





BENCH TEST RESULTS - TM 2 SEASONAL OZONE DEMAND

Stanislaus Regional Water Authority Water Supply Project August 2018

TECHNICAL MEMORANDUM

Stanislaus Regional Water Authority Water Supply Project Bench Test Results - TM 2 Seasonal Ozone Demand

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Subject:	Bench Test Results of Seasonal Ozone Demand and Design Ozone Dose

EXECUTIVE SUMMARY

The Stanislaus Regional Water Authority (SRWA), a joint powers authority between the Cities of Turlock and Ceres, is pursuing a new water supply project to provide treated water from the Tuolumne River as a supplement to their existing groundwater supply. The expected treatment train for the new Water Treatment Plant (WTP) includes pre-oxidation to aid manganese removal, clarification, primary disinfection by intermediate ozonation, dual-media biologically active filtration, final disinfection with free chlorine, and stabilization of the finished water prior to distribution. Within this general treatment train, several options exist for selected treatment steps: primary clarification can be achieved by conventional coagulation, flocculation and sedimentation, or by sand-ballasted clarification; and final disinfection can be achieved either in a chlorine contact basin followed by a clearwell or in a baffled clearwell only.

To design a robust ozonation system, it is necessary to determine the seasonal variability in ozone demand and ozone decay for both raw water and primary treated (in this case, coagulated/settled (C/S)) water and to estimate the appropriate design ozone dose. Trussell Tech conducted monthly ozone demand tests in the Trussell Tech Laboratory (Pasadena, CA) from November 2016 to October 2017 to obtain the necessary data. The bench tests considered two different ozone:TOC (O3:TOC) ratios and three different coagulants—alum, polyaluminum chloride (PACI) and ferric.

Results from these seasonal ozone demand tests indicated:

- Ozone demand of the raw water is greater than the ozone demand of clarified water.
- Ozone demand is associated with the total organic carbon (TOC) concentration of the water.
- The highest raw water TOC concentrations were measured during the winter months (January through March) and were associated with storm events.

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- In general, the ozone demand of the clarified water was higher when PACl was used for coagulation compared to alum.
- Bromate is an ozonation by-product formed through the reaction of ozone with bromide ions. The MCL for bromate is $10 \mu g/L$. Only very low bromate concentrations were measured for the ozonated raw water while concentrations in the ozonated C/S water were always below the analytical detection limit. Thus, bromate formation is not a regulatory concern for this water.

Using pathogen log inactivation calculation procedures provided in the Surface Water Treatment Rule Guidance Manual (USEPA, 1991), and accounting for seasonal variability in raw water and clarified water TOC concentrations, the range of ozone doses needed to both meet the demand of the water and provide 1-log Giardia inactivation and 2-log virus inactivation were:

- 1.2 mg/L to 5.6 mg/L with pre-ozonation, and
- 0.5 mg/L to 2.0 mg/L with intermediate ozonation.

The design ozone dose should be able to deliver the maximum anticipated dose. Therefore, a design ozone dose of 5.6 mg/L is needed, pre-ozonation, and a design ozone dose of 2.0 mg/L is needed for intermediate ozonation.

1 INTRODUCTION

The Stanislaus Regional Water Authority (SRWA), a joint powers authority between the Cities of Turlock and Ceres, is pursuing a new water supply project to provide treated water from the Tuolumne River as a supplement to their existing groundwater supply. Candidate treatment options for the project were evaluated by Trussell Technologies (Trussell Tech) through a year-long bench-scale testing program (November 2016 – October 2017), using water samples collected monthly from the Tuolumne River. Monthly sample collection for the bench tests was part of a parallel source water quality monitoring campaign. Ozone is included in the treatment train for the new water treatment plant (WTP) due to its ability to (1) break down large organic molecules (e.g., TOC, synthetic organic chemicals (SOC/S), and pesticides), (2) address algae by-products and related taste and odor (T&O) compounds should they be present in the river water, and (3) achieve primary disinfection with reduced disinfection by-product (DBP) formation compared with the use of free chlorine. Biologically active carbon (BAC) dual-media filtration (GAC/sand) will follow ozone in the full-scale treatment train to provide enhanced removal of organic compounds. Of particular importance for the water treatment plant design is the impact of seasonal water quality changes on ozone demand. Thus, the bench testing included one year of monthly ozone demand assessment to facilitate selection of the appropriate design ozone dose.

This is the second technical memorandum (TM 2) of three discussing results of bench-scale testing. The bench testing objectives and methodology were summarized in TM 1, along with results and conclusions from testing conducted on samples collected between November 2016 and February 2017. The focus of TM 2 is seasonal changes in ozone demand, characterized on a monthly basis for one year, and selection of an appropriate design ozone dose for the SRWA treatment facility. The selected design ozone dose for the SRWA WTP must consider seasonal changes in water quality as well as historical extremes, particularly for those parameters that affect ozone demand such as TOC and water temperature. Ozone demand and ozone dose are estimated for both the pre-ozonation and intermediate options, even though only intermediate ozone was considered in the Pre-Design TM for the Reference WTP (Trussell Tech, June 2018). A third and final TM in this series, TM 3, will discuss the results of bench testing aimed at manganese removal.

2 TESTING OVERVIEW

This section provides an overview of the Tuolumne River water quality over the year-long sampling campaign as it relates to ozone demand, and the bench-scale testing done to determine the design ozone dose for either pre-ozonation or intermediate ozonation.

2.1 Raw Water Quality and Testing Overview

Important questions raised regarding treatment of Tuolumne River water with ozone include:

- What ozone dose is required to meet the ozone demand?
- How does ozone demand of the raw water (preozonation) compare with ozone demand of coagulated/settled (C/S) water (intermediate ozonation)?
- What is the seasonal variability of the ozone demand?

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• Will the ozonation by-product bromate be formed above regulatory limits with ozone?

To address these questions, twelve rounds of monthly ozone demand tests were completed using Tuolumne River water samples collected by FishBio between late November 2016 and mid-October 2017. Sampling conditions over the year-long sampling campaign are characterized by the associated Tuolumne River flows presented in Figure 2.1. The reported in-stream river flows were measured at the United States Geological Survey (USGS) La Grange Dam flow gauge station, upstream of the monitoring site located at the future infiltration gallery intake location. As depicted in Figure 2.1, the winter months (January through March) were characterized by storms delivering above-average rainfall (snowfall at upper elevations in the watershed), followed by snowmelt and releases from the upstream Don Pedro Dam into June 2017. Raw water quality data from these monthly sampling events are summarized in Table 2.1. TOC is shown in relation to streamflow because ozone demand and ozone decay rate are strongly influenced by TOC concentration in both the raw water and clarified/settled (C/S) water. The raw water TOC increased in response to rapid increases in stream flows, induced by storms starting in late December 2016. After the high stream flows stabilized (starting in late February 2017), the TOC dropped, returning to more normal/prestorm levels by mid-March 2017.



Figure 2.1. Tuolumne River flow measured at USGS La Grange Dam flow gauge station and TOC measured by Eurofins Lab

Sampl Month Collecti		TOC (mg/L)		UV – 254 (cm-1)	SUVA (L/mg∙m)	Alkalinity (mg/L as CaCO3)	Turbidity (NTU)		рН		Temp (°C)	Conductivity (μmhos/cm)
	Date	TT Lab	Eurofins	Eurofins	Eurofins	Eurofins	Field	Eurofins	Field	Eurofins	Field	Field
Nov 2016	11/14/16	1.87	2.1	0.050	2.5	26	0.59	0.72	-	7.4	15.5	61.8
Dec 2016	12/12/16	2.04	2.0	0.052	2.6	26	1.51	1.2	-	7.5	11.9	67.5
Jan 2017	1/9/17	4.08	3.5	0.117	3.0	22	7.63	5.5	7.4	7.4	11.9	59.3
Feb 2017	2/13/17	3.00	7.3	0.086	3.1	18	7.74	5.6	7.9	7.5	10.1	51.0
Mar 2017	3/13/17	2.72	2.3	0.075	3.3	20	11.78	8.8	7.4	7.4	10.7	43.1
Apr 2017	4/10/17	2.46	2.8	0.065	3.0	20	3.32	2.5	7.6	7.4	10.7	43.6
May 2017	5/8/17	2.32	2.2	0.065	3.4	17	2.85	1.3	7.7	7.5	12.0	46.0
June 2017	6/12/17	2.28	2.4	0.064	3.0	15	2.94	1.2	7.7	-	12.2	36.3
July 2017	7/10/17	2.23	2.1	0.059	2.8	12	2.62	0.58	7.4	7.4	13.9	20.8
Aug 2017	8/14/17	2.16	1.9	0.055	3.0	11	2.92	0.75	7.7	7.7	15.1	28.2
Sept 2017	9/11/17	2.01	1.9	0.0520	2.9	11	4.31	1.4	7.2	7.4	15.9	25.4
Oct 2017	10/9/17	2.12	1.8	0.0525	2.9	21	1.88	0.72	7.4	7.3	16.1	62.7

Table 2.1. Raw water quality for year of ozone demand testing (November 2016 to October 2017)

Notes:

All water quality analyses were completed by the Trussell Tech Laboratory (TT Lab), unless otherwise indicated.

