

ABSTRACT

TITLE: "IMPACT OF MIXING CHLORINE WITH CHLORINE DIOXIDE ON TTHMS FORMATION IN DRINKING WATER"

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The Surface Water Treatment Rule emphasizes the need for utilities to meet minimum levels of disinfection for surface waters, whereas the Disinfection-Disinfection By-Products Rule limits the disinfectant by-products levels. Therefore, utilities will have to implement a treatment approach that balances the benefits of disinfection against disinfection by-products. After the *Cryptosporidium* outbreak in Milwaukee during March 1993 (4), many utilities began immediately investigating the use of more advanced disinfectants such as ozone and chlorine dioxide in order to combat the threat from the *Cryptosporidium* protozoan. Chlorine alone was not adequate to inactivate the new target organism. Most disinfectants have their consequences in terms of disinfection by-products causing a potentially long-term adverse health impact from cancer. Although chlorine has served the water industry well for about a century in safeguarding the public health, it is relatively ineffective against *Cryptosporidium* and can cause excessive trihalomethanes in distribution systems (5). THMs were limited in drinking water in 1979 to 100 ppb (THM Rule) (6) and are being lowered to 80 ppb to meet impending regulations because of their potential carcinogenic properties. Although ozone is the strongest and most capable disinfectant against *cryptosporidium*, it can have its dark side by producing excessive bromates, a potential carcinogen, in high bromide water (7). However, chlorine dioxide does not cause bromates and is capable of inactivating *Cryptosporidium* but not as well as Ozone. However, there are concerns about its disinfection by-product, chlorites, identified as causing hemolytic anemia, especially in 13% of black males (8). In El Paso, Texas, the Umbenhauer/Robertson Water plant is mixing 2 mg/l of chlorine with 3 mg/l of chlorine dioxide in the same disinfection zone followed by ferrous chloride to reduce the chlorite by-product. This new treatment process has lowered TTHM formation in the distribution system while increasing the disinfection capability as compared to the same chlorine dioxide dose alone. Therefore, the purpose of this paper is to examine the impact of mixing chlorine with chlorine dioxide on the formation of TTHMs. Laboratory and plant dose-response studies are presented to compare the impact of chlorine dose alone, chlorine dioxide dose alone and in combination with chlorine on the formation of TTHMs. The results presented provide a means for chlorine dioxide users to lower their chlorine dioxide cost in meeting lower TTHMs' levels while increasing their disinfection capability.

INTRODUCTION

The 1986 amendments to the Safe Drinking Water Act (1) are challenging many water utilities to meet stricter water quality requirements. Two rules, the Surface Water Treatment Rule (SWTR) (2) and the Disinfection-Disinfection By-Products (D-DBP) Rule (3), are requiring utilities to implement more advanced technologies in water treatment. The Surface Water Treatment Rule emphasizes the need for utilities to meet minimum levels of disinfection for surface waters, whereas the Disinfection-Disinfection By-Products Rule limits the disinfectant by-products. Therefore, utilities will have to implement a treatment approach that balances the benefits of disinfection against disinfection by-products. After the *Cryptosporidium* outbreak in Milwaukee during March 1993 (4), many utilities began immediately investigating the possible use of more advanced disinfectants such as ozone and chlorine dioxide in order to combat the threat from the *Cryptosporidium* protozoan. Chlorine alone was not adequate to inactivate the new target organism. Most disinfectants have their consequences in terms of disinfection by-products causing a potentially long-term adverse health impact from cancer. Although chlorine has served the water industry well for about a century in safeguarding the public health, it is relatively ineffective against *Cryptosporidium* and can cause excessive trihalomethanes in distribution systems (5). THMs were limited in drinking water in 1979 to 100 ppb (THM Rule) because of their potential carcinogenic properties (6). Although ozone is the strongest and most capable disinfectant against *Cryptosporidium*, it can have its dark side by producing excessive bromates, a potential carcinogen (7). If the choice is chlorine dioxide, it is also capable of inactivating *Cryptosporidium* but not as well as Ozone. However, there are concerns about its disinfection by-products such as chlorites, identified as causing hemolytic anemia, especially in 13% of black males (8). In El Paso, Texas, the Umbenhauer/Robertson Water Plant is adding 2 mg/l of chlorine with 3 mg/l of chlorine dioxide in the same disinfection zone in order to minimize TTHM formation and maximize disinfection capability (Figure 1).

