KELLER ASSOCIATES

Technical Memo

REGISTERED PROFESSIONAL ENGINEER
73236-PE
OREGON
MARCH 11, 2003
BRYAN R. PHINNEY
EXPIRATION DATE: 12/31/18

To: The City of Ashland Public Works

From: Keller Associates

Date: 02/20/2018

Subject: **Ozone demand/decay results, discussion, and conclusions**

Summary

Ozone demand and decay tests are used to determine the optimum ozone dose for a drinking water source. The ozone demand is highly dependent on the water quality characteristics of the source water; therefore, ozone demand and decay tests are needed to estimate the optimum ozone dose. The goal of the ozone testing was to determine the ozone demand of the filtrate water, and to determine the effectiveness of ozone at degrading the Taste and Odor (T&O) compound geosmin at the design criteria. The design criteria are to effectively remove algal toxins by maintaining at least a 0.3 mg/L ozone residual at a 5-minute Hydraulic Detention Time (HDT).

Ozone demand and decay tests were performed by Eurofins Eaton Analytical (EEA) on two samples from the Pall filtrate stream. Samples were taken during Design Run #1 (DR1) and Design Run #3 (DR3) in an attempt to test water that resembles summer conditions in October (9/27/2017) and late fall/winter conditions in November (11/16/2017). Results demonstrated degradation of geosmin in spiked water samples. Removal of geosmin to below the upper Odor Threshold Concentration (OTC) was achieved with a 5-minute HDT by applying a 2.0 mg/L ozone dosage for the DR1. Removal of 65% of geosmin was achieved in the spiked DR3 sample resulting in a residual concentration of 30 ng/L. The dose of 1.0 mg/L ozone was insufficient to degrade geosmin below the OTC for DR3. Results for ozone demand, Initial Demand (ID), ozone decay rates, and ozone half-lives are presented in Tables 1 to 3.

Background

Algal blooms occurring in TID and Reeder Reservoir water have produced the organic compound geosmin which causes T&O issues for the City of Ashland. It is estimated that the OTC for geosmin is 5-10 ng/L (Erin D. Mackey, 2013). Currently, T&O is treated through the addition of Powdered Activated Carbon (PAC). As an alternative to PAC, implementation of ozone treatment to oxidize geosmin and algal toxins could be used. Ozone treatment could be applied seasonally when T&O compounds are prevalent due to algae. Pressurized Granular Activated Carbon (GAC) vessels operating as biofilters could be placed downstream of the ozone treatment to adsorb oxidized and any remaining un-oxidized residual T&O or algal toxins with its main function being to remove oxidized natural organic matter (NOM).

The design criteria of maintaining at least a 0.3 mg/L ozone residual at a 5-minute HDT was selected for the effective removal of microcystin (Chorus, 2018). Ozone demand and decay tests were performed to estimate the minimum applied ozone dosage that would meet the design criteria for algal toxin degradation. Once these concentrations were estimated, sampled water was spiked to 70 ng/L of geosmin and treated with ozone for 5-minutes before the residual geosmin was measured. The geosmin concentration of 70 ng/L was selected because 73.3 n/L was the highest reported concentration in Reeder Reservoir.

Ozone demand, Initial Demand (ID), ozone decay rates, and ozone half-lives were estimated from the ozone demand and decay tests. Ozone demand was estimated as the applied ozone dosage that intersects the x-axis on a plot of residual ozone concentration vs. applied ozone dosage for a fixed HDT of 5-minutes (Mark M. Benjamin, 2013). The ID was estimated as the difference between the applied ozone dosage and the ozone residual after 1-minute (Rakness, 2005). Ozone decay rates were estimated

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as the slopes of the linearized first order decay of ozone for each ozone dosage (Christopher R. Schulz, 2005).

Materials and Methods

Water was sampled from the Pall filtrate (port 8) port and collected in 10-Liter bottles for overnight shipment to Dean Gregory for ozone testing. Samples were refrigerated until testing was performed. Ozone tests were structured with 2 samples x 2 temperatures x 3 doses, for a total of twelve demand and decay tests. Temperatures 3 °C and 21 °C were tested; where 3°C is the minimum temperature reported in the water quality data summary and review, and 21°C is the maximum 7-day rolling average for 2015-2016 between the months of May through November. Three ozone doses were selected with the goal of bracketing the target residual ozone concentration of 0.3 mg/L at 5-minutes of contact time. Water quality data for TOC, DOC, pH, Alkalinity, and Turbidity were measured with each sample. Sampled water was spiked to a target of 70 ng/L of geosmin to match the highest recorded concentration at the Reeder Reservoir. Ozone demand and decay doses that met the criteria of at least 0.3 mg/L ozone at 5-minutes of contact time were used to test the degradation of geosmin. A control for the spiked water was measured followed by measuring the residual geosmin concentration after 5-minutes of contact time.