Field analyses were completed by FishBio, the contract sampling team, using handheld field instruments.

2.2 Test Procedures

The monthly raw water samples were shipped to the Trussell Tech Laboratory (TT Lab) in Pasadena, CA, where all bench testing was performed. Bench testing included jar tests to prepare C/S water and Solution Ozone Tests (SOT) to determine the ozone demand of both the raw water and C/S water. The experimental methods used for bench testing were described previously in Appendix A of TM 1 (Trussell Tech, 2017).

3 OZONE TESTING RESULTS

As discussed previously in TM 1 (Trussell Tech, 2017), ozone is a fast reacting disinfectant/oxidant that typically decays rapidly in water. The decay profile of ozone in natural water is typically characterized by a more rapid initial decay due to the initial ozone demand exerted by reacting constituents in the water, followed by a slower first-order decay profile (Rakness 2005; U.S. EPA 2010). The initial ozone demand of the water is a function of many parameters (e.g., pH, alkalinity, temperature, and natural organic matter (NOM) concentration), but is largely influenced by the NOM (measured as total organic carbon, TOC). Thus, the higher the TOC concentration in the water, the greater the ozone demand. Ozone testing typically involves dosing ozone as a function of the raw water or C/S water TOC concentration (e.g., 0.6 or 1.0 mg/L O₃ per mg/L TOC). Dosing ratios of 0.6 and 1.0 O3:TOC are commonly used as a starting place in establishing an appropriate dosing ratio that will provide an ozone residual after approximately 4 to 6 minutes, representative of the hydraulic detention time of a typical ozone contactor.

The initial November 2016 SOT results, which were conducted at 7°C and 22°C, showed that faster ozone decay occurred under warm water conditions. To be conservative in estimating seasonal ozone demand, subsequent tests were conducted at warm water temperatures of 20°C or greater.

3.1 Ozone Decay Test Conditions

For each of the monthly SOTs (November 2016 – October 2017), decay curves were developed for multiple O3:TOC ratios, for both raw water and C/S water at water temperatures in the range of 20 to 22°C. Ozone applied ahead of the coagulation/flocculation process is considered "pre-ozonation." Ozone applied after coagulation/flocculation (and prior to filtration) is considered "intermediate ozonation."

Raw water ozone demand tests used ozone-to-TOC ratios (O3:TOC) of 0.6, 1.0, and 1.2. The O3:TOC ratio of 0.6 was used only from November 2016 to February 2017 because very little ozone residual remained in solution after 1 minute, making it difficult to estimate the decay rate after the initial demand was met. For this reason, the O3:TOC ratio of 0.6 was not considered for the analysis of design ozone dose with pre-ozonation. All raw water ozone decay curves from November 2016 to October 2017 are presented in Appendix A of this TM, in Figure A.1, Figure A.2, and Figure A.3.

Intermediate ozone demand was evaluated using the C/S prepared water at O3:TOC ratios of 0.6 and 1.0. Ferric chloride (ferric) was the coagulant used during the early tests (November and December 2016), but was not continued since aluminum-based coagulants were selected

as the preferred chemicals for the full-scale WTP. Subsequent testing involved C/S waters prepared with molar-equivalent doses (e.g., equivalent mM of active meal ions) of aluminum sulfate (alum) and polyalumnium chloride (PACl). As discussed in TM 1 (Trussell Technologies, 2017), parallel testing of all three candidate coagulants—ferric, alum, and PACl—at equivalent molar doses, resulted in approximately the same percentage TOC removal during clarification. Ozone decay curves for all monthly SOTs using C/S water are presented in Appendix A, in Figure A.4, Figure A.5 and Figure A.6.

The coagulant type and corresponding dose (mg/L of coagulant) used to prepare the C/S water is specified in Table 3.1, along with the raw water TOC, clarified water TOC and resulting percentage TOC removal. An equivalent molar dose of 0.049 mM was used for all three coagulants. TOC removal varied throughout the year with removals ranging from roughly 25% to 40%. Erroneous TOC removal was measured in January and August and is likely the result of floc carryover in the C/S water. Dissolved organic carbon (DOC) removals ranged from 30% to 42%, with no erroneous measurements since the samples were filtered prior to DOC analysis. For raw water with TOC between 2 and 4 mg/L and alkalinity below 60 mg/L as CaCO3, the Stage 1 Disinfectants and Disinfection Byproducts Rule (D/DBP Rule) requires 35% TOC removal. Therefore, the ozone demand tests conducted on the C/S water had TOC concentrations consistent with the D/DBP Rule requirements. Further optimization of coagulant dose was addressed in TM 1 (Trussell Tech, 2017).

Month	Coag- ulant	Coag. Dose** (mg/L)	Raw Water TOC (mg/L)	Raw Water DOC (mg/L)	Raw Water Alkalinity (mg/L as CaCO ₃)	C/S Water TOC (mg/L)	C/S Water DOC (mg/L)	TOC Removal (%)	DOC Removal (%)
Nov 2016	Ferric	7.9	1.92	1.89	26	1.21		37.0	
Dec 2016	Ferric	7.9	2.04	1.95	28	1.29		35.5	
lan 2017	Ferric	7.9	4.00	4.00	20	4.24***	2.80	-1.4	30.0
Jan 2017	Alum	14.6	4.08	4.00	22	3.04***	2.32	27.3	42.0
Feb 2017	Alum	14.6	3.0	2.07	20	1.8	1.80	41.3	39.4
	PACI	14.5	3.0	2.97	20	1.88	1.87	38.7	37.0
Mar 2017	Alum	14.6	2.72	2.67	19	1.77	1.50	35.0	43.9
	PACI	14.5	2.12	2.07		1.81	1.57	33.6	41.3
Apr 2017	Alum	14.6	2.46	2.28	10	1.56	1.44	36.6	39.5
Api 2017	PACI	14.5	2.40	2.30	19	1.57	1.52	36.2	36.1
May 2017	Alum	14.6	2.22	2.24	10	1.7	1.53	26.7	34.6
May 2017	PACI	14.5	2.32	2.34	19	1.71	1.52	26.3	35.0
lun 2017	Alum	14.6	2.28	2 20	17	1.43	1.34	37.3	41.5
	PACI	14.5	2.20	2.23	17	1.4	1.38	38.6	39.7
Jul 2017	Alum	14.6	2.23	2.16	15	1.5	1.29	32.7	40.3

Table 3.1. Coagulant type and dose for clarified (C/S) water preparation, as well as C/S water TOC used in ozone demand testing*

Month	Coag- ulant	Coag. Dose** (mg/L)	Raw Water TOC (mg/L)	Raw Water DOC (mg/L)	Raw Water Alkalinity (mg/L as CaCO ₃)	C/S Water TOC (mg/L)	C/S Water DOC (mg/L)	TOC Removal (%)	DOC Removal (%)
	PACI	14.5				1.68	1.36	24.7	37.0
Aug 2017	Alum	14.6	0.16	2.07	15	1.96***	1.29	9.3	37.7
	PACI	14.5	2.16			2.16***	1.22	0.0	41.1
Son 2017	Alum	14.6	2.01	2.04	14	1.98	1.33	1.5	34.8
Sep 2017	PACI	14.5	2.01	2.04	14	1.93	1.33	4.0	34.8
0-+ 0017	Alum	14.6	2 1 2	2 11	21	1.44	1.30	32.1	38.4
	PACI	14.5	2.12	2.11	21	1.45	1.39	31.6	34.1

* Analyses conducted in Trussell Tech laboratory.

** These coagulant doses all have an equivalent metal ion concentration of 0.049 mmol/L

*** Poor settling and floc carry-over in the jar tests resulted in erroneous TOC data.

3.2 Ozone Demand and Ozone Decay

SOT data were used to calculate initial ozone demand and the rate of ozone decay for both raw water and clarified waters. The ozone demand is considered to be the amount of ozone consumed in the first 60 seconds of reaction time (Rakness, 2005). The 60-second ozone demand is described by the following equation:

60-sec O₃ demand (mg/L) = Transferred O₃ dose (mg/L) – 60-sec O₃ residual (mg/L)

In test procedures that bubble ozone gas through the sample as the means of dosing ozone, the ozone transfer efficiency has to be taken into account to calculate the transferred ozone dose. This requirement adds both complexity and potential error to the experiment. The SOT uses a concentrated ozone solution (i.e., approximately 65 to 70 mg/L ozone) instead of ozone gas to dose the samples. As a result, with the SOT, the applied ozone dose equals the transferred ozone dose.

The ozone decay coefficient associated with each SOT was determined using the equation for first order decay:

$$\frac{dC}{dt} = -kC \tag{Eqn 3-1}$$

Through integration, this equation becomes:

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{Eqn 3-2}$$

which in the linearized form is:

$$\ln(C) = -kt + \ln(C_0) \tag{Eqn 3-3}$$

where: C_0 = initial ozone concentration (mg/L) C = residual ozone concentration (mg/L) k = ozone decay coefficient (min⁻¹) t = reaction time, or hydraulic detention time (min)

The ozone decay coefficient is the slope of the best fit line through a plot of ln(C) versus reaction time. Regression plots for the raw water SOTs (i.e., pre-ozonation) are provided in Appendix B, in Figure B.1, Figure B.2, and Figure B.3. Regression plots for intermediate ozonation (C/S water SOTs) are included in Appendix B, in Figure B.4, Figure B.5, and Figure B.6.

