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DISINFECTION BY-PRODUCTS IN

UNITED STATES DRINKING WATERS

FINAL REPORT

November 1989

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LIST OF ABBREVIATIONS

ACETAL	Acetaldehyde
ALD	Aldehyde
AMWA	Association of Metropolitan Water Agencies
AWWARF	American Water Works Association Research Foundation
BCAN	Bromochloroacetonitrile
Br^-	Bromide
C	Concentration
C_0	Concentration at time zero
CDHS	California Department of Health Services
CE	Clearwell effluent
CH	Chloral hydrate
$CHBr_3$	Bromoform
$CHBr_2Cl$	Dibromochloromethane
$CHBrCl_2$	Bromodichloromethane
$CHCl_3$	Chloroform
CHP	Chloropicrin
Cl^-	Chloride
Cl_2	Chlorine
Cl_2/NH_3	Prechlorine/postammonia
ClO_2	Chlorine dioxide
cm^{-1}	Inverse centimeter
/cm	Inverse centimeter
CNCl	Cyanogen chloride
CONV	Conventional treatment
CP	Chlorophenol
CPHF	California Public Health Foundation
DBAA	Dibromoacetic acid
DBAN	Dibromoacetonitrile
DBP	Disinfection by-product
DCAA	Dichloroacetic acid
DCAN	Dichloroacetonitrile

DCP	2,4-dichlorophenol
1,1-DCP	1,1-dichloropropanone
DF	Direct filtration
DIS	Disinfection only
EBCT	Empty bed contact time
FE	Filter effluent
FI	Filter influent
FRM	Formaldehyde
FS	Flowing stream
GAC	Granular activated carbon
GC	Gas chromatograph
GW	Groundwater
H_2O_2	Hydrogen peroxide
HAA	Haloacetic acid
HAN	Haloacetonitrile
HK	Haloketone
HOBr	Hypobromous acid
ID	Identification
JMM	James M. Montgomery, Consulting Engineers, Inc.
LAA	Los Angeles Aqueduct
LR	Lake/reservoir
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MCL	Maximum contaminant level
Metropolitan	Metropolitan Water District of Southern California
μg/L	Microgram per liter
mg/L	Milligram per liter
mgd	Million gallons per day
MRL	Minimum reporting level
MS	Mass spectrometer
n	Number of samples
NA	Not analyzed
ND	Not detected
NH_2Cl	Chloramines

nm	Nanometer
O_3	Ozone
PCP	Pentachlorophenol
PI	Plant influent
r	Correlation coefficient
SDS	Simulated distribution system
SDWA	Safe Drinking Water Act
SFT	Softening
SPW	State Project Water
t	Time
TCAA	Trichloroacetic acid
TCAN	Trichloroacetonitrile
TCP	2,4,6-trichlorophenol
1,1,1-TCP	1,1,1-trichloropropanone
THM	Trihalomethane
TOC	Total organic carbon
TOX	Total organic halide
TTHM	Total trihalomethanes
u	Number of utilities
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UV-254	Ultraviolet absorbance at 254 nanometers
XDBP	Halogenated disinfection by-product
$XDBP_{sum}$	Sum of measured halogenated disinfection by-products

Executive Summary

EXECUTIVE SUMMARY

INTRODUCTION

The United States Environmental Protection Agency (USEPA) will be developing regulations to control disinfection by-products (DBPs) in drinking water as a result of the 1986 amendments to the Safe Drinking Water Act. Although the schedule for promulgation of regulations under these amendments remains uncertain at this time, the anticipated regulations require that the presence and control of target DBPs be fully understood. Thus, in October, 1987, the Association of Metropolitan Water Agencies (AMWA) entered into a cooperative agreement with the USEPA to perform a study of the formation and control of DBPs in full-scale drinking water systems. The study was performed by the Metropolitan Water District of Southern California (Metropolitan) and James M. Montgomery, Consulting Engineers, Inc. (JMM).

Specific objectives of the project included determining the occurrence of DBPs at 25 drinking water treatment facilities around the nation; determining the seasonal nature of DBP occurrence as a function of temperature, total organic carbon (TOC), pH and other water quality parameters; and determining the effect of changes in treatment processes and/or disinfectants on the production of DBPs at up to 10 drinking water treatment facilities. The study focused on the identification of DBPs as a function of source water quality, water treatment process selection and operation, and disinfection processes and chemicals. The target DBP compounds for the study are listed in Table ES-1. Target compounds included trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), aldehydes (ALDs), chloropicrin, chloral hydrate, cyanogen chloride, and 2,4,6-trichlorophenol. A companion study, funded by the California Department of Health Services (CDHS) through a grant to the California Public Health Foundation (CPHF), was also conducted by Metropolitan and JMM. This study evaluated DBP production at 10 drinking water treatment facilities in California.

The first year of the two-year USEPA study focused on establishing and verifying the analytical procedures used in the study, selecting utilities to participate in the study, developing DBP baseline data through implementation of a quarterly sampling program at the participating utilities, and conducting process modification studies at two utilities. During the second year of the project, baseline data collection was completed and process modification studies were conducted at six utilities.

Baseline data collection for the 35 utilities participating in the combined USEPA and CDHS studies involved sampling of clearwell effluents (after final disinfection but before distribution) on a quarterly basis for one year. The first sampling quarter (mid-March through April, 1988) corresponded to the spring season, and subsequent samplings corresponded to the summer, fall and winter seasons. Utilities were sent sampling kits containing the sample bottles, detailed instructions for sampling, and a sample information sheet on which to record plant operating conditions on the day of sampling.

TABLE ES-1

LIST OF COMPOUNDS TARGETED IN STUDY

Compounds

Trihalomethanes

chloroform
bromodichloromethane
dibromochloromethane
bromoform

Haloacetonitriles

trichloroacetonitrile
dichloroacetonitrile
bromochloroacetonitrile
dibromoacetonitrile

Haloketones

1,1-dichloropropanone
1,1,1-trichloropropanone

Miscellaneous chloro-organics

chloropicrin
chloral hydrate
cyanogen chloride

Haloacetic acids

monochloroacetic acid
dichloroacetic acid
trichloroacetic acid
monobromoacetic acid
dibromoacetic acid

Chlorophenols

2,4-dichlorophenol*
2,4,6-trichlorophenol
pentachlorophenol*

Aldehydes

formaldehyde
acetaldehyde

* These chlorophenols were only analyzed for during the first sampling quarter.

Treatment modification studies were conducted to identify, in a preliminary manner, the impact of processes or process modifications on DBP production. Thus, the following full-scale and/or pilot studies were conducted: five studies involving a change from chlorine or chloramines to ozone/chlorine or ozone/chloramines; two studies on alum coagulation for DBP precursor removal; two studies involving a change from chlorine to chlorine dioxide/chlorine; and one study of granular activated carbon (GAC) for DBP precursor removal.

UTILITY SELECTION

An information request form was sent to 104 potential participants in the study, and from the 78 responses received, utilities were selected to complete the matrix shown in Table ES-2. The matrix was divided into two major categories, treatment type (conventional, direct filtration, softening and disinfection only) and source water type (groundwater, lake/reservoir and flowing stream). Within these categories, geographical location and disinfectant type were also considered. In addition, two other categories were utilized in developing the selection matrix: population and THM level.

METHODOLOGY

Grab samples were collected at clearwell effluents (after final disinfection but before distribution) for DBP and TOC analyses. For those plants which did not have clearwells, samples were collected at specified points after final disinfection. Additional analyses were performed on plant influents: TOC, bromide, chloride and aldehydes. TOC was also measured at filter influents, if filtration was employed as a treatment process. Holding studies performed by Metropolitan were conducted to identify preservatives and holding times for the DBP samples.

The THM liquid/liquid extraction (LLE) gas chromatograph (GC) method was modified by Metropolitan to include THMs, HANs, HKs and chloropicrin. Chloral hydrate was analyzed by a separate LLE/GC method. HAAs and 2,4,6-trichlorophenol were analyzed by an acidic salted LLE and GC. Cyanogen chloride was analyzed by a purge-and-trap gas chromatograph/mass spectrometer (GC/MS) method. Aldehydes were analyzed by a derivatization/extraction GC method.

DATA MANAGEMENT AND ANALYSIS

The large database developed during the study required a strict data handling protocol to ensure its accuracy and reliability. Some of the elements of this protocol included use of signatures by responsible project team members, use of data-sheet reference numbers for each individual project data sheet, and a tracking system for the status of each group of data.

Nonparametric statistical methods were used to analyze data from this study. Nonparametric methods do not require an assumed parametric distribution for the data, and cases below the detection limits can be incorporated more readily as compared to parametric methods. A "five-number summary", including the minimum value, 25th percentile, median, 75th percentile and maximum value of the data set, was used to present a simple summary of the data. Notched box-and-whisker plots were used also

TABLE ES-2

DISINFECTION BY-PRODUCTS IN DRINKING WATER STUDY

UTILITY SELECTION MATRIX

TREATMENT	GROUNDWATER	LAKE/RESERVOIR	FLOWING STREAM
CONVENTIONAL	Clermont Co., OH 1 Long Beach, CA 2	Norwich, CT* 1B MWD, CA -Mills $2^a,5^b$ Arlington, TX* 2A Hackensack, NJ 2^e MWD, CA -Weym. 2 San Francisco, CA 1 Big Spring, TX* 5 Shreveport, LA $6^a,8^b$	Cape Girardeau, MO* 2A Cincinnati, OH 1 Contra Costa WD, CA 2A Sacramento, CA 1 Santa Clara Valley, CA 2 Newport News, VA 1A
DIRECT FILTRATION		East Bay MUD, CA 1 Las Vegas, NV 1 Little Rock, AR 1 Aurora, CO $1^aA,5^bA$	Los Angeles DWP, CA 3
SOFTENING	Palm Beach Co., FL 2 Wausau, WI* 1 Minot, ND 1 Santa Monica, CA 1	Macomb, IL* 1A Galveston,TX $7^c,4^d$	Louisville, KY 2 Ft. Meyers, FL* 1 Emporia, KN* 2A Omaha, NB 1A
DISINFECTION ONLY	Mesa Consol., CA 3	North Skagit Co., WA* 1 New York City, NY 1 Newark, NJ 1	

Note: Utilities participating in the California Public Health Foundation study are listed in bold type.
* Population under 50,000; all others over 50,000.

Key for chemical addition:

1 - chlorine only
2 - chlorine + chloramines
3 - ozone + chlorine
4 - chlorine + chlorine dioxide
5 - chloramines only
6 - chloramines + chlorine dioxide
7 - chlorine + chloramines + chlorine dioxide
8 - ozone + chloramines
A - powdered activated carbon
B - potassium permanganate

[a] - first quarter only
[b] - second through fourth quarters
[c] - first through third quarters
[d] - fourth quarter only
[e] - clearwell effluent sampled
    before ammonia addition

used for presentation of project data. This type of plot is presented and described in Figure ES-1.

BASELINE SAMPLING RESULTS AND DISCUSSION

Table ES-3 summarizes the baseline median DBP values for each quarter as well as for all four sampling quarters combined. It should be noted that these data represent clearwell effluent samples or samples collected at specified points after disinfection for those plants without clearwells. Some distribution system sampling was performed for the process modification studies (discussed in more detail below). Results of the process modification studies indicated that some DBPs, such as THMs, increased in the chlorinated distribution systems of some utilities, while their concentrations did not change in the chloraminated systems of other utilities. In addition, it is important to note that the disinfection practices of some of the participating utilities, such as the use of chloramines, are utilized to meet the current TTHM regulation and not to meet requirements of the proposed Surface Water Treatment Rule (SWTR). Thus, some utilities would produce different DBP levels if their current disinfection practices required modification in order to meet proposed concentration-time (CT) requirements of the SWTR.

Figure ES-2 is a summary of the four-quarter median concentrations of each DBP class measured in this study. The median value of total THMs (TTHMs) was 36 μg/L, and the median value of HAAs was 17 μg/L during the four quarters of baseline data collection. On a weight basis, THMs were the largest class of DBPs detected in this study (54.5 percent of the total measured DBPs), and HAAs were the second largest fraction (25.4 percent of the total) (see Figure ES-3). A running annual average of TTHMs is utilized to determine compliance with the TTHM maximum contaminant level (MCL) of 0.10 mg/L. When the running annual average (i.e., the mean of the four baseline TTHM values) was computed for each utility, the 35-utility median TTHM concentration was 39 μg/L.

TOC analyses were performed on plant influent samples after the first sampling quarter. Figure ES-4 is a box-and-whiskers plot of the plant influent TOC data for the summer, fall and winter quarters. Note that the "notches" in the plots of the three quarters overlap, indicating that there is not a statistically significant difference, at 95 percent confidence, between the medians of any two quarters. In Figure ES-5, influent TOC values are plotted by source water type. Again, there is no statistically significant difference between the medians of any two sources.

Figure ES-6 is a plot of TTHMs by sampling quarter. As would be expected, TTHM levels were highest in the summer quarter when water temperatures were the highest, lower in the fall, and lowest in the winter and spring quarters, although these differences were not statistically significant at a 95 percent confidence level. Figure ES-7 shows TTHM levels plotted as a function of the influent water temperatures measured during baseline data collection. In this plot, the median TTHM level is significantly higher in the highest temperature range than in the lower three ranges, illustrating the dependence of TTHM production on water temperature.

Figure ES-8 illustrates TTHM levels as a function of the disinfection scheme in use by the utilities on the day of sample collection. Only chlorination, prechlorination/

GUIDE TO NOTCHED BOX-AND-WHISKER PLOTS

$+$ ◄— **EXTREME OUTLIER**
any value outside 3 interquartile ranges
measured from the 25 and 75 percentiles

☐ ◄— **OUTLIER**
any value outside 1.5 interquartile ranges
measured from the 25 and 75 percentiles

◄— **MAXIMUM VALUE**
this is the largest value (excluding outliers)

◄— **75 PERCENTILE**
75% of the data are less than or
equal to this value (including outliers)

INTERQUARTILE RANGE
contains the data between
the 25 and 75 percentiles

95% CONFIDENCE INTERVAL
for the median (including outliers)

◄— **MEDIAN**
50% of the data are above or
below this value (including outliers)

◄— **25 PERCENTILE**
25% of the data are less than or
equal to this value (including outliers)

NOTE: Horizontal width of box is
proportional to square root of sample size (N)

◄— **MINIMUM VALUE**
this is the lowest value (excluding outliers)

FIGURE ES-1

TABLE ES-3

DISINFECTION BY-PRODUCTS IN DRINKING WATER

SUMMARY OF BASELINE SAMPLING MEDIAN VALUES

Disinfection By-Products (μg/L)	1st Quarter (Spring)	2nd Quarter (Summer)	3rd Quarter (Fall)	4th Quarter (Winter)	All Quarters Combined
Trihalomethanes					
Chloroform	15	15	13	9.6	14
Bromodichloromethane	6.9	10	5.5	4.1	6.6
Dibromochloromethane	2.6	4.5	3.8	2.7	3.6
Bromoform	0.33	0.57	0.88	0.51	0.57
Total Trihalomethanes	34	44	40	30	36
Haloacetonitriles					
Trichloroacetonitrile	<0.012	<0.012	<0.029	<0.029	<0.029
Dichloroacetonitrile	1.2	1.1	1.1	1.2	1.2
Bromochloroacetonitrile	0.50	0.58	0.70	0.59	0.57
Dibromoacetonitrile	0.54	0.48	0.51	0.46	0.50
Total Haloacetonitriles	2.8	2.5	3.5	4.0	3.3
Haloketones					
1,1-Dichloropropanone	0.52	0.46	0.52	0.55	0.52
1,1,1-Trichloropropanone	0.80	0.35	0.60	0.66	0.60
Total Haloketones	1.4	0.94	1.0	1.8	1.2
Haloacetic acids					
Monochloroacetic acid	<1.0	1.2	<1.0	1.2	<1.0
Dichloroacetic acid	7.3	6.8	6.4	5.0	6.4
Trichloroacetic acid	5.8	5.8	6.0	4.0	5.5
Monobromoacetic acid	<0.5	<0.5	<0.5	<0.5	<0.5
Dibromoacetic acid	0.9	1.5	1.4	1.0	1.1
Total Haloacetic acids	18	20	21	13	17

Table ES-3

Disinfection By-Products In Drinking Water
Summary of Median Values, Continued

	1st Quarter (Spring)	2nd Quarter (Summer)	3rd Quarter (Fall)	4th Quarter (Winter)	All Quarters Combined
Aldehydes					
Formaldehyde	NA	5.1	3.5	2.0	3.6
Acetaldehyde	NA	2.7	2.6	1.8	2.2
Total Aldehydes	NA	6.9	5.5	4.2	5.7
Miscellaneous					
Chloropicrin	0.16	0.12	0.10	0.10	0.12
Chloral hydrate	1.8	3.0	2.2	1.7	2.1
Cyanogen chloride	0.45	0.60	0.65	0.80	0.60
2,4,6-Trichlorophenol	<0.3	<0.4	<0.4	<0.4	<0.4
Halogenated DBP$_{sum}$	64	82	72	58	70
Total Organic Halide	150	180	170	175	170
Plant Influent Characteristics					
Total Organic Carbon, mg/L	NA	2.9	2.9	3.2	3.0
Ultraviolet absorbance, cm^{-1}	NA	0.11	0.11	0.13	0.11
Chloride, mg/L	NA	28	32	23	29
Bromide, mg/L	NA	0.07	0.10	0.07	0.08

NA = Not Analyzed

Note (1): Total class median values are not the sum of the medians of the individual compounds, but rather the medians of the sums of the compounds within that class.

Note (2): The halogenated DBP$_{sum}$ median values are not the sum of the class medians for all utilities, but rather the medians of the halogenated DBP$_{sum}$ values for all utilities. This value is only the sum of halogenated DBPs measured in this study.

Disinfection By–Product Concentration
by DBP Class – Four Quarters

FIGURE ES-2

Percent of Sum of DBP Class Medians
By DBP Class – Four Quarters
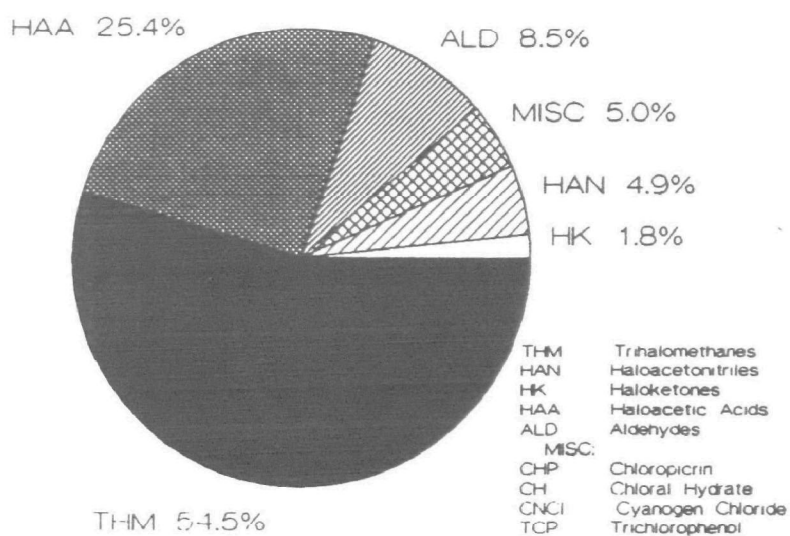
FIGURE ES-3

Influent Total Organic Carbon
By Quarter
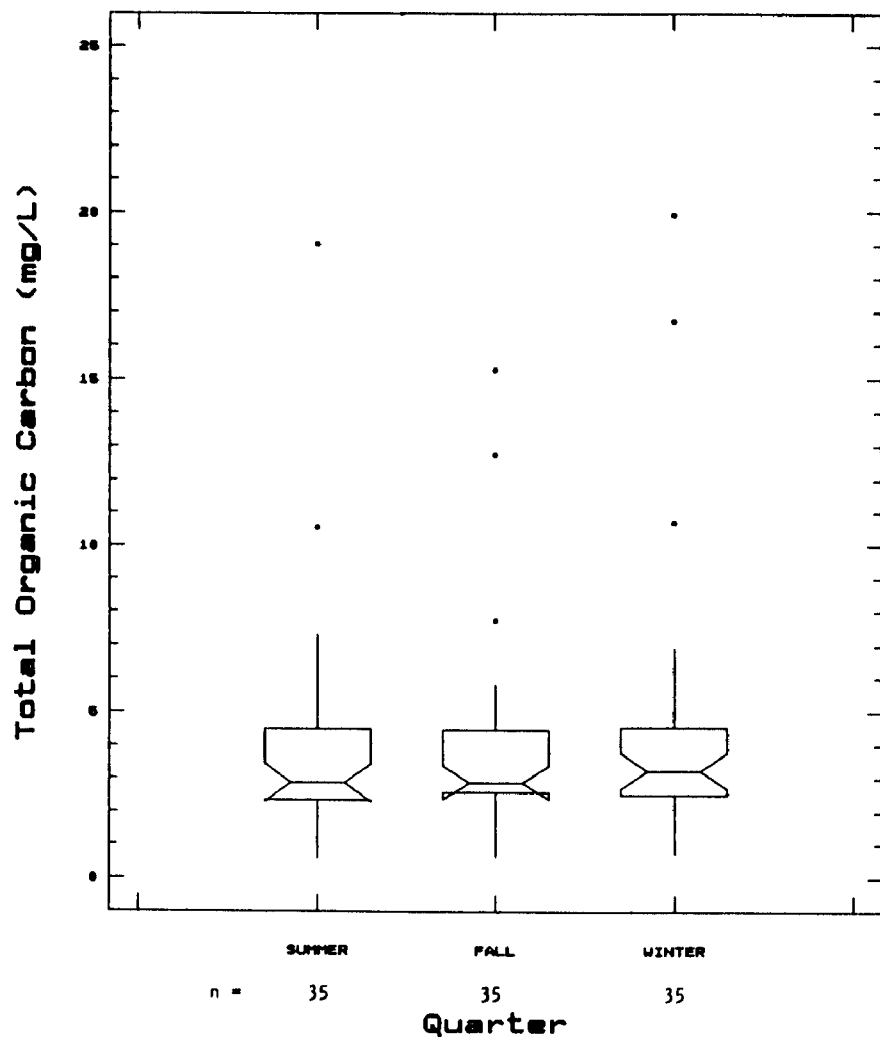
FIGURE ES-4

Influent Total Organic Carbon
By Source
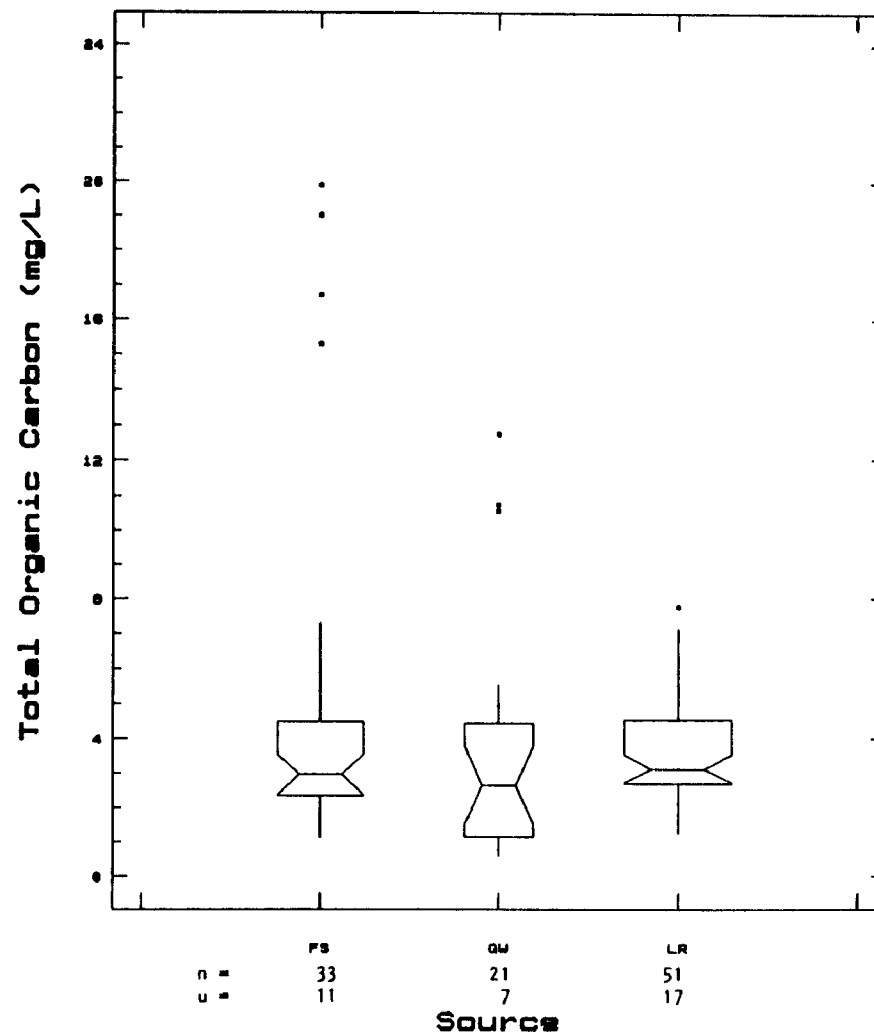
FIGURE ES-5

Trihalomethanes
By Quarter
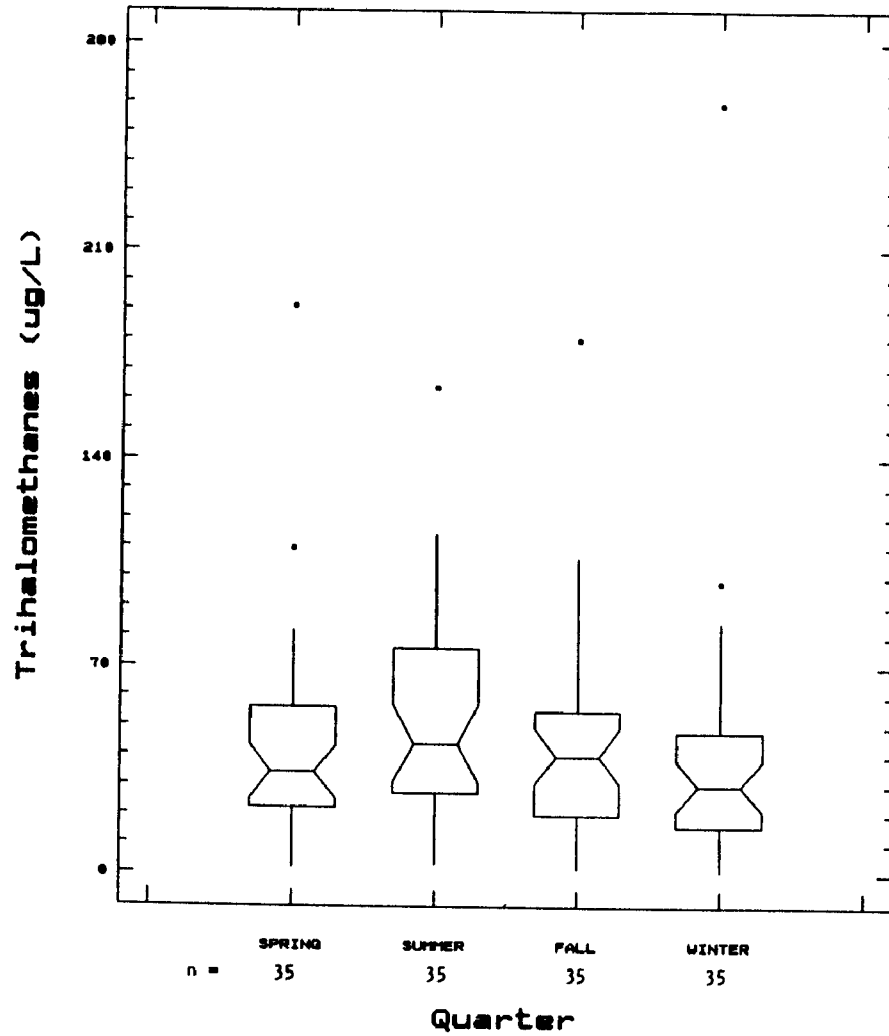
FIGURE ES-6

Trihalomethanes
By Influent Temperature
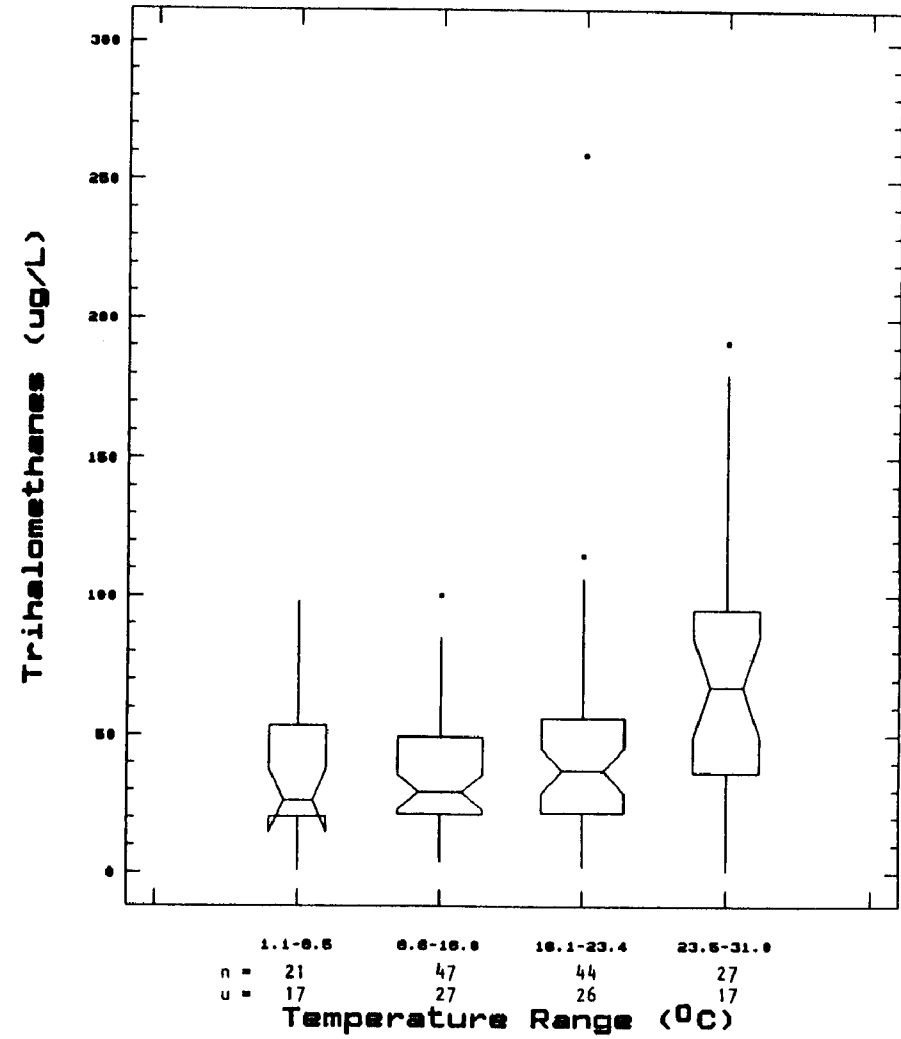
FIGURE ES-7

postammoniation, and chloramination are shown since other disinfection schemes (such as preozonation/postchlorination) had very small sample sizes. All other factors being equal, it would be expected that the chlorinating utilities would produce a higher median TTHM level than utilities using the other two disinfection schemes. However, Figure ES-8 indicates that the prechlorinating/postammoniating utilities had a higher median TTHM level than utilities employing the other two disinfection scenarios, and this difference was significant at a 95 percent confidence level. The same trend was observed for the median level of the sum of halogenated DBPs ($XDBP_{sum}$) measured in this study. The reasons for this trend are not immediately apparent from the median influent TOC levels for the three disinfection schemes, which occurred within the narrow range of 2.8 to 3.2 mg/L. However, the median values of ultraviolet absorbance at 254 nanometers (UV-254) for the prechlorinating/postammoniating utilities, indicate that these utilities had a higher UV-254 level than utilities employing either of the other two disinfection schemes, although the difference was not statistically significant at a 95 percent confidence level. The higher UV-254 levels may indicate higher levels of DBP precursors even though higher precursor levels were not reflected in the TOC results. Thus, the chlorinating utilities participating in this study may have been able to use free chlorine for oxidation/disinfection and still meet the TTHM MCL of 0.10 mg/L, while other utilities have had to employ free chlorine for oxidation/disinfection and then use ammonia at some point in their process trains in order to meet the TTHM MCL.

In all, over 300 correlations were determined for the baseline data collected in this study. Correlations of non-THM DBPs with THMs were performed in order to explore the potential of using TTHMs as a surrogate for other DBPs such as HAAs or HANs, since performing analyses for several different DBPs is beyond the scope of a utility's routine monitoring program. Figure ES-9 illustrates the correlations of THMs with $XDBP_{sum}$, the sum of non-THM DBPs, and HANs. As illustrated in the figure, there was a strong correlation between TTHMs and $XDBP_{sum}$ (r=0.96). Since THMs represent the largest DBP fraction detected in this study, the data were re-evaluated by correlating TTHMs with the sum of non-THM DBPs (XDBPs - THMs). In this instance, r decreased to 0.76. However, this lower correlation coefficient does not mean that THMs cannot be used as a surrogate or predictor of the sum of all XDBPs. It should be noted, though, that correlations between some classes of compounds were low (for instance, comparing TTHMs to haloketones yielded an r of only 0.06), whereas for TTHMs and HANs, r was equal to 0.78.

Figure ES-10 illustrates the correlation of influent chloride levels with influent bromide. There was a strong correlation between these two parameters (r=0.97), and these results indicate that chloride may be used as a predictor for bromide. Using all of the data points collected in the baseline sampling program (excluding three outlier values from a utility with atypically high bromide levels), linear regression analysis yielded the following equation:

$$[Br^-] = -0.0071 + 0.0034[Cl^-]$$

It is significant to note that high bromide levels were detected not only at utilities impacted by tidal influences or saltwater intrusion, but at inland utilities as well.

Trihalomethanes
By Disinfection Scheme
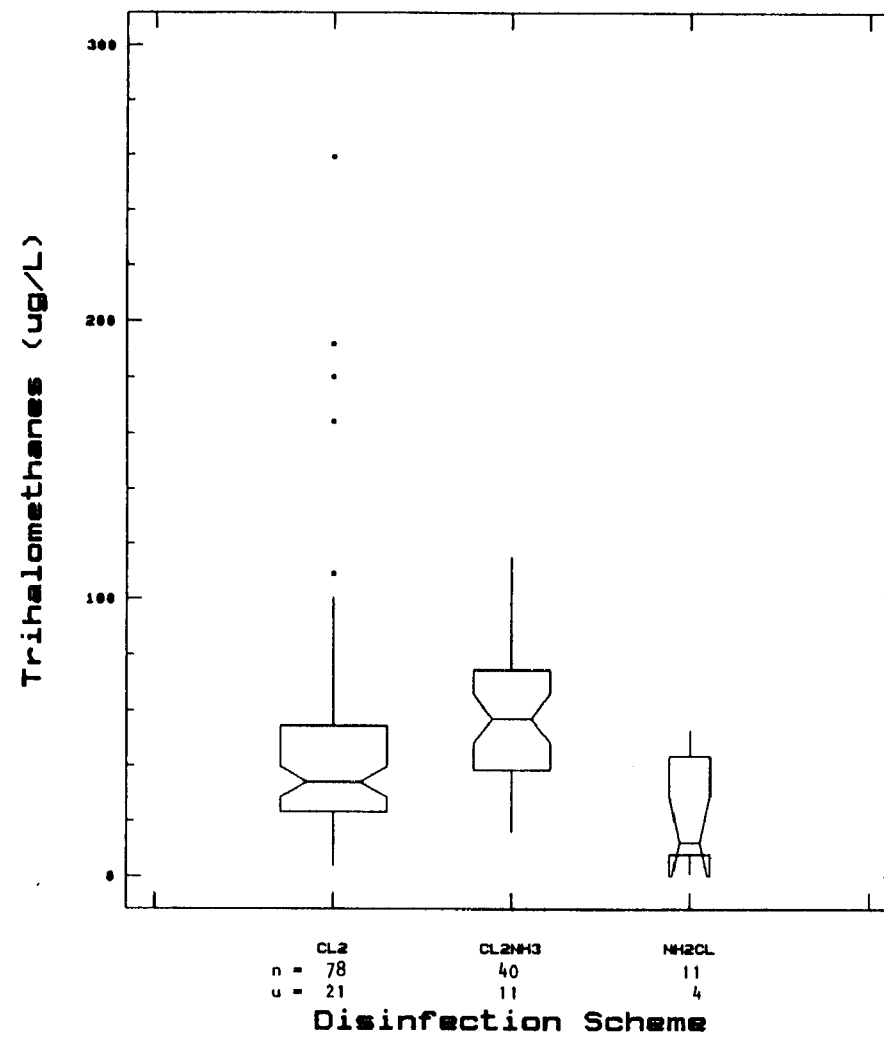
FIGURE ES-8

Correlations with Trihalomethanes
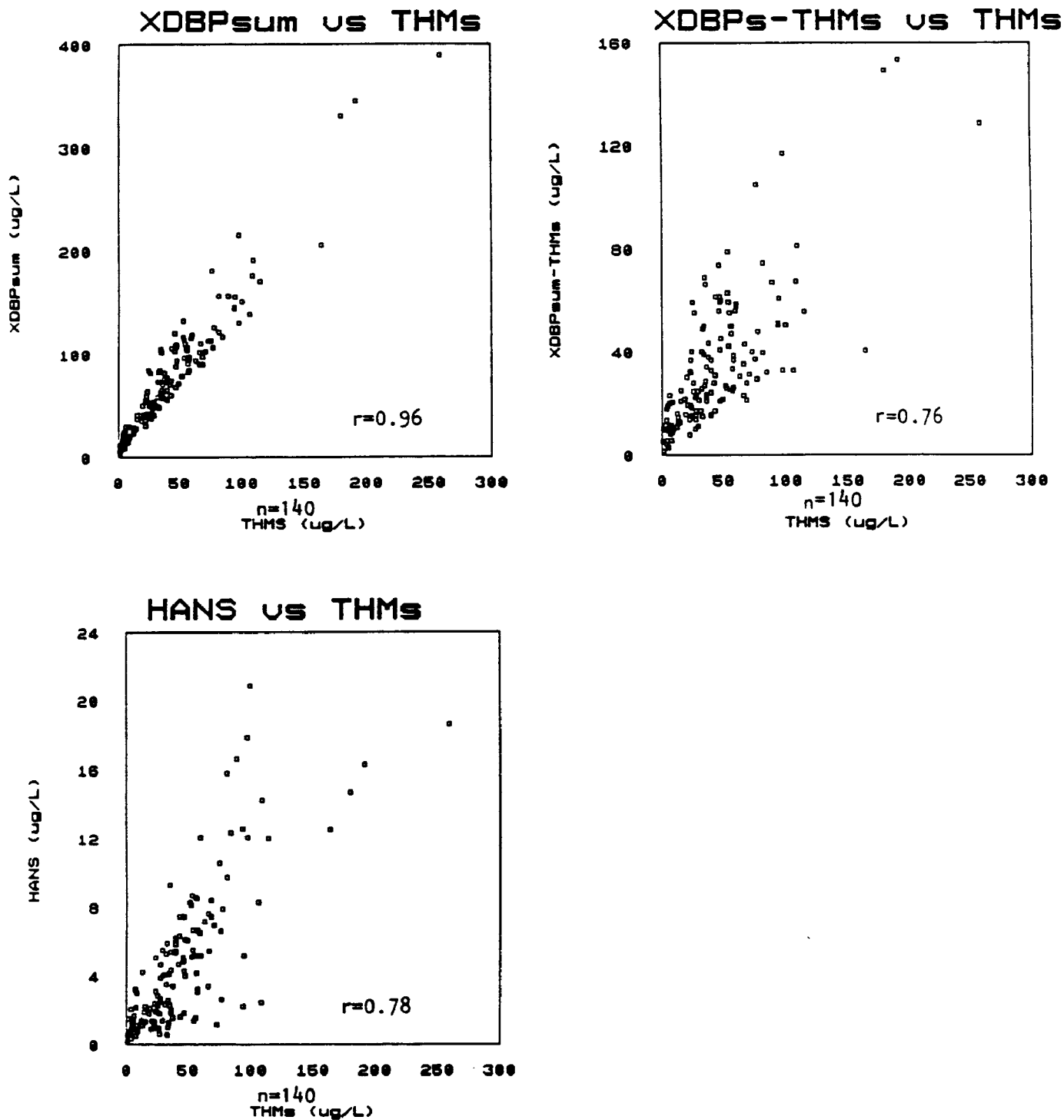
FIGURE ES-9

Correlations with Influent
Chloride and Bromide

Br- vs CL-

Influent Bromide (mg/L)

r=0.97, 0.86*

n=105, 102*

Influent Chloride (mg/L)

CHBr3 vs Br-

Bromoform (ug/L)

r=0.57, 0.69*

n=105, 102*

Influent Bromide (mg/L)
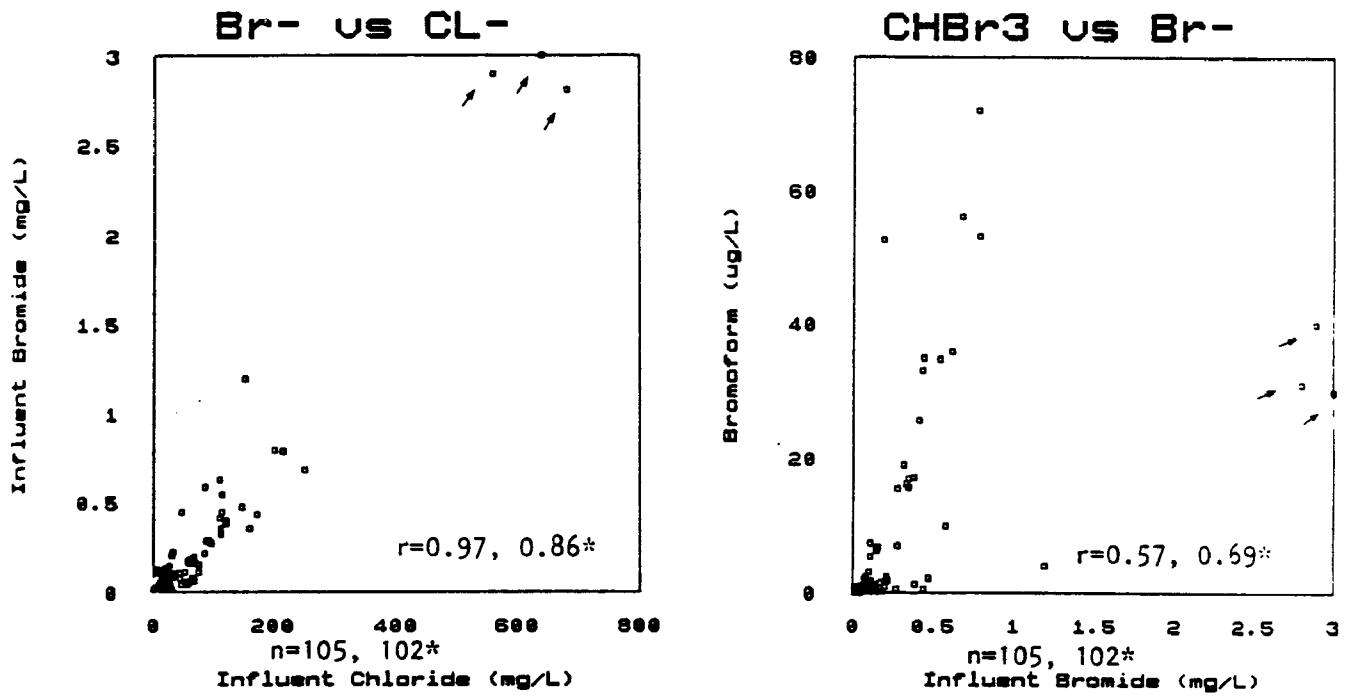
* Excludes indicated outliers

FIGURE ES-10

Figure ES-11 shows the relationship of influent bromide to levels of chloropicrin, 1,1,1-trichloropropanone (1,1,1-TCP) and trichloroacetic acid (TCAA) measured during baseline data collection. In each case, an exclusion relationship is demonstrated, i.e., the presence of bromide appeared to exclude the presence of the particular DBP. Correlations of the four THM compounds with dichloroacetic acid (DCAA) are illustrated in Figure ES-12. The best correlation was found with chloroform (r=0.86). However, as the THMs shift to the more brominated species, the correlation coefficients decrease until an exclusion relationship is observed between DCAA and bromoform (r=-0.33). This progression is consistent with the finding that bromide and various chlorinated DBPs were related by exclusion.

Of the 35 utilities included in this study, only three employed ozone, yet almost all had detectable levels of formaldehyde and acetaldehyde in the clearwell effluent samples. These aldehydes were also found in some plant influent samples, and chlorination alone was found to produce these compounds.

Chloramines are recognized as an effective control strategy for THMs and other DBPs. However, for most waters studied in this project, concentrations of cyanogen chloride were found to be significantly higher in chloraminated waters as compared to chlorinated waters. Moreover, it was possible to statistically divide the distribution of cyanogen chloride into two groups, depending on whether the final disinfectant was chlorine or chloramines.

Figure ES-13 illustrates the removal of TOC within the filtering plants included in the baseline sampling program. Overall, TOC removal within these plants averaged approximately 24 percent. It should be noted that the treatment practices of the utilities participating in the baseline sampling program most likely focused on turbidity control and were not optimized with respect to TOC removal. Results of the two treatment modification studies on improved coagulation (described in more detail below) indicated that these two utilities were able to achieve higher TOC removals than those indicated in Figure ES-13; however this ability may be source-water specific.

The TTHM data from this study of 35 utilities was compared to that of the THM survey conducted by the American Water Works Association Research Foundation in 1987, which involved 727 utilities around the nation. Since compliance with the TTHM MCL of 0.10 mg/L is based on a running annual average, mean TTHM values were computed for each of the 35 utilities in this study for the 4 sampling quarters. The AWWARF survey utilized the means of three years of quarterly data. The TTHM means for both projects are plotted in Figure ES-14, which illustrates that the two frequency distributions were very similar.

TREATMENT MODIFICATION STUDIES - RESULTS AND DISCUSSION

Ozonation Studies

Because of the increasing use of ozone in the United States for disinfection and control of DBPs, five treatment modification studies focused on the use of ozone at various water treatment plants.

Correlations with Influent Bromide

CHP vs Br-

Chloropicrin (ug/L)

r=-0.22, -0.25*

n=104, 101*
Influent Bromide (mg/L)

1,1,1-TCP vs Br-

1,1,1-Trichloropropanone (ug/L)

r=-0.26, -0.35*

n=105, 102*
Influent Bromide (mg/L)

TCAA vs Br-

Trichloroacetic Acid (ug/L)

r=-0.27, -0.35*

n=105, 102*
Influent Bromide (mg/L)

CHC13 vs Br-

Chloroform (ug/L)

r=-0.25, -0.29*

n=105, 102*
Influent Bromide (mg/L)
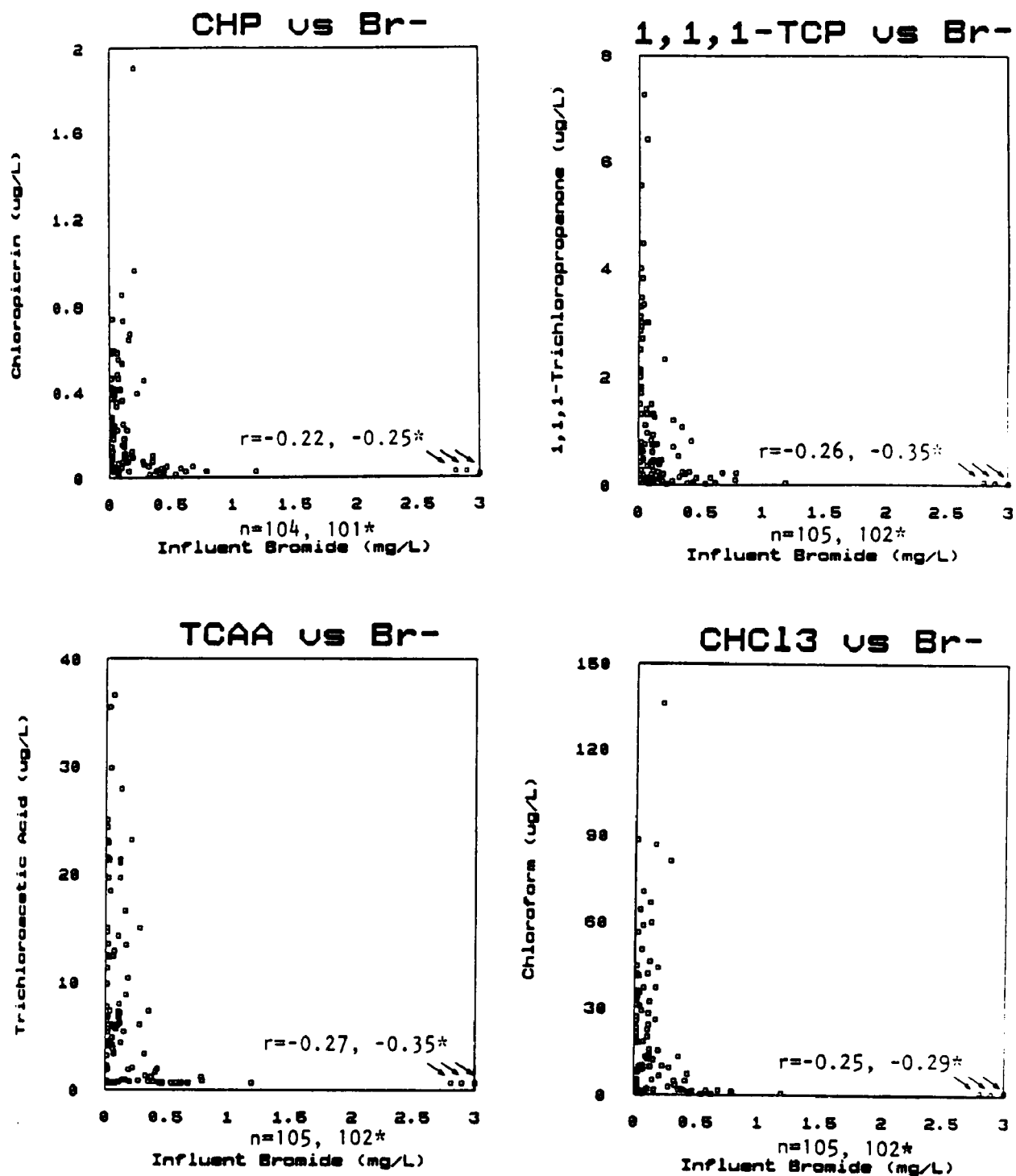
* Excludes indicated outliers

FIGURE ES-11

Correlations with Dichloroacetic Acid
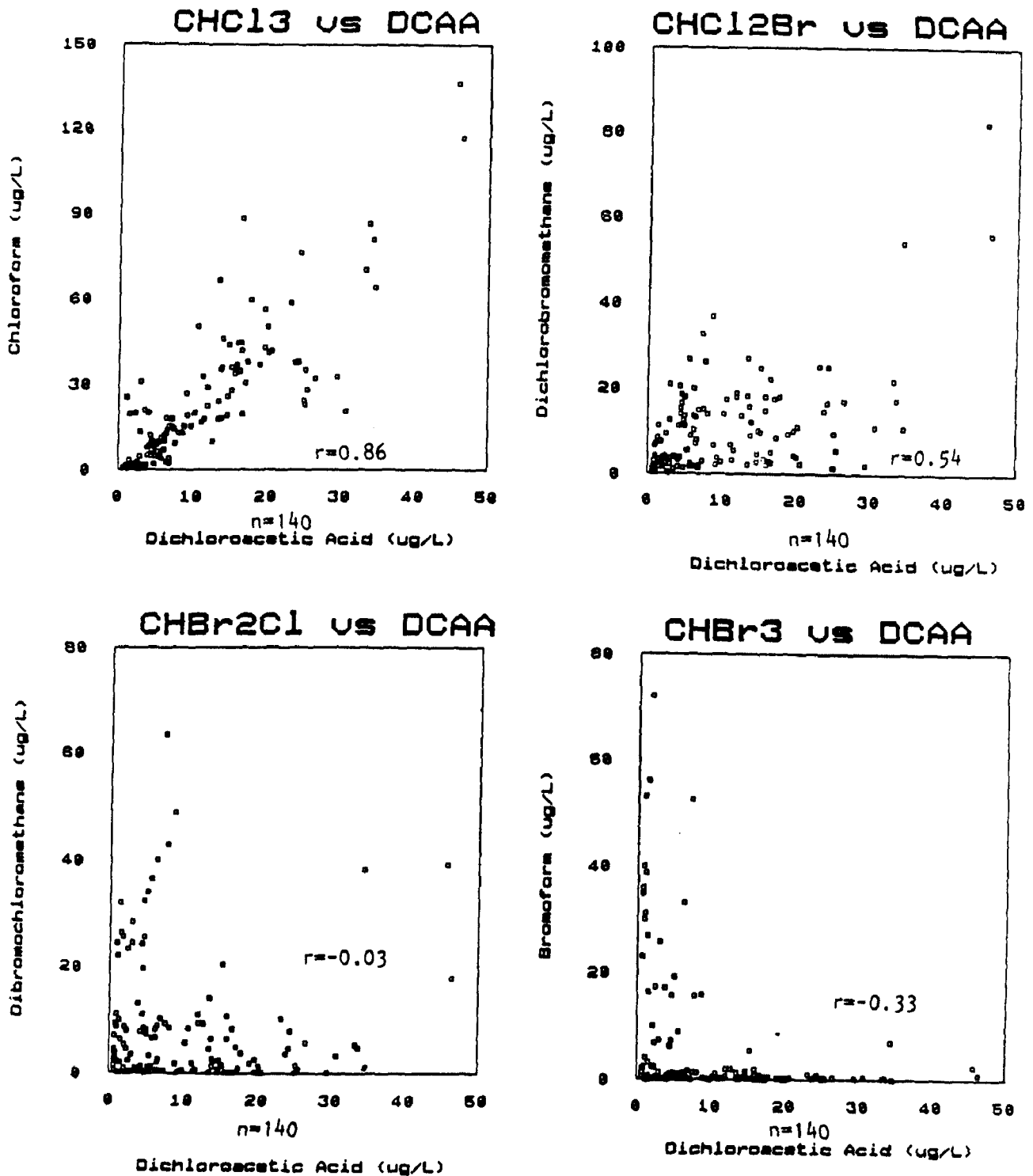
FIGURE ES-12

Mean Total Organic Carbon Removal
Through Filtering Utilities' Processes

PI   Plant Influent
FI   Filter Influent
EFF   Clearwell Effluent

Mean PI TOC = 4.0 mg/L
Mean EFF TOC = 2.8 mg/L
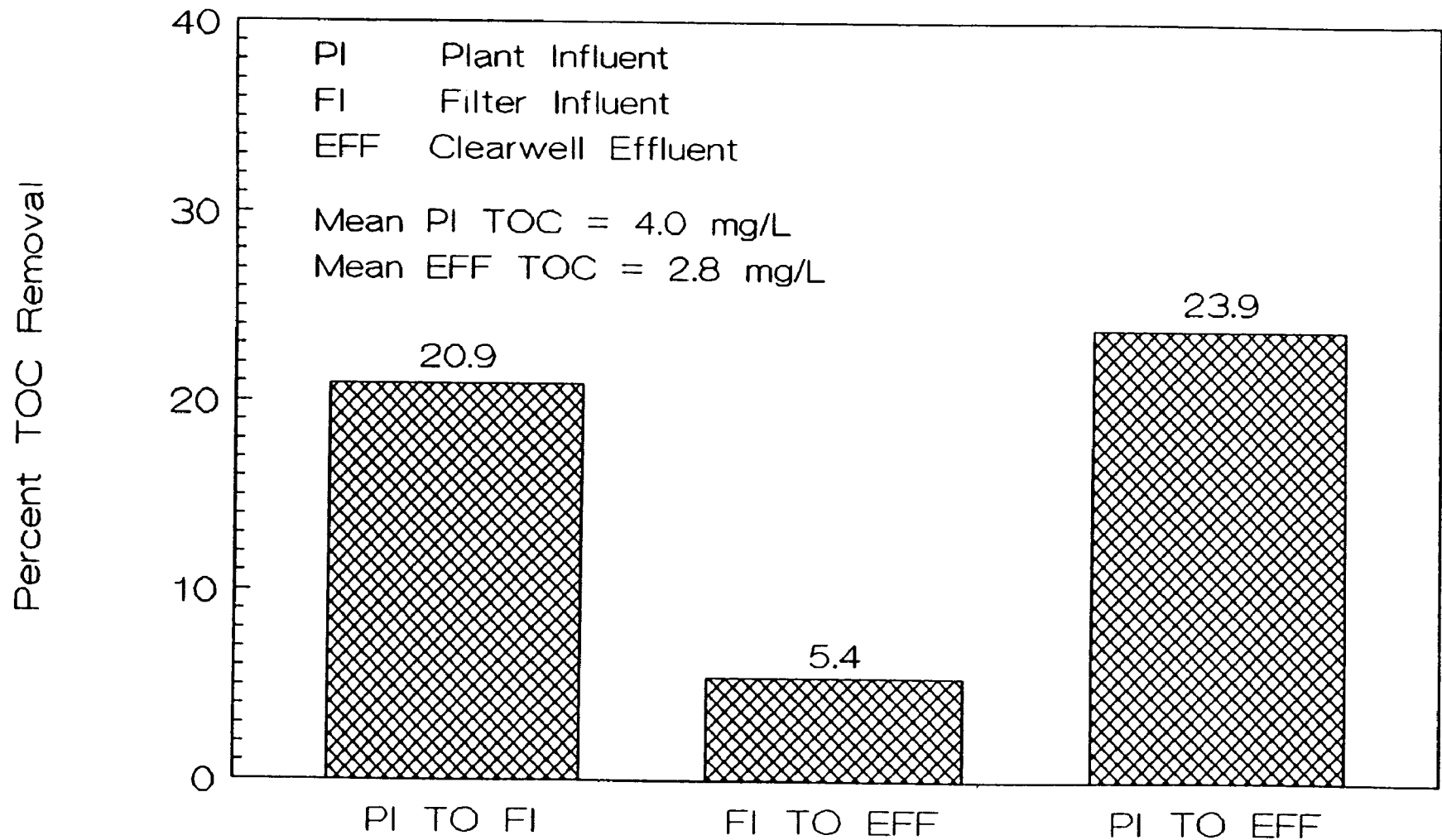
FIGURE ES-13

AWWARF 12-Quarter vs. USEPA 4-Quarter Means
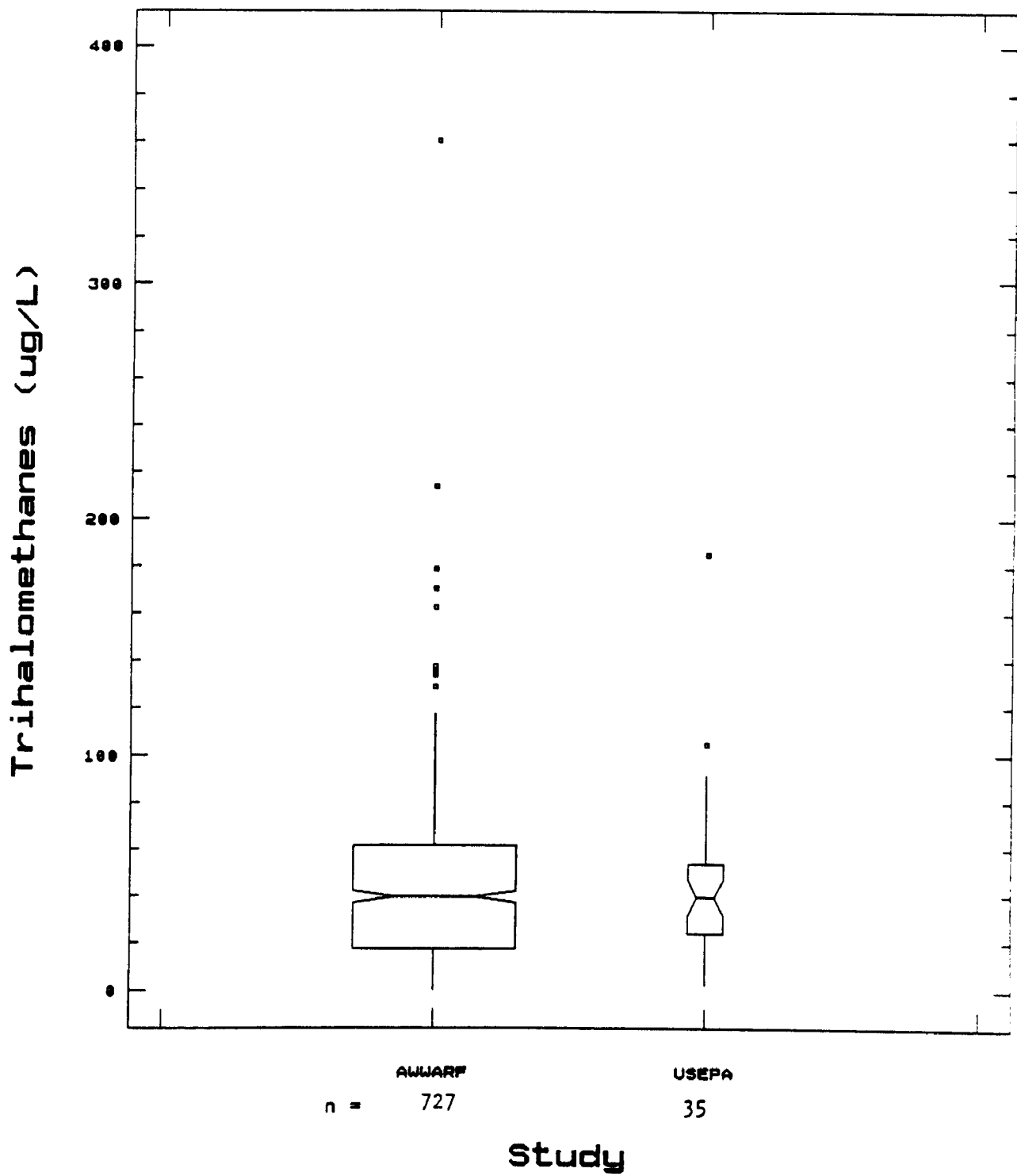
FIGURE ES-14

The study at Utility 6 involved sampling before and after ozonation was incorporated into the treatment process of a 52-mgd plant treating a reservoir water. A conventional treatment process was used before ozonation was installed, with chlorine added to the plant influent, flocculator influent, and filter influent and effluent. Ammonia was added after filtration. When ozonation was installed (in combination with the rapid mix process) the plant was modified to direct filtration, with flotation and skimming replacing the flocculation and sedimentation processes. As a result of ozone implementation, the plant was able to reduce chlorine doses and free chlorine contact time. The "before" and "after" samples (before and after ozonation was placed on-line) were collected approximately five months apart. Figure ES-15 summarizes the impact of ozonation on DBP levels measured in the utility's distribution system after a residence time of approximately 7 hours. The figure illustrates that reductions of 56 to 66 percent occurred for all XDBP classes after the implementation of ozonation, with the exception of HKs which increased slightly. Chloral hydrate, chloropicrin and cyanogen chloride concentrations also decreased. However, from this study, it was not possible to attribute the lower levels of most DBPs directly to ozone since changes in treatment process, and lower chlorine doses and shorter contact times were employed. It cannot be determined if ozone caused a decrease or modification of DBP precursor material or if lower DBP levels can be attributed solely to the decreased use of chlorine. From a full-scale perspective, however, it is notable that the application of ozone decreased the dependence on chlorine for oxidation and disinfection, with the overall result of decreased DBP concentrations.

Three different treatment scenarios were studied at Utility 7, which operates a 400-mgd conventional treatment plant. Chlorine-only (using chlorine doses of 2.3 mg/L at the plant influent and 1.1 mg/L at the filter influent) and prechlorination/postammoniation (chlorine doses of 2.3 mg/L at the plant influent and 0.6 mg/L at the filter influent; ammonia dose of 0.49 mg/L as ammonia-nitrogen at the filter effluent) were studied at full scale and a 6-gpm pilot plant was utilized to study preozonation/postchloramination (ozone dose of 2.0 mg/L before rapid mix; and 0.5 mg/L ammonia and 1.5 mg/L chlorine at the filter effluent). Samples were collected for each scenario after 2-hour and 24-hour simulated distribution system (SDS) tests were conducted. In these tests, samples were dosed with disinfectants and held under conditions representative of Utility 7's distribution system to provide an estimate of the levels of DBPs that would have been produced under realistic environmental conditions. The effects of ozonation on DBP levels after the 24-hour SDS test are illustrated in Figure ES-16. Preozonation followed by concurrent addition of ammonia and chlorine after filtration decreased the levels of THMs, HAAs, HANs, and chloral hydrate as compared to chlorine-only or prechlorination/postammoniation treatment. Concentrations of 1,1,1-TCP were lowest for ozone/chloramines treatment, higher for prechlorination/postammoniation and highest for chlorination treatment, while 1,1-dichloropropanone (1,1-DCP) concentrations exhibited the opposite trend. Very little difference in chloropicrin levels were observed between the three treatment schemes; however, all levels were less than 1 μg/L. Cyanogen chloride levels were highest for the ozone/chloramines treatment after 2 hours of holding time, but after 24 hours, there was very little difference in cyanogen chloride concentrations between the three treatments. Aldehydes were not measured at this utility in this study.

Utility 19 operates a large (600-mgd) preozonation/direct filtration facility. Chlorine-only (1.8 mg/L of chlorine added to the plant influent and 0.3 mg/L added to the filter

Effect Of Cl2,NH2Cl and O3,Cl2,NH2Cl
on DBP Formation (Utility 6)
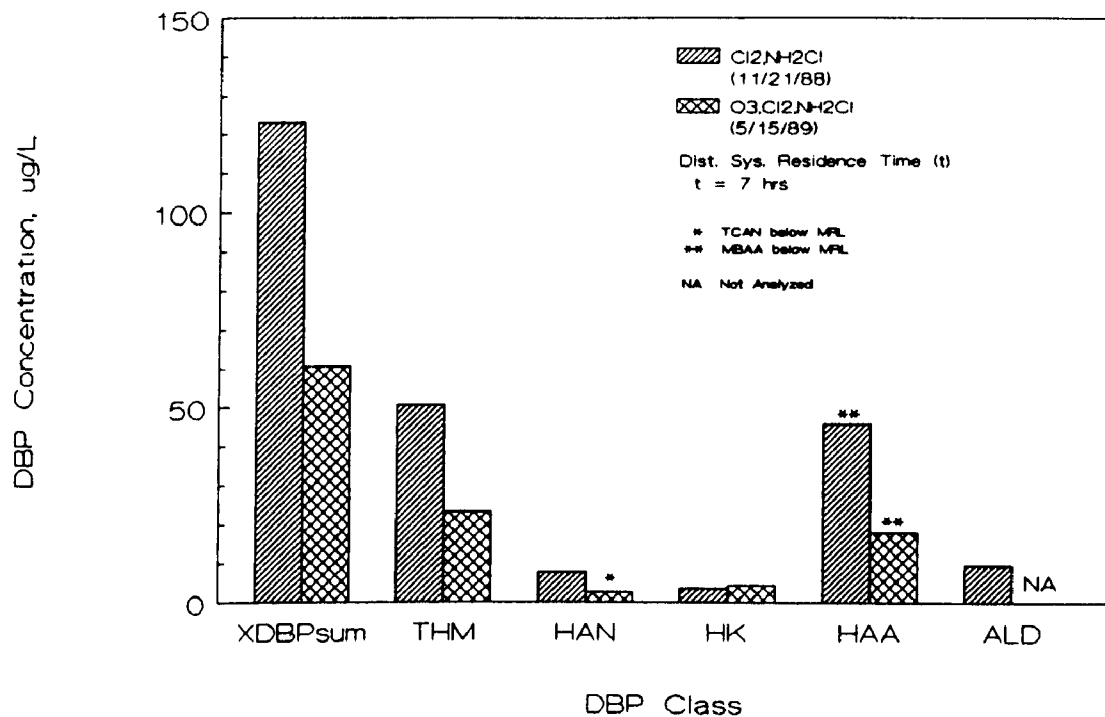
FIGURE ES-15

Effect Of Cl2, Cl2/NH3 & O3/NH3/CL2
on DBP Formation (Utility 7)
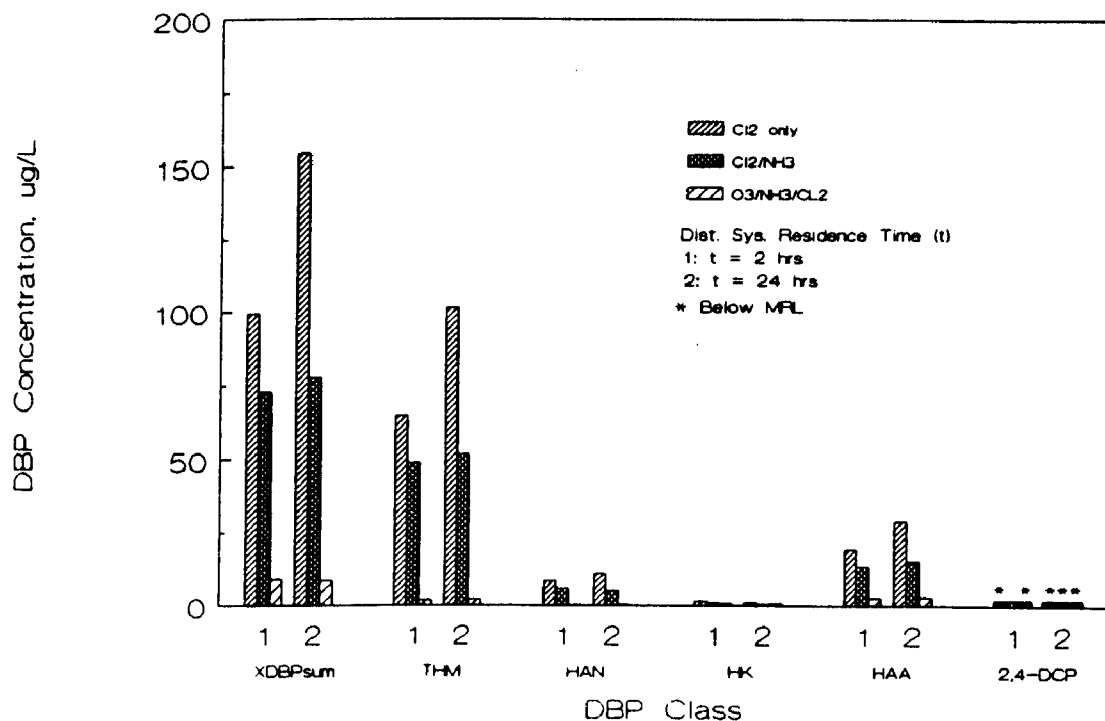
FIGURE ES-16

effluent) and preozonation/postchlorination (ozone dose of 1.7 mg/L, and chlorine dose of 1.5 mg/L added to the filter effluent) treatments were studied. Samples were collected at the plant's clearwell effluent and in the distribution system at residence times of 4.3 and 11 hours. Figure ES-17 shows concentrations of DBPs after 11 hours of residence time in the distribution system. Decreases of 13 μg/L and 8.7 μg/L were observed for TTHMs and HAAs, respectively, after implementation of ozonation with subsequent chlorination. A 2.3 μg/L increase in chloral hydrate was observed. After ozonation, HANs were decreased by 1.2 μg/L, and small increases were observed for HKs and chloropicrin. The cyanogen chloride analysis was not performed during the ozonation trial, and this compound was only slightly detected during the chlorine-only trial.

Sampling at Utility 25 was conducted at full scale at a 90-mgd conventional treatment facility. Samples were collected before the plant went on-line with two-stage ozonation. Chloramines-only treatment was utilized before ozonation was implemented, with disinfectant addition limited to the concurrent addition of ammonia (1.6 mg/L) and chlorine (8.0 mg/L) at the rapid mix. After the ozone system was placed on-line, ozone was applied to both the raw and settled water at 4.0 mg/L per stage, and chlorine (5.0 mg/L) and ammonia (1.0 mg/L) were added concurrently prior to filtration. Samples were collected at various points in the plant: 2nd-stage ozone contactor influent (2OI), filter influent (FI), filter effluent (FE), clearwell effluent (CE); and at four distribution system locations: at 4 to 5 hours of residence time (L1), 8 to 9 hours of residence time (L2), 9 to 10 hours of residence time (L3), and 18 to 20 hours of residence time (L4). Figure ES-18 presents the profile of TTHM concentrations through the plant and distribution system. The data show that for both treatment scenarios, THMs were formed immediately after chlorine and ammonia addition and remained stable through the plant and into the distribution system, but TTHM concentrations were significantly lower after ozone was incorporated into the plant's treatment process. The same trend was observed for levels of XDBP$_{sum}$ and HAAs. The unexpectedly high levels of DBPs produced by chloramines-only treatment at Utility 25 may have been due to poor mixing upon concurrent addition of chlorine and ammonia, and/or to the high influent TOC concentration of this utility's source water (7.7 mg/L). Concentrations of chloropicrin and ALDs were substantially higher in the plant and distribution system during the ozonation trial compared to the chloramines-only experiment.

At Utility 36, a 5-gpm pilot plant was employed to evaluate the effect of five different treatment scenarios on the formation of DBPs. Conventional treatment was employed with options to add preozonation (2 mg/L), with and without hydrogen peroxide addition (0.67 mg/L), and free chlorine (6.5 mg/L) or chloramines (2.1 mg/L chlorine and 0.5 mg/L ammonia) as disinfectants in the rapid mix. Samples were collected from the filter effluent and held for 24 hours at ambient temperature in order to simulate the residence time in a distribution system. Figure ES-19 illustrates the effect of the five different disinfection schemes on various DBP classes and chloral hydrate. The highest levels of TTHMs, HAAs, HANs and chloral hydrate were observed with those disinfection schemes which employed chlorine as the final disinfectant. Preozonation/postchlorination appeared to slightly increase the level of TTHMs and slightly decrease the concentration of HAAs; chloral hydrate was increased. Large decreases were observed under any disinfection scheme which employed chloramines as a disinfectant. For example, as compared to chlorine-only treatment, chloramines-only,

EFFECT OF VARIOUS DISINFECTION SCHEMES ON DISINFECTION BY-PRODUCTS FORMATION AT UTILITY 19
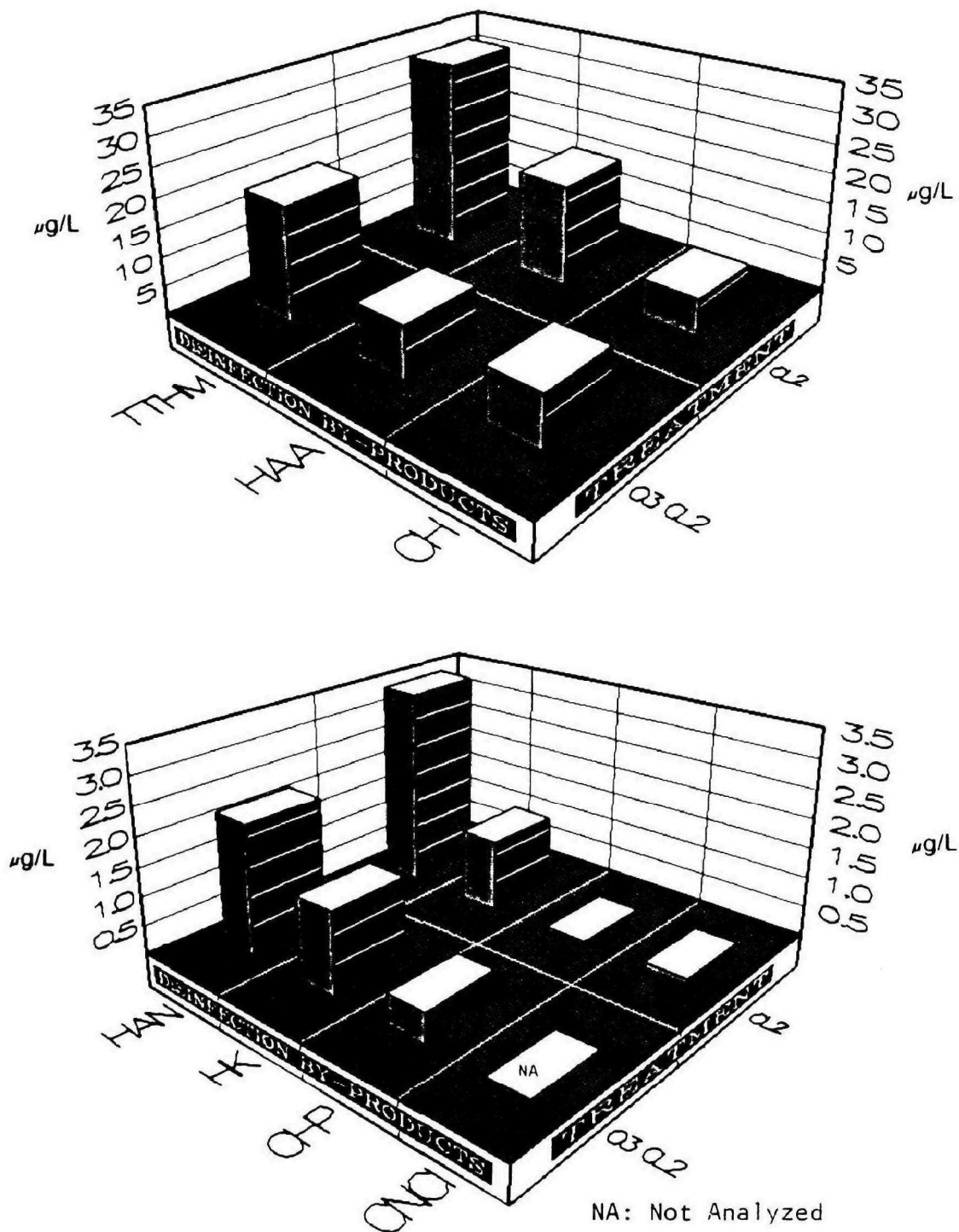
FIGURE ES-17

Effects of NH2Cl and O3/NH2Cl Treatment
on Total THM Formation at Utility 25

NA = Not analyzed
** = No lime addition

NH2Cl
O3/NH2Cl

Treatment & Residence Time
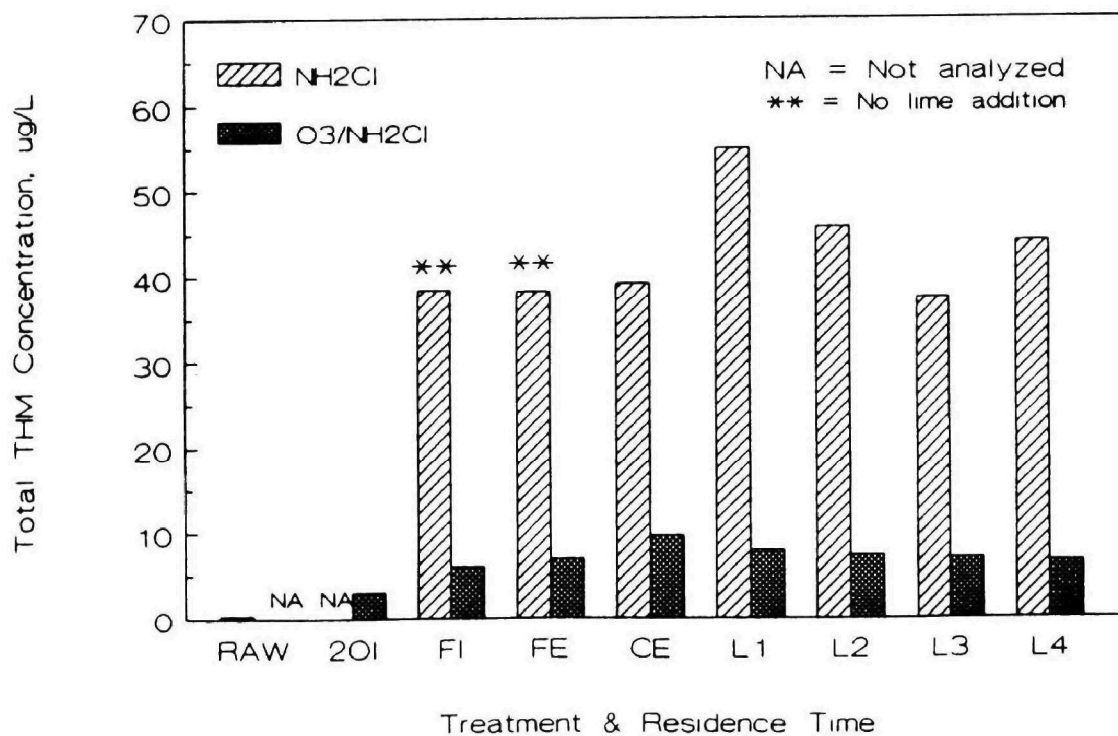
FIGURE ES-18

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY—PRODUCT FORMATION AT UTILITY 36
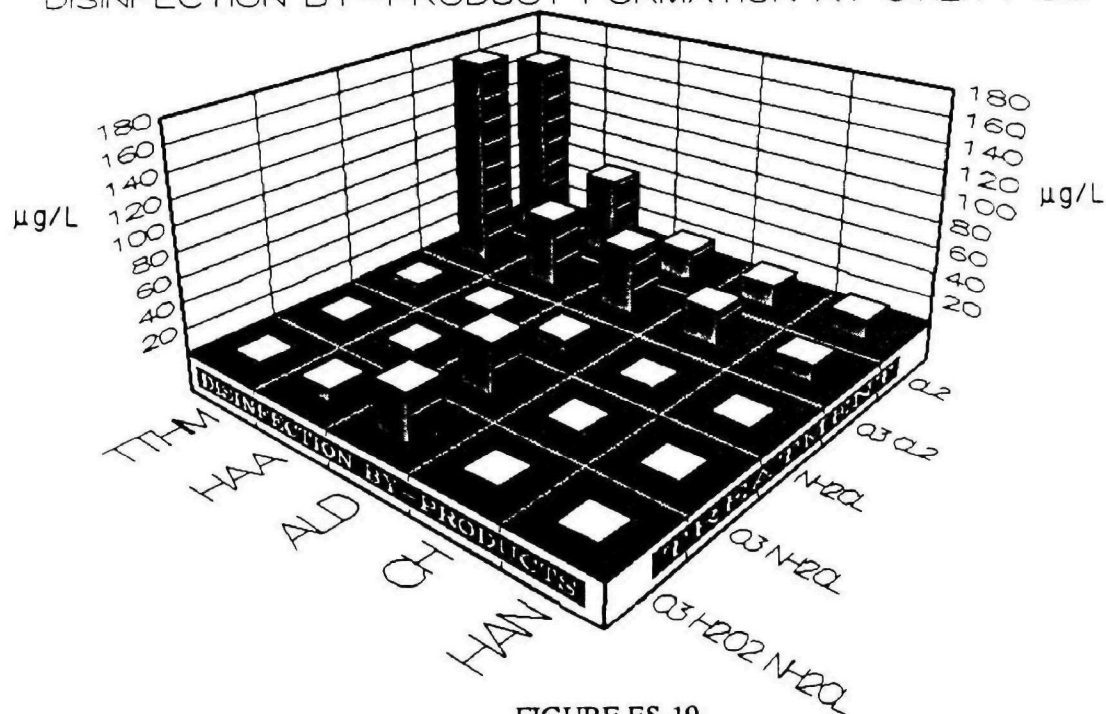
FIGURE ES-19

ozone/chloramines and ozone/hydrogen peroxide/chloramines decreased TTHM levels by 96, 97 and 98 percent, respectively.

At Utilities 19 and 36, the use of preozonation/postchlorination resulted in a shift to the brominated THMs and HAAs. Ozone can react with bromide ions in the raw water causing the formation of hypobromous acid (HOBr). Reactions of HOBr with natural organic material can produce bromoform, dibromoacetic acid, and other brominated DBPs. This was found to occur even at a utility with low levels of influent bromide, such as Utility 19, which typically treats water having an influent bromide concentration of only 0.04 mg/L.

Ozonation was found to increase aldehyde concentrations at Utilities 6, 25 and 36. Aldehydes were not measured at Utilities 7 and 19 during the treatment modification studies. However, subsequent pilot testing at Utility 7 indicated that aldehydes were formed in the ozone contactors. When the pilot filters at this utility were operated without the upstream addition of a secondary disinfectant, aldehyde concentrations in the filter effluent were lowered to detection limits or below, suggesting that biological activity within the filter bed was responsible for aldehyde removal. Utilities 6, 19, 25 and 36 employed secondary disinfection prior to filtration and, thus, may have precluded or reduced the potential for aldehyde removal within their filters. Furthermore, when Utility 7 applied chloramines before the pilot filters, aldehyde concentrations were not reduced through the filtration step.

Chlorine Dioxide Studies

Chlorine dioxide studies were conducted at two utilities. Both studies evaluated the combination of chlorine dioxide/chlorine as a DBP control method compared to free chlorine.

Utility 16 operates a 400-mgd direct filtration treatment system with free chlorine for both preoxidation and final disinfection, but periodically switches to chlorine dioxide preoxidation to control THMs and taste and odor. Samples were collected in the plant and at two distribution system locations (approximate residence times of 45 minutes and 7 days). On the chlorine-only sample date, chlorine doses were 2.0 mg/L at the plant influent and 1.0 mg/L at the filter effluent. For the chlorine dioxide test, the chlorine dioxide dose was 0.5 mg/L at the plant influent and the chlorine dose was 1.9 mg/L at the filter effluent. Figure ES-20 illustrates levels of DBPs measured in the distribution system. There were very little differences observed in DBP levels produced by the two different oxidation/disinfection schemes.

Utility 37's 30-mgd treatment facility provides for two separate treatment trains, one of which has provision for chlorine dioxide preoxidation, and one which employs free chlorine. Both treatment trains have free chlorine as a final disinfectant. For this study, 0.9 mg/L of chlorine dioxide was added to the flocculator effluent of one treatment train, and 2.25 mg/L of chlorine was added to the other treatment train for preoxidation. Although detectable levels of free chlorine were measured in the chlorine dioxide treatment train, and vice versa, the preoxidant in one treatment train was predominantly chlorine dioxide (referred to as "chlorine dioxide" treatment), and in the other train, the preoxidant was predominantly chlorine (referred to as "chlorine" treatment). Samples were collected at the plant's sedimentation basin effluent, after a

residence time of approximately 2.5 hours and before chlorine was added for residual disinfection. Figure ES-21 shows the effect of the two different preoxidants on the sum of measured halogenated DBPs and the DBP classes. From this figure, it is apparent that even in the relatively short detention time in the sedimentation basins, the use of chlorine dioxide preoxidation resulted in lower levels of all measured DBPs compared to chlorine treatment. $XDBP_{sum}$ was almost 50 percent lower with chlorine dioxide treatment.

Coagulation Studies

Coagulation studies were conducted at two utilities to evaluate the effect of coagulant dose on DBP formation. These utilities were selected because they had the capabilities to adjust alum doses at full scale without severely compromising the quality of their finished water.

Utility 3 operates a conventional treatment facility with a 10.5-mgd capacity. Alum doses were varied from low (10 mg/L) to medium (19 mg/L) to high (40 mg/L) for the study, and coagulation pH was held constant at pH 5.5. Chlorine was not added until the clearwell influent; therefore, samples were collected at the filter effluent and 24-hour SDS tests were conducted using a chlorine dose of 3.5 mg/L. Removal of TOC increased from 25 to 50 percent in the filter influent as the alum dose increased from 10 to 40 mg/L. At the low alum dose, a greater percent of TOC was removed through filtration (20 percent) than at the medium and high alum doses (15 and 9 percent, respectively). This was most likely due to the better settling characteristics of the floc at the higher doses. Figure ES-22 illustrates the effect of increasing alum dose on $XDBP_{sum}$ and the DBP classes. In general, DBPs decreased with increasing alum dose. $XDBP_{sum}$ was lowered from 150 to 94 μg/L, and TTHMs from 86 to 55 μg/L as alum doses increased from 10 to 40 mg/L.

The study at Utility 12 was conducted at a conventional treatment facility with a capacity of 72 mgd. Chlorine was added at two locations in the plant: before the rapid mix (1.8 mg/L dose) and before filtration (1.3 mg/L dose). The total chlorine contact time was approximately 100 minutes. Ammonia was added approximately 4 minutes after filtration, prior to the clearwell. Samples were collected at the plant influent, sedimentation basin effluent, filter effluent and clearwell effluent. Alum doses were varied from low (24.6 mg/L) to medium (45.7 mg/L) to high (73 mg/L) for the study. Since the plant had no capability to control pH before or during the sedimentation process, the pH values decreased as the alum doses increased. The low alum dose removed 33 percent of the influent TOC, while the medium and high alum doses removed 47 and 46 percent, respectively, as measured in the filter effluent. Most of the TOC removal occurred in the sedimentation basins, with little or no additional removal occurring through filtration. Figure ES-23 illustrates the effect of alum dose on DBP concentrations by class. For $XDBP_{sum}$, concentrations decreased from 87 to 69 μg/L as the alum dose increased from 25 to 75 mg/L. For TTHMs, the levels decreased from 53 to 39 μg/L. In general, individual THMs and HAAs decreased slightly with increasing alum dose; little or no change was observed for HKs, HANs or ALDs. That greater DBP removal was not observed with increasing alum dose was due to the utility's prechlorination practices. Approximately 1.8 mg/L of free chlorine was added to the raw water, with 75 minutes of contact time from the point of addition to

Effect Of Cl2 and ClO2/Cl2
on DBP Formation (Utility 16)
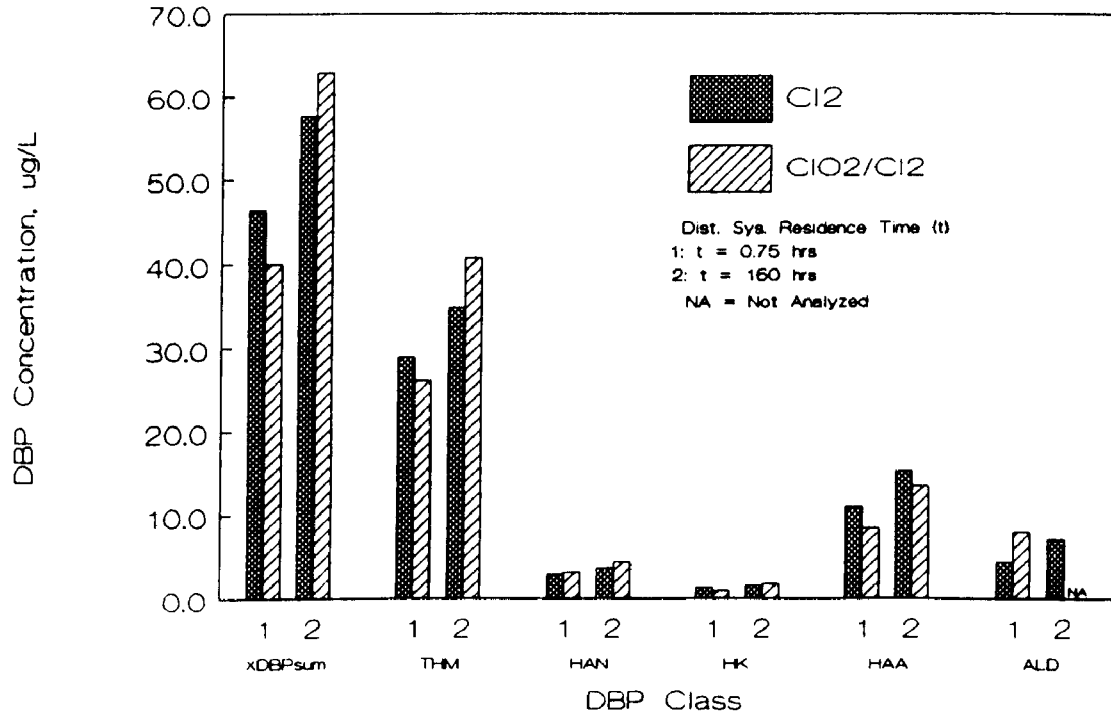
FIGURE ES-20

Effect of Cl2 AND ClO2
on DBP Formation (Utility 37)
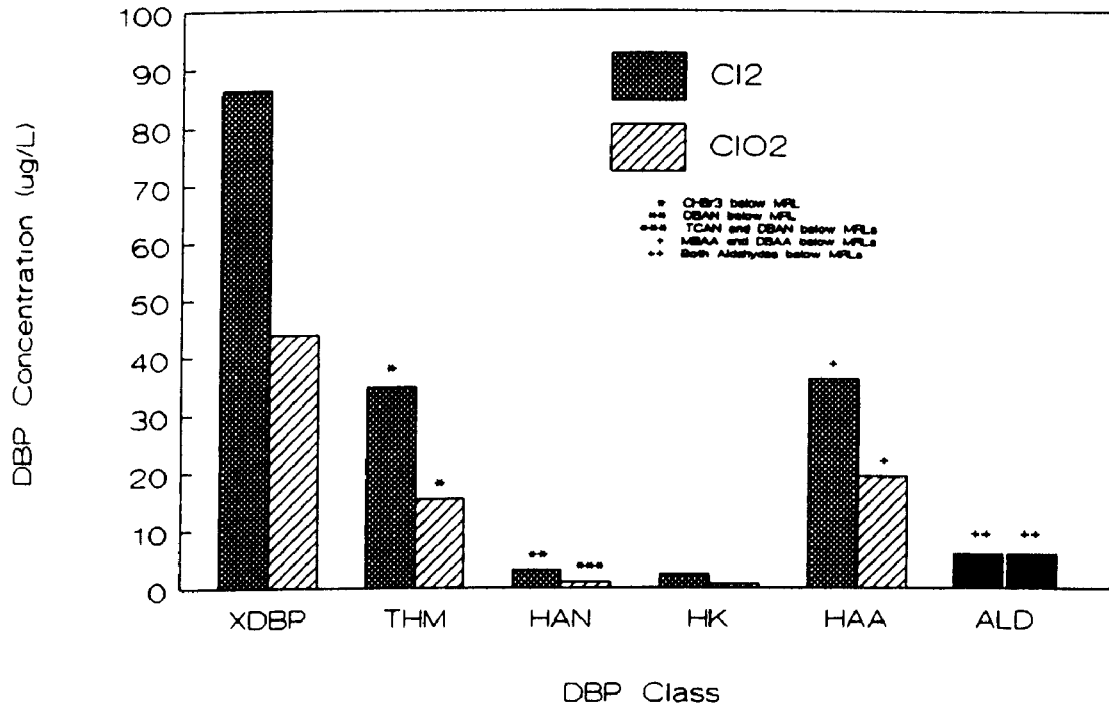
FIGURE ES-21

Effect of Alum Dose
on DBP Formation (Utility 3, SDS)
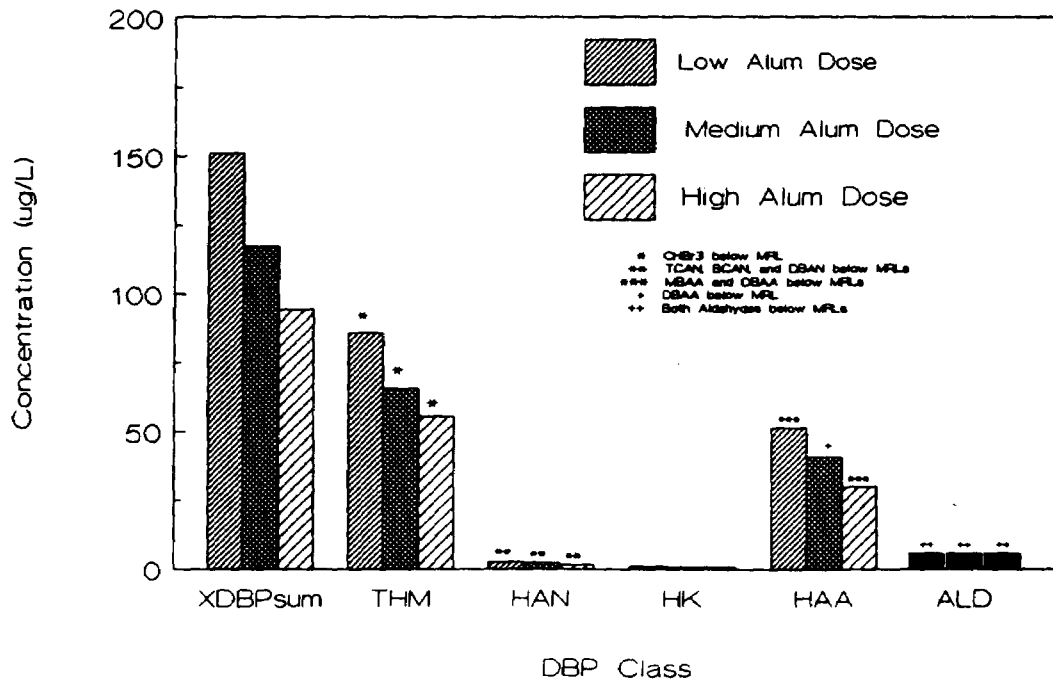
FIGURE ES-22

Effect of Alum Dose
on DBP Formation (Utility 12)
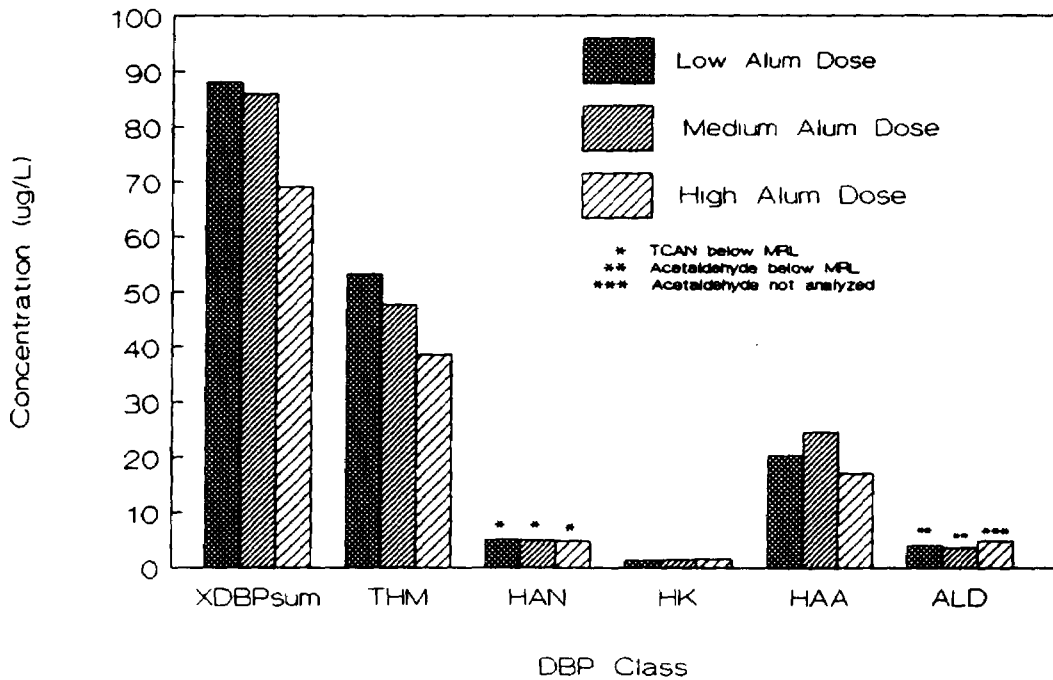
FIGURE ES-23

the sedimentation basin effluent. Consequently, DBP formation occurred before and during TOC removal processes.

As discussed previously, mean overall TOC removal through the filtering plants participating in the baseline sampling program was 24 percent. It is important to note that for those utilities capable of increasing TOC removal by increasing applied alum doses, the enhanced precursor removal represents only an incremental increase over that achieved under normal operation. For example, at Utility 12, TOC removals of 24 to 35 percent were observed from plant influent to clearwell effluent during baseline data collection (normal operation), and TOC removals up to 47 percent were achieved by increasing alum doses in the treatment modification study.

Granular Activated Carbon Study

The granular activated carbon (GAC) study involved the collection of samples in Utility 11's 235-mgd conventional treatment facility and 2-mgd GAC demonstration plant over a period of approximately 4 months. Unchlorinated water was diverted from the conventional plant after presedimentation (alum and polymer addition followed by lamella separation and 3-days of off-line storage), and through a rapid sand filter before application to the GAC column. The GAC was Filtrasorb 400 (12 x 40 mesh) and the column was operated with an empty bed contact time of 15 minutes. Samples were collected at the GAC column influent and effluent and 3-day SDS tests were performed using 4.5 mg/L of chlorine in order to evaluate DBP production. Samples were collected on GAC column Run Days 0.2, 13, 25, 54, 82 and 95. The TOC removal performance of the GAC column is illustrated in Figure ES-24. The GAC was very effective for TOC removal at Utility 11, although research at other utilities indicates that this technology has site-specific benefits. For the first 25 run days, the column effluent TOC remained the same as that measured on Run Day 0.2 (0.1 mg/L), which represents the non-adsorbable fraction of the TOC. On Run Day 54, the column effluent TOC had only increased to 0.2 mg/L, and it was not until the 82nd run day that a substantial increase in column effluent TOC was observed (0.6 mg/L). The impact of TOC removal on levels of SDS THMs is illustrated in Figure ES-25. This figure shows that SDS TTHMs were extremely low (approximately 6 μg/L or less) in the column effluent for the first 54 run days, indicating very effective removal of THM precursors. After 82 run days, SDS TTHMs had increased to 34 μg/L and after 95 run days, SDS TTHMs were 47 μg/L. Comparing levels of SDS TTHMs in the column influent and effluent, GAC treatment led to reductions in SDS TTHM levels of >97, >92, >97 and >96 percent on each sampling day through the 54th run day, and 71 and 65 percent on the 82nd and 95th run days, respectively.

Despite the low bromide levels in Utility 11's raw water (less than or equal to 0.06 mg/L), GAC effluent SDS samples on the 82nd and 95th run days had levels of bromoform and dibromoacetic acid that exceeded levels in the GAC influent SDS samples. The increase in the percentage of brominated THMs and HAAs may be due, at least in part, to the increased ratio of bromide to precursor material after significant levels of TOC have been removed in the GAC contactor.

TOC vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+GAC Inf   Δ·····ΔGAC Eff
Immediate   Immediate
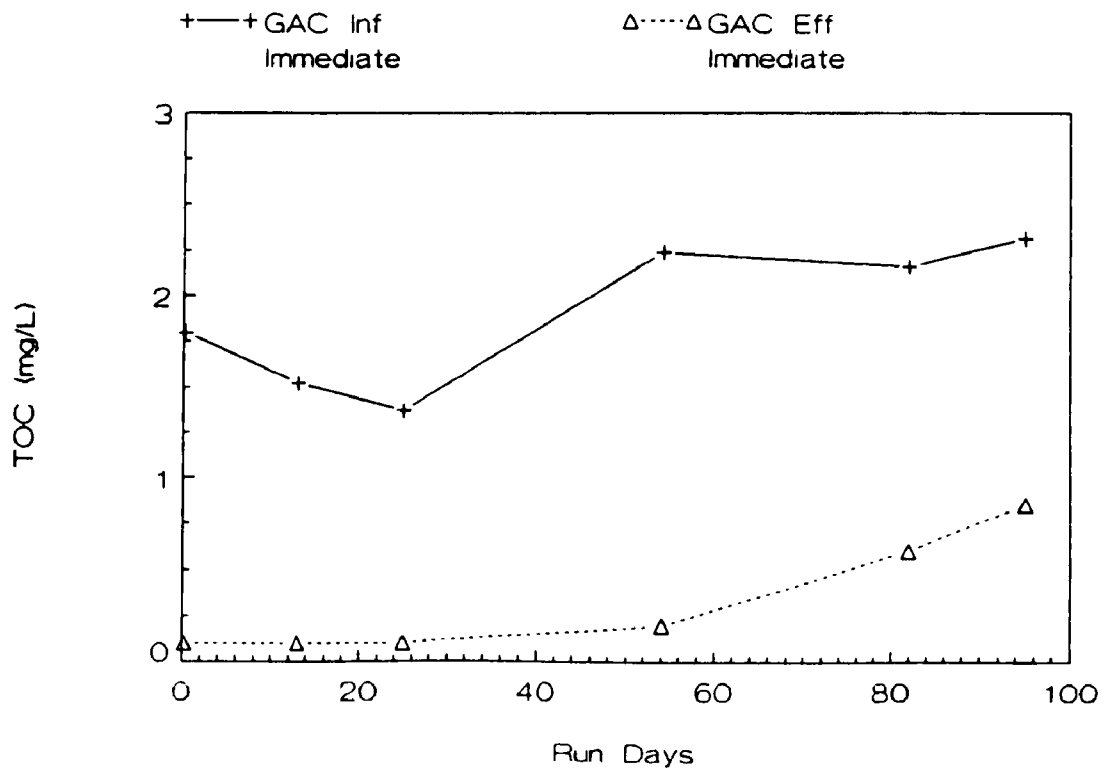
FIGURE ES-24

SDS TTHMs vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+GAC Inf   Δ·····ΔGAC Eff
3-day SDS   3-day SDS
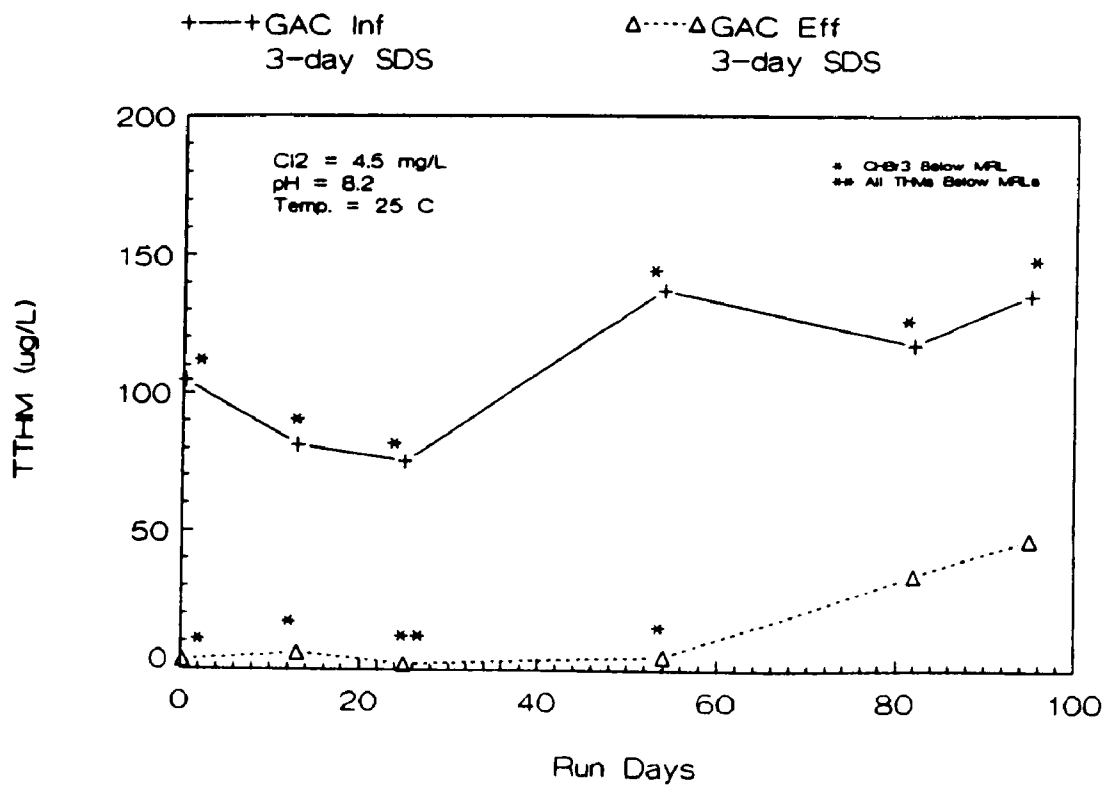
FIGURE ES-25

SUMMARY AND CONCLUSIONS

THMs. on a weight basis, represented the largest class of DBPs measured in this study and the median TTHM value for the four quarters of baseline sampling of clearwell effluents was 39 μg/L (computed as the median of running annual average TTHMs for each individual utility). HAAs were the second largest fraction detected, and aldehydes were the third largest. Little difference was observed in the concentrations of influent water quality parameters and concentrations of DBPs on a seasonal basis when considering the overall medians for all 35 participating utilities: however, seasonal variations were observed for individual utilities. In addition, levels of $XDBP_{sum}$ and TTHMs were found to depend on water temperature.

The numerous correlations conducted for this study indicated that TTHMs correlated well with the sum of halogenated DBPs measured in this study and with some DBP classes (e.g., HANs), while correlations between THMs and other classes of DBP compounds (e.g., HKs) were low; that bromide levels could be predicted from chloride concentrations; and that bromide present in raw waters impacted the speciation of THMs, HANs and HAAs. In addition, the shift in speciation to brominated DBPs occurred even in inland utilities not impacted by saltwater intrusion, and in waters low in bromide after preozonation or GAC treatment.

Ozone in conjunction with chlorine or chloramines as final disinfectants was generally effective in lowering concentrations of classes of halogenated DBPs. The extent to which halogenated DBP levels were decreased or increased after implementation of ozonation depended primarily on the final disinfectant which was employed. Aldehyde levels were found to increase upon ozonation, although it was found in one case possible to remove aldehydes within the treatment plant when filters were operated without a residual disinfectant.

Chlorine dioxide was effective for controlling DBPs at one utility, while at another, no difference from DBP levels resulting from the utility's normal chlorination practices was observed. Coagulation was effective in removing DBP precursors at the two utilities studied, as long as chlorine was not added before the DBP precursors were removed in the coagulation, flocculation, sedimentation and filtration processes. GAC was an effective technique for controlling levels of DBPs by removing precursors at the one utility studied.

Section 1

Introduction

SECTION 1

INTRODUCTION

The United States Environmental Protection Agency (USEPA) will be developing regulations to control disinfection by-products (DBPs) in drinking water as a result of the 1986 amendments to the Safe Drinking Water Act (SDWA). Under these amendments. the USEPA is required to develop a priority list of chemicals that may be present in drinking water and to develop maximum contaminant levels (MCLs) for those compounds. Included on this list are disinfectants, trihalomethanes (THMs) and other DBPs. Although the schedule for promulgation of regulations under the SDWA amendments remains uncertain at this time, the USEPA anticipates proposing DBP regulations in September, 1991 and finalizing the regulations by September, 1992. If the provisions of the SDWA are to be met within the required regulatory timetable, the presence and control of the target DBPs must be fully understood.

PROJECT BACKGROUND AND OBJECTIVES

In October. 1987. the Association of Metropolitan Water Agencies (AMWA) entered into a cooperative agreement with the USEPA to develop information on the formation and control of DBPs in full-scale drinking water treatment systems. AMWA contracted with the Metropolitan Water District of Southern California (Metropolitan) to perform the study. Engineering services for the study were provided by James M. Montgomery, Consulting Engineers, Inc. (JMM) through a subcontract with Metropolitan.

Project Objectives

The principal objective of the study was to collect data from representative water utilities in the United States on the occurrence and control of DBPs in drinking water.

Specific objectives of the project included:

o   Determine the occurrence of DBPs at 25 drinking water treatment facilities around the nation. Facilities were selected to provide a broad range of source water qualities and treatment processes.

o   Determine the seasonal nature of the occurrence of DBPs as a function of temperature, total organic carbon (TOC), pH, and other water quality parameters.

o   Determine the effect of changes in treatment processes and/or disinfectants on the production of DBPs at bench, pilot and/or full scale at up to 10 drinking water treatment facilities.

The study focused on the identification of DBPs expected in United States drinking waters as a function of source water quality, water treatment process selection and operation, and disinfection processes and chemicals. Previous studies or those currently underway at the USEPA have been designed to define the occurrence and levels of DBPs in a broad sampling of water treatment systems. This study, however, focused

on the relationships between source water quality, processes employed at water treatment facilities, and the level and frequency of occurrence of DBPs.

Target Compounds

The DBPs of interest to the project are listed in Table 1-1, and include THMs, haloacetonitriles (HANs), haloketones (HKs), haloacetic acids (HAAs), chloropicrin, chloral hydrate, cyanogen chloride. 2,4,6-trichlorophenol, and aldehydes (ALDs). The chemical structure of each of the target compounds is illustrated in Figure 1-1.

All of the halogenated DBP compounds selected for study appear on the USEPA's Drinking Water Priority List of contaminants expected to be regulated by 1991. The aldehydes (formaldehyde and acetaldehyde) were added to the study since ozonating utilities were included in the study and these compounds have been identified as by-products of the ozonation process (and speculated to be chlorination by-products as well). In addition, the USEPA is considering the regulation of these aldehydes as part of an ozone DBP priority list.

California Department of Health Services/California Public Health Foundation DBP Study

The USEPA DBP project was conducted in conjunction with a similar study being funded by a grant from the California Department of Health Services (CDHS) and the California Public Health Foundation (CPHF). Metropolitan and JMM also conducted the CDHS study. The CDHS study involved 10 utilities around the State of California selected to provide a broad range of source water qualities and treatment processes. The CDHS study focused on utilities with source waters representative of supplies used by the majority of consumers in California.

Conducting the two studies simultaneously has been beneficial for both the USEPA and the CDHS. Data for all 35 utilities involved in the combined studies has been available to both funding agencies by providing each agency with copies of progress reports prepared for the other agency's study. In addition, the combined USEPA/CDHS studies provided the opportunity to study a larger number of utilities, allowing a more representative selection of utilities. Data in this report reflect results from the 35 utilities participating in the combined USEPA/CDHS studies. A separate report was prepared for the CDHS study (Metropolitan, 1989), focusing on the 10 California utilities.

PROJECT DESCRIPTION

The USEPA project has been conducted over a period of two years. The first year of the project (October, 1987 through September, 1988) focused on establishing and verifying the analytical procedures at Metropolitan's Water Quality Laboratory, selecting utilities to participate in the study, developing DBP baseline data through implementation of a quarterly sampling program at the 25 utilities, and performing process modification studies at two utilities. During the second year of the project (October, 1988 through September, 1989), baseline data collection was completed and process modification studies were conducted at six utilities. Project status has been summarized in quarterly progress reports submitted to the USEPA.

TABLE 1-1

LIST OF COMPOUNDS TARGETED IN STUDY

Compounds

Trihalomethanes

  chloroform
  bromodichloromethane
  dibromochloromethane
  bromoform

Haloacetonitriles

  trichloroacetonitrile
  dichloroacetonitrile
  bromochloroacetonitrile
  dibromoacetonitrile

Haloketones

  1,1-dichloropropanone
  1,1,1-trichloropropanone

Miscellaneous chloro-organics

  chloropicrin
  chloral hydrate
  cyanogen chloride

Haloacetic acids

  monochloroacetic acid
  dichloroacetic acid
  trichloroacetic acid
  monobromoacetic acid
  dibromoacetic acid

Chlorophenols

  2,4-dichlorophenol*
  2,4,6-trichlorophenol
  pentachlorophenol*

Aldehydes

  formaldehyde
  acetaldehyde

* These chlorophenols were only analyzed for during the first sampling quarter.

TRIHALOMETHANES
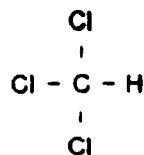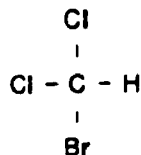
$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-H$$

CHLOROFORM

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-H$$

DICHLOROBROMO-
METHANE
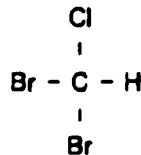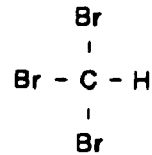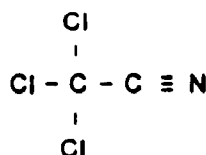
$$Br-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-H$$

DIBROMOCHLORO-
METHANE

$$Br-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-H$$

BROMOFORM

HALOACETONITRILES

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-C\equiv N$$

TRICHLORO-
ACETONITRILE

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C\equiv N$$

DICHLORO-
ACETONITRILE

$$Cl-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C\equiv N$$

BROMOCHLORO-
ACETONITRILE

$$Br-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C\equiv N$$

DIBROMO-
ACETONITRILE

HALOKETONES

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

1,1-DICHLOROPROPANONE

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

1,1,1-TRICHLOROPROPANONE

MISCELLANEOUS

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-NO_2$$

CHLOROPICRIN
(TRICHLORONITROMETHANE)

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-OH$$

CHLORAL HYDRATE

$$Cl-C\equiv N$$
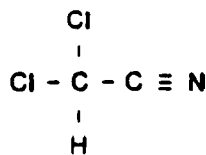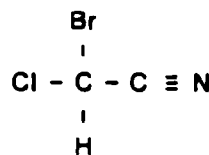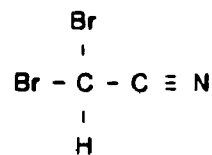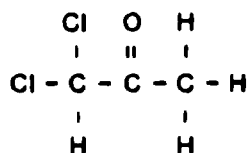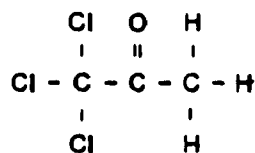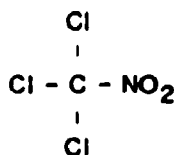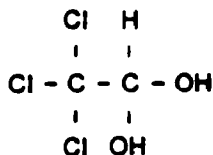
CYANOGEN CHLORIDE

Structural Formulas for Disinfection By-Products

FIGURE 1-1

HALOACETIC ACIDS
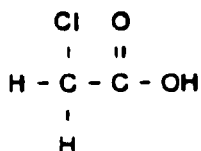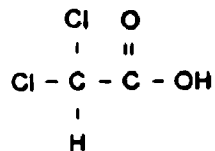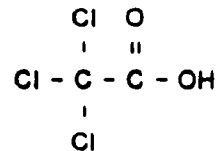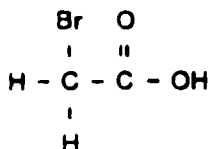
Cl O
| ||
H - C - C - OH
|
H

MONOCHLOROACETIC
ACID

Cl O
| ||
Cl - C - C - OH
|
H

DICHLOROACETIC
ACID

Cl O
| ||
Cl - C - C - OH
|
Cl

TRICHLOROACETIC
ACID

Br O
| ||
H - C - C - OH
|
H

MONOBROMOACETIC
ACID

Br O
| ||
Br - C - C - OH
|
H

DIBROMOACETIC
ACID

CHLOROPHENOLS

2,4-DICHLOROPHENOL

2,4,6-TRICHLOROPHENOL

PENTACHLOROPHENOL

ALDEHYDES

H   H
| |
H - C - C = O
|
H

ACETALDEHYDE

H
|
H - C = O
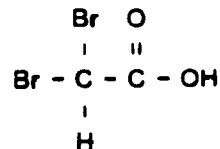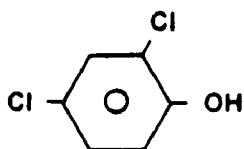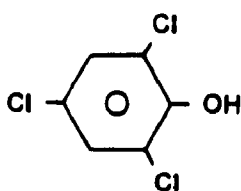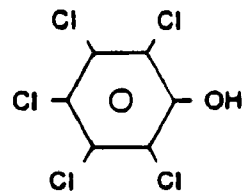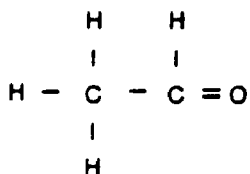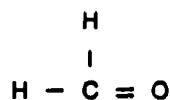
FORMALDEHYDE

Structural Formulas for Disinfection By-Products

FIGURE 1-1   (Continued)

Introduction

For the CDHS study, the first "year" of the project (February, 1988 through June, 1988) included utility selection, baseline data collection at the 10 utilities, and performance of process modification studies at two utilities. During the second year of the study (July, 1988 through June, 1989), baseline data collection was completed.

The major components of the project, the baseline data collection and the process modification studies, are described in more detail below. The utility selection process is described in Section 2 of this report.

Baseline Data Collection

A sampling schedule for the 35 utilities participating in the USEPA and CDHS studies was developed which provided for sampling of clearwell effluents (after final disinfection but before distribution) in the selected plants on a quarterly basis for one year. The first sampling date was March 14, 1988 and the fourth sampling was completed in February, 1989. The first sampling quarter (i.e., mid-March through April) corresponded to the spring season. The subsequent sampling quarters corresponded to the summer, fall and winter seasons (i.e., July through August, October through November, and late December through February, respectively). Furthermore, the utilities were sampled each quarter in the same order where possible. In this manner, each utility was sampled four times, each time representing different seasonal conditions in terms of temperature and water quality.

Utilities were sent coolers containing the sample bottles, packing material, blue ice, detailed sampling instructions and a sample information sheet. Utility personnel collected the grab samples at the designated sampling locations on the designated sampling dates. The utilities were asked to fill in the sample information sheet with plant operating information such as chemical dosages and locations of chemical addition on the day of sampling. After sampling, the utilities returned the sampling kits via overnight mail to Metropolitan for analysis.

The results of the baseline data collection achieved project objectives by providing information on the occurrence of DBPs on a seasonal basis at the selected utilities. These results are reported and discussed in detail in Section 5 of this report.

