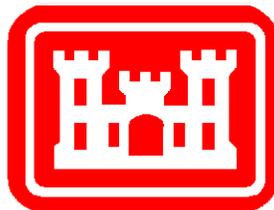


PUBLIC WORKS TECHNICAL BULLETIN 200-1-63  
1 JANUARY 2009

**ALTERNATIVES TO CHLORINE DISINFECTION  
AT THE FORT BRAGG, NC, DRINKING WATER  
TREATMENT PLANT**



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Facilities Engineering  
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ALTERNATIVES TO CHLORINE DISINFECTION AT  
THE FORT BRAGG, NC, DRINKING WATER  
TREATMENT PLANT

1. Purpose.

a. The purpose of this Public Works Technical Bulletin (PWTB) is to make available the results of a study conducted at Fort Bragg, NC, that evaluated alternatives to the existing chlorine disinfection used at their drinking water treatment plant.

b. All PWTBs are available electronically (in Adobe® Acrobat® portable document format [PDF]) through the World Wide Web (WWW) at the National Institute of Building Sciences' Whole Building Design Guide web page, which is accessible through URL:

[http://www.wbdg.org/ccb/browse\\_cat.php?o=31&c=215](http://www.wbdg.org/ccb/browse_cat.php?o=31&c=215)

2. Applicability. This PWTB applies to all U.S. Army facilities engineering activities having responsibility for the operation, or contracted operation, of a drinking water treatment plant.

3. References.

a. Army Regulation (AR) 200-1, "Environmental Protection and Enhancement," 13 December 2007.

b. Public Law 104-182, "Safe Drinking Water Act," as amended 1996.

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c. Title 40 Code of Federal Regulations, Part 141.70-141.75 (40 CFR 141.70-141.75), "Surface Water Treatment Rule and Interim Enhanced Surface Water Treatment Rule," February 1999.

d. 40 CFR 141, "Disinfectants/Disinfection Byproducts Rule," December 1998.

e. U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory (ERDC-CERL) Waste Minimization and Pollution Prevention (WM&PP) Program.

#### 4. Discussion.

a. AR 200-1 contains policy that requires that Army installations comply with Federal and State environmental regulations.

b. The Safe Drinking Water Act was passed by Congress in 1974 to ensure safe drinking water in the United States. An amendment to that Act in 1996 required that the U.S. Environmental Protection Agency (EPA) regulate certain microbial contaminants and disinfection by-products. This led to the Interim Enhanced Surface Water Treatment Rule and the Disinfectants/Disinfection Byproducts (D/DBP) Rule.

c. The Surface Water Treatment Rule and Interim Enhanced Surface Water Treatment Rule, both included in 40 CFR 141, regulate the removal of *Giardia* and *Cryptosporidium* from drinking water.

d. The D/DBP Rule is also included in 40 CFR 141. This Rule established drinking water quality standards and sampling requirements for trihalomethanes (THM), haloacetic acids (HAA), and halo ketones.

e. The ERDC-CERL WM&PP Program funded the demonstration of environmental management technologies at Army installations. The demonstration research program was funded by the Office of the Assistant Deputy Secretary of the Army - Installations and Environment. The program was managed and executed by the U.S. Army Engineer Research and Development Center Construction Engineering Research Laboratory. All research was conducted through a contract with MSE Technology Application, Inc., located in Butte, MT. Funding for this program ended in Fiscal Year (FY) 2005, with work continuing through December 2006. The results and documentation of the studies completed through this program were intended for the use of the host installations. In most cases, however, the results of the studies would be of

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benefit to many other Army and Department of Defense installations. Funding constraints did not allow formal publication of most of the final reports generated by the WM&PP Program. The PWTB program is now providing a mechanism to transfer the results of some of those studies.

f. Appendices A and B contain the majority of the information in the MSE final report: Chlorine Disinfection Alternatives Feasibility Study/Pilot Study at Fort Bragg including evaluation of Mixed Oxidants (MIOX), Sodium Hypochlorite, and Chlorine Dioxide Treatment Technologies, and the Magnetic Ion Exchange (MIEX<sup>®</sup>) Dissolved Organic Carbon Removal Process. That report was written in August 2005.

g. The Fort Bragg drinking water treatment plant uses chlorine gas for both primary and secondary disinfection. While chlorine is an effective, inexpensive disinfectant, there are many negative aspects to its use. Storing large quantities of chlorine gas triggers regulatory thresholds and requires the facility to submit a Risk Management Plan to the U.S. Environmental Protection Agency (EPA) for the use and handling of this chemical. The storage of large amounts of this toxic, poisonous gas also presents a security risk to Fort Bragg and the surrounding community.

h. Another negative consequence of using chlorine-based disinfection processes is the potential formation of halogenated organic by-products such as THM, HAA, and halo ketones. These disinfection by-product (DBP) compounds are regulated by EPA's D/DBP Rule and have regulatory levels that have been exceeded at Fort Bragg. The installation has received notices of violation and has been assessed penalties for exceeding these levels.

i. As a result of these problems, Fort Bragg proposed that the WM&PP Program investigate alternatives to the current gas chlorine disinfection system. That investigation would recommend a disinfection technology that would (1) not pose a threat to force protection (by not compromising the ability to adequately disinfect the water), (2) not trigger an EPA Risk Management Plan, (3) not produce further-regulated by-products, and (4) reduce risk to on-site plant personnel.

j. After completing a site investigation, MSE Technology Applications, Inc. (MSE) performed a preliminary evaluation of alternatives to gas chlorination and ranked them for purposes of pilot-scale testing. The first alternative selected for testing was a mixed oxidant technology marketed by the MIOX Corporation

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of Albuquerque, New Mexico. Other disinfection technologies chosen for investigation were sodium hypochlorite (NaOCl) and chlorine dioxide (ClO<sub>2</sub>). In addition to disinfection alternatives, it was decided to test a method to remove organic carbon from the source water prior to chlorination (to reduce DBP formation). The MIEX® process was chosen for this test.

k. MIOX, ClO<sub>2</sub>, and hypochlorite treatment processes all resulted in effective disinfection of the Fort Bragg source water. These technologies easily performed as well as the current chlorination treatment method. When used at levels equivalent to traditional chlorination, MIOX and NaOCl treatments did not appear to significantly reduce DBPs. Chlorine dioxide treatment resulted in fewer traditional DBPs but increased levels of chlorate and chlorite, which are also regulated by the EPA under the D/DBP Rule.

l. An analysis was performed to evaluate water plant operations data to determine if a correlation existed between DBP formation and parameters other than the obvious ones of organic content and chlorine usage. Several years of plant operational data were examined for statistical correlation to HAA concentration. Of the 38 parameters evaluated, the ones that had a significant correlation were color, hardness, manganese, alum added, and alkali added. Most of these are interrelated and could be affected by the organic content of the source water; therefore, it is not surprising that they correlate to the HAA level. Unexpectedly, chlorine usage did not correlate to DBP formation. These variables were then used in a linear regression analysis to attempt to predict the HAA level prior to measuring it. The resulting correlation coefficient (R) 0.85 and the variance (R<sup>2</sup>) 0.73 were reasonably good fits. While there were no unexpected results, in the future, more rigorous analyses may result in better correlations.

m. The analysis of Fort Bragg data showed, and the literature supports, that the occurrence of DBPs is directly related to the quantity of organic carbon in the source water. Since this is the case, it would be advantageous for Fort Bragg to seriously consider a process to remove dissolved organic carbon (DOC). After testing several chlorination alternatives, a number of DOC removal technologies were evaluated for testing. As a result, the MIEX® process was selected for demonstration at Fort Bragg. This technology removed approximately half of the organic content of the water and reduced the HAAs by approximately two-thirds; THMs were unaffected.

n. The most inexpensive way for Fort Bragg to meet the goals of eliminating chlorine gas and reducing DBPs is the implementation of ClO<sub>2</sub> disinfection. Other alternatives, such as ozone disinfection or DOC removal combined with either MIOX or hypochlorite would also be effective but significantly more costly. However, the long-term regulatory status of chlorate and chlorite is questionable. Table 1 summarizes the comparison of estimated costs of each of the alternatives evaluated.

Table 1. Economic analysis results.

Technology	Capital Cost	Increased Annual Operating Cost	Net Present Value
NaOCl	\$16,370	\$19,500	\$240,033
MIOX	\$276,019	\$13,950	\$436,024
ClO <sub>2</sub>	\$64,000	\$42,860	\$555,601
Ultraviolet radiation	\$1,153,000	\$11,600	\$1,286,051
Ozone	\$2,446,000	\$184,600	\$4,563,347
MIEX <sup>®</sup> DOC Removal	\$3,900,000	\$187,000	\$6,044,875

o. It is difficult to predict the long-term performance of a technology without measuring it during all seasons and all water conditions. Short-term studies such as this one give a good indication of potential problems, and are valuable for eliminating inappropriate technologies from consideration. But a longer pilot-scale study should be completed prior to selecting a specific technology.

p. Several years of daily process data were examined in an attempt to correlate DBP formation with other parameters. Disinfection by-products correlated well with several parameters, primarily related to the organic carbon content of the water. It would be useful to perform a larger study using more data.

q. In small-scale batch tests, the MIEX<sup>®</sup> process effectively reduced the organic carbon content of the water, which resulted in a decrease of HAA by two thirds. A larger-scale study is needed to validate this promising DOC control alternative. NOTE: Due to constraints to publishing proprietary information, the data for the MIEX<sup>®</sup> technology has been removed from the report and is not included in Appendices A and B.

r. A glossary of acronyms and abbreviations is included in Appendix A following the Index.

5. Points of Contact (POCs). Headquarters U.S. Army Corps of Engineers (HQUSACE) is the proponent for this document. The POC

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### ACRONYMS AND ABBREVIATIONS

AWWA	American Water Works Association
CaCO <sub>3</sub>	calcium carbonate (limestone)
CERL	U.S. Army Construction Engineering Research Laboratory
CFU	colony-forming units
ClO <sub>2</sub>	chlorine dioxide
ClO <sub>2</sub> <sup>-</sup>	chlorite ion
ClO <sub>3</sub> <sup>-</sup>	chlorate ion
CO <sub>2</sub>	carbon dioxide
CT	inactivation (concentration multiplied by time)
DBP	disinfection by-products
D/DBP	Disinfectants/Disinfection By-Products Rule
DO	dissolved oxygen
DOC	dissolved organic carbon
EPA	United States Environmental Protection Agency
gpm	gallons per minute
HAA	haloacetic acid
HAA5	haloacetic acids (five compounds)
HCl	hydrochloric acid
HOCl	hypochlorous acid
HPC	heterotrophic plate count
lb	pound
mL	milliliter
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
mgd	million gallons per day
mg/L	milligrams per liter
MIEX <sup>®</sup>	magnetic ion exchange
MIOX	mixed oxidants
Mn <sup>+2</sup>	manganese ion
MSE	MSE Technology Applications, Inc.
MW/cm <sup>2</sup>	megawatt per square centimeter

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NaClO <sub>2</sub>	sodium chlorite
NaOCl	sodium hypochlorite
NOM	natural organic matter
OCl <sup>-</sup>	hypochlorite ion
ppb	parts per billion
ppm	parts per million
RMP	Risk Management Plan
THM	trihalomethane
TOC	total organic carbon
TTHM	total trihalomethanes
µg/L	micrograms per liter
µm	micrometer
UV	ultraviolet
UV254	specific absorption of ultraviolet light at 254 nanometers
WM&PP	Waste Minimization and Pollution Prevention
WTP	water treatment plant

**APPENDIX A**

**1 INTRODUCTION**

**1.1 Background**

The primary Fort Bragg (NC) Water Treatment Plant (WTP) treats and supplies drinking water to the entire cantonment area, including Simmons Army Airfield. The WTP was built in 1918 and, after several upgrades, has a design treatment capacity of 16 million gallons per day (mgd). As shown in Table 1-1, average flow is between 5 and 6 mgd.

The plant uses conventional methods to treat water (see Figure 1-1). Raw water is pumped from the Little River, and lime (to raise pH), alum (for coagulation and flocculation), and poly-aluminum chloride (for coagulation and flocculation) are added prior to mixing. Most solids settle out in the flocculation and sedimentation basins. Effluent from these basins is chlorinated with gaseous chlorine and immediately passes through dual-media filters. Sodium hexametaphosphate (corrosion control) and fluoride are added to the water prior to the first million-gallon clearwell. Ammonia (to form chloramines), chlorine, and lime (to raise pH) are added to the water, which is then pumped to the distribution system. Two additional million-gallon clearwells are used as needed.

Table 1-1. Quantity of water treated at Fort Bragg WTP (millions of gallons).

Month	FY01	FY02	FY03	FY04	FY05
October	254.2	253.5	161.7	172.3	177.6
November	217.5	221.9	150.6	156.3	164.3
December	229.3	200.1	168.9	136.0	162.7
January	226.8	179.1	182.6	134.1	173.2
February	192.8	157.4	180.2	116.2	153.0
March	212.9	180.5	198.6	130.9	- - -
April	145.0	214.7	170.8	154.2	- - -
May	308.9	276.8	184.1	167.2	- - -
June	262.3	266.2	207.4	138.8	- - -
July	279.2	213.6	193.0	155.5	- - -
August	284.8	192.0	181.4	188.0	- - -
September	239.2	175.9	156.9	172.0	- - -
Total	2,853	2,532	2,136	1822	831
Avg. per day	7.8	6.9	5.9	5.0	5.5

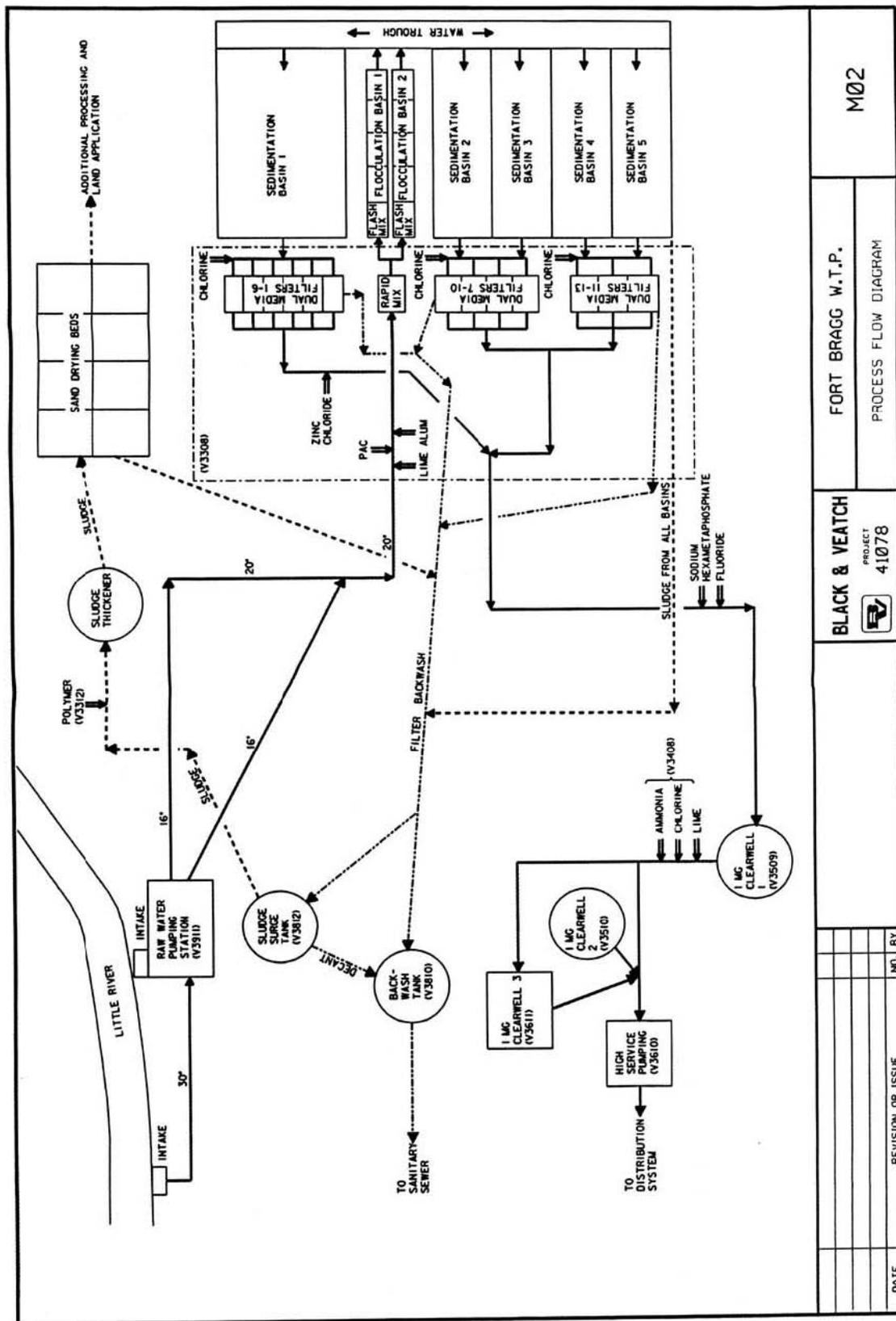


Figure 1-1. Ft. Bragg WTP flow diagram.

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The Fort Bragg drinking WTP uses chlorine gas as a primary and secondary disinfectant. While chlorine is an effective, inexpensive disinfectant, there are negative aspects to its use. The quantity of chlorine gas stored at each facility triggers regulatory thresholds governed by the Clean Air Act Section 112(r) (Prevention of Accidental Releases), and the facility has submitted the required Risk Management Plan (RMP) to the U.S. Environmental Protection Agency (EPA) for the use and handling of this poisonous chemical. While in effect, the RMP requires periodic updates, audits, and operator training on the safe use of chlorine. The storage of large amounts of this poisonous gas also provides a potential target for a terrorist attack, which would significantly impact the surrounding community, Pope Air Force Base, and the operations at Fort Bragg.