The primary purpose of this paper is to examine the impact of adding chlorine with chlorine dioxide on the formation of TTHMs. Laboratory and plant studies are presented to determine the impact of the addition of chlorine alone and in combination with chlorine dioxide on the formation of TTHMs. Since the Eka SVP-Pure Chlorine Dioxide Generator system is a chlorate-based technology and does not have chlorine or chlorite in its generator stock solution, it offers an opportunity for an effective way of identifying the effects of chlorine with chlorine dioxide on the formation of TTHMs. (9)

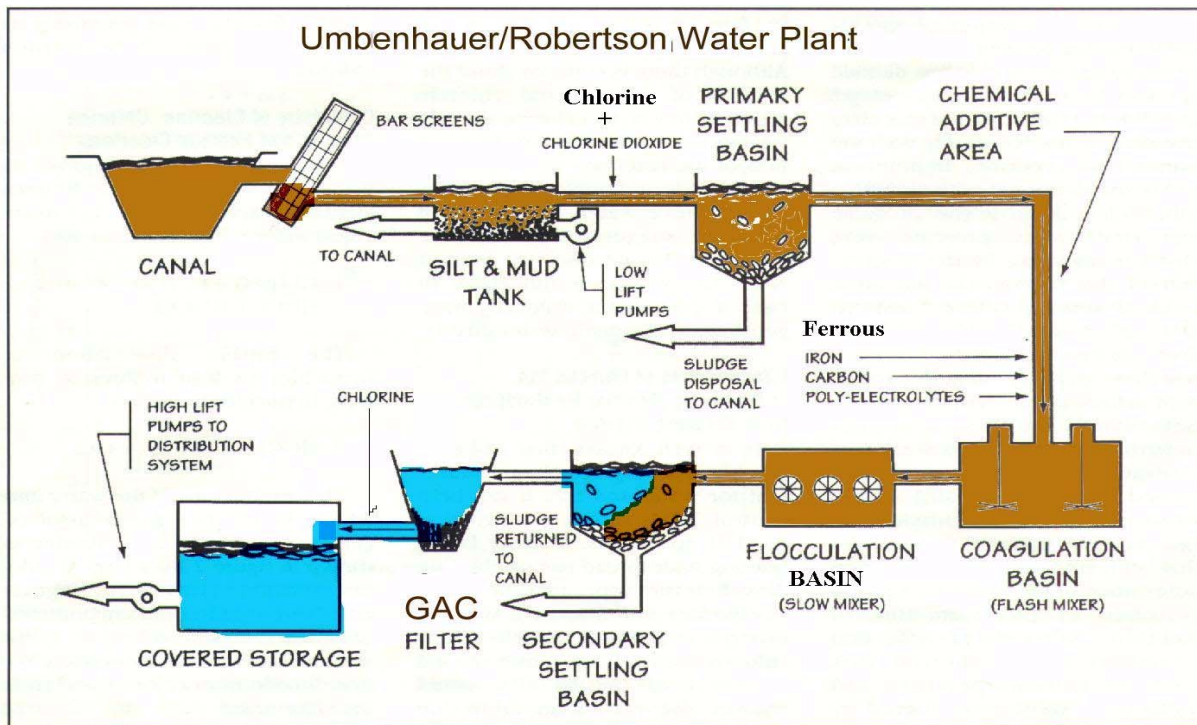


Figure 1 - Umbenhauer/Robertson Water Plant Flow Schematic

LABORATORY STUDY PROCEDURES

This project was carried out using laboratory studies as detailed below. Analyses were performed at the El Paso Water Utilities Central Laboratory and an outside EPA approved laboratory using proper QC/QA procedures. The raw water source for the studies was the Rio Grande River, which was available for treatment normally during the period of March through September in El Paso, Texas. The raw water samples were dosed with chlorine dioxide solutions obtained from the Eka SVP-Pure Chlorine Dioxide Generator utilizing a two solution system containing 40% sodium chlorate/10% hydrogen peroxide (Purate™) and 78% sulfuric acid. (Figure 2). In order to evaluate the impact of adding chlorine with chlorine dioxide on disinfection by-products, raw water samples were dosed with 1, 2, or 3 mg/l of chlorine dioxide and dosed with various amounts of chlorine ranging from 0% (chlorine dioxide alone) to 200% of the chlorine dioxide dose. After the sample sets were initially dosed with chlorine dioxide and chlorine, they were held for about 45 minutes. Then, all of the sample sets were equally dosed with 7 mg/l of chlorine and held for 1-hour contact period in order to compare the effects of various combinations of chlorine dioxide and chlorine on TTHM formation.

