Impact of ClO_2 Pre-oxidation of Ozone on Bromate Formation

by

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Study Objectives

1. Determine effect of O_3 residual & O_3 contact time on Bromates
2. Determine effect of ClO_2 on reducing BrO_3 .
3. Determine effect of ozonation on chlorite and chlorate levels.
4. Maintain chlorite level at less than 0.1 mg/L in the finish water.
5. Develop predictive BrO_3 equations for O_3 alone and O_3 w/ClO_2
6. Increase disinfection capability of the ozone while lowering bromate levels.

Initial Assumptions

* BrO_3 Formation is due to O_3 Concentration & Contact Time

* Peroxone Treatment prevents Bromate Formation

* ClO_2 reduces BrO_3 formation from Ozonation

Background

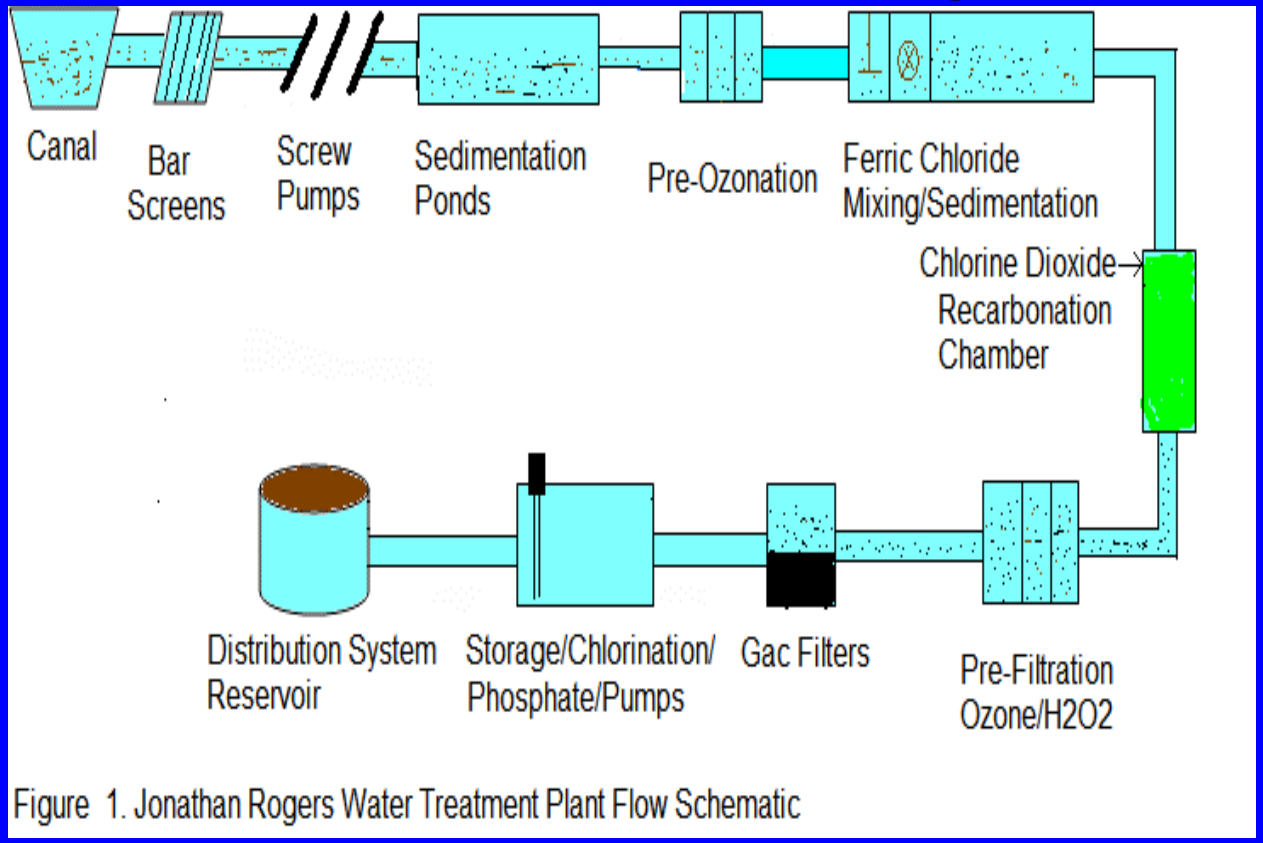


Figure 1. Jonathan Rogers Water Treatment Plant Flow Schematic

Bromate Formation during July, 2002 @ Contra Costa

Condition	Ozone Dose, mg/L	Bromide, ppb	TOC, mg/L	UV 254	Bromate, ppb
Ozone only	2	160	2.0	0.085	24.7
0.5 ClO_2	2	180	2.1	0.095	14.3
1.0 ClO_2	2	180	2.1	0.095	5.2
0.5 NH3-N	2	210	2.0	0.087	16.9
pH 6.5	2	180	2.0	0.085	13.3
pH 6.0	2	180	2.0	0.085	5.6
Ozone only	4	180	2.1	0.095	60.3
0.7 ClO_2	4	180	2.0	0.085	51.1
1.0 ClO_2	4	160	2.0	0.085	57.3

Eka ClO_2 Generator & Rotometers

Purate & Acid Storage

Disinfection Synergy from Combined Oxidants

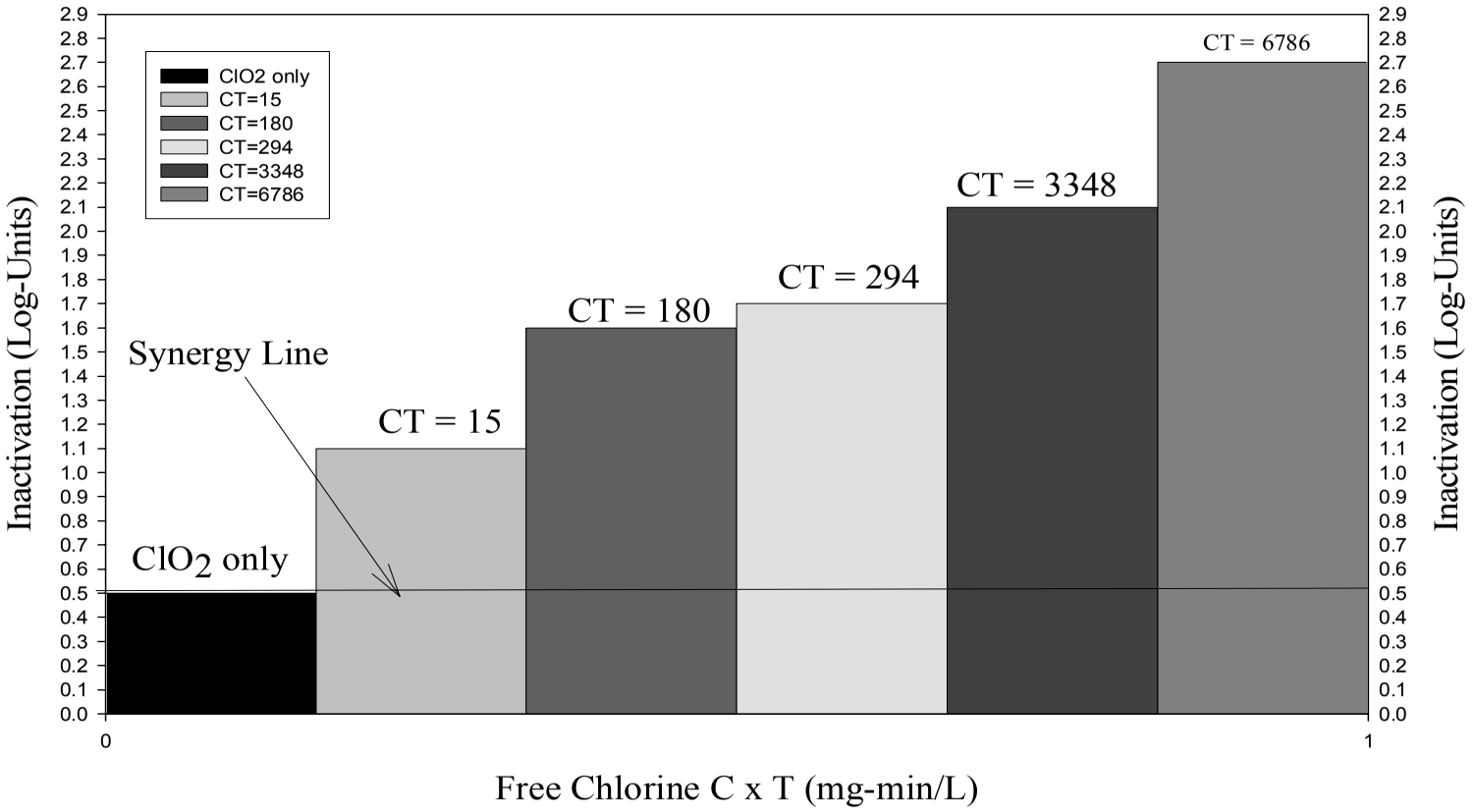


Figure 2. Cryptosporidium Log-Kill by Synergism of Cl_2 after 1.0 mg/l of ClO_2 for 45 minutes