The EPA requires facilities with quantities of hazardous chemicals greater than a specified threshold limit to prepare an RMP that gives details for handling accidental releases of that chemical. This rule was the impetus for Fort Bragg wanting to replace chlorine with an alternative disinfectant. The maximum quantity of chlorine gas allowed on site without an RMP is 2,500 pounds (lb). At the current usage rate of approximately 250 lb/day, that allows for only 10 days storage on site – too little to run an efficient facility.

The RMP threshold limit for chlorine dioxide (ClO<sub>2</sub>) is 1,000 lb. Fortunately the ClO<sub>2</sub> process outlined in this document generates very small quantities of ClO<sub>2</sub> at any one time, and it would not be stored on site in appreciable amounts. However, the best process for manufacturing ClO<sub>2</sub> requires the use of hydrochloric acid (HCl), which has an RMP threshold limit of 15,000 lb. A treatment rate of 5 mgd would require approximately 42 lb of ClO<sub>2</sub> per day. At a ratio of 0.54 lb of HCl per lb, ClO<sub>2</sub> results in 22.5 lb/day of HCl. At this rate, a 15,000-lb supply would last 665 days or nearly 2 years. Since HCl is a common chemical and readily available, it is not necessary to store more than 15,000 lb at any given time.

Figure 1-2 shows Fort Bragg chlorine use for 2 years for both primary and secondary chlorination. The seasonal effects are obvious: more chlorine is typically needed in the warmer months due to higher oxidant demand from the source water. Also, more water is used in the summer for irrigation purposes. Figure 1-2 also shows that the amount of primary chlorination has been decreasing in an attempt to limit DBPs. At the same time, the amount of secondary chlorination has been increasing.

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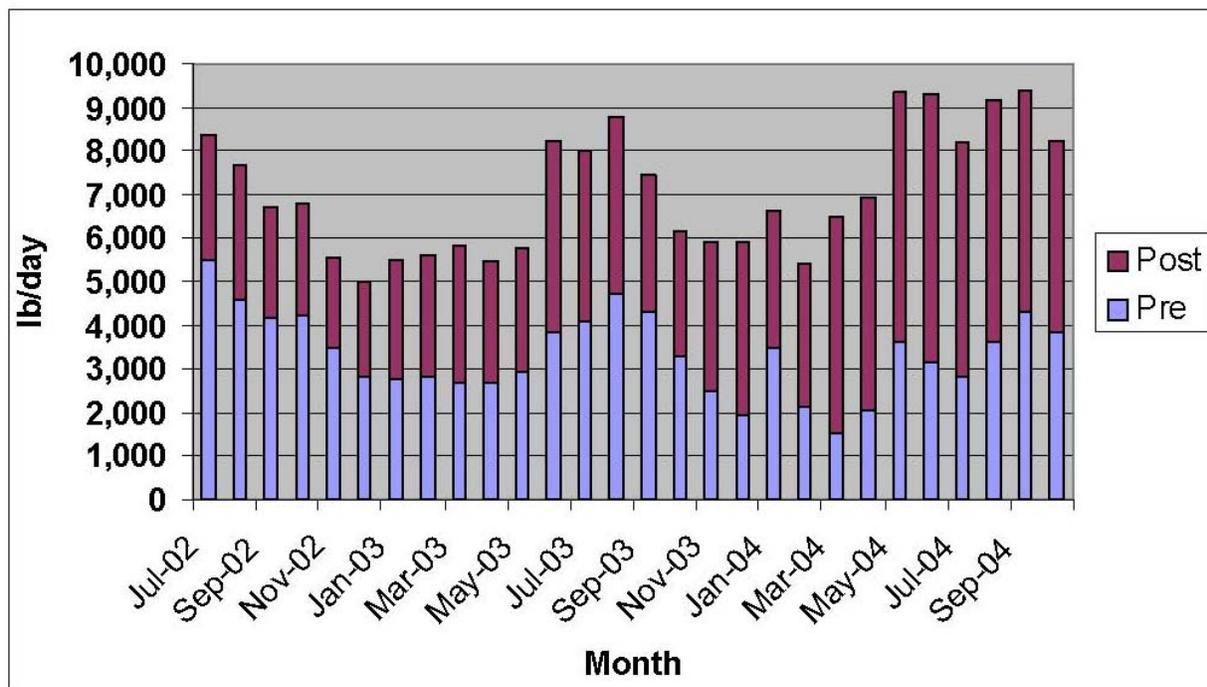


Figure 1-2. Chlorine usage at Fort Bragg WTP for 2002-04.

Halogenated organic by-products such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloketones can be formed when using chlorine- and bromine-based disinfection processes. These DBP compounds are regulated by the EPA's Disinfectants/Disinfection By-Product (D/DBP) Rule and have regulatory levels that have been exceeded at Fort Bragg. The installation has received notices of violation and has been assessed penalties for these exceedances.

In summary, Fort Bragg wanted to investigate alternatives to the current gas chlorine disinfection system that would (1) not pose a threat to force protection (by not compromising the ability to adequately disinfect the water), (2) not trigger an EPA RMP, (3) not produce further-regulated by-products, and (4) reduce risk to on-site plant personnel.

## 1.2 Approach

The existing drinking water treatment process was evaluated extensively including analysis of current baseline data for items such as chlorine usage, DBPs, and flow rates. Alternatives to gas chlorination were then identified and evaluated on the basis of their ability to resolve Fort Bragg's unique problems. A detailed scoring matrix was developed, and the various

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alternatives were ranked. Since Fort Bragg wanted to test more than one technology, this subjective process was developed for the purpose of ranking technologies in order of priority for testing. Mixed oxidant technology was ranked first, and ClO<sub>2</sub> was ranked second. Consequently, it was decided to test these technologies in that order. Fort Bragg also wanted to test sodium hypochlorite (NaOCl). The Construction Engineering Research Laboratory final report dealt primarily with the Mixed Oxidants (MIOX) tests; however, this report also includes the ClO<sub>2</sub> and NaOCl test results.

For all analyses, water was collected and sent to a commercial laboratory certified by the North Carolina State Laboratory Public Health Department to test for conventional water quality parameters, THMs, HAAs, and bacterial concentrations. Resulting data were then evaluated and tabulated in this report.

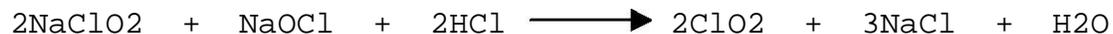
### 1.2.1 MIOX Tests

For the initial pilot test, the MIOX Corporation of Albuquerque, New Mexico, was contacted to obtain a demonstration unit. A pilot-scale unit was installed at the Fort Bragg WTP, and tests were performed on five different days in February and March and on two different days in July 2004. The MIOX unit was run as specified by the manufacturer so the exact concentration of reactants was unknown. The unit was run continuously for several weeks to evaluate its long-term performance.

### 1.2.2 Chlorine Dioxide Tests

Following completion of the MIOX tests, additional tests were performed using ClO<sub>2</sub> and NaOCl technologies. These were performed at several times during the year in an attempt to evaluate seasonal variability. The same basic test setup at Fort Bragg was used for all tests.

A 3,000-milligram per liter (mg/L) stock solution of ClO<sub>2</sub> was prepared using sodium chlorite (NaClO<sub>2</sub>), NaOCl, HCl, and deionized water as shown in the following reaction:



The ClO<sub>2</sub> solution was injected into a 15-gallon per minute (gpm) stream from the sedimentation basins at an initial concentration of 1.0 mg/L per recommendation of the NaClO<sub>2</sub> vendor. In order to assess seasonal variability, five separate tests were performed in April and May 2004, and three tests were run in January 2005. During the January tests, the concentration was raised to 1.3

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mg/L as recommended by the NaClO<sub>2</sub> vendor to ensure adequate disinfection.

### 1.2.3 Sodium Hypochlorite Tests

A 2,000-mg/L NaOCl stock solution was prepared and injected into a 15-gpm stream from the sedimentation basins. For the first five tests, the amount of NaOCl added to the water was matched to the free chlorine concentration of the Fort Bragg filtered water (after primary chlorination). This turned out to be equivalent to 0.6 to 0.7 mg/L free chlorine. In order to assess seasonal variability, two tests were performed in June, one in September, and two in October.

Later, MSE decided to mimic the amount of chlorine added by Fort Bragg rather than trying to simulate the measured chlorine concentration. In November 2004, three additional hypochlorite tests were performed. During November 2003, Fort Bragg used an average concentration of 1.98 mg/L for primary chlorination; therefore, three tests were performed at a free chlorine concentration of approximately 2.0 mg/L, three times the concentration of previous hypochlorite tests.

To calculate equivalent free chlorine the following reactions were assumed:



For both, the reactive species is hypochlorous acid (HOCl). To convert NaOCl to equivalent free chlorine (as Cl<sub>2</sub>), the concentration must be multiplied by a ratio of the molecular weights of chlorine gas and NaOCl or  $70.91 \div 74.44 = 0.953$ .

### 1.2.4 MIEX<sup>®</sup> Tests

Approximately 100 milliliters (mL) of MIEX<sup>®</sup> resin was placed into a clean bucket, to which 1 gallon (3.78 L) of raw source water was added and mixed for 15 minutes. This mixture was allowed to settle and then was decanted into another bucket. This process was repeated two additional times to simulate multiple loading of the ion exchange resin. The composite solution was then filtered through a sand filter into another bucket, and samples were taken for total organic carbon (TOC), dissolved organic carbon (DOC), and specific absorption of ultraviolet (UV) light

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at 254 nanometers (UV254). The above process was then repeated using coagulated water from the sedimentation basins using new MIEX<sup>®</sup> resin and sand.

To simulate chlorination and assess the impact of using MIEX<sup>®</sup> resin on DBP formation, the MIEX<sup>®</sup>-treated water was chlorinated using NaOCl. A 2,000-mg/L stock hypochlorite solution was prepared, and hypochlorite was added in the same concentration as Fort Bragg chlorine gas. As with previous tests, the chlorinated samples were allowed to sit for at least 1 hour to simulate the first clearwell. Samples were then taken for TOC, DOC, UV254, HAA, and THM analyses.

## **2 TECHNOLOGY ASSESSMENT**

To effectively make recommendations, appropriate literature was studied, and disinfection experts were contacted to determine the best methods to disinfect drinking water. The baseline technology for comparison was traditional gas chlorination. Technologies that were evaluated include mixed oxidation, ozonation, UV light, chloramines, filtration, and hypochlorite. Potential site impacts (such as waste disposal) were evaluated prior to pilot testing. A summary of the results of this task is included in Section 2.4, Alternatives to Chlorination.

### **2.1 Chlorine Disinfection**

Chlorine is a disinfectant added to drinking water to reduce or eliminate microorganisms (such as bacteria and viruses) that can be present in water supplies. For more than a century, the safety of drinking water supplies in America has been greatly improved by the addition of chlorine. Disinfecting our drinking water ensures that it is free of the microorganisms that can cause serious and life-threatening diseases. Today, chlorine is the most commonly used drinking water disinfectant, and the one for which we have the most scientific information.

When chlorine gas is added to water, it reacts rapidly to form HOCl and HCl. The formation of HOCl is considered the most important reaction in water chlorination, and the complete reaction occurs within a few tenths of a second. Hypochlorous acid undergoes partial dissociation to form hypochlorite ion (OCl<sup>-</sup>) and, together with HOCl, is termed "free available chlorine." Molecular chlorine is also considered to be free available chlorine but is not usually found in detectable concentrations at most water treatment pH values. Hypochlorous acid is an effective disinfectant for two reasons: (1) HOCl can penetrate cell walls effectively due to its charge neutrality,

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and (2) HOCl is an effective oxidant, having a higher oxidation potential than OCl<sup>-</sup> and chloramines (White 1986).

Total coliform bacteria are often used as indicators of fecal contamination and the potential presence of pathogenic organisms in water. Often a 99% (2-log) deactivation of indicator organisms is achieved by an appropriate combination of disinfectant concentration (C) and time (T), which is termed the CT value. Virus and enterovirus deactivation has been shown to require a higher CT value than bacteria and, more recently, an emerging challenge for disinfection practices has been the deactivation of protozoan cysts and oocysts in surface water supplies. In the case of protozoa, CT values for 99% deactivation of *Giardia* cysts (at 5 °C) has been reported to be 50 to 100 times higher than those for poliovirus and 500 to 10,000 times higher than for the coliform bacteria *Escherichia coli*.

*Cryptosporidium* oocysts are the etiologic agent for the disease cryptosporidiosis, which has been shown to be potentially life threatening in immuno-compromised individuals. Little scientific data are available on the deactivation of these organisms by chlorine or other oxidants; however, initial indications suggest that chlorine and chloramines are relatively ineffective for deactivation of *Cryptosporidium* oocysts (Korich et al. 1990). Consequently a combination of filtration and disinfection is required to meet regulations.

As mentioned above, chlorine acts as an oxidizer. It oxidizes organic and inorganic materials present in treatment waters including reduced metals, bromide ions, sulfides, and organic and inorganic nitrogenous compounds. The reaction of chlorine with organic matter naturally present in water forms a group of chemicals known as DBPs. The most common DBPs are THMs and HAAs. These are also referred to as total trihalomethanes (TTHM) and HAA5 for the five regulated HAAs. The amount of DBPs found in drinking water depends on a number of things, including the season and the source of the water. For example, DBP levels are generally lower in winter than in summer because the amount of natural organic matter (NOM) (chlorine demand) is lower and less chlorine is used. Disinfection by-product levels are also low when the drinking water source is a well or a large lake and higher when rivers or other surface waters are the source, again because of more organic matter in rivers.

## 2.2 Benefits of Chlorine

Chlorine is an effective disinfectant that has been responsible for making the nation's drinking water safe. While chlorine is an effective bactericide and virucide, it is relatively ineffective against protozoa, such as *Giardia* and *Cryptosporidium* (EPA Guidance Manual 1999). Tables 2-1 and 2-2 show CT values for chlorine and alternative disinfectants. In the tables, a 2-log reduction corresponds to 99%; 3-log means 99.9%, 4-log is 99.99%, etc. The chief benefit of chlorinated drinking water is the protection of public health through the control of waterborne diseases. For decades it has played a key role in controlling pathogens in water, as evidenced by the virtual absence of waterborne diseases such as typhoid and cholera in developed countries. A report by Craun et al. (1994) concludes that municipal water systems that are designed to prevent waterborne infectious disease are one of the most effective investments of public funds that society can make and that even conservative estimates of benefit-cost ratios are 3:1 for small systems and 8:1 for large systems.

Table 2-1. CT values for deactivation of viruses (EPA Guidance Manual 1999).

Disinfectant		Units	Deactivation (mg · min/L)		
			2-log	3-log	4-log
Chlorine	mg · min/L	3	4		6
Chloramine	mg · min/L	643	1,067		1,491
ClO <sub>2</sub>	mg · min/L	4.2	12.8		25.1
Ozone	mg · min/L	0.5	0.8		1.0
UV	MW · s/cm <sup>2</sup>	21	36		Not available

CT values were obtained from American Water Works Association (AWWA) 1991.

Note 1 - Values are based on a temperature of 10 °C, pH range of 6 to 9, and a free Cl<sub>2</sub> residual of 0.2 to 0.5 mg/L.

Note 2 - Values are based on a temperature of 10 °C and a pH of 8.

Note 3 - Values are based on a temperature of 10 °C and a pH range of 6 to 9.

Table 2-2. CT values for deactivation of *Giardia* cysts (EPA Guidance Manual 1999).

Disinfectant	Deactivation (mg · min/L)					
	0.5-log	1-log	1.5-log	2-log	2.5-log	3-log
Chlorine	17	35	52	69	87	104
Chloramine	310	615	930	1,230	1,540	1,850
ClO <sub>2</sub>	4	7.7	12	15	19	23
Ozone	0.23	0.48	0.72	0.95	1.2	1.43

CT values were obtained from AWWA 1991.

Note 1 - Values are based on a free Cl<sub>2</sub> residual less than or equal to 0.4 mg/L, temperature of 10 °C, and a pH of 7.

Note 2 - Values are based on a temperature of 10 °C and a pH in the range of 6 to 9.

Note 3 - Values are based on a temperature of 10 °C and a pH of 6 to 9.

### 2.3 Risks of Chlorination By-Products

As discussed previously, chlorination of water can lead to the formation of DBPs. Natural waters and wastewaters commonly contain a very large number of NOM compounds that may react with free chlorine from the disinfection process to form DBPs. The factors affecting the formation of these halogenated DBPs include the type and concentration of NOM, chlorine form and dose, time, bromide ion concentration, pH, organic nitrogen concentration, and temperature. The formation of DBPs is strongly related to the TOC at the point of disinfection and also correlates with the amount of chlorine consumed (Singer et al. 1993). In general, there is higher DBP formation at high pH than at low pH. Brominated and mixed brominated/chlorinated DBPs form when chlorine is used in the presence of bromide (Pourmoghaddas et al. 1993). One utility study found that preozonation, as opposed to prechlorination, was a major factor in reducing the amount of THMs formed, and that seasonal variation in organic matter appeared to be strongly linked with the variation in THMs and HAAs (Serodes et al. 2003).

Trihalomethanes are the most studied of the DBPs formed during chlorination of water and wastewater. The highest concentrations of THMs have been found in finished waters having surface waters as their source (Bellar et al. 1974). Chloroform is a common THM that has been banned by the U.S. Food and Drug Administration for use as an additive in the preparation of food and drugs and is regulated by the EPA in drinking water (Trussel and Umphres 1978).