Eka SVP-Pure Chlorine Dioxide Generator



Figure 2 - Eka SVP Pure Chlorine Dioxide

COMPARISON OF THE EFFECT OF 1 MG/L OF ClO_2 & Cl_2 DOSES ON TTHMS

Figure 3 shows the effect on TTHM formation of 1 mg/L of chlorine dioxide dosages (using a Chlorate-Based Generator solution), spiked with chlorine doses ranging from 0% chlorine to 200% chlorine. Figure 3 shows that the raw sample dosed with 7 mg/l chlorine alone, held for 1 hour contact time, forms about 42 ppb of TTHMs. The 1 mg/l chlorine dioxide dose with 0% chlorine had insignificant reduction in TTHMs. This is to be expected because the initial chlorine dioxide demand (< 1 minute time) of the Rio Grande River water is usually between 1.5 mg/l and 2.0 mg/l, i.e., there seems to be insufficient dosage to cause a long enough contact time of the chlorine dioxide with TTHM precursors to cause a significant reduction in TTHMs. However, when chlorine is added with the 1 mg/l of chlorine dioxide dose, the TTHM levels are reduced at the 33%, 66%, and 100% chlorine levels. At the 150% and 200% levels, the TTHMs are higher than the 0% chlorine and raw TTHM levels. The results imply that the chlorine with 1 mg/L chlorine dioxide is participating in TTHM reduction by possibly reforming chlorine dioxide with the chlorite by product of chlorine dioxide degradation. Since most water plants

dose at the 1 mg/L chlorine dioxide level, the perception, from most water professionals, is that chlorine dioxide at this concentration can only “prevent” TTHM formation, not reduce TTHMs. However, in this testing, it has been shown that TTHM reduction can be accomplished by adding chlorine with chlorine dioxide, even at the 1 mg/L dosage level. When the chlorite byproduct level is exceeded by the amount of the chlorine necessary to reform chlorine dioxide, the excess chlorine will participate in forming higher TTHMs. This also implies that chlorine is able to reduce the chlorite byproduct levels in order to form chlorine dioxide. As shown in the next section, the chlorite and chlorate levels were analyzed at various % chlorine dosages to determine if chlorite was being reduced by the chlorine.