The 60-second ozone demand values and the ozone decay coefficients associated with all of the tested conditions are presented in Table 3.2 for raw water and Tables 3.3 and 3.4 for C/S water. These data show that the ozone demand of the water increases as the TOC concentration of the water increases. The impact of water temperature on ozone demand and ozone decay was evaluated during the November 2016 testing and was discussed in TM 1 (Trussell Tech, 2017). These November 2016 tests showed that both ozone demand and ozone decay rate increase as the water temperature increases. As a result, it was decided to conduct the monthly SOTs under warm water (22°C) conditions rather than cold water (7°C) conditions, to be more conservative in estimates of ozone demand and decay as a function of source water TOC concentration.

The full set of ozone decay data, along with calculated ozone demand and ozone decay coefficients, is provided in Appendix C, with pre-ozonation test results in Table C.1 and intermediate ozonation test results in Table C.2.

	Raw		Raw Water O3:TOC = 1.0		Raw Water O3:TOC = 1.2			
Month TOC (mg/L		Ozone Dose (mg/L)	Measured 60-s Ozone Demand (mg/L)	Ozone Decay Coefficient (min ⁻¹)	Ozone Dose (mg/L)	Measured 60-s Ozone Demand (mg/L)	Ozone Decay Coefficient (min ⁻¹)	
Nov 2016	1.87	1.87	1.16	0.255	not tested			
Dec 2016	2.04	2.04	1.30	0.276	not tested			
Jan 2017	4.08	4.08	3.46	0.285 *	not tested			
Feb 2017	3.00	3.00	1.83	0.285	not tested			
Mar 2017	2.72	2.72	1.88	0.395	3.40**	2.13	0.250	
Apr 2017	2.46	2.46	1.76	0.386	2.95	1.84	0.266	
May 2017	2.32	2.32	1.52	0.349	2.78	1.33	0.210	
June 2017	2.28	2.28	1.62	0.345	2.74	1.54	0.209	
July 2017	2.23	2.23	2.07	0.464	2.68	1.72	0.221	
Aug 2017	2.16	2.16	1.95	0.330	2.59	1.47	0.195	
Sept 2017	2.01	2.01	1.14	0.214	2.41	1.42	0.188	
Oct 2017	2.05	2.05	1.40	0.257	2.46	1.69	0.236	

Table 3.2. SOT ozone demand and decay data for Raw Water

Notes:

* For accurate dose calculations, the February decay coefficient was substituted, because the measured decay coefficient was 1.3592 min⁻¹ (too high)
 ** O3:TOC ratio of 1.25 was used for this SOT.

	C/S	C/:	S Water (using alu O3:TOC = 1.0	m)	C/S Water (using alum) O3:TOC = 0.6			
Month	Water TOC (mg/L)	Ozone Dose (mg/L)	Measured 60-s Ozone Demand (mg/L)	Ozone Decay Coefficient (min ⁻¹)	Ozone Dose (mg/L)	Measured 60-s Ozone Demand (mg/L)	Ozone Decay Coefficient (min ⁻¹)	
Nov 2016	1.21	1.21	0.73 *	0.138 *	0.73	0.41 *	0.171 *	
Dec 2016	1.29	1.29	0.64 *	0.113 *	0.77	0.45 *	0.169 *	
Jan 2017	3.04	3.04	1.45	0.123	2.54	1.07	0.193	
Feb 2017	1.80	1.80	0.86	0.136	1.08	0.66	0.226	
Mar 2017	1.77	1.77	0.74	0.080	1.06	0.52	0.112	
Apr 2017	1.56	1.56	0.67	0.096	0.94	0.56	0.178	
May 2017	1.70	1.70	0.41	0.070	1.02	0.59	0.180	
June 2017	1.43	1.43	0.59	0.091	0.86	0.45	0.136	
July 2017	1.50	1.50	0.60	0.082	0.90	0.51	0.139	
Aug 2017	1.96	1.96	1.05	0.115	1.18	0.74	0.209	
Sept 2017	1.98	1.98	0.84	0.099	1.19	0.63	0.172	
Oct 2017	1.44	1.44	0.70	0.083	0.86	0.50	0.133	
Notes: * Results are	for coagulatior	n with ferric rather than	ı alum.					

Table 3.3. SOT ozone demand and decay data for Coagulated/Settled (C/S) water with alum as coagulant

	C/S	C/S	6 Water (using PA O3:TOC = 1.0	CI)	C/S Water (using PACI) O3:TOC = 0.6			
Month	Water TOC (mg/L)	Ozone Dose (mg/L)	Measured 60-s Ozone Demand (mg/L)	Ozone Decay Coefficient (min ⁻¹)	Ozone Dose (mg/L)	Measured 60-s Ozone Demand (mg/L)	Ozone Decay Coefficient (min ⁻¹)	
Nov 2016		not tested			not tested			
Dec 2016		not tested			not tested			
Jan 2017		not tested			not tested			
Feb 2017	1.88	1.88	1.00	0.178	1.13	0.70	0.297	
Mar 2017	1.81	1.81	0.92	0.119	1.09	0.49	0.130	
Apr 2017	1.57	1.57	0.79	0.157	0.94	0.55	0.177	
May 2017	1.71	1.71	0.59	0.093	1.02	0.49	0.150	
June 2017	1.40	1.40	0.64	0.101	0.84	0.53	0.200	
July 2017	1.68	1.68	0.87	0.117	1.01	0.71	0.285	
Aug 2017	2.16	2.16	1.46	0.177	not tested			
Sept 2017	1.93	1.93	1.27	0.156	0.87	0.68	0.218	
Oct 2017	1.45	1.45	0.73	0.106	1.13	0.55	0.183	

Table 3.4. SOT ozone demand and decay data for C/S water with PACl as coagulant

3.3 Ozone Demand as a Function of Ozone Dose

Raw water ozone demand data were plotted as a function of ozone dose for each of the O3:TOC dosing ratios, and the results are presented in Figure 3.1. Figure 3.1a shows the individual regression lines for the three O3:TOC ratios tested, and Figure 3.1b shows a single regression line for the combined dataset. There was poor correlation between transferred ozone dose and ozone demand for the higher dose ratio of 1.2 O3:TOC (Figure 3.1) possibly because at these higher ozone doses, the dose exceeds the initial demand such that the demand appears somewhat constant over the TOC range considered. The regression equations with all data combined can be used to provide a reasonable estimate of the ozone demand of this raw water as a function of TOC concentration.



(a) Ozone demand as a function of O3:TOC ratio



(b) Ozone demand with all O3:TOC ratios combined

Figure 3.1. 60-Second raw water ozone demand, November 2016 through October 2017

The C/S water ozone demand data are plotted as a function of ozone dose for O3:TOC ratios of 0.6 and 1.0 and presented in Figure 3.2. Data from all three coagulants—ferric, alum, and PACl—were grouped together since all coagulants provided similar TOC removal at equal molar metal ion doses. Figure 3.2a shows the regression lines for the individual O3:TOC ratios, and Figure 3.2b shows the regression for the combined dataset. It should be noted that

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the ozone dose used for the January SOT was too high because it was based on an elevated TOC value resulting from poor settling of the floc in the jar test. Nonetheless, the January water samples used in testing represented the highest influent TOC measured by TT Lab in connection with bench testing (Table 2.1), and the delivered dose and corresponding demand provide a valuable upper dose range to inform the design. The regression equations from the ozone dose and demand plots (Figure 3.2) can be used to estimate the ozone demand of C/S water as a function of TOC concentration and O3:TOC ratio.



(b) Ozone demand of C/S water-alum, PACI, ferric and O3:TOC ratios combined

Figure 3.2. 60-Second ozone demand of C/S water as a function of ozone dose with ferric, alum, and PACl combined, November 2016 through October 2017

Because the ozone dose was a function of the raw water TOC concentration, the regression lines and equations would look identical to what is shown in Figures 3.1 and 3.2 if the data were plotted as a function of TOC concentration rather than ozone dose. Therefore, for both raw water samples and C/S samples (Figure 3.1 and Figure 3.2), the 60-second ozone demand increased with increasing TOC concentrations.

Using the regression equations indicated in Figures 3.1 and 3.2, a summary of ozone demand as a function of raw water and C/S TOC concentrations is presented in Table 3.5. These concentrations are important because the initial ozone demand of the water must be met before residual ozone concentrations can be achieved in the ozone contactor for calculating pathogen disinfection credit. Raw water TOC concentrations for the SOTs ranged from 1.87 mg/L to 4.08 mg/L with an average of approximately 3 mg/L; the maximum TOC of 7.3 mg/L measured by Eurofins was considered erroneous since a duplicate sample analyzed by Trussell Tech was 3.07 mg/L. The historic maximum TOC concentration was 6.5 mg/L (Trussell Tech, March 2018). The C/S TOC concentrations in Table 3.5 assume 35% TOC removal through clarification when the raw water TOC is less than 4 mg/L and 45% TOC removal when the TOC is greater than 4 mg/L, in accordance with the D/DBP Rule Enhanced Coagulation treatment requirements.

