Impact of Combining Chlorine Dioxide and Chlorine in Minimizing Chlorite and THM Levels at Aurora, Colorado and El Paso, Texas

By

Douglas Rittmann, Ph.D., P.E., Consultant, El Paso

Kevin Linder, Superintendent, Aurora Water Utilities

Brad Zachman, Operations Specialist, Aurora Water Utilities

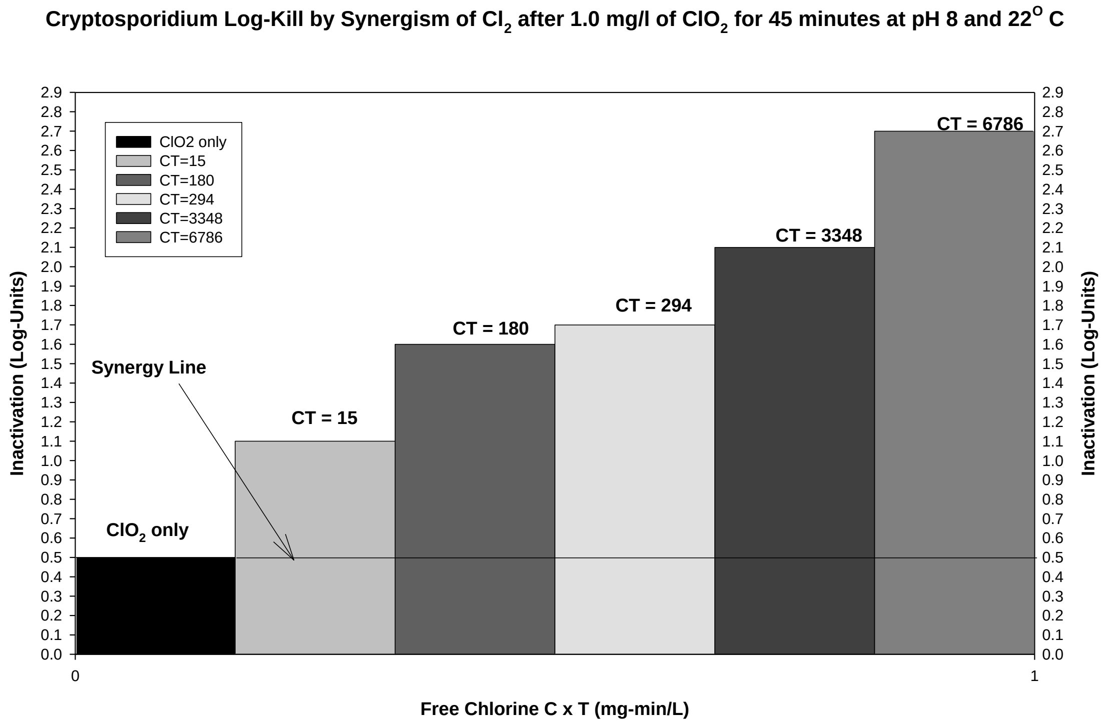
Abstract

The cities of Aurora, Colorado and El Paso, Texas demonstrated through laboratory and plant studies the synergistic benefits of combined treatment of chlorine dioxide and chlorine in reducing chlorite levels and THM levels in the distribution system. Gordon Finch, in the late 90's, has already showed synergistic disinfection benefits from sequential addition of chlorine dioxide and chlorine for *Cryptosporidium sp*. inactivation at lower CT levels than for chlorine dioxide alone. Similarly, this paper will demonstrate the synergistic benefits of additional THM and chlorite reduction from combined disinfectants. Aurora was able to meet lower chlorite and THM levels by mixing chlorine at various ratios with chlorine dioxide. Similarly, El Paso mixed chlorine with chlorine dioxide doses from 3 to 7.5 mg/L using ferrous chloride for chlorite reduction in order to reduce THMs significantly more compared to chlorine dioxide alone. It was shown that chlorine preferentially reacts with the chlorite byproduct from the chlorine dioxide dose and thereby lowered the chlorite level, instead of it reacting first with THM precursors. Linear regression equations were developed to predict THMs with R^2 levels greater than 0.90 based on various independent variable levels for TOC, pH, chlorine dioxide dose, chlorine dose, and contact times. Because chlorine is synergistic with chlorine dioxide and satisfies some of the chlorine dioxide demand, the treatment cost can be lower for meeting disinfection and disinfection byproduct goals compared to using higher chlorine dioxide dosages alone in pretreatment. By combining these oxidants in water treatment, their advantages can be maximized while their disadvantages can be minimized.

Introduction

Gordon Finch, in the late 90's, showed synergistic disinfection benefits from sequential addition of chlorine dioxide and chlorine for *Cryptosporidium sp.* inactivation at lower CT levels than for chlorine dioxide alone (Figure 1).[1] In the last 10 years, El Paso Texas and Aurora Colorado have also shown the synergistic benefits in combining chlorine dioxide with chlorine in reducing chlorite levels and TTHMs levels in laboratory and plant studies. This new research and development is needed and timely because of the implementation of Stage 2 Disinfection and Disinfection By-Products Rule. With increasing disinfection requirements and lower disinfection byproduct levels, water plants will need treatment options that are more capable while being more cost effective. This paper will demonstrate this capability in using the combination of chlorine dioxide and chlorine in pretreatment.

Figure 1 – Combined Effect of Chlorine Dioxide and Chlorine on *Cryptosporidium sp.*