1 MG/L Chlorine Dioxide & % Chlorine Doses

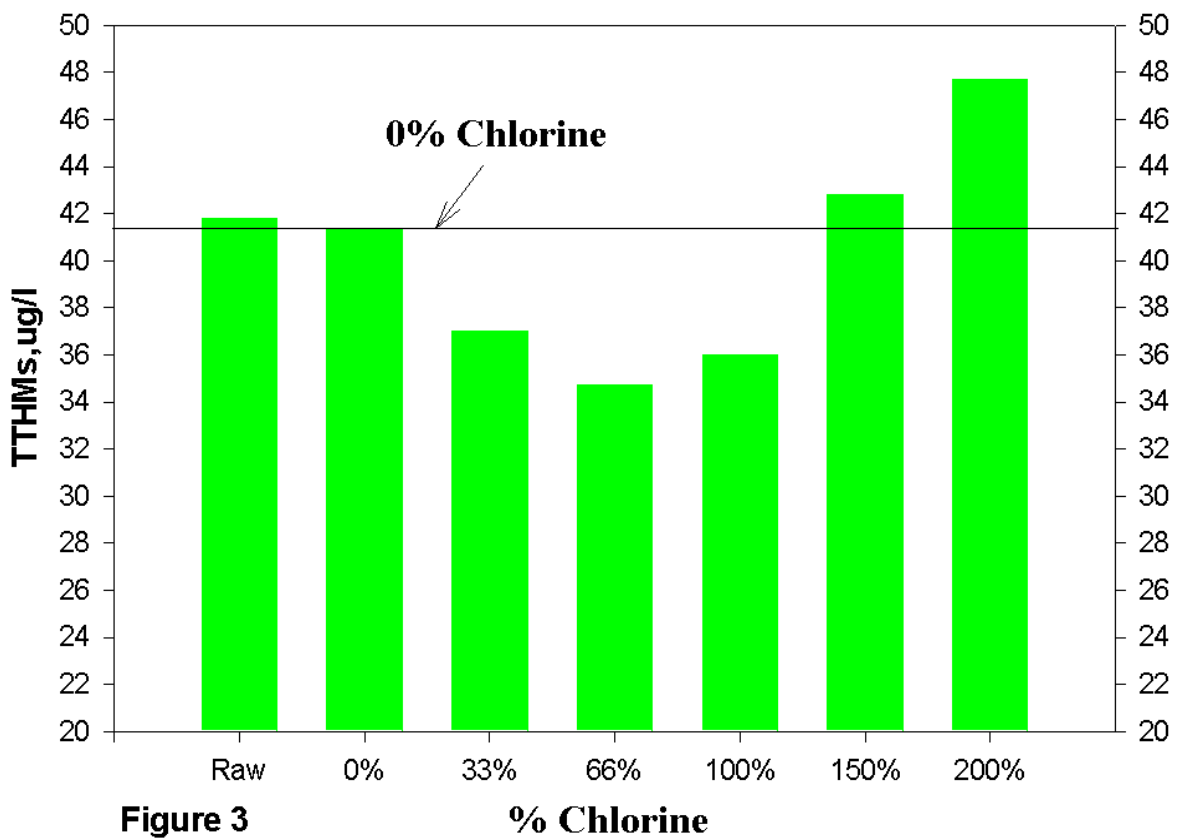


Figure 3

% Chlorine

CHLORINE EFFECT ON CHLORITE AND CHLORATE AT 1 MG/L ClO₂ DOSE

In Figure 4, the chlorite and chlorate levels versus chlorine levels from 0% to 200% are plotted for the same samples depicted in Figure 3. At 0% chlorine, the chlorite level is highest at 0.46 mg/L while the chlorate level is 0.19 mg/L. As the chlorine dosages are increased, the chlorite levels decrease and the chlorate levels are rather flat throughout the range from 0% to 200% chlorine. The overall reduction in chlorite was about 0.10 mg/L (0.46 mg/L to 0.36 mg/L). The chlorate level increase was negligible at about 0.03 mg/L (0.19 mg/L to 0.22 mg/L). Therefore, it seems reasonable that the chlorite reduction is principally caused by the sequence of reactions with chlorine to reform chlorine dioxide, ultimately being reduced to chloride. If the chlorine level exceeds the amount needed by the chlorite level for reforming chlorine dioxide, the amount of the chlorine, not needed for chlorite oxidation, will participate in forming TTHMs. This may be the reason for the lowest TTHM level at about 66% chlorine and the subsequent increase in TTHMs at the 100%, 150%, and 200% chlorine dosages.

Chlorine Effect on Chlorite & Chlorate at 1 MG/L Chlorine Dioxide Dose

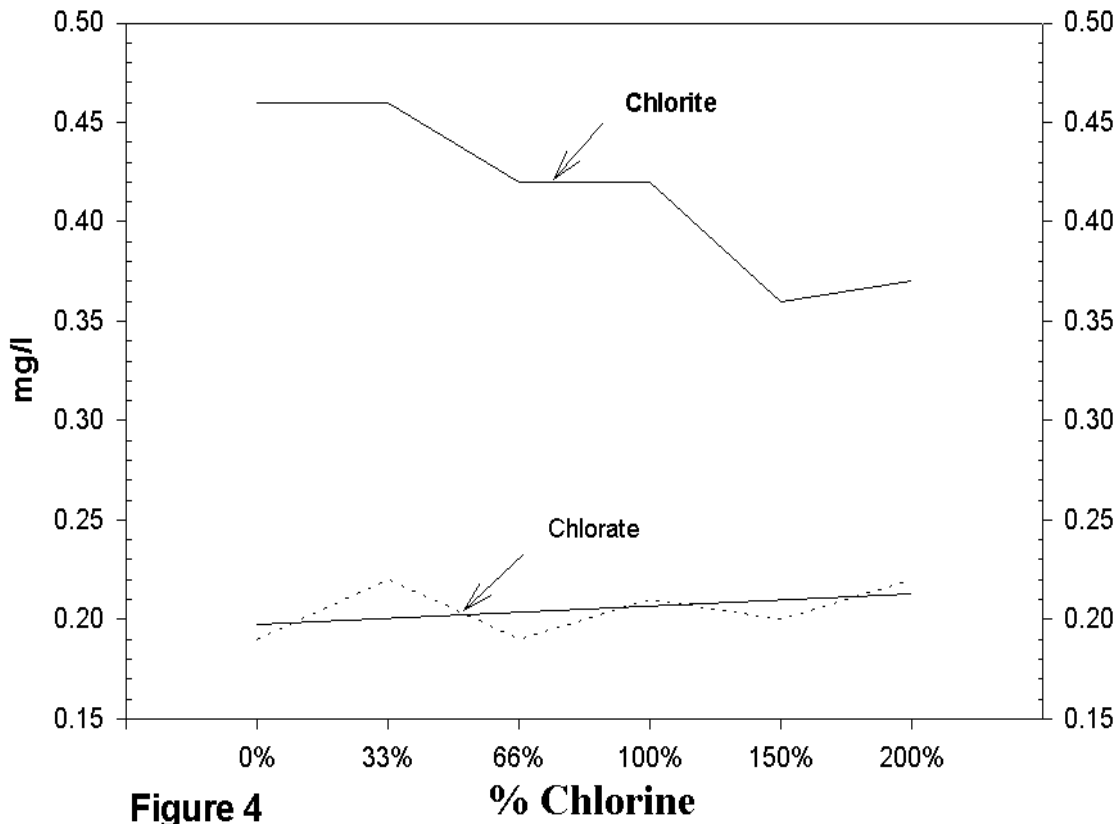
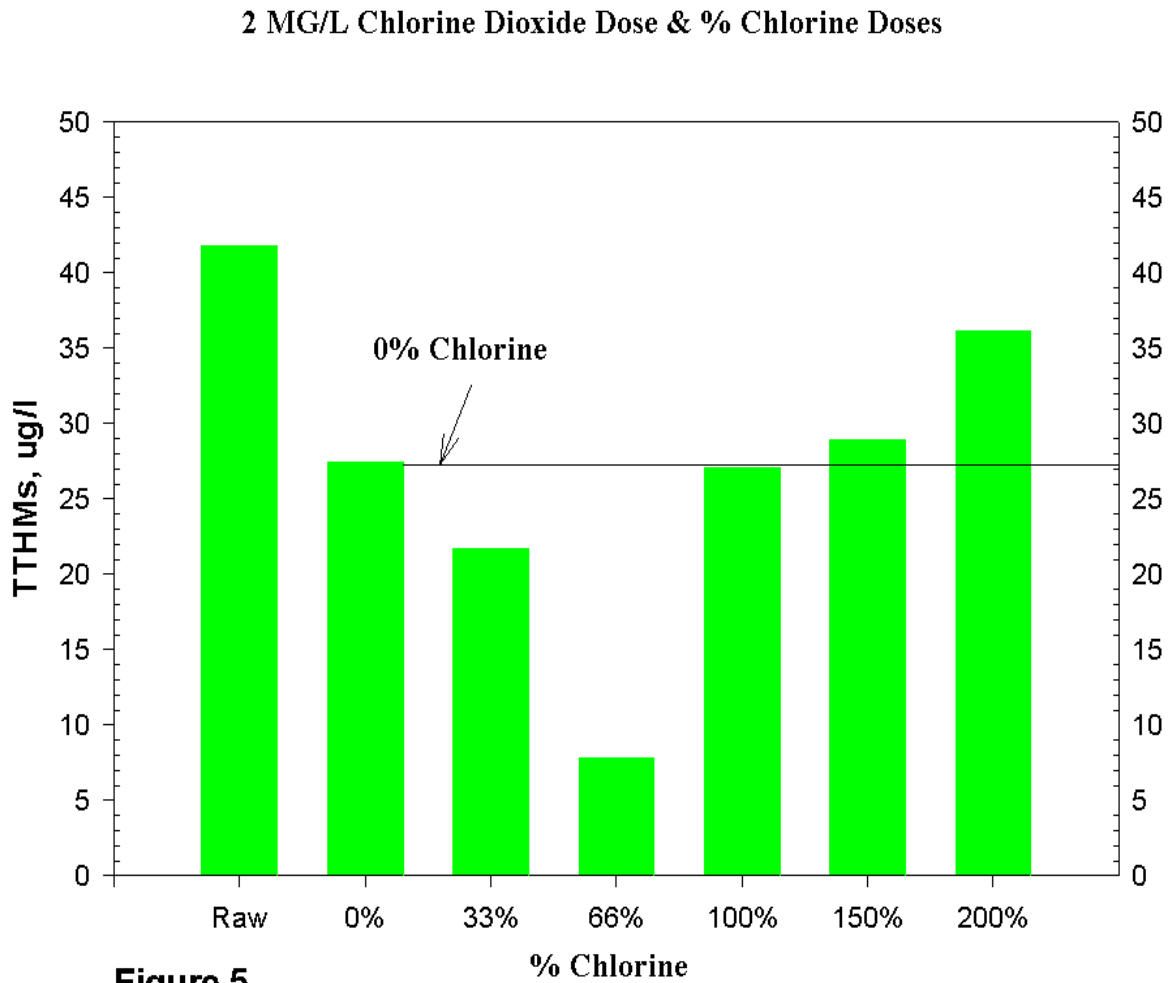


