Appendix F: City of Santa Monica Olympic Well Field Restoration and Arcadia Water Treatment Plant Expansion Project Ultraviolet Advanced Oxidation Process Performance Testing Results

City of Santa Monica

Public Works Department
Water Resources Division

December 26, 2023

Mr. Terry Kim

District Engineer
State Water Resources Control
Board – Division of Drinking Water
500 North Central Avenue, Suite 500
Glendale, CA 91203

City of Santa Monica Olympic Well Field Restoration and Arcadia Water Treatment Plant Expansion Project
Ultraviolet Advanced Oxidation Process (UVAOP) Performance Testing Results

Dear Mr. Kim:

The City of Santa Monica (City) is pleased to submit the attached Performance Test Report for the Olympic Well Field Restoration and Arcadia Water Treatment Plant Expansion TrojanUVFlex200™ – Advanced Oxidation System (Report) for the State Water Resources Control Board, Division of Drinking Water (DDW) review and approval. Performance testing of the Ultraviolet Advanced Oxidation Process (UV/AOP) was conducted by TrojanUV, along with the Contractor (Walsh) and the designer (Brown and Caldwell), from September 22nd to October 5th, 2023. The UV/AOP performance testing was conducted following the "UV/AOP Performance Test Plan" approved by the DDW on August 9, 2023. As discussed with the DDW during the monthly project coordination meeting on August 9, 2023, testing of Olympic Well SM-4 was removed from the test protocol due to diminished pumping capacity. The objective of the performance testing was to demonstrate, after successful functional testing, that the UV AOP equipment and system meets all specified performance requirements.

The testing included a total of 22 test runs with varying operational modes (auto or manual), ultraviolet transmittance (UVT), lamp sections on, lamp power, hydrogen peroxide (H_2O_2) levels, influent concentrations of 1,4-dioxane, and scavenging term. The UV AOP system that was tested is comprised of two separate trains of single chamber TrojanUVFlex200™ reactors, each with 11 populated lamp sections and 1 unpopulated lamp section (264 lamps per reactor) with H_2O_2 dosing to accomplish the compliance level treatment requirement of 2.4 log reduction (LR) of 1,4-dioxane, 2.2 log reduction of TCE and 2.3 log reduction of PCE. Testing was performed on one train as both trains are identical. In auto mode, the UV system control algorithm dynamically adjusted reactor power and H_2O_2 concentration to meet the contaminant treatment removal objectives based upon the following identified process input

parameters: flow rate, UVT, hydroxyl radical scavenging demand, and contaminant influent and target effluent concentration (to calculate target LRs). A safety factor of 1.1 (i.e., 10% higher operating setpoint) was applied to the compliance LR setpoints to constrain the limits of the system's operations.

The City has reviewed the Report dated December 21, 2023, and noted the following conclusions:

- The TrojanUVFlex200 automatic control program appears fully capable of controlling the system operation, as shown in Figure 5-7 of the Report, to reliably meet the contaminant treatment targets, not only at the design conditions, but also when the UVT is below the design value and when the flow per train is below the design value. Inclusion of a 1.1 safety factor provided an additional level of reliability.

- As described in the TrojanUV UV-AOP Performance Test Plan in Appendix D of the Acceptance Test Plan, knowing the LR value for one contaminant in a UV/H2O2-treated water allows the prediction of LR values for other contaminants present in the water and susceptible to UV/H2O2 treatment. Thus 1,4-D spiking and measurement of LRs was used to demonstrate adequate treatment for achievement of all LR goals (e.g., TCE and PCE removal). The validity of this assumption is reviewed in the Addendum to this letter.

- The measured and programmable logic controller-calculated UV influent and effluent H2O2 concentrations were in good agreement. The measured 1,4-dioxane LR values exceeded the operating LR setpoints for all tests for which the 1,4-dioxane compliance LR target was either the design value of 2.4 or the reduced value of 1.8 for both the design scavenging term (ST) value and with a reduced ST value at a reduced influent pH of 6.5. As PCE and TCE were not spiked like 1,4-dioxane, all but one UV effluent PCE (Test 10 – UV effluent concentration of 0.26 μg/L) and all UV effluent TCE concentrations were less than the Maximum Detection Level of 0.18 μg/L at their respective design LR setpoints per Table 4-1 of the Report.

- For those four tests which had a reduced 1,4-dioxane LR target of 1.2, 3 of the 4 runs met or exceeded the compliance target, while test 14 achieved 92% of the compliance target LR (i.e., 1.1 vs 1.2). Trace concentrations of nitrite were detected in three influent water quality samples very near the detection limit and so were qualified. TrojanUV suspects the influence of nitrite contributed to a higher ST than the plan setpoint value. However, the test was conducted without sodium hypochlorite dosing occurring upstream of the pretreatment greensand filtration process. As the water will be chlorinated prior to greensand treatment during normal operations, nitrite is expected to fully oxidize to nitrate, and thus its contribution to the ST will be eliminated.

Based on the testing results, the City proposes to use the Trojan UV "Dynamically Adjusted Control Algorithm" approach with a variable lamp power and H2O2 dose. The City proposes to

use a conservative setting corresponding to the design worst-case LR of 2.4, 2.2, and 2.3 for 1,4-dioxane, TCE and PCE, respectively; the design scavenging term of 130,000/s when operating at ambient influent pH; an operating scavenging term of 90,000/s when operating at an influent pH of 6.6 or lower; and, a 1.1 safety factor (i.e., 10% higher operating setpoint) applied to the compliance LR setpoints. This operation mode would be consistent for both UV AOP treatment trains. Operation of greensand filtration with free chlorine dosing would also be required prior to treatment.

If you have any questions or additional comments pertaining to the Report, and the City's proposed mode of operation for the UV AOP system, please contact me at (424) 299-6733 or via email at alex.waite@santamonica.gov.

Sincerely,

Alex Waite, P.E.

Supervising Civil Engineer
City of Santa Monica
2500 Michigan Ave, Bldg 1
Santa Monica, CA 90404

CC: Saeedreza Hafeznezami, State Water Resources Control Board – Division of Drinking Water (via email)

Matthew Megill, State Water Resources Control Board – Division of Drinking Water (via email)

Jeff Densmore, State Water Resources Control Board – Division of Drinking Water (via email)

Scott Coffin, State Water Resources Control Board – Division of Drinking Water (via email)

Kurt Souza, State Water Resources Control Board – Division of Drinking Water (via email)

Addendum

Rationale for Proposing 1,4-Dioxane Removal Yield as an Indicator for Tetrachloroethene (PCE) and Trichloroethene (TCE) Removal Efficiency from Groundwater with the UV/H2O2 AOP at Water Treatment Facilities
By: Brown and Caldwell using TrojanUV's Test Plan Assumptions

To overcome the challenges and uncertainties associated with spiking PCE and TCE (compounds technically insoluble in water) to the UV influent water, 1,4-dioxane treatment performance (spiking) was used as an indicator of PCE and TCE treatment. As described in the TrojanUV UV-AOP Performance Test Report in Appendix D of the Acceptance Test Plan, using equation (1) from that report, and knowing the LR value for one contaminant in a UV/H2O2-treated water allows the prediction of LR values for other contaminants present in the water and susceptible to UV/H2O2 treatment.

Thus, TrojanUV used the kinetic equation (1) with the ·OH water background demand of 130,000 s^{-1} and the fundamental kinetic parameters for H2O2 and for the three contaminants selected by them from the literature reported values and used with Kinetic Model (proprietary and confidential) to predict the contaminant treatment with the UV/H2O2 AOP, fluence-based pseudo-first order kinetics rate constants were calculated. For a given UV fluence, the LR values relative to PCE, i.e. PCE:1,4-Dioxane:TCE, are estimated to be 1.00:1.13:1.19. Based on the PCE treatment goal of 2.3 LR, the treatment equivalency of the three contaminants would be 2.30-LR PCE, 2.60-LR 1,4-dioxane and 2.73-LR TCE.

Using this ratio, the measured LR values are compared with the predicted LRs for PCE and TCE for the lower LR test points in the following table, where a measurable PCE and TCE residuals were achieved. This data confirms that the assumed log removal for each measured constituent is reasonable with respect to PCE and conservative with respect to TCE. Further, the highest measured concentrations of PCE (28 µg/L in Test 10) and TCE (82 µg/L in Test 12) were both removed to non-detect at the design LR conditions, corresponding to demonstrated LRs of >2.2 and >2.7, respectively.

No.	Test ID	Operating Setpoint			1,4-Dioxane (µg/L)	PCE				TCE			
		1,4-Dioxane (log)	PCE (log)	TCE (log)	Measured LR	UV Feed	Measured LR	Predicted LR from 1,4-D LR	Actual/ Pred	UV Feed	Measured Log Removal	Predicted LR from 1,4-D LR	Actual/ Pred
C1	UV-PTC1	Manual	Manual	Manual	0.00	14	0.00			32	0.00		
C2	UV-PTC2	Manual	Manual	Manual	0.03	13	> 1.9			34	0.36		
1	UV-PT1	Manual	Manual	Manual	3.59	14	> 1.9	3.18		31	> 2.2	3.78	
2	UV-PT2	Manual	Manual	Manual	3.75	14	> 1.9	3.32		31	> 2.2	3.95	
3	UV-PT3	Manual	Manual	Manual	3.49	13	> 1.9	3.08		30	> 2.2	3.67	
4	UV-PT4	2.64	2.53	2.42	2.95	13	> 1.9	2.61		29	> 2.2	3.1	
5	UV-PT5	2.64	2.53	2.42	3.33	11	> 1.8	2.94		27	> 2.2	3.5	
6	UV-PT6	2.64	2.53	2.42	2.46	12	> 1.8	2.18		27	> 2.2	2.59	
7	**UV-PT7**	**1.32**	**1.27**	**1.21**	**1.22**	**14**	**1.20**	**1.08**	**1.11**	**37**	**1.91**	**1.29**	**1.48**
8	**UV-PT8**	**1.32**	**1.27**	**1.21**	**1.20**	**14**	**1.15**	**1.06**	**1.09**	**35**	**1.83**	**1.27**	**1.44**
9	UV-PT9	2.64	2.53	2.42	3.01	16	> 1.9	2.66		33	> 2.2	3.17	
10	UV-PT10	2.64[a]	2.53[a]	2.42[a]	2.93	28	2.03	2.6		2	> 1.0	3.09	
11	UV-PT11	2.6	2.5	2.4	2.86	26	> 2.2	2.53		1.6	> 0.9	3.01	
12	UV-PT12	2.6	2.5	2.4	3.49	2.1	> 1.1	3.09		82	> 2.7	3.68	
13	UV-PT13	2.6	2.5	2.4	3.46	1.9	> 1.0	3.07		78	> 2.6	3.65	
14	**UV-PT14**	**1.32**	**1.27**	**1.21**	**1.10**	**15**	**1.06**	**0.97**	**1.09**	**37**	**1.78**	**1.16**	**1.54**
15	**UV-PT15**	**1.32**	**1.27**	**1.21**	**1.22**	**15**	**1.06**	**1.08**	**0.98**	**35**	**1.73**	**1.29**	**1.34**
16	UV-PT16	1.98	1.9	1.82	2.46	11	> 1.8	2.17		28	> 2.2	2.59	
17	UV-PT17	1.98	1.9	1.82	2.49	13	> 1.9	2.2		30	> 2.2	2.62	
18	UV-PT18	2.6	2.5	2.4	3.45	13	> 1.9	3.06		32	> 2.2	3.64	
19	UV-PT19	2.6	2.5	2.4	3.61	14	> 1.9	3.19		34	> 2.3	3.8	
20	UV-PT20	2.6	2.5	2.4	2.77	16	> 1.9	2.45		36	> 2.3	2.92	

Detection limit = 0.18 µg/L

The City of Santa Monica
Arcadia Water Treatment Plant Expansion

TrojanUVFlex200™ - Advanced Oxidation System

Performance Test Report

December 21, 2023

Contents

1   INTRODUCTION/BACKGROUND

The City of Santa Monica has installed an ultraviolet/hydrogen peroxide (UV/H_2O_2) advanced oxidation process (AOP) system at the Arcadia Water Treatment Plant. This system will provide treatment of groundwater from the Olympic well field for 1,4-dioxane, trichloroethylene (TCE) and tetrachloroethylene (PCE) contamination. The system consists of two trains (1 duty+1 standby) of TrojanUVFlex200^{TM} UV Advanced Oxidation Process (UV-AOP) chambers, along with a hydrogen peroxide (H_2O_2) dosing system. Each chamber contains 11 lamp sections, and each section is comprised of 24-1 kW Solo UV lamps.

Trojan Technologies, along with the Contractor (Walsh) and the designer (Brown and Caldwell), completed on-site performance testing of the UV-AOP system from September 22nd to October 5th, 2023. This report describes the methods, procedures and test conditions used during the performance testing and summarizes the test results based on the analytical data reported from third-party laboratories.

2   OBJECTIVES

The primary objective of TrojanUVFlex200 UV-AOP system performance testing was to verify that the installed UV system is capable of meeting the treatment criteria at the design operating conditions, as summarized in Table 2-1. A secondary objective was to provide a robust set of data demonstrating treatment up to 2.4, 2.2 and 2.3 log removal of 1,4-dioxane, TCE, and PCE, respectively, to determine the operating performance guidelines for review by the California Division of Drinking Water (DDW). The performance testing described herein is intended to provide data to demonstrate that the TrojanUVFlex200 automatic control program can control the system operation to reliably meet the contaminant treatment targets, not only at the design conditions, but also when the UVT is below the design value and when the flow per train is below the design value.

Table 2-1 summarizes the UV/H_2O_2 AOP system design criteria. The installed system includes two trains (1 duty + 1 standby) of single chamber TrojanUVFlex200™ reactors, each with 11 populated lamp sections (264 lamps per reactor). The one duty train will provide up to 2.4 log reduction of 1,4-dioxane, 2.2 log reduction of TCE and 2.3 log reduction of PCE from 2,000 gpm of 96% UVT water with up to 40 mg/L H_2O_2.

Table 2-1: Summary of UV-AOP Design Conditions.

Total Flow, GPM	2,000
Duty/Redundant Trains	1/1
Total System Power (kW)	329
1,4-Dioxane Influent concentration (ug/L)	54
1,4-Dioxane Effluent concentration (ug/L)	0.2
1,4-Dioxane Log_{10} Reduction	≥2.4
TCE Influent concentration (ug/L)	34
TCE Effluent concentration (ug/L)	0.2
TCE Log_{10} Reduction	≥2.2
PCE Influent concentration (ug/L)	42
PCE Effluent concentration (ug/L)	0.2
PCE Log_{10} Reduction	≥2.3
Nitrate Concentration (mg/L as N)	8.0
Minimum UV Transmittance at 254 nm, %	96
Design Hydroxyl Radical Scavenging Demand (s^{-1})	130,000
Design Maximum Influent [H2O2] (mg/L)	40

3   UV-OXIDATION FUNDAMENTALS

3.1   TREATMENT MECHANISMS

UV light-based advanced oxidation processes (UV-AOPs) rely upon the simultaneous mechanisms of direct UV photolysis and hydroxyl radical-induced oxidation to degrade chemical contaminants in water. UV-photolysis is the process by which chemical bonds in the contaminant structures are broken by the energy associated with the UV light absorbed by those compounds. UV-photolysis does *not* require the addition of H_2O_2. A UV-AOP process in the presence of an oxidant (*e.g.,* H_2O_2) relies on the *in-situ* generation of hydroxyl radicals (•OH) through the UV-photolysis of H_2O_2 which is dosed to the water, and the subsequent oxidation of chemical contaminants initiated by hydroxyl radicals.

Hydrogen peroxide is commercially available as aqueous solutions of varying strength. It is a relatively weak absorber of UV light having a molar absorption coefficient at 254 nm of 19.6 L mol^{-1} cm^{-1}. Nevertheless, the quantum yield of hydroxyl radical formation from hydrogen peroxide UV photolysis approaches unity. Therefore, the UV/H_2O_2 process is one of the most efficient advanced oxidation processes.

Hydroxyl radicals are extremely reactive, short lived and unselective transient species. Due to their high reactivity in natural waters, especially in the presence of naturally occurring organic matter (NOM) and alkalinity, these radicals will instantly react with the water constituents and do not exist beyond the boundaries of the UV reactor volume.

Hydroxyl radicals can oxidize organic and inorganic compounds by various types of reactions, comprising electron transfer, hydrogen abstraction and electrophilic addition reactions. In UV oxidation treatment processes, the yield of hydroxyl radicals is optimized based on the H_2O_2 required for a given contaminant treatment level for a given water quality, flow, and UV system operating conditions.