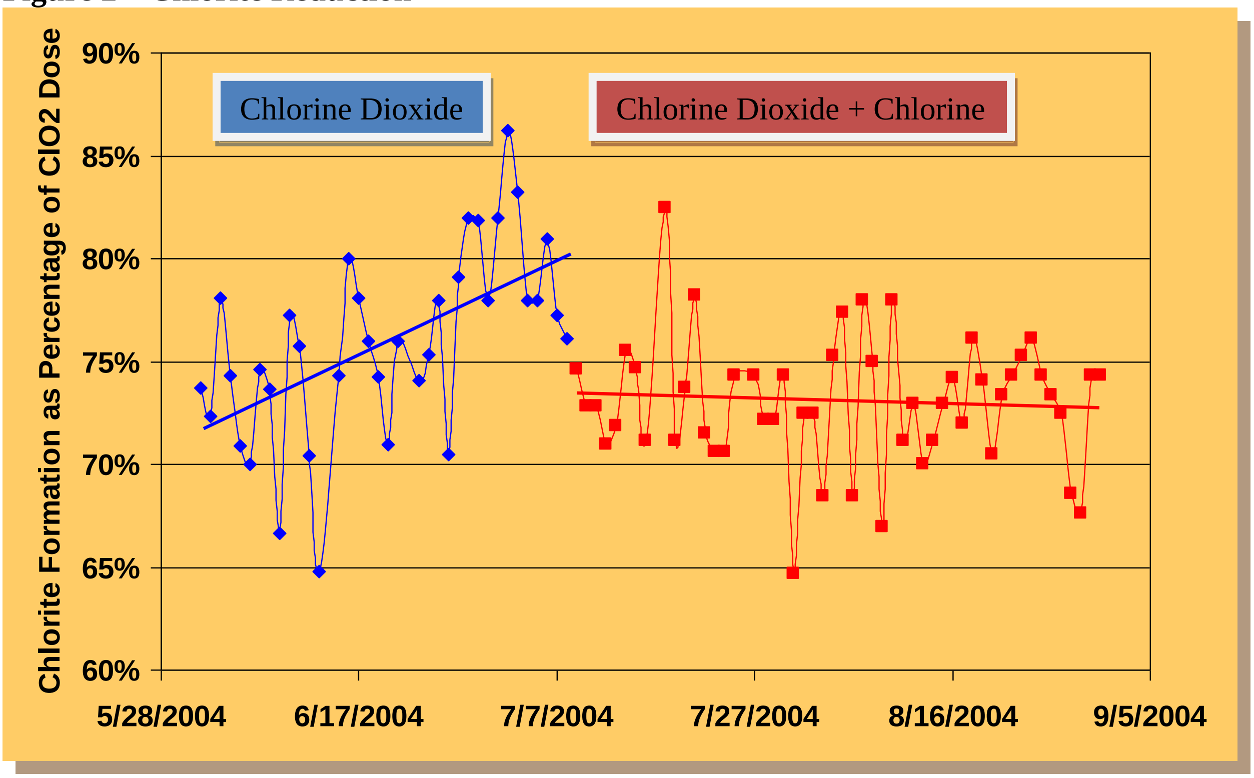


Reducing Chlorite Formation at Aurora, Colorado

Aurora Water's 80-mgd Wemlinger Water Treatment Facility was modified in 2002 by replacing chlorine with chlorine dioxide as the primary disinfectant. Chlorine dioxide use eliminated the need to construct new chlorine contact basins while meeting the Stage 2 Disinfectants and Disinfection byproducts Rule with a relatively small capital investment. Although the chlorine dioxide dose was not to exceed 1.4 mg/L in order to meet the 1.0 mg/L chlorite maximum contaminant level (MCL), the chlorite formation was 85% of the chlorine dioxide dose instead of the typical 70% maximum amount (Figure 2). Also, the decay rate of the chlorine dioxide was more rapid than expected. Therefore, the Wemlinger operations group faced the challenge of providing adequate CT while meeting the chlorite MCL goal. Based on Dr. Douglas Rittmann's research, the co-application of chlorine dioxide and chlorine could reduce the chlorite level and TTHM levels in the distribution system. Another benefit was that the co-application of chlorine and chlorine dioxide permitted both chemicals to satisfy the CT requirement in the same disinfection zone by the Colorado Drinking Water Regulations.

When both chemicals are fed together, it was hypothesized that the chlorite byproduct from the chlorine dioxide reacted preferentially with the free chlorine to re-form chlorine dioxide while reducing the chlorite level to 73% of the chlorine dioxide dose from 80% to 85% observed at startup. Also, the chlorine satisfies some of the demand that was previously required for the chlorine dioxide. Bench-scale results demonstrated that a 1:1 ratio of chlorine to chlorine dioxide was ideal in reducing chlorite and TTHM levels in the distribution system.

Figure 2 – Chlorite Reduction



<u>Distribution TTHMs from Chlorine Only Treatment at Aurora Colorado</u>

Table 1 reports the actual versus predicted TTHMs from chlorine only treatment during the period of February, 2001 to October, 2003 prior to the use of chlorine dioxide mixed with chlorine treatment at the Wemlinger Water Plant starting about May, 2004. The actual distribution system average THMs were 20.8 µg/L to 53.5 µg/L. The distribution system uses chloramination to minimize THM formation. Without pre-chlorination treatment, THMs were reduced to less than the Stage 2 maximum requirement but the plant needed to have a pre-disinfectant capability for additional safety from potential bacteriological breakthrough of the filters. Therefore, replacement of pre-chlorination with chlorine dioxide was determined a feasible alternative to pre-chlorination with the possibility of reducing TTHMs even more.

Figure 3 depicts table 1 data. A standard least squares JMP software model with effect leverage was used to determine predictive TTHMs based on the independent variables of finished water chlorine dosages, finished water pH levels, and finished water TOC levels. Although temperature and contact time are usually important variables in predicting TTHMs, they were not significant to more accurate results. The finished water temperatures for the samples were 6 degrees C to 16.6 degrees C which reflected a wide range of temperature conditions and certainly influenced the actual THMs to some degree. Also, the contact time would not have significant leverage to the predicted model likely due to the chloramination treatment in the distribution system as free chlorination would have in the El Paso Water System.

Table 1 – Distribution TTHMs Model Data using Chlorine Only at Wemlinger Plant

Sample Number	Date	Distribution THM Average, µg/L	Predicted THM Average, µg/L	Residuals, µg/L	Final Cl_2 Dose, mg/L	Finished Water TOC, mg/L	Finished Water pH
1	2/23/2001	20.8	23.7	- 2.9	3.7	1.27	7.43
2	4/20/2001	30	27.2	+2.8	3.8	1.48	7.44
3	9/19/2001	42.6	40.8	+1.8	4.2	1.99	7.73
4	11/12/2001	31.1	26.2	+4.9	4.2	1.36	7.45
5	1/11/2002	21.5	24.0	- 2.5	4.0	1.34	7.36
6	2/8/2002	22.4	24.2	- 1.8	4.0	1.30	7.41
7	3/8/2002	22.8	25.9	- 3.1	4.0	1.26	7.54
8	5/17/2002	26.3	26.1	+0.2	4.2	1.31	7.49
9	5/9/2003	47.7	50.8	- 3.1	5.2	2.8	7.51
10	6/13/2003	53.5	53.4	+0.1	8.0	2.69	7.51
11	9/22/2003	35.7	32.7	+3.0	4.3	1.9	7.34
12	10/6/2003	41.7	41.0	+0.7	5.2	2.3	7.39
	Maximum	53.5	53.4	+4.9	8.0	2.8	7.73
	Minimum	20.8	23.7	-3.1	3.7	1.26	7.34
	Average	33.0	33.0	.008	4.6	1.75	7.47