Considering the full range of measured Raw Water TOC concentrations, the ozone demand ranges from approximately 1 mg/L to 4.5 mg/L. The ozone demand of the C/S water ranges from approximately 0.5 mg/L to 2.3 mg/L. The design ozone dose will have to exceed the ozone demand of the water.

Figure 3.3 compares the ozone demand with the O3:TOC ratio of 0.6 with the ratio of 1.0. The demand increases with increased ozone dose (higher O3:TOC), because the reaction kinetics are faster.



Figure 3.3 Ozone demand for C/S water for O3:TOC ratios of 0.6 versus 1.0

Raw Water TOC		C/S TOC**	Ozone Demand fo	or Pre-Ozonation	Ozone Demand for Intermediate Ozonation			
Basis	mg/L	mg/L	O3:TOC Ratio=1.0 Regression	All Data Regression	O3:TOC Ratio=0.6 Regression	O3:TOC Ratio=1.0	All Data Regression	
Historical Max	6.5	3.6	5.6	4.5	2.7	2.3	2.1	
SRWA Sampling Program Max*	4.2	2.3	3.4	2.9	1.7	1.3	1.3	
SRWA Sampling Program Avg	2.3	1.5	1.6	1.5	1.0	0.7	0.8	
SRWA Sampling Program Min	1.6	1.0	0.9	1.1	0.6	0.3	0.5	

Table 3.5. Summary of raw water and C/S ozone demand as a function of raw water TOC

Notes:

* Eurofins measured a maximum value of 7.3 mg/L. Based on a duplicate sample collected at the same time but analyzed by TT with a concentration of 3.07 mg/L, the Eurofins measured maximum was considered erroneous.

**The assumed percentage TOC removal during clarification is based on the D/DBP Rule Enhanced Coagulation requirements of 35% when the raw water TOC is between 2.0 and 4.0 mg/L and 45% when the raw water TOC is greater than 4.0 mg/L (alkalinity \leq 60 mg/L as CaCO3)

3.4 Ozone Decay as a Function of Ozone Dose

Ozone decay rates as a function of ozone dose is shown in Figure 3.4. For the purposes of this figure, the data for alum, PACl, and ferric were combined, but dose data were separated into O3:TOC ratios of 0.6 and 1.0. Figure 3.4a excludes the decay rate for the one erroneously high ozone dose applied in January, while Figure 3.4b includes the January data points. For all cases, the correlations were poor.



(a) Ozone decay as a function of ozone dose in C/S water, with January results excluded.



(b) Ozone decay as a function of ozone dose in C/S water, with January results included.

Figure 3.4 Ozone decay for C/S water as a function of ozone dose, for O3:TOC ratios of 1.0 and 0.6—alum, PACI, and ferric data combined

Figure 3.5 compares the ozone decay rates with alum versus PACl for the same ozone doses. The ozone decay rate is higher when PACl is used for coagulation compared with alum. Alum consumes 0.5 mg/L as CaCO₃ of alkalinity per mg/L used in coagulation, while PACl does not consume alkalinity. Alum—a strong acid—reduces the pH of the C/S water while PACl does not reduce the pH. The chemistry of ozone in water is very complex with many pathways for the reaction of ozone with dissolved constituents. Ozone decay is a function of both pH and alkalinity. The rate of ozone decay is influenced by the formation of hydroxyl radicals which serve to consume molecular ozone, and the concentration of radical scavengers such as carbonate and bicarbonate ions, which slow the decay of ozone by the radicals. As discussed by Gardoni, et al (2012), the rate of ozone decay is faster at a higher pH—which supports the faster ozone decay for the PACl tests compared to alum.



Figure 3.5 - Comparison of ozone decay rates for alum versus PACI as coagulants

3.5 Bromate Formation

Bromate is an ozonation by-product formed through the reaction of ozone with bromide ions. To understand the potential for bromate formation with the Tuolumne River source water, an assessment of bromate formation as a function of ozone dose was completed in tandem with the monthly ozone demand tests. The results are summarized in Table 3.6. Bromide was detected in only four of the twelve raw water samples. However, bromate was detected in two of the preozonated samples and only at the highest O3:TOC dosing ratio of 1.2. All other ozonated raw water and C/S samples were non-detect (ND) for bromate, with a method reporting limit of 1 μ g/L. For reference, the MCL for bromate is 0.010 mg/L (10 μ g/L). Thus, bromate formation is not a regulatory concern for this source water.

Table 3.6 -	Summary of raw water bromide and ozonated water bromate results associated with monthly ozone decay testing,
November	2016 through October 2017.

		Preozonation			Intermediate Ozonation							
Sampling	Raw Water				C/S 7.9 m	C/S 7.9 mg/L ferric		C/S 14.6 mg/L alum		C/S 14.5 mg/L PACI		
Date	μg/L)	0.6 O3:TOC	1.0 O3:TOC	1.2 03:TOC	0.6 O3:TOC	1.0 O3:TOC	0.6 O3:TOC	1.0 O3:TOC	0.6 O3:TOC	1.0 O3:TOC		
		Bromate Concentration in Ozonated Water (μg/L) – Detection Limit in ()										
11/28/16	8	ND (1)	1.0		ND (1)	ND (1)						
12/12/16	8.6	ND (1)	ND (1)		ND (1)	ND (1)						
1/9/17	ND (5)	ND (1)	ND (1)		ND (1)	ND (1)	ND (1)	ND (1)				
2/13/17	ND (5)	ND (1)	ND (1)				ND (1)	ND (1)	ND (1)	ND (1)		
3/13/17	ND (5)		ND (1)	ND (1) ¹			ND (1)	ND (1)	ND (1)	ND (1)		
4/10/17	ND (5)		ND (1)	ND (1)			ND (1)	ND (1)	ND (1)	ND (1)		
5/8/17	ND (5)		ND (1)	ND (1)			ND (1)	ND (1)	ND (1)	ND (1)		
6/12/17	2.4		ND (1)	1.1			ND (1)	ND (1)	ND (1)	ND (1)		
7/10/17	ND (5)		ND (1)	ND (1)			ND (1)	ND (1)	ND (1)	ND (1)		
8/14/17	ND (5)		ND (1)	ND (1)			ND $(1)^2$	ND (1)	ND $(1)^2$	ND (1)		
9/11/17	ND (5)		ND (1)	ND (1)			ND (1)	ND (1)	ND (1)	ND (1)		
10/9/17	8.2		ND (1)	1.2			ND (1)	ND (1)	ND (1)	ND (1)		

¹ The 3/13/17 sample was preozonated with an O3:TOC ratio of 1.25.

 2 The 8/14/17 intermediate ozonation with PACl included an O3:TOC ratio of 1.25 instead of 0.6.

4 DESIGN OZONE DOSAGES

Per initial discussions with DDW, total required pathogen treatment credit for the Reference WTP is 2-log *Cryptosporidium*, 4-log *Giardia* and 5-log virus. Conventional treatment with filtration will achieve 2-log *Cryptosporidium*, 2.5-log *Giardia*, and 2-log virus treatment credit by meeting regulatory filter effluent turbidity requirements. Based on initial monitoring data, the source water is assumed to fall in Bin 1 of the Long-Term 2 Enhanced Surface Water Treatment Rule (LT2) and no additional *Cryptosporidium* removal or inactivation is needed with either ozone or free chlorine. Ozonation will provide 1-log *Giardia* and 2-log virus inactivation. Free chlorine will be used to achieve the additional target pathogen inactivation of 0.5-log for *Giardia* and 1-log for virus. This section discusses the ozone dose needed to provide 1-log Giardia and 2-log virus inactivation through ozone.

4.1 Disinfection Credit with Ozone

Details for calculating *Giardia* and virus inactivation credit through an ozone contactor are discussed in the SWTR Guidance Manual (U.S. EPA 1991). Disinfection credit is based on meeting a required CT to achieve the desired pathogen inactivation, where C is the residual ozone concentration and T is the hydraulic detention time. The CT required for Giardia and virus inactivation is defined in the SWTR Guidance Manual (U.S. EPA, 1991) as a function of water temperature. The CT required for *Cryptosporidium* inactivation is described in the LT2 Toolbox Guidance Manual (U.S. EPA, 2010). Figure 4.1 compares the relative inactivation rates with ozone for virus, *Giardia*, and *Cryptosporidium* as a function of water temperature. As illustrated, it is rarely practical in water treatment to use ozone for *Cryptosporidium* inactivation because of the large CT required.



Figure 4.1 - Virus, Giardia, and Cryptosporidium inactivation with ozone

A schematic of the ozone contactor for the Reference WTP with side-stream injection is provided in Figure 4.2. The first chamber of the ozone contactor is the "dissolution

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chamber," referred to as the "dissolution zone," where the ozone is rapidly dissolving into solution and meeting the initial ozone demand of the source water. As discussed earlier in this TM, the ozone demand is considered to be the amount of ozone consumed in the first 60 seconds of reaction time (Rakness, 2005). During this first 60 seconds, the ozone decay is very rapid and not first-order. For purposes of estimating the design ozone dose, the ozone concentration in the dissolution chamber is not considered stable due to rising bubbles and very rapid reaction and decay.