Disinfection Synergy from Combined Oxidants

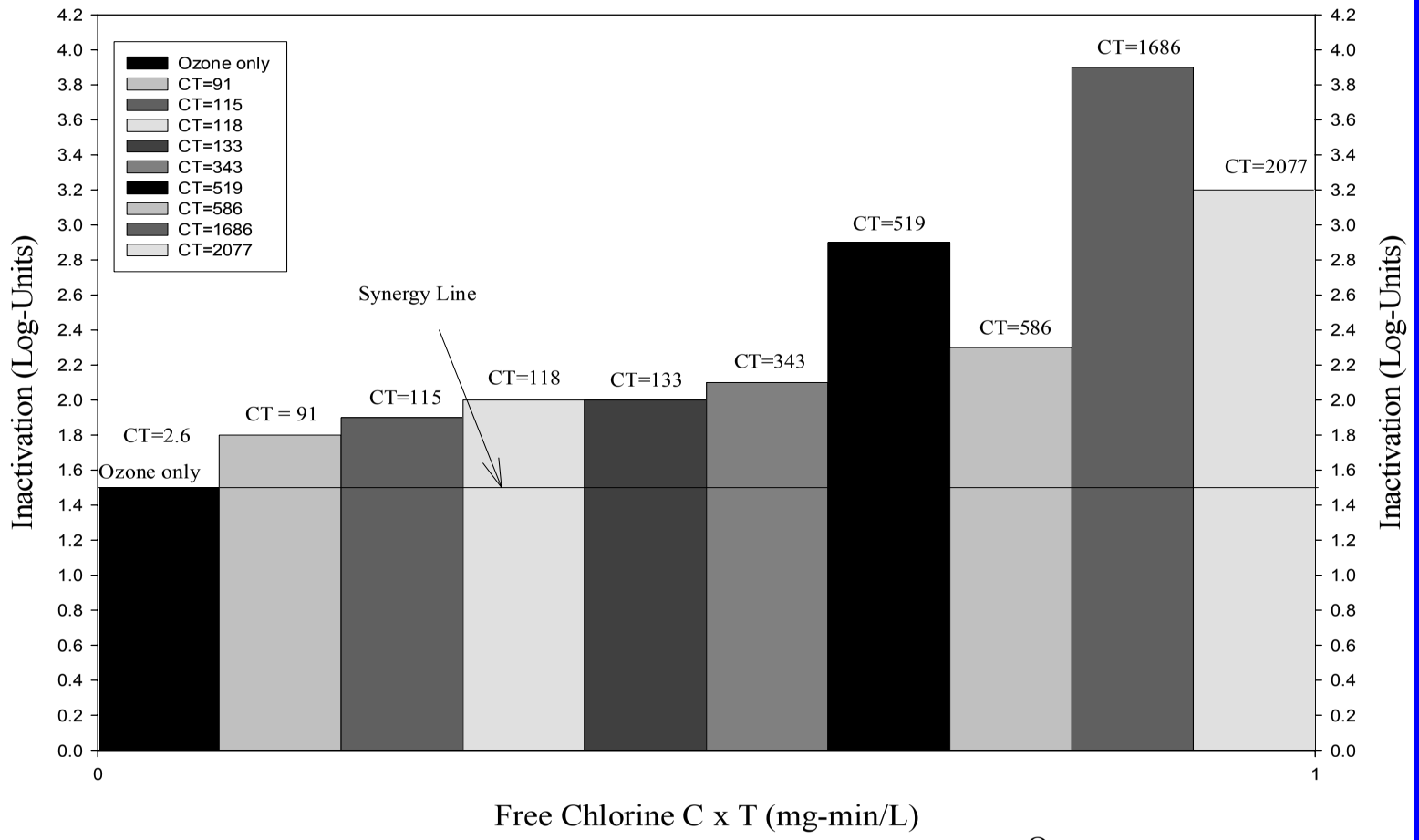
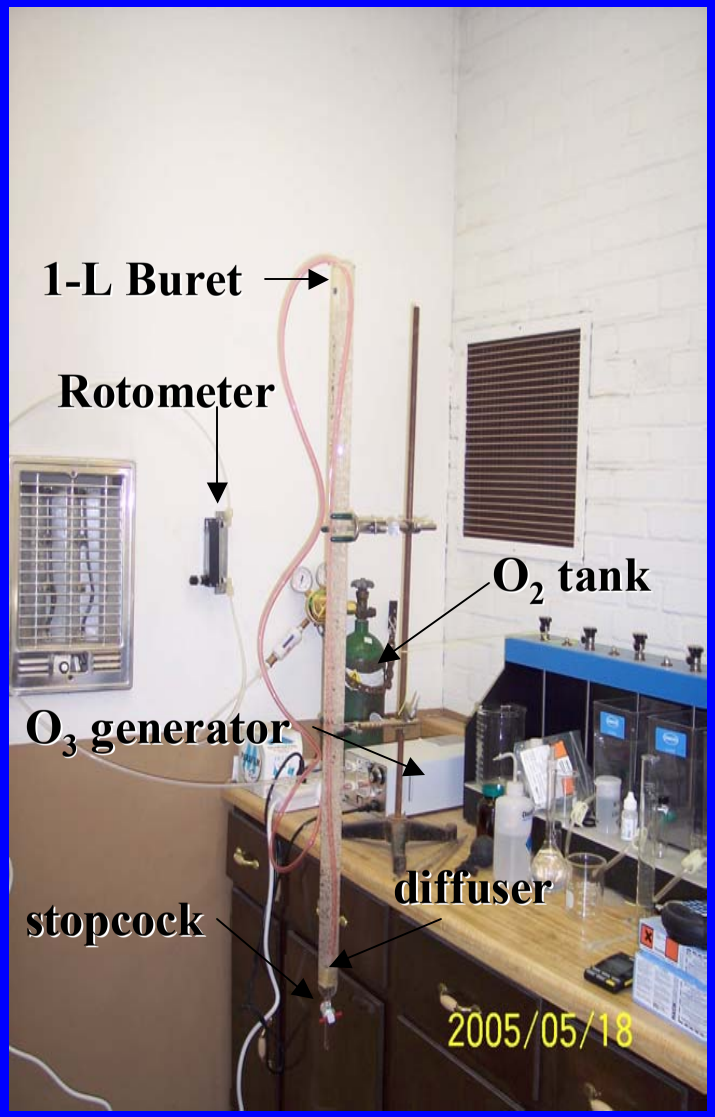
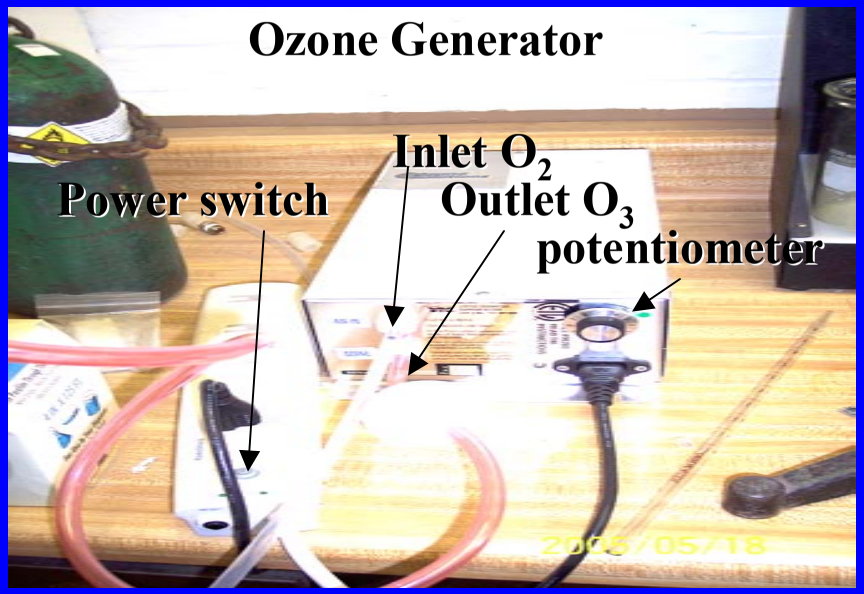
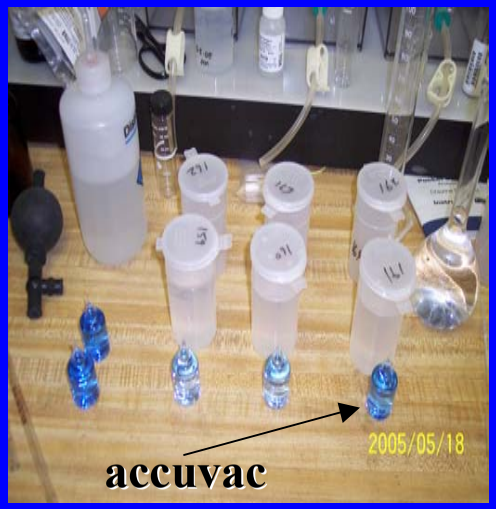


Figure 3. Inactivation of *C. parvum* oocysts by O_3 and Cl_2 at pH 6 and 22^{O} C