Figure 4

% Chlorine

COMPARISON OF THE EFFECT OF 2 MG/L OF ClO₂ & Cl₂ DOSES ON TTHMS

Figure 5 shows the effect on TTHM formation of 2 mg/L of chlorine dioxide dosages with chlorine doses ranging from 0% chlorine to 200%. The 0% chlorine sample shows a 15 ppb reduction of TTHMs from the raw TTHM level of 42 ppb. The 2 mg/L chlorine dioxide dose is apparently sufficient to exceed the immediate chlorine dioxide demand than the 1 mg/L dose. At the 33% and 66% chlorine doses, the TTHMs are reduced significantly more than the 1 mg/L chlorine dioxide dose with comparable chlorine levels, indicating that more chlorine dioxide is being formed from the reaction between the chlorite byproduct and free chlorine. As before, the 100%, 150%, and 200% chlorine dosages are showing increasing TTHM levels but lower than comparable chlorine levels with 1 mg/L chlorine dioxide doses.



CHLORINE EFFECT ON CHLORITE AND CHLORATE AT 2 MG/L ClO₂ DOSE

Figure 6 shows the chlorite and chlorate levels plotted for chlorine levels from 0% to 200% for the same samples depicted in Figure 5. As before, the chlorite levels are decreasing while the chlorate level increases at a lower rate. The chlorite levels range from 0.90 to 0.69 or 0.21 mg/L difference as compared to the chlorate difference of 0.11 mg/L. The difference in the chlorite range of values is twice the amount compared to the 1 mg/L chlorine dioxide dose indicating that more chlorine dioxide reformation is possible with the greater amount available from the higher chlorine dioxide dose. Therefore, the 2 mg/L chlorine dioxide doses with chlorine reactions seems to have a similar consistent pattern as the 1 mg/L chlorine dioxide doses.

