

# 9. COMBINED DISINFECTANTS

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Multiple disinfectants, the sequential or simultaneous use of two or more disinfectants, have been used with increasing frequency in recent years. This trend is attributed to the fact that:

- Less reactive disinfectants, such as chloramines, have proven to be quite effective in reducing DBPs formed during disinfection and are more effective for controlling biofilms in the distribution system.
- Regulatory and consumer pressure to produce water that has been disinfected to achieve high inactivation for various pathogens, has pushed the industry towards more effective disinfectants. Sometimes more effective disinfection meant using higher disinfectant doses which also produces more DBPs.
- Recent research has shown that the application of sequential disinfectants is more effective than the added effect of the individual disinfectants. This process where two (or more) disinfectants produce a synergistic effect by either simultaneous or sequential application to achieve more effective pathogen inactivation, is referred to as *interactive disinfection* in this manual.

This chapter discusses recent industry applications of multiple disinfectants to meet the varied requirements for inactivation and reduction in DBPs. The initial discussion focuses on traditional disinfectants used in primary and secondary application. This is followed by a discussion of interactive disinfectants where two disinfectants are applied together specifically to achieve primary disinfection. Note that the IESWTR does not have any provision for additional credits for interactive disinfection or taking additional credit for the synergistic effects from interactive disinfection. Until such credit is established, interactive disinfection is considered an emerging technology. This chapter does not discuss mixed oxidant systems, which are designed to generate mixed oxidants on-site for drinking water disinfection, and are also considered an emerging technology.

## 9.1 Primary and Secondary Disinfectants

By separating the inactivation function and residual disinfection function in water treatment, each can be optimized independently. Thus, the combination of disinfectants currently used in disinfection is typically identified as a primary or secondary disinfectant, as follows:

- Primary disinfection refers to the inactivation of microorganisms to meet the regulatory bacteriological requirements. This requirement typically is met by achieving certain CT requirements to assure a target log inactivation of target organisms as set forth in the Surface Water Treatment Rule (SWTR) (AWWA, 1991).
- Secondary disinfection refers to application of a disinfectant to meet regulatory requirements for distribution system bacteriological quality as set forth in the Total Coliform Rule (TCR). The SWTR requires that a residual disinfectant be measured in the distribution system, or that the bacteriological quality meet certain standards (heterotrophic plate count (HPC) less than 500/100mL).

To be an effective primary disinfectant, the disinfectant should effectively inactivate the target organism. Table 9-1 lists potential primary disinfectants as discussed in Chapters 2 through 8.

**Table 9-1. Potential Primary Disinfectants**

Target Organism	Potential Primary Disinfectants	
	With Filtration <sup>1</sup>	Without Filtration
Coliform Bacteria	Chlorine Chloramines Chlorine dioxide Ozone UV Interactive disinfection	Chlorine Chlorine dioxide Interactive disinfection <sup>3</sup>
Giardia cysts	Chlorine <sup>2</sup> Chlorine dioxide <sup>2</sup> Ozone <sup>2</sup> Interactive disinfection	Chlorine <sup>2</sup> Chlorine dioxide <sup>2</sup> Interactive disinfection <sup>3</sup>
Viruses	Chlorine <sup>2</sup> Chlorine dioxide <sup>2</sup> Ozone <sup>2</sup> UV <sup>2</sup> Interactive disinfection	Chlorine <sup>2</sup> Chlorine dioxide <sup>2</sup> UV <sup>2</sup> Interactive disinfection <sup>3</sup>
Cryptosporidium oocysts	Chlorine dioxide Ozone Interactive disinfection	Chlorine dioxide Interactive disinfection <sup>3</sup>

<sup>1</sup> Natural or treatment filtration reduces disinfection inactivation requirements.

<sup>2</sup> Inactivation credit established in SWTR.

<sup>3</sup> Any interactive disinfection that uses ozone or peroxone without filtration is strongly discouraged.

As discussed in earlier chapters, certain disinfectants (e.g., ozone, UV, peroxone, and in some cases chlorine dioxide), while being effective disinfectants, do not leave a long-lasting residual disinfectant. Therefore, secondary disinfection is limited to those disinfectants that remain stable in the distribution system. In order of decreasing stability, these secondary disinfectants are chloramines, chlorine, and chlorine dioxide.

Based on the above, the combinations of disinfectants that are viable options to meet the disinfection requirements can be determined for various treatment trains. These combinations are shown for various treatment objectives. Note that the treatment objectives are dependent on the treatment currently in place.

To meet DBP, and specifically, THM limits, several studies have evaluated the application of various primary/secondary disinfectants. Table 9-2 presents the typical application of these combined disinfectants.

**Table 9-2. Primary/Secondary Disinfectant Combinations and Typical Applications in Water Treatment**

Primary / Secondary	Typical application*	Comment
Chlorine/Chlorine	Low THMFP raw water, low TOC, conventional treatment with optimal coagulation.	Most commonly used disinfection scheme. Effective system.
Chlorine/Chloramine	Moderate THM production situation, typically with conventional treatment.	Chlorine to provide disinfection and monochloramine to limit DBP formation.
Chlorine dioxide/Chlorine dioxide	High DBP production, require filter process to remove <i>Cryptosporidium</i> , low chlorine dioxide demand in treated water.	Primary and secondary usage requires a limit on chlorine dioxide dose to reduce residual chlorate/chlorite.
Chlorine dioxide/Chloramine	High DBP production, require filtration to remove <i>Cryptosporidium</i> .	Primary chlorine dioxide dose limited to residual chlorate/chlorite. Stable, low reactive secondary disinfectant.
Ozone/Chlorine	Moderate DBP formation, direct or no filtration, low THMFP.	Highly effective disinfection to achieve high log inactivation; low THMFP to accept free chlorine.
Ozone/Chloramine	Moderate DBP formation, direct or no filtration, higher THMFP.	Highly effective disinfection to achieve high log inactivation, low THMFP to require combined chlorine residual.
UV/Chlorine	Requires membrane treatment to provide effective <i>Giardia</i> and <i>Cryptosporidium</i> removal. UV only for virus inactivation; ground water disinfection; low THMFP.	Rare application but feasible in special circumstances. Little <i>Giardia</i> and no <i>Cryptosporidium</i> inactivation.
UV/Chloramine	Requires membrane treatment to provide effective <i>Giardia</i> and <i>Cryptosporidium</i> removal. UV only for virus inactivation; ground water disinfection, moderate THMFP.	Rare application but feasible in special circumstances. No <i>Giardia</i> or <i>Cryptosporidium</i> inactivation.

Notes:

\* Low DBP formation is defined as producing less than the Stage 2 D/DBP Proposed Standard (less than 0.040 mg/L TTHM; less than 0.030 mg/L HAA5). Moderate DBP formation is defined as producing less than the Stage 1 D/DBP Standard and more than the Stage 2 D/DBP Proposed Standard. High DBP formation is defined as producing more than the Stage 1 D/DBP Standard (greater than 0.080 mg/L TTHM; greater than 0.060 mg/L HAA5).

### 9.1.1 DBP Formation with Various Primary and Secondary Disinfectant Combinations

The concentrations and types of DBPs formed depend on, among other things, the combination of disinfectants used to achieve primary and secondary disinfection and the water quality. For example, under certain water quality conditions, ozone/chloramine disinfection is known to produce lower THM concentrations than chlorine/chloramine disinfection. However, the ozone/chloramine alternative can increase the formation of other DBPs such as aldehydes and BOM. No single

combination of disinfectants is applicable to all situations. Table 9-3 summarizes the potential DBPs formed by various combinations of disinfectants. The disinfection byproducts referenced here are discussed in greater detail in earlier chapters of this manual.

**Table 9-3. DBPs Associated with Various Combined Oxidation/Disinfection Processes**

Alternative			Potential DBPs	Remarks
Preoxidation	Primary Disinfection	Secondary Disinfection		
Chlorine	Chlorine	Chlorine	XDBPs*	Maximum XDBP formation compared to all other strategies. Principal components are TTHMs and HAAs.
			Aldehydes	Formed at relatively low levels.
Chlorine	Chlorine	Chloramine	XDBPs Cyanogen chloride Cyanogen bromide	Formation of XDBPs (specifically TTHMs and HAA5s) significantly reduced compared to chlorine/ chlorine/ chlorine.
			Aldehydes	Formed at relatively low levels.
Chlorine dioxide	Chlorine dioxide	Chlorine	XDBPs	Formation of XDBPs may be decreased by delaying the point of chlorine addition.
			Aldehydes, carboxylic acids, maleic acids	Formed at relatively low levels.
			Chlorate Chlorite	Chlorite is a major breakdown product of chlorine dioxide.
Chlorine dioxide	Chlorine dioxide	Chloramine	XDBPs	Formation of XDBPs (especially TTHMs and HAA5s) minimized by avoiding use of free chlorine.
			Aldehydes, carboxylic acids, maleic acid	Formed at relatively low levels.
			Chlorate Chlorite	Chlorite is a major breakdown product of chlorine dioxide.
Potassium permanganate	Chlorine	Chlorine	XDBPs	Formation of XDBPs may be decreased by delaying the point of chlorine addition.
			Aldehydes	Formed at relatively low levels.
Potassium permanganate	Chlorine	Chloramine	XDBPs Cyanogen chloride Cyanogen bromide	Formation of XDBPs may further be decreased compared to potassium permanganate/ chlorine/ chlorine.
			Aldehydes	Formed at relatively low levels.
Ozone	Ozone	Chlorine	XDBPs	Formation of certain XDBPs may increase or decrease compared to chlorine/ chlorine/ chlorine. Brominated byproducts may be of concern when bromides are present in the raw water.
			Bromate, Aldehydes, carboxylic acids	Although formed at relatively high levels significant amounts of this BOM can be removed through biological filtration.
Ozone	Ozone	Chloramine	XDBPs Cyanogen chloride  Cyanogen bromide	Formation of XDBPs (especially TTHMs) minimized by avoiding use of free chlorine.
			Bromate, Aldehydes, carboxylic acids	Although formed at relatively high levels significant amounts of this BOM can be removed through biological filtration.