Figure 4.2 – Zones within Ozone Contactor with Sidestream Injection

In order to receive disinfection credit with ozone, the ozone demand of the water must first be met and then an ozone residual must be provided to achieve the required CT for disinfection credit. Per the regulations, one way to achieve ozone disinfection credit is to meet the ozone demand of the water and then maintain an ozone residual above 0.3 mg/L out of the first chamber of the ozone contactor. When this condition is met, the SWTR regulations allow 0.5-log *Giardia* inactivation credit and 1-log virus inactivation credit—referred to as "Direct Credit". Additional CT credit is achieved by monitoring ozone residual throughout the remainder of the ozone contactor. Based on experience in applying the direct credit approach (to a plant utilizing bubble diffusers in the first cell), the ozone demand of the water is not met prior to CT credit. In addition, the ozone residual out of the first chamber is not stable because of poor mixing in the first cell and because the downward water velocity can push rising bubbles downward—resulting in unrealistically high ozone concentrations leaving the first chamber. Lastly, testing has indicated the CT credit needed for 0.5-log Giardia inactivation is not actually achieved in the first cell (Rakness, 2014). Thus, disinfection credit in this dissolution zone is not considered in the following calculations of design ozone dose.

Disinfection credit is determined by multiplying CT obtained through the ozone contactor by the pathogen inactivation rate constant, according to the following equation (Chick-Watson Model, Crittenden et al., 2013, eq. 13-4):

$$-Log\left(\frac{N}{N_o}\right) = k_p \ge CT$$

where:

 $-Log\left(\frac{N}{N_o}\right) = log inactivation$ $N_o = concentration of organisms at time = 0 (org/L)$

N = concentration of organisms at time = t (org/L)

 k_p = pathogen inactivation rate constant (k_v for virus, k_G for Giardia, k_C for Cryptosporidium)

CT = ozone residual concentration x contact time

The pathogen inactivation rate constants with ozone as a function of water temperature (°C) are the following (LT2ESWTR, 2010):

$k_v = 2.1744 \mathrm{x} (1.0726)^{Temp}$	Eqn. 4-2
$k_G = 1.0380 \mathrm{x} (1.0741)^{Temp}$	Eqn. 4-3
$k_c = 0.0397 \mathrm{x} (1.09757)^{Temp}$	Eqn. 4-4

The method used to calculate pathogen inactivation through the reaction zone of the ozone contactor is the *extended integration method* (USEPA 2010), which allows pathogen inactivation credit for the complete area under the ozone decay curve with a residual ≥ 0.05 mg/L. This method is preferable to the *effluent method* (USEPA 1991), which allows inactivation credit only for the summation of CT measurements made through the ozone contactor. These inactivation approaches are illustrated in Figure 4.3.



Figure 4.3 – Comparison of *Extended Integration Method* to *Effluent Method* for calculation of CT

For the *extended integration method*, CT is calculated according to Equation 4-5 (Rakness, 2005, Eqn. 2-21).

$$CT_{total} = \left(\frac{T_{10}}{T}\right) x \left(\frac{C_o}{k^*}\right) x \left(e^{k^* x H D T} - 1\right)$$
 Eqn. 4-5

where:

 $T_{10}/T = Baffle factor$

 C_o = ozone concentration at the start of the reactive zone

k* = maximum decay rate through the contactor; assumed to be decay rate
 determined from the SOTs (decay rates are negative in this equation)

HDT = hydraulic detention time

and

$$Log Inactivation = k_p \ge CT_{total}$$
 Eqn. 4-6

Table 4.1 indicates the CT required for 1.0-log and 1.5-log *Giardia* inactivation, and the CT required for 2-log and 3-log virus inactivation with ozone as a function of water temperature

(USEPA, 1991). The CT needed for 1-log *Giardia* inactivation is approximately equal to the CT needed for 2-log virus inactivation. Therefore, the log-removal value (LRV) calculations and ozone doses discussed in this section center around *Giardia* inactivation, knowing that if *Giardia* inactivation is achieved with ozone, the required virus inactivation will be concurrently achieved. Also, additional virus inactivation, if needed, is easily achieved during final disinfection with free chlorine.

	Temperature (°C)								
Inactivation	5	10	15	20	25				
Giardia, 1-log	0.63	0.48	0.32	0.24	0.16				
Giardia, 1.5-log	0.95	0.72	0.48	0.36	0.24				
Viruses, 2-log	0.6	0.5	0.3	0.25	0.15				
Viruses, 3-log	0.9	0.8	0.5	0.4	0.25				

Table 4.1 – CT required for Giardia and virus inactivation with ozone (USEPA, 1991)

Using the *extended integration method*, the estimated ozone doses necessary to meet the demand of the water <u>and</u> achieve the required 1-log *Giardia* and 2-log virus inactivation with a baffle factor of 0.6 (consistent with the Reference WTP pre-design) were calculated using each month's SOT results. This approach was used rather than basing the calculation on the previously shown ozone demand and ozone decay regression equations (Figures 3.2 and 3.4) because the relationship between ozone dose and ozone decay rate indicated a poor correlation (Figure 3.4). Results from these monthly *extended integration method* calculations for 1-log *Giardia* inactivation with pre-ozonation are shown in Table 4.2. Monthly *extended integration method* dose calculations for 1-log Giardia inactivation with pre-ozonation at 03:TOC ratios of 1.0 and 0.6 are shown in Tables 4.3 and 4.4.

Month	O3:TOC Ratio	Ozone Dose (mg/L)	Ozone Decay Coefficient (min-1)	60-s Ozone Demand (mg/L)	CT Value for 1-log Giardia Inactivation	Giardia Inactivation Rate Constant (k _G)	HDT of Reaction Zone (min)	Ozone Dose Needed for 1- log Giardia LRV in Reaction Zone (mg/L)	Ozone Dose to Meet 60-s Demand and 1-log Giardia Inactivation (mg/L)			
November	1.0	1.87	0.255	1.16	0.2310	4.3288	5	0.136	1.30			
December	1.0	2.04	0.276	1.30	0.2310	4.3288	5	0.142	1.45			
January	1.0	4.08	0.285*	3.46	0.2310	4.3288	5	0.145	3.60			
February	1.0	3.00	0.285	1.83	0.2310	4.3288	5	0.145	1.98			
March	1.0	2.72	0.395	1.88	0.2310	4.3288	5	0.177	2.05			
April	1.0	2.46	0.386	1.76	0.2310	4.3288	5	0.174	1.93			
May	1.0	2.32	0.349	1.52	0.2310	4.3288	5	0.163	1.68			
June	1.0	2.28	0.345	1.62	0.2310	4.3288	5	0.162	1.78			
July	1.0	2.23	0.464	2.07	0.2310	4.3288	5	0.198	2.27			
August	1.0	2.16	0.330	1.95	0.2310	4.3288	5	0.157	2.11			
September	1.0	2.01	0.214	1.14	0.2310	4.3288	5	0.125	1.27			
October	1.0	2.05	0.257	1.40	0.2310	4.3288	5	0.137	1.54			
Notes: * The February	Notes: * The February decay coefficient was substituted because the measured decay coefficient was 1.3592 min ⁻¹ and considered erroneously high.											

Table 4.2 - Ozone dose needed to meet ozone demand and 1-log Giardia inactivation, with Pre-Ozone ($T_{10}/T = 0.6$, Temp=20°C)

Table 4.3 - Ozone dose needed to meet ozone demand and 1-log	Giardia inactivation, with Intermediate-Ozone (O3:TOC Ratio =
1.0; $T_{10}/T = 0.6$; Temp=20°C)	

Month	O3:TOC Ratio	Ozone Dose (mg/L)	Ozone Decay Coefficient (min-1)	60-s Ozone Demand (mg/L)	CT Value for 1-log Giardia Inactivation	Giardia Inactivation Rate Constant (k _G)	HDT of Reaction Zone (min)	Ozone Dose Needed for 1- log Giardia LRV in Reaction Zone (mg/L)	Ozone Dose to Meet 60-s Demand and 1-log Giardia Inactivation (mg/L)
Coagulant =	Alum (14.6	mg/L)							
January	1.0	3.04	0.123	1.45	0.2310	4.3288	5	0.103	1.55
February	1.0	1.80	0.136	0.86	0.2310	4.3288	5	0.106	0.96
March	1.0	1.77	0.080	0.74	0.2310	4.3288	5	0.093	0.83
April	1.0	1.56	0.096	0.67	0.2310	4.3288	5	0.097	0.77
May	1.0	1.70	0.070	0.41	0.2310	4.3288	5	0.091	0.50
June	1.0	1.43	0.091	0.59	0.2310	4.3288	5	0.096	0.69
July	1.0	1.50	0.082	0.60	0.2310	4.3288	5	0.094	0.70
August	1.0	1.96	0.115	1.05	0.2310	4.3288	5	0.101	1.15
September	1.0	1.98	0.099	0.84	0.2310	4.3288	5	0.098	0.94
October	1.0	1.44	0.083	0.70	0.2310	4.3288	5	0.094	0.79
Coagulant =	PACI (14.5	mg/L)			•	•		•	
February	1.0	1.88	0.178	1.00	0.2310	4.3288	5	0.116	1.12
March	1.0	1.81	0.119	0.92	0.2310	4.3288	5	0.102	1.02
April	1.0	1.57	0.157	0.79	0.2310	4.3288	5	0.111	0.90
May	1.0	1.71	0.093	0.59	0.2310	4.3288	5	0.096	0.68
June	1.0	1.40	0.101	0.64	0.2310	4.3288	5	0.098	0.74
July	1.0	1.68	0.117	0.87	0.2310	4.3288	5	0.102	0.97
August	1.0	2.16	0.177	1.46	0.2310	4.3288	5	0.116	1.58
September	1.0	1.93	0.156	1.27	0.2310	4.3288	5	0.111	1.38
October	1.0	1.45	0.106	0.73	0.2310	4.3288	5	0.099	0.83