Treatment Modification Studies

Treatment modification studies are described in detail in Section 6 of this report. The utilities at which these studies were conducted were selected based on the representative nature of their normal treatment process, the flexibility offered by their treatment plant design or other facilities (i.e., pilot plant facilities), and their willingness to contribute resources to the study.

The principal goal of conducting the treatment modification studies was to identify, in a preliminary manner, the processes or process modifications having the greatest impact on DBP production. To achieve this goal, the following treatment modification studies were conducted:

o   Utility 3: Full-scale study of effects of alum dose on DBP precursor removal by coagulation at pH 5.5.

Introduction

o   Utility 6:   Full-scale study of effects of changing oxidant/disinfectant (chlorine/chloramines and ozone/chloramines).

o   Utility 7:   Pilot and full-scale study of effects of changing oxidant/disinfectant (chlorine only, chlorine/chloramines, and ozone/chloramines).

o   Utility 11:   Demonstration-scale study of granular activated carbon (GAC) adsorption for removal of DBP precursors.

o   Utility 12:   Full-scale study of effects of alum dose on DBP precursor removal by coagulation.

o   Utility 16:   Full-scale study of effects of changing oxidant/disinfectant (chlorine only and chlorine dioxide/chlorine).

o   Utility 19:   Full-scale study of effects of changing oxidant/disinfectant (chlorine only and ozone/chlorine).

o   Utility 25:   Full-scale study of effects of changing oxidant/disinfectant (chloramines and ozone/chloramines).

o   Utility 36:   Pilot study of effects of changing oxidant/disinfectant (chlorine only, chloramines only, ozone/chlorine, ozone/chloramines and ozone/hydrogen peroxide/chloramines).

o   Utility 37:   Full-scale study of treating parallel trains with different preoxidants/disinfectants (chlorine and chlorine dioxide).

Eight of the treatment studies were performed for the USEPA study and two were performed for the CDHS study.   Utilities 36 and 37 were selected for process modification studies but did not participate in the baseline sampling program.   The results of all ten studies are reported and discussed in Section 6.

Section 2

Utility Selection

SECTION 2

UTILITY SELECTION

Twenty-five utilities around the United States were selected for participation in the USEPA project. The first task of the selection process was the development of a criteria matrix and an information request to be filled in by potential participants. Then the potential utilities were screened and the utilities were selected for participation based on the criteria matrix developed for the study.

INFORMATION REQUEST

An information request packet was sent to 104 potential participants in the study, along with a cover letter introducing the study and providing some background information which would familiarize the recipients with the study and emphasize the study's importance to the water utility industry. The letter also indicated the level of commitment from each participant that would be required for the study. In some instances. a particular plant owned/operated by the utility was identified in the information request and in other cases where the utility had more than one treatment plant. they were asked to respond for the plant producing the highest levels of THMs. Copies of the information request form and cover letter are provided in Appendix A of this report.

The information request was to be filled in by each recipient, providing data on the plant's treatment processes, chemical doses and contact times, and the quality of the plant's raw water. finished water and distributed water. Responses were received from 78 utilities. a response rate of 75 percent.

Not only did the completed information requests provide the basis of the selection process. but as the study progressed. the information was a valuable reference for interpreting baseline data as they were collected.

SELECTION MATRIX

The 35 utilities (25 for the USEPA study and 10 for the CDHS study) were selected for participation in the study from those responding to the information request based on the following criteria:

- o Utility willingness to participate,
- o Disinfectant/oxidant(s) in use or available,
- o Source water type.
- o Source water quality,
- o Geographical location.
- o Treatment process configuration,
- o Ability to alter or segregate treatment processes, and
- o On-site pilot plant capabilities.

The resulting matrix of utilities is presented in Table 2-1. The matrix is divided into two major categories. treatment type (conventional. direct filtration, softening and

2-1

TABLE 2-1

DISINFECTION BY-PRODUCTS IN DRINKING WATER STUDY

UTILITY SELECTION MATRIX

TREATMENT	GROUNDWATER	LAKE/RESERVOIR	FLOWING STREAM
CONVENTIONAL	Clermont Co., OH 1 Long Beach, CA 2	Norwich, CT* 1B MWD, CA -Mills $2^a,5^b$ Arlington, TX* 2A Hackensack, NJ 2^e MWD, CA -Weym. 2 San Francisco, CA 1 Big Spring, TX* 5 Shreveport, LA $6^a,8^b$	Cape Girardeau, MO* 2A Cincinnati, OH 1 Contra Costa WD, CA 2A Sacramento, CA 1 Santa Clara Valley, CA 2 Newport News, VA 1A
DIRECT FILTRATION		East Bay MUD, CA 1 Las Vegas, NV 1 Little Rock, AR 1 Aurora, CO $1^aA,5^bA$	Los Angeles DWP, CA 3
SOFTENING	Palm Beach Co., FL 2 Wausau, WI* 1 Minot, ND 1 Santa Monica, CA 1	Macomb, IL* 1A Galveston,TX $7^c,4^d$	Louisville, KY 2 Ft. Meyers, FL* 1 Emporia, KN* 2A Omaha, NB 1A
DISINFECTION ONLY	Mesa Consol., CA 3	North Skagit Co., WA* 1 New York City, NY 1 Newark, NJ 1	

Note: Utilities participating in the California Public Health Foundation study are listed in bold type.
* Population under 50,000; all others over 50,000.

Key for chemical addition:

1 - chlorine only
2 - chlorine + chloramines
3 - ozone + chlorine
4 - chlorine + chlorine dioxide
5 - chloramines only
6 - chloramines + chlorine dioxide
7 - chlorine + chloramines + chlorine dioxide
8 - ozone + chloramines
A - powdered activated carbon
B - potassium permanganate

[a] - first quarter only
[b] - second through fourth quarters
[c] - first through third quarters
[d] - fourth quarter only
[e] - clearwell effluent sampled
    before ammonia addition

disinfection only) and source water type (groundwater, lake/reservoir, and flowing stream). Within these categories, geographical location and disinfectant type (free chlorine. chloramines, chlorine dioxide, and/or ozone) were also considered. Population was also used as a category in developing the selection matrix (<50,000 and >50,000). as was TTHM level (<25 μg/L, 25 to 50 μg/L, and >50 μg/L).

The selection process was aided by data from the THM survey conducted for the American Water Works Association Research Foundation (AWWARF) in 1987 (McGuire and Meadow. 1988). Using the AWWARF data plus the questionnaire responses. the selection process was aimed at filling the utility selection matrix as completely as possible based on the criteria described above.

To illustrate the nation-wide distribution of the selected utilities. a map showing their locations is presented in Figure 2-1. It should be noted that 10 of the 11 participating utilities in California were involved in the CDHS study.

PROCESS TRAINS OF THE PARTICIPATING UTILITIES

Simplified schematics of the process trains employed at each participating utility are shown in Figure 2-2 by utility identification number. The figure indicates that of the 35 utilities participating in the combined USEPA and CDHS studies:

- o Sixteen utilized a conventional treatment process with coagulation, flocculation. sedimentation and filtration;
- o Five employed a direct filtration treatment process;
- o Ten softened; and
- o Four employed disinfection only.

The schematics, in addition to the information provided in Table 2-1. indicate the following disinfection schemes for the participating utilities (during the majority of baseline data collection):

- o Nineteen of the utilities used only free chlorine throughout their treatment trains and as a final disinfectant;
- o Nine utilities used free chlorine and provided for some free chlorine contact time before the addition of ammonia (either with or without further chlorine addition) to form chloramines as the final disinfectant;
- o Three utilities used only chloramines (concurrent addition of chlorine and ammonia. with no free chlorine contact time) throughout their treatment trains and as a final disinfectant;
- o One utility employed chlorine with subsequent ammonia addition to form chloramines. in addition to chlorine dioxide;
- o Three utilities used ozone (two utilities employed ozone and free chlorine. and one utility utilized ozone, chloramines, and chlorine dioxide).

Several utilities had changes in their disinfection schemes during the course of the baseline sampling. For instance, Utility 4 changed from prechlorination/ postammoniation to concurrent addition of chlorine and ammonia after the first quarter. Utility 18 changed from chlorine to chloramines after the first quarter. Utility 25 switched from chloramines to ozone/chloramines after the 1st quarter. Utility 27, a

UTILITIES PARTICIPATING IN DBP STUDY

FIGURE 2-1

| AERATION | RAPID MIX | FLOCCULATION | SEDIMENTATION | FILTRATION |

UTILITY 1

UTILITY 2

UTILITY 3

UTILITY 4 *

* Configuration during last 3 quarters; during 1st quarter same as Utility 7

FIGURE 2-2

FIGURE 2-2 (Continued)

UTILITY 9

Lime
Chlorine
Polymer
Alum
Powdered Activated
Carbon (Intermittent)

Ammonia
Fluoride
Chlorine, Lime

UTILITY 10

Ammonia
Chlorine
Lime (Intermittent)
Alum

UTILITY 11

Alum
Polymer

Lamella Settler

Reservoir Storage (3 days)

Chlorine
Lime
Fluoride
Ferric Sulfate*

Hydraulic Jump

Chlorine

Chlorine

* Ferric Sulfate added intermittently (in use on 5/8/89, 6/12/89 and 7/17/89)

FIGURE 2-2 (Continued)

UTILITY 12

Chlorine
Alum
Powdered Activated
Carbon (Intermittent)

Lime, Fluoride
Chlorine, Polymer

Caustic Soda
Ammonia

UTILITY 13

Chlorine
Alum

Polymer
(Intermittent)

Chlorine
Lime

UTILITY 14

Chlorine
Polymer

Polymer

Chlorine
Alum

Meter
Box

Solids
Contact
Clarifier

Polymer

Chlorine
Ammonia

FIGURE 2-2 (Continued)

UTILITY 15

Alum
Chlorine
Fluoride

Chlorine
Lime

UTILITY 16

Chlorine

Polymer
Ferric Chloride

Sodium Hydroxide
Sodium Silicate
Chlorine

UTILITY 17

Chlorine
Alum

Lime, Phosphate
Fluoride, Chlorine

FIGURE 2-2 (Continued)

UTILITY 18 *

Chlorine, Polymer
Powdered Activated Carbon,
Ammonia

Polymer
Alum

Powdered Activated Carbon
Polymer, Fluoride
Ammonia

Chlorine
Ammonia
Fluoride

* Used Chlorine only during 1st quarter

UTILITY 19

Ferric Chloride
Polymer
Chlorine

Chlorine- intermittent

Chlorine

UTILITY 20

Chlorine

Powdered Activated Carbon
(Intermittent)

Alum
Lime

Chlorine, Fluoride
Phosphate, Lime

FIGURE 2-2 (Continued)

UTILITY 21

Chlorine
Lime
Polymer

Solids Contact Clarifier

Chlorine   Ammonia

UTILITY 22

Alum, Lime,
Activated Silica

Aeration

Solids Contact Clarifier

Recarbon-ation

Fluoride

Carbon Dioxide

Chlorine

UTILITY 23

Aeration

Lime
Sodium Aluminate
Polymer

Solids Contact Clarifier

Recarbon-ation

Fluoride
Phosphate
Chlorine

Carbon Dioxide

Chlorine

UTILITY 24

Chlorine

Aeration

Ion Exchange

Caustic Soda
Chlorine

FIGURE 2-2 (Continued)

UTILITY 25 *

Chlorine Dioxide

Chlorine
Ammonia

Chlorine**, Ammonia **
Alum
Polymer

Lime

Fluoride
Chlorine Dioxide

* No Ozonation during 1st quarter
** 1st quarter only.

UTILITY 26

Alum
Polymer
Lime
Powdered Activated Carbon
(Intermittent)

Solids
Contact
Clarifier

Recarbon-
ation

Chlorine

Carbon Dioxide

Chlorine

UTILITY 27 *

Chlorine Dioxide
Polymer

Lime
Ferric Sulfate

Solids
Contact
Clarifier

Polymer
Carbon Dioxide
Chlorine

Phosphate, Fluoride
Chlorine Dioxide
Ammonia

* Ammonia off-line during 4th quarter

FIGURE 2-2 (Continued)

UTILITY 28

Alum
Polymer

Chlorine

Fluoride
Carbon Dioxide

Ammonia
Lime
Soda Ash

Chlorine, Ammonia →

UTILITY 29

Alum
Polymer
Chlorine

Solids Contact Clarifier

Aeration

Solids Contact Clarifier

Chlorine
Phosphate →

Alum

Polymer
Lime, Chlorine

Chlorine →

UTILITY 30

Ammonia
Lime, Alum

Ammonia
Chlorine
Fluoride
Carbon Dioxide

Polymer
Chlorine

**Recarbon-
ation**

Carbon Dioxide →

Powdered Activated Carbon

FIGURE 2-2 (Continued)

FIGURE 2-2 (Continued)

prechlorine/postammonia/chlorine dioxide utility, had their ammonia off-line on the 4th quarter sampling date. Additionally, although Utility 6 employed prechlorination/ postammoniation, the clearwell effluent samples were collected before the ammonia addition point, therefore it is classified as a chlorinating utility.

In all, 35 utilities were each sampled four times during the course of baseline data collection, yielding 140 total data points. Of the 140 disinfection schemes in use during baseline data collection, 78 (or 56 percent) were free chlorine only, 40 (29 percent) were prechlorination/postammoniation, 11 (8 percent) were chloramines only, 8 (6 percent) were ozone/chlorine, and 3 (2 percent) were ozone/chloramines.

The schematics indicate the following coagulants were used by the utilities:

o   Seven of the utilities employed alum only;
o   Ten used alum with a polymer as a coagulant aid;
o   One utility used polymer as a primary coagulant;
o   Two used ferric chloride and polymer; and
o   Six utilities used no coagulant.

Additionally, the softening utilities used a variety of coagulants in several different combinations:

o   Lime plus polymer;
o   Lime, alum and polymer (three utilities);
o   Alum/polymer in one solids contact clarifier for color removal and lime/polymer in a second unit for softening;
o   Lime, alum and activated silica;
o   Lime, sodium aluminate and polymer;
o   Lime, ferric sulfate and polymer; and
o   Lime, alum, ferric sulfate, activated silica and polymer.

Eight of the 35 utilities utilized powdered activated carbon, at least on an intermittent basis. Only one utility added potassium permanganate as a preoxidant. One utility employed ion exchange for softening.
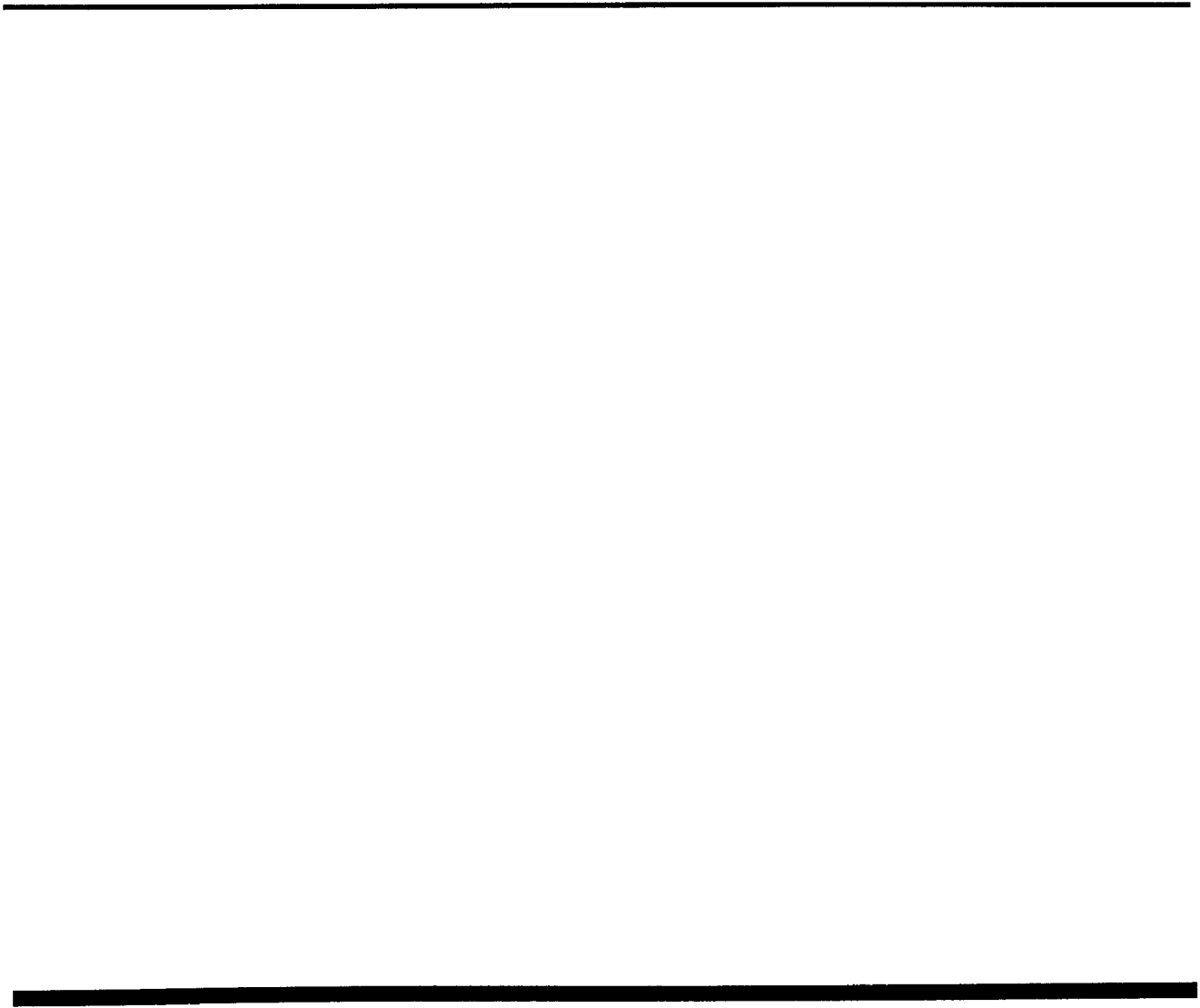
Section 3

Methodology

SECTION 3

METHODOLOGY

This section briefly describes the sampling and analytical methodology of the study. References are provided for further information. In addition, detailed analytical protocols are provided in Appendix C of this report.

SAMPLING PROCEDURE

The sampling instructions (Appendix B) included in each sampling kit provided detailed information to the utilities on how to properly sample for the study. A project engineer contacted each utility to arrange the sampling date for each quarter. At that time, if water quality conditions or treatment plant operations were deemed unacceptable (non-representative), the sampling date was postponed. Typically, on the sampling date, all sample collection was completed by a utility within 1 to 2 hours. Evaluation of plug flow conditions in each plant was not within the scope of the study.

Grab samples (see Table 3-1) were collected by utility personnel at clearwell effluents (after final disinfection but prior to distribution). Starting with the second sampling quarter, TOC samples were collected each sampling date at plant influents and filter influents. Also starting with that quarter, ultraviolet (UV) absorbance measurements were made at all three sampling points, the bromide and chloride levels of plant influents were determined, and formaldehyde and acetaldehyde analyses were made of the clearwell effluents. Some plant influents were analyzed for these aldehydes during the third sampling quarter; aldehyde determinations were made for all plant influents during the fourth sampling quarter.

Plant influent samples were collected at the head of the treatment plants and corresponded to "raw" water before the addition of disinfectant/oxidant, coagulant, lime, etc. This sampling location was important in enabling the characterization of the DBP precursors (i.e., as measured by TOC and UV-254) prior to the addition of any treatment chemicals. In addition, bromide measurements were made on plant influent water to determine the influence of this ion on the production of brominated DBPs. Since strong oxidants such as chlorine or ozone can convert bromide to hypobromous acid, bromide samples were collected upstream of the preoxidation point.

Samples were dechlorinated and/or preserved as outlined in Table 3-1 and were analyzed as soon as possible within established holding times. Holding times are described in Table 3-2. The dechlorination agents and preservatives for the DBP fractions were evaluated in holding studies to ensure that analyte concentrations held to +/- 20 percent of their initial values. Total organic halide (TOX) samples were dechlorinated with a sodium sulfite solution. Because sampling kits were prepared and shipped to field locations at least 2 weeks prior to sampling, the instability of the dechlorination solution required that TOX samples be dechlorinated and preserved upon receipt at the laboratory. Standard Methods (1985) establishes a 28-day maximum storage for bromide samples. This holding time is only applicable to unchlorinated samples, as an unquenched free chlorine residual can lower the level of bromide. In this study, bromide samples were collected upstream of chlorine addition points.

TABLE 3-1

SAMPLING KIT CONTENTS

Analytical Fraction	Sample Bottles Number	Size	Dechlorination Agent and/or Preservative[a]
Plant influent sample bottles:			
Formaldehyde/acetaldehyde	3,	40 mL	None; $HgCl_2$ solution + NH_4Cl crystals[b]
Bromide/chloride	1,	60 mL	None
TOC/UV	3,	60 mL	None[a]
Filter influent sample bottles:			
TOC/UV	3,	60 mL	None[a]
Clearwell effluent sample bottles:			
PE-DBPs[c]	3,	40 mL	65 mg NH_4Cl crystals
Chloral hydrate	3,	40 mL	20 mg ascorbic acid
Haloacetic acids[d]	4,	40 mL	65 mg NH_4Cl crystals
Cyanogen chloride	4,	40 mL	20 mg ascorbic acid
Formaldehyde/acetaldehyde	3,	40 mL	None; $HgCl_2$ solution + NH_4Cl crystals[b]
TOX	2,	250 mL	None[a]
TOC/UV	3,	60 mL	None[a]
Additional bottles in kit:			
Travel blank--NH_4Cl	2,	40 mL	65 mg NH_4Cl crystals
Travel blank--ascorbic acid	2,	40 mL	20 mg ascorbic acid
Travel blank--formaldehyde	2,	40 mL	None; $HgCl_2$ solution + NH_4Cl crystals[b]

[a]For the following analytical fractions, additional reagents are added after sampling as soon as possible after receipt at Metropolitan:
TOC/UV: Acidify with reagent-grade phosphoric acid to pH < 2.
TOX: Dechlorinate and acidify, respectively, by addition of ½ mL of 50% sulfuric acid and 3 drops (utilizing a 3½" pasteur pipette) of a fresh saturated sodium sulfite solution.

[b]No dechlorination agent and preservative used during second and third sampling quarter; 40 μL of a 10 mg/mL mercuric chloride solution plus 65 mg ammonium chloride crystals used during fourth sampling quarter.

[c]PE-DBPs (pentane-extractable disinfection by-products) are THMs. HANs. haloketones. and chloropicrin.

[d]Includes 2.4.6-trichlorophenol.

TABLE 3-2

SAMPLE HOLDING TIMES

Analytical Fraction	Sample Holding Limit	Extract Holding Limit
PE-DBPs	Extract immediately	2 weeks
Chloral hydrate	21 days	15 days
Haloacetic acids	9 days	7 days
Cyanogen chloride	Analyze immediately	Not applicable
Formaldehyde/acetaldehyde	Extract immediately	14 days
TOX	2 weeks	Not applicable
TOC/UV	28 days	Not applicable
Bromide/chloride	28 days	Not applicable

ANALYTICAL METHODS

A method was developed for the analysis of THMs, HANs, haloketones. and chloropicrin that employed modified THM liquid/liquid extraction (LLE) (Koch et al., 1988). For this analytical fraction, pentane was used as the extraction solvent, sodium sulfate was added to improve the partitioning from the aqueous phase to the solvent, and a capillary gas chromatograph/electron capture detector (GC/ECD) was utilized for adequate resolution of the analytes. The more polar chloral hydrate required a similar LLE method, but methyl t-butyl ether was used as the extraction solvent (Krasner et al., 1989). HAAs and 2,4,6-trichlorophenol were analyzed by an acidic, salted ether LLE, and they required esterification with diazomethane prior to GC/ECD analysis (Krasner et al., 1989). Cyanogen chloride was analyzed by a purge-and-trap gas chromatograph/mass spectrometer (GC/MS) method (Krasner et al., 1989). Formaldehyde and acetaldehyde were analyzed by a derivatization/extraction GC/ECD method (Yamada and Somiya, 1989; Glaze et al., 1989b)

The TOC measurements were performed according to the persulfate-ultraviolet Standard Method 505B (1985). TOC samples were acidified with reagent-grade phosphoric acid to a pH of less than 2 after receipt of the samples at Metropolitan's laboratory. This preservation technique was also used on UV samples. UV was measured at 254 nanometers (nm) with a UV-visible spectrophotometer (Lambda 5, Perkin-Elmer Corp., Norwich, CT) and a 1-cm quartz cell. The UV was also measured at 800 nm to provide a correction for the presence of turbidity or suspended solids. Because some plant effluent samples were chloraminated, monochloramine (which has UV absorbance at 243 nm) could have presented an interference problem. However, the acid preservation converted monochloramine to dichloramine in approximately 2 hours. The latter species has a UV peak at 293 nm, so it did not present an interference problem. To evaluate the effect of the phosphoric acid on the UV results, some unpreserved parallel effluent samples were also analyzed, and these yielded comparable results to the acidified samples.

Bromide and chloride analysis was conducted with an ion chromatograph (Model 2000, Dionex Corp.. Sunnyvale, CA), a 20-μL or 50-μL sample loop, a high-performance ion chromatography analytical column (AS4A, Dionex Corp.), an anion micromembrane suppressor. and a conductivity detector. The eluant was a solution of 2 millimolar Na_2CO_3 and 1 millimolar $NaHCO_3$.

The TOX analysis was performed using USEPA Method 9020 from SW 846 Test Method for Evaluating Solid Waste, Physical/Chemical Methods (Second Edition).

SIMULATED DISTRIBUTION SYSTEM TESTING

Some samples in this study were analyzed using a simulated distribution system (SDS) test protocol (Koch et al.. 1989) developed at Metropolitan. In this protocol, samples are chlorinated and incubated under conditions which simulate actual full-scale conditions in Metropolitan's distribution system. Typically, samples are chlorinated at a level which will leave a chlorine residual of at least 0.5 mg/L at the end of the incubation period. Firstly, this mimics typical distribution system practices of providing some minimal chlorine residual to consumers, and secondly, some DBPs are unstable when the chlorine residual has gone to zero. Samples are buffered to a pH of

8.2, which is consistent with many utilities' practice of corrosion control. Some DBPs will undergo some hydrolysis at this pH, as would be experienced in actual distribution systems operating at such a pH. The samples are incubated at 25°C, which will produce maximum levels of THMs and other DBPs, as would be experienced in summer months. The samples are incubated for one to three days, to provide a measure of DBP levels that would be expected in a distribution system with such a detention time. Most importantly, the use of standardized SDS conditions enables a consistent set of data to be produced that often cannot be realized in a distribution system which may be influenced by other confounding variables. Also, the use of SDS testing allows evaluation of expected distribution system DBP levels when studying pilot plant and demonstration-scale facilities (see Section 6).

For the GAC study at Utility 11 (see Section 6), SDS tests were performed. The SDS test was selected to provide a standard set of conditions by which to evaluate DBP precursor removal at Utility 11's GAC demonstration plant. For example, Utility 11's ambient water temperature ranged from 11 to 27°C during the course of the study. However, with SDS testing, all samples were incubated at 25°C. During the day 13 and day 25 samplings, some additional SDS tests were set up at ambient water temperature. The results are shown in Tables 3-3 and 3-4.

An SDS test can only mirror a limited number of actual operating conditions. For example, routine SDS samples at Utility 11 received a 4.5 mg/L chlorine dose, in order to provide adequate chlorine for a 3-day incubation period. However, the actual plant dosed different amounts of chlorine, depending on current demand requirements. In addition, the actual plant applied chlorine in three locations, two before conventional filtration and one after. The pH of SDS samples are buffered to a pH of 8.2 to 8.3, whereas the pH ranged from 8.4 to 8.8 in Utility 11's actual distribution system during the course of this study.

For some DBPs, the distribution value is between that detected in the two SDS tests at Utility 11 (Tables 3-3 and 3-4). For example, for the Day 13 testing, chloroform was 42, 31, and 55 μg/L in the distribution, ambient SDS, and standard SDS samples, respectively. At that same time, 1,1,1-trichloropropanone had values of 0.55, 1.2, and 0.28 μg/L, respectively. Since this ketone is an intermediate DBP (chloroform is the stable endproduct of 1,1,1-trichloropropanone), it appears as if the elevated temperature of the standard SDS test drove the reaction of 1,1,1-trichloropropanone hydrolysis the furthest. During the Day 25 testing, this ketone was detected at levels of 0.18, 1.5, and 0.36 μg/L in the distribution, ambient SDS, and standard SDS samples, respectively. The lowest ketone value was found in the distribution system where the elevated pH (i.e., 8.8) probably resulted in base-catalyzed hydrolysis of this DBP.

In general, though, the SDS tests yield comparable DBP levels as that detected in the actual distribution system. Unless noted, SDS tests were performed at the standard SDS condition of 25°C.

Another SDS consideration was that the GAC effluent would not have as high a chlorine demand as the GAC influent. Thus, GAC effluents were analyzed by two different SDS tests, one at a chlorine dose of 4.5 mg/L and another at 2.0 mg/L. The latter dose is a more realistic chlorine level for Utility 11's GAC effluent when TOC removal is high. Since the chlorine dose may influence the level of DBP production,

TABLE 3-3

UTILITY 11 GAC STUDY: DAY 13 DBP RESULTS

Parameter	Distribution System	Ambient SDS GAC Inf.[#]	SDS Blank	Standard SDS GAC Inf.[#]	SDS Blank
Temperature. °C	15	12	12	25	25
pH	8.7	8.41	8.51	8.44	8.51
Detention time/ incubation. days	3 (approx.)	3	3	3	3
Cl_2 dose*. mg/L		4.5	4.5	4.5	4.5
Cl_2 residual. mg/L	0.7	2.2	3.6	1.34	4.05
DBPs, μg/L:					
$CHCl_3$	42	31	0.70	55	0.79
$CHBrCl_2$	15	13	<0.22	20	0.29
$CHBr_2Cl$	6.0	4.8	<0.48	6.4	<0.48
$CHBr_3$	0.49	<0.91	<0.91	<0.91	<0.91
TCAN	<0.03	<0.03	<0.03	<0.03	<0.03
DCAN	1.8	2.0	<0.04	1.3	<0.04
BCAN	0.55	0.59	<0.19	0.71	<0.19
DBAN	0.64	<1.20	<1.20	<1.20	<1.20
1.1-DCP	0.34	0.80	0.35	0.70	0.18
1.1.1-TCP	0.55	1.2	<0.03	0.28	<0.03
MCAA	1.6	<1.7	<1.7	2.1	<1.7
DCAA	15	13	2.1	19	2.1
TCAA	9.4	7.9	<1.5	9.1	<1.5
MBAA	<0.5	<0.5	<0.5	0.5	<0.5
DBAA	1.4	1.0	<0.6	1.3	<0.6
Chloropicrin	0.60	0.42	<0.04	0.56	<0.04
Chloral hydrate	9.9	6.3	0.92	12	0.79

These SDS results are raw data before blank subtraction was performed.
* In SDS tests. entire Cl_2 dose delivered to GAC influent samples (conventional filtered water): whereas. distribution system sample received Cl_2 in plant at three locations--two before filters and one after filters.

TABLE 3-4

UTILITY 11 GAC STUDY: DAY 25 DBP RESULTS

Parameter	Distribution System	Ambient SDS GAC Inf.#	Ambient SDS SDS Blank	Standard SDS GAC Inf.#	Standard SDS SDS Blank
Temperature. °C	16	14	14	25	25
pH	8.8	8.22	8.29	8.28	8.29
Detention time/ incubation. days	3 (approx.)	3	3	3	3
Cl_2 dose*. mg/L	2.7	4.5	4.5	4.5	4.5
Cl_2 residual. mg/L	0.7	0.90	NA	1.0	NA
DBPs, μg/L:					
$CHCl_3$	52	33	0.88	53	1.1
$CHBrCl_2$	16	14	0.40	18	1.2
$CHBr_2Cl$	6.1	5.0	<0.48	5.8	0.54
$CHBr_3$	0.27	<0.91	<0.91	<0.91	<0.91
TCAN	<0.03	<0.03	<0.03	<0.03	<0.03
DCAN	0.75	1.6	<0.04	0.56	<0.04
BCAN	0.49	0.57	<0.19	0.36	<0.19
DBAN	0.20	<1.20	<1.20	<1.20	<1.20
1.1-DCP	0.25	0.76	<0.09	0.54	0.15
1.1.1-TCP	0.18	1.5	0.03	0.36	<0.03
MCAA	1.7	<1.7	<1.7	2.0	<1.7
DCAA	17	13	2.2	17	2.3
TCAA	8.4	8.3	<1.5	9.6	<1.5
MBAA	<0.5	<0.5	<0.5	<0.5	<0.5
DBAA	1.1	0.76	<0.6	0.94	<0.6
Chloropicrin	0.65	0.48	<0.04	0.50	<0.04
Chloral hydrate	11	6.9	0.70	10	0.50

These SDS results are raw data before SDS blank subtraction was performed.
* In SDS tests. entire Cl_2 dose delivered to GAC influent samples (conventional filtered water): whereas. distribution system sample received Cl_2 in plant at three locations--two before filters and one after filters.
NA = Not available.

Methodology

the GAC effluent was dosed at the same concentration as the GAC influent in order that comparisons could be made where the TOC level was the only variable.

A comparison of SDS data for the GAC effluent is made for the two SDS protocols used at Utility 11 (see Table 3-5). The standard SDS conditions for the GAC influent of a 4.5 mg/L chlorine dose and buffering to pH 8.2 were followed on one set of GAC effluents. The other set of GAC effluents received 2.0 mg/L chlorine and were not buffered (pH approximately 7.5). On Day 82, there was 0.60 mg/L of TOC in the GAC effluent, and the chlorine demand was 0.7 and 1.4 mg/L for the 2.0 and 4.5 mg/L dosed tests, respectively. On Day 95, there was 0.85 mg/L of TOC in the GAC effluent, and the chlorine demand was 1.0 and 1.5 mg/L for the 2.0 and 4.5 mg/L dosed tests, respectively. The difference in chlorine demands between the two SDS protocols may, in part, be related to the differences in pH of the two tests. On both days, the THMs were higher in the 4.5 mg/L chlorine dose tests; however, the difference was less pronounced when there was higher TOC present (i.e., 38 and 47 μg/L TTHMs in the 2.0 and 4.5 mg/L chlorine dose tests, respectively). The HANs and the 1,1,1-TCP were lower in the 4.5 mg/L chlorine dose tests. As these DBPs are reactive intermediates, the higher chlorine dose and pH probably resulted in their degradation (and resultant formation of other DBPs as stable endproducts).

SDS tests involve preparation of blanks (i.e., distilled water plus a bromide spike at the level occurring in the raw water). There are low levels of DBPs detected in SDS blanks. Whether these are formed due to DBP precursors in the distilled water, SDS bottle, reagents used, or a combination of these is uncertain. If the blank levels are due to precursors in the bottle and/or reagents, then SDS blanks should be subtracted from the SDS sample results. For example, the ambient SDS test performed on Day 13 samples from Utility 11 had 0.80 and 0.35 μg/L 1,1-dichloropropanone in the SDS sample and blank, respectively. If blank subtraction is performed, the difference of 0.45 μg/L compares well with the 0.34 μg/L found in the distribution sample. Thus, data reported in Section 6 reflect SDS blank subtraction.

SDS blank subtraction was performed in a previous GAC study performed by Metropolitan (McGuire et al., 1989). In the latter study, SDS samples of virgin GAC effluents each typically had levels of 1 to 2 μg/L of dichloroacetic acid (DCAA), when different empty bed contact times were evaluated in parallel (i.e., 7.5, 15, 30, and 60 minutes). One explanation was that this DBP formation was due to a nonadsorbable fraction of TOC. However, SDS blanks tended to have, within analytical error, the same values for DCAA, which tended to support that these levels were background levels in all samples. To resolve this issue for the current study, minimum reporting levels (MRLs) for SDS testing were calculated based upon the analysis of seven SDS blank samples (see discussion in Quality Assurance section below). Thus, relatively high MRLs were obtained for SDS samples as contrasted to instantaneous samples (see Table 3-6). SDS data that were less than these values were not reported, thus precluding the need for SDS background subtraction in many instances. However, when higher blank levels were detected, they were subtracted from SDS sample results. For example, the standard SDS tests at Utility 11 for the Day 13 samples (see Table 3-3) for trichloroacetic acid (TCAA) in the GAC influent and blank yielded values of 19 and 2.1 μg/L, respectively. Thus, a blank-subtracted result of 17 μg/L was reported. As in this example, the blank subtraction often resulted in a number which did not differ from the uncorrected value within analytical error. The evaluation of SDS data is

3-4

TABLE 3-5

UTILITY 11 TREATMENT STUDY
COMPARISON OF GAC EFFLUENT SDS TESTS:
EFFECT OF CHLORINE DOSE AND pH ON DBPs

	Day 82 GAC Effl. SDS*		Day 95 GAC Effl. SDS#	
Chlorine Dose:	2.0 mg/L	4.5 mg/L	2.0 mg/L	4.5 mg/L
pH	7.55	8.28	7.45	8.20
Cl_2 residual, mg/L	1.30	3.10	1.0	3.0
DBPs, μg/L:				
$CHCl_3$	4.0	8.9	8.8	14
$CHCl_2Br$	7.9	12	13	15
$CHClBr_2$	8.5	11	14	15
$CHBr_3$	1.8	2.0	2.2	2.8
TCAN	<0.029	<0.029	<0.029	<0.029
DCAN	0.40	0.20	0.63	0.30
BCAN	0.47	<0.27	1.1	0.52
DBAN	<1.1	<1.1	1.2	<1.1
1.1-DCP	<0.09	<0.09	0.11	<0.09
1.1.1-TCP	0.37	0.096	0.66	0.14
MCAA	<1.0	2.4	<1.0	1.0
DCAA	2.5	4.0	4.9	6.7
TCAA	1.2	1.8	1.6	3.3
MBAA	0.5	<0.5	0.6	0.5
DBAA	2.7	3.0	3.9	4.6
Chloropicrin	0.07	<0.07	0.11	0.07
Chloral Hydrate	1.8	2.3	3.2	4.0

* TOC of GAC effluent on day 82 = 0.60 mg/L
# TOC of GAC effluent on day 95 = 0.85 mg/L

more complex, though, when SDS results approach the same value as that detected in SDS blanks. For this reason, MRLs are set at higher values for SDS testing, since quantification can only be reliable when SDS values are significantly higher than blank levels.

QUALITY ASSURANCE

Metropolitan is certified by the CDHS for the analysis of THMs and volatile organic compounds. Furthermore, Metropolitan obtained permission to utilize the THM/HAN/haloketone/chloropicrin method described above for THM compliance monitoring. For the list of DBPs under investigation, no officially-approved USEPA methods exist. To validate all the DBP methods used for this study, Cincinnati tap water and Metropolitan's Weymouth plant were both sampled as is and a separate set of bottles was spiked with all the target-compound DBPs. These samples were split between Metropolitan, Montgomery Laboratories (Montgomery), and the Technical Support Division (TSD) and the Environmental Monitoring Support Laboratory (EMSL) of the USEPA (not all laboratories ran each analytical fraction).

Metropolitan's, Montgomery's, and TSD's laboratories all agreed on THM, HAN, haloketone, and chloropicrin results (Fair, 1988a). Metropolitan and TSD obtained comparable results for chloral hydrate and cyanogen chloride (Fair, 1988a). Metropolitan and TSD had comparable TOC results, and Montgomery and TSD had comparable TOX data (Fair, 1988a). In addition, Metropolitan, TSD and EMSL, in both this initial cross-calibration and a subsequent one which also included 2,4,6-trichlorophenol, obtained comparable HAA results (Fair, 1988a; Fair, 1988b).

Finally, Metropolitan submitted a 16-point Quality Assurance (QA) Project Plan for the USEPA study, which was approved by the USEPA QA officer Audrey D. Kroner (McGuire, 1988). The QA protocol covers accuracy, precision, independent verification and the use of an internal standard. Accuracy is dependent on many factors, but the most important is the calibration curve. Accuracy was monitored by calculating the recoveries of samples which had been enhanced with known concentrations of the compounds of interest. Precision is another parameter that is dependent on more than one factor. The precision of a method was monitored by analyzing samples in duplicate and calculating the difference between the two analyses. Independent verification of a method was done by interlaboratory calibration (discussed above). The internal standard was used to insure that there were consistent injections into the GC of samples and standards.

All of the above mentioned parameters were important in assuring that good quality data were produced. It is important to note that all portions of the QA program met the established standards in order for an analysis to be considered in control.

Initial calculations of the method detection limits (MDLs) were made according to the Code of Federal Regulations 40 Part 136, July 1, 1987. A set of 7 standards were prepared in organic-pure water at 1 to 5 times the estimated detection limit. Each standard was analyzed according to the method and the standard deviation of the 7 replicate measurements for each analyte was determined. These MDLs were used as minimum reporting levels (MRLs), except where the instrumental detection limit has proved to be higher. Often, the MRLs corresponded to the lowest level standard on the

calibration curve. The MRL for each analyte is shown in Table 3-6. Since some DBPs were detected in the SDS blanks, a higher MRL was used for SDS samples, the value based on a calculation utilizing the results from 7 SDS blank samples.

At the beginning of this study, many MRLs corresponded to the MDL-calculated values, even though the calibration curves did not include a standard at that low of a level. Thus, MRLs were either raised to correspond to the lowest level standard analyzed (e.g., chloroform MDL was 0.021 μg/L, but lowest level standard run was 0.102) or the calibration curve was expanded to include a lower level standard at the same level as the calculated MDL (e.g., dichloroacetonitrile MDL was 0.025 μg/L, but lowest level standard had initially been 1 μg/L; thus a 0.027 μg/L level standard was added to the curve). As was discussed in the previous section on SDS testing, SDS samples require a higher MRL to remove the uncertainty in reporting SDS data that are comparable to those levels detected in SDS blanks.

Quantitation was done using an external standard calibration curve. Standards were prepared in organic-pure water spiked with the appropriate DBPs and extracted, derivatized, or purged with the samples. The extracted or purged standards were used to compensate for the varying extraction or purging efficiencies of the different compounds in the analysis. Samples with analytes outside the range of the calibration curve required re-analysis with an appropriate dilution.

An internal standard was spiked into each sample or extract. The purpose of the internal standard was to monitor injections made into the GC. A sample injection was deemed acceptable if the area counts of the internal standard peak did not vary more than +/- 10 percent from other samples which were extracted or purged on the same date.

Sample spikes were analyzed to monitor the extraction or purging efficiency of specific analytes in sample matrices. This measured the accuracy of the method in a natural matrix. The spiked samples were analyzed at a frequency of at least 10 percent of the samples. The samples were spiked at the levels that are typically found in samples. Data were entered into the quality control (QC) table directly after the analysis. The QC charts were reviewed by the analyst and the immediate supervisor. All spike recoveries must fall within the upper and lower control limits to be acceptable. If a spike recovery was not acceptable, then the samples were re-analyzed from the point where the last spike was in control and a sample was re-spiked and re-analyzed only for those analytes that were out of control.

Initial control limits were defined by calculating the mean percent recovery from the most recent 50 sample spike data points. The 99 percent confidence interval is +/- three times the standard deviation, which defined the control limits. Warning limits were defined as +/- two times the standard deviation. If a sample recovery was above or below the warning limit this indicated there was a potential problem. The problem was determined and corrected before the analysis was out of control. Control limits and warning limits were re-calculated on a semiannual basis using the most recent 50 spiked sample percent recovery values. Data points that were out of control were not included in the re-calculation of new control limits.

TABLE 3-6

MINIMUM REPORTING LEVELS (MRLs)

Analyte	Minimum Reporting Levels					
DBPs, μg/L:	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr	Spring/ Summer 1989	Cl₂ SDS Tests
Trihalomethanes						
Chloroform	0.021	0.021	0.102	0.102	0.102	0.52
Bromodichloromethane	0.020	0.020	0.103	0.103	0.103	0.22
Dibromochloromethane	0.017	0.017	0.108	0.108	0.108	0.48
Bromoform	0.013	0.013	0.101	0.101	0.101	0.91
Haloacetonitriles						
Trichloroacetonitrile	0.012	0.012	0.029	0.029	0.029	0.03
Dichloroacetonitrile	0.025	0.025	0.027	0.027	0.027	0.04
Bromochloroacetonitrile	0.035	0.035	0.027	0.027	0.04	0.19
Dibromoacetonitrile	0.076	0.076	0.028	0.028	0.08	1.20
Haloketones						
1.1-Dichloropropanone	0.030	0.030	0.026	0.026	0.026	0.09
1.1.1-Trichloropropanone	0.013	0.013	0.029	0.029	0.029	0.03
Haloacetic Acids						
Monochloroacetic acid	1.0	1.0	1.0	1.0	1.0	1.7
Dichloroacetic acid	0.6	0.6	0.6	0.6	0.6	2.1
Trichloroacetic acid	0.6	0.6	0.6	0.6	0.6	1.5
Monobromoacetic acid	0.5	0.5	0.5	0.5	0.5	0.5
Dibromoacetic acid	0.6	0.6	0.6	0.6	0.6	0.6
Chlorophenols						
2.4-Dichlorophenol	2.0	NA	NA	NA	NA	NA
2.4.6-Trichlorophenol	0.3	0.4	0.4	0.4	0.4	0.4
Pentachlorophenol	0.4	NA	NA	NA	NA	NA
Aldehydes						
Formaldehyde	NA	1.0	1.0	1.0	3.0	1.7
Acetaldehyde	NA	1.0	1.0	1.0	3.0	1.8
Miscellaneous DBPs						
Chloropicrin	0.010	0.010	0.026	0.026	0.026	0.04
Chloral hydrate	0.2	0.2	0.050	0.050	0.050	0.43
Cyanogen chloride	0.02	0.1	0.1	0.1	0.2	0.1

Table 3-6, Continued

Minimum Reporting Levels (MRLs)

Analyte	Minimum Reporting Levels					
	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr	Spring/ Summer 1989	Cl_2 SDS Tests
Other Analytes						
Total organic carbon, mg/L	0.05	0.05	0.05	0.05	0.05	NA
Total organic halide, μg/L	10	10	10	10	10	10
Ultraviolet absorbance, cm^{-1}	NA	0.005	0.001	0.001	0.001	NA
Chloride, mg/L	NA	0.1	0.1	0.1	0.1	NA
Bromide, mg/L	NA	0.01	0.01	0.01	0.01	NA

NA = Not Analyzed
SDS = Simulated Distribution System

Methodology

Prior to the calculation of initial control limits for spike recoveries, control limits of +/- 20 percent were used for all DBP fractions except for cyanogen chloride. For the latter analyte, control limits from EPA Method 525.2 for volatile organic compounds were preliminarily used (i.e., +/- 40 percent; however, warning limits were set at +/- 20 percent). As the data in Table 3-7 indicate, calculated control limits were consistent with the preliminary assumptions. For the HAAs, the use of +/- three standard deviations created control limits that were relatively high due to some outlier values affecting the statistics. In fact, virtually all spike recoveries fell within +/- two standard deviations; therefore, the control limits for these analytes were based on the latter statistics.

Sample duplicates were analyzed in order to monitor the precision of the method. Duplicates were analyzed on randomly selected samples at a frequency of at least 10 percent of the samples. Data were entered into the QC table after the analytical run was completed. The QC charts were reviewed by the analysts and the immediate supervisor. Control limits were determined by calculating the range as a function of the relative standard deviation (coefficient of variation) as specified in Standard Methods proposed Method 1020B. The normalized range (R_n) was calculated as follows:

$$R_n = |x_1 - x_2| / [(x_1 + x_2)/2]$$

where x_1 and x_2 are the duplicate values.

A mean normalized range (R_m) was calculated for 50 pairs of duplicate data points:

$$R_m = \frac{\Sigma R_n}{n}$$

where n = number of duplicate pairs.

The variance (s^2) of the normalized ranges was calculated:

$$s^2 = \frac{\Sigma (R_n - R_m)^2}{n-1}$$

The standard deviation (s) was calculated as the square root of the variance. The upper and lower control limits were defined as R_m + 3s and zero, respectively. All duplicates must fall within the control limits to be acceptable. If a duplicate was not acceptable, then the samples were re-analyzed from the point where the last duplicates were in control and a duplicate was re-analyzed only for those analytes that were out of control. The upper warning limit was defined as R_m + 2s. If an R_n was outside the warning limit, this indicated there was a potential problem. The problem was investigated before the analysis was out of control. Control limits were recalculated on a semi-annual basis using the most recent 50 points. Data points that were out of control were not included in the recalculation of new control limits.

TABLE 3-7

DBP QUALITY CONTROL LIMITS

Analyte	Period Covered	Spike Quality Control Limits				Duplicate Limits	
		UCL	UWL	LWL	LCL	UCL	UWL
			Percent Recovery			Normalized Range	
CHCl$_3$	Preliminary	120			80	0.2	
	Initial	121	113	83	75	0.2	
	Recalculated	119	111	81	73	0.14	0.10
CHCl$_2$Br	Preliminary	120			80	0.2	
	Initial	123	116	86	79	0.2	
	Recalculated	119	112	84	77	0.10	0.076
CHClBr$_2$	Preliminary	120			80	0.2	
	Initial	125	117	86	78	0.2	
	Recalculated	126	117	82	73	0.13	0.099
CHBr$_3$	Preliminary	120			80	0.2	
	Initial	120	113	87	81	0.2	
	Recalculated	120	112	81	73	0.13	0.095
TCAN	Preliminary	120			80	0.2	
	Initial	122	114	77	68	0.2	
	Recalculated	116	110	85	78	0.2*	
DCAN	Preliminary	120			80	0.2	
	Initial	126	119	91	84	0.2	
	Recalculated	134	124	84	74	0.21	0.15
BCAN	Preliminary	120			80	0.2	
	Initial	131	122	87	78	0.2	
	Recalculated	141	129	82	71	0.20	0.15
DBAN	Preliminary	120			80	0.2	
	Initial	134	124	82	71	0.2	
	Recalculated	135	124	84	74	0.19	0.14
1,1-DCP	Preliminary	120			80	0.2	
	Initial	123	116	88	81	0.2	
	Recalculated	126	119	87	79	0.20	0.15

Table 3-7, Continued

DBP Quality Control Limits

Analyte	Period Covered	Spike Quality Control Limits UCL	UWL	LWL	LCL	Duplicate Limits UCL	UWL
		Percent Recovery				Normalized Range	
1.1.1-TCP	Preliminary	120			80	0.2	
	Initial	121	113	82	75	0.2	
	Recalculated	127	118	81	72	0.17	0.13
Chloropicrin	Preliminary	120			80	0.2	
	Initial	123	115	81	73	0.2	
	Recalculated	120	113	86	79	0.15	0.11
Chl Hydrate	Preliminary	120			80	0.2	
	Initial	124	113	72	62	0.2	
	Recalculated	130	119	74	63	0.074	0.057
MCAA	Preliminary	120			80	0.2	
	Initial	120#			87#	0.2	
	Recalculated	119#			76#	0.21	0.16
DCAA	Preliminary	120			80	0.2	
	Initial	129#			74#	0.2	
	Recalculated	129#			74#	0.16	0.12
TCAA	Preliminary	120			80	0.2	
	Initial	137#			81#	0.2	
	Recalculated	134#			78#	0.16	0.12
MBAA	Preliminary	120			80	0.2	
	Initial	122#			82#	0.2	
	Recalculated	120#			82#	0.20	0.15
DBAA	Preliminary	120			80	0.2	
	Initial	121#			82#	0.2	
	Recalculated	123#			74#	0.19	0.15
TCP	Preliminary	120			80	0.2	
	Initial	133#			70#	0.2*	
CNCl	Preliminary	140	120	80	60	0.2	
	Initial	138	126	75	63	0.28	0.21

Table 3-7, Continued

DBP Quality Control Limits

UCL = Upper control limit
UWL = Upper warning limit
LWL = Lower warning limit
LCL = Lower control limit

* Not enough points for calculation of control limits.
# The calculated control limits were relatively high due to some outlier values affecting the statistics; therefore, the calculated warning limits were used as the control limits in order to keep closer control over the analysis.

Methodology

Prior to the calculation of initial control limits for the precision of replicate analyses, control limits of 0.2 for a normalized range were used for all DBP fractions. As Table 3-7 indicates, calculated control limits were determined later in the study; however, these values were consistent with initial assumptions.

ON-SITE EXTRACTION STUDIES

For the DBP studies, samples were collected from 35 utilities throughout the United States. These samples were collected in bottles containing a dechlorination agent and/or preservative to ensure the integrity of the sample during shipping and storage prior to analysis. To evaluate how effective the preservation methods were in different matrices, two of Metropolitan's laboratory staff extracted samples on-site at Utility 2. In addition, split samples were preserved and brought back to the laboratory for analysis. The latter samples were stored at 4°C for 24 hours to simulate typical overnight shipping conditions. Samples were analyzed in triplicate, both on-site and at the laboratory, to provide adequate statistics. For the Metropolitan laboratory extractions, the pentane-extractable DBPs were extracted upon receipt (after the 24-hour shipping period). The chloral hydrate and HAA samples were extracted in the laboratory within the established holding period (see Table 3-2).

Both the chlorinated filter effluent and chloraminated clearwell effluent were sampled in order to evaluate the effects of the dechlorination agents/preservatives on both disinfectants. Ammonium chloride is added to samples to convert free chlorine to chloramines as a means of preserving pentane-extractable DBPs (i.e., THMs, HANs, haloketones, and chloropicrin). Since the clearwell effluent is already chloraminated, that location was sampled on-site both with and without the addition of ammonium chloride for this analytical fraction. Other analytical fractions evaluated included chloral hydrate (dechlorinated with ascorbic acid) and HAAs (preserved with ammonium chloride).

A concern in this special study was the effect of the dechlorination agents/preservatives on the pH of samples. The table below shows the pH drop brought about by these reagents:

		pH	
Sample	Actual	+ Ammonium Chloride	+ Ascorbic Acid
Filter effluent	7.48	7.27	3.78
Clearwell effluent	7.55	7.16	4.42

The data are presented in Tables 3-8 and 3-9; the findings are as follows:

1. The THMs, chloropicrin, choral hydrate, and the HAAs were stable to +/- 20 percent between extractions on-site and in the laboratory in both samples. Note (in Table 3-9) that monochloroacetic acid was 27 percent higher in the clearwell sample analyzed in the laboratory. However, if one examines the number of significant figures in the results (i.e., 2) and the relative standard deviation of the on-site results (i.e., standard deviation divided by the mean,

3-8

TABLE 3-8

UTILITY 2: CHLORINATED FILTER EFFLUENT

ON-SITE AND LAB EXTRACTION

Compound	On-Site Extraction Mean* (µg/L)	Std. Dev.	Lab Extraction Mean* (µg/L)	Std. Dev.	Percent Stability[#]
Chloroform	60.3	2.1	58.6	3.2	97
Bromodichloromethane	15.6	0.31	14.6	0.73	94
Dibromochloromethane	3.41	0.05	3.00	0.25	88
Bromoform	0.15	0.003	0.13	0.007	87
Trichloroacetonitrile	0.32	0.01	0.14	0.006	44
Dichloroacetonitrile	13.1	0.35	10.9	0.47	83
Bromochloroacetonitrile	3.08	0.05	2.03	0.17	66
Dibromoacetonitrile	0.63	0.04	0.24	0.05	38
1.1-Dichloropropanone	0.83	0.02	0.66	0.06	80
1.1.1-Trichloropropanone	2.26	0.06	1.91	0.11	85
Monochloroacetic Acid	1.2	NA	1.3	0.1	108
Dichloroacetic Acid	15.5	0.67	14.2	0.45	92
Trichloroacetic Acid	24.6	0.61	23.3	1.0	95
Monobromoacetic Acid	ND	NA	ND	NA	NA
Dibromoacetic Acid	0.6	0	0.6	0	100
Chloropicrin	0.10	0.002	0.09	0.008	90
Chloral Hydrate	7.02	0.35	6.3	0.26	90

*   Some mean data reported to three digits to enable percent stability calculations;
     however, data only good to two significant figures.
#   Percent Stability = 100 x (mean of lab extraction)/(mean of on-site extraction)
NA = Not analyzed
ND = Not detected

TABLE 3-9

UTILITY 2: CHLORAMINATED CLEARWELL EFFLUENT

ON-SITE AND LAB EXTRACTION

| Compound | On-Site Extraction | | | | Lab Extract. | | |
| | Unpreserved* | | Preserved** | | Preserved** | | |
	Mean# (µg/L)	Std. Dev.	Mean# (µg/L)	Std. Dev.	Mean# (µg/L)	Std. Dev.	Percent Stability##
Chloroform	56.2	1.0	56.0	0.46	49.8	3.4	89
Bromodichloromethane	14.7	0.30	14.7	0.03	13.0	1.1	89
Dibromochloromethane	3.00	0.11	3.03	0.03	2.47	0.29	82
Bromoform	0.14	0.005	0.14	0.001	0.12	0.008	86
Trichloroacetonitrile	0.21	0.004	0.19	0.004	0.097	0.005	51
Dichloroacetonitrile	12.7	0.37	12.6	0.17	9.90	0.62	79
Bromochloroacetonitrile	2.66	0.07	2.69	0.03	1.84	0.23	68
Dibromoacetonitrile	0.47	0.01	0.47	0.009	0.18	0.21	38
1.1-Dichloropropanone	1.43	0.11	0.98	0.02	0.58	0.04	59
1.1.1-Trichloropropanone	1.71	0.06	1.80	0.01	1.46	0.14	81
Monochloroacetic Acid	NA	NA	1.1	0.21	1.4	0.12	127
Dichloroacetic Acid	NA	NA	13.6	0.10	13.7	0.06	101
Trichloroacetic Acid	NA	NA	22.9	0.47	21.7	0.35	95
Monobromoacetic Acid	NA	NA	ND	NA	ND	NA	NA
Dibromoacetic Acid	NA	NA	0.5	0.05	0.6	0	120
Chloropicrin	0.13	0.04	0.12	0.00	0.10	0.005	83
Chloral Hydrate	NA	NA	6.74	0.07	6.2	0.02	92

*   Results from an unpreserved sample (i.e., no ammonium chloride).
** Results from a preserved sample (ammonium chloride for all but chloral hydrate, which was ascorbic acid preserved).
#   Some mean data reported to three digits to enable percent stability calculations; however, data only good to two significant figures.
% Stability = 100 x [(mean of lab extraction)/(mean of preserved on-site extraction)]
NA = Not analyzed
ND = Not detected

thus 19 percent), the calculation of the stability is affected by the uncertainty in the former data.

2. Trichloroacetonitrile (TCAN), as in Metropolitan water in previous studies (Koch et al., 1988), degraded to 44 to 51 percent of its initial value in 24 hours. In Metropolitan's previous studies, the other HANs were stable to at least 80 percent of their initial value; however, the same situation was not experienced at Utility 2. Bromochloro- and dibromoacetonitrile (DBAN) degraded to 66-68 and 38 percent, respectively, of their initial (on-site) values in 24 hours; although, dichloroacetonitrile (DCAN) did remain stable (i.e., to 79-83 percent). Note that DBAN experienced a high standard deviation in the clearwell samples.

3. Both haloketones were stable in the filter effluent samples; however, 1,1-dichloropropanone (1,1-DCP) degraded to 59 percent of its on-site value in 24 hours in the clearwell sample. Also note that clearwell samples collected with and without preservative yielded similar on-site results for all pentane-extractable DBPs, except for 1,1-DCP. The unpreserved sample had 1.43 μg/L 1,1-DCP; whereas, the ammonium-chloride-preserved sample yielded an on-site 1,1-DCP value of 0.98 μg/L.

To continue to evaluate the preservation techniques, a laboratory analyst from Metropolitan performed on-site extractions at Utility 33. This utility was chosen for its low alkalinity and lack of natural buffering capacity. This matrix is ideal for studying the pH change and effects caused by the addition of these preservatives. Samples that were extracted in the field included the pentane-extractable DBPs and chloral hydrate. The pH of the water was measured in the field as is and at the laboratory after field preservation and overnight shipment. The results are as follows:

	pH		
Sample	Actual	+ Ammonium Chloride	+ Ascorbic Acid
Effluent	6.96	6.31	3.46

The data on the chlorinated effluent are presented in Table 3-10; and the findings are as follows:

1. There was little in the way of brominated DBPs, due to the low bromide level in the source water. Thus, it was difficult to evaluate those data, as on-site results were close to the minimum reporting levels. However, data for the other DBPs indicate that chloroform, bromodichloromethane, the haloketones, chloropicrin, and chloral hydrate were stable to +/- 20 percent of their on-site values.

2. The major HAN present was DCAN; although, the levels detected were less than 1.0 μg/L. The laboratory result was higher by 0.24 μg/L.

During the field study, an attempt was made to analyze some samples where the chlorine residual was not quenched or converted to chloramines. This utility practices

TABLE 3-10

UTILITY 33: CHLORINATED EFFLUENT

ON-SITE AND LAB EXTRATION

Compound	On-Site Extraction		Lab Extraction		Percent Stability[#]
	Mean (μg/L)	Std. Dev.	Mean (μg/L)	Std. Dev.	
Chloroform	22	1.1	23	0.51	105
Bromodichloromethane	1.3	0.06	1.4	0.03	108
Dibromochloromethane	ND	NA	ND	NA	NA
Bromoform	0.16	0.01	<0.101	NA	NA*
Trichloroacetonitrile	ND	NA	ND	NA	NA
Dichloroacetonitrile	0.61	0.02	0.85	0.03	139
Bromochloroacetonitrile	0.07**	0.0	<0.027	NA	NA*
Dibromoacetonitrile	0.09	0.12	<0.028	NA	NA*
1,1-Dichloropropanone	1.8	0.04	2.0	0.03	111
1,1,1-Trichloropropanone	3.3	0.14	3.1	0.08	94
Chloropicrin	0.50**	0.02	0.59	0.02	118
Chloral Hydrate	1.7	0.04	1.8	0.02	106

Percent stability = 100 x [(mean of lab extraction)/(mean of on-site extraction)]
*   On-site result too close to minimum reporting level to be able to evaluate stability
** Tentative result due to unacceptable quality control for these compounds only
NA = Not analyzed
ND = Not detected

disinfection only, so the effluent sample is located, in time, very close to the point of chlorine application. Thus, a high free chlorine residual was present in the effluent sample (i.e., 2.5 mg/L). The field laboratory where on-site extractions were performed was located approximately two hours away from the effluent sample tap. Thus, unpreserved samples continued to react with free chlorine yielding high DBP levels (e.g., 62 μg/L of chloroform was detected; whereas, preserved samples yielded 22 μg/L). These results emphasize the need for a dechlorination agent or preservative to stop the reaction of free chlorine in forming DBPs after a sample is collected.

One final utility (Utility 6) was selected for an on-site study. The pH results are as follows:

| | | pH | |
Sample	Actual	+ Ammonium Chloride	+ Ascorbic Acid
Clearwell effluent	8.00	7.19	4.66

At Utility 6, chloraminated clearwell effluent was sampled for pentane-extractable DBPs and chloral hydrate. In addition, water was collected with no preservatives. The data from Table 3-11 indicate the following:

1. The THMs, chloropicrin, and chloral hydrate were stable to +/- 20 percent.

2. TCAN was not detected in these samples. The other HANs, unlike at Utility 2, were all stable. The laboratory results were higher than the on-site values; however absolute differences were $\leq$0.24 μg/L for each HAN.

3. The haloketones were stable between the on-site and laboratory analyses of preserved samples ($<$0.25 μg/L for each compound). As observed at Utility 2, the unpreserved sample had 1.6 μg/L 1,1-DCP, while the preserved sample had 0.91 μg/L.

Overall, the on-site experiments confirm the findings of Metropolitan's holding studies (Koch et al. 1988; Krasner et al, 1989), that the chosen dechlorination agents and preservatives for the pentane-extractable DBPs, chloral hydrate, and HAAs do result in laboratory results representative of the DBP levels at the time of sampling. Furthermore, in continuing to evaluate the stability of the pentane-extractable DBPs, nine different utilities' clearwell effluents were sampled and shipped (overnight) to Metropolitan. They were extracted upon receipt, plus a second set of aliquots were extracted four days after the initial sampling. The results were essentially the same (within analytical error) on both days (see Table 3-12). TCAN, though, did degrade between the two extraction dates, which is consistent with previous results on this unstable HAN. Similar experiments have been performed with the HAAs and chloral hydrate, and re-extractions have yielded comparable data. More holding studies need to be performed in other matrices in order to better define the validity of these dechlorination agents and preservatives. The data, however, do support the idea that samples can be shipped to the laboratory for analysis.

TABLE 3-11

UTILITY 6: CHLORAMINATED CLEARWELL EFFLUENT

ON-SITE AND LAB EXTRACTION

| | On-Site Extractions | | | | Lab Extract. | | |
| | Unpreserved* | | Preserved** | | Preserved** | | |
Compound	Mean (μg/L)	Std. Dev.	Mean (μg/L)	Std. Dev.	Mean (μg/L)	Std. Dev.	Percent Stability#
Chloroform	6.9	0.17	6.5	0.06	7.2	0.4	111
Bromodichloromethane	6.4	0.21	6.2	0.06	6.6	0.4	106
Dibromochloromethane	3.5	0.12	3.4	0.1	3.8	0.36	112
Bromoform	0.45	0.01	0.43	0.1	0.43	0.03	100
Trichloroacetonitrile	ND	NA	ND	NA	ND	NA	NA
Dichloroacetonitrile	0.81	0.09	0.79	0.02	1.0	0.06	127
Bromochloroacetonitrile	0.50	0.03	0.50	0.03	0.63	0.06	126
Dibromoacetonitrile	0.57	0.03	0.63	0.10	0.87	0.23	138
1,1-Dichloropropanone	1.6	0.17	0.91	0.07	1.1	0.12	121
1,1,1-Trichloropropanone	0.87	0.1	0.95	0.06	1.2	0.06	126
Chloropicrin	0.20	0.01	0.20	0	0.21	0.01	105
Chloral Hydrate	3.2	0.04	2.6	0.02	2.7	0.09	104

*   Results from an unpreserved sample (i.e., no ammonium chloride).
**   Results from a preserved sample (ammonium chloride for all but chloral hydrate. which was ascorbic acid preserved).
#   Percent stability = 100 x [(mean of lab extraction)/(mean of preserved on-site extraction)]
NA = Not analyzed
ND = Not detected

TABLE 3-12

PENTANE-EXTRACTABLE DISINFECTION BY-PRODUCTS: MATRIX HOLDING STUDY

Utility/Number of Days after Sampling	Concentration (µg/L)										
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TCAN	DCAN	BCAN	DBAN	1,1-DCP	1,1,1-TCP	CHP
Utility 1											
1 Day	0.80	1.5	2.3	1.3	ND	0.15	0.36	0.90	ND	0.067	0.010
4 Days	1.1	2.2	3.4	2.0	ND	0.16	0.45	1.2	0.11	0.087	0.015
Utility 3											
1 Day	2.3	1.2	0.26	0.080	0.009	0.67	0.12	0.060	1.1	1.6	0.082
4 Days	2.4	1.2	0.27	0.074	ND	0.68	0.12	0.054	1.0	1.5	0.083
Utility 23											
1 Day	1.9	3.8	5.3	2.3	ND	0.97	1.3	1.9	0.26	0.097	0.043
4 Days	1.8	3.6	5.0	2.1	ND	0.99	1.3	2.0	0.25	0.12	0.053
Utility 24											
1 Day	0.81	0.85	4.5	23	ND	ND	0.31	5.2	ND	ND	ND
4 Days	0.76	0.81	4.3	21	ND	ND	0.27	4.1	ND	ND	ND
Utility 26											
1 Day	43	10	2.5	0.10	0.017	3.6	1.2	0.29	0.52	2.0	0.86
4 Days	40	9.9	2.4	0.097	ND	3.6	1.1	0.28	0.51	1.8	0.78
Utility 27											
1 Day	6.9	19	26	7.2	ND	0.94	2.0	3.7	0.41	0.66	0.058
4 Days	7.2	18	23	7.2	ND	1.0	2.0	3.5	0.48	0.50	0.13
Utility 29											
1 Day	117	56	18	0.76	0.055	10	4.8	1.2	1.5	4.4	0.38
4 Days	114	50	17	0.74	0.027	9.8	4.5	1.1	1.5	4.3	0.41
Utility 31											
1 Day	36	15	6.5	0.61	ND	1.4	1.2	0.62	0.35	0.41	0.29
4 Days	34	14	6.2	0.62	ND	1.3	1.0	0.59	0.33	0.40	0.28
Utility 35											
1 Day	20	2.4	0.11	ND	ND	0.85	0.046	ND	1.1	2.0	0.16
4 Days	19	2.3	0.10	ND	ND	0.85	0.043	ND	1.1	1.9	0.17

ND = Not detected

ALDEHYDE DERIVATIZATIONS/EXTRACTIONS ON-SITE

When aldehyde analysis was added to the scope of work, a new preservation concern developed. Formaldehyde in particular is a very unstable compound. Thus, samples were analyzed upon receipt at the laboratory. Another investigator performed derivatizations and extractions in the field for aldehyde analyses of four utilities (Glaze et al. 1989b); however, such an action is cost prohibitive when 35 utilities nationwide are being analyzed on a quarterly basis. Therefore, on-site evaluations were performed at Utilities 33 and 6 for the aldehyde fraction.

A combination of two preservatives for aldehyde fractions was evaluated. Mercuric chloride was added as a biocide, in order to inactivate microorganisms capable of either producing or degrading aldehydes. In addition, ammonium chloride was added to convert free chlorine to chloramines, as it was suspected that a free chlorine residual could continue to form additional aldehydes. At Utility 33 (see Table 3-13), it is clear that the addition of mercuric chloride was essential for the influent sample, as unpreserved samples had no detectable levels of the measured aldehydes after the 24-hour shipping period. Levels of aldehydes at this utility, which utilizes free chlorine, were low (≤ 5 μg/L of each aldehyde), and the coefficient of variation was high for some of the analyses.

However, when Utility 6 implemented ozonation, it was expected that higher levels of aldehydes would be produced, which would yield more conclusive results on the use of preservatives and the ability to ship aldehyde samples back for laboratory analysis. In this experiment, unpreserved samples on-site were compared to fully preserved samples analyzed after a 24-hour shipping period. As Table 3-14 shows, formaldehyde levels were identical between on-site and laboratory analyses (e.g., the ozone contactor effluent had 16 and 15 μg/L of formaldehyde for on-site and laboratory analyses, respectively). Most of the acetaldehyde results were comparable as well (e.g., 7.4 versus 5.7 μg/L for the plant effluent analyzed on-site and in the laboratory, respectively). However, the on-site extraction blank contained 3.2 μg/L of acetaldehyde, while none was detected in the laboratory extraction blank, so it was difficult to compare the two sets of results due to a possible acetaldehyde contamination problem on-site. However, these data do indicate that aldehyde samples can be preserved and shipped to the laboratory for analysis of these analytes upon receipt.

PRESERVATION OF TOX SAMPLES

For this study, total organic halide (TOX) samples were collected with no dechlorination agent or preservative in the field and shipped iced overnight to Metropolitan's laboratory. After receipt, the samples were dechlorinated with a fresh sodium sulfite solution and preserved with sulfuric acid. Several studies were performed to evaluate to what extent TOX formation occurred during the 24-hour shipping period. TOX bottles were shipped with (1) no preservative reagents and (2) only sodium sulfite. Contrary to expectations, the latter samples yielded TOX results which were generally much higher than those dechlorinated in the laboratory. For example, the TOX results for Utility 33 were 680 μg/L for a laboratory-dechlorinated sample and 880 μg/L for the sample shipped with sulfite. These data suggested to some USEPA scientists (Sorrell and Brass, 1988) that the sodium sulfite solution was unstable and, perhaps, samples collected in bottles shipped with this chemical were not

TABLE 3-13

UTILITY 33: ALDEHYDE RESULTS

ON-SITE AND LAB EXTRACTION

| Location/Compound | On-Site Extractions | | | | Laboratory Extractions | | | |
| | Unpreserved | | Preserved* | | Unpreserved | | Preserved* | |
	Mean (μg/L)	Std. Dev.	Mean (μg/L)	Std. Dev.	Mean (μg/L)	Std Dev.	Mean (μg/L)	Std. Dev.
Influent/ Formaldehyde	2.3	2.9	NA	NA	< 1.0	NA	3.8	1.7
Effluent/ Formaldehyde	3.4	0.1	1.8	0.1	5.1	0.58	3.6	0.46
Influent/ Acetaldehyde	1.6	0.2	NA	NA	< 1.0	NA	1.0	0.33
Effluent/ Acetaldehyde	4.0	0.3	2.2	0.3	1.9	0.48	1.4	0.17

* Ammonium chloride added on-site; mercuric chloride plus ammonium chloride added for samples shipped back to laboratory.

NA = Not analyzed

TABLE 3-14

UTILITY 6: FORMALDEHYE RESULTS

ON-SITE AND LAB EXTRACTION

Location	On-Site Extract.[*] Mean (μg/L)	Std. Dev.	Lab Extract.[*] Mean (μg/L)	Std. Dev.	Percent Stability[#]
Plant Influent	0.63[**]	0.06	0.83[**]	0.12	NA[**]
O₃ Contactor Eff.	16	0	15	0.58	94
Plant Effluent	16	0	16	0.58	100

[*] On-site samples contained no preservatives; laboratory samples contained mercuric chloride and ammonium chloride.

[#] Percent Stability = 100 x [(mean of lab extraction)/(mean of on site extraction)]

[**] Levels detected below minimum reporting level of 1.0 μg/L

NA = Not analyzed

being dechlorinated in the field. When the next set of samples was received, TOX bottles shipped with the sulfite solution were analyzed for chlorine residual and, indeed, a residual remained. Because sampling kits were prepared and shipped to field locations at least two weeks prior to sampling, the instability of the dechlorination solution required that TOX samples be dechlorinated and preserved upon receipt at the laboratory. Samples dechlorinated at Metropolitan's laboratory were treated with a fresh sodium sulfite solution each time in order to ensure that the samples were dechlorinated.

To test the importance of timing of the addition of preservation agents, the following experiments were performed. Metropolitan's chlorinated filter effluent and chloraminated plant effluent were sampled and stored at 4°C for 24 hours to simulate overnight shipping conditions. Then the samples were preserved with those reagents not originally present in the TOX bottle at time of sampling. These data (Table 3-15) indicate that in Metropolitan's matrix, results were the same when fully dechlorinated and preserved at the time of sampling or after 24 hours at 4°C. However, samples only dechlorinated at the time of sampling had a slight loss of TOX when not acidified immediately.

When on-site extractions were performed at Utility 2, another experiment was performed with TOX samples as well (Table 3-16). Samples were evaluated by on-site dechlorination (with fresh sodium sulfite) and preservation (with sulfuric acid) versus dechlorination/preservation at the laboratory (after 24-hour storage at 4°C). The chloraminated water had the same TOX when dechlorinated/preserved on-site or in the laboratory. However, the chlorinated water did appear to increase by 16 percent during shipment/storage with no dechlorination at time of sampling.

When on-site analyses were conducted at Utility 33, special TOX sampling was included (Table 3-16). The sample dechlorinated and acidified in the field contained 390 μg/L of TOX, while the sample dechlorinated/preserved 24 hours later contained 610 μg/L. There was a 56 percent increase in TOX during the shipping period. These results reflect the fact that even during refrigerated shipping, the free chlorine was able to react with the sample matrix and produce additional TOX during the 24-hour period. Since Utility 33 practiced disinfection only and the sample tap was located near the point of chlorination, the large amount of free chlorine residual (i.e., 2.5 mg/L) and short contact time before sampling resulted in the sample containing sufficient chlorine and precursors to produce the additional TOX during shipping.

Further TOX experiments were carried out at Utility 6 (Table 3-16). Utility 6's filter influent was sampled, since it represented a point close to initial chlorination (at the time of this sampling). TOX was 60 μg/L when dechlorinated on-site and 110 μg/L when dechlorinated in the laboratory. The filter effluent samples had a longer contact time with chlorine prior to sampling and there was a smaller difference in TOX results between the on-site and laboratory-dechlorinated samples (77 μg/L on-site versus 110 μg/L in the laboratory). The chloraminated plant effluent samples were less affected by the timing of dechlorination (mean results of 78 μg/L of TOX for on-site dechlorination and 89 μg/L for the laboratory dechlorination). Samples collected from Utility 6's distribution system (water temperature 6°C) had 76 to 89 μg/L of TOX (dechlorinated in the laboratory), suggesting that the TOX did not increase over time in this utility's cold, chloraminated distribution system.

TABLE 3-15

TOX PRESERVATION STUDY

Sample[1]	Preservatives at Time of Sampling	Preservatives Added after 24 hr @ 4°C	TOX, μg/L (Replicates)	Percent Diff.[#]
Filter Effluent[2]	Sulfite[*]/acid	None	170, 160	Control
" "	None	Sulfite/acid	160, 170	0
" "	Sulfite	Acid	130, 150	-15%
Plant Effluent[3]	Sulfite/acid	None	150, 150	Control
" "	None	Sulfite/acid	130, 170	0
" "	Sulfite	Acid	130, 140	-10%

Percent difference = 100 x [(mean TOX value - "control" mean TOX value)/ "control" mean TOX value]
   where "control" sample = sample dechlorinated and acidified at time of sampling.
* Fresh sodium sulfite solution used.
[1] Samples from Metropolitan's Weymouth filtration plant.
[2] Chlorinated water
[3] Chloraminated water

TABLE 3-16

ON-SITE TOX PRESERVATION STUDIES

Sample Location	Cl_2 Dose (mg/L)	NH_3 Dose (mg/L)	Residual Cl_2 (mg/L)	TOX, μg/L[p] On-Site[*]	MWDSC Lab[#]	Percent Diff.[δ]
Utility 2						
Filter Effluent	8.8		2.67 total	310, 320	380, 350	+16%
Clearwell Effl.		0.5	2.2 total	330, 270	310, 295	+1%
Utility 33						
Plant Effluent	NA		2.5 free[X]	390	610	+56%
Utility 6						
Filter Influent	2		0.5 free	60, 61	110, 110	+82%
Filter Effluent			0.12 free	76, 78	110, 110	+43%
Plant Effluent	1	0.4	0.95 total	80, 75	98, 80	+15%
Distrib. Loc. #1			0.70 total	NA	82	
Distrib. Loc. #2			0.80 total	NA	76	
Distrib. Loc. #3			0.40 total	NA	89	

p Replicate analyses when available.
* Fresh sodium sulfite solution + acid added on-site.
# Sodium sulfite solution + acid added at MWDSC lab.
δ Percent difference = 100 x |(mean MWDSC lab TOX - mean on-site TOX)/ mean on-site TOX)|
X Very short free Cl_2 contact time before sample site.
NA = Not analyzed.

Methodology

The TOX experiments to date suggest that for chloraminated waters, dechlorination after receipts of samples was not problematic. However, the results indicate that chlorinated waters would continue to produce additional TOX, which appears to be related to the amount of chlorination that occurred prior to sampling. That is, if samples were collected shortly after chlorination, TOX values would be off by a high degree, whereas samples collected after sufficient chlorine contact time had already occurred in the treatment plant probably would not continue to produce a significant amount of TOX during refrigerated shipping. Since 14 of the 35 utilities in this study used chloramines as a final disinfectant, those TOX data are probably representative of values at the time of sampling. The largest error in interpreting the TOX data will probably be for disinfection-only utilities; however, only four of these were included in the study. The on-site TOX experiment at Utility 33, though, provides some data for interpreting the TOX results of a disinfection-only utility.

Experiments on dechlorination of TOX samples are very difficult, in that specific DBPs cannot be isolated for study as was performed for the pentane-extractable DBP fraction (see discussion above). In fact, Croue and Reckhow (1988) demonstrated that sodium sulfite (the TOX dechlorination agent) readily destroys many DBPs, including some of particular health concern (including a reduction in the mutagenicity of a sample). For this study, it was found to be impractical to have the individual utilities perform the proper dechlorination/preservation at time of sampling (e.g., the sulfite solution is unstable and has been shown to be difficult to ship to participating utilities). For field surveys, it appears that the dechlorination and preservation of TOX samples requires more study.

Section 4

Data Management and Analysis

SECTION 4

DATA MANAGEMENT AND ANALYSIS

This chapter discusses the organization of the database used in the study in terms of the individual database files. the fields contained in each, and their interrelationships; the data handling and tracking protocol; and the statistical and graphical methods by which data were analyzed and summarized.

DATABASE

The conceptual design of the database involved two main data files. The first data file, called UTILITIES, contained information about each participating utility. Each utility record (one per utility) had fields to store information such as utility identification (ID) number. name, water source, treatment type, population size, geographic location, coagulant type. and disinfectant type. The second data file, called RESULTS, stored all sampling results. Each measured value was stored in a separate record. The fields of the record included utility ID, location of sampling point, analysis code, sampling quarter. detection limit flag, and the measured value of the analysis compound or parameter. In addition to the two main data files, minor files were used to translate the various abbreviation codes into their full-length descriptions. This complete set of data files and their interlinking key fields is referred to as a "relational database". The database was implemented using the commercial software package dBASE III PLUS™ (Ashton-Tate) on an IBM compatible PC.

DATA HANDLING PROTOCOL

The basic elements of data handling protocol for this study were: 1) use of signatures by responsible team members, 2) data-sheet reference numbers for each individual project data sheet. and 3) tracking the status of each group of data. Figure 4-1 shows the various protocol steps performed at Metropolitan and JMM.

The first component of protocol involved the sign-off procedures used by Metropolitan in transferring data from laboratory analysts' notebooks to the data-entry sheets sent to JMM. Data sheets were signed or initialed by the transcriber and subsequently by the person performing a transcription check. The second protocol step took place at JMM when data was entered into the database. Every individual piece of paper (data sheet) was assigned a sequential number referred to as the Reference Number. As data were entered into the computer data-entry screens. the data-entry clerk typed in the Reference Number for each screen/sheet (screens and sheets correspond one-to-one) of data. and all data from that sheet were stored in the database tagged with that Reference Number. The purpose of the Reference Number is to allow any data point printed from the database into a report, table or graphics file to be traced back to the original paper data sheet from which it came, and from there back to the individual lab analyst's notebook, if necessary. A Data Entry Status Log kept at the computer work area was continually updated to prevent use of duplicate Reference Numbers. The data-entry clerk signed off on each data sheet as it was entered.
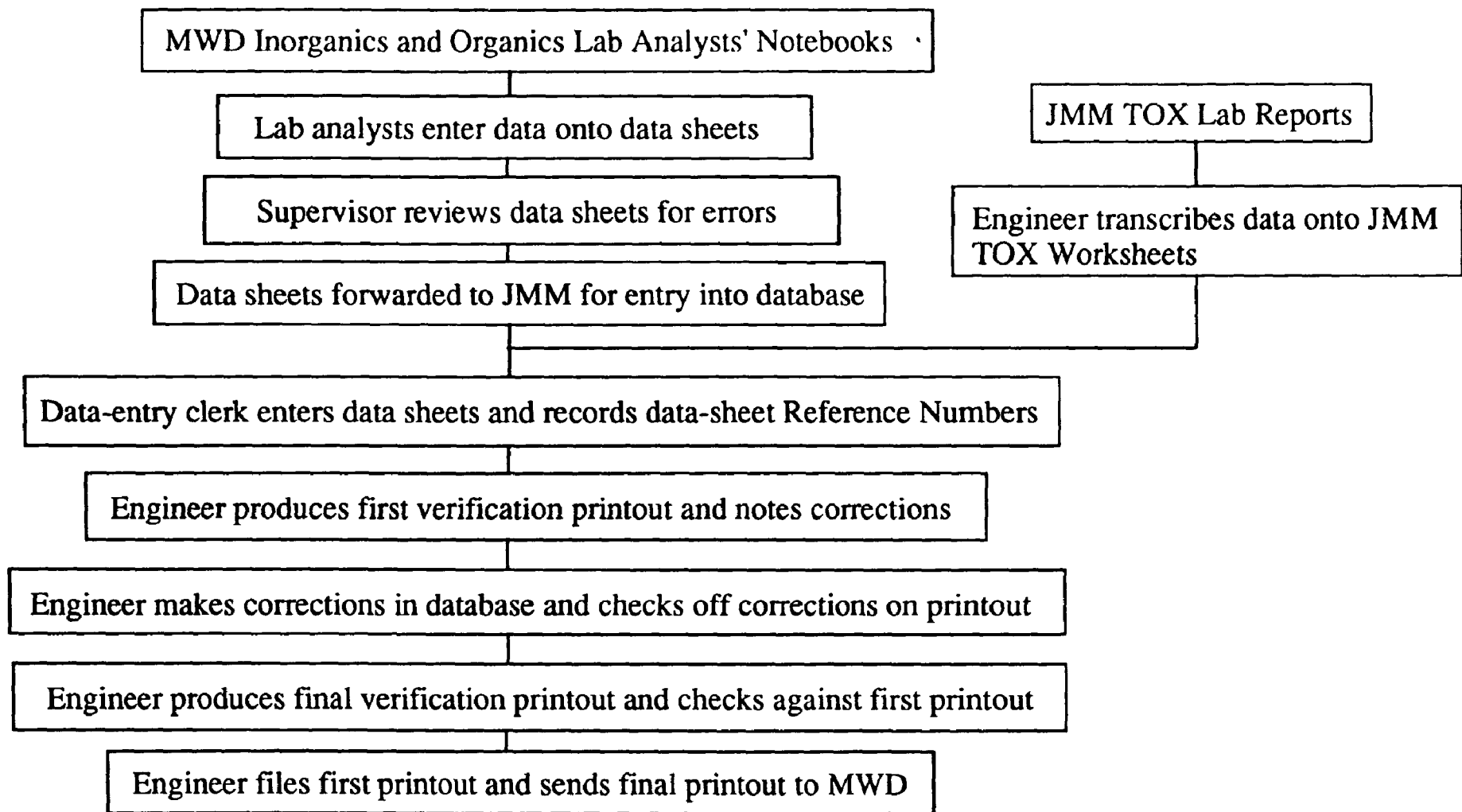
DATA-SAMPLING PROTOCOL

FIGURE 4-1

The next protocol step was to create a data verification computer printout for the range of newly-entered Reference Numbers. A single dBASE software program was created to produce the printout for all project data, referred to as the Verification Report. The output format of the report was virtually identical to the original data-entry sheets, allowing rapid visual comparison of the printout to the originals. An engineer familiar with the project performed the data-verification step. The printout was compared to the originals, and any needed corrections were marked on the printout with a colored pen. As this verification took place, the engineer signed off on each of the original data sheets.

Following verification, the engineer went into the computer database files with the dBASE data-file editor and manually performed the necessary corrections. As each correction was made, it was checked off on the verification printout using a second pen of a different color. The final protocol step was the production of a final Verification Report, which was compared to the original, marked-up verification printout to ensure that all necessary corrections were made. Completion of each of the above steps was duly noted on the Data Entry Status Log.

The use of signatures by all responsible parties and the careful checking of data at each step resulted in an extremely reliable database.

SUMMARY STATISTICS

The data from this study consist of plant influent and filter influent (where applicable) water quality characteristics and clearwell effluent DBPs from 35 water utilities' treatment plants. As described in preceding chapters, each plant was sampled once every quarter for a total of four quarters (although not all analytes were determined every quarter). For each DBP compound or water quality parameter, it is of interest to examine and compare the set of values (one per plant) for particular quarters, and the complete annual set of values (from all plants for all quarters sampled). This large amount of data created the need for a way to summarize the various data sets.

For conveying the essential features of any set of data, it is desired to express both a measure of central tendency and a measure of variability. The traditional parametric approach consists of reporting the sample mean and sample standard deviation. However, this approach suffers from several drawbacks:

1. **Assumed Distribution:** In the water quality field, it is frequently assumed that all water quality data is either normally or log-normally distributed. This assumption is perhaps based on a limited understanding of statistics, and on studies involving a few conventional water quality parameters or compounds which were found to be adequately modeled by normal or log-normal distributions. Thus, a wholesale tendency has emerged to apply parametric techniques based on those distributions, frequently without testing the validity of the assumption. It is not always recognized that the common practice of computing the mean and standard deviation is rooted in the statistical methodology of estimation, in this context the estimation of the population parameters of a normal distribution from a limited sample assumed to be drawn from the population. In association with the computation of the sample mean, the 95% confidence interval for the mean is also frequently reported as a measure of the accuracy of the population estimate.

Data Management and Analysis

With these classical statistical methods (in the early phase of this project), the sample means of compounds and class totals across the 35 utilities, and their associated 95% confidence intervals based on the normal distribution, were computed. Subsequent testing of the individual DBP compounds and chemical class totals indicated that they followed different distributions, and that neither the normal nor log normal distribution seemed to apply in some cases. Furthermore, upon careful reflection it was realized that a major objective of the study was to explore, describe, and summarize the sample data, not to estimate the parameters of an underlying distribution for a larger population, such as the population of all United States water utilities, for example. Even if this were a major objective, it is possible that the non-randomized sample of 35 utilities with different selected source waters and treatment practices would be inadequate to do so.

2. **Sensitivity to Outliers:** A single or several extremely outlying data values can have a substantial adverse impact on both the sample mean and sample standard deviation. Especially for exploratory data analysis, it is often advantageous to use simpler summaries based on sorting and counting which are more resistant: that is, an arbitrary change in a small part of the data set can have only a small effect on the summary.

3. **Loss of Information:** Information about the characteristics of a data set can be obscured by reducing the data to one or two summary numbers such as the mean and standard deviation. For example, the minimum and maximum values cannot be discerned, and questions about how many of the values in the sample are above or below a specified level cannot be answered.

4. **Censored data:** Data for compounds which are reported as below detection limits (in this study, Minimum Reporting Levels (MRLs)) complicate the issue of how to compute summary statistics such as the mean and standard deviation. Various approaches for handling such "left-censored" data (below detection limits) are encountered in practice, including treating these values as equal to zero, equal to the detection limit, or equal to one-half the detection limit. However, each of these techniques bears conceptual difficulties and objections (Helsel and Cohn, 1988).

Consideration of the above discussion led to a decision to utilize nonparametric measures to analyze the data from this study. Nonparametric statistical methods do not require an assumed parametric distribution for the data, and cases below the detection limits can be incorporated. In the area of applied statistics called exploratory data analysis, the data in a sample set are sorted in ascending order of magnitude, and then characterized by counting up from the lowest value and determining percentages called percentiles. In particular, the "five-number summary" (Tukey, 1977) is frequently used to summarize a data set.

The five-number summary consists of the minimum value, 25th percentile, median, 75th percentile, and maximum value from the data set. The "nth" percentile is the value below which n percent of the data lie. The most familiar percentile is the median, the 50th percentile, above and below which 50 percent of the data lie. Because the 25th, 50th, and 75th percentiles divide the data set into four quarters, the 25th and 75th percentiles are frequently referred to as the lower and upper quartiles,

respectively. The difference or spread between the lower and upper quartiles is known as the interquartile range, and it encompasses the middle 50 percent of the data values. Thus, in nonparametric statistics, the median and interquartile range are analogous to the mean and one standard deviation above and below the mean in parametric statistics. They also provide much more resistant measures of central tendency and variability. For example, all the values below the lower quartile including the minimum can change in magnitude, even drastically, without affecting the values of the median and interquartile range.

The five-number summary gives five pieces of information about a data set instead of just one or two. It also allows very useful but simple statements to be made, such as "75 percent of the chloral hydrate data for the utilities sampled fell below 1.1 μg/L." Lastly, medians and other percentiles can still be determined for data sets containing censored data. For example, for the following data set (n = 9):

$$<0.1, <0.1, <0.1, <0.1, 0.12, 0.43, 1.1, 2.0, 3.5$$

the lower quartile is <0.1, the median is 0.12, and the upper quartile is 1.1. The proper statement is that the lower quartile is <0.1; that is, "the lower 25 percent of the observations in the data set fell below 0.1."

One of the major benefits of the use of the five-number summary (or any other desired percentiles) is how well they lend themselves to graphical portrayal of a data set and its essential characteristics. The following sections describe the types of graphical data presentations used for this study.

GRAPHICAL PRESENTATION OF DATA

Box-and-Whisker Plots

The box-and-whisker plot (Tukey, 1977) is a direct graphical representation of the five-number summary. Box-and-whisker plots are most useful for comparing several different batches of data side by side. A variation of regular box-and-whisker plots called notched box-and-whisker plots (McGill et al., 1978) was used in this study (Figure 4-2).

As shown in Figure 4-2, the lower and upper quartiles form the lower and upper edges of the "box", with the median drawn as a horizontal line dividing the box into the two middle quarters of the data. The "whiskers" are vertical lines extending from the box edges (quartiles) to the minimum and maximum values of the data set. More specifically, the whiskers extend to the maximum and minimum values, but exclude outliers. In this form of exploratory data analysis, outliers are determined by a rule-of-thumb criterion. Outliers are defined as those points which lie outside a specified "distance" (range), equal to 1.5 times the interquartile range, measured from the upper and lower quartiles.

To clarify this, first consider the interquartile range, which is the distance in data units between the lower and upper quartiles. Multiply this distance by one-and-a-half, and measure that distance upward from the upper quartile and downward from the lower quartile. Any data point falling outside of those "outer cutoff" limits is classified as an

GUIDE TO NOTCHED BOX-AND-WHISKER PLOTS

+ ← **EXTREME OUTLIER**
any value outside 3 interquartile ranges
measured from the 25 and 75 percentiles

☐ ← **OUTLIER**
any value outside 1.5 interquartile ranges
measured from the 25 and 75 percentiles

← **MAXIMUM VALUE**
this is the largest value (excluding outliers)

← **75 PERCENTILE**
75% of the data are less than or
equal to this value (including outliers)

INTERQUARTILE RANGE
contains the data between
the 25 and 75 percentiles

95% CONFIDENCE INTERVAL
for the median (including outliers)

← **MEDIAN**
50% of the data are above or
below this value (including outliers)

← **25 PERCENTILE**
25% of the data are less than or
equal to this value (including outliers)

NOTE: Horizontal width of box is
proportional to square root of sample size (N)
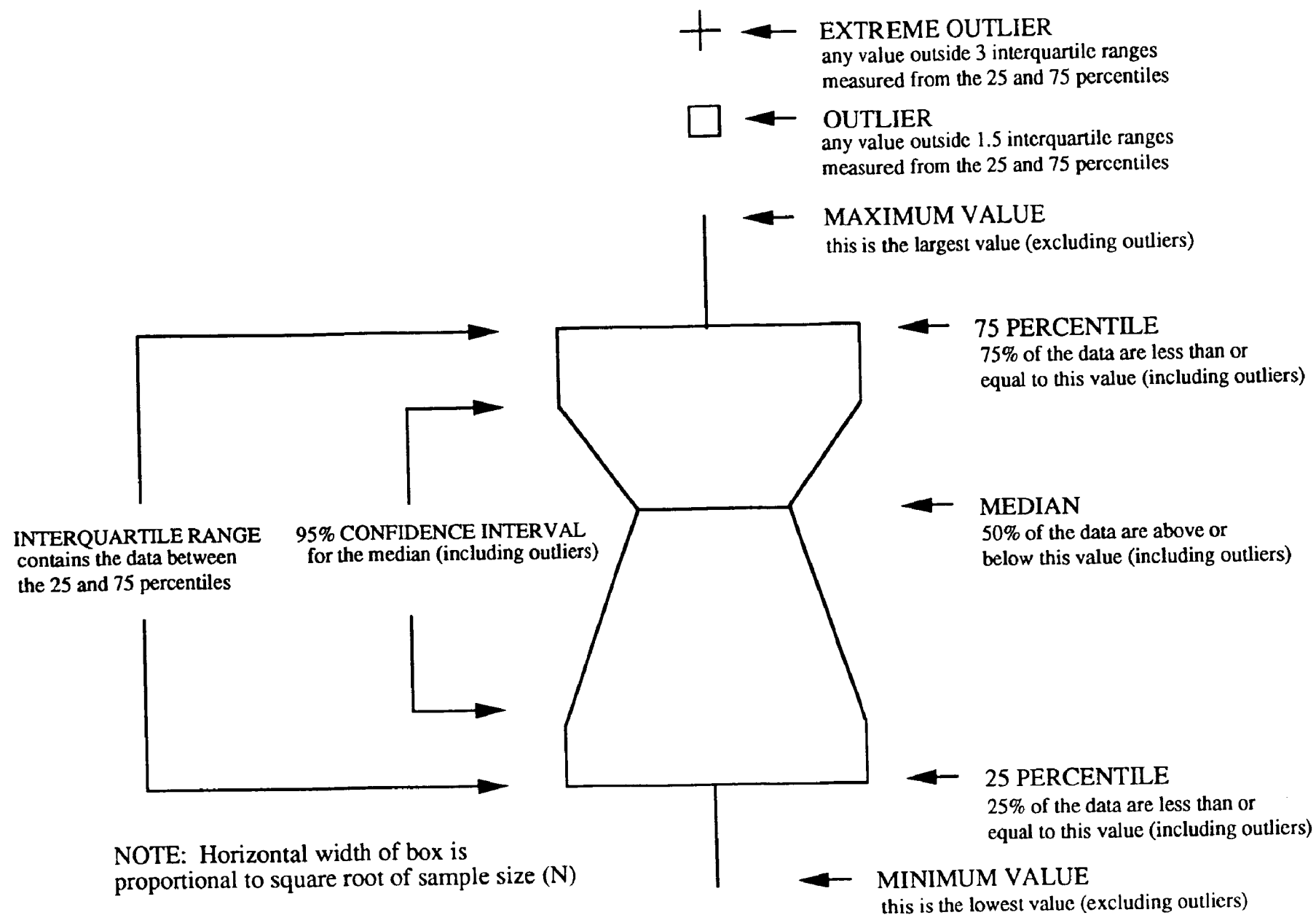
← **MINIMUM VALUE**
this is the lowest value (excluding outliers)

FIGURE 4-2

outlier, and is excluded when determining the minimum and maximum for setting the endpoints of the whiskers. For a perfectly symmetric normal distribution, the choice of the 1.5 interquartile range cutoffs correspond to a probability of only 0.7 percent (p = 0.007, 0.0035 in each tail of the distribution) for a data point to lie outside those limits (Hoaglin, Mosteller, and Tukey, 1983). The outlier criterion is only a guide as to which data points should be more carefully scrutinized as potential outliers, not an absolute rule.

Notched box-and-whisker plots portray the 95 percent confidence interval about the median as a notch-width in the box. This confidence interval can be used to test the pairwise significance of differences in medians between two data sets, which is a nonparametric analog of the classical t-test for the significance of differences in means of normally distributed data sets. An example is shown in Figure 4-3. In comparing the box-and-whisker plots for three data sets (A, B and C in Figure 4-3), the 95 percent confidence interval (notch-width) for one data set (A) would be compared to that of the second data set (B), and then to that of the third data set (C). If the 95 percent confidence intervals of any two medians do not overlap (medians for A and B, and A and C), then the difference between those medians is statistically significant at a 95 percent confidence level. If the 95 percent confidence intervals of the medians of any two data sets overlap (B and C), then the difference between those two medians is not statistically significant at a 95 percent confidence level. It should be noted that this type of comparison is pairwise only. In other words, even if box-and-whisker plots from three different data sets are being compared, the 95 percent confidence intervals for only two at a time (A and B, A and C, and B and C) can be compared for determining whether or not there are statistically significant differences between the two at a 95 percent confidence level. A more detailed discussion of the 95 percent confidence interval about the median has been prepared by McGill, et al. (1978).

Bar Charts

A derivative form of the box-and-whisker plot was also created and used for this study. As shown in Figure 4-4, standard bar graphs were made with the height of the bar equal to the median of the data set. The interquartile range was then superimposed on the bar, being drawn as an I-shaped "error bar" (more properly, "variability bar") with the horizontal cross-members of the "I" at the lower and upper quartiles. Thus, this form of bar chart represents a "three-number summary", omitting the minimum and maximum values. These graphs were used in cases where multiple compounds or chemical class totals were portrayed on the same graph, for which differences in medians are not relevant. Rather, they provide a relative indication of location (central tendency) and spread (variability). For those DBPs that had relatively high MRL values and the 25th percentile, median and 75th percentile were less than the MRL, the bar chart might be interpreted as giving a misleading representation of the concentration. In such circumstances, the bar was drawn solid black rather than cross-hatched. For purposes of comparison, the MRL is indicated on the bar chart in some figures where the median was greater than the MRL, as shown in Figure 4-4.

Star Symbol Plots

Another type of graphical presentation that was used for this study was the star symbol plot (STSC Inc., 1987). The star symbol plot is not part of the standard repertoire of

Example of Notched Box-and-Whisker Plot for Three Data Sets

A   B   C
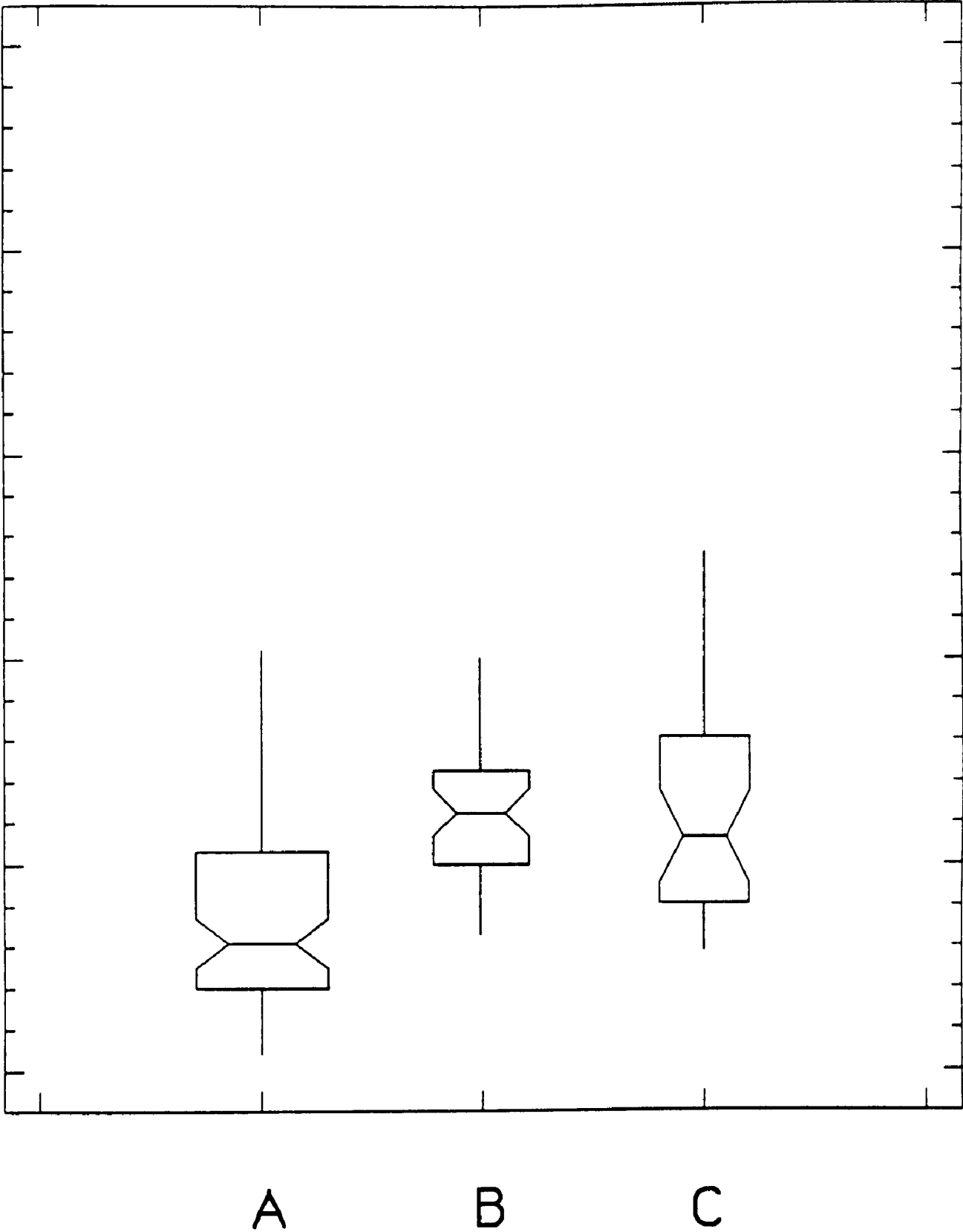
FIGURE 4-3

GUIDE TO BAR CHARTS USING MEDIAN, PERCENTILES AND MINIMUM REPORTING LEVEL

75 PERCENTILE
75% of the data are less than
or equal to this value

MEDIAN
50% of the data are above
or below this value

INTERQUARTILE RANGE
contains the data between
the 25 and 75 percentiles

25 PERCENTILE
25% of the data are less than
or equal to this value

MINIMUM REPORTING LEVEL
lower limit of quantitation
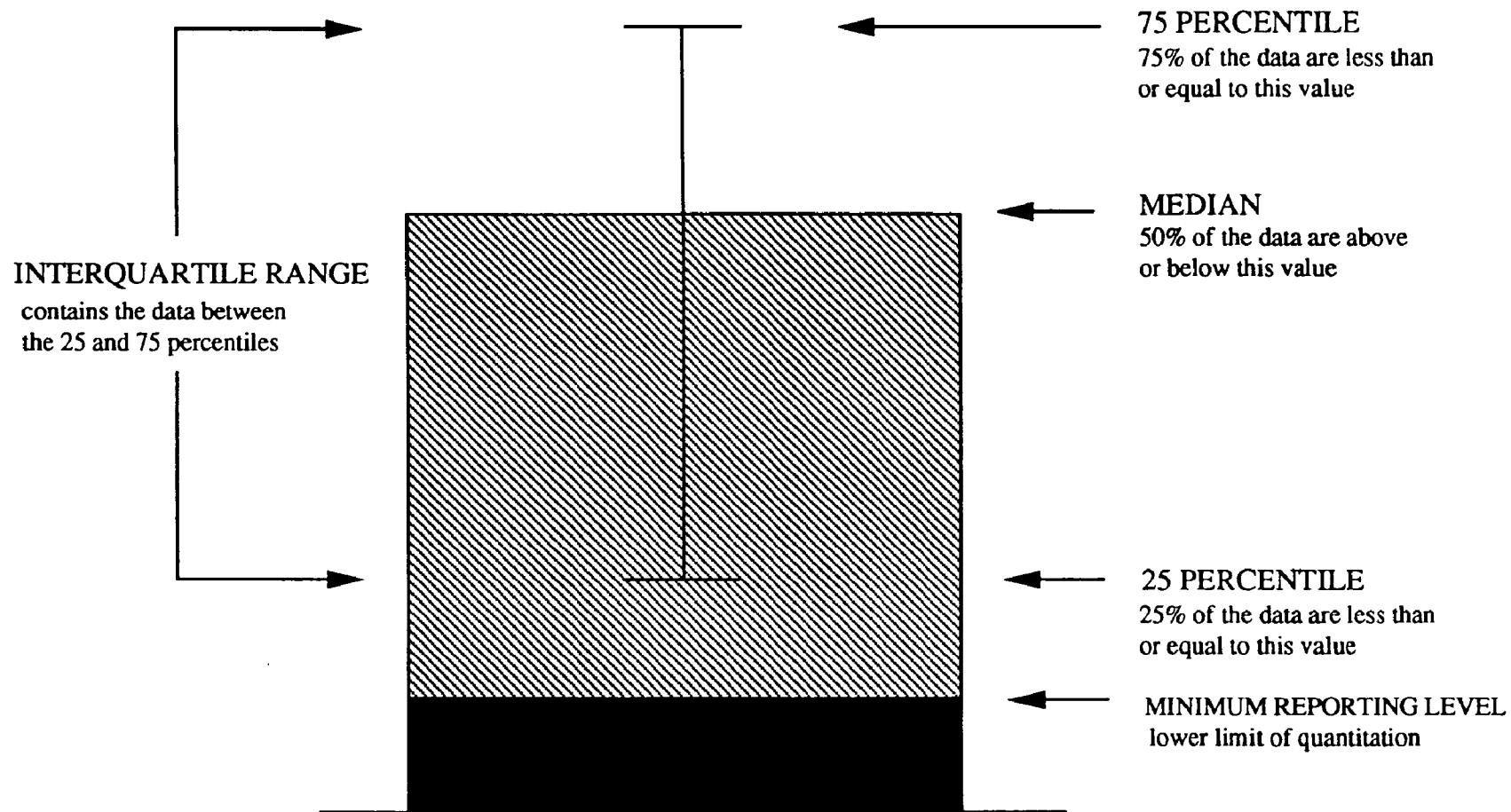
NOTE - ASTERISKS ON CHARTS INDICTE THE FOLLOWING:
*   25 percentile < Minimum Reporting Level
**   25 percentile and median < Minimum Reporting Level
***   25 percentile, median, and 75 percentile < Minimum Reporting Level

FIGURE 4-4

exploratory data analysis and nonparametric statistics, as are box-and-whisker plots. It is. however. a unique way of visually portraying differences in multivariate (multiple variable) "profiles" between entities.

A star symbol plot is used to graphically display the relative magnitude of the values of multiple variables for two or more entities. As an example, consider the four compounds which make up the regulated quantity. total trihalomethanes as the four variables to be portrayed. This example is illustrated in Figure 4-5. On a star symbol plot. the magnitude of each variable is plotted as a "ray" of a "star" emanating from a common center point. starting with the first variable at a "0 degrees" position, and with the remaining variables being spaced evenly around the full 360 degrees of a circle as in trigonometry. For the four trihalomethanes, a four-ray star results, with each ray of the star at 0. 90. 180, and 270 degrees (right angles), respectively. For the general case of "n" variables. n rays of the star will be plotted. each separated by an angle of 360/n degrees.

Chapter 5 of this report presents the actual application of star symbol plots to this study. at which point this concept will be made more discernible.

EXAMPLE GUIDE TO STAR PLOTS
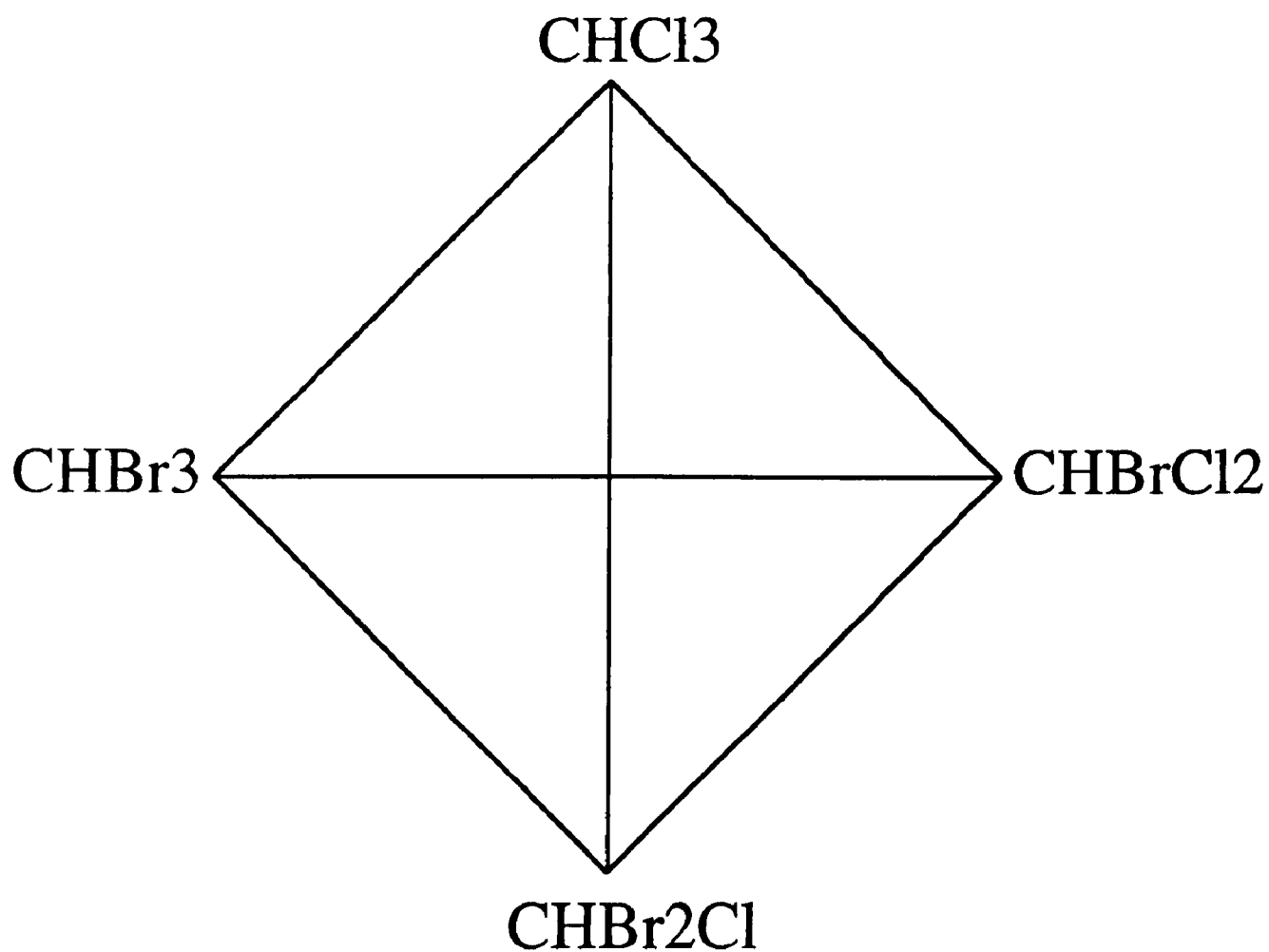
FIGURE 4-5

Section 5

Baseline Sampling Results and Discussion

SECTION 5

BASELINE SAMPLING RESULTS AND DISCUSSION

In this section, results of the quarterly baseline sampling are presented and discussed. Methods of data analysis and presentation were described in Section 4. Table 5-1 lists the abbreviations used in the figures in this section.

OVERVIEW OF BASELINE DATA

Figures 5-1 through 5-10 present an overview of the results of the baseline sampling program for all four quarters combined. Table 5-2 shows the baseline median DBP values for each quarter as well as for all four sampling quarters combined. It should be noted that a class total median value is not the sum of the medians of individual compounds, but rather the median value of the sum of all the compounds within that class. To illustrate, the median for a compound (chloroform, for example) during a sampling quarter was the median of the 35 measured values of chloroform for that quarter. For each utility, the sum of the individual compounds within each class (THMs, for example) was computed, and then the median of these 35 sums was determined. Finally, the sum of the individual halogenated DBP compounds measured in this study ($XDBP_{sum}$) was computed, and then the median of these 35 sums was determined.

In examining these data, it should be noted that they represent clearwell effluent samples. Distribution system sampling, which was performed for some of the process modification studies described in Section 6 of this report, indicated that some DBPs (such as THMs) increased in the chlorinated distribution systems of some utilities, while the same compounds remained stable in chloraminated distribution systems. In addition, it is important to note that the disinfection practices of some of the 35 participating utilities, such as the use of chloramines, were employed to meet the current TTHM MCL of 0.10 mg/L, and not to meet the requirements of the proposed Surface Water Treatment Rule (SWTR). Thus, DBP levels at some utilities would most likely be different if their current disinfection practices required modification in order to meet proposed concentration-time (CT) requirements of the SWTR.

Figure 5-1 is a summary of the four-quarter median concentrations of each DBP class (THMs, HANs, HKs, HAAs and ALDs) and the miscellaneous compounds. The median value of THMs was 36 μg/L, and the median value of HAAs was 17 μg/L. On a weight basis, ALDs were the next most prevalent compound, with a total median concentration of 5.7 μg/L.

Figure 5-2 shows the contribution of each of the median class totals and miscellaneous compounds to the total concentration of DBPs measured in this study. On a weight basis, THMs were the largest class of DBPs detected in this study, comprising 54.5 percent of the total measured DBPs. The second largest fraction was HAAs, comprising 25.4 percent of the total. The data indicate that the median level of THMs was approximately twice that of HAAs. Figure 5-2 also shows that the third largest fraction detected was the ALDs (formaldehyde and acetaldehyde), which comprised 8.5 percent of the measured DBPs. These two low molecular weight aldehydes were

TABLE 5-1

LIST OF ABBREVIATIONS USED IN DBP STUDY

ABBREVIATION[1]	DEFINITION
Disinfection By-Products	
DBP	Disinfection by-product
$XDBP_{sum}$	Sum of measured halogenated disinfection by-products
Haloacetic acids	
HAA	Haloacetic Acid
MCAA	Monochloroacetic Acid
DCAA	Dichloroacetic Acid
TCAA	Trichloroacetic Acid
MBAA	Monobromoacetic Acid
DBAA	Dibromoacetic Acid
Haloketones	
HK	Haloketone
1,1-DCP	1,1-Dichloropropanone
1,1,1-TCP	1,1,1-Trichloropropanone
Haloacetonitriles	
HAN	Haloacetonitrile
DCAN	Dichloroacetonitrile
TCAN	Trichloroacetonitrile
BCAN	Bromochloroacetonitrile
DBAN	Dibromoacetonitrile
Aldehydes	
ALD	Aldehydes
FRM	Formaldeyde
ACETAL	Acetaldehyde

TABLE 5-1

List of Abbreviations, Continued

ABBREVIATION[1]	DEFINITION

Chlorophenols

CP	Chlorophenol
DCP	2,4-Dichlorophenol
TCP	2,4,6-Trichlorophenol
PCP	Pentachlorophenol

Other Disinfection By-Products

CH	Chloral Hydrate
CHP	Chloropicrin
CNCl	Cyanogen Chloride

Others

PI	Plant Influent
FI	Filter Influent
FE	Filter Effluent
CE	Clearwell Effluent
MRL	Minimum Reporting Level
NA	Not analyzed
THM	Trihalomethane
TOC	Total Organic Carbon
TOX	Total Organic Halogen
UV-254	Ultraviolet light absorbance at 254 nanometers

[1]Disinfection by-products not listed are represented by their chemical formulas.

TABLE 5-2

DISINFECTION BY-PRODUCTS IN DRINKING WATER

SUMMARY OF BASELINE SAMPLING MEDIAN VALUES

Disinfection By-Products (μg/L)	1st Quarter (Spring)	2nd Quarter (Summer)	3rd Quarter (Fall)	4th Quarter (Winter)	All Quarters Combined
Trihalomethanes					
Chloroform	15	15	13	9.6	14
Bromodichloromethane	6.9	10	5.5	4.1	6.6
Dibromochloromethane	2.6	4.5	3.8	2.7	3.6
Bromoform	0.33	0.57	0.88	0.51	0.57
Total Trihalomethanes	34	44	40	30	36
Haloacetonitriles					
Trichloroacetonitrile	<0.012	<0.012	<0.029	<0.029	<0.029
Dichloroacetonitrile	1.2	1.1	1.1	1.2	1.2
Bromochloroacetonitrile	0.50	0.58	0.70	0.59	0.57
Dibromoacetonitrile	0.54	0.48	0.51	0.46	0.50
Total Haloacetonitriles	2.8	2.5	3.5	4.0	3.3
Haloketones					
1,1-Dichloropropanone	0.52	0.46	0.52	0.55	0.52
1,1,1-Trichloropropanone	0.80	0.35	0.60	0.66	0.60
Total Haloketones	1.4	0.94	1.0	1.8	1.2
Haloacetic acids					
Monochloroacetic acid	<1.0	1.2	<1.0	1.2	<1.0
Dichloroacetic acid	7.3	6.8	6.4	5.0	6.4
Trichloroacetic acid	5.8	5.8	6.0	4.0	5.5
Monobromoacetic acid	<0.5	<0.5	<0.5	<0.5	<0.5
Dibromoacetic acid	0.9	1.5	1.4	1.0	1.1
Total Haloacetic acids	18	20	21	13	17

Table 5-2

Disinfection By-Products In Drinking Water
Summary of Median Values, Continued

	1st Quarter (Spring)	2nd Quarter (Summer)	3rd Quarter (Fall)	4th Quarter (Winter)	All Quarters Combined
Aldehydes					
Formaldehyde	NA	5.1	3.5	2.0	3.6
Acetaldehyde	NA	2.7	2.6	1.8	2.2
Total Aldehydes	NA	6.9	5.5	4.2	5.7
Miscellaneous					
Chloropicrin	0.16	0.12	0.10	0.10	0.12
Chloral hydrate	1.8	3.0	2.2	1.7	2.1
Cyanogen chloride	0.45	0.60	0.65	0.80	0.60
2,4,6-Trichlorophenol	<0.3	<0.4	<0.4	<0.4	<0.4
Halogenated DBP$_{sum}$	64	82	72	58	70
Total Organic Halide	150	180	170	175	170
Plant Influent Characteristics					
Total Organic Carbon, mg/L	NA	2.9	2.9	3.2	3.0
Ultraviolet absorbance, cm^{-1}	NA	0.11	0.11	0.13	0.11
Chloride, mg/L	NA	28	32	23	29
Bromide, mg/L	NA	0.07	0.10	0.07	0.08

NA = Not Analyzed

Note (1): Total class median values are not the sum of the medians of the individual compounds, but rather the medians of the sums of the compounds within that class.

Note (2): The halogenated DBP$_{sum}$ median values are not the sum of the class medians for all utilities, but rather the medians of the halogenated DBP$_{sum}$ values for all utilities. This value is only the sum of halogenated DBPs measured in this study.