Alternative			Potential DBPs	Remarks
Preoxidation	Primary Disinfection	Secondary Disinfection		
Peroxone	Chlorine or Ozone	Chlorine	XDBPs	Formation of certain XDBPs may increase or decrease compared to chlorine/ chlorine/ chlorine.
			Bromate, Aldehydes, carboxylic acids	Although formed at relatively high levels significant amounts of this BOM can be removed through biological filtration. Also, the formation of bromate will increase if peroxone is used.
Peroxone	Chlorine or Ozone	Chloramine	XDBPs Cyanogen chloride Cyanogen bromide	Formation of XDBPs may decrease compared to peroxone/ chlorine/ chlorine.
			Bromate, Aldehydes, carboxylic acids	Although formed at relatively high levels significant amounts of this BOM can be removed through biological filtration. Also, the formation of bromate will increase if peroxone is used.
Chlorine	UV**	Chloramine	XDBPs Cyanogen chloride Cyanogen bromide	May form XDBP from pre-oxidation.
			Aldehydes	Low levels.
Potassium Permanganate	UV**	Chloramine	XDBPs	Very low due to less reactive oxidants.
			Aldehydes, carboxylic acids	Very low, if any, due to less reactive oxidants.

\* XDBPs - Halogenated Disinfection Byproducts.

\*\* Although "conventional" UV use as primary disinfectant is limited to virus inactivation (may require membrane filtration), pulsed UV may be able to inactivate *Giardia* and *Cryptosporidium*.

Source: Adopted in part from USEPA, 1992; Richardson et al., 1994.

Raw water chlorination, applied prior to natural organic matter (NOM) removal processes, combined with chlorination for residual disinfection produces the greatest concentrations of halogenated DBPs. Studies indicate that pre-oxidation of raw water with ozone or chlorine dioxide can reduce the formation of halogenated DBPs because it shifts the point of chlorine application from raw water to settled or filtered water which has lower DBP precursor concentrations (MWDSC and JMM, 1989).

The use of ozone can reduce the formation of halogenated byproducts in waters containing low concentrations of bromide. However, ozone increases BOM and may encourage bacterial growth in the distribution system. Removal of AOC with biological filtration (e.g., biological activated carbon) reduces the potential for bacterial growth in the distribution system. The use of chloramines as a secondary disinfectant instead of chlorine shortens the chlorine contact time and thus reduces the formation of chlorinated byproducts. However, chloramine produces by-products of its own (cyanogen chloride and cyanogen bromide). In addition, a short chlorine contact time prior to ammonia addition will help inactivate heterotrophic plate count bacteria that are found in the effluent of a biologically active filter. Bench or pilot studies will be required to evaluate the trade-offs in DBP formation for various disinfectant combinations for a specific application.

The application of ozone should be carefully considered because it produces aldehydes, aldoketoacids, and carboxylic acids. However, these can be removed in a biologically active filter.

In bromide-containing waters, ozonation can increase the formation of brominated organic DBPs and form bromate.

In pilot plant studies for water containing low concentrations of bromide, Lykins et al. (1991) determined that ozonation followed by chloramination produced the lowest levels of halogenated disinfection byproducts. However, this is not applicable to source waters containing significant bromide concentrations due to the potential for bromate formation and brominated THMs and HAAs. The addition of chlorine dioxide will produce chlorite and chlorate and may form some oxygenated DBPs (e.g., maleic acids).

### 9.1.2 Impact of Modifying Disinfection Practices

EPA and the Association of Metropolitan Water Agencies funded a 2-year study of 35 water treatment facilities to evaluate DBP production. Among four of the facilities, eleven alternative disinfection strategies were instigated to evaluate the difference in DBP production from the plants' previously existing disinfection strategies. Three reports (MWDSC and JMM, 1989; Jacangelo, 1989; USEPA, 1992) analyzed and documented different aspects of the study. Table 9-4 shows the eleven potential strategies used for primary and secondary disinfection. Table 9-5 shows the changes in DBP production observed in the four plants after eight of these new strategies were implemented. Following are overviews of the potential implications of these strategies, as detailed by the three reports.

**Table 9-4. Strategies for Primary and Secondary Disinfectants**

<i>Base Disinfection Condition</i>	<i>Modified Disinfection Practice</i>
Chlorine/Chlorine	Chlorine/Chloramine
Chlorine/Chlorine	Chloramine/Chloramine
Chlorine/Chlorine	Chlorine Dioxide/Chloramine
Chlorine/Chlorine	Ozone/Chlorine
Chlorine/Chlorine	Ozone/Chloramine
Chlorine/Chlorine	Chlorine Dioxide/Chlorine
Chlorine/Chlorine	Chlorine Dioxide/Chlorine Dioxide
Chlorine/Chloramine	Ozone/Chloramine
Chlorine/Chloramine	Chlorine Dioxide/Chloramine
Ozone/Chlorine	Ozone/Chloramine
Chloramine/Chloramine	Ozone/Chloramine

Note: Disinfectants are listed as primary disinfectant/secondary disinfectant

**Table 9-5. Impacts of Disinfection Practice on DBP Formation**

Disinfection Byproduct	Change in Disinfection Practice (Primary Disinfectant/Secondary Disinfectant)				
	Chlorine/Chlorine to Chlorine/Chloramine	Chlorine/Chlorine to Ozone/Chlorine		Chlorine/Chloramine to Ozone/Chloramine	Chlorine/Chlorine to Chloramines/Chloramines
	Utility #7	Utility #19	Utility #36	Utility#7	Utility #36
Total Trihalomethanes	decrease	decrease	no change	decrease	decrease
Total Haloacetic Acids	decrease	decrease	no change	decrease	decrease
Total Haloacetonitriles	decrease	decrease	no change	decrease	decrease
Total Haloketones	decrease	no change	increase	increase	decrease
Total Aldehydes	not analyzed	not analyzed	increase	not analyzed	decrease
Chloropicrin	no change	increase	increase	decrease	no change
Chloral Hydrate	decrease	increase	increase	decrease	decrease
Cyanogen Chloride	no change	not analyzed	no change	no change	increase
Disinfection By-Product	Change in Disinfection Practice (Primary Disinfectant/Secondary Disinfectant)				
	Ozone/Chlorine to Ozone/Chloramine	Chloramines/Chloramines to Ozone/Chloramines		Chlorine/Chlorine to Ozone/Chloramine	
	Utility #36	Utility #25	Utility #36	Utility #7	Utility #36
Total Trihalomethanes	decrease	decrease	no change	decrease	decrease
Total Haloacetic Acids	decrease	decrease	no change	decrease	decrease
Total Haloacetonitriles	decrease	no change	no change	decrease	decrease
Total Haloketones	decrease	no change	increase	decrease	decrease
Total Aldehydes	decrease	increase	increase	not analyzed	increase
Chloropicrin	increase	increase	increase	decrease	increase
Chloral Hydrate	decrease	decrease	increase	decrease	decrease
Cyanogen Chloride	increase	increase	increase	no change	increase

Notes: Results based on full scale evaluation at Utilities #19 and #25 and on pilot scale evaluations at Utilities #7 and #36.

Free chlorine contact time was 4 hours for Utility #7 during use of chlorine/chloramine strategy.

Systems must demonstrate efficacy of chloramines as a primary disinfectant if they are to be used as such.

Source: USEPA, 1992; Jacangelo, et al., 1989.

### 9.1.3 Chlorine/Chlorine to Chlorine/Chloramine

Chloramines as a secondary disinfectant shortens the free chlorine contact time and, therefore, reduce the formation of most halogenated DBPs, including TTHM. However, the consumer is exposed to a chloramine residual that has a different health concern (i.e., can cause methemoglobinemia and adversely affect the health of kidney dialysis patients) than chlorine residual. For maximum benefit in reducing halogenated byproducts, the ammonia/chlorine mixing conditions should be optimized to quickly remove free chlorine from the system, with the optimal pH for the chlorine/ammonia reaction considered to be pH 8.3. In one case, changing the secondary disinfectant from chlorine to chloramines resulted in a reduction in average TTHM concentrations from 105 µg/L to 45 µg/L with most (80 percent) of the TTHM formation in the chloraminated system occurring prior to the addition of ammonia (Singer, 1988).