The whole model graph in figure 3 depicts the actual versus predicted TTHMs. The R-Square was excellent at 0.94 for the range of independent variables. The leverage graphs (3a, 3b, 3c) determine if the independent variables are significant in predicting the dependent variable of average distribution system TTHMs. When the leverage graph passes at an angle across the mean line, then the independent variable is significant in its leverage. The best leverage was TOC at P = 0.0005 while pH at P = 0.1008 and chlorine dose at P = 0.2734 are less significant. The lower the P value the more significant the leverage on the dependent variable. The TTHM data average was 33 µg/L for the actual and predicted values with the residuals range from -3.1µg/L to + 4.9 µg/L, which is within the experimental error of THM analysis. The TTHMs predictive equation is: Predictive Average Distribution TTHMs, µg/L = -133.5 + (1.5 * Final Cl_2 Dose, mg/L) + (15.3 * Finished Water TOC, mg/L) + (17.8*Finished Water pH).

Figure 3- Actual versus Predicted THMs Model

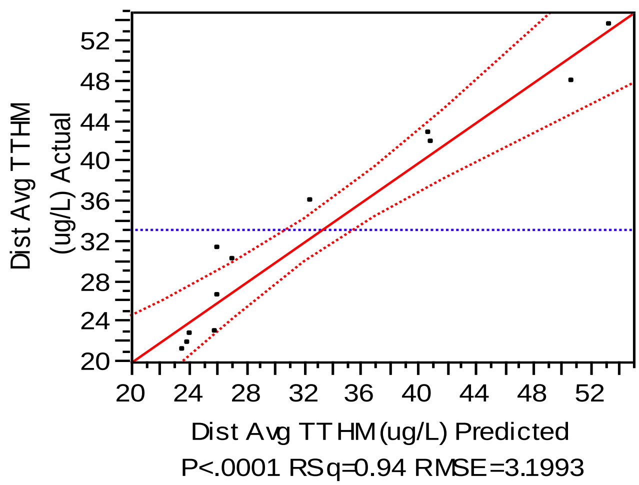


Figure 3a – THMs versus TOC Leverage

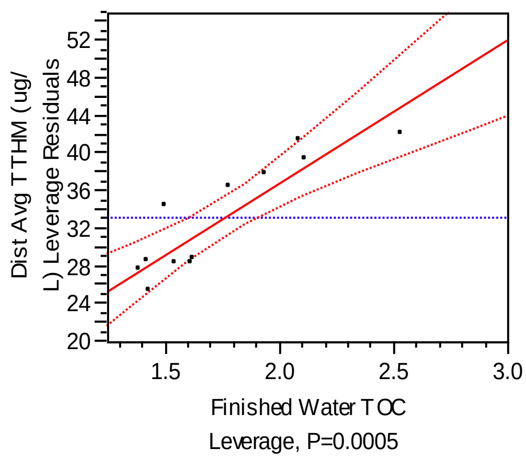


Figure 3b – THMs versus pH Leverage

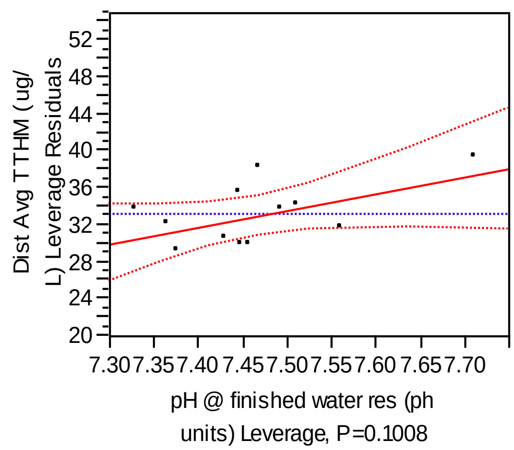
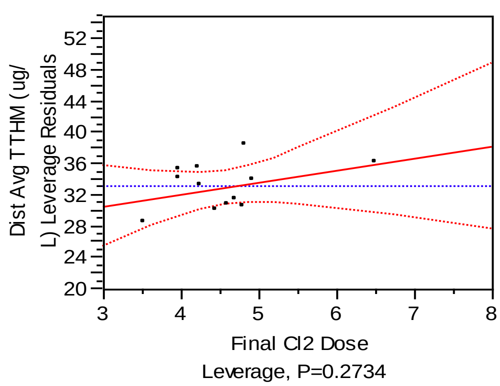


Figure 3c – THMs versus Chlorine Dose Leverage



Distribution TTHMs using Chlorine Dioxide mixed with Chlorine at Wemlinger Plant

Table 2 reports on 23 samples of actual versus predicted TTHMs from chlorine dioxide combined with chlorine in pretreatment at Wemlinger Water Plant during the period of July, 2004 to October, 2008. The actual distribution system average TTHMs were 9.8 µg/L to 26.3 µg/L with an average of 16.4 µg/L. The chlorine dioxide dosages were 0.55 mg/L to 1.05 mg/L combined with chlorine dosages of 0.4 mg/L to 1.2 mg/L. The final pH levels of the water were 7.27 to 7.8 but had little leverage on the prediction model and therefore were not included in the equation. This was expected because the range of values was small and chloramines minimized their effect on TTHM formation. The water temperatures were 5.8 degrees C to 19 degrees C and the finished TOC were 1.18 mg/L to 3.2 mg/L but they had reduced effect on the model outcome which was, again, minimized by chloramination. However, they were included.