Disinfection By-Product Concentration
by DBP Class – Four Quarters

THM   Trihalomethanes
HAN   Haloacetonitriles
HK   Haloketones
HAA   Haloacetic Acids
ALD   Aldehydes
CHP   Chloropicrin
CH   Chloral Hydrate
CNCl   Cyanogen Chloride
TCP   Trichlorophenol

***   25th percentile, median, and
        75th percentile values below MRL

FIGURE 5-1

Percent of Sum of DBP Class Medians
By DBP Class – Four Quarters

HAA 25.4%   ALD 8.5%
                MISC 5.0%
                HAN 4.9%
                HK 1.8%

THM 54.5%

THM   Trihalomethanes
HAN   Haloacetonitriles
HK   Haloketones
HAA   Haloacetic Acids
ALD   Aldehydes
  MISC:
CHP   Chloropicrin
CH   Chloral Hydrate
CNCl   Cyanogen Chloride
TCP   Trichlorophenol
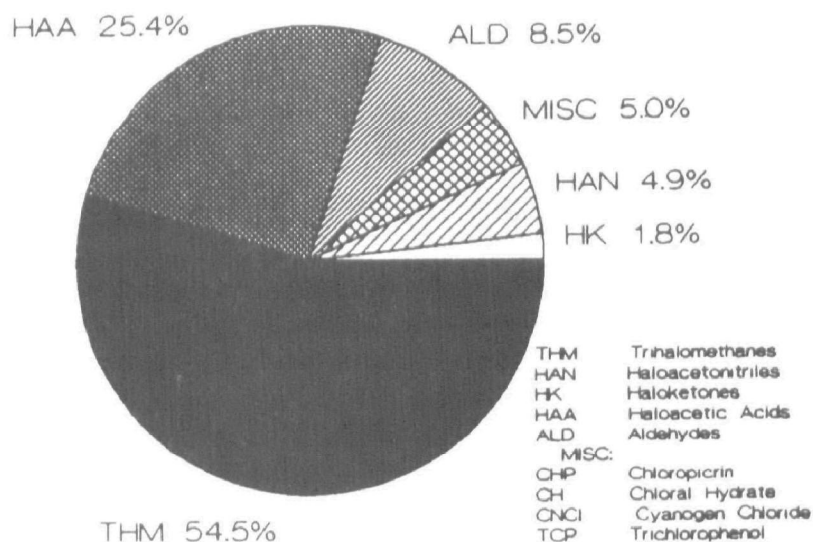
FIGURE 5-2

initially discovered as by-products of ozonation (Glaze et al., 1989a; Yamada and Somiya, 1989), and they also appear to be by-products of chlorination.

A breakdown of the class medians of the non-THM DBPs measured in this study is shown in Figure 5-3 on a weight basis. HAAs are by far the largest contributor to non-THM DBPs, comprising 56.8 percent of the total measured compounds. The two next largest fractions are ALDs and HANs, comprising 19.0 and 11.0 percent of the total, respectively. Chloral hydrate was the next largest fraction, comprising 6.9 percent of the total measured non-THM compounds on a weight basis.

Figure 5-4 shows the four-quarter median concentrations of the four THM compounds. Additionally, Figure 5-5 shows the same data as a percentage of the total level of THMs. These figures indicate that chloroform was detected at the highest levels for the THM compounds, comprising 56.2 percent of the total. The four quarter median level of chloroform was 14 μg/L. Bromodichloromethane and dibromochloromethane had median levels of 6.6 and 3.6 μg/L, respectively. The median level of bromoform was 0.57 μg/L, representing 2.3 percent of the total THMs.

Figure 5-6 presents the median HAA concentrations by compound for the four sampling quarters. Trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA) were the two HAAs detected in the highest concentrations, with median levels of 5.5 and 6.4 μg/L, respectively. These results are consistent with those of other researchers, which have shown that the aqueous chlorination of humic and fulvic acids yielded TCAA and DCAA as the major chlorinated by-products (Quimby et al., 1980; Christman et al., 1983; Miller and Uden, 1983; DeLeer et al., 1985). Dibromoacetic acid (DBAA) was detected at a four-quarter median concentration of 1.1 μg/L. The median concentrations of both monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA) were below their minimum reporting levels of 1.0 and 0.5 μg/L, respectively.

Four-quarter median concentrations of the HKs are presented in Figure 5-7. Both of these compounds had median levels less than 1 μg/L.

Median HAN concentrations for the baseline sampling are shown in Figure 5-8. Dichloroacetonitrile was detected at the highest concentration among the HANs, with a median level of 1.2 μg/L. Bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) had median levels of 0.57 and 0.50 μg/L, respectively. The median concentration of trichloroacetonitrile (TCAN) was below its minimum reporting level of 0.029 μg/L.

Figure 5-9 presents the median levels of cyanogen chloride, chloral hydrate, chloropicrin and 2,4,6-trichlorophenol (TCP). Chloral hydrate had the highest concentration of these miscellaneous compounds (2.1 μg/L), followed by cyanogen chloride (0.60 μg/L). The median concentration of chloropicrin was 0.12 μg/L. During the first sampling quarter, TCP was detected at low levels at four of the 22 utilities sampled for this compound, yet it was not detected in any samples collected in subsequent sampling quarters. Pentachlorophenol analyses were conducted for 22 utilities during the first sampling quarter, but was not detected in any of the samples. Analyses were also conducted for 2,4-dichlorophenol at 12 utilities during the first sampling quarter. This compound was only detected at one utility, at a concentration equal to the detection limit (2 μg/L).

Percent of Sum of Non–THM DBP
Class Medians by Class – Four Quarters

ALD 19.0%

HAN 11.0%

CH 6.9%

HK 3.9%

CNCl 2.0%

CHP 0.4%

HAA 56.8%

THM	Trihalomethanes
HAN	Haloacetonitriles
HK	Haloketones
HAA	Haloacetic Acids
ALD	Aldehydes
CHP	Chloropicrin
CH	Chloral Hydrate
CNCl	Cyanogen Chloride
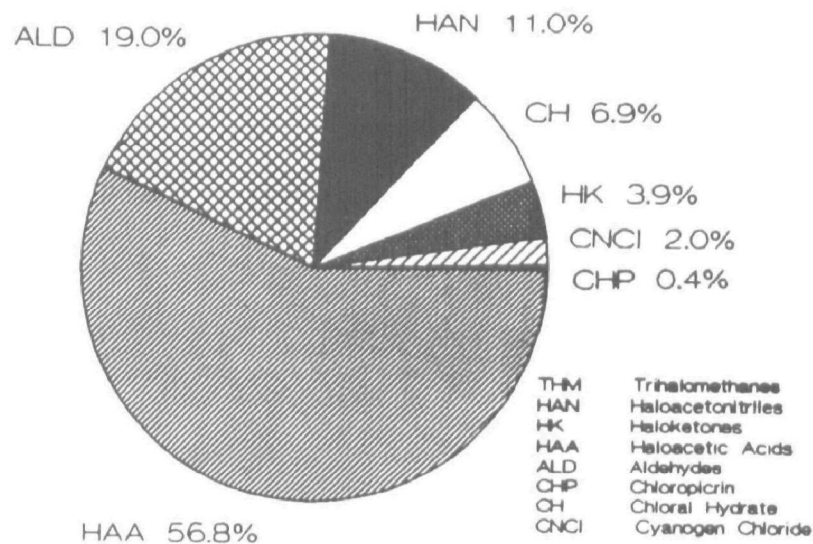
FIGURE 5-3

Trihalomethane Concentrations
by THM Compound – Four Quarters

Median THM Concentration (ug/L)

THM Compound

CHCl3   CHBrCl2   CHBr2Cl   CHBr3
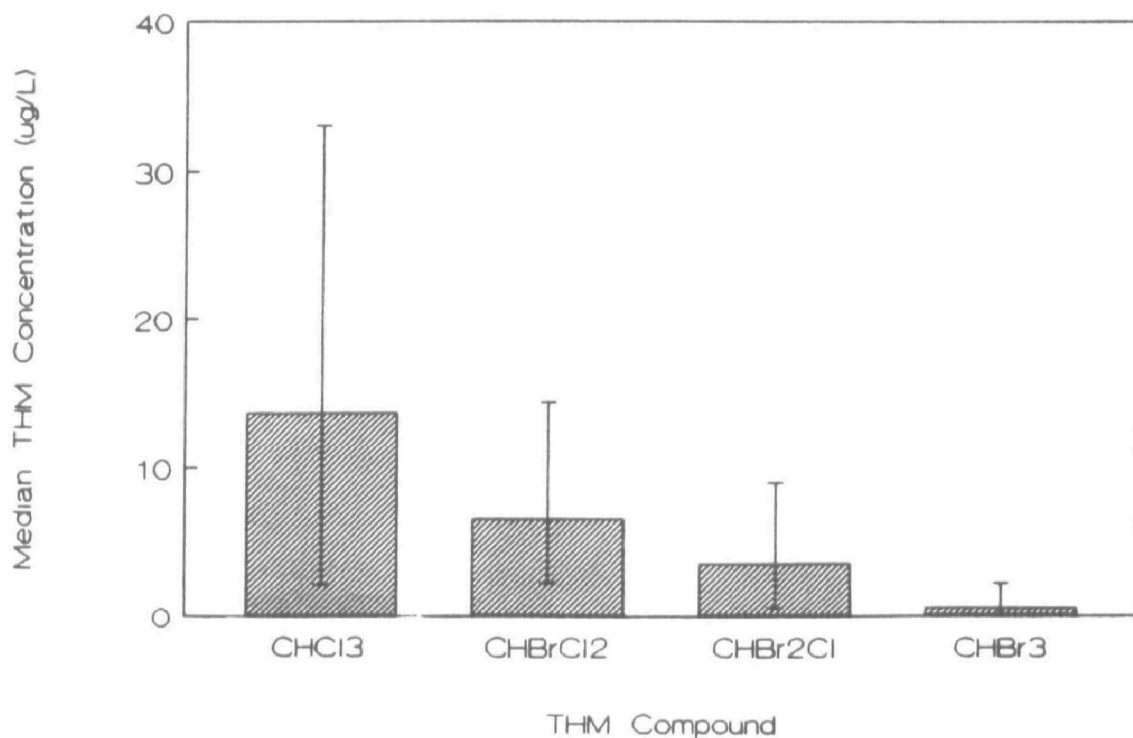
FIGURE 5-4

Percent of Sum of THM Compound Medians
by Compound – Four Quarters

CHBrCl2 26.9%

CHBr2Cl 14.6%

CHBr3 2.3%

CHCl3 56.2%
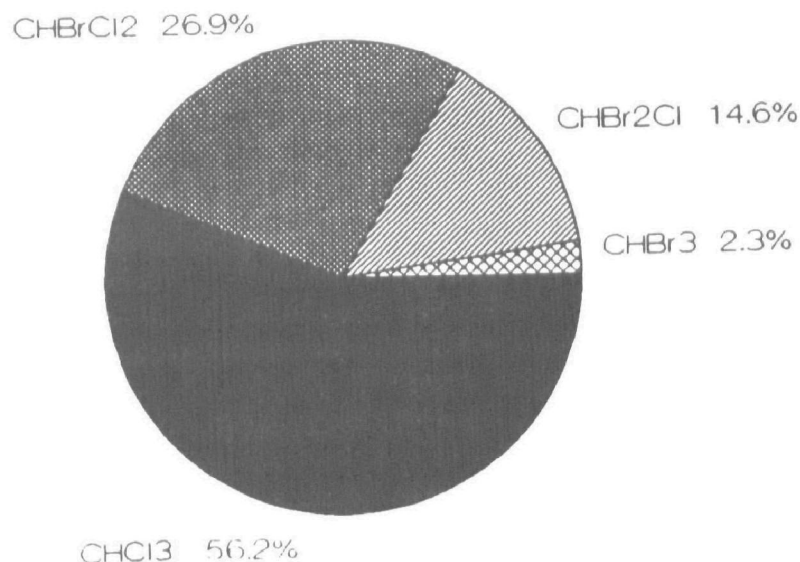
FIGURE 5-5

Haloacetic Acid Concentrations
by HAA Compound – Four Quarters

MCAA = Monochloroacetic Acid
DCAA = Dichloroacetic Acid
TCAA = Trichloroacetic Acid
MBAA = Monobromoacetic Acid
DBAA = Dibromoacetic Acid

* 25th percentile value below MRL
** 25th percentile and median values below MRL

Y-axis: Median HAA Concentration (ug/L)

X-axis: HAA Compound — MCAA, DCAA, TCAA, MBAA, DBAA
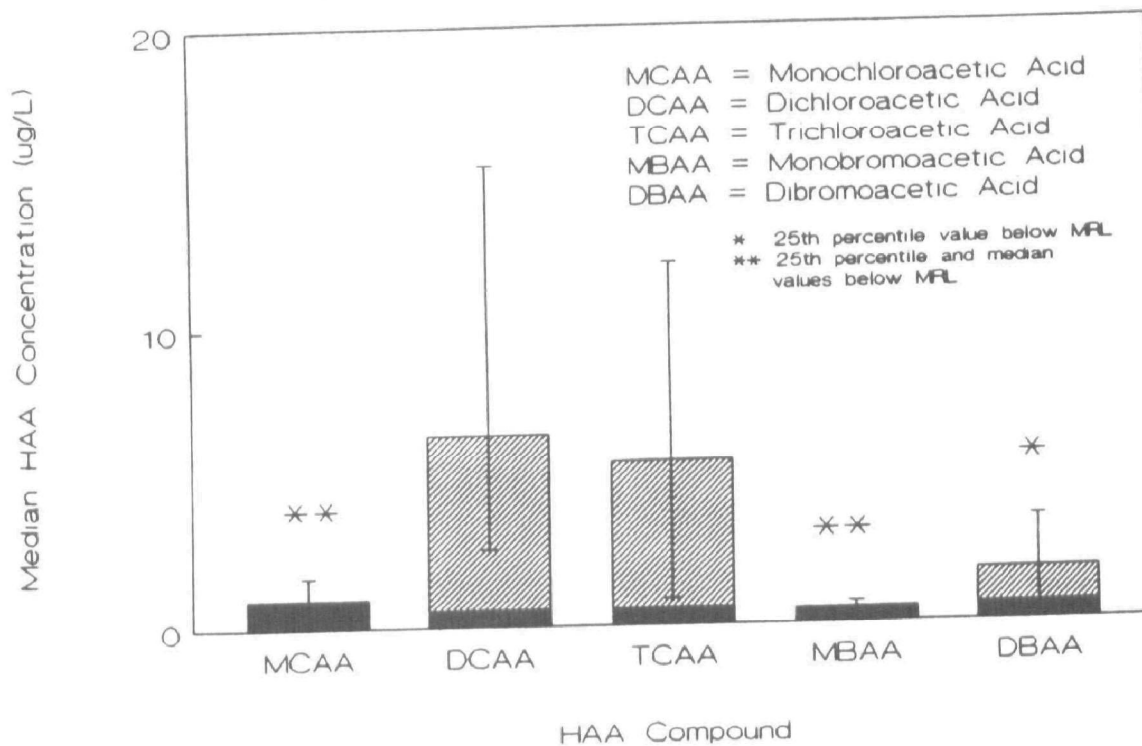
FIGURE 5-6

Haloketone Concentrations
by HK Compound — Four Quarters

1,1-DCP   1,1-Dichloropropanone
1,1,1-TCP   1,1,1-Trichloropropanone
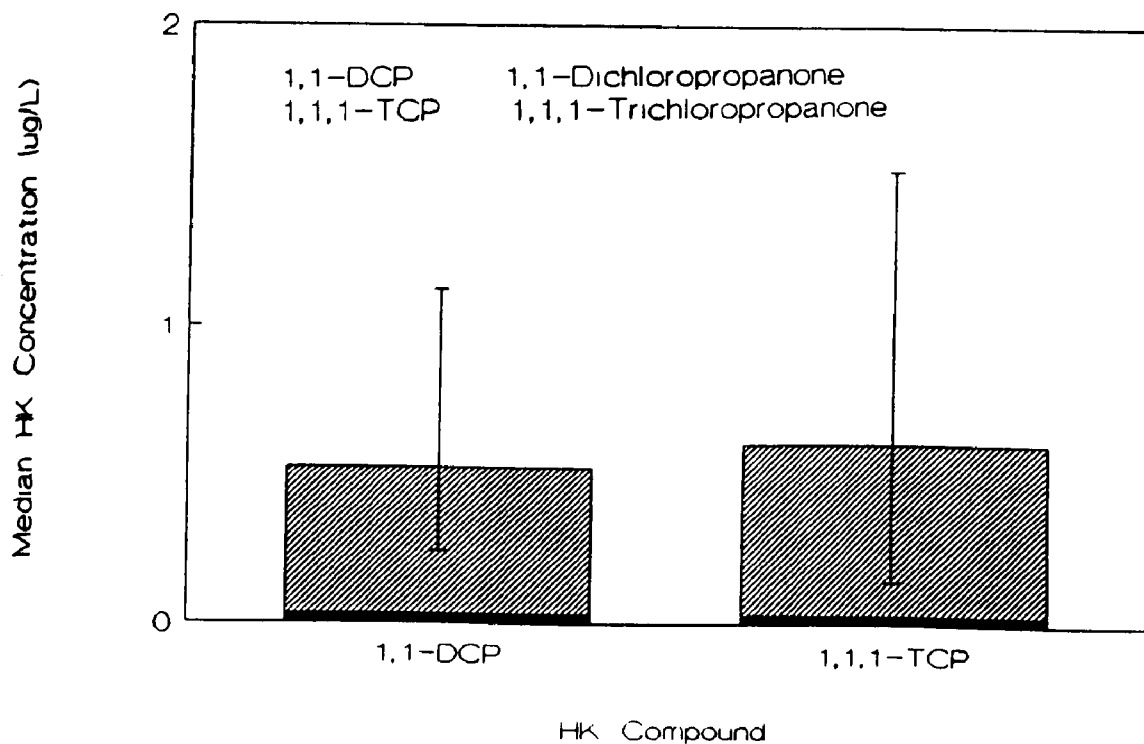
FIGURE 5-7

Haloacetonitrile Concentrations
by HAN Compound — Four Quarters

TCAN   Trichloroacetonitrile
DCAN   Dichloroacetonitrile
BCAN   Bromochloroacetonitrile
DBAN   Dibromoacetonitrile

*** 25th percentile, median, and 75th
    percentile values below MRL

FIGURE 5-8

Miscellaneous DBP Concentrations
by Compound — Four Quarters

FIGURE 5-9
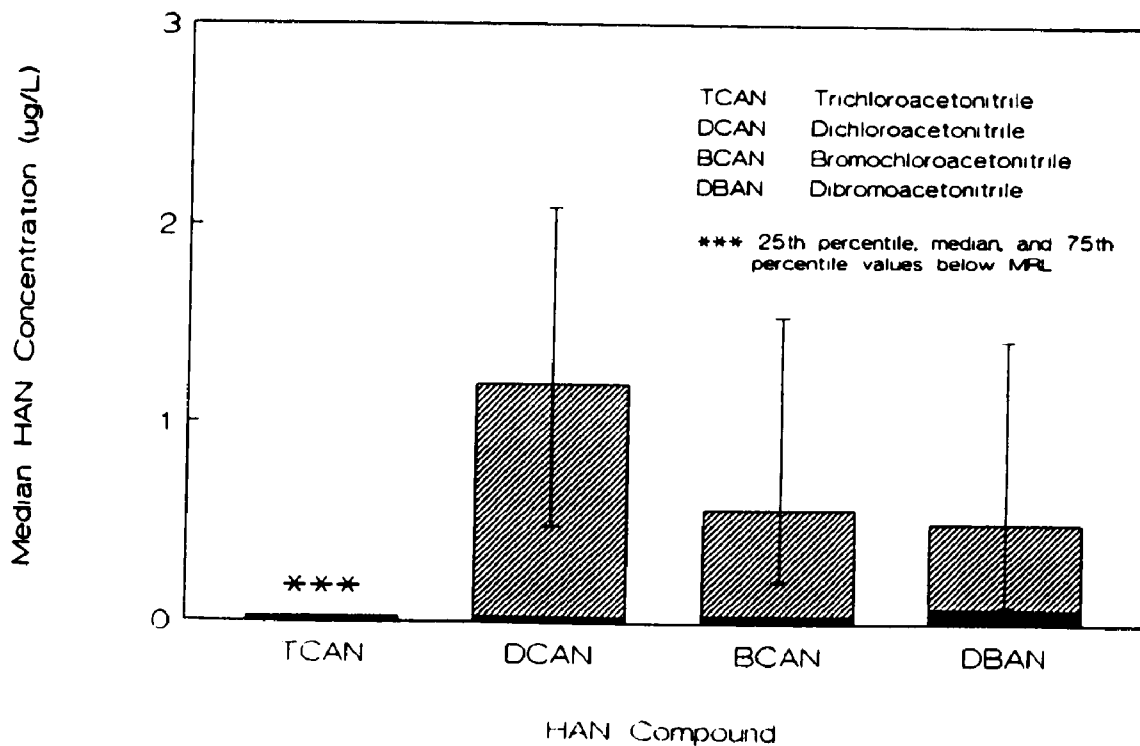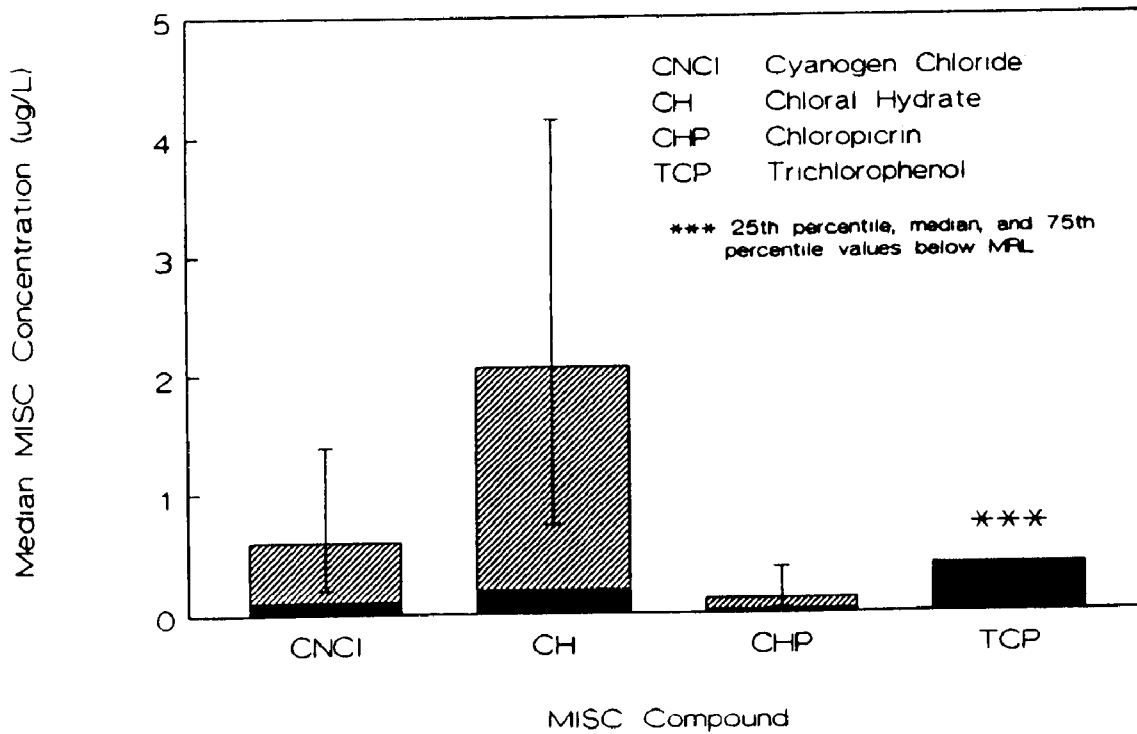
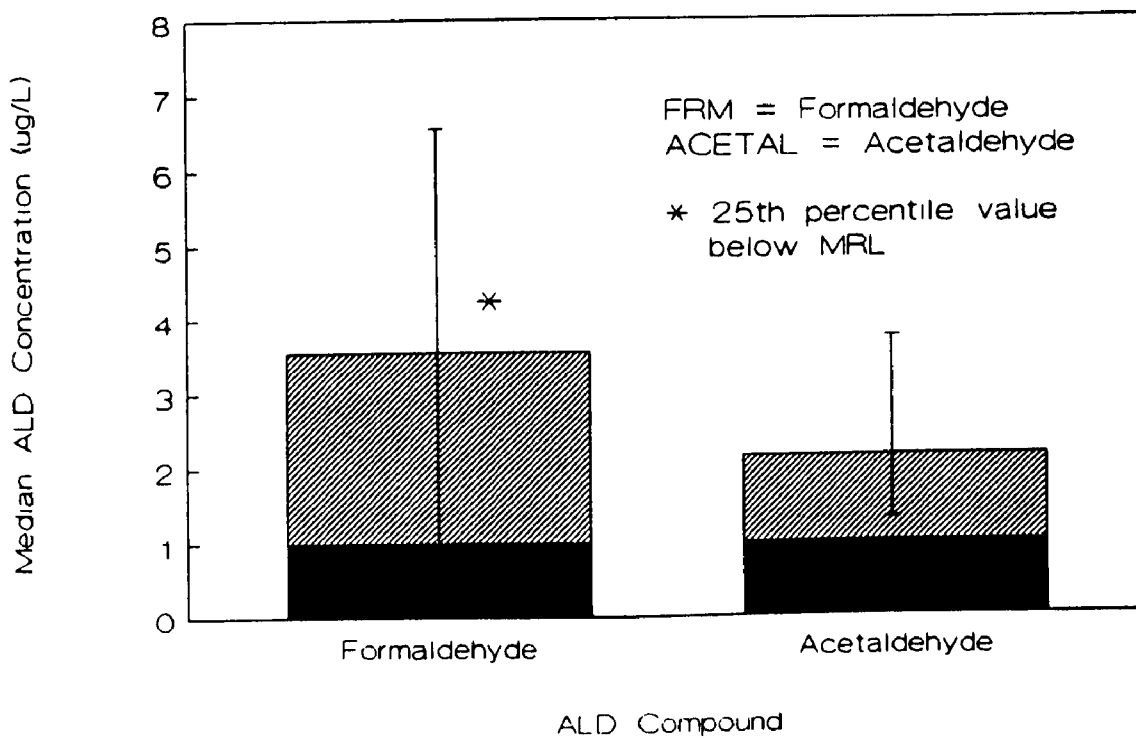# Aldehyde Concentrations
by Compound — Four Quarters

FIGURE 5-10

Baseline Sampling Results and Discussion

Median concentrations of the ALDs are shown in Figure 5-10. The four-quarter median level of formaldehyde was 3.6 μg/L and the median level of acetaldehyde was 2.2 μg/L.

STAR PLOT ANALYSES

One of the stated objectives of this study was to "determine the seasonal nature of DBPs as a function of temperature, total organic carbon, pH, and other water quality parameters; and to determine the effects of changes in treatment processes and/or disinfectants on the production of DBPs". Under ideal conditions, these objectives could be approached and properly treated as a problem in formal statistical experimental design. The ideal conditions would include a very large population of United States utilities staffed and equipped for DBP sampling, with the investigator free to perform any adjustments necessary at each plant to implement strict experimental controls in a classical statistical level-response context. Furthermore, approximately equal numbers of utilities would be using the same raw water source types, influent water quality levels, and oxidation/disinfection schemes. However, ideal conditions are not possible in field studies such as this one. Rather, the group of 35 utilities represented an unbalanced mixture of differing source waters, raw water qualities, treatments and disinfection schemes. The following paragraphs illustrate these points with the aid of star symbol plots.

Figure 5-11 shows the guide to the star plots used in this section. Using data from the summer sampling quarter for each plant in the study, the raw water characteristics of TOC and UV-254 absorbance were plotted at 0 and 180 degrees to form what can be termed the "organics axis", while raw water bromide and chloride levels were plotted at 90 and 270 degrees to form the "inorganics axis". It should be noted that the magnitude of each ray of the star plots is normalized to the utility with the highest level of the parameter under consideration. Utility 10 had the highest chloride and bromide levels (640 mg/L and 3.00 mg/L, respectively) and Utility 29 had the highest TOC and UV-254 levels (19.04 mg/L and 0.697 cm^{-1}, respectively). However, because the levels of these parameters were so high at these two utilities, relative differences between levels of these parameters for the other utilities tended to be minimized. Thus, these two utilities were excluded from all star plots and the plots were normalized to the utilities with the next highest levels of these influent parameters, Utility 24 (115 mg/L of chloride, 0.54 mg/L of bromide) and Utility 21 (10.57 mg/L of TOC, and UV-254 equal to 0.358 cm^{-1}).

Figure 5-12 shows the star plots for the 33 utilities (excluding Utilities 10 and 29), labeled by utility number. From the relative sizes and various shapes of the "stars", it is immediately apparent that the raw water quality characteristics varied considerably among the participating utilities.

Figure 5-13 presents the same star plots, but with the utilities sorted by source water type, each source water type on a separate page of the figure. This plot clearly begins to illustrate the problem of trying to ascribe differences in DBP production to discrete and unrelated causal factors, in this case source water origin. The star plots for the groundwater sources are a good illustration of this point. The groundwater "stars" vary widely in both size and shape; and thus, in the relative influences of bromide and organic carbon, both of which have a major impact on the level and speciation of DBPs

GUIDE TO STAR SYMBOL PLOTS
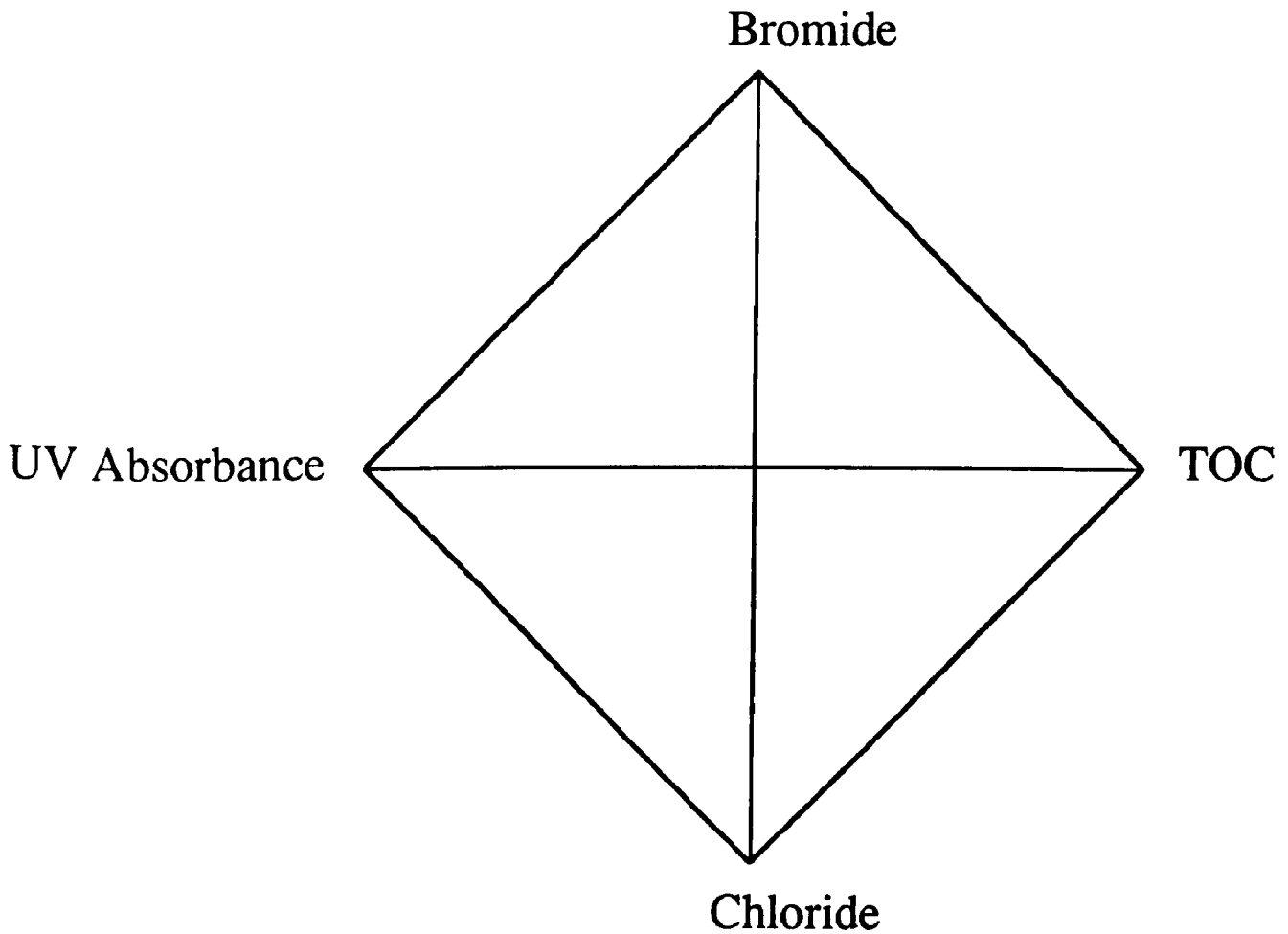
Each "ray" of the star emanating from the center point represents the relative magnitude of that parameter

FIGURE 5-11

Plant Influent By Utility ID Number
Summer Quarter

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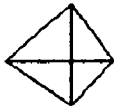
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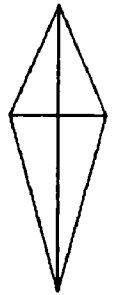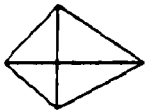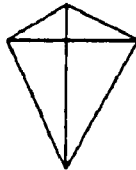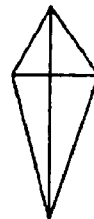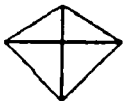
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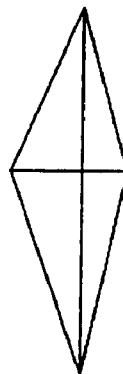
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FIGURE 5-12

Plant Influent By Utility ID Number
Summer Quarter
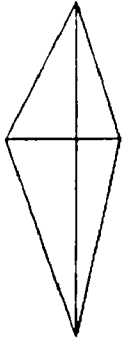
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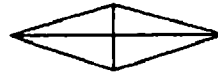
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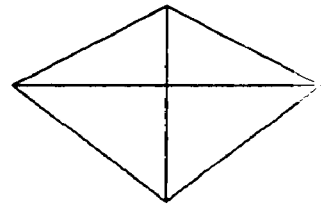
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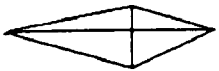
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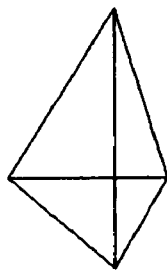
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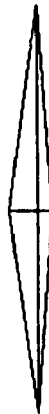
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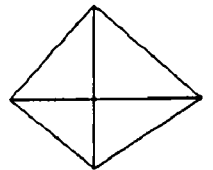
25

FIGURE 5-12   (Continued)

Plant Influent By Utility ID Number
Summer Quarter
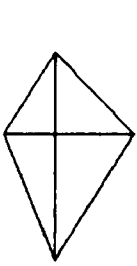
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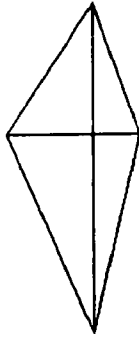
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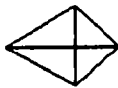
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FIGURE 5-12   (Continued)

Plant Influent by Source Water Type
Lake/Reservoir Sources
Summer Quarter
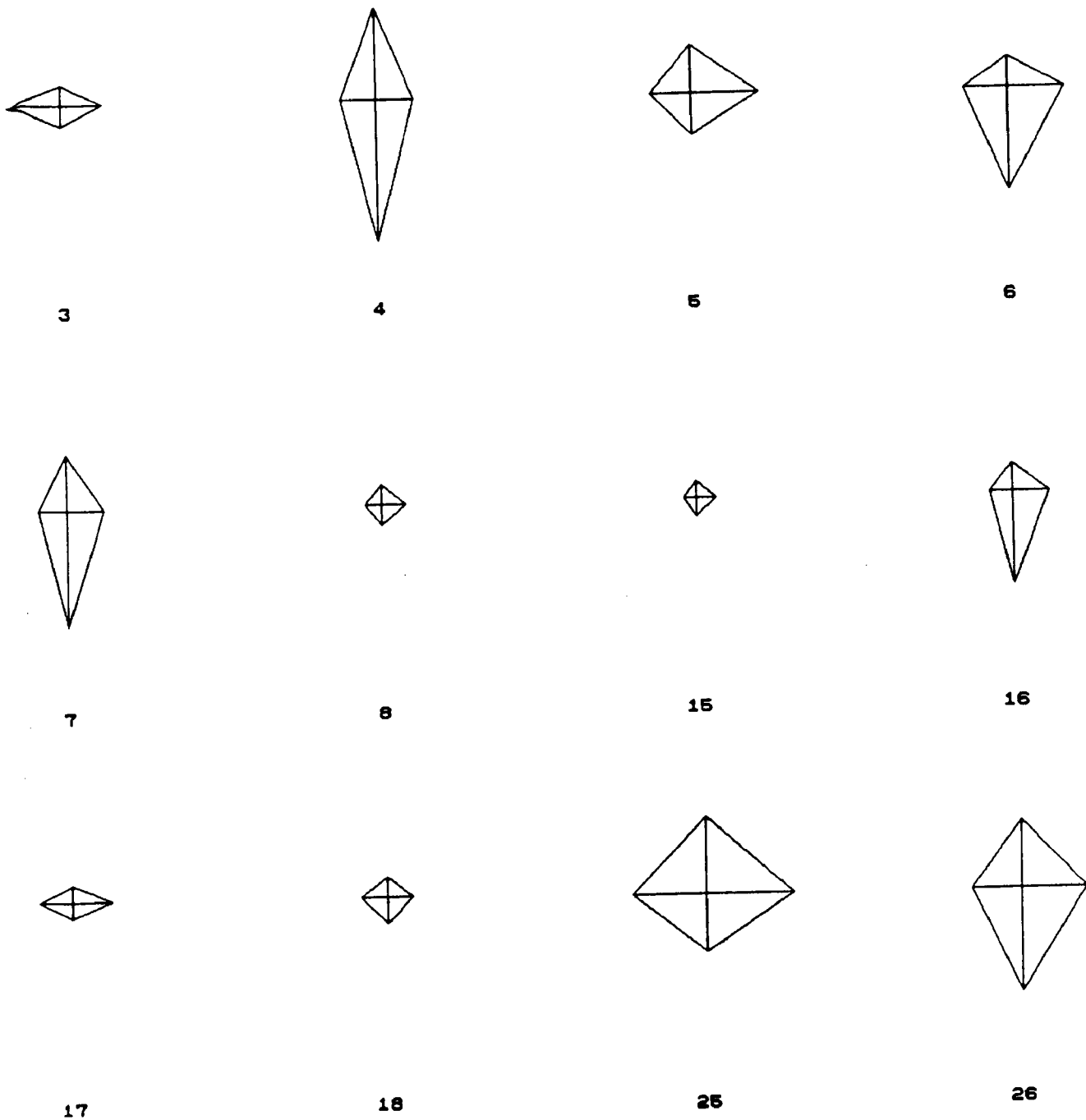
FIGURE 5-13

Plant Influent by Source Water Type
Lake/Reservoir Sources
Summer Quarter
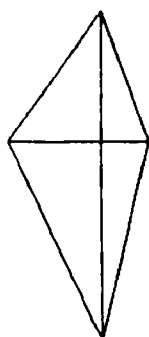
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FIGURE 5-13 (Continued)

Plant Influent by Source Water Type
Flowing Stream Sources
Summer Quarter
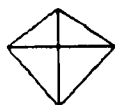
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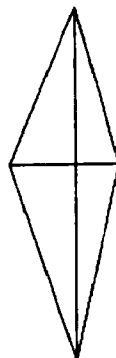
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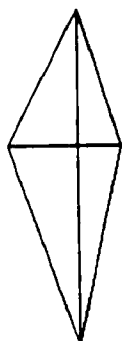
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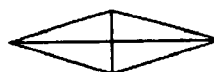
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FIGURE 5-13 (Continued)

Plant Influent by Source Water Type
Groundwater Sources
Summer Quarter

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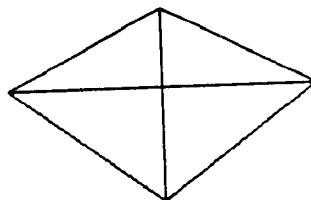
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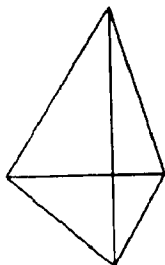
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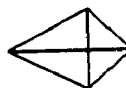
FIGURE 5-13 (Continued)

produced upon oxidation/disinfection of that water. For example, Utility 24 has a high level of bromide, while the level of TOC at this utility is relatively low. Utility 21 treated a colored groundwater with a high concentration of TOC. Finally, Utility 1's source water was a groundwater low in both inorganic and organic constituents. The plots from the flowing stream and lake/reservoir illustrate similar conditions.

The next set of star plots (Figure 5-14) depicts each utility again, but sorted by treatment type. Some overall trends are apparent in these plots. For instance, the direct filtration and disinfection only utilities generally have relatively small "stars", indicating the presence of relatively low levels of organics and inorganics, and hence the ability to employ less-extensive treatment systems for these source waters. The fact that the characteristics of the source water dictate to a large degree the type of treatment required for that water serves to confound an attempt to ascribe differences in clearwell effluent DBP levels simply to treatment type. It may be misleading to consider concentrations of TTHMs, for instance, produced by plants utilizing direct filtration or disinfection only and conclude that THM concentrations at these plants were caused solely by the treatment practices of the plants.

Figure 5-15 presents utilities labeled by disinfection scheme. In theory, this would seem to be the most promising classification for identifying causal differences in DBP production. However, examination of these star plots reveals several confounding factors. For example, all other parameters being equal, chlorine-only utilities would be expected to have higher TTHMs than the chloraminating utilities. However, the four-quarter median TTHM value was actually higher for the prechlorinating/postammoniating utilities (approximately 57 μg/L) than for the chlorine-only utilities (approximately 34 μg/L). (These findings will be discussed in more detail later in this section.) This may be understood, in part, by considering the widely varying raw water qualities of the utilities employing these two disinfection scenarios, as shown in Figure 5-15. While it appears that, in general, the prechlorinating/postammoniating utilities may have a higher percentage of relatively large "stars" compared to the chlorinating utilities, the differences in these influent parameters between the two disinfection schemes were not found to be statistically significant (as will be discussed later in this section). However, it may be the combination of high organics and bromide levels that required four of the 10 prechlorinating/postammoniating utilities to use postammoniation for THM control. No overall trend in raw water quality characteristics is observed in the star plots of any of the disinfection schemes. Thus, characteristics such as reactivity of precursor material, chlorine dose and contact time, pH, water temperature, and precursor removal within the treatment processes must also play a role in the formation and speciation of DBPs. The star plots presented here illustrate some of the difficulties arising from attempts to find discrete, unrelated causal factors for DBP production.

SEASONAL VARIATION

Figures 5-16 through 5-34 show the variation in the water quality parameters and DBPs measured in this study as a function of sampling season. The data are presented as notched box-and-whisker plots, showing the median, interquartile range, minimum and maximum values, outliers, and the 95 percent confidence intervals of the medians. The number of samples (n) is also shown on each plot. A more detailed discussion of this type of data presentation was included in Section 4 of this report.

Plant Influent By Treatment Type
Conventional Utilities, Summer Quarter

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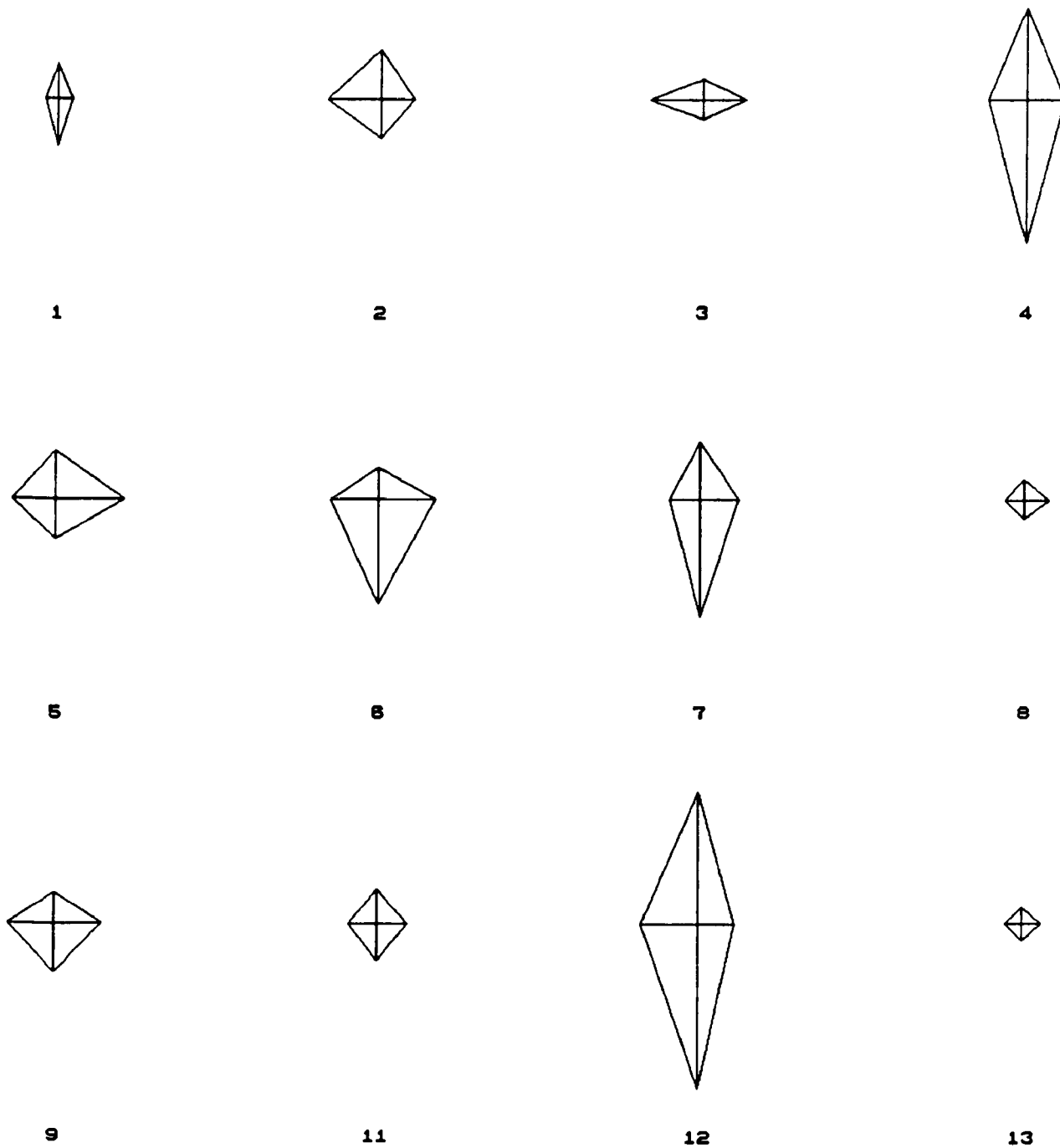
FIGURE 5-14

Plant Influent By Treatment Type
Conventional Utilities, Summer Quarter
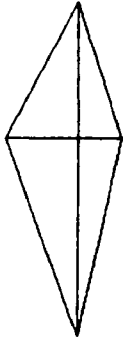
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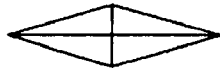
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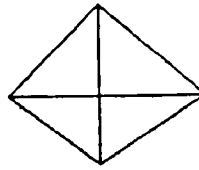
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FIGURE 5-14 (Continued)

Plant Influent By Treatment Type
Softening Utilities, Summer Quarter
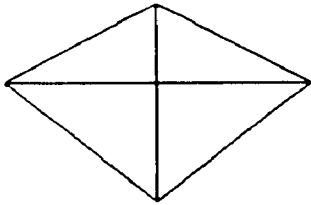
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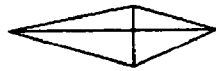
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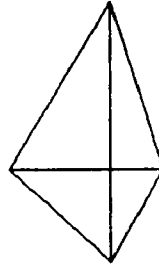
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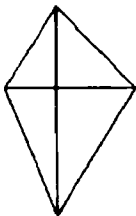
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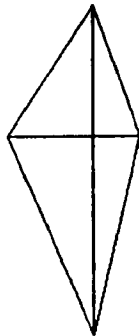
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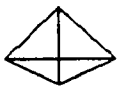
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FIGURE 5-14 (Continued)

Plant Influent By Treatment Type
Direct Filtration Utilities, Summer Quarter

15
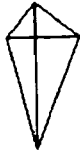
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19

FIGURE 5-14 (Continued)

Plant Influent By Treatment Type
Disinfection-Only Utilities, Summer Quarter
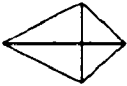
32

33

34

35

FIGURE 5-14 (Continued)

Plant Influent By Disinfection Scheme
Chlorine Only, Summer Quarter

1

3
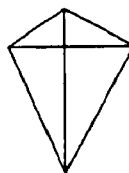
6

8

11

13

15
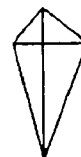
16

17

20
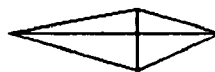
22
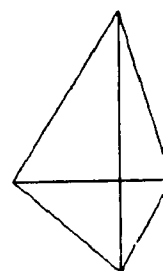
23

FIGURE 5-15

Plant Influent By Disinfection Scheme
Chlorine Only, Summer Quarter

24
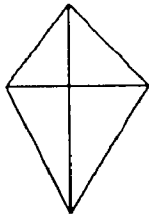
26

31

33

34

35

FIGURE 5-15 (Continued)

Plant Influent By Disinfection Scheme
Chlorine /Ammonia, Summer Quarter

2
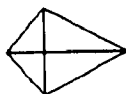
5

7

9
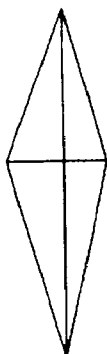
12
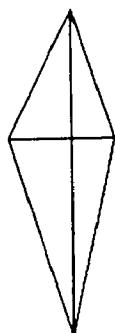
14
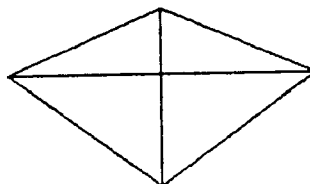
21
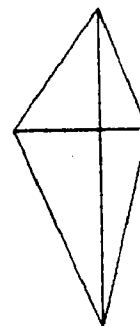
27

28

30

FIGURE 5-15 (Continued)

Plant Influent By Disinfection Scheme
Summer Quarter

Chloramines Only
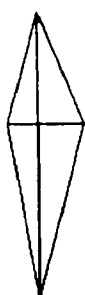
4

18

Ozone/Chlorine

19
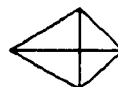
32

Ozone/Chloramines
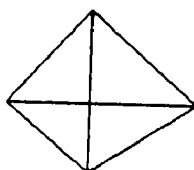
25

FIGURE 5-15 (Continued)

Baseline Sampling Results and Discussion

Influent Water Quality

The seasonal effects on influent water quality parameters measured in this study (TOC, UV-254, chloride and bromide) are shown in Figures 5-16 through 5-19. Data from only the summer, fall and winter quarters are presented since these influent analyses were not instituted until the second sampling quarter.

As shown in Figure 5-16, median levels of TOC did not change appreciably by season, ranging from 2.9 to 3.2 mg/L. The three-quarter median influent TOC level was 3.0 mg/L. There was not a significant difference in the medians of any two sets of quarterly influent TOC data. In other words, the 95 percent confidence interval for the spring quarter median was compared to that of the summer quarter, then to the fall quarter. The overlapping 95 percent confidence intervals indicate that the difference in the median TOC levels of any two quarters is not statistically significant. The "folded over" box for the fall quarter data shown in Figure 5-16 results from the 95 percent confidence interval of the median extending lower than the 25th percentile value. The notch width corresponds to the 95 percent confidence interval of the median, and the horizontal line across the box corresponds to the 25th percentile value.

Figure 5-17, a plot of UV-254 absorbance as a function of sampling quarter, indicates a trend similar to the influent TOC levels. Although the winter median (0.13 cm^{-1}) appears slightly higher than the summer or fall medians (0.11 cm^{-1} for both quarters), the medians of the summer and fall seasons are within the 95 percent confidence interval for the median of the winter quarter, indicating no statistical difference in the medians of any two seasons.

A plot of influent chloride levels by season is shown in Figure 5-18. Again, there is little seasonal variation indicated in this figure. The highest median influent chloride level was 32 mg/L, occurring in the fall season. The three-quarter median chloride level was 29 mg/L. Figure 5-19 shows the seasonal variation in influent bromide levels on a seasonal basis. Quarterly medians ranged from 0.07 to 0.10 mg/L of bromide, with a three-quarter median of 0.08 mg/L. Note the presence of one outlying data point in each quarter that occurs at substantially higher concentrations than the 75th percentiles and other outliers. These outlying data points represent Utility 10, which had extremely high influent bromide levels. Bromide and its impact on DBP formation and speciation will be discussed in detail later in this section.

Classes of DBP Compounds

Figure 5-20 is a plot of the seasonal variation of the sum of halogenated DBPs (XDBP$_{sum}$) measured in this study. The median of the summer quarter (82 μg/L) is higher than the median of the winter quarter (58 μg/L); however, this difference is not statistically significant since the 95 percent confidence intervals about the medians of both quarters overlap. The median values of XDBP$_{sum}$ for the spring and fall quarters were 64 and 72 μg/L, respectively.

Figure 5-21 is a plot of TTHMs by sampling quarter. As would be expected based on seasonal temperature differences, the highest median TTHM level occurred in the summer season and the next highest in the fall. For many utilities in California and the South, the fall season can be almost as warm as the summer. The lowest median

Influent Total Organic Carbon By Quarter
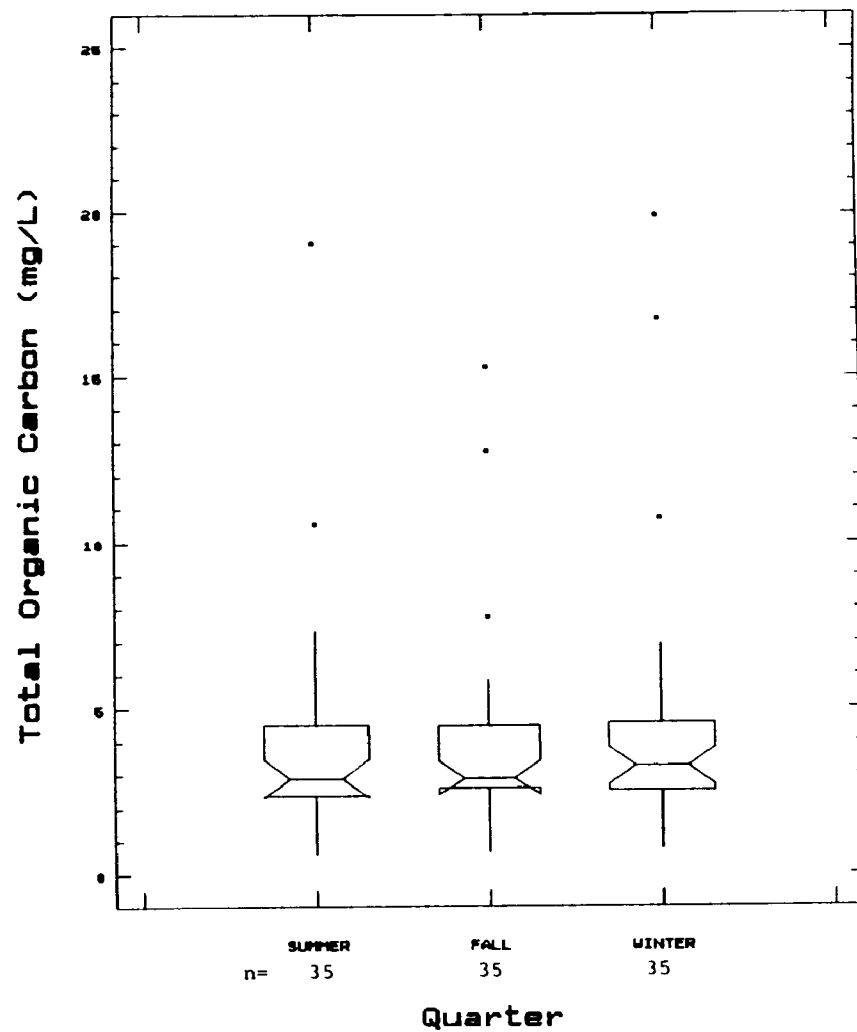
FIGURE 5-16

Influent UV Absorbance By Quarter
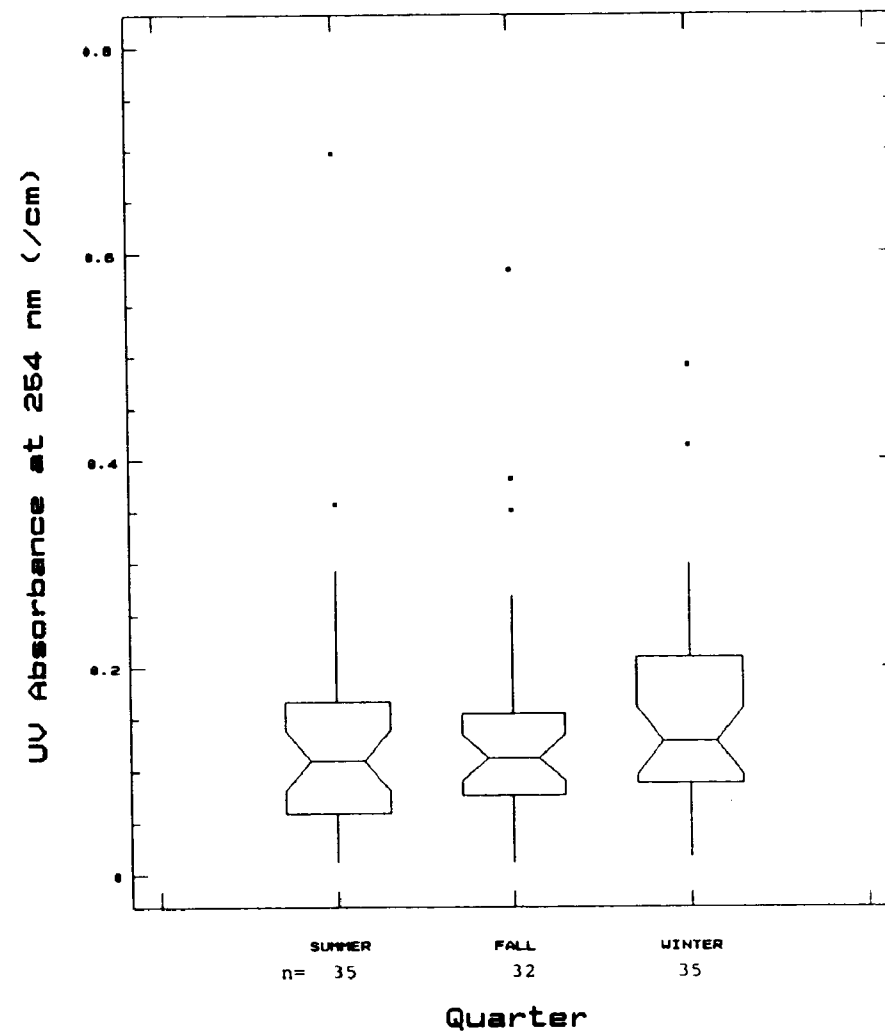
FIGURE 5-17

Influent Chloride By Quarter
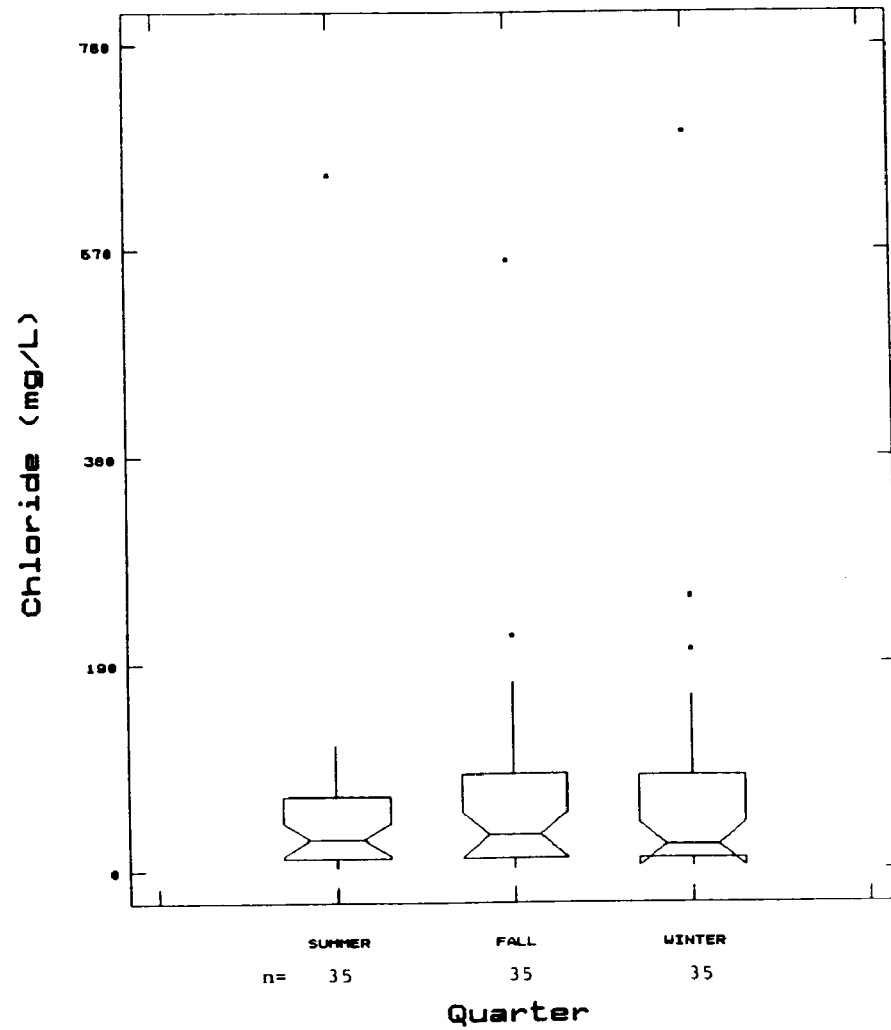
Influent Bromide By Quarter
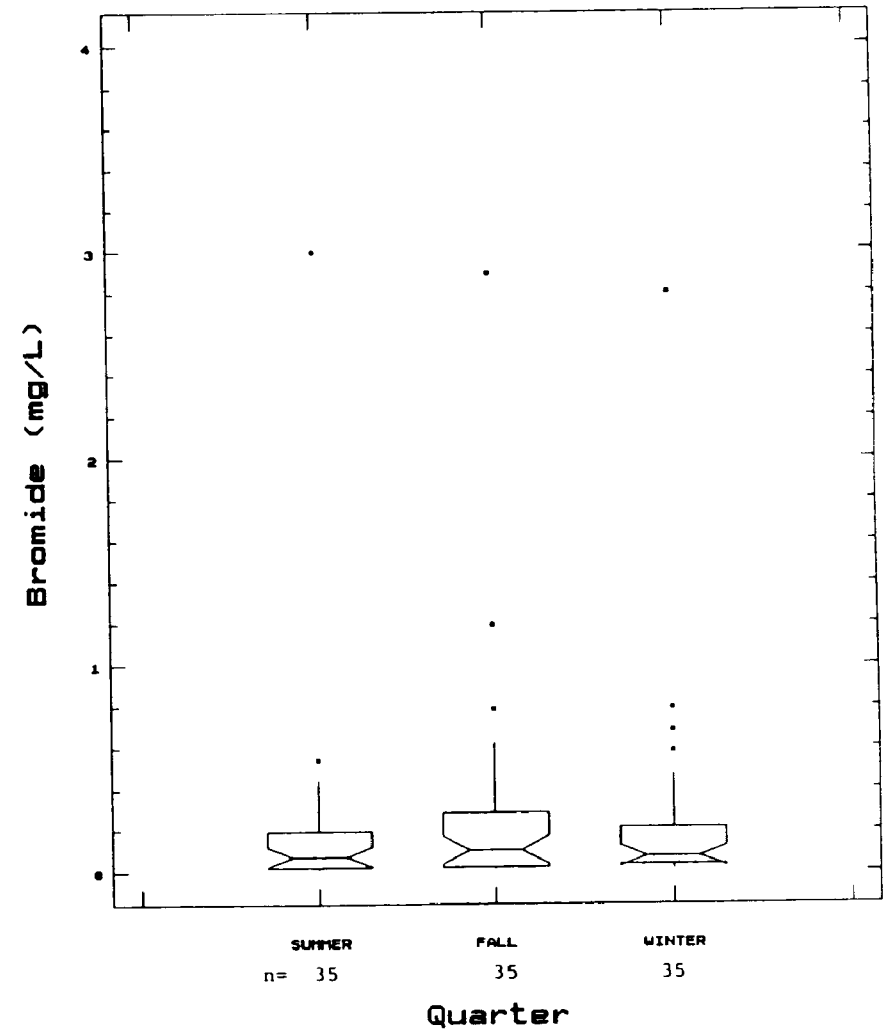
FIGURE 5-18

FIGURE 5-19

XDBPsum by Quarter
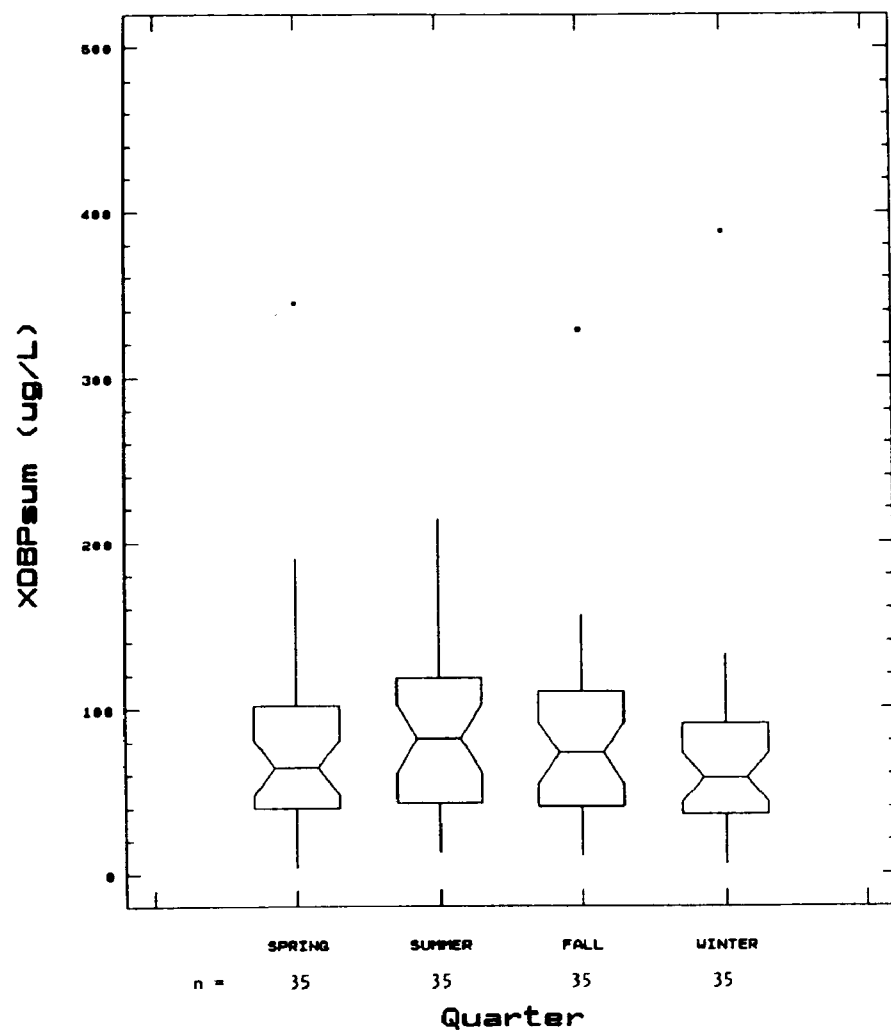
FIGURE 5-20

Trihalomethanes

By Quarter
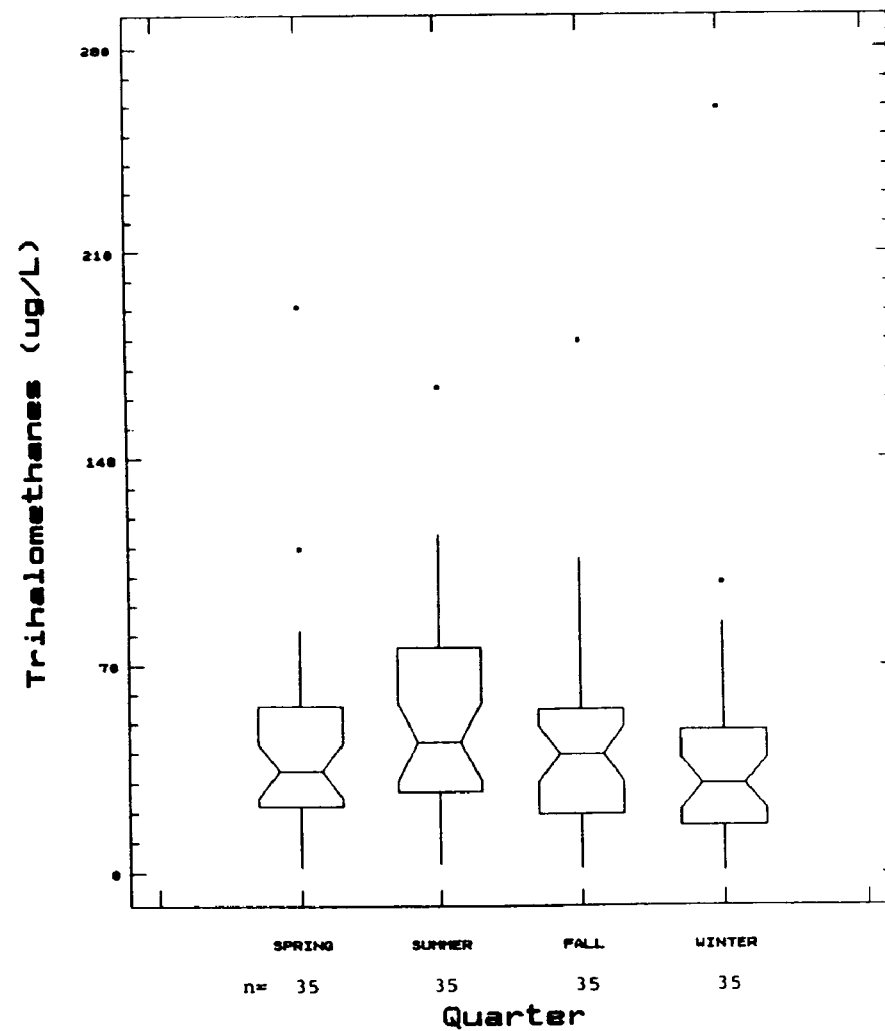
FIGURE 5-21

TTHM level occurred in the winter. The impact of water temperature on the formation of THMs and other DBPs will be discussed in detail later in this section. Figure 5-22 is a plot of median chloroform levels by sampling quarter. There are no significant differences between the medians of any two quarters and only three outliers appear on the plot. However, plots of bromodichloromethane, dibromochloromethane and bromoform (Figures 5-23, 5-24 and 5-25, respectively) indicate progressively greater numbers of outliers, although there are no statistically significant differences between the medians of any two quarters for these compounds. The increasing number of outliers is most likely due to the presence of high levels of brominated THMs in utilities with high influent bromide concentrations. Note the extremely high levels of bromoform (over 50 μg/L) of several of the outliers in Figure 5-25. The impact of influent bromide levels on the production of brominated DBPs is discussed in detail later in this section.

Following the same trend as median TTHM levels, median total HAA levels were higher in summer (20 μg/L) and fall (21 μg/L) than in winter and spring (13 and 18 μg/L, respectively), as shown in Figure 5-26. However, there was no statistical difference between the medians of any two quarters. Figures 5-27 and 5-28 show DCAA and DBAA concentrations on a quarterly basis. Neither of these plots indicate a significant difference between the medians of any two quarters. However, following the same trend observed in the plots of chloroform and bromoform, the plot of DBAA shows many more outliers than the plot of DCAA.

In contrast to the trend of increasing median concentrations with increasing seasonal temperatures seen in the TTHM and HAA plots, Figure 5-29 shows that the median level of total HANs was highest in winter and lowest in summer, although the differences were not statistically significant. This same trend is observed in the plot of quarterly median HK concentrations, Figure 5-30. The role of HANs and HKs as reactive intermediates rather than stable endproducts of chlorination reactions is discussed later in this section.

Figure 5-31 illustrates the seasonal variation in aldehyde concentrations. Only three quarters of data are presented since the ALD analysis was not instituted until the second sampling quarter. The plot indicates that the level of ALDs in the summer quarter (6.9 μg/L) was higher than winter median (4.2 μg/L), but the difference was not statistically significant at a 95 percent confidence level.

The chloropicrin levels shown in Figure 5-32 indicate that there was little seasonal variation, with all four quarterly medians falling within the range 0.10 to 0.16 μg/L. Figure 5-33 indicates the same lack of significant variation in quarterly cyanogen chloride medians. The median concentrations of cyanogen chloride were within the range 0.45 to 0.80 μg/L for the four sampling quarters. The plot of chloral hydrate concentrations shows no significant difference between the medians of any two quarters (Figure 5-34).

Although Figures 5-20 through 5-34 do not show statistically significant differences between the median DBP concentrations from season to season, seasonal variation in DBP levels is demonstrated in Table 5-3. In this table, DBP values for the 35 utilities are presented for the 25th percentile, median and 75th percentile for the four sampling quarters. For TTHMs, the 25th percentiles for the summer and winter quarters were

Chloroform By Quarter

Chloroform (ug/L)

SPRING   SUMMER   FALL   WINTER
n=   35   35   35   35
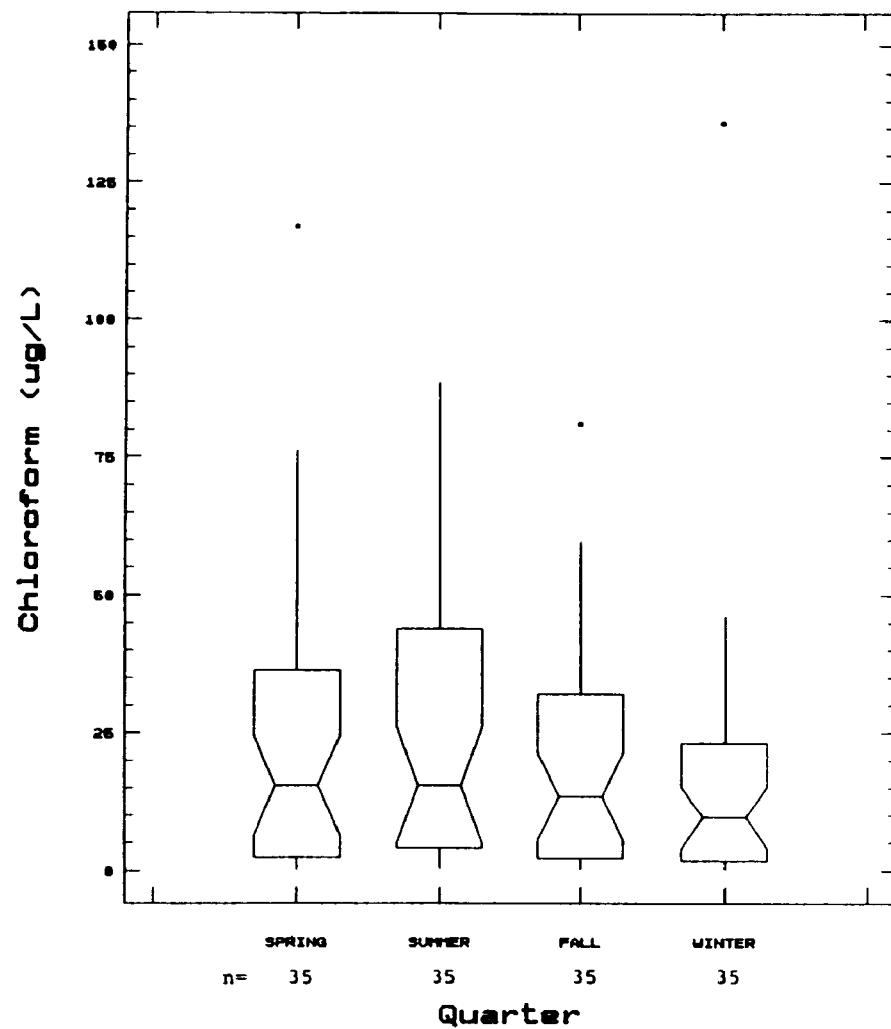
Quarter

FIGURE 5-22

Bromodichloromethane
By Quarter

Bromodichloromethane (ug/L)

SPRING   SUMMER   FALL   WINTER
n=   35   35   35   35
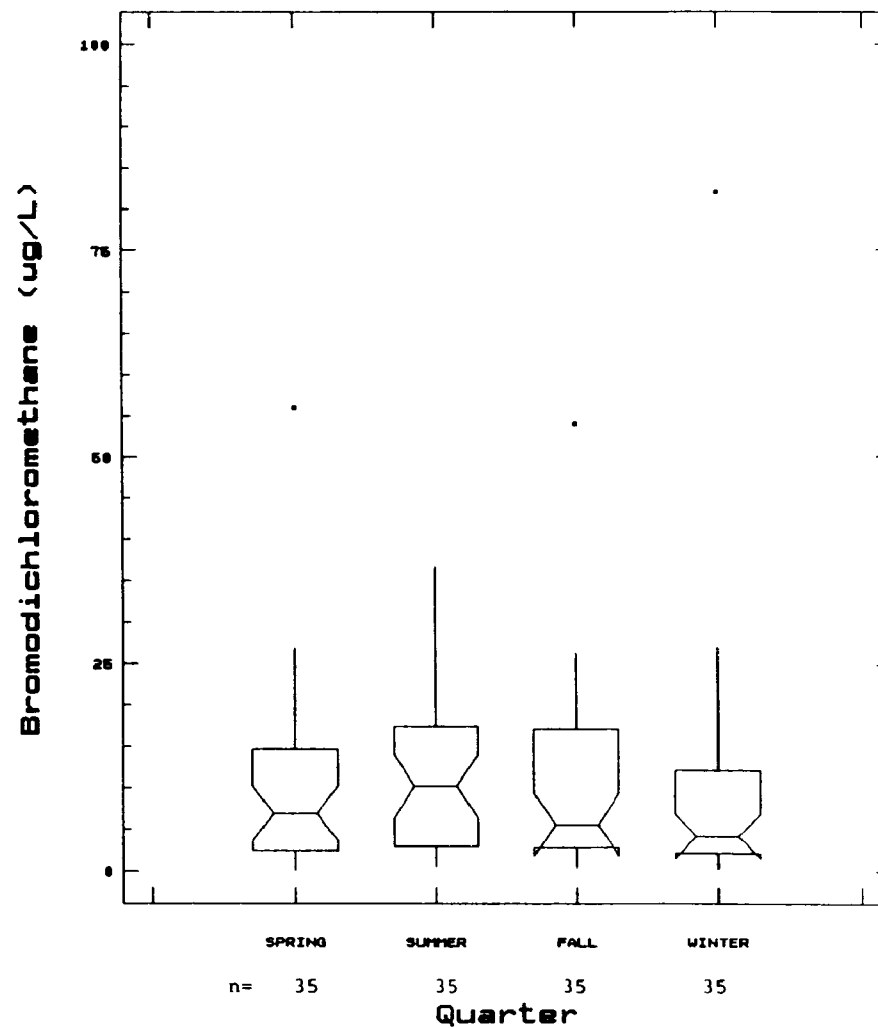
Quarter

FIGURE 5-23

Dibromochloromethane By Quarter
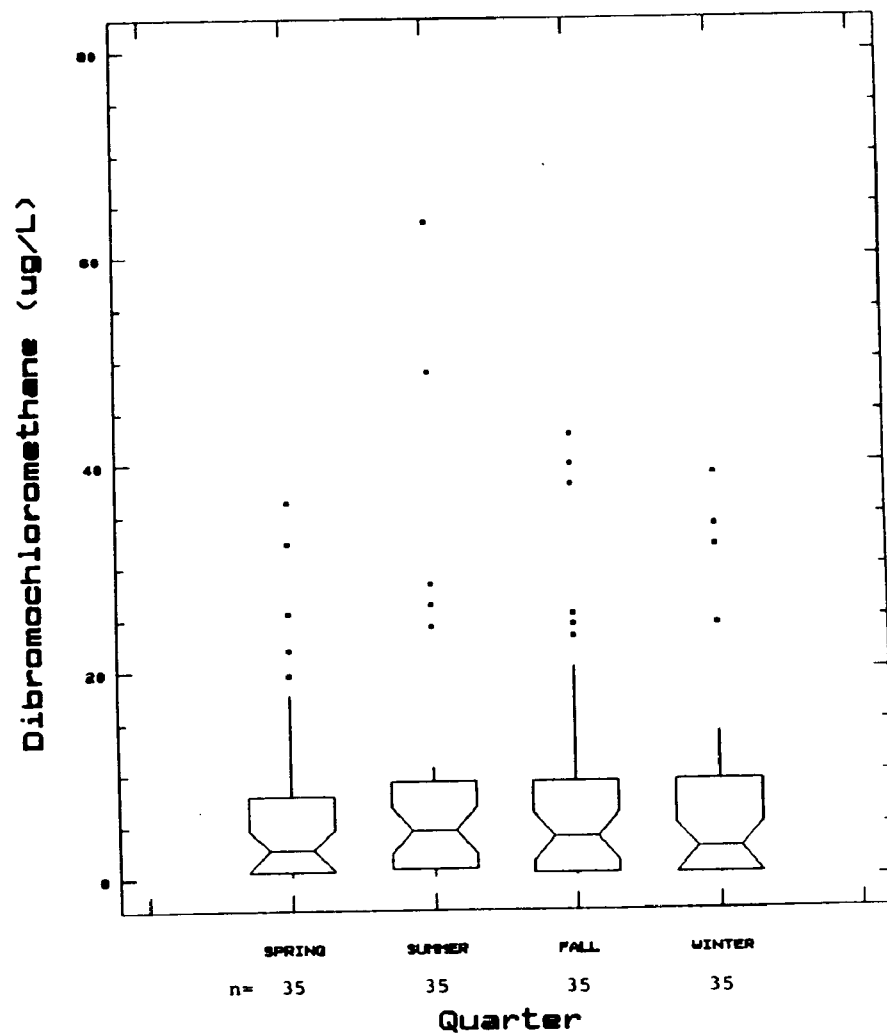
FIGURE 5-24

Bromoform By Quarter
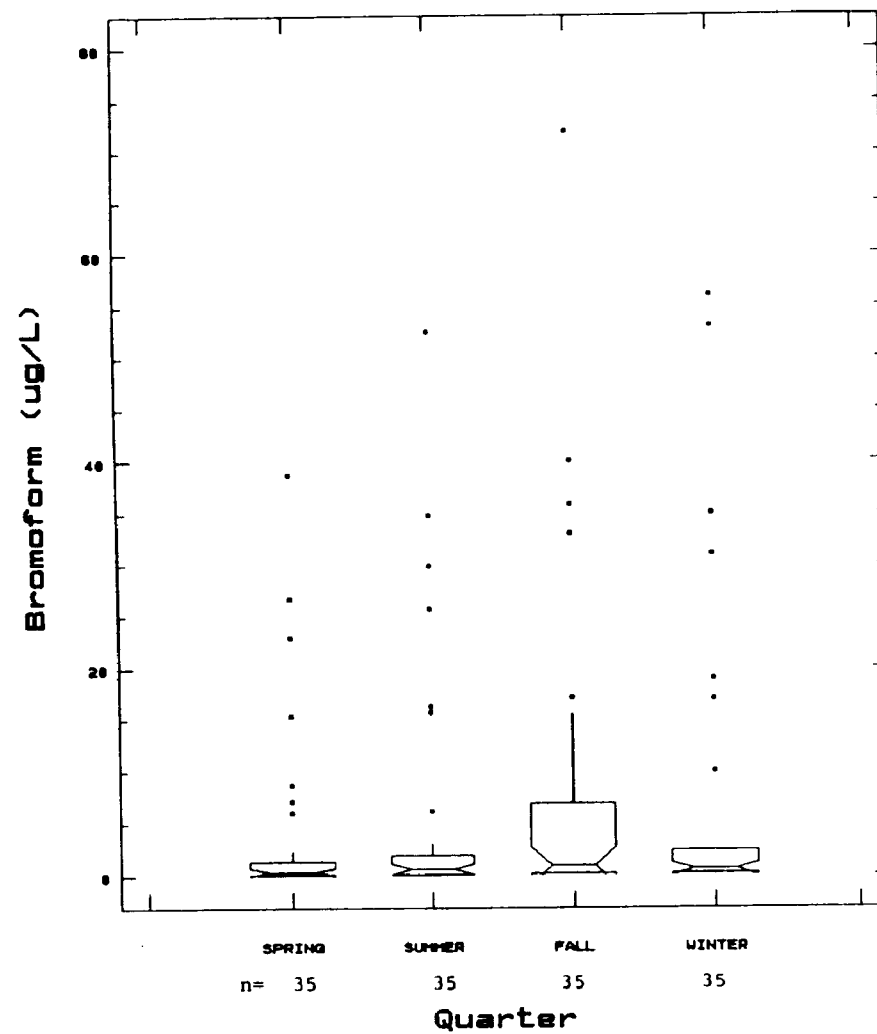
FIGURE 5-25

Haloacetic Acids
By Quarter

Haloacetic Acids (ug/L)

FIGURE 5-26

Dichloroacetic Acid
By Quarter

Dichloroacetic Acid (ug/L)
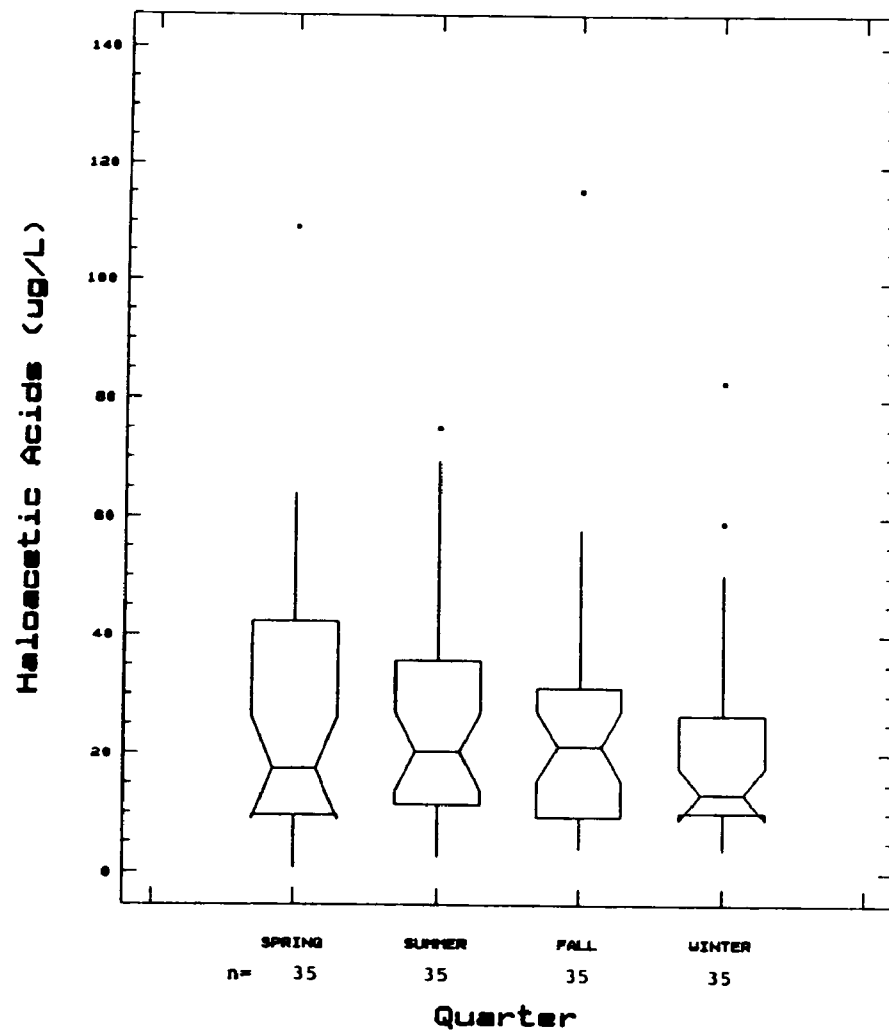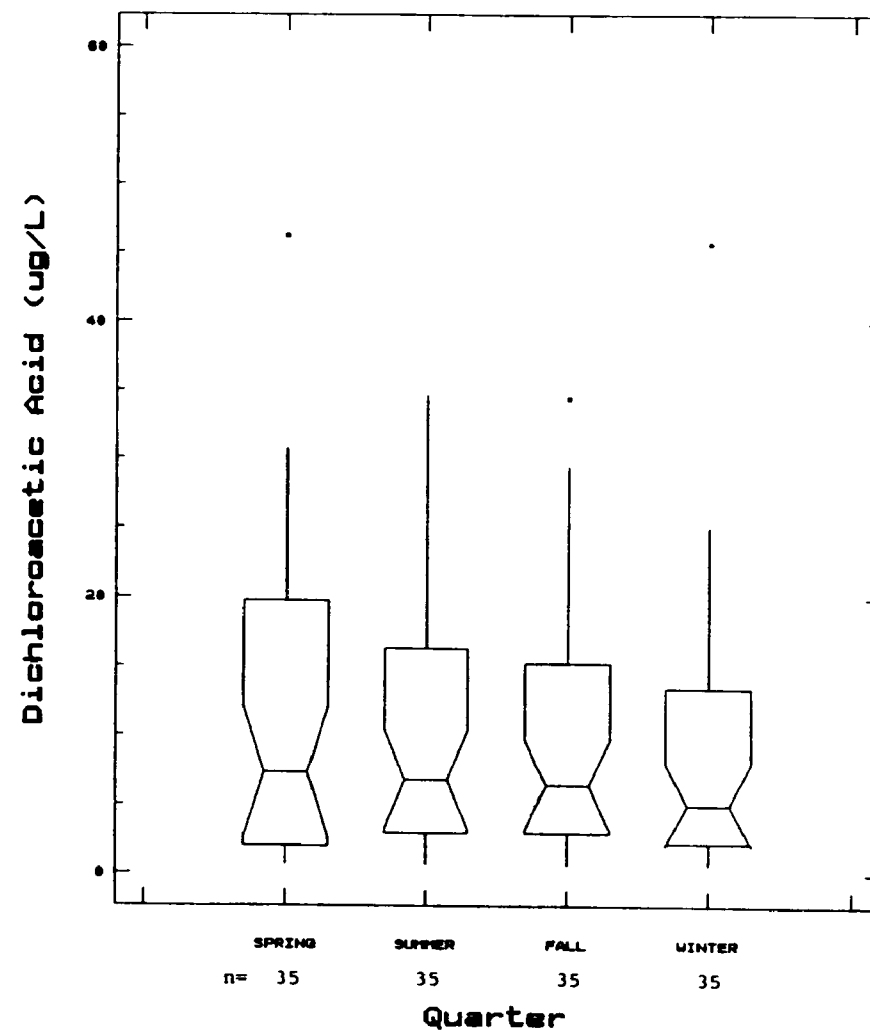
FIGURE 5-27

Dibromoacetic Acid
By Quarter
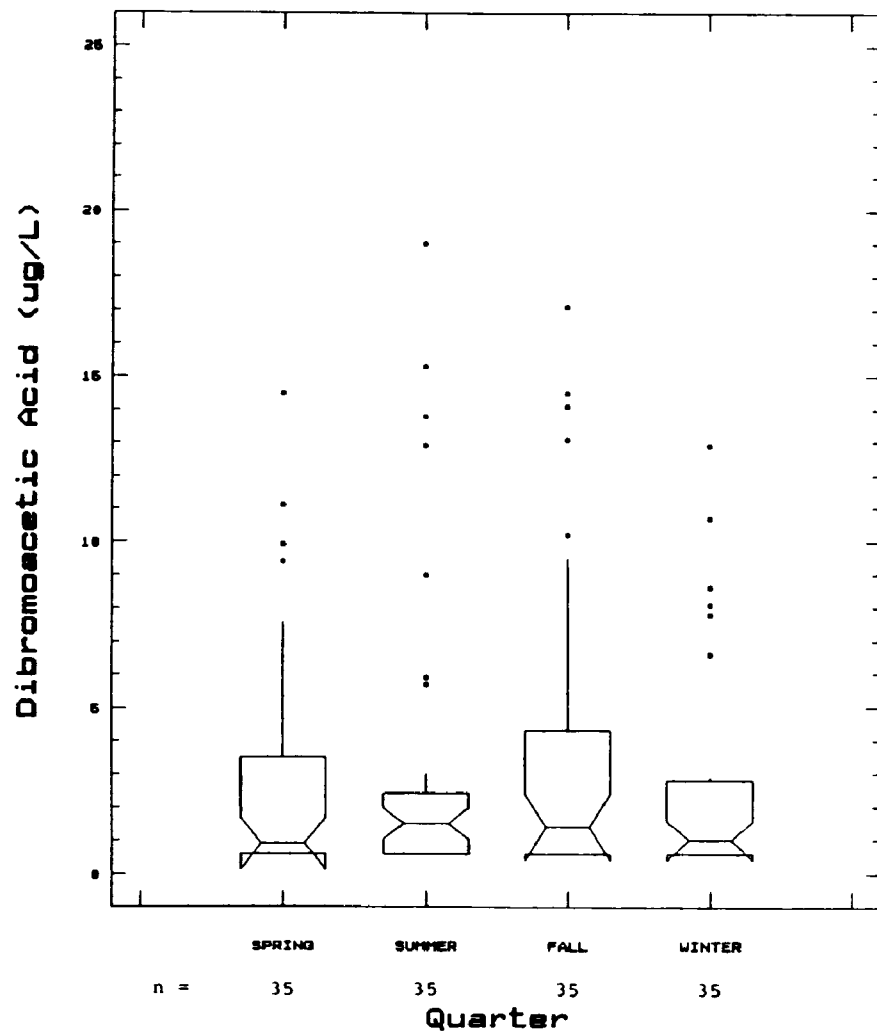
FIGURE 5-28

Haloacetonitriles
By Quarter
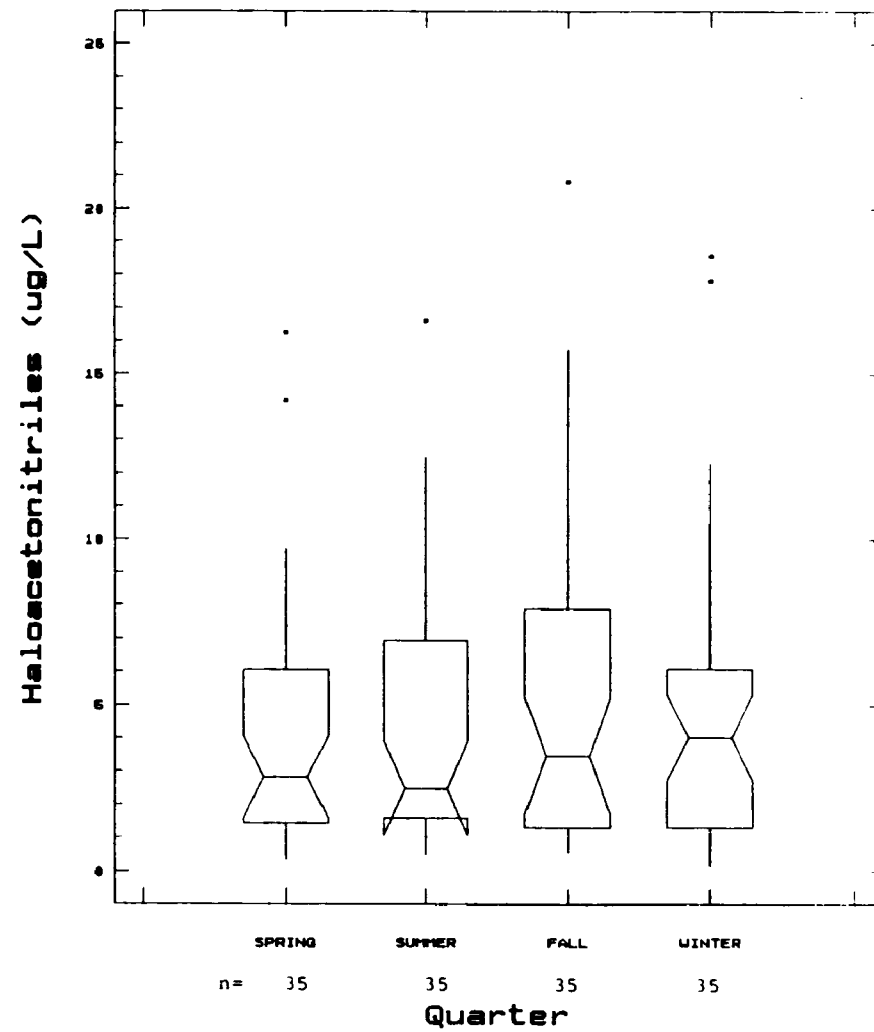
FIGURE 5-29

Haloketones
By Quarter
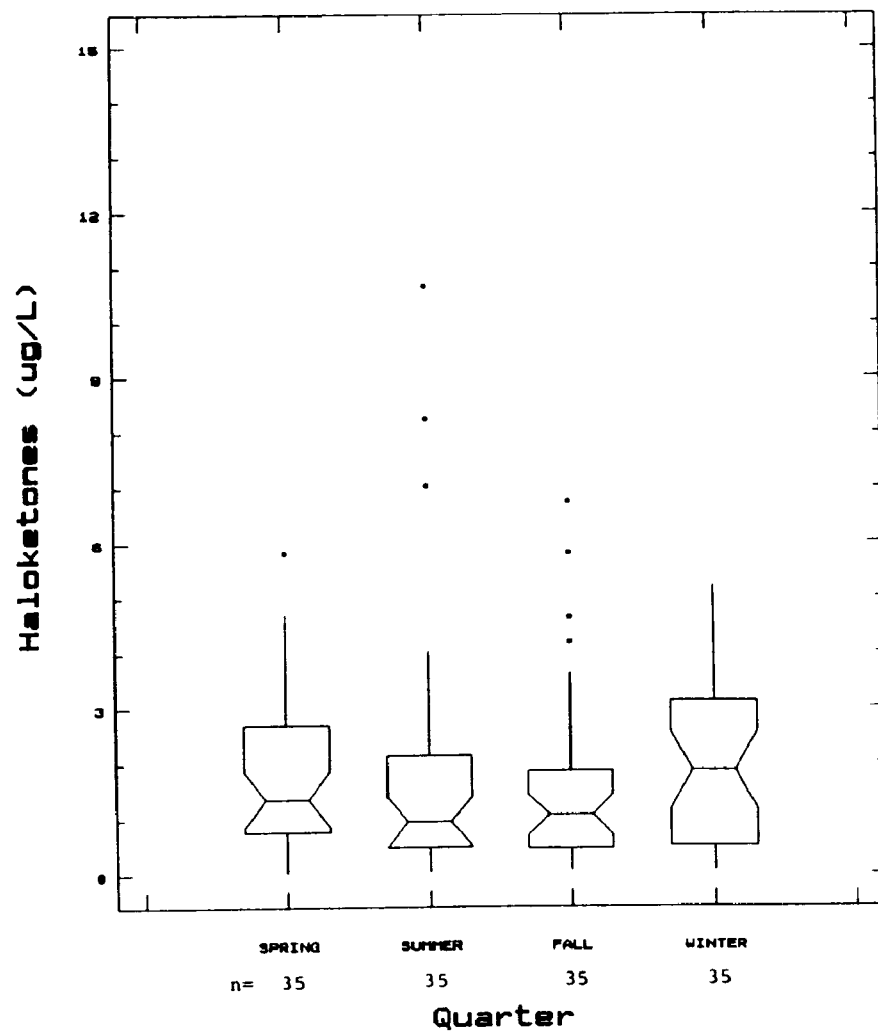
FIGURE 5-30

Aldehydes by Quarter
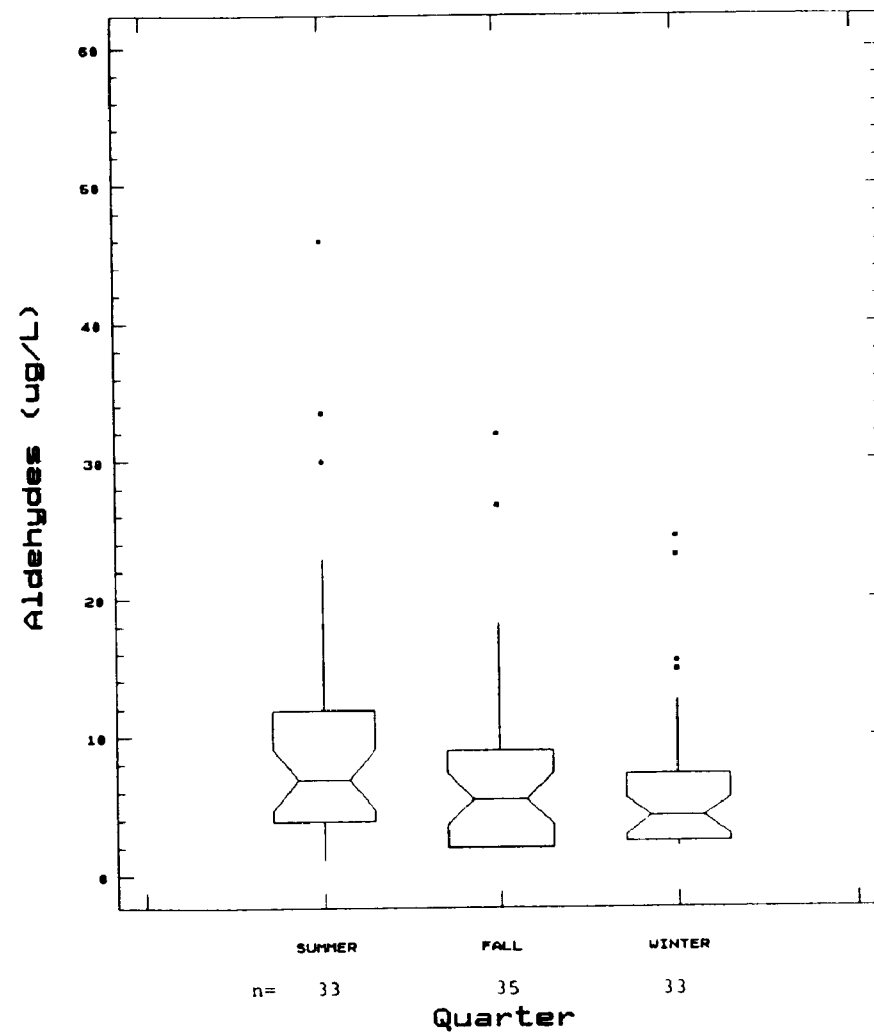
FIGURE 5-31

Chloropicrin By Quarter

Chloropicrin (ug/L)

	SPRING	SUMMER	FALL	WINTER
n=	35	35	34	35
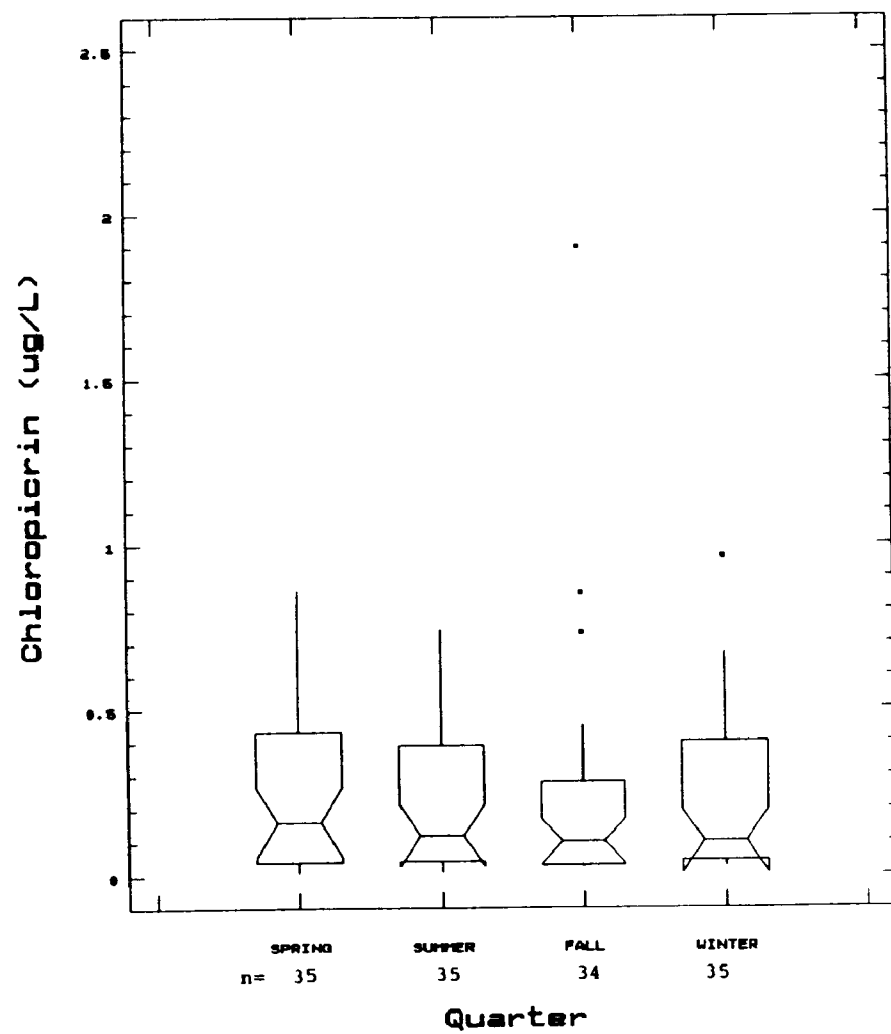
Quarter

FIGURE 5-32

Cyanogen Chloride By Quarter

Cyanogen Chloride (ug/L)

	SPRING	SUMMER	FALL	WINTER
n=	20	35	34	35
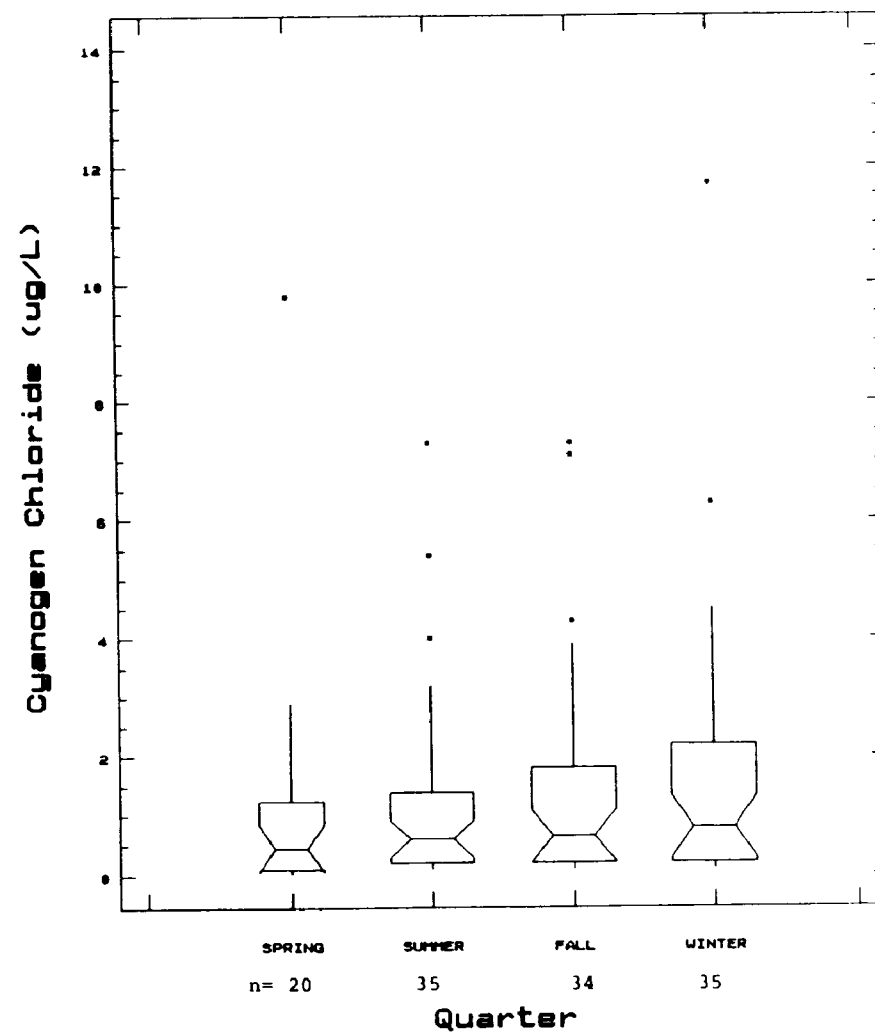
Quarter

FIGURE 5-33

Chloral Hydrate By Quarter
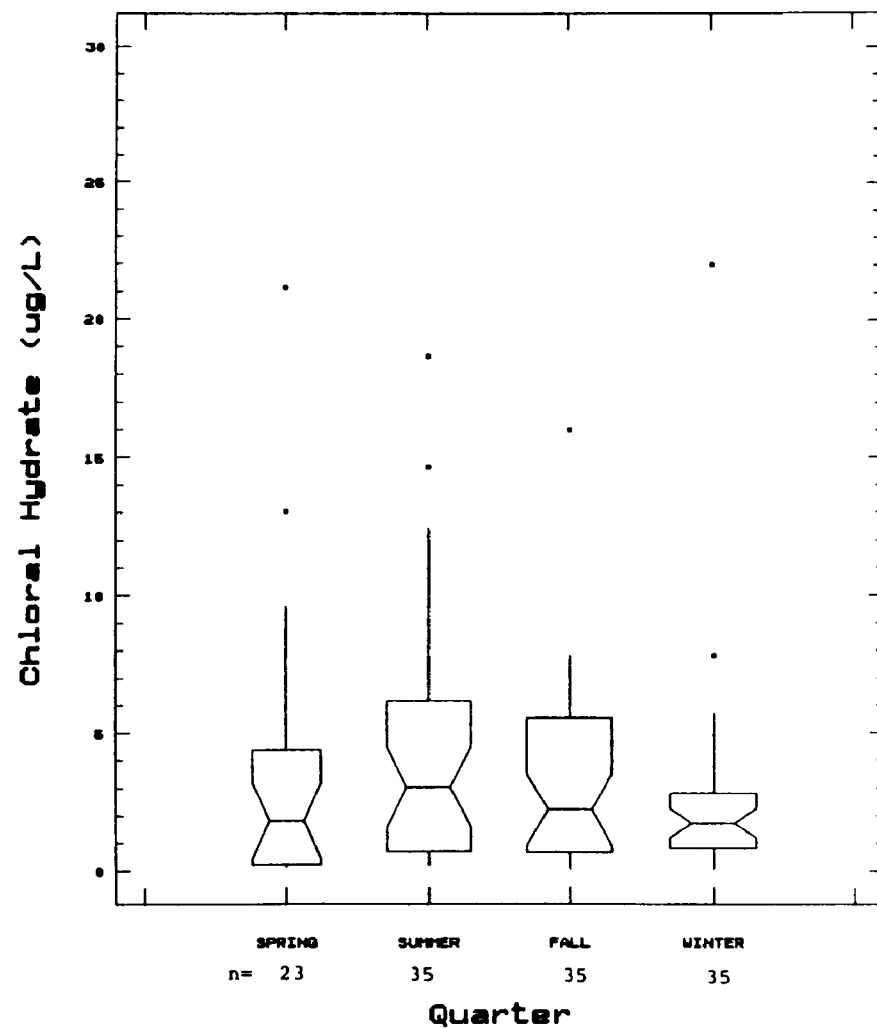
FIGURE 5-34

Influent Total Organic Carbon
By Treatment
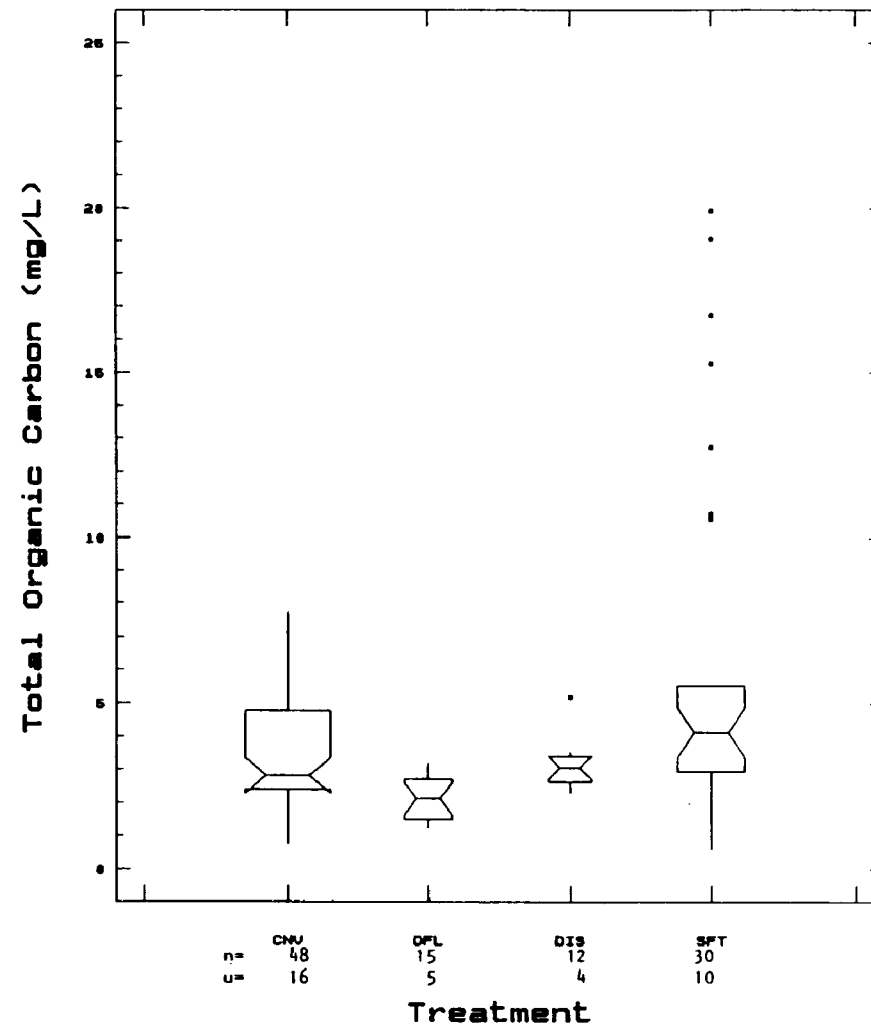
FIGURE 5-35

TABLE 5-3

COMPARISON OF SEASONAL DBP LEVELS

Quarter	25th Percentile	Median	75th Percentile
Total Trihalomethanes (μg/L)			
Spring	22	34	57
Summer	28	44	76
Fall	20	40	54
Winter	15	30	48
Sum of Haloacetic Acids (μg/L)			
Spring	10	17	42
Summer	11	20	35
Fall	9	21	31
Winter	10	13	26
Sum of Haloacetonitriles (μg/L)			
Spring	1.4	2.8	6.0
Summer	1.6	2.5	7.0
Fall	1.3	3.4	7.8
Winter	1.3	4.1	6.0
Sum of Aldehydes (μg/L)			
Summer	4	7	12
Fall	2	5.5	9
Winter	2.3	4	7

28 and 15 μg/L, respectively, indicating a decrease of almost 50 percent from summer to winter. The 75th percentile for TTHMs was 76 μg/L in the summer and 48 μg/L in the winter, indicating a decrease of almost 40 percent from summer to winter. Although the seasonal differences for HAAs, HANs and ALDs were not as substantial as those observed for THMs, seasonal differences for these DBPs are apparent in the table. For instance, the 75th percentile for the sum of HAAs was 42 μg/L in the spring, and decreased almost 40 percent to 26 μg/L in the winter. Furthermore, the medians for HAAs were highest in the summer and fall, but the 75th percentile was highest in the spring. From the data presented in Table 5-3, it is clear that seasonal variations influenced levels of DBPs measured over the sampling period.

Table 5-4 is a summary of clearwell effluent TTHMs and influent temperature, TOC and bromide levels for all 35 utilities, comparing data from the summer and winter quarters. This table illustrates that seasonal variations in the reported parameters were different for individual utilities. For instance, Utility 1 had a summer water temperature of 18°C and a winter temperature of 14°C. Bromide and TOC levels at Utility 1 varied only slightly as well, and this lack of variability is reflected in the TTHM levels (7.9 and 9.0 μg/L in the summer and winter quarters, respectively). At Utility 20, there was essentially no seasonal variation in TOC and bromide concentrations, but water temperature varied from 26 to 8°C from summer to winter, and TTHM levels in the summer were significantly higher (76 and 24 μg/L in the summer and winter quarters, respectively). At Utility 23, the water temperature was similar both quarters (10°C in the summer and 8°C in the winter); however, TOC and bromide levels were higher in the winter (4.49 mg/L and 0.58 mg/L, respectively) than in the summer (3.27 mg/L and 0.44 mg/L, respectively). These differences are reflected in the higher TTHMs in the winter versus the summer quarter (24 versus 3.8 μg/L, respectively). From the data presented in this table, it is apparent that seasonal variations in influent water quality and effluent DBPs do not exist uniformly for utilities around the nation, but rather for individual utilities.

VARIATION BY TREATMENT TYPE

Figure 5-35 shows the three-quarter influent TOC levels as a function of treatment type (conventional, direct filtration, disinfection only, and softening). The plot includes the number of data points in each category (n) as well as the number of utilities within each category (u). There is no statistically significant difference between the median values for conventional, direct filtration and disinfection only utilities. However, the softening utilities participating in this study had a significantly higher median influent TOC than either conventional or direct filtration utilities. This is perhaps due to the inclusion of several utilities treating highly-colored ground and surface waters by softening.

Figure 5-35 is the only plot of water quality parameters as a function of treatment type. As discussed above regarding the star plot analyses, levels of DBPs measured in this limited study of 35 utilities cannot be ascribed simply to discrete causal factors such as treatment type and source water type. Thus, plots of DBP levels as a function of treatment type are relatively meaningless and could be misleading if taken out of context. However, some special issues relating to DBP levels in disinfection-only utilities are discussed later in this section.

TABLE 5-4

COMPARISON OF SEASONAL TTHMs AND INFLUENT WATER QUALITY

Utility	Summer Quarter Effluent TTHMs (μg/L)	Summer Influent Values Temp. (°C)	Summer Influent Values TOC (mg/L)	Summer Influent Values Br⁻ (mg/l)	Winter Quarter Effluent TTHMs (μg/L)	Winter Influent Values Temp. (°C)	Winter Influent Values TOC (mg/L)	Winter Influent Values Br⁻ (mg/L)
1	7.9	18	0.75	0.07	9.0	14	0.96	0.08
2	90	30	2.4	0.12	60	27	2.5	0.12
3	6.1	28	3.2	0.02	6.1	4.5	3.2	0.02
4	9.1	23	2.8	0.27	12	9.6	2.7	0.47
5	42	30	5.4	0.12	32	15	5.5	0.13
6	98	24	4.5	0.06	33	4.0	4.9	0.07
7	63	21	2.8	0.15	30	13	2.7	0.07
8	27	20	1.6	0.02	12	9.5	1.7	0.02
9	95	31	3.6	0.06	40	5.0	4.5	0.10
10	43	28	4.6	3.0	47	6.0	5.3	2.8
11	67	27	2.1	0.07	28	8.4	3.0	0.06
12	71	23	2.6	0.41	85	9.0	2.8	0.79
13	24	19	1.1	1.0	26	11	1.5	0.01
14	114	22	2.6	3.5	76	11	3.9	0.32
15	27	19	1.3	0.01	22	13	1.4	0.01
16	28	15	2.7	0.05	36	12	2.7	0.07
17	94	30	3.0	0.01	29	9.5	3.2	0.01
18	7.6	17	1.8	0.02	0.7	4.5	1.9	0.03
19	15	20	1.8	0.10	5.9	5.0	1.5	0.04
20	76	26	7.4	0.04	24	8.1	6.9	0.03
21	56	25	11	0.18	48	23	11	0.17
22	60	6.6	5.5	0.02	38	10	4.0	0.02
23	3.8	10	3.3	0.44	24	8.1	4.5	0.58
24	40	22	0.60	0.54	43	20	0.74	0.44
25	34	NA	7.1	0.22	9.1	18	6.9	0.14
26	164	27	5.2	0.19	98	3.0	3.7	0.68
27	57	30	2.9	0.33	36	10	3.8	0.35
28	36	28	2.4	0.09	16	4.5	2.6	0.04
29	108	29	19	0.16	259	23	17	0.21
30	73	27	3.6	0.10	66	2.0	20	0.11
31	77	28	3.0	0.05	57	1.1	3.2	0.05
32	3.1	26	2.6	0.07	0.8	24	2.5	0.06
33	44	18	3.2	0.01	25	3.1	3.5	0.01
34	46	15	2.6	0.01	53	6.2	3.3	0.03
35	38	18	3.1	0.01	20	2.8	3.5	0.01

NA = Not analyzed

VARIATION BY SOURCE WATER TYPE

Figures 5-36 through 5-39 show the influent water quality parameters measured in this study as a function of source water type (flowing stream, groundwater, and lake/reservoir). The 105 TOC measurements performed for this study had a minimum of 0.6 mg/L and a maximum of 19.9 mg/L. As seen in Figure 5-36, there is very little difference between the medians of any two source water types. The highest TOC levels occurring in this study were measured at Utility 29, treating a highly-colored surface water, and one anomalous reading at Utility 30 in the winter quarter. The other two influent TOC measurements at Utility 30 were less than 5 mg/L. The 25th percentile TOC level for the groundwater sources was the lowest; however, the presence of colored groundwaters resulted in a median TOC value statistically comparable to that of the other two source water types.