### 9.1.4 Chlorine/Chlorine to Ozone/Chlorine

A change from chlorine to ozone for primary disinfection is attractive because ozone generally produces fewer regulated DBPs than chlorine. However, as mentioned in previous chapters, ozone will react with organic compounds to produce BOM, aldehydes, organic acids, and ketones, many of which are biodegradable. In addition, for water sources containing significant bromide ion concentrations, site-specific engineering evaluations should be completed prior to using ozone as a primary disinfectant due to the potential formation of bromate ion or brominated organic byproducts. At low pH values, the brominated organic byproducts are favored, while at higher pH values, bromate ion formation is favored. Therefore, changing from chlorine to ozone may be limited in cases where the source water contains bromide ion. In the ozone/chlorine strategy, bromine has the opportunity to react with NOM prior to chlorine application, potentially increasing the extent of bromine incorporation into DBPs. Also, in this situation, switching to biological filtration can increase regrowth and corrosion rates in the distribution system.

In systems containing negligible concentrations of bromide ion, replacement of pre-chlorination with ozonation may allow for the point of chlorine addition to be moved beyond clarification or filtration. The principal benefit derived from using ozone for controlling THM formation is that it allows free chlorine to be applied later in the treatment process after precursors have been removed. This would be expected to result in reduced formation of chlorinated DBPs due to the reduced chlorine dose requirement and the reduced NOM concentrations following treatment. Replacement of chlorine with ozone appears to be most effective in decreasing chlorinated DBPs when it eliminates the need for pre-chlorination. However, replacing chlorine with ozone while maintaining free chlorine as a secondary disinfectant has produced mixed results, with some byproduct concentrations being reduced at the expense of increasing the concentrations of others. *The human health implications of this trade-off are largely unknown.* It has been shown that substituting ozone for chlorine as a primary disinfectant, while maintaining free chlorine as a secondary disinfectant when not practicing pre-chlorination, resulted in an increased THM formation in raw waters for the Cities of Phoenix and San Diego (Malcolm Pirnie, 1989; Malcolm Pirnie, 1990).



An operational consideration of the ozone/chlorine system is the application point for chlorine. The ozone should be completely decomposed or chemically quenched prior to chlorine addition. If ozone is present when chlorine is added, the ozone will react with the chlorine and NOM present to form chlorinated DBPs.

Ozonation converts NOM into low molecular weight humic NOM and may increase the concentrations of precursors to some DBPs. For instance, ozonation followed by chlorination as a secondary disinfectant may yield high concentrations of chloral hydrate (Logsdon et al., 1992; McKnight and Reckhow, 1992). This may occur because the byproduct of ozonation, acetaldehyde, is a known precursor for chloral hydrate, a byproduct of chlorination. Enhancement of chloral hydrate has not been observed when biologically active filtration is used following ozonation and prior to chlorination (Singer, 1992). In addition to chloral hydrate, ozonation followed by chlorination can produce greater THM and halo ketones levels than chlorination alone, particularly when chlorine is applied at high pH levels (Jacangelo et al., 1989; Reckhow et al., 1986). Ozonation followed by chlorination or chloramination can increase chloropicrin and cyanogen chloride concentrations above those observed with chlorination or chloramination alone (Jacangelo et al., 1989). The most promising treatment strategy for preventing the enhancement of these biodegradable ozonation byproducts and BOM is to locate ozonation after sedimentation and follow it by biologically active GAC.

### 9.1.5 Chlorine/Chlorine to Ozone/Chloramine

In addition to the concerns addressed in Sections 9.1.3 and 9.1.4, switching from chlorine to chloramine residual exposes the consumer to a residual that may be a more significant health concern (particularly for kidney dialysis patients). The impact of switching from chlorine/chlorine to ozone/chloramines on the production of byproducts was investigated in a 5 gpm pilot study (MWDSC and JMM, 1989; Jacangelo et al., 1989). That switch produced greater concentrations of chloropicrin, cyanogen chloride, formaldehyde and total aldehydes than in the original chlorine/chlorine strategy. Concentrations of TTHMs, total haloacetic acids, total haloacetonitriles, total halo ketones and chloral hydrate were lower with ozone/chloramine. Brominated DBPs were not reported. Ozonation followed by chloramination has been observed to increase cyanogen chloride concentrations beyond those observed with chlorination only (Jacangelo et al., 1989). Increased chloral hydrate has not been observed when monochloramine is applied as the secondary disinfectant (Singer, 1992).

### 9.1.6 Chlorine/Chlorine to Chlorine Dioxide/Chlorine

Use of chlorine dioxide as a pre-oxidant to replace chlorine may allow moving the point of chlorination downstream in the process train for application to water with lower NOM concentrations. The reduced precursor concentration and the reduced chlorine dose should result in a reduction of chlorinated DBPs. However, if excess chlorine is present in the chlorine dioxide feed stream, it would react with NOM prior to removal in sedimentation and filtration if pre-oxidation is practiced. Switching from chlorine/chlorine to chlorine dioxide/chlorine produces mixed results.

Like ozone, chlorine dioxide alters the nature of NOM molecules, potentially forming greater precursor concentrations for some DBPs while reducing the precursor concentrations for other DBPs. *The human health implications of these trade-offs are largely unknown.* Chlorine dioxide/chlorine appears to be most effective in decreasing chlorinated DBPs when it can replace the need for pre-chlorination. However, for facilities that use pre-chlorination but do not require it, continuing to use chlorine/chlorine while eliminating pre-chlorination may be as effective in decreasing chlorinated DBPs.

### 9.1.7 Chlorine/Chlorine to Chlorine Dioxide/Chlorine Dioxide

The potential to apply chlorine dioxide as both a primary and secondary disinfectant is limited because:

- Chlorine dioxide is a strong oxidant and dissipates rapidly in both raw and treated waters; and
- Approximately 50 to 70 percent of chlorine dioxide is converted to the inorganic byproducts chlorite and chlorate.

On the positive side, chlorine dioxide/chlorine dioxide application will significantly lower the formation of organic DBPs.

### 9.1.8 Chlorine/Chloramine to Ozone/Chloramine

In addition to the concerns raised in Sections 9.1.4 and 9.1.5, switching from chlorine/chloramine to ozone/chloramine resulted in reduced formation of most of the halogenated DBPs (MWDSC and JMM, 1989). Other studies also indicate reduction in the formation of most halogenated DBPs but increased formation of 1,1-dichloropropanone (MWDSC and JMM, 1989). The primary difference in chlorinated DBP formation when switching from chlorine/chloramine to ozone/chloramine could be attributed to the shorter contact time with free chlorine.

### 9.1.9 Chlorine/Chloramine to Chlorine Dioxide/Chloramine

The Louisville Water Company evaluated the feasibility of switching from a chlorine/chloramine to chlorine dioxide followed by chloramine to control THM formation (Hubbs et al., 1981). The treatment plant includes lime soda-ash for softening. Disinfection occurs prior to the lime treatment step. Ammonia is added to form chloramine before the water enters the softening phase. There is a 10 minute lag period between the first disinfectant (chlorine or chlorine dioxide) and second disinfectant (chloramine) addition. The study showed a significant decrease in THM formation from 25 µg/L with chlorine to 5 µg/L using chlorine dioxide as the initial disinfectant. At the same time, treated water coliform densities were essentially unchanged; however, results showed slightly more scattered data during the chlorine dioxide test period. Based on these results, the Water Company decided to use chlorine/chloramine to meet disinfection and THM targets. No other DBPs were measured during the test period.

### 9.1.10 Ozone/Chlorine to Ozone/Chloramine

In addition to concerns raised in Sections 9.1.4 and 9.1.5, when compared with ozone/chlorine, ozone/chloramine produced greater concentrations of cyanogen chloride. Concentrations of TTHM, total haloacetic acids, total haloacetonitriles, total haloketones, chloral hydrate, total aldehydes and formaldehyde were lower with ozone/chloramine than with ozone/chlorine. Ozone/chloramine produces some chlorinated DBPs at greater concentrations than ozone/chlorine; however, ozone/chloramine significantly reduces TTHMs compared to ozone/chlorine (LeLacheur et al., 1991).

### 9.1.11 Summary

EPA is not encouraging systems to switch to different disinfectants due to unknown risks to public health. When needed for compliance with regulations or increasing *Cryptosporidium* inactivation, careful selection of alternative disinfectants as primary and secondary disinfectants, can produce less DBPs and increase inactivation. In general, the results followed the characteristic DBPs associated with the primary disinfectant (halogenated DBPs with chlorine compounds or ozone in the presence of bromide oxidized organics, AOC with ozone or peroxone). However, by carefully selecting the primary and secondary disinfectant and avoiding long contact times and high dosages of halogens (chlorine, bromine), the total DBP formation declined. The quantity and types of DBPs that form are site-specific, depending on the water quality, disinfectant dose and type, and are best determined by bench testing. Note that any system changing disinfectants is subject to the profiling and benchmarking requirements as described in Section 1.3.1 and specified in 40 CFR § 141.172.