3.2   WATER QUALITY PARAMETERS

UV Transmittance

UV transmittance (UVT) is the spectral radiant power (P_λ) transmitted through a medium (*e.g.*, water sample) across a particular pathlength (l) divided by the spectral radiant power incident on the sample (P_λ^0). UVT is measured using a UV spectrophotometer. Reagent grade water is used to zero the instrument (*i.e.*, UVT = 100%). UV absorbance (A) at a given wavelength (**λ**) correlates to the amount of light absorbed by a solution over a given pathlength (l). UVT and UV absorbance are related through the following equation:

$$UVT(\lambda, \%) = 10^{-A(\lambda)} \times 100$$

The typical cell pathlength is 1 cm and both transmittance and absorbance values are commonly reported per cm. A key reference wavelength and one at which UVT is often reported is 254 nm, which is also the radiation emitted from the excited state of mercury atoms in the low-pressure mercury vapor arc lamps. UV Transmittance depends on the concentration of UV light-absorbing compounds and particles (which also scatter the light) present in the water matrix. The higher the water background UV absorption, the lower is the UV light availability to H_2O_2 for hydroxyl radical generation and to organic contaminants for the direct UV photolysis. The UV transmittance is one of the key water quality parameters used in the UV equipment sizing for a given application.

Hydroxyl Radical Scavenging Demand

While the desired reactions in UV oxidation processes are between photo-generated hydroxyl radicals and contaminant molecules, the non-selective nature and high reactivity of hydroxyl radicals result in reactions between these species and various organic and inorganic water constituents, which always occur at much higher concentrations than the target micropollutants. Examples of such hydroxyl radical scavengers are the dissolved natural organic matter (NOM), carbonate and/or bicarbonate ions, iron and manganese ions, etc. Hydrogen peroxide itself reacts with hydroxyl radical; thus, the kinetic model used to determine the UV/H_2O_2 process conditions and to size the UV equipment optimizes the H_2O_2 concentration required to generate the highest •OH yield, while affecting a minimum •OH demand. The •OH water background demand has a negative impact on the steady-state concentration of hydroxyl radicals in the

water. Since the rate of contaminant degradation is proportional to the steady-state concentration of hydroxyl radicals, these hydroxyl radical scavenging reactions reduce the rate of contaminant degradation. The $\bullet$OH water background demand (also known as 'scavenging term'; $\sum k_s[S]$ or S.T.) is water matrix-specific and must be determined experimentally through a properly developed and validated method. Trojan routinely determines the scavenging demand of water samples at its laboratory in London, Ontario. The $\bullet$OH water background demand is another key water quality parameter used by the kinetic model for sizing the UV equipment for a given UV/H_2O_2 AOP application.

In principle, the method for the $\bullet$OH water background demand relies on the competition kinetics for the hydroxyl radicals between the water matrix constituents and a probe compound which is added to the sample (Zhou and Mopper, 1996; Rosenfeldt and Linden, 2007; Rosenfeldt, 2010; Lee and von Gunten, 2010; Keen *et al.*, 2014; Kwon *et al.*, 2014; Gerrity *et al.*, 2016; Wang *et al.*, 2020). The most used probe compound is para-chlorobenzoic acid (pCBA) providing its well characterized rate constant for the OH radical reaction (5.0×10^9 M^{-1} s^{-1}; Buxton *et al.*, 1988) and known quantum yield and molar absorption coefficient at 254 nm. Upon reviewing the literature published over the years and extensive use of pCBA for quantification of OH radical steady state concentration, Trojan adopted and used pCBA as a probe for the $\bullet$OH water background demand determination in samples collected from water treatment plants in the past.

In a recent article, Kim *et al.* (2021) reported for the first time in the literature on a potential unidentified reaction of pCBA in the UV/H_2O_2 process in addition to the known $\bullet$OH- and direct photolysis-based degradation. The authors examined several chemical compounds of various structures as potential $\bullet$OH chemical probes, among which, pCBA. The experimental data indicated that para-substituted benzoic acids, in particular, are vulnerable to attack by an unknown reactive species, leading to false quantification of $\bullet$OH. As a result, the $\bullet$OH water background demand measured using these probes, including pCBA, would be underestimated.

The authors postulated the triplet excited state of H_2O_2 as the reactive species responsible for the degradation of pCBA in addition to the $\bullet$OH and direct photolysis pathways. Although there is no direct experimental evidence in the public domain on the decay of H_2O_2 excited states, Kim *et al.* advanced the idea of pCBA degradation *via* a H_2O_2 triplet state based on the observed pCBA byproducts containing the oxygen isotope (^{18}O) atom when they used $H_2^{18}O_2$.

Based on their experimental results, Kim *et al.* concluded that the impact of the reaction of $(H_2O_2)^*$ on the degradation kinetics of the $\bullet$OH probe compound (*e.g.*, pCBA) would be more significant under the following conditions: (*a*) presence of high concentrations of $\bullet$OH scavengers; (*b*) high concentration of H_2O_2 dosed to the water sample subject to $\bullet$OH water background demand measurement; and (*c*) low concentration of dissolved oxygen. The higher the contribution of $(H_2O_2)^*$ to the kinetics of pCBA decay, the greater the underestimation of the $\bullet$OH water background demand.

Providing the recent literature information and additional in-house investigation on pCBA suitability as a probe for the OH radical water matrix demand determination, Trojan decided not to use this compound as a probe anymore. Further proprietary research studies conducted

at Trojan resulted in adopting a reliable probe compound for OH radical water matrix demand. That compound has been used over the past 3-4 years.

Santa Monica Olympic wellfield water samples were submitted to Trojan in 2020 for determination of the hydroxyl radical scavenging demand and associated water quality parameters. The results are listed in Table 3-1, and they were all determined using pCBA as an •OH probe compound. The maximum value measured was for the SM-4 sample ($90,400$ s^{-1}). Nevertheless, this result measured using pCBA as the scavenging probe needed to be adjusted to the value believed to be more representative of the true value. Trojan has observed that this ratio can be up to 1.5 and therefore, the pCBA scavenging result was adjusted to a value of $130,000$ s^{-1} and this was the value used as the basis for the UV AOP system sizing and subsequently programmed into the UV system PLC during commissioning.

Table 3-1: Water Quality Analysis: Basis for UV System Design.

Sample ID	Date	Total chlorine (ppm)	Free chlorine (ppm)	pH	Total Alkalinity	%UVT$_{254}$	TOC	Total Iron	Nitrate (ppm as NO$_3$)	OH* Scavenging
		(ppm)	(ppm)		(ppm as CaCO$_3$)	(%)	(ppm)	(ppm)	UV spec	(s-1)
SM-9	6/1/2020	N.D.	N.D.	7.17	423	98.1	0.317	0.06	15.6	86,500
SM-8	6/11/2020	N.D.	N.D.	7.66	240	95.0	0.265	0.22	3.0	51,800
SM-4 Filtered through 8 μm	7/3/2020	N.D.	N.D.	8.18	359	98.5	0.590	N.D.	28.0	90,400
SM-3	12/15/2020	N.D.	N.D.	7.67	323	98.9	0.353	0.02	24.6	42,900
SM-3 pH 6.3	12/15/2020	__	__	__	__	__	__	__	__	25,400

Note: The STs listed in the table were adjusted prior to design to correct for underestimated results based on use of pCBA as described above.

3.3 TROJAN UV/H$_2$O$_2$ SYSTEM CONTROLS

The operation of Trojan UV-Oxidation Systems for contaminant treatment is based on the calculation of an instantaneous contaminant log-reduction (LR) as a function of the fundamental contaminant kinetic parameters, system flow, UV transmittance, hydroxyl radical scavenging demand, H$_2$O$_2$ concentration and UV reactor intensity sensor values. The methodology is based on a contaminant treatment kinetic model that combines a fundamental photochemical kinetic model with an empirically validated UV dose model to accurately predict the degradation of contaminants in a UV-oxidation system (i.e., UV alone or combined with an oxidant to generate hydroxyl radicals).

Therefore, the UV system control algorithm provides a dynamically adjusted system based upon the identified process input parameters. These include flow rate, UVT, hydroxyl radical scavenging demand, and contaminant influent and target effluent concentration (to calculate target LRs). Further, by inputting the H$_2$O$_2$ and electrical energy costs, the algorithm calculates the combination of reactor power and H$_2$O$_2$ concentration that meets the contaminant treatment objective at the lowest operating cost. Specific constraints on the limits of the system operation can also constrain the operating conditions.

The fundamental photochemical kinetic model is based upon a contaminant-specific pseudo-first order UV fluence-based reaction rate constant (k′, cm^2/mJ) that accounts for contaminant

reduction due to both UV direct photolysis and hydroxyl radical oxidation. In addition to the contaminant-specific fundamental kinetic parameters (i.e., quantum yield (Φ_C), molar absorption coefficient (ε_C) & second order hydroxyl radical rate constant $k_{C,OH}$), this fluence-based rate constant k′ is dependent upon the H_2O_2 concentration and the hydroxyl radical scavenging demand of the water ($\sum k_s[S]$ or S.T.). Typically, the scavenging demand of the water is considered to be either a constant value (based upon historical measurements) or linked to certain measurable water quality parameters. The H_2O_2 concentration is a control variable that can be monitored and adjusted together with the UV reduction equivalent dose (RED) to provide the target LR of the contaminant. The fluence-based rate constant for contaminant treatment with the UV/H_2O_2 AOP is calculated using the following equation:

$$\frac{k_c}{I_{avg.}} = k_c' = \frac{\phi_c \varepsilon_c LN(10)}{U} + \frac{LN(10)\phi_{OH}\varepsilon_{H_2O_2}k_{c,OH}[H_2O_2]}{U(k_{H_2O_2,OH}[H_2O_2] + \sum k_{s,OH}[S])}$$

Eq. 1

where,

Symbol	Description
U	Photon energy at 253.7 nm (J/einstein)
ϕ_C	Quantum Yield of contaminant at 254 nm
ϕ_{OH}	Quantum Yield of OH radical formation from hydrogen peroxide photolysis
ε_C	Molar absorption coefficient of contaminant at 254 nm, $M^{-1} cm^{-1}$
ε_{H2O2}	Molar absorption coefficient of hydrogen peroxide at 254 nm, $M^{-1} cm^{-1}$
$k_{C,OH}$	Reaction rate constant of contaminant with OH radical, $M^{-1} s^{-1}$
$k_{H2O2,OH}$	Reaction rate constant of H_2O_2 with OH radical, $M^{-1} s^{-1}$
$k_{s,OH}[S]$	Hydroxyl radical scavenging for various constituents S in the water matrix, s^{-1}

Equation 1 is provided and discussed further by Stefan (2018). Inspection of equation 1 shows that for a given contaminant and water quality (i.e., ($\sum k_s[S]$), the H_2O_2 concentration is the only independent variable.

This rate constant has the units cm^2 /mJ. The UV dose required to achieve 90% removal of a chemical pollutant (D_{10}, mJ/cm^2) is related to the fluence-based rate constant k_C' through equation (1):

D_{10} = Ln(10)/k_c′   *Eq. 2*

Therefore, for a given H_2O_2 concentration, a target LR (LR_t) is achieved by delivering the required UV dose i.e., the reduction equivalent dose (RED, mJ/cm^2).

RED_t = D_{10} x LR_t   *Eq. 3*

The UV dose delivered by a UV reactor is a function of various parameters among which the water flow rate and UVT, the lamp power level, the quartz sleeve transmittance (including fouling) and the UV reactor efficiency. The flowrate and UVT are measured parameters. The lamp power level is the controlled/independent variable.

In disinfection applications, the RED for a UV reactor is calculated using a bioassay-generated validated equation in which RED is a function of UV lamp power level/UV intensity measurement, flowrate, UVT and D_{10} (i.e., the dose per log inactivation of a microorganism). Similarly, for UV-AOP applications, Trojan has developed a RED equation for the TrojanUVFlex200 reactor using an empirically validated computational fluid dynamics (CFD) model to relate RED to the UV intensity sensor values, flowrate, UVT, and contaminant D_{10}.

The control algorithm evaluates various combinations of lamp power and related RED and H_2O_2 dose and related D_{10}, all of which meet the contaminant LR target and selects that combination which represents the minimum operating cost.

4 METHOD

4.1 EXPERIMENTAL SET UP

UVT Modifier, Hydrogen Peroxide and Contaminant Dosing

To produce UV influent water quality that matches the design UVT value, Aqua Hume solution was injected into the 12-inch diameter greensand effluent pipe approximately 250 feet upstream of the UV reactors. A Blue-White peristaltic pump was used to inject diluted Aqua Hume at rates between about 9 ml/min to 250 ml/min. An injection wand was assembled that delivered the Aqua Hume solution into the center of the greensand effluent pipe.

The permanent H_2O_2 delivery system was used to inject H_2O_2 from the H_2O_2 storage tank containing 50% H_2O_2 into the 12-inch diameter UV influent pipe approximately 65 feet upstream of the reactors.

To quantitatively demonstrate the required log reduction targets of 1,4-dioxane, the 1,4-dioxane concentrations required in the UV influent were chosen such that the contaminant concentrations could be accurately measured in both UV influent and UV effluent samples. Therefore, the influent contaminant concentrations needed to be high enough to ensure that the 1,4-dioxane concentrations in the UV effluent samples would exceed the analytical method reporting limit (MRL). The analytical method employed for 1,4-dioxane analysis was EPA Method 522, which has an MRL of 0.070 µg/L and an MDL of 0.028 µg/L. Since it was recommended to avoid working at concentrations approaching the MRL, a target UV effluent 1,4-dioxane concentration of 0.1 µg/L was chosen.

The 1,4-dioxane injection stock was prepared by diluting between 6.2 grams and 146 grams of >99.5% pure 1,4-dioxane (Sigma Millipore #34857 batch #MKCQ8470) to 1.0 L with distilled water to prepare stock solutions ranging from 6,200 mg/L to 146,000 mg/L. These stocks were injected using a peristatic pump into the UV influent piping adjacent to the Aqua Hume injection location described above.

Achievement of Steady State Operation

A critical requirement is that the UV system be operating at steady state prior to collection of the UV reactor influent-effluent sample pairs. A tracer test was performed to determine the time required for the system to reach steady state following a process change. The UVT modifier Aqua Hume (UAS of America), which is a liquid concentrate natural organic matter, was used as the tracer compound. A step change in the UVT was made and samples were collected at specified time intervals at both the reactor influent and effluent sample ports. The reactor lamps were off during this test. The samples were analyzed on-site for UVT to determine the time required for the system to reach steady state following a change in process conditions.

4.2   TEST PROCEDURE

The general procedure for each test completed was:

- Set and verify stable system flow at the target value.
- Begin injection of Aqua Hume (i.e., UVT modifier) and H_2O_2.
- Select the UV system control mode.
- Ensure that the correct ST is entered in the PLC.
- If local control is selected, turn on the desired number of lamp sections and set the lamp power level.
- If remote (i.e., auto) control is selected ensure that the correct contaminant log reduction targets are entered.
- Confirm that the target UV influent UVT and H_2O_2 dose is achieved.
- Confirm that the UV reactor operation is stable (i.e., number of lamp sections and power level).
- Begin injection of 1,4-dioxane stock solution.
- Wait for steady state time to elapse.
- Record the relevant data.
- Collect the influent and effluent sample pairs.
- Measure hydrogen peroxide and UVT in the UV influent and UV effluent grab samples.

Test Matrix

Table 4-1 presents the test matrix and summarizes the operational setpoints and predicted conditions as well as the notes describing the rationale for each specific test condition.

Near-ambient UVT (~98.5%) was tested as well as the design UVT of 96% and a minimum UVT target of 93%.

All tests were completed with combinations of wells SM-8 and SM-9 and using UV Train 2. Well SM-4 was not operational during the performance test. Whereas the test matrix states that UV Train 1 will be tested, an issue with the Train 1 outlet valve control resulted in the switch to test Train 2. The design and performance of the two parallel trains are considered to be identical, which is the basis for only testing one train. The first five tests, including two control tests, were to be performed in manual (i.e., local control) mode to ensure testing took place

under the conditions tied to the maximum power draw and peroxide dose set out in the contract documents. To conduct these tests in manual mode, the number of lamp sections operating, lamp power and H_2O_2 dose were manually set to the specified values. Tests 1, 2 and 3 were all performed at a BPL of 84% to simulate end of lamp life and sleeve fouling design conditions.

The two control tests were performed to demonstrate the expected result that no 1,4-dioxane treatment is achieved in the absence of both UV and H_2O_2 and that reduction of PCE and especially TCE is minimal by direct UV photolysis only (i.e., in the absence of H_2O_2). The tests were also included to assess the integrity of sample collection, handling, and analytical quality control.

Tests 4, 5 and 6 were performed in automatic control mode at the design flow and design LR target of 2.4 LR 1,4-dioxane, 2.2 LR TCE and 2.3 LR PCE. Test 4 is at the design UVT of 96%, test 5 is at 93% UVT and test 6 is at ambient UVT. These tests will demonstrate the ability of the system controls to respond to water quality changes. Tests 7 and 8 targeted a lower 1,4-dioxane LR (i.e., 1.2 log) with the design ST ($130,000$ s^{-1}) and measured ST ($124,000$ s^{-1}) entered into the UV PLC. Test 9 is a duplicate of test 6 but at the lower flow of 1,500 gpm. Tests 10 through 13 were conducted at 1,000 gpm each and show the impact of well blend. Tests 10 and 11 were performed with SM-9 only while tests 12 and 13 were performed with well SM-8 only. The paired tests utilize the design and measured ST values. Tests 14 and 15 are duplicate tests that targeted a lower 1,4-dioxane LR (i.e., 1.2 log) from water with a reduced pH (i.e., 6.5). Tests 16 and 17 are duplicates of test 6 but with a lower 1,4-dioxane LR (i.e., 1.8 log) and with the design and measured ST values entered in the PLC. Tests 18, 19 and 20 were performed with low pH water (i.e., 6.5). Tests 18 and 19 were performed at the ambient UVT and design UVT (96%) respectively and at the design flow and ST. Test 20 was performed at the ambient UVT, design flow and measured ST.