Influent UV-254 absorbance by source water type is illustrated in Figure 5-37. Although the median UV-254 absorbance level is higher for the groundwater utilities than the flowing stream or lake/reservoir utilities, the difference is not statistically significant. The outlier points shown for the flowing stream utilities are the three quarterly readings from Utility 29, reflecting the high organic content of this utility's source water.

The influent chloride levels plotted by source water type in Figure 5-38 show very little variability in chloride concentrations from source to source. The influent bromide data plotted in Figure 5-39 indicate the same lack of variation between the source water types. The highest outlier points on both plots represent Utility 10, treating a lake/reservoir source with extremely high chloride and bromide levels. No plots of DBP concentrations by source water type are included for the reasons discussed previously with respect to the star plot analyses and the variation of DBP data by treatment type.

VARIATION BY DISINFECTION SCHEME

Figures 5-40 through 5-54 illustrate influent parameters and DBP levels measured in this study as a function of disinfection scheme (chlorine only, "Cl2"; prechlorination and postammoniation, "Cl2NH3"; and chloramination, "NH2Cl"). Results for the preozonation/postchlorination and preozonation/postchloramination utilities are not presented here because the very small number of data points precluded meaningful observations about those data. However, aldehyde data from the ozonating utilities will be discussed later in Section 5, and further discussion will be included with the results of the ozonation treatment studies in Section 6.

Influent Parameters

Figure 5-40 shows the overall influent TOC levels as a function of disinfection scheme. The medians show very little variation among utilities using the various disinfection practices. Although Figure 5-41, a plot of influent UV-254 absorbance as a function of disinfection scheme, does not show statistically significant differences between the three categories, this figure does indicate that prechlorinating/postammoniating utilities had higher influent UV-254 levels than the chlorinating or chloraminating utilities. One

Influent Total Organic Carbon
By Source
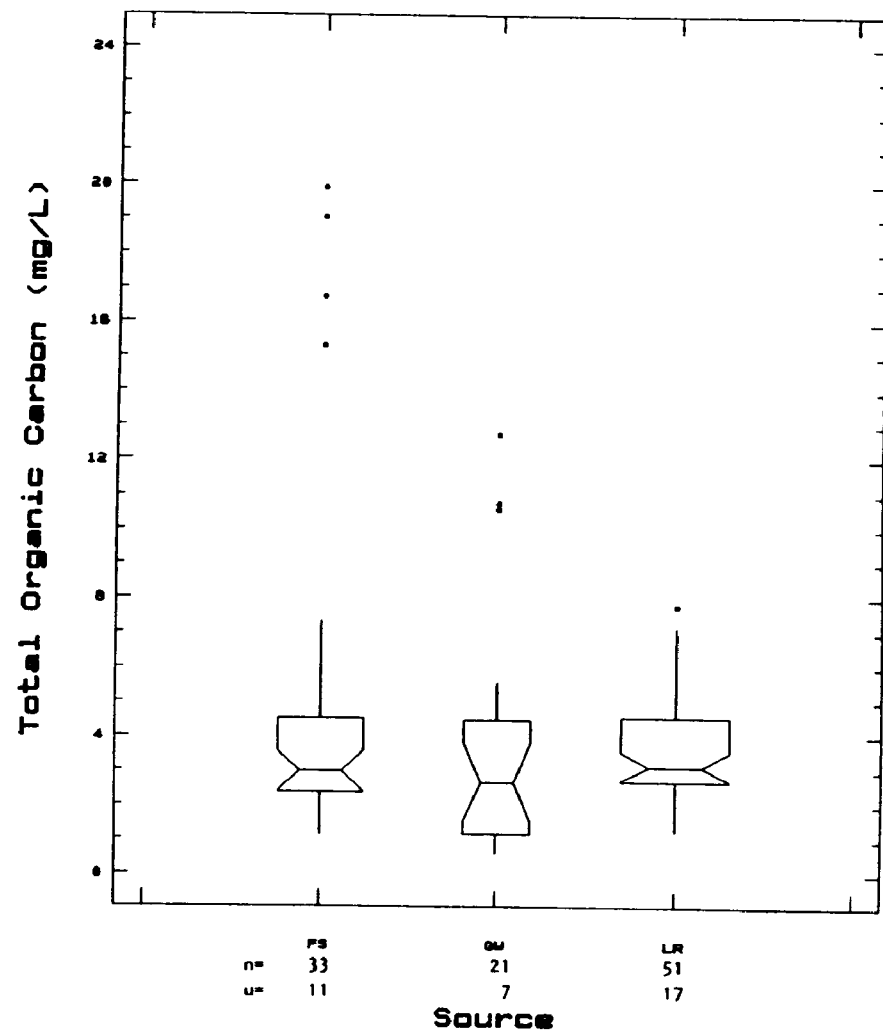
FIGURE 5-36

Influent UV-254 Absorbance
By Source
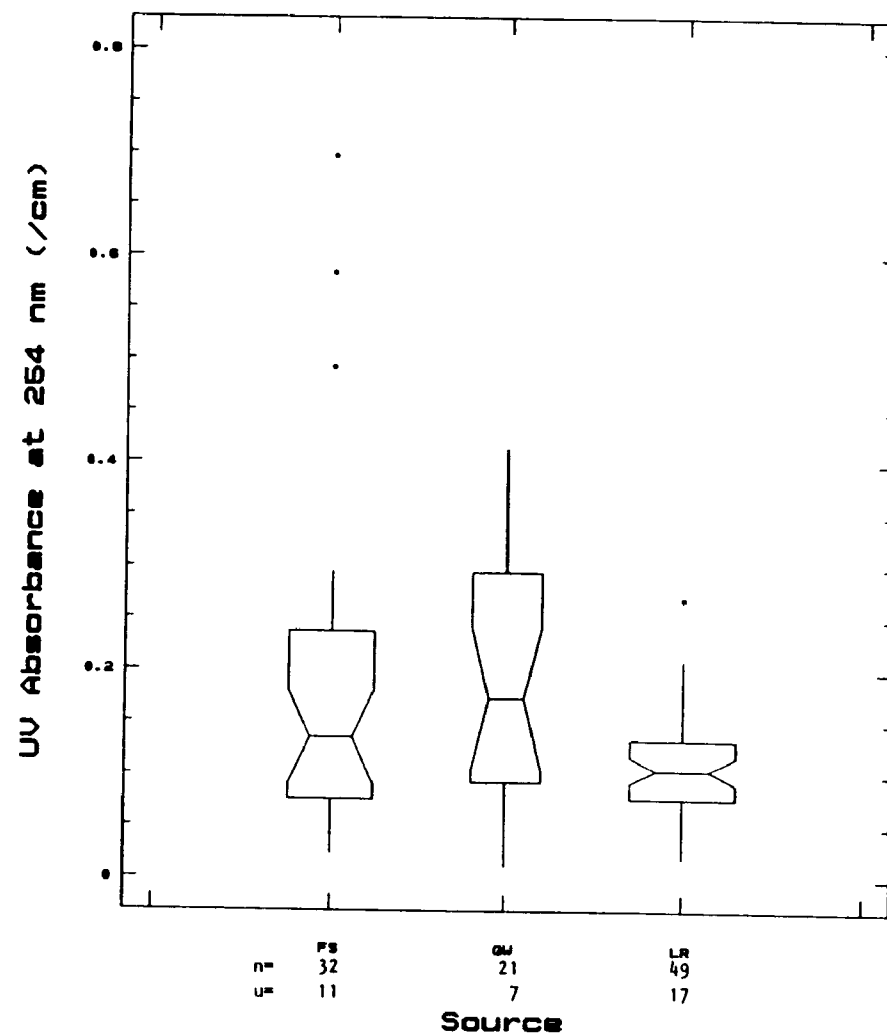
FIGURE 5-37

Influent Chloride by Source
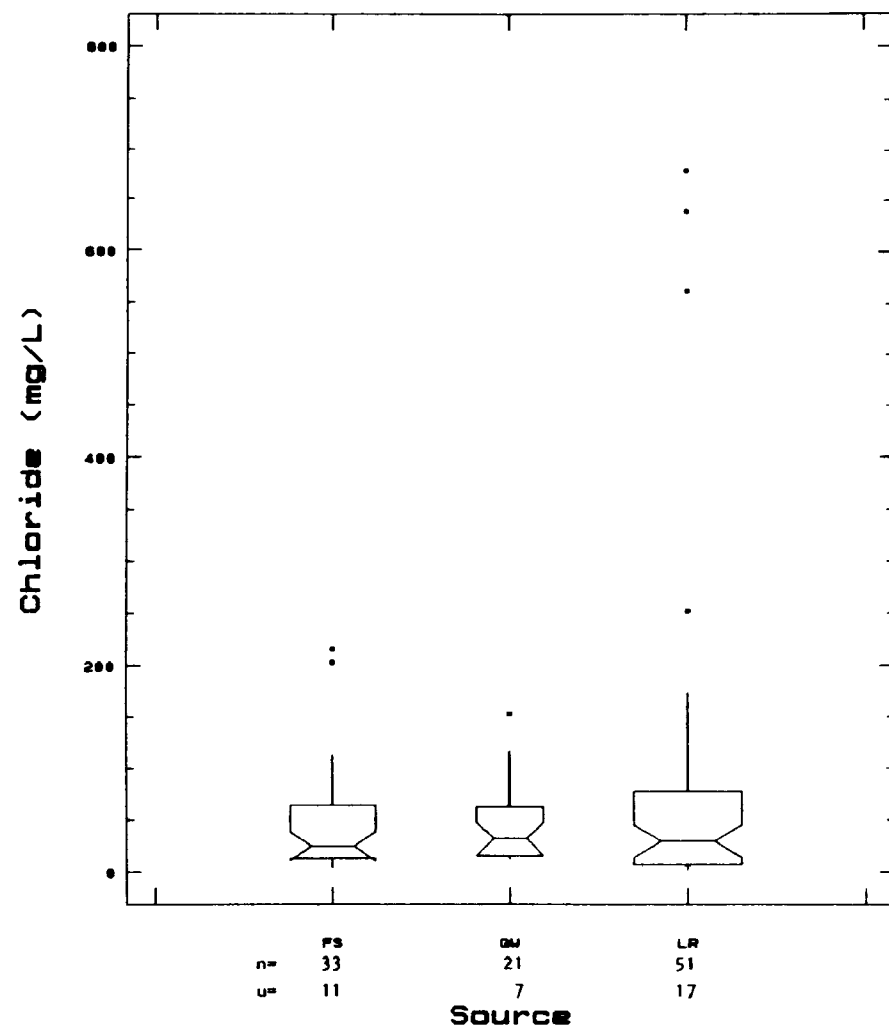
FIGURE 5-38

Influent Bromide by Source
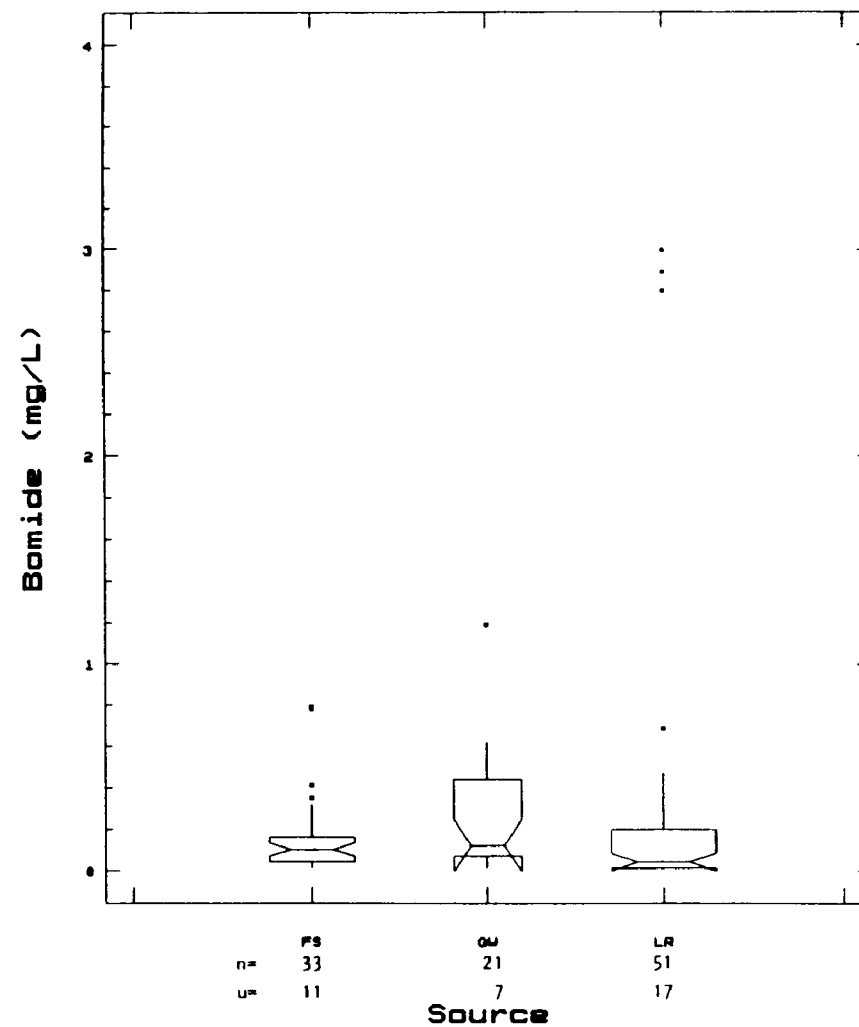
FIGURE 5-39

Influent Total Organic Carbon By Disinfection Scheme
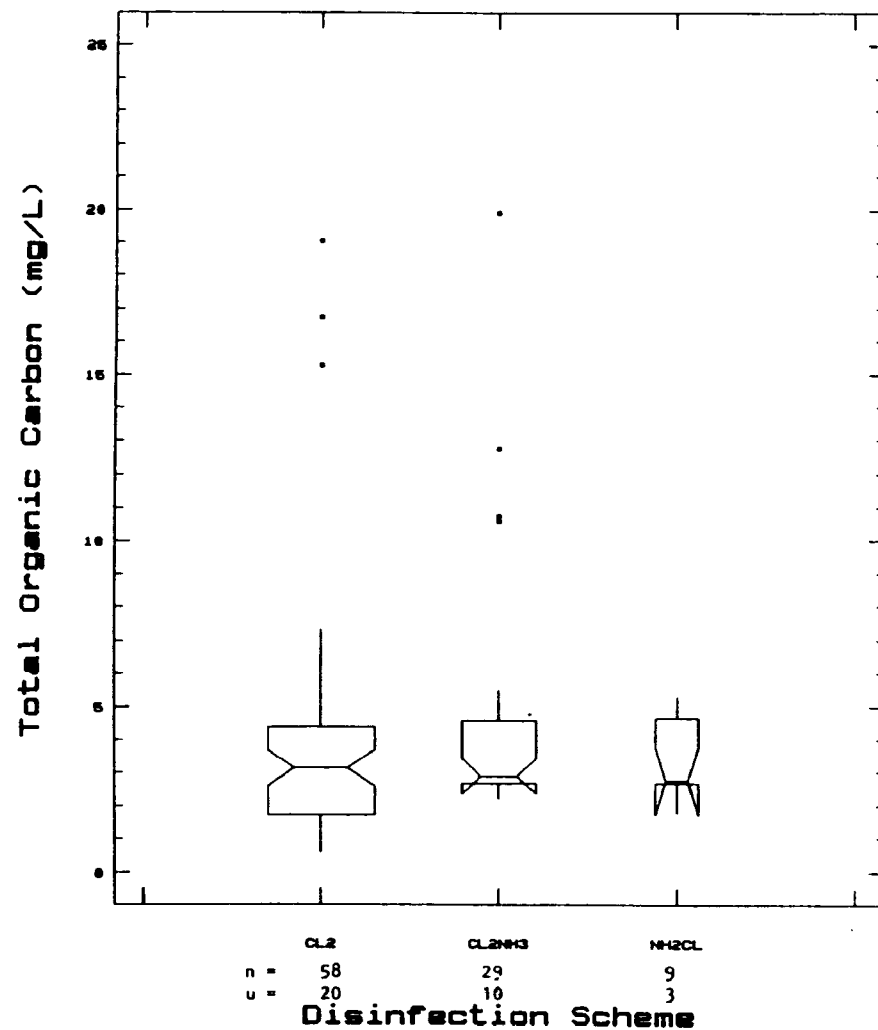
FIGURE 5-40

Influent UV Absorbance By Disinfection Scheme
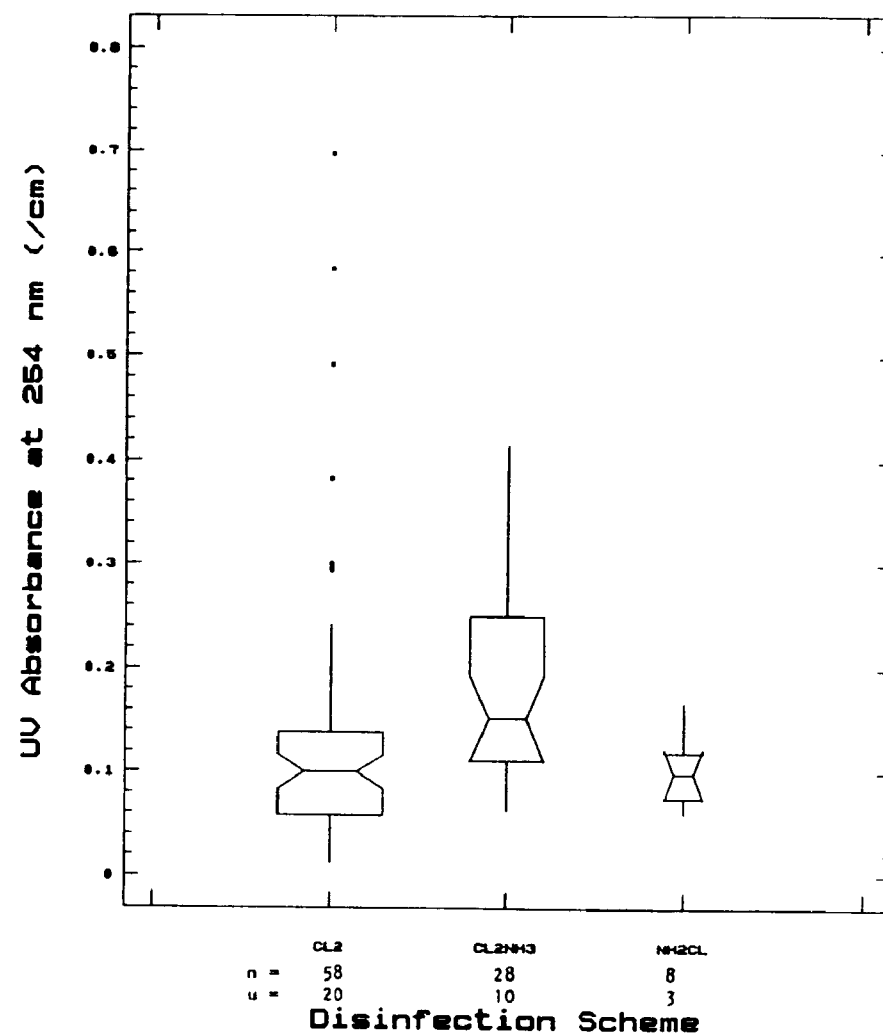
FIGURE 5-41

possible explanation for these results is that utilities with high UV-254 absorbance most likely have high color levels and require free chlorine contact time for color removal. However, the high UV-254 levels also indicate the presence of dissolved organic matter which could function as THM precursors. Thus, subsequent ammonia addition is required in order to control THMs.

Figures 5-42 and 5-43 illustrate overall influent chloride levels plotted with and without the inclusion of Utility 10, respectively. Because of the relatively small number of data points in the chloraminating category, the inclusion of Utility 10's extremely high influent chloride levels produces an oddly-shaped box-and-whisker plot. Whether or not Utility 10 is included, however, the overlapping 95 percent confidence intervals indicate there is no statistical difference between the medians of any two quarters. In Figures 5-44 and 5-45, influent bromide levels are plotted by disinfection scheme both with and without the inclusion of Utility 10. In both plots, prechlorinating/postammoniating utilities have a higher median influent bromide level than chlorinating utilities, and the difference is statistically significant at a 95 percent confidence level.

Classes of DBP Compounds

Figure 5-46 illustrates levels of $XDBP_{sum}$ by disinfection scheme. The plot indicates that the prechlorinating/postammoniating utilities have a higher median value of $XDBP_{sum}$ (approximately 94 μg/L) than either the chlorinating or chloraminating utilities (approximately 62 and 23 μg/L, respectively), and that the median $XDBP_{sum}$ level of the chlorinating utilities is higher than that of the chloraminating utilities. These differences are statistically significant at a 95 percent confidence level.

Figure 5-47, a plot of overall median TTHM levels by disinfection scheme, reflects the same trend observed in Figure 5-46. The median TTHM level for the prechlorinating/postammoniating utilities (approximately 57 μg/L) was significantly higher than that of the chlorinating and chloraminating utilities (approximately 34 and 12 μg/L, respectively), and the median TTHM level of the chlorinating utilities was substantially higher than that of the chloraminating utilities, although the difference was not statistically significant.

The fact that the prechlorinating/postammoniating utilities produced higher levels of $XDBP_{sum}$ than the chlorinating utilities is contrary to an intuitive expectation. While the plots of influent water quality parameters did not indicate significant differences in TOC or UV-254 levels between the three disinfection schemes (Figures 5-40 and 5-41), the median UV-254 level was higher for the prechlorinating/postammoniating utilities than for the other two disinfection schemes. The higher levels of UV-254 absorbance for the prechlorinating/postammoniating utilities may indicate higher levels of DBP precursors (i.e., higher humic substances content of the dissolved organic matter) than in the influents of utilities using the other disinfection schemes. Thus, the higher median level of $XDBP_{sum}$ may reflect the higher concentrations of DBP precursors in the prechlorinating/postammoniating utilities.

Another factor contributing to the unexpectedly high levels of DBPs occurring at the prechlorinating/postammoniating utilities may be the higher bromide levels measured at these utilities. The data plotted in Figure 5-45 indicated that the

Influent Chloride
By Disinfection Scheme
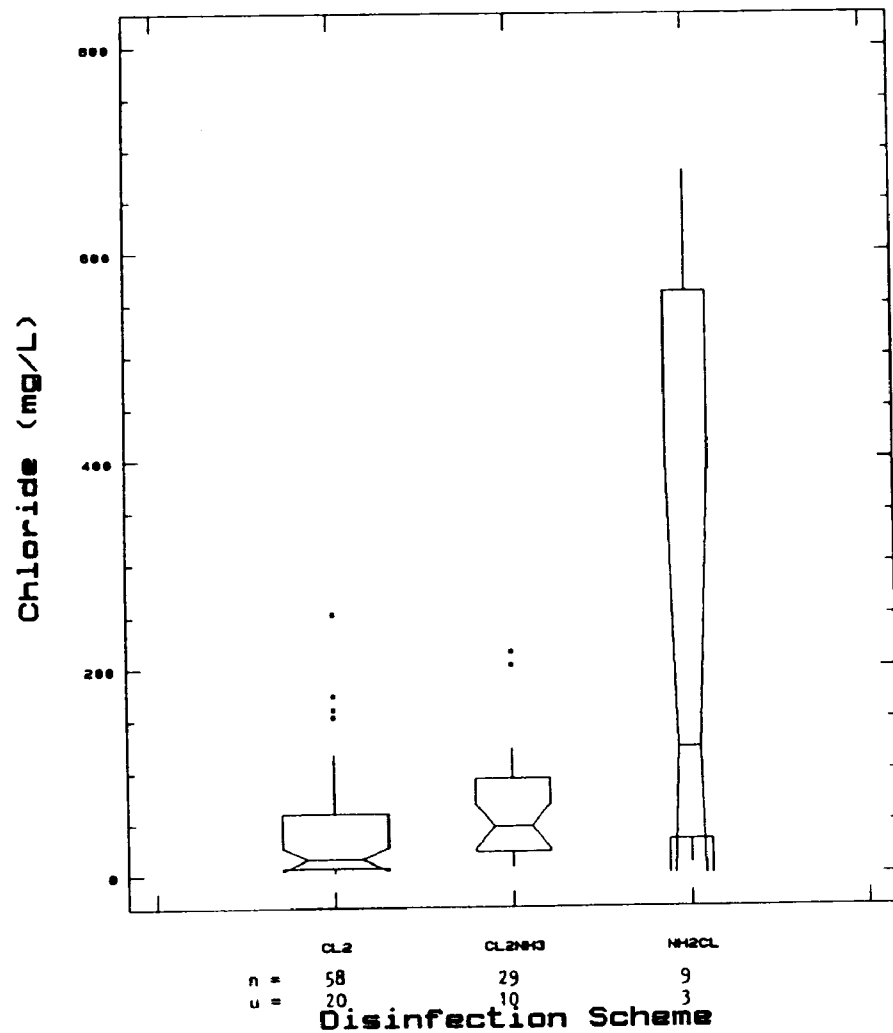
FIGURE 5-42

Influent Chloride
By Disinfection Scheme (w/o #10)
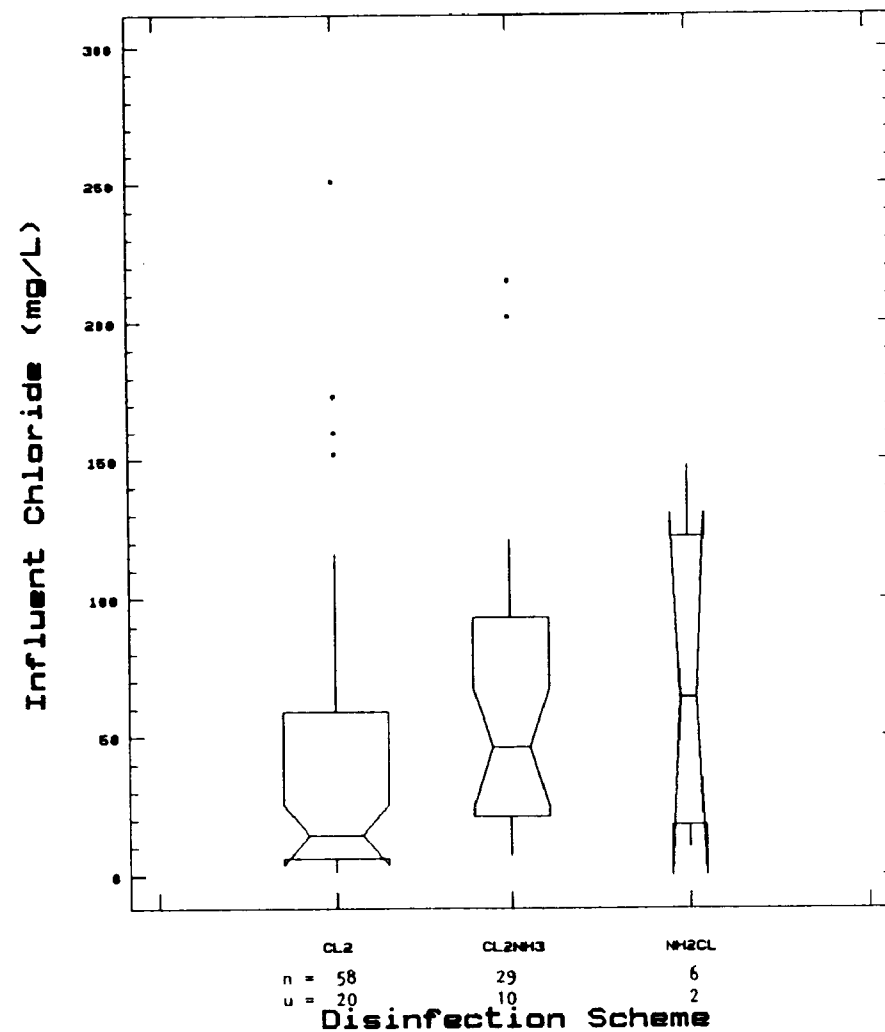
FIGURE 5-43

Influent Bromide
By Disinfection Scheme

Bromide (mg/L)

	CL2	CL2NH3	NH2CL
n =	58	29	9
u =	20	10	3

Disinfection Scheme
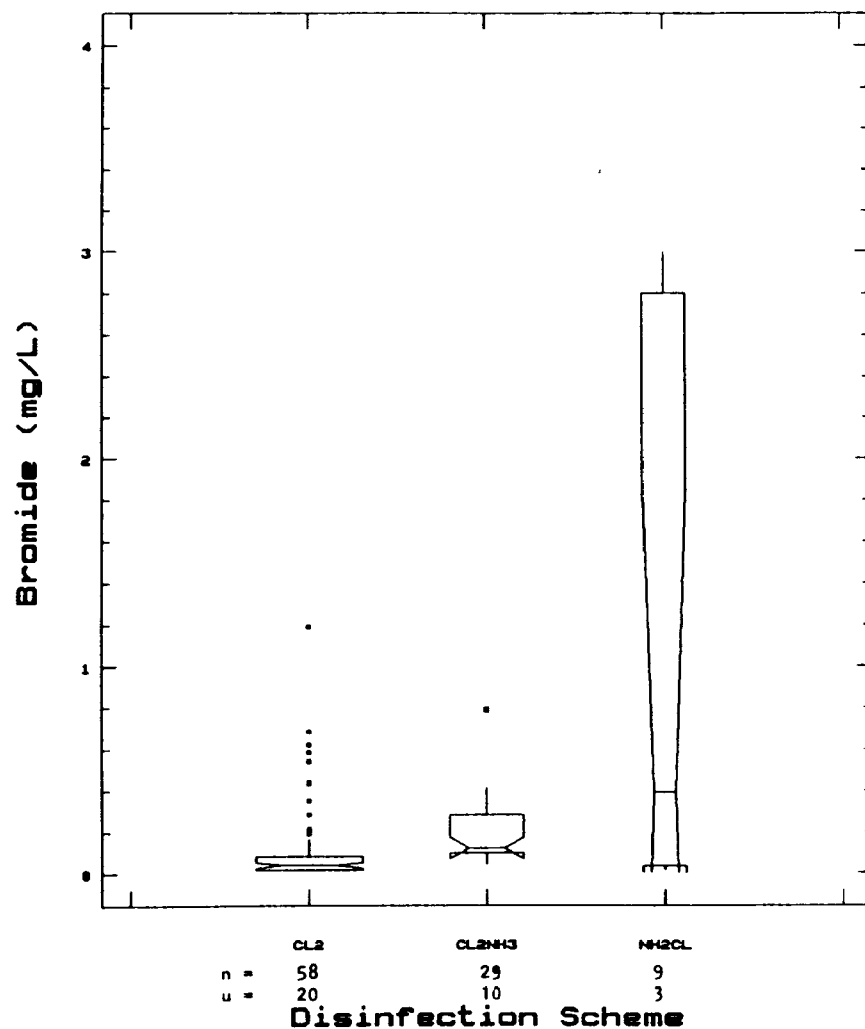
FIGURE 5-44

Influent Bromide
By Disinfection Scheme (w/o #10)
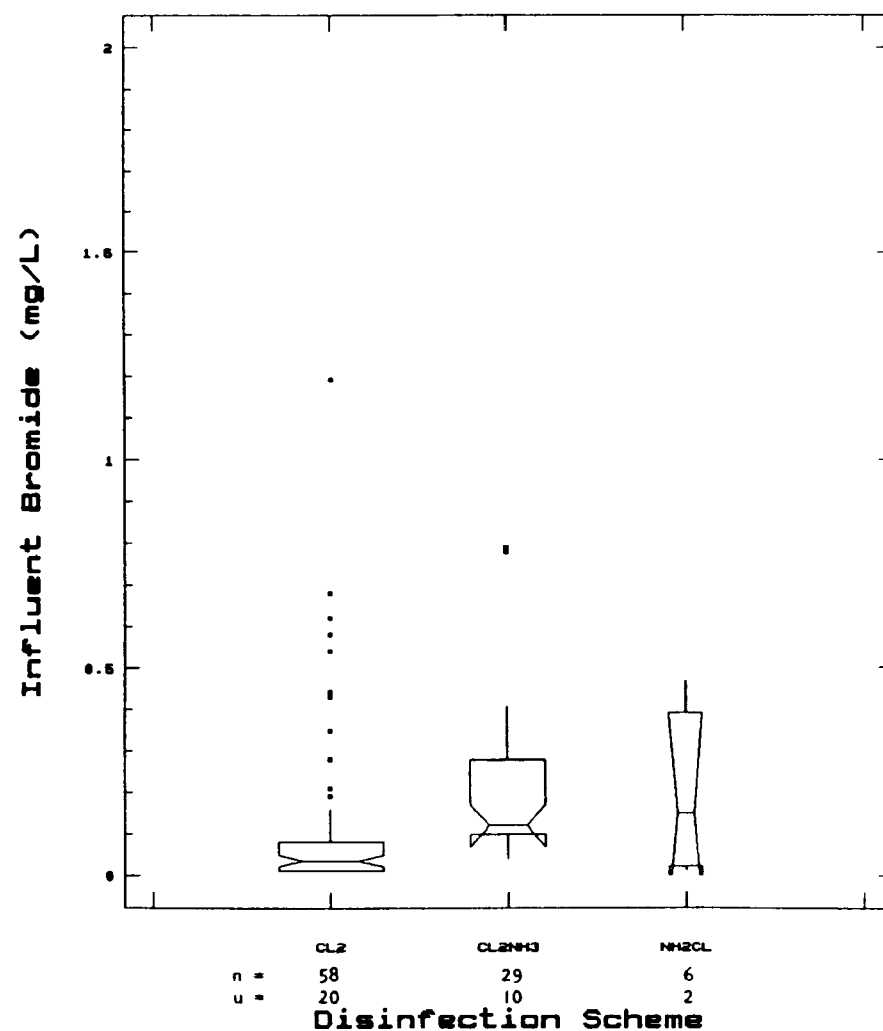
Influent Bromide (mg/L)

	CL2	CL2NH3	NH2CL
n =	58	29	6
u =	20	10	2

Disinfection Scheme
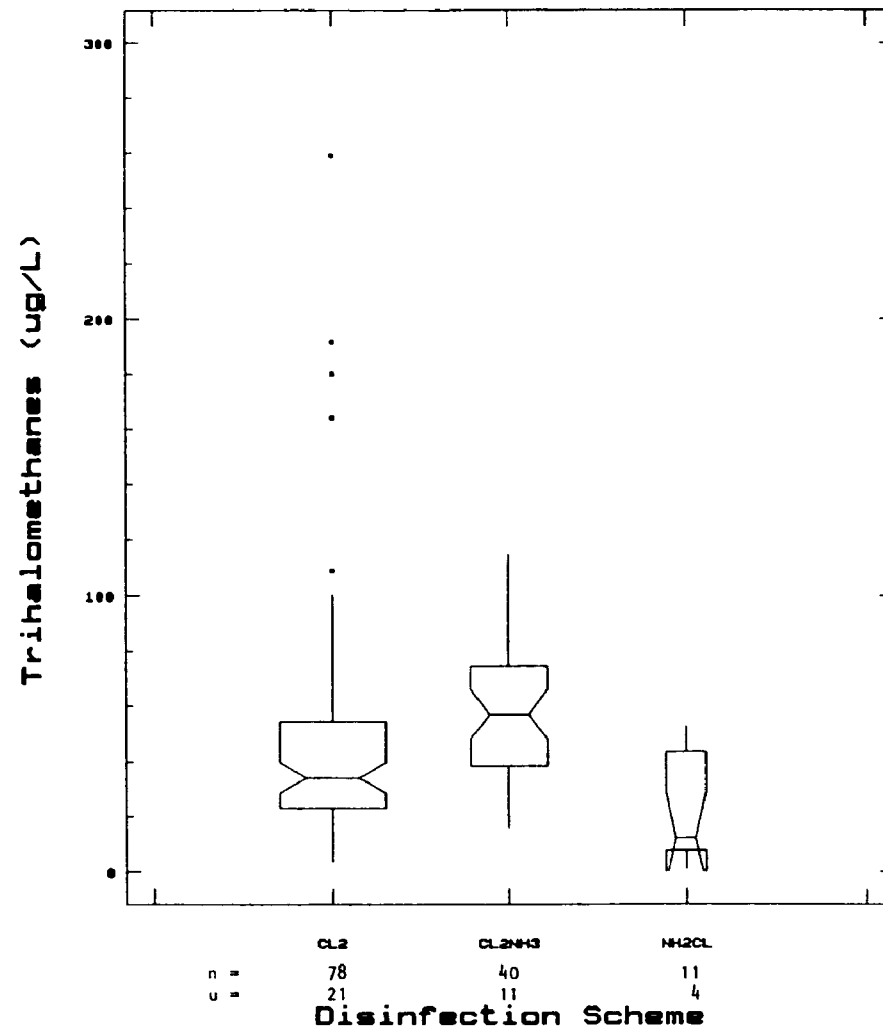
FIGURE 5-45

FIGURE 5-46

FIGURE 5-47

prechlorinating/postammoniation utilities had a higher median influent bromide level than the chlorinating utilities, and this difference was statistically significant at a 95 percent confidence level. Research by Aizawa, et al. (1989) found "...the concentration of total THM increased with the augmentation of bromide ions with the same amount of chlorine dosage. The increase in THMs is up to two times higher than in the absence of bromide ions." As discussed later in this section, utilities treating waters high in bromide had relatively high concentrations of bromoform and other brominated DBPs. Since bromoform is the heaviest of the THM compounds, its presence can result in elevated TTHM levels.

In interpreting the DBP data presented as a function of disinfection scheme, it should be noted that baseline data samples for this study were collected at the clearwell effluents of the participating utilities. Figure 2-2 illustrated the process trains of the plants at which samples were collected. Of the 11 prechlorinating/postammoniating utilities participating in this study, eight did not add ammonia until the filter effluent and filtration was the process immediately upstream of the clearwell. Thus, these utilities maintained a free chlorine residual throughout most of the in-plant detention time, and levels of DBPs measured at these utilities reflect the free chlorine contact time. The differences in DBP concentrations between the prechlorinating/postammoniating utilities and the chlorinating utilities would be more apparent had the sampling taken place within the distribution systems of the participating utilities.

As discussed previously in the section entitled "Star Plot Analyses", all other factors being equal, it would be expected that the chlorinating utilities would have the highest median TTHM level compared to utilities employing the other two disinfection schemes. Figures 5-46 and 5-47 highlight the danger of oversimplifying the influences of causal factors on DBP production. Taken out of context, these two figures could give the impression that based on median levels, prechlorinating/postammoniating utilities could not meet a revised THM standard if it were lowered to 50 μg/L, while utilities utilizing only free chlorine would be able to meet this lower standard. Such a perception would not consider other potential causal factors found in this and other DBP studies, such as influent TOC levels, influent UV-254 absorbance, influent bromide concentration, free chlorine contact time, pH, and temperature, among others. A correct interpretation of the results presented in Figures 5-46 and 5-47 is that, of the 35 utilities participating in this study, the utilities practicing prechlorination/postammoniation had higher median levels of halogenated DBPs and TTHMs than the utilities employing chlorination or chloramination. The UV-254 data presented previously in Figure 5-41 may suggest that these results are due to the presence of THM and DBP precursors in higher levels in the source waters of the prechlorinating/postammoniating utilities, and that prechlorination/postammoniation may be the most effective oxidation/disinfection method for such source waters.

Figure 5-48 shows overall HAA concentrations by disinfection scheme. Both chlorinating and prechlorinating/postammoniating utilities had significantly higher HAA levels than chloraminating utilities. The chlorinating and prechlorinating/postammoniating utilities had median HAA levels of approximately 22 and 19 μg/L, respectively, while the chloraminating utilities had a median HAA level of only 8 μg/L.

Haloacetic Acids
By Disinfection Scheme
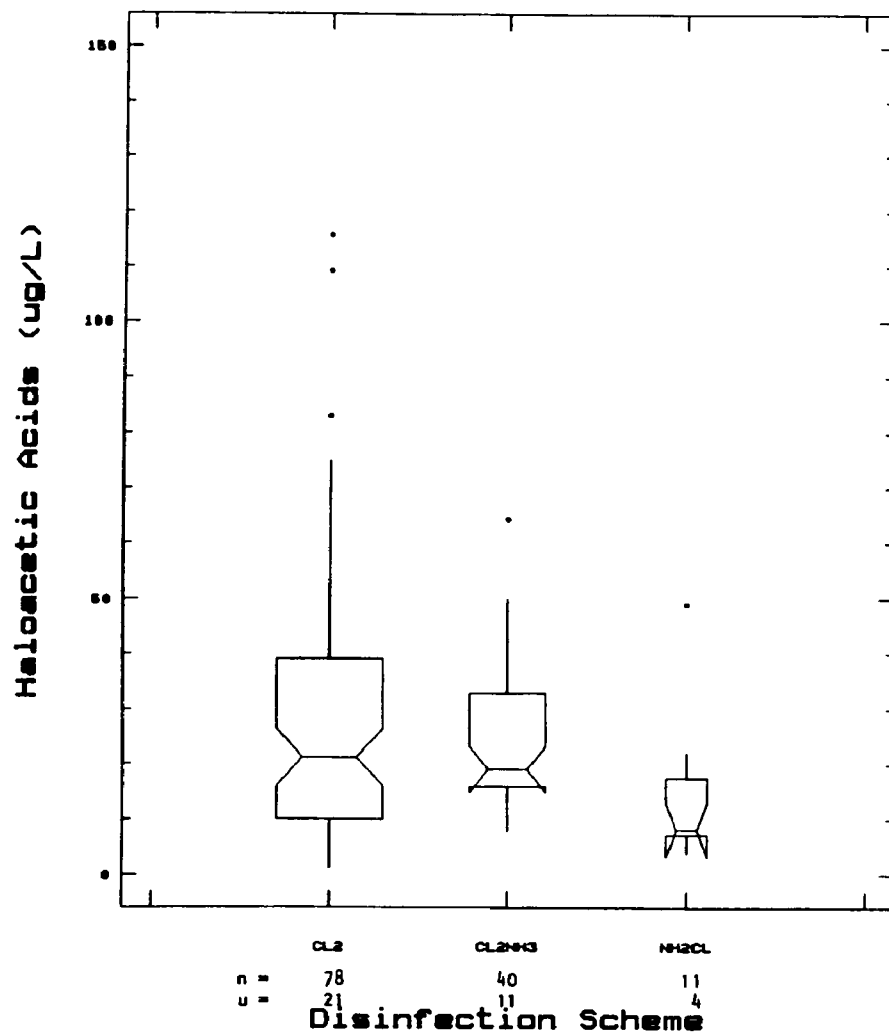
FIGURE 5-48

Haloacetonitriles
By Disinfection Scheme
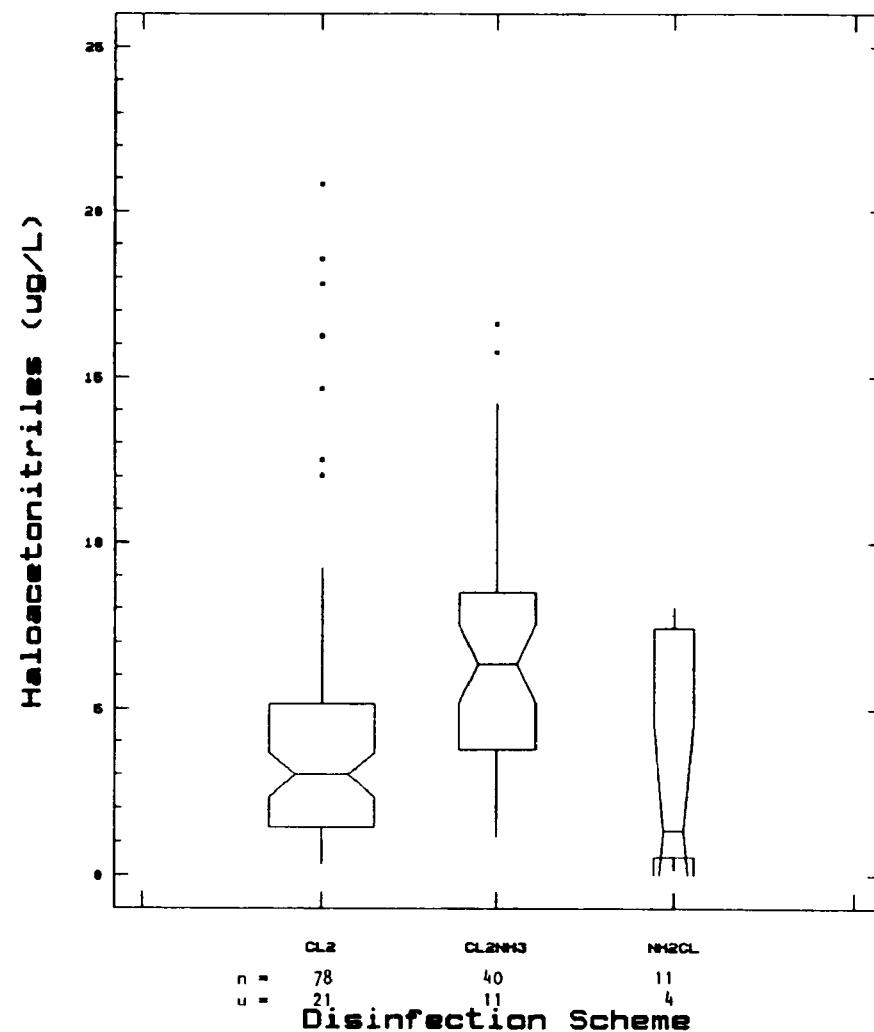
FIGURE 5-49

Overall HAN levels are shown in Figure 5-49 by disinfection scheme. This plot reflects the same trend seen in the plots of XDBP$_{sum}$ and TTHM levels as a function of disinfection scheme; that is, a significantly higher HAN concentration for the prechlorinating/postammoniating utilities compared to either the chlorinating or chloraminating utilities. However, in contrast to the plots of XDBP$_{sum}$ and TTHM medians, Figure 5-49 shows a number of outliers at high levels for the chlorinating utilities, indicating that some chlorinating utilities produced relatively high levels of HANs (in the approximate range of 12 to 21 μg/L).

Figure 5-50 is a plot of overall HK concentrations by disinfection scheme. This plot indicates that the median level of HKs was significantly higher for chlorinating and prechlorinating/postammoniating utilities compared to chloraminating utilities.

Figure 5-51 shows ALD levels as a function of disinfection scheme. In this plot, prechlorinating/postammoniating utilities produced the highest median ALD concentration, significantly higher than either the chlorinating or chloraminating utilities. Influent ALD levels and ALD production as a function of the oxidation/disinfection schemes utilized by water treatment facilities will be discussed later in this section and in Section 6.

Overall chloropicrin and chloral hydrate levels are shown in Figure 5-52 and 5-53, respectively, as a function of disinfection scheme. Both plots suggest the same trend of the highest median for chlorinating utilities, lower for prechlorinating/postammoniating utilities, and the lowest median for chloraminating utilities. For chloropicrin levels, the differences between medians are significant for the chlorinating and chloraminating utilities. For chloral hydrate, the median level is significantly higher for chlorinating and prechlorinating/postammoniating utilities compared to chloraminating utilities.

Figure 5-54 is a plot of cyanogen chloride data for the three disinfection scenarios. The plot indicates that the prechlorinating/postammoniating utilities had a significantly higher cyanogen chloride level (approximately 2 μg/L) compared to both the chlorinating and chloraminating utilities (less than 0.5 μg/L). These results will be evaluated in detail later in this section in the "Special Issues" discussion.

DBP AND INFLUENT PARAMETER CORRELATIONS

The objective of this section is to examine correlations of various DBP classes, individual DBPs and various water quality parameters. Correlations were determined between:

- o DBP classes
- o Individual DBPs
- o Individual DBPs and influent water quality parameters
- o Influent water quality parameters

In total, over 300 correlations, as shown in Appendix D, were determined. Figures 5-55 to 5-68 present a selected number of these. Note that in some figures, the correlations are re-evaluated without including certain outliers. In some cases, the outlier is an anomalous data point not observed in other samplings at the same utility. In other cases, utilities with very high concentrations of the parameter under

Haloketones
By Disinfection Scheme

	CL2	CL2NH3	NH2CL
n =	78	40	11
u =	21	11	4

Disinfection Scheme
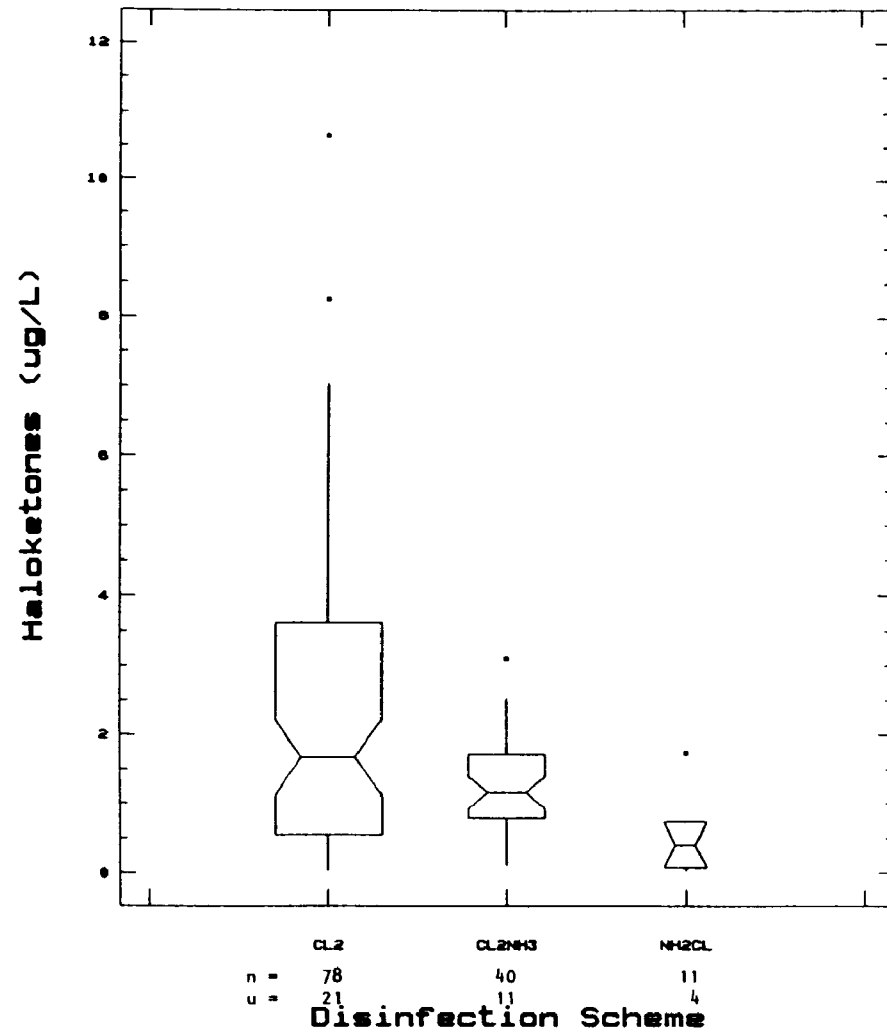
FIGURE 5-50

Aldehydes By Disinfection Scheme

	CL2	CL2NH3	NH2CL
n =	55	28	9
u =	20	13	3

Disinfection Scheme
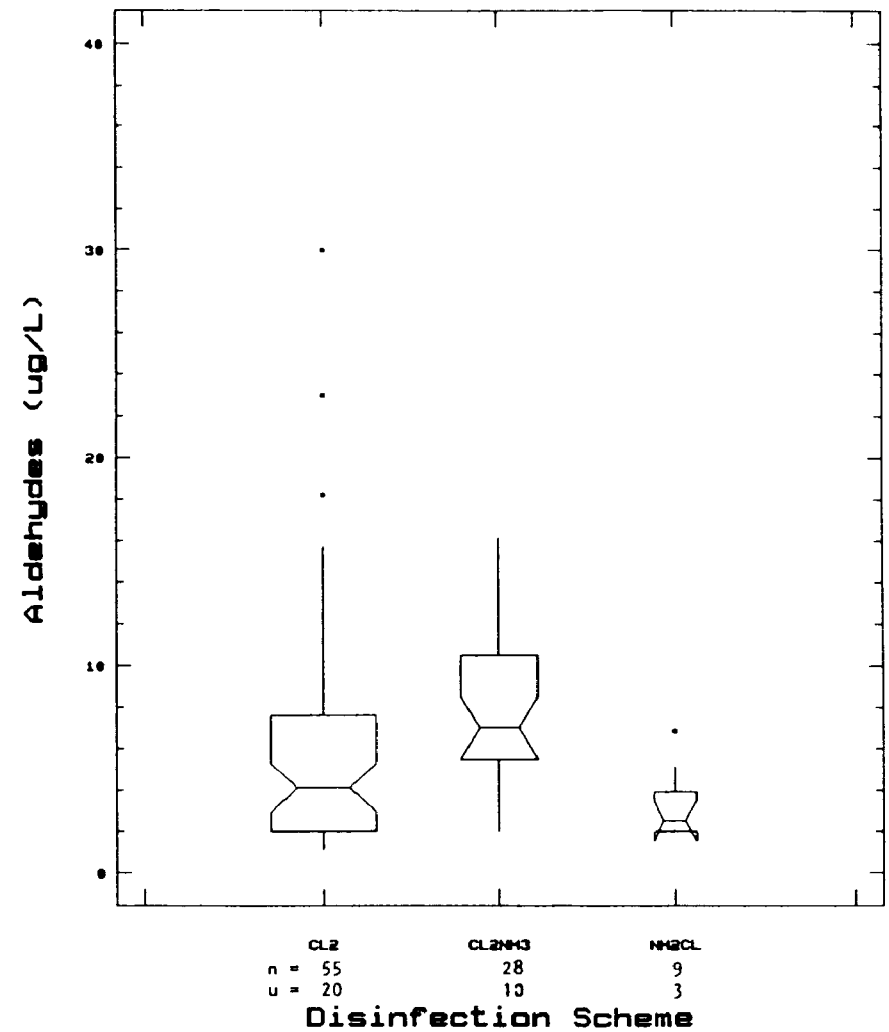
FIGURE 5-51

Chloropicrin By Disinfection Scheme

Chloropicrin (ug/L)

CL2   CL2NH3   NH2CL
n =   78   40   11
u =   21   11   4

Disinfection Scheme
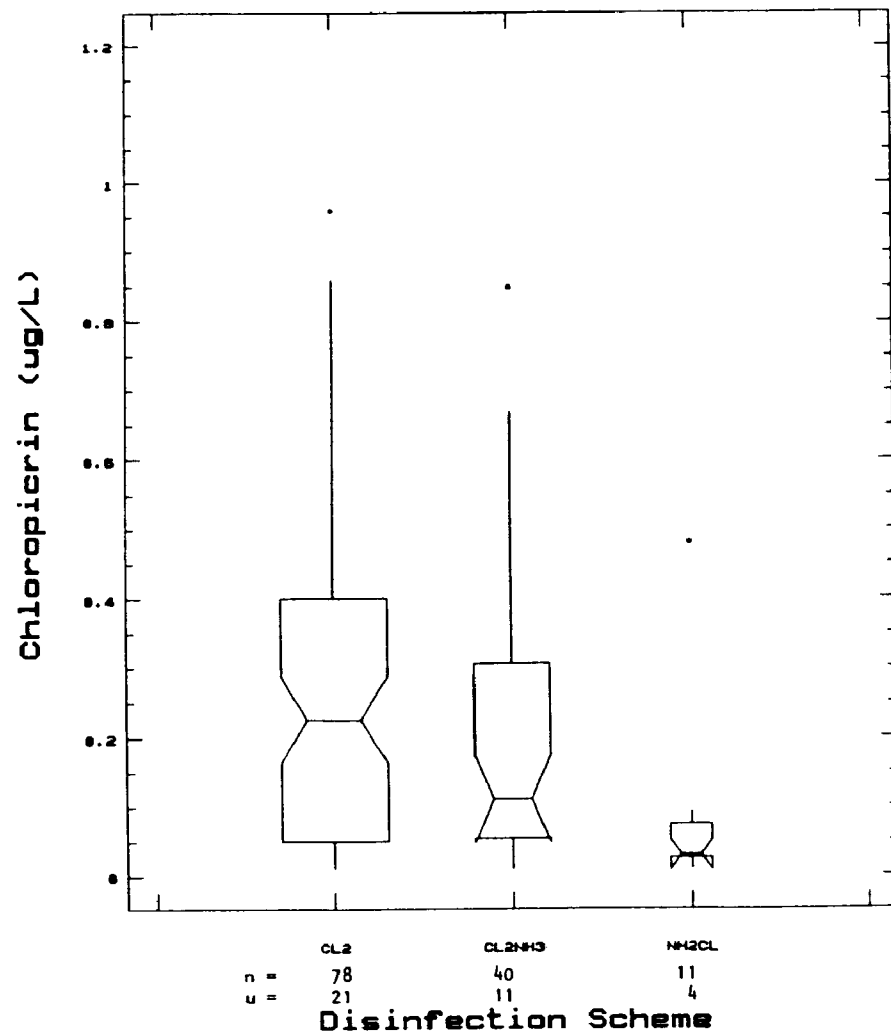
FIGURE 5-52

Chloral Hydrate
By Disinfection Scheme

Chloral Hydrate (ug/L)

CL2   CL2NH3   NH2CL
n =   72   34   11
u =   21   10   4

Disinfection Scheme
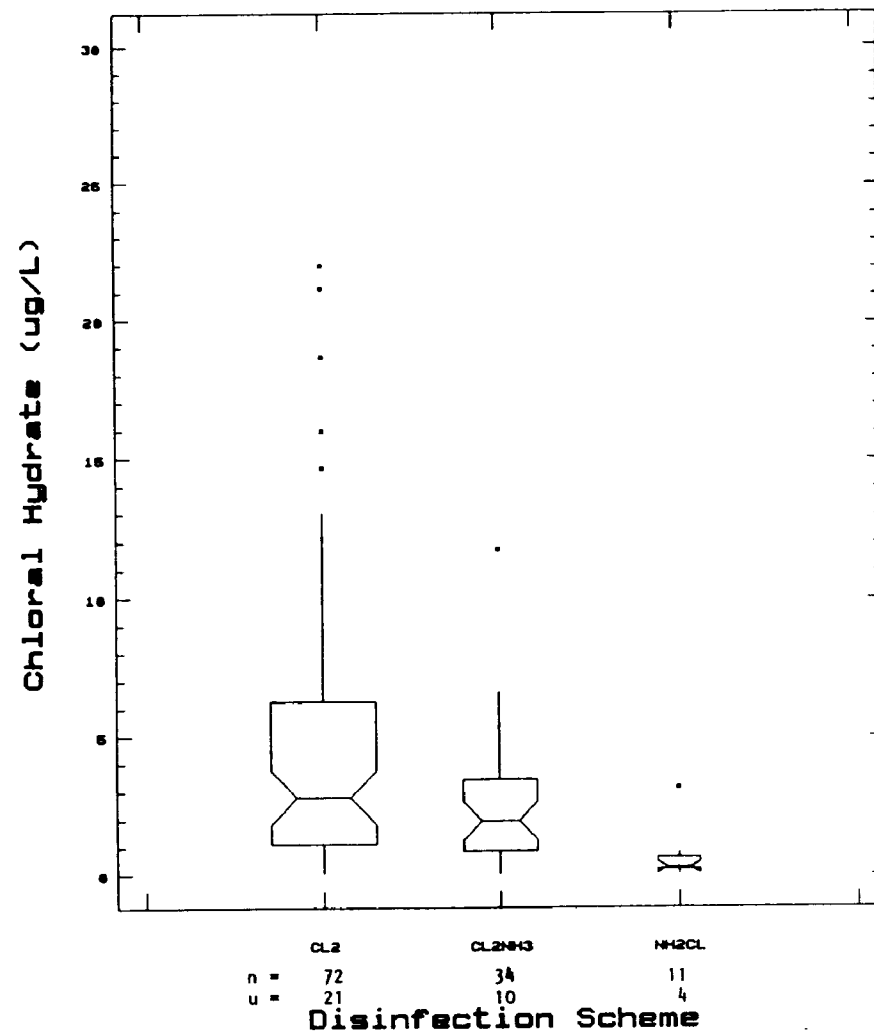
FIGURE 5-53

Cyanogen Chloride
By Disinfection Scheme
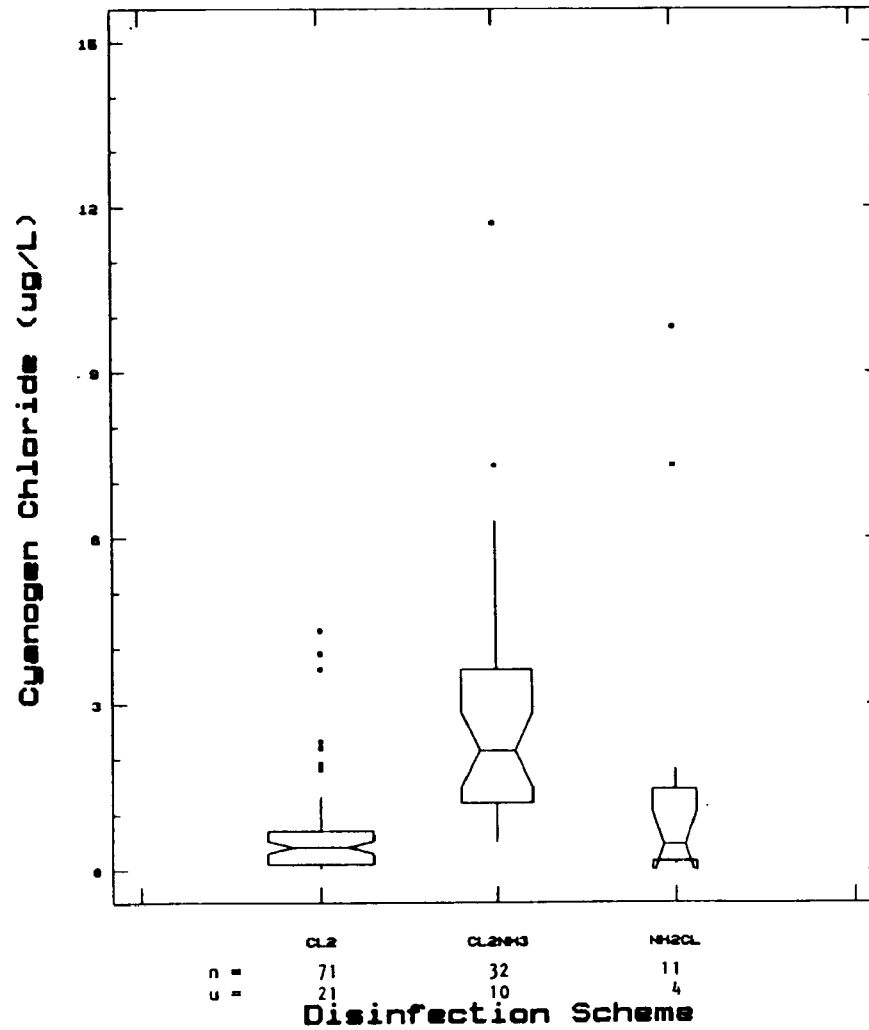
FIGURE 5-54

consideration can create what may be an artificially high correlation coefficient; thus a more realistic value is obtained by treating those utilities as outliers.

Correlations with THMs

In this study, analyses were performed through four analytical fractions for a total of 19 individual halogenated DBPs (XDBPs). Concerns have been expressed as to the practicality of performing several different DBP analyses in a utility's routine monitoring program, and the question of employing a surrogate has been raised. Figure 5-55 presents various correlations with THMs. There was a strong correlation between TTHMs and the sum of XDBPs measured in this project (r=0.96). As THMs represent the largest DBP fraction detected in this study, the data were reevaluated by comparing TTHMs to the sum of non-THM XDBPs. In this instance, r decreased to 0.76. However, the latter comparison does not mean that THMs cannot be used as a surrogate or predictor of the sum of all XDBPs. It should be noted, though, that correlations between classes of compounds were often low (e.g., comparing TTHMs to haloketones yields an r of only 0.06). Additionally, some of the other individual DBPs may require separate monitoring based on their health effects and their formation and control relative to THMs. For example, THM production can be minimized with the use of chloramines, whereas cyanogen chloride formation can be increased, as will be discussed in detail later in this section.

Figure 5-55 also presents the correlation of HANs with THMs (r=0.78). The median ratio of the sum of the HANs to THMs for all four quarters was 0.11 (the 25th percentile was 0.073 and the 75th percentile was 0.15). The linear regression equation for this relationship is:

$$[HANs] = 0.78 + 0.087[THMs]$$

In general, it appears that the concentrations of HANs were approximately one-tenth of the concentrations of THMs. Another study found that the concentration of DCAN averaged about 10 percent of the THM concentration (Oliver, 1983). The variations from these generalized relationships are probably due, at least in part, to the different effect of pH on these two DBP classes; this is discussed in greater detail later in this section.

Correlation with HAAs

Figure 5-56 presents various correlations with HAAs. The correlation of HAAs with $XDBP_{sum}$ was 0.87. If THMs are not included in the correlation, r increases to 0.98. However, HAAs comprise approximately 57 percent of the non-THM XDBPs (see Figure 5-3). If both HAAs and THMs are subtracted from the $XDBP_{sum}$ and then correlated with HAAs, r equals 0.77. Furthermore, a correlation of 0.74 is found if only HAAs are subtracted from $XDBP_{sum}$. The latter two correlations may be useful in helping to predict the sums of non-THM, non-HAA XDBPs.

Correlations with Influent Water Quality Parameters

The correlations of TOC with THMs and UV-254 absorbance, and UV-254 absorbance with THMs, are shown in Figure 5-57. Several researchers have investigated the

Correlations with Trihalomethanes

XDBPsum vs THMs

r=0.96

n=140
THMS (ug/L)

XDBPs-THMs vs THMs

r=0.76

n=140
THMS (ug/L)

HANS vs THMs

r=0.78

n=140
THMs (ug/L)
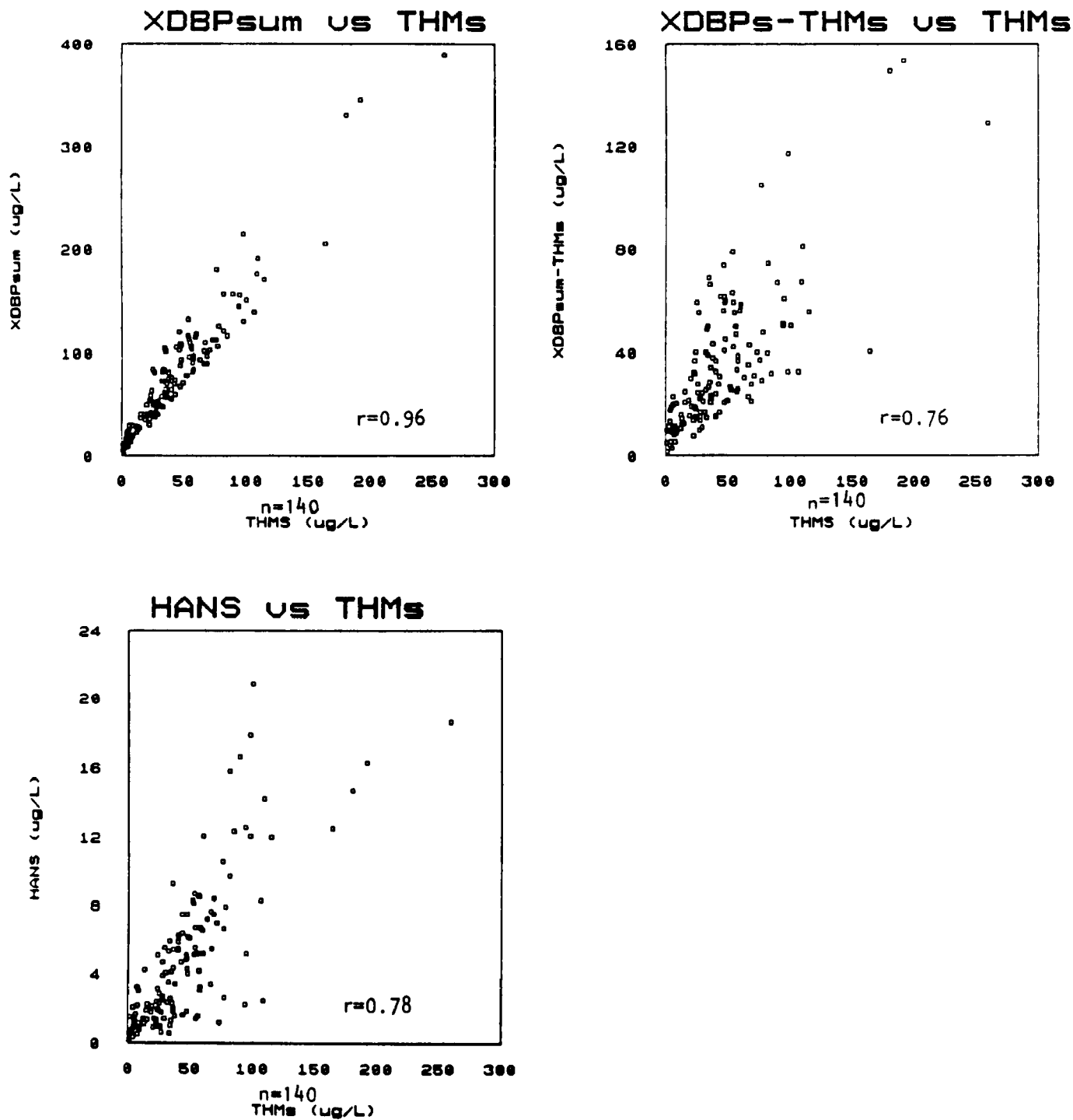
FIGURE 5-55

Correlations with Haloacetic Acids

XDBPsum vs HAAs

r=0.87

n=140
HAAS (ug/L)

XDBPs-THMs vs HAAs

r=0.98

n=140
HAAS (ug/L)

XDBPsum-HAAS vs HAAS

r=0.77

n=140
HAAS (ug/L)

XDBPsum-THMs-HAAS vs HAAS

r=0.74

n=140
HAAS (ug/L)
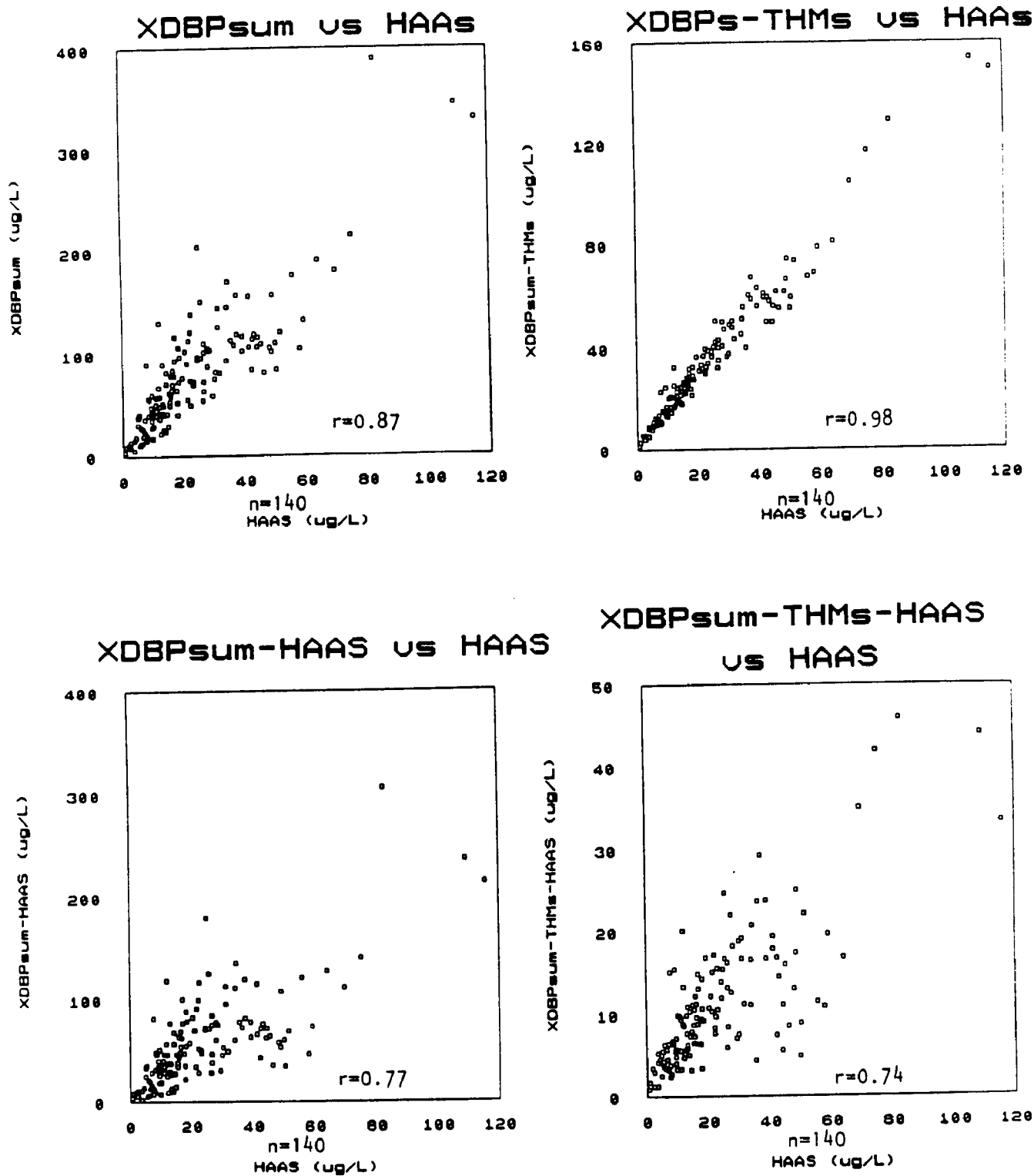
FIGURE 5-56

Correlations with Influent Parameters
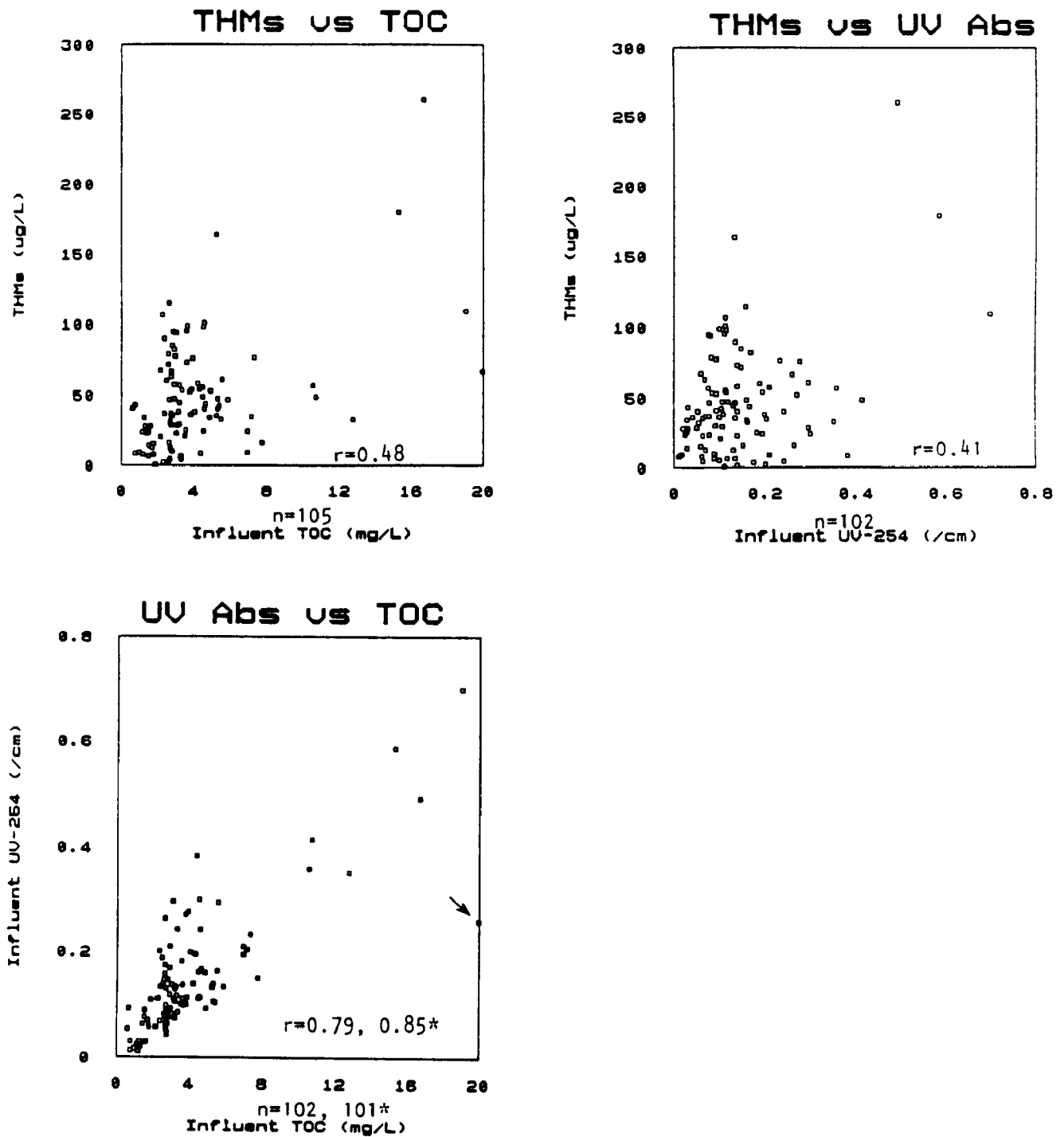
THMs vs TOC
r=0.48
n=105
Influent TOC (mg/L)

THMs vs UV Abs
r=0.41
n=102
Influent UV-254 (/cm)

UV Abs vs TOC
r=0.79, 0.85*
n=102, 101*
Influent TOC (mg/L)

* Excludes indicated outlier

FIGURE 5-57

relationships among TOC, UV-254 absorbance, and THM formation potential (THMFP) (AWWA Organic Contaminants Committee, 1985; Amy et al., 1987; Chowdhury et al., 1988). For this study, the correlation between the UV-254 and TOC of plant influents was high (i.e., r=0.85, without outlier). Determining this correlation by water source did not improve the correlation (Figure 5-58). It should be noted that neither TOC or UV-254 correlated well with the TTHMs of the plant effluents. Specifically, during the last three sampling quarters, the correlation of TTHMs with influent TOC was 0.48; and for TTHMs with UV-254, r=0.41. Because utilities apply chlorine doses based on numerous considerations (e.g., the chlorine demand of the water, disinfection requirements, taste and odor control), in actuality the TTHMs detected do not necessarily reflect the THMFP of that water. Also, since a large percentage of the utilities in this study used chloramines and several utilized ozone as a preoxidant, it is not surprising to find a poor correlation between the influent TOC and the effluent DBPs. A mathematical model accounting for chlorine dose, TOC concentration, bromide level, temperature, pH and other parameters is currently being explored by other researchers to determine whether THM levels are predictable (Amy et al., 1987).

Correlations with Bromide and Brominated DBPs

Figure 5-59 presents correlations of plant influent chloride with plant influent bromide, and influent bromide with bromoform. Influent chloride had a very high correlation with influent bromide (r=0.97). The three outliers noted were from the same utility; if these are not included, the correlation coefficient decreases to 0.86. Because of the high correlations, chloride may be used as a predictor for bromide. Using all the data, linear regression analysis yields the equations:

$$[Br^-] = -0.0500 + 0.0044[Cl^-] \text{ (with outliers)}$$

$$[Br^-] = -0.0071 + 0.0034[Cl^-] \text{ (without outliers)}$$

The correlation of influent bromide with bromoform is also presented in Figure 5-59. The correlation for this relationship was 0.57 unless the noted outliers are excluded (r=0.69).

Relationships of influent bromide with chloropicrin, 1,1,1-TCP, TCAA and chloroform are presented in Figure 5-60. In each case, an exclusion relationship is demonstrated, i.e., the presence of bromide appeared to exclude the presence of the particular DBP, and the inverse was also observed. Mutual exclusion of bromide with these compounds is also demonstrated by their negative correlation coefficients.

The formation of chloropicrin due to chlorination of: 1) nitrogenous organic compounds, 2) non-nitrogenous organic substances in the presence of nitrites, and 3) humic substances, has been well documented in the literature (Coleman et al., 1976; Sayato et al., 1982; Duguet et al., 1984; Thibaud et al., 1986). Additionally, bromide has been shown by many researchers to play an important role in the formation of trihalomethanes (Rook, 1976). This study has shown, however, that bromide may also play a significant role in precluding the formation of certain other compounds. The exclusion relationship of bromide with chloropicrin is consistent with that observed by Thibaud, et al. (1988). These researchers showed that increasing bromide

Correlations with Influent Parameters

Water Source is FS

Water Source is GW

Water Source is LR

r = 0.82, 0.90 *

n = 35, 34 *

r = 0.84

n = 21

r = 0.66

n = 46
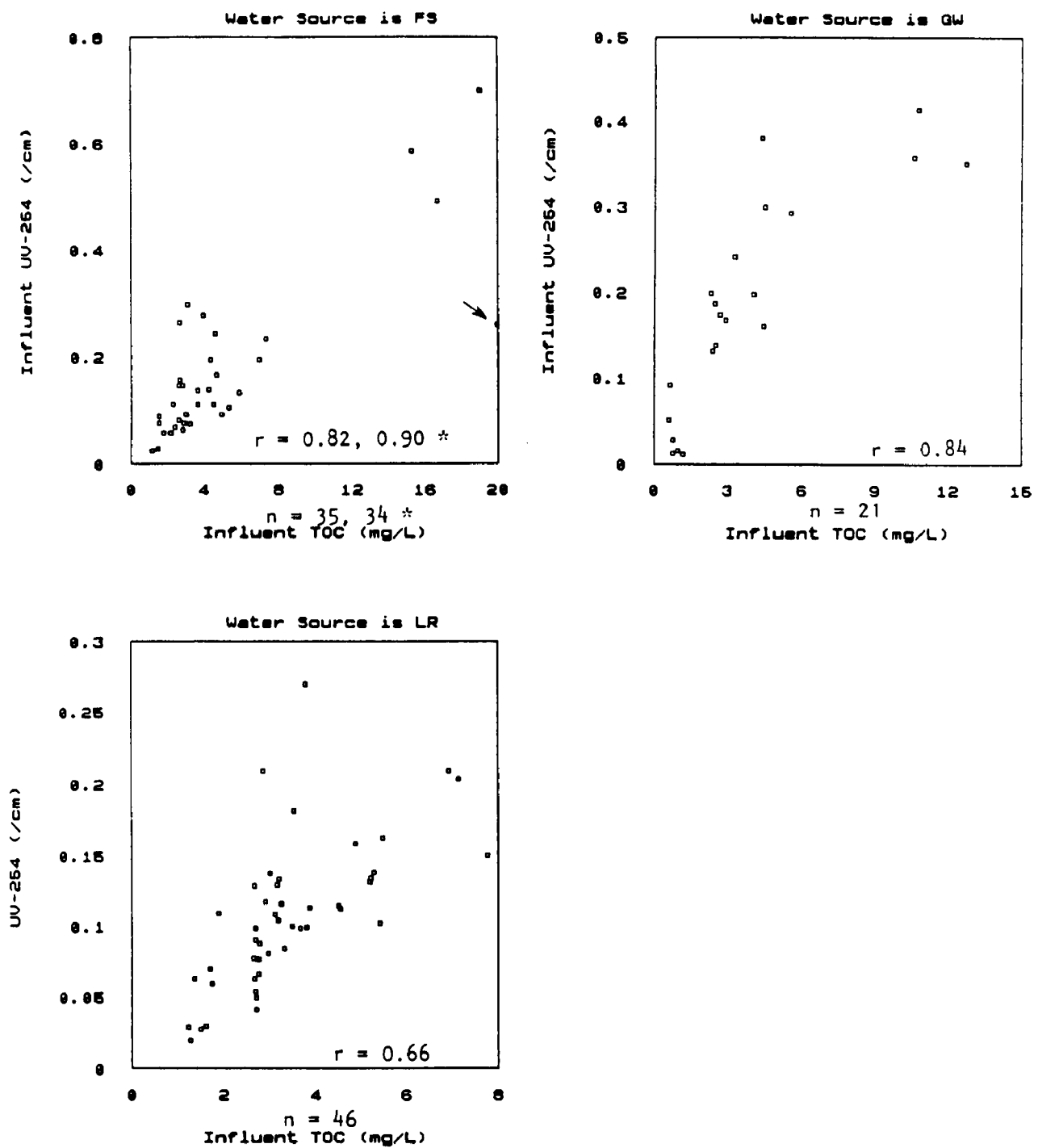
* Excludes Indicated Outlier

FIGURE 5-58

Correlations with Influent
Chloride and Bromide
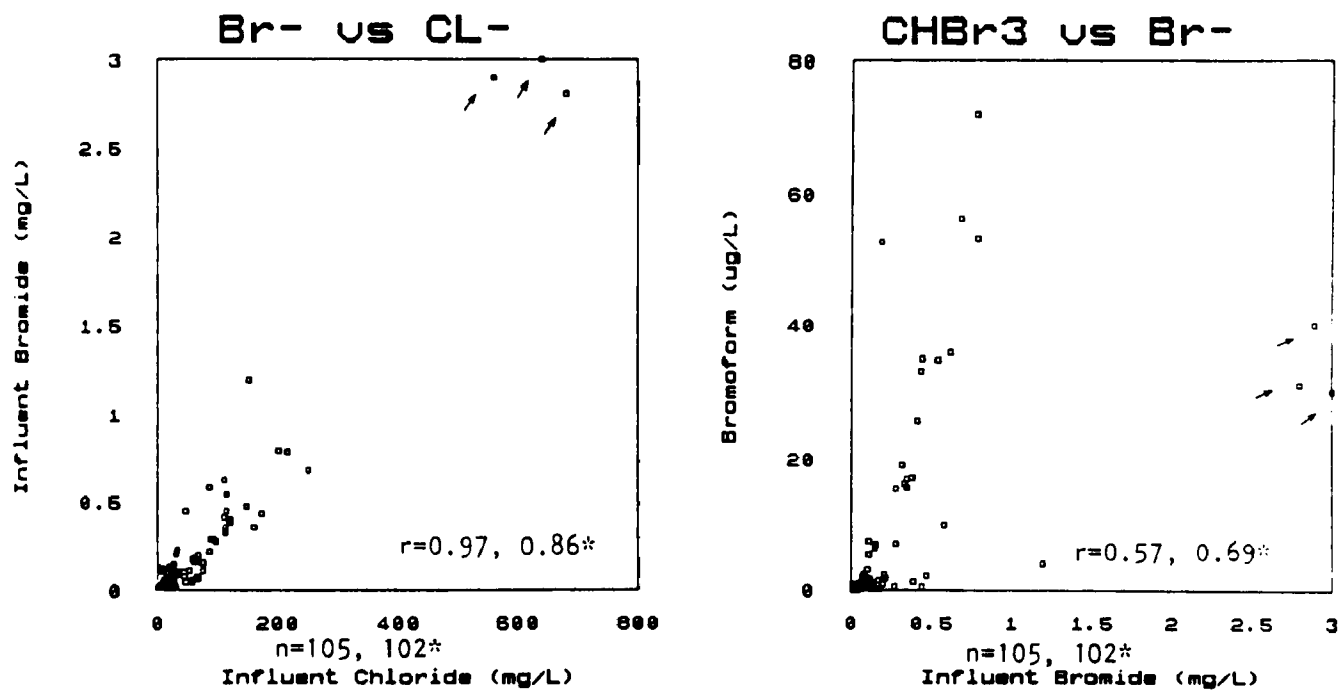
FIGURE 5-59

Correlations with Influent Bromide
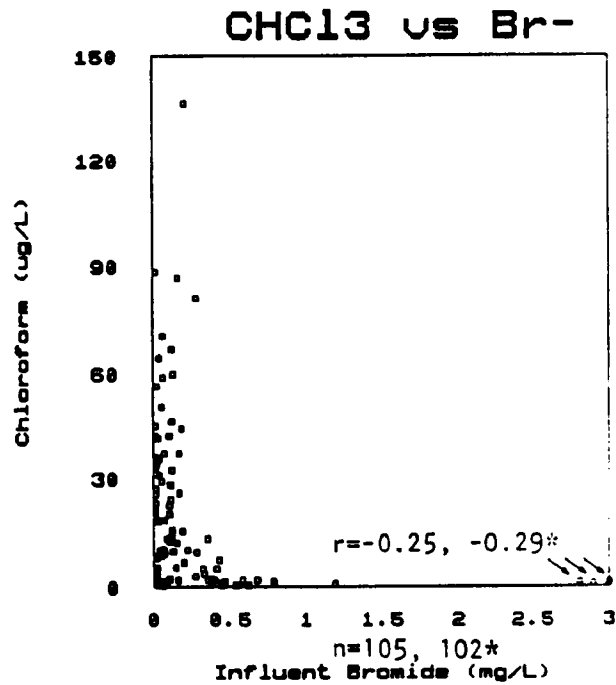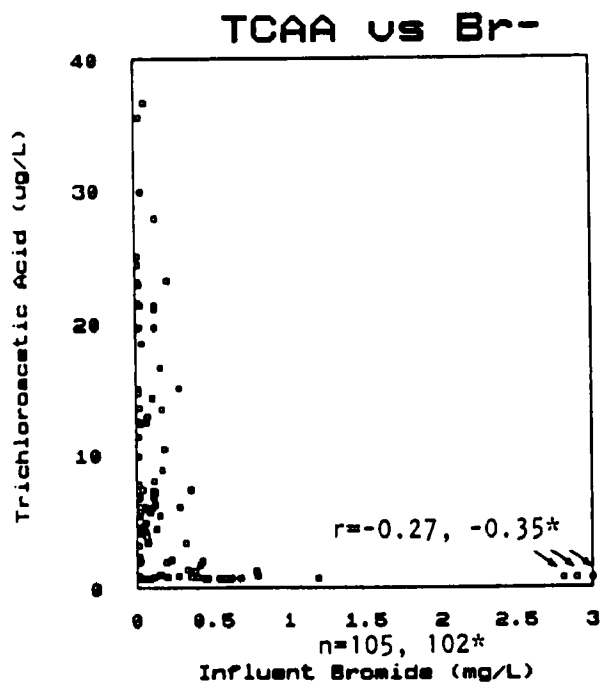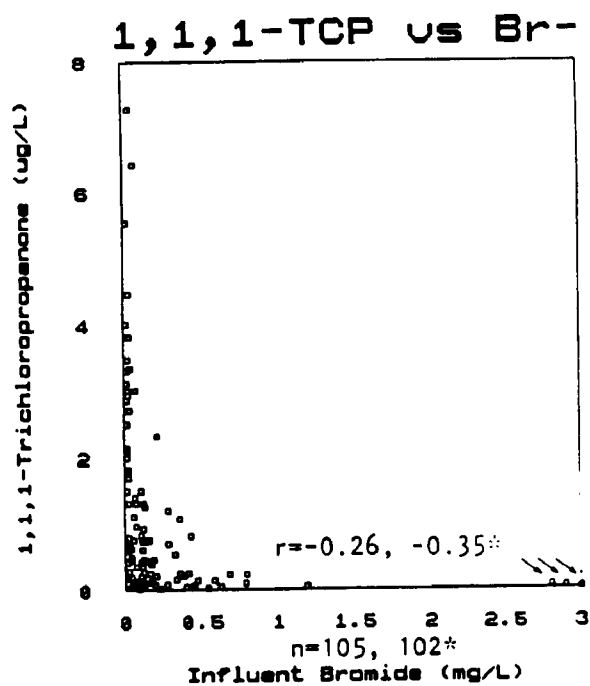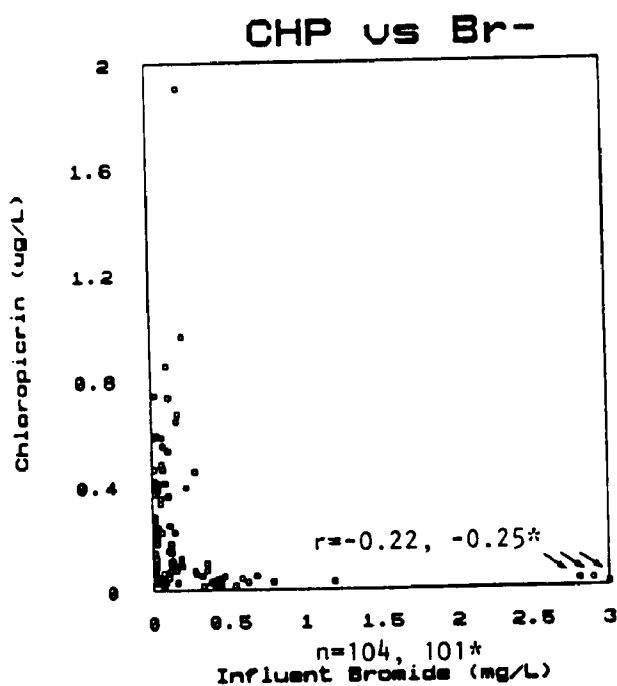
CHP vs Br⁻

Chloropicrin (ug/L)
Influent Bromide (mg/L)
r=-0.22, -0.25*
n=104, 101*

1,1,1-TCP vs Br⁻

1,1,1-Trichloropropanone (ug/L)
Influent Bromide (mg/L)
r=-0.26, -0.35*
n=105, 102*

TCAA vs Br⁻

Trichloroacetic Acid (ug/L)
Influent Bromide (mg/L)
r=-0.27, -0.35*
n=105, 102*

CHCl3 vs Br⁻

Chloroform (ug/L)
Influent Bromide (mg/L)
r=-0.25, -0.29*
n=105, 102*

* Excludes indicated outliers

FIGURE 5-60

concentrations led to a decrease in the production of chloropicrin (trichloronitromethane) and to the formation of brominated halopicrins (i.e., bromodichloronitromethane, dibromochloronitromethane and tribromonitromethane). These halopicrins are analogous to the THMs and appear to be influenced by bromide in a similar manner.

The exclusion relationship of bromide with 1,1,1-trichloropropanone is supported by work performed by Croue and Reckhow (1988). These researchers showed that in the presence of 0.4 mg of bromide per mg of carbon, the chlorination of a particular fulvic acid yielded decreased concentrations of 1,1,1-TCP. Additionally, several new brominated compounds were detected including chloro-, bromopropanones. As 1,1,1-TCP has been demonstrated to be an intermediate DBP which can hydrolyze to chloroform. the chloro-, bromopropanones may be precursors of the brominated THMs. Since bromide appears to play an important role in DBP formation, it is not unusual that other exclusion relationships such as with TCAA and chloroform were observed, as shown in Figure 5-60. A more detailed discussion of the effect of bromide levels on DBP production is presented later in this section.

The pattern of exclusion relationships with bromide and chorinated DBPs is similar to that shown with bromoform and chlorinated DBPs. Figure 5-61 presents correlations of chloroform, 1,1,1-TCP, chloral hydrate and TCAA with bromoform. In each case a negative correlation was observed. Koch and Krasner (1989) observed that chloral hydrate concentrations were higher in two water sources low in bromide when compared to a third source water high in bromide. Additionally, in this study, when bromoform was correlated with a brominated compound such as dibromoacetonitrile (Figure 5-62). a fairly high correlation was achieved (r=0.88). A similarly high correlation was observed when dibromoacetic acid was correlated with dibromoacetonitrile (r=0.85).

Correlations with Chloroform

In an effort to evaluate whether chloroform could be employed as a surrogate parameter for other selected DBPs, various correlations with this compound were determined. Figure 5-63 shows the correlations of chloroform with DCAA and TCAA. Correlations with all utilities participating in the study and with non-ozonating utilities are presented because it has been shown that ozonation can reduce TCAA precursors (Reckhow and Singer. 1984; Bruchet et al., 1985; Lykins et al., 1986; Dore et al., 1988). Additionally, it has been shown conceptually that ozonation can shift the DBP speciation from chloroform and TCAA to DCAA (Reckhow and Singer, 1985). There was very little difference observed whether or not ozonating utilities were included in the correlation for either compound; however, only three utilities utilized ozone in the baseline studies and, thus, may not have impacted the overall correlations for the 35 utilities. Correlations for DCAA and TCAA with chloroform when all utilities were included were 0.85 and 0.80, respectively.

Correlations of chloroform with chloral hydrate, 1,1,1-TCP and chloropicrin are presented in Figure 5-64. The best correlation among the three compounds was with chloral hydrate (r=0.85). The poor correlation with 1,1,1-TCP (r=0.52) may be attributed to the instability of the compound. Reckhow and Singer (1985) showed that 1,1,1-TCP was an intermediate of chloroform. They reported that approximately 7.5

Correlations with Bromoform
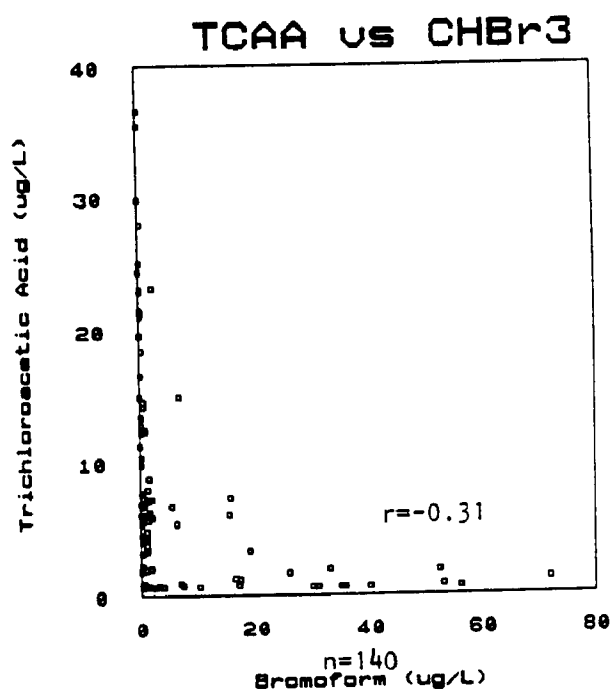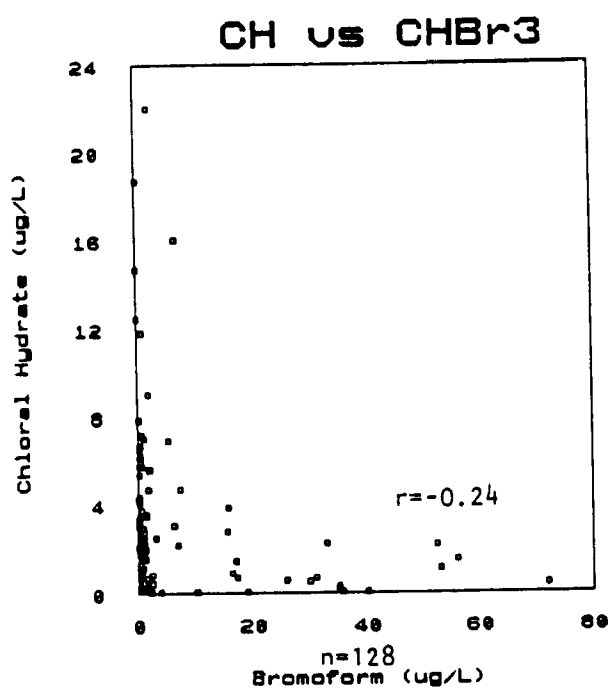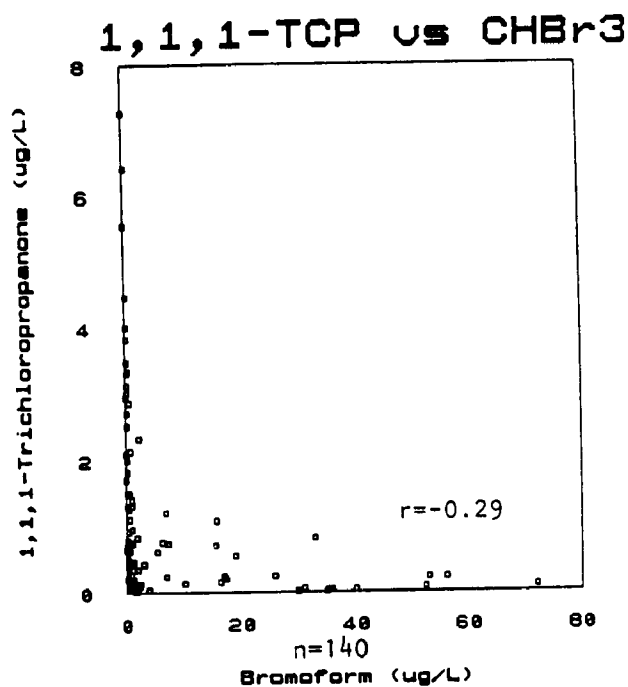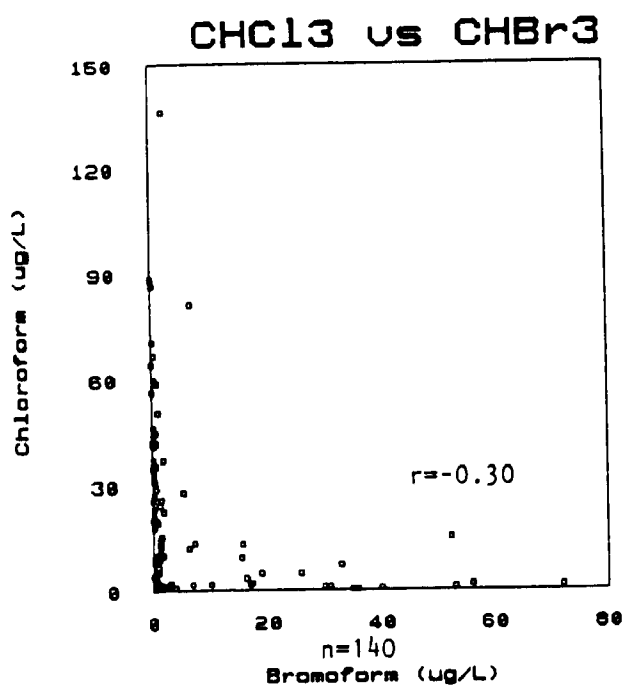
FIGURE 5-61

Correlations with Dibromoacetonitrile

CHBr3 vs DBAN

DBAA vs DBAN
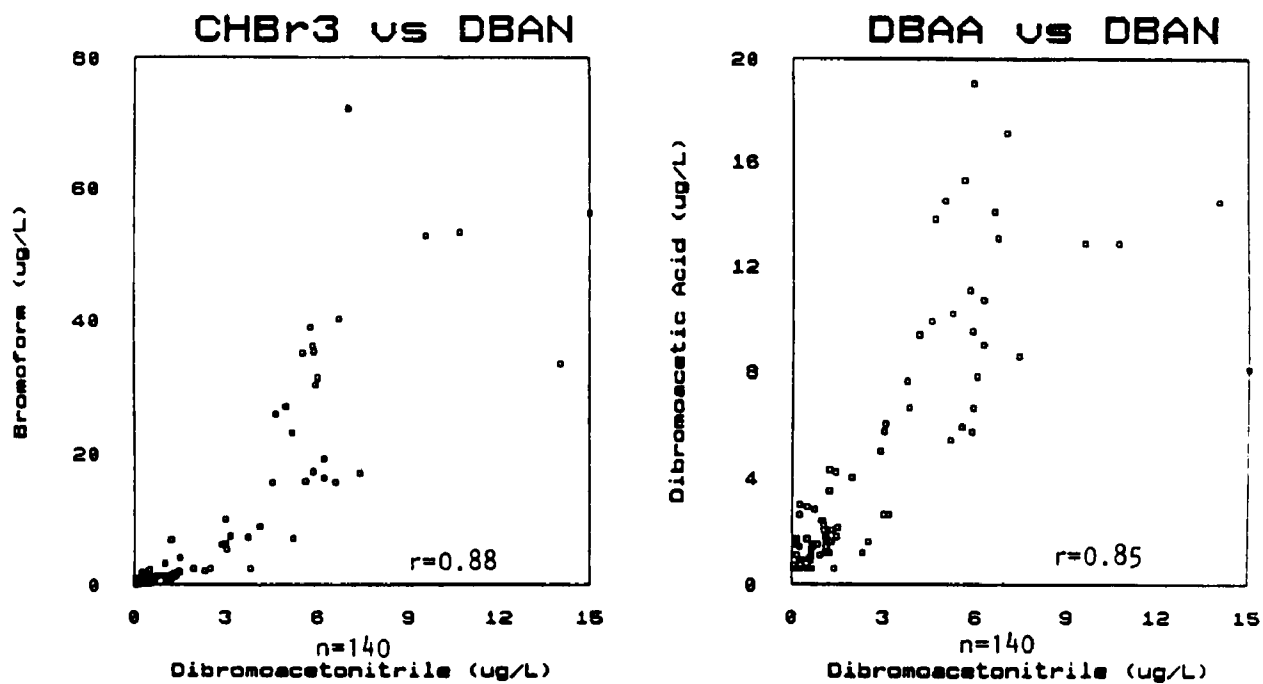
FIGURE 5-62

Correlations with Chloroform

DCAA vs CHCl3
All Utilities

DCAA vs CHCl3
Utilities w/o Ozone

TCAA vs CHCl3
All Utilities

TCAA vs CHCl3
Utilities w/o Ozone
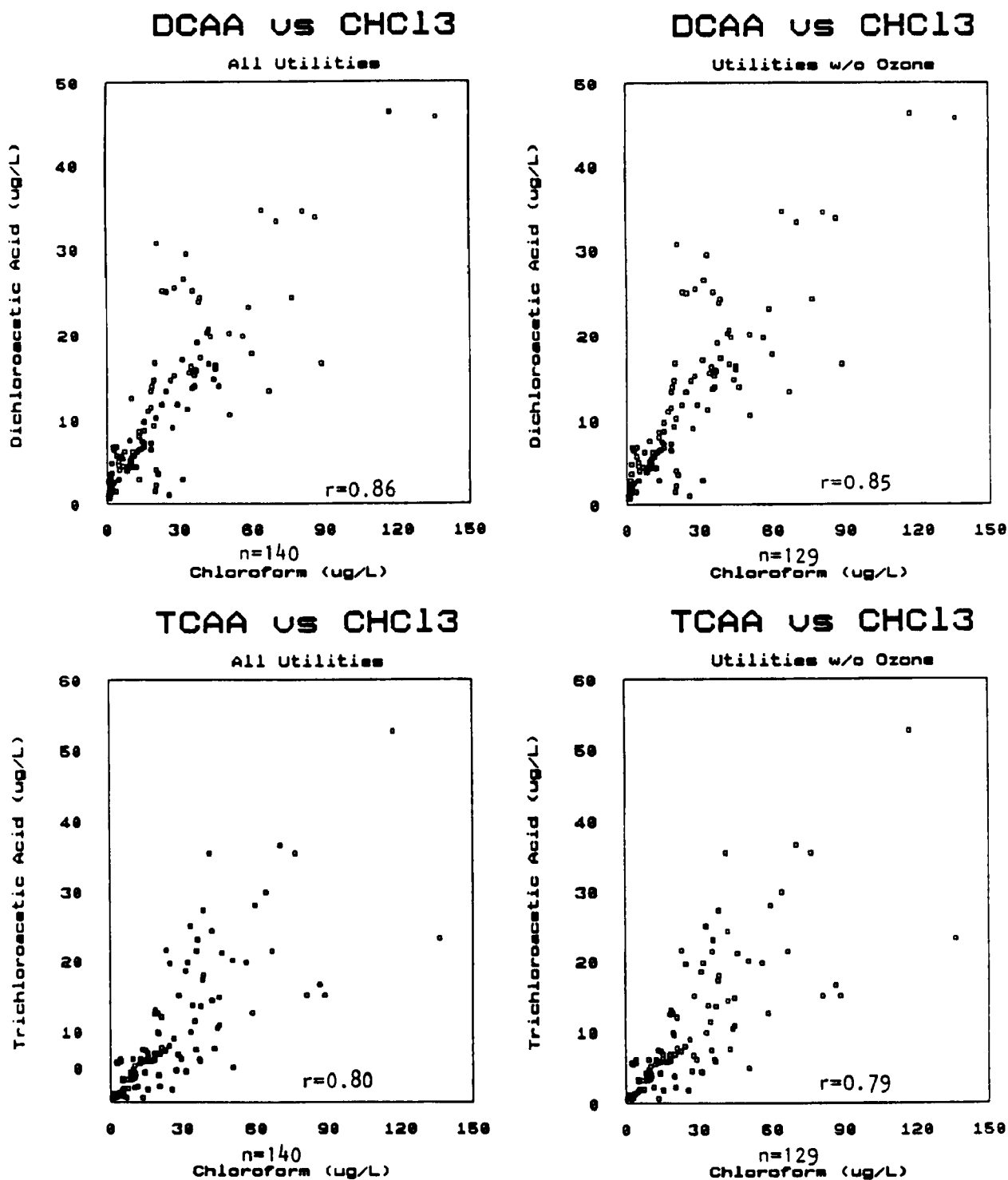
FIGURE 5-63

Correlations With Chloroform
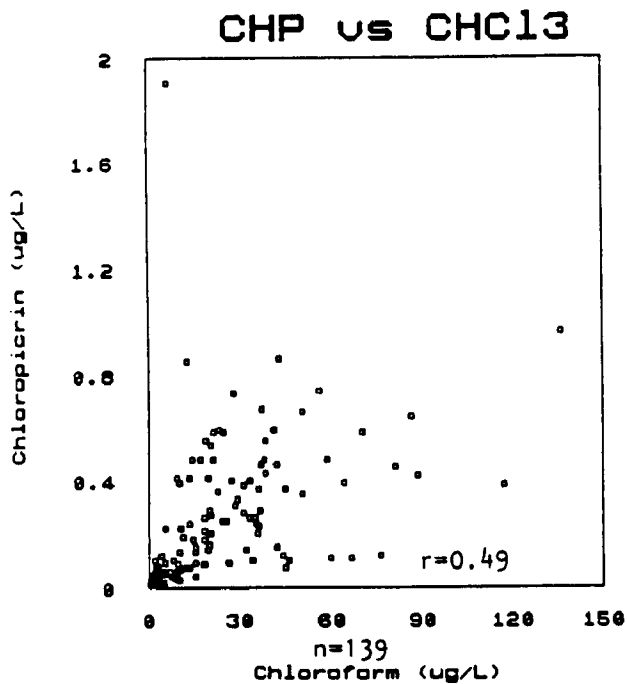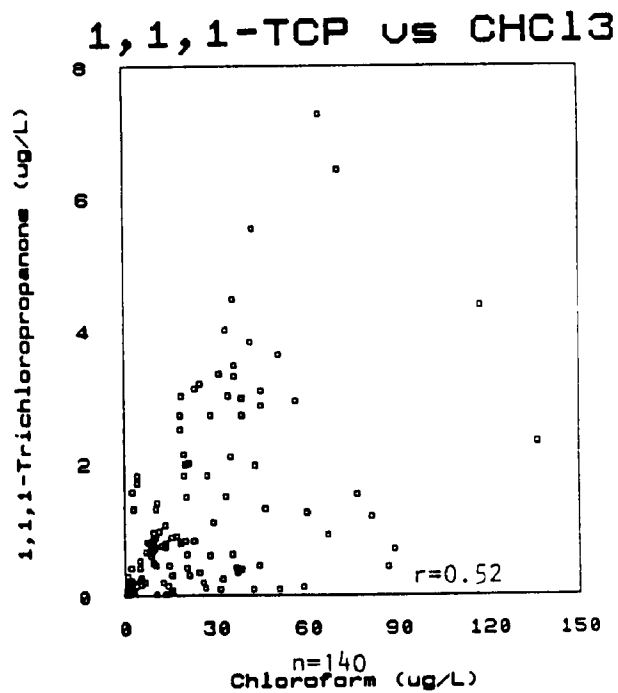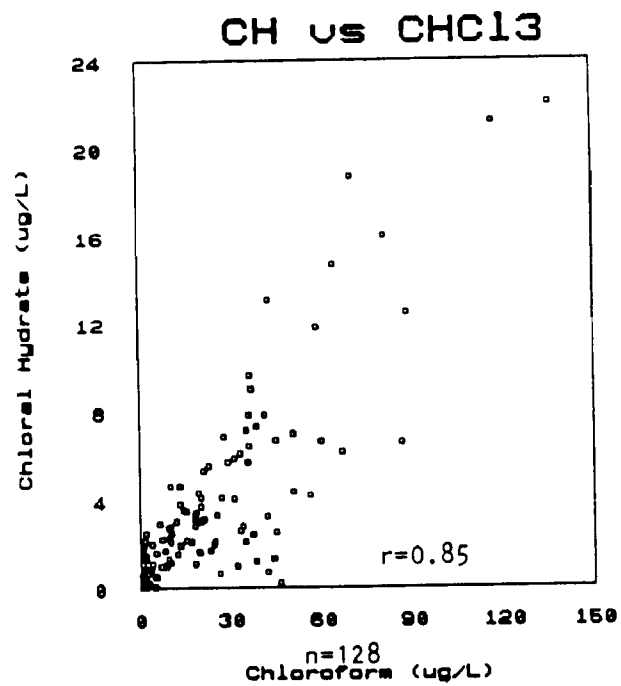
FIGURE 5-64

percent of the chloroform produced following 72 hours of reaction time between chlorine and a particular fulvic acid at pH 7 passed through the 1,1,1-TCP intermediate. This issue will be expanded upon later in Section 5.

Chloroform correlated poorly with chloropicrin (r=0.49). This may be due to several factors, including the concentration of nitrogenous organic compounds. That chloropicrin can be formed by nitro-compounds and amino acids has been reported by several researchers (Coleman et al., 1976; Sayato et al., 1982; Thibaud et al., 1986). Additionally, chloropicrin precursors can be produced during the oxidation of various non-nitrogenous compounds, such as phenols, if nitrite is present (Duguet et al., 1985).

Correlations with DCAA and TCAA

Correlations of the four trihalomethanes and DCAA are shown in Figure 5-65. The best correlation was found with chloroform (r=0.86). However, as the THMs shift to the more brominated species, the correlations decrease until an exclusion relationship is observed between DCAA and bromoform (r=-0.33). This progression is consistent with the bromide correlations discussed above, which showed that bromide and various chlorinated DBPs were related by exclusion.

Figure 5-66 presents correlations with TCAA. The correlation of DCAA with TCAA was 0.85, while that with DCAN was 0.76. The figure also shows that the correlation with 1,1,1-TCP was 0.77. The latter correlation was better than that discussed above between 1,1,1-TCP and chloroform (r=0.52). This observation is consistent with the fact that at high pH, chloroform is stable while the other two compounds may undergo hydrolysis.

Correlations with Formaldehyde

The correlation of acetaldehyde and formaldehyde is shown in Figure 5-67. A correlation of 0.64 was observed between the two. Because it has been shown in this study and in others (Lykins et al., 1986; Glaze et al., 1989a) that ozonation produces aldehydes during water treatment, correlation of acetaldehyde with formaldehyde were determined for only non-ozonating utilities. Excluding the outlier, the correlation improved to 0.78.