Effect of Chlorine on Chlorite & Chlorate at 2 MG/L Chlorine Dioxide

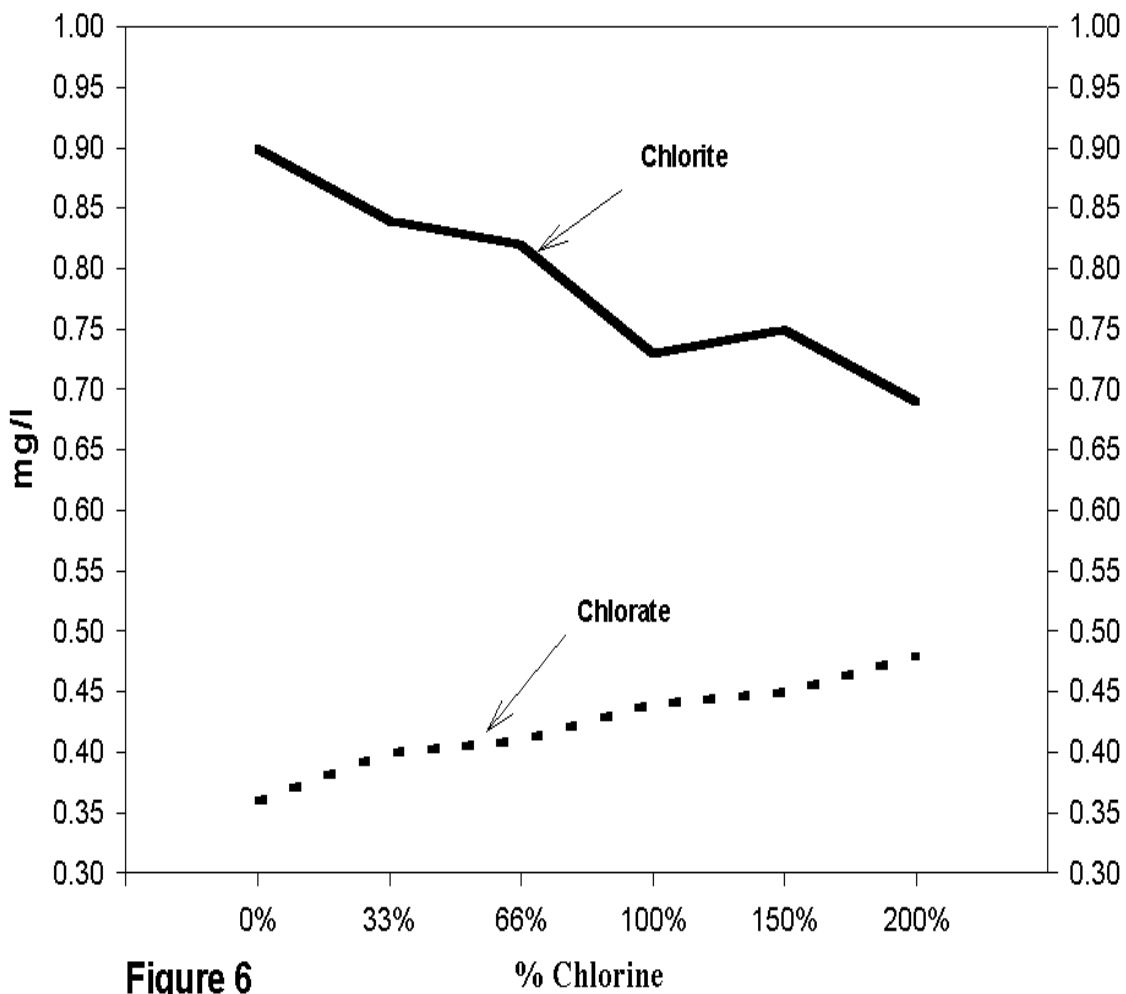


Figure 6

% Chlorine

COMPARISON OF 3 MG/L OF ClO₂ AND EXCESS Cl₂ DOSES ON TTHMS

Figure 7 shows the average effect on TTHM formation from two sets of data depicting 3 mg/L of chlorine dioxide dosages with chlorine doses ranging from 0% chlorine to 200% chlorine level. The 25 ppb TTHM reduction from the raw to the 0% chlorine dose is greater than the 15 ppb reduction obtained at the previous 2 mg/l chlorine dioxide dose. Again, the 25% and 50% chlorine doses show decreasing TTHMs while the 75%, 100%, 150%, and 200% chlorine doses have increasingly higher TTHM values. It seems apparent that 66% chlorine is the most beneficial for TTHM reduction for all three chlorine dioxide dosages.