Sample Handling

Sample bottles were provided by Weck Laboratories Inc. (Industry, CA) for 1,4-dioxane, VOC and typical water quality parameter analyses. UV influent samples were collected first followed by the UV effluent samples, ensuring the steady-state operating conditions upon any change in the test variables (see Table 4-1). Separate containers were used to obtain pre-H_2O_2 influent, post-H_2O_2 influent and UV effluent samples for UVT and H_2O_2 on site analysis, with the analysis being completed by Trojan within approximately 15 minutes of sample collection. Samples were placed in coolers with ice and collected by the Weck sample couriers, with Chain of Custody procedures followed.

UV Transmittance (UVT)

Samples for the "background" water UVT analysis (prior to H_2O_2 injection but after UVT modification) were collected from the online UVT meter (i.e., Trojan Optiview) sample line that is drawn from the common influent header immediately upstream of the H_2O_2 injection port. The hydraulic retention time (HRT) between this port and the Aqua Hume injection port is approximately 1 minute at a flow of 2,000 gpm. Grab samples for the background water and from

the UV influent and effluent sample ports were measured using a 4-cm path length quartz cell and a RealUVT™ 254 nm portable photometer (RealTech Inc., Canada).

Hydrogen Peroxide

Hydrogen peroxide was measured using the DPD/peroxidase method described by Bader *et al*. (1988). In this procedure, hydrogen peroxide reacts with DPD reagent (Hach Company) through a reaction catalysed by the peroxidase enzyme (horseradish peroxidase, Millipore Sigma USA).

Hydroxyl Radical Scavenging Demand

As mentioned in section 3.2.2, Trojan routinely determines the scavenging demand of water samples at its laboratory in London, Ontario. The scavenging determination SOP involves spiking into an aliquot of the water sample a probe compound, for which the rate constant for the •OH reaction is available in the published literature and which was also confirmed by Trojan, and H_2O_2. The spiked water samples are irradiated to precise UV doses at 253.7 nm from a UV lamp mounted in a low-pressure collimated beam apparatus. The *quasi*-parallel UV light beam is perpendicular to the water sample surface. UV fluence rate at the water surface is measured using a calibrated radiometer (International Light Technologies Inc.) and the exposure times with NIST traceable stopwatches. The sample results are used to develop a UV dose-response relationship, from which the probe degradation kinetics is calculated, and subsequently the •OH water matrix scavenging capacity is determined.

1,4-Dioxane and Remaining Parameters

All analyses were performed by Weck Laboratories, Inc. (Industry, CA). Chain-of-custody forms were used, and the laboratory reports were sent to Walsh and Brown and Caldwell. TCE and PCE were analyzed using USEPA method 524.2, with MRLs of 0.50 µg/L and MDLs of 0.18 µg/L. 1,4-Dioxane analysis was performed using USEPA method 522 with an MRL of 0.070 µg/L and a method detection limit (MDL) of 0.028 µg/L. All parameter method details are listed in Table 4-2.

Table 4-2: Analytical details for Weck Laboratory methods.

ANALYTE	METHOD	MDL	MRL	UNITS
1,4-Dioxane	EPA 522	0.028	0.07	µg/L
TCE	EPA 524.4	0.18	0.5	µg/L
PCE	EPA 524.4	0.18	0.5	µg/L

Table 4-1: Planned test matrix.

No.	Test ID	Well Blend SM-4 (gpm)	SM-8 (gpm)	SM-9 (gpm)	System Flow Rate (gpm)	Train in Operation	Mode	Lamp Power (%)	H2O2 Setpoint (mg/L)	Scavenging s^{-1}	1,4-D Log Setpoint	TCE Log Setpoint	PCE Log Setpoint	Predicted 1,4-D Log Reduction	Predicted TCE Log Reduction	Predicted PCE Log Reduction	Lamp Sections On	1,4-D (µg/L)	UVT (%)	pH	Notes
C1	UV-PTC1	0	1000	1000	2,000	1	Manual	0	40	130,000	-	-	-	0			0	spike	amb.	amb.	Control 1: H2O2 Only
C2	UV-PTC2	0	1000	1000	2,000	1	Manual	100	0	130,000	-	-	-	0			11	spike	amb.	amb.	Control 2: UV Only
1	UV-PT1	0	1000	1000	2,000	1	Manual	84	40	130,000	-	-	-	3.54	3.68	3.14	11	spike	96	amb.	Design flow, UVT, ST conditions
2	UV-PT2	0	1000	1000	2,000	1	Manual	84	40	130,000	-	-	-	3.54	3.68	3.14	11	spike	96	amb.	Duplicate design flow, UVT, ST conditions
3	UV-PT3	0	1000	1000	2,000	1	Manual	84	40	124,000	-	-	-	3.54	3.68	3.14	11	spike	96	amb.	Duplicate design flow and UVT with measured ST
4	UV-PT4	0	1000	1000	2,000	1	Auto	97.5	35.20	130,000	2.4	2.2	2.3	2.85	2.97	2.56	8	spike	96	amb.	Design flow, UVT, ST conditions in auto mode
5	UV-PT5	0	1000	1000	2,000	1	Auto	94.5	35.20	130,000	2.4	2.2	2.3	2.86	2.97	2.56	11	spike	93	amb.	Design flow and ST conditions in auto mode with lower UVT
6	UV-PT6	0	1000	1000	2,000	1	Auto	97	37.34	130,000	2.4	2.2	2.3	3.30	3.43	2.95	7	spike	amb.	amb.	Design flow and ST conditions in auto mode at ambient UVT
7	UV-PT7	0	1000	1000	2,000	1	Auto	88.5	35.20	130,000	1.2	1.1	1.15	1.45	1.51	1.28	3	spike	amb.	amb.	Added - Design flow and ST at ambient UVT with lower LRV
8	UV-PT8	0	1000	1000	2,000	1	Auto	85.5	35.20	124,000	1.2	1.1	1.15	1.42	1.47	1.25	3	spike	amb.	amb.	Added - Design flow at ambient UVT with lower LRV and measured ST
9	UV-PT9	0	750	750	1,500	1	Auto	87.5	36.27	130,000	2.4	2.2	2.3	2.86	2.97	2.56	5	spike	amb.	amb.	This is run 6 with a lower flow rate
10	UV-PT10	0	0	1000	1,000	1	Auto	72	34.67	130,000	2.4	2.2	2.3	2.74	2.85	2.49	4	spike	amb.	amb.	Vary well blends with Design LRV, ambient UVT at a lower flow and design ST
11	UV-PT11	0	0	1000	1,000	1	Auto	69.5	34.67	124,000	2.4	2.2	2.3	2.68	2.79	2.43	4	spike	amb.	amb.	Vary well blends with Design LRV, ambient UVT at a lower flow and measured ST
12	UV-PT12	0	1000	0	1,000	1	Auto	74	34.67	130,000	2.4	2.2	2.3	2.91	3.03	2.62	4	spike	amb.	amb.	Vary well blends with Design LRV, ambient UVT at a lower flow and design ST
13	UV-PT13	0	1000	0	1,000	1	Auto	71.5	34.67	124,000	2.4	2.2	2.3	2.86	2.97	2.57	4	spike	amb.	amb.	Vary well blends with Design LRV, ambient UVT at a lower flow and measured ST
14	UV-PT14	0	1000	1000	2,000	1	Auto	65	34.67	90,000	1.2	1.1	1.15	1.48	1.54	1.26	3	spike	amb.	6.5	Included to provide more data related to low-pH operation
15	UV-PT15	0	1000	1000	2,000	1	Auto	65	34.67	90,000	1.2	1.1	1.15	1.48	1.54	1.26	3	spike	amb.	6.5	Included to provide more data related to low-pH operation
16	UV-PT16	0	1000	1000	2,000	1	Auto	80.5	35.74	130,000	1.8	1.65	1.73	2.17	2.25	1.92	5	spike	amb.	amb.	This is run #6 with a lower LRV
17	UV-PT17	0	1000	1000	2,000	1	Auto	78	34.67	124,000	1.8	1.65	1.73	2.11	2.19	1.88	5	spike	amb.	amb.	This is run #16 with measured ST
18	UV-PT18	0	1000	1000	2,000	1	Auto	97	37.335	130,000	2.4	2.2	2.3	4.11	4.26	3.55	7	spike	amb.	6.5	This is run 6 with reduced pH and design ST
19	UV-PT19	0	1000	1000	2,000	1	Auto	97.5	35.203	130,000	2.4	2.2	2.3	3.56	3.70	3.08	8	spike	96	6.5	This is run 18 with design UVT and ST
20	UV-PT20	0	1000	1000	2,000	1	Auto	93	35.736	90,000	2.4	2.2	2.3	2.97	3.08	2.56	5	spike	amb.	6.5	This is run 6 with reduced pH and measured ST (at the lower pH)

Note that Lamp Power, H₂O₂ Setpoint and Lamp Sections On values for Auto control mode runs (i.e., 4 to 20) are estimates based on specified operating conditions and design water quality.

5 RESULTS

5.1 MIXING AND STEADY STATE

A mixing/steady state test was completed on September 21st, 2023. The test was performed at a flow of approximately 1,000 gpm through UV train 2 with the UV reactor off and using Aqua Hume as the tracer compound. At time t=0 minutes Aqua Hume injection was started and samples were collected from the UV influent and UV effluent sample ports at various times up to 32 minutes. The grab samples were measured for UVT using the bench-top Real Tech photometer.

UVT values were converted to UV absorbance (UVA = -Log(UVT)) and the test results are plotted versus time in Figure 5-1. UVT was reduced by Aqua Hume from 97.5% to about 85.7%. The data in Figure 5-1 shows that UVA had reached steady state at the UV influent port about 3 or 4 minutes after beginning Aqua Hume injection and it took at least 6 minutes more before steady state UVA was reached at the UV effluent sample port. There was an anomalous UV influent UVA result for the sample collected at 10 minutes, where the UVA decreased significantly to 0.0567 cm^{-1} before increasing again in the next sample at 15 minutes to 0.0671 cm^{-1}. Because of this anomalous sample, it was decided to conclude that steady state with respect to UVA/UVT at the UV effluent sample port is achieved 20 minutes after beginning Aqua Hume injection. Given that the 1,4-dioxane stock solution is injected at approximately the same location as the Aqua Hume injection port, the 1,4-dioxane would also reach steady state at the UV effluent port 20 minutes after beginning injection. Therefore, for a system flow of approximately 1,000 gpm the UV effluent samples were collected a minimum of 20 minutes after beginning Aqua Hume and 1,4-dioxane injection. Assuming that time to reach steady state is inversely proportional to flow, for flows of 1,500 gpm and 2,000 gpm, samples were collected 15 minutes and 10 minutes, respectively, after beginning injection at those flowrates. Given that the calculated HRT in the UV reactor at the design flow of 2,000 gpm is approximately 3 minutes, UV influent samples were collected up to 3 minutes prior to collecting the UV effluent samples.
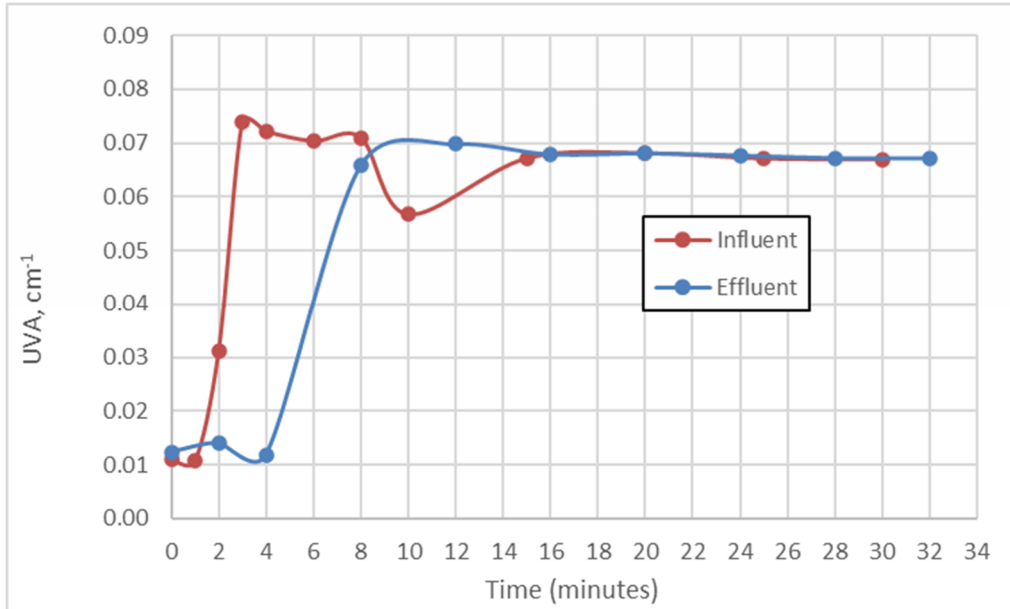
Figure 5-1 Mixing/steady state test results performed at 1,000 gpm through UV Train #2.

5.2 WATER QUALITY

Water samples were collected from the site on each of the five test days of Performance Testing (September 22 and October 2-5) and sent to the Trojan Laboratory for analysis of water quality parameters. The sampling location varied and included the pre- and post-greensand filtration ports and pre- and post- 1,4-dioxane and UVT modifier spiking (in post-greensand filtration samples) ports. One sample was collected at the UV effluent port for the purpose of examining the change in the water quality parameters relative to those of the UV influent sample. Therefore, one should differentiate between the water quality parameters representative to the well water and/or well water blend and those which are representative to the actual test conditions (i.e., in the presence of 1,4-dioxane with or without Aqua Hume addition). The only sample containing H_2O_2 was the sample collected at the UV effluent port. The samples collected during the Performance Testing and their description along with the water quality parameters reported by the Trojan Laboratory are summarized in Table 5-1.

As shown in Table 5-1, the well blend samples were collected once per day. If the water quality parameters did not change during the day of testing, then the analytical data shown in Table 5-1 would be valid for all tests performed on that day. However, should the water quality vary during the day, the data reported in the table should be considered with caution as it may represent only the water parameters associated with the tests performed at the time of sampling.

Table 5-1: Trojan water quality results for Arcadia WTP samples.

	SM8 Post-greensand (Sep 22 13:00)	UV-PT2 Post-greensand pre-spike (Oct 2 15:40)	UV-PT2 UV Influent pre-H2O2 (Oct 2 ~15:40)	Pre-Greensand (Oct 3 15:45)	Pre-H2O2 (Oct 3 15:45)	PT20 Pre-H2O2 (Oct 4 15:00)	PT20 UV Effluent (Oct 4 15:00)	PT9 Pre-H2O2 (Oct 5 9:00)	SM9 PT10 pre-H2O2 (Oct 5 13:25)
Well Blend	SM-8	50:50 Blend of SM-8:SM-9	50:50 Blend of SM-8:SM-9	50:50 Blend of SM-8:SM-9	50:50 Blend of SM-8:SM-9	50:50 Blend of SM-8:SM-9	50:50 Blend of SM-8:SM-9	50:50 Blend of SM-8:SM-9	SM-9
Ammendments	No 1,4-Dioxane spike; ambient UVT & pH	No 1,4-Dioxane spike; ambient UVT & pH	350 ug/L 1,4-Dioxane spike; 96% UVT & ambient pH	No 1,4-Dioxane spike; ambient UVT & pH	No 1,4-Dioxane spike; ambient UVT & pH	176 ug/L 1,4-Dioxane spike; ambient UVT & reduced pH	176 ug/L 1,4-Dioxane spike; ambient UVT & reduced pH	No 1,4-Dioxane spike; ambient UVT & pH	No 1,4-Dioxane spike; ambient UVT & pH
UVT (%)	96.7%	98.3%	96.4%	99.0%	98.5%	98.6%	99.2%	99.1%	98.8%
pH	7.35	7.57	7.70	7.71	7.58	6.96	6.79	7.22	7.61
TOC (mg/L)	1.03	0.54	0.76	0.95	0.55	0.65	0.62	0.49	0.87
Alkalinity (mg/L as $CaCO_3$)	335	377	387	385	379	305	307	377	432
Nitrate (mg/L as NO_3^-)	29.1	23.5	23.6	22.7	22.8	22.7	22.5	25.0	19.0
Nitrite (mg/L as NO_2^-)	na	0.011	0.014	na	0.013	0.011	0.103	0.010	na
OH Radical ST (s^{-1})	86,250	na	128,000	na	107,530	85,300	na	na	90,000

Sample SM8 post-greensand filtration was collected and analyzed in September 2023 when tests PT12 and PT13 were performed. The data shown in Table 5-1 for the 50:50 SM8:SM9 well water blend used in all October tests except PT10 and PT11 (100% SM9 well water) may not reflect the average of the parameters listed for the SM8 (Sep 2023) and SM9 (Oct 2023) samples, as the water quality of SM8 well water may have varied from September to October.

The next paragraphs are concerned with a brief data interpretation of the Trojan analytical results for the samples shown in Table 5-1.