Correlations with Total Organic Halide

Figure 5-68 presents the correlations of $XDBP_{sum}$ with TOX on a molar basis. With all utilities included in the analysis, the correlation was 0.70. However, if disinfection-only utilities are not used (since TOX increased in concentration between time of sampling to time of receipt at Metropolitan's laboratory; see Section 3 of this report for details), the correlation improved to 0.86, or 0.77 without the outliers. When only utilities which employ chloramines as a final disinfectant are included in the correlation (since TOX concentrations in chloraminated effluent appeared to be least affected by transit time to Metropolitan's laboratory for preservation; see Section 3 for details), r is equal to 0.78. The correlations found in this study are not as high as those found by Singer (1988) who correlated the THM formation potential with the TOX formation potential of various raw waters (r=0.96, n=60, reported on μg/L basis). However, the correlation found by this researcher between TTHMs and TOX on finished waters

Correlations with Dichloroacetic Acid
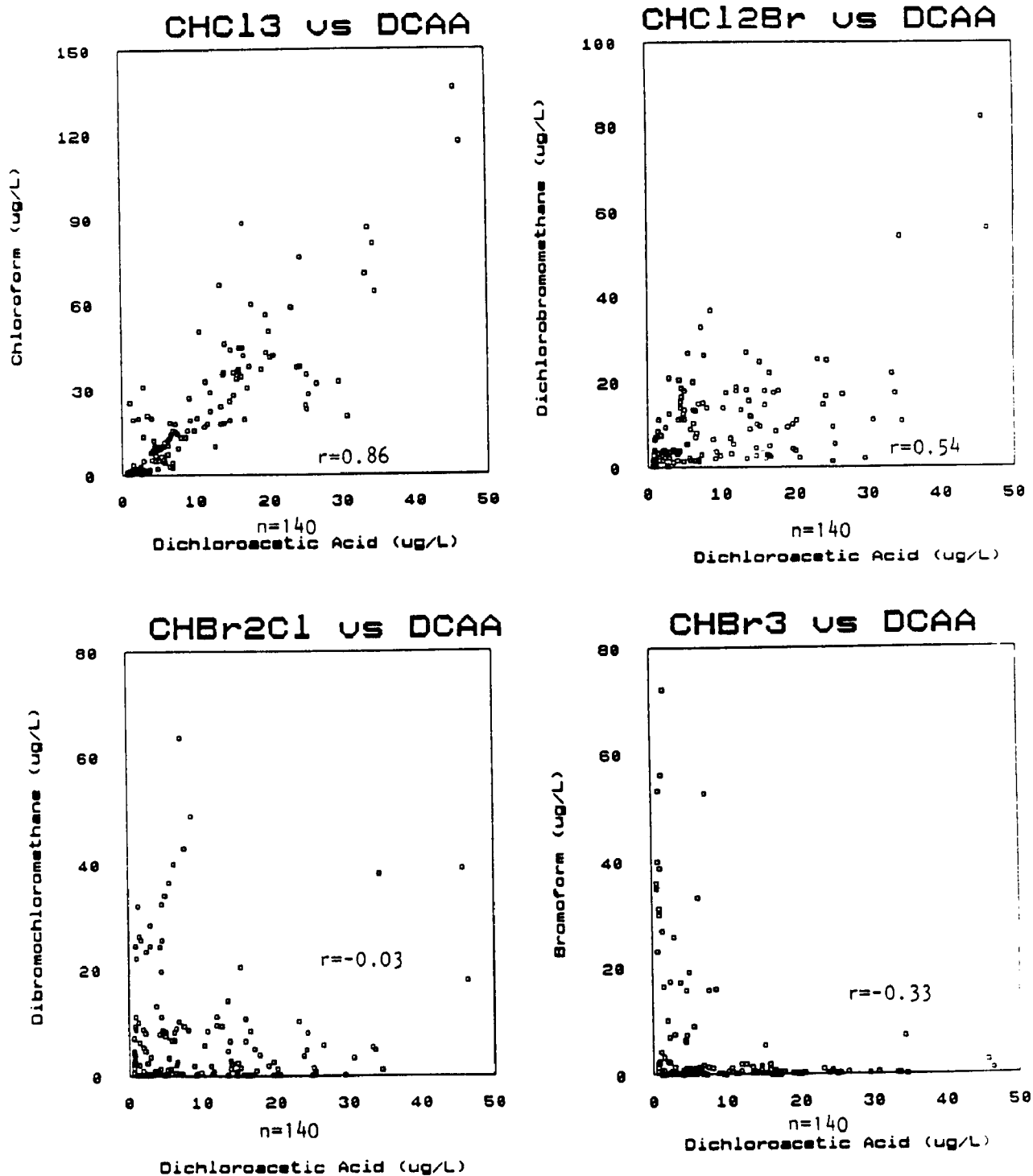
FIGURE 5-65

Correlations with Trichloroacetic Acid
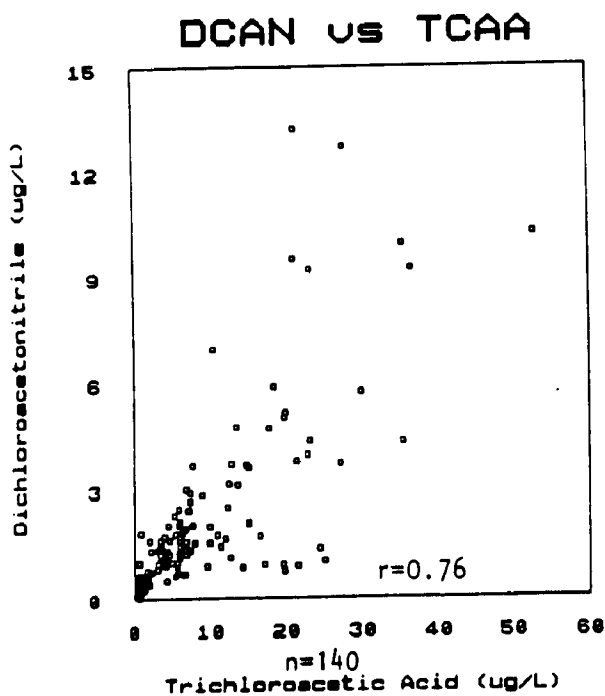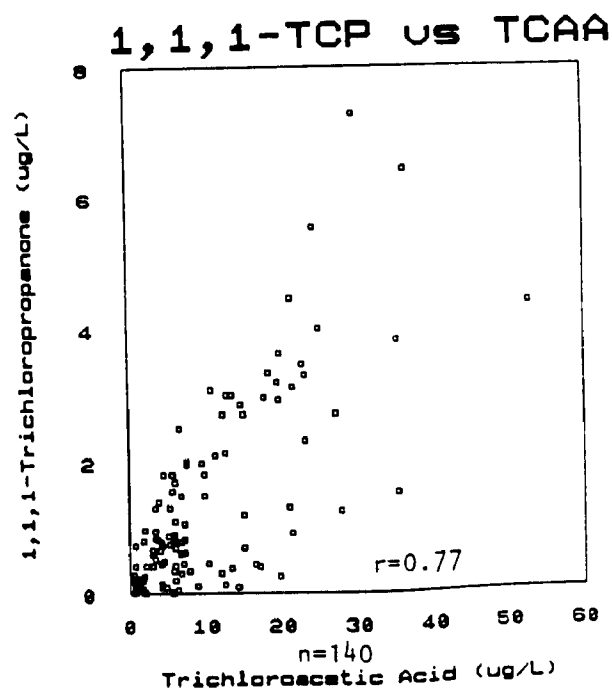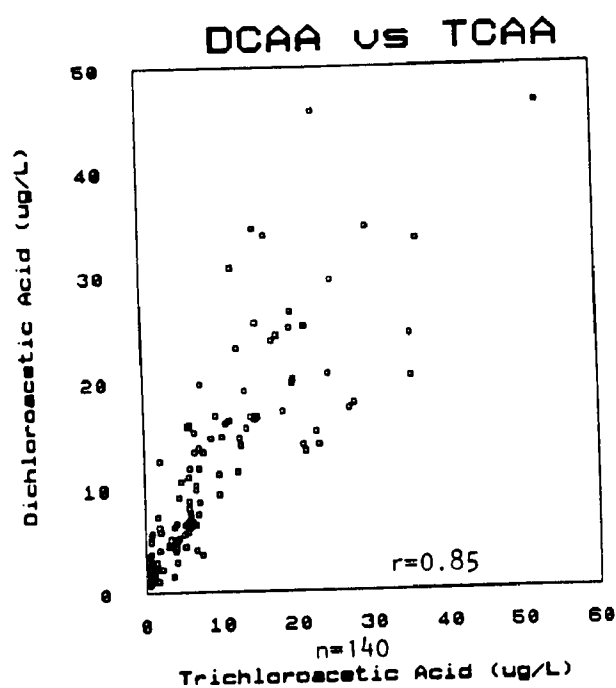
FIGURE 5-66

Correlation with Formaldehyde

Non-Ozonating Utilities
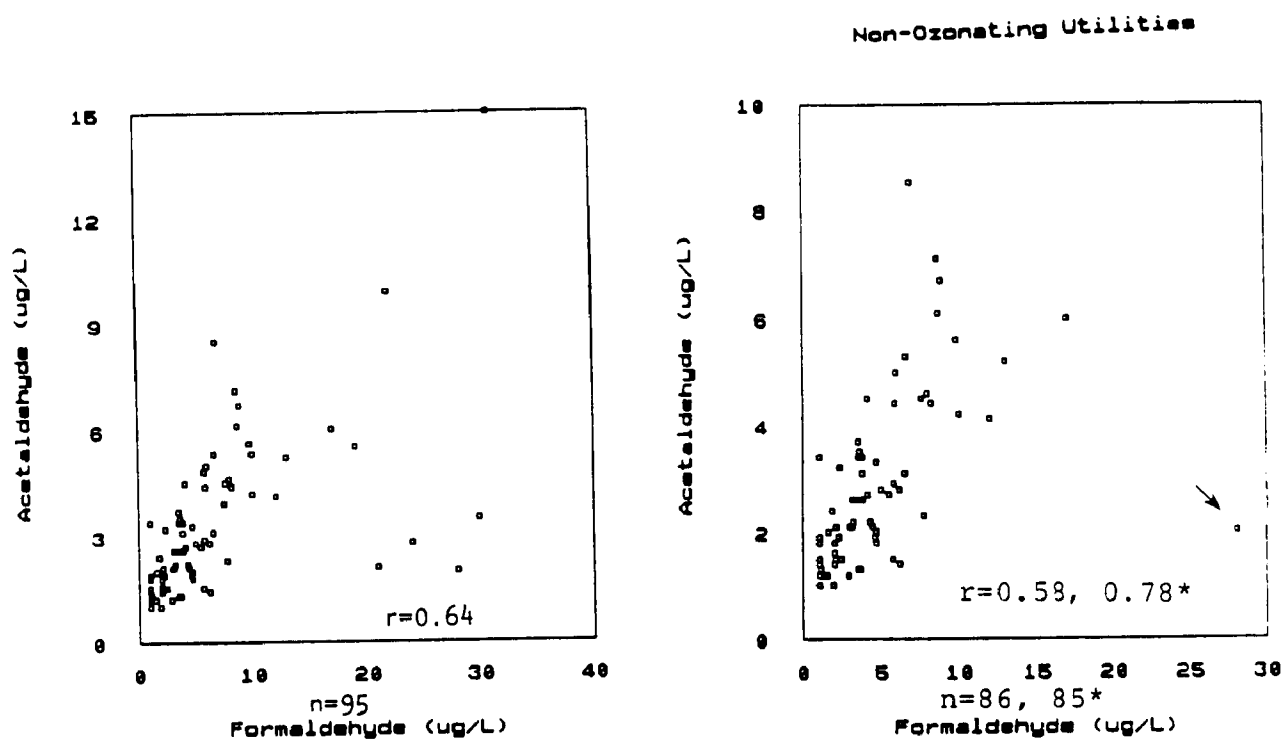
* Excludes indicated outlier

FIGURE 5-67

Molar XDBPs versus Molar TOX
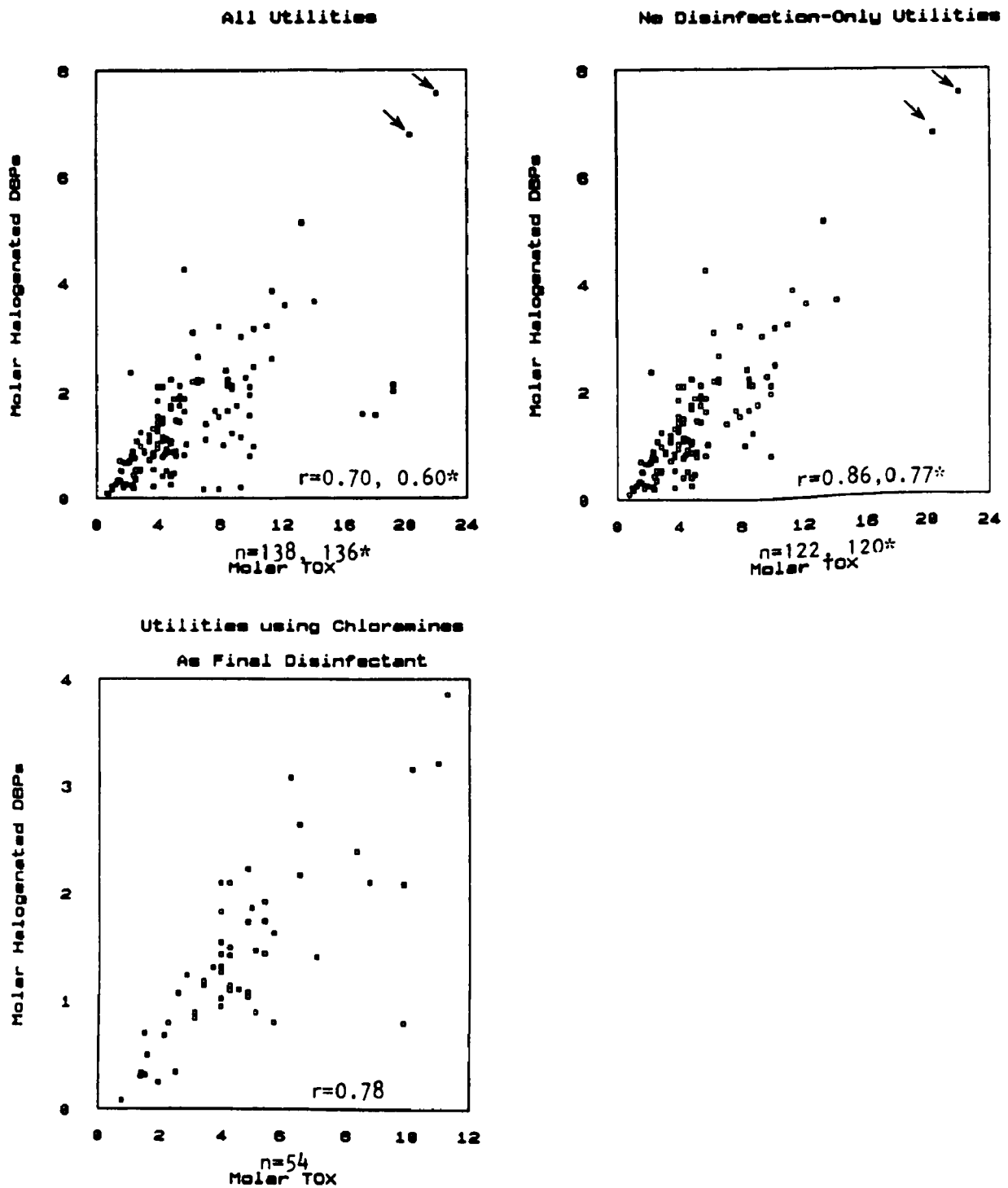
All Utilities

r=0.70, 0.60*

n=138, 136*
Molar TOX

No Disinfection-Only Utilities

r=0.86, 0.77*

n=122, 120*
Molar TOX

Utilities using Chloramines As Final Disinfectant

r=0.78

n=54
Molar TOX

* Excludes Indicated Outliers

FIGURE 5-68

(r=0.89. n=166) was closer to the correlation found in this study. The difference in correlations between the formation potentials of raw water and instantaneous measurements on finished water is probably due to the variety of conditions with which each plant treats its water.

SPECIAL ISSUES

In evaluating the results of the baseline data collection for this study, a number of issues were identified which could not be classified under the previous headings of this section. These special issues are discussed below.

Effect of pH

The HAN and HK data presented in Figures 5-29 and 5-30 tend to support relationships reported by other researchers in which HANs and HKs were found to be reactive intermediates rather than stable endproducts such as THMs. For instance, Reckhow and Singer (1985) reported that when a fulvic acid solution was chlorinated, concentrations of DCAN and 1,1,1-trichloropropanone (1,1,1-TCP) declined over time after quickly reaching an initial peak while chloroform, TCAA and DCAA increased in concentration with increasing contact time. These researchers also found the same trend with increasing pH. demonstrating that DCAN and 1,1,1-TCP hydrolyzed at high pH: while chloroform concentrations increased with increasing pH, indicating that this compound is a product of the hydrolysis reactions of DCAN and 1,1,1-TCP. Additionally. Gurol. et al. (1983) found that the presence of free chlorine greatly increased the degradation rate of 1,1,1-TCP and the formation of chloroform.

In order to investigate the impact of pH on the DBP concentrations measured in this study, several DBPs were plotted as a function of clearwell effluent pH. In actuality, it is the pH (which varies) throughout the treatment process that impacts DBP formation, but it is the final pH which determines the stability of the DBPs and their fate in the distribution system (i.e.. that received by consumers). In these plots, clearwell effluent pH values from all four quarters of baseline data collection were divided into four intervals of varying magnitude, but with an equal number of measurements in each interval. (Usually. plots with equal interval widths would be a preferable way to show the data: however. because there were very few data points in the lowest pH interval and most of the data points were in the highest pH interval, the plot was prepared with varying interval widths and equal numbers of data points in each interval.) Figure 5-69 illustrates the levels of $XDBP_{sum}$ plotted in this manner. No significant difference between $XDBP_{sum}$ values are indicated by the data in Figure 5-69. The problems inherent in any attempts to ascribe differences in DBP levels to single causal factors such as pH have been discussed previously in this section; and Figure 5-69 may indicate the influence of many confounding factors. However, it may also be the case that pH impacts the levels of individual DBP compounds which make up the parameter $XDBP_{sum}$. rather than influencing the level of $XDBP_{sum}$ itself.

To further explore this issue. TTHMs were plotted as a function of clearwell effluent pH in Figure 5-70. As observed in the plot of $XDBP_{sum}$, there are no statistically significant differences between the median levels of TTHMs at a 95 percent confidence level. HANs are plotted as a function of pH in Figure 5-71. This plot, in general, indicates decreasing levels of HANs with increasing pH. When clearwell effluent pH

XDBPsum By Effluent pH

	4.6-7.55	7.56-8.23	8.24-8.7	8.71-9.78
n =	34	33	34	33
u =	13	14	14	13

pH Range
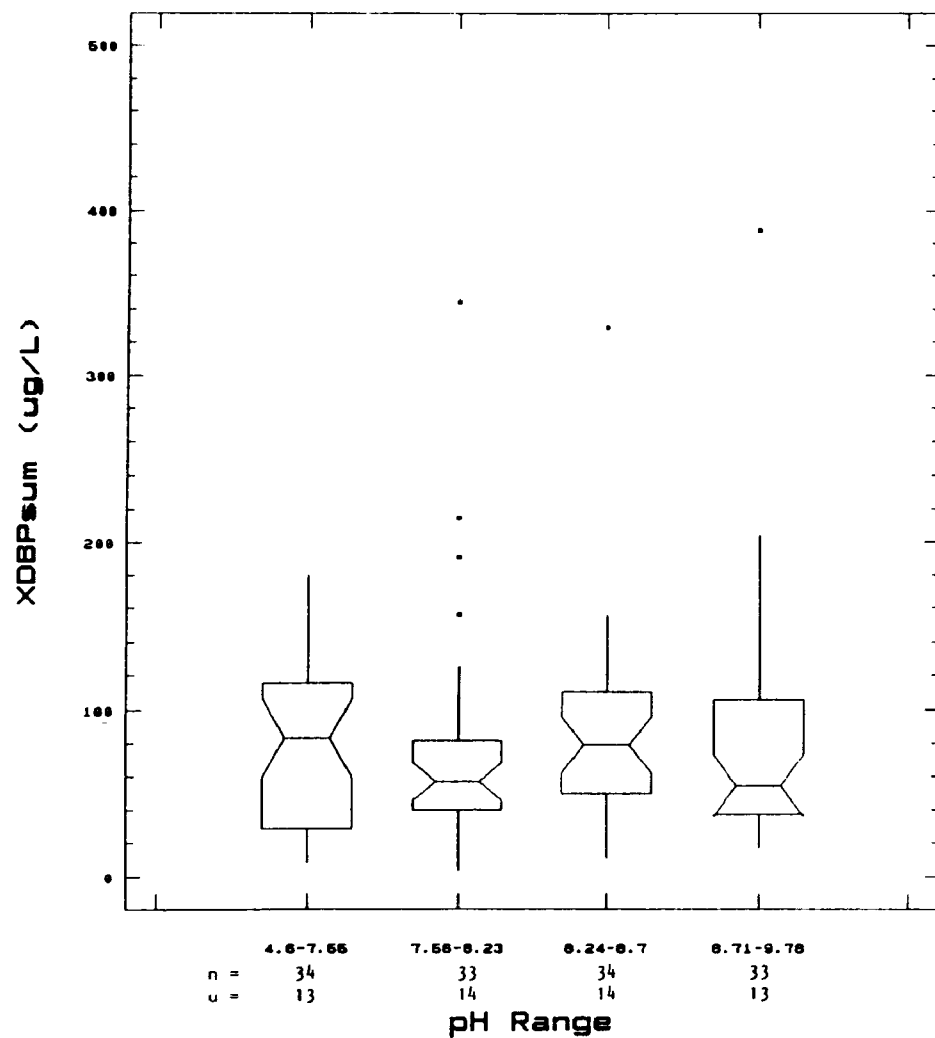
FIGURE 5-69

Trihalomethanes
By Effluent pH

	4.6-7.55	7.56-8.23	8.24-8.7	8.71-9.78
n =	34	33	34	33
u =	13	14	14	13

pH Range
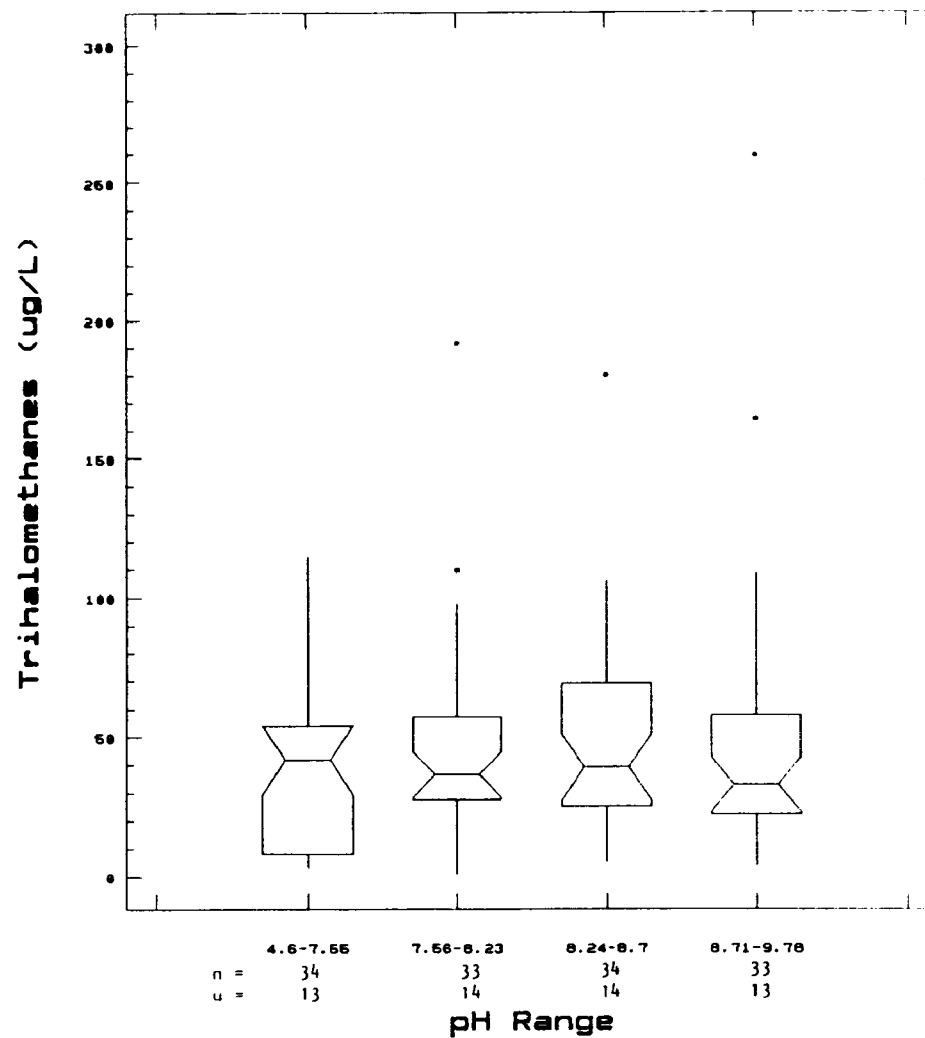
FIGURE 5-70

Haloacetonitriles
By Effluent pH
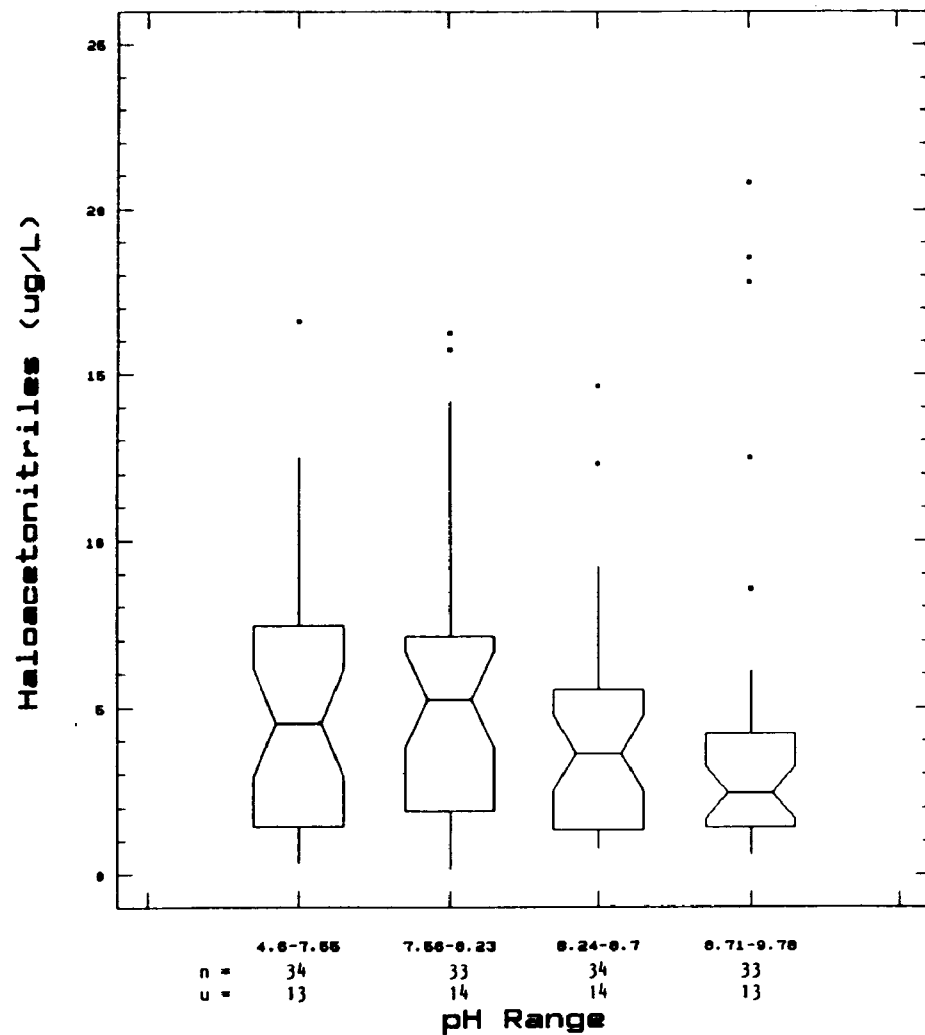
FIGURE 5-71

Dichloroacetonitrile
By Effluent pH
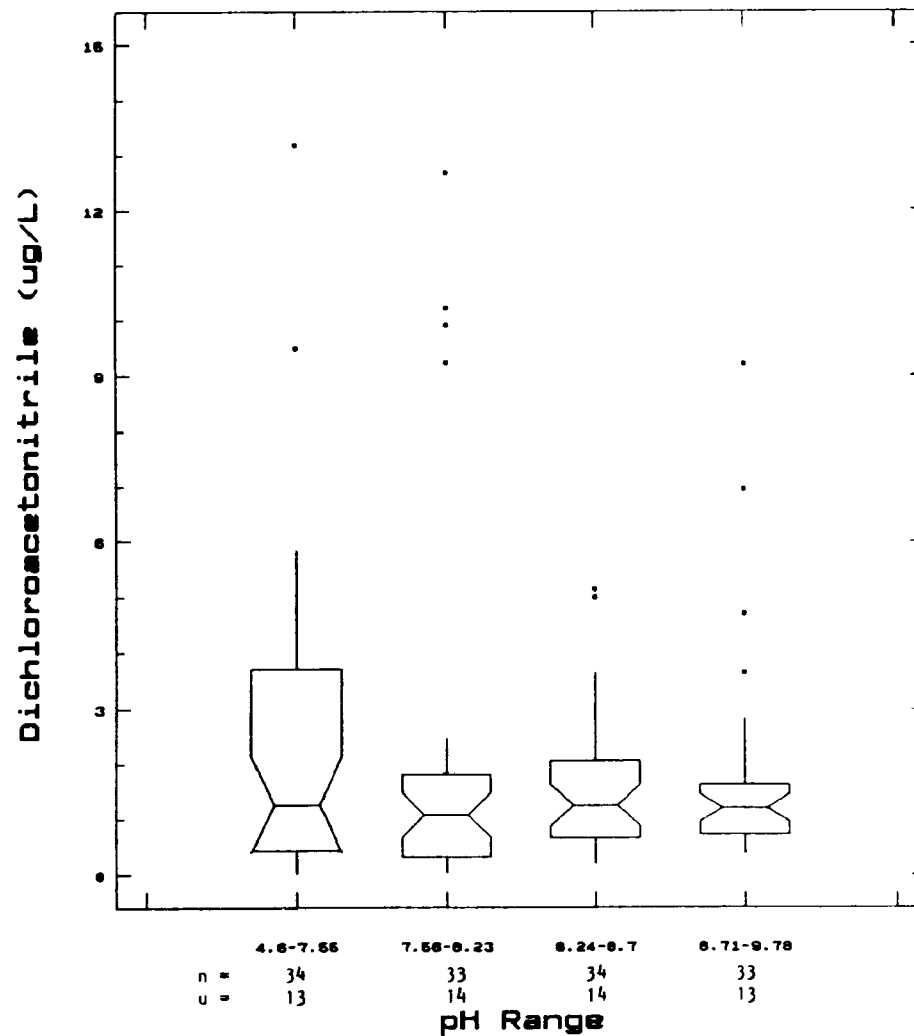
FIGURE 5-72

values occurred within the range 8.24 to 9.78, the median level of HANs was approximately 2.5 to 3.5 μg/L, whereas the HAN medians were 4.5 to 5.5 μg/L in the 4.6 to 8.23 pH ranges. The difference between the median HAN concentrations for the 7.56 to 8.23 pH range and the 8.71 to 9.78 pH range is statistically significant at a 95 percent confidence level. Thus, Figure 5-71 tends to support the finding that HANs hydrolyze at high pH. When DCAN was plotted as a function of clearwell effluent pH, no statistically significant difference in median concentrations occurred over the four pH ranges (Figure 5-72). However, the 75th percentile value for the 4.6 to 7.55 pH range (3.7 μg/L) is approximately twice the 75th percentile value for the 7.56 to 9.78 pH ranges (1.6 to 2.0 μg/L).

A plot of 1,1,1-TCP as a function of pH is shown in Figure 5-73. This figure illustrates that statistically significant differences occurred between 1,1,1-TCP concentrations at low pH (4.6 to 7.55) and at high pH (7.56 to 9.78). Figure 5-73 is thus an indication that hydrolysis of this haloketone occurred at basic pH. This same trend was observed in a plot of TCAA as a function of pH. The median TCAA concentration was higher within the pH range 4.6 to 7.55 than within the pH ranges greater than 7.55; however, the differences were not significant at a 95 percent confidence level. Miller and Uden (1983) reported that TCAA concentrations declined substantially as pH increased from 6 to 10 in the chlorination of a fulvic acid solution. Miller and Uden (1983) also found that chloral hydrate increased in concentration from pH 4 to pH 7, and then decreased as pH increased to 10. These researchers reported that the product of chloral hydrate decomposition at elevated pH was chloroform. However, chloral hydrate results from the baseline data of this study indicated that there were no statistically significant differences between the median concentrations of this compound occurring within the four clearwell effluent pH ranges.

Effect of Temperature

Seasonal effects on DBP levels were discussed previously in this section. Plots of DBP concentrations showed some indications of temperature-related effects, although some seasonal impacts may be due to changes in the nature of naturally-occurring organics as well. The impact of temperature on THM formation has been documented by a number of researchers over the past decade, including Stevens, et al. (1976), who found that chloroform concentrations more than doubled (from approximately 100 to over 225 μg/L) when incubation temperature was increased from 25 to 40°C in raw Ohio River water receiving 10 mg/L of chlorine.

In order to evaluate temperature effects on DBP levels measured in this study, $XDBP_{sum}$, TTHMs and HANs were plotted as a function of influent water temperature. Data from all four quarters of baseline data were divided into four temperature ranges of equal magnitude. Figure 5-74 illustrates that levels of $XDBP_{sum}$ were strongly influenced by temperature. Although there is very little difference in the three lower temperature ranges (from 1.1 to 23.4°C), in the range 23.5 to 31.0°C, $XDBP_{sum}$ was significantly higher at a 95 percent confidence level. The same trend is observed in Figure 5-75, a plot of TTHMs by temperature range. In the three lower temperature ranges, median TTHMs varied between approximately 25 and 35 μg/L, while in the highest temperature range, the median TTHM concentration was over 65 μg/L. The same trend was observed for HANs as a function of temperature, as shown in Figure 5-76, although the differences were not statistically significant.

1,1,1-Trichloropropanone
By Effluent pH

	4.6-7.55	7.56-8.23	8.24-8.7	8.71-9.78
n =	34	33	34	33
u =	13	14	14	13

pH Range
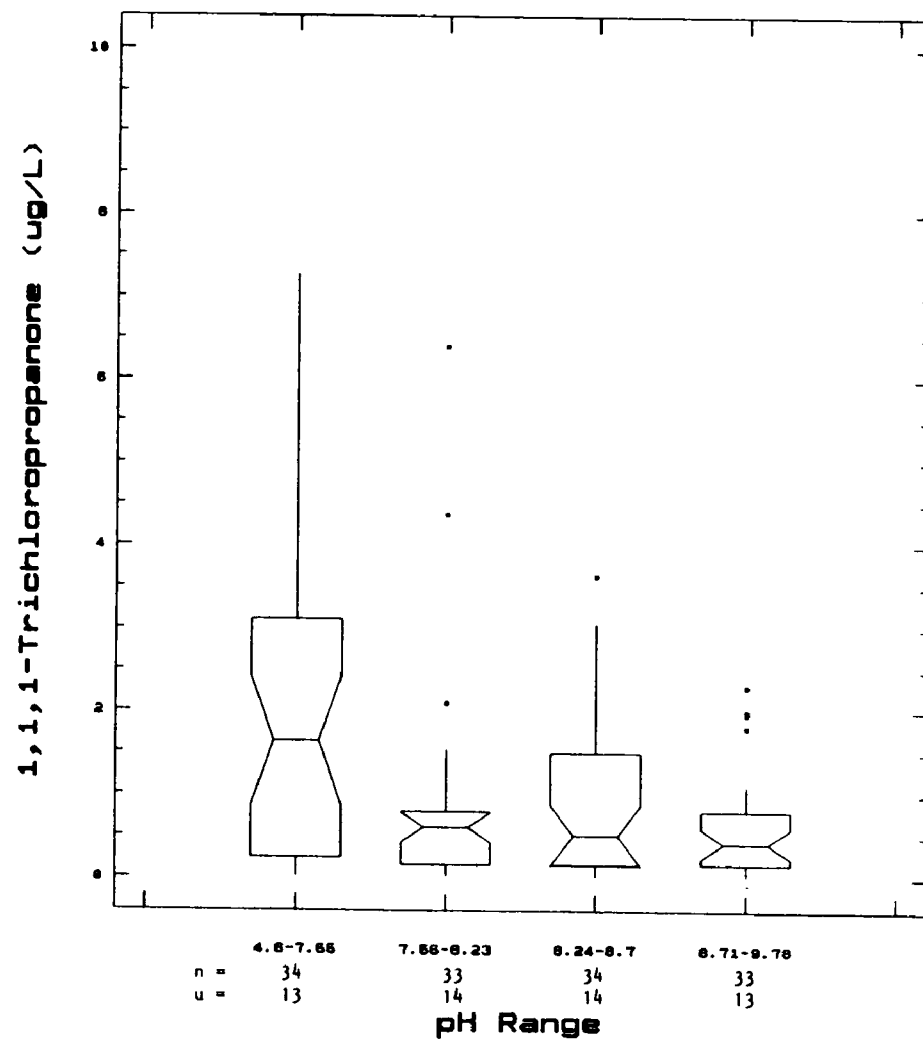
FIGURE 5-73

Sum of Halogenated DBPs
By Influent Temperature

	1.1-8.5	8.6-16.0	16.1-23.4	23.5-31.0
n =	21	47	44	27
u =	17	27	26	17

Temperature Range (^{0}C)
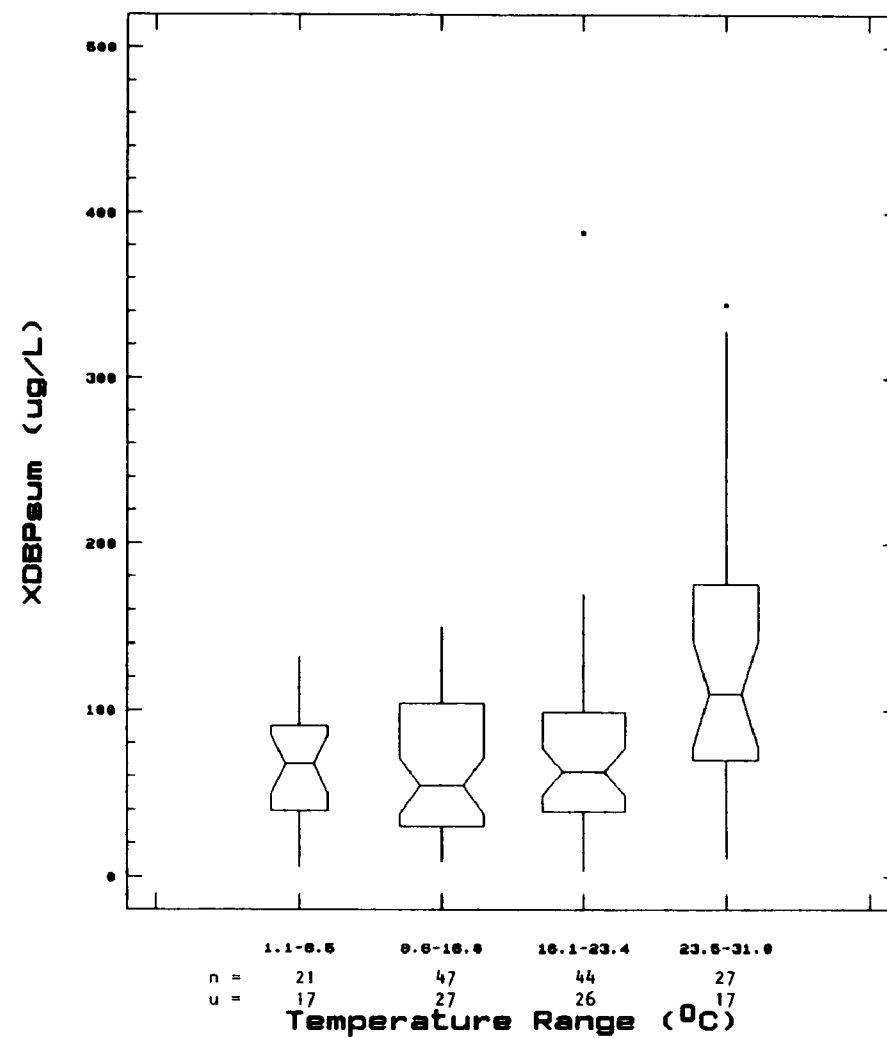
FIGURE 5-74

Trihalomethanes
By Influent Temperature
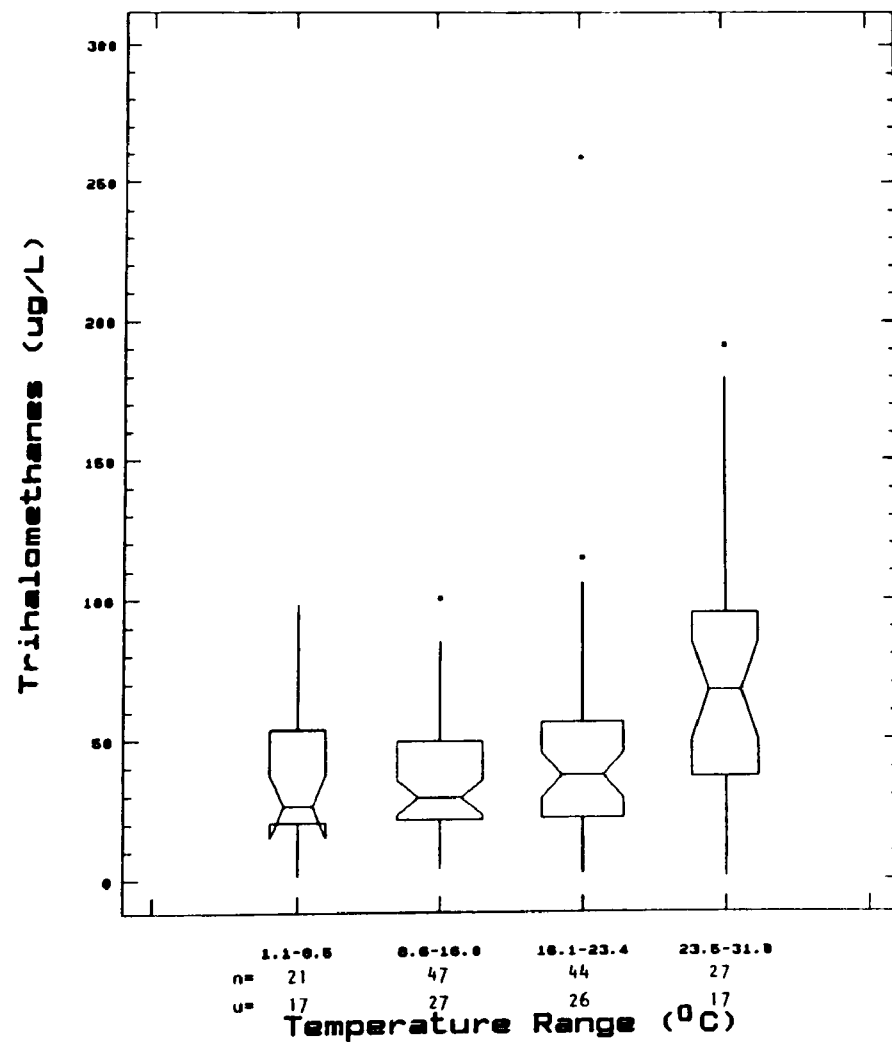
FIGURE 5-75

Haloacetonitriles
By Influent Temperature
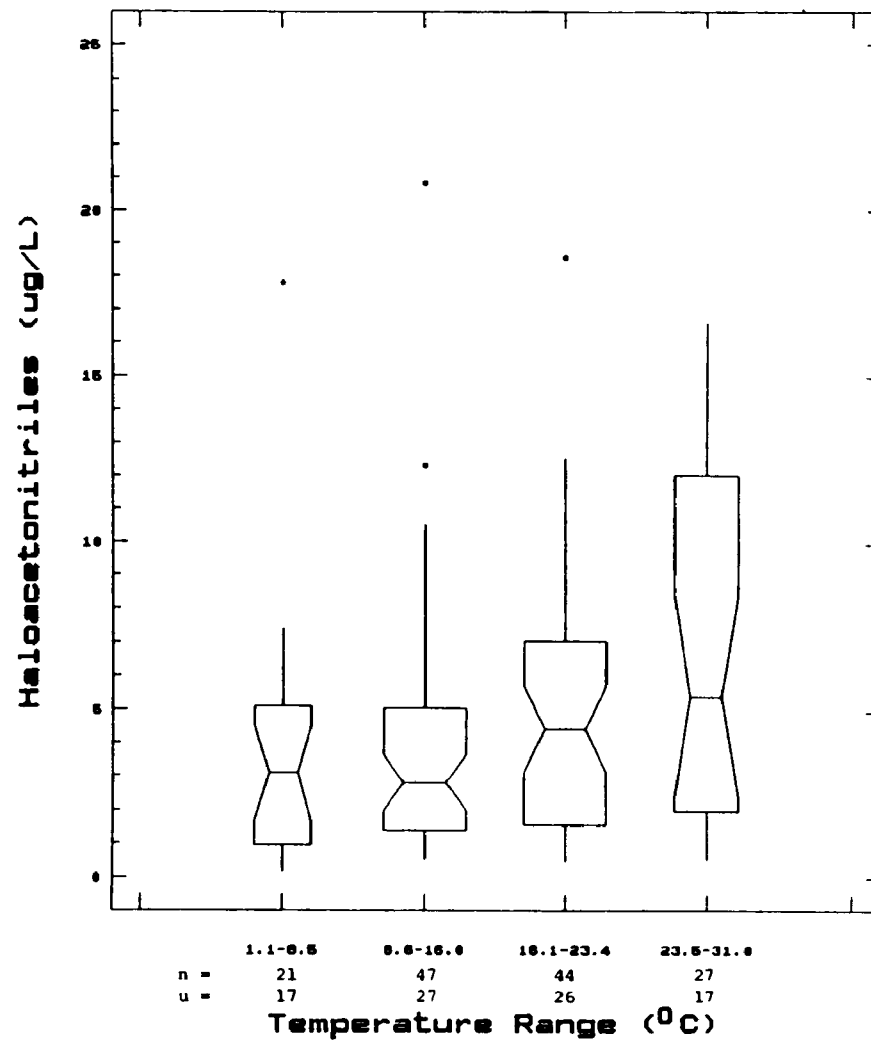
FIGURE 5-76

Baseline Sampling Results and Discussion

Brominated DBPs

During the first quarter of baseline sampling, a high correlation was found between dibromoacetic acid (DBAA) and dibromochloromethane (correlation coefficient $r = 0.91$). In addition, relatively high levels of the measured brominated DBPs were detected at some utilities. These findings suggested that the influence of bromide present in the raw water should be evaluated; therefore, bromide and chloride analyses of the plant influents were added beginning with the second quarter of baseline sampling.

Among the 35 utilities in this project, bromide levels in the plant influents ranged from <0.01 to 3.00 mg/L. High bromide levels were found in each of the three types of source waters. Figure 5-19 presented the raw water bromide levels at the 35 utilities for the latter three sampling quarters.

Table 5-5 shows DBP data for a utility with high bromide levels (Utility 12). Not only was there a shift in THMs to the more brominated species at high bromide levels, but the same situation existed for the HANs and HAAs. Dichloro- and trichloroacetic acid (DCAA and TCAA), which are commonly found in other DBP studies (Uden and Miller, 1983; Norwood et al., 1986) as well as this one, were detected at low levels at Utility 12 when bromide levels were high; instead, DBAA was the major HAA detected.

Additionally, there were seasonal shifts in the raw water bromide concentration at this utility. Such shifts were observed in some utilities as a result of drought conditions and saltwater intrusion problems. During the summer of 1988, 0.41 mg/L bromide was detected at Utility 12. In the fall of 1988 and winter of 1989, higher bromide levels were detected (0.78 to 0.79 mg/L). As Table 5-5 shows, the change in distribution of brominated DBPs was consistent with the change in bromide level. For example, bromoform and dibromoacetonitrile (DBAN) represented (on a weight basis) 36 and 67 percent of the sum of their respective class fractions in the summer, when the bromide level was lowest. These percentages increased to approximately 66 and 85, respectively, in the fall and winter, when the bromide levels were higher. Similar results have been documented by other researchers, such as Lange and Kawczynski (1978), when investigating the impact of bromide concentration on THM speciation.

When bromide levels at Utility 12 increased from 0.41 to 0.78 mg/L from summer to fall, 1988, there was a shift to a higher percentage of brominated DBPs, as discussed above. This shift is illustrated in Figure 5-77. However, this figure indicates that the shift for the HANs and HAAs was less dramatic than that for the THMs, as the majority of HANs and HAAs were already brominated during the summer, 1988 sampling. However, bromoform only represented 36 percent of the THMs in summer sampling, while it increased significantly (to 68 percent) by the fall. One possible explanation is that the kinetics for the formation of DBAN and DBAA may be faster than that for bromoform. If this is the case, this could explain why the correlation coefficients for DBAN and DBAA versus bromoform (i.e., 0.88 and 0.82, respectively) are not higher, as the formation of the fully brominated species for each DBP class may proceed to completion at different kinetic rates.

TABLE 5-5

DBP CONCENTRATIONS AT UTILITY
WITH SEASONAL CHANGE IN BROMIDE LEVELS

	Utility 12*			
Component	Summer 1988	Fall 1988	Winter 1989	Summer# 1989

PLANT INFLUENT VALUES, mg/L

Total Organic Carbon	2.6	2.2	2.8	2.9
Chloride	111	215	202	44
Bromide	0.41	0.78	0.79	0.14

CLEARWELL EFFLUENT VALUES, µg/L

Chloroform	4.7	1.4	0.86	18
Bromodichloromethane	13	7.5	6.5	17
Dibromochloromethane	28	25	24	11
Bromoform	26	72	53	1.7
Total Trihalomethanes	72	106	84	48
Trichloroacetonitrile	<0.012	<0.029	<0.029	<0.029
Dichloroacetonitrile	0.74	0.24	0.19	2.2
Bromochloroacetonitrile	1.6	0.96	1.4	1.8
Dibromoacetonitrile	4.6	7.0	11	1.0
Total Haloacetonitriles	6.9	8.2	13	5.0
Monochloroacetic Acid	<1.0	<1.0	<1.0	2.4
Dichloroacetic Acid	2.9	1.7	0.9	11
Trichloroacetic Acid	1.6	1.2	0.8	8.0
Monobromoacetic Acid	1.0	1.6	1.3	0.9
Dibromoacetic Acid	14	17	13	2.6
Total Haloacetic Acids	20	22	16	25
1.1-Dichloropropanone	0.36	0.031	0.074	0.77
1,1,1-Trichloropropanone	0.24	0.077	0.21	0.71
Total Haloketones	0.60	0.11	0.28	1.5
Chloropicrin	0.018	<0.026	<0.026	0.10
Chloral Hydrate	0.53	0.38	1.1	3.3
Cyanogen Chloride	2.3	0.6	0.8	3.7

* Data for spring 1988 not included because bromide was not measured that quarter; not sampled in Spring 1989.

\# Used data for medium alum treatment study.
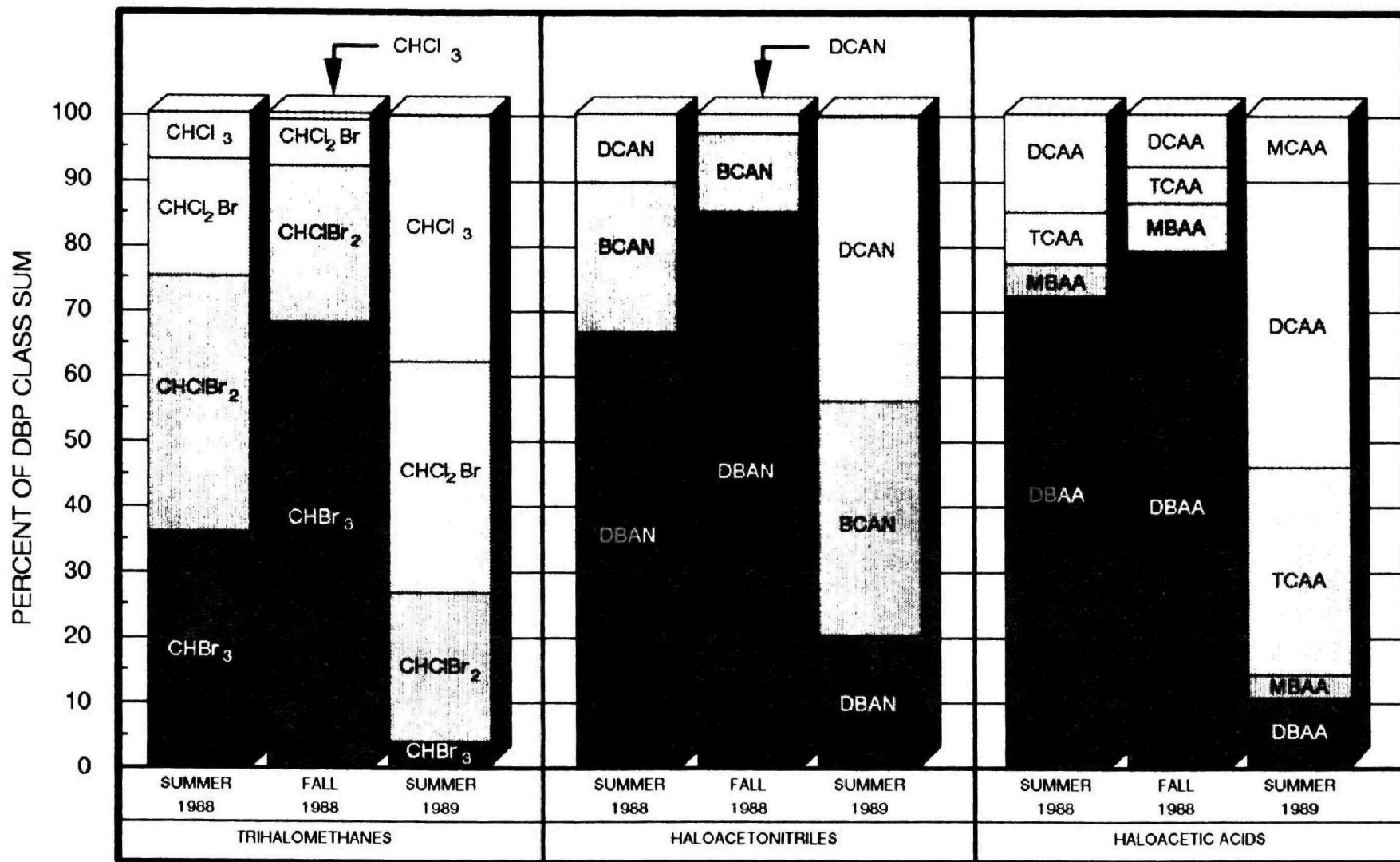
UTILITY 12 DISINFECTION BYPRODUCTS SPECIATION

FIGURE 5-77

Baseline Sampling Results and Discussion

When the bromide level at Utility 12 decreased to 0.14 mg/L in the summer of 1989, chlorinated DBPs began to predominate. As would be expected from the bromide/chlorinated DBP exclusion relationships, the highest levels of chlorinated ketones, chloropicrin and chloral hydrate were detected during the low bromide sampling period.

The high bromide concentrations and associated impacts on DBP speciation observed at Utility 12 were the result of saltwater intrusion. However, high levels of chloride and bromide were measured in waters not limited to coastal origins with modern saltwater intrusion problems. A mid-South utility (Utility 10), which is located inland, derives it waters from two lakes, one of which is high in mineral content. In dry years, evaporation results in an increase in salinity, and in particular, chloride levels. During the three quarters that chloride and bromide were measured, levels ranged from 561 to 680 mg/L and 2.8 to 3.0 mg/L, respectively. In the Midwest, high bromide levels were detected in waters from two utilities (Utilities 23 and 26). Utility 23 had 47 to 152 mg/L chloride and 0.44 to 1.19 mg/L bromide. Utility 26 had 69 to 251 mg/L chloride and 0.19 to 0.68 mg/L bromide. As Table 5-6 indicates, these utilities have a higher level of brominated DBPs than chlorinated ones, due to the presence of high bromide levels. Thus, the presence of brominated DBPs is not restricted to coastal areas, such as in California or Florida, experiencing saltwater intrusion problems in their source waters. According to Standard Methods (1989), the bromide content of groundwaters and stream base-flows can also be affected by connate water (ancient seawater that was trapped in sedimentary deposits at the time of geological formation). In addition, industrial and oil-field brine discharges can contribute to the bromide in source waters.

In the 35-utility study, there was a very good correlation between bromide and chloride levels (correlation coefficient r = 0.97), as discussed previously in this section. Since the levels of these ions were atypically high at Utility 10, the data were re-examined by excluding the levels detected at that utility. The correlation was still high (r = 0.86). As discussed previously, an equation for predicting bromide levels from chloride levels was determined, excluding the outlier points from Utility 10:

$$[Br^-] = -0.0071 + 0.0034[Cl^-]$$

This equation was then applied to the data from Utility 12, where the source of chloride and bromide is due to saltwater intrusion problems, and the results are reported in Table 5-7. The measured and predicted bromide levels agreed to 10 percent, on the average. Furthermore, the concentrations of chloride and bromide in seawater are 18,980 and 65 mg/L, respectively (Sverdrup et al., 1942). From these data, if chloride and bromide were only from sea water diluted with unsalty freshwater, then:

$$[Br^-] = 0.0034[Cl^-]$$

Despite the similarity of the equations, there will be more variability in the prediction when more than modern sea water intrusion is involved. However, since the correlation holds in general for the 35 utilities, one should be able to predict a relative level of bromide in waters where only chloride measurements were made.

TABLE 5-6

DBP CONCENTRATIONS AT INLAND UTILITIES
WITH HIGH BROMIDE LEVELS*

Component	Mid-South Util. #10	Midwest Util. #23	Midwest Util. #26
PLANT INFLUENT VALUES, mg/L			
Total Organic Carbon	4.9	4.4	4.5
Chloride	561	152	173
Bromide	2.9	1.2	0.43
CLEARWELL EFFLUENT VALUES, μg/L			
Chloroform	0.59	0.62	7.1
Bromodichloromethane	2.9	1.3	20
Dibromochloromethane	9.2	2.1	40
Bromoform	40	3.9	33
Total Trihalomethanes	**53**	**7.9**	**100**
Trichloroacetonitrile	<0.029	<0.029	<0.029
Dichloroacetonitrile	0.24	0.50	1.6
Bromochloroacetonitrile	1.1	1.1	5.2
Dibromoacetonitrile	6.7	1.5	14
Total Haloacetonitriles	**8.0**	**3.1**	**21**
Monochloroacetic Acid	<1.0	2.3	<1.0
Dichloroacetic Acid	0.8	1.1	6.2
Trichloroacetic Acid	<0.6	<0.6	1.9
Monobromoacetic Acid	1.2	0.7	1.9
Dibromoacetic Acid	13	2.1	14
Total Haloacetic Acids	**15**	**6.2**	**24**

*Third quarter results.

TABLE 5-7

UTILITY 12: INFLUENCE OF SALTWATER INTRUSION

| Sampling Period | Chloride mg/L | Bromide Level | | |
		Measured mg/L	Predicted[#] mg/L	Percent Difference[*]
Summer 1988	111	0.41	0.37	9.8
Fall 1988	215	0.78	0.72	7.7
Winter 1989	202	0.79	0.68	14
Summer 1989	44	0.14	0.14	0.0

[*]Percent difference = 100 x |measured - predicted|/measured.

[#]Prediction based on relationship derived from this study:
$[Br^-] = -0.0071 + 0.0034[Cl^-]$

As indicated above. the production of THMs in those utilities with high bromide levels can shift to the more brominated species. The same phenomenon was observed for HAAs and HANs. It is fortunate that many brominated DBPs were included in the study; otherwise, the DBP levels of some utilities would be misrepresented. Yet, research has shown that other brominated species exist which were not included in the analytical methods for this DBP study. GC/MS analysis revealed the presence of HAAs containing both bromine and chlorine atoms (Slocum et al., 1987) as is observed with THMs; however, analytical standards for these compounds did not exist commercially. Research also indicated the formation of brominated trihalonitromethanes in a manner similar to the production of chloropicrin (trichloronitromethane) (Thibaud et al., 1988). These findings emphasize the fact that brominated DBPs, not just chlorinated DBPs, are important in chlorinated drinking water.

Aldehydes

Results of aldehyde analyses of clearwell effluents were discussed previously in this section. When ALDs were added to the list of analytes after the second quarter, and it became clear that ALDs were occurring in the effluents of many of the 35 utilities (not exclusively ozonating utilities). the issue of whether these compounds were originating in the plant influents or within the plant still needed to be resolved. To determine if formaldehyde and acetaldehyde were produced by the disinfectants/oxidants used at the plants or if these compounds originated from the source water (e.g., from a biogenic process). all 35 utilities were sampled at the plant influents (preserved with mercuric chloride) during the fourth quarter of baseline sampling.

Table 5-8 shows the aldehyde levels in the plant influents and effluents. Formaldehyde was found in 16 of the 34 influents analyzed, at levels of 1.2 to 13 μg/L. The median level of formaldehyde in plant influents for all 34 utilities was < 1.0 μg/L, and the median level for only the 16 utilities where formaldehyde was detected in the influents was 2.8 μg/L. Acetaldehyde was found in 12 of the 33 influents analyzed, at levels of 1.1 to 16 μg/L. The median level of acetaldehyde in plant influents for all 33 utilities was < 1.0 μg/L. and the median level for only the 12 utilities where acetaldehyde was detected in the influents was 2.0 μg/L.

At the three ozone plants, it is clear that formaldehyde was a product of the oxidation/disinfection process. Acetaldehyde was found in the effluents of all three ozone plants; however, it was detected at a higher level in the plant influent of Utility 25. The other plants shown in Table 5-8 employed either free chlorine only or chloramination (primarily with pre-chlorination). At some plants, no formaldehyde or acetaldehyde was detected in the plant influent, but these aldehydes were detected in the effluent. Where these aldehydes were detected in the influent, they were either at a very low level compared to that detected in the effluent (e.g., Utility 29, a chlorinating utility. had 2.0 versus 8.0 μg/L formaldehyde in the plant influent and effluent, respectively) or at a level comparable to that detected in the effluent (e.g., Utility 14 had 6.4 versus 4.1 μg/L formaldehyde in the plant influent and effluent. respectively). From these limited data. formaldehyde and acetaldehyde appear to be present because of a combination of the effects of plant disinfection processes and influent water quality. the combination varying from one utility to another.

TABLE 5-8

ALDEHYDE LEVELS IN PLANT INFLUENTS AND EFFLUENTS*

Utility Number	Disinfection Scheme	Formaldehyde, μg/L Plant Influent	Formaldehyde, μg/L Clearwell Effluent	Acetaldehyde, μg/L Plant Influent	Acetaldehyde, μg/L Clearwell Effluent
4	NH_2Cl	ND	ND	ND	1.5
10	NH_2Cl	1.7	ND	ND	1.2
18	NH_2Cl	1.2	ND	1.9	1.5
2	Cl_2, NH_3	NA	NA	NA	NA
5	Cl_2, NH_3	4.9	ND	4.5	3.4
7	Cl_2, NH_3	ND	ND	ND	1.8
9	Cl_2, NH_3	3.9	8.7	4.4	6.1
12	Cl_2, NH_3	ND	2.0	ND	1.6
14	Cl_2, NH_3	6.4	4.1	2.4	4.5
21	Cl_2, NH_3	3.0	6.9	10	8.5
28	Cl_2, NH_3	2.7	3.5	1.7	3.0
30	Cl_2, NH_3	ND	4.3	1.3	2.2
1	Cl_2	ND	ND	ND	ND
3	Cl_2	ND	ND	ND	ND
6	Cl_2	13	7.6	NA	NA
8	Cl_2	ND	NA	ND	NA
11	Cl_2	3.4	2.0	ND	1.8
13	Cl_2	ND	1.1	2.1	1.3
15	Cl_2	ND	ND	ND	ND
16	Cl_2	ND	1.6	ND	2.0
17	Cl_2	ND	ND	1.6	ND
20	Cl_2	ND	ND	1.4	ND
22	Cl_2	1.2	4.3	ND	2.2
23	Cl_2	ND	ND	ND	1.0
24	Cl_2	1.4	ND	ND	1.4
26	Cl_2	ND	2.1	ND	2.1
29	Cl_2	2.0	8.0	ND	4.6
31	Cl_2	ND	3.3	ND	2.6
33	Cl_2	5.8	3.6	ND	1.3
34	Cl_2	ND	1.8	ND	2.4
35	Cl_2	ND	2.1	ND	1.5
27	Cl_2, ClO_2	1.4	4.6	1.1	1.9
25	O_3, NH_2Cl	3.2	19	16	5.5
19	O_3, Cl_2	ND	7.5	ND	3.9
32	O_3, Cl_2	1.4	21	ND	2.1

* Fourth sampling quarter.
ND = Not detected (< 1.0 μg/L).
NA = Not analyzed; analytical problem with sample.

Baseline Sampling Results and Discussion

Table 5-9 lists the aldehyde levels at three ozone plants during baseline sampling and at four plants that utilized only chlorination or prechlorination/postammoniation but had high formaldehyde levels ($\geq$ 10 μg/L during at least one sampling). The latter four utilities had 10 μg/L or more of formaldehyde at a time when they had approximately 100 μg/L (or more) TTHMs. These limited data suggest that when a chlorinating utility's water quality and treatment practices produce a high level of THMs, they can potentially produce a high level of formaldehyde as well. As will be discussed in Section 6 regarding treatment studies where ozonation was implemented, there can be a "tradeoff" of halogenated DBPs for aldehydes in implementing ozonation. Levels of halogenated and non-halogenated DBPs in the clearwell effluents and distribution systems of ozonation plants will be discussed in Section 6. In addition, the issue of the formation and removal of aldehydes in ozonation plants will also be discussed in Section 6.

Cyanogen Chloride Results

Typically, chloramines are used as a means of lowering THM levels in treated waters. Of the 142 cyanogen chloride analyses conducted for this study (35 utilities for three to four quarters), 32 samples represented prechlorination/postammoniation and another 11 represented chloramines only. As seen in Figure 5-54 (presented previously), the prechlorinating/postammoniating utilities had a significantly higher cyanogen chloride median concentration (approximately 2 μg/L) compared to either the chlorinating or chloraminating utilities (both of which had medians of less than 0.5 μg/L). Additionally (not shown in Figure 5-54), one utility with preozonation/postchloramination had a median cyanogen chloride level of approximately 7 μg/L. Since some of these disinfection schemes represent small data sets, making it difficult to interpret the data, Figure 5-78, a plot of cyanogen chloride by final disinfectant (regardless of whether prechlorination/postammoniation or chloramination were used) was generated. As seen in the figure, the utilities that deliver chloraminated water were demonstrated to have a statistically higher level of cyanogen chloride.

Research in Japan has shown that cyanogen chloride was sometimes formed in the presence of certain amino acids and hypochlorous acid, but was always formed in the presence of the amino acids tested when both hypochlorous acid and the ammonium ion (i.e., chloramines) were present (Hirose et al., 1988). Other research (Ohya and Kanno, 1985) found that cyanogen chloride was formed by the reaction of humic acid with hypochlorous acid in the presence of the ammonium ion. It was found that the amount of cyanogen chloride was at a maximum when the reaction mixture contained a ratio of 8 to 9 ppm of chlorine to 1 ppm of ammonia (as nitrogen), and that the maximum yield of cyanogen chloride increased as increasing amounts of hypochlorous acid were added. Furthermore, these formation patterns were reproduced with three raw waters from Japan. These data imply that cyanogen chloride may be more readily formed in chloraminated systems.

In separate research endeavors, N-chloroglycine was formed as a result of the reaction of monochloramine with glycine under conditions typical for drinking water (Margerum and Gray, 1978), and it has been suggested that the formation of cyanogen chloride is caused by the reaction of glycine with chlorine (Kopfler et al., 1975). Studies have demonstrated the formation of organochloramines by the use of inorganic chloramines

TABLE 5-9

LEVELS OF ALDEHYDES AND THMS IN SELECTED CLEARWELL EFFLUENTS

Utility	Formaldehyde, μg/L			Acetaldehyde, μg/L			TTHMs, μg/L		
	Summer 1988	Fall 1988	Winter 1989	Summer 1988	Fall 1988	Winter 1989	Summer 1988	Fall 1988	Winter 1989
Chlorine or Chloramine Plants:									
2	10	8.2	NR*	4.2	4.4	NR	90	82	60
9	12	6.2	8.7	4.1	2.8	6.1	95	54	40
26	17	8.6	2.1	6.0	7.1	2.1	164	100	98
29	NR	13	8.0	4.3	5.2	4.6	109	180	259
Ozone Plants:									
19	5.8	10	7.5	4.8	5.3	3.9	15	20	5.9
25	31	22	19	15	9.9	5.5	34	16	9.0
32	30	24	21	3.5	2.8	2.1	3.1	1.4	0.72

*NR = not reported; analytical problem with sample.

Cyanogen Chloride
By Final Disinfectant
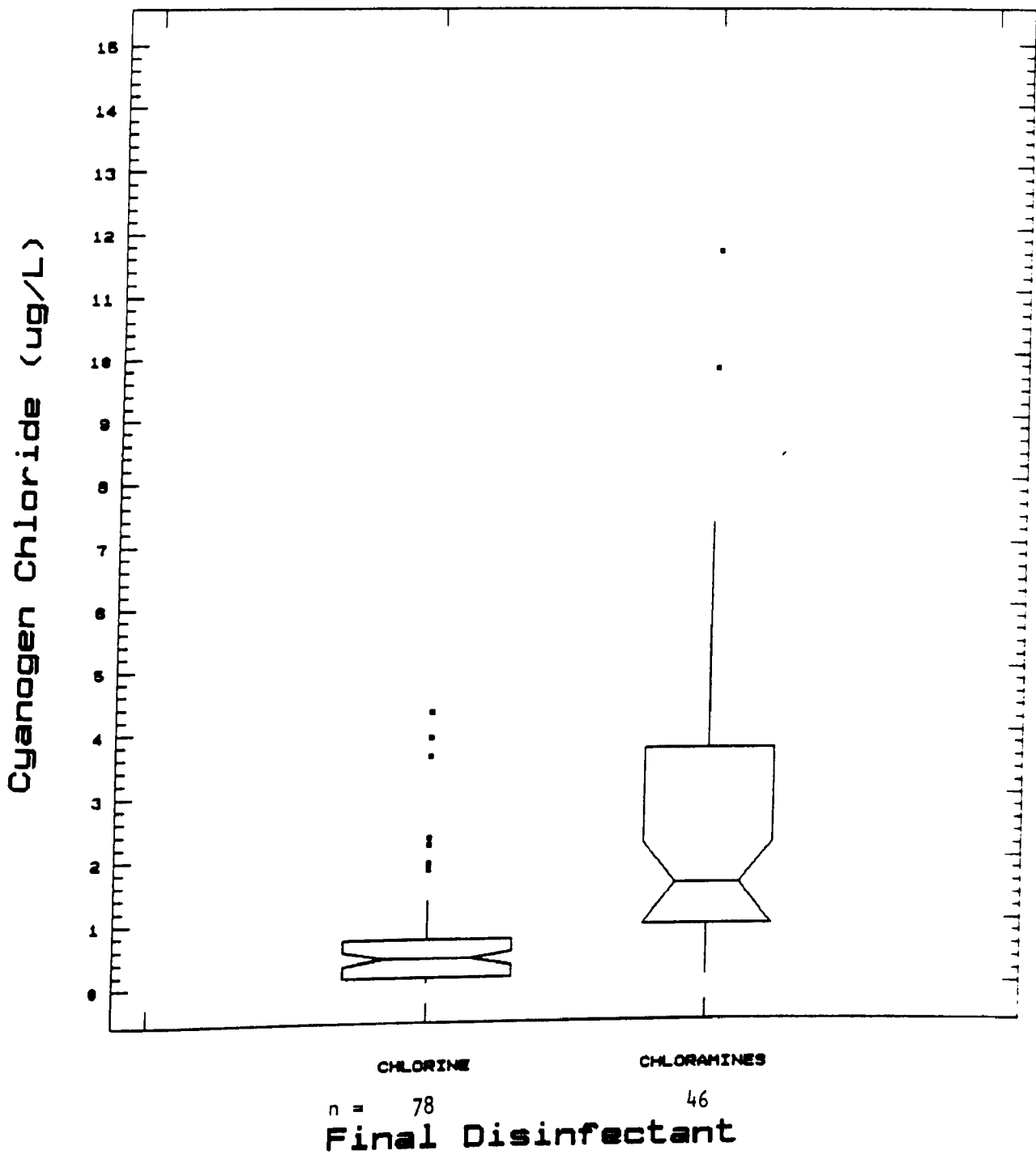
FIGURE 5-78

in the treatment of water (Scully and Bempong, 1982). The cyanogen chloride results presented above, as well as the presence of moderate concentrations of TOX in chloraminated waters with low levels of TTHMs, indicate a need to further identify chloramine by-products.

DBP Levels of Disinfection-Only Utilities

Figure 5-35, presented previously, illustrated influent TOC levels as a function of treatment type. DBP levels as a function of treatment type have not been discussed further in this section for the reasons presented previously in Section 5, under the heading "Star Plot Analyses". However, some findings of this study with respect to DBP levels occurring in disinfection-only utilities warrant further evaluation.

The overall median concentration of TTHMs for direct filtration and disinfection-only utilities were the lowest of the four treatment types, although the differences were not statistically significant. However, the median level of HAAs in disinfection-only utilities (approximately 35 μg/L) was significantly higher than that of either conventional or direct filtration utilities (approximately 17 and 9 μg/L, respectively); and this difference was significant at a 95 percent confidence level. Additionally, the median concentration of HAAs for softening utilities was only approximately 23 μg/L, although this was not significantly lower than the HAA median for disinfection-only utilities. This trend was even more pronounced when comparing the median HK concentrations of disinfection-only utilities (approximately 3.8 μg/L) with those of conventional, direct filtration and softening utilities (all of which occurred within the approximate range of 0.8 to 1.4 μg/L), and the differences were statistically significant at a 95 percent confidence level.

Samples from the disinfection-only utilities were collected very shortly after the addition of the disinfectant (in all cases, free chlorine, although one disinfection-only utility also employed preozonation). There was very little free chlorine contact time before sample collection since none of these utilities had detention time in a clearwell after the addition of chlorine.

The role of HKs as reactive intermediates rather than stable endproducts was discussed previously. The HK data from the disinfection-only utilities seem to suggest that this class of compounds are formed very rapidly upon chlorination, and there was insufficient contact time before sampling for the reaction to proceed further toward the formation of chloroform. A factor that may influence HAA formation in disinfection-only utilities is that the disinfectant is applied directly to the organic material present in the raw water, before the precursor material has been lowered in concentration, or altered in molecular weight distribution or other characteristics, by the addition of treatment chemicals, filtration or other treatment processes.

Removal of TOC During Treatment

Figure 5-79 illustrates the removal of TOC within the filtering plants included in this study. The percent removal of TOC from the plant influent to the filter influent of each plant was calculated, and the mean value of percent removal was plotted in the figure. In a similar manner, the removal from the filter influent to the clearwell effluent, and from the plant influent to the clearwell effluent were also calculated and
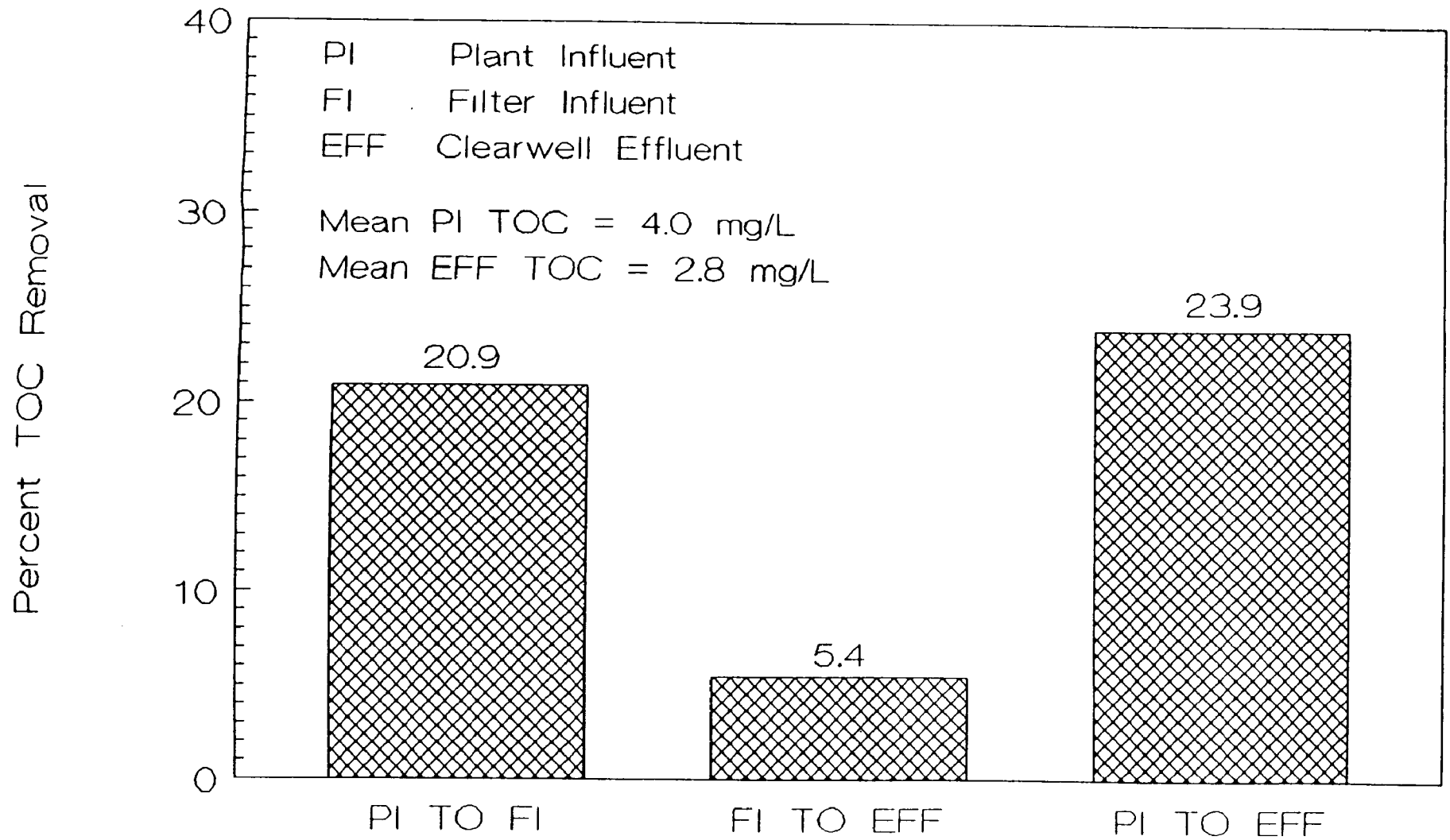
FIGURE 5-79

are shown in the figure. The plot indicates that most of the TOC removal (approximately 21 percent) occurred prior to filtration, that is, by sedimentation, and only 5 percent of the remaining TOC was removed by filtration. Overall, TOC removal within the filtering plants averaged approximately 24 percent.

The data shown in Figure 5-79 reflect the TOC removal achieved by the participating utilities, where much of the process operation is most likely focused on turbidity control. In Section 6, results are presented for two utilities that were able to achieve higher TOC removals than the mean values noted in Figure 5-79. (It should be noted that for one of the two utilities which were capable of increasing TOC removal by increasing alum doses, the enhanced precursor removal was only an incremental increase over that achieved in the baseline sampling.) From the data collected for this study, it is not possible to draw conclusions as to whether or not the levels of TOC removal illustrated in Figure 5-79 can be improved under all or most circumstances by optimizing the coagulation process. Further research in this area is required, especially since the TOC in some surface waters does not appear amenable to removal by conventional treatment (Chadik and Amy, 1983).

TOC removal by coagulation may be further optimized by controlling coagulation pH, although many utilities do not have the capability to control pH at the rapid mix basin. Of course, the economics of increased chemical consumption and associated sludge production, as well as increases in total dissolved solids due to acid and base addition, must be weighed against the advantages of enhancing precursor removal by increasing coagulant doses and adjusting the coagulation pH. The coagulation studies will be discussed in detail in Section 6 of this report.

Comparison of THM Levels from USEPA DBP Study and AWWARF THM Survey

The median TTHM levels previously reported in Table 5-2 were 34, 44, 40 and 30 μg/L for the spring, summer and fall quarters of 1988 and the winter quarter of 1989. These data were compared to the TTHM values obtained in a survey of 727 utilities around the United States conducted for the American Water Works Association Research Foundation (AWWARF) in 1987 (McGuire and Meadow, 1988). The median TTHM concentrations in the AWWARF survey for the spring, summer, fall and winter seasons were 40, 44, 36 and 30 μg/L, respectively. (The AWWARF survey reflected more than 67 percent of the population represented by water utilities serving more than 10,000 customers.)

Because of the similarity of TTHM levels for the DBP study and the AWWARF survey, the data were further evaluated. Compliance with the THM regulation is based on a running annual average for each utility (USEPA, 1979); therefore, mean values were computed for each of the 35 utilities for the four sampling quarters. The AWWARF survey utilized the means of three years of quarterly data. The means for both projects are plotted on a frequency distribution curve in Figure 5-80. A log scale was used for the ordinate axis in order to compress the displayed range, not to imply a log-normal distribution. Visually, the 35-utility DBP study appears to represent a THM frequency distribution very similar to that of the 727-utility AWWARF survey. The major difference is in the data for low TTHM levels (less than or equal to 25 μg/L). As discussed in Section 2 of this report, utility selection for this study attempted to achieve a balance among utilities which had reported low, medium and high TTHM levels in

FREQUENCY DISTRIBUTIONS OF THM SURVEY DATA
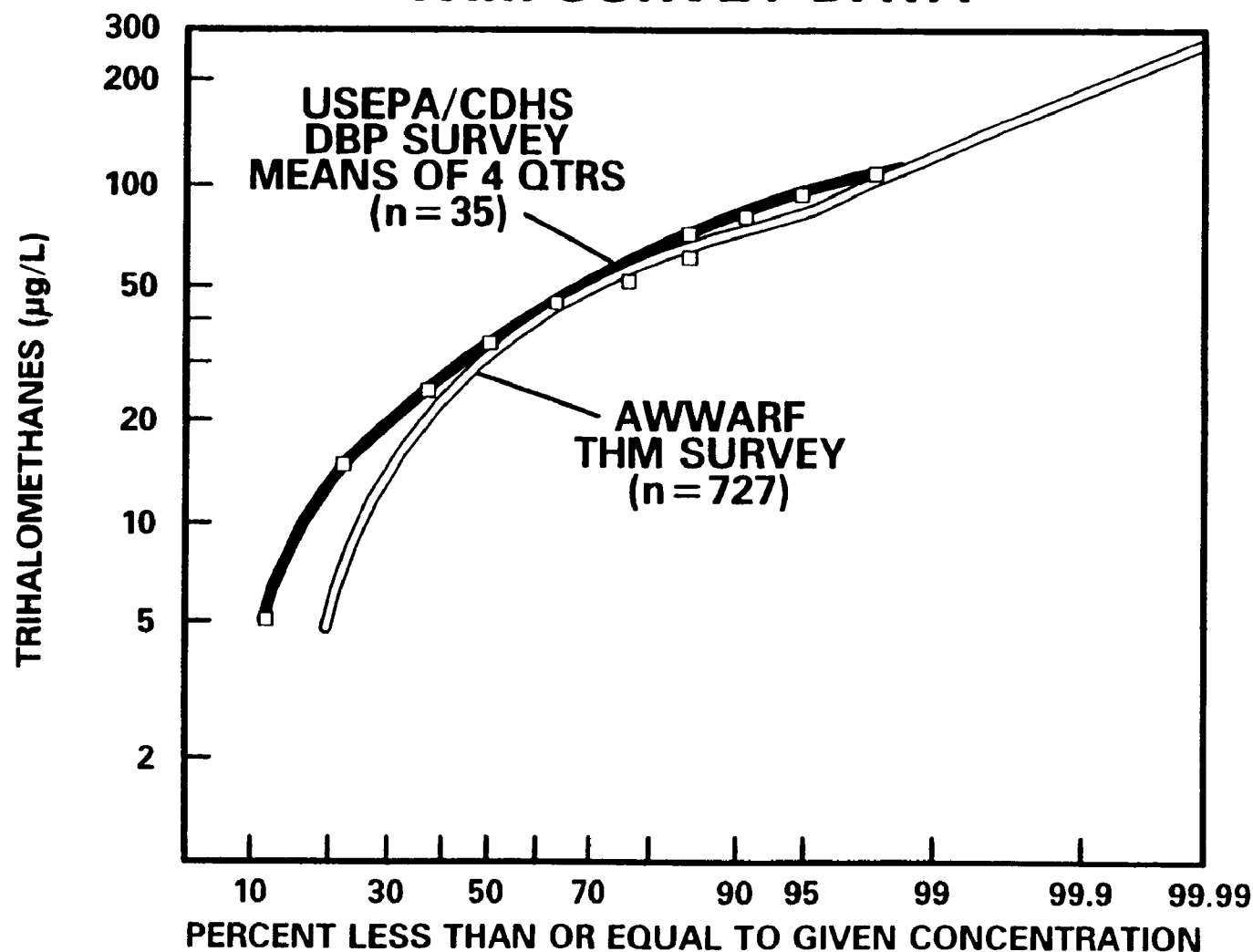
FIGURE 5-80

the AWWARF survey. Thus, fewer utilities with very low TTHM levels were included in the DBP study than are found nationwide, and this may be the cause of the differences in the data below 25 μg/L of TTHMs between the two surveys. A statistical comparison of the two distributions, by means of a Kolmogorov-Smirnov test (Hoel, 1971), indicates that the hypothesis that these samples are from the same distribution is not rejected at a significance level of 0.01.

In addition, a notched box-and-whisker plot of the TTHM levels from the two surveys is shown in Figure 5-81. Both sets of survey results have median TTHM values of 39 μg/L, and the 95 percent confidence intervals for the two medians overlap, indicating that the two groups are statistically similar in terms of central tendency. Furthermore, their minima and maxima are comparable, indicating a similarity in variability.

It should be noted that the AWWARF survey reported distribution system THM data, whereas results of this study represent clearwell effluent THM levels. THM levels from the clearwell effluents of utilities employing chloramines as a final disinfectant may reflect more closely the THM levels found in their distribution systems.

Comparison of USEPA Study and CDHS DBP Study Results

Figure 5-82 illustrates the levels of XDBP$_{sum}$ for the 25 utilities participating in the USEPA study and the 10 utilities in the CDHS study, as well as for the combined 35 utilities. The four-quarter median level of XDBP$_{sum}$ was substantially lower for the CDHS study, approximately 48 μg/L, compared to approximately 75 μg/L for the USEPA study, although the difference was not statistically significant at a 95 percent confidence level. Additionally, the 75th percentile values from each study are approximately equal, as are the ranges.

AWWARF 12-Quarter vs. USEPA
4-Quarter Means
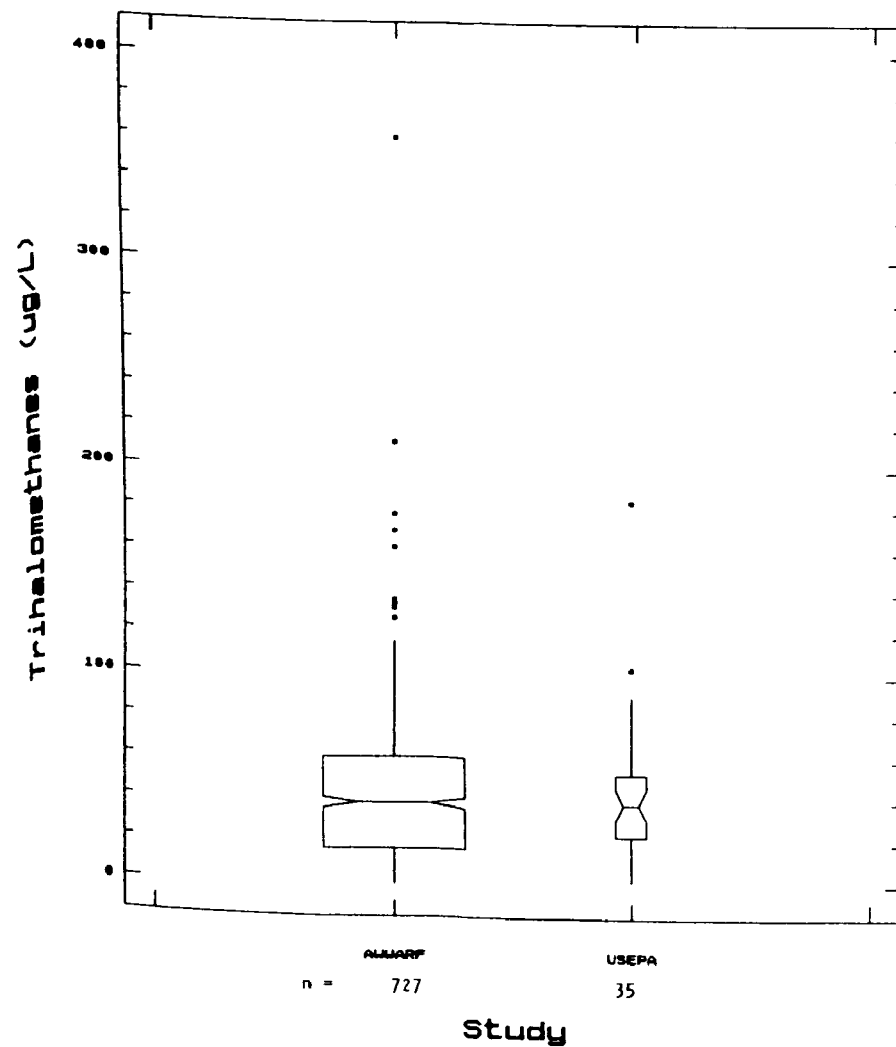
FIGURE 5-81

Total Halogenated DBPs
By Study
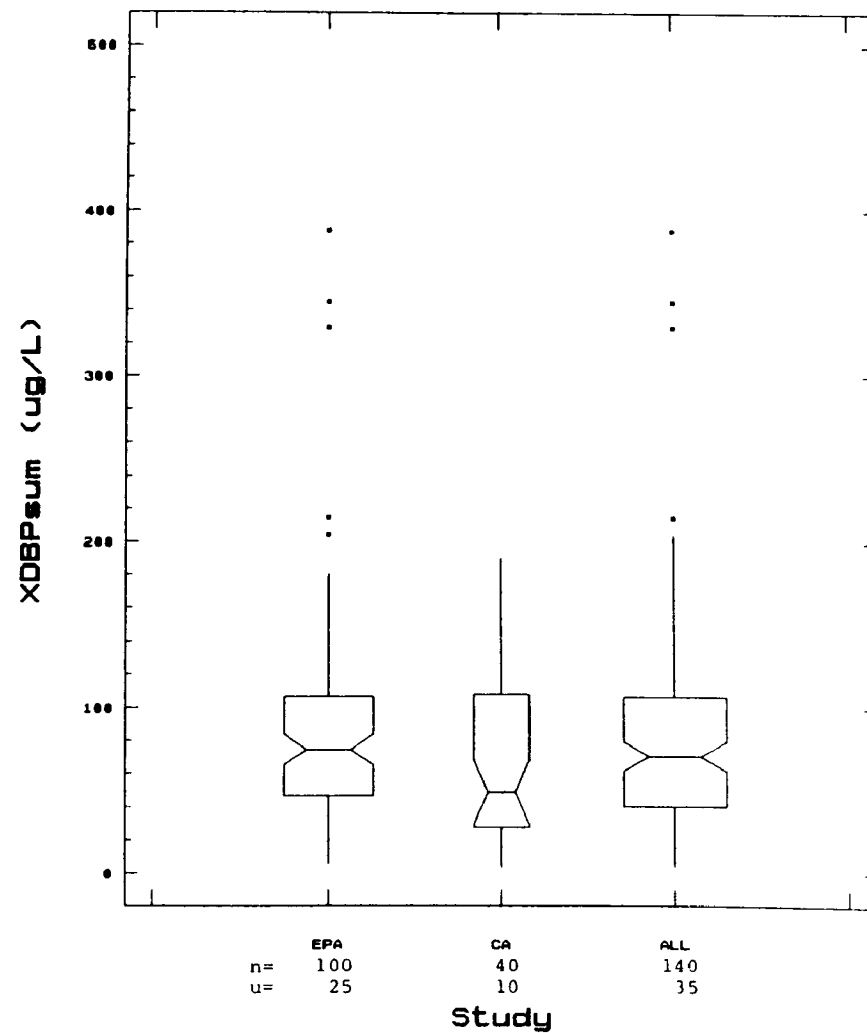
FIGURE 5-82

Section 6

Treatment Modification Studies - Results and Discussion

SECTION 6

TREATMENT MODIFICATION STUDIES - RESULTS AND DISCUSSION

In this section, results of the treatment modification studies will be presented and discussed. A total of ten studies were performed for the combined USEPA and CDHS DBP projects. Five of these studies focused on the use of ozonation as a method of DBP control, two investigated coagulation for DBP precursor removal, two studies evaluated chlorine dioxide for DBP control, and one involved the use of GAC to lower concentrations of DBP precursors.

OZONATION STUDIES

Because of the increasing use of ozone in the United States for disinfection and control of DBPs, five treatment modification studies focused on the use of this oxidant at various water treatment plants. The utilities which participated in this project were selected because ozonation processes were installed at their treatment plant or because they were able to provide a pilot plant which could evaluate ozonation. Table 6-1 shows the type of source water and various disinfection schemes employed at each utility in order to evaluate the effect of ozone on the formation of DBPs.

Utility 6

Utility 6 operates a plant in the eastern United States which had a capacity of 52 mgd at the time of the study. Sampling at this plant was conducted before and after ozone was incorporated into the treatment process, which is presented schematically in Figure 6-1. As a conventional treatment plant, chlorine was added in four places: to the raw water, before flocculation, and before and after filtration. Ammonia was also added after filtration to convert the free chlorine to chloramines for residual disinfection. As the schematic shows, there was a change to direct filtration when ozonation was installed, the flocculation and sedimentation basins having been converted to flotation/skimming tanks. As a result of changing the plant configuration and implementing ozone, the utility was able to employ lower doses of chlorine for shorter contact times. Under this configuration, chlorine was applied before and after filtration, ammonia being added before the second chlorination point to produce chloramines for residual disinfection. Therefore, free chlorine contact time was limited to that required to prevent biological growth in the filters.

Sampling locations included distribution system Location 3, which corresponds to a residence time of 7 hours. Because of delays in the switch to ozone and changes in water quality, the "before" and "after" samples (before and after the implementation of preozonation) were taken approximately four to six months apart. The first "after" sample was collected on March 13, 1989. However, as indicated in Table 6-2, the temperature at Location 3 was 7°C lower as compared to the November 21, 1988 conventional treatment sampling at that location. The raw water TOC concentration was also lower in March compared to November. Consequently, a second ozonated "after" sample was collected on May 15, 1989 when the distribution system water temperature was comparable to that of the November sampling. Additionally, Table 6-2 shows that the samples collected on this sampling date and on November 21, 1988,

TABLE 6-1

DISINFECTION SCENARIOS, PLANT SCALES AND SOURCES
FOR UTILITIES PARTICIPATING IN STUDY

Utility	Scale	Source Water	Disinfection Scenarios	Abbreviations
6	Full	Reservoir	1) Prechlorination, postammoniation	Cl_2, NH_3
			2) Preozonation, postchlorination postammoniation	O_3, Cl_2, NH_3
7	Full/ Pilot	Reservoir	1) Pre- and postchlorination (full scale)	Cl_2
			2) Prechlorination, postammoniation (full scale)	Cl_2, NH_3
			3) Preozonation, postchloramination (pilot scale)	O_3, NH_2Cl
19	Full	Flowing Stream	1) Pre- and post chlorination	Cl_2
			2) Preozonation, postchlorination	O_3, Cl_2
25	Full	Lake	1) Prechloramination only	NH_2Cl
			2) Pre- and postozonation, post chloramination	O_3, NH_2Cl
36	Pilot	Lake	1) Prechlorination only	Cl_2
			2) Prechloramination only	NH_2Cl
			3) Preozonation, prechlorination	O_3, Cl_2
			4) Preozonation, prechloramination	O_3, NH_2Cl
			5) Preozonation with hydrogen peroxide addition, prechloramination	O_3, H_2O_2, NH_2Cl

Note: The prefix "pre-" in disinfection scenarios denotes addition prior to the rapid mix. The prefix "post-" denotes addition directly before or after filtration.

PRECHLORINATION / POSTAMMONIATION
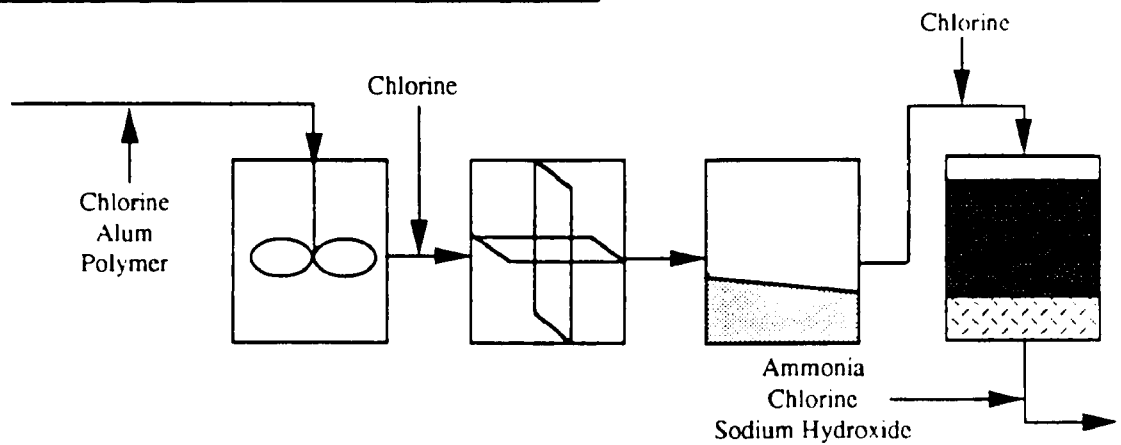
OZONE / CHLORINE / CHLORAMINES
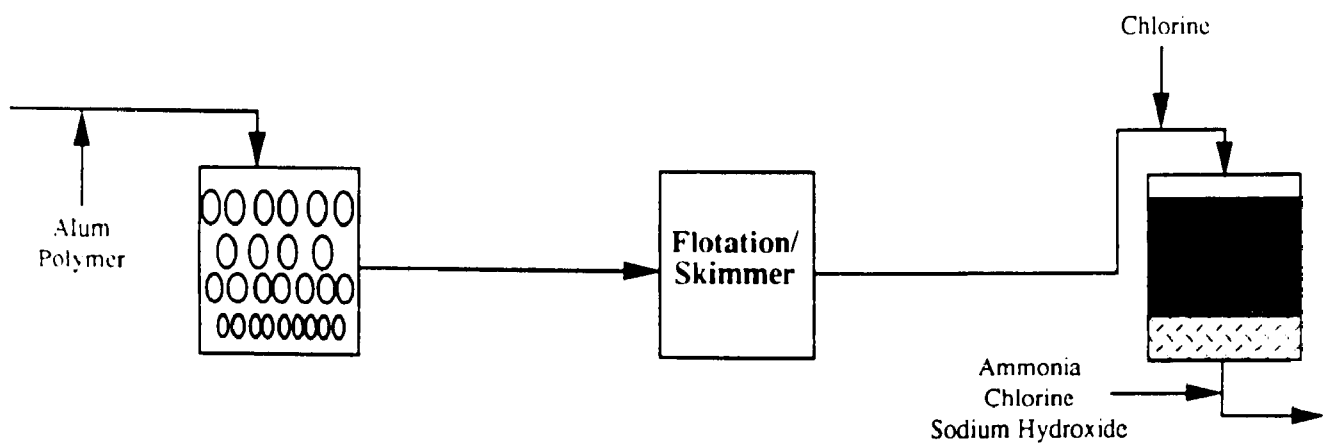
SCHEMATIC OF UTILITY 6 TREATMENT PROCESSES

FIGURE 6-1

TABLE 6-2

UTILITY 6 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	UV Absorbance at 254 nm (cm⁻¹)	Chloride (mg/L)	Bromide (mg/L)	TOX (μg/L)	pH	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)	Temp. (°C)
CONVENTIONAL (11/21/88 DBP Sampling)									
Raw Water	4.25	0.178	43	0.05	NA	7.8	NA	NA	9
Location 3	2.84	0.102	NA	NA	240	7.6	NA	>2.0	13
OZONE (5/15/89 DBP Sampling)									
Raw	4.28	0.144	66	0.06	NA	7.5	NA	NA	14
Location 3	3.60	0.059	NA	NA	100	7.8	ND	2.0	15
OZONE (3/13/89 Aldehyde Profile)									
Raw Water	3.75	0.137	66	0.07	NA	7.7	NA	NA	6
Ozone Contactor Effluent (OCE)	3.72	0.093	NA	NA	NA	8.0	NA	NA	5
Filter Influent (FI)	3.64	0.092	NA	NA	60*	7.6	0.5	1.0	5
Filter Effluent (FE)	3.18	0.070	NA	NA	76*	8.0	0.1	0.5	5
Plant Effluent (PE)	3.20	0.069	NA	NA	80*	8.0	NA	1.0	5
Location 1 (L1)	3.18	0.071	NA	NA	82	8.1	NA	0.7	7
Location 2 (L2)	3.23	0.072	NA	NA	76	8.1	NA	0.8	6
Location 3 (L3)	3.20	0.070	NA	NA	89	8.2	NA	0.4	6

NA = Not Analyzed

ND = Not Detected

Note:
1. All comparisons of conventional versus ozone treatment are made with samples collected on 11/21/88 and 5/15/89, repectively. The data on these two sampling dates represent the water quality parameters associated with Figures 6-2 to 6-9.

2. Locations represent distribution system sampling points in order of increasing residence time.

*These TOX samples were dechlorinated and preserved in the field.

had similar raw water TOC and pH. Consequently, all comparison of "before" and "after" ozonation samples were made using data from these two sampling dates. Table 6-2 shows that the total chlorine residual at Location 3 with preozonation (May 15, 1989 sampling) was 2.0 mg/L. Before ozone was implemented, the measured distribution system residual was greater than 2.0 mg/L; historical records showed that the residual at this point was usually 2.8 mg/L. The table also indicates that TOX decreased by 58 percent with the preozonation disinfection scheme, despite the higher concentration of TOC measured in the distribution system. However, it should be noted that less free chlorine and a shorter contact time were employed when preozonation was utilized.

The effects of ozonation on DBPs measured at Location 3 is presented in Figures 6-2 to 6-9. As shown in Figures 6-2 through 6-4, a reduction of 56 to 66 percent was observed for all XDBP classes except HKs, which increased slightly from 3.6 to 4.4 μg/L. Chloral hydrate, chloropicrin and cyanogen chloride decreased slightly. Figures 6-5, 6-6 and 6-7 show that most of the individual THMs, HAAs, and HANs decreased in concentration. Because of the low bromide levels in the raw water (0.05 to 0.06 mg/L), there were no observed increases in concentrations of brominated DBPs. The only individual DBP compound to increase in concentration was 1,1-DCP (1.4 to 2.8 μg/L), as shown in Figure 6-8. Concentrations of the miscellaneous compounds are illustrated in Figure 6-9.

The effect of water temperature on formation of DBPs after ozonation was implemented is shown in Figure 6-10. Samples were collected when the temperature was 6°C and approximately 2 months later when the temperature had increased to 15°C. The residence time at the distribution sampling point was 7 hours. The data show that DBP class totals increased only slightly with the 9 degree increase in water temperature.

From this study, it is not possible to directly attribute the reduction in most XDBPs to ozone since lower doses of chlorine and shorter contact times were employed. It cannot be determined if ozone caused a decrease or modification of DBP precursor material or if lower DBP levels can be attributed solely to a decreased use of chlorine. Examination of Figure 6-6 shows that the use of preozonation affected individual HAAs differently (50 percent reduction in DCAA versus a 78 percent decrease in TCAA). For this study, the following order of increasing effect of preozonation on controlling the formation of these DBPs was:

$$1,1,1\text{-TCP} < \text{DCAA} < \text{TOX} \leq \text{CHCl}_3 < \text{DCAN} < \text{TCAA}$$
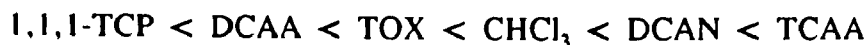
According to bench-scale research on preozonation/postchlorination treatment of fulvic acids by Reckhow and Singer (1985), the following order of increasing precursor destruction for nearly all of the investigated doses were:

$$1,1,1\text{-TCP} < \text{DCAA} < \text{TOX} \leq \text{CHCl}_3 \leq \text{TCAA} < \text{DCAN}$$
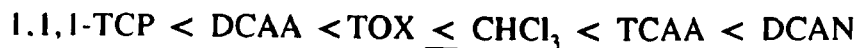
Thus, the plant-scale study results at Utility 6 were quite comparable to the bench-scale testing noted above. In addition, it is notable that the full-scale application of ozone decreased the dependence on chlorine for oxidation and disinfection.

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY—PRODUCT FORMATION AT UTILITY 6
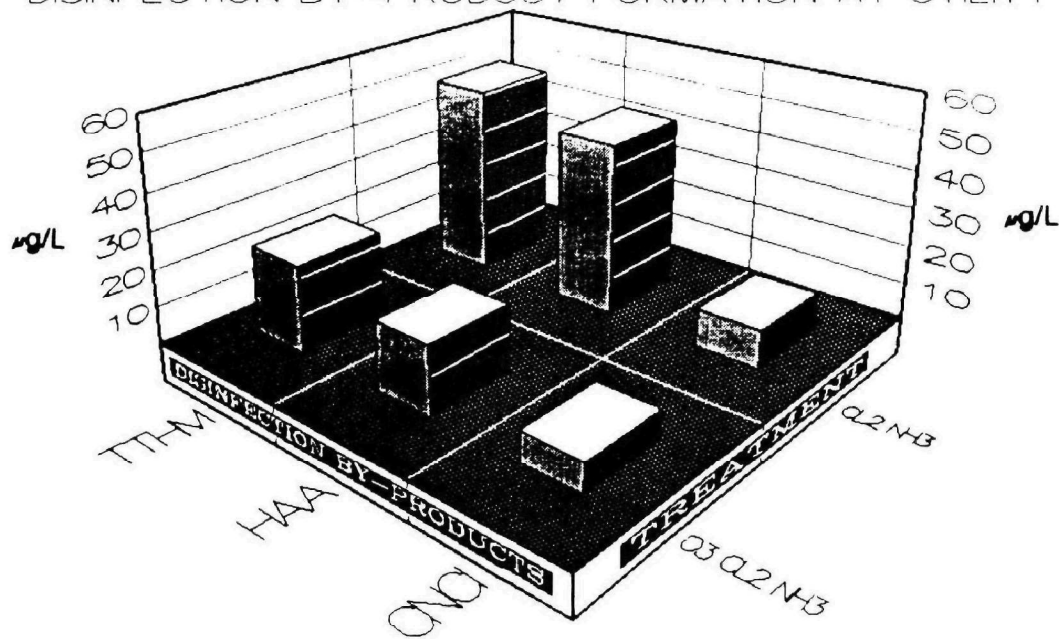
FIGURE 6-2

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY—PRODUCT FORMATION AT UTILITY 6
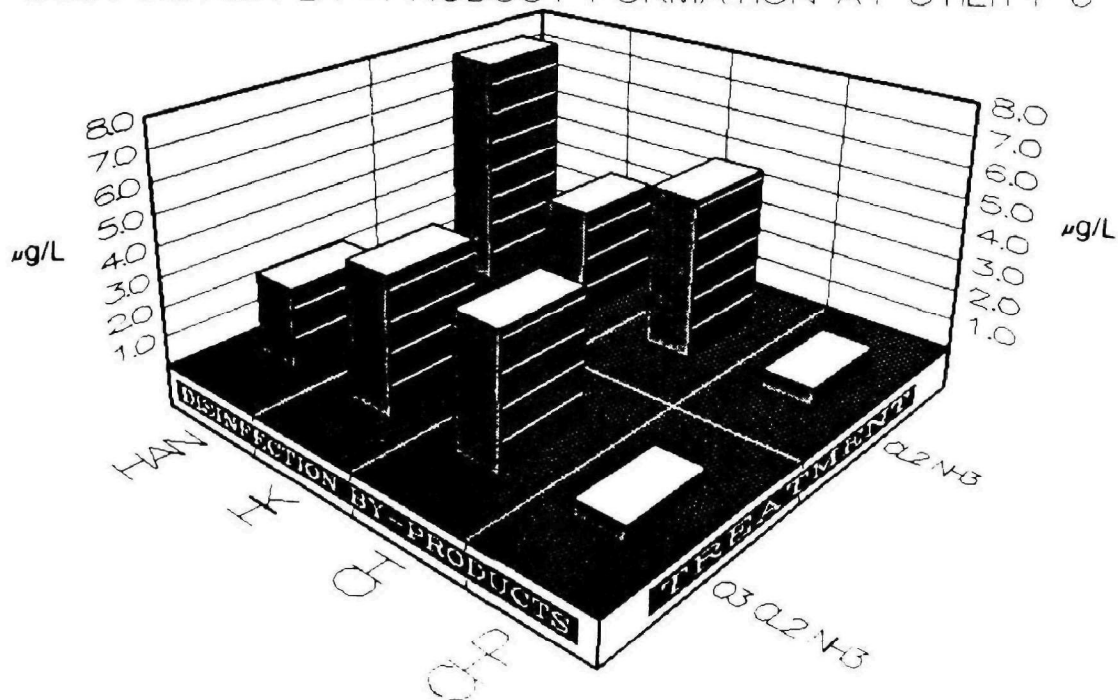
FIGURE 6-3

Effect Of Cl2,NH2Cl and O3,Cl2,NH2Cl on DBP Formation (Utility 6)
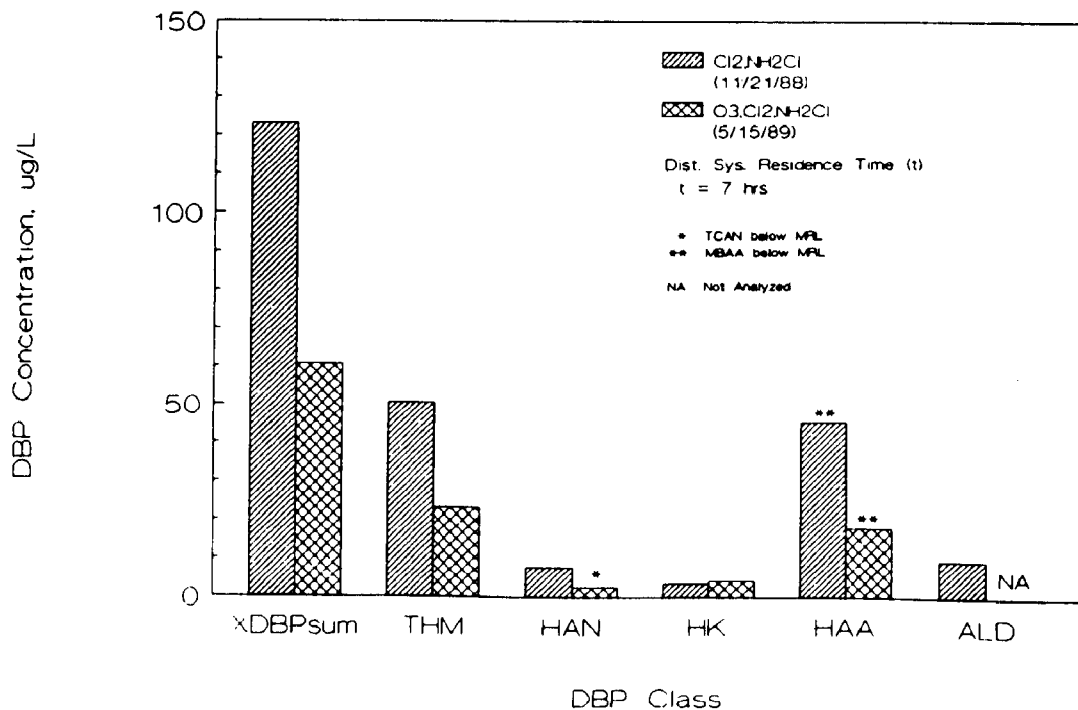
FIGURE 6-4

Effect Of Cl2,NH2Cl and O3,Cl2,NH2Cl on THM Formation (Utility 6)
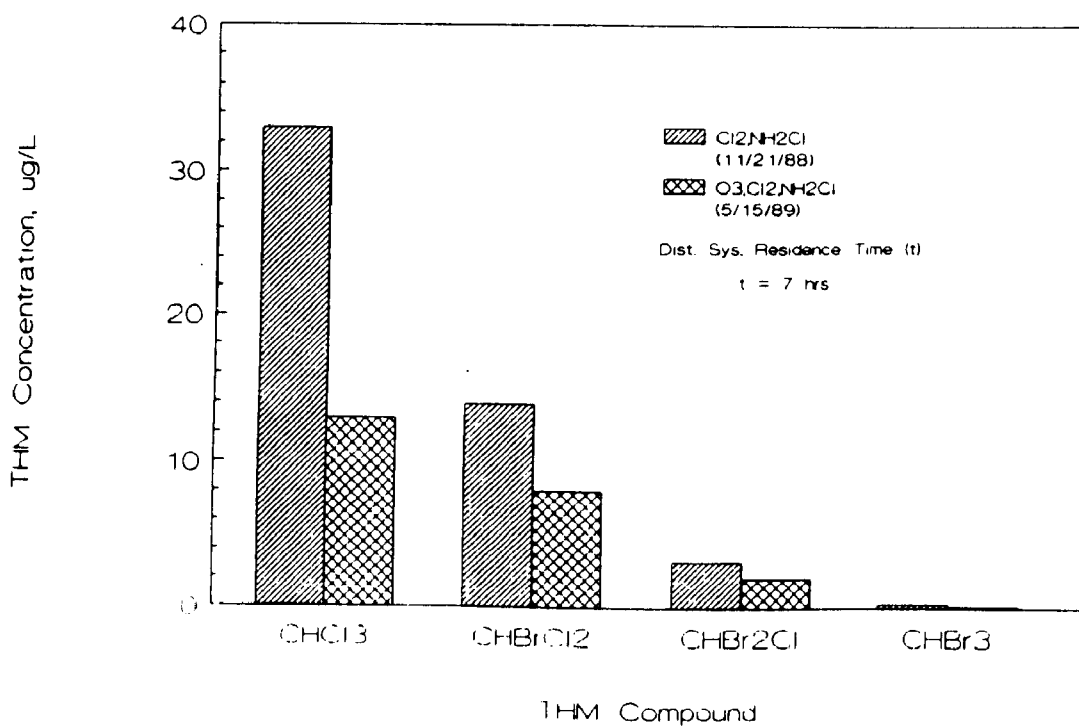
FIGURE 6-5

Effect of Cl2,NH2Cl and O3,Cl2,NH2Cl on HAA Formation (Utility 6)
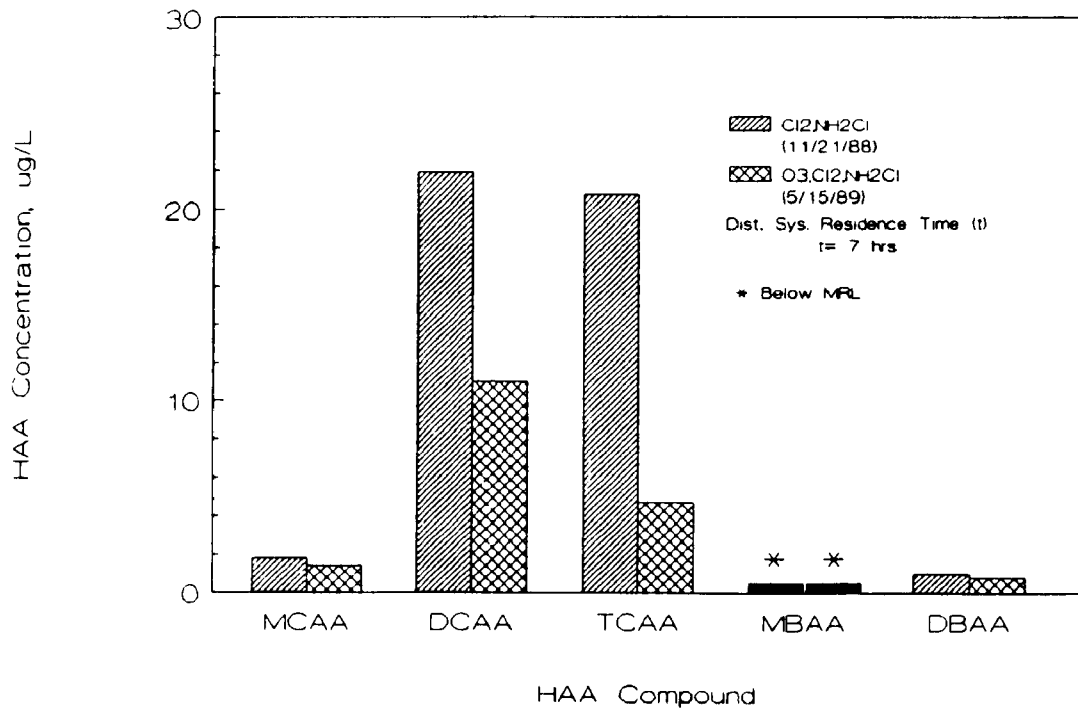
FIGURE 6-6

Effect Of Cl2,NH2Cl and O3,Cl2,NH2Cl on HAN Formation (Utility 6)
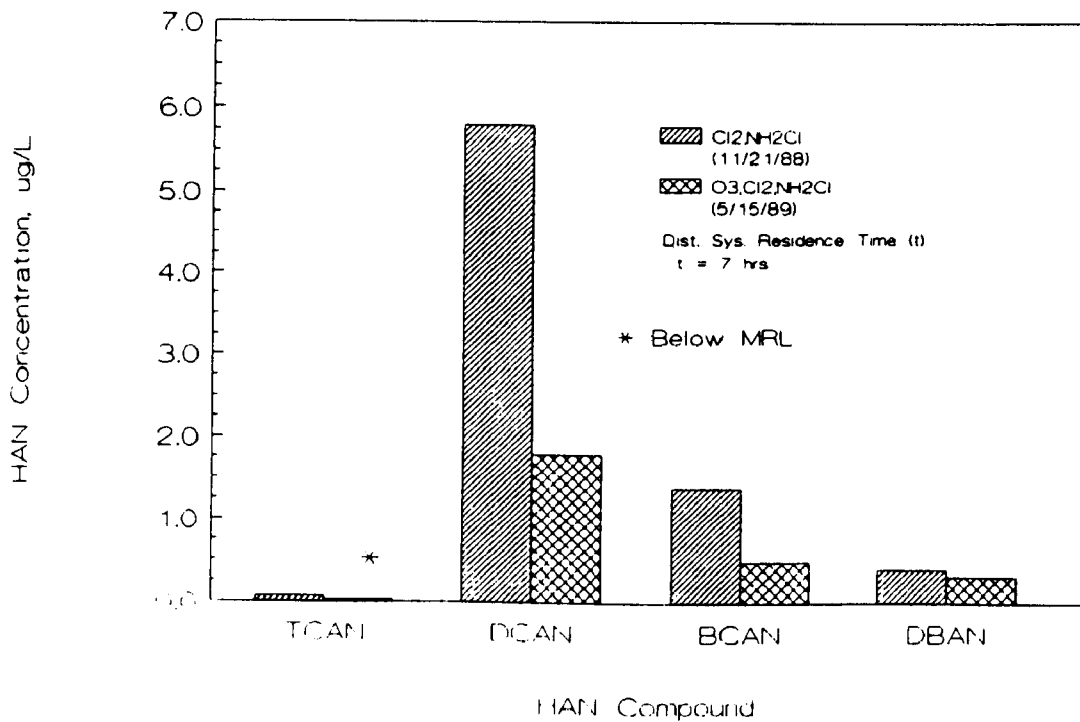
FIGURE 6-7

Effect Of Cl2,NH2Cl and O3,Cl2,NH2Cl on HK Formation (Utility 6)
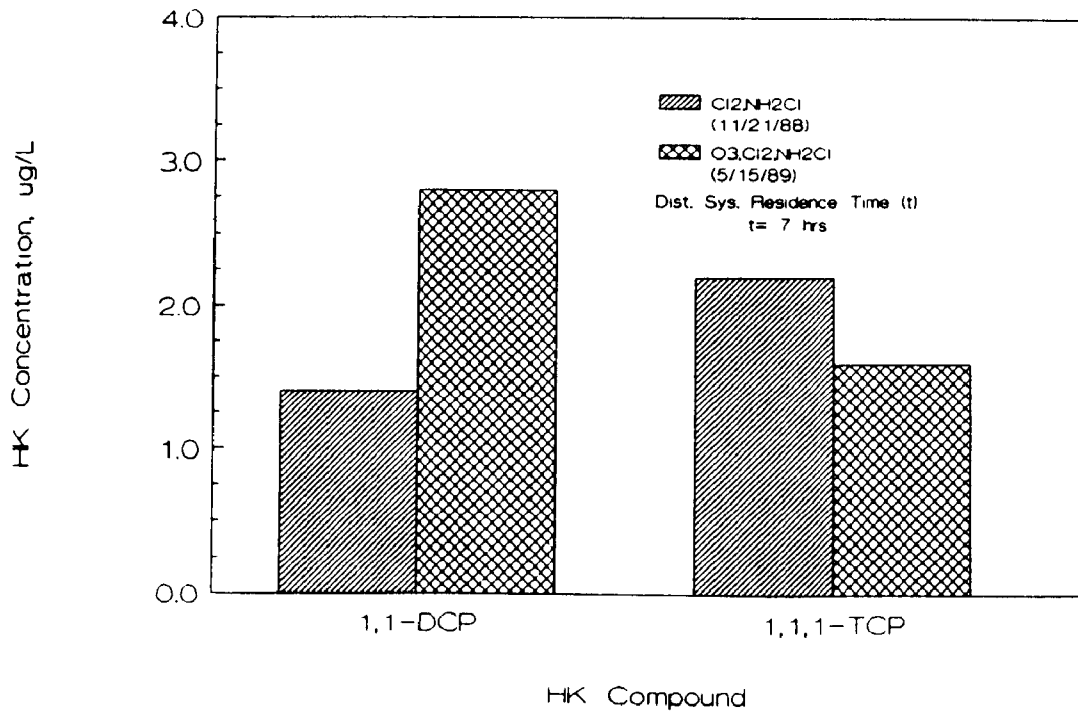
FIGURE 6-8

Effect of Cl2,NH2Cl and O3,Cl2,NH2Cl On Misc. DBP Formation (Utility 6)
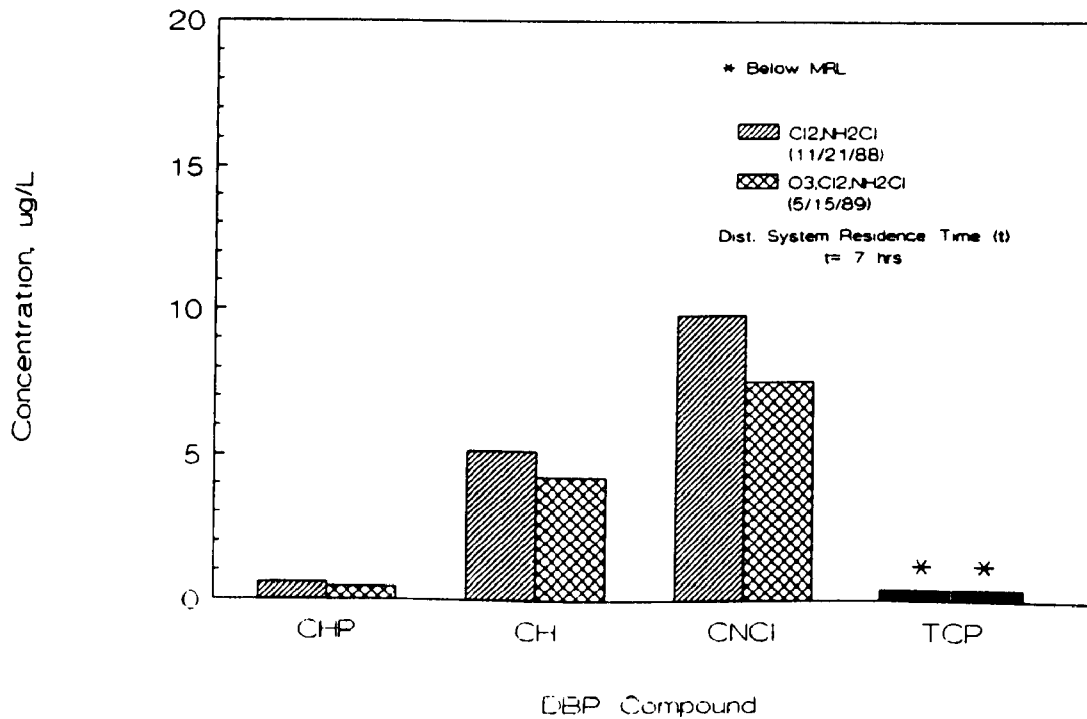
FIGURE 6-9

Effect Of Seasonal Temperatures
on DBP Formation (Utility 6)
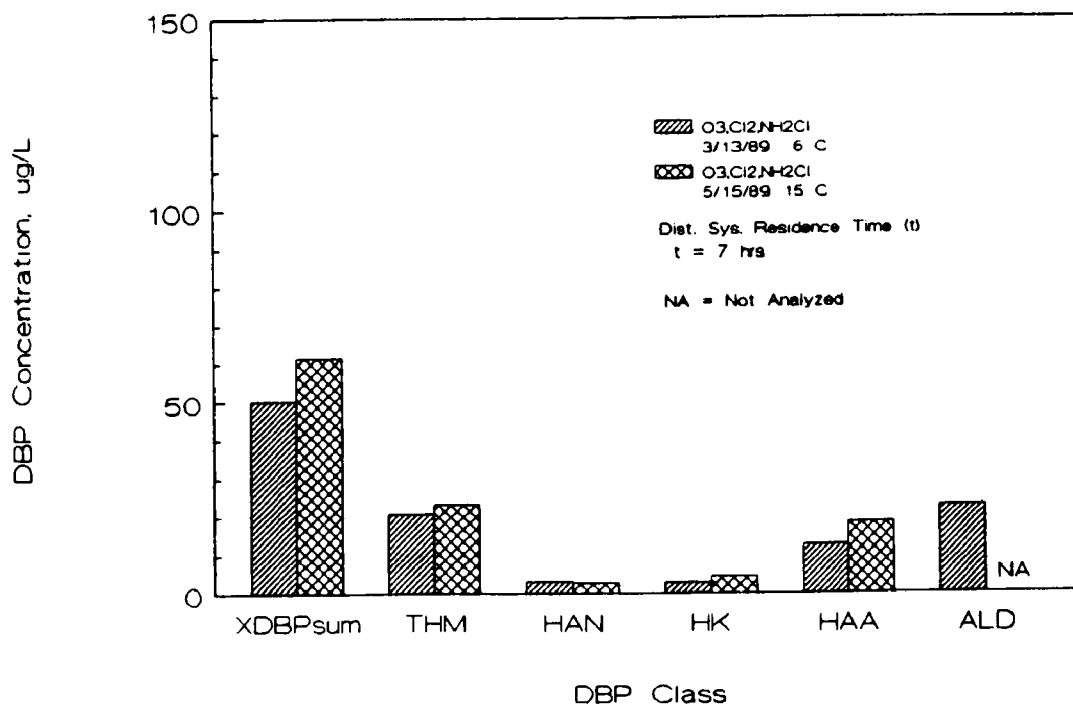
FIGURE 6-10

Effect Of O3,Cl2,NH2Cl
on Aldehydes Formation (Utility 6)
(3/13/89)
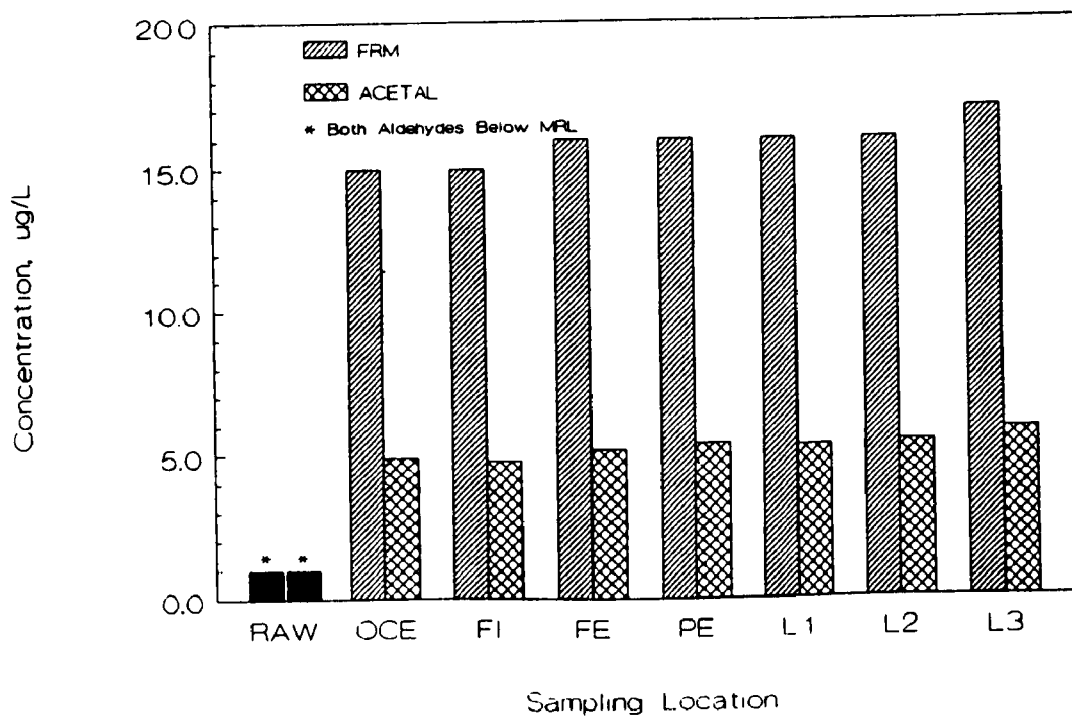
FIGURE 6-11

Stability of Aldehydes Through the Plant and Distribution System. The effect of ozone on the formation of aldehydes is presented in Figure 6-11. No formaldehyde or acetaldehyde was detected in the plant influent. Immediately after ozonation, though, concentrations of formaldehyde and acetaldehyde increased to approximately 15 and 5 μg/L. respectively. The plant and distribution system profile shows that these compounds were stable after formation. As noted above, chlorine is added in the treatment process before filtration; a 0.5 mg/L free residual (1.0 mg/L total residual) was detected in the filter influent. As will be discussed in more detail below, the maintenance of a disinfectant residual through the filter most likely precluded the aldehyde-removal capabilities of the filter.