Table 2 – Actual THMS versus Predicted THMs using ClO2 mixed with Cl2

Sample	Date	Actual Dist. Average THMs, µg/L	Pred. Dist. Average THMs µg/L	Residuals, µg/L	ClO_2, mg/L	Cl_2 Feed mg/L	Final Cl_2 Dose mg/L	Finish pH	Finish Temp., C^o	Finish TOC, mg/L
1	7/23/04	26.3	26.0	0.3	1.05	1	1.9	7.3	19	1.9
2	8/6/04	24.9	25.8	-0.9	1.05	1	1.95	7.38	18.4	2.5
3	9/10/04	25.4	25.1	0.3	1	0.85	2	7.32	17.7	3.2
4	10/8/04	23.8	23.6	0.2	1	0.85	2	7.45	15.6	1.96
5	3/11/05	13.7	14.7	-1.0	0.68	0.45	1.9	7.61	9	1.51
6	4/8/05	13.8	14.0	-0.2	0.65	0.43	1.95	7.62	10	1.66
7	6/10/05	21.9	21.6	0.3	0.9	0.75	2.1	7.29	16.6	2.57
8	9/9/05	18.1	18.3	-0.2	0.7	1	1.5	7.42	17.9	1.85
9	11/4/05	17.8	16.4	1.4	0.7	0.7	1.7	7.58	12.4	1.57
10	12/16/05	12.3	11.1	1.2	0.6	0.6	2	7.8	8.4	1.66
11	1/13/06	11.1	11.6	-0.5	0.6	0.6	1.9	7.59	7.3	1.63
12	2/10/06	12.6	13.8	-1.2	0.65	0.65	1.85	7.54	9.5	1.81
13	3/10/06	13.1	12.9	0.2	0.65	0.7	2	7.76	8.9	2.66
14	4/7/06	12.7	13.6	-0.9	0.65	0.7	1.95	7.62	11.6	1.75
15	5/5/06	11.3	12.4	-1.1	0.6	0.7	2.1	7.48	15	1.46
16	6/9/06	15.3	14.6	0.7	0.65	0.75	2	7.57	17	1.6
17	10/6/06	13.4	14.1	-0.7	0.7	0.9	2.15	7.79	15.4	2.05
18	11/3/06	13.4	13.0	0.4	0.7	0.9	2.1	7.76	11.5	1.61
19	6/8/07	20.3	20.6	-0.3	0.9	1.2	2	7.41	17	2.92
20	10/5/07	18.2	17.5	0.7	0.75	0.95	2	7.53	17.9	2.69
21	2/8/08	11.8	11.3	0.5	0.6	0.6	1.95	7.27	6.3	1.18
22	3/10/08	9.8	9.4	0.4	0.55	0.7	1.9	7.53	5.8	1.32
23	10/10/08	15.6	15.2	0.4	0.7	0.4	2.35	7.4	14.3	2.01
Max.		26.3	26.0	+1.4	1.05	1.2	2.35	7.8	19	3.2
Min.		9.8	9.4	-1.2	0.55	0.4	1.5	7.27	5.8	1.18
Avg.		16.4	16.4	0.10	0.74	0.76	1.97	7.52	13.1	2.00

The whole model graph in figure 4 depicts the actual versus predicted TTHMs. The R-Square value was excellent at 0.98 for the range of independent variables. The leverage graphs (4a, 4b, 4c, 4d, 4e) determine if the independent variables are significant in predicting the dependent variable of average distribution system TTHMs. As before, when the leverage graph passes at an angle across the mean line, then the independent variable is significant in its leverage. The leverage was excellent for the chlorine dioxide dose ($P<0.0001$), chlorine feed ($P = 0.008$), final chlorine dose ($P=0.0005$), and water temperature ($P=0.0006$) but the final TOC ($P=0.2554$) had reduced effect. The pH effect was not significant because of the narrow range of values and the chloramines effect. The TTHM data average was 16 µg/L for the actual and predicted values which were about one half of the chlorination only model of 33 µg/L. The residuals were -1.2 µg/l to +1/4 µg/L which, again, were within the experimental error of THM analysis. The predictive equation factors of the independent variables show two negative effects on THMs from chlorine feed and the final chlorine dose which may indicate the re-formation of chlorine dioxide by the reaction of free chlorine with the chlorite byproduct but the positive factor for chlorine dioxide dosage may indicate that the chlorine dioxide has a significant effect but not participating in oxidation of humic and fulvic acids (THMs) due to its low dosage and relatively short persistence in the water. The re-formation of chlorine dioxide may also slow the rate of THM formation until ammonia is added for chloramines treatment as compared to when free chlorine is only available. The chlorination only model also showed a greater positive effect on THMs from pH and TOC. Whatever is the exact cause of the lower THMs from combining chlorine dioxide and chlorine, the important fact is that 50% reduction is real and significant and should not be dismissed.[2]

On the other hand, the El Paso Water Plant equations showed negative factors for chlorine dioxide and TOC because their chlorine dioxide dosage is much higher at 3 mg/l mixed with 2 mg/L chlorine which permit sufficient oxidation and duration for reduction of THM precursors. The literature also states that chlorine dioxide is effective in oxidizing THM precursors when chlorine dioxide dosages are greater than 2.0 mg/L but, typically, plants that dose at less than 1.4 mg/L show THM reductions because they are replacing free chlorine in pretreatment.[3] The combined effect of chlorine dioxide and chlorine seems to enhance THM reduction at lower dosages too which was also shown in El Paso's bench-scale testing. The TTHMs predictive equation is: Predictive TTHMs, µg/L = 4.90 + (27.6 * ClO_2, mg/L) + (-4.1 * Cl_2 feed, mg/L) + (-5.5* Final Cl_2 dose) + (0.29 * Final Temperature, C^o) + (0.56 * Final TOC, mg/L).

The El Paso Water Utility management wanted to meet the TTHM goal by using free chlorine in the distribution system instead of chloramines as was done in Aurora. This would be challenging because the Rio Grande River water source in El Paso had double the available TOC (4.0 mg/L average) at higher water temperatures with longer chlorine contact times in the distribution system. Over a three year period, bench-scale and plant studies were performed. There were three treatment scenarios compared in the evaluation. They were: 1). chlorine only in pretreatment through finished water; 2). chlorine dioxide in pretreatment with free chlorine in finished water; 3). chlorine combined with chlorine dioxide in pretreatment followed by free chlorine in finished water. The pretreatment contact time was one hour and the finished water had an average of 24 hours contact time at maximum water demand.