Laboratory animals exposed to very high levels of THMs have an increased risk of cancer. Several studies on humans have also found a link between long-term exposure to high levels of chlorination by-products and a higher risk of cancer. For instance, a recent study showed an increased risk of bladder and possibly colon cancer in people who drank chlorinated water for 35 years or more (King and Marrett 1996). Another group also found a significant correlation between years of exposure to chlorinated surface water and the risk for bladder cancer ( $p = 0.0007$ ) (McGeehin et al. 1993). Studies have also shown that there is increased risk of cancer and intrauterine growth retardation from exposure to drinking waters containing THMs (Williamson 1981; Cantor et al. 1978; Kramer et al. 1992). Villaneuva et al. (2004) found in a pooled analysis that the risk of bladder cancer is increased in long-term exposure to DBPs at levels currently observed in many industrialized countries. Dodds et al. (2004) conducted a population-based

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case-control study in Nova Scotia and Eastern Ontario, Canada, to examine the effect of THMs on stillbirth risk. The results provided evidence of increased risk of stillbirth associated with exposure to chlorination by-products through ingestion, showering, and bathing.

Pursuant to requirements of the Safe Drinking Water Act Amendments of 1996, EPA is developing interrelated regulations to control microbial pathogens and disinfectant residuals and DBPs in drinking water. Collectively these rules are intended to address complex risk tradeoffs between the desire to deactivate pathogens and the need to reduce DBPs. The EPA has lowered the Maximum Contaminant Levels (MCLs) for total THMs and extended the MCL for THMs to all size systems; established MCLs for HAAs, bromate, and chlorate; and established Maximum Contaminant Level Goals (MCLGs) for other currently unregulated DBPs.

As a result of DBP concerns from chlorine, the EPA has placed more emphasis on the use of disinfectants other than chlorine. Some of these alternatives have also been found to produce DBPs as a result of either reactions between disinfectants and compounds in the water or as a natural decay product of the disinfectant itself. These DBPs include halogenated organics, organic oxidation products, and halogenated inorganics. As discussed above, the type and amount of DBPs produced during treatment depend on the disinfectant type, water quality, treatment sequences, contact time, temperature, and pH.

When considering the use of alternative disinfectants, systems should ensure that the deactivation of pathogenic organisms is not compromised. Pathogens pose an immediate critical public health threat due to the risk of an acute disease outbreak.

#### **2.4 Alternatives to Chlorination**

In the past few decades, an increasing emphasis has been placed on the application of alternative methods of drinking water disinfection, primarily due to the formation of undesirable DBPs and to the resistance of *Cryptosporidium* oocysts to traditional disinfectants. The Stage 1 D/DBP Rule and the Interim Enhanced Surface Water Treatment Rule, both promulgated in December 1998, seek to reduce concentrations of DBPs and to enhance the efficiency and reliability of filtration processes to remove pathogens, respectively.

### 2.4.1 Chloramines

Chloramines are formed when water containing ammonia is chlorinated or when ammonia is added to water containing chlorine (hypochlorite or HOCl). Chloramines are an effective bactericide but provide weaker oxidation and disinfection capabilities than free chlorine. The mechanism of deactivation appears to be reaction of monochloramine with four amino acids: cysteine, cystine, methionine, and tryptophan (Jacangelo et al. 1987). Chloramines are much less effective against viruses or protozoa such as *Giardia* and *Cryptosporidium*. Chloramines are very effective as residual disinfectants in the distribution system, minimize taste and odor problems, produce lower levels of THMs and HAAs, and may be more effective against biofilms in the distribution system. However, chloramines produce DBPs such as chloral hydrate and HAAs, cause eye irritation at high levels, require higher dosages and contact times (e.g., high CT values), and can promote algae growth in reservoirs and increase bacteria in the distribution system due to residual ammonia. Chloramines also present problems to individuals on dialysis machines where chloramines residuals in tap water may pass through membranes in the dialysis machines and directly induce oxidant damage to red blood cells.

Monochloramine addition can also impact other processes at a water treatment facility. Ammonia can serve as a nutrient for nitrifying bacterial growth in the distribution system, which can cause increased nitrate levels, and imbalances in chlorine and ammonia levels can cause breakpoint chlorination reactions to occur in the distribution system.

### 2.4.2 Hypochlorite

Sodium and calcium hypochlorite are effective disinfection agents that are used in drinking water systems throughout the United States. Sodium hypochlorite (often referred to as liquid bleach) is a chemical compound used to add chlorine to water. It is transported and stored in solutions containing 5 to 20% chlorine. It can be generated on site but is more commonly shipped by truck in containers ranging from 55 to 5,000 gallons (208-18,900 L). Calcium hypochlorite is another chlorinating chemical that is available in granular and tablet forms.

As stated previously, the hypochlorite ion (OCl<sup>-</sup>) that is produced by the addition of sodium or calcium hypochlorite solutions is a weaker disinfection agent than HOCl. Recent tests by MSE at the Fort Bragg WTP indicate that NaOCl treatment may

result in a reduction in HAAs as compared to gas chlorination. Sodium hypochlorite disinfection was shown by Weinberg et al. (2001) to add bromate to drinking water in quantities significant to be a health concern.

According to the American Water Works Association (AWWA 1998), approximately 20% of large treatment systems (more than 10,000 users) use NaOCl as a disinfection agent. Use of calcium hypochlorite is much less common.

### **2.4.3 Chlorine Dioxide**

Chlorine dioxide is a stronger oxidant than free chlorine and does not form halogenated by-products typically associated with chlorine, including THMs and HAAs. However, ClO<sub>2</sub> does react to form chlorite (ClO<sub>2</sub><sup>-</sup>) and chlorate (ClO<sub>3</sub><sup>-</sup>) ions, which may be toxic in high concentrations. Studies have shown disparate results regarding the deactivation of *Cryptosporidium*; consequently, it is not known if this disinfectant is indeed effective for deactivation of this organism (Chauret et al. 2001; Finch and Li 1999). Chlorine dioxide is generated on site at water treatment facilities and does not hydrolyze in water but remains in solution as a dissolved gas. It is approximately 10 times more soluble than chlorine (above 11 °C) and can be easily removed from solution by aeration with carbon dioxide (CO<sub>2</sub>). Most commercial generators use NaClO<sub>2</sub> as the common precursor feedstock chemical to generate ClO<sub>2</sub> for drinking water application. Recently ClO<sub>2</sub> production from sodium chlorate, a procedure traditionally used in pulp and paper applications, has been tested at U.S. municipal WTPs.

Chlorine dioxide generators are operated to obtain the maximum production while minimizing free chlorine or residual oxidant formation. The specified yield for ClO<sub>2</sub> generators is typically greater than 95%. In addition, the measurable excess chlorine should be less than 2% by weight in the generator effluent.

The advantages of ClO<sub>2</sub> are: (1) it acts as an excellent virucide, (2) it does not react with ammonia nitrogen to form chlorinated amines, (3) it does not react with oxidizable material to form THMs, (4) it destroys up to 30% of THM precursors, (5) it destroys phenols that cause taste and odor problems in potable water supplies, (6) it forms fewer chlorinated DBPs such as THMs and HAAs, (7) it improves removal of iron and manganese by rapid oxidation and settling of oxidized compounds, (8) it does not react with bromide to form

bromate or brominated by-products, and (9) it has enhanced turbidity removal under certain conditions.

The disadvantages of ClO<sub>2</sub> as a disinfectant for drinking water are that (1) it reacts with NOM and forms the inorganic by-products chlorite and, to a lesser extent, chlorate; (2) it requires on-site generation equipment and handling of chemicals; and (3) it occasionally poses unique odor and taste problems. Also, ClO<sub>2</sub> has a lower allowable dose so it may not maintain a residual in the distribution system.

#### **2.4.4 Ozone**

Ozone is an allotrope of oxygen, having three oxygen atoms to each molecule, and is a powerful oxidizing agent. Ozone is formed by passing dry air or oxygen through a system of high-voltage electrodes. For drinking water applications, ozone requires shorter contact time and dosage than chlorine and is widely used as a primary disinfectant in many parts of the world, although it is relatively new to the United States. Ozone does not directly produce halogenated organic materials unless bromide ions are present. Ozone is a very effective disinfectant and has been shown to be effective against *Cryptosporidium* (Korich et al. 1990); however, since it breaks down quickly, small amounts of chlorine or other disinfectants must still be added.

Since ozone, like chlorine, is a powerful oxidant, it can be used for a variety of purposes in drinking water treatment including taste and odor control, color removal, coagulation, and disinfection. In addition, ozone can be used to destroy pesticides and toxic industrial chemicals. Ozone has proved to be a more effective bactericide and virucide than chlorine. It is a better disinfectant for *Giardia* and *Cryptosporidium* oocysts than chlorine, chloramines, and ClO<sub>2</sub>. Ozone produces oxygenated by-products that are less toxic and less persistent than chlorination by-products. It also tends to produce lower levels of THMs and HAAs. Today, there are more than 3,000 drinking WTPs using ozone worldwide. However, ozonation produces higher levels of aldehydes and other by-products than does chlorination. Also, because ozone degrades rapidly, it cannot provide adequate protection from recontamination within distribution systems. Furthermore, it breaks up large organic molecules into smaller ones, which are more suitable for feeding microorganisms and can lead to biofilm growth. A recent EPA nationwide DBP occurrence study (September 2002) has shown that DBPs can form during

subsequent chlorination of ozone-treated waters. Renovating WTPs to use ozone also can be very expensive.

#### 2.4.5 Ultraviolet Irradiation

Ultraviolet radiation is generated by a special lamp and can penetrate the cell walls of microorganisms to disrupt genetic material and render the cells unable to reproduce. Ultraviolet radiation effectively destroys bacteria and viruses, although a secondary disinfectant must be used to prevent regrowth of microorganisms and to protect distribution systems from contamination. As a primary disinfectant for small systems, UV radiation can be attractive because it is readily available, produces few known toxic residuals, requires short contact times, and the equipment is easy to operate and maintain. Although typical DBP formation is minimal or absent, UV has been shown to form formaldehyde when used for disinfection of surface waters (Malley et al. 1995). Ultraviolet radiation deactivates *Cryptosporidium* oocysts (Shin et al., 2001). A 2- to 3-log reduction in the viability of *Cryptosporidium* oocysts was achieved in a low-pressure UV system with a theoretical minimum intensity of 14.58 megawatts per square centimeter (mW/cm<sup>2</sup>) and contact time of 10 minutes (UV dose=8,748 mW\*s/cm<sup>2</sup>) as shown by Campbell et al. (1995).

In contrast to chemical disinfectants, UV light acts physically on the genetic structure of microbes to deactivate them. As a result of its physical (rather than chemical) nature, UV disinfection does not appear to produce many DBPs. Ultraviolet light is an excellent germicide; it is highly effective at deactivating bacteria and viruses, although it is less effective in deactivating protozoans like *Giardia* and *Cryptosporidium*. Ultraviolet radiation can be one of the cheapest alternatives to chlorination. By 1990, Europe had approximately 2,000 UV drinking WTPs. Ultraviolet light is strictly a disinfectant; unlike oxidants, it cannot be used to control taste, odor, or color.

Producing UV radiation requires electricity to power special lamps, which are typically quartz tubes filled with an inert gas and small quantities of mercury. A UV lamp operates in much the same way as a fluorescent lamp; UV radiation is emitted from an electron flow through ionized mercury vapor to produce UV energy in most systems. While the fluorescent tube is coated with phosphorous to convert the UV to visible light, UV lamps are not coated and transmit the UV radiation generated by the arc. Low- and medium-pressure lamps are used for disinfection, and the

latter have much greater intensity so fewer lamps are required for an equivalent dosage. However, it is recommended that low-pressure lamps be used for small systems since several low-pressure lamps provide greater reliability than a single medium-pressure lamp.

Two emerging technologies in UV reactor design are microscreening UV and pulsed UV. The former uses two treatment chambers, each containing a 2-micrometer ( $\mu\text{m}$ ) nominal porosity screen so that *Cryptosporidium* oocysts can be temporarily captured on the filters and exposed to a total preset UV dose. The pulsed UV system uses capacitors to build up and deliver electricity pulses to xenon flash bulbs in a flow-through chamber. The unit provides microsecond pulses that give off high intensity, broadband radiation via flash tubes. Since UV is a physical process that requires a contact time to accomplish pathogen deactivation, these new systems increase the UV contact and dose to the treated water.

To achieve deactivation, UV radiation must be absorbed into the target microorganism. Anything that prevents UV rays from reacting with microorganisms will decrease the disinfection efficacy. While pH does not appear to have any effect on UV disinfection (Scheibel and Bassell 1981), several factors that do are the development of chemical and biological films on the lamp surface, dissolved organics and inorganics, clumping or aggregation of microorganisms, turbidity, color, and short-circuiting of water flow through the UV contactor.

#### **2.4.6 Mixed Oxidants**

This patented system generates a mixture of chemically oxidizing species from electrolysis of a sodium chlorine brine solution. The MIOX Corporation claims that electrolysis converts the brine solution to a mixture of free chlorine,  $\text{ClO}_2$ , hydrogen peroxide, ozone, and other short-lived oxidants. Although this technology has been developed over several decades, the chemical components of the mixture, as well as the efficacy of pathogen reduction, have been the focus of very few studies. One study showed MIOX to be a practical and effective disinfectant against even the most resistant pathogens (Venczel et al. 1997). However, it was not shown how long after generation the mixed-oxidant solution is effective. Since many powerful oxidant species are short-lived, it is possible to lose a significant amount of effectiveness in a short time after generation. Therefore, residual effectiveness might be quite different than the initial solution. Additionally, Venczel et al. have not been able to

successfully repeat their results (CRC 2001). Mixed oxidant systems have been shown to reduce biofilm growth, eradicate coliform bacteria, and, in side-by-side tests with hypochlorite, indicate an equivalent or better effectiveness and operation, although the MIOX system capital cost plus installation greatly exceeded the cost of a hypochlorite system (Camper 1998).

On their web site, the MIOX Corporation claims "mixed oxidants can help water systems comply [with the D/DBP Rule] since users typically see a reduction in trihalomethane formation of about 30% to 50% when compared to chlorine." Several examples of full-scale treatment facilities are listed on the web site.

#### **2.4.7 Filtration**

Biological/physical filtration methods of water treatment are good ways to reduce or eliminate by-products from primary disinfection and the need for residual disinfection. Many of these methods basically mimic nature's methods for cleaning water. Major biological/physical filtration methods currently available include biologically active carbon treatment, slow sand filtration, and membrane filtration.

Biologically active carbon filtration is able to remove aldehydes and many other by-products of primary disinfection and significantly reduce production of DBPs by residual chlorination. Studies comparing slow sand filters to other methods of water treatment (including chlorine, ClO<sub>2</sub>, and ozone) found slow sand filters to be the most effective in removing bacteria, viruses, cysts, and spores. Slow sand filtration is an essential element of water treatment works in London, Amsterdam, Paris, and other European cities and is recommended by the World Health Organization and the United Nations Environment Program as the preferred method of water treatment in developing countries. Slow sand filters are limited in their ability to break down industrially produced organic pollutants like pesticides. A promising approach is to add a small amount of ozone, breaking up the large organic compounds into smaller ones that are biodegradable and suitable for feeding microorganisms in a biological filter.

Both slow sand and activated carbon filters are effective in removing easily biodegradable compounds present in the water after chemical disinfection, thus decreasing problems in the distribution system caused by regrowth of bacteria. By combining the treatment steps of ozonation, biologically active carbon

and/or slow sand filtration, drinking water of a high quality and a high biological stability can be achieved.

#### **2.4.8 Organic Carbon Removal**

Disinfection by-products are a result of the reaction of chlorine with organic carbon. Therefore, it makes sense to attempt to eliminate (or significantly reduce) one or both of these elements. Following are technologies that can significantly reduce organic carbon content in drinking water. These alternatives are excerpted from Fearing (2004).

- Coagulation - This is the process by which small colloid materials and small particles are combined into larger aggregates for adsorbing dissolved organic matter on these aggregates, facilitating their removal in subsequent filtration.
- Adsorption
  - Activated carbon - Discussed in the previous section, considered the "best available technology" for organic carbon removal.
  - Ion exchange resins - Several anion exchange resins are capable of adsorbing organic matter in water. One of the most promising is MIEX<sup>®</sup>, which is discussed in more detail below.
  - Carbonaceous resins - These act similarly to granular activated carbon.
  - Metal oxides - Activated alumina and iron oxides can effectively bind the weak acid groups found in organic matter.
  - Metal hydroxides - These are flocculants with similar adsorption mechanism as metal oxides.
- Oxidation - Strong oxidants, such as ozone, are used to react with organic matter to form simpler products. Another step is then needed to biodegrade these substances.
- Membranes - Ultrafiltration and nanofiltration can be used to effectively remove organic compounds; however, membrane fouling is a problem.

A recent development that looks promising, the MIEX<sup>®</sup> DOC process, was selected for testing at the Fort Bragg WTP. The remainder of this section will focus on this innovative organic removal technology.

#### **2.4.9 MIEX<sup>®</sup> DOC Process Description**

The MIEX<sup>®</sup> DOC process is a continuous ion exchange process designed for the removal of DOC from a source water. The process uses a patented magnetized ion exchange resin, the MIEX<sup>®</sup> DOC resin.

The MIEX<sup>®</sup> DOC resin has been developed to enable adsorption of DOC to occur in a stirred contactor, much like a flash mixer in a conventional WTP. The MIEX<sup>®</sup> DOC resin beads are much smaller (around 150 microns) than conventional resin beads to allow rapid DOC adsorption kinetics in the contactor vessel. Under mixing conditions, the resin beads are dispersed to provide the maximum surface area available for adsorption of DOC.

The resin suspension then passes to a separating stage where the resin is recovered and recycled. A magnetic component is dispersed within the resin particle structure so that, when passed to a settler, the fine resin beads rapidly agglomerate into larger, fast settling particles. Resin recovery rates of greater than 99.9% are achieved at settler rise rates of over 10 meters/hour. Most of the settled resin is recycled to the front of the process while a small side stream is removed and sent for regeneration. The MIEX<sup>®</sup> DOC resin is regenerated in a brine (NaCl) solution where adsorbed organics are substituted for chloride ions.