## 9.2 Pathogen Inactivation with Interactive Disinfectants

In 1988, several reports appeared on the combined efficiency of some disinfectants on pathogen inactivation. Worley and Williams (1988) reported that a mixture of free chlorine and organic *N*-halamine produced higher levels of inactivation of a variety of bacteria. The combination of free chlorine and sodium bromide was also investigated and found to be more effective than using free chlorine alone (Alleman et al., 1988). In a study at the University of Arizona, the synergistic inactivation of *E. coli* and MS-2 coliphage was demonstrated by the combined application of chloramine and cupric chloride (Straub et al., 1994).

Recently there has been a great deal of interest in the potential of interactive disinfectants because reports showed that some of these combinations are more effective for inactivating *Cryptosporidium* (Finch et al., 1994). Research on interactive disinfectants for primary pathogen inactivation is under way for several combinations of disinfectants:

- Chlorine followed by chloramine;
- Chlorine dioxide followed by chlorine;
- Chlorine dioxide followed by chlorine dioxide;

- Chlorine dioxide followed by chloramine;
- Ozone followed by chlorine;
- Ozone followed by chlorine dioxide; and
- Ozone followed by chloramine.

### 9.2.1 Inactivation Mechanism

Bernbaum (1981 and 1985) developed a testing method for determining the kind of interaction that can be expected when agents are combined to produce a given observation. Synergism can be tested using the mathematical model developed by Bernbaum and modified for disinfection kinetics by Kouame and Haas (1991). The principle is that, if the agents in a given combination do not interact in producing the effect observed, then regardless of the effect relations, the following equation is satisfied:

$$\sum_{i=1}^n \frac{x_i}{y_i} = 1$$

where:

- $x_i$  = Concentration of the individual agent in the combination
- $y_i$  = Concentration of the agents that individually would produce the same magnitude of effect as that of the combination
- $i$  = Individual agent
- $n$  = Total number of agents

The sum calculated from this equation for a set of data is interpreted as follows:

- The sum is less than 1 in the case of synergistic interaction;
- The sum is greater than 1 in the case of antagonistic interaction; and
- The sum is equal to 1 in the case of additivity (zero interaction).

Using this approach, Kouame and Haas (1991) showed that a synergistic interaction exists in the inactivation of *E. coli* when exposed simultaneously to free chlorine and monochloramine.

The authors described a possible mechanism in which both of the disinfectants work together to inactivate bacteria. The researchers hypothesized that bacterial inactivation is caused by monochloramine penetrating the cell and oxidizing thiol groups, which in turn causes structural changes in the cell membrane. Once these changes have been made, copper is allowed to pass into the cell and binds either to sulfhydryl groups of respiratory enzymes or nucleic acids. More recently, the researchers investigating *E. coli* inactivation hypothesized that a potential synergistic mechanism consisting of sub-lethal injury caused by free chlorine resulted in enhanced sensitivity to monochloramine (Kouame and Haas, 1991).

Another hypothesis for the increased effectiveness of interactive disinfectants is that the first oxidant (i.e., chlorine, chlorine dioxide, or ozone) conditions the outer membrane of *Cryptosporidium* oocysts so that the secondary oxidant (i.e., chlorine, chlorine dioxide, and monochloramine) can penetrate the oocyst more easily (Liyanage et al., 1996). For example, preliminary work on the disinfection of *Cryptosporidium parvum* using free chlorine followed by monochloramine suggested that there may be a synergism involving two chlorine species. Sequential treatment of these chlorine species was found to provide greater inactivation than expected from the additive effects of the two disinfectants used alone (Gyurek et al., 1996).

Recent studies have utilized a straight forward method to determine if synergism has occurred based on measured inactivation (Finch, 1997; Gyurek et al., 1996; and Liyanage et al., 1996). According to this approach, synergism is demonstrated if the sequential application of disinfectants provides more inactivation than is expected from the additive effects of the individual, separate disinfectants. In addition, the magnitude of the synergistic effects is equal to the difference in the level of inactivation achieved from multiple disinfectants and the additive inactivations achieved from the single disinfectants.

## 9.2.2 Environmental Effects

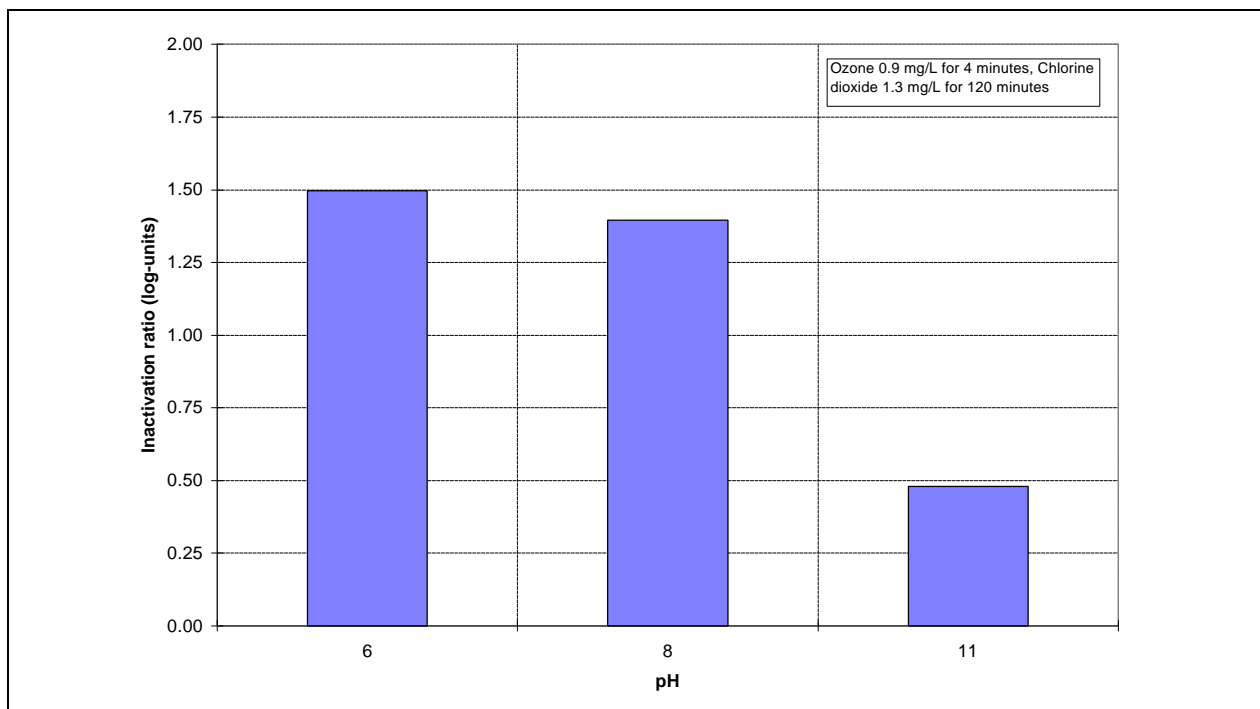
Similar to most chemical disinfectants, the preliminary results from an AWWARF ongoing study suggest that pH and temperature affect the amount of synergistic inactivation achieved by sequential applications of disinfectants (Finch, 1997). The following sections briefly describe the effects these parameters have on pathogen inactivation.

### 9.2.2.1 pH

The level of inactivation due to the sequential application of chemical disinfectants is believed to be pH dependent (Finch, 1997). Figure 9-1, Figure 9-2, and Figure 9-3 illustrate the impact of pH on the log inactivation of *Cryptosporidium parvum* attributed to synergistic effects for three sequential combinations of ozone-chlorine dioxide, chlorine dioxide-free chlorine, and chlorine dioxide-chloramine, respectively. As shown in these figures, the amount of log inactivation due to synergistic effects is lower at high pH (e.g., pH = 11). These results show that neutral pH is more effective than low pH except for ozone-chlorine dioxide.