Table 4.4 -	- Ozone d	ose needed	to meet ozor	e demand	and 1-log (Giardia in	activation,	with Inter	mediate-Ozo	one (O3:TOC	Ratio =
0.6; T_{10}/T	= 0.6; Ter	mp=20°C)									

Month	O3:TOC Ratio	Ozone Dose (mg/L)	Ozone Decay Coefficient (min-1)	60-s Ozone Demand (mg/L)	CT Value for 1-log Giardia Inactivation	Giardia Inactivation Rate Constant (k _G)	HDT of Reaction Zone (min)	Ozone Dose Needed for 1- log Giardia LRV in Reaction Zone (mg/L)	Ozone Dose to Meet 60-s Demand and 1-log Giardia Inactivation (mg/L)
Coagulant =	Alum (14.6	mg/L)							
January	0.6	1.82	0.193	1.07	0.2310	4.3288	5	0.120	1.19
February	0.6	1.08	0.226	0.66	0.2310	4.3288	5	0.129	0.79
March	0.6	1.06	0.112	0.52	0.2310	4.3288	5	0.101	0.62
April	0.6	0.94	0.178	0.56	0.2310	4.3288	5	0.116	0.67
May	0.6	1.02	0.180	0.59	0.2310	4.3288	5	0.117	0.71
June	0.6	0.86	0.136	0.45	0.2310	4.3288	5	0.106	0.55
July	0.6	0.90	0.139	0.51	0.2310	4.3288	5	0.107	0.62
August	0.6	1.18	0.209	0.74	0.2310	4.3288	5	0.124	0.86
September	0.6	1.19	0.172	0.63	0.2310	4.3288	5	0.115	0.75
October	0.6	0.86	0.133	0.50	0.2310	4.3288	5	0.105	0.61
Coagulant =	PACI (14.5	mg/L)	•						
February	0.6	1.13	0.297	0.70	0.2310	4.3288	5	0.148	0.85
March	0.6	1.09	0.130	0.49	0.2310	4.3288	5	0.105	0.60
April	0.6	0.94	0.177	0.55	0.2310	4.3288	5	0.116	0.67
Мау	0.6	1.02	0.150	0.49	0.2310	4.3288	5	0.110	0.60
June	0.6	0.84	0.200	0.53	0.2310	4.3288	5	0.122	0.65
July	0.6	1.01	0.285	0.58	0.2310	4.3288	5	0.145	0.73
August	0.6	1.16	0.218	0.68	0.2310	4.3288	5	0.126	0.80
September	0.6	0.87	0.183	0.55	0.2310	4.3288	5	0.117	0.67
October	0.6	1.13	0.297	0.70	0.2310	4.3288	5	0.148	0.85

Linear regression equations were calculated for the relationship between TOC concentration and the required ozone dose for 1-log *Giardia* inactivation. Figure 4.4 shows the regression for ozone dose as a function of raw water TOC (i.e., pre-ozonation), using an O3:TOC ratio of 1.0. Figure 4.5 shows the regression equations for ozone dose as a function of C/S TOC (i.e., intermediate ozonation) for the combined alum and PACl datasets. These regression equations were then used to calculate ozone doses for both pre-ozonation and intermediate ozonation for a range of anticipated raw water TOC concentrations: (a) historical maximum TOC, (b) SRWA measured maximum TOC, (c) SRWA average measured TOC, and (d) SRWA minimum measured TOC. The range of ozone doses needed for pre-ozonation are summarized in Table 4.2 and vary from a low of 1.2 mg/L to a maximum dose of 5.6 mg/L. For intermediate ozonation, the range of ozone doses needed for the anticipated TOC concentrations are summarized in Table 4.3 and range from 0.5 mg/L to 2.0 mg/L.

The design ozone dose should be able to meet the maximum anticipated ozone dose. For the raw water, a design ozone dose of 5.6 mg/L is needed, and for intermediate ozonation, a design ozone dose of 2.0 mg/L is needed.



Figure 4.4 – Ozone dose required to achieve 1.0-log Giardia inactivation in raw water (pre-ozonation)



Figure 4.5 – Ozone dose required to achieve 1.0-log Giardia inactivation for C/S (intermediate ozonation), based on alum and PACI SOT results combined

Table 4-5.	Estimated	ozone do	se to	achieve	1-log	Giardia	and	2-log	virus	inactiva	tion
with pre-oz	zonation (T	$\mathbf{T}10/\mathbf{T}=0.$	6; T	emperat	ure =	20°C)					

Scenario	O3:TOC Ratio	Historical Max TOC	SRWA Measured Max TOC	SRWA Measured Avg TOC	SRWA Measured Min TOC
Raw TOC (mg/L)		6.5	4.2	2.8	1.8
Calculated Ozone Dose (mg/L)	1.0	5.64	3.53	1.79	1.15

	`				
Scenario	O3:TOC Ratio	Historical Max TOC	SRWA Measured Max TOC	SRWA Measured Avg TOC	SRWA Measured Min TOC
C/S TOC (calculated, mg/L)*		6.5 x 0.55 = 3.6	2.3	1.8	1.2
Calculated Ozone Dose	1.0	2.03	1.28	0.80	0.53
(Alum+PACI)	0.6	1.41	0.95	0.66	0.50

Table 4.6. Estimated ozone dose to achieve 1.0-log Giardia and 2-log virus inactivation with intermediate ozonation (T10/T = 0.6; Temperature = 20° C)

* C/S water TOC concentration was calculated based on the raw water TOC concentration and the D/DBPR Enhanced Coagulation TOC removal requirements:

• 45% TOC removal if the raw water TOC \geq 4 mg/L

• 35% TOC removal is required if the raw water TOC > 2 mg/L and < 4 mg/L.

5 CONCLUSIONS

What ozone dose is required to meet the ozone demand?

The ozone dose was correlated with 60-second ozone demand based on monthly SOT results for source water samples collected between November 2016 and October 2017. Based on the correlation shown in Figure 3.1 for raw water and the historical maximum TOC value (Table 3.5), the ozone demand is expected to range from approximately 1 to 5.5 mg/L for the range of TOC concentrations observed in the river. The correlation for C/S water was shown in Figure 3.2, from which the demand is expected to range from 0.5 to 2.3 mg/L depending on the percentage TOC removed during coagulation.

What is the seasonal variability of the ozone demand?

The winter water quality represented by the January through March 2017 samples were characterized by higher turbidity (5-12 NTU vs. <4 NTU) and higher TOC (>2.7 mg/L vs. <2.5 mg/L), which gradually tapered off with the decreased flows in the river (Figure 2.1). The increase in turbidity and TOC for the winter water samples yielded increased ozone demand in the raw source water. The measured ozone demand of the raw water ranged from 1.1 mg/L to 3.5 mg/L, and the measured ozone demand of the C/S water ranged from 0.5 mg/L to 1.5 mg/L. In general, the ozone demand of the C/S water was higher when PACI was used for coagulation compared to alum.

Is bromate formation a concern for this water?

Results indicate that bromate formation is not expected to be an issue for this source water, regardless of the location of ozonation—pre-ozonation (raw water) or intermediate ozonation (clarified water).

What is the estimated design ozone dose to achieve 1.0-log *Giardia* inactivation?

A design ozone dose of 5.6 mg/L is needed for pre-ozonation, and a design ozone dose of 2.0 mg/L is needed for intermediate ozonation.

6 REFERENCES

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Appendix A – SOT Decay Profiles A.1 Monthly Pre-ozonation Decay Curves

Figure A.1. Raw water ozone decay curves for November 2016 – February 2017 samples.

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Figure A.2. Raw water ozone decay curves for March – June 2017 samples.



Figure A.3. Raw water ozone decay curves for July – October 2017 samples.







Figure A.4. Clarified water ozone decay curves for November 2016 – February 2017 samples. Coagulants and doses used to prepare clarified water are specified for each test.



Figure A.5. Clarified water ozone decay curves for March – June 2017 samples. Coagulants and doses used to prepare clarified water are specified for each test.



Figure A.6. Clarified water ozone decay curves for July – October 2017 samples. Coagulants and doses used to prepare clarified water are specified for each test.

APPENDIX B – First-Order Ozone Decay

B.1 Monthly Pre-ozonation Results

Ln(C) versus reaction time is plotted for the raw water dosed with 0.6, 1.0, and 1.2 O3:TOC in Figure B.8 for the November, December, January, and February bench tests. The residual ozone concentrations measured at 60 seconds and beyond were used in developing these regression lines. The data associated with the 0.6 ozone-to-TOC ratio doses from the December, January, and February samples was too limited to calculate initial demand and decay coefficients because the ozone dose was not high enough to maintain a residual for a long enough time to collect enough data points for a regression line.