The MIEX<sup>®</sup> DOC process differs significantly from conventional ion exchange processes. In conventional ion exchange columns, as the ion exchange capacity is progressively exhausted, the water produced deteriorates in quality. The leakage of undesired ions eventually reaches the point where product water is not of an acceptable quality. At that point, the column has to be taken off line and the resin regenerated. In contrast, the overall ion exchange capacity in the MIEX<sup>®</sup> DOC process is continuously maintained. As a consequence, the treated water from the MIEX<sup>®</sup> DOC process is of a consistent quality with breakthrough of DOC controlled at a predetermined level.

Unlike conventional ion exchange processes, the MIEX<sup>®</sup> DOC process does not require pretreatment for solids removal. Therefore, this process can be used to treat raw water at the start of a treatment chain or as a polishing step at the end. High

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turbidity levels do not interfere with the adsorption of DOC. When used to treat raw water, further treatment downstream of the MIEX<sup>®</sup> DOC process is required for turbidity removal. Because this process causes a slight increase in turbidity due to a small amount of resin carryover from the settler, a subsequent filtration stage is required.

## 2.5 Summary

Alternatives to chemical disinfection are considered due to concerns over DBPs, hazardous chemical storage, disinfectant-related tastes and odors, and the emergence of chlorine-resistant protozoan parasites. Changes in the quantity and quality of water sources and environmental pressure to reduce the production and use of chlorine-based chemicals provide additional reasons to consider alternative methods of water treatment.

Alternatives to conventional chemical disinfection include physical and chemical barriers to contamination. These include filtration, ozonation, and UV irradiation. Both ozone and UV irradiation are effective against bacteria, viruses, and parasitic protozoa. Filtration processes may also remove undesirable substances, such as NOM, prior to disinfection, which can lead to a reduction in the concentrations of chemical disinfectants needed and their resulting by-products.

However, ozonation and UV irradiation do not provide residuals and thus would require the addition of a chemical to maintain residual disinfection in the distribution system. The main consequence of operating without a disinfectant residual would be lack of a preservative effect and loss of a useful indicator for failure of disinfection or serious post-treatment contamination. Before operating without a residual, considerable renovation and cleaning of mains would be required. Intensive water quality monitoring would be needed until it was established that water quality in distribution was acceptable. Also, at present, U.S. regulations do not permit the distribution of water without a residual.

Ozonation in combination with biotreatment and possibly residual UV treatment or chloramination prior to distribution appears to pose the best available alternative for larger water supply systems. Ultraviolet treatment in combination with filtration and, in some cases, residual chloramination provides the best currently available option for small groundwater treatment plants free of protozoan pathogens. While each of the above

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chlorine-free alternatives has its own set of strengths and weaknesses, combinations of them can be used to eliminate or vastly reduce chlorine use for virtually all of its uses in water disinfection. By using mainly nonchemical methods of water treatment and improving the system and maintenance of the distribution system, it is feasible to cease using chlorine entirely.

The main implications for water treatment and process monitoring when changing to alternatives to chemical disinfection would be the need to ensure the efficacy of disinfection. While there is no reason to impose tighter standards for nonconventional treatment methods, there is no simple surrogate, like chlorine residual measurement, to assess the integrity of physical processes.

Taking these concerns into account when alternative processes are to be used for primary disinfection, a low dose of chemical disinfectant might still be added to provide a residual within distribution. This would enable effective disinfection and DBP precursor removal, resulting in low production of by-products while still ensuring microbiological safety. The applicability of alternative processes should be considered on a case-by-case basis, taking into account source water characteristics, existing treatment, the nature of the distribution system, and the need to ensure protection of public health.

Table 2-3 summarizes salient points for the baseline technology (chlorine gas) and several alternatives. Table 2-4 shows the original ranking of the alternative technologies based on some of these points. As stated previously, the ranking process was subjective; its purpose was to prioritize appropriate technologies to help with the decision-making process. Ranking categories included treatment effectiveness, DBPs, residual, safety, and cost. Sources included literature, university professors, and industry experts. The "Knowledge of DBP" category was intended to indicate that MSE has extensive knowledge (good) of potential dangerous by-products of certain technologies but very little knowledge about others (bad).

Table 2-3. Chlorination alternatives summary.

Disinfectant	Advantages	Disadvantages
<b>Chlorine Gas</b>	Very effective against most pathogens Usually most cost-effective option Well understood and accepted Good residual disinfection	DBP formation (THMs, HAAs) Additional regulatory requirements (EPA's Risk Management Program) Ineffective against <i>Giardia</i> and <i>Cryptosporidium</i>
<b>Chloramines</b>	Reduced formation of THMs and HAAs More stable residual than chlorine Good secondary disinfectant	Weaker disinfectant than chlorine Requires shipments and use of ammonia Toxic for kidney dialysis patients Potential for nitrification
<b>Sodium hypochlorite (NaOCl)</b>	Same efficacy and residual protection as chlorine gas Fewer training requirements than chlorine gas Fewer regulations than chlorine gas	Limited shelf-life Same by-products as chlorine gas, plus bromate and chlorate Higher chemical costs than chlorine gas Corrosive; needs special handling
<b>Calcium Hypochlorite (Ca(ClO)<sub>2</sub>)</b>	Same efficacy and residual protection as chlorine gas More stable than NaOCl, allowing long-term storage Fewer regulations than chlorine gas	Same by-products as chlorine gas Higher chemical costs than chlorine gas Fire or explosive hazard if handled improperly
<b>MIOX</b>	Economical to operate Potentially lower DBP Good residual disinfection Safe, no toxic chemicals used	New technology - little history High capital costs Significant operator interface High energy costs Only one published study with <i>Cryptosporidium</i> Unknown stability of disinfectant
<b>Ozone</b>	Produces no chlorinated THMs or HAAs Effective against <i>Cryptosporidium</i> and <i>Giardia</i> Better taste and odor control than chlorination	More complicated than chlorine or UV systems No residual protection Hazardous gas requires special handling By-products consist of bromate, brominated organics, and ketones High capital and operating costs
<b>UV</b>	No chemical generation, storage, or handling Effective against <i>Cryptosporidium</i> and <i>Giardia</i> No known by-products at levels of concern	No residual protection Less effective in turbid water No taste and odor control Higher cost than chlorine High maintenance
<b>Chlorine dioxide (ClO<sub>2</sub>)</b>	Possibly effective against <i>Cryptosporidium</i> Low formation of THMs/HAAs Better taste and odor control than chlorination	Hazardous by-product formation (chlorite, chlorate) Requires on-site generation equipment and handling of chemicals Higher cost than chlorine Studies not conclusive showing effectiveness against <i>Cryptosporidium</i>
Adapted from <a href="http://www.c3.org/chlorine_issues/disinfection/water_disinfection.html#dm">http://www.c3.org/chlorine_issues/disinfection/water_disinfection.html#dm</a> and other sources		

*Table 2-4. Chlorination alternative ranking (original list).*

Alternative	Effectiveness			Disinfection Byproducts		Residual Disinfection	Safety	Cost		Total	Rank
	Giardia & Crypto	Color	Taste & Odor	Formation	Knowledge			Capital	Operating		
<b>Weighting</b>	10	5	5	10	3	7	10	5	5		
Chlorine gas	4	4	4	1	5	4	1	4	4	183	4
Chloramine	3	2	3	2	2	5	2	4	4	176	6
Hypochlorite	3	3	3	2	4	4	2	3	3	170	8
ClO <sub>2</sub>	4	4	4	3	4	3	2	3	3	193	2
Mixed oxidants	4	4	4	3	2	4	4	4	4	224	1
Ozone	4	4	4	1	2	1	4	2	2	163	9
UV	3	2	2	5	2	1	4	2	2	173	7
Biological Activated Carbon	3	3	3	5	2	1	4	2	2	183	4
Membrane Filtration	4	3	2	5	2	1	4	2	2	188	3
Sand Filtration	2	2	2	5	2	1	4	2	2	163	9

**Scale:**  
 5 = Very good  
 4 = Good  
 3 = Neutral  
 2 = Bad  
 1 = Very bad

### 3 PILOT-SCALE TESTS

Pilot-scale tests were performed on three disinfection technologies: MIOX, ClO<sub>2</sub>, and NaOCl. Tests were also performed on the MIEX<sup>®</sup> DOC removal process. Details for each test follow.

#### 3.1 MIOX Test Description

According to the manufacturer, the MIOX system produces mixed oxidants by electrolyzing salt water (brine) and separating the resulting products (see Figure 3-1). Strong oxidants, referred to as MIOX solution, are produced within the cell, discharged at the top of the cell, and collected into a holding tank until they are mixed with untreated water. These oxidants act together as a disinfectant that is reported to be more effective than any single oxidant.

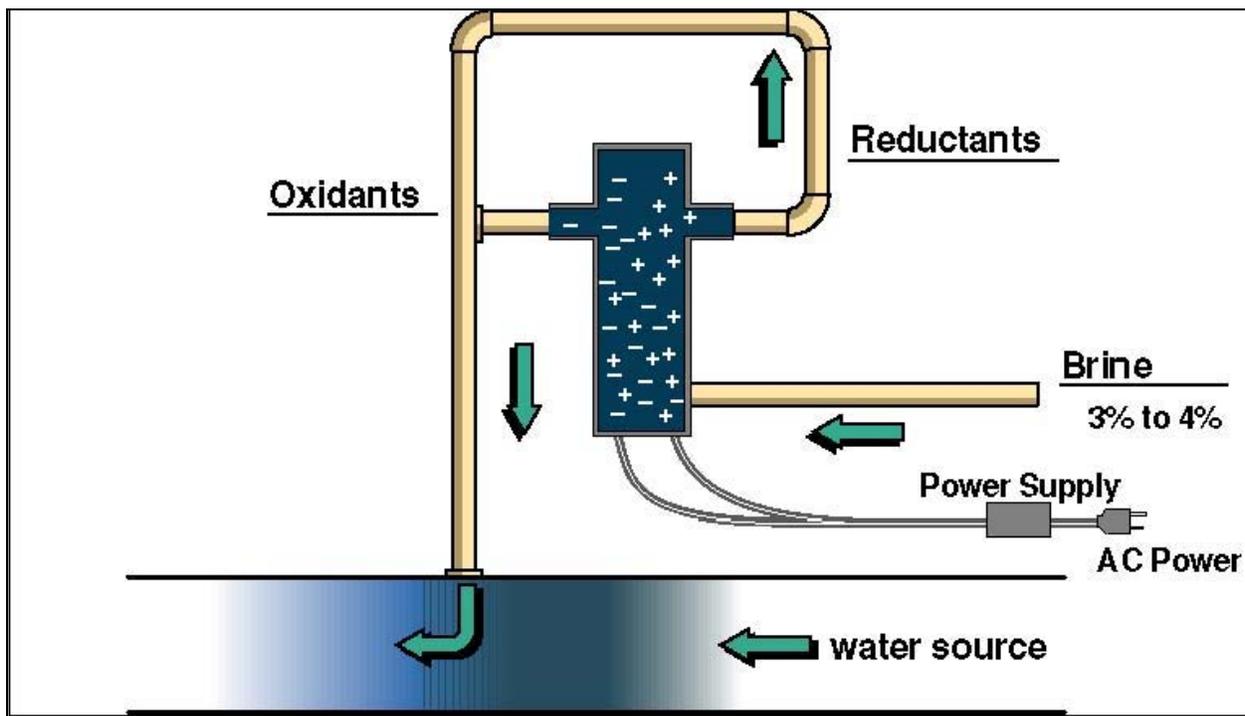


Figure 3-1. Conceptual diagram of the MIOX process.

The Fort Bragg WTP chlorinates at two points. Primary chlorination of raw water is accomplished with gaseous chlorine prior to filtration, and secondary chlorination is then accomplished by using gaseous chlorine and ammonia as part of a chloramine process. The MIOX unit was used to simulate Fort Bragg's primary chlorination step. These samples were then held for a retention time similar to the current Fort Bragg process

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(approximately 2 hours) to assess effects similar to those in the plant from the passage of chlorinated water through the treatment process. Samples of Fort Bragg water were also tested at the point immediately following the primary chlorination step.

For this demonstration, a MIOX SAL-80 was used. This unit has the capability to produce up to 10 lb/day of free available chlorine. The equipment was installed at the Fort Bragg WTP to test water prior to primary chlorination. The MIOX unit was installed and started up with assistance from the manufacturer. The general layout is shown in Figure 3-2. MIOX solution was injected into an approximate 15-gpm flow from the sedimentation basins. Chlorine was analyzed immediately using a Hach kit and compared to the Fort Bragg filtered water sample. Adjustments were made as necessary to the MIOX injection rate. It was assumed that the 50 feet of piping between the MIOX injection point and the sample point was sufficient for proper mixing. After samples were taken, they were held for approximately 2 hours to simulate the WTP Clearwell #1.

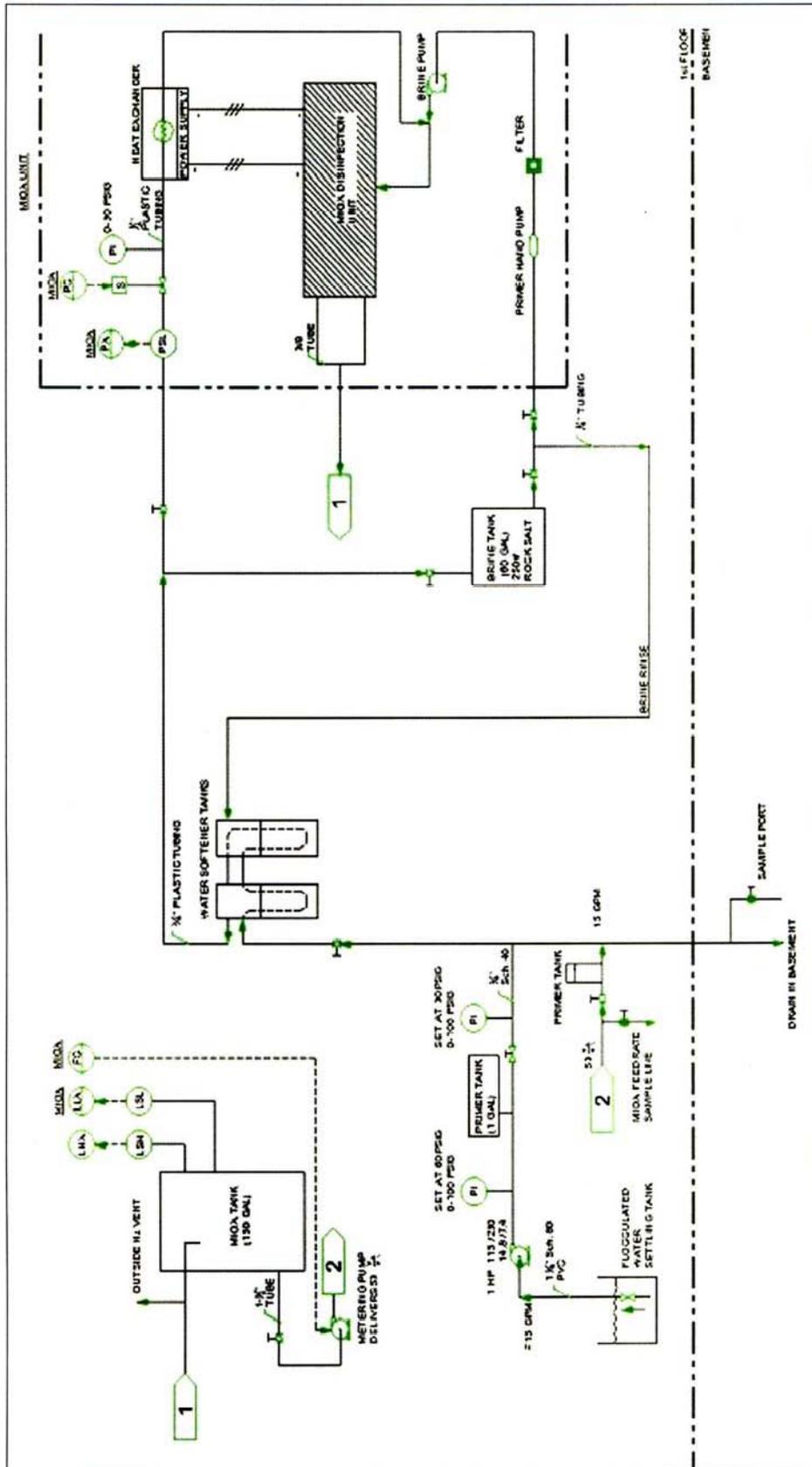


Figure 3-2. MIOX unit process flow diagram.

### **3.2 Chloride Dioxide Test Description**

Chlorine dioxide tests were performed after extensive consultation with drinking water experts and International Dioxide, Inc., a major manufacturer of  $\text{NaClO}_2$  (which is used to prepare  $\text{ClO}_2$ ). A 3,000-mg/L  $\text{ClO}_2$  solution was prepared by mixing  $\text{NaClO}_2$ ,  $\text{NaOCl}$ , and  $\text{HCl}$  as specified by International Dioxide. This solution was then injected into a 15-gpm stream from the Fort Bragg sedimentation basins. The initial concentration was set at 1.0 mg/L for the first five tests and at 1.3 mg/L for later samples. Chlorine dioxide concentration was measured immediately using a colorimetric Hach test kit. It was assumed that the 50 feet of piping between the injection point and the sample point was sufficient for proper mixing.

As with the MIOX process, the  $\text{ClO}_2$  unit was used to simulate Fort Bragg's primary chlorination step. These samples then were held for a retention time similar to the current Fort Bragg process (approximately 2 hours) to assess effects similar to those in the plant from the passage of chlorinated water through the treatment process. Samples of Fort Bragg water were also taken at the point immediately following the primary chlorination/filtration step.