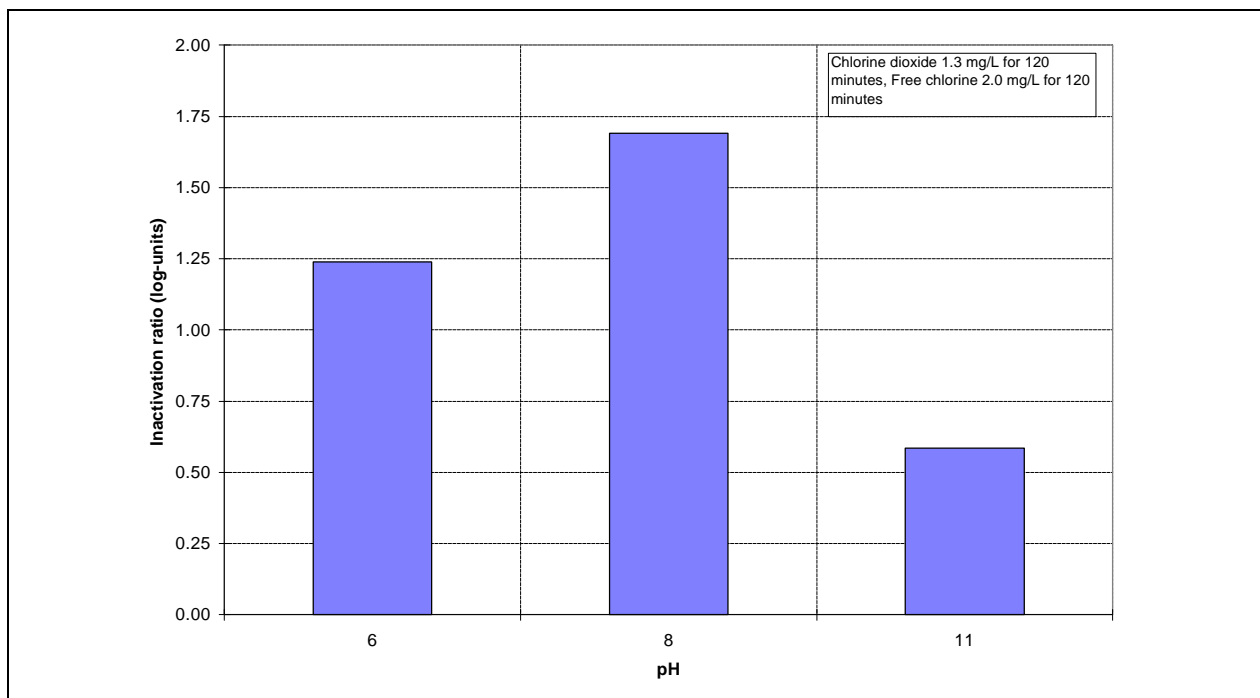
### 9.2.2.2 Combination of Low Temperature and pH

The combined effect of low temperature and high pH is believed to significantly reduce the amount of *Cryptosporidium* inactivation attributed to synergism (Finch, 1997). One possible explanation for this reduction is that the oocysts contract under these conditions and become harder to penetrate. However, significant reduction in *Cryptosporidium* oocysts inactivation is true under reduced water temperature and high pH whether interactive disinfection is practiced or not. Therefore, reduced inactivation may not be necessarily due to synergism between combined disinfectants.



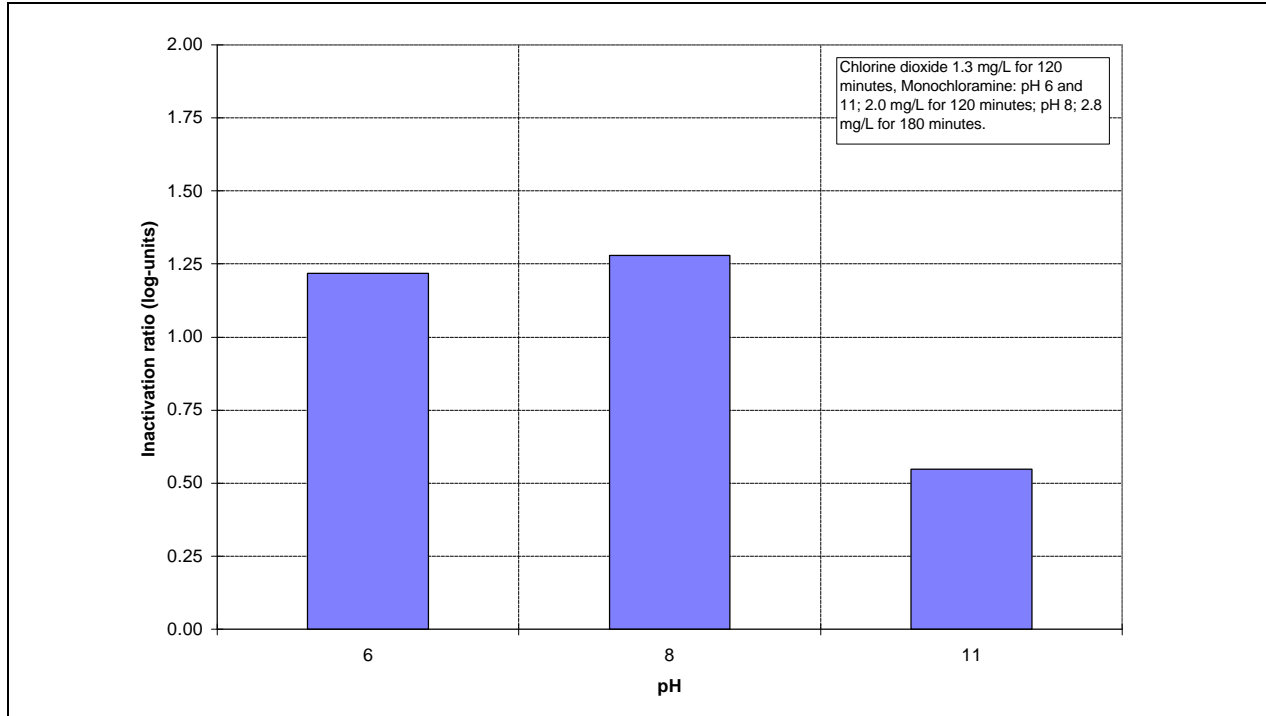
Source: Finch, 1997.

**Figure 9-1. Inactivation of *C. parvum* Attributed to Synergistic Effects. Application of Ozone Followed by Chlorine Dioxide**



Source: Finch, 1997.

**Figure 9-2. Inactivation of *C. parvum* Attributed to Synergistic Effects. Application of Chlorine Dioxide Followed by Free Chlorine**



Source: Finch, 1997.

**Figure 9-3. Inactivation of *C. parvum* Attributed to Synergistic Effects. Application of Chlorine Dioxide Followed by Monochloramine**

### 9.2.2.3 Pathogen Susceptibility

*Cryptosporidium* oocysts are more susceptible to inactivation by combinations of disinfectants than by individual disinfectants. *Giardia* cysts were also found to have a similar response to:

- Ozone followed by free chlorine;
- Ozone followed by monochloramine;
- Chlorine dioxide followed by free chlorine;
- Chlorine dioxide followed by monochloramine; and
- Free chlorine followed by monochloramine.

However, no synergism was observed with bacterial spores, specifically *Bacillus cereus* spores (Finch, 1997). These results suggest that encysted parasites might show more susceptibility to synergistic effects than bacterial spores. Masking effects caused by turbidity for interactive disinfectants are expected to be similar to those of the individual disinfectants.

### 9.2.3 Pathogen Inactivation Efficiency Using Interactive Disinfectants

Within the last few years there have been several studies to investigate interactive disinfectants. These studies were conducted under various conditions of pH, bench or laboratory scale, and using various organisms:

- Battigelli and Sobsey (1993) studied viral inactivation under lime softening conditions using sequential addition of chlorine and monochloramine;
- Kouame and Haas (1991) determined *E. coli* inactivation during simultaneous addition of free chlorine and monochloramine;
- Finch (1997) is studying various combinations of chlorine, chlorine dioxide, ozone, and monochloramine on inactivation of *Cryptosporidium parvum* oocysts, *Giardia muris* cysts, and *Bacillus cereus* spores under laboratory conditions; and
- Oppenheimer (1997) is developing CT requirements for *Cryptosporidium parvum* inactivation in a variety of natural waters using ozone followed by chlorine.

The following is a summary of the findings of these studies to date.

#### 9.2.3.1 Virus Inactivation Using Chlorine and Monochloramine Under High pH

One of the primary objectives of the Battigelli and Sobsey study (1993) was to evaluate the disinfection efficiency under high pH conditions encountered in conventional lime softening treatment with and without the addition of chlorine and monochloramine. The three microorganisms selected for evaluation were hepatitis A virus, poliovirus 1, and MS-2 coliphage.

During the study, the inactivation kinetics of the three test viruses were determined when 2.0 mg/L monochloramine were formed dynamically after the viruses had been exposed to lime solution and free chlorine for 60 seconds. The authors believed that this approach simulates the conditions typically encountered in a water softening facility where ammonia is applied post-chlorination.

Results indicated that a high degree of inactivation occurs during the first 60 seconds of chlorine addition at approximately 2.4 mg/L free chlorine.

Table 9-6 shows the amount of inactivation attributed to the lime solution, free chlorine, and monochloramine for the three viruses. The table also contains the amount of inactivation attributed to the sequential application of lime solution, free chlorine and monochloramine previously described (simultaneous chloramination). Results shown in Table 9-6 are based on a pH of 11.0 and a total contact time of 360 minutes.

Except for poliovirus 1, the summation of the individual disinfectants was greater than the level of inactivation achieved from the simultaneous chloramination. These results imply that the sequential addition of free chlorine and monochloramine after lime addition to raise the pH to 11, form an



antagonistic (negative) interaction for inactivation of hepatitis A virus and MS-2 coliphage. For poliovirus 1, under similar conditions, an enhancement of 1.4 log inactivation was achieved suggesting positive synergism for poliovirus 1 inactivation.