Figure B.7. Raw water first-order ozone decay for November 2016 – February 2017 samples.





Figure B.8. Raw water first-order ozone decay for March – June 2017 samples.



Figure B.9. Raw water first-order ozone decay for March – June 2017 samples.

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B.2 Monthly Intermediate Ozonation Results

As with the raw water, ln(C) versus reaction time is plotted for the clarified water dosed with 0.6 and 1.0 O3:TOC in Figure B.12 for the November, December, January, and February bench tests. In addition to the two ozone doses (0.6 and 1.0 O3:TOC), the plots in Figure B.12 characterize the first-order ozone decay of the waters clarified using different coagulants. Millimolar-per-liter equivalent doses of ferric (November, December, and January), alum (January through October), and PACI (February through October) were used to prepare the clarified water.

SRWA – Ozone Demand Bench Testing TM2 (continued)



Figure B.10. Clarified water first-order ozone decay for November 2016 – February 2017 samples. Coagulants and doses used to prepare clarified water are specified for each test.



Figure B.11. Clarified water first-order ozone decay for March – June 2017 samples. Coagulants and doses used to prepare clarified water are specified for each test.



Figure B.12. Clarified water first-order ozone decay for July – October 2017 samples. Coagulants and doses used to prepare clarified water are specified for each test.

APPENDIX C – Summary of Ozone Demand Results

C.1 Monthly Pre-ozonation Results

Table C.1. Initial and 60-second ozone demand of Raw Tuolumne River water as a function of ozone dose and water temperature.

Target	Transferred Water Ozone Decay Ozone Ozone Ozone Ozone Ozone Ozone Ozone							e (mg/L)				
Ratio	(mg/L)	(°C)	<i>k</i> (min ⁻¹)	Residual Demand (mg/L) (mg/L)	Demand (mg/L)	0 min	0.5 min	1 min	2 min	3 min	4 min	5 min	6 min
Nov. 2016 Te	st Results	TOC =	1.87	Blue=7°C;	Red=22°C								
0.6	1.12	9.7	0.1138	0.49	0.64	1.12	0.63	0.49	0.42	0.40	0.30	0.31	0.28
1	1.87	8.7	0.0835	0.98	0.89	1.87	1.06	0.98	0.94	0.85	0.76	0.72	0.74
0.6	1.12	22.0	0.4988	0.34	0.78	1.12	0.42	0.34	0.24	0.14	0.09	0.06	0.03
1	1.87	22.1	0.2552	0.71	1.16	1.87	0.75	0.71	0.53	0.45	0.31	0.26	0.19
Dec. 2016 Te	st Results	TOC =	2.04										
0.6	1.22	20.2	0.9114	0.19	1.04	1.22	0.26	0.19	0.07	0.03			
1	2.04	19.9	0.2764	0.74	1.30	2.04	0.84	0.74	0.54	0.41	0.30	0.22	0.20
January 2017	Test Results	TOC =	4.08										
0.6	2.45	25.9	n/a ^(B)	n/a ^(B)	n/a ^(B)	2.45	0.09						
1	4.08	25.5	1.3592	0.62	3.46	4.08	1.03	0.62	0.23	0.04			
February 201	7 Test Results	TOC =	3.0										
0.6	1.80	21.4	0.464	0.16	1.64	1.80	0.32	0.16	0.01	0.06			
1	3.00	21.2	0.2851	1.17	1.83	3.00	1.48	1.17	0.80	0.56	0.40	0.29	0.31
March 2017 T	est Results	TOC =	2.72	-									
1	2.72	19.4	0.3954	0.84	1.88	2.72	1.08	0.84	0.58	0.43	0.29	0.19	0.11
1.25	3.40	18.9	0.2498	1.27	2.13	3.40	1.51	1.27	0.98	0.74	0.59	0.47	0.36
April 2017 Tes	st Results	TOC =	2.46										
1	2.46	20.8	0.3857	0.70	1.76	2.46	0.89	0.70	0.47	0.34	0.23	0.16	0.10
1.2	2.95	21.2	0.2661	1.11	1.84	2.95	1.37	1.11	0.85	0.64	0.49	0.38	0.29
May 2017 Tes	st Results	TOC =	2.32										
1	2.32	21.9	0.3485	0.80	1.52	2.32	0.89	0.80	0.58	0.41	0.30	0.21	0.14
1.2	2.78	21.6	0.2104	1.46	1.33	2.78	1.66	1.46	1.21	0.98	0.78	0.65	0.51
June 2017 Te	st Results	TOC =	2.28										
1	2.28	20.7	0.3453	0.66	1.62	2.28	0.84	0.66	0.47	0.33	0.25	0.17	0.11

SRWA – Ozone Demand Bench	Testing	TM2 (continued)
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Target	Transferred Ozone Dose	Water Temp.	Ozone Decay Coefficient ^(A) , <i>k</i> (min ⁻¹)	60-Sec. Ozone Residual (mg/L)	60-Sec Ozone Demand	Ozone Residual after SOT Sampling Time (mg/L)								
Ratio	(mg/L)	(°C)			Demand (mg/L)	0 min	0.5 min	1 min	2 min	3 min	4 min	5 min	6 min	
1.2	2.74	20.4	0.2092	1.20	1.54	2.74	1.33	1.20	0.94	0.76	0.61	0.51	0.42	
July 2017 Tes	t Results	TOC =	2.23											
1	2.23	21.5	0.4642	0.57	1.66	2.23	0.65	0.57	0.36	0.25	0.16	0.10	0.05	
1.2	2.68	21.1	0.2209	0.96	1.72	2.68	1.10	0.96	0.75	0.59	0.48	0.39	0.31	
August 2017	Fest Results	TOC =	2.16											
1	2.16	21.9	0.3298	0.58	1.58	2.16	0.72	0.58	0.37	0.29	0.21	0.15	0.11	
1.2	2.59	21.7	0.1954	1.12	1.47	2.59	1.29	1.12	0.86	0.70	0.60	0.49	0.41	
Sept. 2017 Te	est Results	TOC =	2.01											
1	2.01	20.6	0.2143	0.87	1.14	2.01	1.12	0.87	0.67	0.55	0.44	0.36	0.30	
1.2	2.41	20.6	0.1878	0.99	1.42	2.41	1.10	0.99	0.78	0.64	0.55	0.46	0.38	
October 2017	Test Results	TOC =	2.05											
1	2.05	21.1	0.2573	0.65	1.40	2.05	0.79	0.65	0.48	0.38	0.30	0.23	0.18	
1.2	2.46	21.5	0.2362	0.77	1.69	2.46	0.90	0.77	0.59	0.46	0.37	0.30	0.23	

(A) These ozone decay coefficients are based on ozone residual concentrations measured after one minute or more of reaction time. Thus, the decay coefficients exclude the initial period of rapid decay when the ozone demand of the water is being met.

(B) The ozone dosed was insufficient to exceed the ozone demand and maintain an ozone residual for the 6 minutes of decay testing; no ozone demand values could be calculated.

C.2 Monthly Intermediate Ozonation Results

Table C.2. Initial and 60-second ozone demand of clarified water as a function of ozone dose and water temperature.

Target	Transferred Ozone Dose (mg/L)	Water Temp. (°C)	Ozone Decay Coefficient ^(A) , <i>k</i> (min ⁻¹)	60-Sec. Ozone Residual (mg/L)	60-Sec Ozone Demand (mg/L)	Ozone Residual after SOT Sampling Time(mg/L)								
Ratio						0 min	0.5 min	1 min	2 min	3 min	4 min	5 min	6 min	
November 2	016 Test Results	s (7.9 m	g/L Ferric, C/S W	ater TOC =	1.21 mg/L)									
0.6	0.73	7.2	0.080	0.32	0.41	0.73	0.38	0.32	0.28	0.26	0.26	0.22	0.08	
1	1.21	6.8	0.089	0.73	0.48	1.21	0.78	0.73	0.62	0.55	0.50	0.50	0.45	
0.6	0.73	22.1	0.171	0.31	0.41	0.73	0.37	0.31	0.25	0.22	0.18	0.16	0.13	