Utility 7

Three different treatment scenarios were studied at Utility 7 (Figure 6-12), which is a 400-mgd conventional treatment plant. Chlorine-only and prechlorination/ postammoniation options were studied at full scale. A chlorine dose of 2.3 mg/L was applied at the plant influent. Additional chlorine was dosed at the filter influent: 1.1 mg/L during the chlorine-only test and 0.6 mg/L during the postammoniation option. Chlorine-only DBP samples were collected from the filter effluent just prior to postammoniation; the prechlorination/postammoniation samples were taken just after ammonia (0.49 mg/L as nitrogen) was added to the filter effluent. There were approximately 4 hours of free chlorine contact time under this scenario. In order to study preozonation at this utility, a 6-gpm pilot plant was employed. The pilot plant followed similar treatment processes as the full-scale plant but included ozone, which was applied at a dose of 2.0 mg/L. The pilot filter effluent was chloraminated (0.5 mg/L ammonia as nitrogen. 1.5 mg/L chlorine) with no free chlorine contact time.

Samples for each scenario were collected after 2 and 24 hours using the simulated distribution system (SDS) protocol. The SDS test was described in detail in Section 3 of this report. In these tests. samples were dosed with disinfectants and held under conditions representative of Utility 7's distribution system to give an estimate of the levels of DBPs that can be formed under realistic environmental conditions (Koch et al., 1989). For the SDS tests performed at Utility 7, samples were incubated at 25°C for 2 and 24 hours to simulate samples from the clearwell effluent and the distribution system. respectively. The preozonated pilot-plant sample was buffered to pH 8.2 to 8.3. The chloraminated filter effluent sample had received final pH adjustment in the treatment plant. However, the chlorinated filter effluent sample was collected at a point in the plant prior to final pH adjustment, so the SDS sample was raised to a pH of 8.2 by the addition of a 1-percent sodium hydroxide solution. The latter two samples had sufficient chlorine or chloramine levels for the SDS testing. The preozonated pilot plant effluent required a 1.5 mg/L chloramine dose, with ammonia added prior to chlorine dosing.

The chlorine residuals at the sampling locations, as well as other water quality parameters. are shown in Table 6-3. The data indicate that the pH and temperature at the sampling points for all the disinfection schemes were similar. The pilot plant received the same raw water as the full-scale plant, so the observed difference in treated-water TOC levels was probably due to a slightly greater TOC removal during the ozone-treatment trial.

CHLORINE ONLY

Polymer
Chlorine

Chlorine
Alum
Polymer

PRECHLORINATION/ POSTAMMONATION ONLY

Polymer
Chlorine

Chlorine
Alum
Polymer

Ammonia
Sodium Hydroxide

OZONE / CHLORAMINES

Polymer

Alum
Polymer
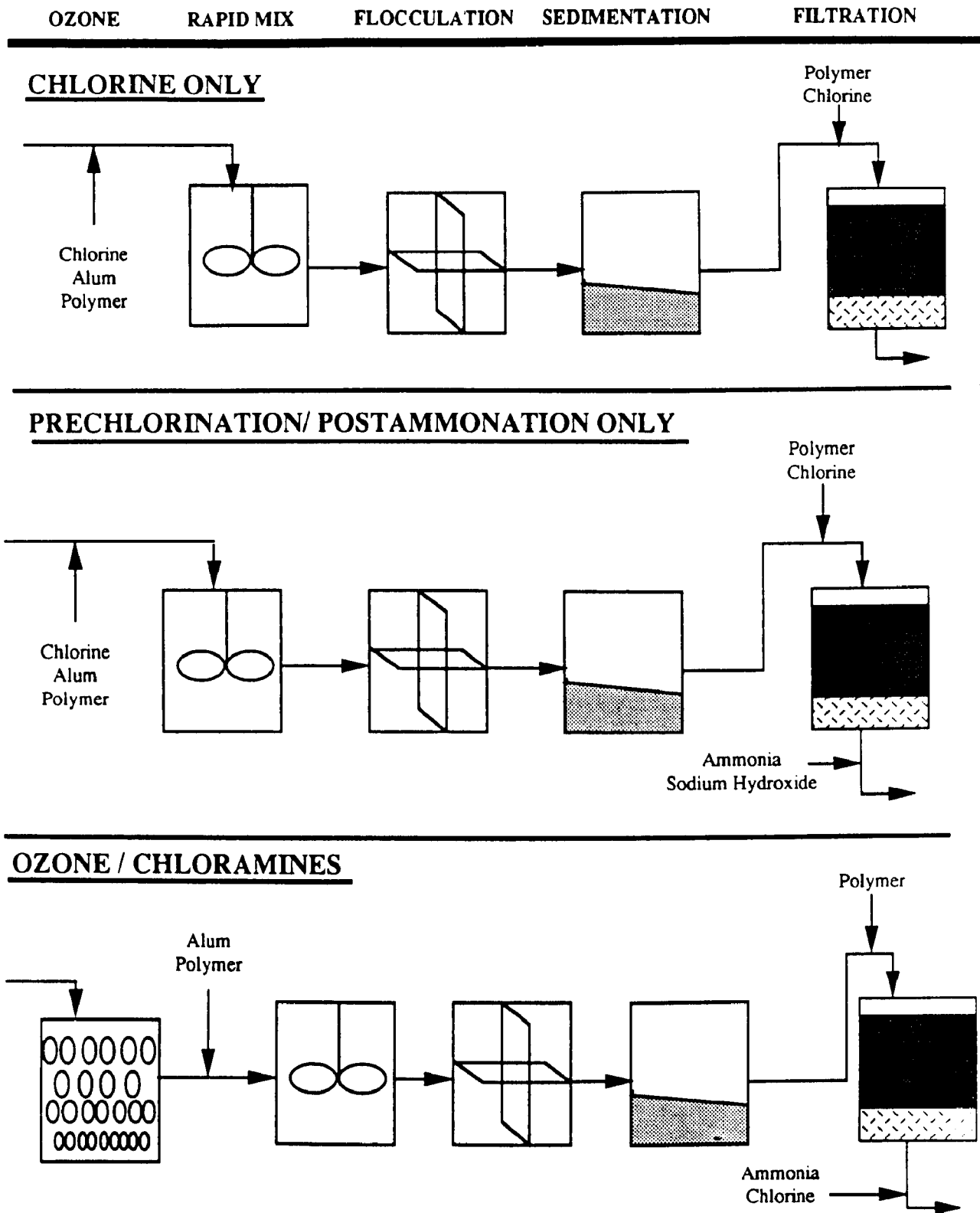
Ammonia
Chlorine

SCHEMATIC OF UTILITY 7 TREATMENT PROCESSES

FIGURE 6-12

TABLE 6-3

UTILITY 7 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	Pre-Ozone Dose (mg/L)	Chlorine Dose Pre, Post (mg/L)	Post-Ammonia Dose (mg/L as NH_3-N)	TOX (μg/L)	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)	pH	Temp. (°C)
Simulated Clearwell Effluent (2 hours)									
Cl_2	2.72	0	2.3, 1.12	0.0	180	1.13	1.32	8.14	25
Cl_2/NH_3	2.63	0	2.3, 0.60	0.49	150	<0.1	1.47	8.24	25
O_3/NH_2Cl	2.49	2.0	0.0, 1.5	0.5	31	<0.1	1.40	8.28	25
Simulated Distr. System (24 hours)									
Cl_2	2.72	0	2.3, 1.12	0.0	210	0.30	NA	8.19	24.8
Cl_2/NH_3	2.71	0	2.3, 0.60	0.49	130	NA	1.35	8.09	24.8
O_3/NH_2Cl	2.46	2.0	0.0, 1.5	0.5	38	NA	1.29	8.22	24.8

NA = Not analyzed.

Effects of ozonation on DBPs at Utility 7 after the 24-hour SDS tests are shown in Figures 6-13 and 6-14. Preozonation followed by concurrent addition of ammonia and chlorine after filtration decreased the levels of THMs, HAAs, HANs, and chloral hydrate as compared to chlorination-only or prechlorination/postammoniation. Very little difference in concentrations of HKs, cyanogen chloride or chloropicrin was observed between any of the treatments.

Aldehydes were not analyzed at the time of the study. However, subsequent pilot testing at Utility 7 indicated formation of aldehydes in the ozone contactors, the levels of which (1) remained the same through the filtration step when chloramines were applied upstream of the filters, and (2) decreased through the filtration step when chloramines were not added until after filtration (Montgomery, 1989), as shown in Figures 6-15 and 6-16 for formaldehyde. Since the ozone residual is short-lived, when no chlorine or chloramines were added prior to filtration, it is probable that biological activity had developed on the filter media; the data suggest that this activity was capable of removing biodegradable material produced by ozonation, such as the two aldehydes studied here. This is consistent with other studies which have shown that biologically operated filters can decrease materials such as assimilable organic carbon (Van der Kooij et al., 1982; Montgomery, 1989).

The use of filtration with biological activity is typical of many European ozone plants; however, it is atypical in water treatment plants in the United States. As the plant schematics for the other ozonating utilities in this study indicate (see Figures 6-1, 6-23, 6-32 and 6-46), chlorine or chloramines were added after the ozone contactor and before the filters, thus probably minimizing microbiological growths in the filters. An important finding of the ozonation studies conducted for this project is the large increases observed in aldehyde formation whenever ozonation is employed followed by secondary disinfection prior to filtration (see Figures 6-33 and 6-47). The placement of secondary disinfection with respect to filtration requires further study in order to minimize aldehyde levels in the finished waters of ozonating plants.

Table 6-3 shows that 24-hour SDS TOX concentrations decreased as free chlorine contact time decreased in each successive treatment train, the lowest (38 μg/L) being observed when ozonation/chloramination (with no free chlorine contact time) was tested.

Figures 6-17 to 6-22 present the DBP data for the treatment modification study as a function of contact time. Results from SDS tests at 2 and 24 hours are shown. Under the chlorine-only scenario, all DBPs increased with increasing residence time except for the haloketones and chloropicrin. Under the prechlorination/postammoniation scheme, all DBPs were relatively stable between the 2-hour and 24-hour tests, except for 1,1,1-TCP which decreased and cyanogen chloride which increased. For the preozonation/postchloramination treatment scenario, most DBPs remained at or below 1 to 2 μg/L each, except for cyanogen chloride, which was detected at 2.3 to 3.4 μg/L.

Utility 19

This utility, which was studied at full scale (Figure 6-23), is a 600-mgd preozonation/direct filtration facility. During the trial when only chlorine was employed, ozone was taken offline and pre- and post-chlorine doses were applied to

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY-PRODUCT FORMATION AT UTILITY 7

*Includes 4 hours of free chlorine
contact time before postammoniation
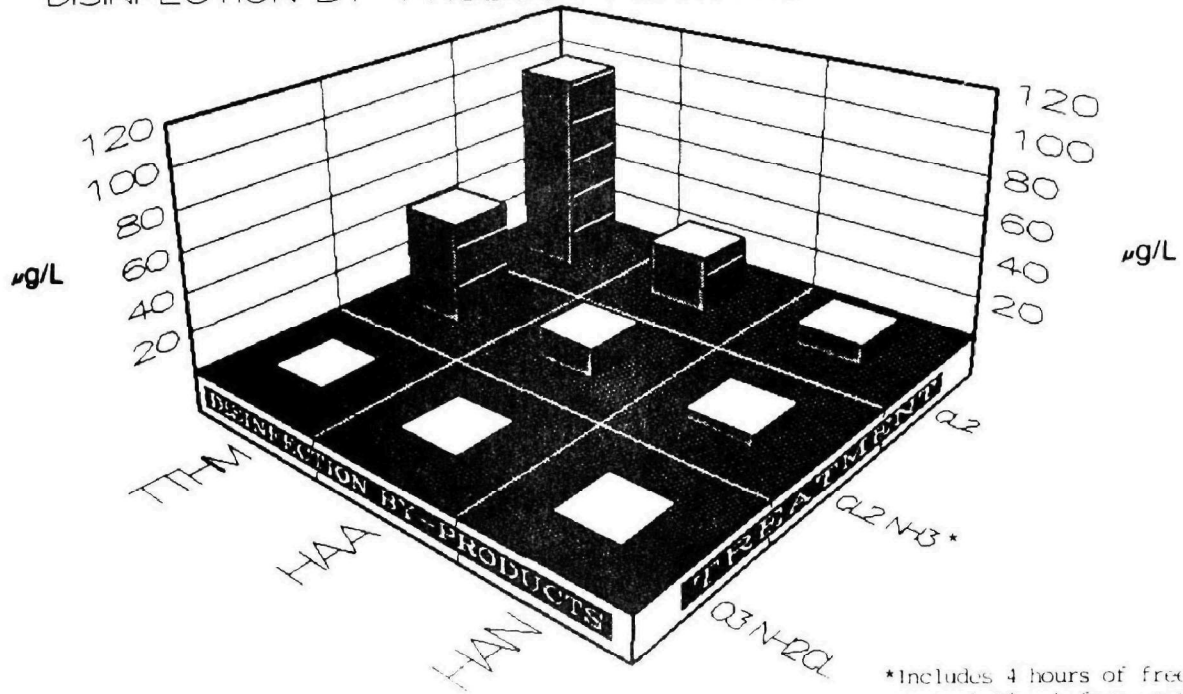
FIGURE 6-13

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY-PRODUCT FORMATION AT UTILITY 7

*Includes 4 hours of free chlorine
contact time before postammoniation

FIGURE 6-14

CHANGE IN FORMALDEHYDE CONCENTRATION
THRU PROCESS TRAIN, STATE PROJECT WATER
Reference: Montgomery, 1989

GUIDE TO FIGURES:

PIA = plant influent
OE3 = ozone contactor effluent
FI = filter influent
FE = filter effluent

Disinfectants
Upstream of Filters

+——+ 2 mg/L O3,
no NH2Cl

△——△ 2 mg/L O3,
1.5mg/L NH2Cl

O——O 2 mg/L O3,
1.5mg/L NH2Cl

PLANT LOCATION
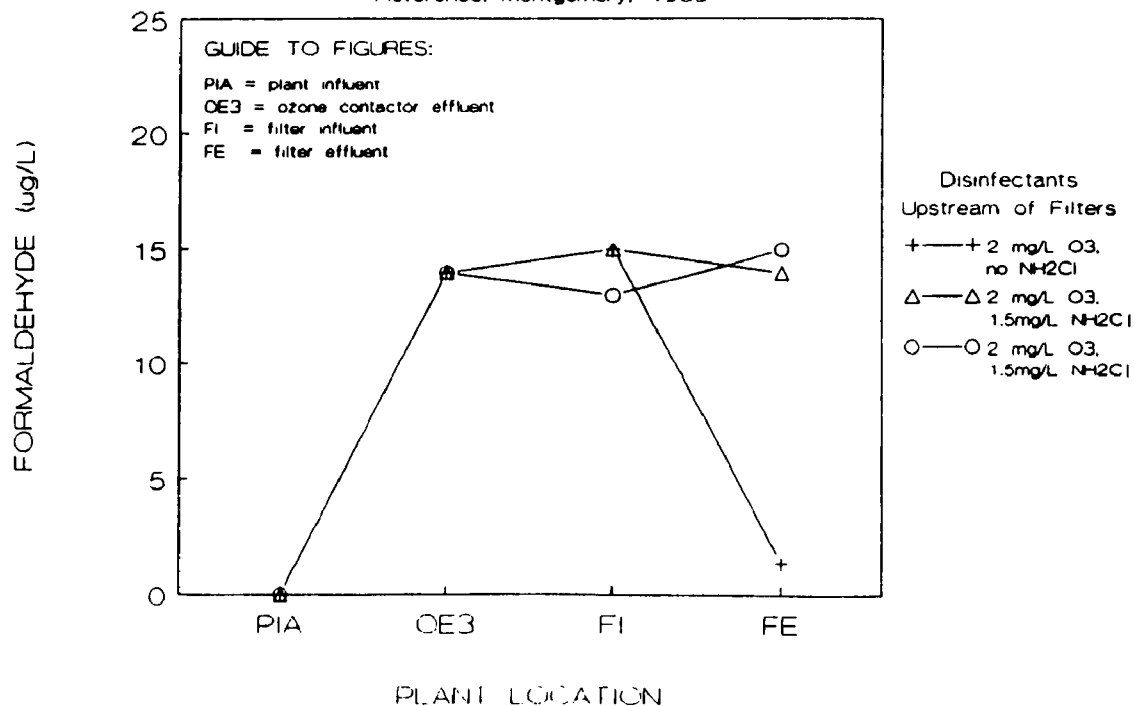
FIGURE 6-15

CHANGE IN FORMALDEHYDE CONCENTRATION
THRU PROCESS TRAIN, COLORADO RIVER WATER
Reference: Montgomery, 1989

GUIDE TO FIGURES:

PIA = plant influent
OE3 = ozone contactor effluent
FI = filter influent
FE = filter effluent

Disinfectants
Upstream of Filters

+——+ 2 mg/L O3,
no NH2Cl

△——△ 2 mg/L O3,
1.5mg/L NH2Cl

O——O 2 mg/L O3,
1.5mg/L NH2Cl

PLANT LOCATION
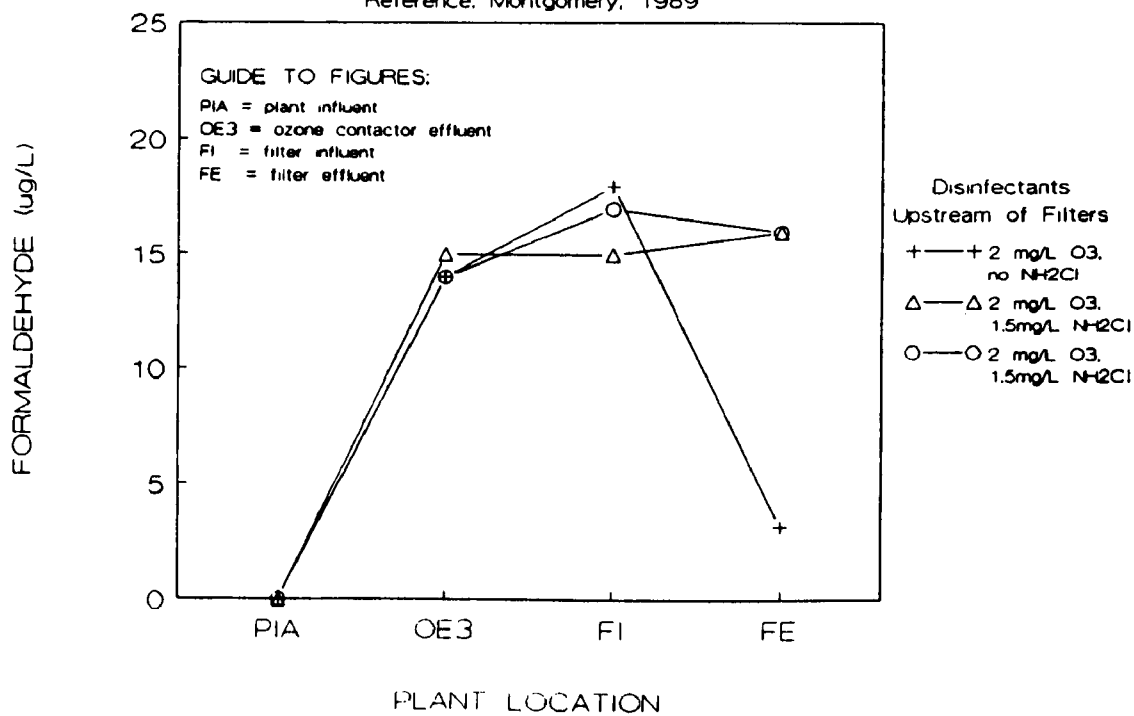
FIGURE 6-16

Effect Of Cl2, Cl2/NH3 & O3/NH3/CL2 on DBP Formation (Utility 7)
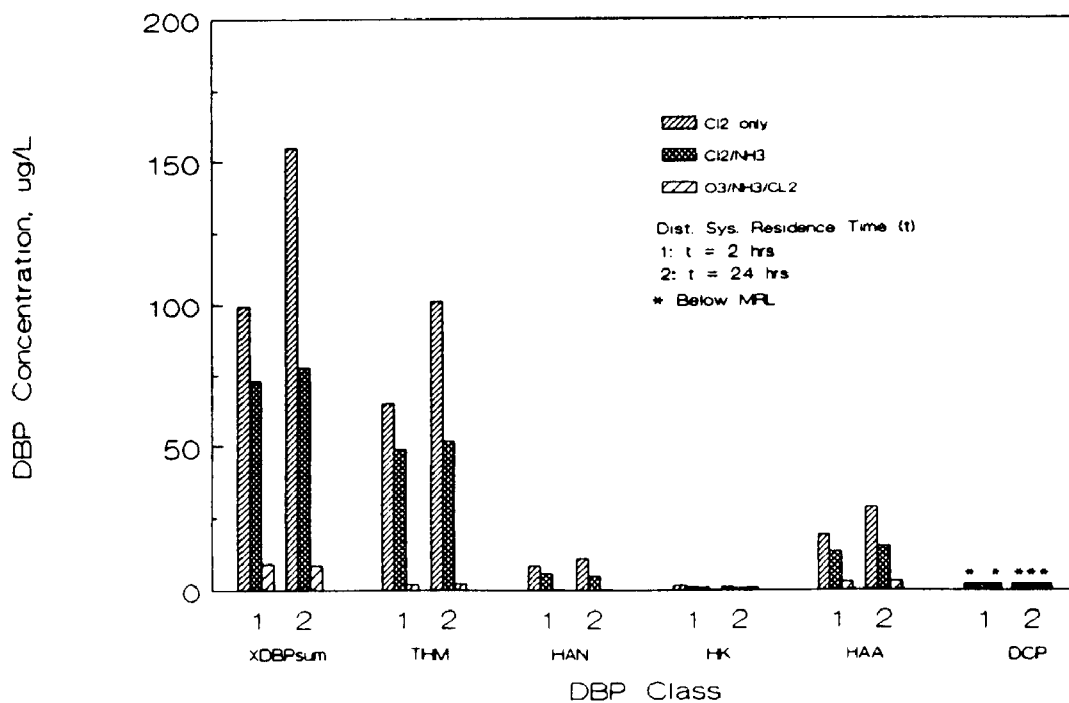
FIGURE 6-17

Effect Of Cl2, Cl2/NH3 & O3/NH3/CL2 on THM Formation (Utility 7)
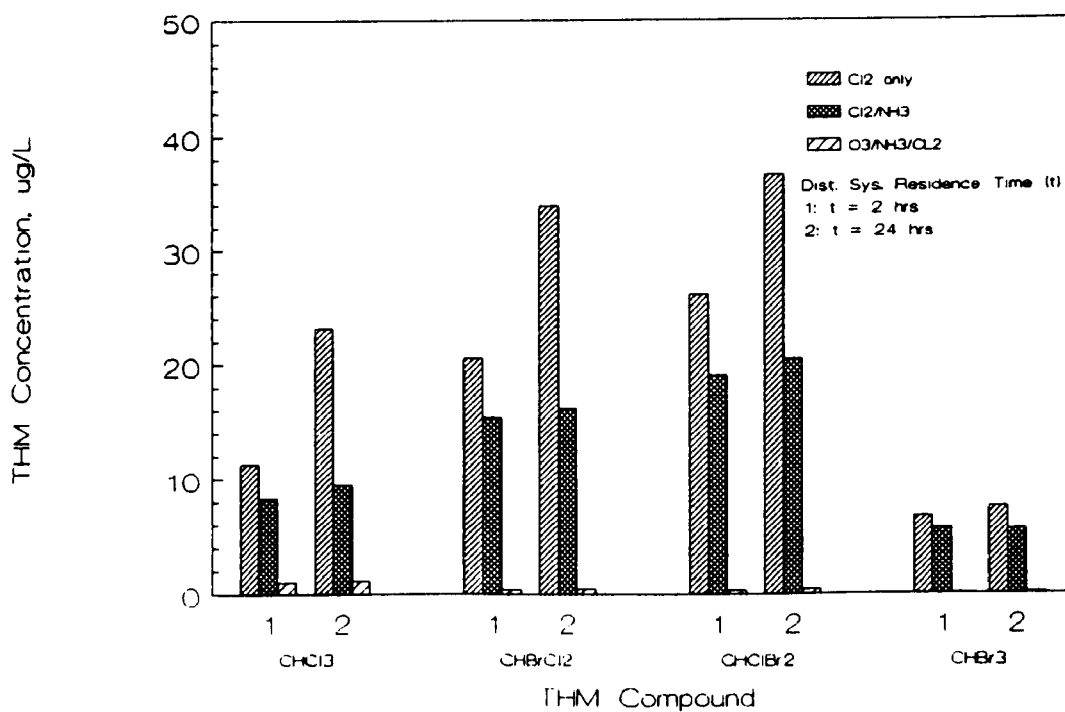
FIGURE 6-18

Effect Of Cl2, Cl2/NH3 & O3/NH3/Cl2 on HAN Formation (Utility 7)
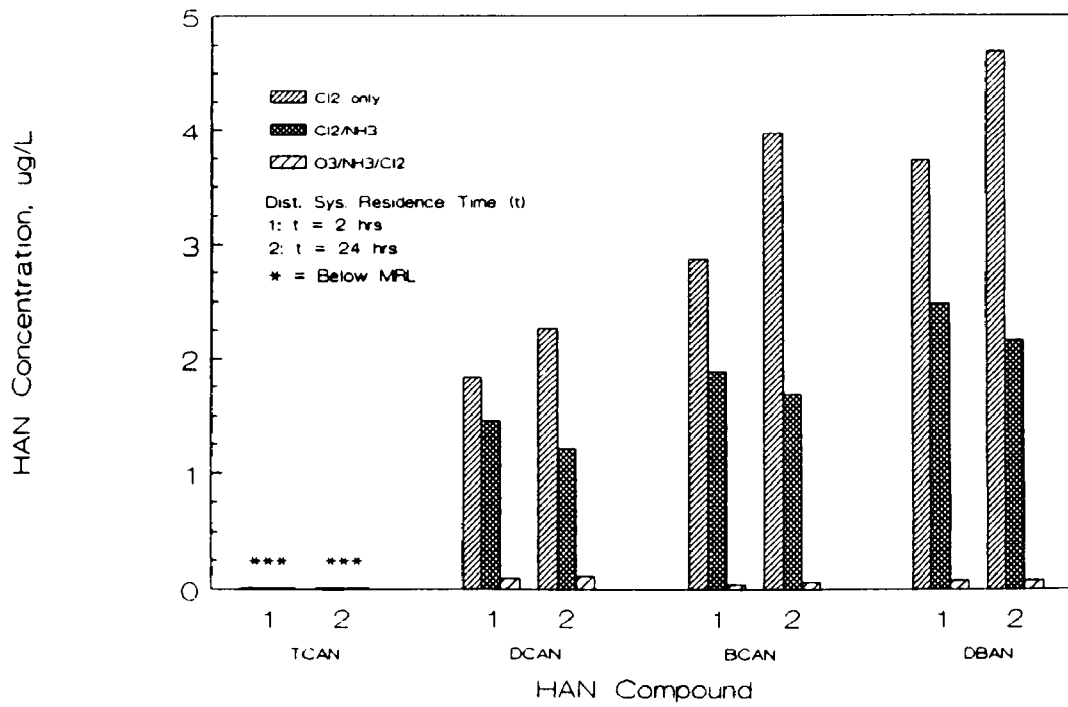
FIGURE 6-19

Effect Of Cl2, Cl2/NH3 & O3/NH3/Cl2 on HK Formation (Utility 7)
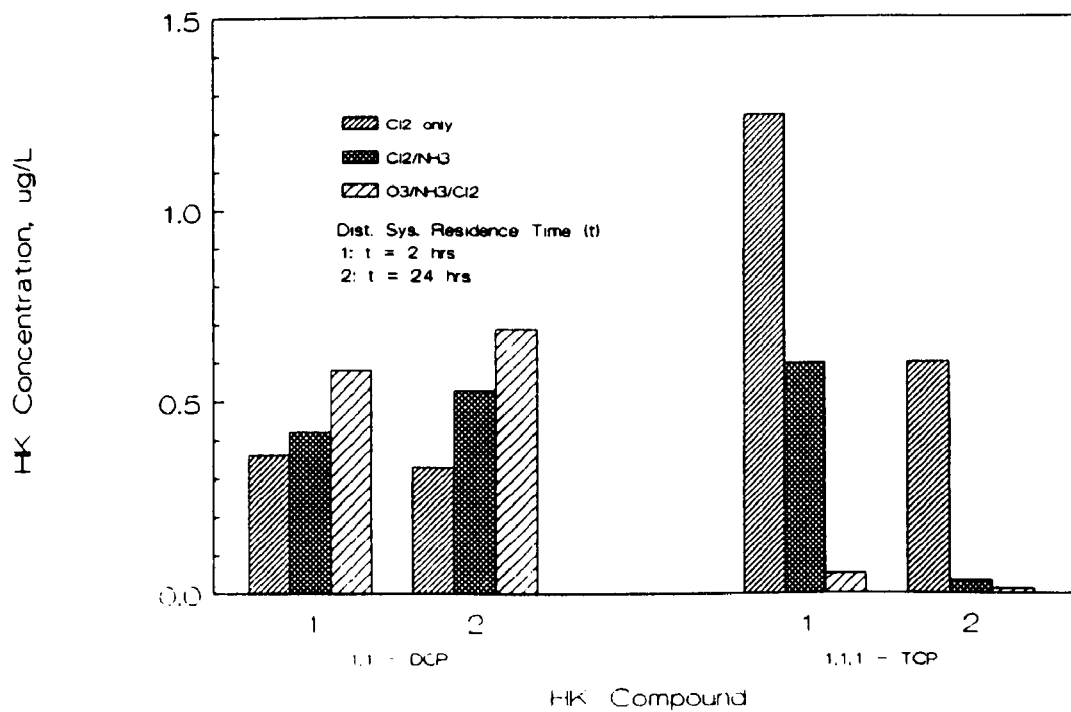
FIGURE 6-20

Effect Of Cl2, Cl2/NH3 & O3/NH3/Cl2 on HAA Formation (Utility 7)
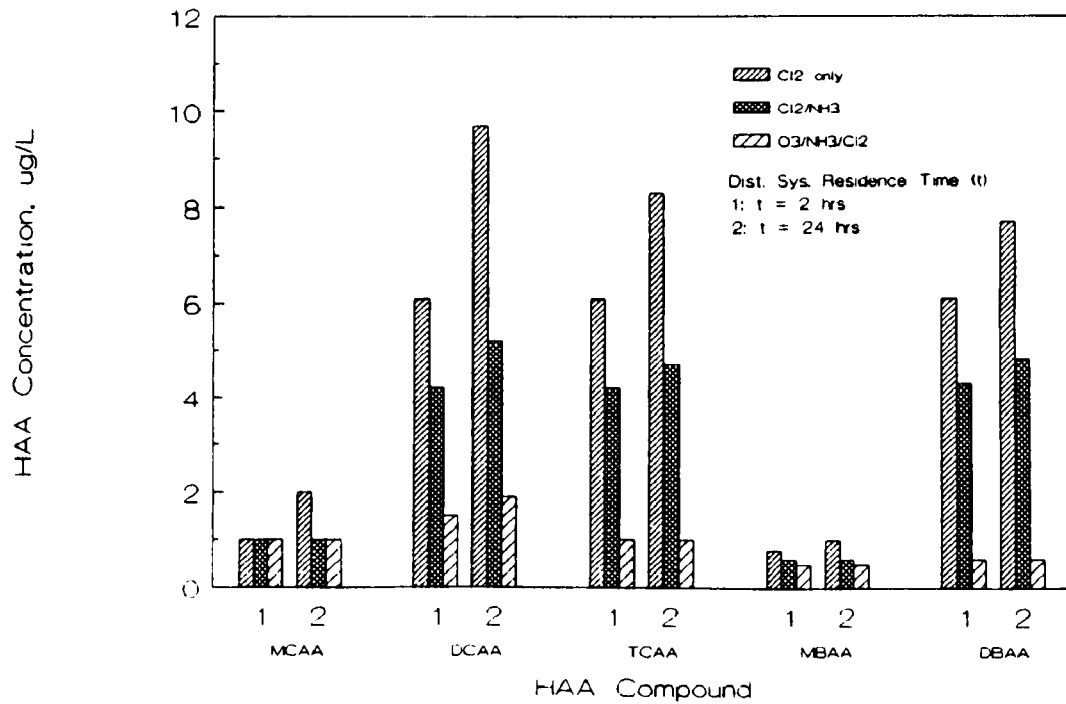
FIGURE 6-21

Effect Of Cl2, Cl2/NH3 & O3/NH3/Cl2 on Misc. DBP Formation (Utility 7)
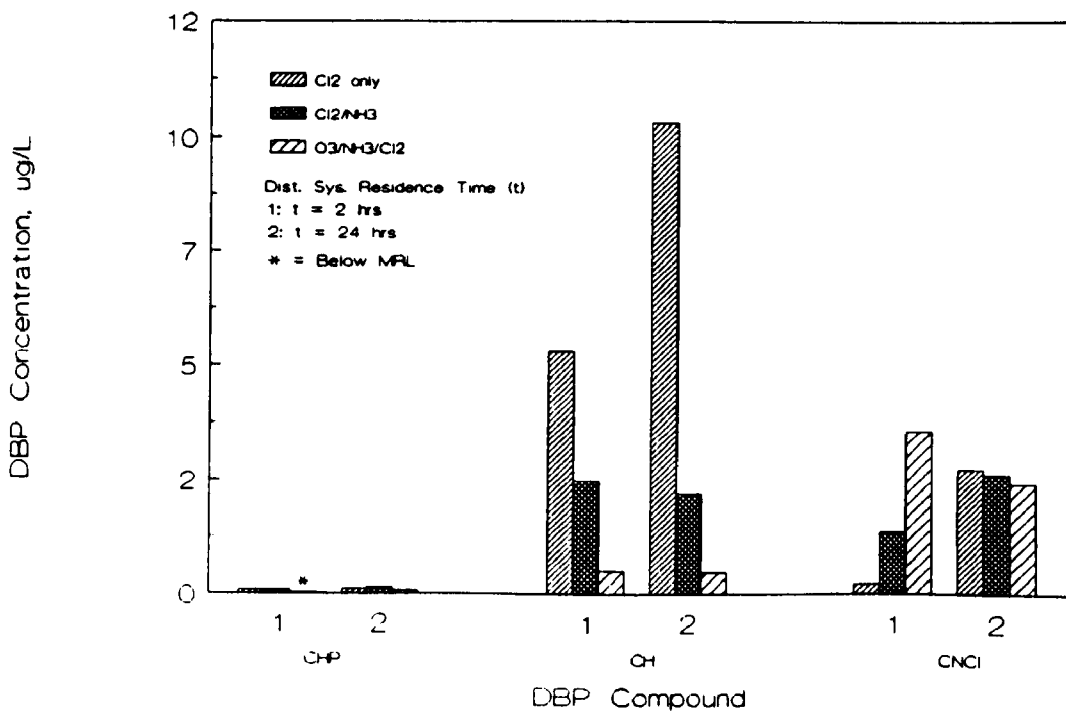
FIGURE 6-22

CHLORINE ONLY

Ferric Chloride
Polymer
Chlorine

Chlorine ———▶

OZONE / CHLORINE

Ferric Chloride
Polymer
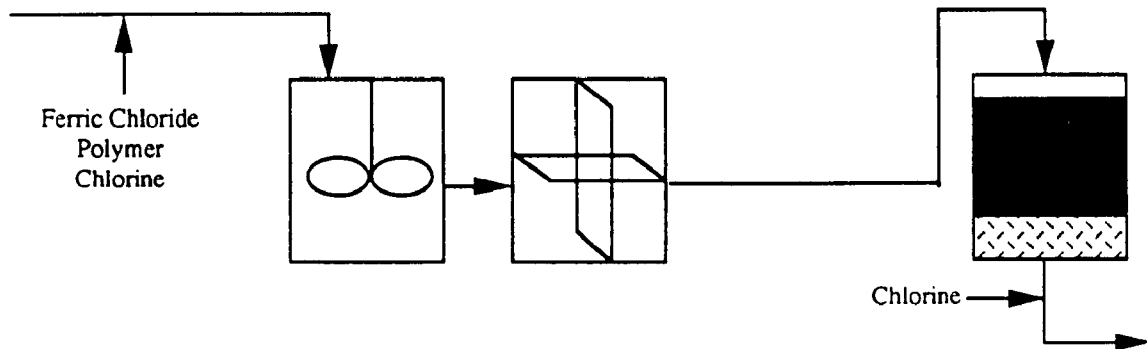
Chlorine -
Intermittent *
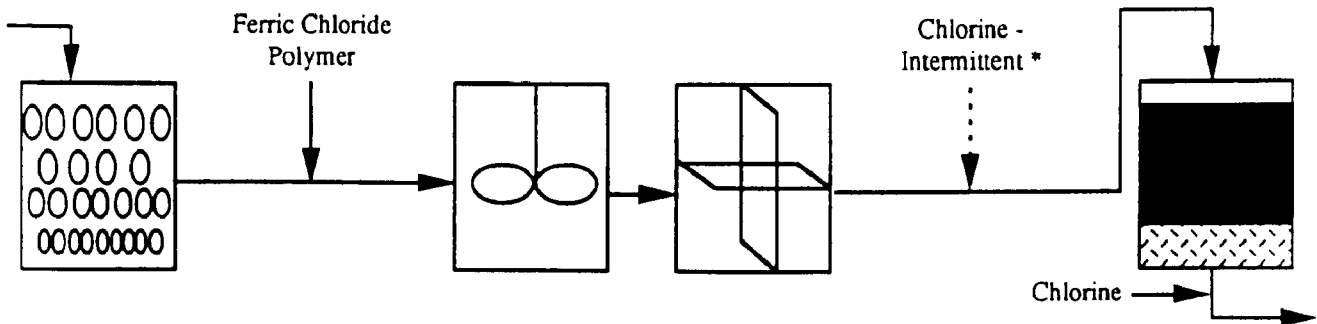
Chlorine ———▶

SCHEMATIC OF UTILITY 19 TREATMENT PROCESSES

FIGURE 6-23

* Chlorine was not added at this point on day of sampling.

100 percent Los Angeles Aqueduct (LAA) water for five days with doses on the day of sampling of 1.8 and 0.3 mg/L, respectively. On the fifth day, samples were collected at predetermined points: at the clearwell effluent and in the distribution system at residence times of 4.3 and 11 hours. When preozonation was reinstated, prechlorination was stopped and an ozone dose of 1.3 mg/L was applied; a post-chlorine dose of 1.0 mg/L was used. However, during this ozone/chlorine treatment, the treatment plant was using 78 percent LAA water/22 percent State Project water (SPW). Therefore the ozone/chlorine treatment was repeated when the plant was utilizing 100 percent LAA water. At that time, an ozone dose of 1.7 mg/L was applied and a 1.5 mg/L post-chlorine dose was used. The chlorine residuals at the sampling locations, as well as other water quality parameters, are shown in Table 6-4. Free and total chlorine residuals and TOC concentrations were similar in the "before" and "after" samplings when 100 percent LAA water was treated. The temperature for the chlorine-only samples was slightly lower. The blended water had a higher TOC level, since SPW has a higher TOC than LAA water.

Figures 6-24 and 6-25 present concentrations of DBP classes and the miscellaneous DBPs. All data are presented after 11 hours of residence time in the distribution system and represent only the 100 percent LAA water samplings. As shown in Figure 6-24, decreases of 13 μg/L and 8.7 μg/L were observed for TTHMs and HAAs, respectively, after ozone implementation with subsequent chlorination. A 2.3 μg/L increase in chloral hydrate was observed. The effect of ozonation on HANs, HKs and chloropicrin formation is shown in Figure 6-25. After ozone addition, the concentration of HANs was reduced by 1.2 μg/L, while small increases were observed for HKs and chloropicrin. Cyanogen chloride analysis was not performed during the ozonation trial; it was only detected at levels equal to or slightly above the MDL during the chlorine-only experiment. Changes in TOX concentrations before and after ozonation are presented in Table 6-4. For the 100 percent LAA water studies at the 11-hour residence time samplings, a decrease in TOX of 62 μg/L was observed after ozonation was applied.

Figures 6-26 to 6-31 present the data for the treatment modification study in relation to residence time in the distribution system. Levels of XDBP classes and individual DBPs are shown at the three different distribution system residence times: 0 hours (clearwell effluent), and 4.3 and 11 hours. In addition, ozone/chlorine data are presented when the treatment plant was using 100 percent LAA water versus 78 percent LAA water/22 percent SPW. In general, the data show that all DBPs increased with increasing residence time except for 1,1-DCP and cyanogen chloride.

Figure 6-26 shows that when only LAA water was used, decreases were observed in the DBP class totals for THMs, HAAs and HANs with ozone implementation. However, as shown in Figures 6-27 to 6-29, the di- and tri-brominated species of these DBP classes increased with ozonation. Although the level of total HAAs decreased with ozone implementation by approximately 50 percent at the 11-hour residence time sample point, the level of DBAA increased by more than 100 percent. At Utility 19, bromide was not assayed at the time of the study; however, 0.04 mg/L was detected in a subsequent sampling of the same raw water source.

The change in source water from 100 percent LAA water to a blend with SPW further shows the effect of bromide on concentrations of DBPs produced by ozonation followed

TABLE 6-4

UTILITY 19 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	Pre-Ozone Dose (mg/L)	Chlorine Dose Pre, Post (mg/L)	TOX (μg/L)	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)	pH	Temp. (°C)
Clearwell Effluent								
O_3/Cl_2[a]	1.50	1.3	0.0, 1.0	73	0.7	0.9	8.1	17.5
O_3/Cl_2[b]	1.22	1.7	0.0, 1.5	68	1.1	1.2	8.1	18
Cl_2[b]	1.20	0.0	1.8, 0.3	140	1.0	.15	8.1	15.2
Distr. Pt. 1 (4.25 hours)								
O_3/Cl_2[a]	1.48	1.3	0.0, 1.0	100	0.68	0.71	7.7	16.8
O_3/Cl_2[b]	1.20	1.7	0.0, 1.5	79	1.0	1.0	8.1	19.0
Cl_2[b]	1.25	0.0	1.8, 0.3	140	0.92	1.00	7.9	15.0
Distr. Pt. 2 (11 hours)								
O_3/Cl_2[a]	1.56	1.3	0.0, 1.0	92	0.55	0.68	7.8	16.8
O_3/Cl_2[b]	1.21	1.7	0.0, 1.5	88	0.52	0.54	8.2	19.5
Cl_2[b]	1.28	0.0	1.8, 0.3	150	0.63	0.68	7.9	15.5

[a]Source water was 78 percent LA Aqueduct water and 22 percent State Project Water.
[b]Source water was 100 percent LA Aqueduct water.

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY—PRODUCT FORMATION AT UTILITY 19
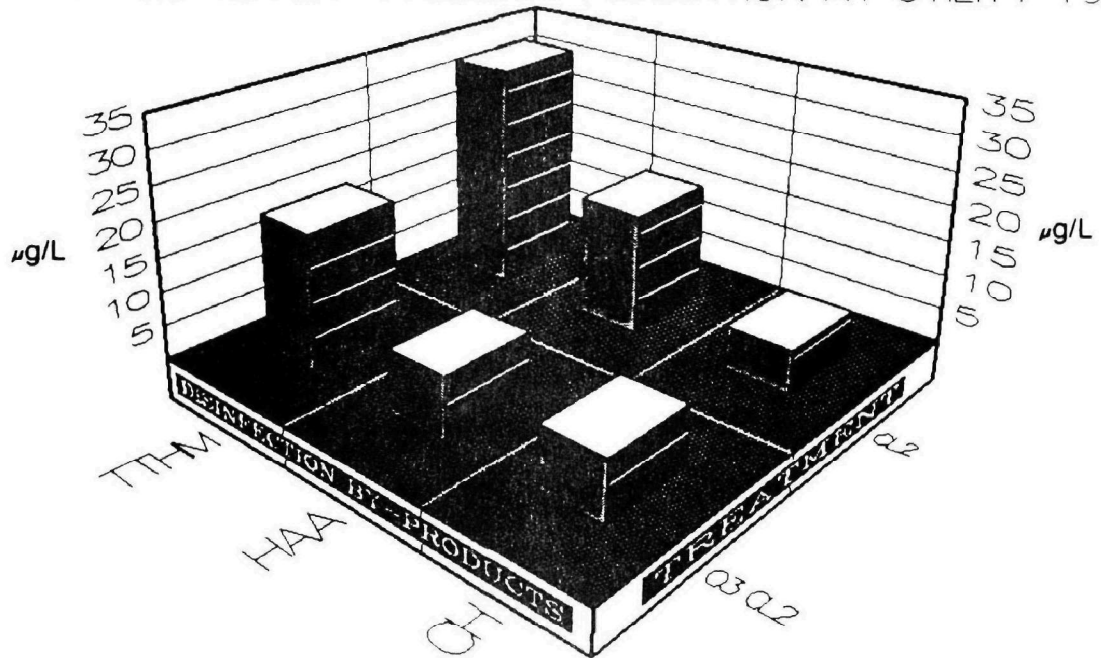
FIGURE 6-24

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
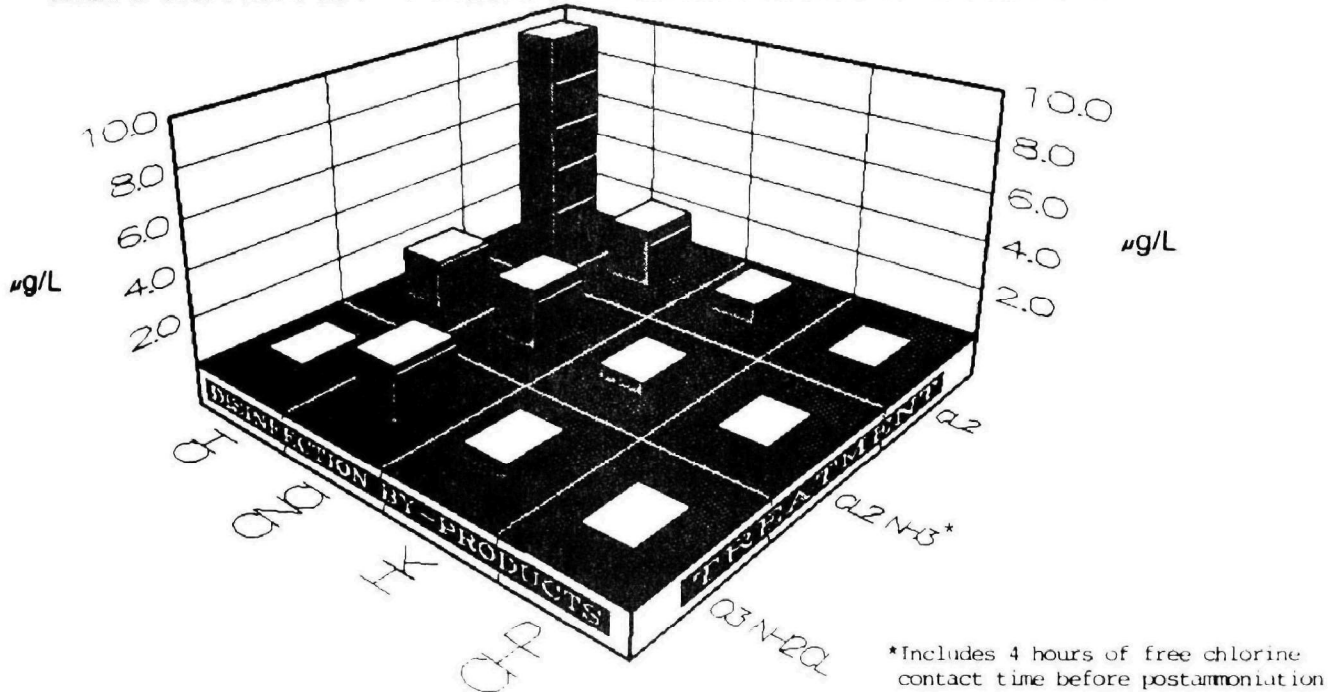DISINFECTION BY—PRODUCT FORMATION AT UTILITY 19
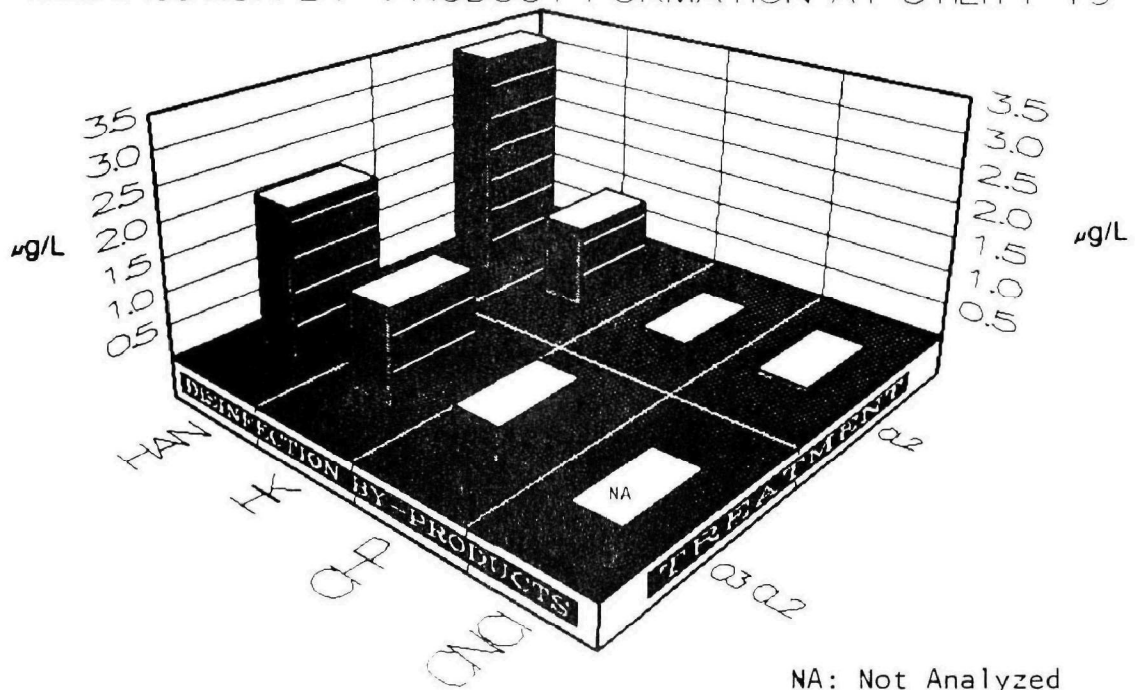
NA: Not Analyzed

FIGURE 6-25

Effect of O3/Cl2 & Cl2 Only on
DBP Formation (Utility 19)
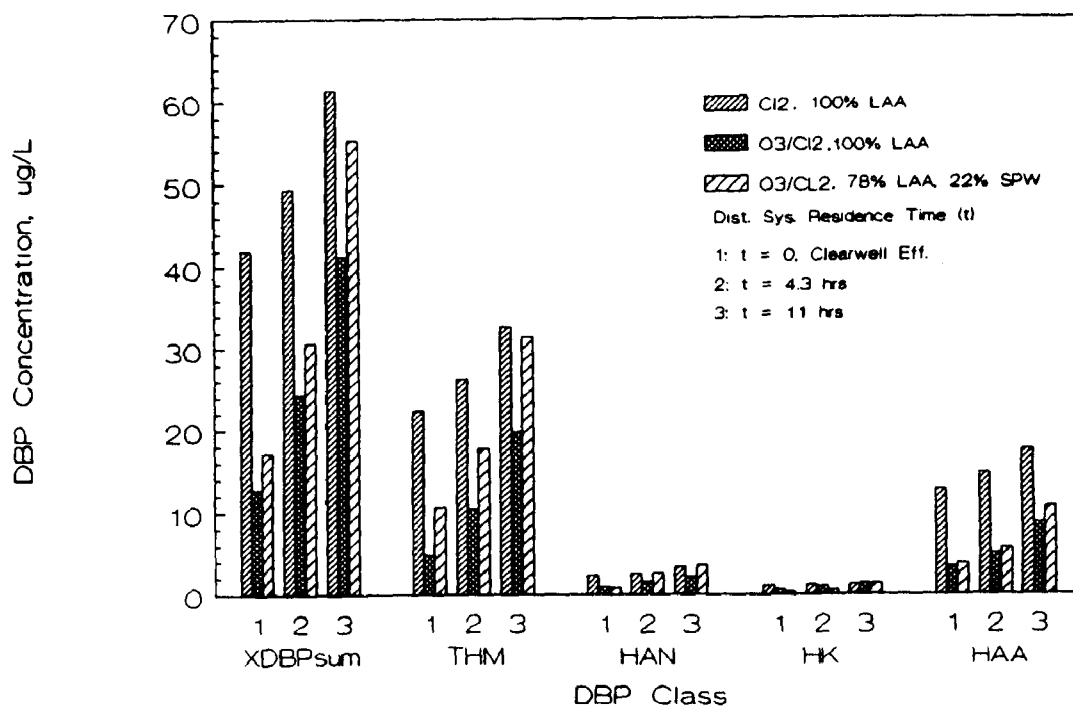
FIGURE 6-26

Effect of O3/Cl2 & Cl2 Only on
THM Formation (Utility 19)
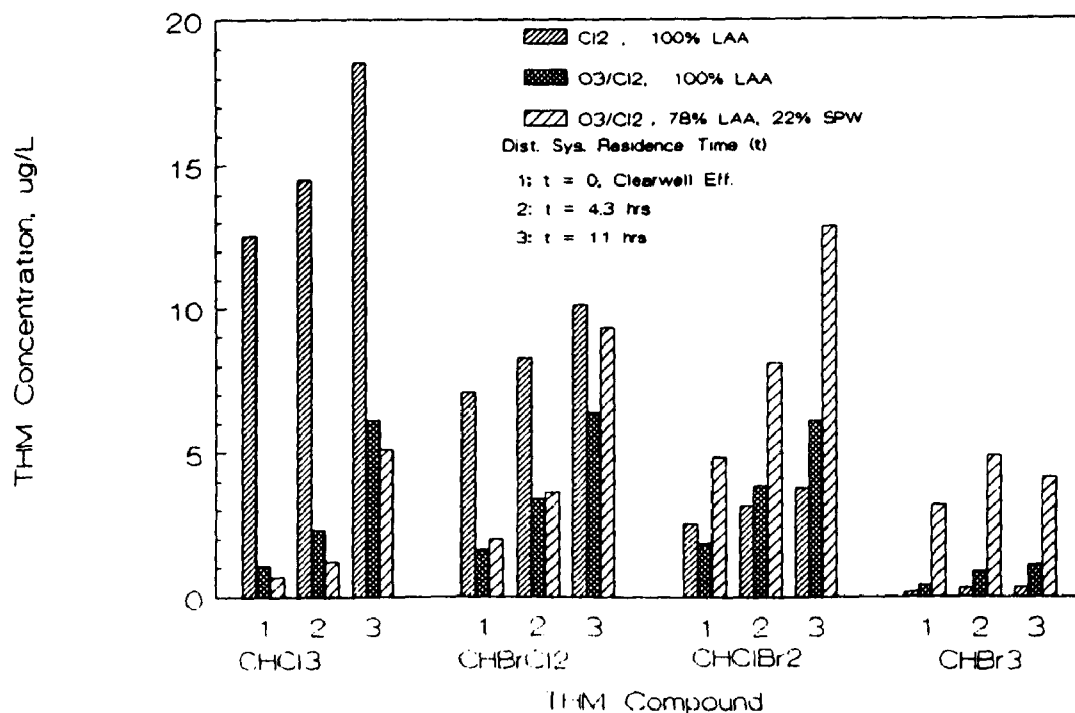
FIGURE 6-27

Effect of O3/Cl2 & Cl2 Only on HAA Formation (Utility 19)
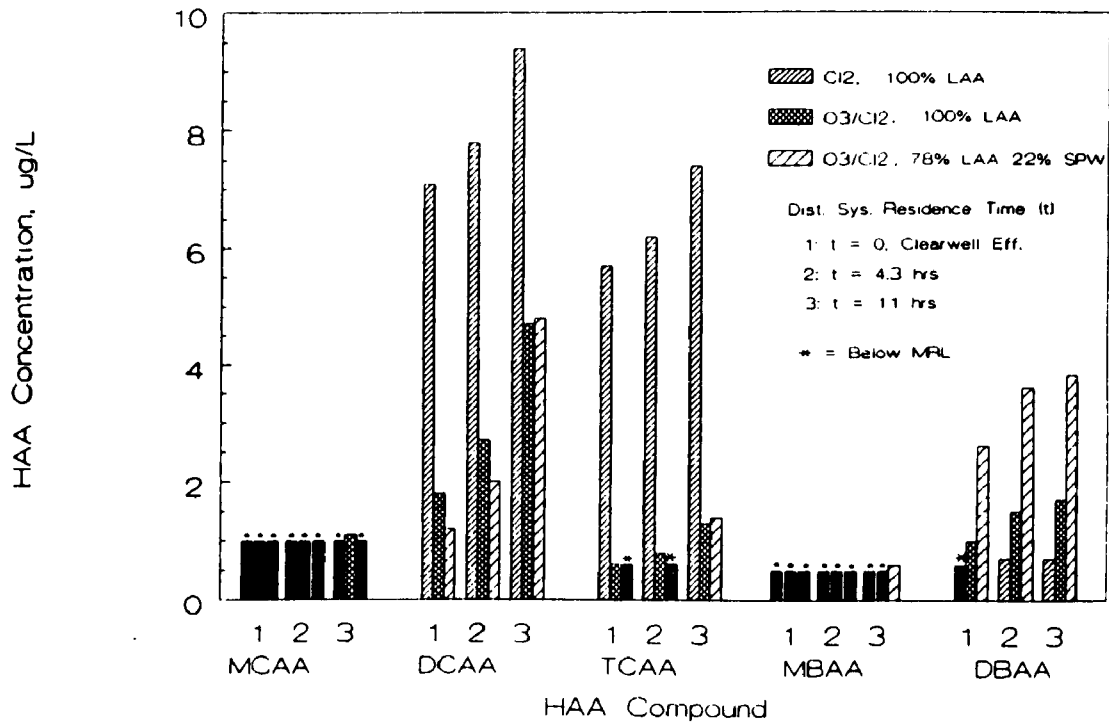
FIGURE 6-28

Effect of O3/Cl2 & Cl2 Only on HAN Formation (Utility 19)
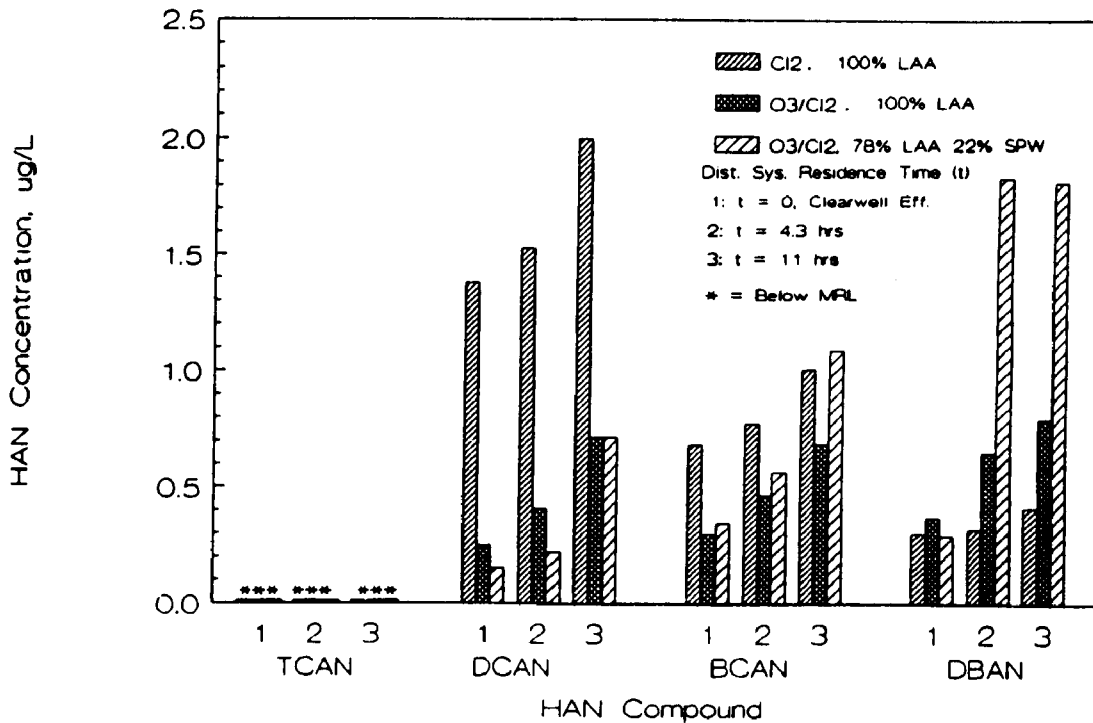
FIGURE 6-29

Effect of O3/Cl2 & CL2 Only on HK Formation (Utility 19)
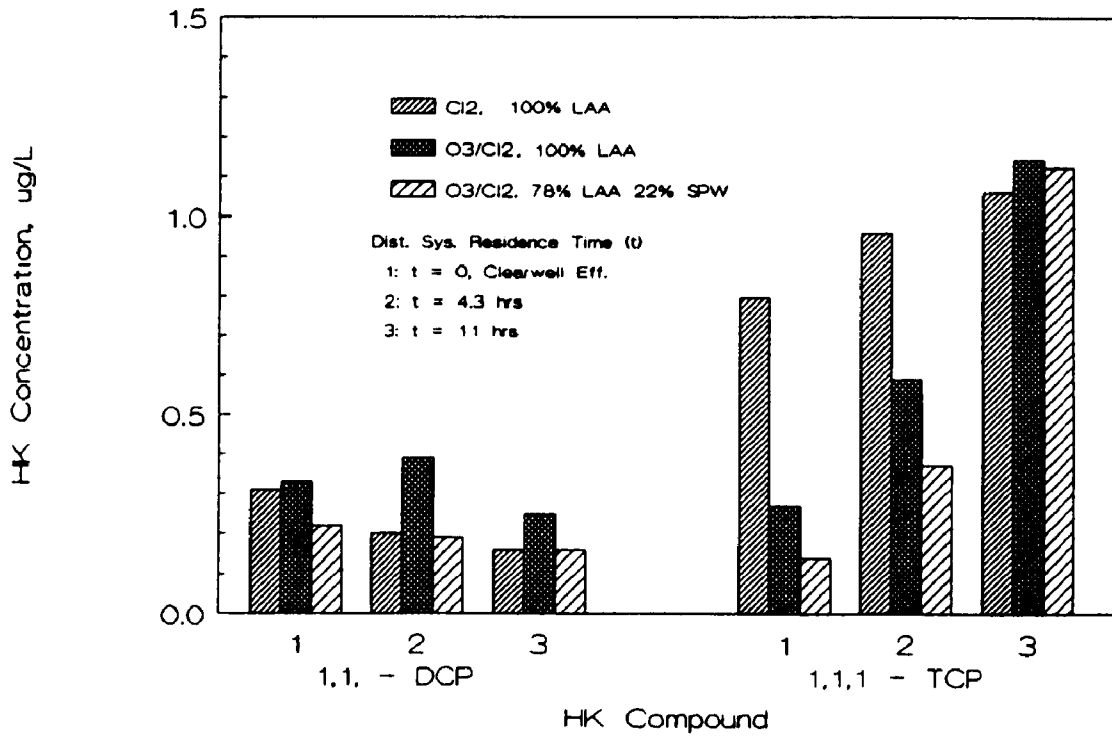
FIGURE 6-30

Effect of O3/Cl2 & Cl2 Only on Misc. DBP Formation (Utility 19)
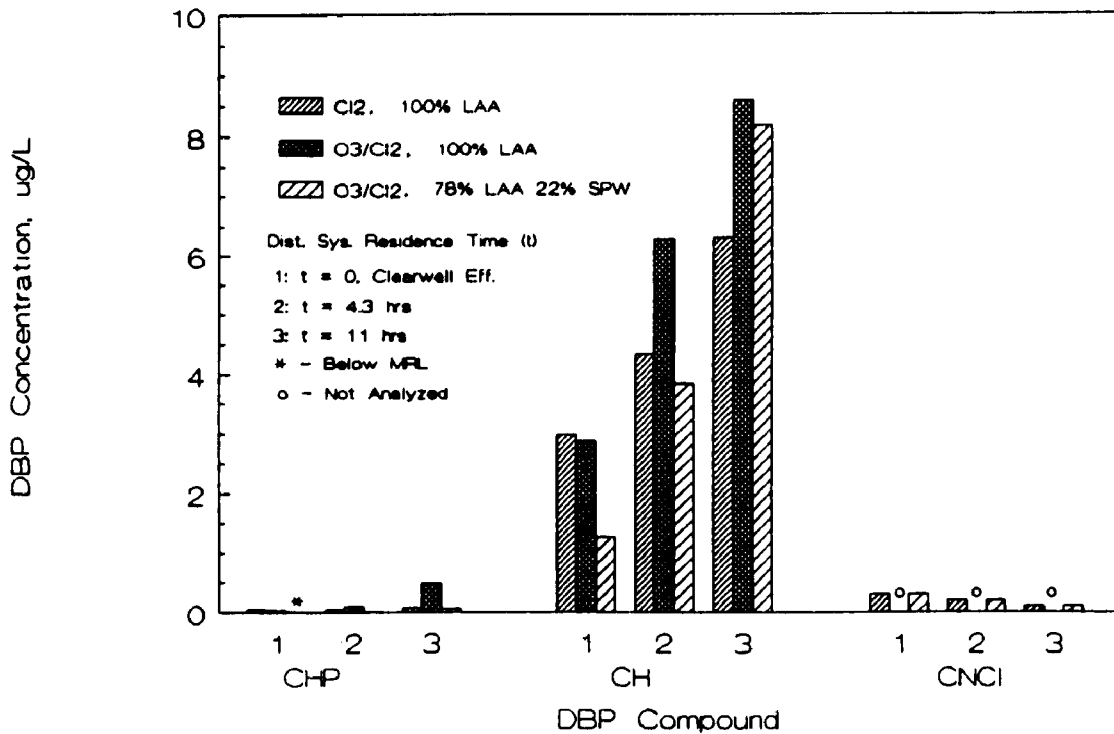
FIGURE 6-31

by chlorination. A comparison of the two shows that when SPW was employed, a shift to increasing concentration of the brominated species occurred. Although bromide was not measured during this treatment scenario, a subsequent sample of a blend of 74 percent LAA water and 26 percent SPW showed that the bromide level had increased to 0.1 mg/L. These data are consistent with those discussed in Section 5 regarding Utility 12, where seasonal shifts in bromide concentrations promoted increases in some brominated DBPs. In addition, ozone can react with bromide ions in the raw water, causing the formation of hypobromous acid (HOBr) (Dore et al., 1988). Reactions of HOBr with natural organic material can produce bromoform and other brominated DBPs, as evidenced at Utility 19.

Utility 25

Sampling at Utility 25 was conducted at full scale at a conventional treatment plant with a capacity of 90 mgd. A schematic of the plant before and after the implementation of ozonation is presented in Figure 6-32. Samples were collected before the plant went online with two-stage ozonation. During this period, concurrent addition of ammonia (1.6 mg/L) and chlorine (8.0 mg/L) was practiced at the rapid mix; there were no other points of disinfectant addition. Sampling of ozonated water was conducted seven days after the plant switched to routine operation of ozonation to insure that the distribution system was well-flushed with ozonated water. The oxidant was applied to both raw and settled water at 4 mg/L per stage, and chlorine (5.0 mg/L) and ammonia (1.0 mg/L) were added concurrently prior to filtration. Both before and after ozone implementation, samples were collected at various points in the plant and distribution system. Water quality parameters of the raw water and at the various sampling points are shown in Table 6-5.

The effects of the treatment modification on concentrations of DBPs for this utility are shown in Figures 6-33 and 6-34. In these plots, data from Location 4 in the distribution system (residence time of 18 to 20 hours) are employed. The DBP classes with the highest concentrations when chloramines-only were employed were TTHMs and HAAs. It should be noted, though, that the total chlorine dose and residual concentrations were higher during this sampling than during the ozone study. Despite concurrent addition of chlorine and ammonia, Figure 6-33 shows that under the chloramines-only scheme, the TTHM and HAA concentrations were relatively high, both being 44 μg/L. This is in contrast to the study at Utility 36 which showed that the chloramines-only scenario was very effective in limiting the formation of these compounds. The relatively high levels of these DBP classes at Utility 25 were probably a result of some free chlorine contact time due to inadequate mixing and/or the high raw water TOC concentration (7.7 mg/L).

Concentrations of TTHMs and HAAs were reduced to 6.7 μg/L and 15 μg/L, respectively, after the treatment modification was implemented. Concentrations of the measured aldehydes increased from 10 to 57 μg/L with the switch to ozone. Figure 6-34 shows that the ozone/chloramines treatment slightly decreased the concentration of chloral hydrate and HANs as compared to chloramines only; however, small increases were observed for HKs, cyanogen chloride and chloropicrin. Finally, Table 6-5 shows that TOX decreased by 89 μg/L when ozone treatment was implemented.

CHLORAMINES ONLY

Polymer
Alum
Chlorine
Ammonia

Lime

OZONE / CHLORAMINES

Polymer
Alum

Lime
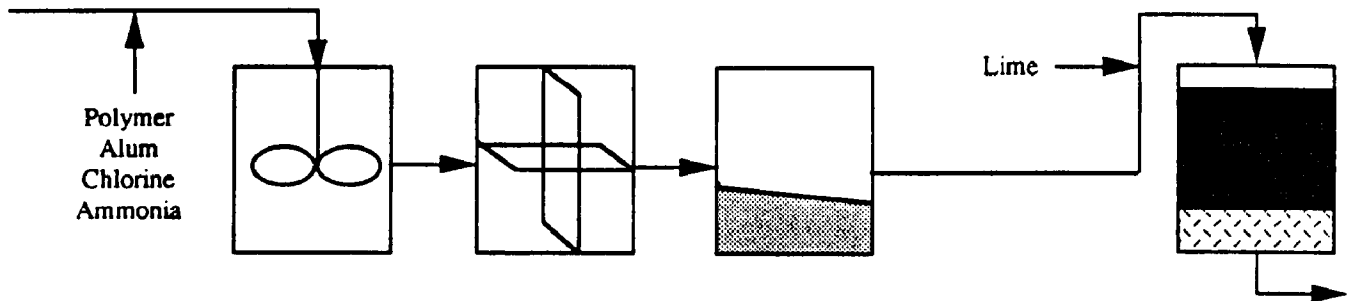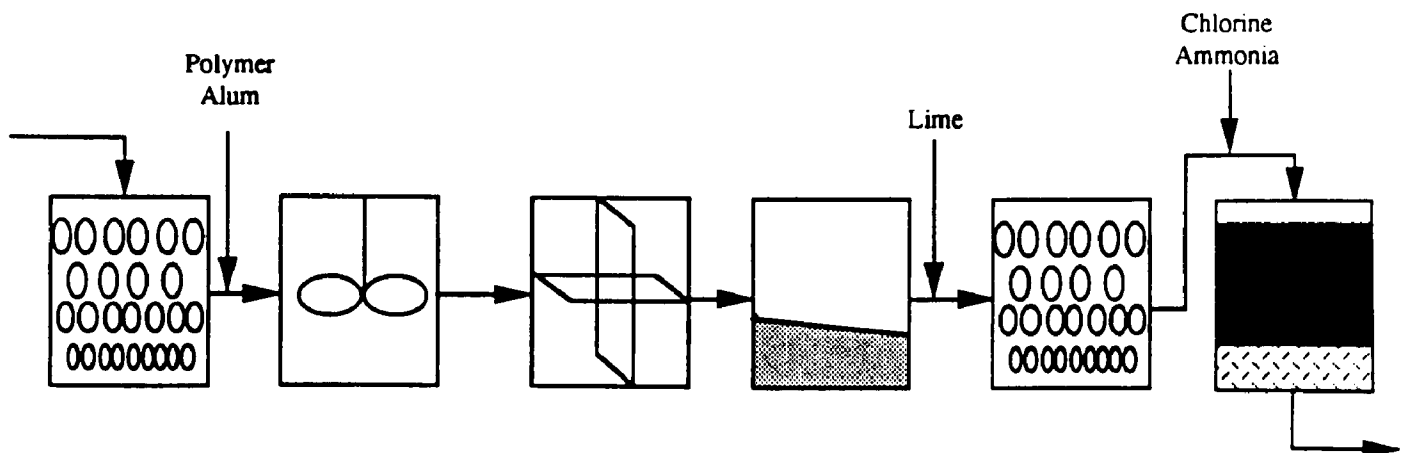
Chlorine
Ammonia

SCHEMATIC OF UTILITY 25 TREATMENT PROCESSES

FIGURE 6-32

TABLE 6-5

UTILITY 25 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	UV Absorbance at 254 nm (cm^{-1})	Chloride (mg/L)	Bromide (mg/L)	TOX (μg/L)	pH	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)
CONVENTIONAL								
Raw	7.72	0.255	34	0.22	20	8.3	NA	NA
Filter Influent[1]	4.63	0.096	NA	NA	180	7.3	NA	4.0
Filter Effluent[1]	4.63	0.081	NA	NA	200	8.1	NA	4.0
Clearwell Effluent	4.85	0.095	NA	NA	170	9.0	NA	3.5
Location 1	4.67	0.087	NA	NA	150	9.0	0.1	2.9
Location 2	4.72	0.091	NA	NA	140	8.9	0.1	3.2
Location 3	4.69	0.086	NA	NA	150	8.9	0.1	3.5
Location 4	4.76	0.088	NA	NA	150	9.0	0.1	3.5
OZONE								
Raw	8.01	0.233	34	0.23	NA	NA	NA	NA
2nd O$_3$ Contactor Inf.	5.47	0.054	NA	ND	29	9.8	NA	ND
Filter Influent	5.25	0.067	NA	ND	57	9.2	NA	2.7
Filter Effluent	5.06	0.041	NA	ND	65	9.2	NA	2.7
Clearwell Effluent	5.23	0.046	NA	ND	67	9.4	NA	2.2
Location 1	5.65	0.050	NA	ND	64	9.2	NA	1.8
Location 2	5.48	0.049	NA	ND	56	9.3	NA	1.2
Location 3	5.44	0.053	NA	ND	64	9.4	NA	1.3
Location 4	5.51	0.047	NA	ND	61	9.3	NA	1.1

[1] No lime added
NA = Not Analyzed
ND = Not Detected
Note: Temperature for all studies ranged from 26.0 to 30.0°C.
Locations represent distribution system sampling points in order of increasing residence time.

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY—PRODUCT FORMATION AT UTILITY 25
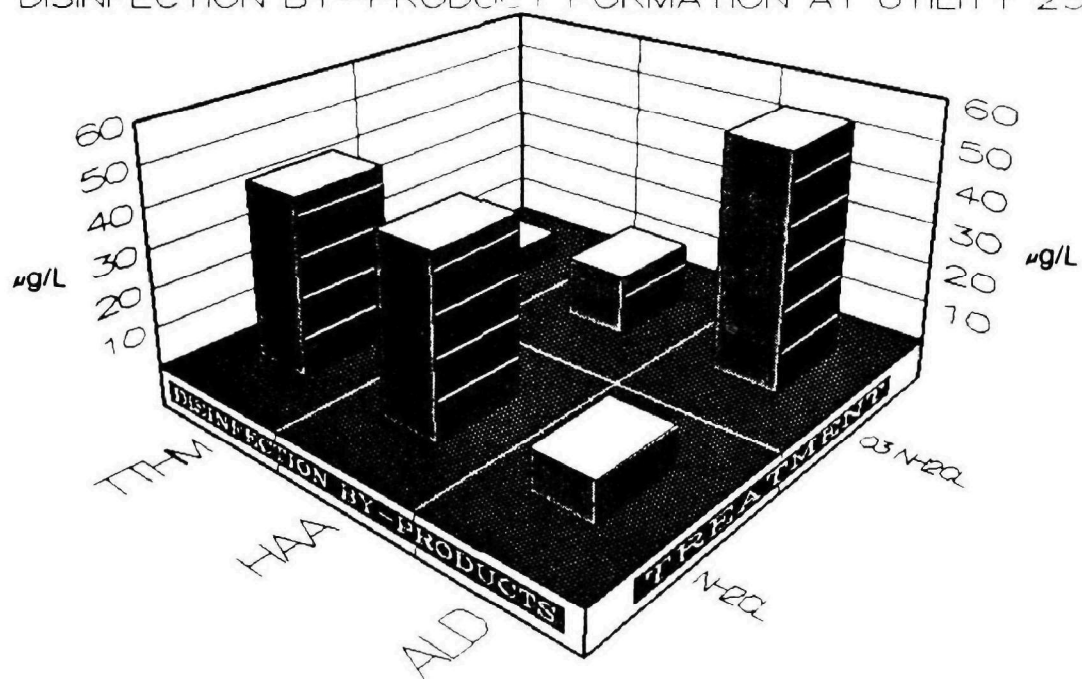
FIGURE 6-33

EFFECT OF VARIOUS DISINFECTION SCHEMES ON
DISINFECTION BY—PRODUCT FORMATION AT UTILITY 25
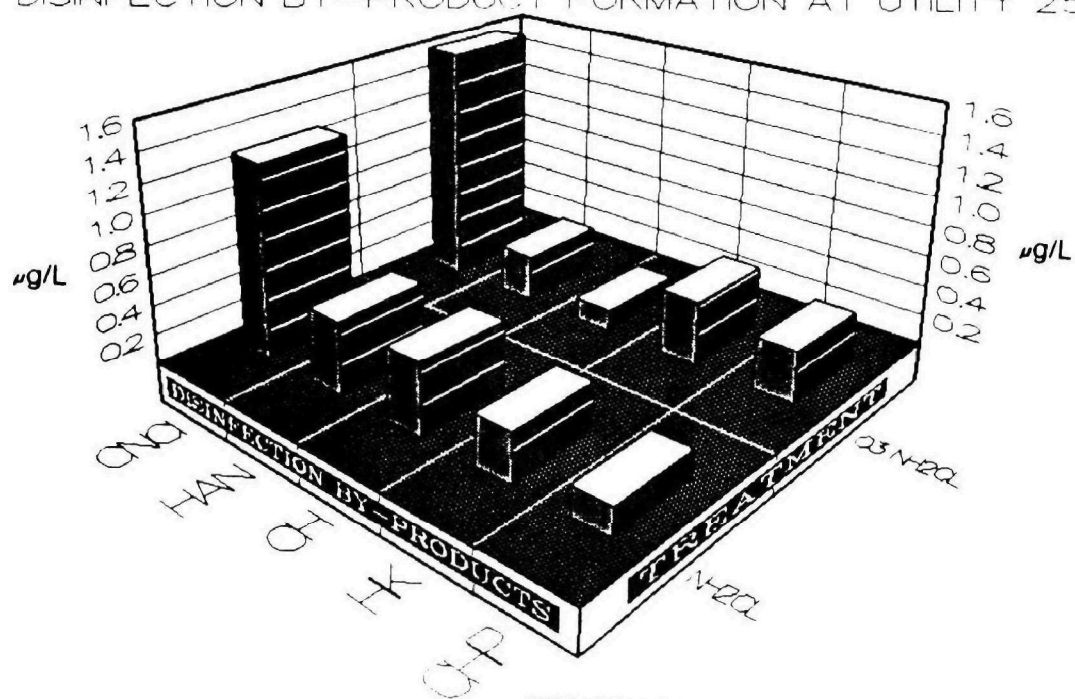
FIGURE 6-34

Treatment Modification Results and Discussion

Stability of DBPs Through the Plant and Distribution System. Figures 6-35 to 6-45 show a profile of DBPs through the treatment plant and at four locations in the distribution system. Explanations of abbreviations used in the figures and distribution system residence times at the point of sampling are presented in Table 6-6. During the sampling for conventional treatment, the plant temporarily went offline and lime was not applied immediately after startup. The filter influent and filter effluent samples were collected after the plant startup, so these samples had abnormally low pH values (7.3 and 8.1, respectively, as compared to 8.9 to 9.0 at the distribution system sampling points which represents water produced when lime addition was underway) as shown in Table 6-5.

Figures 6-35 to 6-39 present the DBP profiles for $XDBP_{sum}$, THMs, HAAs, DCAA and chloropicrin. The data show that for both treatment scenarios, the DBPs were formed immediately after chlorine and ammonia addition and remained stable through the plant and into the distribution system. During the ozonation study, some low levels of DBPs were detected in the second-stage ozone influent. It is believed that some minimal level of chlorine or chloramines was added in the treatment train prior to this sampling point.

DBP profiles of HANs, HKs, and chloral hydrate are depicted in Figures 6-40 to 6-42. In each case, during the chloramines-only treatment scenario, higher concentrations were found in the filter influent and filter effluent than in the clearwell effluent or distribution system. As noted above, the pH values were 0.8 to 1.7 units lower for these two sampling points during the chloramine-only study because of a temporary discontinuation of lime addition. The data suggest that at the higher pH values these compounds are unstable and break down to other final products. As discussed in Section 5, other researchers have reported that HANs and HKs were reactive intermediates rather than stable endproducts such as THMs and HAAs (Reckhow and Singer, 1985). They also found that with increasing pH, DCAN and 1,1,1-TCP underwent hydrolysis. Likewise, Miller and Uden (1983) found that chloral hydrate decomposed at elevated pH. When ozonation was applied, smaller concentrations of these compounds were detected, but similar trends in relation to stability were observed. In each case, concentrations in high pH waters decreased with increasing residence time.

The cyanogen chloride profile (Figure 6-43) indicates that this compound was unstable in Utility 25's distribution system. In contrast, cyanogen chloride increased in Utility 6's distribution system (e.g., from 4.7 μg/L at the clearwell effluent to 9.9 μg/L at location 3 during the chlorine/chloramines study). Both utilities have chloramines as the final disinfectant; however, the pH of Utility 6's distribution system was 7.5 to 8.0. These limited data imply that cyanogen chloride may be unstable at a pH of 9, as evidenced at Utility 25.

Figures 6-44 and 6-45 show the profiles for the aldehyde sum and for formaldehyde only, respectively. In the chloramines-only scenario, these compounds were formed after disinfectant addition and remained relatively stable through the plant and distribution system. In the ozone/chloramines treatment scenario, higher concentrations of aldehydes were detected and a similar stability profile was observed. It should also be noted that these data are consistent with those described above at Utility 6.

TABLE 6-6

EXPLANATION OF ABRREVIATIONS USED IN UTILITY 25 DBP PROFILES AND RESIDENCE TIME OF DISTRIBUTION SYSTEM SAMPLING POINTS

Abbreviation	Explanation
RAW	Plant Influent raw water
2OI	Second stage ozonation influent
FI	Filter Influent
FE	Filter Effluent
CE	Clearwell Effluent
L1	Location 1 in Distribution System (4-5 hours residence time)
L2	Location 2 in Distribution System (8-9 hours residence time)
L3	Location 3 in Distribution System (9-10 hours residence time)
L4	Location 4 in Distribution System (18-20 hours residence time)

Effects of NH2Cl and O3/NH2Cl Treatment on Halogenated DBP Formation, Utility 25
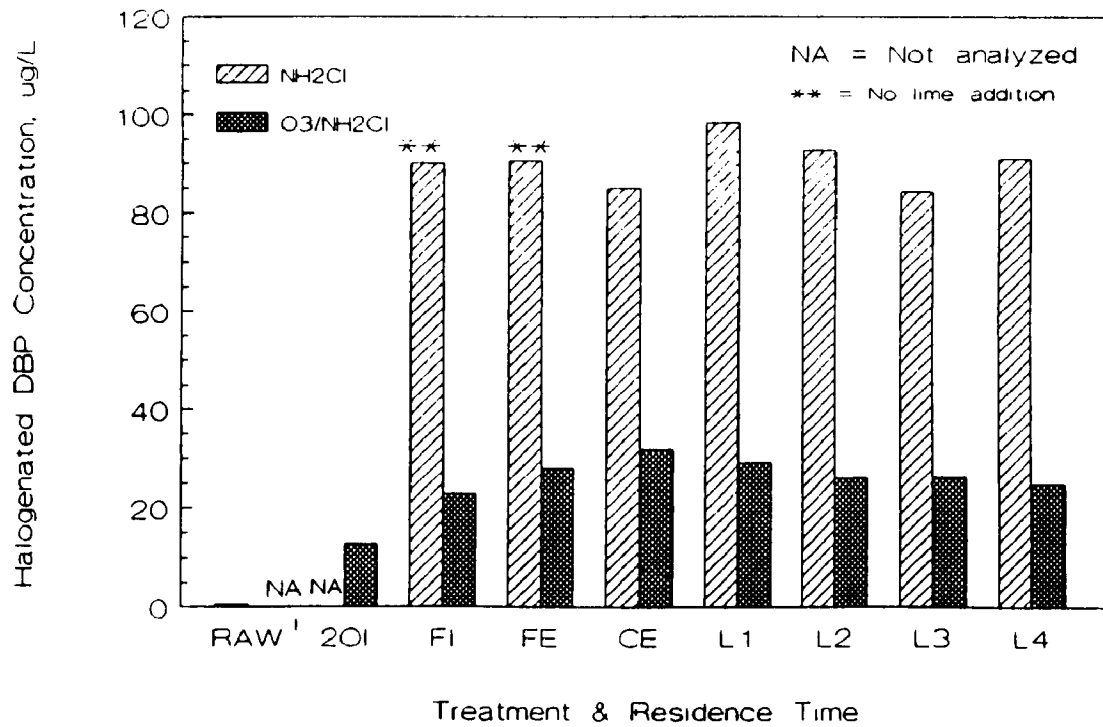
FIGURE 6-35

Effects of NH2Cl and O3/NH2Cl Treatment on Total THM Formation at Utility 25
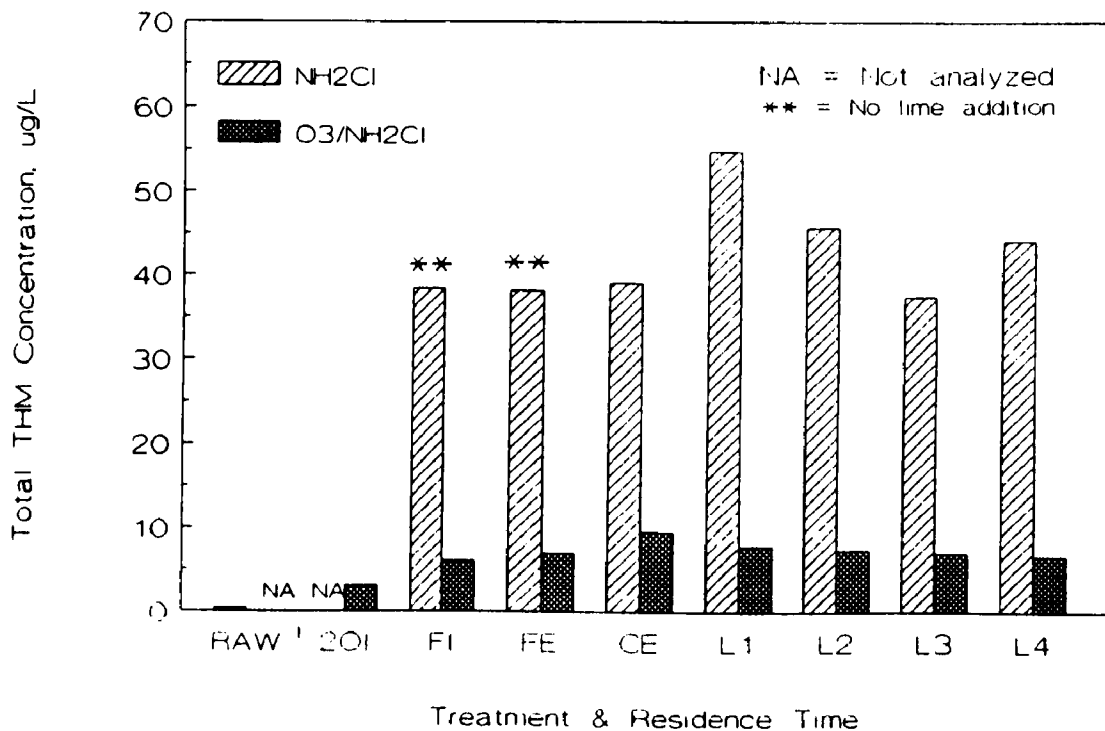
FIGURE 6-36

Effects of NH2CI and O3/NH2CI Treatment on HAA Formation at Utility 25
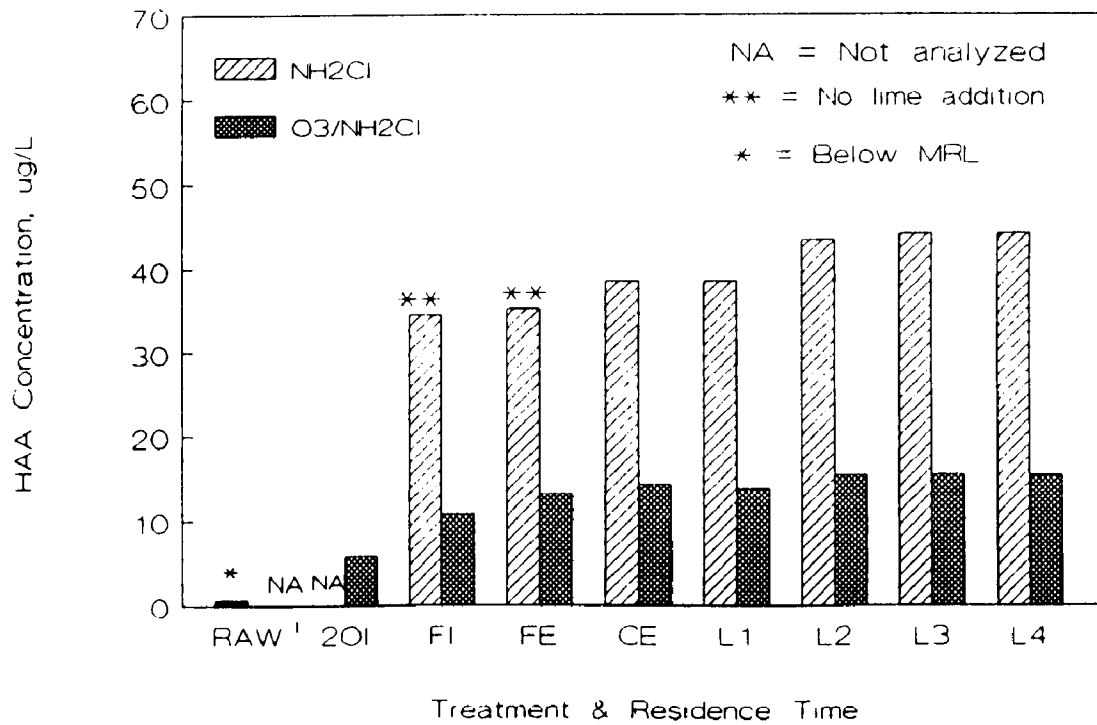
FIGURE 6-37

Effects of NH2CI and O3/NH2CI Treatment on DCAA Formation at Utility 25
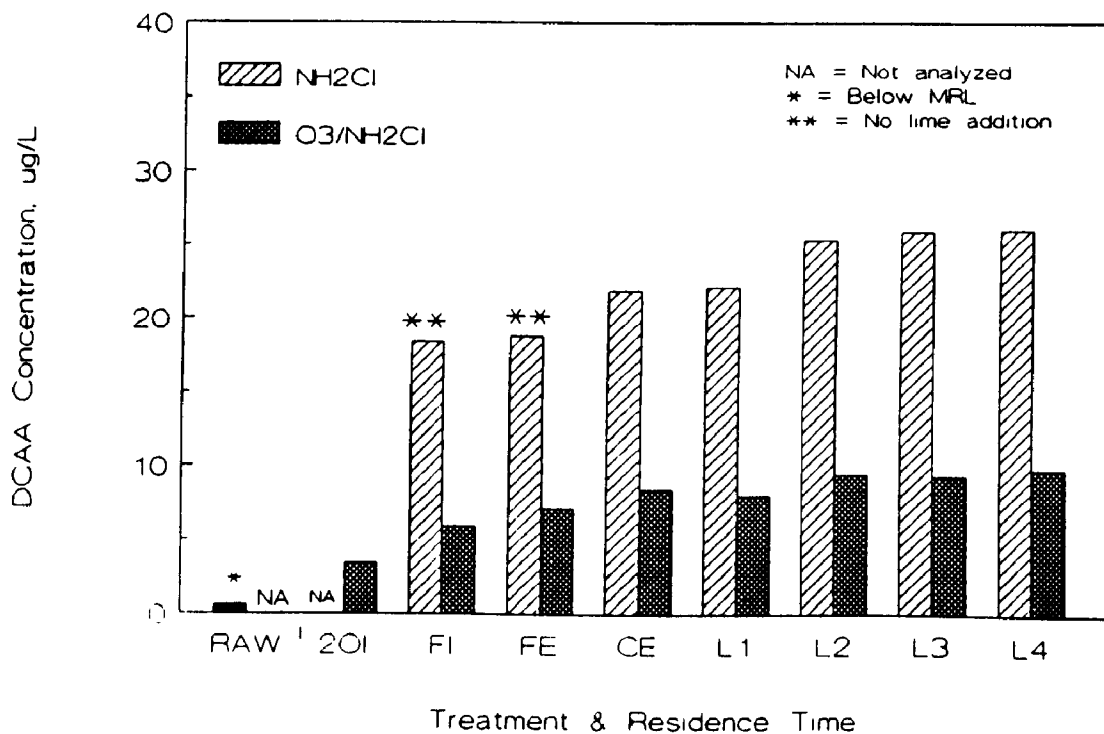
FIGURE 6-38

Effects of NH2Cl and O3/NH2Cl Treatment
on Chloropicrin Formation at Utility 25
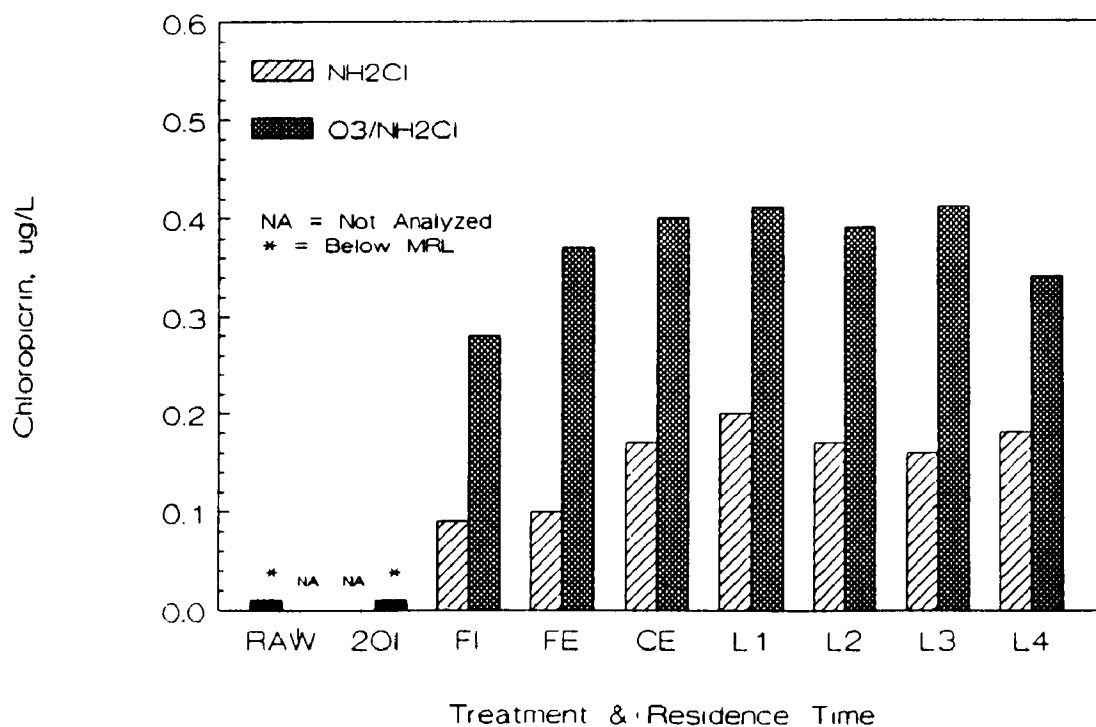
FIGURE 6-39

Effects of NH2Cl and O3/NH2Cl Treatment
on HAN Formation at Utility 25
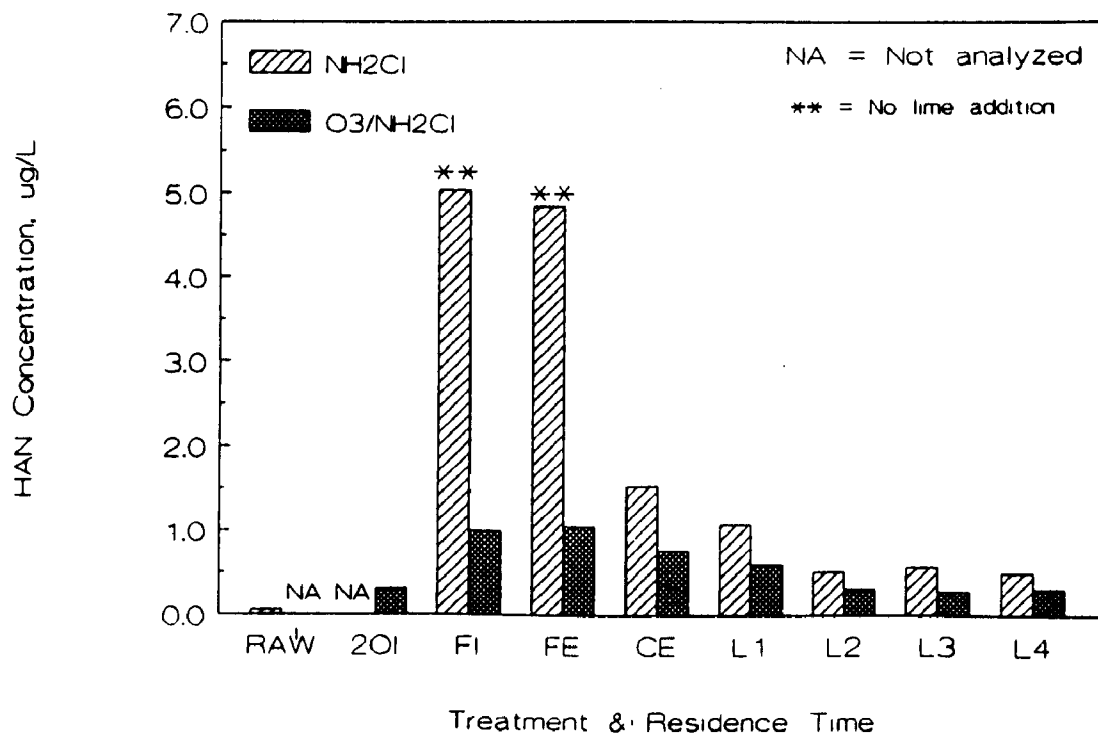
FIGURE 6-40

Effects of NH2Cl and O3/NH2Cl Treatment on HK Formation at Utility 25
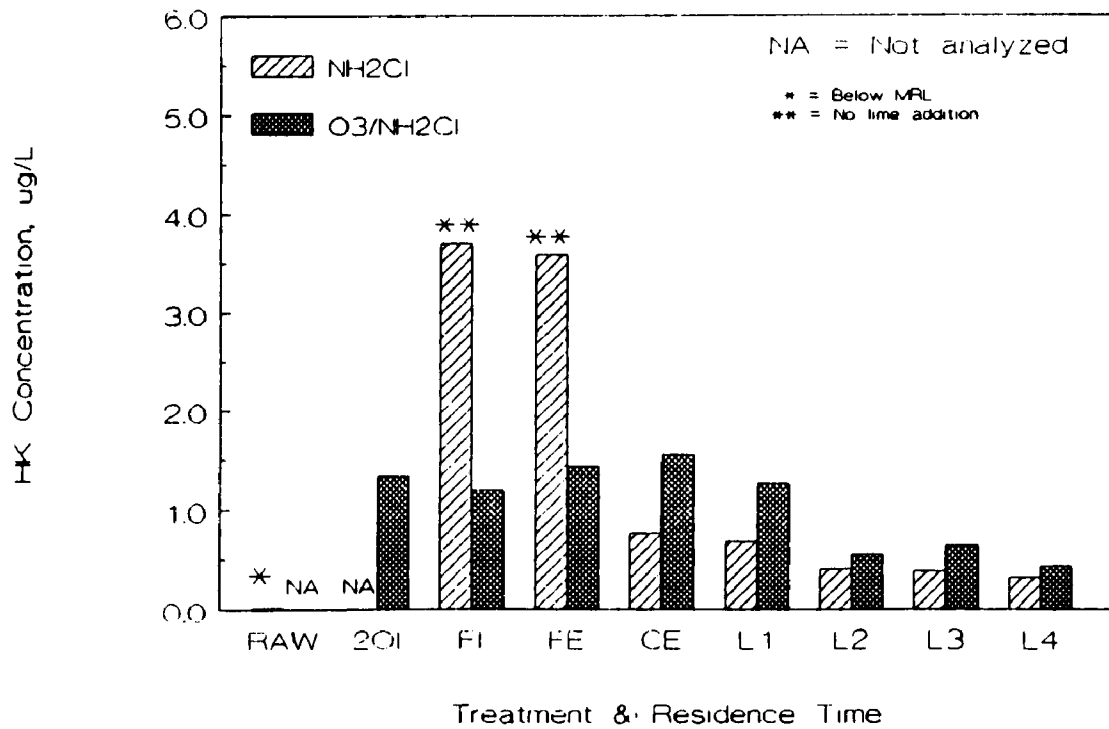
FIGURE 6-41

Effects of NH2Cl and O3/NH2Cl Treatment on Chloral Hydrate Formation Utility 25
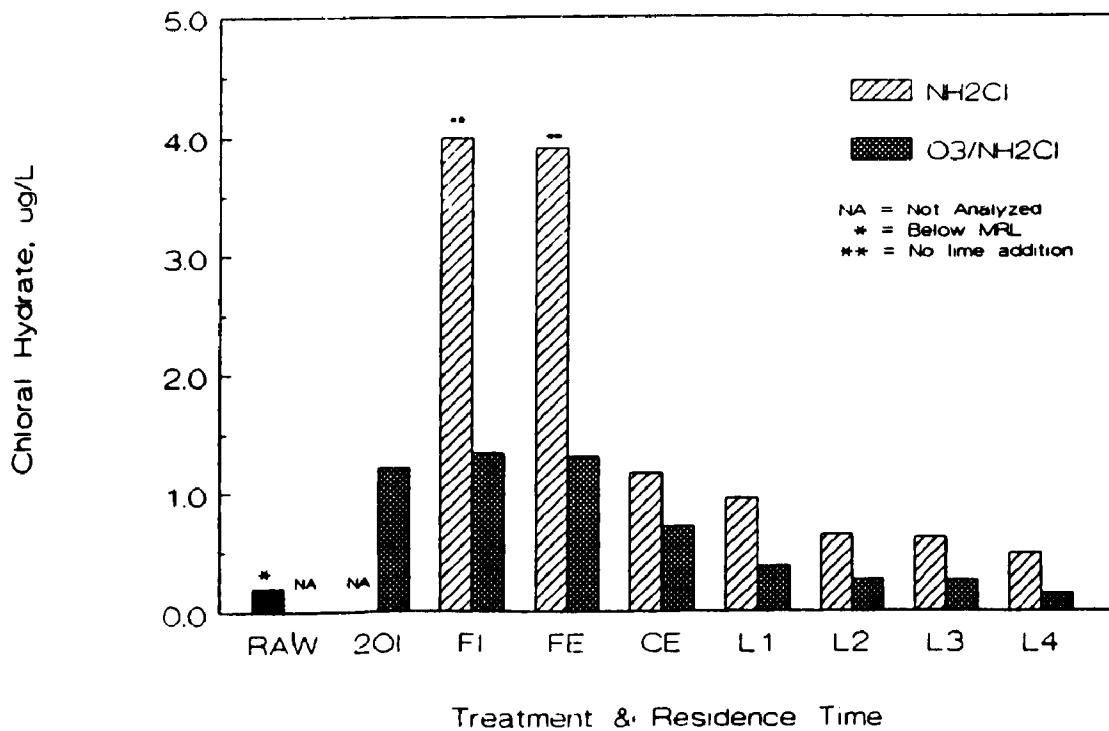
FIGURE 6-42

Effects of NH2Cl and O3/NH2Cl Treatment on CNCl Formation at Utility 25
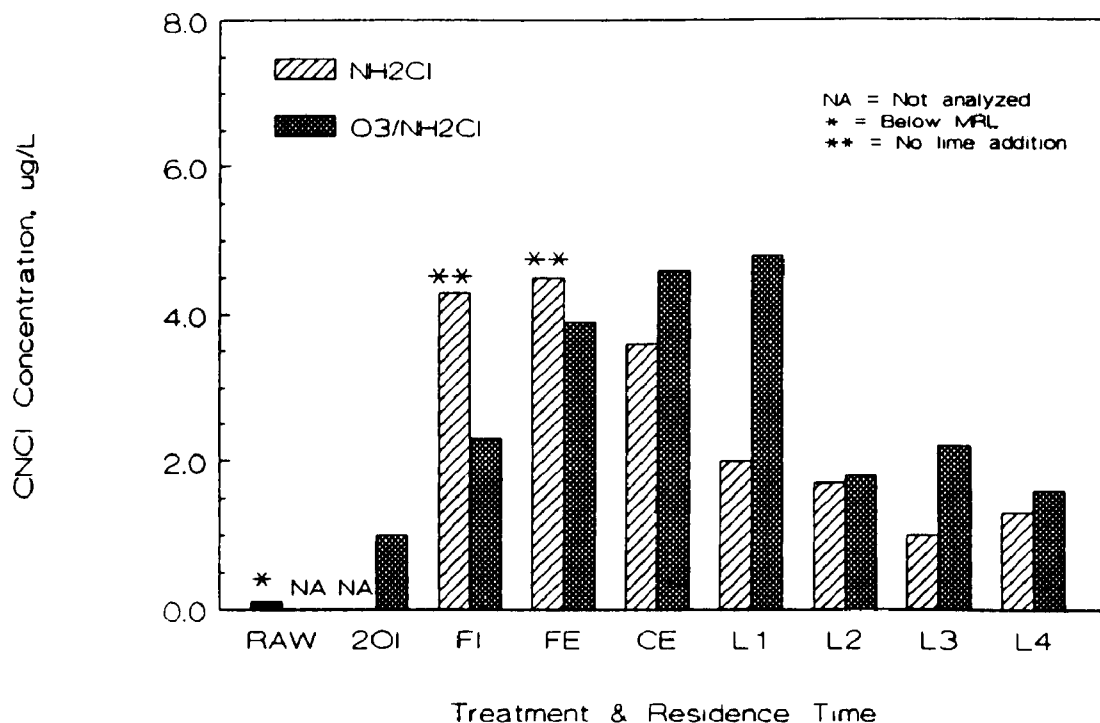
FIGURE 6-43

Effects of NH2Cl and O3/NH2Cl Treatment on ALD Formation at Utility 25
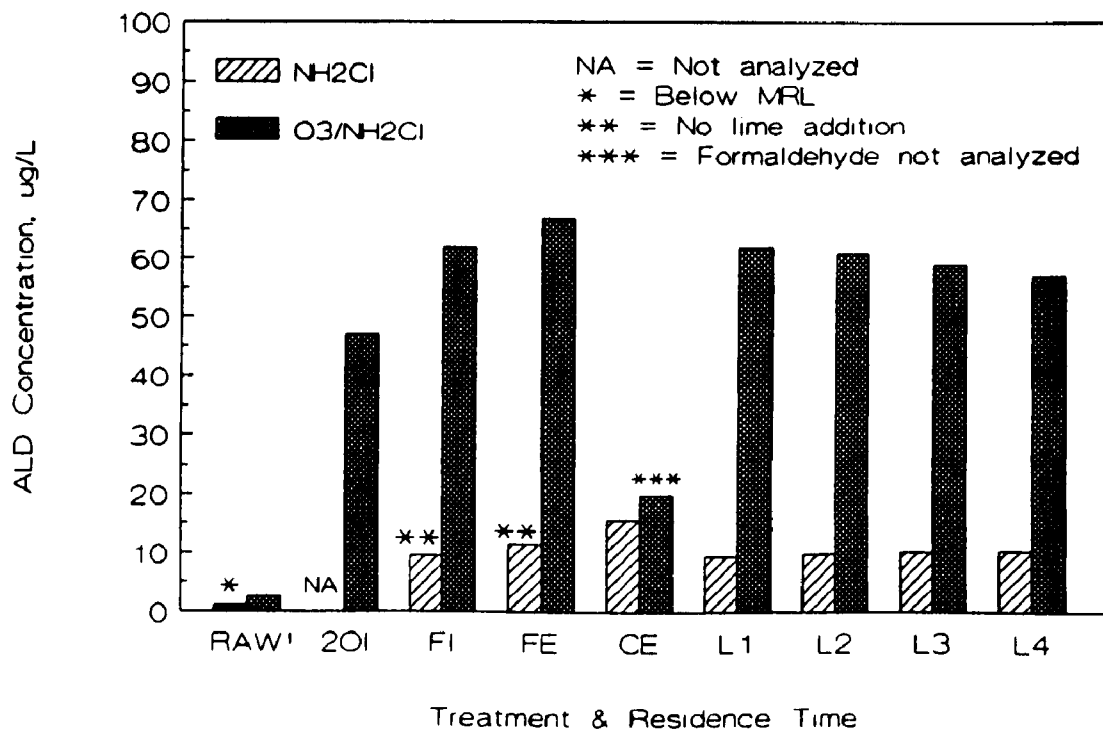
FIGURE 6-44

Effects of NH2Cl and O3/NH2Cl Treatment on Formaldehyde Formation at Utility 25
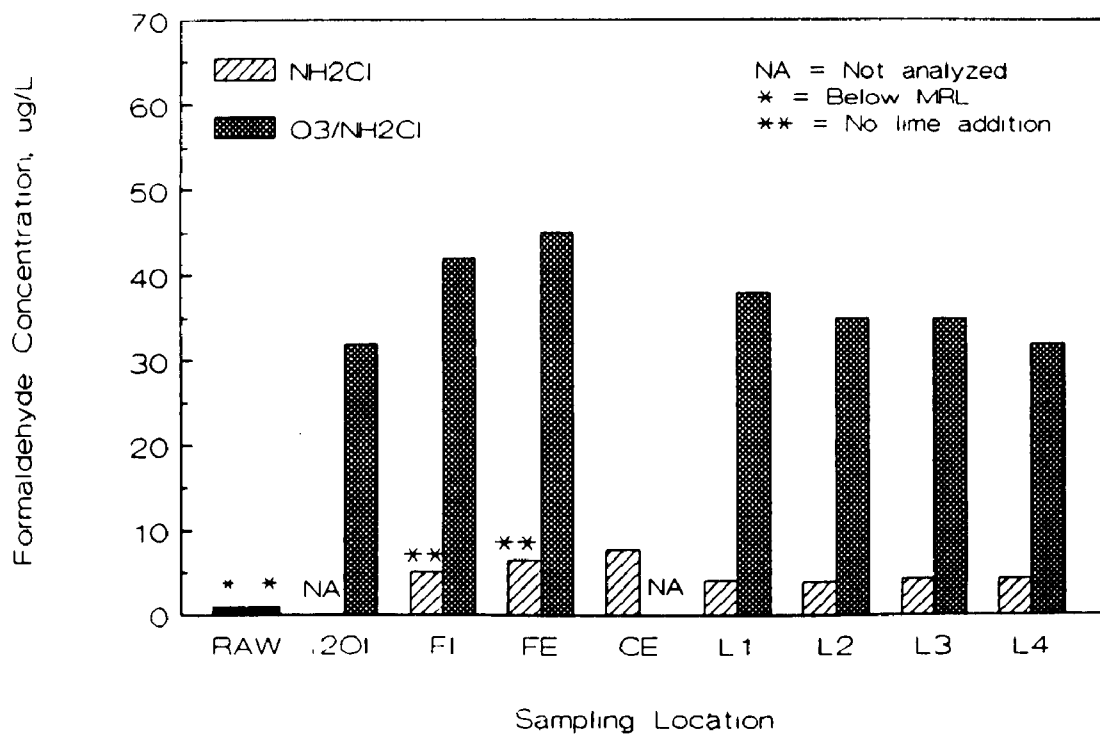
FIGURE 6-45

Treatment Modification Results and Discussion

Moreover, since disinfectant was applied before filtration, there was probably no opportunity for biological degradation of these compounds in the filters.

Utility 36

At Utility 36, a pilot plant with a flow rate of 5 gallons per minute was employed to evaluate five different treatment scenarios on the formation of DBPs. Conventional treatment was employed with options to add preozonation (2 mg/L), with and without hydrogen peroxide addition (0.67 mg/L), and free chlorine (6.5 mg/L) or chloramines (2.1 mg/L chlorine and 0.5 mg/L ammonia) as disinfectants in the rapid mix. The various treatment scenarios are shown in Figure 6-46. Samples were collected from the filter effluent and held for 24 hours at ambient temperature in order to simulate the retention time in a distribution system. After the 24-hour incubation time, samples were transferred to individual sample bottles containing the appropriate dechlorination agents and preservatives. Various water quality parameters are shown in Table 6-7.

Table 6-8 shows the effect of ozonation on the individual DBP compounds produced with chlorination in 24-hour samples. With ozonation, chloroform decreased from 42 to 37 μg/L. However, increases were observed for the brominated THMs, resulting in an increase in TTHMs. The level of bromide measured in the raw water at Utility 36 was 320 μg/L. Dichloroacetic acid was essentially the same level, with and without preozonation, while trichloroacetic acid was reduced by 50 percent with preozonation. The varying effect of ozone on HAA precursors is consistent with bench-scale experiments performed by Reckhow and Singer (1985). Other notable changes were observed for formaldehyde and acetaldehyde, which increased from 13 to 36 μg/L and 11 to 16 μg/L, respectively, with ozonation. Additionally, chloral hydrate increased from 19 to 28 μg/L. Figure 6-47 shows the effect of the five different disinfection schemes on various DBP classes and chloral hydrate. The highest levels of TTHMs, HAAs, HANs and chloral hydrate were observed with those schemes which employed chlorine as a final disinfectant. By comparison, large decreases were observed under any disinfection scheme which employed chloramines. For example, as compared to the chlorine-only disinfection scenario, chloramines-only, ozone/chloramines, and ozone/hydrogen peroxide/chloramines reduced TTHM levels by 96, 97 and 98 percent, respectively.

When chloramines-only were applied, only 6.1 μg/L of TTHMs were formed. This result is in contrast to that found during the the study at Utility 25, where fairly high levels of TTHMs (44 μg/L) were formed when chloramines-only were employed. Thus, Utility 36 data further support the probability that there was some free chlorine contact time at Utility 25 although concurrent addition of ammonia and chlorine was practiced.