**Table 9-6. Virus Inactivation By Individual Disinfectants and Simultaneous Chloramination**

Disinfectant(s)	Log Survival <sup>1</sup>			Condition
	Hepatitis A Virus	Poliovirus	MS-2 Coliphage	
Lime solution only	-3.0	-0.5	-4.0	360 min contact time
Free chlorine	-1.8	-1.2	-1.6	60 second contact time, 2.5 mg/L chlorine
Monochloramine	-3.7	-1.9	-3.8	2.0 mg/L monochloramine
Summation free+monochloramine	-5.5	-3.1	-5.4	Additive
Simultaneous chloramination	-4.5	-4.5	-4.5	2.4 mg/L chlorine 60 second contact time, 2.0 mg/L monochloramine, 359 minutes.

<sup>1</sup> All data at pH 11 after lime addition  
Source: Battigelli and Sobsey, 1993.

### 9.2.3.2 Inactivation of *E. coli* Under Simultaneous Free and Combined Chlorination

The inactivation of *E. coli* bacteria by the simultaneous application of free chlorine and monochloramine was investigated at the Illinois Institute of Technology (Kouame and Haas, 1991). Figure 9-4 shows the level of *E. coli* inactivation by free chlorine and monochloramine, separately and combined. The level of inactivation by monochloramine alone after a contact time of 300 seconds was found to be significantly less than that of free chlorine. Therefore, the sum of the individual inactivation by free chlorine and monochloramine was assumed to be equal to that of free chlorine alone. Note that in this case, the residual disinfectant rapidly disappeared due to the breakpoint reactions that occur when monochloramine and free chlorine are combined.

The surviving fraction of bacteria following the simultaneous application of free chlorine and monochloramine is substantially less than what would be expected by adding the individual levels of inactivation. In other words, at similar doses and contact times, the amount of inactivation from the combined disinfectants was greater than the sum of the inactivation due to free chlorine alone and monochloramine alone.

In summary the Kouame and Haas (1991) study showed that high levels of bacteria inactivation can be achieved when free chlorine and monochloramine exist simultaneously in a continuous flow system and that the combined action of both chemicals on the bacteria is synergistic.

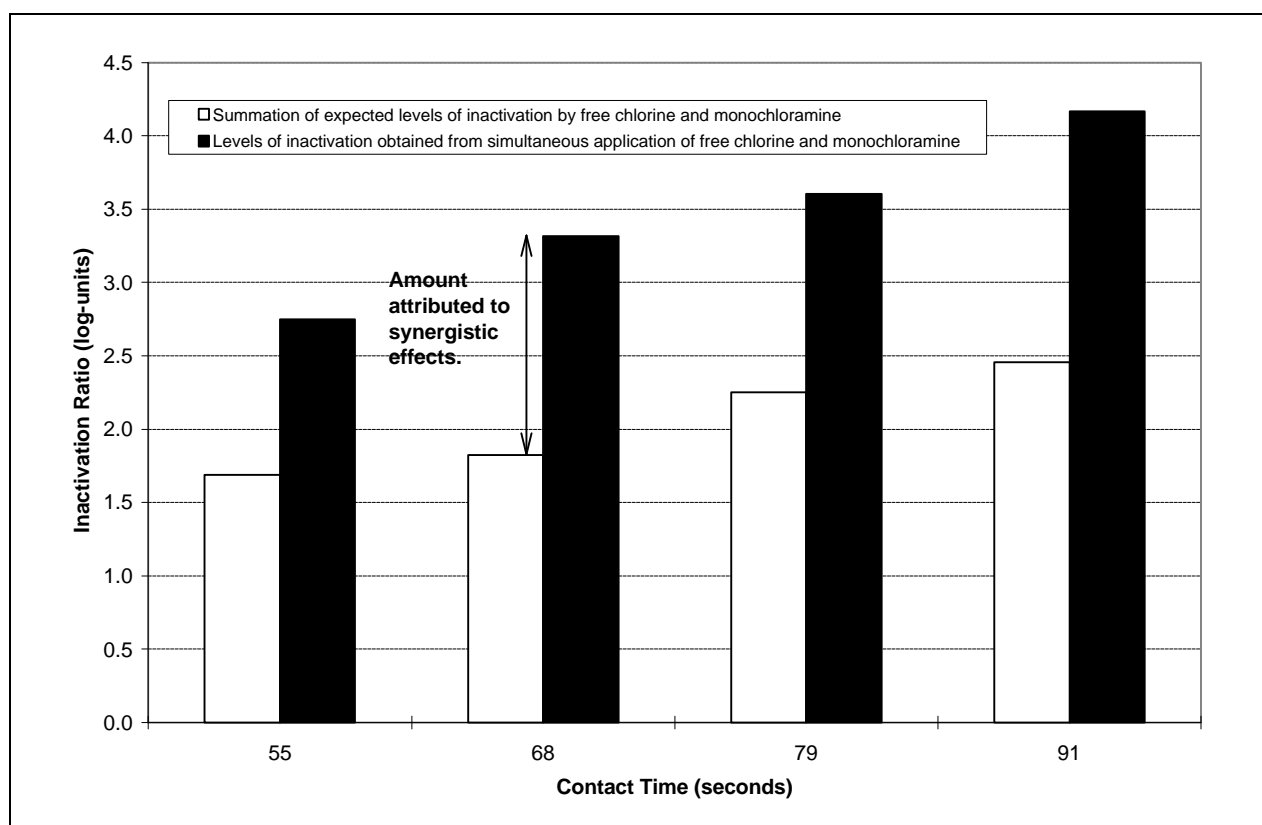
### 9.2.3.3 *Cryptosporidium*, *Giardia*, and *Bacillus* Inactivation in Laboratory Grade Water

The preliminary results of an AWWARF study that investigated the application of multiple disinfectants was presented at a American Water Works Association Technology Transfer Conference in Portland, OR, in August 1997. The objectives of this study were to screen interactive chemical disinfectants (ozone, chlorine, chlorine dioxide, and monochloramine) for inactivation of *Cryptosporidium parvum*, *Giardia muris*, and *Bacillus cereus* and develop design criteria for *Cryptosporidium parvum* inactivation using the best combinations.

#### Ozone Followed By Chlorine Dioxide

Table 9-7 shows the results obtained from ozone and chlorine dioxide application for the inactivation of *Cryptosporidium parvum*.

Based on the data shown in Table 9-7, ozone followed by chlorine dioxide was the most effective disinfectant combination for *Cryptosporidium* inactivation. A total contact time of 124 minutes was required to achieve 3 to 4-log inactivation with ozone and chlorine dioxide residuals of 0.9 and 1.3 mg/L, respectively.



Source: Kouame and Haas, 1991.

**Figure 9-4. Inactivation of *E. coli* Using Free Chlorine and Monochloramine**

**Table 9-7. *C. parvum* Inactivation Using Ozone Followed by Chlorine Dioxide**

Disinfectant	Level of Inactivation (log-units)		
	pH 6.0	pH 8.0	pH 11.0
Ozone	1.6	0.8	0
Chlorine dioxide	0.9	1.4	2.4
Ozone followed by chlorine dioxide	4.0	3.6	2.9
Inactivation attributed to synergism	1.5	1.4	0.5

Source: Finch, 1997.

Ozone: 0.9 mg/L for 4 minutes, chlorine dioxide 1.3 mg/L for 120 minutes.

### Chlorine Dioxide Followed by Free Chlorine

Table 9-8 through Table 9-10 summarize of the results obtained for chlorine dioxide followed by free chlorine for *Cryptosporidium parvum*, *Giardia muris*, and *Bacillus cereus*, respectively.

**Table 9-8. *C. parvum* Inactivation Using Chlorine Dioxide Followed by Free Chlorine**

Disinfectant	Level of Inactivation (log-units)		
	pH 6.0	pH 8.0	pH 11.0
Chlorine dioxide	1.0	1.4	1.6
Free chlorine	0	0	0
Chlorine dioxide followed by free chlorine	2.2	3.0	2.3
Inactivation attributed to synergism	1.2	1.6	0.7

Source: Finch, 1997.

Chlorine dioxide 1.3 mg/L for 120 minutes, free chlorine 2.0 mg/L for 120 minutes.

**Table 9-9. *G. muris* Inactivation Using Chlorine Dioxide Followed by Free Chlorine**

Disinfectant	Level of Inactivation (log-units)	
	pH 6.0	pH 8.0
Chlorine dioxide	0.8	0.8
Free chlorine	0.8	0.6
Chlorine dioxide followed by free chlorine	2.2	2.0
Inactivation attributed to synergism	0.6	0.6

Source: Finch, 1997.

Chlorine dioxide: 1.0 mg/L for 10 minutes, free chlorine 2.0 mg/L for 30 minutes.

**Table 9-10. *B. cereus* Inactivation Using Chlorine Dioxide Followed by Free Chlorine**

Disinfectant	Level of Inactivation (log-units)	
	pH 6.0	pH 8.0
Chlorine dioxide	1.8	
Free chlorine	1.2	
Chlorine dioxide followed by free chlorine	2.9	
Inactivation attributed to synergism	0	

Source: Finch, 1997.