UV Transmittance (UVT). The UVT in samples collected under ambient water quality conditions varied from 98.3% to 99.1% (October samples), with the UVT of 96.7% measured for SM8 sample collected and analyzed in September. Sample UV-PT2 UV Influent pre-H_2O_2 contained Aqua Hume, which was intentionally added to the well water blend for testing the UV/H_2O_2 system performance at the design UVT. The UVT data reported by Trojan Laboratory agree well with the UVT data recorded at the site for the tests performed in those days.

Water pH. The pH data for the October samples collected from test runs at the ambient water pH condition spanned from ~7.2 (PT9 pre-H_2O_2) to ~7.7 (Pre-greensand and PT2 post-greensand pre-spike); pH of SM8 sample collected during Performance Testing event in September was also within this range. All these values are larger than those recorded at the site (~6.8 – 7.1). The pH values in samples from PT20 test (pre-H_2O_2 and UV Effluent) were ~7.0 and 6.9, respectively, also greater than those measured at the site, i.e., 6.5. Of note, for this PT20 test, pH was intentionally depressed at the site to examine the impact of pH on 1,4-dioxane, PCE and TCE degradation yields relative to those observed in tests at ambient pH. The water in the two wells (SM8 and SM9) are high in alkalinity. Since carbonic acid pK_{a1} is 6.35, lowering pH would reduce the concentration of bicarbonate ion in the favor of carbonic acid, thus, reducing the OH radical ST capacity of the water; $k(\bullet OH,HCO_3^-) = 8.5E+06$ M^{-1} s^{-1}; $k(\bullet OH,CO_2) = <1E+06$ M^{-1} s^{-1}; Buxton et al., 1988). The overall alkalinity (as $CaCO_3$) in a given water sample would be quasi-similar at pH ~7 and ~6.5, while the contribution of bicarbonate to the overall OH radical water matrix demand would be different due to the pH-driven distribution of the two carbonate species (H_2CO_3 and HCO_3^-). Therefore, in a given water, a lower ST is expected at pH 6.5 than at pH~7, and that is reflected in Table 5-1 which shows the lowest ST in PT20 pre-H_2O_2 sample of pH 6.5 as measured at site.

Total Organic Carbon (TOC). The TOC concentration was very low in all samples and varied from ~0.5 to ~1.0 mg/L. These low TOC levels explain the high UVT values measured for the samples at ambient water quality condition and, although the TOC speciation (i.e., composition) is not known, it would indicate a relatively small contribution of the organics constituting TOC to the overall OH radical water matrix demand.

Of note, the difference of ~0.2 mg/L in the TOC measured in samples PT2 post-greensand pre-spike and UV-PT2 pre-H_2O_2 is attributed to the organic matter contained in the Aqua Hume amount added to the water as a UVT modifier, and it is associated with the observed change in UVT.

Alkalinity (expressed as CaCO₃). Alkalinity was high in all samples and ranged from 377 to 387 mg/L in greensand-filtered 50:50 SM8:SM9 well blend samples at their ambient pH. The PT20 samples (UV influent and UV effluent) had similar alkalinity (~305 mg/L) and lower than observed in the other samples (50:50 well blend), due to the lower pH in these samples. The alkalinity concentration measured in the SM8 (September) and SM9 (October) water samples was 335 and 432 mg/L, and bracketed the values determined in the blended water. At a 50:50 SM8:SM9 blending ratio, the calculated alkalinity would be ~384 mg/L, which is also within the measured range, and may indicate that the alkalinity in wells SM8 and SM9 was constant throughout the Performance Testing event.

Nitrate. Except for the SM8-only and SM9-only samples, all the other samples represent a 50:50 well water blend. Nitrate ranged from 22.5 to 25.0 mg/L as NO_3^-. Nitrate in the SM8 (September) and SM9 (October) samples were quantified as 29.0 and 19.0 mg/L as NO_3^-, which bracketed the data for the blended water, but also indicated a significant difference in water quality of the two wells. Nitrate is a rather poor absorber of the 253.7 nm radiation (molar absorption coefficient of ~4 M^{-1} cm^{-1}), but in high concentrations and at high UV doses, its photolysis to *intermediates* leading to nitrite becomes significant. Therefore, *in-situ* formation of nitrite and its reaction with hydroxyl radical is not negligible. Moreover, pH, alkalinity and H_2O_2 concentrations play important roles in nitrate photolysis to nitrite, with nitrite increasing as these parameters' values increase. The mechanism is complex and not fully elucidated in the literature studies.

Nitrite. The nitrite levels measured by Trojan in all samples except for the PT20 UV Effluent sample were very low and approached the 10 micrograms/L detection limit of the ion-chromatography method used by Trojan. The nitrite measured in the PT20 UV Effluent was ~103 micrograms/L. During UV-AOP treatment nitrite is simultaneously formed through direct UV photolysis of nitrate and destroyed through rapid reaction with the OH radical. This rapid reaction with the OH radical means that nitrite has the potential to be a significant OH radical scavenger. The UV-AOP controls program accounts for this formation of nitrite and its impact on the ST. However, if significant nitrite ion was present in the UV influent water and if its concentration in the influent water was variable during the Performance Testing, then it could cause unrecognized variability in the ST from test to test. It is also important to mention that nitrite is slowly oxidized to nitrate by dissolved oxygen and this reaction could have occurred between the time of sample collection and nitrite analysis. Therefore, it is conceivable to assume that the levels reported by Trojan in Table 5-1 could be lower than those in the samples at their collection time.

A sample identified as PT-SW8-S4 was collected by Brown and Caldwell at the greensand influent port on the morning of Oct 4th (PT8 test condition) and submitted to Weck Laboratories for comprehensive analysis. According to Weck's report, the sample contained 50 micrograms/L nitrite-N, which is equivalent to 164 micrograms/L NO_2^-. It is unclear whether the greensand filter would remove nitrite, and whether the water quality parameters of the well water blend varied during the day of Oct 4th. Nitrite is a strong OH radical scavenger and its contribution to the ST at a 164 microgram/L level would be approximately 36,000 s^{-1}, estimated using $k(\bullet OH, NO_2^-)$=1.0E+10 M^{-1} s^{-1} (Buxton et al. 1988).

It should be noted that typical operation of the greensand filters will involve injection of sodium hypochlorite upstream of the filters and this would oxidize any nitrite ion, converting it to nitrate. However, hypochlorite was not injected during any of these performance tests and therefore nitrite ion present in the well water could have increased the ST during these performance tests.

OH Radical water matrix "demand" (also commonly known as OH radical term, ST). The OH radical ST (s^{-1}) was determined only for some of the samples received by Trojan. Note that the OH radical ST for SM8 Post-greensand sample was determined in September and it would be characteristic to the water used in those tests (PT12 and PT13). 1,4-Dioxane in that water sample would have been at its ambient level. The same statement is valid for the Pre-H_2O_2 (Oct 3 15:45) and SM9 PT10 Pre-H_2O_2, i.e., the listed OH radical STs are representative to the 50:50 well water blend and 100% SM9 well water, respectively. However, should the well blend quality vary from one day to another or during the day of testing, the analytical data shown in Table 5-1 would be representative only to the test(s) conducted at the time of sample collection. All OH radical STs shown in Table 5-1 include the contributions of alkalinity, organic and inorganic compounds present or added to the water (except for H_2O_2) and of nitrite present and/or formed from the intermediates of nitrate photolysis.

The OH radical STs determined in the samples listed in Table 5-1 are dominated by the contribution of alkalinity, e.g., 74.5% (SM-8 Post-greensand); 56.5% (UV-PT2 UV Influent pre-H_2O_2); 66% (Oct 3rd Pre-H_2O_2); 62% (PT20 pre-H_2O_2); 90% (SM9 PT10 pre-H_2O_2). The largest value of 128,000 s^{-1} was observed for the UV-PT2 UV Influent pre-H_2O_2 sample, which contained both 1,4-dioxane and Aqua Hume spiked during that test. Therefore, along with the contributions of alkalinity, of nitrite formed from nitrate photolysis and subsequent reactions of its intermediates, and of 1,4-dioxane, there is some contribution from Aqua Hume to the ST of the October 3rd UV Influent pre-H_2O_2 sample.

As expected, the lowest OH radical ST across all samples collected from the October tests (85,300 s^{-1}) was determined in the PT20 Pre-H_2O_2 (Oct 4 15:00) sample. That is essentially explained by a lower contribution of alkalinity to the overall ST than in the other samples due to the lower pH (6.5) of the water in this test. Note that 1,4-dioxane was also present in this sample received from the site and nitrite was also formed during the procedure of ST determination.

The lower ST at a low pH is primarily explained by the reaction of peroxynitrite ($ONOO^-$), which is the key intermediate in nitrate photolysis, with CO_2 (higher concentration at low pH than at neutral pH) leading to nitrate and to the decomposition of peroxynitrous acid (ONOOH), which is the conjugate acid of peroxynitrite, to nitrate (70%), both of which reduce the nitrite yield [pK_a(ONOOH)=6.8; pK_a(H_2CO3)=6.35].

5.3 ON-SITE DATA AND MEASUREMENTS

Table 5-2 presents several key on-site measurements recorded for each test run. These include the measured flow and the estimated percent well blend, the number of lamp sections operating, and the percent lamp power level, the control mode (i.e., manual or automatic), the ST value entered into the PLC, the online influent (i.e., pre-H_2O_2) UVT value, the PLC-calculated influent H_2O_2 concentration and predicted effluent H_2O_2 concentration. The compliance and operating log reduction targets for 1,4-dioxane, TCE, and PCE are also listed, along with the PLC-calculated (i.e., predicted) log reductions for each contaminant in all tests. The default PLC program does not provide performance predictions when the system is in local control mode and the entered target log reduction values are irrelevant. A subsequent update of the PLC program enabled these performance predictions to be provided when the system was operated in local control mode.

Table 5-3 lists the results of on-site benchtop analyses, including measured UVTs and H_2O_2 concentrations, for UV influent and UV effluent samples for each test. Also presented in Table 5-3 are the UV influent 'background' UVTs provided by the Trojan Optiview online UVT meter and the 'background' UVTs of grab samples collected upstream of H_2O_2 injection and downstream of Aqua Hume injection and measured on-site using the benchtop photometer. The presented background influent UVT and background effluent UVT values are calculated from the measured influent and effluent UVTs by subtracting the contribution to those UVTs by the measured H_2O_2 concentrations. The background water includes the impact of Aqua Hume on UVT. The online pH meter values are also provided for each test.

UVT Measurements and PLC calculations
Figure 5-2 compares the online UVT measurements to the background UVT grab samples measured using the bench-top photometer. The results are in very good agreement, suggesting that the online UVT meter will provide a highly accurate UVT signal upon which the PLC can base contaminant log reduction predictions. Furthermore, as presented in Table 5-3, the calculated influent background UVT based on the analyses of influent UVT and H_2O_2 also agree very well with both the online and grab sample measurements. The agreement among the three UV influent background UVT sets also validates the calculation method, which is the same calculation method used by the PLC to determine the UVT of the influent water. The same calculation method is also used to predict the background UVT of the water leaving the UV reactor (i.e., UVT of water in absence of H_2O_2). For the control test for which the UV reactor was off, we see that the calculated effluent background UVT is almost identical to the influent background UVT, as expected. Nevertheless, for all other tests the effluent background UVT has increased relative to the influent UVT and especially so for those tests in which Aqua Hume was injected. While this change is difficult to predict, it is not unexpected and is thought to be due to partial AOP treatment of the UV absorbing molecules in the Aqua Hume (e.g., humic & fulvic acids) resulting in decreased UV absorbance, as discussed in Section 5.2. The data for these tests show that the absolute change in UVT is inversely proportional to the UVT of the influent water. That is, Test 5 resulted in ~2.5% increase in UVT across the reactor while tests 1 to 4 averaged about a 1.94% increase and the remaining tests averaged about a 0.74% increase. That is, the higher the concentration of Aqua Hume that was dosed, the larger the increase in UVT. It is also observed that the increase in background UVT was less (i.e., 0.46%

average) for the tests targeting the lowest treatment levels (i.e., tests 7, 8, 14 & 15) and conducted at ambient UVT. That is, when less AOP treatment was applied, there was less apparent degradation of the UV-absorbing compounds.

Table 5-2: Test Data Recorded from UV HMI

Test ID	Date/Time	Well Blend		Total Flow	Control Mode	Lamp Sections	Lamp Power	Entered Scavenging Term	Online UVT	Online H2O2		Compliance Setpoint			Operating Setpoint			PLC Calculated LR		
		SM-8	SM-9							Feed	Residual	1,4-Dioxane	PCE	TCE	1,4-Dioxane	PCE	TCE	1,4-Dioxane	PCE	TCE
		(%)	(%)	(gpm)			(%)	(S⁻¹)	(%)	(mg/L)	(mg/L)	(log)	(log)	(log)	(log)	(log)	(log)	(log)	(log)	(log)
UV-PTC1	10/2/2023 13:10	50%	50%	2,000	Manual	0	0%	130,000	97.80%	39.60	39.60	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual
UV-PTC2	10/2/2023 14:37	50%	50%	2,003	Manual	11	100%	130,000	97.61%	0.00		Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual
UV-PT1	10/2/2023 15:35	50%	50%	1,997	Manual	11	84%	130,000	95.64%	39.73	-	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual
UV-PT2	10/2/2023 15:40	50%	50%	1,997	Manual	11	84%	130,000	95.69%	39.70	-	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual
UV-PT3	10/2/2023 16:22	50%	50%	1,999	Manual	11	83%	124,000	95.76%	36.98	-	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual	Manual
UV-PT4	10/3/2023 10:45	50%	50%	1,982	Auto	10	77.5%	130,000	95.89%	30.71	16.13	2.4	2.3	2.2	2.64	2.53	2.42	2.66	2.55	2.78
UV-PT5	10/3/2023 11:30	50%	50%	1,981	Auto	11	95%	130,000	93.45%	38.30	21.38	2.4	2.3	2.2	2.64	2.53	2.42	2.76	2.54	2.87
UV-PT6	10/3/2023 14:04	50%	50%	1,988	Auto	7	82%	130,000	98.54%	28.59	14.18	2.4	2.3	2.2	2.64	2.53	2.42	2.65	2.59	2.77
UV-PT7	10/4/2023 8:50	50%	50%	1,972	Auto	4	64.5%	130,000	98.45%	23.44	16.97	1.2	1.15	1.1	1.32	1.27	1.21	1.33	1.30	1.39
UV-PT8	10/4/2023 9:10	50%	50%	1,970	Auto	4	61.5%	124,000	98.62%	22.19	16.02	1.2	1.15	1.1	1.32	1.27	1.21	1.33	1.31	1.39
UV-PT9	10/5/2023 8:48	50%	50%	1,449	Auto	6	70.5%	130,000	98.55%	27.32	12.81	2.4	2.3	2.2	2.64	2.53	2.42	2.67	2.65	2.79
UV-PT10	10/5/2023 14:35	0%	100%	988	Manual	5	58.5%	130,000	98.82%	--		2.4	2.3	2.2	2.64	2.53	2.42	Manual	Manual	Manual
UV-PT11	10/5/2023 15:20	0%	100%	989	Auto	5	57%	124,000	98.82%	23.21	9.47	2.4	2.3	2.2	2.6	2.5	2.4	2.66	2.8	2.79
UV-PT12	9/22/2023 15:00	100%	0%	1,000	Auto	5	56.5%	130,000	97.73%	26.67	11.90	2.4	2.3	2.2	2.6	2.5	2.4	2.67	2.67	2.79
UV-PT13	9/22/2023 16:00	100%	0%	1,000	Auto	5	57.5%	124,000	97.53%	25.37	11.21	2.4	2.3	2.2	2.6	2.5	2.4	2.67	2.69	2.80
UV-PT14	10/4/2023 15:25	50%	50%	1,973	Auto	3	67.5%	90,000	98.57%	22.11	16.78	1.2	1.15	1.1	1.32	1.27	1.21	1.38	1.27	1.43
UV-PT15	10/4/2023 16:00	50%	50%	1,971	Auto	3	66.5%	90,000	98.64%	22.16	16.83	1.2	1.15	1.1	1.32	1.27	1.21	1.38	1.27	1.43
UV-PT16	10/3/2023 14:30	50%	50%	1,985	Auto	6	71.5%	130,000	98.63%	23.78		1.8	1.73	1.65	1.98	1.9	1.82	NA	NA	NA
UV-PT17	10/3/2023 14:53	50%	50%	1,990	Auto	6	77%	124,000	98.61%	23.07	12.00	1.8	1.73	1.65	1.98	1.9	1.82	NA	2.27	2.35
UV-PT18	10/4/2023 14:20	50%	50%	1,973	Auto	8	70%	130,000	98.64%	26.02	12.16	2.4	2.3	2.2	2.6	2.5	2.4	2.65	2.66	2.78
UV-PT19	10/4/2023 13:43	50%	50%	1,972	Auto	10	74.5%	130,000	96.02%	31.24	16.49	2.4	2.3	2.2	2.6	2.5	2.4	2.68	2.55	2.80
UV-PT20	10/4/2023 14:50	50%	50%	1,972	Auto	7	62.5%	90,000	98.49%	22.33	11.56	2.4	2.3	2.2	2.6	2.5	2.4	2.67	2.55	2.79

Table 5-3: Measured UVT and H₂O₂ results.