Figure 4 – Actual THMs vs. Predicted THMs

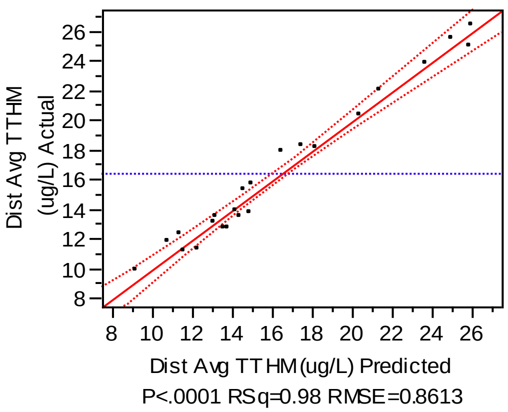


Figure 4a – Actual THMs vs. ClO_2 Feed

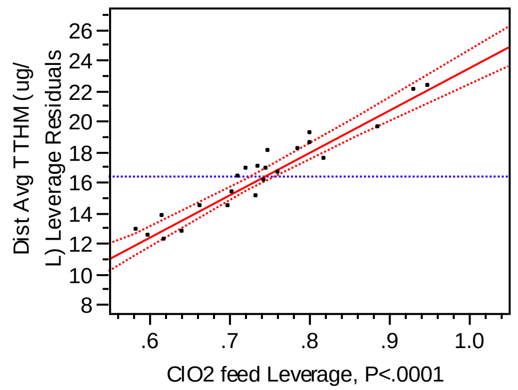


Figure 4b- Actual THMs vs. Cl_2 Feed

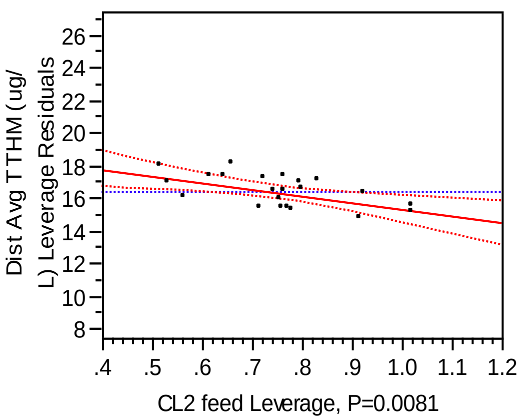


Figure 4c – Actual THMs vs. Temperature

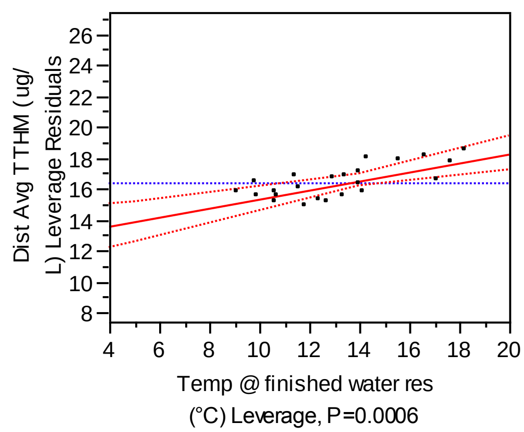


Figure 4d = Actual THMs vs. TOC

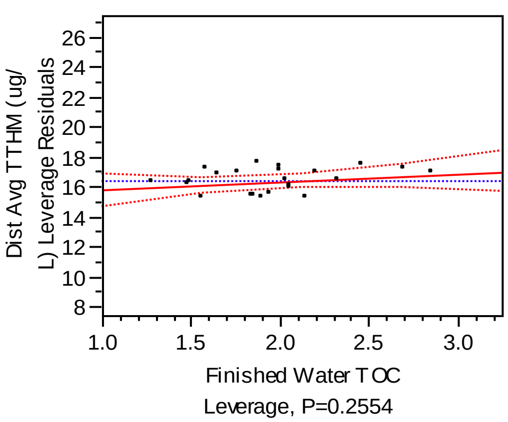
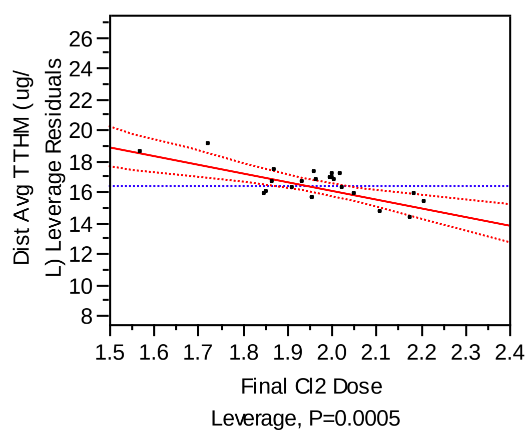


Figure 4e – Actual THMs vs. Final Cl_2 Dose

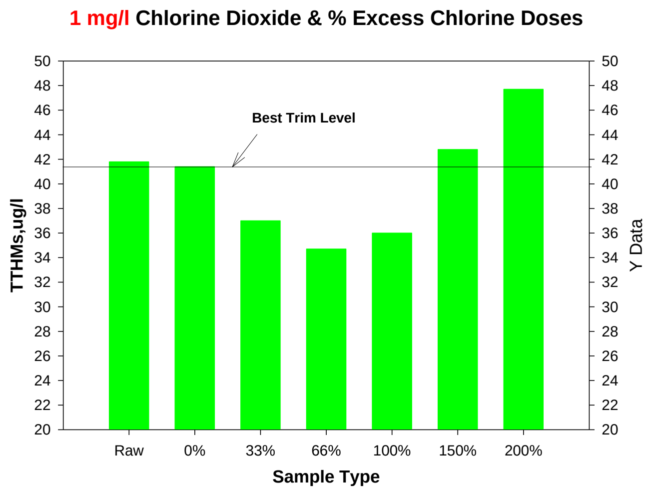


Laboratory Bench-Scale Testing at El Paso Canal Water Plant

This project began by performing 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 (PurateTM) and 78% sulfuric acid. 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% 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 ratios of chlorine dioxide and chlorine on TTHM formation.

Figure 5 shows the effect on TTHM formation of 1 mg/L of chlorine dioxide dosages (using a Eka Chlorate-Based Chlorine Dioxide Generator solution), spiked with chlorine doses ranging from 0% chlorine (chlorine dioxide only) to 200% chlorine dose of the chlorine dioxide dose. The Figure 5 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 (chlorine only). 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 reality is that chlorine dioxide at this concentration can “prevent” TTHM formation, not reduce TTHMs compared to post chlorination only. 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 compared to post chlorination only. 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 re-form chlorine dioxide. As shown in figure 6, the chlorite and chlorate levels were analyzed at various % chlorine dosages to determine if chlorite was being reduced by the chlorine.