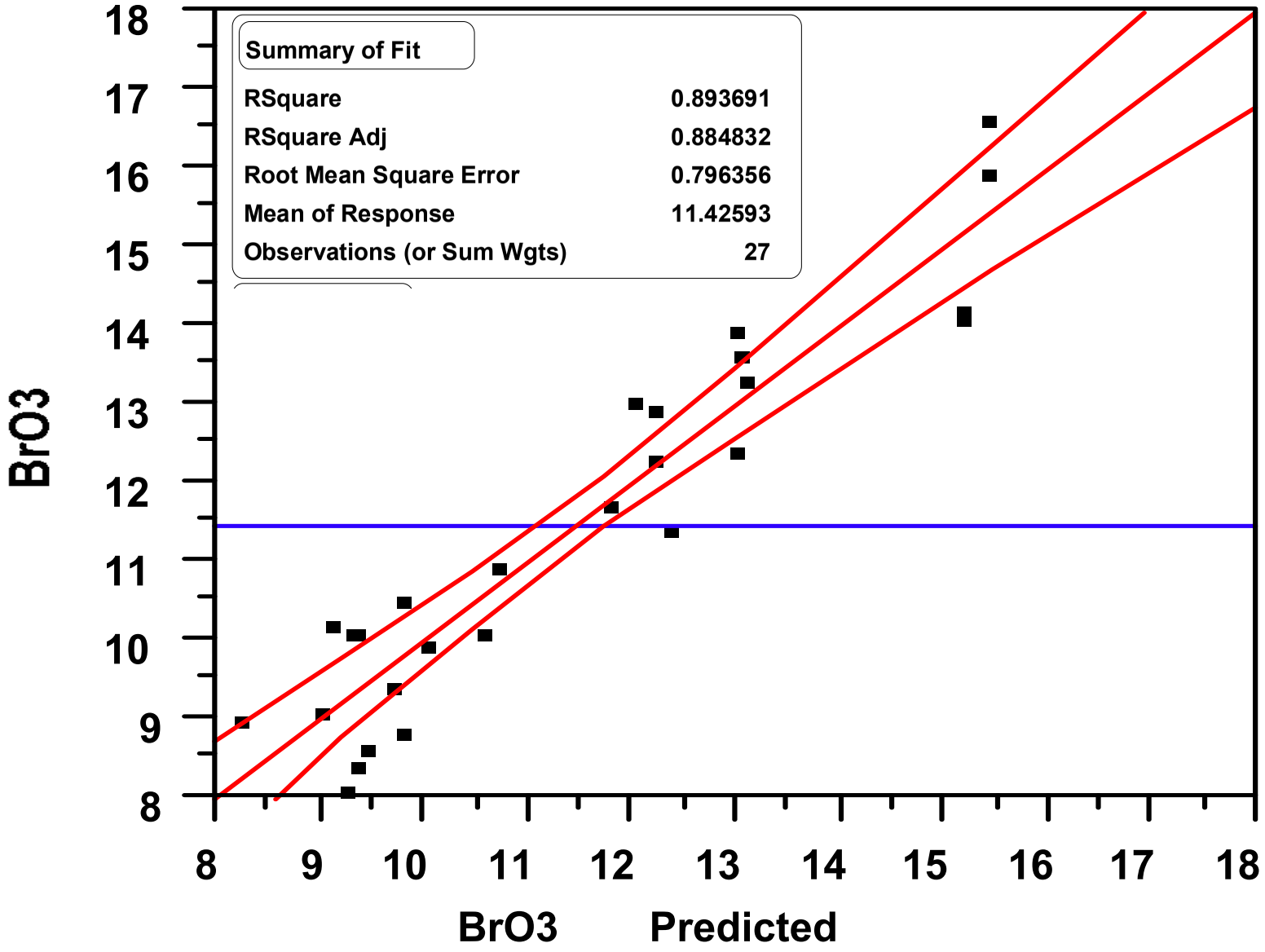
2005 Lab Procedures



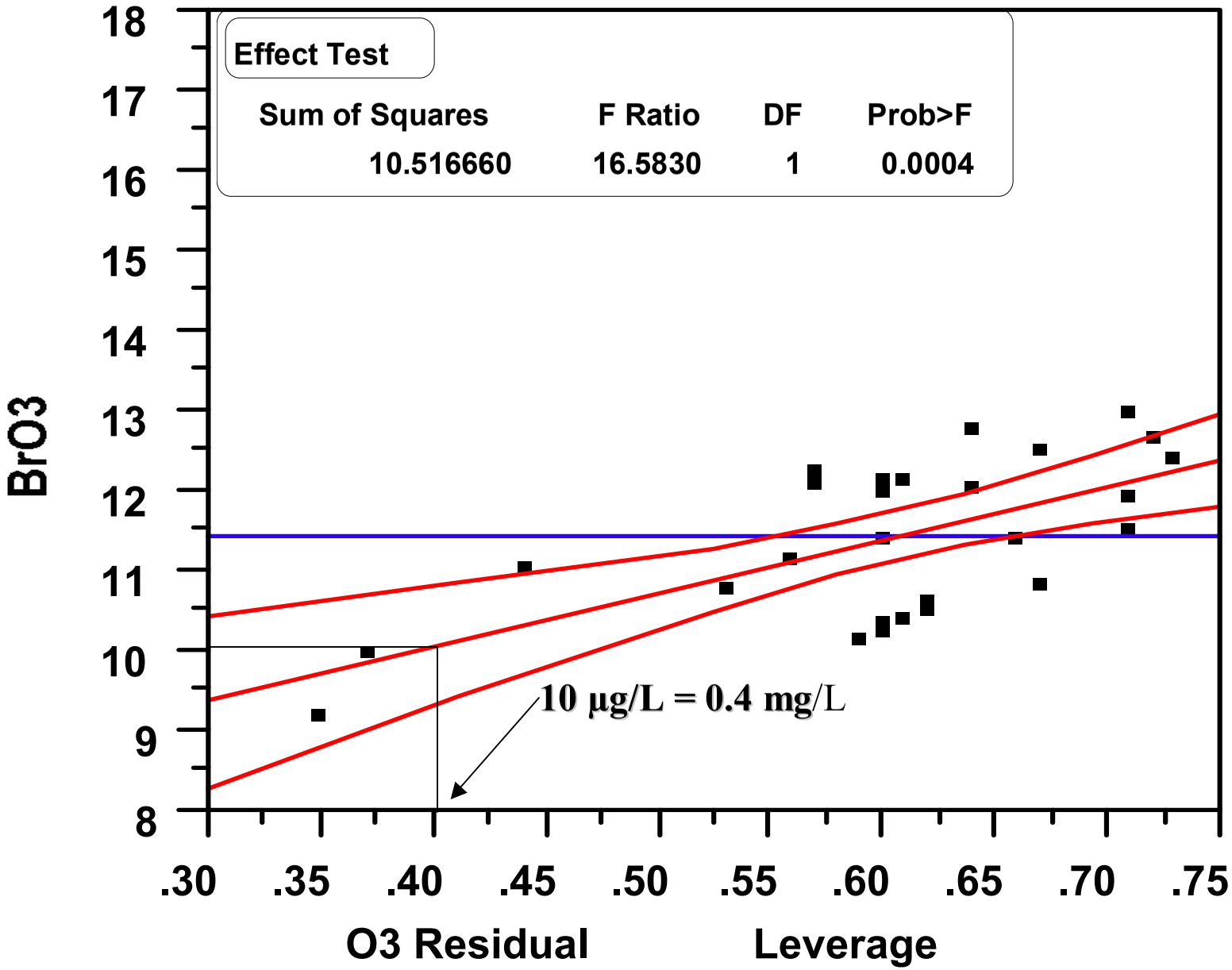




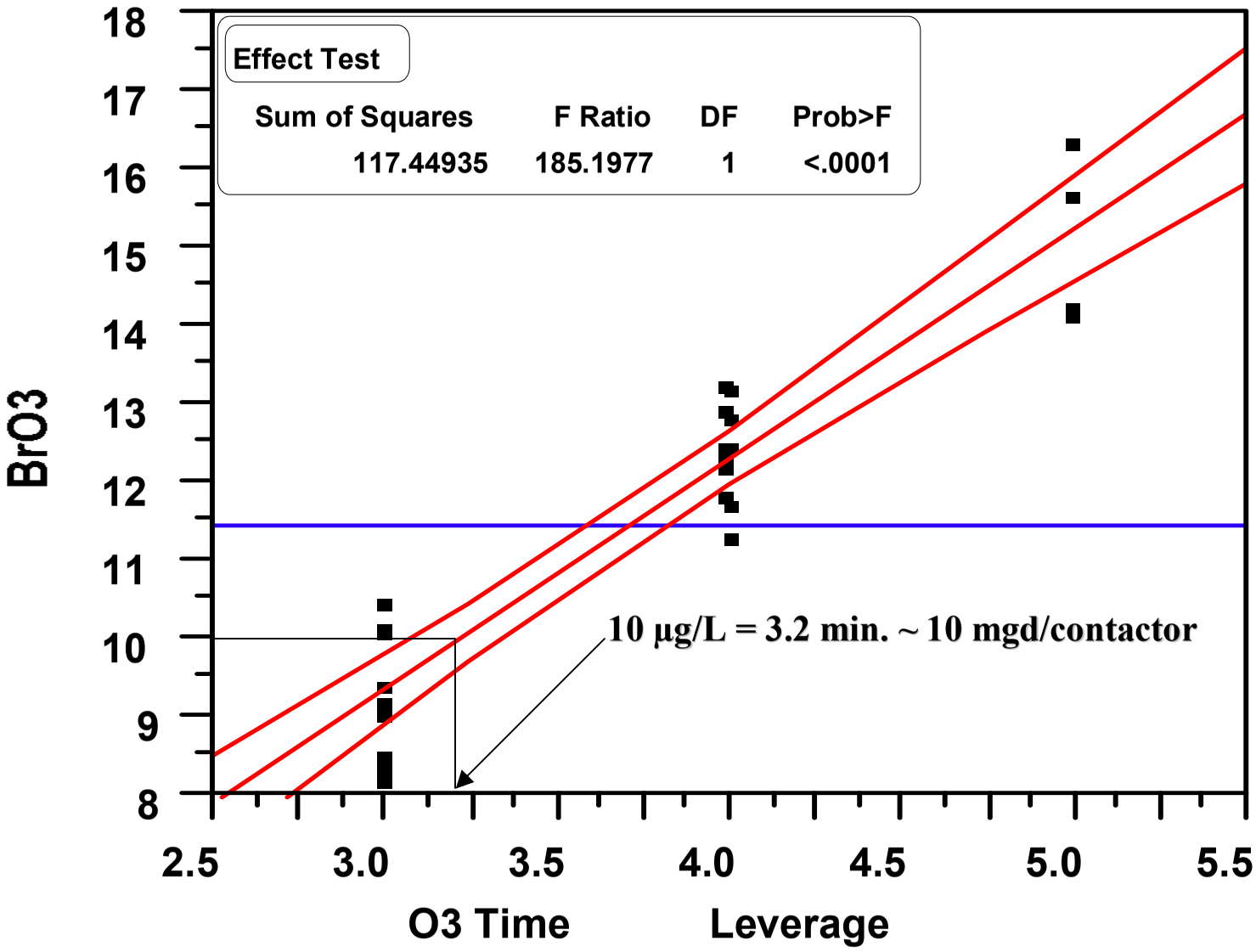
Predicted vs. Actual Bromates Model with O_3 Only