### **3.3 Sodium Hypochlorite Test Description**

Drinking water treatment experts and several literature sources were consulted prior to performing  $\text{NaOCl}$  tests. A concentrated hypochlorite solution was prepared by mixing sufficient 6% household bleach in deionized water to obtain a 2,000-mg/L solution. As with the other mixtures, this solution was injected into a 15-gpm flow from the sedimentation basins. Initially the treatment concentration was set by attempting to emulate the free chlorine level of the Fort Bragg filtered water. Later, the amount of hypochlorite added simulated the quantity of chlorine gas added by Fort Bragg. Free chlorine concentration was measured immediately using a colorimetric Hach test kit. It was assumed that the 50 feet of piping between the injection point and the sample point was sufficient for proper mixing.

As with the other technologies, the  $\text{NaOCl}$  unit was used to simulate Fort Bragg's primary chlorination step. These samples then were held for a retention time similar to the current Fort Bragg process (approximately 2 hours) to assess effects similar to those in the WTP from the passage of chlorinated water through the treatment process. Samples of Fort Bragg water were

also taken at the point immediately following the primary chlorination/filtration step.

### **3.4 MIEX<sup>®</sup> DOC Removal Test Description**

The MIEX<sup>®</sup> DOC process is normally a continuous ion exchange process. However, for MSE's purposes, it was run as a series of batch processes. Raw water from the river was collected and placed in a bucket with the MIEX<sup>®</sup> ion exchange resin. After a 15-minute contact time (as recommended by the manufacturer), the water was decanted off and placed in another vessel. The treated water was filtered using the same sand used in the Fort Bragg sand filters. Then, NaOCl was added at a level equivalent to the gaseous chlorine added by Fort Bragg. After a 1-hour reaction period, sample bottles were filled and sent to a certified laboratory for testing. These tests were repeated for coagulated water from the Fort Bragg sedimentation basins.

### **3.5 Analytical Tests**

Analytical tests were performed to evaluate the effectiveness of each of the alternative technologies, and that effectiveness was compared to conventional chlorination.

#### **3.5.1 Sample Locations**

The following locations were used to collect samples to show the effectiveness of the various disinfectants. Not all locations were used for each test.

- Raw - These samples were taken from the raw water tap in the WTP laboratory. The water had not passed through chlorination and flocculation steps.
- Filtered - These samples were taken immediately after the primary chlorination and dual media filtration prior to entering Clearwell #1. It was too complicated to take samples after chlorination but prior to filtration. This sample point was selected to be similar to the MIOX, hypochlorite, and ClO<sub>2</sub> samples, but the filtration step made it slightly different.
- MIOX - Flocculated water was taken from the sedimentation basin, MIOX solution was added, and it traveled through approximately 50 feet of pipe prior to being sampled. The turbulent flow in the pipe ensures it was well mixed.

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- Hypochlorite - These are similar to the MIOX samples except that a NaOCl solution is added to the flocculated water. Several different concentrations of hypochlorite were used to fully evaluate the technology.
- Chlorine Dioxide - These are similar to the MIOX samples except that a ClO<sub>2</sub> solution is added to the flocculated water. Several different concentrations of ClO<sub>2</sub> were used to fully evaluate the technology.
- Clearwell - These samples were taken from the Clearwell #1 tap in the WTP laboratory. The first clearwell is a 1 million-gallon tank in which the water is held immediately following primary chlorination and filtration. Assuming this tank is about half full, the average residence time is 2 to 3 hours.
- Tap - These samples were taken from the finished tap water location in the WTP laboratory.

The Fort Bragg filtered water and the MIOX-, ClO<sub>2</sub>-, and hypochlorite-treated samples were allowed to sit for 1 to 2 hours prior to adding neutralizers and placing in sample bottles. This rest period allowed the oxidant time to react fully and to somewhat simulate the residence time in the first clearwell. Using a colorimetric Hach kit, residual chlorine and ClO<sub>2</sub> levels were measured immediately after sampling and then prior to placing sample in bottles.

### **3.5.2 Test Parameters**

The following analytical tests were used to evaluate the effectiveness of the various disinfection treatment technologies.

#### **3.5.2.1 Color**

Color in water comes from many sources and is removed to make the water suitable for drinking water applications. While color can indicate potential problems, it is primarily a concern to consumers for aesthetic reasons. True color does not include turbidity or suspended matter. Spectrophotometric analysis of filtered samples is the preferred method.

#### **3.5.2.2 Oxidant Demand**

Oxidant demand refers to the difference between the added oxidant and residual oxidant concentration measured after a

prescribed contact time. The oxidant in this case refers to both the existing chlorine and the proposed mixed oxidant solution. Since these oxidants react with many substances in drinking water over time, the sampling and testing must be performed on a consistent time-increment basis.

#### **3.5.2.3 Alkalinity**

Alkalinity is a measure of the acid-neutralizing capacity of water. Alkalinity of most drinking waters is primarily a function of carbonate, bicarbonate, and hydroxide content. An acid titration method is typically used to determine alkalinity, which is expressed as milligrams calcium carbonate (CaCO<sub>3</sub>) per liter of water.

#### **3.5.2.4 Total Organic Carbon**

The organic carbon in water is composed of a variety of organic compounds in various oxidation states. To determine the quantity of organic carbon, the organic molecules must be broken down to single carbon units and converted to a molecular form that can be measured quantitatively. The combustion-infrared method oxidizes all organic carbon to CO<sub>2</sub>, which is then measured by an infrared analyzer. It is desirable to remove organic carbon from drinking water to prevent problems with DBPs.

#### **3.5.2.5 Dissolved Organic Carbon**

Dissolved organic carbon is defined as the fraction of TOC that passes through a 0.45-micron filter. Particulates are not included.

#### **3.5.2.6 UV254**

This test refers to the sample's specific absorption of UV light at 254-nanometer wavelength and is an indicator of the humic content of water. Humic substances are organic residues of decaying organic matter.

#### **3.5.2.7 Chlorine Residual**

Free chlorine and other chlorine species are destroyed as they oxidize organic matter in the water. To ensure the safety of consumers, water treatment facilities in the United States are required to have a residual quantity of chlorine remaining in the water following treatment. The DPD colorimetric method is one of the most commonly used test methods for residual chlorine.

### **3.5.2.8 Heterotrophic Plate Count**

The heterotrophic plate count (HPC) is the procedure for estimating the number of live heterotrophic bacteria in water. The measurement is colony-forming units (CFU) per milliliter of water. Although the premise is that each colony arises from a single cell, clusters of cells may also produce colonies. While many of these bacteria are harmless, the presence of heterotrophic bacteria in drinking water supplies can indicate bigger problems.

### **3.5.2.9 Coliforms (Fecal and Total)**

Coliforms are defined as all aerobic and facultative anaerobic, gram-negative, nonspore-forming, rod-shaped bacteria that develop a red colony with a metallic sheen within 24 hours at 35 °C on an Endo-type medium containing lactose. The membrane filter technique for measuring coliforms is often used. Coliform bacteria are often used as indicators of fecal contamination and the potential presence of pathogenic organisms in water. It is very important that these be eliminated from drinking water.

### **3.5.2.10 Total Trihalomethanes**

Trihalomethanes are a group of four chemicals that are formed along with other DBPs when chlorine or other disinfectants react with naturally occurring organic and inorganic matter in water. The major THMs are chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Since THMs are suspected carcinogens, EPA has published the Stage 1 D/DBP Rule to regulate THMs at a maximum allowable annual average level of 80 parts per billion (ppb). The Stage 2 Rule is more restrictive in that it will require that MCLs be calculated for each monitoring location.

### **3.5.2.11 Total Haloacetic Acids**

Haloacetic acids are a group of chemicals that are formed along with other DBPs when chlorine or other disinfectants react with naturally occurring organic and inorganic matter in water. The regulated HAAs are monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. Since HAAs are suspected carcinogens, EPA has published the Stage 1 D/DBP Rule to regulate HAAs at 60 ppb annual average. The Stage 2 Rule is more restrictive in that it will require that MCLs be calculated for each monitoring location.

### **3.5.2.12 Chlorate and Chlorite**

When ClO<sub>2</sub> is used to treat water, it results in residual levels of both ClO<sub>3</sub><sup>-</sup> and ClO<sub>2</sub><sup>-</sup> ions. The final concentrations of these substances are limited to less than 1.0 ppm by EPA's Stage 1 D/DBP Rule.

### **3.6 Pilot-Scale Test Results and Discussion**

Three different disinfection technologies were evaluated at the pilot scale at the Fort Bragg WTP. These included MIOX, NaOCl, and ClO<sub>2</sub> technologies. Detailed data summary tables are shown at the end of this section (Tables 3-1 through 3-9). In addition to the disinfection processes, an organic carbon removal process (MIEX<sup>®</sup>) was examined in detail. A detailed explanation for each parameter follows.

#### **3.6.1 Color**

The color of all the treated samples was consistently higher than the Fort Bragg filtered samples. This was likely due to the fact that the MIOX-, hypochlorite, and ClO<sub>2</sub>-treated samples were not filtered after treatment, which may have left suspended solids in the samples, contributing to the color. Also, the pilot-scale injection system incorporated iron pipe that could have contributed to the sample color in the form of rust.

#### **3.6.2 Chlorine Demand**

Chlorine demand data showed that this parameter was more a function of the organic content of the water than the technology being tested. As the water's organic content rose in the summer and fall, the chlorine demand for both the raw water and the treated water went up significantly. As expected, the raw water chlorine demand was significantly higher than that for treated water. This result also shows that improvement is needed in reducing the organic content of the treated water prior to chlorination.

#### **3.6.3 Alkalinity**

The alkalinity in the samples treated with alternative technologies was typically greater than the Fort Bragg filtered water samples, but they were similar enough to be essentially indistinguishable. The values obtained by this study were comparable to Fort Bragg historical data.

### **3.6.4 Total Organic Carbon and Dissolved Organic Carbon**

During these tests, the organic carbon content of the raw water varied between 4 and 10 mg/L with 95% typically in the dissolved form. This is similar to previous compliance data collected by Fort Bragg. However, historical data from Fort Bragg showed that the organic carbon content could rise higher. In August 2003 the TOC of the source water spiked to a high of 15.5 mg/L.

All three alternative treatment technologies were similar for organic carbon content. Water treated with MIOX, hypochlorite, and ClO<sub>2</sub> had 50% to 60% of the DOC level of raw water. Total organic carbon removal was similar; however, the Fort Bragg process typically removed about 10% more organic carbon than the alternatives tested. This difference was undoubtedly due to Fort Bragg's filtration process removing particulate matter that is part of the TOC but not DOC. Alternative treatment technologies did not have a filtration step.

### **3.6.5 UV254**

The trends in these results were consistent with the TOC and DOC results. Since this test measures humic content (a significant organic component of the water), it would be expected to be similar to TOC and DOC.

### **3.6.6 Chlorine Residual**

**MIOX tests** - Chlorine content of the samples was measured on site using a Hach test kit. The chlorine value was measured primarily for process control purposes and to ensure that the MIOX process was similar to the Fort Bragg primary chlorination step. Residual chlorine was also measured at the contracted test laboratory, and very little free chlorine remained in the samples. This is to be expected as the samples had continued reaction time during transport and storage.

Figure 3-3 shows residual chlorine levels in a water sample to which MIOX solution was added and then tested with a Hach kit every 15 to 30 minutes. It shows that most of the available chlorine was used up within the first 2 hours; additional contact time was unnecessary.

**Hypochlorite tests** - Chlorine residual values were very similar to those for the MIOX and Fort Bragg filtered water samples.

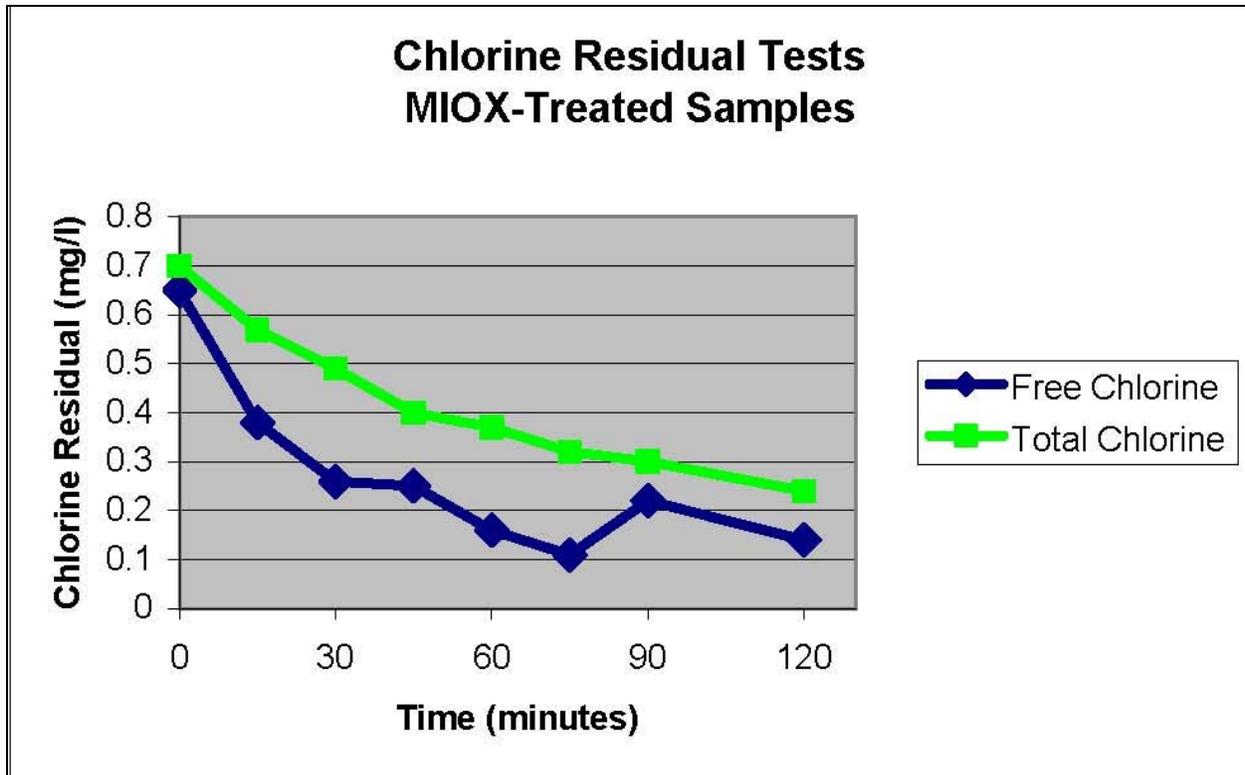


Figure 3-3. Chlorine consumption of MIOX-treated samples.

**Chlorine Dioxide tests** - Instead of chlorine residual, ClO<sub>2</sub> residual was measured with a Hach kit. When it was measured, the ClO<sub>2</sub> content decreased over time as it apparently reacted with substances in the water.

### 3.6.7 Heterotrophic Plate Count

The number of culturable heterotrophic bacteria in all the treated samples was significantly lower than that in the raw water. This is to be expected and shows the effectiveness of these treatments. The HPC values for the MIOX- and ClO<sub>2</sub>-treated samples were consistently slightly higher than the Fort Bragg samples; however, the difference is not significant and is likely due to lack of optimization of these treatments. Heterotrophic plate count values for hypochlorite-treated water were similar to the Fort Bragg filtered water, especially when increased concentrations were used.

### 3.6.8 Coliforms

The raw water samples consistently showed the presence of both fecal and total coliforms. No coliforms were detected in any of the MIOX-treated samples, the hypochlorite-treated samples, or

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the Fort Bragg filtered samples, which showed the effectiveness of these disinfection methods.

However, the ClO<sub>2</sub> test results were not as clear cut. Two of the initial five ClO<sub>2</sub>-treated samples had positive hits for total coliforms but not fecal coliforms (Table 3-3). MSE was unsure if this was a problem with the technology or a misapplication of the method. According to the ClO<sub>2</sub> experts consulted, disinfection failures are very uncommon. Therefore, MSE performed additional ClO<sub>2</sub> tests to confirm the effectiveness of the technology (Table 3-4). In addition to the original 1.0-mg/L target, these tests were also run at a concentration of 1.3 g/L ClO<sub>2</sub>. Neither level had positive hits for coliforms, which indicates that ClO<sub>2</sub> technology should be entirely appropriate for application at Fort Bragg.

### 3.6.9 Trihalomethanes

Concurrent tests of Fort Bragg tap water showed that the majority of the THM formation occurs at some point following primary chlorination. On the other hand, HAA formation occurs immediately after primary treatment. The reaction kinetics of THM formation are apparently much slower than those for HAA formation. Recent data by Xie and Zhou (2002) indicates that HAAs are biodegraded in granular activated carbon, which leads MSE to believe that they may also be degraded slowly in water distribution systems.

**MIOX tests** - As shown in Table 3-1, the THM content of both the MIOX-treated samples and Fort Bragg filtered water samples was much lower than the regulatory limit of 80 micrograms/liter ( $\mu\text{g/L}$ ). The average filtered water value was 7.2  $\mu\text{g/L}$ , or approximately 33% lower than the average MIOX treated value of 10.8  $\mu\text{g/L}$ . At these low levels, this difference is insignificant and within the range of error for the analytical instruments. However, the MIOX samples were not filtered after treatment, which could have contributed to higher THM values because of slightly higher organic levels remaining in the samples (as shown by DOC and TOC data).

For a more realistic picture, these tests were also run in July when the organic carbon levels are typically higher. However, the resulting THM values were not much higher than earlier in the year (see Table 3-2). Also, in a reversal of previous results, the MIOX-treated values were lower than the Fort Bragg filtered water samples.

**Hypochlorite tests** - During initial hypochlorite tests, the goal was to add enough NaOCl to simulate the free chlorine content of the Fort Bragg filtered samples. The resulting treated water had a THM content similar to Fort Bragg's chlorinated water samples. When it was pointed out that Fort Bragg was adding significantly more free chlorine during primary chlorination, the procedure was changed. Therefore, during later tests, enough hypochlorite was added to be equivalent to the chlorine gas in the Fort Bragg samples. This caused the THM levels to be substantially higher than the Fort Bragg filtered water results.