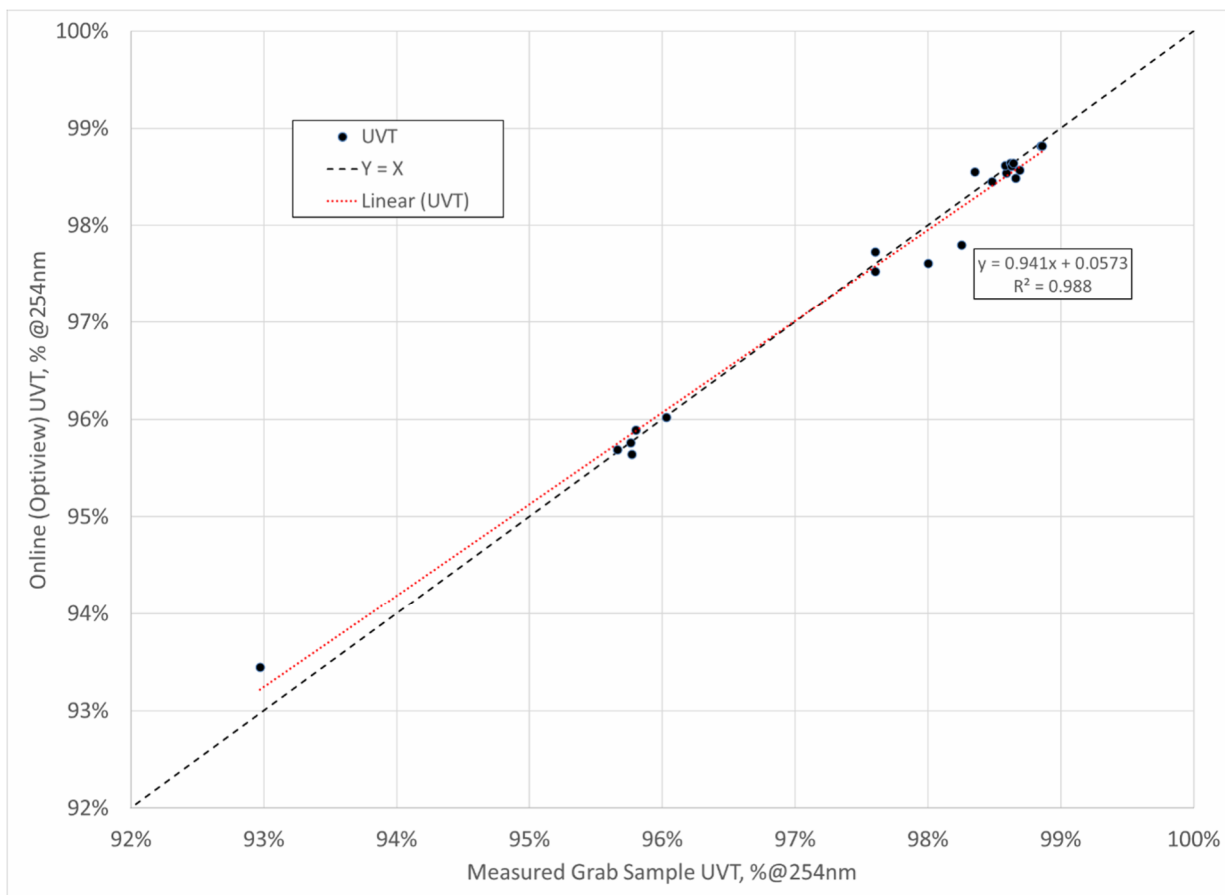| Test ID	UVT								Feed pH	Online H2O2		Measured H2O2	
	Online (Optiview) Pre-H2O2	Measured UV Inf Pre-H2O2	Measured UV Influent Post-H2O2	PLC Calculated Inf. UVT (Online + H2O2)	Calculated Background Inf UVT (Inf UVT - H2O2)	PLC Calculated Eff. UVT (Online + Residual H2O2)	Measured UV Effluent	Calculated Background Eff UVT (Eff UVT - H2O2)		PLC Requested Dose	PLC Calculated Residual	UV Influent (S9)	UV Effluent (S10)
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(SU)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
UV-PTC1	97.80%	98.25%	93.22%	92.79%	98.2%	92.8%	93.20%	98.3%	7.06	39.60	39.60	39.6	40.5
UV-PTC2	97.61%	98.00%	98.00%	97.61%	98.0%	97.6%	98.23%	98.2%	7.02	0.00	0.00	0.0	0.0
UV-PT1	95.64%	95.77%	90.59%	90.73%	95.6%	N.A.	94.55%	97.5%	7.03	39.73	N.A.	40.8	23.3
UV-PT2	95.69%	95.66%	90.42%	90.78%	95.5%	N.A.	94.56%	97.5%	7.02	39.70	N.A.	41.2	23.0
UV-PT3	95.76%	95.76%	90.98%	91.17%	95.7%	N.A.	94.92%	97.6%	7.02	36.98	N.A.	37.9	21.3
UV-PT4	95.89%	95.80%	91.84%	92.06%	95.7%	93.9%	95.22%	97.6%	6.95	30.71	16.13	30.7	18.2
UV-PT5	93.45%	92.97%	88.64%	88.82%	93.2%	90.8%	92.80%	95.7%	7.11	38.30	21.38	37.4	23.0
UV-PT6	98.54%	98.59%	94.88%	94.87%	98.6%	96.7%	97.04%	99.3%	7.10	28.59	14.18	29.3	17.0
UV-PT7	98.45%	98.48%	95.47%	95.43%	98.5%	96.3%	96.63%	99.1%	6.90	23.44	16.97	23.5	18.7
UV-PT8	98.62%	98.58%	95.83%	95.76%	98.6%	96.5%	96.87%	99.1%	6.91	22.19	16.02	21.6	16.8
UV-PT9	98.55%	98.35%	94.83%	95.04%	98.5%	96.9%	97.29%	99.2%	6.83	27.32	12.81	28.3	14.9
UV-PT10	98.82%	98.85%	95.42%	95.26%	99.0%	N.A.	97.61%	99.7%	6.87	N.A.	N.A.	27.7	15.7
UV-PT11	98.82%	98.86%	95.77%	95.82%	99.0%	97.6%	97.89%	99.5%	6.85	23.21	9.47	24.7	12.0
UV-PT12	97.73%	97.60%	94.73%	94.33%	98.3%	96.2%	97.61%	99.3%	6.83	26.67	11.90	28.1	13.2
UV-PT13	97.53%	97.60%	94.85%	94.30%	98.1%	96.1%	97.54%	99.1%	6.97	25.37	11.21	25.4	12.0
UV-PT14	98.57%	98.69%	95.72%	95.72%	98.8%	96.4%	96.70%	99.3%	6.50	22.11	16.78	24.0	19.7
UV-PT15	98.64%	98.62%	95.67%	95.78%	98.8%	96.5%	96.67%	99.2%	6.60	22.16	16.83	24.0	19.2
UV-PT16	N.A.	98.61%	95.49%	N.A.	98.6%	N.A.	97.23%	99.3%	7.04	N.A.	N.A.	24.2	15.8
UV-PT17	98.61%	98.63%	95.54%	95.64%	98.6%	97.1%	97.45%	99.3%	6.92	23.07	12.00	24.0	14.2
UV-PT18	98.64%	98.64%	95.16%	95.29%	98.6%	97.1%	97.29%	99.2%	6.52	26.02	12.16	26.9	14.9
UV-PT19	96.02%	96.03%	91.92%	92.12%	95.9%	93.9%	95.42%	97.8%	6.52	31.24	16.49	31.7	18.7
UV-PT20	98.49%	98.66%	95.67%	95.61%	98.7%	97.0%	97.44%	99.3%	6.50	22.33	11.56	23.7	14.4

Figure 5-2: Comparison between online UVT and measured background UVT.

The experimental data presented in Table 5-3 were also used to demonstrate how accurately the UV system control algorithm predicts the UV influent and UV effluent UVTs. The control algorithm calculates the UV influent UVT from the online UVT value and the H_2O_2 concentration. To exemplify, the control algorithm equation was used with the online pre-H_2O_2 UVTs with the PLC-requested H_2O_2 concentrations to calculate the UV influent UVT. A similar approach was used to calculate the UV effluent UVTs, that is, taking the online UVT adjusted for the PLC-calculated residual H_2O_2 concentration. These calculated UVT values are included in Table 5-3. The calculations assume that no or negligible changes would occur in the water background UVT during the UV/AOP treatment. Figure 5-3 (A) shows the comparison between measured UV influent UVTs and PLC-calculated UV influent UVTs. The agreement is very good for the UV influent data, thereby providing confidence in the calculation method used by the system controls to predict the influent UVT. Figure 5-3 (B) shows the comparison between measured UV effluent UVTs and PLC-calculated UV effluent UVTs. While the calculated effluent UVT trends well with the measured values, all measured effluent UVT values are higher than the predicted values and the discrepancy is greater for the lower UVT test conditions. This discrepancy corresponds to the observed increase in the background UVT across the reactor discussed above. The UVT modifier (Aqua Hume) is not a naturally occurring

constituent of the well water; thus, the UVT changes observed in the Aqua Hume-spiked tests are not representative to treatment conditions of typical well water.
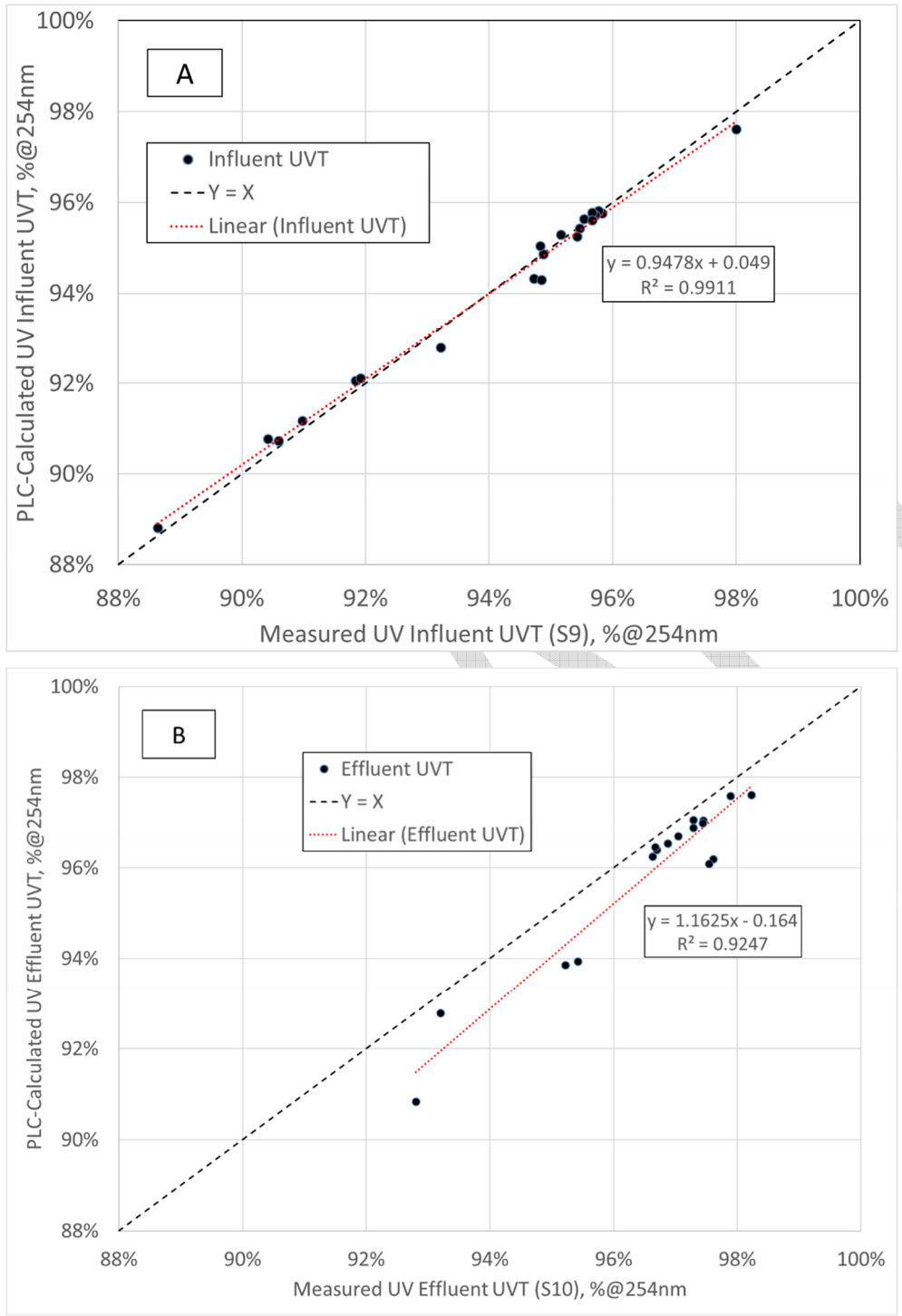

Figure 5-3: Comparison between measured and PLC-Calculated UVT

Hydrogen peroxide Measurements and PLC calculations

The PLC-requested UV influent H_2O_2 concentrations and PLC-predicted residual (i.e., UV effluent) H_2O_2 concentrations are plotted against the measured values in Figure 5-4. The measured H_2O_2 values plotted in Figure 5-4 are the results of the influent and effluent grab sample measurements. The PLC-calculated influent H_2O_2 concentrations for tests 10 and 16 were inadvertently not recorded. Also, the PLC-predicted H_2O_2 residuals were not available for the manual tests 1 to 3, 10, and 16. Figure 5-4 demonstrates very good agreement between the predicted and measured data. The excellent agreement between the predicted and measured influent H_2O_2 concentrations provides confidence in the reliance on the predicted concentrations in the absence of a reliable online analytical instrument. The PLC calculates the UV effluent H_2O_2 concentration based on the UV influent concentration and the predicted H_2O_2 destruction through the reactor. The UV influent and effluent H_2O_2 concentrations are then used to determine the average H_2O_2 concentration through the UV chamber, and subsequently the contaminant log reductions. Figure 5-4 shows that while the measured and PLC-predicted UV effluent H_2O_2 concentrations trend very well, the measured UV effluent H_2O_2 concentrations are consistently slightly higher than the predicted effluent concentrations. The impact of that underpredicted effluent H_2O_2 concentration is to add some conservatism to the predicted contaminant treatment.
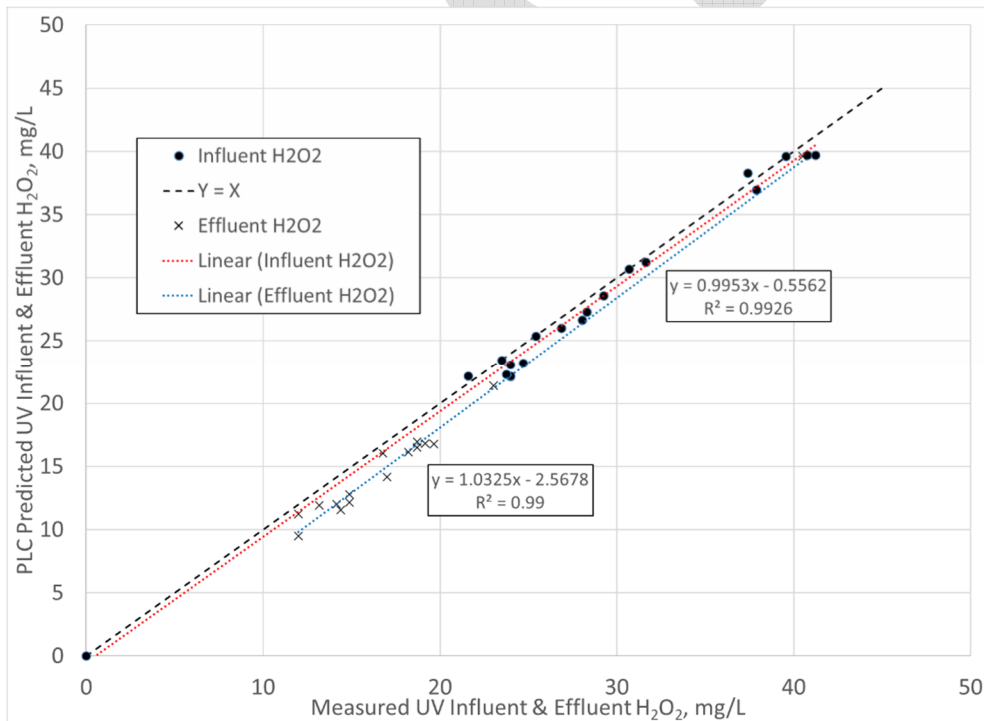

Figure 5-4: Comparison between measured and PLC H₂O₂ concentrations.

5.4   TARGET CONTAMINANT TREATMENT

Table 5-5 lists the 1,4-dioxane data reported by Weck Laboratories, while the TCE and PCE analytical data are reported in Tables 5-6 and 5-7, respectively. As well as the analytical data

reported by Weck for the duplicate influent and effluent samples, these tables also list the relative standard deviation (RSD) of the duplicate analyses and the average contaminant log reduction for each test. The average log reduction is calculated by taking the log of the average influent concentration divided by the average effluent concentration (i.e., Log(avg inf/avg eff)). The PLC-entered compliance and operating LR setpoints as well as the PLC-predicted LRs for each test are also included.