BrO_3 vs. O_3 Residual with O_3 only



BrO_3 vs. O_3 Time with O_3 only



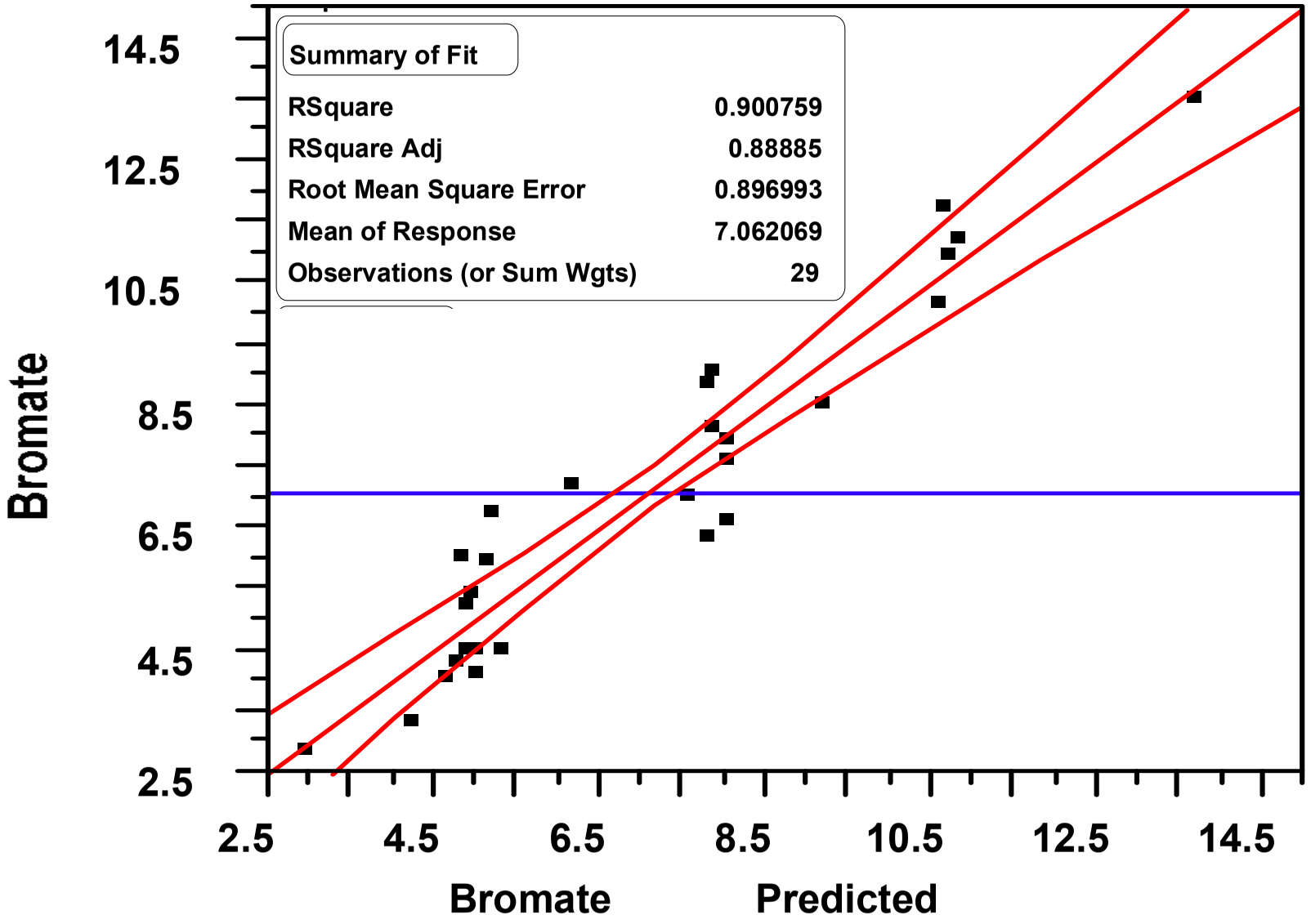
Prediction Equation for Bromate Formation with O_3 only

Bromates, µg/L = -3.49 + (2.94 * O_3 Time, minutes) + (6.70 * O_3 Residual, mg/L)
R^2 = 0.89, N = 27

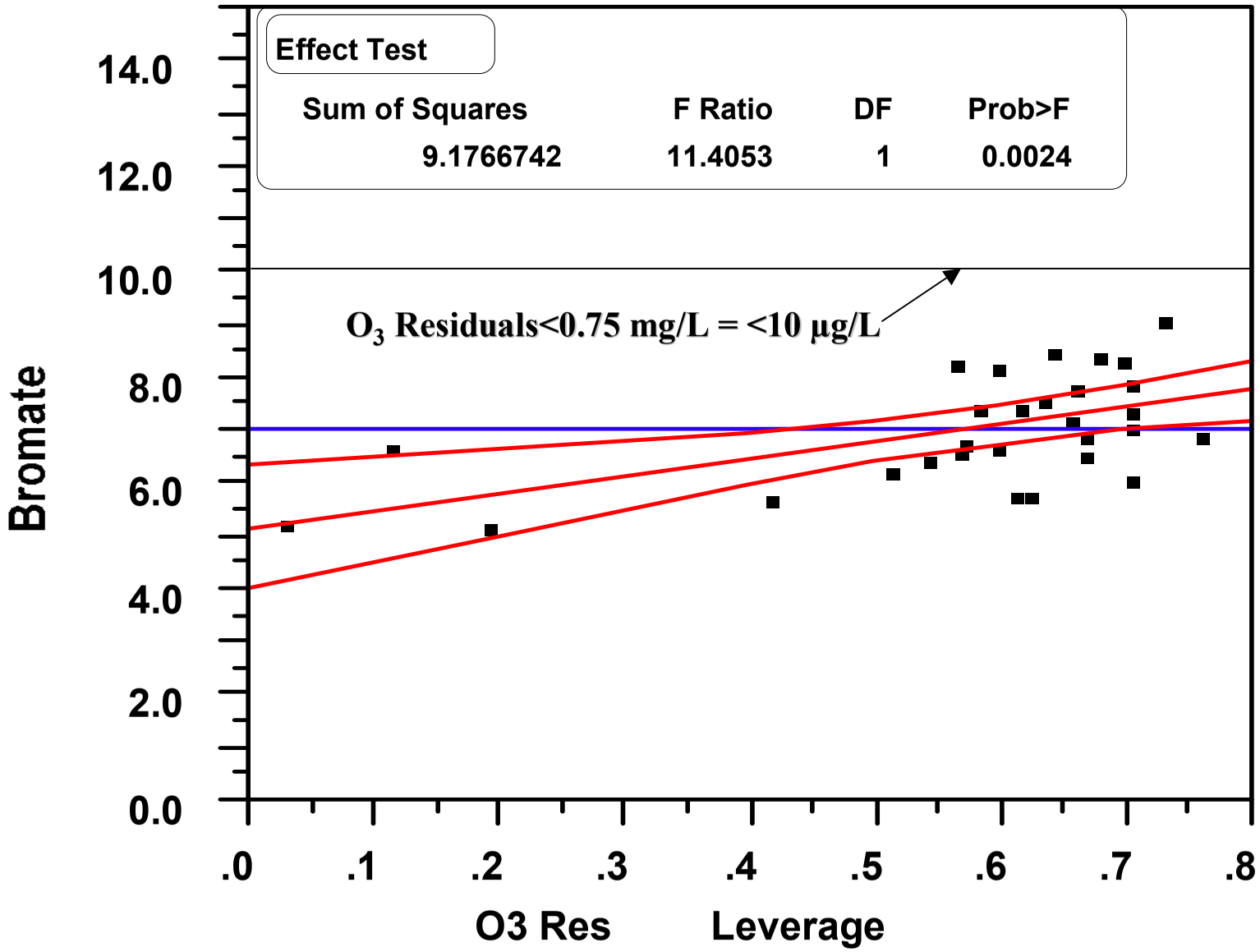
Prediction Parameters are:

1. **Range of Ozone Residuals = 0.35 to 0.73**
2. **Range of Ozone Contact Times = 3 to 5 minutes**
3. **Range of Actual Bromates = 8.1 to 16.6 µg/L**
4. **Range of Predicted Bromates = 8.3 to 15.5 µg/L**
5. **Range of Residuals = -1.2 µg/L to +1.1 µg/L**
6. **Range of Bromide Levels = 170 to 220 µg/L**