**Chlorine Dioxide tests** - As expected, the THM content of the ClO<sub>2</sub>-treated samples was either at or below the detection limit for these substances. Concurrent Fort Bragg chlorinated water samples had typical levels of THMs.

### 3.6.10 Haloacetic Acids

**MIOX tests** - Initially the HAA content of both the MIOX-treated samples and Fort Bragg filtered water samples was much lower than the proposed regulatory limit of 60 µg/L (see Table 3-1). The average filtered water value was 4.4 µg/L, or about 21% lower than the average MIOX-treated value of 5.6 µg/L. This difference is insignificant and, at these low levels, within the range of error for the analytical instruments. In any case, the MIOX samples were not filtered after treatment. Filtering could have contributed to higher HAA values because more organic compounds remained in the sample as shown by the DOC and TOC data in Tables 3-1 and 3-2. For a more realistic picture, these tests were also run in July when the organic carbon levels are typically higher. As expected, the overall HAA values were significantly higher than earlier in the year (see Table 3-2). Also, the MIOX process produced a much lower level of HAAs than the Fort Bragg filtered water samples. This may show that the MIOX process has the potential to help Fort Bragg with periodic HAA exceedances. However, the HAA level was potentially complicated by inadequate MIOX solution, as explained in the following section. Since the manufacturer's recommendations were used for MIOX addition, there was no way to compare it directly to gas chlorine addition.

**Hypochlorite tests** - During initial tests the goal was to add enough NaOCl to simulate the free chlorine content of the Fort Bragg filtered samples. The resulting treated water had a significantly lower HAA content than the filtered water. When it was pointed out that Fort Bragg was adding significantly more free chlorine during primary chlorination, the procedure was

changed. During later tests, therefore, sufficient hypochlorite was added to be equivalent to the chlorine gas added. This caused the HAA levels to be more in line with the Fort Bragg filtered water results.

**Chlorine Dioxide tests** - As expected, the samples treated with ClO<sub>2</sub> formed substantially fewer HAAs than the Fort Bragg chlorinated water.

### 3.6.11 Chlorate and Chlorite

**MIOX tests** - Chlorate and chlorite were not measured.

**Hypochlorite tests** - Chlorate and chlorite were not measured.

**Chlorine Dioxide tests** - Chlorates and chlorites are the only significant DBPs of ClO<sub>2</sub> testing. The results of this testing showed the chlorate concentration was between 0.2 and 0.4 mg/L and chlorite between 0.3 and 0.6 mg/L, well below the 1.0-mg/L limit mandated by EPA's Stage 1 D/DBP Rule. In later tests, when the initial ClO<sub>2</sub> level was increased by 30%, the chlorate and chlorite levels increased by about 18%, but still never rose above 0.6 mg/L. Figure 3-4 charts the DBPs data.

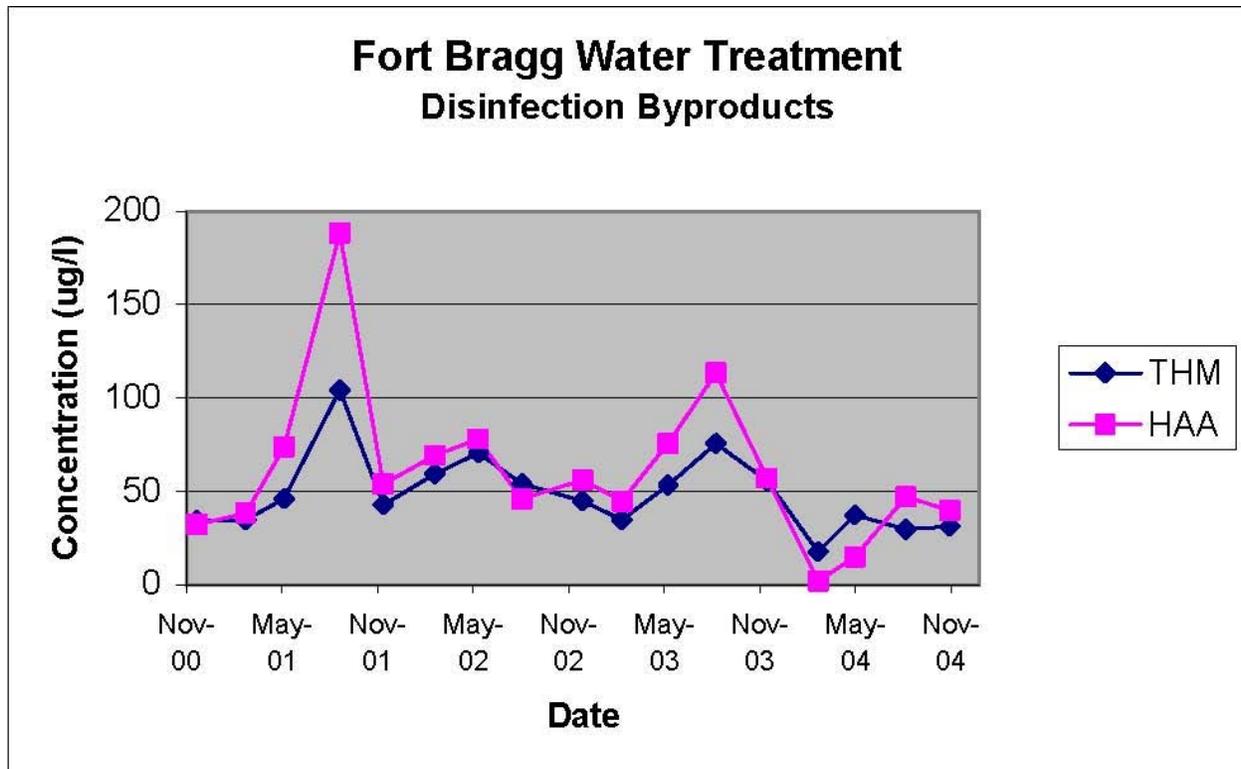


Figure 3-4. Disinfection by-product data.

### 3.7 Organic Carbon Removal

For the first two tests, the MIEX<sup>®</sup> process was applied to both source water and coagulated water. Use of the MIEX<sup>®</sup> resin on source water did not have the desired effect from a DBP elimination standpoint; therefore, that portion was eliminated for the last two tests.

MIEX<sup>®</sup> treatment of Fort Bragg coagulated water was very successful in terms of removing the organic compounds responsible for DBP formation, especially those responsible for HAAs. The TOC and DOC content of the treated water was similar for both MIEX<sup>®</sup>-treated and Fort Bragg samples. However, the UV254 values for the MIEX<sup>®</sup>-treated samples were significantly lower than the Fort Bragg samples.

The average THM content of MIEX<sup>®</sup>-treated water was 3.4 µg/L, slightly lower than the Fort Bragg filtered water level of 3.9 µg/L. However, the HAA results were more dramatic. The average HAA content of MIEX<sup>®</sup>-treated water was 7.3 µg/L, about two-thirds lower than the Fort Bragg filtered water level of 21.5 µg/L. Since HAAs are the primary DBP of concern for Fort Bragg, these results are very encouraging. The sampling results for the MIEX<sup>®</sup> DOC removal process are not shown because of a proprietary agreement.

Table 3-1. Historical Fort Bragg DBP data (average of four point-of-use compliance locations).

Sample Date	Average THM (µg/L)	Average HAA (µg/L)
February 2001	34.6	38.3*
May 2001	46.1	73.8*
August 2001	104.3	188.2*
November 2001	42.8	53.8*
February 2002	59.3	69.3
May 2002	70.5	78.0
August 2002	54.0	46.0
November 2002	44.8	55.5
February 2003	34.8	44.8
May 2003	53.5	75.8
August 2003	75.5	113.3
November 2003	55.8	57.0
February 2004	17.8	2.0
May 2004	37.3	15.0
August 2004	29.8	47.0
November 2004	31.3	39.8
New Regulatory Limit	80.0	60.0

\* HAA data prior to 2002 was not compliance data, but was for information only.

Table 3-2. Initial MIOX test results.

Parameter	Units	February 16, 2004			March 2, 2004			March 4, 2004			March 9, 2004			March 11, 2004				
		Raw	MIOX	Filtered	Raw	MIOX	Filtered	Raw	MIOX	Filtered	Raw	MIOX	Filtered	Raw	MIOX	Filtered	Clear-well	
Initial residual chlorine level	mg/L	-----	0.69	0.72	-----	0.29	0.51	-----	0.32	0.28	-----	0.65	0.25	0.34	-----	0.62	0.13	0.33
Time prior to filling sample bottles	min	-----	105	103	-----	141	110	-----	-----	-----	-----	120	120	-----	-----	120	120	-----
Final residual chlorine level	mg/L	-----	0.21	0.72	-----	0.13	0.48	-----	-----	-----	-----	0.21	0.19	-----	-----	0.24	0.05	-----
Alkalinity as CaCO <sub>3</sub>	mg/L	-----	1.0	<0.1	-----	0.5	<0.1	-----	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-----	1.0	<0.1	<0.1
Laboratory chlorine residual	mg/L	-----	0.3	0.6	-----	0.3	0.3	-----	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	-----	<0.3	<0.3	<0.3
Chlorine demand (4 hour)	mg/L	4.6	<0.3	<0.3	1.6	<0.3	<0.3	1.2	<0.3	<0.3	<0.3	3.3	0.7	0.5	3.5	1.1	0.8	1.0
Color (apparent)	units	-----	18	6	-----	13	4	-----	10	3	-----	27	6	6	-----	22	3	2
DOC	mg/L	4.0	2.0	2.0	4.4	2.3	2.5	4.7	2.4	2.1	5.4	2.6	2.5	1.9	4.7	2.6	2.4	2.1
TOC	mg/L	4.2	2.9	3.5	5.2	2.9	2.6	4.7	2.5	2.2	5.8	3.7	2.7	2.6	4.8	3.1	2.7	2.4
HPC	CFU/ml	350	12	<1	115	6	<1	148	1	<1	81	14	<1	<1	147	19	3	3
Total coliform	colonies	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	Absent	Present	Absent	Absent	Absent
Fecal coliform	colonies	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	Absent	Present	Absent	Absent	Absent
UV254	m <sup>-1</sup>	15.5	3.00	3.30	15.8	2.98	3.45	15.7	3.15	3.70	17.7	3.90	4.00	3.90	16.8	3.65	3.90	3.80
TTHM	µg/L	-----	6	11	-----	9	4	-----	13	10	-----	14	7	13	-----	12	4	5
Total HAA	µg/L	-----	2	<2	-----	5	6	-----	13	5	-----	3	3	5	-----	5	6	3

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Table 3-3. Supplemental MIOX test results.

Parameter	Units	July 14, 2004			July 15, 2004		
		Raw	MIOX	Filtered	Raw	MIOX	Filtered
Initial residual chlorine level	mg/L	- - - -	0.35	0.32	- - - -	0.43	0.32
Time prior to filling sample bottles	min	- - - -	113	105	- - - -	147	145
Final residual chlorine level	mg/L	- - - -	0.09	0.04	- - - -	0.03	0.05
Alkalinity as CaCO <sub>3</sub>	mg/L	- - - -	1.5	<1	- - - -	<1	<1
Chlorine Demand (4 hour)	mg/L	10.7	4.2	3.4	8.8	4.5	2.2
Color (apparent)	units	- - - -	20	6	- - - -	20	9
DOC	mg/L	5.76	2.66	2.63	5.39	2.45	2.48
TOC	mg/L	6.01	3.07	2.71	5.51	2.93	2.52
HPC	CFU/ml	505	2	< 1	170	< 1	< 1
Total Coliform	colonies	Present	Absent	Absent	Present	Absent	Absent
Fecal Coliform	colonies	Present	Absent	Absent	Present	Absent	Absent
UV254	m <sup>-1</sup>	26.8	5.10	4.85	25.63	5.00	4.70
TTHM	µg/L	< 1.0	7.0	12.2	< 1.0	8.8	12.6
Total HAA	µg/L	< 2.0	16.1	44.3	< 2.0	14.4	28.2

Table 3-4. Chlorine dioxide test results.

Parameter	Units	21-April-04			04-May-04			05-May-04			19-May-04			20-May-04		
		Raw	ClO <sub>2</sub>	Filtered	Raw	ClO <sub>2</sub>	Filtered	Raw	ClO <sub>2</sub>	Filtered	Raw	ClO <sub>2</sub>	Filtered	Raw	ClO <sub>2</sub>	Filtered
Calculated initial ClO <sub>2</sub> concentration	mg/L	-----	1.05	-----	-----	0.94	-----	-----	1.04	-----	-----	-----	-----	1.01	-----	-----
Measured initial chlorine or ClO <sub>2</sub> level	mg/L	-----	0.49	0.33	-----	0.46	0.78	-----	0.63	0.27	-----	-----	-----	0.50	0.30	0.22
Time prior to filling sample bottles	Min	-----	65	65	-----	97	90	-----	120	117	-----	-----	-----	100	100	105
Measured final chlorine or ClO <sub>2</sub> level	mg/L	-----	0.13	0.14	-----	0.04	0.08	-----	0.19	0.06	-----	-----	-----	0.03	0.01	0.02
Alkalinity as CaCO <sub>3</sub>	mg/L	-----	<1	<1	-----	<1	<1	-----	<1	<1	-----	-----	-----	5	<1	<1
Chlorine Demand (4 hour)	mg/L	6.9	2.2	1.6	10.9	3.8	2.7	12.6	3.4	4.8	7.4	7.4	8.7	4.0	1.1	1.3
Color (apparent)	units	72	18	6	-----	19	9	-----	11	<5	-----	-----	-----	26	7	8
DOC	mg/L	6.94	2.25	1.97	9.41	3.62	4.15	7.47	3.01	2.96	7.07	7.07	7.44	3.0	2.9	3.09
TOC	mg/L	7.00	2.80	2.45	9.67	4.45	4.79	7.56	3.54	3.16	8.16	8.16	7.86	3.79	2.98	3.15
HPC	CFU/ml	45	2	1	500	13	<1	137	3	<1	51	51	45	1	<1	<1
Total Coliform	Colo-nies	Present	Absent	Absent	Present	Present	Absent	Present	Absent	Absent	Present	Present	Present	Present	Absent	Absent
Fecal Coliform	Colo-nies	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	Present	Present	Present	Absent	Absent	Absent
UV254	m <sup>-1</sup>	21.8	4.60	4.10	36.3	7.6	7.6	29.7	6.00	5.40	34	34	37	6	5.45	5.95
TTHM	µg/L	-----	<1.0	5.6	-----	<1.0	7.8	-----	<1.0	3.6	-----	-----	-----	1.1	7.6	10.4
Total HAA	µg/L	-----	3.5	26.6	-----	7.2	67.8	-----	4.4	29.9	-----	-----	-----	5.0	31.4	39.0
Chlorate	mg/L	-----	0.33	<0.10	-----	0.29	<0.01	-----	0.20	<0.01	-----	-----	-----	0.361	<0.01	<0.01
Chlorite	mg/L	-----	0.59	<0.01	-----	0.32	<0.01	-----	0.32	<0.01	-----	-----	-----	0.395	<0.01	<0.01

Table 3-5. Supplemental ClO<sub>2</sub> test results.

Parameter	Units	January 26, 2005				January 27, 2005				January 28, 2005				
		Raw	Low ClO <sub>2</sub>	High ClO <sub>2</sub>	Tap	Raw	Low ClO <sub>2</sub>	High ClO <sub>2</sub>	Filtered	Tap	Raw	Low ClO <sub>2</sub>	High ClO <sub>2</sub>	Clear-well #1
Calculated initial ClO <sub>2</sub> concentration	mg/L	----	1.02	1.32	----	----	1.01	1.32	----	----	1.01	1.31	----	----
Initial measured ClO <sub>2</sub> level	mg/L	----	0.82	0.92	----	----	0.46	0.73	----	----	0.63	0.84	----	----
Final measured ClO <sub>2</sub> level	mg/L	----	0.18	0.22	----	----	0.22	0.37	----	----	0.37	0.50	----	----
Alkalinity as CaCO <sub>3</sub>	mg/L	3	1	2	1	1	4	5	1	2	<1	<1	<1	<1
Chlorine Demand (4 hour)	mg/L	10.0	3.0	3.4	3.8	13.2	4.8	4.6	3.8	9.4	3.8	4.0	3.2	----
Color (apparent)	units	100	20	20	6	70	18	12	<5	90	22	18	7	----
DOC	mg/L	3.88	1.35	1.39	1.37	4.88	2.47	2.30	2.15	5.18	2.15	2.24	2.13	----
TOC	mg/L	4.37	2.23	2.09	1.67	5.07	2.94	2.79	2.24	5.3	3.16	3.26	2.34	----
HPC	CFU/ml	507	43	42	5	216	13	15	<1	151	10	17	<1	----
Total Coliform	colonies	Present	Absent	Absent	Absent	Present	Absent	Absent	Absent	Present	Absent	Absent	Absent	----
Fecal Coliform	colonies	Present	Absent	Absent	Absent	Present	Absent	Absent	Absent	Present	Absent	Absent	Absent	----
UV254	m <sup>-1</sup>	15.2	3.80	2.75	2.30	15.5	4.00	3.60	2.35	17.6	2.70	2.80	3.05	----
TTHM	µg/L	----	<1	<1	3.8	13.2	<1	<1	4.7	15.5	<1	<1	4.3	10.9
Total HAA	µg/L	----	2.7	4.4	39.5	34.1	3.9	3.5	27.2	36.2	3.3	2.9	37.4	22.5
Chlorate	mg/L	----	0.23	0.29	<0.01	----	0.27	0.33	<0.01	----	0.23	0.24	<0.01	----
Chlorite	mg/L	----	0.46	0.56	<0.01	----	0.43	0.52	<0.01	----	0.51	0.58	<0.01	----

Table 3-6. Hypochlorite test results.