Figure 5 – Effect on TTHMs from 1 mg/LClO_2 & Cl_2



In Figure 6 the chlorite and chlorate levels versus chlorine levels from 0% to 200% of the 1 mg/L chlorine dioxide dosages are plotted for the same samples depicted in Figure 5. At 0% chlorine (chlorine dioxide only), 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 0.36mg/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.

Figure 6 – Effect on Chlorite and Chlorate levels at 1 mg/L ClO_2 & Cl_2

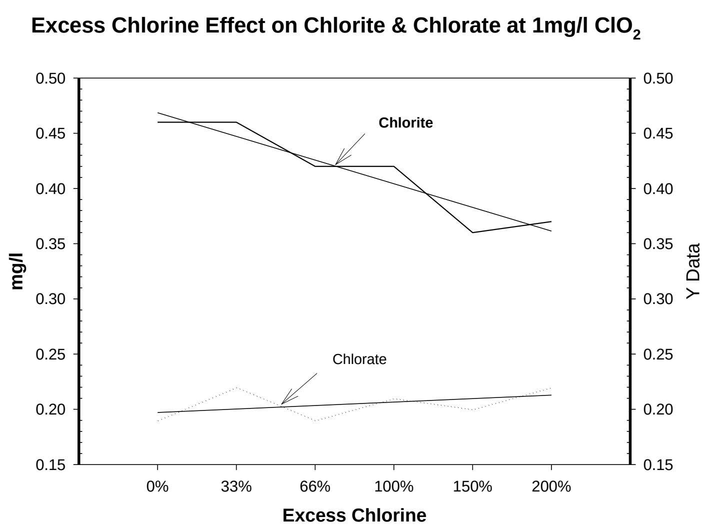


Figure 7 shows the effect on TTHM formation of 2 mg/L of chlorine dioxide dosages with chlorine doses ranging from 0% chlorine to 200%. The 0% chlorine sample (chlorine dioxide only) shows a 15 ppb reduction of TTHMs from the raw TTHM level of 42 ppb. The 2 mg/L chlorine dioxide dose is apparently sufficient 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.

Figure 7 – Effect on TTHMs 2 mg/L ClO_2 & Cl_2

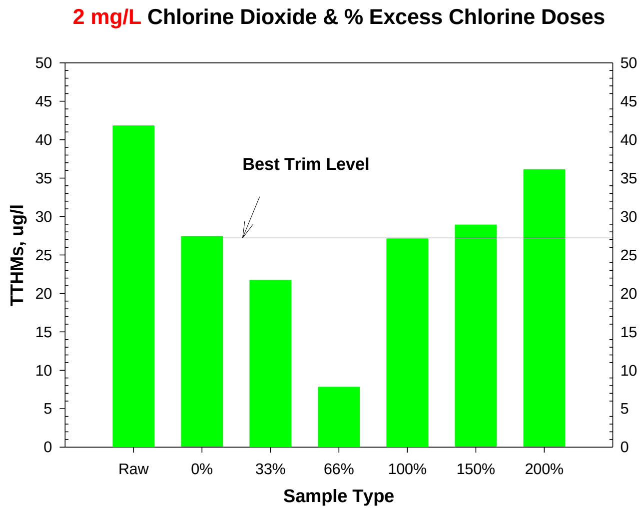


Figure 8 shows the chlorite and chlorate levels plotted for chlorine levels from 0% to 200% for the same samples depicted in Figure 6. As before, the chlorite levels are decreasing while the chlorate level increases at a lower rate. The chlorite levels range from 0.90 to 0.69 or 0.21 mg/L difference 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 re-formation is possible with the greater amount available from the higher chlorine dioxide dose. Therefore, the 2 mg/L chlorine dioxide dosages with chlorine reactions seem to have a similar consistent pattern as the 1 mg/L chlorine dioxide doses. The chlorate levels were determined to originate from the addition of chlorine in the hypochlorite solutions and not from the reaction of chlorine with the chlorite.

Figure 8 – Effect on Chlorite and Chlorate Levels at 2 mg/L ClO_2 & Cl_2

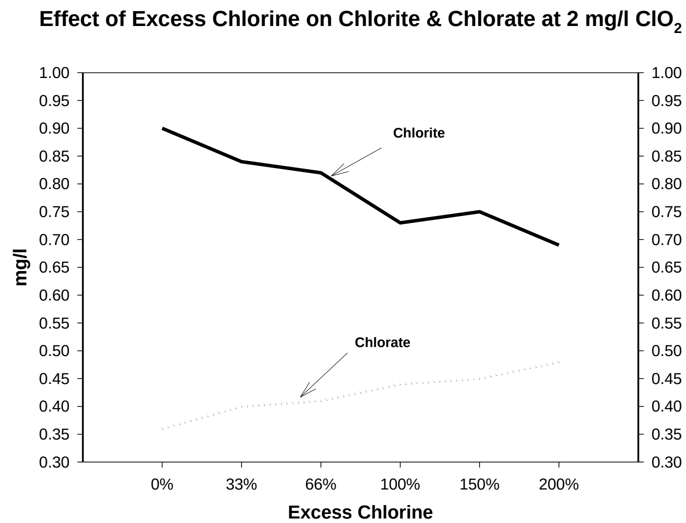
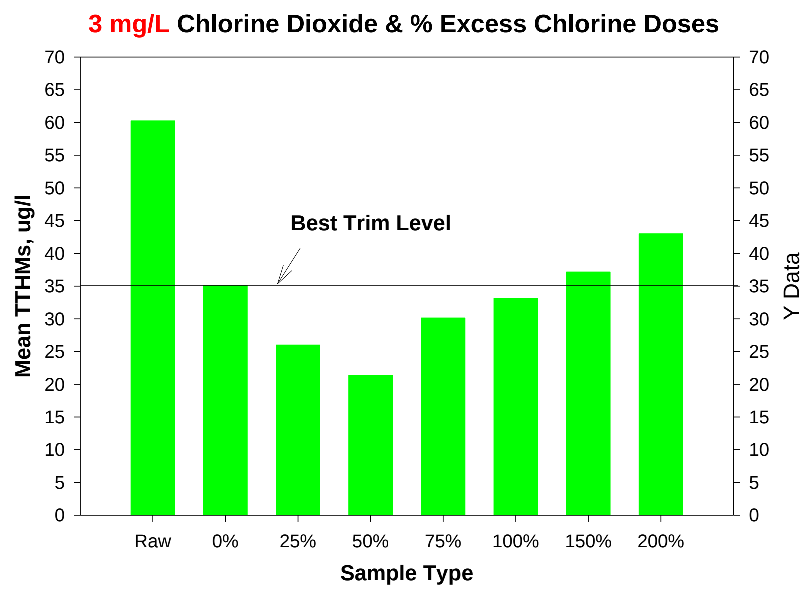


Figure 9 shows the average effect on TTHM formation from two sets of data depicting 3 mg/L of chlorine dioxide dosages with chlorine doses ranging from 0% chlorine to 200% chlorine level. The 25 ppb TTHM reduction from the raw at the 0% chlorine dose is greater than the 15 ppb reduction obtained at the 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.