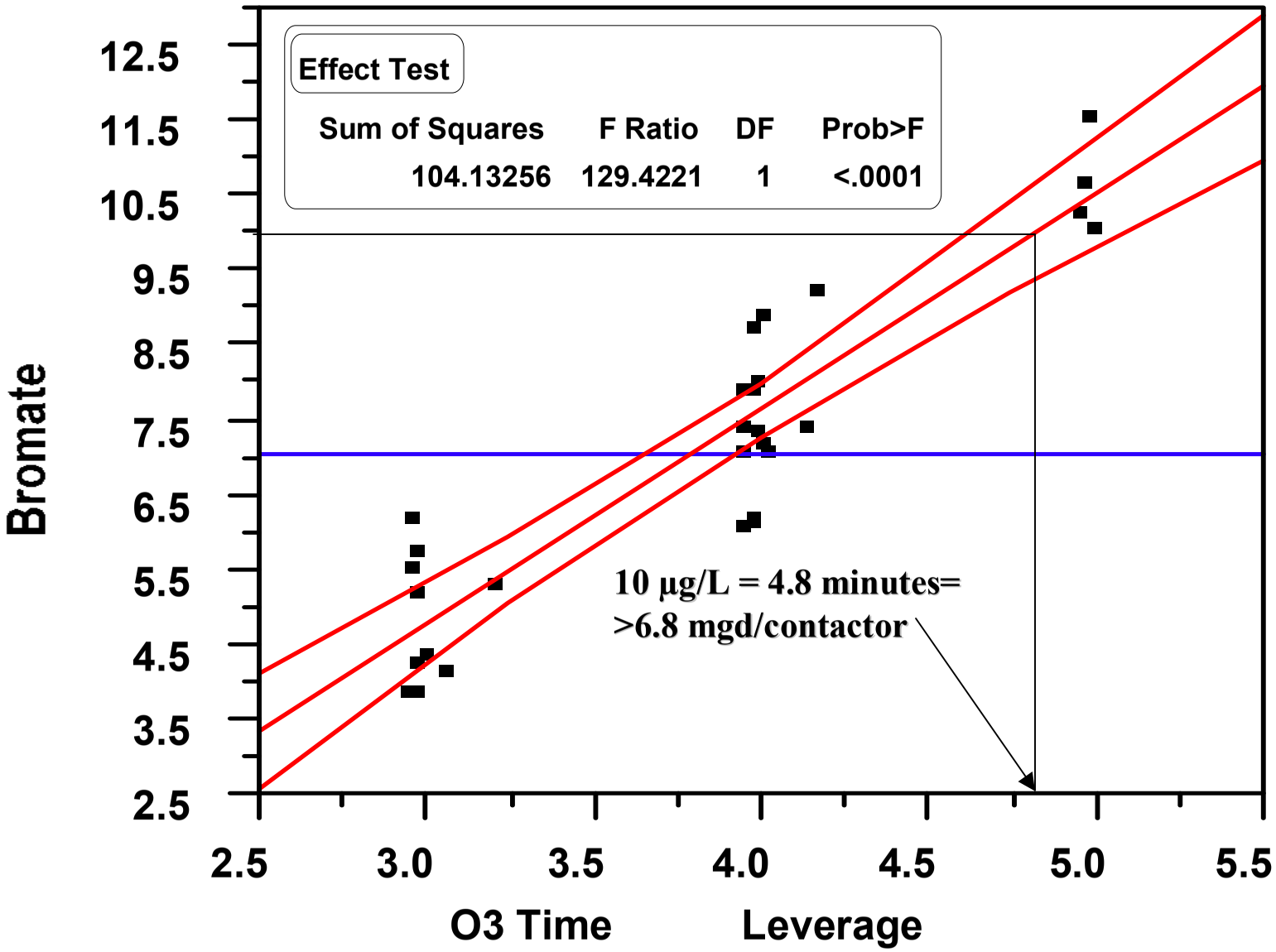
Predicted vs. Actual Bromate Model with ClO_2



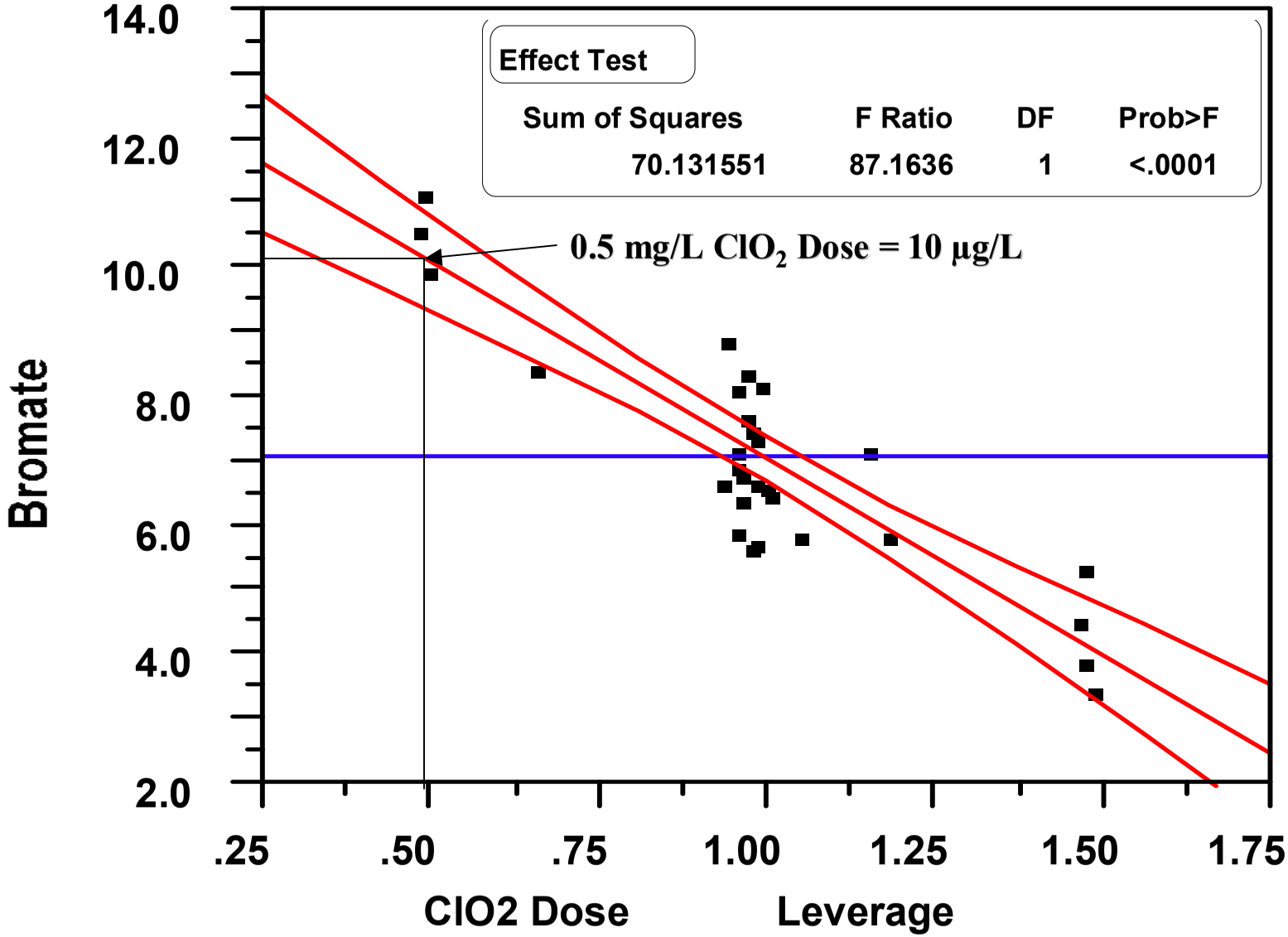
Bromates vs. O_3 Residuals with ClO_2



Bromate vs. O_3 Time with ClO_2



Bromates vs. ClO_2 Dose



Predictive Equation for Bromate Formation with ClO_2

Bromates, µg/L = 0.40 + (2.87 * O_3 Time, minutes) + (3.23 * O_3 Residual, mg/L) + (-6.09 * ClO_2 Dose, mg/L) R^2= 0.90, N = 29

Bromates, µg/L = -3.49 + (2.94 * O_3 Time, minutes) + (6.70 * O_3 Residual, mg/L)

R^2 = 0.89, N = 27 Ozone Dose Only Equation

Prediction Parameters are:

1. Range of Ozone Residuals = 0.01 to 0.74 mg/L
2. Range of Ozone Contact Times = 3 – 5 minutes
3. Range of ClO_2 Dosage = 0.5 to 1.5 mg/L
4. ClO_2 contact time = 1 to 2 minutes
5. Range of Actual Bromates = 2.9 to 13.6 µg/L
6. Range of Predicted Bromates = 2.9 to 13.7 µg/L
7. Range of Residuals = -1.4 to 1.3 µg/L
8. Range of Bromide Levels = 170 µg/L to 220 µg/L