Parameter	Units	June 23, 2004			June 24, 2004			September 16, 2004			October 20, 2004			October 21, 2004			
		Raw	Treated	Filtered	Raw	Treated	Filtered	Raw	Treated	Filtered	Raw	Treated	Filtered	Raw	Treated	Filtered	Tap
Pre-chlorine added as Cl <sub>2</sub>	mg/L	----	0.63	3.08	----	0.63	3.06	----	0.79		----		----	0.69		----	
Alkalinity as CaCO <sub>3</sub>	mg/L	----	1	<1	----	2	<1	----	1	<1	----		----	<1	3	<1	----
Chlorine Demand (4 hour)	mg/L	6.6	1.0	1.5	6.3	0.6	1.3	13.3	6.0	5.2	----	5.70	0.5	0.7	1.1	0.8	----
Color (apparent)	units	----	13	3	----	11	8	----	40	17	----	----	<5	<5	15	7	----
DOC	mg/L	5.37	2.37	2.25	5.13	2.02	1.91	9.27	4.22	4.83	----	5.70	2.23	2.43	2.02	2.02	----
TOC	mg/L	5.44	2.46	2.34	5.15	2.06	1.97	9.59	5.42	4.97	----	6.04	2.52	2.46	2.51	2.04	----
HPC	CFU/ml	267	3	<1	344	4	<1	220	16	<1	----	287	<1	<1	2	4	----
Total Coliform	colonies	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	----	Present	Absent	Absent	Absent	Absent	----
Fecal Coliform	colonies	Present	Absent	Absent	Present	Absent	Absent	Present	Absent	Absent	----	Present	Absent	Absent	Present	Absent	----
UV254	m <sup>-1</sup>	29.1	3.30	3.45	29.5	4.40	4.25	39.9	9.80	11.6	----	23.3	3.65	3.40	3.90	3.80	----
TTHM	µg/L	<1.0	8.6	9.6	<1.0	6.6	6.3	----	2.8	7.6	24.1	----	3.3	4.3	5.6	5.9	36.3
Total HAA	µg/L	<2.0	10.6	33.4	<2.0	10.5	28.3	----	20.5	65.5	74.7	----	15.5	44.1	18.7	28.9	38.7

Table 3-7. Supplemental hypochlorite test results.

Parameter	Units	November 9, 2004				November 10, 2004				November 11, 2004						
		Raw	Low Hypo-chlorite	High Hypo-chlorite	Filtered	Tap	Raw	Low Hypo-chlorite	High Hypo-chlorite	Filtered	Tap	Raw	Low Hypo-chlorite	High Hypo-chlorite	Filtered	Tap
Pre-chlorine added as Cl <sub>2</sub>	mg/L	-----	0.66	1.98	-----	-----	-----	0.68	2.03	-----	-----	-----	0.68	2.03	-----	-----
Alkalinity as CaCO <sub>3</sub>	mg/L	-----	< 1	-----	< 1	-----	< 1	< 1	-----	-----	-----	< 1	< 1	-----	< 1	-----
Chlorine Demand (4 hour)	mg/L	12.0	3.1	-----	4.7	-----	8.3	3.4	-----	2.4	-----	2.0	3.4	-----	2.0	-----
Color (apparent)	units	-----	20	-----	< 5	-----	-----	20	-----	8	-----	-----	9	-----	4	-----
DOC	mg/L	4.98	2.09	-----	2.14	-----	4.73	1.93	-----	2.10	-----	-----	2.01	-----	2.08	-----
TOC	mg/L	5.18	2.56	-----	2.22	-----	4.92	2.60	-----	2.11	-----	-----	2.36	-----	2.14	-----
HPC	CFU/ml	239	4	< 1	< 1	-----	> 738	2	< 1	< 1	-----	-----	< 1	< 1	3	-----
Total Coliform	colonies	Present	Absent	Absent	Absent	-----	Present	Absent	Absent	Absent	-----	-----	Present	Absent	Absent	-----
Fecal Coliform	colonies	Present	Absent	Absent	Absent	-----	Present	Absent	Absent	Absent	-----	-----	Present	Absent	Absent	-----
UV254	m <sup>-1</sup>	25.8	4.60	-----	4.70	-----	22.3	4.40	-----	4.40	-----	-----	4.10	-----	3.70	-----
TTHM	µg/L	-----	< 1	8.6	4.1	24.1	-----	< 1	5.1	2.6	21.9	-----	< 1	3.7	1.9	19.9
Total HAA	µg/L	-----	14.8	56.5	40.1	37.7	-----	16.1	37.1	35.8	25.6	-----	13.7	22.8	37.5	39.1

#### 4 FORT BRAGG DBP DATA ANALYSIS

During late 2004, Fort Bragg started experiencing higher than normal levels of DBPs, especially HAAs. As a result, MSE was asked to evaluate data related to WTP operations to determine if there was a correlation of DBP formation to a parameter other than the obvious ones of organic content and chlorine usage. Several years of plant operational data (July 2002 through January 2005) were examined for statistical correlation. Section 4.1 lists the 38 parameters that were compared, and Table 4-1 highlights the ones with the highest statistical correlation to HAA concentration.

Table 4-1. Correlation coefficient between HAA concentration and WTP variables.

Dependent Variable	Days Prior to HAA Sampling						Average of 2-4
	1	2	3	4	5	6	
Color - raw water	0.61	0.67	0.65	0.64	0.61	0.62	0.71
Color - finished water		0.70		0.61	0.60		0.73
pH filtered water	-0.67						
Hardness finished water	0.70			0.70			0.67
Manganese raw water		0.75					0.66
Manganese finished water	0.68	0.83					
Alum used		0.63					
Pre-alkali used					0.61		

Regulated DBPs (HAAs and THMs) are typically tested only on a monthly basis. Since the HAA and THM samples are collected at several points in the distribution system, it is difficult to correlate these results to daily production data collected at the WTP. A process change made at the WTP may take several days to show up at any one of the DBP sampling points. To account for this delay, the DBP data were compared to plant operation data at 0, 1, 2, 3, 4, 5, 6, and 7 days prior to DBP sampling. Variation is wide in DBP measurements at the various sample points; on a given sampling day, one measurement can be high while another is almost zero. Averages are used; however, the intrinsic variation complicates the analysis. Due to these complications, the resulting correlation is rough at best.

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**4.1 Daily Parameters Evaluated**Total finished water quantity (mgd)Chemicals added

Alum (lb)

Pre-alkali (lb)

Post-alkali (lb)

Prechlorine (lb)

Post-chlorine (lb)

Fluoride (lb)

Phosphate (lb)

Carbon (lb)

Ammonia (lb)

Finished water properties

Color

pH

CO<sub>2</sub>

Alkalinity

Hardness

Iron

Manganese

Fluoride

Total phosphate

Ortho phosphate

Raw water properties

Temperature

Turbidity

Color

pH

CO<sub>2</sub>

Alkalinity

Hardness

Dissolved oxygen

Iron

Manganese

Fluoride

Total phosphate

Filtered water properties

pH

CO<sub>2</sub>

Alkalinity

Residual chlorine - Clearwell #1

Residual chlorine at point of exit

Calculated CT

**4.2 Results of Correlation Analysis**

Since HAAs are currently a bigger problem than THMs for Fort Bragg, the correlation looked primarily at how well the data values correlated with HAA. Correlation coefficients were

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considered significant if greater than 0.60 or less than -0.60. The use of 0.60 as a cutoff point is somewhat arbitrary, but it seemed logical after examining the results. The variance for a correlation coefficient of 0.60 is  $(0.60)^2 = 0.36$  or 36% variance between data sets. Days 0 and 7 had no significant correlations.

Many of the above parameters are interrelated, so it is not surprising that they all correlate fairly well to HAA concentration. The parameters listed in Table 4-1 could all conceivably affect or be affected by the organic content of the source water. Color is an obvious visual indication of humic substances in the water. Waters with greater organic content would be expected to contain more impurities and also require greater quantities of treatment chemicals.

It was surprising that the level of manganese in the finished water turned out to be the best predictor of HAA content 2 days later. Manganese is a natural constituent of bottom sediments of surface waters but is typically found in the insoluble oxide form. During warm weather, however, the dissolved oxygen (DO) content in the water near these bottom sediments is reduced. As the DO level decreases, manganese is converted from insoluble oxides through bacterial action to very soluble manganese ions ( $Mn^{+2}$ ) that can leach from the sediments. Since the level of known DBP precursors, such as humic content, also increases during the summer months, it is not surprising that manganese content correlates well with DBP precursors; however, it is odd that it is the best predictor of HAA content.

One purpose for performing this data analysis was to attempt to discover a not-so-obvious correlation in the data (i.e., to find an unknown parameter that was impacting DBP concentration). To uncover such a parameter would be a tremendous help to Fort Bragg because presumably controlling this parameter would lower DBPs. Unfortunately, everything that correlated well with DBP formation also was related to the organic content of the source water.

The correlation analysis resulted in a few surprises. It seemed odd that neither the quantity of prechlorine or post-chlorine showed up as significant to the formation of HAAs or THMs. The level of organic compounds in the water is the determining factor for DBP formation. Excess chlorine is present at all times; however, this is significant only when the organic level rises. Since regulations mandate a chlorine residual, the quantity of chlorine added is difficult to reduce. Fort Bragg

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appears to be making progress to optimize this by decreasing primary chlorination while increasing secondary chlorination with chloramines. Reducing the organic content of the water would obviously have the biggest impact.

To examine the effects and interactions of multiple variables, a linear regression was performed using data from Day #2 (2 days prior to DBP sample collection). This day was chosen because it had the most significant correlations of HAA content with process data. Haloacetic acid concentration was the independent variable, and raw water color, finished water color, raw water manganese, finished water manganese, and amount of alum added were the dependent variables. The resulting correlation coefficient was 0.88 (R) and the variance (R<sup>2</sup>) was 0.78. The following graph (Figure 4-1) shows the predicted HAA value that was calculated using these five variables and compares that to the measured HAA values. The general correlation is good; however, individual data points are widely variable.

However, correlation with only one of these variables, manganese content of the finished water, is almost as good (see Figure 4-2).

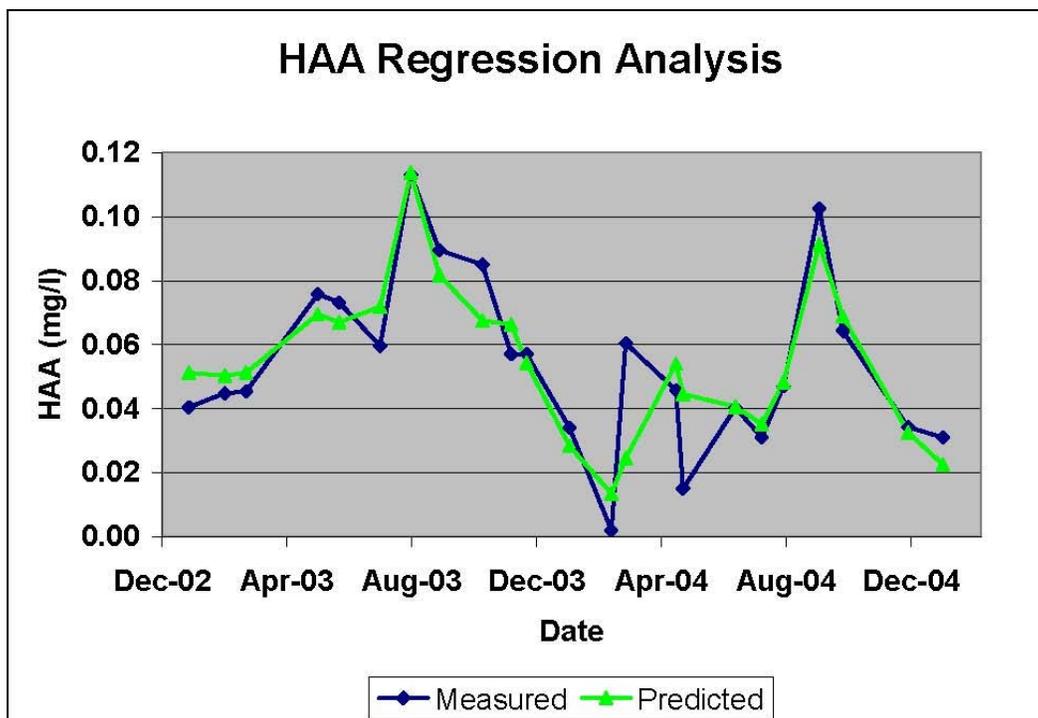


Figure 4-1. HAA regression analysis.

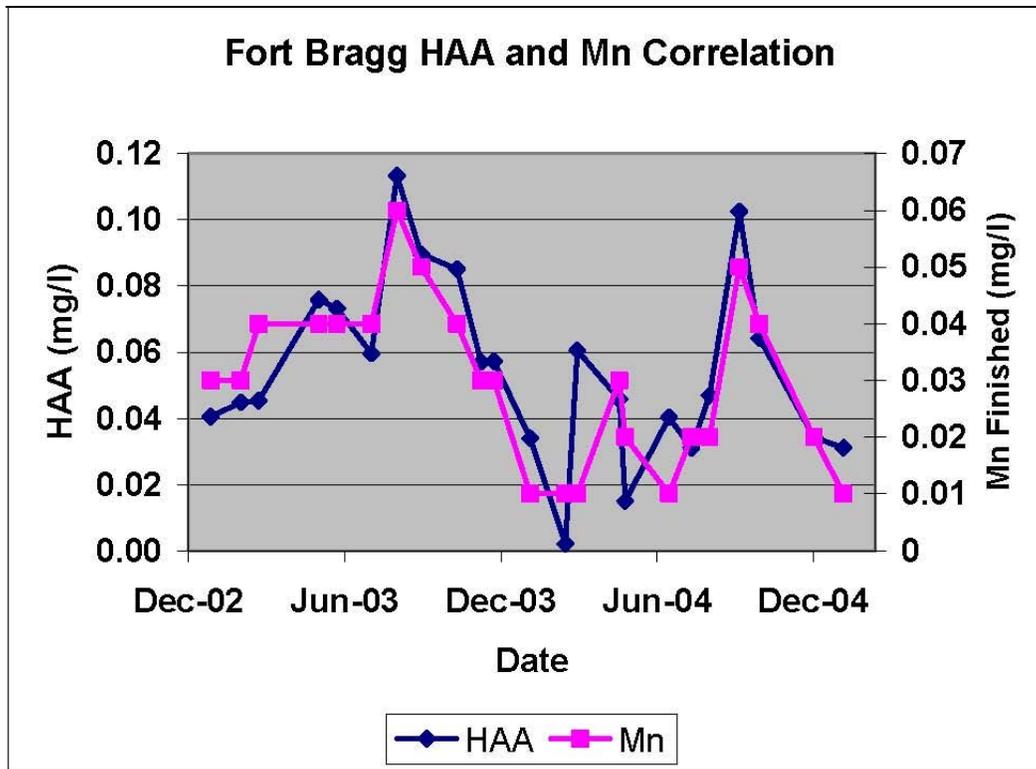


Figure 4-2. HAA and manganese correlation.

## 5 ECONOMIC ANALYSIS

An economic analysis was performed on the main technology alternatives evaluated in this report. Those included: MIOX (mixed oxidants), ClO<sub>2</sub>, NaOCl, ozone, and UV radiation. While it was not a disinfection technology, the MIEX<sup>®</sup> DOC removal process was also evaluated. Detailed calculations are found in Appendix B.

### 5.1 Basis

All capital equipment was sized based on a 10-mgd WTP. This corresponds to the greatest flow seen at the Fort Bragg WTP during the years listed in Table 1-1. Operating costs were based on a 5.5-mgd flow, which is similar to the average treated water flow for FY04-05.

### 5.2 Results

Alternatives were evaluated economically by using a simple capital and operating costs technique. To obtain the net operating cost, the current cost of chlorine gas was subtracted from the calculated operating cost of each alternative. A

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discounted cash flow analysis method was used to compare alternatives, and Table 5-1 shows the results. Net present value was calculated using a discount rate of 6% and a term of 20 years.

Table 5-1. Economic analysis results.

Technology	Capital Cost	Increased Annual Operating Cost	Net Present Value
NaOCl	\$16,370	\$19,500	\$240,033
MIOX	\$276,019	\$13,950	\$436,024
ClO <sub>2</sub>	\$64,000	\$42,860	\$555,601
Ultraviolet radiation	\$1,153,000	\$11,600	\$1,286,051
Ozone	\$2,446,000	\$184,600	\$4,563,347
MIEX <sup>®</sup> DOC Removal	\$3,900,000	\$187,000	\$6,044,875

### 5.3 Conclusions

Costs for NaOCl addition were significantly lower than the other alternatives, with both low capital and operating expenses. Costs for the next two alternatives listed (MIOX and ClO<sub>2</sub>) were very similar. Mixed oxidant technology by the MIOX Corporation has a fairly high initial capital investment; however, operating costs are very low. Both NaOCl and ClO<sub>2</sub> treatments have a much lower capital investment but higher operating costs. Ultraviolet and ozone are both significantly more expensive than conventional treatments.

The MIEX<sup>®</sup> DOC removal process has a high capital cost. Budd (2005) expects this cost to decrease as the process is implemented at a greater number of sites. Implementation of MIEX<sup>®</sup> supposedly results in a significant reduction in chemical costs (specifically alum, chlorine, and polymer); however, this was not quantified.

## 6 RECOMMENDATIONS

Installations should consider the following criteria when making a decision regarding selection of a drinking water disinfection technology. The first two criteria were specified by Fort Bragg.