Figure 9 - Effect on TTHMs 3 mg/L ClO_2 & Cl_2



Model Equations for Cl_2 only, ClO_2 only, and Combined Cl_2 with ClO_2

Three model equations were developed to determine the effects of chlorine, chlorine dioxide, TOC, contact time, and pH on TTHMs in laboratory experiments at a constant temperature of 23 degrees C. Based on these model equations, figure 10 depicts the comparison of the results for three conditions of 1). 7 mg/L chlorine dosage alone for 24 hours contact time, 2). 3 mg/L chlorine dioxide dosage alone for 1 hour contact time followed by 7 mg/L of chlorine dose for 24 hours contact time 3). 3 mg/L chlorine dioxide dosage mixed with 2 mg/L chlorine for 1 hour contact time followed by 7 mg/L chlorine dosage for 24 hours contact time. Samples were also pH adjusted from 5 to 9 prior to adding oxidants. The regression equation calculations reflect the maximum level of TOC formed at 5 mg/L and 24 hours contact time. The 7 mg/L chlorine dosage for 24 hours contact time calibrated well with the maximum TTHMs formed in the El Paso distribution system at various pH levels.

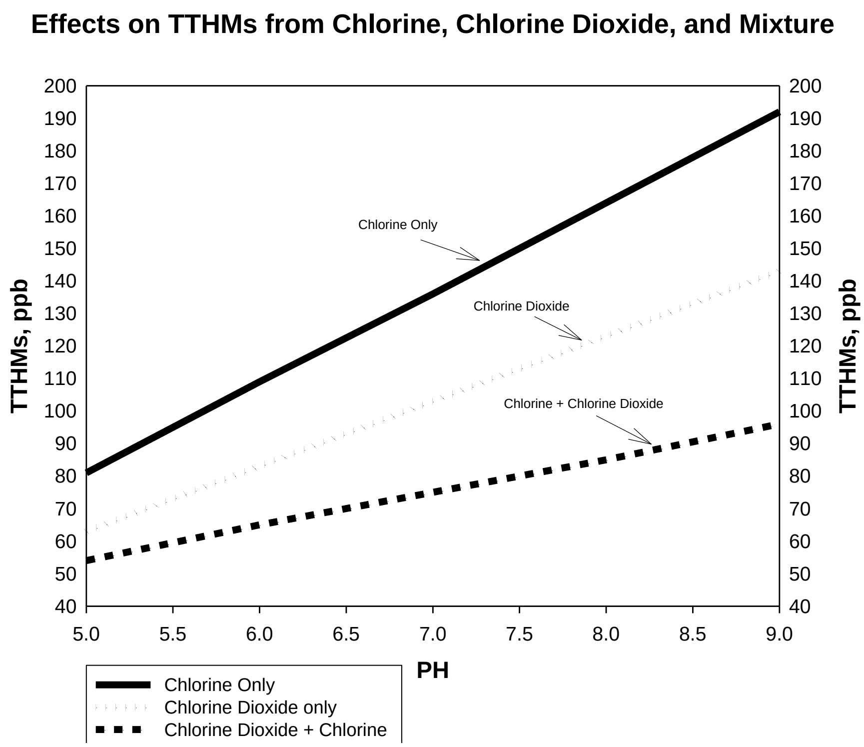
The predictive equation for chlorine dosages alone was: Predicted TTHMs, µg/L = -201.6 + (0.87 * Cl_2, mg/L) + (4.88 * Time, hours) + (4.27 * TOC, mg/L) + (27.69 * pH). The ranges of the independent variables for the chlorine alone model were as follows: 1). chlorine dosages were 2 mg/L to 100 mg/L, 2). pH levels were from 5 to 9, 3). TOC levels were 2.8 to 5.9 mg/L, and 4). contact times were 1 hour and 24 hours. There were 27 samples analyzed with an R- square of 0.94. The leverage effect was significant (P = <0.0005) from chlorine, contact time, and pH but had a reduced effect from TOC (P= 0.4931)

The chlorine dioxide only model predicted THM results based on 3 to 7.5 mg/L chlorine dioxide dosages at 1 hour contact time followed by chlorine dosages of 2 to 7 mg/L at contact times of 1 hour and 24 hours for pH levels from 5 to 9 and TOC concentrations ranging from 2.8 to 5.3 mg/L. Seventeen samples were analyzed. The whole model equation was as follows: Predicted THMs, µg = -89.4 + (-11.2* ClO_2, mg/L) + (4.1 * Cl_2, mg/L) + (3.8 * Time, hours) + (-11.4 * TOC, mg/L) + (21.8 * pH). The R square was excellent at 0.94 with a mean of response of 60.5 ppb THMs and all independent variables had significant leverage (P = <0.0005). The negative factors for chlorine dioxide dose and TOC of -11.2 ppb and -11.4 ppb per mg/L, respectively, showed the oxidation potential of chlorine dioxide in reducing THM precursors (humic acid and fulvic acid) because, in these experiments, the TOC was not removed by coagulation or filtration, i.e., each raw sample was dosed only with the oxidants.