Figure 6-47 shows that at Utility 36, chloramines only were as effective in reducing the levels of chlorinated DBPs as ozone/chloramines or ozone/hydrogen peroxide/chloramines. Similar findings are shown in Table 6-7 for TOX concentrations. Unlike the study at Utility 25, where the chloramine dose was reduced after preozonation, the chloramine doses and residuals at Utility 36 were similar whether or not ozone was employed. Aldehydes were produced in greatest concentrations under the disinfectant schemes which employed ozone. The level of the

CHLORINE ONLY

Chlorine
Ferric Sulfate
Polymer

CHLORAMINES ONLY

Chlorine
Ammonia
Ferric Sulfate
Polymer
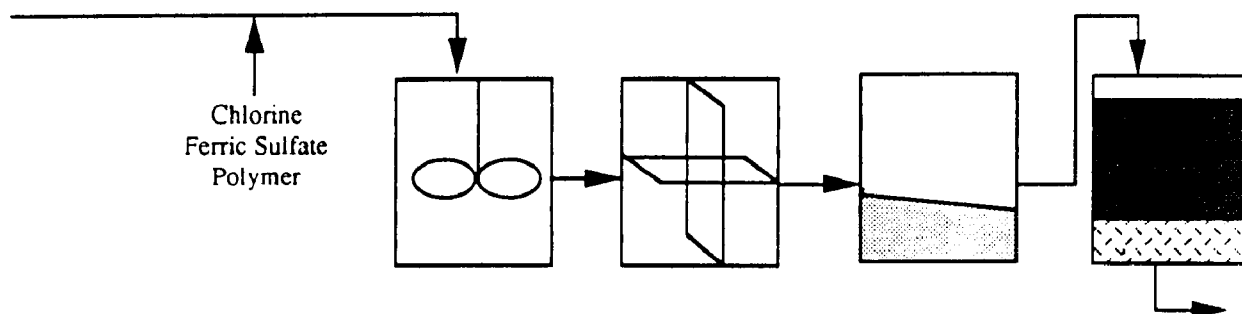
OZONE / CHLORINE
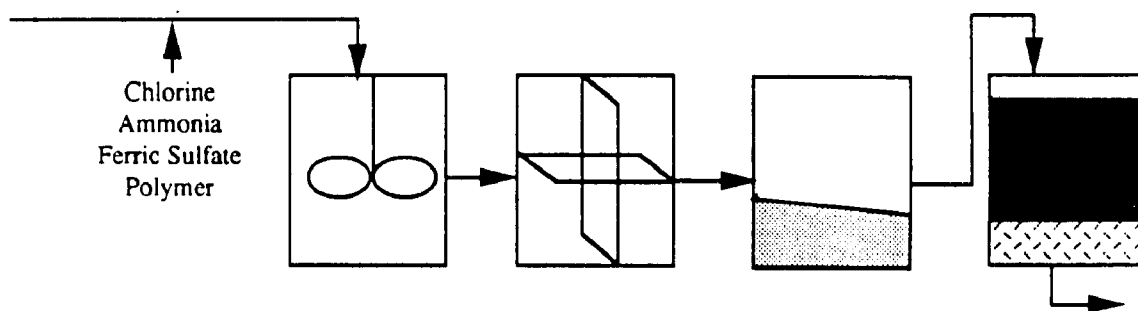
Chlorine
Ferric Sulfate
Polymer
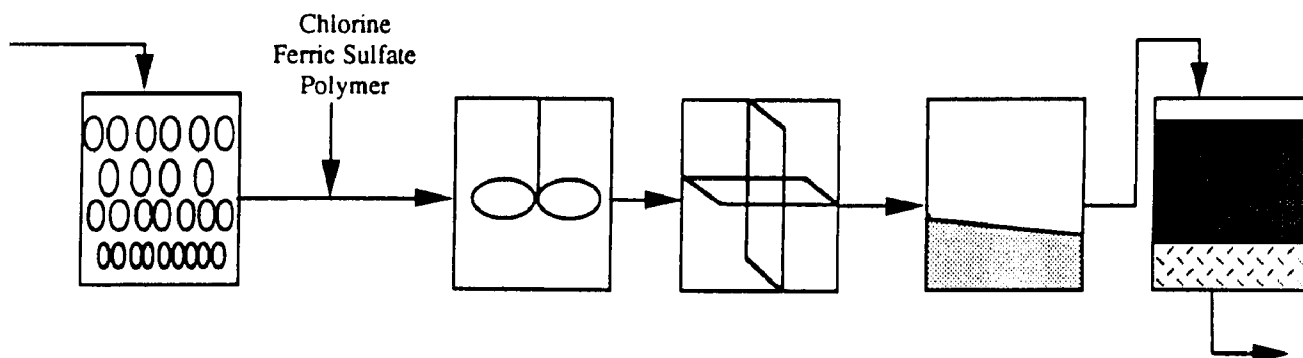
SCHEMATIC OF UTILITY 36 TREATMENT PROCESSES

FIGURE 6-46

OZONE / CHLORAMINES

Chlorine
Ammonia
Ferric Sulfate
Polymer
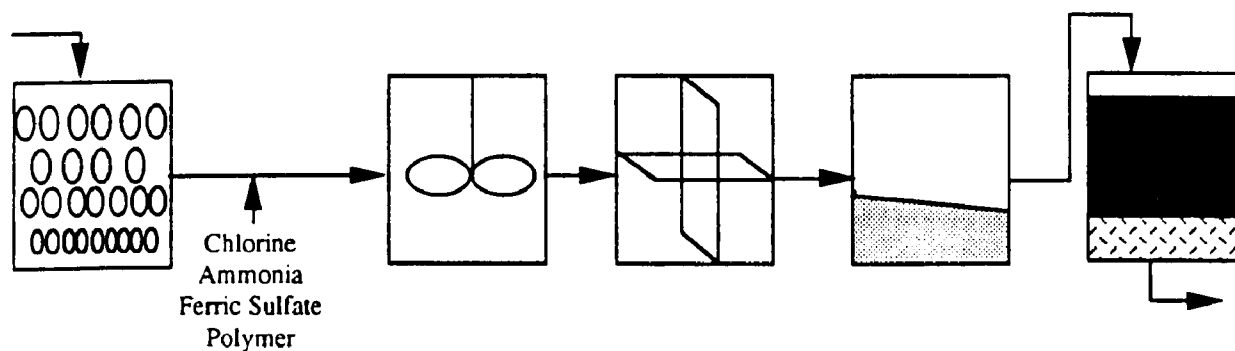
OZONE AND PEROXIDE / CHLORAMINES

Hydrogen
Peroxide

Chlorine
Ammonia
Ferric Sulfate
Polymer
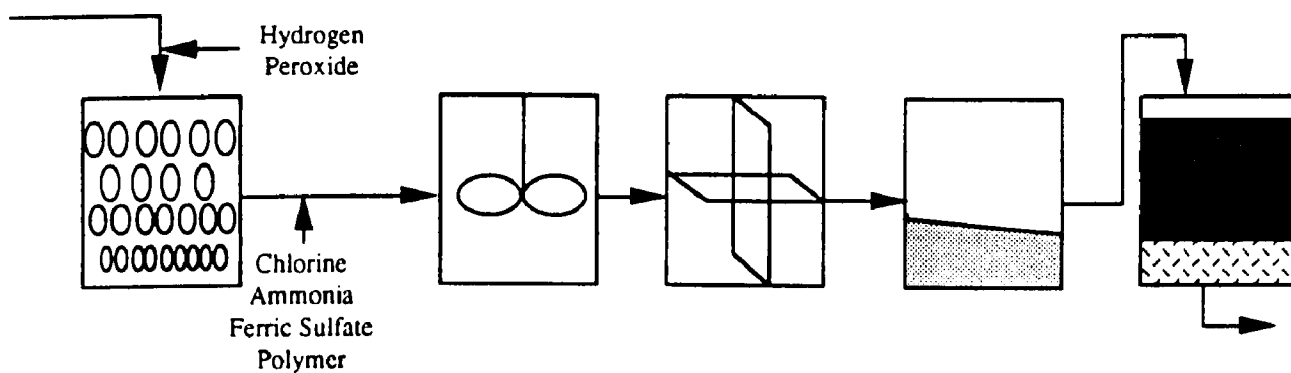
SCHEMATIC OF UTILITY 36 TREATMENT PROCESSES

FIGURE 6-46 (Continued)

TABLE 6-7

UTILITY 36 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	UV Absorbance at 254 nm (cm^{-1})	Chloride (mg/L)	Bromide (mg/L)	TOX (μg/L)	pH	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)
INFLUENT (at 9 a.m.)	4.28	0.091	46	0.32	NA	8.24	NA	NA
FILTER EFFLULENT (Immediate)								
Cl_2	4.01	0.045	NA	NA	300	7.63	2.9	3.4
NH_2Cl	3.87	0.060	NA	NA	67	7.55	NA	1.4
O_3 and Cl_2	4.10	0.036	NA	NA	280	7.72	1.6	2.1
$O_3.NH_2Cl$	4.03	0.044	NA	NA	59	NA	NA	1.3
$O_3/H_2O_2.NH_2Cl$	4.00	0.044	NA	NA	81	7.71	NA	1.3
FILTER EFFLUENT ($SDS_{24\ hours}$)								
Cl_2	3.87	0.031	NA	NA	380	7.56	0.8	1.4
NH_2Cl_2	3.83	0.049	NA	NA	75	7.59	NA	1.0
O_3 and Cl_2	4.05	0.034	NA	NA	330	7.61	0.2	0.3
$O_3.NH_2Cl$	3.91	0.034	NA	NA	69	7.76	NA	0.8
$O_3/H_2O_2.NH_2.Cl$	3.88	0.035	NA	NA	73	7.69	NA	0.8

NA = Not Analyzed
ND = Not Detected
Note: Temperature for all studies ranged from 24.8°C to 26.9°C.

TABLE 6-8

DISINFECTION BY-PRODUCT CONCENTRATIONS

BEFORE AND AFTER OZONE ADDITION AT UTILITY 36

Disinfection By-Products	Chlorine Only (μg/L)	Ozone/ Chlorine (μg/L) ⌣
Trihalomethanes		
Chloroform	42	37
Bromodichloromethane	50	54
Dibromochloromethane	50	62
Bromoform	9.5	17
Total Trihalomethanes	152	170
Haloacetic Acids		
Monochloroacetic Acid	4.0	5.1
Dichloroacetic Acid	23	21
Trichloroacetic Acid	22	13
Monobromoacetic Acid	3.8	3.2
Dibromoacetic Acid	11	13
Total Haloacetic Acids	64	55
Haloketones		
1.1-Dichloropropanone	0.24	0.28
1.1.1-Trichloropropanone	1.8	2.7
Total Haloketones	2.0	3.0
Haloacetonitriles		
Trichloroacetonitrile	<0.012	<0.012
Dichloroacetonitrile	4.5	3.3
Bromochloroacetonitrile	5.5	4.3
Dibromoacetonitrile	5.8	5.3
Total Haloacetonitriles	16	13
Aldehydes		
Formaldehyde	13	36
Acetaldehyde	11	16
Total Aldehydes	24	52
Miscellaneous		
Chloropicrin	0.25	0.57
Chloral Hydrate	19	28
Cyanogen Chloride	0.2	0.2

Note: Values less than the minimum reporting level not included in calculation of total class values.

EFFECT OF VARIOUS DISINFECTION SCHEMES ON DISINFECTION BY-PRODUCT FORMATION AT UTILITY 36
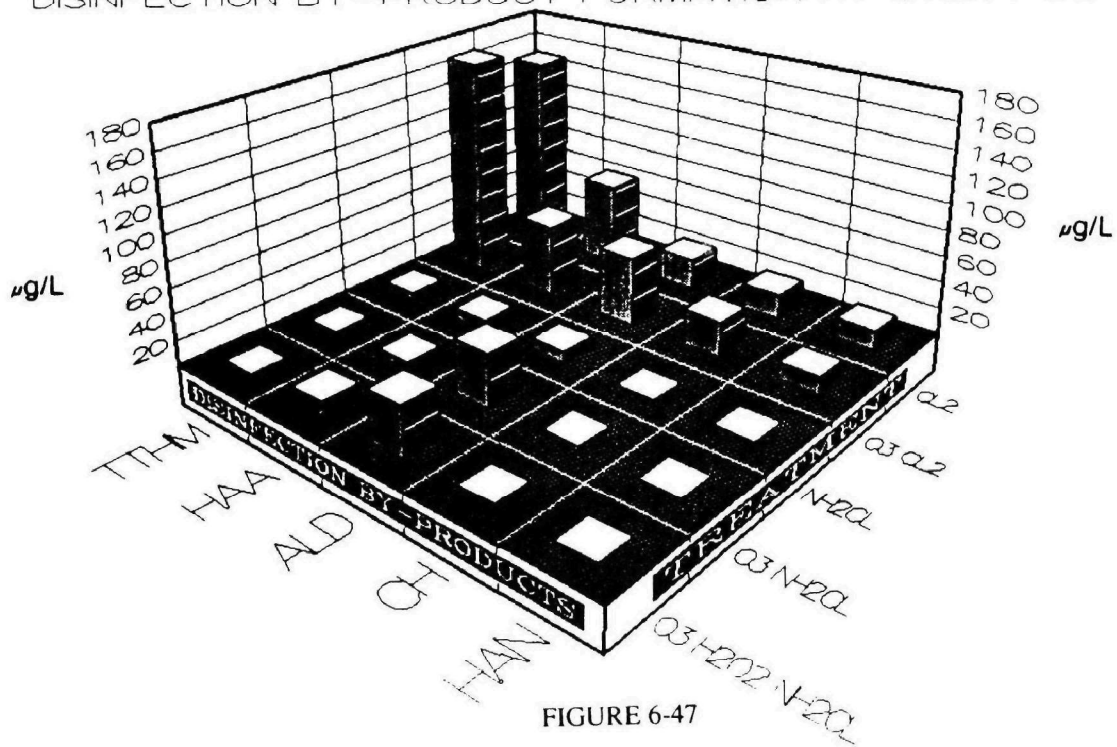
FIGURE 6-47

EFFECT OF VARIOUS DISINFECTION SCHEMES ON DISINFECTION BY-PRODUCT FORMATION AT UTILITY 36
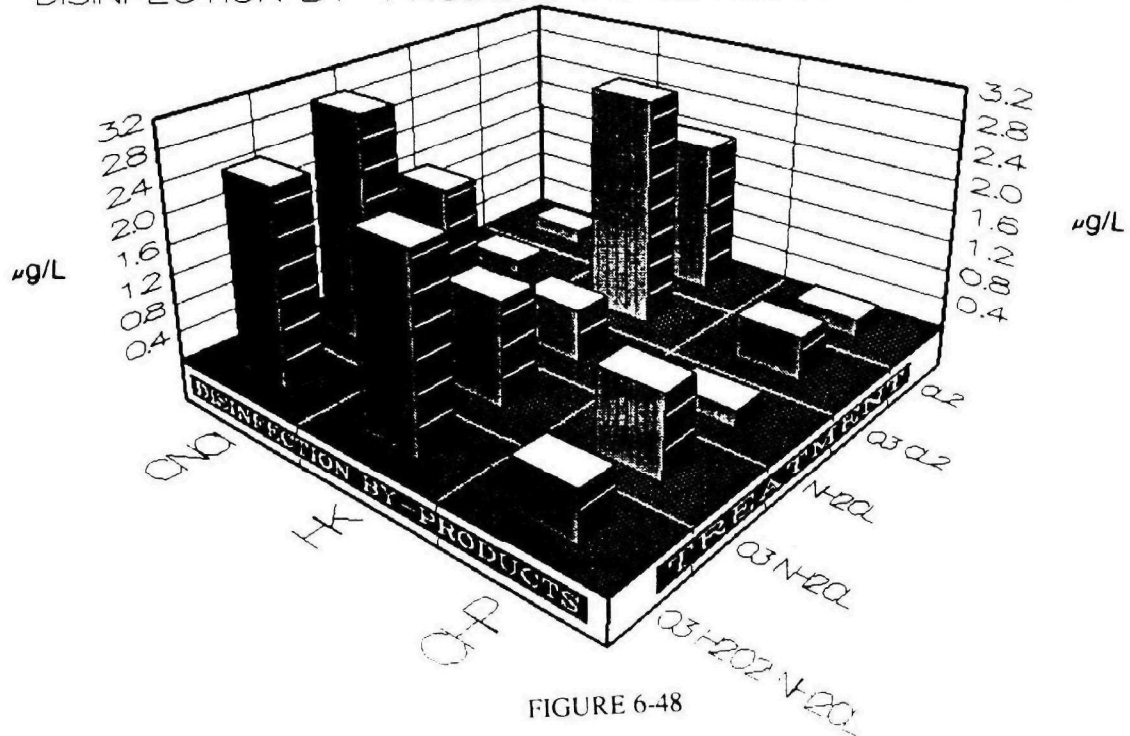
FIGURE 6-48

measured aldehydes for ozone/chlorine was 52 μg/L as contrasted to 24 μg/L and 9.1 μg/L for chlorine-only and chloramines-only schemes, respectively.

Figure 6-48 shows the effect of the five different treatments on HKs, cyanogen chloride and chloropicrin. The data indicate that formation of cyanogen chloride was most influenced by the final disinfectant. For those disinfection schemes which employed chloramines, cyanogen chloride levels were approximately 8 to 15 times greater than those which employed chlorine as a final disinfectant. Additionally, preozonation resulted in a higher cyanogen chloride level than that produced by chloramines alone.

Chloropicrin concentrations were approximately 2 to 4 times greater when the disinfection scheme employed preozonation. Although these results were consistent with those found by others (Becke et al., 1984; Hoigne and Bader, 1988), the levels of chloropicrin detected were low, ranging from 0.22 to 1.07 μg/L. The cited studies reported increases in chloropicrin in systems where preozonation was followed by chlorine addition. At Utility 36, the highest increase in chloropicrin concentration was observed in the trial which employed ozone followed by chloramination.

The use of hydrogen peroxide in conjunction with ozone has been shown to enhance the efficiency of ozone in oxidizing some organic materials (Glaze et al., 1987; Aieta et al., 1988; Wallace et al., 1988). In this study, peroxide was added at a ratio of 0.3 to 1 (hydrogen peroxide to ozone) on a weight basis; chloramines were employed as the final disinfectant. When compared to ozone/chloramine treatment, only small changes were observed in DBP formation using the ozone/hydrogen peroxide combination.

Effects of Holding Time on DBPs. Figures 6-49 to 6-58 show the effect of holding time on levels of DBPs which were measured in the pilot plant effluent (t=0; the residual disinfectant contact time through the plant before filtration was approximately one hour) and after 24 hours. The greatest increases in $XDBP_{sum}$ or XDBP class total concentrations over 24 hours were observed in the treatment scenarios which employed free chlorine as a final disinfectant (Figures 6-49 to 6-53). Similar results were observed for chloral hydrate (Figure 6-54). For chloropicrin, however, the ozone/chloramines treatment scenario produced the greatest increase over a 24 hour period (Figure 6-55). It should be noted, though, that the concentration even after the 24-hour holding time was low (1.07 μg/L).

As noted above, cyanogen chloride levels after 24 hours were 8 to 15 times greater under treatment scenarios which employed chloramines as a final disinfectant. Figure 6-56 shows that levels of this compound increased over the holding time under the ozone/chloramines scenario, while it decreased under those which employed chlorine as a final disinfectant.

Figure 6-57 and 6-58 show that once aldehydes were formed, they remained stable over 24 hours. This is consistent with the data found at Utility 6. It should also be noted that since a disinfectant residual was carried through the filter, there was probably no significant biological activity to lower the aldehyde levels formed from the various disinfectants.

Effects of Various Treatments on Halogenated DBP Formation at Utility 36
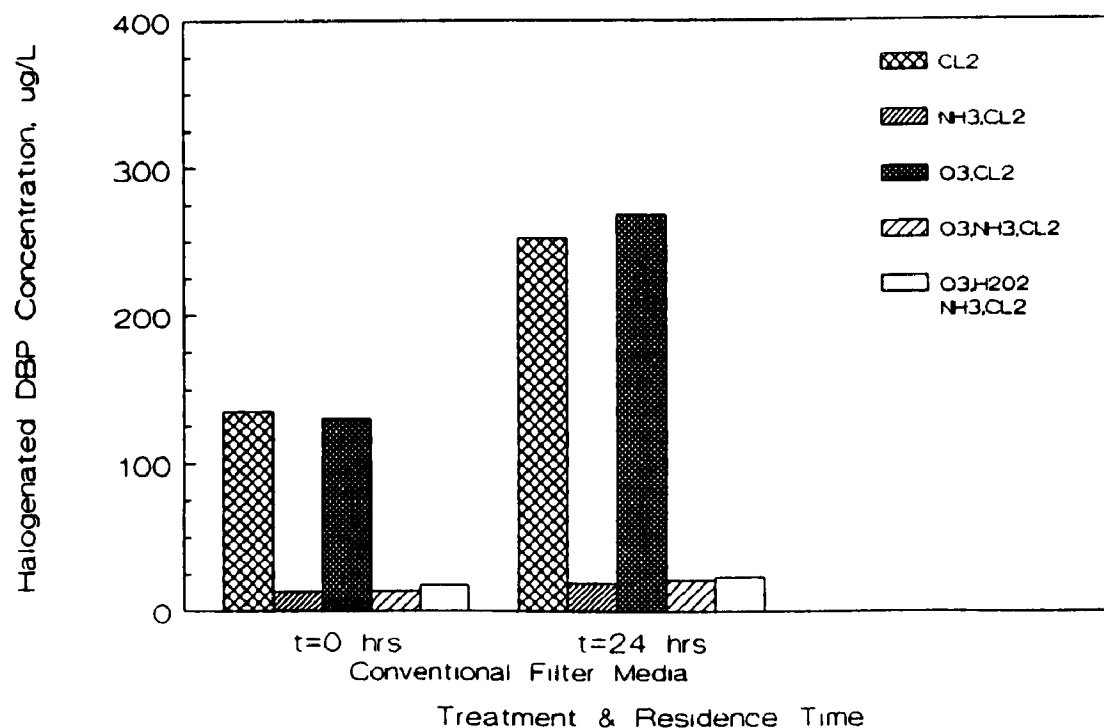
FIGURE 6-49

Effects of Various Treatments on THM Formation at Utility 36
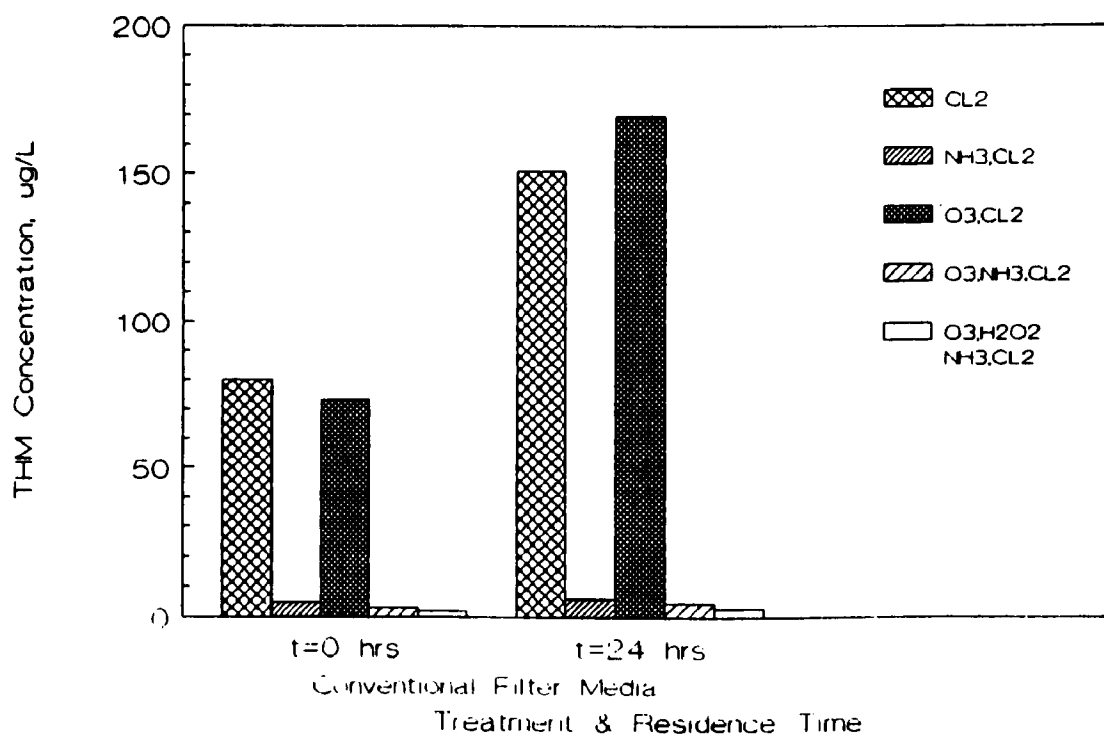
FIGURE 6-50

Effects of Various Treatments on HAA Formation at Utility 36
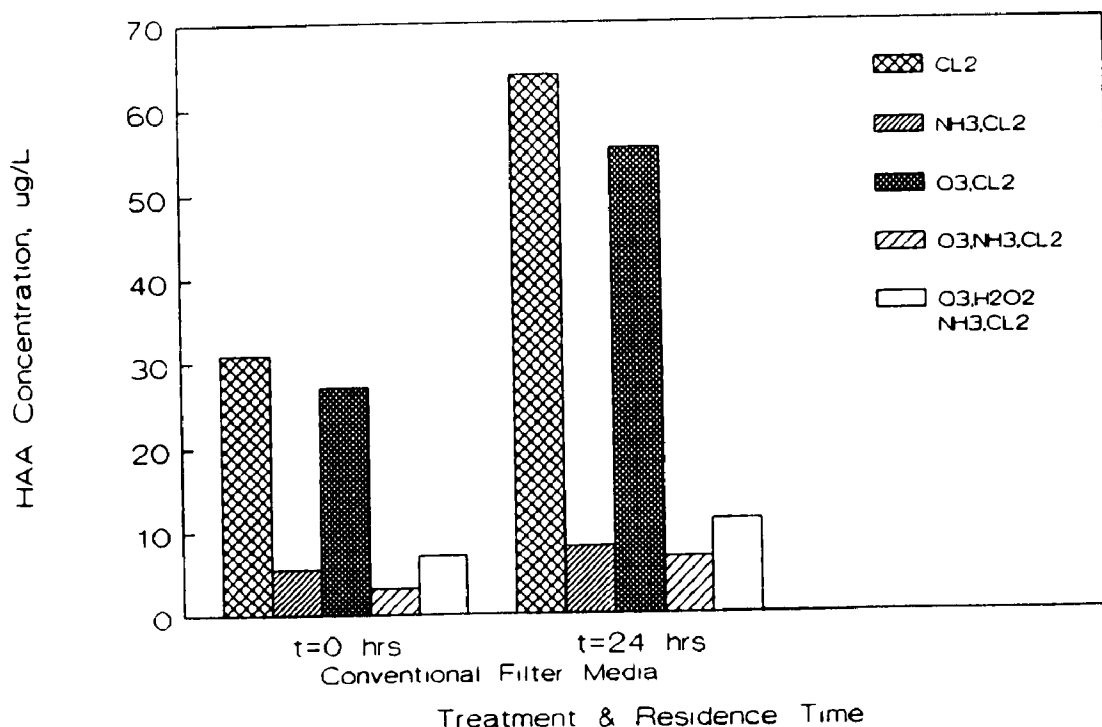
FIGURE 6-51

Effects of Various Treatments on HAN Formation at Utility 36
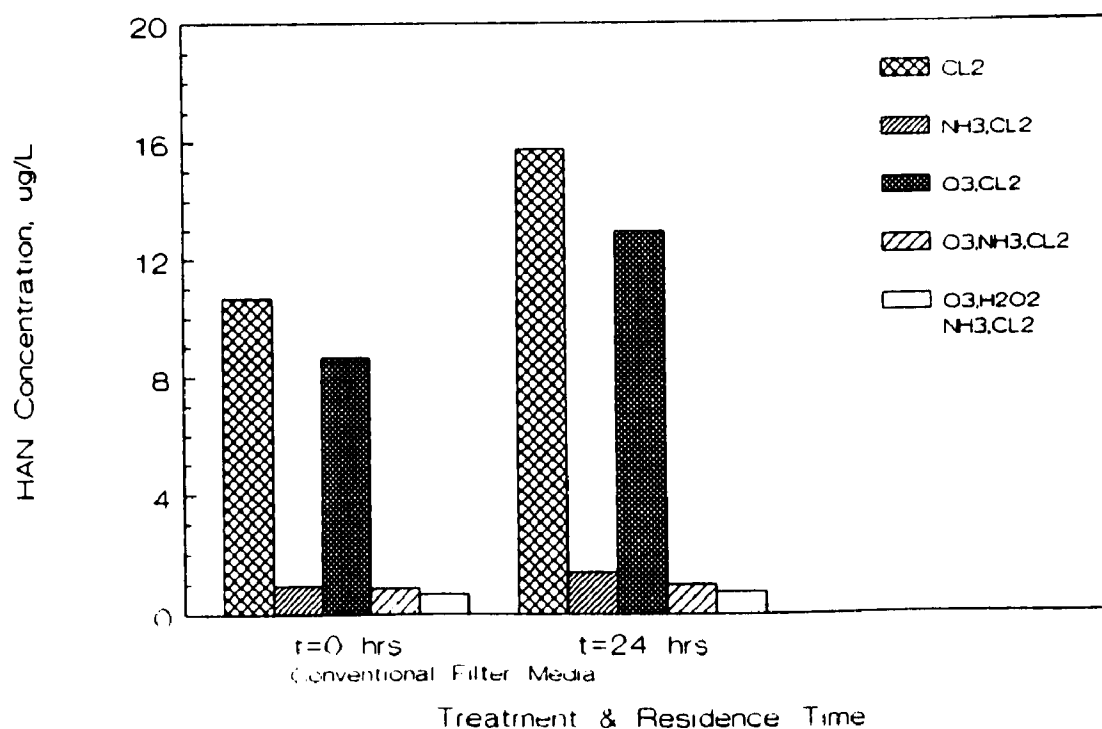
FIGURE 6-52

Effects of Various Treatments on HK Formation at Utility 36
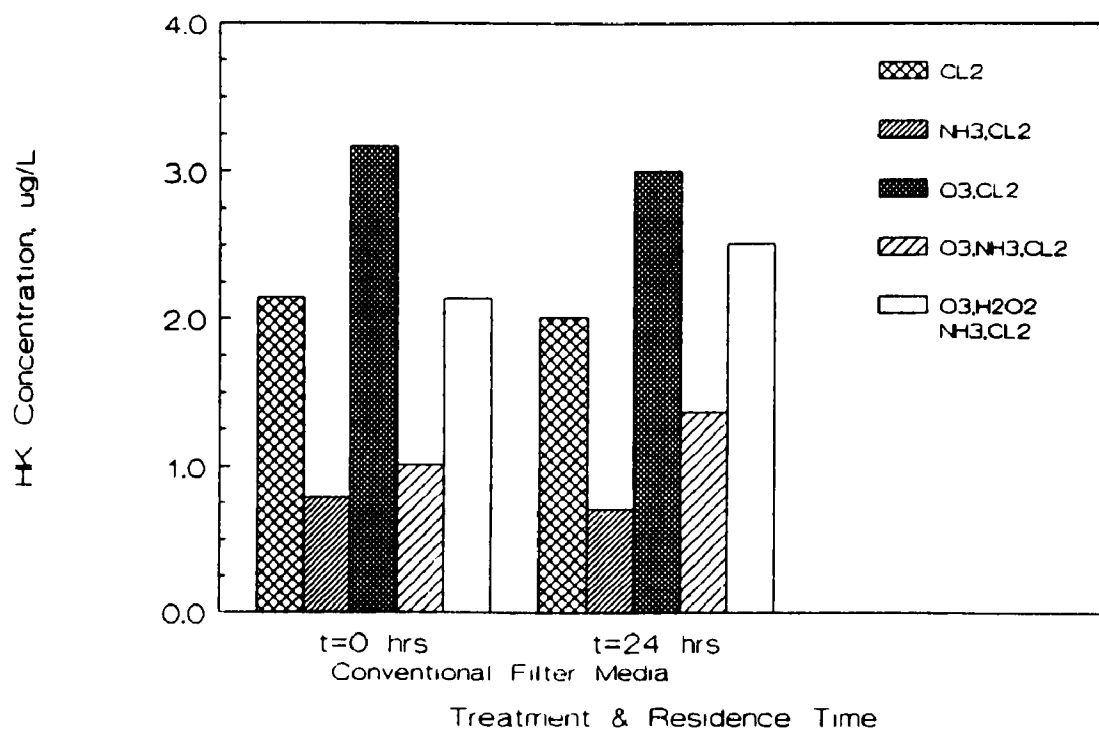
FIGURE 6-53

Effects of Various Treatments on CH Formation at Utility 36
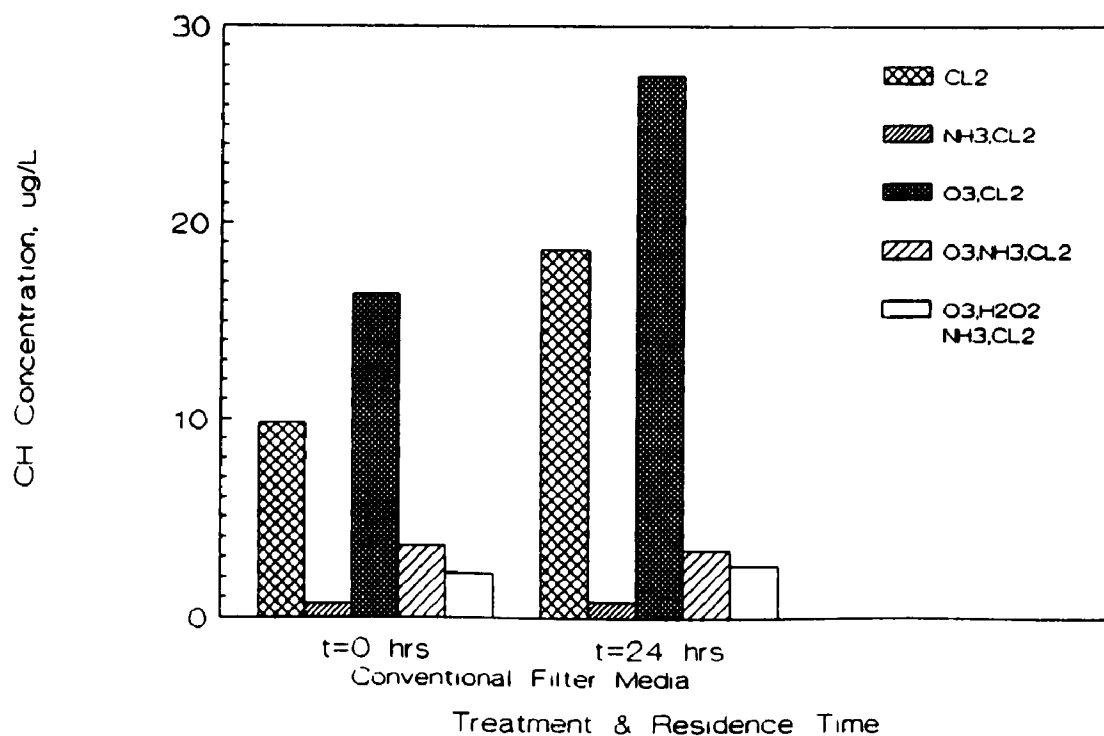
FIGURE 6-54

Effects of Various Treatments on CHP Formation at Utility 36
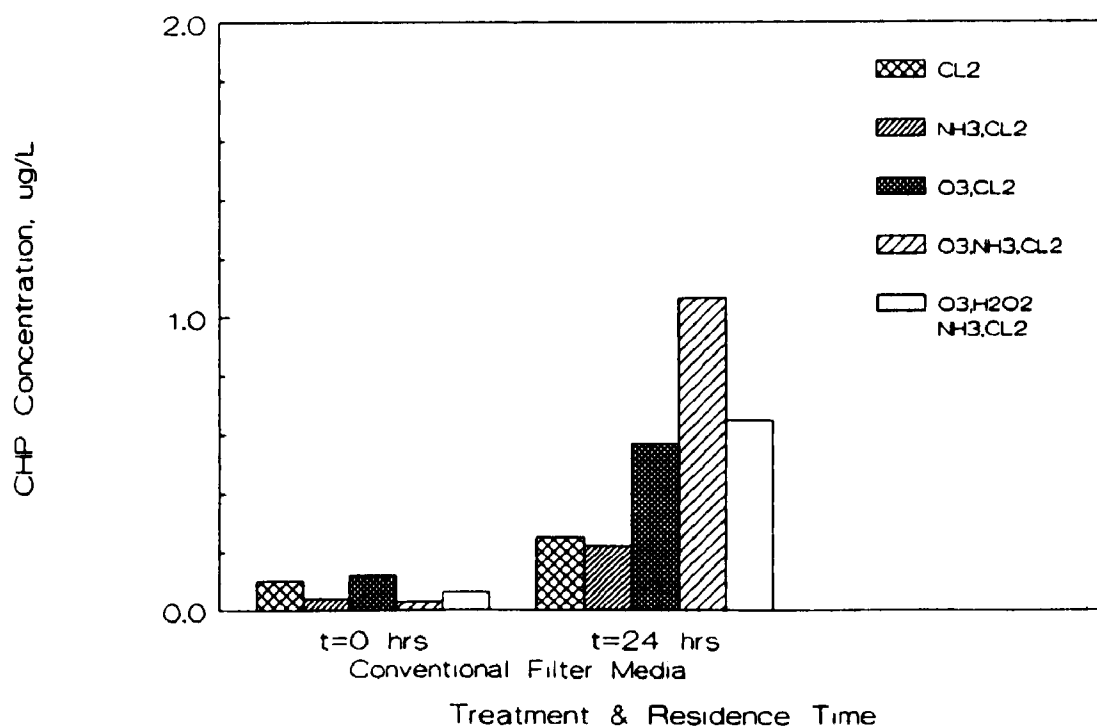
FIGURE 6-55

Effects of Various Treatments on CNCl Formation at Utility 36
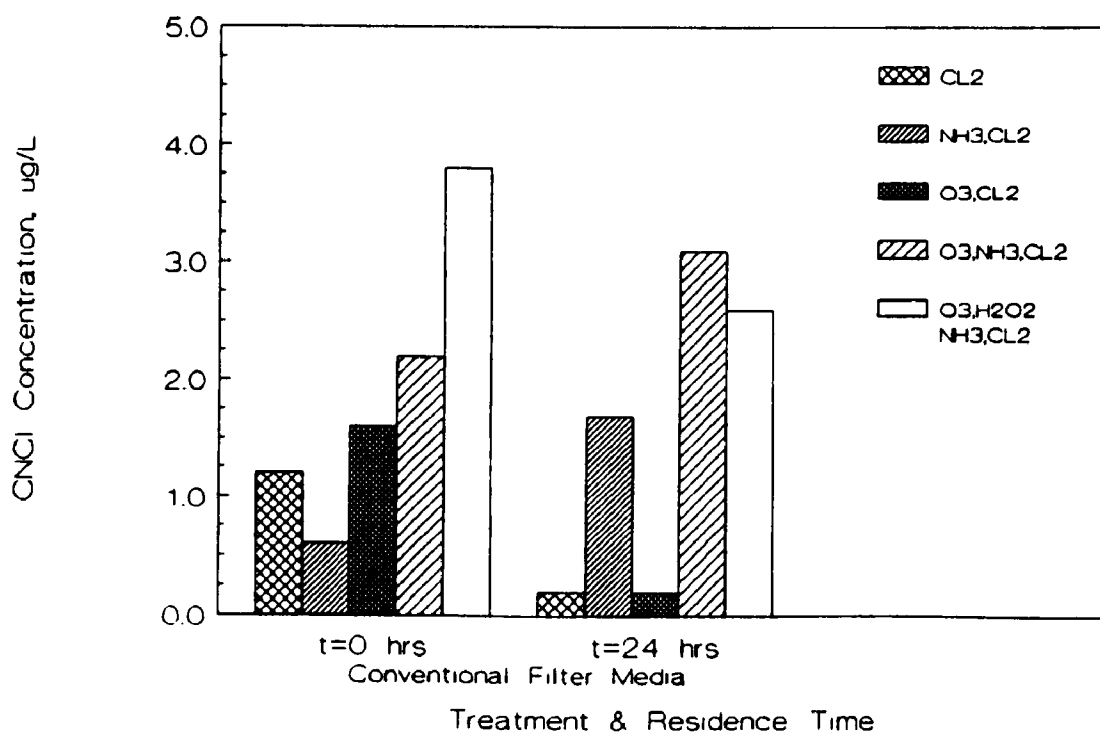
FIGURE 6-56

Effects of Various Treatments on ALD Formation at Utility 36
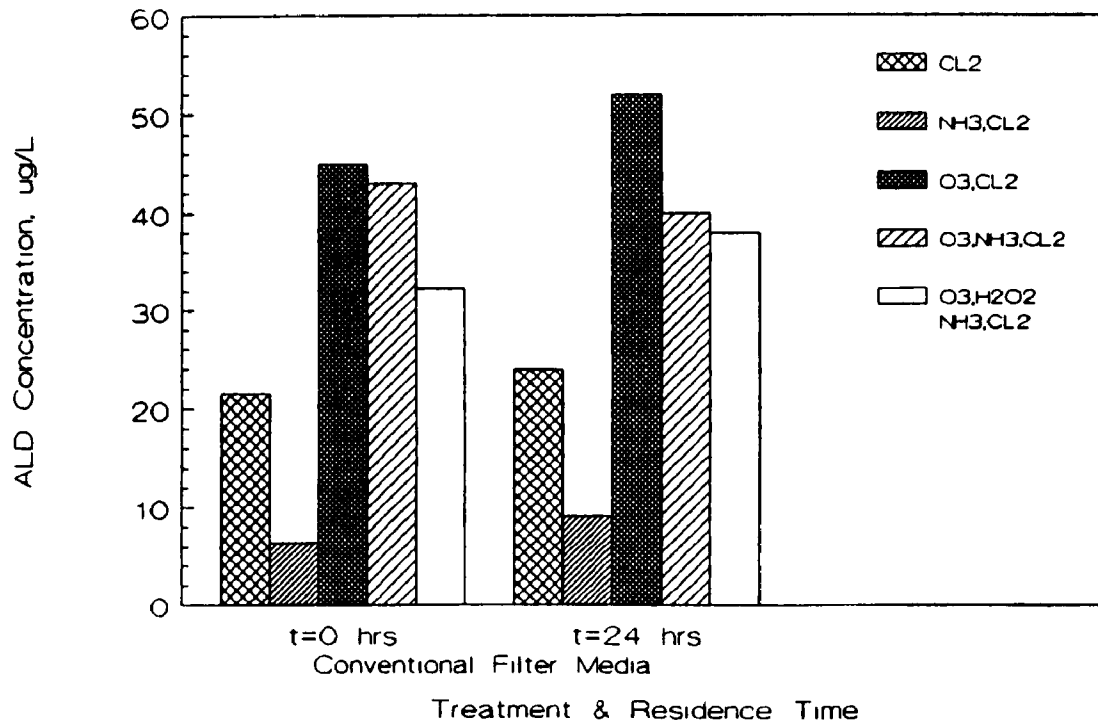
FIGURE 6-57

Effects of Various Treatments on Formaldehyde Formation at Utility 36
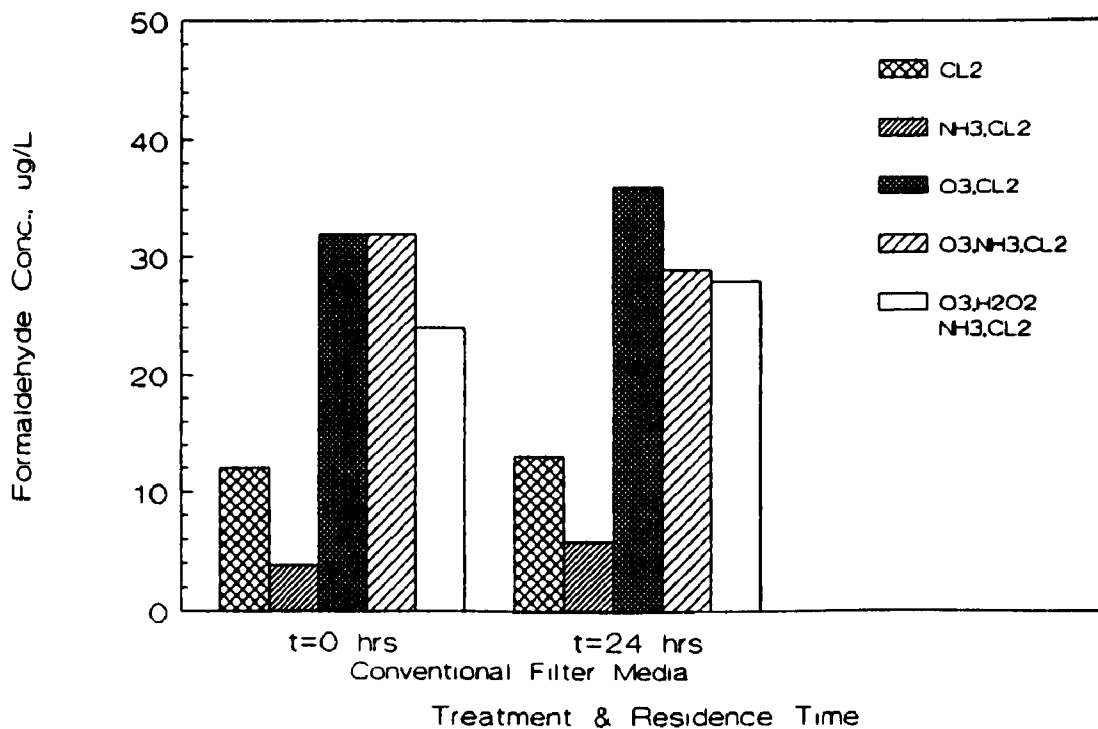
FIGURE 6-58

Treatment Modification Results and Discussion

Discussion

As shown in the ozonation studies discussed above, the formation of DBPs is strongly influenced by the particular disinfection scheme employed at the treatment plant. In order to meet the anticipated Surface Water Treatment Rule disinfection requirements as well as DBP regulations, many utilities are faced with selecting alternative treatments. Three general disinfection treatment change scenarios for utilities considering ozonation include:

1) Those which currently employ only free chlorine for disinfection in their treatment process and will switch to ozone and chlorine for primary and residual disinfection, respectively;

2) Those which currently employ only chloramines for disinfection, but will switch to ozonation followed by chloramination;

3) Those which currently employ only free chlorine in their treatment and will switch to ozonation followed by chloramination.

Figures 6-59 to 6-64 summarize results from this study based on the above DBP control options. All the data represented in these figures correspond to the terminal distribution system points studied. Changes in concentrations of TOX, $XDBP_{sum}$ and other DBP classes except HKs are presented as percent change. Individual compounds and HKs are shown as actual changes in concentration. Changes were calculated by comparing concentrations of DBPs before and after ozonation was added to the treatment process.

Modification from Chlorine to Ozone/Chlorine. Figures 6-59 and 6-60 present data for utilities where treatment plants were modified from employing only chlorine for disinfection to ozone/chlorine treatment. At Utility 19, preozonation decreased the concentration of TOX and most classes of the measured DBPs. In contrast, a 7 percent increase in $XDBP_{sum}$ was observed at Utility 36; this was primarily due to the observed increase in TTHM concentration. That ozonation can increase TTHMs has been observed in other studies (Riley et al., 1978; Lawrence, 1977; Umphres et al., 1979). Increased levels of THMs after preozonation may be attributed to an increase in precursor materials by formation of: 1) m-hydroxy aromatic compounds; or 2) secondary precursors, i.e., aliphatic carbonyl compounds (Glaze et al., 1982); or to an increase in brominated THMs due to bromide ion in the raw water (Dore et al., 1988).

Figures 6-24 and 6-25, and Table 6-8, show the individual DBP concentrations which were measured during the modification studies at Utilities 19 and 36. As mentioned previously, the data show decreases in chloroform for the two utilities and a general shift to the brominated THMs after ozonation. This was particularly evident at Utility 36 where the increase in TTHMs after ozone addition was due primarily to increases in dibromochloromethane and bromoform. These changes were greater than the upper control limits of the respective compounds, i.e., the differences were not due to analytical variability. As discussed in Section 5, levels of brominated THMs in treated water have been shown to be associated with bromide concentrations in the raw water. The same shift to the brominated species is seen to varying extents upon examination of

Percent Change in DBP Concentrations due to Switch from
CHLORINE ONLY to OZONE/CHLORINE Treatment

% Change in DBP and TOX Concentrations
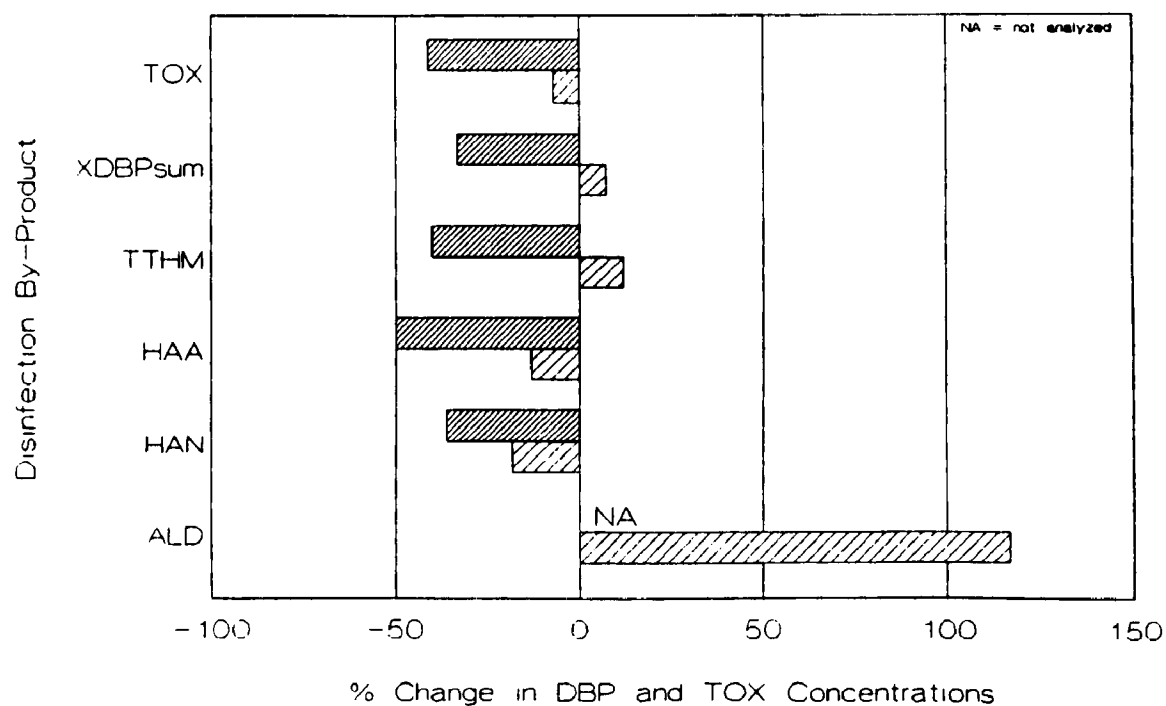
FIGURE 6-59

Change in DBP Concentrations due to Switch from
CHLORINE ONLY to OZONE/CHLORINE Treatment

Change in DBP Concentration (ug/L)
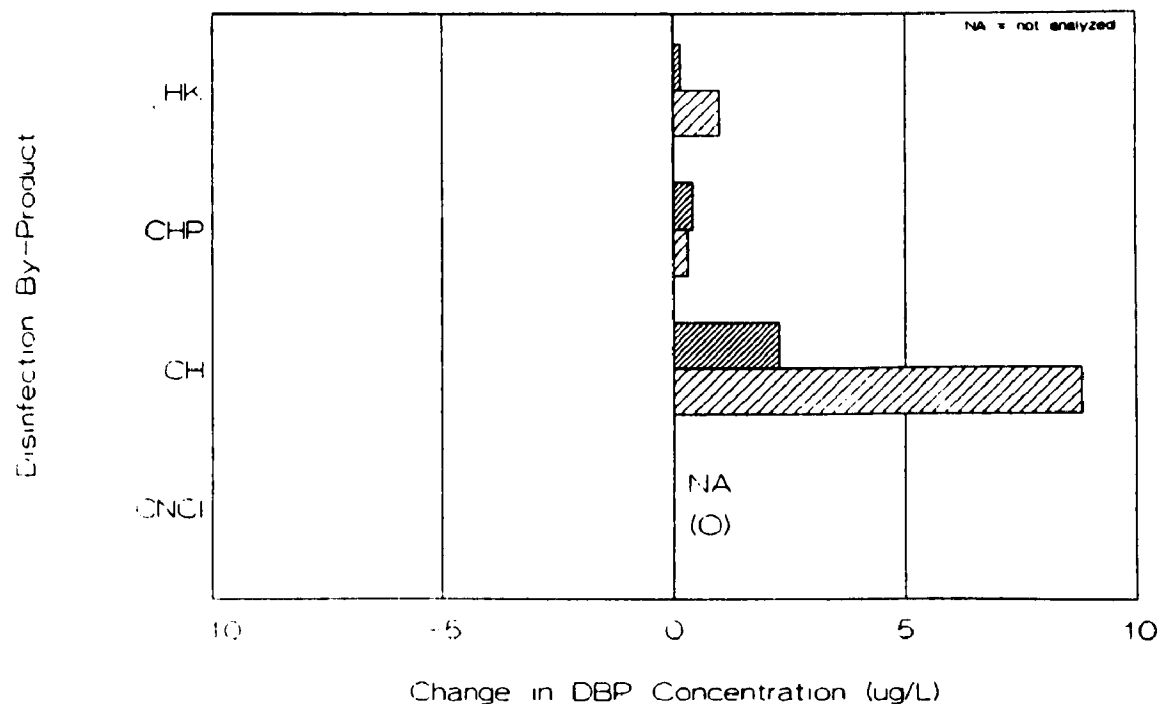
FIGURE 6-60

the concentrations of dibromoacetic acid. Although the levels of total HAAs decreased by approximately 50 and 14 percent at Utilities 19 and 36, respectively, the level of dibromoacetic acid increased by more than 100 percent at Utility 19, and by 18 percent at Utility 36. Ozone can react with bromide ions in the raw water causing the formation of hypobromous acid (HOBr) (Dore et al., 1988). Reactions of HOBr with natural organic matter can produce bromoform and other brominated DBPs. When preozonation and postchlorination is practiced, competition exists between hypochlorous acid and HOBr for organic matter, leading to varying concentrations of chlorinated and brominated DBPs (Dore et al., 1988).

In this study, HAAs represented the second largest fraction of halogenated DBPs on a weight basis. The data presented in Figure 6-28 and Table 6-8 confirm work by other researchers who found DCAA and TCAA to be major by-products of chlorination of humic and fulvic acids (Quimby et al., 1980; Christman et al., 1983; Miller and Uden, 1983; DeLeer et al., 1985). At Utility 19, chloroform and TCAA were decreased by 68 and 82 percent after preozonation and postchlorination. DCAA was decreased by 50 percent, but remained the largest contributor to the HAA fraction. At Utility 36, the TCAA concentration was decreased by 41 percent while DCAA decreased only slightly. Dore, et al. (1988) showed that ozonation followed by chlorination of fulvic acids reduced TCAA levels but did not greatly affect DCAA. Reckhow and Singer (1985) demonstrated decreases in chloroform and TCAA precursors after similar treatment while DCAA precursors remained largely unchanged. Moreover, the latter researchers predicted the destruction of dichloroacetonitrile precursors and an enhancement of 1,1,1-TCP. In this study, ozone addition resulted in a decrease in HANs and a small increase in HKs at Utilities 19 and 36, respectively.

At Utility 36, 19 μg/L of chloral hydrate were detected after the chlorination-only treatment, and at Utility 19, 6.3 μg/L. After ozonation and chlorination, those concentrations were increased to 28 and 8.6 μg/L, respectively.

Modification from Chloramines to Ozone/Chloramines. Four utilities modified treatment from chloramines-only or prechlorination/postammoniation to ozone/chloramines. Figures 6-61 and 6-62 show that, in each study, the modification was effective in reducing levels of all classes of halogenated DBP compounds except for HKs. However, increases in this DBP class were less than 0.7 μg/L in all cases. Small increases were observed for chloropicrin and cyanogen chloride in two of the studies, while chloral hydrate decreased in three of them. The most significant increase was observed in the concentrations of aldehydes. Preozonation increased the sum of formaldehyde and acetaldehyde over 300 percent in the utilities where these compounds were measured.

Modification from Chlorine to Ozone/Chloramines. Figures 6-63 and 6-64 present a summary of the results of the two plants which modified treatment from chlorine-only as a disinfectant to ozone/chloramines. Decreases of at least 80 percent in concentrations of TOX, XDBP$_{sum}$ and sums of all halogenated classes of DBP compounds except for HKs were observed. Aldehydes increased by 67 percent and cyanogen chloride by 2.9 μg/L for the treatment modification study at Utility 36. The greatest decrease among the other compounds was detected in concentrations of chloral hydrate, which was reduced by approximately 9 and 15 μg/L at Utilities 7 and 36, respectively.

Percent Change in DBP Concentrations due to Switch from
CHLORAMINES ONLY to OZONE/CHLORAMINES Treatment

UTILITY 7*   UTILITY 25   UTILITY 36   UTILITY 6

% Change in DBP and TOX Concentrations
* Includes 4 hours of free chlorine contact time before postammoniation

FIGURE 6-61

Change in DBP Concentrations due to Switch from
CHLORAMINES ONLY to OZONE/CHLORAMINES Treatment

UTILITY 7*   UTILITY 25   UTILITY 36   UTILITY 6

Change in DBP Concentration (ug/L)
* Includes 4 hours of free chlorine contact time before postammoniation

FIGURE 6-62

Percent Change in DBP Concentrations due to Switch from
CHLORINE ONLY to OZONE/CHLORAMINES treatment

▨ UTILITY 7   ▨ UTILITY 36

% Change in DBP and TOX Concentrations

FIGURE 6-63

Change in DBP Concentrations due to Switch from
CHLORINE ONLY to OZONE/CHLORAMINES Treatment

▨ UTILITY 7   ▨ UTILITY 36

Change in DBP Concentration (ug/L)

FIGURE 6-64

Treatment Modification Results and Discussion

CHLORINE DIOXIDE STUDIES

Chlorine dioxide studies were conducted at Utility 16 and Utility 37. Both utilities employed chlorine dioxide as a preoxidant, and used chlorine as a final disinfectant.

Utility 16

Utility 16 operates a large (400 mgd) direct filtration treatment system for a low-organics reservoir water in the western United States. The plant utilizes free chlorine for both preoxidation and final disinfection for most of the year, but periodically switches to chlorine dioxide preoxidation to control THMs and taste and odor. The plant utilized chlorine-only treatment for all quarterly baseline samples collected for this study. The plant was sampled on November 21, 1988 for the chlorine-only treatment, and on March 21, 1989 for the chlorine dioxide/chlorine treatment. Figure 6-65 illustrates the treatment trains employed on the two sampling days.

Samples were collected at the plant influent. filter influent, clearwell effluent. and at two distribution system locations (approximate residence times of 45 minutes and 7 days). DBP analyses were conducted on the clearwell effluent and distribution system samples only. On the chlorine-only sample date. the plant was operating with a pre-chlorine dose of 2 mg/L (applied to the plant influent) and a post-chlorine dose of 1 mg/L (applied to the filter effluent). On the chlorine dioxide/chlorine sample date, the plant was operating with a chlorine dioxide dose of 0.5 mg/L (plant influent) and a chlorine dose of 1.9 mg/L (filter effluent).

An emergency situation occurred on the March sampling date. A chlorine storage tank developed a leaky valve. requiring that the tank be emptied. The contents of the tank were discharged into the water being treated in the plant, resulting in a significant amount of free chlorine in addition to the chlorine dioxide. Thus, the in-plant samples were unusable for purposes of this study. However, the two distribution system samples were collected prior to the chlorine leak problem and the results from these samples are reported in Table 6-9 and illustrated in Figure 6-66.

Figure 6-66 indicates very little difference in the levels of DBPs produced by the two different oxidation/disinfection schemes. In fact, at distribution system Location 2, the chlorine dioxide/chlorine treatment produced slightly higher levels of $XDBP_{sum}$, THMs. HANs and HKs than the chlorine-only treatment. With both chlorine dioxide/chlorine and chlorine-only treatment. levels of all DBPs increased with increasing residence time in the distribution system.

Chlorine dioxide residual. and chlorite and chlorate levels were measured at the laboratory of Dr. Gilbert Gordon at Miami University in Oxford, Ohio. Preserved samples were shipped overnight to Dr. Gordon on both the November and March sampling dates. Dr. Gordon's laboratory utilized a flow injection analysis method to analyze for chlorine dioxide, chlorite and chlorate (Gordon et al., 1989; Themelis et al., 1989). Chlorine dioxide residual levels are reported in Table 6-9. Neither chlorite nor chlorate were detected in either of the chlorine-only samples. However, for the chlorine dioxide/chlorine samples, 0.30 mg/L of chlorite and 0.14 mg/L of chlorate were detected at Location 1. Also, 0.09 mg/L of chlorite and 0.28 mg/L of chlorate were detected at Location 2.

CHLORINE ONLY

Chlorine   Ferric Chloride

Chlorine
Zinc Orthophosphate

CHLORINE DIOXIDE / CHLORINE

Chlorine Dioxide   Ferric Chloride
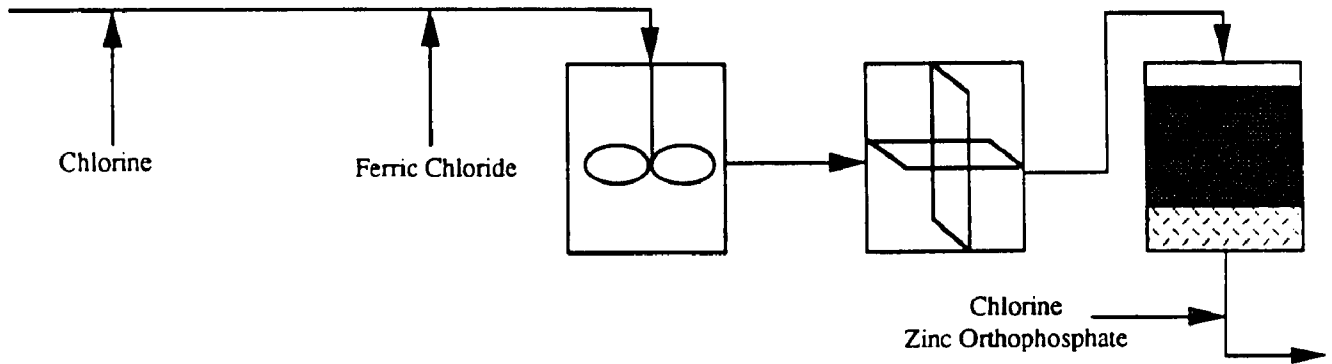
Chlorine
Zinc Orthophosphate
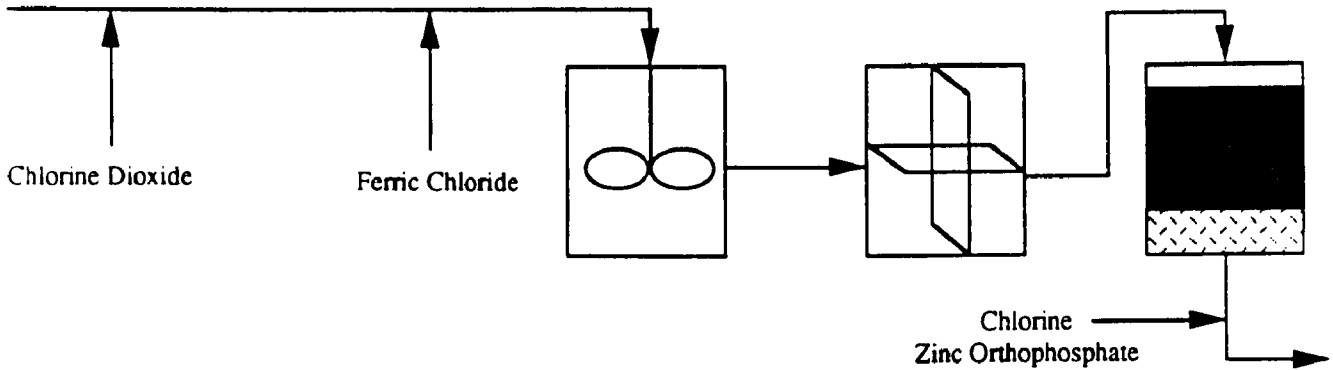
SCHEMATIC OF UTILITY 16 TREATMENT PROCESSES

FIGURE 6-65

TABLE 6-9

UTILITY 16 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	UV Absorbance (cm⁻¹)	pH	Temp. (°C)	Chlorine Residual (mg/L) Free	Chlorine Residual (mg/L) Total	Chlorine Dioxide Residual (mg/L)	Chlorite (mg/L)	Chlorate (mg/L)	TOX (μg/L)
CHLORINE ONLY										
Raw Water	2.69	0.098	7.72	14.8	NA	NA	ND	ND	ND	< 10
Location 1	2.64	0.083	7.59	15.1	0.6	0.9	ND	ND	ND	140
Location 2	2.62	0.082	7.65	16.5	0.9	1.5	ND	ND	ND	150
CHLORINE DIOXIDE/ CHLORINE										
Raw Water	2.81	0.088	7.79	16.1	0.05	0.05	NA	NA	NA	NA
Location 1	2.63	0.075	7.83	11.6	0.7	NA	0.26	0.30	0.14	93
Location 2	2.69	0.075	7.73	16.6	0.6	NA	0.16	0.09	0.28	120

NA = Not Analyzed
ND = Not Detected
Note: Locations represent distribution system sampling points in order of increasing residence time.

Effect Of Cl2 and ClO2/Cl2 on DBP Formation (Utility 16)
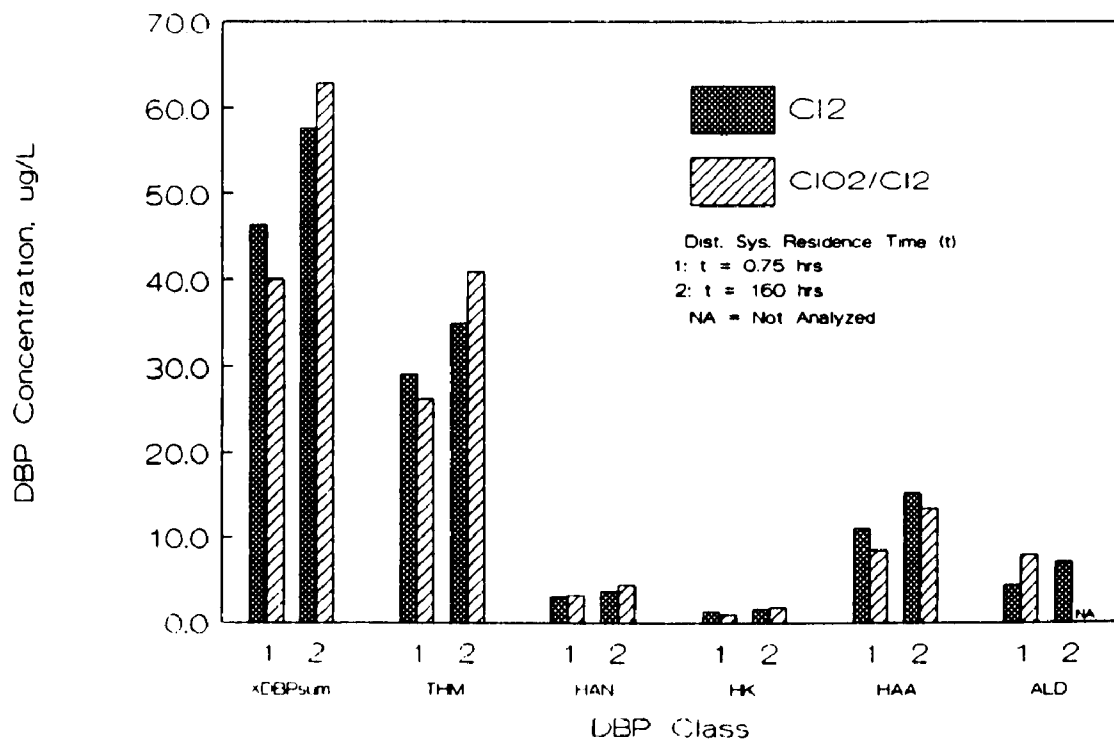
FIGURE 6-66

Treatment Modification Results and Discussion

Utility 37

Utility 37 did not participate in the quarterly baseline sampling program for this study, but was selected for a treatment study because the plant's configuration and operation offered a unique opportunity for a side-by-side comparison of DBP levels produced by chlorine dioxide and chlorine-only preoxidation. This Southeastern utility treats a low-organics river water with a conventional treatment process. The plant typically treats approximately 30 mgd.

The configuration of the plant provides for two separate treatment trains. In 1981, the plant began seasonal use of chlorine dioxide preoxidation (added following flocculation) in one of the trains for THM control. The other train has chlorine preoxidation. Free chlorine is used for residual disinfection in both trains; however, samples were collected before the addition of chlorine for residual disinfection. Schematic diagrams of the two treatment trains are shown in Figure 6-67.

The chlorine dioxide dose was approximately 0.9 mg/L and the chlorine dose was approximately 2.25 mg/L for preoxidation. However, the chlorine dioxide generator product could not be analyzed directly; it could only be analyzed after addition of the generator product to the flocculation basin effluent. Because chlorine dioxide reacts very rapidly, the actual dose was most likely higher than 0.9 mg/L, although the sample was taken immediately after addition of the generator product to the flocculated water. To further illustrate this point, plant operations personnel reported that the applied chlorine dose was 2.25 mg/L; however, the total chlorine residual measured immediately after application of the chlorine to the flocculated water was only 1.15 mg/L.

All samples for this study were collected on May 19, 1989. Water quality parameters for this utility are reported in Table 6-10. On the sampling date, it was determined that there was some degree of mixing between the two treatment trains, since low levels of chlorine dioxide were measured in the chlorine-only treatment train and vice versa. Additionally, although the chlorine dioxide generator was operated to produce the lowest practical levels of free chlorine in the generator product, detectable levels of free chlorine were measured immediately after addition of the generator product to the flocculated water (0.2 mg/L). Thus, the preoxidant in one treatment train was predominantly chlorine dioxide (referred to as the "chlorine dioxide" treatment train), and the preoxidant in the other train was predominantly free chlorine (referred to as the "chlorine" treatment train).

Samples were collected at the plant influent and sedimentation basin effluent. DBP analyses were performed on the sedimentation basin effluent samples. The sedimentation basins had a detention time of approximately 2.5 hours. Following the sedimentation basins, there was mixing of the two trains in the filter influent flume.

Chlorine dioxide, chlorite and chlorate measurements were performed on-site by flow injection analysis. Chlorite levels were 1.16 mg/L in the chlorine dioxide treatment train and 0.07 in the chlorine train (measured at the sedimentation basin effluent). Chlorate concentrations were 0.53 and 0.22 mg/L in the chlorine dioxide and chlorine treatment trains, respectively (sedimentation basin effluent).

CHLORINE

Polymer

Chlorine

Baffle Mixing

Solids Contact Clarifier

Lime
(Not Operational)

Fluoride
Chlorine

CHLORINE DIOXIDE / CHLORINE

Polymer

Chlorine Dioxide

Baffle Mixing

Solids Contact Clarifier

Lime
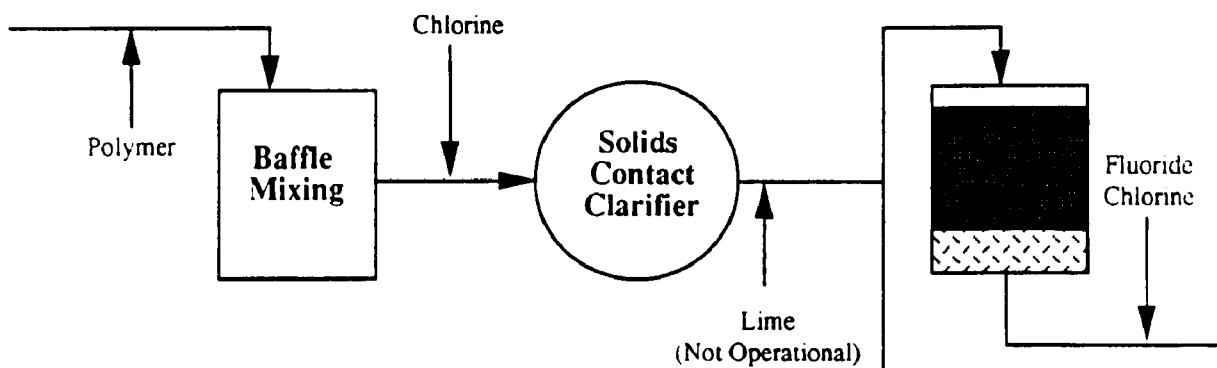
Fluoride
Chlorine
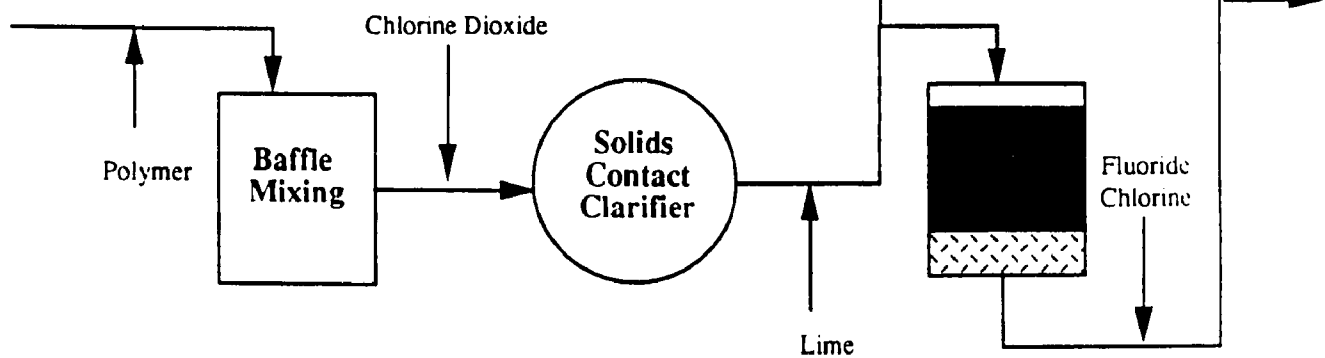
SCHEMATIC OF UTILITY 37 TREATMENT PROCESSES

FIGURE 6-67

TABLE 6-10

UTILITY 37 TREATMENT STUDY
Water Quality Parameters

	TOC (mg/L)	UV Absorbance at 254 nm (cm⁻¹)	pH	Temp (°C)	Chlorine Residual (mg/L) Free	Chlorine Residual (mg/L) Total	Chlorine Dioxide Residual (mg/L)	Chlorite (mg/L)	Chlorate (mg/L)	TOX (μg/L)
Raw Water	1.01	0.050	7.0	15	ND	ND	NA	NA	NA	NA
CHLORINE										
Sed Basin Effluent	1.03	0.023	6.7	15	0.2	0.35	0.19	0.07	0.22	140
CHLORINE DIOXIDE										
Sed Basin Effluent	1.11	0.028	6.8	15	0.05	0.06	0.21	1.16	0.53	69

NA = Not Analyzed
ND = Not Detected

Treatment Modification Results and Discussion

Results of the DBP sampling are presented in Figures 6-68 through 6-73. Figure 6-68 shows the effect of the two different preoxidants on $XDBP_{sum}$ and the DBP classes. From this figure, it is apparent that even in the relatively short detention time in the sedimentation basins, the use of chlorine dioxide preoxidation resulted in lower levels of all measured DBPs compared to chlorine treatment. $XDBP_{sum}$ was almost 50% lower with chlorine dioxide treatment. However, the figure indicates that chlorine dioxide treatment produced detectable levels of DBPs, most likely due, at least in part, to the presence of free chlorine in the chlorine dioxide generator product.

Figure 6-69 illustrates THM levels resulting from the two preoxidation schemes. The advantages of chlorine dioxide as a THM control method are apparent, since levels of chloroform, bromodichloromethane and dibromochloromethane were 52, 75 and 74 percent lower, respectively, with the chlorine dioxide treatment compared to the chlorine-only treatment.

HAN formation was also substantially lower with the chlorine dioxide treatment, as illustrated in Figure 6-70. The concentration of DCAN was over 60 percent lower with chlorine dioxide preoxidation (1.0 μg/L) compared to free chlorine preoxidation (2.9 μg/L). Figure 6-71 shows HK levels produced by the two preoxidation schemes. Again, chlorine dioxide treatment produced significantly lower levels of the two HK compounds. The concentration of 1,1,1-TCP was significantly lower for the chlorine dioxide treatment (0.2 μg/L) as compared to the chlorine treatment (1.6 μg/L). As this ketone is a chloroform precursor, the previously discussed lower TTHM concentration with the use of chlorine dioxide treatment is consistent.

HAA levels are plotted in Figure 6-72. MCAA concentrations were approximately the same for the two treatments and DCAA levels were only 28 percent lower for the chlorine dioxide treatment. However, the concentration of TCAA was over 70 percent lower with chlorine dioxide treatment. Figure 6-73 shows the levels of miscellaneous compounds for the two treatments. Very little difference in the concentrations of chloropicrin and cyanogen chloride was observed. Chloral hydrate was significantly lower with chlorine dioxide treatment (1.8 μg/L) compared to chlorine treatment (4.2 μg/L).

Discussion

Use of chlorine dioxide has been identified as a treatment technology capable of enabling utilities to lower THM levels. Chlorine dioxide preoxidation allows chlorine addition to be delayed until after coagulation, sedimentation and filtration processes have removed precursors to some extent. Chlorine dioxide does not form THMs, although a small amount of TOX may be formed (Chow and Roberts, 1981; Fleischacker and Randtke, 1983; Werdehoff and Singer, 1986; Lykins and Griese, 1986). Additionally, some researchers have found that chlorine dioxide is capable of lowering the concentration of THM and TOX precursors by oxidation (Rav-Acha et al., 1985; Werdehoff and Singer, 1986; Lykins and Griese, 1986). Thus, chlorine dioxide preoxidation in combination with free chlorine residual disinfection would be expected to produce lower levels of DBPs.

Although the results of the study at Utility 16 were inconclusive with respect to reductions in levels of DBPs produced by chlorine dioxide preoxidation, Utility 37

Effect of Cl2 AND ClO2
on DBP Formation (Utility 37)
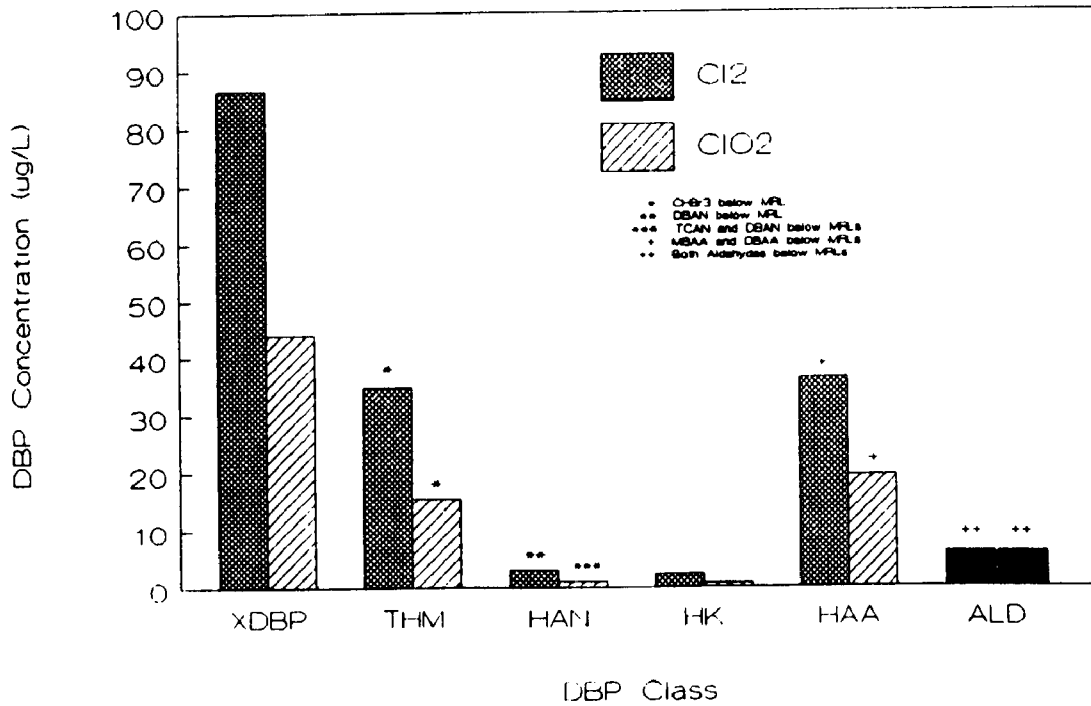
FIGURE 6-68

Effect of Cl2 and ClO2
on THM Formation (Utility 37)
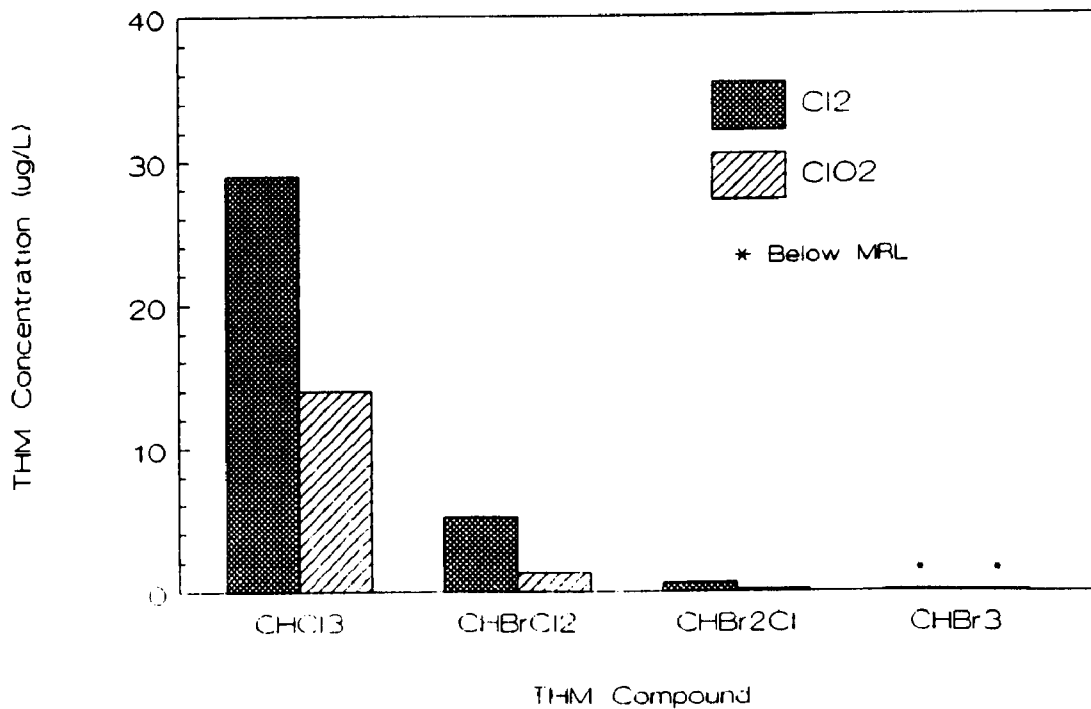
FIGURE 6-69

Effect of Cl2 and ClO2
on HAN Formation (Utility 37)
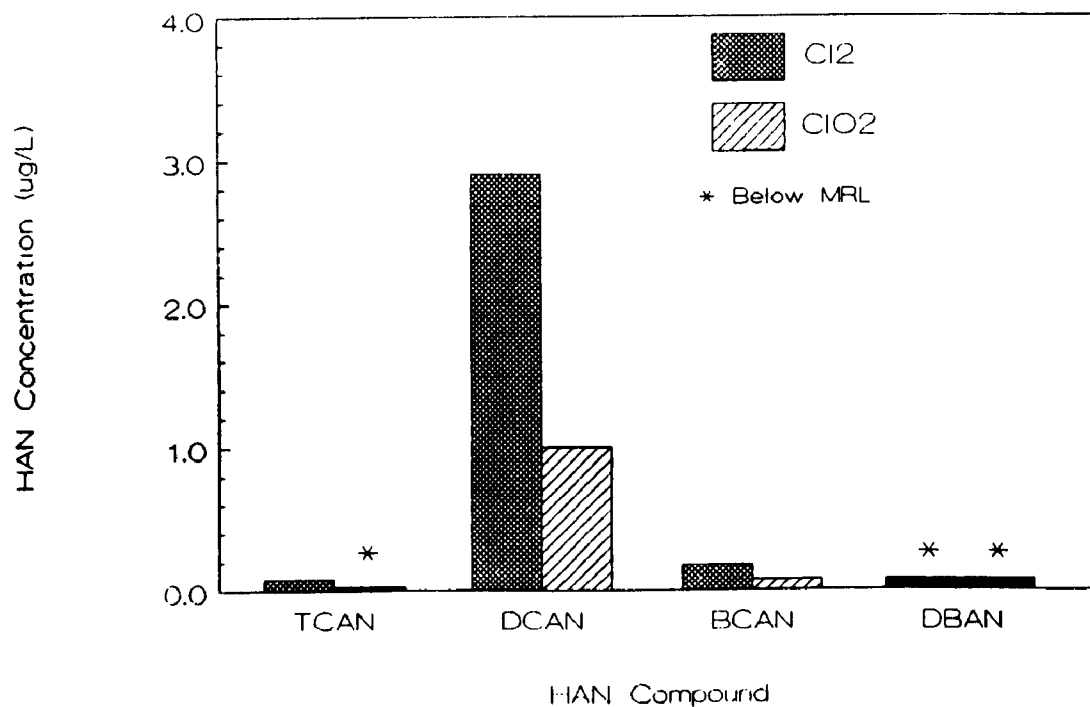
FIGURE 6-70

Effect of Cl2 and ClO2
on Haloketone Formation (Utility 37)
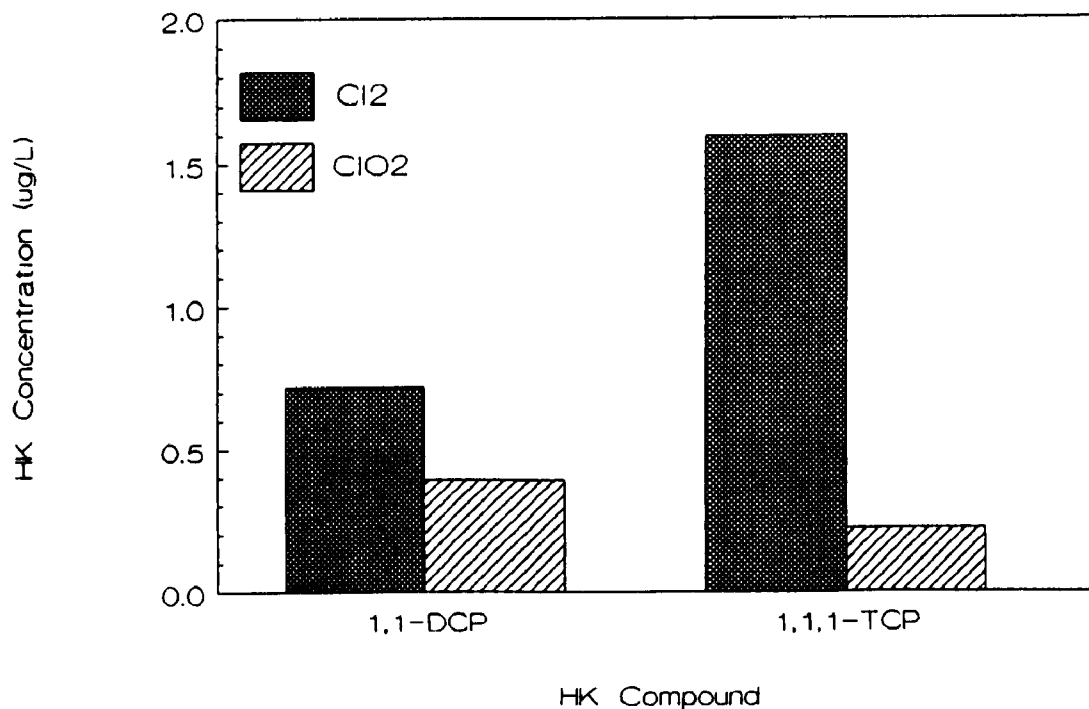
FIGURE 6-71

Effect of Cl2 and ClO2 on
Haloacetic Acid Formation (Utility 37)
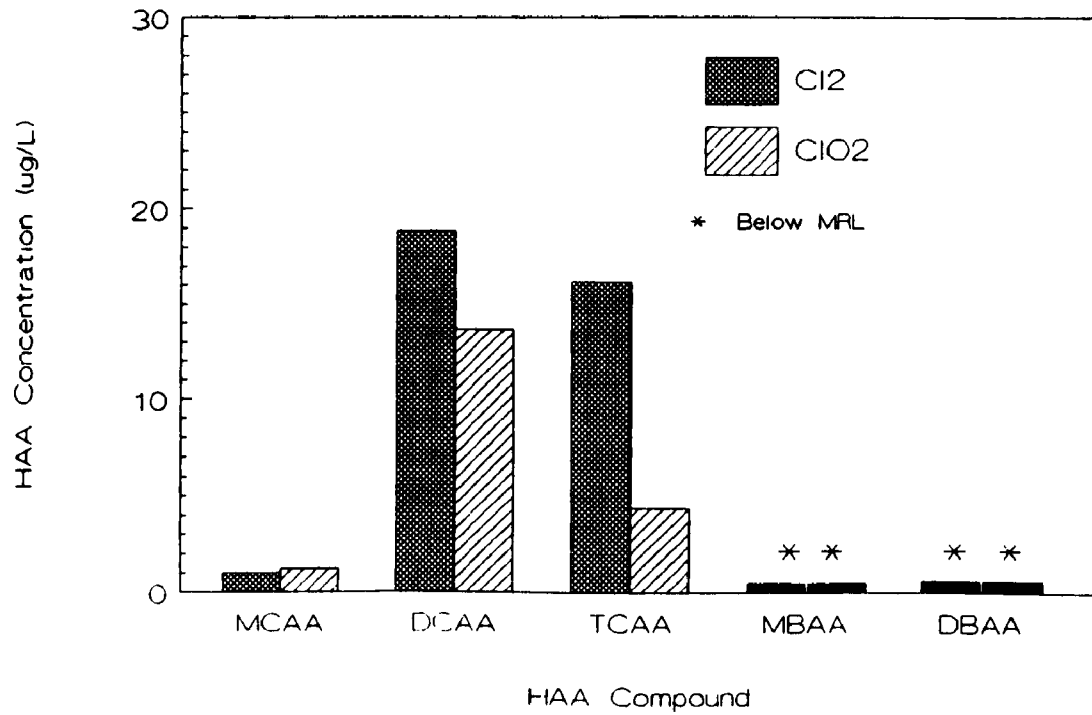
FIGURE 6-72

Effect of Cl2 and ClO2
on Misc. DBP Formation (Utility 37)
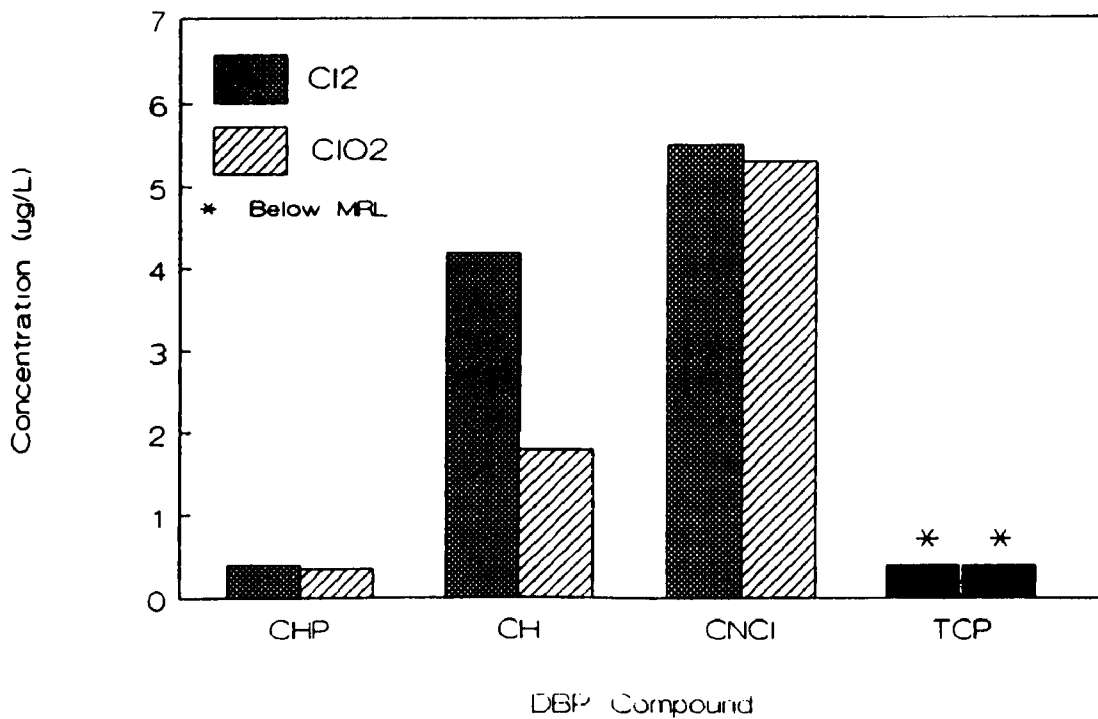
FIGURE 6-73

results indicated that chlorine dioxide preoxidation produced substantially lower levels of many DBPs, even with the presence of free chlorine in the generator product and with some degree of mixing between the two process trains.

The chlorine dioxide generator product was optimized for this study to contain the lowest practical levels of free chlorine. It is interesting to note that routine operation of the generator at Utility 37 resulted in approximately equal amounts of chlorine dioxide and free chlorine in the generator product (before generator optimization, 1.60 mg/L of chlorine dioxide and 1.56 mg/L of total chlorine were measured upon addition of the generator product to the flocculated water). The plant superintendent reported that the generator is operated in this way to avoid "kerosene" and "bleach" odor complaints from consumers that occurred when the level of free chlorine in the generator product was minimized. Household odors associated with chlorine dioxide treatment, including "kerosene" and "chlorinous", have been investigated by Hoehn, et al. (1989). This chlorine dioxide study reports on DBP levels produced when the operation of the chlorine dioxide generator was optimized and does not necessarily reflect the levels experienced under routine operations at Utility 37.

Chlorite and chlorate are inorganic by-products of chlorine dioxide. Currently, the USEPA recommends that the combined residuals of chlorine dioxide, chlorite and chlorate not exceed 1.0 mg/L in distribution systems (USEPA, 1983). Additionally, chlorine dioxide, chlorite and chlorate are among the disinfectants and DBPs targeted by the USEPA's Drinking Water Priority List (Federal Register, 1988).

Levels of chlorite and chlorate in the distribution system samples of Utility 16 were low and the distributed water easily met the recommended level of 1.0 mg/L combined chlorine dioxide, chlorite and chlorate residual. Levels of chlorine dioxide, chlorite and chlorate were not measured in the distribution system of Utility 37, but based on the levels measured in the sedimentation basin effluent, this utility may not have been able to meet the 1.0 mg/L recommended limit under the conditions employed for this study.

COAGULATION STUDIES

Coagulation studies were conducted in order to study the effect of coagulant dose on DBP precursor removal. Utilities 3 and 12 were selected because they were able to adjust their alum dose at full scale without severely compromising the quality of the finished water. Each applied low, medium and high doses of aluminum sulfate, after which samples were collected and analyzed for DBPs and various water quality parameters.

Utility 3

Utility 3 is a conventional treatment plant in the eastern United States with a 10.5-mgd capacity. Figure 6-74 presents a process schematic of the plant and shows the three doses of alum which were applied during the study. Each alum dose was applied on a different day; a period of at least 48 hours passed between initiating each alum dose to assure adequate flushing of the plant before collecting samples. Samples of the plant influent raw water, filter influent and filter effluent were collected and analyzed for TOC and UV-254 absorbance. Turbidity measurements were made on-site at these three locations. Bromide and chloride were also measured in the plant influent.

RAPID MIX   FLOCCULATION   SEDIMENTATION   FILTRATION

ALUM COAGULATION
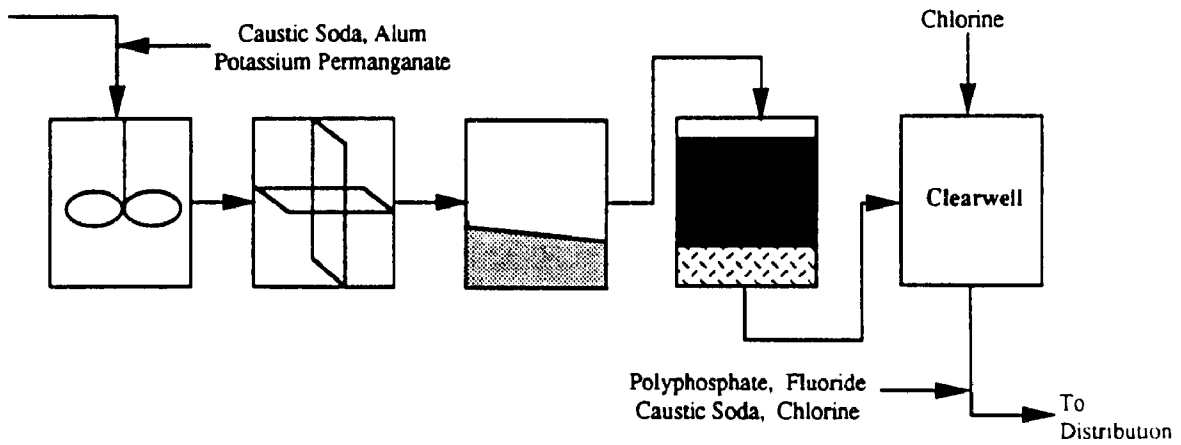
Alum Dosages (ppm)

Low = 10
Medium = 19
High = 40

SCHEMATIC OF UTILITY 3 TREATMENT PROCESS

FIGURE 6-74

Treatment Modification Results and Discussion

Chlorine is normally applied at two places in the plant, at the entrances to the clearwell and to the distribution system. However, during this study, samples from the filter effluent were collected and 24-hour SDS tests were conducted. Thus, no chlorine was applied in the plant to the water that was sampled. A 3.5 mg/L dose of chlorine was applied for the SDS testing. A description of the protocol for the SDS test was provided in Section 3 of this report.

Chlorine residuals, as well as other water quality parameters, are presented in Table 6-11. The table shows that the pH values for each sampling point in the plant were similar for all three alum doses (5.5 to 5.6 at the filter influents and effluents). Additionally, chloride and bromide levels were low, being detected at 5 mg/L and 0.01 to 0.02 mg/L, respectively. Influent turbidity ranged from 1.1 to 1.6 NTU, with filter effluent values of 0.21 NTU for the low alum test and 0.04 to 0.06 NTU for the high and medium alum tests.

Table 6-11 also shows that the influent TOC concentrations ranged between 2.97 and 3.11 mg/L and the UV-254 absorbance between 0.120 and 0.133 cm^{-1}. The percent removals of these water quality parameters at each alum dose are presented in Table 6-12. Percent removals of TOC increased from 25 to 50 percent in the filter influent water as the alum dose increased from 10 to 40 mg/L. At the low alum dose, a greater percent of TOC was removed through filtration (20 percent) than at the medium and high alum doses (15 and 9 percent, respectively); this was probably due to the better settling characteristics of the floc at these doses.

A pattern similar to TOC removal was observed for UV-254 absorbance. Percent removal ranged from 39 to 69 percent through flocculation/sedimentation at the various alum doses. An additional 9 to 26 percent removal was obtained through filtration.

Figure 6-75 presents the effect of increasing alum dose on XDBP$_{sum}$ and DBP classes. In general, DBPs decreased with increasing alum dose. XDBP$_{sum}$ was lowered from 150 to 94 μg/L, and THMs from 86 to 55 μg/L as alum doses increased from 10 to 40 mg/L. Figure 6-76 shows that chloroform was the predominant THM; this is consistent with the low bromide levels found in the plant influent. Chloroform concentrations were reduced from 74 to 45 μg/L as alum doses increased. Changes in coagulant dose had little effect upon the other chlorinated THMs, although these were detected only at levels less than 11 μg/L.

The effect of alum dose on other individual DBPs is presented in Figures 6-77 to 6-80. DCAA and TCAA followed patterns similar to chloroform (Figure 6-77) as did 1,1,1-TCP (Figure 6-78), DCAN (Figure 6-79) and chloral hydrate (Figure 6-80). It should be noted that some DBPs may have undergone hydrolysis since the SDS tests were conducted at pH 8.2; however, this effect would have been consistent for all alum doses tested.

As part of the two coagulation studies, residual aluminum was measured in the plant influent and in the actual distribution system at a residence time of approximately 24 hours. Table 6-11 shows that levels in the plant influent were similar on the three sampling dates (46 to 50 μg/L) and that the levels in the distribution system were higher (75 to 124 μg/L), although residual aluminum was the lowest in the distribution system sample with the highest alum dose.

TABLE 6-11

UTILITY 3 TREATMENT STUDY
Water Quality Parameters

Sampling Location	TOC (mg/L)	UV absorbance (cm⁻¹)	Chloride (mg/L)	Bromide (mg/L)	Turbidity (NTU)	Aluminum (μg/L)	TOX (μg/L)	Free Chlorine Residual (mg/L)	pH	Temp. (°C)
Plant Influent										
Low Alum	3.11	0.122	5	0.02	1.32	47	NA	ND	6.4	14.5
Med Alum	3.08	0.133	5	0.01	1.62	50	NA	NA	6.3	16.0
Hi Alum	2.97	0.120	5	0.02	1.09	46	NA	ND	6.4	14.5
Filter Influent										
Low Alum	2.32	0.074	NA	NA	1.10	NA	NA	ND	5.5	14.0
Med Alum	1.87	0.047	NA	NA	0.68	NA	NA	ND	5.5	16.0
Hi Alum	1.48	0.037	NA	NA	0.44	NA	NA	ND	5.5	13.5
Filter Effluent										
Low Alum	1.71	0.043	NA	NA	0.21	NA	NA	ND	5.5	14.5
Med Alum	1.41	0.030	NA	NA	0.06	NA	NA	NA	5.6	16.0
Hi Alum	1.22	0.026	NA	NA	0.04	NA	NA	ND	5.5	13.5
24 Hr. Simulated Distribution System Test										
Low Alum	NA	NA	NA	NA	NA	124*	240	1.2	8.2	25
Med Alum	NA	NA	NA	NA	NA	87*	190	1.3	8.2	25
Hi Alum	NA	NA	NA	NA	NA	75*	150	1.9	8.2	25

NA = Not Analyzed
ND = Not Detected
* = Aluminum data from actual plant distribution samples.

TABLE 6-12

PERCENT REMOVAL OF TOTAL ORGANIC CARBON
AND ULTRAVIOLET ABSORBANCE AT 254 nm BY
VARIOUS ALUM DOSES AT UTILITY 3

	PLANT INFLUENT TO FILTER INFLUENT (Percent Removal)	PLANT INFLUENT TO FILTER EFFLUENT (Percent Removal)
Total Organic Carbon		
Alum Dose		
Low	25	45
Medium	39	54
High	50	59
UV-254 Absorbance		
Alum Dose		
Low	39	65
Medium	65	77
High	69	78

Effect of Alum Dose
on DBP Formation (Utility 3, SDS)
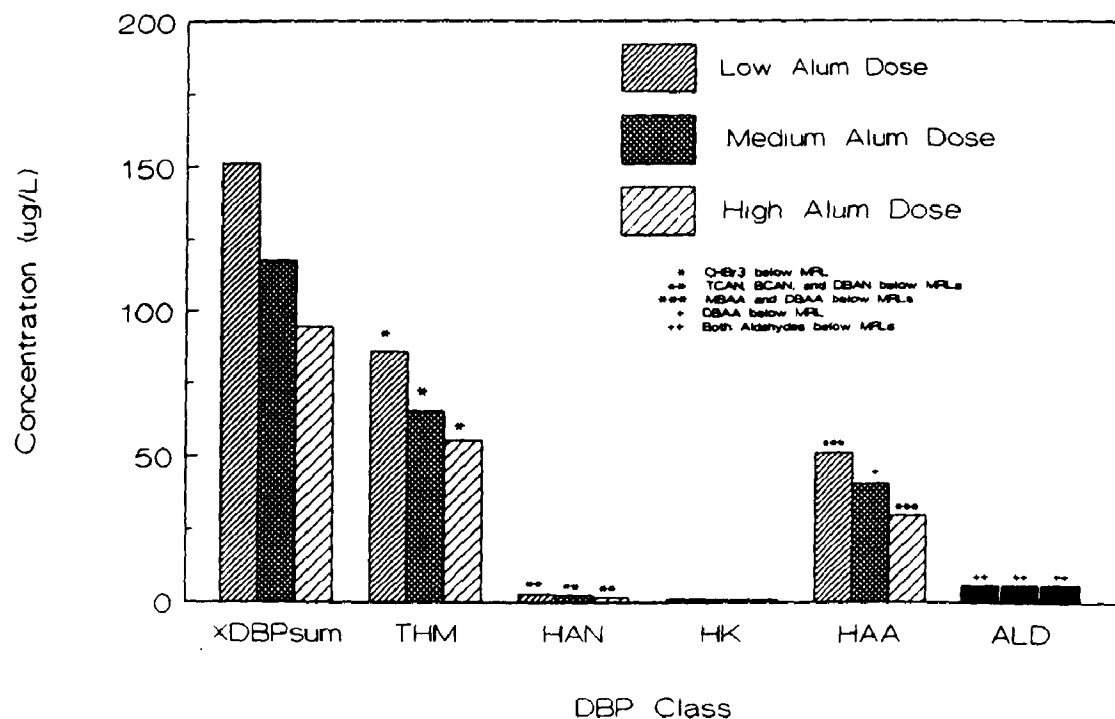
FIGURE 6-75

Effect of Alum Dose
on THM Formation (Utility 3, SDS)

FIGURE 6-76

Effect of Alum Dose
on HAA Formation (Utility 3, SDS)

FIGURE 6-77

Effect of Alum Dose
on HK Formation (Utility 3, SDS)

FIGURE 6-78

Effect of Alum Dose
on HAN Formation (Utility 3, SDS)

FIGURE 6-79

Effect of Alum Dose on
on Misc. DBP Formation (Utility 3, SDS)
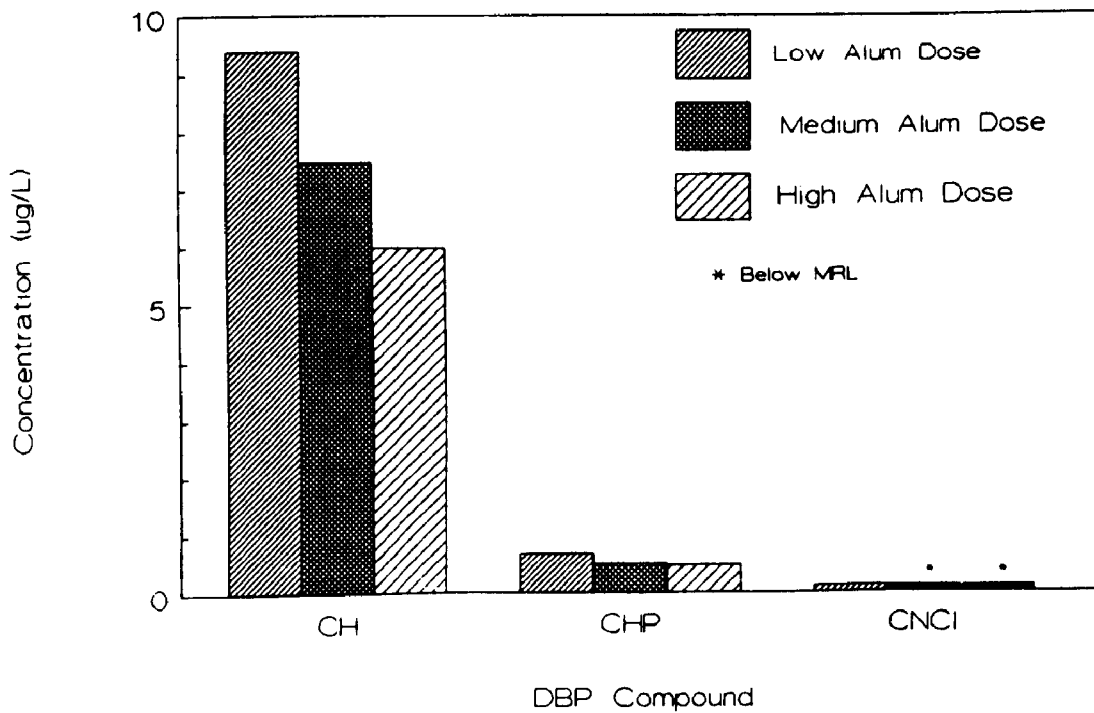
FIGURE 6-80

Treatment Modification Results and Discussion

Utility 12

Utility 12 is a conventional treatment plant in the western United States with a 72-mgd capacity. Figure 6-81 presents a process schematic of the plant and shows the three doses of alum applied during the study. Chlorine was added at two locations in the plant: before the rapid mix (1.8 mg/L dose) and before filtration (1.3 mg/L dose). The total chlorine contact time was approximately 100 minutes. Ammonia was added approximately 4 minutes after filtration, prior to the clearwell, in order to convert the free chlorine residual to chloramines. Chlorine residuals and other water quality parameters are shown in Table 6-13.

Samples of the raw water, sedimentation basin effluent, filter effluent and clearwell effluent were collected and analyzed for all DBPs. Sampling was conducted a minimum of three plant detention times after alum doses were changed.

Table 6-13 presents various water quality parameters for each alum dose applied. Free and total chlorine residuals and temperatures were similar throughout the study. Since the plant had no capability to control pH before or during the sedimentation process, the pH values decreased as alum dose increased. It is important to note that the bromide levels were 0.14 to 0.15 mg/L during the treatment modification study. These bromide levels are in contrast to the quarterly sampling, in which 0.41 mg/L and 0.79 mg/L were detected during the summer, 1988 and winter, 1989 quarters, respectively. The effect of elevated levels of bromide on DBPs as compared to the concentrations found during the treatment study was discussed in more detail in Section 5 of this report.

Residual aluminum was measured in the plant influent and clearwell effluent. Table 6-13 shows that increasing the alum dose did not increase the residual aluminum leaving the plant. In fact, removals of 71 to 76 percent of influent aluminum were observed. These results are in contrast to that observed at Utility 3, indicating a need to better understand aluminum chemistry in relation to the coagulation process. Influent turbidity ranged from 11 to 17 NTU, with clearwell effluent values of 0.14 NTU for the low alum test and 0.06 to 0.07 NTU for the medium and high alum tests.

Table 6-14 shows that the low alum treatment removed 33 percent of the influent TOC, while the medium and high alum doses removed 47 and 46 percent, respectively, as measured in the filter effluent. It is important to note, however, that most of the TOC removal occurred in the sedimentation basins, with little or no additional removal having occurred through filtration. Removal of UV-254 absorbance ranged from 76 to 86 percent from plant influent to filter effluent.

Figures 6-82 to 6-88 present the DBP data from the clearwell effluent in relation to alum dose. Figure 6-82 shows the effect of alum dose on DBP concentrations by class. For XDBP$_{sum}$, concentrations decreased from 87 to 69 μg/L as the alum dose increased from 25 to 75 mg/L; for THMs, the levels decreased from 53 to 39 μg/L. Little or no change was observed for the other DBP classes. Figures 6-83 to 6-88 present individual DBP concentrations by DBP class and the miscellaneous compounds. In general, individual THMs and HAAs decreased slightly with increasing alum dose; little or no change was observed for individual HKs, HANs and ALDs, or for chloropicrin, chloral hydrate, and cyanogen chloride.