### 6.1 Criteria

- Eliminate hazards associated with chlorine gas - This was the original premise for the project (i.e., eliminating chlorine cylinders to reduce risks associated with a gaseous chlorine leak).
- Reduce hazardous DBPs - Reduction of DBPs, especially HAAs, is very important to WTP personnel since new regulations are more restrictive.
- Deactivate *Cryptosporidium* and *Giardia* - Elimination of parasites is becoming increasingly important. There is very little data on how some of the newer disinfection technologies affect *Cryptosporidium* oocysts since these tests are very expensive.
- Maximize safety - Alternatives to chlorine gas have other hazards associated with them. For example, ClO<sub>2</sub> and its precursors can be dangerous to handle.
- Minimize cost - Life-cycle costs should always be analyzed and compared for various alternatives.
- Ensure compliance with other water quality regulations and consumer concerns - Items such as odor, color, taste, etc.

If the only priority were simply eliminating the chlorine gas cylinders, then any of the listed alternatives would work well. If reduction of DBPs is also critical, it is possible that MIOX may be able to accomplish this to a lesser extent; however, the data are inconclusive. Chlorine dioxide, ozone, and UV effectively eliminate THMs and HAAs, but other DBPs can result from these processes, and while the regulatory limits for these other DBPs are still easily met, the regulations are likely to become more stringent in the future, potentially making compliance difficult.

Other factors were used to ensure recommendations were appropriate. For example, public WTPs are required to maintain a

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disinfectant residual in the distribution system. Therefore, a technology that was unable to provide this (i.e., ozone, UV) would be able to replace only primary chlorination at Fort Bragg; a secondary chlorination step would still be needed.

The most inexpensive way for Fort Bragg to meet the goals of eliminating chlorine gas and reducing DBPs is the implementation of ClO<sub>2</sub> disinfection. Other alternatives, such as ozone disinfection or DOC removal combined with either MIOX or hypochlorite would also be effective but significantly more costly. Chlorine dioxide treatment meets the criteria specified above better than any other technology tested. Chlorine gas is eliminated, THMs and HAAs are reduced significantly, it may be effective against *Cryptosporidium*, gas production is relatively safe, it has been shown to be inexpensive, and the water treatment system is easily retrofitted. However, since the long-term regulatory status of chlorate and chlorite is questionable, ClO<sub>2</sub> processes may run into problems in the future.

## 6.2 Additional Work

It is not appropriate to make a specific recommendation for disinfection system replacement with the limited data derived from these small-scale, relatively short-duration tests. It is recommended that Fort Bragg perform the following additional work prior to selecting a drinking water disinfection alternative:

- Chlorine Dioxide Study - To ensure it is an appropriate alternative, MSE recommends performing ClO<sub>2</sub> tests at a larger scale and for a longer time period. It is difficult to determine what long-term impacts a technology will have without measuring it during all seasons and under all water conditions. Small projects give good indications of potential problems and can be used to filter out inappropriate technologies; however, larger pilot-scale work should be completed prior to making any major decisions.
- DBP Regression Analysis - MSE looked at several years of daily process data in an attempt to correlate DBP formation with other parameters. Disinfection by-products correlated well with several parameters - mostly related to the organic carbon content of the water. It would be useful to perform a larger study using more data.
- Organic Carbon Removal - In small-scale batch tests, the MIEX<sup>®</sup> process effectively reduced the organic carbon content of the

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water, which resulted in a decrease of hazardous air pollutants by two-thirds. MSE recommends a larger-scale study to test this promising DOC removal alternative.

## 7 REFERENCES

- American Water Works Association (AWWA) 1998 as referenced in [http://www.c3.org/chlorine\\_issues/disinfection/water\\_disinfection.html#dm](http://www.c3.org/chlorine_issues/disinfection/water_disinfection.html#dm).
- Bellar, T. A., J. J. Lichtenberg, and R. C. Kroner. 1974. The occurrence of organohalides in chlorinated drinking waters. *J AWWA*, December:703-706.
- Budd, G.C. 2005. MIEX<sup>®</sup> Process: Considerations for Application, presented at AWWA Southeastern Regional Technology Transfer Conference, Greenville, SC, January 27-28, 2005.
- Campbell, A. T., L.J. Robertson, M. R. Snowball, and V. H. Smith. 1995. Inactivation of oocysts of *Cryptosporidium parvum* by ultraviolet radiation. *Water Research* 29:2583-2586
- Camper, A. 1998. Validation of mixed oxidants for the disinfection and removal of biofilms from distribution systems. Demonstration Project Summary, Drinking Water Assistance Program for Small Systems, Montana University System Water Center, Montana State University, Bozeman.
- Cantor, K. P., R. Hoover, T. J. Mason, L. J. McCabe. 1978. Associations of cancer mortality with halomethanes in drinking water. *J Natl Cancer Inst.* 61:979-985.
- Chauret, C. P., C. Z. Radziminski, M. Lepuil, R. Creason, and R. C. Andrews. 2001. Chlorine dioxide inactivation of *Cryptosporidium parvum* oocysts and bacterial spore indicators. *Appl Environ Microbiol* 67:2993-3001.
- Craun, G. F., R. J. Bull, R. M. Clark, J. Doull, W. Grabow, G. M. Marsh, D. A. Okun, S. Regli, M. D. Sobsey, and J. M. Symons. 1994. Balancing chemical and microbial risks of drinking water disinfection, Part II. Managing the risks. *J Water SRTÑA Agua.* 43:207-218.
- CRC. 2001. Conference Report. *Cryptosporidium*: From Molecules to Disease, 7-12 October 2001, Fremantle, Western Australia. Health Stream, the Public Newsletter of the Cooperative Research Centre for Water Quality and Treatment. Issue 24, December 2001.
- Dodds, L., W. King, A. C. Allen, G. A. Armson, D. B. Fell, and C. Nimrod. 2004. Trihalomethanes in public water supplies and risk of stillbirth. *Epidemiology* 15:179-186.

EPA Guidance Manual: Alternative Disinfectants and Oxidants. April 1999. U.S. Environmental Protection Agency, Cincinnati, OH.

Fearing, D.A. 2004. Process Options for the Treatment of Humic Rich Waters, PhD Thesis, Cranfield University School of Water Sciences, Bedfordshire.

Finch, G. R. and H. Li. 1999. Inactivation of *Cryptosporidium* at 1 °C using ozone or chlorine dioxide. *Ozone Sci Eng* 21:477-486.

Fort Bragg Integrated Strategic Environmental Plant, Prepared by the Public Works Business Center for Fort Bragg, June 2001.

Jacangelo, J. G., V. P. Oliviera, and K. Kawata. 1987. Mechanism of inactivation of microorganisms by combined chlorine. AWWA Research Foundation, Denver, CO.

King, W. D., and L. D. Marrett. 1996. Case-control study of bladder cancer and chlorination by-products in treated water (Ontario, Canada). *Cancer Causes and Control* 7:596-604.

Korich, D. G., J. R. Mead, M. S. Madore, N. A. Sinclair, and C. R. Sterling. 1990. Effects of ozone, chlorine dioxide, chlorine and monochloramine on *Cryptosporidium parvum* oocyst viability. *Appl. Environ. Microbiol.* 56:1423-1428.

Kramer, M. D., C. F. Lynch, P. Isacson, and J. W. Hanson. 1992. The association of waterborne chloroform with intrauterine growth retardation. *Epidemiology* 3:407-413.

Malley, J. P., J. P. Shaw, and J. R. Ropp. 1995. Evaluations of by-products by treatment of groundwaters with ultraviolet irradiation. AWWA Research Foundation and AWWA, Denver, CO.

McGeehin, M. A., J. S. Reif, J. C. Becher, and E. J. Manione. 1993. Case-control study of bladder cancer and water disinfection methods in Colorado. *Am J Epidemiol.* 138:492-501.

MIOX Corporation Internet Web Site, <http://www.miox.com/>

Pourmoghaddas, H., A. A. Stevens, R. A. Kinman, R. C. Dressman, L. A. Moore, and J. C. Ireland. 1993. Effect of bromide ion on formation of HAAs during chlorination. *J AWWA* 85:82-87.

Scheibel, O. K., and C. D. Bassell. 1981. Ultraviolet disinfection of a secondary wastewater treatment plant effluent.

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EPA600/2-81-152, PB81-242125, U.S. Environmental Protection Agency, Cincinnati, OH

Serodes, J. B., M. J. Rodriguez, H. Li, and C. Bouchard. 2003. Occurrence of THMs and HAAs in experimental chlorinated waters of the Quebec City area (Canada). *Chemosphere* 51:253-263

Shin, G-A, K. G. Linden, M. J. Arrowood, and M. D. Sobsey. 2001. Low-pressure UV inactivation and DNA repair potential of *Cryptosporidium parvum* oocysts. *Appl Environ Microbiol* 67:3029-3032.

Singer, P.C. 1993. Trihalomethanes and other by-products formed from the chlorination of drinking water. National Academy of Engineering Symposium on Environmental Regulation: Accommodating Changes in Scientific, Technical or Economic Information, Washington, DC.

Trussel, R. R., and M. Umphres. 1978. The formation of trihalomethanes. *J AWWA* November:604-612

Tung, Hsin-hsin. 2004. Haloacetic acid removal by granular activated carbon, Penn State University PhD dissertation.

Venczel, L. V., M. Arrowood, M. Hurd, and M. D. Sobsey. 1997. Inactivation of *Cryptosporidium parvum* oocysts and *Clostridium perfringens* spores by a mixed-oxidant disinfectant and free chlorine. *Appl Environ Microbiol.* 63:1598-1601.

Villaneuva, C. M., K. P. Cantor, S. Cordier, J. J. Jaakkola, W. D. King, C. Lynch, S. Porru, and M. Kogevinas. 2004. Disinfection by-products and bladder cancer: a pooled analysis. *Epidemiology* 15:357-367

Weinberg, H. S., S. W. Krasner, S. D. Richardson, and A. D. Truiston Jr. 2002. The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study. National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens, GA.

Weinberg, H. S., C. A. Delcomyn, and P. C. Singer. 2001. *Journal of Chromatography A* 920, 213-219.

White, G. C. 1986. *Handbook of Chlorination*, Van Nostrand Reinhold, New York.

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Williamson, S. J. 1981. Epidemiological studies on cancer and organic compounds in U.S. drinking waters. *Sci Total Environ.* 18:187-203.

Xie, Y., and H. Zhou. 2002. Biologically Active Carbon for HAA removal: Part II, Column Study. *J AWWA* 94:5:126-134.

**Appendix B**

**Economic Analysis Details**

**MIOX**

**Capital costs** - MIOX Corporation sent an estimate to Fort Bragg for a facility that would operate at 15 million gallons per day (mgd) peak flow rate. This was scaled down to 10 mgd to reflect more recent conditions. Following is the pricing summary:

Item	Cost
Mixed oxidant tank generation system	\$223,472
45-ton brine generator	\$23,510
Two 1,000-gallon oxidant storage tanks	\$1,991
Venturi injection system	\$2,344
Piping, valves, and fittings	\$1,588
Spare parts	\$11,114
Installation and startup	\$12,000
<b>Total cost</b>	<b>\$276,019</b>

**Operating costs** - The MIOX Corporation estimate included the following items from the referenced letter. These were scaled for an operation of 5.5-mgd operation.

Item	Annual Amount	Unit Cost	Annual Cost
Additional electricity	245 MWhr	\$0.09 per KWhr	\$22,050
Sodium chloride	33,000 lb	\$0.10 per lb	\$3,300
Additional personnel	Assume none		\$0
<b>Total cost</b>			<b>\$25,300</b>
Chlorine gas savings	40.7 tons	\$280 per ton	\$11,400
<b>Net Cost</b>			<b>\$13,950</b>

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Using a life of 20 years and a discount rate of 6% yields a net present value of \$436,024.

**Source** - 1999 cost estimate by MIOX Corporation, letter from Rodney Harrington to Gary Cullen dated February 24, 1999.

### CHLORINE DIOXIDE

**Capital costs** - Following is the pricing summary from a manufacturer's letter. Originally equipment was sized for 3 mgd and then scaled up to the desired 10-mgd peak flow rate.

Item	Cost
Three chemical generator	\$49,000
Piping, valves, and fittings	\$2,000
Spare parts	\$3,000
Installation and startup	\$10,000
<b>Total cost</b>	<b>\$64,000</b>

**Operating costs** - Includes the following items from the above referenced source. These were scaled for an operation of 5.5 mgd.

Item	Annual Amount	Unit Cost	Annual Cost
Additional electricity	Assume none		\$0
25% NaClO <sub>2</sub>	90,000 lb	\$0.50 per lb	\$45,000
12.5% NaOCl	74,000 lb	\$0.11 per lb	\$8,140
35% HCl	12.9 tons	\$87 per ton	\$1,120
Additional personnel	Assume none		\$0
<b>Total cost</b>			<b>\$54,260</b>
Chlorine gas savings	40.7 tons	\$280 per ton	\$11,400
<b>Net Cost</b>			<b>\$42,860</b>

Using a life of 20 years and a discount rate of 6% yields a net present value of \$555,601.

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**Source** - Information from Bill Demet of International Dioxide, Inc., a major ClO<sub>2</sub> vendor, e-mail to Randy Hiebert dated June 25, 2004.

### SODIUM HYPOCHLORITE

**Capital costs** - Equipment was sized for 3 mgd. To obtain a 10-mgd maximum flow rate, equipment costs were multiplied by the flow ratio to the 0.6 power.

Item	Cost
Metering pump, tanks, switches	\$8,370
Piping, valves, and fittings	\$2,000
Spare parts	\$1,000
Installation and startup	\$5,000
<b>Total cost</b>	<b>\$16,370</b>

**Operating costs** - Includes the following items scaled for a 5.5-mgd operation.

Item	Annual Amount	Unit Cost	Annual Cost
Additional electricity	Assume none		\$0
12.5% NaOCl	281,000 lb	\$0.11 per lb	\$31,000
Additional personnel	Assume none		\$0
<b>Total Cost</b>			<b>\$30,900</b>
Chlorine gas savings	40.7 tons	\$280 per ton	\$11,400
<b>Net Cost</b>			<b>\$19,500</b>

Using a life of 20 years and a discount rate of 6% yields a net present value of \$240,033.

**Source** - *The Economic Advantages of Chlorine Gas Disinfection* by Hydroinstruments, Inc.

<http://www.hydroinstruments.com/economics.shtml>

**OZONE**

**Capital costs** - These values were obtained from a plant that was sized for 34 mgd. To obtain the desired 10-mgd maximum flow rate, equipment costs were multiplied by the ratio of the flow rates to the 0.6 power.

Item	Cost
Ozone disinfection system, including piping, valves, fittings, installation, and startup	\$2,446,000
<b>Total cost</b>	<b>\$2,446,000</b>

**Operating costs** - Includes the following items from the referenced source. These were scaled for a 5.5-mgd operation.

Item	Annual Cost
Additional chemicals, maintenance, electricity	\$162,000
Ozone	\$34,000
Additional personnel	\$0
<b>Total cost</b>	<b>\$196,000</b>
Chlorine gas savings	\$11,400
<b>Net Cost</b>	<b>\$184,600</b>

Using a life of 20 years and a discount rate of 6% yields a net present value of \$4,563,347.

**Source:**

*Custom-Designed Membrane Filtration for Water Treatment Plants - A Technical and Economic Evaluation*, December 2000; prepared by Carollo Engineers for the Energy Center of Wisconsin.

**ULTRAVIOLET RADIATION**

**Capital costs** - Equipment was sized for 34 mgd. To obtain the desired 10-mgd maximum flow rate, equipment costs were multiplied by the ratio of the flow rates to the 0.6 power.

Item	Cost
UV disinfection system, including piping, valves, fittings, installation, and startup	\$1,153,000
<b>Total</b>	<b>\$1,153,000</b>

**Operating costs** - Includes the following items from the referenced source. These were scaled for a 5.5-mgd operation. With the UV bulb maintenance issues experienced at the Fort Bragg wastewater plant, an additional amount was added for extra personnel.

Item	Annual Cost
Operation and maintenance	\$3,000
Additional personnel	\$20,000
<b>Total</b>	<b>\$23,000</b>
Chlorine gas	\$11,400
<b>Net Cost</b>	<b>\$11,600</b>

Using a life of 20 years and a discount rate of 6% yields a net present value of \$1,286,051

**Source:**

*Custom-Designed Membrane Filtration for Water Treatment Plants - A Technical and Economic Evaluation*, December 2000; prepared by Carollo Engineers for the Energy Center of Wisconsin.

**MIEX® DOC REMOVAL**

**Capital costs** - Original equipment sizing was sized for 7-mgd peak flow rate. The figures were for source water that had a very high organic loading and as a result may be somewhat high. These figures were scaled up to 10 mgd. Following is a summary:

Item	Cost
Capital equipment	\$3,716,000
Initial resin	\$390,000
<b>Total cost</b>	<b>\$4,106,000</b>

**Operating costs** - Includes the following items from the referenced source. Again, the figures were for source water that had a very high organic loading and as a result may be somewhat high. These were scaled for a 5.5-mgd operation.

Item	Annual Amount	Unit Cost	Annual Cost
Resin makeup			\$228,000
Additional electricity	321 MWhr	\$0.09 per KWhr	\$28,890
Sodium chloride	843 tons	\$50 per ton	\$42,150
Regenerant disposal	7500 tons	\$50 per ton	\$375,000
Additional personnel	Assume none		\$0
<b>Total cost</b>			<b>\$674,040</b>
Chlorine gas savings (12%)	5 tons	\$280 per ton	\$1,400
Alum savings (48%)	75 tons	\$112 per ton	\$8,400
Alkali savings (25%)	52 tons	\$138 per ton	\$7,200
Sludge disposal	240 tons	\$287 per ton	\$68,880
<b>Net Cost</b>			<b>\$13,950</b>

Using a life of 20 years and a discount rate of 6% yields a net present value of \$436,024.

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**Sources:**

*Selective DBP Precursor Removal with an Innovative Ion Exchange Process* by P.J. Delphos, K. Harr, T.L. Bianco, American Water Works Association, 2001.

*MIEX<sup>®</sup> Process: Considerations for Application* by G.C. Budd, presented at AWWA Southeastern Regional Technology Transfer Conference, Greenville, SC, January 27-28, 2005.

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