Chlorine dioxide: 2.3 mg/L for 20 minutes, free chlorine for 30 minutes.

Chlorine dioxide followed by free chlorine was capable of achieving between 2 and 3 logs of *Cryptosporidium* inactivation following a total contact time of 240 minutes and approximately 2 logs of inactivation of *Giardia* following only 40 minutes of contact time. No synergism was observed with *Bacillus cereus*. However, approximately 3 logs of inactivation after a contact time of 50 minutes were achieved by the additive effects of chlorine dioxide and free chlorine.

### Chlorine Dioxide Followed by Chloramine

Table 9-11 and Table 9-12 show the results of the inactivation of *Cryptosporidium parvum* and *Giardia muris* when using chlorine dioxide followed by monochloramine.

**Table 9-11. *C. parvum* Inactivation Using Chlorine Dioxide Followed by Chloramine**

Disinfectant	Level of Inactivation (log-units)		
	pH 6.0	pH 8.0	pH 11.0
Chlorine dioxide	1.0	1.5	1.6
Monochloramine	0	0	0
Chlorine dioxide followed by monochloramine	2.2	2.8	2.1
Inactivation attributed to synergism	1.2	1.3	0.5

Source: Finch, 1997.

Chlorine dioxide: pH 6, 8, and 11: 1.3 mg/L for 120 minutes. Monochloramine: pH 6 and 11: 2.0 mg/L for 120 minutes, pH 8: 2.8 mg/L for 180 minutes.

**Table 9-12. *G. muris* Inactivation Using Chlorine Dioxide Followed by Chloramine**

Disinfectant	Level of Inactivation (log-units)	
	pH 8.0	pH 11.0
Chlorine dioxide	0.8	0.8
Monochloramine	0.5	0.7
Chlorine dioxide followed by monochloramine	1.7	1.5
Inactivation attributed to synergism	0.4	0

Source: Finch, 1997.

pH 8.0: Chlorine dioxide 1.0 mg/L for 5 minutes, monochloramine 2.0 mg/L for 150 minutes.

pH 11.0: Chlorine dioxide 1.0 mg/L for 5 minutes, monochloramine 2.0 mg/L for 5 minutes.

At similar disinfect residuals and contact times, chlorine dioxide followed by monochloramine was found to achieve the same levels of *Cryptosporidium* inactivation as chlorine dioxide followed by free chlorine at pH values of 6 and 11. However, at pH 8, a higher monochloramine residual and contact time were required to achieve inactivation levels comparable to chlorine dioxide and free chlorine. No synergism was found for *Giardia* inactivation at pH 11.0 with only a minimal increase in effectiveness at pH 8.0.

### Ozone Followed by Free Chlorine

Table 9-13 and Table 9-14 show the levels of inactivation of *Giardia muris* and *Bacillus cereus* obtained by using ozone followed by free chlorine.

**Table 9-13. *G. muris* Inactivation Using Ozone Followed by Free Chlorine**

Disinfectant	Level of Inactivation (log-units)		
	pH 6.0	pH 8.0	pH 11.0
Ozone	0.5	0.8	0.4
Free chlorine	0.8	0.6	0
Ozone followed by free chlorine	2.3	2.2	0.4
Inactivation attributed to synergism	1.0	0.8	0

Source: Finch, 1997.

pH 6.0: ozone 0.1 mg/L for 60 seconds; free chlorine 2.0 mg/L for 30 minutes.

pH 8.0: ozone 0.1 mg/L for 17 seconds; free chlorine 2.0 mg/L for 60 minutes.

pH 11.0: ozone 0.1 mg/L for 5 seconds; free chlorine 2.0 mg/L for 60 minutes.

**Table 9-14. *B. cereus* Inactivation Using Chlorine Dioxide Followed by Free Chlorine**

Disinfectant	Level of Inactivation (log-units)	
	pH 6.0	pH 11.0
Chlorine dioxide	1.4	
Free chlorine	2.0	
Chlorine dioxide followed by free chlorine	3.4	
Inactivation attributed to synergism	0	

Source: Finch, 1997.

Ozone followed by free chlorine was capable of achieving approximately 2 logs of *Cryptosporidium* inactivation at pH 6.0 and 8.0; however, only a 0.4 log inactivation was achieved at pH 11.0. The difference in inactivations was primarily caused by the inability of free chlorine to inactivate *Cryptosporidium* at pH 11.0. Similar to the disinfectant combination of chlorine dioxide and free chlorine, no synergism was observed for *Bacillus cereus* inactivation; however, the additive effects of ozone and free chlorine achieved greater than 3 logs of inactivation.

### Ozone Followed by Monochloramine

Table 9-15 shows the results obtained for *Giardia muris* inactivation by ozone followed by monochloramine.

**Table 9-15. *G. muris* Inactivation Using Ozone Followed by Chloramine**

Disinfectant	Level of Inactivation (log-units)	
	pH 8.0	pH 11.0
Ozone	0.8	0.4
Monochloramine	0.5	0.7
Ozone followed by monochloramine	2.1	1.8
Inactivation attributed to synergism	0.8	0.7

Source: Finch, 1997.

pH 8.0: ozone 0.1 mg/L for 17 seconds; monochloramine 2.0 mg/L for 150 minutes.

pH 11.0: ozone 0.1 mg/L for 5 seconds; monochloramine 2.0 mg/L for 5 minutes.

Because of the different residuals and contact times, inactivation efficiencies of ozone followed by chloramine and ozone followed by free chlorine could not be compared. However, for similar

monochloramine residuals, a very short monochloramine contact time of 5 minutes at pH 11 was found to achieve a greater inactivation than a contact time of 150 minutes at pH 8.

### Free Chlorine Followed by Monochloramine

Table 9-16 shows the results obtained for *Giardia muris* inactivation by free chlorine followed by monochloramine.

Similar to the results obtained for ozone followed by monochloramine, a very short monochloramine contact time of 5 minutes at pH 11 was found to achieve a greater inactivation than a contact time of 150 minutes at pH 8. However, free chlorine did not achieve any inactivation at pH 11.

**Table 9-16. *G. muris* Inactivation by Free Chlorine Followed by Monochloramine**

Disinfectant	Level of Inactivation (log-units)	
	pH 8.0	pH 11.0
Free chlorine	0.6	0
Monochloramine	0.5	0.7
Free chlorine followed by monochloramine	2.4	0.7
Inactivation attributed to synergism	1.3	0

Source : Finch, 1997.

pH 8.0: free chlorine 2.0 mg/L for 60 minutes; monochloramine 2.0 mg/L for 150 minutes.

pH 11.0: free chlorine 2.0 mg/L for 60 minutes, monochloramine 2.0 mg/L for 5 minutes.

### 9.2.3.4 Bench-Scale Tests Using Natural Waters

In another AWWARF study, Oppenheimer (1997) is developing CT requirements for *Cryptosporidium parvum* inactivation in a variety of natural waters, developing design criteria for full-scale contacting systems from bench scale CT values, and investigating the impact of selected variables on CT requirements. To date, samples have been collected and analyzed from 13 geographically disperse locations. Although a significant amount of data were not available, results from the California State Water Project and Ohio River appear to show that the sequential application of ozone and chloramines resulted in an enhanced inactivation of *C. parvum* as shown in Table 9-17. The sequential application of free chlorine and monochloramine appears to enhance *C. parvum* inactivation by providing some synergistic effects. To obtain the log reduction, however, very high ozone residuals were required which appear to be impractical. In addition, bromate formation was also a problem.

**Table 9-17. *C. parvum* Inactivation by Sequential Application of Ozone and Chloramine**

Water Source	Ozone		Chlorine		Chloramine		Log Inactivation Enhancement
	Residual mg/L	Contact min	Residual mg/L	Contact min	Residual mg/L	Contact min	
California State Water Project	0.8	12	1.5	~0	2.5	30	0.3 to > 1.4
Ohio River	4	15	1.5	120	0.5	120	0.9 to 1.4

Source: Oppenheimer, 1997.

## 9.2.4 Summary: Pathogen Inactivation with Interactive Disinfectants

Various studies have shown the synergistic effects of interactive disinfectants: either simultaneous application or sequential application. The improved disinfection efficiency due to interactive disinfection is variable, ranging from negative (antagonistic) effects (in two studies) to positive enhancement of disinfection efficiency. Many of the studies show definite improvement in inactivation for interactive disinfectants.

Several research projects on the effects of combined disinfectants are underway at the time this manual is being prepared. These projects should provide insight on the mechanisms and applicability of multiple disinfectants. Based on current information, EPA believes that under appropriate situations a positive improvement in disinfection efficiency exists. This enhanced inactivation varies from organism to organism, and with different disinfectant combinations. For the key organisms of interest under normal pH conditions:

- Coliform bacteria inactivation appears to increase with combined disinfectants;
- *Giardia* cyst inactivation appears to increase with combined disinfectants;
- Hepatitis A virus and MS<sup>-2</sup> coliphage inactivation using combined disinfectants appears to be less efficient than the individual disinfectants;
- Poliovirus 1 inactivation appears to increase with combined disinfectants;
- *Cryptosporidium* oocyst inactivation appears to increase with combined disinfectants; and
- Inactivation of spores appears neutral.