All UV influent and effluent 1,4-dioxane concentrations were >MDL for all tests and therefore a quantifiable LR value can be reported for each test. Table 5-5 shows that the influent 1,4-dioxane concentrations ranged from 19 μg/L to 470 μg/L, while the effluent concentrations ranged from 0.043 μg/L to 2.5 μg/L, except for the control tests. Recall that 1,4-dioxane was spiked into the UV influent stream at concentrations sufficient to produce UV effluent concentrations that were greater than the MRL. The RSD of the influent duplicates ranged from 0% to 19% for the non-control tests and were all considered acceptable. However, the RSD for the effluent duplicates ranged from 0% to 108% with the effluent results for tests 6 and 16 having RSD values >100%. Looking closer at those test results, it is recommended to consider the Test 6 effluent result of 2.2 μg/L as an anomaly and to use the other replicate value of 0.37 μg/L as the true value. Recalculating the 1,4-dioxane LR for Test 6 results in the value increasing from the average LR of 2.46 to 3.0 using the 0.37 μg/L effluent result. Similarly, for Test 16 it is recommended to consider the effluent result of 2.4 μg/L as an anomaly and to instead rely on the 0.32 μg/L result as the true value. That results in the 1,4-dioxane LR value for Test 16 increasing from 2.46 to 3.08. Other than those two tests with effluent RSD values >100%, the average UV effluent RSD of the 1,4-dioxane analyses for all other tests was 14% and this is considered to be acceptable. The results of the two control tests for which the 1,4-dioxane LRs were reported as 0.00 and 0.03 confirm that treatment is not provided in the absence of both UV energy and H_2O_2 together. We can also conclude from these control test results that the sampling and analytical methods do not contribute to anomalous results.

The analytical test results for PCE and TCE provided in Tables 5-6 and 5-7 respectively are quite different than those for 1,4-dioxane, where quantifiable 1,4-dioxane amounts were in the UV effluent samples. That is because these contaminants were not spiked into the influent stream. The average measured UV influent PCE concentration for the tests treating a 50% blend of wells SM-8 and SM-9 was 13.6 μg/L, whereas the result for SM-8 only was 2.0 μg/L and that for well SM-9 only was 27 μg/L. All UV effluent PCE concentration results were less than the MDL of 0.18 μg/L except for tests C1, 7, 8, 14 and 15, which targeted low treatment levels. The LRs reported in tables 5-5, 5-6 and 5-7 are calculated for each individual test as the Log([inf]/[eff]) where the [inf] term is the average UV influent concentration of the replicate samples and the [eff] term is the average UV effluent concentration of the replicate samples. To calculate the contaminant LR in tests where PCE and TCE in the effluent sample were reported as below the MDL, the MDL value (e.g., 0.18 μg/L for PCE & TCE) was used in the calculation of the average effluent concentration. Since the true concentration value could be less than the MDL, the resulting LR calculations are considered to be conservative.

It is noteworthy that while control test C1 with approximately 40 mg/L H_2O_2 but no UV resulted in no treatment of PCE, control test C2 with all lamps at 100% BPL but no H_2O_2 produced >1.9 LR based on an effluent concentration of <0.18 μg/L. That demonstrates that the contributions to PCE LR from direct UV photolysis are significant.

The average measured UV influent TCE concentration for the tests treating a 50% blend of wells SM-8 and SM-9 was 32 μg/L, whereas the result for SM-8 only was 80 μg/L and that for well SM-9 only was 1.8 μg/L. All UV effluent TCE concentration results were less than the MDL of 0.18 μg/L except for tests C1, C2, 7, 8, 14 and 15, which targeted low treatment levels. It is noteworthy that while control test C1 with approximately 40 mg/L H_2O_2 but no UV resulted in no treatment of TCE, control test C2 with all lamps at 100% BPL but no H_2O_2 produced 0.4 LR. That demonstrates the expected result that direct UV photolysis of TCE is much less significant than that of PCE, but needs to be considered. This observation is also consistent with the photolysis quantum yields reported in the literature for PCE and TCE.

Table 5-5: 1,4-Dioxane data for each test.

Test ID	Date/Time	Compliance Setpoint	Operating Setpoint	PLC Predicted	UV Feed		RSD of Influent Samples	UV Effluent		RSD of Effluent Samples	Average Log Reduction
		(log)	(log)	(log)	Replicate 1	Replicate 2	(%)	Replicate 1	Replicate 2	(%)	
UV-PTC1	10/2/2023 13:10	Manual	Manual	Manual	27	19	25%	23	28	14%	0.00
UV-PTC2	10/2/2023 14:37	Manual	Manual	Manual	23	24	3%	22	22	0%	0.03
UV-PT1	10/2/2023 15:35	Manual	Manual	Manual	340	260	19%	0.073	0.08	6%	3.59
UV-PT2	10/2/2023 15:40	Manual	Manual	Manual	280	280	0%	0.057	0.043	20%	3.75
UV-PT3	10/2/2023 16:22	Manual	Manual	Manual	290	300	2%	0.12	0.073	34%	3.49
UV-PT4	10/3/2023 10:45	2.4	2.64	2.66	330	340	2%	0.46	0.3	30%	2.95
UV-PT5	10/3/2023 11:30	2.4	2.64	2.76	290	240	13%	0.14	0.11	17%	3.33
UV-PT6	10/3/2023 14:45	2.4	2.64	2.65	370	370	0%	0.37	**2.2**	101%	2.46 (3.00)
UV-PT7	10/4/2023 8:50	1.2	1.32	1.33	24	28	11%	1.6	1.5	5%	1.22
UV-PT8	10/4/2023 9:10	1.2	1.32	1.33	26	25	3%	1.7	1.5	9%	1.20
UV-PT9	10/5/2023 20:48	2.4	2.64	2.67	350	320	6%	0.3	0.36	13%	3.01
UV-PT10	10/5/2023 14:35	2.4	2.64	Manual	120	120	0%	0.16	0.12	20%	2.93
UV-PT11	10/5/2023 15:20	2.4	2.6	2.66	150	120	16%	0.17	0.2	11%	2.86
UV-PT12	9/22/2023 15:00	2.4	2.6	2.67	190	160	12%	0.052	0.060	10%	3.49
UV-PT13	9/22/2023 16:00	2.4	2.6	2.67	160	160	0%	0.061	0.049	15%	3.46
UV-PT14	10/4/2023 15:25	1.2	1.32	1.38	30	29	2%	2.5	2.2	9%	**1.10**
UV-PT15	10/4/2023 16:00	1.2	1.32	1.38	27	25	5%	1.9	1.2	32%	1.22
UV-PT16	10/3/2023 14:30	1.8	1.98	NA	390	390	0%	2.4	0.32	108%	2.46 (3.08)
UV-PT17	10/3/2023 14:53	1.8	1.98	NA	85	90	4%	0.32	0.25	17%	2.49
UV-PT18	10/4/2023 14:20	2.4	2.6	2.65	380	470	15%	0.14	0.16	9%	3.45
UV-PT19	10/4/2023 13:53	2.4	2.6	2.68	330	360	6%	0.095	0.076	16%	3.61
UV-PT20	10/4/2023 14:50	2.4	2.6	2.67	210	190	7%	0.34	0.34	0%	2.77

Values in red font highlight anomalous analytical results and the expected true LR while bold LR values highlight LRs below the compliance target.

Table 5-6: PCE data for each test.

Test ID	Date/Time	Compliance Setpoint	Operating Setpoint	PLC Predicted	UV Feed		UV Effluent		Average Log Removal
		(log)	(log)	(log)	Replicate 1	Replicate 2	Replicate 1	Replicate 2	
UV-PTC1	10/2/2023 13:10	Manual	Manual	Manual	14	--	14	--	0.00
UV-PTC2	10/2/2023 14:37	Manual	Manual	2.38	13	--	< 0.18	--	> 1.9
UV-PT1	10/2/2023 15:35	Manual	Manual	Manual	14	--	< 0.18	--	> 1.9
UV-PT2	10/2/2023 15:40	Manual	Manual	Manual	14	--	< 0.18	--	> 1.9
UV-PT3	10/2/2023 16:22	Manual	Manual	Manual	13	--	< 0.18	--	> 1.9
UV-PT4	10/3/2023 10:45	2.3	2.53	2.55	13	--	< 0.18	< 0.18	> 1.9
UV-PT5	10/3/2023 11:30	2.3	2.53	2.54	11	--	< 0.18	--	> 1.9
UV-PT6	10/3/2023 14:45	2.3	2.53	2.59	12	--	< 0.18	--	> 1.9
UV-PT7	10/4/2023 8:50	1.15	1.27	1.30	14	--	0.88	--	1.20
UV-PT8	10/4/2023 9:10	1.15	1.27	1.31	14	15	1.1	0.94	1.15
UV-PT9	10/5/2023 20:48	2.3	2.53	2.65	16	--	< 0.18	--	> 1.9
UV-PT10	10/5/2023 14:35	2.3	2.53	Manual	28	--	0.26	--	**2.03**
UV-PT11	10/5/2023 15:20	2.3	2.5	2.75	26	--	< 0.18	--	> 2.2
UV-PT12	9/22/2023 15:00	2.3	2.5	2.67	2.1	--	< 0.18	--	> 1.9
UV-PT13	9/22/2023 16:00	2.3	2.5	2.69	1.9	--	< 0.18	--	> 1.9
UV-PT14	10/4/2023 15:25	1.15	1.27	1.27	15	--	1.3	--	**1.06**
UV-PT15	10/4/2023 16:00	1.15	1.27	1.27	15	--	1.3	--	**1.06**
UV-PT16	10/3/2023 14:30	1.73	1.9	NA	11	--	< 0.18	--	> 1.9
UV-PT17	10/3/2023 14:53	1.73	1.9	2.27	13	--	< 0.18	--	> 1.9
UV-PT18	10/4/2023 14:20	2.3	2.5	2.66	13	--	< 0.18	--	> 1.9
UV-PT19	10/4/2023 13:53	2.3	2.5	2.55	14	--	< 0.18	--	> 1.9
UV-PT20	10/4/2023 14:50	2.3	2.5	2.55	16	--	< 0.18	--	> 1.9

Bold LR values highlight LRs below the compliance target.

Table 5-7: TCE data for each test.

Test ID	Date/Time	Compliance Setpoint	Operating Setpoint	PLC Predicted	UV Feed		UV Effluent		Average Log Removal
		(log)	(log)	(log)	Replicate 1	Replicate 2	Replicate 1	Replicate 2	
UV-PTC1	10/2/2023 13:10	Manual	Manual	Manual	32	--	32	--	0.00
UV-PTC2	10/2/2023 14:37	Manual	Manual	0.1	34	--	15	--	0.36
UV-PT1	10/2/2023 15:35	Manual	Manual	Manual	31	--	< 0.18	--	> 2.2
UV-PT2	10/2/2023 15:40	Manual	Manual	Manual	31	--	< 0.18	--	> 2.2
UV-PT3	10/2/2023 16:22	Manual	Manual	Manual	30	--	< 0.18	--	> 2.2
UV-PT4	10/3/2023 10:45	2.2	2.42	2.78	29	--	< 0.18	< 0.18	> 2.2
UV-PT5	10/3/2023 11:30	2.2	2.42	2.87	27	--	< 0.18	--	> 2.2
UV-PT6	10/3/2023 14:45	2.2	2.42	2.77	27	--	< 0.18	--	> 2.2
UV-PT7	10/4/2023 8:50	1.1	1.21	1.39	37	--	0.45	--	1.91
UV-PT8	10/4/2023 9:10	1.1	1.21	1.39	35	35	0.52	0.51	1.83
UV-PT9	10/5/2023 20:48	2.2	2.42	2.79	33	--	< 0.18	--	> 2.2
UV-PT10	10/5/2023 14:35	2.2	2.42	Manual	2	--	< 0.18	--	> 1.0
UV-PT11	10/5/2023 15:20	2.2	2.4	2.79	1.6	--	< 0.18	--	> 0.9
UV-PT12	9/22/2023 15:00	2.2	2.4	2.79	82	--	< 0.18	--	> 2.2
UV-PT13	9/22/2023 16:00	2.2	2.4	2.80	78	--	< 0.18	--	> 2.2
UV-PT14	10/4/2023 15:25	1.1	1.21	1.43	37	--	0.61	--	1.78
UV-PT15	10/4/2023 16:00	1.1	1.21	1.43	35	--	0.65	--	1.73
UV-PT16	10/3/2023 14:30	1.65	1.82	NA	28	--	< 0.18	--	> 2.2
UV-PT17	10/3/2023 14:53	1.65	1.82	2.35	30	--	< 0.18	--	> 2.2
UV-PT18	10/4/2023 14:20	2.2	2.4	2.78	32	--	< 0.18	--	> 2.2
UV-PT19	10/4/2023 13:53	2.2	2.4	2.80	34	--	< 0.18	--	> 2.3
UV-PT20	10/4/2023 14:50	2.2	2.4	2.79	36	--	< 0.18	--	> 2.3

1,4-Dioxane Spiking

Given the significant range of expected treatment levels, the spiked concentration of 1,4-dioxane was varied from test to test to target an effluent concentration of around 0.1 μg/L. The measured concentrations of 1,4-dioxane in the UV influent samples should represent the sum of the spiked concentrations and the ambient 1,4-dioxane concentrations in the groundwater. Figure 5-5 compares the calculated spiked concentration to the measured UV influent concentration for each test to demonstrate the correlation. Note that tests C1, C2, 7, 8, 14 and 15 targeted spike levels between 1 μg/L and 6.4 μg/L, given their relatively low target LRs. Those low spike levels were achieved using a 1,4-dioxane stock concentration of 6.2 g/L, whereas all remaining tests used a 1,4-dioxane stock concentration of 146 g/L. Given that the four UV influent samples for the control tests (i.e., C1 & C2) averaged 23 μg/L 1,4-dioxane and only 1 μg/L was spiked. From this it is estimated that the ~50:50 blend of SM-8 and SM-9 well water contained approximately 22 μg/L 1,4-dioxane. Therefore, the ideal result for Figure 5-5 would see all data points in a parallel line below the line of Y = X and offset to the right by 22 μg/L. While there are variable results, Figure 5-5 shows the linear regression line of the data points to almost exactly matched that ideal result. That is, the slope of the regression line is >0.99 with an X-intercept of -23 μg/L. It is suggested that the observed variability is likely due primarily to analytical variability.
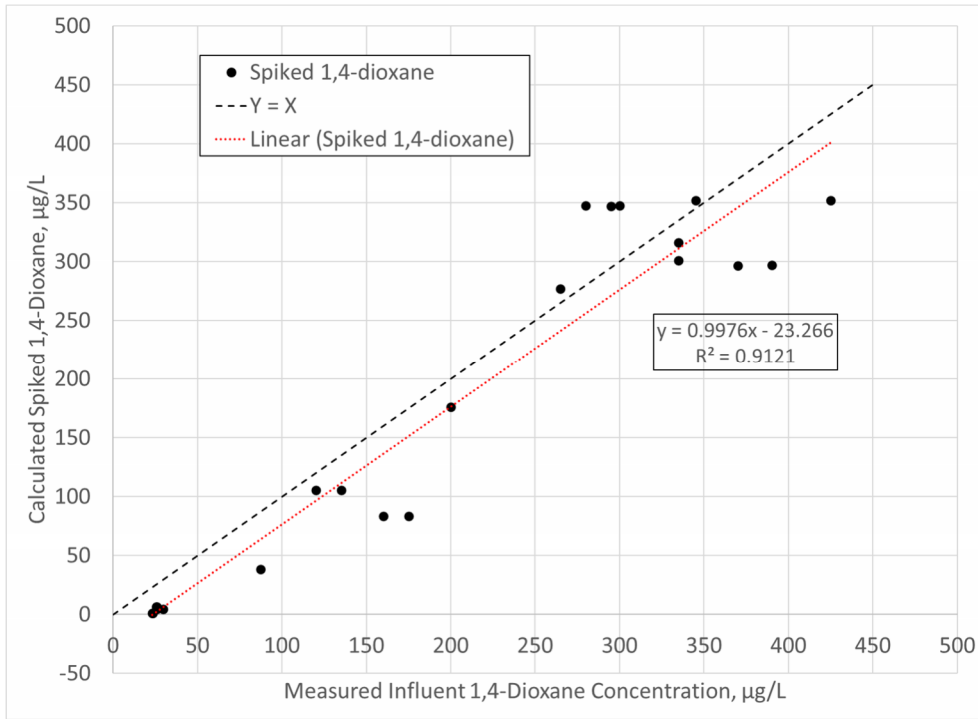
Figure 5-5: Measured UV Influent Contaminant Concentrations versus Calculated Concentrations