6-17

ALUM COAGULATION

Alum
Chlorine

Fluoride, Polymer
Lime, Chlorine

Sodium Hydroxide
Ammonia

Alum Dosages (ppm)

Low = 24.6
Medium = 45.7
High = 73
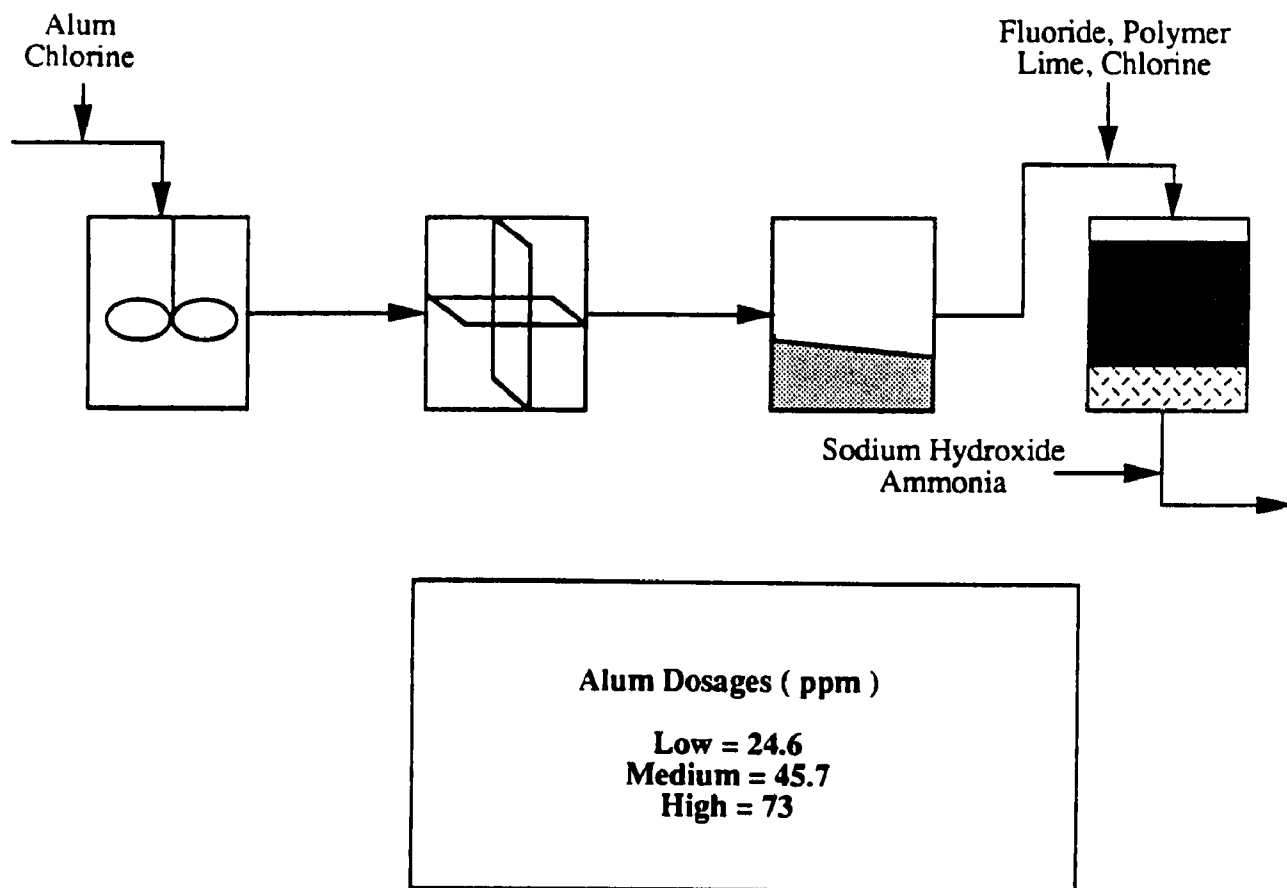
SCHEMATIC OF UTILITY 12 TREATMENT PROCESS

FIGURE 6-81

TABLE 6-13

UTILITY 12 TREATMENT STUDY
Water Quality Parameters

Sampling Location	TOC (mg/L)	UV Absorbance at 254 nm (cm^{-1})	Chloride (mg/L)	Bromide (mg/L)	Turbidity (NTU)	Aluminum (μg/L)	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)	pH	Temp. ($^\circ$C)
Plant Influent										
Low Alum	2.88	0.123	50	0.15	11.0	450	ND	ND	8.6	25
Med. Alum	2.92	0.123	44	0.14	17.0	350	ND	ND	8.5	23
High Alum	2.76	0.121	49	0.15	13.5	370	ND	ND	8.6	23
Sedimentation Basin Effluent										
Low Alum	2.07	0.051	NA	NA	2.2	NA	0.1	0.2	7.4	23
Med. Alum	1.55	0.032	NA	NA	1.2	NA	0.1	0.2	7.0	22
High Alum	1.42	0.027	NA	NA	1.7	NA	0.1	0.5	6.7	22
Filter Effluent										
Low Alum	1.92	0.030	NA	NA	0.13	NA	1.0	1.2	7.4	23
Med. Alum	1.54	0.021	NA	NA	0.04	NA	1.0	1.1	7.4	22
High Alum	1.48	0.017	NA	NA	0.04	NA	0.8	1.0	6.9	22
Clearwell Effluent										
Low Alum	2.00	0.041	NA	NA	0.14	110	0.1	1.0	8.6	23
Med. Alum	1.57	0.025	NA	NA	0.06	94	0.1	1.0	8.7	22
High Alum	1.42	0.022	NA	NA	0.07	107	0.1	1.0	8.6	22

NA = Not Analyzed
ND = None Detected

TABLE 6-14

PERCENT REMOVAL OF TOTAL ORGANIC CARBON
AND ULTRAVIOLET ABSORBANCE AT 254 nm BY
VARIOUS ALUM DOSES AT UTILITY 12

	PLANT INFLUENT TO FILTER INFLUENT (Percent Removal)	PLANT INFLUENT TO FILTER EFFLUENT (Percent Removal)
Total Organic Carbon		
Alum Dose		
Low	28	33
Medium	47	47
High	49	46
UV-254 Absorbance		
Alum Dose		
Low	59	76
Medium	74	83
High	78	86

Effect of Alum Dose
on DBP Formation (Utility 12)
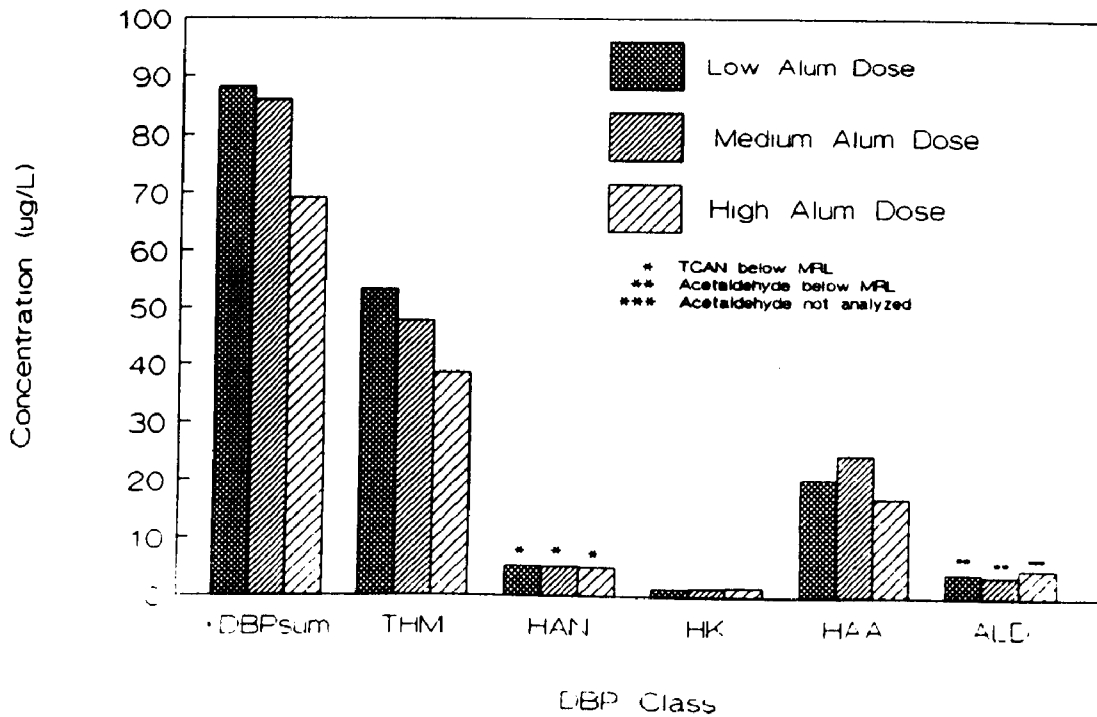
FIGURE 6-82

Effect of Alum Dose
on THM Formation (Utility 12)
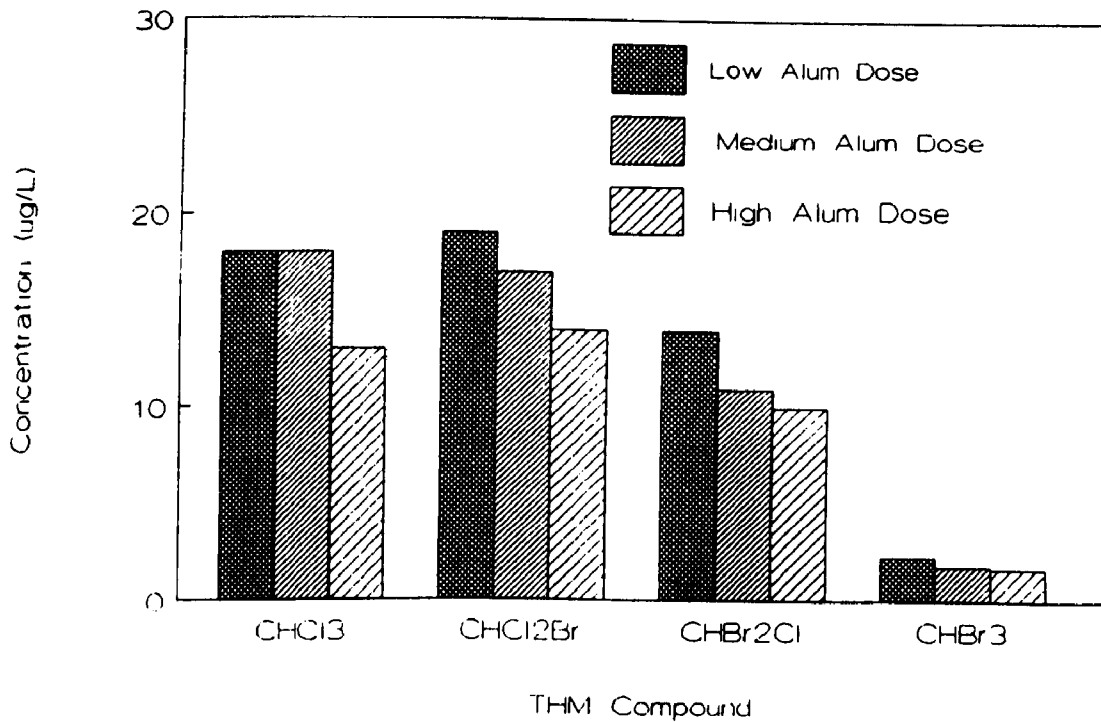
FIGURE 6-83

Effect of Alum Dose
on HAA Formation (Utility 12)
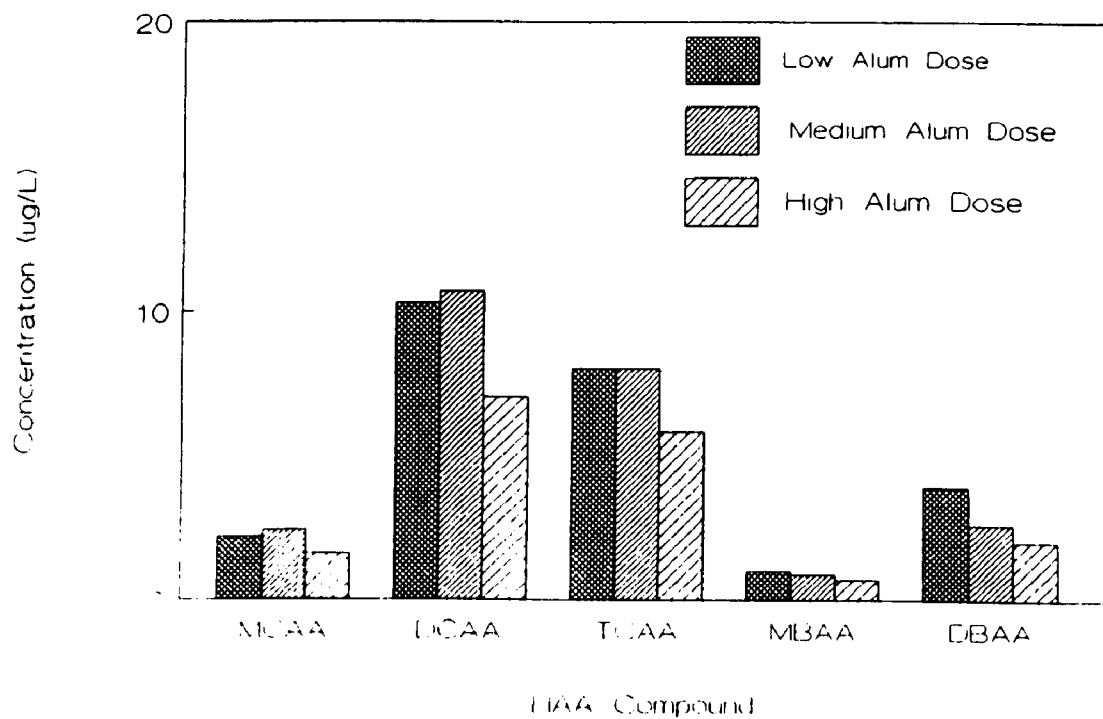
FIGURE 6-84

Effect of Alum Dose
on HK Formation (Utility 12)
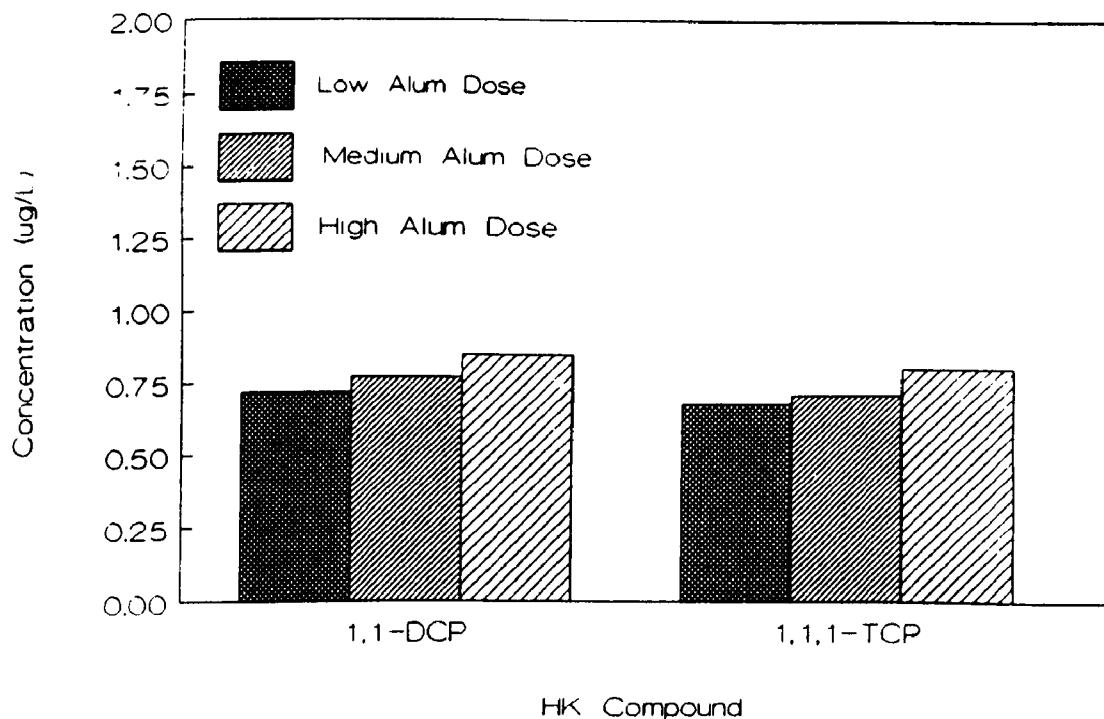
FIGURE 6-85

Effect of Alum Dose
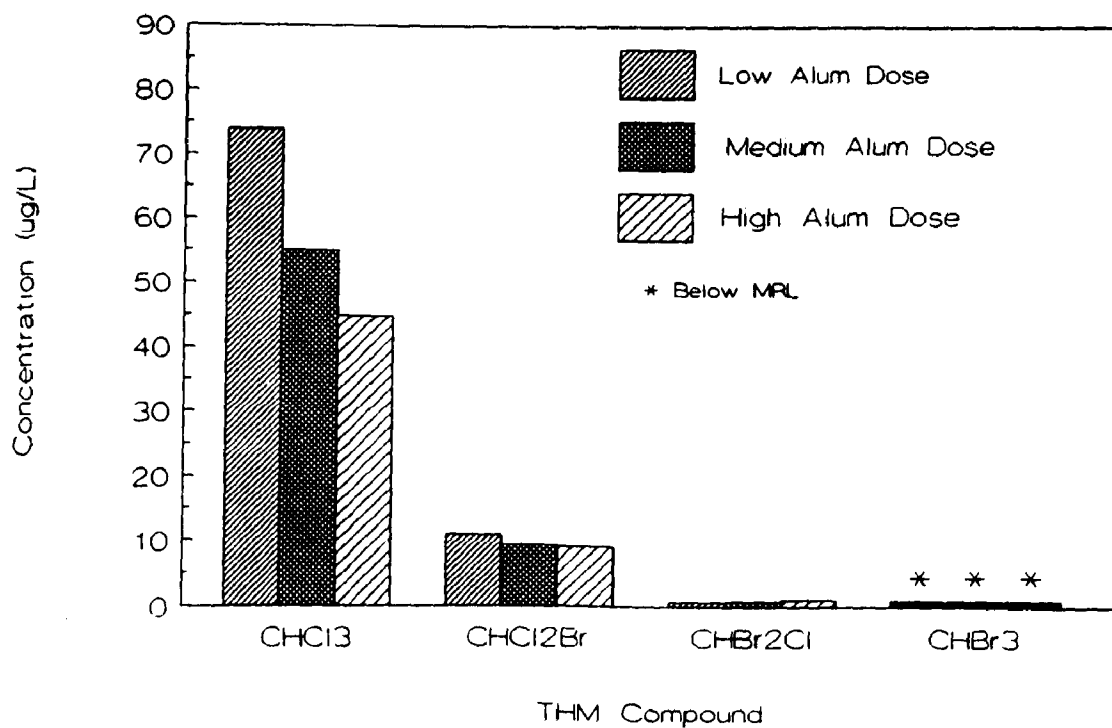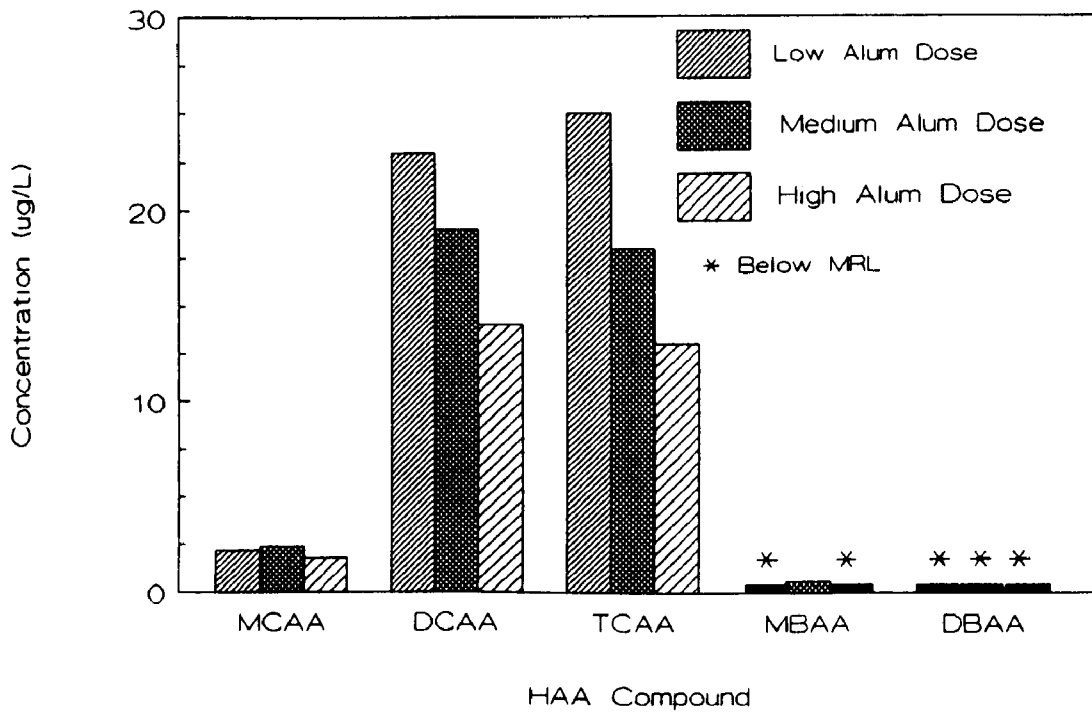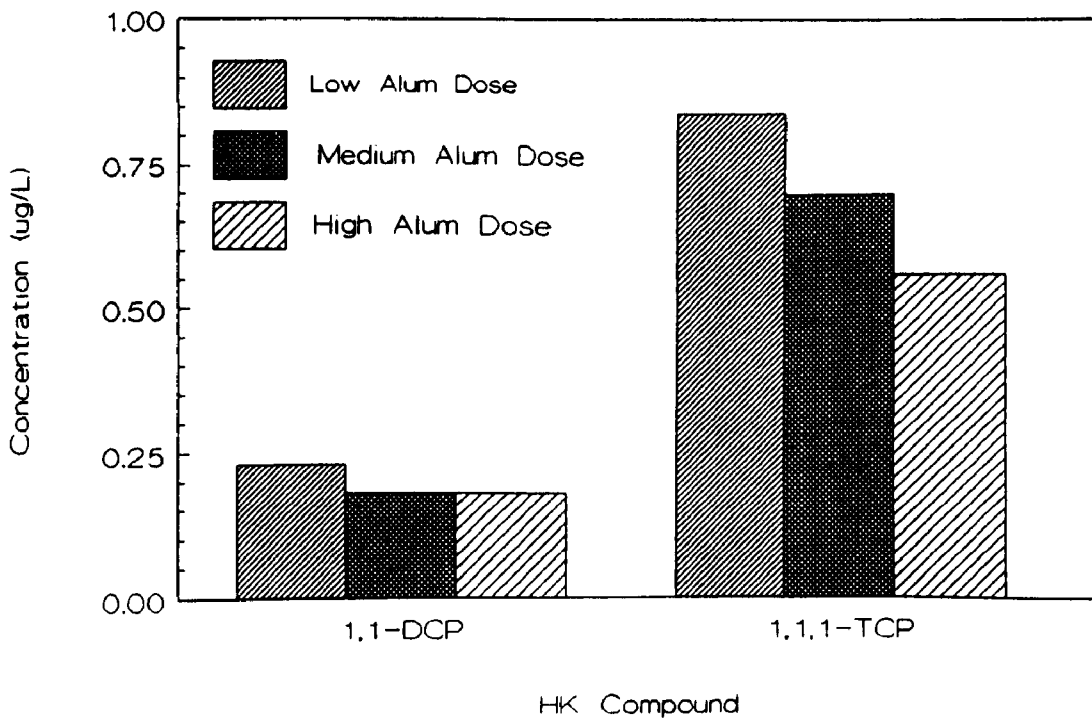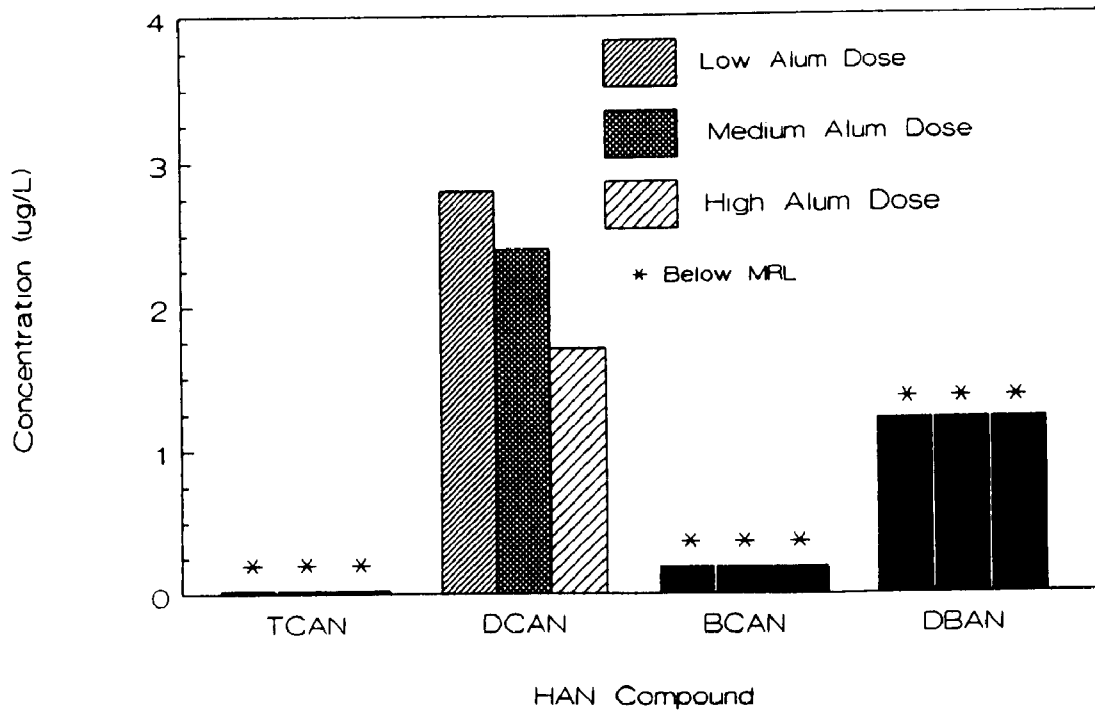## on HAN Formation (Utility 12)
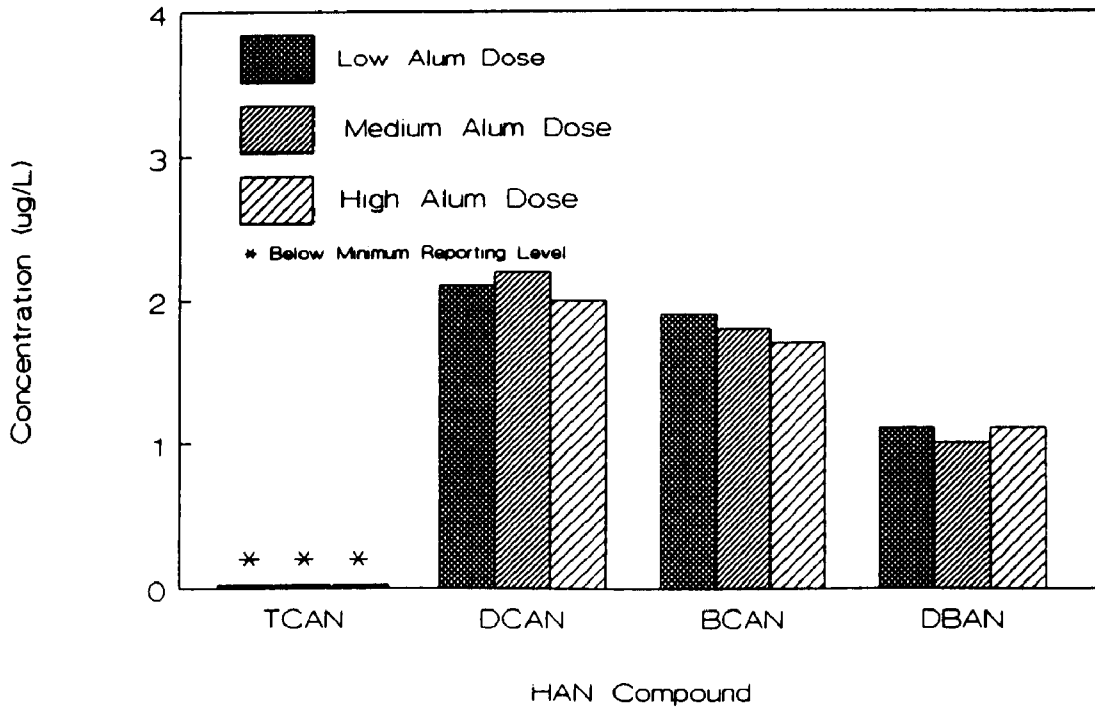
FIGURE 6-86

Effect of Alum Dose
on Misc. DBP Formation (Utility 12)
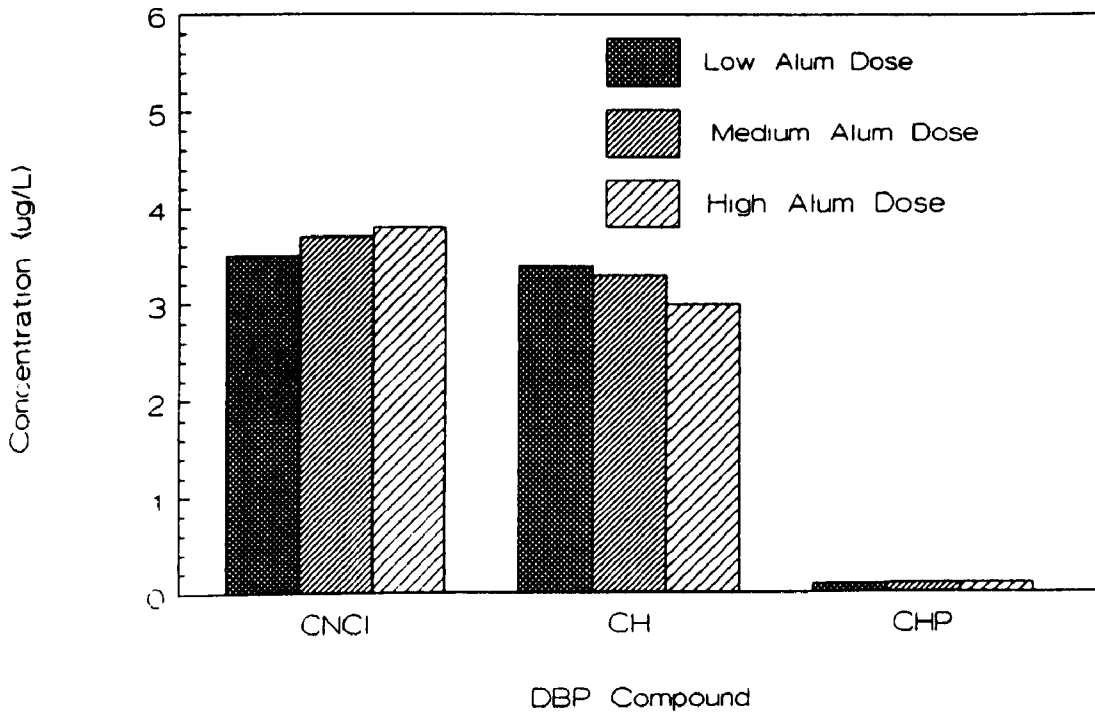
FIGURE 6-87

Effect of Alum Dose
on ALD Formation (Utility 12)
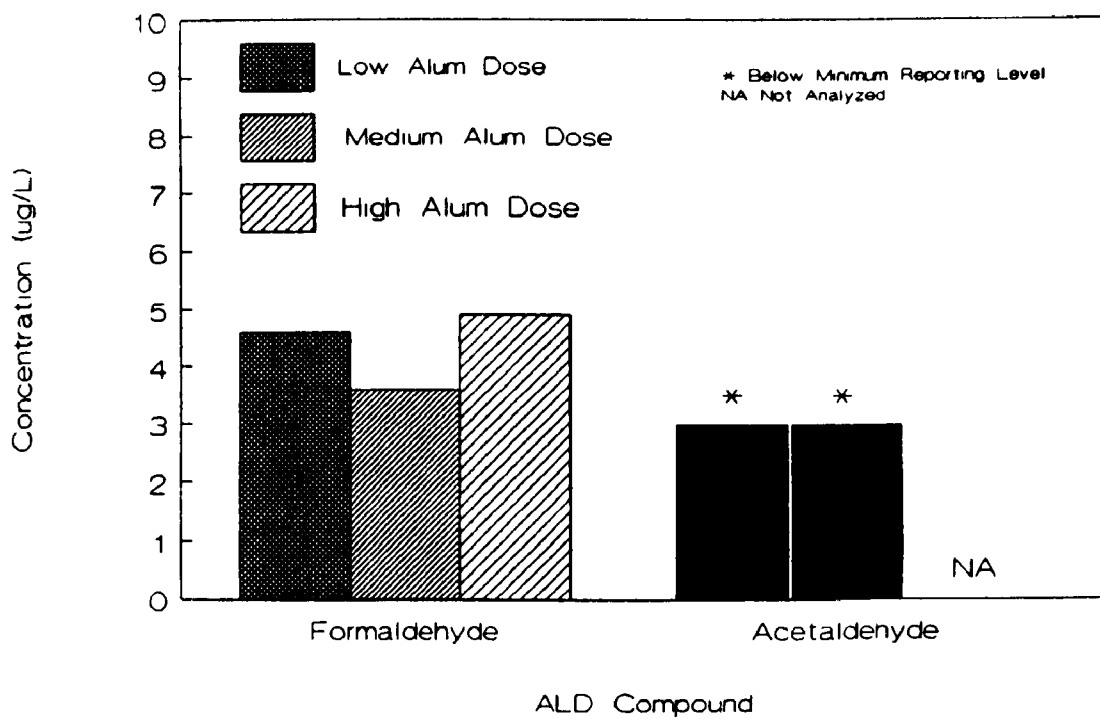
FIGURE 6-88

That greater DBP removal was not observed with increasing alum dose was undoubtedly due to the utility's prechlorination practices. Approximately 1.8 mg/L of free chlorine was added to the raw water, with 75 minutes of contact time from the point of addition to the sedimentation basin effluent. Free chlorine residuals measured in the basin effluent for all three trials were 0.1 mg/L. Consequently, DBP formation occurred before and during TOC removal processes, as demonstrated by the similar concentrations of THMs detected in the sedimentation basin effluent (Table 6-15). However, from the sedimentation basin effluent to the clearwell effluent, an additional 18 μg/L of THMs formed at the low alum dose while only 9 μg/L were produced at high alum dose. A similar trend, although to a lesser extent, was observed for HAAs.

Table 6-15 also shows that THMs increased from the plant influent to the clearwell effluent. However, other classes of DBP compounds such as HKs, and to a lesser extent, HANs, decreased from the filter effluent to the clearwell effluent; similar results were observed for TOX. Since Utility 12 adds sodium hydroxide to increase the pH for corrosion control, the observed decreases were probably due to hydrolysis of these compounds. These results are consistent with those observed by Reckhow and Singer (1984) who showed that TOX and chloroform exhibited opposite pH dependencies. However, as noted in Section 3, problems with on-site dechlorination of TOX samples may have accounted for additional TOX formation during shipping of the chlorinated in-plant samples (this should not have been a problem for the chloraminated clearwell effluent sample). Additionally, Reckhow and Singer (1985) showed the instability of 1,1,1-TCP at high pH, as did Oliver (1983) for DCAN.

Discussion

Several studies have focused upon the use of alum coagulation for removal of THMs and other organic precursor materials from water (Kavanaugh, 1978; Babcock and Singer, 1979; Semmens and Field, 1980; Dempsey et al., 1984; Hubel and Edzwald, 1987). The optimum pH for coagulation of humic substances with alum has been reported to be between 5 and 6 (Kavanaugh, 1978; Babcock and Singer 1979). As noted above, studies at Utility 3 were conducted at pH 5.5 to 5.6. At Utility 12, the pH ranged from 6.7 to 7.4 in the sedimentation basin.

Using a 40 mg/L dose of alum, Utility 3 was able to achieve a TOC removal of 50 percent in the sedimentation basin effluent (filter influent). At this sampling point at Utility 12 for a 73 mg/L alum dose, TOC was reduced by 49 percent. These percent removals are consistent with those reported by Singer (1988), which ranged from 32 to 66 percent. In general, increasing alum dose decreased the levels of DBPs that were produced. At Utility 3, the order of increasing percent removal of DBP and TOX precursors, TOC, and UV-254 absorbance at the high alum dose versus the low alum dose (reference dose) was as follows:

TCAA > UV-254. DCAA > DCAN, TOX, THMs > HKs, TOC

These removals were similar to those reported by Reckhow and Singer (1984) on Black Lake. North Carolina treated water for UV-254, and TOX and DBP precursors:

UV-254 > DCAN, TCAA > TOX, THM, DCAA, > 1,1,1-TCP

TABLE 6-15

CONCENTRATIONS (µg/L) OF VARIOUS DISINFECTION BY-PRODUCTS AND TOTAL ORGANIC HALIDE AT VARYING ALUM DOSES AT UTILITY 12

DBP	Alum Dose	Plant Influent	Sedimentation Basin Influent	Filter Effluent	Clearwell Effluent
Trihalo-	low	0.33	35	45	53
methanes	medium	0.13	34	43	48
	high	0.16	30	36	39
Haloacetic	low	ND	16	27	25
Acids	medium	ND	18	26	25
	high	ND	17	23	17
Haloaceto-	low	ND	4.9	6.1	5.1
nitriles	medium	ND	5.0	6.1	5.0
	high	ND	4.9	6.0	4.8
Haloketones	low	ND	2.5	3.0	1.4
	medium	ND	2.7	3.0	1.5
	high	ND	3.0	3.2	1.6
Chloropicrin	low	ND	0.059	0.088	0.088
	medium	ND	0.068	0.094	0.10
	high	ND	0.070	0.10	0.094
Chloral	low	ND	2.6	3.6	3.4
Hydrate	medium	ND	2.8	3.6	3.3
	high	ND	2.6	3.1	3.0
Cyanogen	low	ND	2.0	2.7	3.5
Chloride	medium	ND	2.1	2.9	3.7
	high	ND	2.2	3.3	3.8
Total Organic	low	18	140	210	140
Halide	medium	18	110	170	120
	high	16	120	170	110

ND = Not Detected

Treatment Modification Results and Discussion

It was not possible to assess removals of these compounds for Utility 12 since the plant influent was chlorinated. It is important to note that Utility 12 practices prechlorination for disinfection and taste-and-odor control. Thus, the advantages of optimized coagulation can be lost if a suitable preoxidant/disinfectant is not available.

Utilities 3 and 12 showed greater TOC removal (39 to 50 percent, from plant influent to filter influent) at the medium and high alum doses as compared to the average TOC removal by the filtering utilities participating in this study (21 percent). It should be noted, however, that the treatment practices by the various utilities surveyed focused on turbidity, rather than on TOC removal. It is not possible to determine whether high TOC removals, as observed at Utilities 3 and 12, would result at other utilities by improving the coagulation process. Such an assessment would need to be conducted on a case by case basis, since some surface waters may not be amenable to greater TOC removals by conventional treatment.

Assessing costs associated with increased alum doses was not part of the scope of this project. However, applying higher alum doses for greater DBP precursor removal will, in many cases, increase the concentrations of total dissolved solids due to pH adjustment for coagulation. This is particularly the case for well buffered waters. Moreover, the amount of chemical sludge produced due to elevated alum doses will be increased. Therefore, costs associated with additional sludge handling, treatment and disposal should be considered.

GRANULAR ACTIVATED CARBON STUDY

The GAC study conducted at Utility 11 was unique among the treatment studies conducted for this project, in that samples were collected during a GAC contactor run, rather than collecting one or two sets of samples at different treatment conditions. In all, six sets of samples were collected over a period of almost four months.

Process Description

Utility 11 operates a large (235 mgd) conventional treatment facility for a low-organics river water. This Midwestern utility also operates demonstration facilities for GAC adsorption and regeneration at the site of the full-scale plant. Numerous pilot and demonstration-scale studies have been conducted at this utility in recent years to evaluate the performance and economic feasibility of GAC for removing trace organic compounds from the plant's source water, a river water receiving industrial discharges and susceptible to spill events. Studies at this utility have also evaluated the feasibility of GAC treatment for removing THM and TOX precursors (McGuire et al., 1989; DeMarco et al., 1981; Clark, 1987; Miller and Hartman, 1982).

A schematic diagram of the full-scale and demonstration facilities is presented in Figure 6-89. The full-scale plant's process train includes rapid mix with alum or alum and polymer addition; flocculation; lamella separation; reservoir storage for 3 days; addition of lime, fluoride and intermittent addition of ferric sulfate to a hydraulic jump; sedimentation and filtration. Free chlorine is added at the hydraulic jump, and at the filter influent and effluent. For the GAC demonstration facilities, a sidestream was diverted after presedimentation to a rapid sand filter (identical to the full-scale plant's filters) and then to two separate GAC contactors, each with a hydraulic capacity of 1
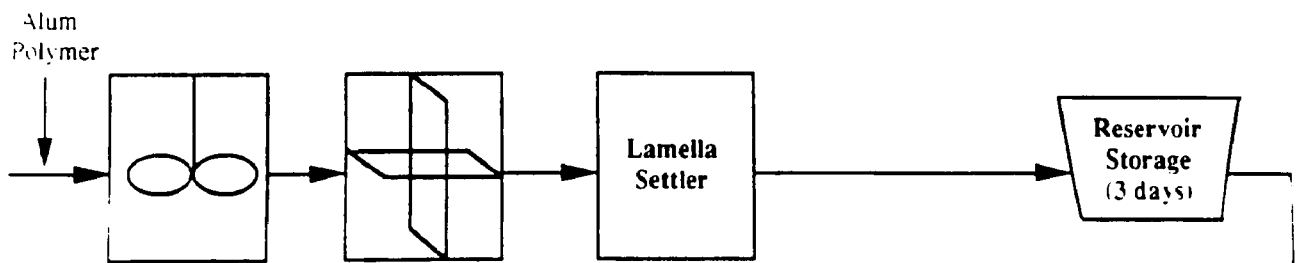
PRETREATMENT:

Alum
Polymer

Lamella
Settler

Reservoir
Storage
(3 days)

CONVENTIONAL PLANT:

Chlorine
Lime
Fluoride
Ferric Sulfate*

Chlorine

Hydraulic
Jump

Chlorine

Chlorine

DEMONSTRATION PLANT:

GAC

Fluoride
Ferric Sulfate*
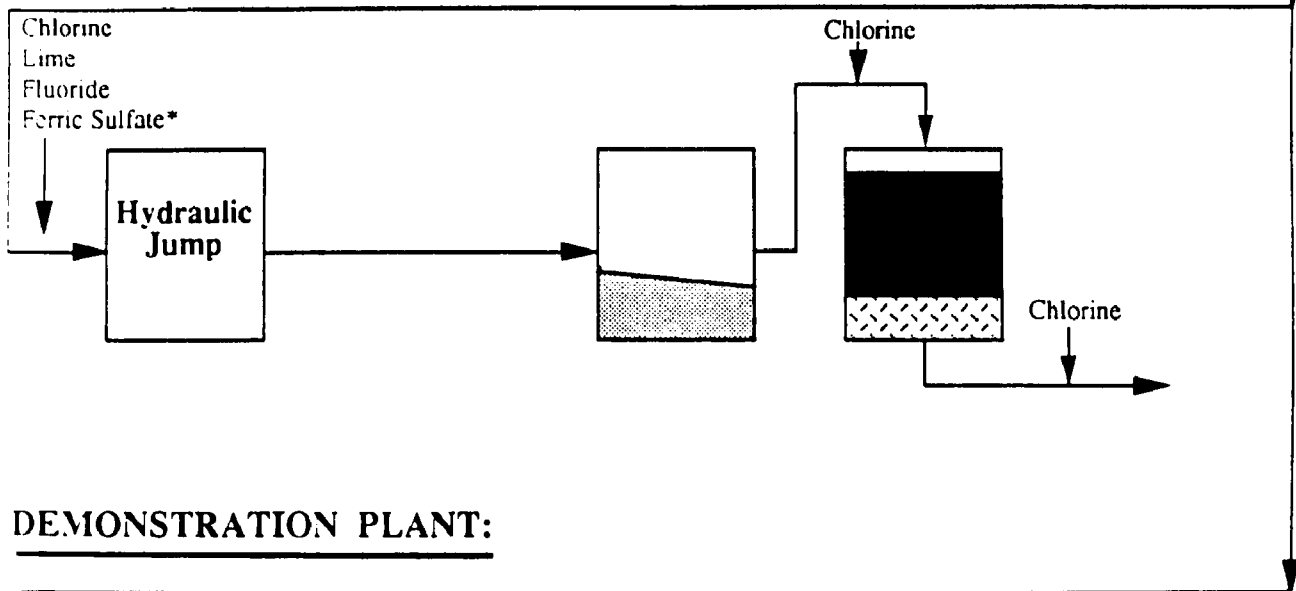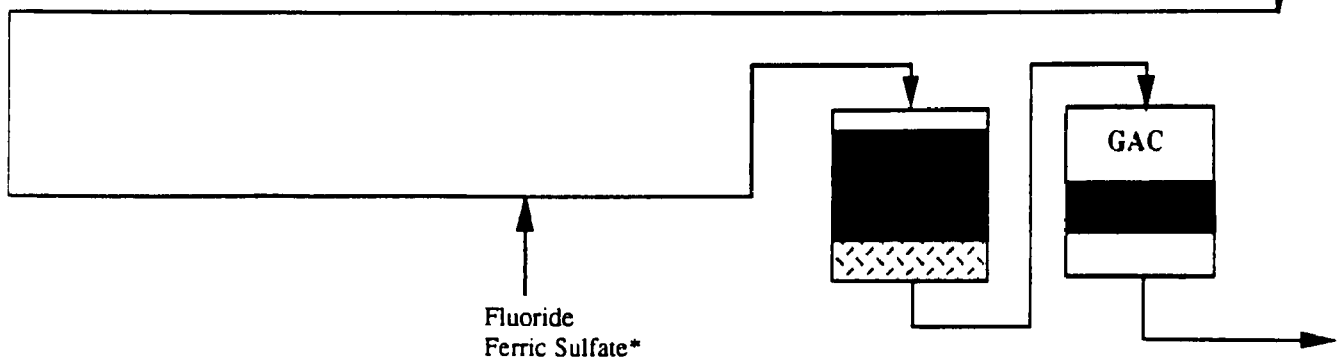
* Ferric Sulfate added intermittently (in use on 5/8/89, 6/12/89 and 7/17/89)

SCHEMATIC OF UTILITY 11 TREATMENT PROCESS

FIGURE 6-89

mgd. The GAC facilities received unchlorinated water and no chlorine was added during treatment in the demonstration plant until after GAC treatment (GAC effluent samples for this study were collected before the addition of chlorine).

The GAC contactors have a diameter of 11 feet. The contactor sampled for this study had a 15-foot carbon depth and was operated at an empty bed contact time (EBCT) of 15 minutes. The carbon was Calgon Filtrasorb 400 (12x40 mesh).

GAC Contactor Operation

Previous studies at this utility have found that dioxins were formed upon regeneration of GAC if chlorinated water had been applied to the carbon, due to the combustion of adsorbed chlorinated compounds (DeMarco et al.. 1988). Thus, recent operation of the GAC contactors at this utility involves somewhat intermittent operation to avoid application of chlorinated water to the GAC.

At Utility 11, the rapid sand filter upstream of the GAC contactors is backwashed with chlorinated (finished plant) water. Filter run lengths varied during the GAC contactor run from approximately 12 to 50 hours. When backwash was initiated, the GAC contactor was taken off-line. The sand filter was backwashed and then flushed with unchlorinated water until such time as residual chlorine was undetectable in the filter effluent. For this reason, each time the dual media filter was backwashed, the GAC contactor was off-line for periods of 1.5 to as much as 4 hours. Thus, the GAC contactor was operated somewhat intermittently, and the "run time" of the contactor did not coincide with "calendar time". Although the sampling period for this study was April 10. 1989 to July 31. 1989, a period of 113 calendar days, the actual run time of the GAC contactor was 95 days. One "run day" of the GAC contactor was defined by the utility as the time required to pass 1 million gallons of water through the contactor at the 1-mgd nominal hydraulic loading rate of the contactor.

Treatment Study Description

The objectives of the treatment study at Utility 11 were twofold:

o   To evaluate the effectiveness of GAC over time in removing DBP precursors: and
o   To determine DBP levels produced by conventional treatment as practiced in the full-scale plant.

The first objective was achieved by sampling the GAC column influent and effluent and performing SDS tests on those samples. Immediate DBP samples were also collected at the GAC influent and effluent as a control (no chlorine added). to determine if the source water contributed to measured levels of DBPs. The second objective was achieved by collection of DBP samples in the conventional plant and at one distribution system location.

Table 6-16 summarizes the sampling plan for the treatment study. The sampling locations are defined in Table 6-17. Six sample sets were collected during the treatment study. Samples were collected at the conventional and demonstration plants on Mondays. Bottles were filled for immediate DBP analyses, as well as for SDS

TABLE 6-16

UTILITY 11 TREATMENT STUDY
SAMPLING PLAN

Sample Location	Sample Type	pH	Temp.	Cl_2	TOC/UV	Cl^-/Br^-	DBPs (incl. ALDs)	ALDs Only	Comments
1. Raw	Immediate	X	X	X	X	X		X	
2. A1	Immediate	X	X	X	X				
3. A2	Immediate	X	X	X	X		X		
4. B1	Immediate	X	X	X	X				
5. B2	Immediate	X	X	X	X		X		
6. B2[1]	SDS 4.5	X	X	X			X		
7. B2[2]	SDS 4.5 Amb.	X	X	X			X		
8. B3	Immediate	X	X	X		X	X		
9. B3[1]	SDS 4.5	X	X	X			X		
10. B3[3]	SDS 2.0	X	X	X			X		
11. A3	Immediate	X	X	X	X		X		Collected 3 days after collection of Samples 1 - 10
12. Blank	SDS 4.5	X	X	X			X		Buffered to pH 8.2, addition of Br^- to level measured in raw water

Note: DBP analyses include THMs, HANs, HKs, HAAs, CH, CHP, CNCl and ALDs.
1. SDS protocol: Cl_2 dose = 4.5 mg/L, pH = 8.2, Temp. = 25°C, Time = 3 days.
2. SDS protocol: Cl_2 dose = 4.5 mg/L, pH = 8.2, Temp. = Temp. of clearwell effluent at time of sampling, Time = 3 days.
3. SDS protocol: Cl_2 dose = 2.0 mg/L, pH = ambient, Temp. = 25°C, Time = 3 days.

TABLE 6-17

UTILITY 11 SAMPLING LOCATIONS

ABBREVIATION	LOCATION
Raw	Plant Influent
A1	Full-Scale Plant. Filter Influent (After primary and secondary sedimentation, and prechlorination)
A2	Full-Scale Plant. Clearwell Effluent
A3	Full-Scale Plant. Distribution System (Detention time = 3 days)
B1	Demonstration Plant. Filter Influent (After primary sedimentation, no chlorination)
B2	Demonstration Plant, Filter Effluent/GAC Contactor Influent
B3	Demonstration Plant, GAC Contactor Effluent

Treatment Modification Results and Discussion

testing of the unchlorinated GAC influent and effluent, and were shipped overnight to Metropolitan for analysis and set-up of the 3-day SDS tests. On Thursdays following the Monday sampling dates, the distribution system was sampled. A distribution system sampling point was selected which had an approximate residence time of 3 days, determined by fluoride tracer studies (conducted by Utility 11) and checked monthly (by Utility 11) by comparing simulated distribution system THM and actual distribution system THM sample results. Thus, the water sampled at this point on a given Thursday was the same water leaving the plant's clearwell effluent the previous Monday. In this way, formation of DBPs in the distribution system could be evaluated, although not on a strictly controlled basis.

Simulated Distribution System Testing

The SDS test protocol was described in Section 3. For this study, all SDS testing was performed at Metropolitan according to Metropolitan's SDS protocol, which had not been developed specifically to simulate Utility 11's distribution system. The protocol called for buffering to pH 8.2, and incubating at 25°C for three days. The applied chlorine dose of 4.5 mg/L was determined adequate to insure a chlorine residual of at least 0.5 mg/L after 3 days of incubation. Two separate chlorine demand tests were conducted on Utility 11's unchlorinated GAC column influent water, one in mid-February and the other in early April, 1989, before start-up of the GAC column. Although the GAC column was expected to remove a substantial amount of the chlorine demand, especially at the beginning of the column run, it was determined that the dose of 4.5 mg/L would be applied to both the GAC column influent and effluent in order to provide a basis of comparison for the SDS DBPs in the column influent and effluent. In practice, the chlorine dose required by the GAC column effluent is significantly lower than that required by the column influent.

An additional SDS sample was run on the GAC column effluent at identical conditions as the other contactor effluent SDS samples, except the chlorine dose was 2.0 mg/L and the samples were run at ambient pH. These samples were run to approximate operating conditions anticipated by Utility 11 when future full-scale GAC facilities are on-line (i.e., lower chlorine dose and no lime addition) (see Section 3 of this report). On two sampling dates, a third SDS protocol was used, in which a GAC influent sample was incubated at the temperature of Utility 11's clearwell effluent at the time of sample collection. Results of this test provided a basis of comparison between actual and SDS data (see Section 3 of this report).

Simulated Distribution System Testing Results and Discussion

Water quality parameters for the immediate samples collected on all six sampling dates are reported in Table 6-18. As reported in the table, TOC levels in the raw water ranged from 1.75 to 2.83 mg/L, and TOC levels in the GAC column influent (sampling point "B2") fell within the range 1.37 to 2.31 mg/L. The TOC removal performance of the GAC column is plotted in Figure 6-90. TOC breakthrough, defined by Utility 11 as a TOC concentration of 1.0 mg/L in the combined effluent of on-line GAC contactors (only one of which was sampled for this study), did not occur within the 95-day sampling period. The GAC was very effective for TOC removal. For the first 25 run days, the contactor effluent TOC remained the same as that measured on Run Day 0.2 (0.1 mg/L), which represents the non-adsorbable fraction of the TOC. After

TABLE 6-18

UTILITY 11 TREATMENT STUDY
Water Quality Parameters

Sampling Location	TOC (mg/L)	Absorbance at 254 nm (cm⁻¹)	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)	pH	Temp. (°C)
Run Day 0.2 (4/10/89)						
Raw	2.83	0.175	NA	NA	7.6	10
A1	1.88	0.072	2.08	2.30	8.2	16
A2	1.77	0.063	1.60	1.78	8.6	9
A3 (4/13/89)	1.78	0.062	0.9	NA	8.6	11
B1	1.88	0.074	NA	NA	7.0	9
B2	1.80	0.070	NA	NA	7.1	12
B3	0.10	0.032	NA	NA	10.0	9.4
Run Day 13 (4/24/89)						
Raw	2.10	0.148	NA	NA	7.6	14
A1	1.54	0.050	2.23	2.41	8.5	12
A2	1.51	0.048	1.66	1.75	8.5	12
A3 (4/27/89)	1.52	0.021	0.7	0.8	8.7	15
B1	1.87	0.058	NA	NA	7.3	12
B2	1.52	0.058	NA	NA	7.3	12
B3	0.10	0.029	NA	NA	7.3	13
Run Day 25 (5/8/89)						
Raw	1.75	0.161	ND	ND	7.6	15
A1	1.59	0.094	2.10	2.30	9.0	16
A2	1.56	0.024	1.64	1.88	8.9	14
A3 (5/11/89)	1.49	0.022	0.7	0.8	8.8	16
B1	1.60	0.087	ND	ND	7.2	15
B2	1.37	0.042	NA	NA	NA	16
B3	0.10	0.003	ND	ND	6.8	15
Run Day 54 (6/12/89)						
Raw	2.47	0.116	ND	ND	7.7	23
A1	2.24	0.066	1.94	2.23	8.6	23
A2	2.15	0.034	1.53	1.68	8.4	23
A3 (6/15/89)	2.00	0.042	0.3	0.4	8.6	22
B1	2.14	0.058	ND	ND	7.4	23
B2	2.24	0.054	ND	ND	7.5	23
B3	0.20	0.003	ND	ND	7.2	23

TABLE 6-18 (Continued)

UTILITY 11 TREATMENT STUDY
Water Quality Parameters

Sampling Location	TOC (mg/L)	Absorbance at 254 nm (cm^{-1})	Free Chlorine Residual (mg/L)	Total Chlorine Residual (mg/L)	pH	Temp. (°C)
Run Day 82 (7/17/89)						
Raw	2.42	0.090	ND	ND	7.6	27
A1	2.22	0.066	1.58	1.82	8.7	27
A2	2.08	0.032	2.08	2.48	8.4	27
A3 (7/20/89)	1.95	0.036	0.4	0.5	8.4	26
B1	2.15	0.056	ND	ND	7.5	27
B2	2.16	0.056	ND	ND	7.4	27
B3	0.60	0.009	ND	ND	7.2	27
Run Day 95 (7/31/89)						
Raw	2.59	0.098	NA	NA	7.7	27
A1	2.39	0.115	1.71	1.96	8.7	27
A2	2.13	0.035	2.05	2.18	8.4	27
A3 (8/3/89)	2.17	0.038	0.3	0.4	8.5	NA
B1	2.30	0.064	NA	NA	7.6	27
B2	2.31	0.060	NA	NA	7.4	27
B3	0.85	0.015	NA	NA	7.2	27

NA = Not Analyzed
ND = Not Detected

TOC vs Run Time for GAC
Column Influent and Effluent, Utility 11

+———+GAC Inf
Immediate

Δ······ΔGAC Eff
Immediate
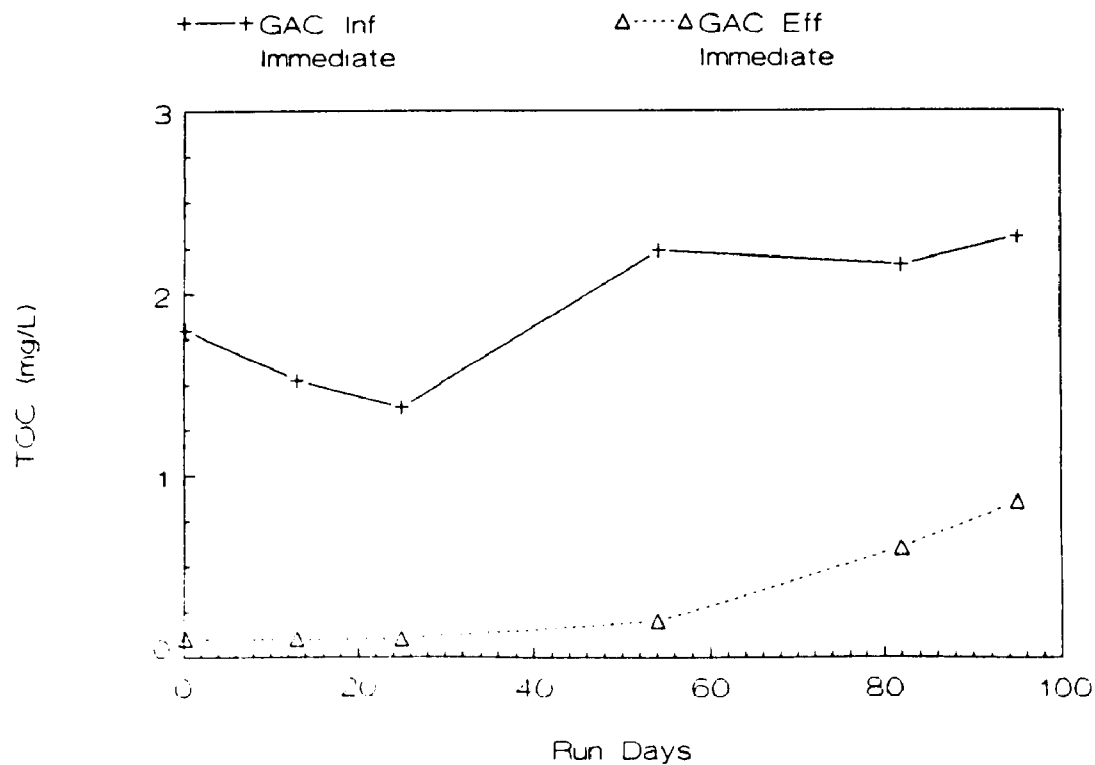
Run Days

FIGURE 6-90

TOC Breakthrough Profile
At Utility 11
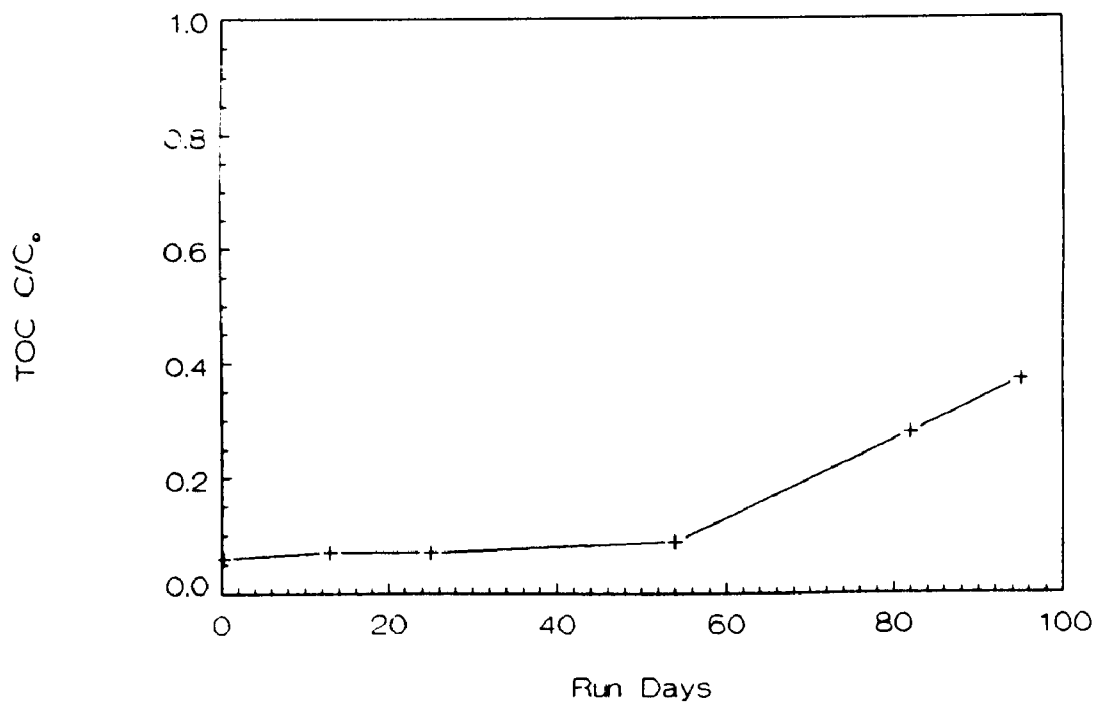
Run Days

FIGURE 6-91

another 29 run days, contactor effluent TOC had only increased to 0.2 mg/L. It was not until the sampling on the 82nd run day that a substantial increase in contactor effluent TOC was measured (0.6 mg/L). A further 13 run days had increased the contactor effluent TOC to 0.85 mg/L, showing evidence of imminent TOC breakthrough.

These TOC removal results are consistent with published data from previous GAC runs at Utility 11's demonstration facilities. DeMarco, et al. (1981) reported a non-adsorbable TOC level of approximately 0.2 mg/L in an example plot of a GAC run at Utility 11 (16-minute EBCT). For the same run, the column effluent TOC was within the range of 0.8 to 1.2 mg/L after 95 days, while column influent TOC values ranged from approximately 1.3 to 2.8 mg/L during the first 95 days of column operation. Additionally, Lykins, et al. (1988) reported non-adsorbable TOC levels of 0.2 from a GAC run at Manchester, New Hampshire (23-minute EBCT), and 0.5 mg/L from Jefferson Parish, Louisiana (20-minute EBCT).

Figure 6-91 is the TOC breakthrough profile for Utility 11, plotted in the form C/C_0 as a function of run time. Additionally, Figure 6-92 shows breakthrough profiles from three previous GAC column runs at Utility 11 (15-minute EBCT) published by Miller and Hartman (1982). In comparing Figures 6-91 and 6-92, even though the shapes of the curves are different, the values of C/C_0 at approximately 90 to 100 days range from approximately 0.4 to 0.6 in the breakthrough profiles shown in Figure 6-92, and the value of C/C_0 at 95 days is approximately 0.4 in Figure 6-91. It is interesting to note that the operation of the GAC columns for the data in Figure 6-92 included prechlorination upstream of the columns, which prevented or at least reduced the potential for microbiological activity within the GAC bed. The curve shown in Figure 6-91 was produced from data without chlorination upstream of the GAC column.

The TOC removal results from Utility 11 are favorable compared to published results from other utilities. For example, in an extensive pilot study conducted by Metropolitan (McGuire et al., 1989), influent TOC values for Colorado River water ranged from approximately 2.0 to 3.1 mg/L (only slightly higher than the influent TOC range for Utility 11). However, using a pilot GAC column with an EBCT of 15 minutes and 12x40 mesh carbon, a column effluent TOC of 0.85 mg/L occurred after only 30 run days, and after 95 run days, the column effluent TOC was 1.7 mg/L.

TOC removal results from GAC studies at other utilities occur between the favorable results achieved at Utility 11 on the one hand, and the relatively unfavorable results of Metropolitan on the other. A pilot study was conducted at Jefferson Parish, Louisiana using Mississippi River water and 1-mgd GAC contactors with a 20-minute EBCT. Results of this study, reported by Lykins, et al. (1988) and McGuire, et al. (1989), indicated that TOC was steadily removed by the GAC columns for up to 160 days, with C/C_0 continuing to increase during that time. Influent TOC concentrations generally ranged from approximately 2.5 to 3.5 mg/L. After 120 to 160 days, C/C_0 was reported in the range of 0.6 to 0.7 in three separate column runs at Jefferson Parish. At Manchester, New Hampshire, pilot study results indicted that after approximately 35 days, C/C_0 had increased to approximately 0.7 and fluctuated around that value for the remainder of the 130-day column run (Lykins et al., 1988). Influent TOC for the lake water used in this study generally ranged from 2.2 to 2.8 mg/L. Results of a pilot study conducted at Philadelphia, Pennsylvania, on Delaware River water was reported
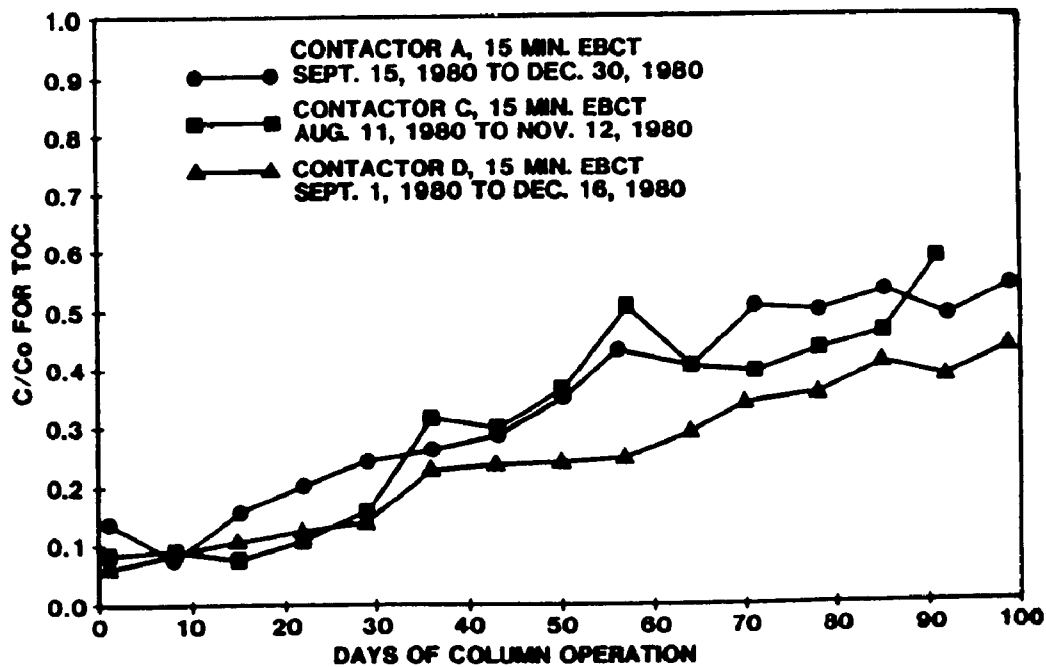
TOC Breakthrough Profiles for Three
Demonstration-Scale Contactor Runs
at Utility 11 (McGuire et al., 1989).

FIGURE 6-92

SDS TTHMs vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf
3-day SDS

Δ-----Δ GAC Eff
3-day SDS
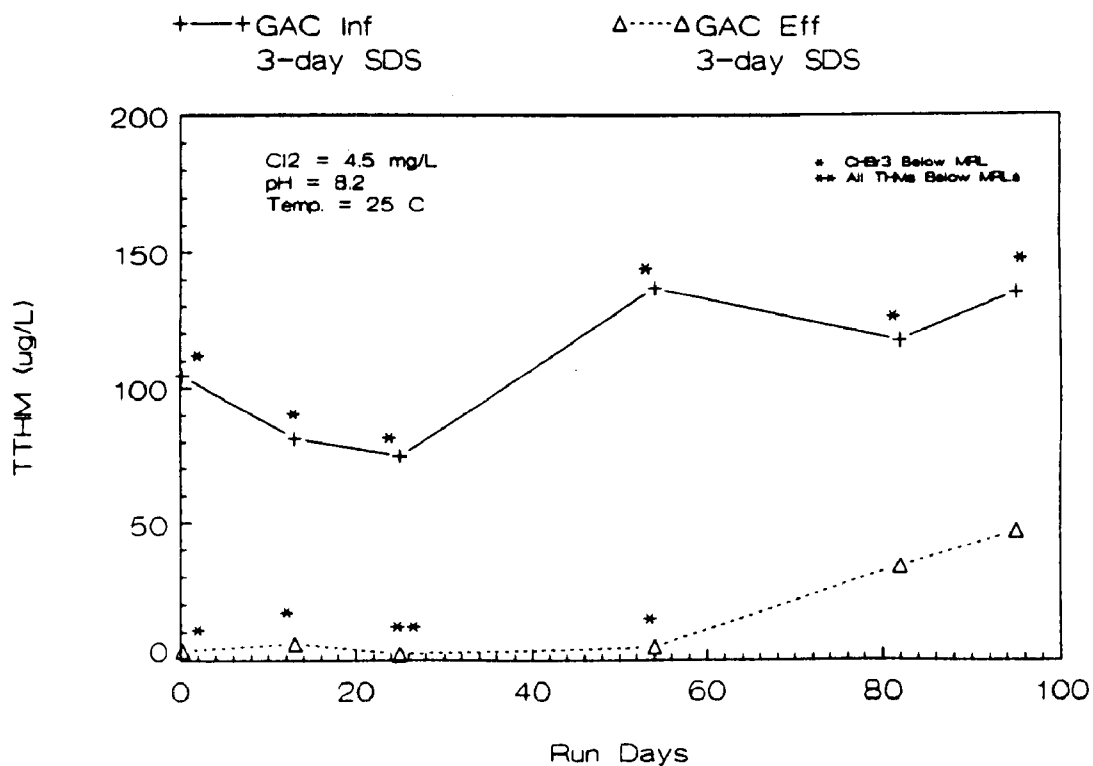
FIGURE 6-93

by McGuire, et al (1989). In this study, influent TOC concentrations ranged from 1.86 to 2.94 mg/L and the columns were operated at an EBCT of 15 minutes. C/C_0 increased steadily over the first 65 days of the column run to approximately 0.4, then increased rapidly after that time until C/C_0 reached 0.6 after 85 days. Thus, it is apparent that the effectiveness of GAC for DBP precursor removal, and hence the feasibility of GAC as a DBP control method, is site-specific, with Utility 11's results being favorable compared to those of some other utilities.

It was beyond the scope of the treatment study at Utility 11 to completely characterize TOC and SDS DBP removal through the entire duration of the GAC contactor run. Rather, the objectives of this study focused on TOC and SDS DBP removal in the early breakthrough stage. Thus, as seen in Figures 6-90 and 6-91, sampling did not extend into the steady state region of the TOC breakthrough curve.

GAC treatment was also effective in removing UV-254, as is apparent in examining the data presented in Table 6-18. The initial UV-254 data appear anomalous, in that GAC effluents had 0.03 cm⁻¹ UV-254 values during the first two samplings and 0.003 cm⁻¹ for the next two samples, even though TOC in the GAC effluent remained low (0.1 to 0.2 mg/L) during this period. However, as TOC concentrations in the GAC effluent increased on Run Days 54, 82 and 95 (GAC effluent TOC of 0.20, 0.60 and 0.85 mg/L, respectively), the UV-254 steadily increased from 0.003 to 0.009 and 0.015 cm⁻¹, respectively.

The impact of GAC treatment on levels of SDS DBPs is illustrated in Figures 6-93 through 6-102. The GAC contactor influent and effluent SDS values plotted in these figures were measured in the samples dosed at 4.5 mg/L of chlorine, buffered to pH 8.2, and incubated for 3 days at 25°C. As shown in Figure 6-93, SDS TTHMs were extremely low (approximately 6 µg/L or less) in the contactor effluent for the first 54 run days, indicating very effective removal of THM precursors. After 82 run days, SDS TTHMs had increased to 34 µg/L and after 95 run days, SDS TTHMs increased to 47 µg/L. SDS TTHMs in the contactor influent were 104, 80, 74, 136, 116 and 134 in the 0.2, 13, 25, 54, 82 and 95 run day samples, respectively. Thus, GAC treatment led to reductions in SDS TTHM levels of >97, >92, >97 and >96 percent on the first four sampling days, respectively; and 71 and 65 percent on the 82nd and 95th run days, respectively.

DeMarco, et al. (1981) reported similar simulated distribution system THM results for a previous GAC contactor run at Utility 11 (16-minute EBCT). The SDS procedure used by these researchers included adding sufficient chlorine to produce an initial free chlorine residual of 2.5 mg/L, buffering to pH 8.2 and incubating for three days at the temperature of the full-scale plant's finished water. After 95 days of column operation, column effluent SDS TTHMs were less than 30 µg/L, while column influent SDS TTHMs ranged from approximately 60 to 160 µg/L during the first 95 days of column operation.

As was the case for TOC removal, the effectiveness of THM precursor removal by GAC is also site specific. For example, SDS THM data published by McGuire, et al. (1989) from GAC pilot studies conducted by Metropolitan on Colorado River water indicate much less effective THM control than was achieved at Utility 11. Metropolitan's SDS

conditions for the latter testing included adding 1 mg/L of chlorine, buffering to pH 8.2 and incubating for five days at 25°C. For a 15-minute EBCT (12x40 mesh carbon), SDS TTHMs in the column effluent were approximately equal to the SDS TTHM levels in the column influent (40 to 52 μg/L) after only 30 days of column operation.

Figures 6-94 and 6-95 illustrate the levels of chloroform and bromoform at Utility 11 in the 3-day SDS$_{4.5}$ (4.5 mg/L of chlorine, buffered to pH 8.2, 25°C) GAC contactor influent and effluent samples. SDS chloroform concentrations in the GAC influent occurred within the range 52 to 100 μg/L. All of the SDS chloroform levels in the GAC effluent samples were less than 2 μg/L through the first 54 run days, then increased to 8.9 and 14 μg/L on the 82nd and 95th run days, respectively. Thus, GAC treatment was very effective for lowering the levels of chloroform in the SDS samples.

Figure 6-95 illustrates SDS$_{4.5}$ bromoform levels in the GAC influent and effluent samples. Bromoform was not detected in any of the contactor influent SDS samples, and was not detected in the contactor effluent samples for the first 54 run days. However, after 82 run days, bromoform was detected in the contactor effluent SDS samples, at 2.0 and 2.8 μg/L on the 82nd and 95th run days, respectively. These data indicate that GAC caused a shift from the chlorinated species to the brominated species in the column effluent samples. This is reported by Utility 11 to be a typical, though unexplained, phenomenon at their GAC facilities. To further illustrate this occurrence, on the 82nd and 95th run days, chloroform comprised 70 and 72 percent, respectively, of the SDS TTHMs in the contactor influent; while chloroform only comprised 30 and 26 percent of the SDS TTHMs in the contactor effluent on those sampling days. On those same sampling days, bromoform comprised less than 1 percent of the SDS TTHMs in the contactor influent, but 6 percent of the contactor effluent SDS TTHMs were contributed by bromoform.

Similar trends to those observed for SDS THMs were found for SDS HAAs. Figure 6-96 shows the SDS$_{4.5}$ results for HAAs in the GAC column influent and effluent. For the first 25 run days, no HAAs were detected in the contactor effluent SDS samples, although the contactor influent SDS samples contained HAA levels ranging from approximately 25 to 40 μg/L during that time. SDS HAA levels gradually increased in the contactor effluent samples over the subsequent sampling dates, although the GAC remained very effective at lowering SDS HAA concentrations over the 95 days of sampling. The shift from chlorinated to brominated species in the GAC contactor effluent SDS samples is seen in Figures 6-97 and 6-98. DCAA in the contactor effluent SDS samples remains significantly lower than in the contactor influent SDS samples. However, DBAA concentrations in the contactor influent SDS samples remained low throughout the sampling period (less than or equal to 1.8 μg/L), while SDS DBAA levels in the effluent samples (3.0 and 4.6 μg/L on the 82nd and 95th run days, respectively) exceeded those in the influent SDS samples after 82 run days. In the SDS samples from the 82nd and 95th run days, DBAA accounted for approximately 3 percent of the total measured HAAs in the GAC influent, but accounted for 26 to 29 percent of the total measured HAAs in the contactor effluent.

Raw water bromide levels were 0.03, 0.05, <0.01, 0.05, 0.04 and 0.06 mg/L in the 0.2, 13, 25, 54, 82 and 95 run day samples, respectively. Referring to Table 5-2, the 3-quarter median influent bromide level of the 35 utilities participating in the baseline sampling program was 0.08 mg/L, indicating that Utility 11 had relatively low levels of

SDS CHCl3 vs Run Time For GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf   Δ····Δ GAC Eff
3-day SDS   3-day SDS

FIGURE 6-94

SDS CHBr3 vs Run Time For GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf   Δ····Δ GAC Eff
3-day SDS   3-day SDS
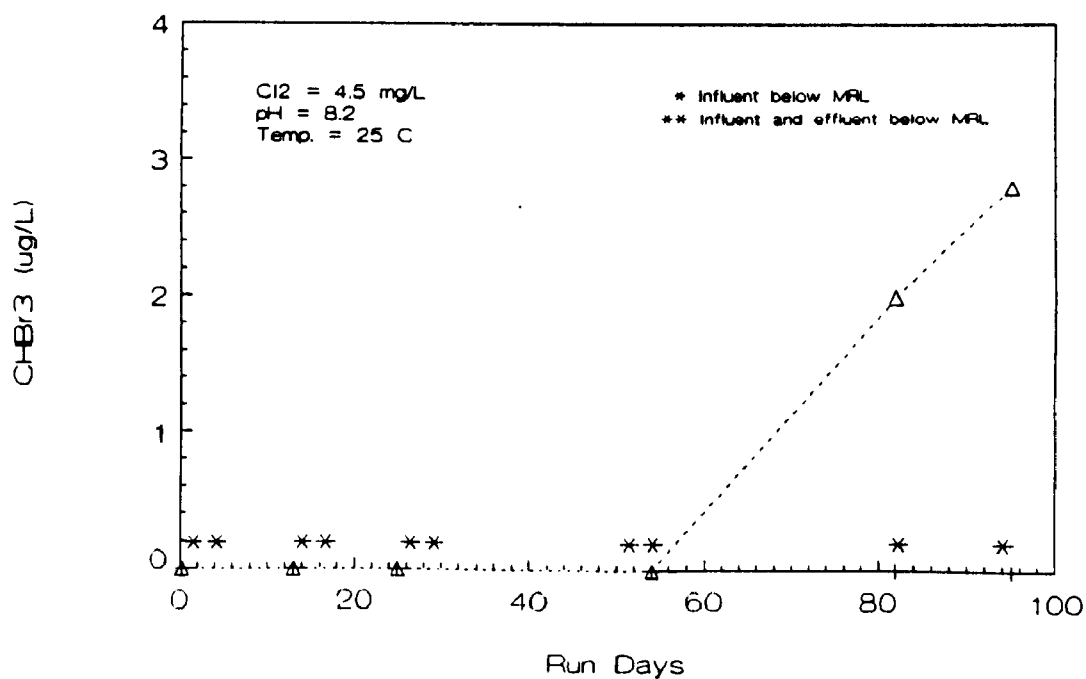
FIGURE 6-95

SDS HAAs vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf
3-day SDS

Δ·····Δ GAC Eff
3-day SDS

Cl2 = 4.5 mg/L
pH = 8.2
Temp. = 25 C

* All HAAs below MRLs
** MCAA, TCAA, and MBAA below MRLs
*** MBAA below MRL

FIGURE 6-96

SDS DCAA vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf
3-day SDS

Δ·····Δ GAC Eff
3-day SDS

Cl2 = 4.5 mg/L
pH = 8.2
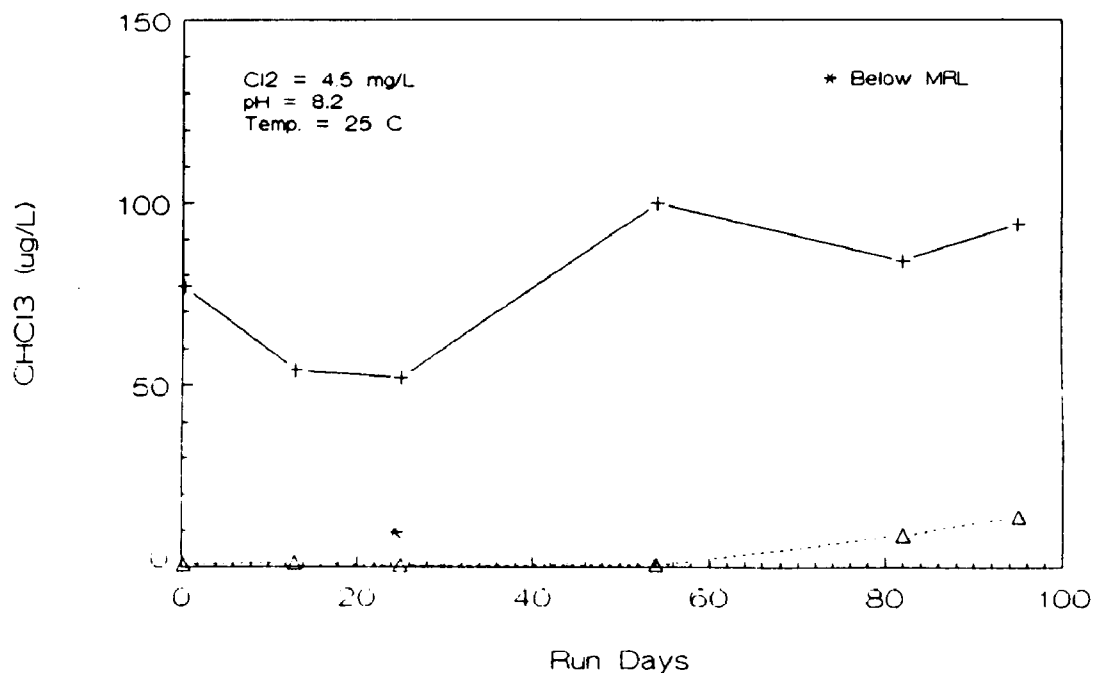Temp. = 25 C

* Below MRL

FIGURE 6-97

SDS DBAA vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf
3-day SDS
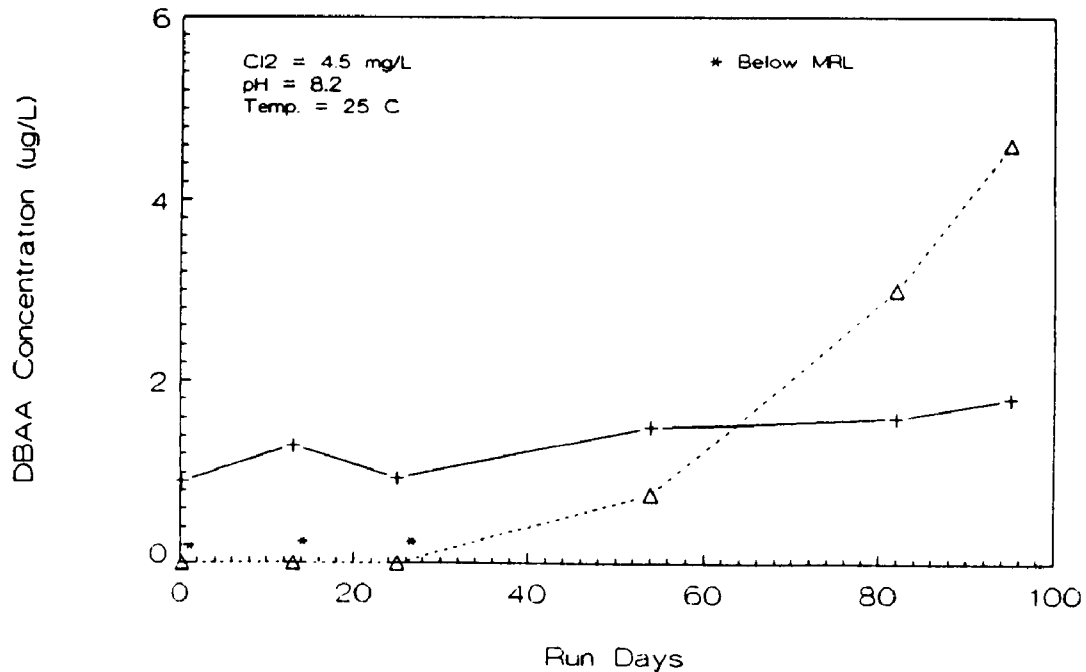
Δ·····Δ GAC Eff
3-day SDS

FIGURE 6-98

SDS HANs vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf
3-day SDS

Δ·····Δ GAC Eff
3-day SDS
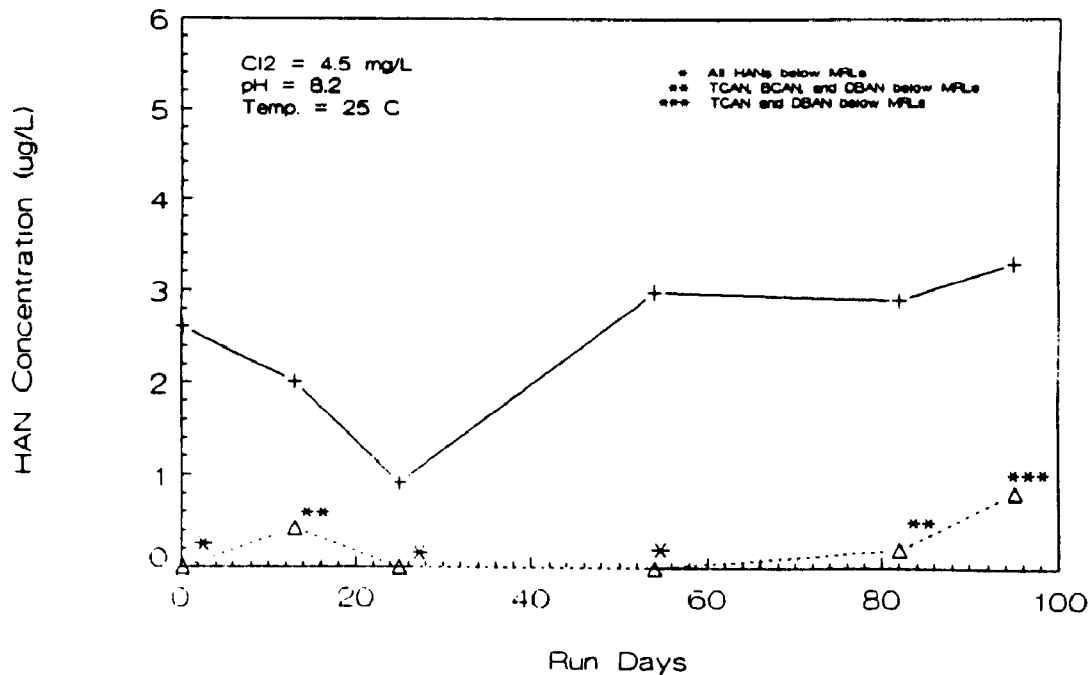
FIGURE 6-99

influent bromide. This low level of bromide did not lead to bromoform production and caused only low levels of DBAA formation in the column influent SDS samples. The shift in speciation from chlorinated to brominated compounds in the GAC contactor effluent may be due to the following:

o Because bromide is not adsorbed by GAC, it is possible that the increased percentage of brominated THMs and HAAs in the column effluent is due to the increased ratio of bromide to precursor material after significant levels of TOC have been removed in the GAC contactor. Bench-scale TOC dilution experiments conducted at Metropolitan (McGuire et al., 1989) indicated that as the TOC of a water was diluted while the bromide concentration was held constant. the speciation of THMs shifted toward the brominated compounds.

o Some researchers have found that the selectivity of precursors for either bromination or chlorination reactions may be a function of precursor molecular weight (Schnoor et al., 1979), and the average of which is most likely altered significantly by adsorption within the column. However, other researchers have found no relation between THM speciation and molecular weight (Glaze et al., 1980).

Removal of SDS HANs by GAC treatment is plotted in Figure 6-99. Very low levels of HANs were observed in the GAC contactor effluent SDS samples. with HAN concentrations showing evidence of slightly increasing toward the end of the sampling period. SDS HK removal is illustrated in Figure 6-100. Overall, very low concentrations of HKs were found in the GAC contactor effluent SDS samples.

SDS chloral hydrate levels are plotted in Figure 6-101 for the GAC column influent and effluent. Contactor influent levels are relatively high, in the range of 9.5 to 22 μg/L. The GAC was very effective in removing SDS chloral hydrate for the first 54 days of column operation. with concentrations at or near detection limits for the first four samples. However. concentrations gradually increased in the next two contactor effluent SDS samples. with a level of 4.0 μg/L measured on the 95th run day. As will be discussed below. chloral hydrate levels in Utility 11's distribution system were also relatively high.

SDS chloropicrin concentrations in the contactor influent and effluent are plotted in Figure 6-102. Levels of this compound in the GAC column effluent SDS samples were at or near detection limits throughout the sampling period. Cyanogen chloride and 2,4,6-trichlorophenol were not detected in any GAC column influent or effluent SDS$_{4,5}$ samples.

Table 6-19 summarizes TOX results for the six sampling dates at all sampling locations. Because the GAC facilities received unchlorinated water, data from the GAC column influent (B2) indicate that some TOX was present in the raw water (12 to 26 μg/L). which would be expected due to the industrial nature of the raw water source. On Run Days 0.2 through 82, the 12 to 16 μg/L of TOX in the GAC column influent was removed (or lowered in concentration) by GAC treatment, since no TOX was detected (detection limit equals 10 μg/L) in the GAC effluent on those days. However, on the 95th run day, 26 μg/L of TOX was measured in the unchlorinated GAC column influent and 21 μg/L of TOX was measured in the unchlorinated GAC column effluent,

SDS HKs vs Run Time for GAC
Column Influent and Effluent, Utility 11

+——+ GAC Inf
3-day SDS

Δ----Δ GAC Eff
3-day SDS

Run Days
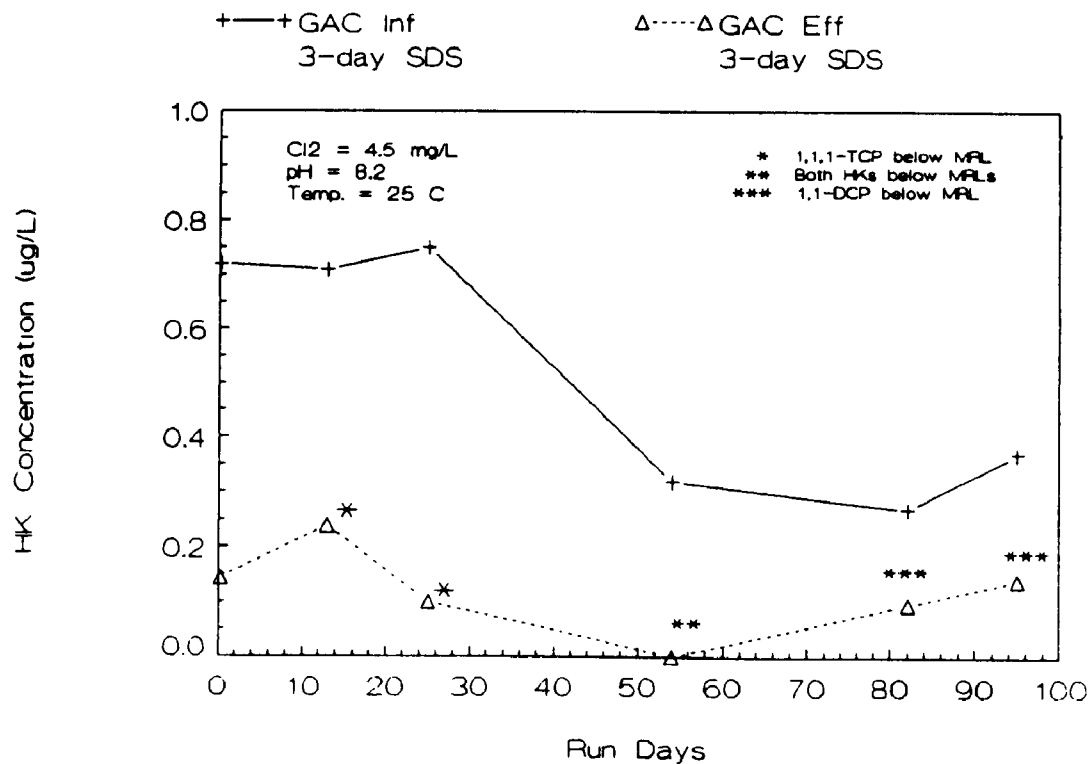
FIGURE 6-100

SDS CH vs Run Time for GAC
Column Influent and Effluent, Utility 11

—+— GAC Inf
3-day SDS

--Δ-- GAC Eff
3-day SDS
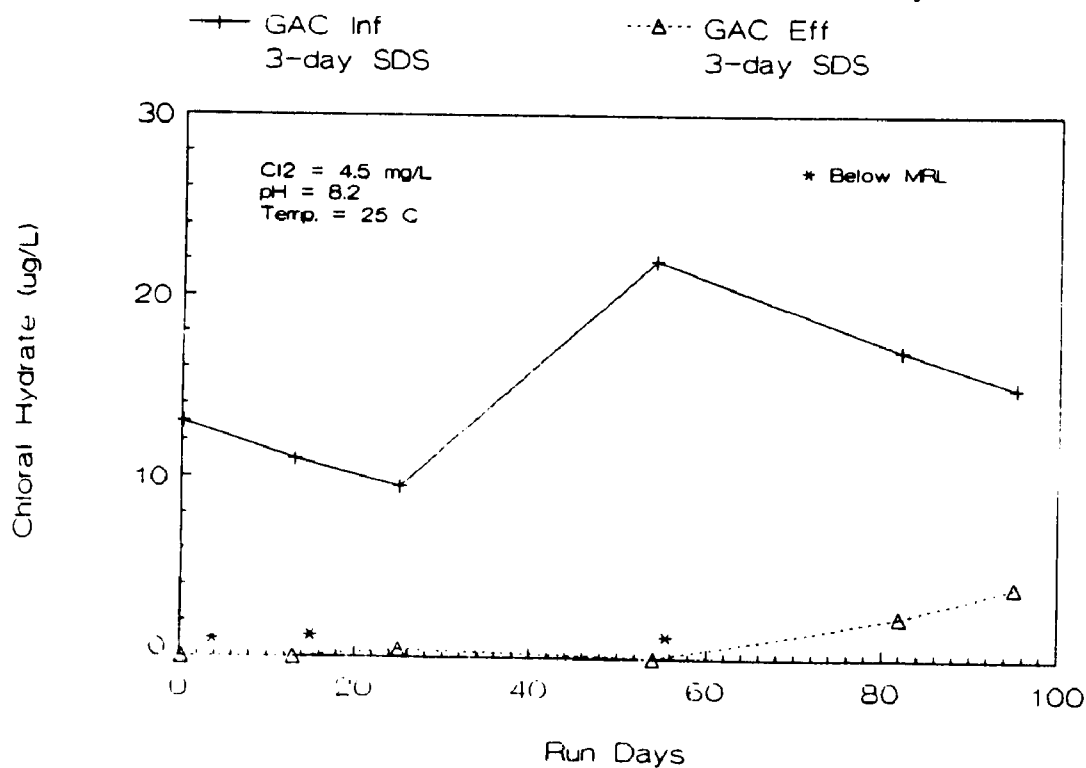
Run Days

FIGURE 6-101

SDS CHP vs Run Time for GAC
Column Influent and Effluent, Utility 11
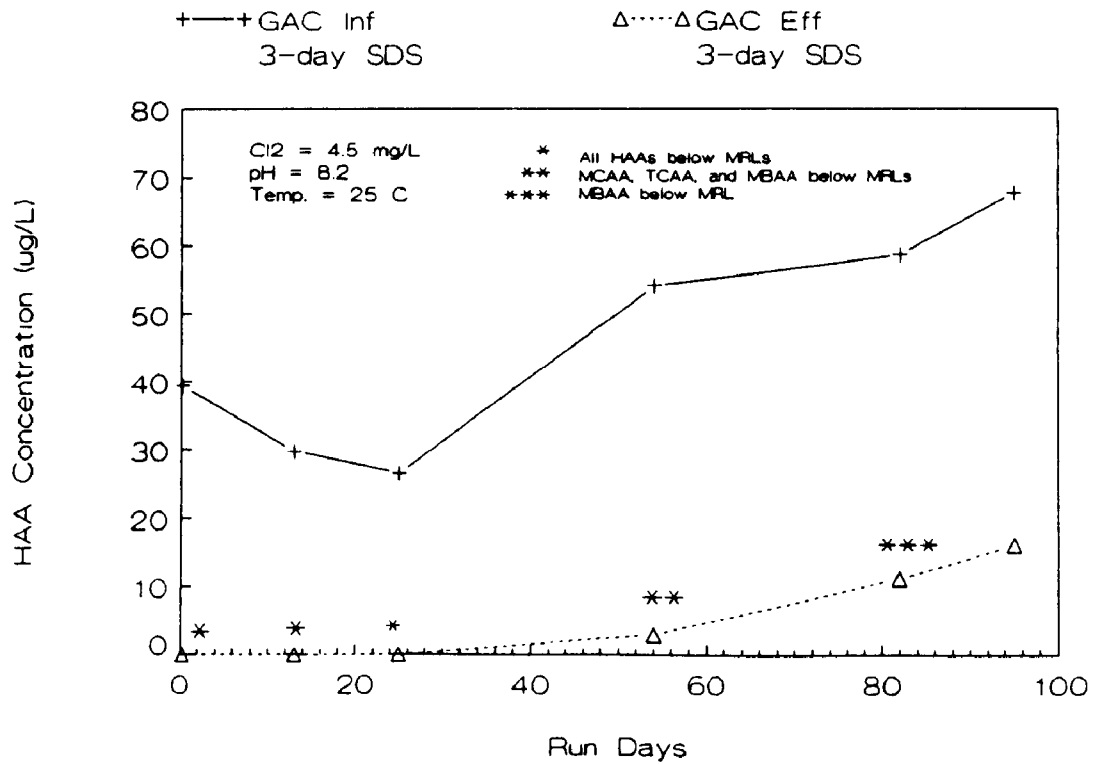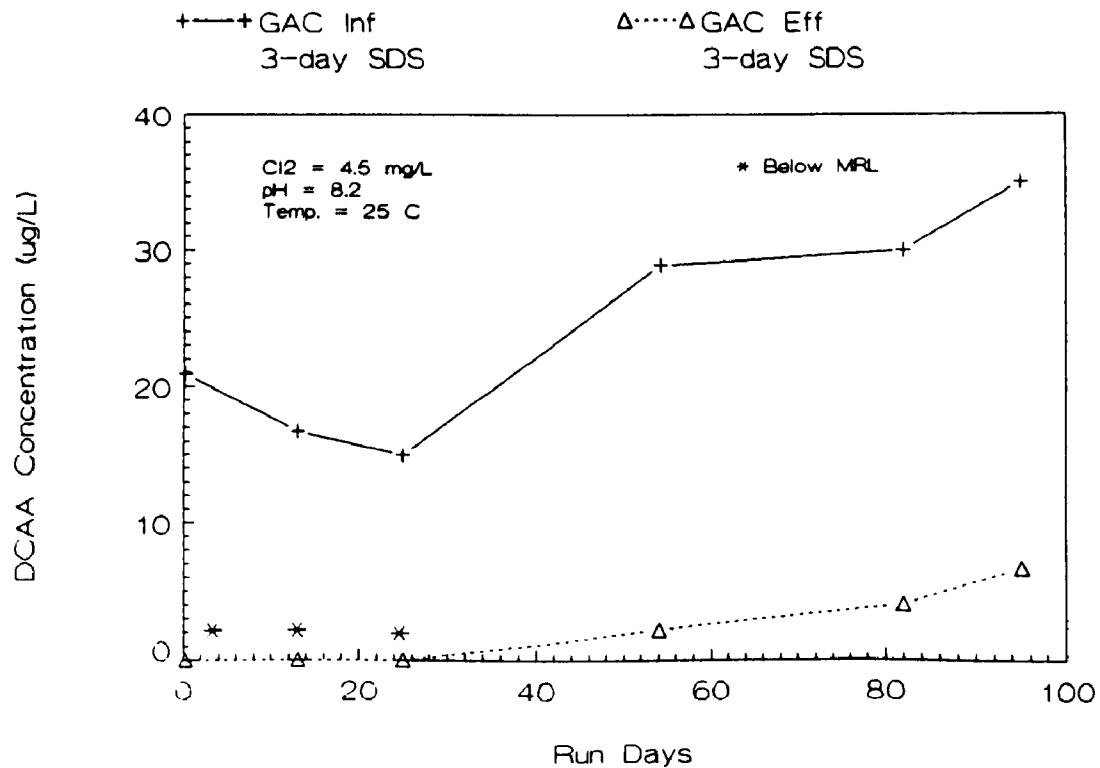
+——+GAC Inf   Δ·····ΔGAC Eff
3-day SDS   3-day SDS

Cl2 = 4.5 mg/L
pH = 8.2
Temp. = 25 C

* Below MRL
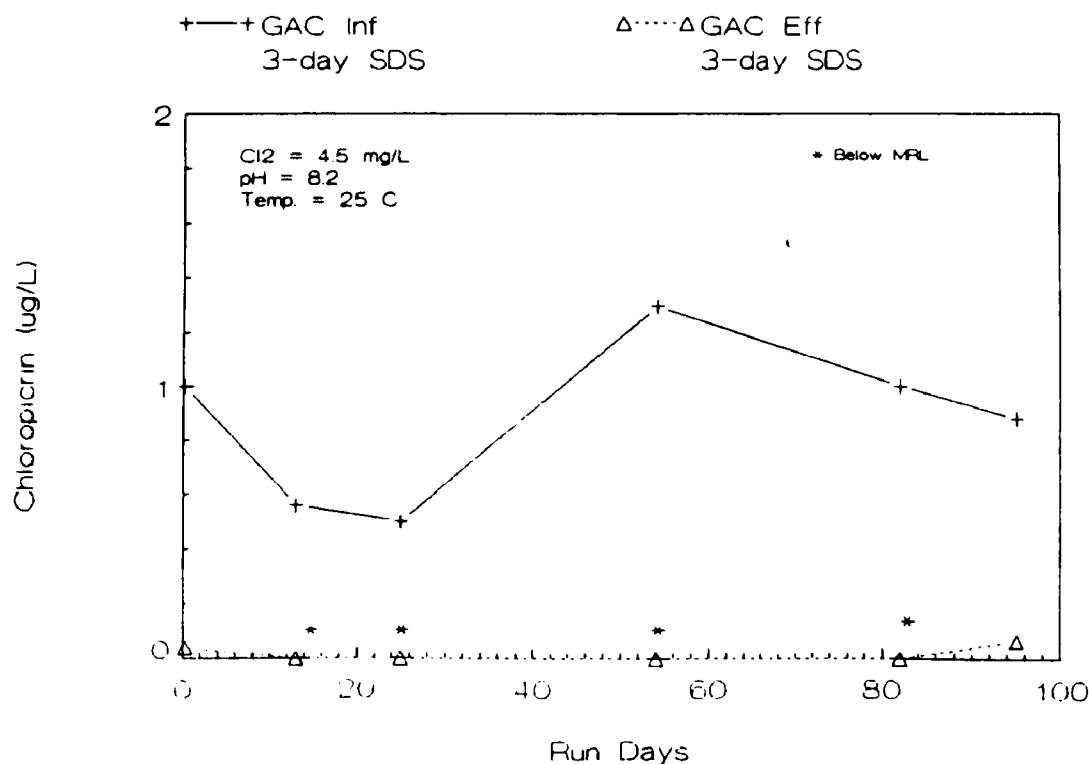
Run Days

FIGURE 6-102

Formation of TTHMs
In Distribution System (Utility 11)

▨ Clearwell   ■ Dist System
Effluent   T = 3 days

* CHBr3 below MRL

Sampling Date (Week of)
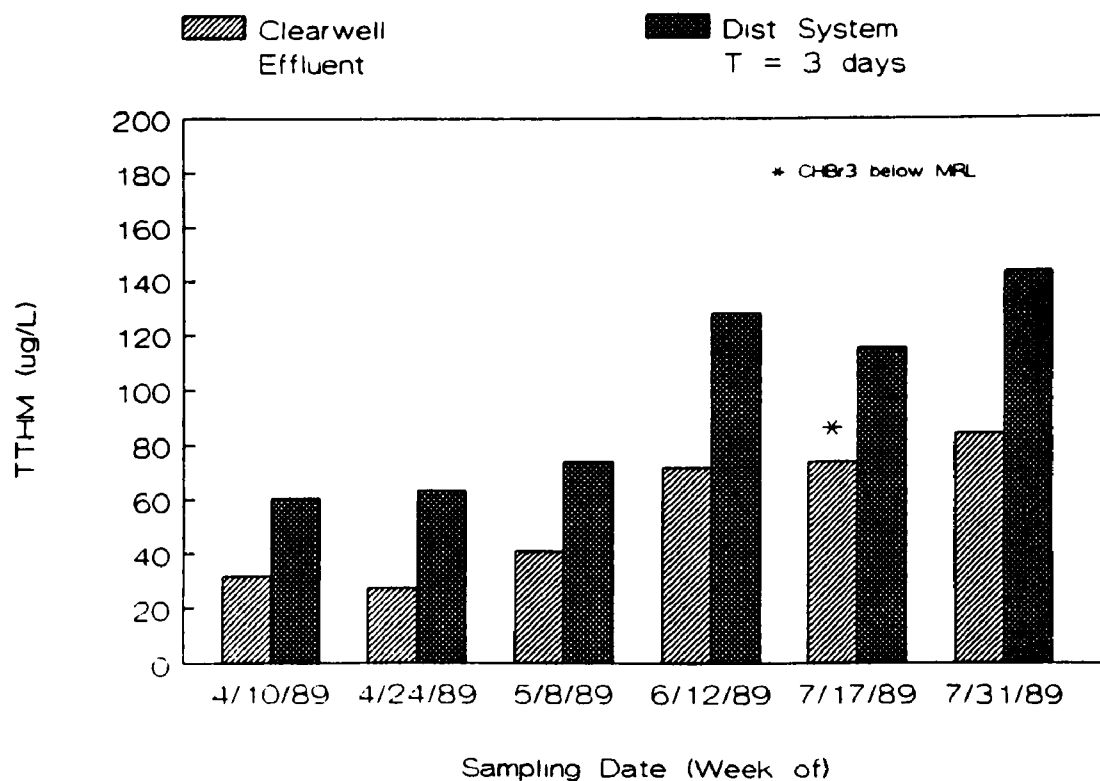
FIGURE 6-103

TABLE 6-19

UTILITY 11 TREATMENT STUDY
TOX RESULTS (in μg/L)

Run Day Sampling Date	0.2 4/10/89	13 4/24/89	25 5/08/89	54 6/12/89	82 7/17/89	95 7/31/89
Location/ Condition						
A2/Immed.[1]	140	110	150	250	260	290
A3/Immed.[2]	180	150	170	240	270	341
B2/Immed.	16	12	13	16	14	26
B2/SDS 4.5[3]	220	170	180	270	270	300
B3/Immed.	<10	<10	<10	<10	<10	21
B3/SDS 4.5[3]	10	16	18	17	42	86
B3/SDS 2.0[4]	<10	11	<10	<10	41	63

[1] Immediate
[2] Immediate, sampled 3 days after collection of in-plant samples
[3] Simulated Distribution System, Cl_2 = 4.5 mg/L, pH = 8.2,
Temp = 25°C, Time = 3 days
[4] Simulated Distribution System, Cl_2 = 2.0 mg/L, pH = ambient
(except pH = 8.2 for 4/10/89 sample), Temp = 25°C, Time = 3 days

indicating that the halogenated organic compounds present in the raw water were not removed by GAC treatment.

As indicated in Table 6-19, the $SDS_{4.5}$ TOX concentrations in the GAC column influent samples ranged from 170 to 300 μg/L, while concentrations in the GAC effluent samples ranged from only 10 to 86 μg/L. $SDS_{4.5}$ TOX levels in the GAC effluent remained below 20 μg/L in samples collected during the first 54 run days, but more than doubled on each successive sampling date after 54 run days.

A comparison of SDS data with actual in-plant and distribution system data is made in Table 6-20 for three of the six sampling days for the levels of chloroform, TTHMs, DCAA, HAA_{sum} and TOX. The demonstration plant filter effluent (B2) $SDS_{4.5}$ was run to provide a controlled basis of comparison with the $SDS_{4.5}$ GAC column effluent (B3) samples as discussed in the previous paragraphs. The distribution system sampling point (A3) had an approximate residence time of 3 days, but actual in-plant chlorine doses varied between 2.7 and 4.8 mg/L, temperatures in the distribution system varied between 11 and 27°C, and distribution system pH ranged from 8.4 to 8.8 over the 95-day sampling period.

In comparing the DBPs measured in the B2 SDS and A3 samples, varying results are seen. For the samples collected the week of 4/10/89, there are substantial differences in the levels of chloroform and TTHMs between the B2 $SDS_{4.5}$ and A3 samples. These differences were probably due, in part, to the difference in temperatures (A3 was 11°C and B2 was incubated at 25°C). However, for the samples collected the week of 7/31/89, the SDS and actual conditions were very similar, and the DBP data shown in Table 6-20 for that week agree to 22 percent or better. The data presented in Table 6-20 illustrate the importance of utilizing a standardized SDS protocol for the evaluation of DBP precursor removal by GAC at Utility 11. By conducting SDS tests, variables such as pH, temperature, chlorine dose and holding time were held constant over the sampling period so that the only independent variable was TOC.

DBP Levels Produced by Conventional Treatment: Results and Discussion

Although the primary objective of the treatment study at Utility 11 was to evaluate removal of DBP precursors by GAC adsorption, the sampling program at this utility offered an opportunity to investigate levels of DBPs produced in conventional treatment and in a chlorinated distribution system, and thus expand upon the DBP data collected under the baseline sampling program.

Figure 6-103 illustrates TTHM levels measured in Utility 11's clearwell effluent and distribution system. As noted previously, the clearwell effluent (A2) was sampled on Monday of each sampling week, and the distribution system sampling point (A3), having an approximate residence time of 3 days in the system, was sampled 3 days later. This figure illustrates two important points. First, the seasonal change in THM production from spring to summer conditions is apparent as the water temperature at A2 increased from 9 to 27°C. Additionally, the chlorine demand of the water increased over the sampling period, since applied chlorine doses increased from 2.7 to 4.8 mg/L in the plant, while free chlorine residuals at the distribution system sampling point decreased from 0.9 to 0.3 mg/L from the 4/13/89 to the 8/3/89 samples (see Table 6-18). TTHMs measured at A2 increased from 32 to 84 μg/L from the early April to

TABLE 6-20

UTILITY 11 TREATMENT STUDY
COMPARISON OF SDS AND DISTRIBUTION SYSTEM RESULTS

Location	Temp. °C	pH	Cl_2 Dose (mg/L)	Free Cl_2 Residual (mg/L)	TOC (mg/L)	$CHCl_3$ (ug/L)	TTHMs (ug/L)	DCAA (ug/L)	HAA_{sum} (ug/L)	TOX (ug/L)
4/10/89										
A3 (4/13/89)	11	8.6	2.7	0.9	1.78	42	61	18	33	180
B2/SDS 4.5	25	8.35	4.5	1.35	1.80*	77	104	21	39	220
5/8/89										
A3 (5/11/89)	16	8.8	2.7	0.7	1.49	52	74	17	28	170
B2/SDS 4.5	25	8.28	4.5	1.0	1.37*	52	74	15	28	180
7/31/89										
A3 (8/3/89)	27**	8.5	4.8	0.3	2.17	105	144	28	57	341
B2/SDS 4.5	25	8.26	4.5	0.95	2.31*	94	134	35	68	300

A3= Distribution system sampling point.
B2= GAC influent.
* Level of TOC in immediate B2 sample prior to SDS set up.
** Clearwell effluent temperature during that samplng period.

the late July samples. Increased formation of THMs in the warm weather months was observed in the baseline data collected for this study and DBP production was found to be strongly influenced by water temperature (see Section 5). It is apparent that the increase at Utility 11 is caused by factors such as the higher water temperatures and higher TOC levels. TOC levels at A2 were 1.77, 1.51, 1.56, 2.15, 2.08 and 2.13 mg/L on the 6 sampling dates (in chronological order), indicating an increase from April to July. It is interesting to note, however, that UV-254 values at A2 exhibit a different trend than TOC, with UV-254 equal to 0.063, 0.048, 0.024, 0.034, 0.032 and 0.038 cm⁻¹ on successive sampling days from early April to late July.

The second important issue illustrated in Figure 6-103 is the production of DBPs in the distribution system of Utility 11. TTHMs measured at A3 were substantially higher than levels measured at A2 on all six sampling dates. For the first two sampling dates, TTHM concentrations were approximately double after 3 days of retention in the distribution system compared to the clearwell effluent TTHMs. For the six samples collected for this study, increases of 29, 36, 33, 57, 42 and 60 μg/L of TTHMs occurred in the distribution system.

Figure 6-104 shows the fate of DCAN in Utility 11's distribution system. In contrast to the increased levels of TTHMs observed in the previous figure, DCAN levels decreased with residence time in the distribution system, with the decrease increasing in magnitude over the six sampling dates. This figure highlights an issue discussed in Section 5, where results of this study confirmed the results of other researchers who found that DCAN was a reactive intermediate rather than a stable endproduct of the chlorination of natural organic matter. DCAN is known to undergo a base-catalyzed decomposition (Trehy and Bieber, 1981), and the hydrolysis rate is significantly higher at pH 8.5 than at neutral pH (Croue and Reckhow, 1988) (the pH at A3 ranged from 8.4 to 8.8.).

Chloral hydrate levels at Utility 11 measured during the baseline data collection were relatively high compared to other utilities, exceeding the 75th percentile values in the summer and fall samples. The chloral hydrate concentrations measured in Utility 11's clearwell effluent samples in April through July, 1989 are consistent with those recorded in the summer quarter baseline sample in 1988. Figure 6-105 illustrates the concentrations of chloral hydrate at A2 and A3 for the six sampling dates. In the first four samples, chloral hydrate levels approximately doubled from A2 to A3, however the increase measured at A3 was significantly lower in the last two samples. In the 6/12/89 sample, the highest level of chloral hydrate was measured (20 μg/L), and this compound was the fourth most prevalent of the measured DBP compounds on a weight basis, exceeded only by chloroform (94 μg/L), bromodichloromethane (26 μg/L), and DCAA (26 μg/L).

Formation of DCAN
In Distribution System (Utility 11)

▨ Clearwell
Effluent

■ Dist System
T = 3 days

DCAN (ug/L)

Sampling Date (Week of)
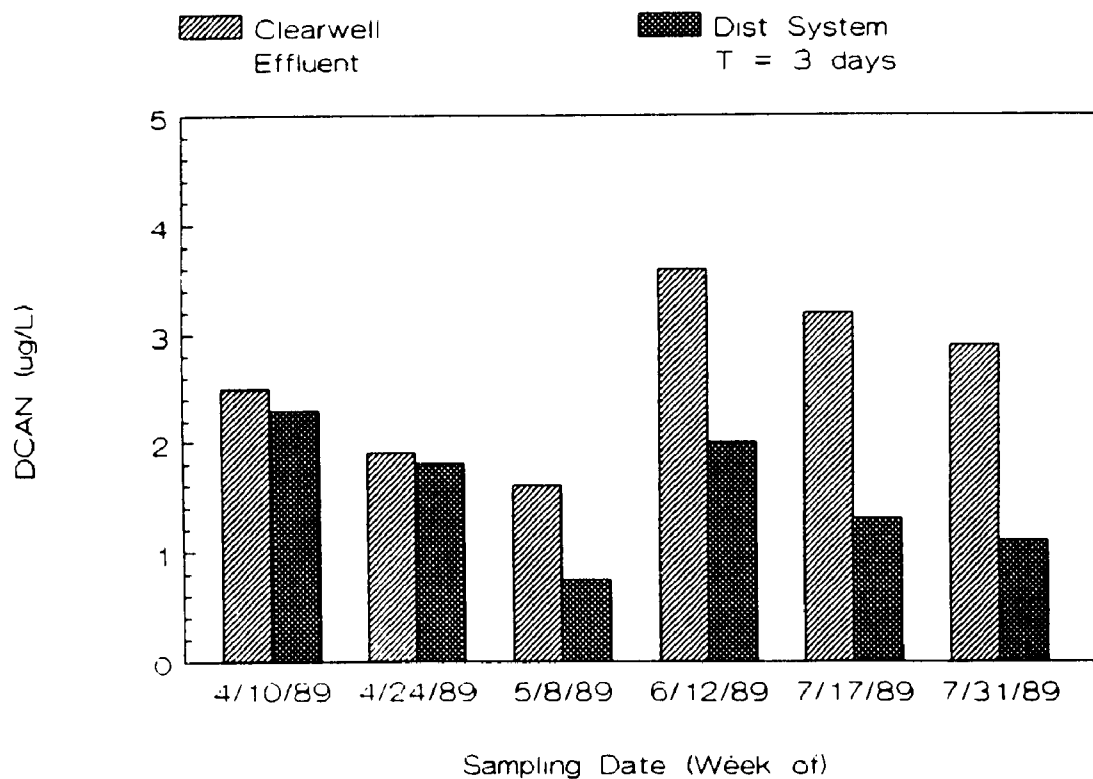
FIGURE 6-104

Formation of CH
In Distribution System (Utility 11)

▨ Clearwell
Effluent

■ Dist System
T = 3 days

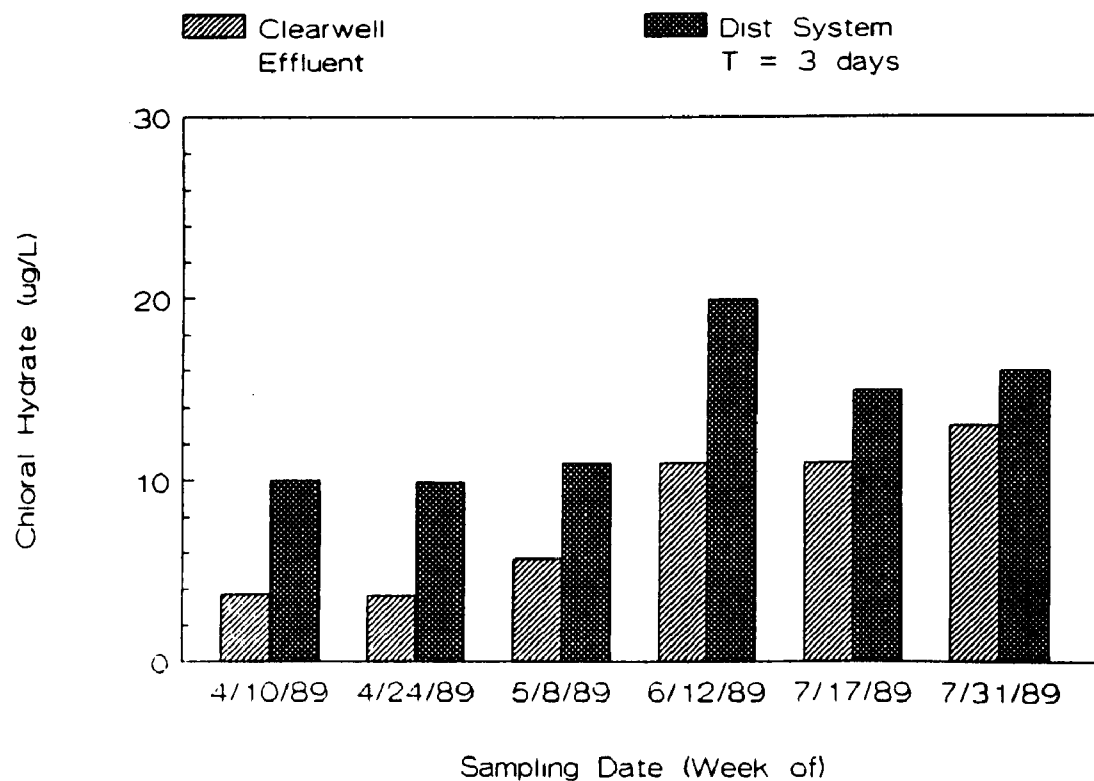Chloral Hydrate (ug/L)

Sampling Date (Week of)

FIGURE 6-105

Section 7

Summary and Conclusions

SECTION 7

SUMMARY AND CONCLUSIONS

In this section, major study results are summarized and conclusions based on study results are drawn. Additionally, research needs arising from study results are discussed.

BASELINE RESULTS

The median TTHM value for the four quarters of baseline sampling at clearwell effluents was 39 μg/L (computed on a running annual average basis for each individual utility). The THMs represented the largest class of DBPs measured in this study (on a weight basis), comprising approximately 54 percent of the measured compounds. The second largest DBP fraction measured in this study was HAAs, with a median concentration of 17 μg/L, which represents approximately 25 percent of the measured compounds. Thus, the median level of TTHMs was approximately twice that of HAAs. The third largest fraction detected was the aldehydes, comprising approximately 9 percent of the measured compounds, with a median concentration of 5.7 μg/L.

Little difference was observed in the overall median concentrations of influent water quality parameters and concentrations of DBP compounds in clearwell effluents from quarter to quarter in the baseline samples. Because of the nationwide distribution of participating utilities and the wide variations in seasonal weather conditions and water temperatures, "season" or "sampling quarter" proved to be a somewhat arbitrary method of categorizing the data. Water temperature, however, was found to have a significant impact on concentrations of DBP compounds. Levels of XDBP$_{sum}$ and THMs were found to be higher in the highest temperature range when the data were sorted into four equal temperature ranges. The differences in DBP levels between the highest temperature range and any of the three lower ranges were statistically significant at a 95 percent confidence level. In addition, plant effluent pH was found to strongly impact a number of DBPs which are unstable and hydrolyze at high pH.

Raw water quality characteristics varied considerably among the 35 participating utilities. Relative concentrations of TOC, UV-254 absorbance, chloride and bromide indicated that classification of the utilities and their DBP levels by source water type, treatment type and disinfection scheme was too simplistic to account for other factors having considerable impact on DBP production.

Classification of the utilities by disinfection scheme indicated that influent parameters varied considerably among the utilities within each category. Prechlorinating/postammoniating utilities were found to have a higher median influent bromide concentration than chlorine-only utilities, with the difference being statistically significant at a 95 percent confidence level. Significant differences were also observed between median concentrations of some DBPs as a function of disinfection scheme. Median levels of XDBP$_{sum}$ and TTHMs for the prechlorinating/postammoniating utilities (approximately 94 and 57 μg/L, respectively) were significantly higher than those of either chlorinating (62 and 34 μg/L, respectively) or chloraminating utilities

Summary and Conclusions

(23 and 12 μg/L, respectively). The same trend was observed in median concentrations of HANs, aldehydes and cyanogen chloride, and the differences were also statistically significant at a 95 percent confidence level. However, the prechlorinating/ postammoniating utilities treated water with the highest median level of UV-254 (0.15 cm^{-1} as compared to 0.10 cm^{-1} for chlorine-only and chloraminating utilities). Since UV-254 may be an indicator of THM formation potential, the former utilities may require postammoniation to minimize further THM formation in their systems.

A strong correlation was found between TTHMs and the sum of measured halogenated DBPs (r=0.96). However, since TTHMs represented over 50 percent of XDBP$_{sum}$, the correlation coefficient for TTHMs and the sum of non-THM DBPs was determined and found to be 0.76. Some of the other DBP classes correlated well with TTHMs (e.g., HANs), while others correlated poorly with TTHMs (e.g., HKs).

HAAs correlated strongly (r=0.98) with the sum of non-THM XDBPs. When both HAAs and TTHMs were subtracted from XDBP$_{sum}$, and were then correlated with HAAs, r equaled 0.77. In addition, a correlation of 0.74 resulted between HAAs and XDBP$_{sum}$ minus HAAs. The latter two correlations may be useful in helping to predict the sums of non-THM, non-HAA XDBPs.

The correlation between the UV-254 absorbance and TOC of plant influent samples was strong (r=0.85), although neither UV-254 nor TOC correlated well with the TTHMs of plant effluents. Influent chloride correlated strongly with influent bromide (r=0.97); thus, chloride may be used as a predictor for bromide. Exclusion relationships were found for bromide with chloropicrin, 1,1,1-TCP, TCAA, chloroform, and other chlorinated DBPs; that is, the presence of bromide appeared to exclude the presence of the particular DBP, and the inverse was also observed.

Bromide present in the source water was found to shift the distribution of THMs, HANs and HAAs to the more brominated species. High bromide levels were observed not only in utilities susceptible to tidal influences and saltwater intrusion, but at inland utilities as well.

Of the 35 utilities included in this study, only three employed ozone, yet almost all 35 had detectable levels of formaldehyde and acetaldehyde. These aldehydes were found in some plant influent samples, and chlorination alone was found to produce these compounds.

Chloramines are recognized as an effective control strategy for THMs and other DBPs. However, for most waters studied in this project, cyanogen chloride was found to be preferentially produced in chloraminated water. The distribution of cyanogen chloride could statistically be divided into two groups, depending on whether the final disinfectant was chlorine or chloramines.

The TOC removal within filtering plants included in the baseline sampling program averaged approximately 24 percent. It should be noted that the treatment practices of the utilities participating in the baseline sampling most likely focused on turbidity control and were not optimized with respect to TOC removal.

The TTHM data from this study of 35 utilities was compared to that of the THM survey conducted by the American Water Works Association Research Foundation in 1987. which involved 727 utilities around the nation. Based on running annual averages. frequency distribution curves for the two sets of data were similar. The hypothesis that the data from the two studies were from the same distribution was not rejected at a significance level of 0.01, using a Kolmogorov-Smirnov test.

PROCESS MODIFICATION RESULTS

Ozone in conjunction with chlorine or chloramines as final disinfectants was generally effective in lowering concentrations of classes of halogenated DBPs, except for HKs. However. observed increases in HKswere equal to or less than 1.0 μg/L. The extent to which DBP levels were decreased or increased after implementation of ozonation depended primarily on the final disinfectant which was employed. Where comparable, ozonation followed by chloramination was more effective in reducing levels of halogenated DBP classes and chloral hydrate than ozone followed by chlorination. For all ozone studies. ozone addition resulted in decreased TOX concentrations.

Although the use of ozone and chlorine or chloramines appeared to be effective in minimizing the formation of compounds in the major halogenated DBP classes, shifts to greater concentrations of the brominated species were observed for THMs and HAAs when free chlorine was used as a final disinfectant. Increases in chloropicrin were observed in some cases where ozone was used first, regardless of the final disinfectant: however. these increases were always less than 1.0 μg/L. When chloramines were employed after ozonation. increases in cyanogen chloride concentrations were observed at some utilities.

Aldehyde concentrations increased substantially whenever ozonation was employed. These increases ranged from 67 to 459 percent. depending on the treatment modification implemented. However, at one utility, the use of filtration to which a disinfectant was not applied. indicated that these aldehydes could be removed. It is important to note that free chlorine also produced aldehydes, although to a lesser extent than ozone.

At one utility studied. chlorine dioxide preoxidation with free chlorine for residual disinfection was not found to lower concentrations of DBPs when compared to chlorine-only oxidation/disinfection. However, at another utility, chlorine dioxide preoxidation was found to be an effective control method for DBPs compared to chlorine preoxidation. even though free chlorine was detected in the chlorine dioxide generator product. Use of chlorine dioxide preoxidation at this utility led to decreases of approximately 50 percent in levels of $XDBP_{sum}$, TTHMS, HANs, HKs and HAAs compared to free chlorine preoxidation.

At two utilities studied. increasing alum dose increased removal of DBP precursors and resulted in lower concentrations of DBPs. However, at one utility. chlorine was added before the removal of TOC in the coagulation. flocculation, sedimentation and filtration processes. resulting in less effective DBP control.

At one utility, GAC was very effective in removing TOC during the initial 54 days of column operation. After the 54th run day. TOC in the column effluent increased steadily. Levels of DBPs in column influent and effluent samples which were chlorinated and held under strictly controlled conditions indicated that DBPs followed the same trend as TOC: that is, very low levels for the first 54 days of column operation, followed by a steady increase. Concentrations of individual THMs and HAAs in the GAC filter effluent indicated that GAC treatment caused a shift from chlorinated to brominated species.

Although this study focused on DBP concentrations and control of DBPs by treatment modifications, it should be noted that in full-scale applications, DBP control strategies must be evaluated not only on their effectiveness for limiting concentrations of DBPs, but on their economic and operational feasibility as well. Evaluation of these aspects of DBP control at full scale were beyond the scope of this study.

RESEARCH NEEDS

Several areas warranting further research are apparent from the study results. Additional research on the effectiveness of currently accepted DBP control methods, such as chloramination and ozonation, is justified due to the detection of chloramination by-products, such as cyanogen chloride, and ozonation by-products, such as formaldehyde, in this and other studies. Additionally, this study focused on the occurrence and control of DBPs, rather than the economic and operational feasibility of the DBP control strategies investigated, subjects of critical importance for utilities faced with meeting future DBP regulations. Consequently, operation and maintenance considerations and associated costs are subjects in need of further investigation.

Another area of needed effort is the development of water quality data for utilities around the nation for modeling purposes, especially TOC and bromide data. In order to develop a background of information on the present and projected future treatment capabilities of the nation's utilities with respect to DBPs and DBP precursors, it is essential that TOC be more routinely measured. The feasibility of monitoring plant performance based on TOC, instead of a parameter such as turbidity, in order to control DBP production also warrants investigation.

Treatment modification studies at two utilities also demonstrated that incremental increases in TOC removal could be accomplished by increasing alum doses. More research needs to be focused on enhancing TOC removal by increased coagulant doses and on overall optimization of the coagulation process. Moreover, data from such research needs to be developed on a nationwide basis.

This study highlighted the role of bromide in the formation of DBPs and the importance of brominated analogs, such as brominated HAAs and possibly brominated picrins. Further investigation of brominated DBP compounds is required for continued progress in the characterization of compounds contributing to TOX.

A great deal of effort in this project was devoted to development of analytical methods for the compounds of interest, and effective sampling and preservation techniques.

Summary and Conclusions

Further research is needed to expand the list of analytes investigated in future studies and protect valuable data by improving sample preservation methods.

This study focused on levels of DBPs produced in full-scale drinking water treatment facilities. In evaluating DBP production within plants and distribution systems, bench-scale (simulated distribution system) research was also conducted for this study to provide a controlled environment from which comparisons between various treatments could be made. In this report, results of a great deal of laboratory research from other studies were compare with the results of this study. However, further research is required to more fully apply the results of strictly controlled laboratory research to "real world" applications in full-scale water treatment facilities. Operation of full-scale facilities is not easily compared to laboratory experiments, in that raw water quality and plant operation may vary from day to day or season to season, and oxidants and disinfectants are added at multiple points with various contact times and degrees of mixing, among other differences. Further research in these areas will increase understanding of the presence and control of DBPs in drinking water.

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