Interactive disinfection is still however considered an emerging technology. As such, CT credits for interactive disinfectants have not yet been established.

## 9.3 Analytical Methods

In general, most of the analytical methods for residual disinfectants are impacted negatively by the presence of other disinfectants. Fortunately, for most of the disinfectants and oxidants listed below, at least one method exists that can be used successfully in the presence of other oxidizing agents. For analytical method details, see the individual disinfectant chapters.

### 9.3.1 Ozone

Residual ozone analysis cannot be performed in the presence of other oxidizing agents including chlorine, chloramine, and potassium permanganate. Typically, the ozone analytical methods exhibit interferences from chlorine, bromine, iodine, and manganese ions. The ACVK is the least susceptible to interference and can be used when manganese concentrations are less than 1 mg/L and free or combined chlorine concentrations are less than 10 mg/L (Gordon et al., 1992).

### **9.3.2 Chlorine Dioxide**

Some of the analytical methods for chlorine dioxide, chlorate, and chlorite cannot be performed in the presence of oxidizing agents. Amperometric and iodometric methods cannot be used in the presence of metal ions such as manganese. Analytical methods that can be used in the presence of other disinfectants and oxidants include UV spectrophotometric methods and ion chromatography (Gordon et al., 1992).

### **9.3.3 Potassium Permanganate**

The atomic adsorption method for permanganate analysis can be performed in the presence of any of the other disinfectants (Standard Methods, 1995).

### **9.3.4 Chloramine**

None of the colorimetric analytical methods for chloramine can be performed in the presence of oxidizing agents such as ozone or hydrogen peroxide. Analytical methods that can be used in the presence of other disinfectants and oxidants include the UV spectrophotometric method and the amperometric titration methods (Gordon et al., 1992).

### **9.3.5 Hydrogen Peroxide**

The analytical procedures for hydrogen peroxide in drinking water are all impacted by other oxidizing species such as ozone and chlorine (Gordon et al., 1992).

### **9.3.6 UV Radiation**

There are no known interferences from other disinfectants with the measurement of UV radiation (DeMers and Renner, 1992).

### **9.3.7 Summary of Analytical Methods**

Ozone analysis in the presence of chlorine is limited. However, these disinfectants are not commonly present simultaneously, especially with the rapid decomposition of ozone.

Hydrogen peroxide analysis is difficult in the presence of ozone and other oxidizing agents. However, when using peroxone, the ozone residual is the analyte used to meet disinfection requirements.

All of the other disinfectants and oxidizing agents can be selectively monitored in the presence of other disinfectants.



## 9.4 Summary

Table 9-18 summarizes, in general, the factors and uses of combined disinfectants. Specific considerations depend on the actual combination of disinfectants used.

**Table 9-18. Summary of Combined Disinfectants**

Consideration	Description
Generation	Generation depends on the type of chemicals used. Ozone, chlorine dioxide, and chloramines require on-site generation.
Primary uses	Two separate disinfectants can be used to provide primary and secondary disinfection. By separating the primary and secondary disinfection functions, the processes can be optimized for maximum inactivation and minimum DBP formation.  Interactive disinfection (using synergism between two disinfectants to enhance inactivation) can serve as a primary disinfectant.
Inactivation efficiency	The use of interactive disinfection as primary disinfectant for inactivation of <i>Giardia</i> , <i>Cryptosporidium</i> , and viruses are feasible. Interactive disinfection is typically more effective than the individual disinfectants.
Byproduct formation	DBP formation is in general reduced by using combined disinfectants. Specifically, continued use of chlorine in combination with other disinfectants can reduce DBP formation.
Limitations	Data on the inactivation efficiency of combined disinfectants are still being generated with much information coming from controlled laboratory studies. Additional information is still needed, specifically on full-scale implementation. Dual (primary/secondary) disinfection for DBP control is well established as a preferred treatment option.
Point of application	Applied for primary and secondary disinfection. Ozonation should occur after settling and prior to biofiltration.
Special considerations	The efficiency and application of combined disinfectants follow to a large extent the limitations and features of the individual disinfectant. The combined disinfectant is often a more effective disinfectant.

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<b>9.</b>	<b>COMBINED DISINFECTANTS.....</b>	<b>9-1</b>
9.1	PRIMARY AND SECONDARY DISINFECTANTS .....	9-1
9.1.1	DBP Formation with Various Primary and Secondary Disinfectant Combinations .....	9-3
9.1.2	Impact of Modifying Disinfection Practices .....	9-6
9.1.3	Chlorine/Chlorine to Chlorine/Chloramine.....	9-8
9.1.4	Chlorine/Chlorine to Ozone/Chlorine.....	9-8
9.1.5	Chlorine/Chlorine to Ozone/Chloramine .....	9-9
9.1.6	Chlorine/Chlorine to Chlorine Dioxide/Chlorine .....	9-9
9.1.7	Chlorine/Chlorine to Chlorine Dioxide/Chlorine Dioxide .....	9-10
9.1.8	Chlorine/Chloramine to Ozone/Chloramine .....	9-10
9.1.9	Chlorine/Chloramine to Chlorine Dioxide/Chloramine .....	9-10
9.1.10	Ozone/Chlorine to Ozone/Chloramine .....	9-11
9.1.11	Summary.....	9-11
9.2	PATHOGEN INACTIVATION WITH INTERACTIVE DISINFECTANTS .....	9-11
9.2.1	Inactivation Mechanism.....	9-12
9.2.2	Environmental Effects .....	9-13
9.2.3	Pathogen Inactivation Efficiency Using Interactive Disinfectants .....	9-16
9.2.4	Summary: Pathogen Inactivation with Interactive Disinfectants.....	9-23
9.3	ANALYTICAL METHODS.....	9-23
9.3.1	Ozone .....	9-23
9.3.2	Chlorine Dioxide.....	9-24
9.3.3	Potassium Permanganate .....	9-24
9.3.4	Chloramine .....	9-24
9.3.5	Hydrogen Peroxide.....	9-24
9.3.6	UV Radiation.....	9-24
9.3.7	Summary of Analytical Methods.....	9-24
9.4	SUMMARY .....	9-25
9.5	REFERENCES .....	9-26

Table 9-1.	Potential Primary Disinfectants .....	9-2
Table 9-2.	Primary/Secondary Disinfectant Combinations and Typical Applications in Water Treatment.....	9-3
Table 9-3.	DBPs Associated with Various Combined Oxidation/Disinfection Processes .....	9-4
Table 9-4.	Strategies for Primary and Secondary Disinfectants.....	9-6
Table 9-5.	Impacts of Disinfection Practice on DBP Formation.....	9-7
Table 9-6.	Virus Inactivation By Individual Disinfectants and Simultaneous Chloramination.....	9-17
Table 9-7.	<i>C. parvum</i> Inactivation Using Ozone Followed by Chlorine Dioxide .....	9-19
Table 9-8.	<i>C. parvum</i> Inactivation Using Chlorine Dioxide Followed by Free Chlorine .....	9-19
Table 9-9.	<i>G. muris</i> Inactivation Using Chlorine Dioxide Followed by Free Chlorine .....	9-19
Table 9-10.	<i>B. cereus</i> Inactivation Using Chlorine Dioxide Followed by Free Chlorine .....	9-19
Table 9-11.	<i>C. parvum</i> Inactivation Using Chlorine Dioxide Followed by Chloramine .....	9-20
Table 9-12.	<i>G. muris</i> Inactivation Using Chlorine Dioxide Followed by Chloramine .....	9-20
Table 9-13.	<i>G. muris</i> Inactivation Using Ozone Followed by Free Chlorine.....	9-21
Table 9-14.	<i>B. cereus</i> Inactivation Using Chlorine Dioxide Followed by Free Chlorine .....	9-21
Table 9-15.	<i>G. muris</i> Inactivation Using Ozone Followed by Chloramine.....	9-21
Table 9-16.	<i>G. muris</i> Inactivation by Free Chlorine Followed by Monochloramine.....	9-22
Table 9-17.	<i>C. parvum</i> Inactivation by Sequential Application of Ozone and Chloramine.....	9-22
Table 9-18.	Summary of Combined Disinfectants .....	9-25

Figure 9-1.	Inactivation of <i>C. parvum</i> Attributed to Synergistic Effects. Application of Ozone Followed by Chlorine Dioxide .....	9-14
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Figure 9-2. Inactivation of *C. parvum* Attributed to Synergistic Effects. Application of Chlorine Dioxide Followed by Free Chlorine..... 9-14

Figure 9-3. Inactivation of *C. parvum* Attributed to Synergistic Effects. Application of Chlorine Dioxide Followed by Monochloramine..... 9-15

Figure 9-4. Inactivation of *E. coli* Using Free Chlorine and Monochloramine..... 9-18