Comparison of Measured and Target Contaminant Log Reductions

The 1,4-dioxane compliance and operating LR setpoints, PLC-predicted LRs, and measured LRs that are provided in Table 5-5 are plotted in Figure 5-6. The measured LRs are represented by the blue bars and the arrows above those for tests 6 and 16 are to indicate that the true measured LRs should likely be 3.0 and 3.08, respectively, as discussed above. The associated compliance and operating LR setpoints as well as the PLC-predicted LR values are represented by the red, green, and purple bars. The compliance LR setpoints were selected according to the test matrix presented in Table 4-1, whereas the operating setpoints were set to be 10% higher than the compliance level. The UV system PLC will operate the system to target the operating LR setpoints for the three controlling contaminants (e.g., 1,4-dioxane, PCE & TCE). Thus, the operating setpoint represents an adjustable operational conservatism relative to the compliance setpoint. The PLC-predicted LRs are calculated by the PLC based on the live online inputs of flow, UVT, H_2O_2 dose, UVI data and number of operating lamp sections, plus the manually entered hydroxyl radical ST and nitrate level as well as the kinetic parameters for each contaminant. As previously described, predicted LRs are not available for all manual mode runs. Furthermore, LR setpoints are irrelevant for manual mode runs since the PLC is not controlling to them. Most tests had a 1,4-dioxane compliance LR setpoint at the design value of 2.4 with the operating target at 2.64. The PLC-predicted LRs are just slightly above the operating target for all those tests, as expected.
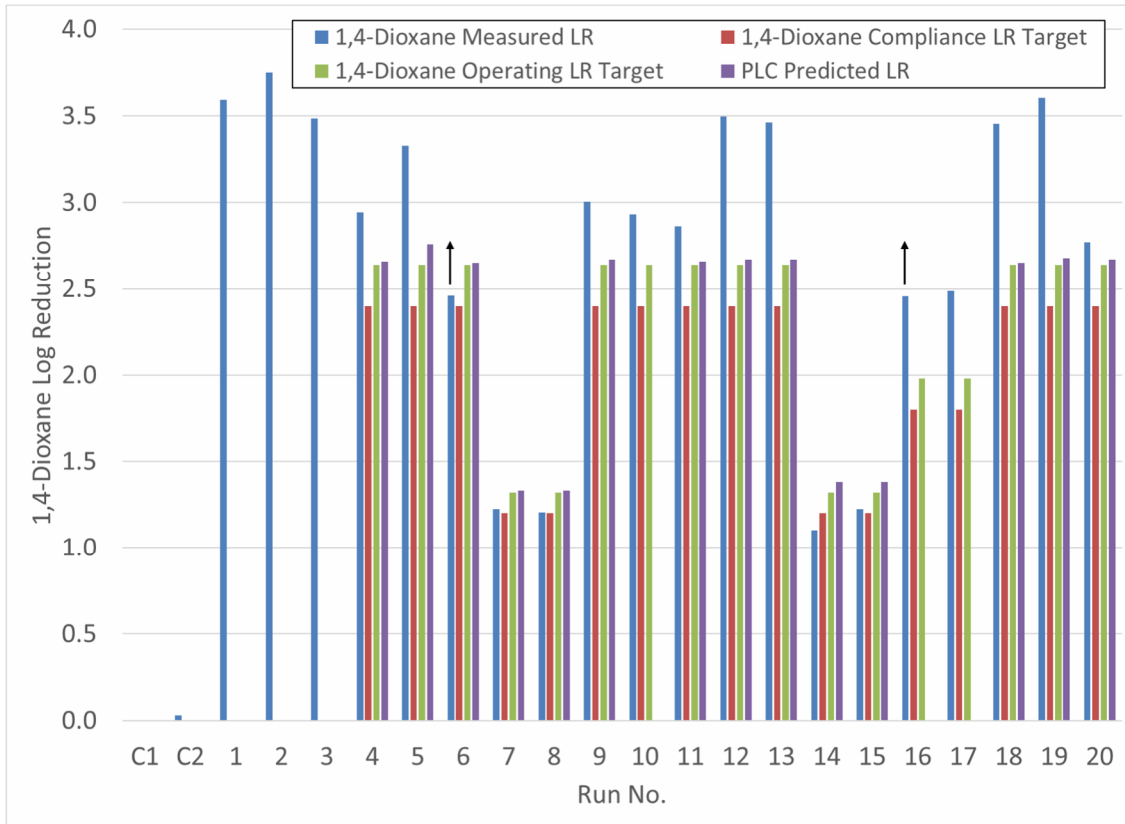
Figure 5-6: 1,4-Dioxane Log Reduction Values: Comparison of Measured, Target and Predicted Values.

Table 5-5 and Figures 5-6 demonstrate that the measured 1,4-dioxane LR values exceeded the target and predicted values for all tests except runs 7, 8, 14 and 15. For those four tests, which had a reduced 1,4-dioxane LR target of 1.2, 3 of the 4 runs met or exceeded the compliance target, while test 14 achieved 92% of the compliance target LR (i.e., 1.1 vs 1.2). Tests 14 and 15 are duplicate tests with the same operating conditions and treatment targets. Nevertheless, run 15 measured 1.22 LR 1,4-dioxane while run 14 measured 1.1 LR. This relatively minor discrepancy is likely due to analytical uncertainty as the range of LRs calculated from both sets of analytical data (i.e., both tests 14 & 15) is from 1.0 to 1.4. As listed in Table 5-2, tests 14 and 15 were performed with the pH reduced to 6.5, which was expected to have an associated reduced ST. As such, the ST entered into the PLC for those tests was 90,000 s^{-1} whereas the measured ST value was slightly lower as presented in Table 5-1. To reiterate, the "measured" ST value corresponds to PT20 pre-H$_2$O$_2$ sample associated with test PT20 which was run on the same day as tests PT14 and PT15, but earlier in the day.

Another means of viewing the comparison between target and measured LR values is the X-Y plot presented in Figure 5-7. In this figure the measured 1,4-dioxane LR values are compared to both the compliance LR setpoint and the operating LR setpoint. Data points below the line of unity (i.e., Y = X) represent test conditions where the measured LR exceeded the setpoint target. Figure 5-7 presents a clearer view of the overall performance that was described in run-by-run detail in Figure 5-6. That is, Figure 5-7 shows that 13 of the 17 runs performed in 'auto' control mode exceeded both the compliance and operating LR targets. Furthermore, of the 4

test conditions with the lowest LR setpoints for which the operating setpoint was not achieved, 3 of those tests demonstrated measured LRs that met or exceeded the compliance setpoint.
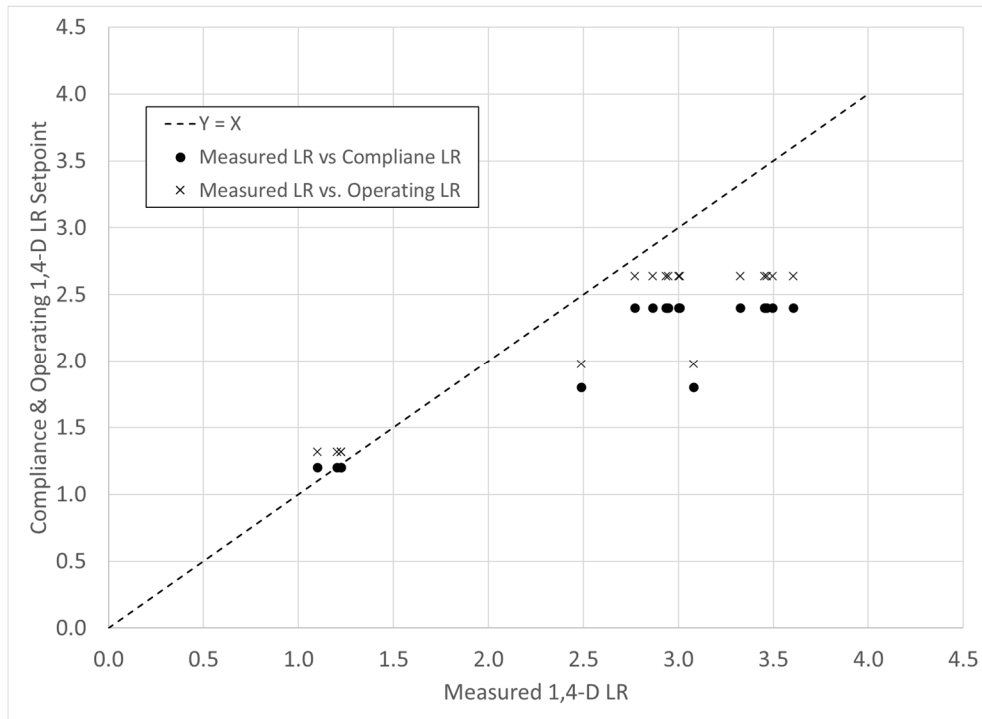

Figure 5-7: Comparison of Measured 1,4-Dioxane LR to the Compliance and Operating LR Setpoints

The PCE compliance and operating LR setpoints, PLC-predicted LRs and measured LRs that are provided in Table 5-6 are plotted in Figure 5-8. The measured LRs are represented by the dark blue bars and the arrows above those bars are to indicate that the true measured LRs should likely be higher based on the measured effluent PCE concentrations being less than the MDL of 0.18 μg/L. The associated compliance and operating LR setpoints as well as the PLC-predicted LR values are represented by the red, green and purple bars. The compliance LR setpoints were selected according to the test matrix presented in Table 4-1 whereas the operating setpoints were set to be 10% higher than the compliance level. The PLC-predicted LRs are calculated by the PLC based on the live online inputs of flow, UVT, H_2O_2 dose, UVI data and number of operating lamp sections plus the manually entered hydroxyl radical ST and nitrate level as well as the kinetic parameters. As previously described, the setpoint and predicted LRs are not available for all manual mode runs. Most tests had a PCE compliance LR setpoint at the design value of 2.3 with the operating target at 2.53. The PLC-predicted LRs for most runs are just slightly (i.e., <5%) above the operating target, although there are a few runs for which the predicted LRs are more than slightly (i.e., 6% to 19%) above the operating target. 1,4-dioxane was the controlling contaminant for those runs (i.e., runs 9, 11, 12, 13 & 17) and the PLC-predicted PCE LR value was higher than required to meet the setpoint. It is noteworthy that the predicted PCE LR for the direct photolysis control test (i.e., C2) is 2.38, whereas the analytical

data demonstrated it to be greater than 1.9, with an effluent PCE concentration less than the MDL.

As shown in Table 5-6 and Figure 5-8 it cannot be definitively concluded that the measured PCE LR values exceeded the target and predicted values because most tests produced effluent PCE concentrations below the MDL of 0.18 μg/L. During the planning phase of this work, Trojan prepared a document titled "*Rationale for Proposing 1,4-Dioxane Removal Yield as an Indicator for Tetrachloroethene (PCE) and Trichloroethene (TCE) Removal Efficiency from Groundwater with the UV/H2O2 AOP at Water Treatment Facilities*". This document explains how the known photochemical kinetic parameters for 1,4-dioxane, PCE and TCE can be applied together with the water quality parameters to calculate their fluence-based rate constants and that the LR ratios of the contaminants are proportional to these rate constants. For example, in that document, it was concluded that the LR ratio would be 1.00:1.00:1.22 for 1,4-dioxane:PCE:TCE when treating the design water quality (i.e., ST=130,000 s^{-1}; NO$_3^-$ 35 mg/L) at the reactor average H$_2$O$_2$ dose of 31 mg/L. The Trojan PLC program and Trojan's offline kinetic model have the photochemical kinetic parameters and fluence-based rate constant equation incorporated as part of the calculations. One discrepancy between these models and the referenced document is that they use the lowest reported value for the rate constant for the reaction of OH radicals with PCE (i.e., 2.0E+09 M^{-1}s^{-1}) as opposed to the average value (i.e., 2.33±0.41E+09 M^{-1}s^{-1}) and so the models are more conservative with respect to PCE treatment when compared with the predictions in the document. Similarly, the kinetic models also use a more conservative OH radical rate constant for TCE (i.e., 2.9E+09 M^{-1}s^{-1}) than the average value (i.e., 3.39±0.70E+09 M^{-1}s^{-1}) used in the document. Both of these models can be used to generate the expected ratio of PCE LR to 1,4-dioxane LR for each test condition. Using the offline kinetic model together with the measured water quality, this ratio ranged from 0.91 to 1.02 and was used to generate predicted PCE LRs based on the measured 1,4-dioxane LRs and these predicted PCE LRs are presented as the light blue bars in Figure 5-8. Recent literature studies showed that the superoxide radical anion (O$_2^{\bullet-}$) contributes to PCE and TCE degradation in H$_2$O$_2$-catalyzed processes (Watts and Teel, 2019). In high alkalinity waters this radical reaches relatively high steady-state concentrations because it is formed from both OH and carbonate radical reactions with H$_2$O$_2$. There are other routes to the formation of this radical, but of a minor importance. The reactions of with PCE and TCE are not included in Trojan's kinetic model, as, to the best of our knowledge, no rate constants are available in the public domain.

The predicted PCE LR exceeds the operating setpoint for all tests for which the effluent PCE concentration was below the MDL. The measured effluent PCE concentration for run 10 was above the MDL and below the MRL and resulted in a measured LR of 2.03 whereas the compliance target was 2.3. It should be noted that analytical data that is below the MRL has a greater uncertainty associated with its quantification. Tests 10 and 11 were performed with well SM-9 only at a flow of 1,000 gpm. Run 10, which had a higher ST entered into the PLC, was performed with slightly higher UV power and higher H$_2$O$_2$ and so it should have provided more treatment than run 11, which produced an effluent PCE concentration below the MDL. The test 10 result also disagrees with the predicted PCE LR based on the measured 1,4-dioxane LR value. For all these reasons, the test 10 PCE result is considered to be an anomaly. Furthermore, similar to the 1,4-dioxane results, runs 7, 8, 14 and 15 did produce effluent PCE concentrations greater than the MDL and the resulting LRs were less than the predicted LRs. For those four tests which had a reduced PCE LR target of 1.15, 2 of the 4 runs met or exceeded the compliance

target while tests 14 and 15 achieved 92% of the compliance target LR (i.e., 1.06 vs 1.15). The predicted PCE LR based on the measured 1,4-dioxane LRs are also lower than the operating target for all 4 runs and lower than the compliance target for run 14. The strong correlation between the measured and predicted LRs for these runs provides confidence in those PCE LR predictions based on the measured 1,4-dioxane LRs.
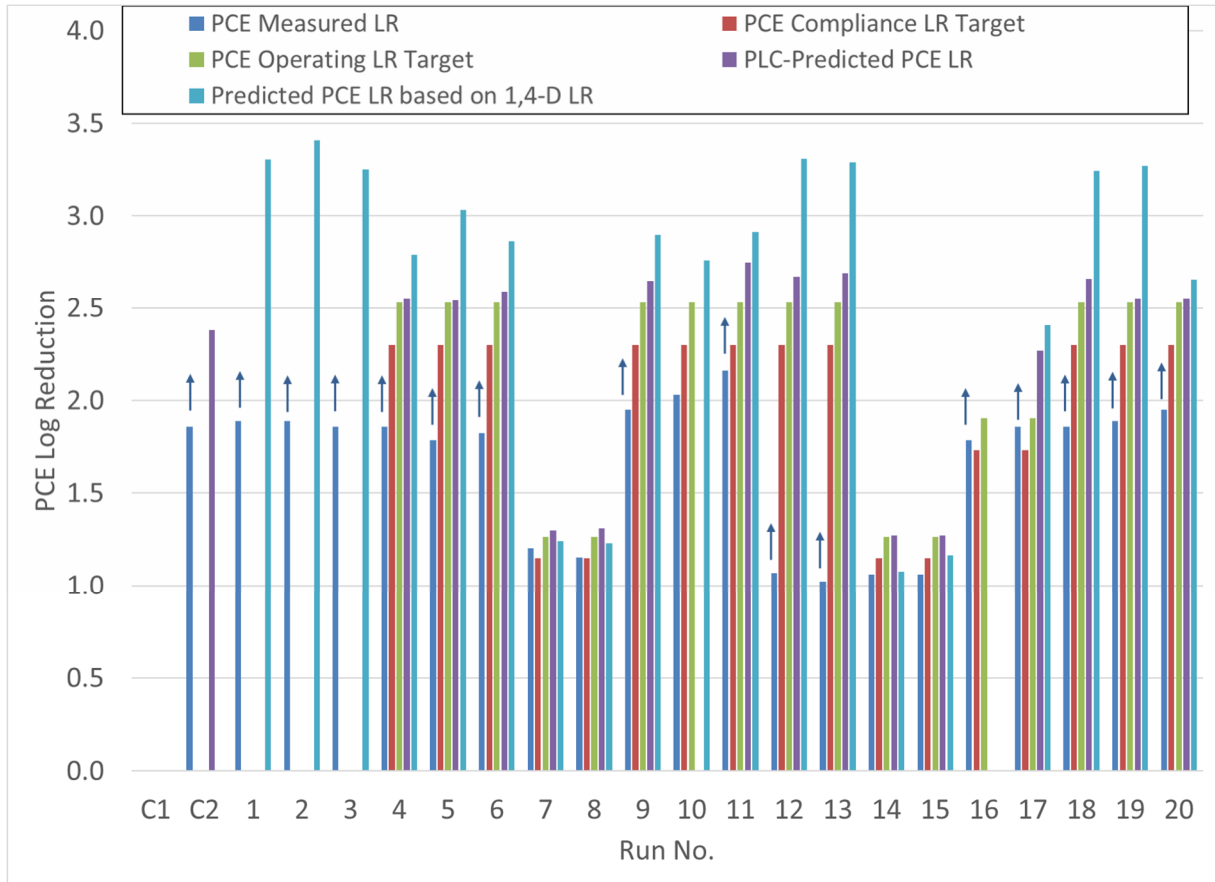

Figure 5-8: PCE Log Reduction Values: Comparison of Measured, Target and Predicted Values.