The combined chlorine dioxide and chlorine dosages were generated in a Rio Linda Chlorine dioxide generator (25% chlorite with chlorine gas) by over-feeding the chlorine up to 75% over the best trim setting for chlorine dioxide generation. Twenty sample runs were performed under the following test conditions: 1). chlorine dioxide dosages were 3 to 7.5 mg/L, 2). The chlorine dosages added for TTHM formation potential were from 0 to 100 mg/L, 3). The chlorine contact times were 1 hour and 24 hours, 4). The TOC concentrations were 2.6 mg/L to 5.1 mg/L, 5). The pH levels were adjusted from 5 to 9. The predicted TTHMs, µg/L = -154.0 + (- 1.63 * ClO_2, mg/L) + (0.60 * Cl_2, mg/L) + (3.61 * Time, hours) + (14.4 * TOC, mg/L) + (12.74 * pH units). R-square was equal to 0.95 with a mean response of 64.4 ppb. The leverage was significant (P = <0.05) for the independent variables except the chlorine dioxide dose had a reduced effect (P = 0.3133). The factors for the intercept, chlorine, and pH were significantly lower compared to the chlorine dioxide only model. The whole model equation predicted TTHMs at about 1/3 of the chlorine only model and about ½ of the chlorine dioxide model. The rate of TTHM reduction per mg/L of chlorine dioxide was 18 ppb with 1:0.66 ratio of dosages compared to 8 to 10 ppb per mg/L of chlorine dioxide dose in the chlorine dioxide only model. The Wemlinger Plant's rate of TTHM reduction per mg/l was 22 ppb at a ratio of 1:1 chlorine dioxide to chlorine dosages.

In figure 10, the raw water dosed with 7 mg/l of chlorine only had a 28 µg/L TTHM increase per pH unit ranging from 81 ppb at pH 5 to 192 ppb TTHMs at pH 9. The 3 mg/L chlorine dioxide dose with 7 mg/L finished water chlorine dose had 20 µg/L increase of TTHMs per pH unit ranging from about 62 ppb to 142 ppb TTHMs at pH 9. The 3 mg/L chlorine dioxide dose mixed with 2 mg/L of chlorine followed by 7 mg/L finished water chlorine dose had 10 ppb increase per pH unit ranging from 54 µg/L at pH 5 to 95 ppb at pH 9. This last treatment scenario was chosen as the preferred option for full scale operation. In the early 1990's, based on Mark Griese's[4] and Iatrou's[5] papers concerning chlorite reduction by ferrous ion, El Paso began using ferrous chloride to reduce excessive chlorites from a 2.5 mg/L chlorine dioxide dose. However, in 1999, El Paso decided to increase the chlorine dioxide dose to 3.0 mg/L mixed with 2 mg/L of chlorine in order to reduce TTHMs further. The plant has been able to meet the Stage 2 Disinfection/Disinfection By-Product Rule requirements with the 3 mg/L chlorine dioxide dose mixed with 2 mg/L chlorine dose at finish water pH 7.0 as predicted in figure 10 below.

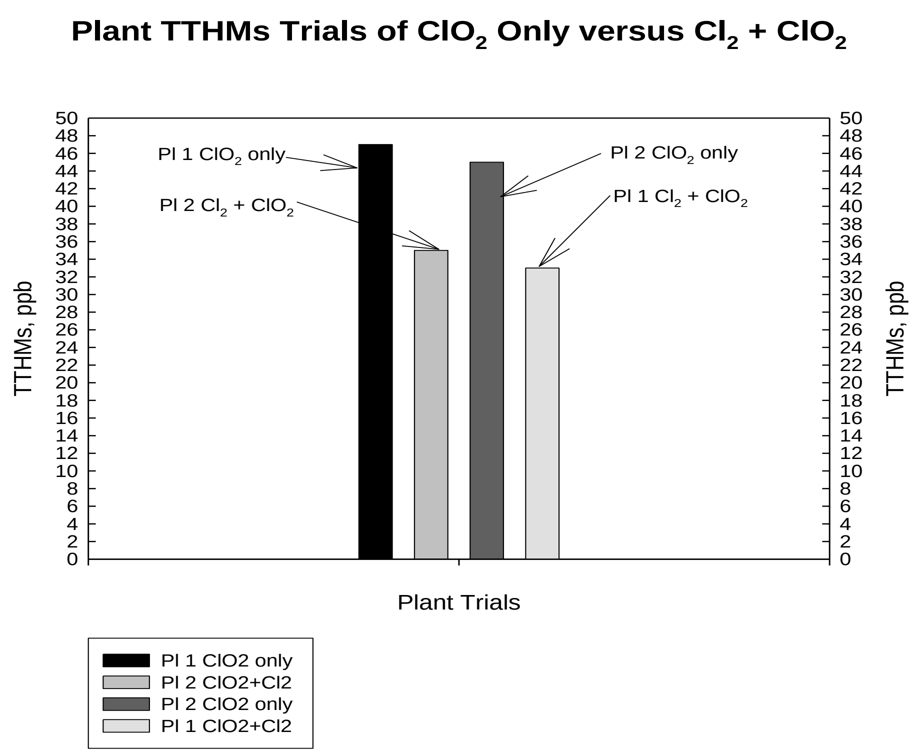
Figure 10 – Linear Model Equations Calculated Effects on TTHMs



Plant Studies at Canal Water Plant in El Paso, Texas

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 11 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 mixed with about 50% chlorine or 1.25 mg/L. The results showed that plant 2 with the chlorine & chlorine dioxide 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.[6,7]

Figure 11 – Canal Plant Testing of ClO_2 versus Cl_2 & ClO_2



Conclusions

The following conclusions can be made with reasonable certainty:

1. The Wemlinger Plant in Aurora Colorado has shown through bench-scale and plant studies that the chlorite level can be reduced by mixing chlorine and chlorine dioxide.
2. The TTHM system data average was 16 µg/L with combined chlorine dioxide and chlorine dosages at 1:1 ratio for the Wemlinger Plant, which was about one half of the chlorine only TTHM distribution system average of 33 µg/L.
3. The TTHM reduction was 22 µg/L per mg/L of chlorine dioxide mixed with chlorine at 1:1 ratio from Wemlinger Plant compared to El Paso Canal Plant's 18 µg/L per mg/L of chlorine dioxide mixed with chlorine at 1:0.66 ratio.
4. El Paso bench-studies showed that 1 mg/L ClO_2 dose to raw water had no reduction in TTHM formation potential but 1 mg/L ClO_2 mixed with 0.66 mg/L Cl_2 reduced TTHMs formation potential by 19%.
5. El Paso bench-scale studies showed that chlorine dioxide mixed with chlorine at a ratio of 1:0.66, respectively, is optimum for THM reduction.
6. El Paso lowered TTHMs at the rate of 18 µg/L per mg/L chlorine dioxide mixed with chlorine in the range of 3 to 7.5 mg/L of chlorine dioxide dose compared to 8 to 10 µg/l per mg/L when chlorine dioxide only is used.
7. The combined chlorine dioxide and chlorine whole model equation predicted TTHMs at about 1/3 of the chlorine only model and about ½ of the chlorine dioxide only model in El Paso.

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