3 MG/L Chlorine Dioxide & % Chlorine Doses

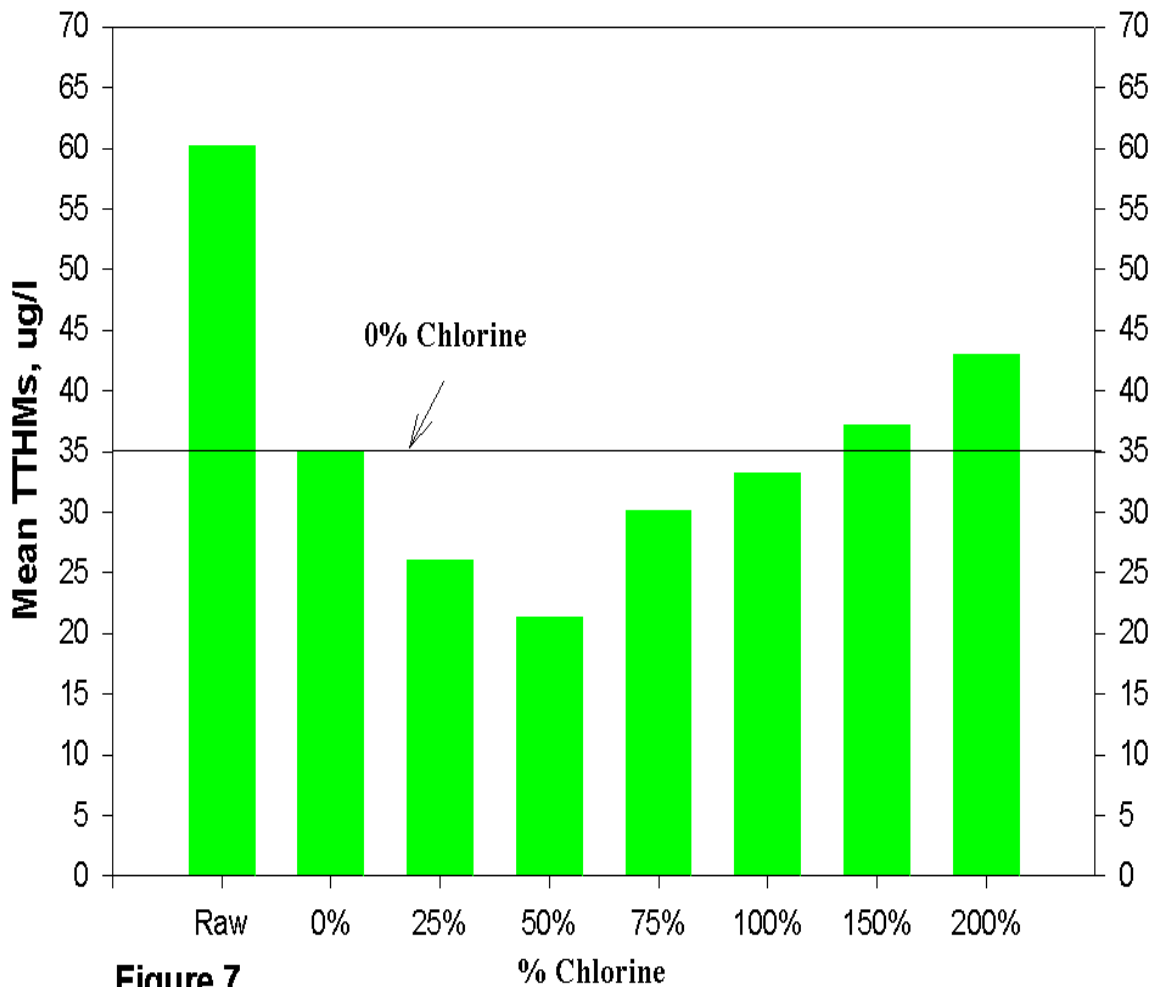


Figure 7

FULL PLANT STUDIES

Since the previous laboratory studies indicated that mixing chlorine with chlorine dioxide is beneficial in reducing TTHM formation, it was important to verify the results on a plant scale. Because El Paso's Canal Plant has two-20 mgd treatment trains, it was ideal for comparison testing of the chlorine dioxide alone versus chlorine dioxide with chlorine doses. Figure 8 depicts TTHM results for samples taken from Plant 1 and Plant 2 secondary effluents. The samples were spiked, like previous laboratory samples, with 7- mg/l chlorine and held for 1-hour contact time in order to form TTHMs. In the first round of plant testing, the Plant 1 raw water was dosed with about 2.5 mg/l chlorine dioxide only. At the same time, plant 2 was also dosed with 2.5 mg/L of chlorine dioxide, but with about 50% chlorine. The results showed that plant 2 with the chlorine had a greater reduction by about 12 ppb TTHMs as compared to Plant 1 with chlorine dioxide alone. Next, it was decided to repeat the experiment by reversing the treatments for each plant. If there were other factors affecting the results in the plant processes, then the results would not repeat. In the second round of plant testing, Plant 1 received the chlorine with chlorine dioxide while Plant 2 received only chlorine dioxide. The TTHM results were almost the same, showing a significantly greater reduction in Plant 1, which was receiving the chlorine dioxide with chlorine.