Table 1 - Comparison of Lab Bromate Levels

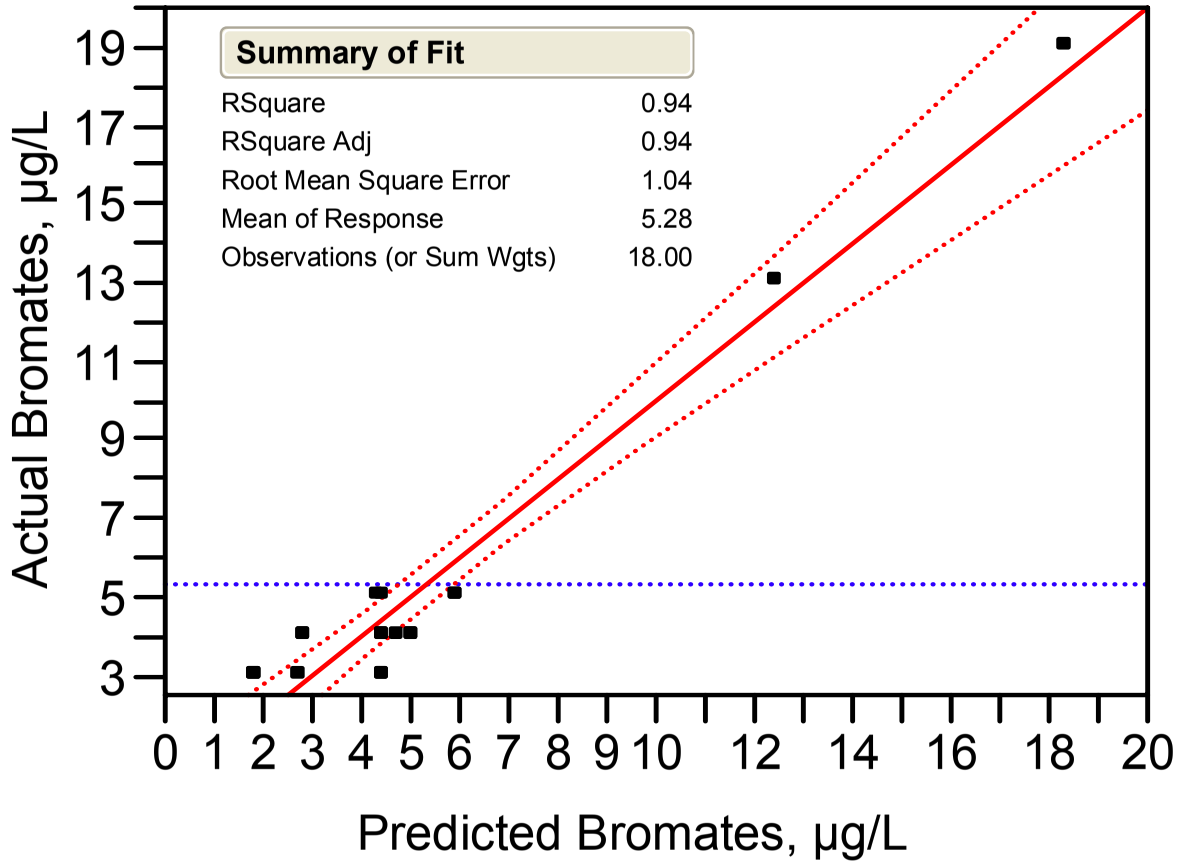
MGD Per Contactor	Contact Minutes	O_3 Residual, mg/L	1.5 mg/L ClO_2, µg/L	1.0 mg/L ClO_2, µg/L	0.5 mg/L ClO_2, µg/L	0zone only, µg/L	% Reduction Range with ClO_2
5.0	6.5	0.3	10.0	13.1	16.2	17.6	8% to 42%
6.0	5.4	0.3	7.0	9.9	13.4	14.4	7% to 51%
7.0	4.64	0.3	5.2	7.8	10.8	12.2	11% to 57%
8.0	4.06	0.3	3.1	6.1	9.2	10.5	12% to 70%
9.0	3.61	0.3	1.8 (<2.0)	4.8	7.9	9.1	13% to 80%
10.0	3.25	0.3	0.76 (<2.0)	3.8	6.9	8.1	15% to 91%

2005 Lab Study of ClO_2 Dose versus ClO_2^- & ClO_3^- Levels

Sample ID	ClO_2 Dose, mg/L	ClO_2^-, mg/L	ClO_3^-, mg/L	% Total Oxidants of ClO_2 dose
137	1.0	0.0	0.731	73.1
138	1.0	0.0	0.731	73.1
139	1.0	0.0	0.734	73.4
140	1.0	0.0	0.691	69.1
141	1.0	0.0	0.671	67.1
142	1.0	0.0	0.664	66.4
143	0.5	0.0	0.293	58.6
144	0.5	0.0	0.284	56.8
145	0.5	0.0	0.293	58.6
156	1.0	0.0	0.716	71.6
157	1.0	0.0	0.718	71.8
158	1.0	0.0	0.72	72.0

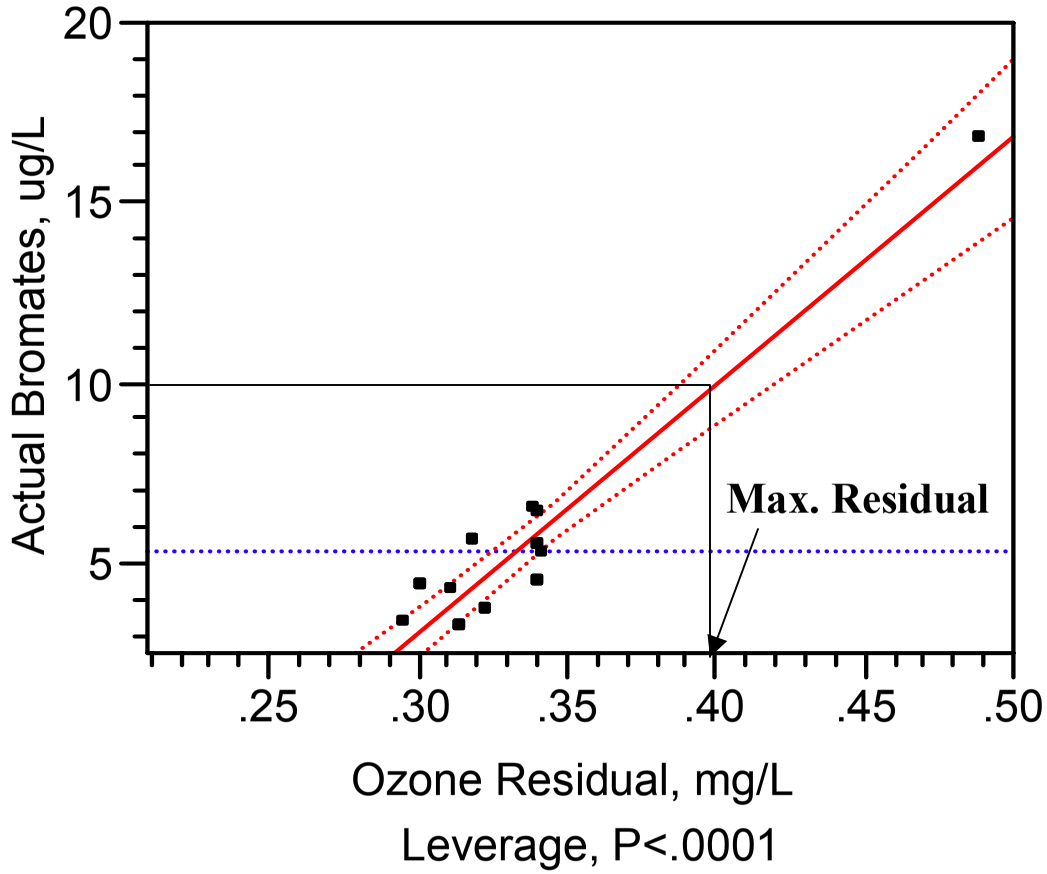
* Plant Study averaged 62% total oxidants of ClO_2 Dose

Plant Study for Actual versus Predicted Bromates Using O_3 Only

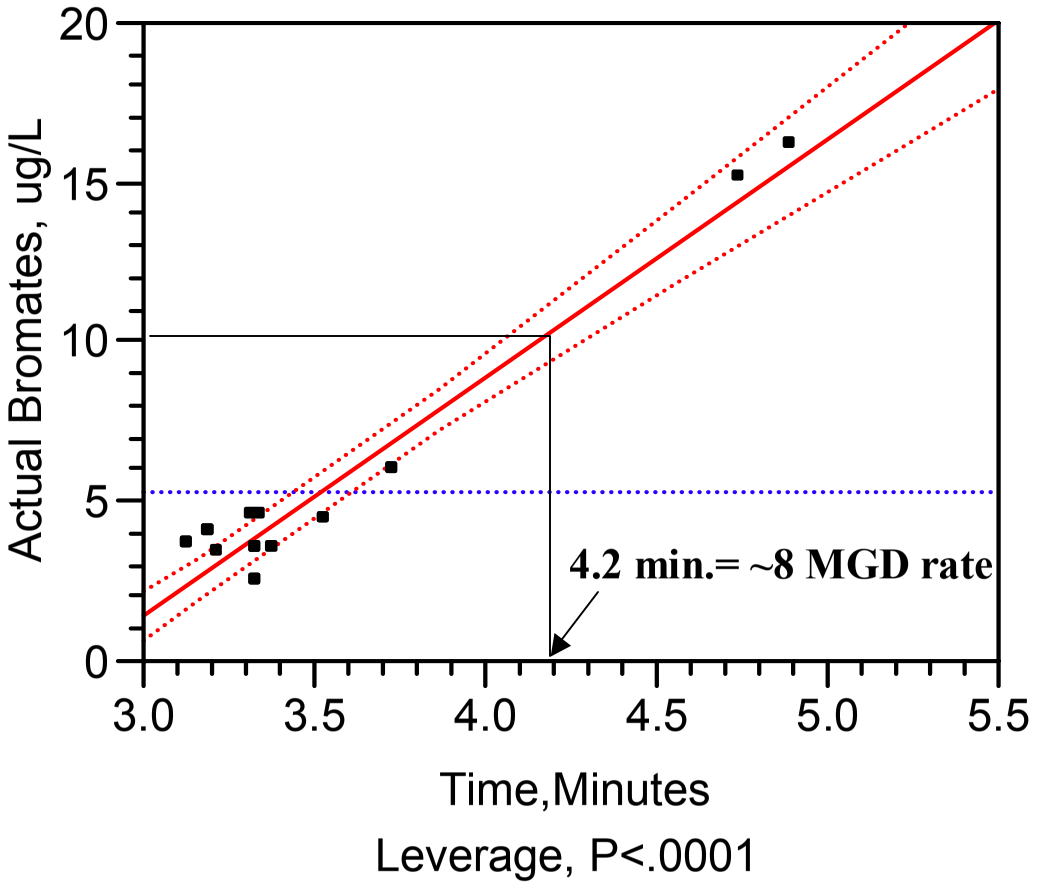


Bromates, µg/L = -43.8 + (68.6 x O_3 Res., mg/L) + (7.46 x Time, minute)