The TCE compliance and operating LR setpoints, PLC-predicted LRs and measured LRs that are provided in Table 5-7 are plotted in Figure 5-8. The measured LRs are represented by the blue bars and the arrows above those bars are to indicate that the true measured LRs should likely be higher based on the measured effluent TCE concentrations being less than the MDL of 0.18 μg/L. The associated compliance and operating LR setpoints as well as the PLC-predicted LR values are represented by the red, green and purple bars. The compliance LR setpoints were selected according to the test matrix presented in Table 4-1 whereas the operating setpoints were set to be 10% higher than the compliance level. The PLC-predicted LRs are calculated by the PLC based on the live online inputs of flow, UVT, H_2O_2 dose, UVI data and number of operating lamp sections plus the manually entered hydroxyl radical ST and nitrate level. As previously described, the setpoint and predicted LRs are not available for all manual mode runs. Most tests had a TCE compliance LR setpoint at the design value of 2.2 with the

operating target at 2.44. The PLC-predicted LRs for most runs are significantly above the operating target. 1,4-dioxane was the controlling contaminant for those runs and the associated predicted TCE LR value was higher than required. As shown in Table 5-7 and Figure 5-8 most tests produced effluent TCE concentrations below the MDL of 0.18 μg/L. Nevertheless, given the higher ambient concentration of TCE than PCE in the SM-8 well water, most tests were able to demonstrate that the compliance LR target was exceeded. That was also true for runs 7, 8, 14 and 15 which did produce effluent TCE concentrations greater than the MDL and the resulting LRs were significantly greater than the predicted LRs. As described for PCE above, the Trojan offline kinetic model was used to generate the expected ratio of TCE LR to 1,4-dioxane LR for each test condition. This ratio was pseudo-constant at 1.03 and was used to generate predicted TCE LRs based on the measured 1,4-dioxane LRs and these predicted TCE LRs are presented as the light blue bars in Figure 5-9. The predicted TCE LR exceeds the operating setpoint for all tests except tests 14 and 15 however, as noted above, the measured TCE LRs for tests 14 and 15 were greater than the operating setpoint and the PLC-predicted values. The overall conclusion regarding TCE treatment is that the compliance LR target is met or exceeded provided sufficient TCE is present to demonstrate the required LR. Only tests 10 and 11 were not able to definitively demonstrate that the compliance target was met because the influent TCE concentrations were too low.
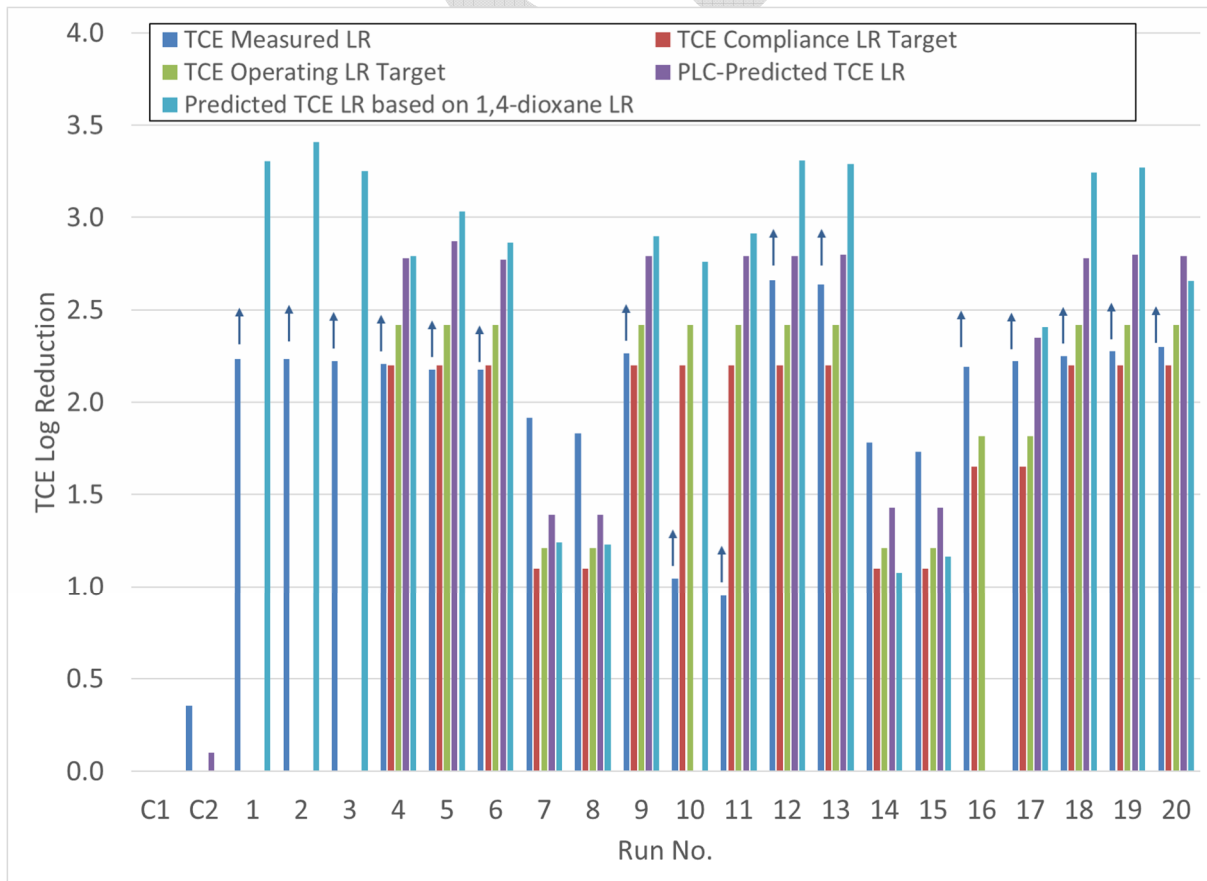

Figure 5-9: TCE Log Reduction Values: Comparison of Measured, Target and Predicted Values.

The overall conclusion from the data presented above is that the measured 1,4-dioxane LR values exceeded the operating LR setpoints for all tests for which the 1,4-dioxane compliance LR target was either the design value of 2.4 or the reduced value of 1.8. For those runs with a 1,4-dioxane compliance target of 1.2 LR, 3 of the 4 runs demonstrated 1,4-dioxane LRs that met or exceeded the compliance LR setpoint. Although tests 14 and 15 are duplicate test runs, only test 14 provided a measured 1,4-dioxane LR value below the compliance setpoint of 1.2 LR. Similarly, although only 6 of the 22 test conditions, including the control tests, produced effluent PCE concentrations >MDL, based on the measured 1,4-dioxane LRs and the predicted ratio of PCE:1,4-dioxane LR, all tests except test 14 are predicted to exceed the compliance setpoints. Only 6 of 22 test conditions produced effluent TCE concentrations >MDL nevertheless, ambient TCE concentrations were high enough to demonstrate that the compliance setpoint was met or exceeded for all tests.

Test runs 14, 15 and 20 were all performed at a reduced pH of ~6.5 and a ST of 90,000 s^{-1} entered into the PLC. The measured 1,4-dioxane and PCE LRs for tests 14 and 15 did not exceed the operating target and run 20 only exceeded that LR target by <5%. While water samples for ST determination were not taken during tests 14 or 15, the sample taken following test 20 measured 85,300 s^{-1} as reported in Table 5-1. It is suggested that this measured ST value, while apparently very accurate for test 20, underestimated the ST of the water for tests 14 and 15. Trojan has calculated that a ST value of 112,500 s^{-1} entered into the UV PLC would have resulted in the contaminant LRs exceeding the operating target (i.e., 1.32 LR for 1,4-D & 1.27 for PCE) for those two runs.

The measured 1,4-dioxane and PCE LRs for tests 7 and 8 were also lower than their respective operating target setpoints. Although those tests were operated using the 50:50 well blend, there was not a specific water sample evaluated for ST for the water treated during tests 7 and 8. Of note, tests 7 and 8 were the first tests performed on October 4th (8:50 and 9:10), whereas tests 14 and 15 were the last tests performed that day (15:25 and 16:00). A few source water samples were collected from the greensand influent during the October Performance Testing by Brown and Caldwell and sent for analysis to Weck Laboratories. The nitrite data reported by Weck for these samples and the corresponding calculated contribution of nitrite to the ST are shown in Table 5-8.

Table 5-8: Nitrite data for source water samples and its contribution to ST

Sample ID	Date and time of sampling	Nitrite (ug/L as N)	ST(NO2-), s-1
PT-SWC2-S4	10/2/2023 13:00	51	36429
PT-SW4-S4	10/3/2023 9:53	ND	NA
PT-SW8-S4	10/4/2023 9:17	50	35714
PT-SW9-S4	10/5/2023 8:50	ND	NA

The information provided in Table 5-8 indicates the well blend quality varies from one day to another, and this observation is supported by other analytes quantified in these samples and not shown herein. The only source water collected on October 4th is PT-SW8-S4 and the sampling was done right after completion of tests 7 and 8. As stated earlier, there was no sample collected

for ST determination at the same time with either PT-SW8-S4 or tests 7 or 8. Furthermore, the $ST(NO_2^-)$ of 35,714 s^{-1} corresponding to the nitrite level of 50 µg/L as N quantified in PT-SW8-S4 sample, is far too high to be part of (i.e., included) in the ST of 85,300 s^{-1} measured experimentally at Trojan for the test 20 sample (pH 6.5) collected on October 4th. Note that the ST measured for the test 20 sample covers the contributions of alkalinity (52,800 s^{-1}), nitrite formed and reacted during the ST determination (observed NO_2^- residual was quantified ~90 µg/L, i.e., much more was formed during the UV/AOP) and of initial organic compounds originally present in the well blend (~10,000 s^{-1}) and added to the sample (e.g., 1,4-dioxane; ST~6,360 s^{-1}). This highly simplified interpretation of the available data indicates that (1) nitrite was likely present in the well blend used for tests 7 and 8, and (2) presumably, there was a variation in nitrite concentration in the well blend used in the tests of October 4th over time. Trojan has calculated that a ST value of 144,750 s^{-1} entered into the UV PLC would have resulted in the contaminant LRs exceeding the operating target (i.e., 1.32 LR for 1,4-D & 1.27 for PCE) for runs 7 and 8. If this increased ST value (i.e., 14,750 s^{-1}) were to be explained by an increased nitrite concentration then that would only require an additional 19 μg/L of NO_2^--N. Therefore, based on the measured nitrite concentrations, it is feasible that variable nitrite levels in the UV influent water could explain the lower treatment efficiency observed for tests 7 and 8. As previously stated, typical operation of the greensand filters will involve injection of sodium hypochlorite upstream of the filters and this would eliminate any contributions to the ST due to nitrite in the groundwater—i.e., the ST under the same feed water quality conditions would be proportionally lower (and hence performance would be higher).

6 CONCLUSIONS & RECOMMENDATIONS

This report documents the on-site performance tests for the TrojanUVFlex200 AOP system installed at the Santa Monica Arcadia Water Treatment Plant. All tests were completed with combinations of wells SM-8 and SM-9 and using UV Train 2. Whereas the test matrix states that UV Train 1 will be tested an issue with the Train 1 outlet valve control resulted in the switch to test Train 2. The design and performance of the two parallel trains are considered to be identical, which is the basis for only testing one train. The background UVT (i.e., pre-H_2O_2) of the tested water ranged from 93.0% to 98.7% and the UV influent H_2O_2 concentrations ranged from 22 to 39.7 mg/L. 1,4-dioxane log reductions from 1.1 to 3.75 were demonstrated, along with PCE log reductions of 1.06 to >2.03 and TCE log reductions of 1.73 to >1.91.

The key conclusions drawn from the performance test are:

- The specified water quality and operating conditions as defined in the test matrix were met for each test. Specifically, the measured flow rates were all within the acceptable range; the measured UV influent background UVT values were within the expected range; the measured UV influent H_2O_2 concentrations were all less than the maximum allowed; 1,4-dioxane was spiked sufficiently to produce effluent concentrations above the MDL for all tests; and the measured UV influent STs were less than the PLC-entered design value.

- The test results clearly demonstrate that the TrojanUVFlex200 UV-AOP system is capable of meeting the guaranteed treatment criteria at the design operating conditions,

as summarized in Table 2-1. Specifically, tests 1, 2 and 3 were all operated at the design conditions and at 84% BPL to simulate the lamp output at the EOLL value of 0.86 and the measured 1,4-dioxane LR values averaged 3.6, which significantly exceeded the design LR of 2.4. These test conditions also treated the ambient concentrations of PCE and TCE to less than the MDL. While ambient TCE concentrations were sufficient to demonstrate LRs at least as high as the design LR, PCE concentrations were not high enough to show this. However, Trojan's kinetic model is able to provide conservatively predicted LRs for both PCE and TCE based on the measured LR of 1,4-dioxane. Those predicted PCE and TCE LRs were shown to exceed the required treatment at the design conditions.

- Results presented demonstrate how the system accurately calculates UV influent UVT from the sum of the measured background UVT and the UV absorbance contribution from injected H_2O_2. Similarly, it was also demonstrated that the calculation of the UV effluent UVT based on the sum of the measured background UVT and the absorbance contribution from the predicted residual H_2O_2 concentration is slightly conservative due to a slight increase in the background UVT across the reactor.

- The results demonstrate that the measured and PLC-calculated UV influent and effluent H_2O_2 concentrations are in good agreement.

- The measured 1,4-dioxane LR values exceeded the operating LR setpoints for all tests for which the 1,4-dioxane compliance LR target was either the design value of 2.4 or the reduced value of 1.8. For those runs with a 1,4-dioxane compliance target of 1.2 LR, 3 of the 4 runs demonstrated 1,4-dioxane LRs that met or exceeded the compliance LR setpoint. Test 14 did not meet the compliance target and was performed at a reduced pH for which it is suggested that the ST entered into the PLC was underestimated. Trojan has calculated that a ST value of 112,500 s^{-1} entered into the UV PLC would have resulted in the contaminant LRs exceeding the operating target (i.e., 1.32 LR for 1,4-D & 1.27 for PCE) for those two runs. Therefore, if the plant controls the UV influent pH to 6.5 or less then it is recommended that a ST value of 112,500 s^{-1} be entered into the UV PLC.

- The measured 1,4-dioxane and PCE LRs for tests 7 and 8 were also lower than their respective operating target setpoints. Evaluation of the greensand influent water at 9:17 AM on October 4th reveals the presence of an estimated 50 μg/L NO$_2^-$-N as reported by Weck. Trojan has calculated that a ST value of 144,750 s^{-1} entered into the UV PLC would have resulted in the contaminant LRs exceeding the operating target (i.e., 1.32 LR for 1,4-D & 1.27 for PCE) for runs 7 and 8. If this increased ST value (i.e., 14,750 s^{-1}) were to be explained by an increased nitrite concentration then that would only require an additional 19 μg/L of NO$_2^-$-N. Therefore, based on the measured nitrite concentrations it is feasible that variable nitrite levels in the UV influent water could explain the lower treatment efficiency observed for tests 7 and 8. However, since typical operation of the greensand filters will involve injection of sodium hypochlorite upstream of the filters, this would eliminate any contributions to the ST due to nitrite in the groundwater. Therefore, the design ST value of 130,000 s^{-1} is considered to be conservative during normal plant operation.

- Although 17 of 22 UV effluent PCE concentrations were less than the MDL, the predicted PCE LRs based on the measured 1,4-dioxane LRs exceed the operating setpoint for those 17 tests. Only tests 14 and 15 performed at the reduced pH had measured PCE LRs below the compliance target due to underestimated ST value entered into the PLC, as discussed above. The overall conclusion regarding PCE treatment is that the compliance LR target will be met when the correct ST value is entered into the PLC.

- Similarly, although most UV effluent TCE concentrations were less than the MDL, only tests 9 and 10 were not able to definitively demonstrate that the compliance target was met because the influent TCE concentrations were too low. However, the conservatively predicted TCE LRs based on the measured 1,4-dioxane LRs exceed the operating setpoints for those all tests except tests 14 and 15. For tests 14 and 15, the measured TCE LRs were shown the significantly exceed both the predicted LRs and the operating targets.

- The overall agreement between measured and model-predicted contaminant LRs provides a high level of confidence in the ability of Trojan's UV/H$_2$O$_2$ AOP control algorithm to accurately predict performance and ultimately to control the system to meet the target contaminant treatment objectives when the system is operated in automatic log reduction-based control.

Overall, the TrojanUVFlex200 AOP performance test results described in this report demonstrate that the system is properly designed to meet and exceed the guaranteed contaminant treatment objectives. The data presented has also shown that select calculations used for the automatic control system are accurate based on measured results, and this provides confidence that the system can reliably operate over a broad range of flows, water qualities and treatment targets.

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