Plant 1 & 2 Studies of Chlorine Dioxide and with Chlorine

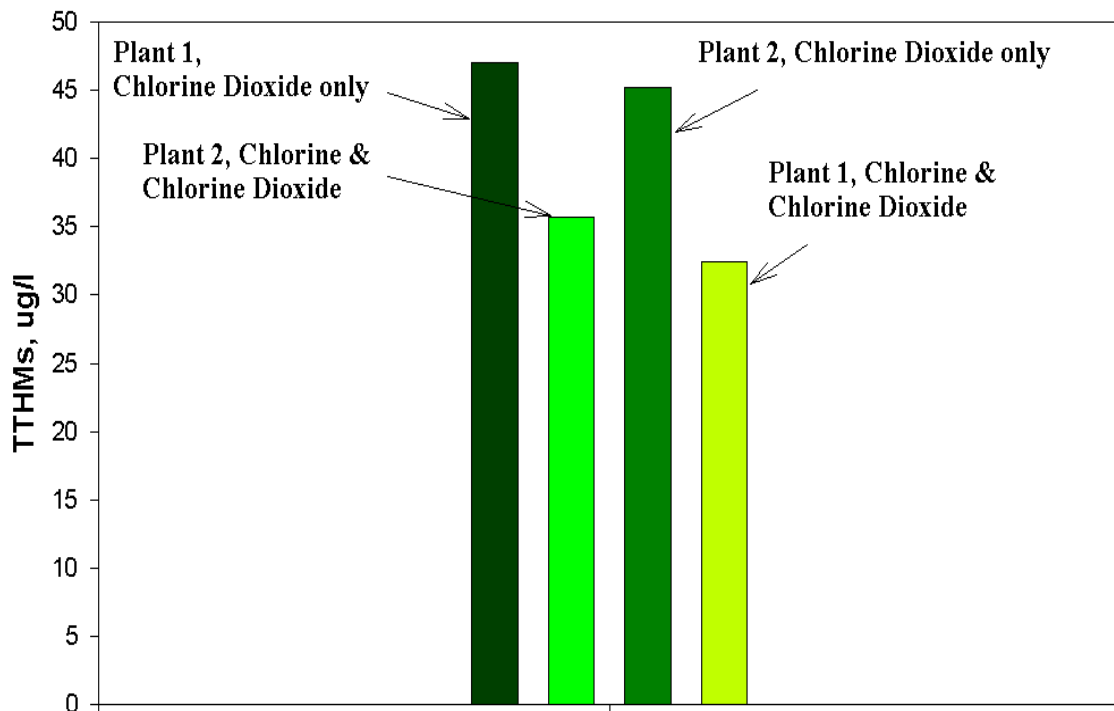


Figure 8

CONCLUSIONS

Based on the laboratory and plant studies conducted in this investigation, the following conclusions can be made with reasonable certainty:

- 1). A 1 mg/L chlorine dioxide dose alone, chlorine dioxide did not reduce TTHMs significantly. However, at 1 mg/L chlorine dioxide dose with 66% chlorine, TTHMs were reduced by 7 ppb or 15%.
- 2). The 2 mg/L and 3 mg/L chlorine dioxide doses with 0% chlorine were able to reduce the TTHMs. However, the 66% chlorine dose in combination with these higher chlorine dioxide doses was able to reduce TTHM formation considerably more.
- 3). Increasing Chlorine Dioxide doses with 66% chlorine showed a higher rate of TTHM reduction, perhaps, because higher chlorite by-product levels are available for reaction with higher chlorine levels to reform chlorine dioxide.
- 4). The laboratory and plant data suggest that about 66% chlorine mixed with chlorine dioxide reduces TTHMs better than chlorine dioxide alone at all three chlorine dioxide dosages studied in this investigation.
- 5). Chlorite reduction occurs at a greater rate than chlorate formation with increasing chlorine doses added to chlorine dioxide.
- 6). The Eka SVP-Pure Chlorine Dioxide Generator was able to obtain additional TTHM reduction when chlorine was added.

RECOMMENDATIONS

On the basis of the results presented in this paper, additional investigations are warranted to:

- 1). Determine if synergistic disinfection benefits are possible with 66% chlorine mixed with chlorine dioxide.
- 2). Determine if CT disinfection credit can be determined for both the chlorine and chlorine dioxide in the same disinfection zone.
- 3). Determine if the oxidation of iron and manganese occurs with the 66% chlorine mixed with chlorine dioxide and if TTHM reduction is adversely impacted when these elements are present.

ACKNOWLEDGEMENTS

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