Target	Transferred Ozone Dose (mg/L)	Water Temp. (°C)	Ozone Decay Coefficient ^(A) , <i>k</i> (min ⁻¹)	60-Sec. Ozone Residual (mg/L)	60-Sec Ozone Demand (mg/L)	Ozone Residual after SOT Sampling Time(mg/L)							
Ratio						0 min	0.5 min	1 min	2 min	3 min	4 min	5 min	6 min
1	1.21	22	0.138	0.48	0.73	1.21	0.56	0.48	0.39	0.32	0.28	0.26	0.24
December 2016 Test Results (7.9 mg/L Ferric, C/S Water TOC = 1.29 mg/L)													
0.6	0.77	21.0	0.169	0.32	0.45	0.77	0.34	0.32	0.27	0.23	0.19	0.17	0.14
1	1.29	21.2	0.113	0.65	0.64	1.29	0.62	0.65	0.56	0.52	0.47	0.38	0.38
January 2017 Test Results (7.9 mg/L Ferric, C/S Water TOC = 4.24 mg/L)													
0.6	2.54	20.7	0.953	0.61	1.94	2.54	0.79	0.61	0.23	0.09	0.00		
1	4.24	21	0.345	1.42	2.82	4.24	1.85	1.42	0.99	0.71	0.49	0.32	0.27
January 20	17 Test Results	(14.6 m	g/L Alum, C/S Wa	ater TOC = 3	.04 mg/L)			-					
0.6	1.82	21.1	0.193	0.75	1.07	1.82	0.92	0.75	0.59	0.48	0.39	0.34	0.28
1	3.04	21.2	0.123	1.59	1.45	3.04	1.71	1.59	1.35	1.18	1.07	0.95	0.85
February 20	17 Test Results	(14.6 m	ig/L Alum, C/S Wa	ater TOC = 1	1.80 mg/L)		A 1A					0.10	
0.6	1.08	23.5	0.226	0.42	0.66	1.08	0.49	0.42	0.26	0.24	0.20	0.16	0.12
1	1.80	23.6	0.136	0.94	0.86	1.80	1.06	0.94	0.79	0.69	0.61	0.53	0.47
February 20	17 Test Results	(14.5 m	ig/L PACI, C/S Wa	ater TOC = 2	1.88 mg/L)								
0.6	1.13	23.4	0.297	0.43	0.70	1.13	0.54	0.43	0.31	0.23	0.18	0.12	0.10
1	1.88	23.3	0.178	0.88	1.00	1.88	1.01	0.88	0.71	0.57	0.51	0.42	0.35
March 201	7 Test Results	(14.6 mg	/L Alum, C/S Wat	ter $IOC = 1$.	77 mg/L)				a 1=				
0.6	1.06	18.2	0.112	0.54	0.52	1.06	0.60	0.54	0.47	0.41	0.37	0.34	0.31
1	1.77	18.8	0.080	1.03	0.74	1.77	1.10	1.03	0.92	0.85	0.79	0.74	0.68
March 201	7 Test Results	(14.5 mg	/L PACI, C/S Wat	er TOC = 1.	81 mg/L)	4.00	0.00	0.00	0.54	0.11	0.00	0.05	0.04
0.6	1.09	18.6	0.130	0.60	0.49	1.09	0.66	0.60	0.51	0.44	0.39	0.35	0.31
1	1.81	19.1	0.119	0.89	0.92	1.81	0.99	0.89	0.77	0.69	0.62	0.54	0.49
April 2017	Test Results	(14.6 mg/	L Alum, C/S Wate	r TOC = 1.5	6 mg/L)	0.04	0.45	0.00	0.00	0.05	0.04	0.40	0.40
0.6	0.94	21.5	0.178	0.38	0.56	0.94	0.45	0.38	0.30	0.25	0.21	0.18	0.16
1	1.56	21.6	0.096	0.89	0.67	1.56	0.99	0.89	0.78	0.69	0.65	0.58	0.55
April 2017	April 2017 Test Results (14.5 mg/L PACI, C/S Water TOC = 1.57 mg/L)						0.47	0.00	0.04	0.00	0.00	0.40	0.40
0.6	0.94	21.5	0.177	0.39	0.55	0.94	0.47	0.39	0.31	0.26	0.22	0.19	0.16
1	1.57	21.8	0.157	0.78	0.79	1.57	0.91	0.78	0.66	0.58	0.50	0.41	0.36
May 2017	I EST RESULTS	(14.6 mg/	LAIUM, C/S Wate	r 100 = 1.7	U mg/L)	1.00	0 5 4	0.40	0.40	0.00	0.00	0.00	0.40
0.6	1.02	21.3	0.180	0.43	0.59	1.02	0.54	0.43	0.40	0.33	0.28	0.22	0.18
1	1.70	21.9	0.070	1.29	0.41	1.70	1.33	1.29	1.21	1.12	1.02	0.99	0.91



Target	Transferred Ozone Dose (mg/L)	Water Temp. (°C)	Ozone Decay Coefficient ^(A) , <i>k</i> (min ⁻¹)	60-Sec. Ozone Residual (mg/L)	60-Sec Ozone Demand (mg/L)	Ozone Residual after SOT Sampling Time(mg/L)							
Ratio						0 min	0.5 min	1 min	2 min	3 min	4 min	5 min	6 min
May 2017	Test Results	(14.5 mg/	L PACI, C/S Wate	er TOC = 1.7	1 mg/L)								
0.6	1.03	21.1	0.150	0.53	0.50	1.03	0.57	0.53	0.44	0.37	0.31	0.24	0.27
1	1.71	19.4	0.093	1.12	0.59	1.71	1.05	1.12	0.88	0.87	0.82	0.70	0.68
June 2017 Test Results (14.6 mg/L Alum, C/S Water TOC = 1.43 mg/L)													
0.6	0.86	21.2	0.136	0.41	0.45	0.86	0.46	0.41	0.34	0.30	0.26	0.23	0.20
1	1.43	20.8	0.091	0.84	0.59	1.43	0.86	0.84	0.74	0.74	0.63	0.57	0.54
June 2017	7 Test Results	(14.5 mg/	L PACI, C/S Wate	er TOC = 1.4	0 mg/L)								
0.6	0.84	21.2	0.200	0.31	0.53	0.84	0.36	0.31	0.25	0.21	0.17	0.14	0.12
1	1.40	21.4	0.101	0.76	0.64	1.40	0.81	0.76	0.66	0.60	0.55	0.48	0.46
July 2017	Test Results	(14.6 mg/l	_ Alum, C/S Wate	er TOC = 1.5	0 mg/L)								
0.6	0.90	21.0	0.139	0.39	0.51	0.90	0.43	0.39	0.32	0.28	0.26	0.21	0.19
1	1.50	21.4	0.082	0.90	0.60	1.50	0.92	0.90	0.78	0.72	0.67	0.62	0.58
July 2017	Ily 2017 Test Results (14.5 mg/L PACI, C/S Water TOC = 1.68 mg/L)												
0.6	1.01	21.2	0.285	0.30	0.71	1.01	0.34	0.30	0.21	0.16	0.12	0.09	0.07
1	1.68	20.8	0.117	0.81	0.87	1.68	0.89	0.81	0.70	0.62	0.55	0.50	0.45
August 2017 Test Results (14.6 mg/L Alum, C/S Water TOC = 1.96 mg/L)													
0.6	1.18	22.2	0.209	0.44	0.74	1.18	0.52	0.44	0.33	0.26	0.22	0.18	0.15
1	1.96	22.1	0.115	0.91	1.05	1.96	1.01	0.91	0.77	0.68	0.61	0.55	0.51
August 201	7 Test Results	(14.5 mg	/L PACI, C/S Wa	ter TOC = 2.	16 mg/L)								
1	2.16	22.2	0.177	0.70	1.46	2.16	0.84	0.70	0.57	0.50	0.40	0.35	0.28
1.2	2.59	22.1	0.132	1.13	1.46	2.59	1.31	1.13	0.94	0.84	0.73	0.65	0.58
September 2017 Test Results (14.6 mg/L Alum, C/S Water TOC = 1.98 mg/L)													
0.6	1.19	21.3	0.172	0.56	0.63	1.19	0.63	0.56	0.44	0.37	0.32	0.27	0.23
1	1.98	20.8	0.099	1.14	0.84	1.98	1.23	1.14	1.00	0.89	0.79	0.76	0.69
September 2017 Test Results (14.5 mg/L PACI, C/S Water TOC = 1.93 mg/L)												'	
0.6	1.16	21.3	0.218	0.48	0.68	1.16	0.57	0.48	0.37	0.29	0.24	0.20	0.16
1	1.93	21.4	0.156	0.66	1.27	1.93	0.80	0.66	0.55	0.47	0.40	0.35	0.30
October 2017 Test Results (14.6 mg/L Alum, C/S Water TOC = 1.44 mg/L)													
0.6	0.86	21.9	0.133	0.36	0.50	0.86	0.41	0.36	0.30	0.26	0.22	0.21	0.18
1	1.44	22.1	0.083	0.74	0.70	1.44	0.81	0.74	0.67	0.61	0.57	0.52	0.49
October 2017 Test Results (14.5 mg/L PACI, C/S Water TOC = 1.45 mg/L)													



Target Ozone/TOC Ratio	Transferred Ozone Dose (mg/L)	Water Temp. (°C)	Ozone Decay Coefficient ^(A) , <i>k</i> (min ⁻¹)	60-Sec. Ozone Residual (mg/L)	60-Sec Ozone Demand (mg/L)	Ozone Residual after SOT Sampling Time(mg/L)							
						0 min	0.5 min	1 min	2 min	3 min	4 min	5 min	6 min
0.6	0.87	22.2	0.183	0.32	0.55	0.87	0.37	0.32	0.25	0.22	0.18	0.15	0.13
1	1.45	22.2	0.106	0.72	0.73	1.45	0.77	0.72	0.63	0.57	0.51	0.46	0.42

(A) These ozone decay coefficients are based on ozone residual concentrations measured after one minute or more of reaction time. Thus, the decay coefficients exclude the initial period of rapid decay when the ozone demand of the water is being met.