Plant Study of Bromates versus Ozone Residuals for O_3 Only



Plant Study of Bromates versus Time, Minutes for O_3 Only



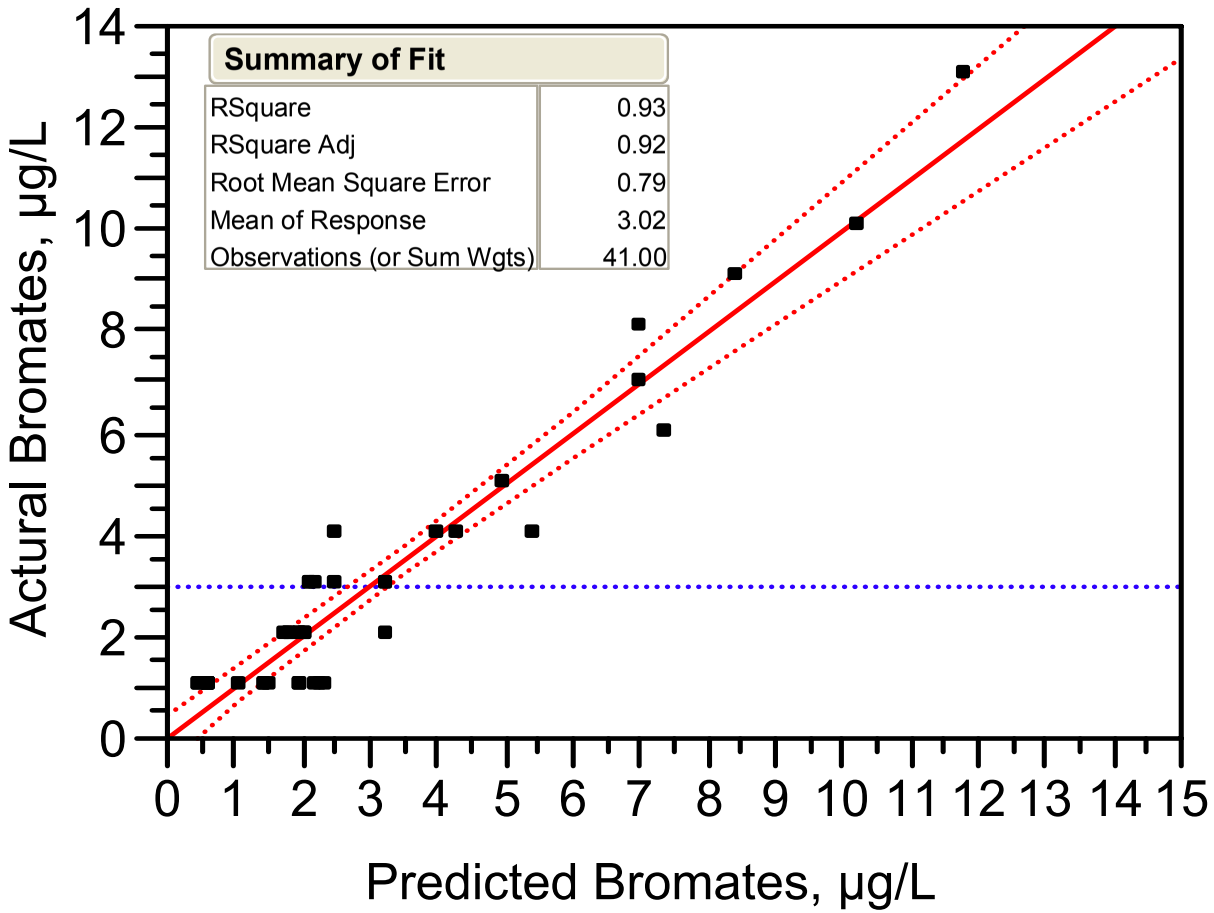
Predictive Equation for Bromate Formation with O_3 alone in Plant Study

Bromates, µg/L = -43.8 + (68.6 x O_3 Res., mg/L) + (7.46 x Time, minute)

Prediction Parameters are:

1. **Range of Ozone Residuals = 0.22 to 0.47 mg/L**
2. **Range of Ozone Contact Times = 3.20 to 5.5 minutes**
3. **Range of Actual Bromates = 3.0 to 19.0 µg/L**
4. **Range of Predicted Bromates = 1.8 to 18.3 µg/L**
5. **Range of Residuals = -1.4 to +1.2 µg/L**
6. **Range of Bromide Levels = 170 µg/L to 220 µg/L**

Plants Study for Actual versus Predicted Bromates with O_3 & ClO_2



Bromates, µg/L = -1.95 + 4.0 x O_3 Res, mg/L + 2.09 x Time, min. + (-6.35 x ClO_2, mg/L)

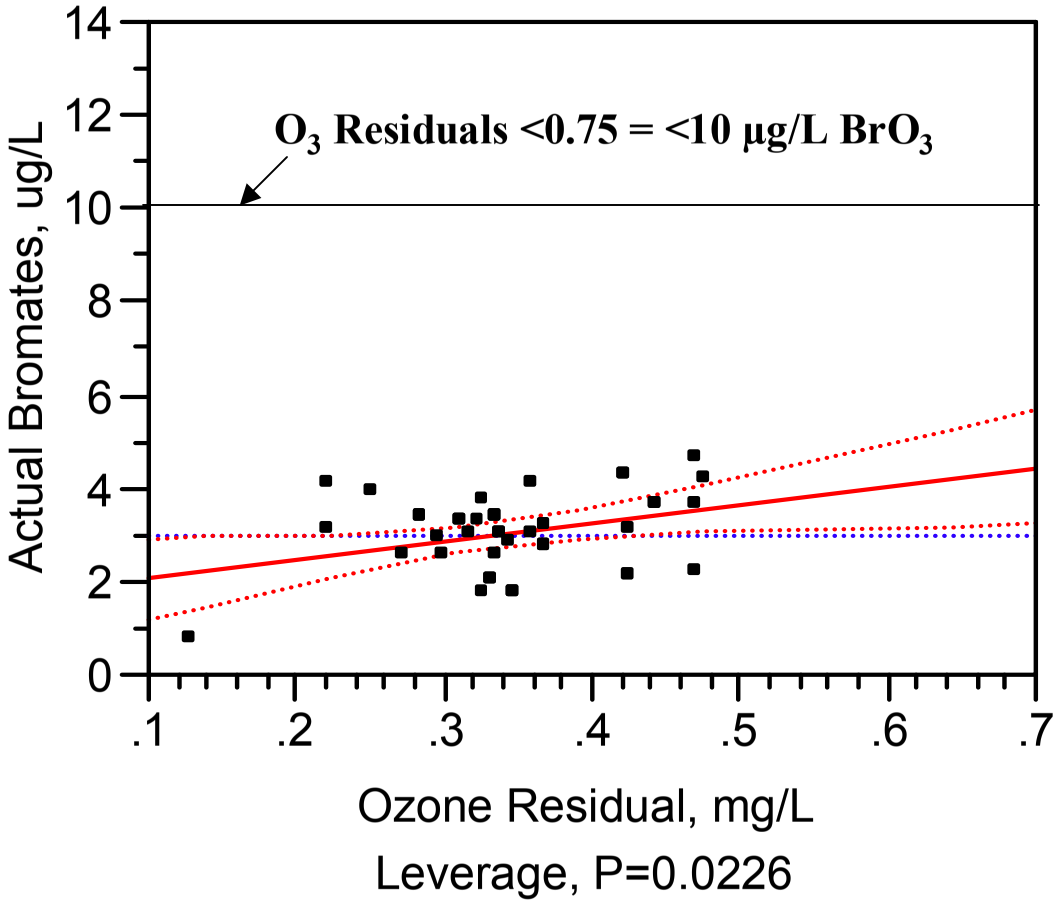
Predictive Equation for Bromate Formation with ClO_2 in Plant Study

Bromates, µg/L = -1.95 + 4.0 x O_3 Res, mg/L + 2.09 x Time, minutes + (-6.35 x ClO_2 , mg/L). R square = 0.93, N = 41 observations.

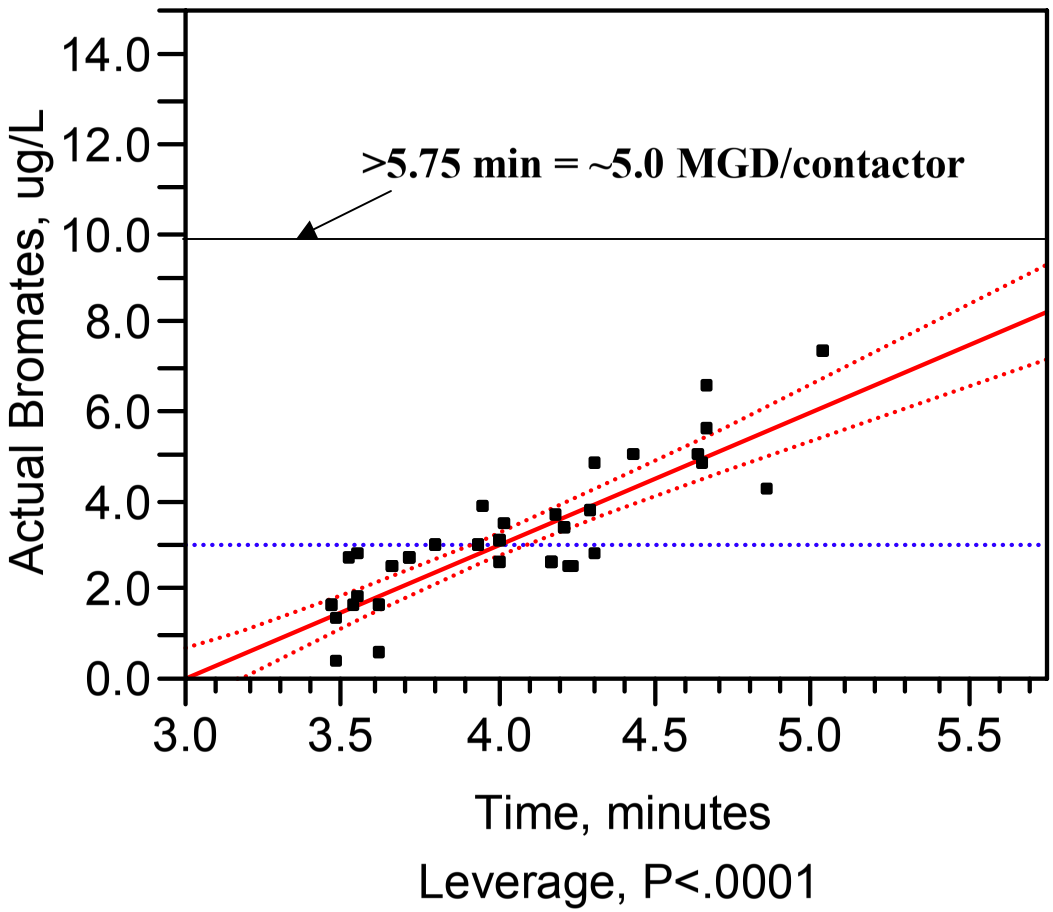
Prediction Parameters are:

1. **Range of Ozone Residuals = 0.15 to 0.65 mg/L**
2. **Range of Ozone Contact Times = 3.28 to 5.01 minutes**
3. **Range of ClO_2 Dosage = 0.44 to 1.67 mg/L**
4. **Range of Actual Bromates = 1.0 to 13.0 µg/L**
5. **Range of Predicted Bromates = 0.5 to 11.7 µg/L**
6. **Range of Residuals = -1.4 to 1.6 µg/L**
7. **Range of Bromide Levels = 170 µg/L to 220 µg/L**

Plant Study of Bromates versus Ozone Residuals with ClO_2



Plant Study of Bromates versus Time, minutes with ClO_2



Plant Study of Bromates versus ClO_2 Dose Leverage

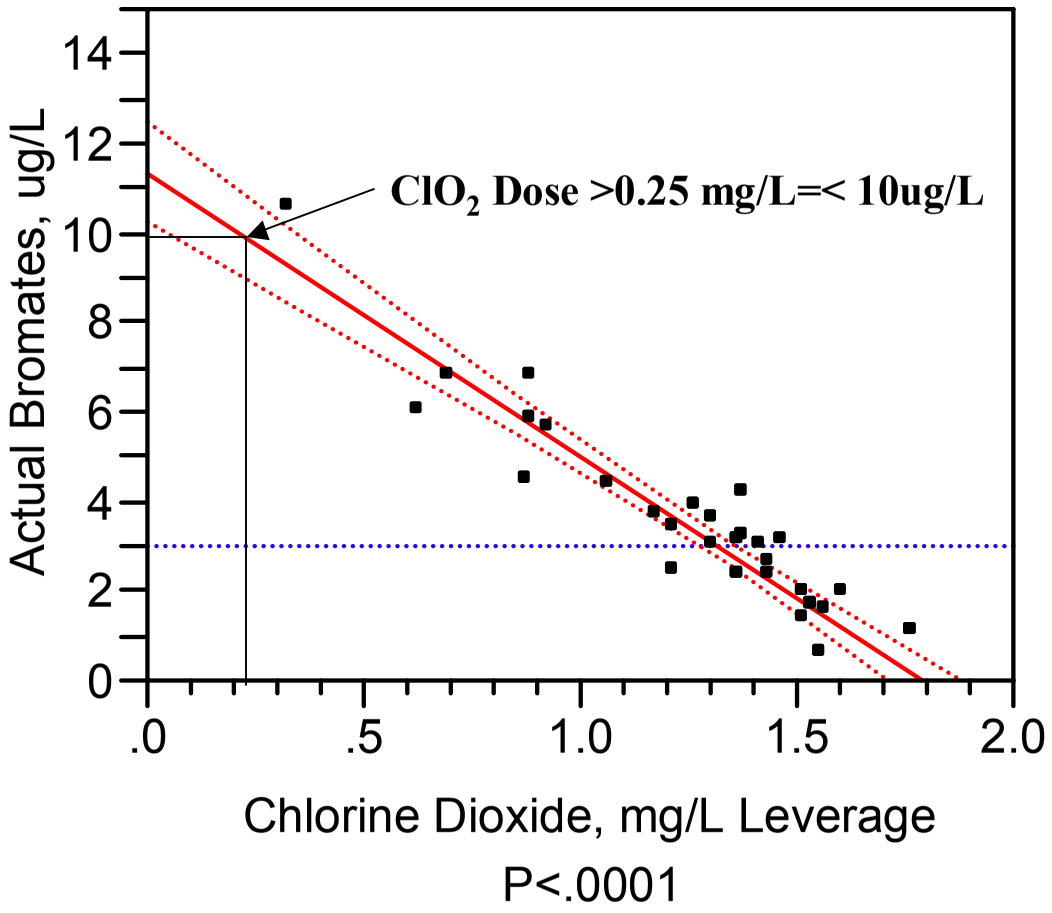


Table 7. Bromate Formation for 3 Chlorine Dioxide Doses and Ozone only at 0.3 Ozone Residual in Plant Study

Flow, MGD	Time, minutes	Ozone Residual mg/L	1.5 mg/L ClO_2 Dose, µg/L	1.0 mg/L ClO_2 dose, µg/L	0.5 mg/L ClO_2 dose, µg/L	Ozone Dose only, µg/L	% Reduction Range
5.0	6.5	0.3	9.1	12.3	15.4	25.3	39 to 64
6.0	5.4	0.3	5.8	9.0	12.2	17.1	29 to 79
7.0	4.64	0.3	3.6	6.7	9.9	11.4	13 to 68
8.0	4.06	0.3	1.8	5.0	8.2	7.1	0 to 75
9.0	3.61	0.3	<1.0	3.7	6.8	3.8	0 to ~80
10.0	3.25	0.3	<1.0	2.6	5.8	<1.0	0

Bromates, µg/L = -43.8 + (68.6 x O_3 Res., mg/L) + (7.46 x Time, minute)

Bromates, µg/L = -1.95 + (4.0 x O_3 Res, mg/L) + (2.09 x Time, min.) + (-6.35 x ClO_2, mg/L)

Table 8. Bromate Formation for 3 Chlorine Dioxide Doses and Ozone Only at 0.4 mg/L Ozone Residual in Plant Study

Flow, MGD	Time, minute	Ozone Residual, mg/L	1.5 mg/L ClO_2 Dose, µg/L	1.0 mg/L ClO_2 dose, µg/L	0.5 mg/L ClO_2 dose, µg/L	Ozone Dose only	% Reduction Range
5.0	6.5	0.4	9.5	12.7	15.8	32.2	51 to 70
6.0	5.4	0.4	6.2	9.4	12.6	24.0	48 to 74
7.0	4.64	0.4	4.0	7.1	10.3	18.3	44 to 78
8.0	4.06	0.4	2.2	5.3	8.6	14.0	39 to 84
9.0	3.61	0.4	<1.0	4.0	7.2	10.6	32 to 91
10.0	3.25	0.4	<1.0	2.9	6.1	7.9	23 to ~94

Bromates, µg/L = -43.8 + (68.6 x O_3 Res., mg/L) + (7.46 x Time, minute)

Bromates, µg/L = -1.95 + (4.0 x O_3 Res, mg/L) + (2.09 x Time, min.) + (-6.35 x ClO_2, mg/L)

Conclusions

The following conclusions from the 2005 Laboratory and Plant Studies, can be made with reasonable certainty:

1. The lab and plant studies predict accurately the effect of ozone residual, contact time, and chlorine dioxide dose on bromate formation.

2. Bromates were reduced by 6.1 µg/L and 6.34 µg/L per mg/L of chlorine dioxide dose in the lab and the plant studies respectively.

3. Chlorite residuals were less than 0.01 mg/L after ozonation at all chlorine dioxide doses.

4. Chlorate levels were 67% and 62% of the applied chlorine dioxide dose in the lab and plant studies, respectively.

5. Ozone alone can comply with the 10 µg/L bromate MCL at contact times of 4.06 minutes or less (>8.0 MGD rate per contactor) with 0.3 mg/L ozone residual but at the 0.4 mg/L ozone residual level, the contact time of 3.61 minutes or less (>9.0 MGD rate per contactor) is necessary to comply with the bromate MCL.

6. The average bromate reduction was 78% at 1.5 mg/L chlorine dioxide dose compared to the Contra Costa study of 78% reduction at 1.0 mg/L chlorine dioxide dose.

7. Since the plant can now operate at the higher ozone residual level of 0.4 mg/L, the plant should have consistent disinfection capability for *Giardia sp* inactivation while increasing TOC removal and resulting in lower TTHM levels in the distribution system.

Special Acknowledgements

Without reliable and accurate laboratory analyses provided by the Laboratory Chemists of The El Paso Water Utilities, this project would not have been possible. Special thanks to Ruben Rodriquez, Chemist who performed the analyses and Miquel Venegas, Laboratory Supervisor, who facilitated the availability of equipment and supplies for successful completion of the laboratory study. Also, special thanks to Fernando Rico, P.E., Water Supply Manager, for his initial support of this project, and Art Ruiz, Plant Superintendent & Robert Riley, Plant Superintendent for their cooperation and support. In addition, I appreciate John Balliew, P.E., Water Division Manager and David Brosman, P.E., Chief Operations Officer for their continual support of practical research projects to improve water quality and treatment operations.

Questions???