Results and Discussion

Testing conditions, water quality information, and estimated values are summarized in Tables 1 to 3 and Figures 1 to 3. The overall ozone demand of DR1 was ~50% greater than DR3 at the 5-minute, 21 °C test. This is likely due to the greater TOC of DR1 than of DR3, 2.54 and 0.78 mg/L, respectively. It has been found that TOC and Natural Organic Matter (NOM) cause a greater ID which contributes to the ozone demand. Ozone decay rates varied with the applied ozone dosage and with temperature; this variability is expected because it has been shown that the ozone decay rate is a function of both temperature and of the ozone dosage (Christopher R. Schulz, 2005). It was found that the decay rates increased with decreasing ozone dosages and increased with increasing temperatures. These findings agree with the results of other research (Christopher R. Schulz, 2005).

The design criteria of at least 0.3 mg/L ozone residual at a 5-minute HDT was accomplished with a 2.0 mg/L and 1.0 mg/L applied ozone dosage for DR1 and DR3, respectively. At these doses, a 90% removal of geosmin was achieved in DR1 and a 65% removal of geosmin in DR3. The DR1 ozone dose achieved a residual geosmin concentration of 6.5 ng/L which is close to the lower limit of the OTC of 5–10 ng/L (Figure 3). The DR3 ozone dose degraded geosmin to a concentration of 30 ng/L. The greater concentration could be due to the lower ozone dose applied, compared to DR1 and is likely also the result of a greater initial geosmin concentration of 85 ng/L. The greater initial geosmin concentration may be resultant from the background concentrations of geosmin detected on 10/31/2017 of 19 ng/L from Port 1 combined with spiking the water with geosmin.

Conclusion

For this analysis, degradation of the T&O compound geosmin was studied. Ozone demand and decay tests demonstrated degradation of geosmin in the spiked water samples. Removal of geosmin to below the upper OTC was achieved with a 5-minute HDT with an applied ozone dose of 2.0 mg/L for the DR1 water sample but was not removed sufficiently with the 1.0 mg/L ozone dose for DR3. It is likely that the 3.0 mg/L ozone dosage recommended in the process selection report will degrade geosmin to below the OTC for the water quality of both design runs, but additional testing should be performed to verify this. The breakdown of algal toxins will also occur with ozone treatment, but this was not the focus of this study. Considerations should be given to the degradation of algal toxins during the design of the ozone contactor.

The City reported having less algal growth this year, and it is recommended that testing be performed year-round to fully capture the ozone demand. Values for ozone demand, Initial Demand (ID), ozone decay rates, and ozone half-lives were estimated from the ozone demand and decay tests and are summarized in Tables 1 to 3 and are shown in Figures 1 to 3.

Table 1. Design Run #1 – TID Water (Pall filtrate)

Desing Run #1 - TID Water (Pall filtrate)								
Testing Conditions								
Variable	Unit	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	
Applied ozone dosage	mg/L	1.02	2.01	3.01	2.02	1.01	1.52	
Temperature	°C	21	21	21	3	1	1	
Water Quality Data of Sampled Water								
Constituent	Unit	Value						
TOC	mg/L	2.54						
DOC	mg/L	2.51						
pH	std. units	6.68						
Alkalinity	mg/L as $CaCO_3$	14						
Turbidity	NTU	0.13						
Color	std. Pt/Co units	8						
Estimated Values From Experimental Information								
Variable	Unit	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	
Ozone decay rate	$min.^{-1}$	-0.940	-0.232	-0.122	-0.0461	-0.128	-0.0647	
Ozone half life	min.	0.737	2.98	5.69	15.0	5.42	10.7	
Initial Demand	mg/L	0.76	1.04	0.72	0.61	0.51	0.56	
		5-minute HDT (21 °C)			5-minute HDT (3 °C)			
Ozone Demand	mg/L	1.09			0.68			

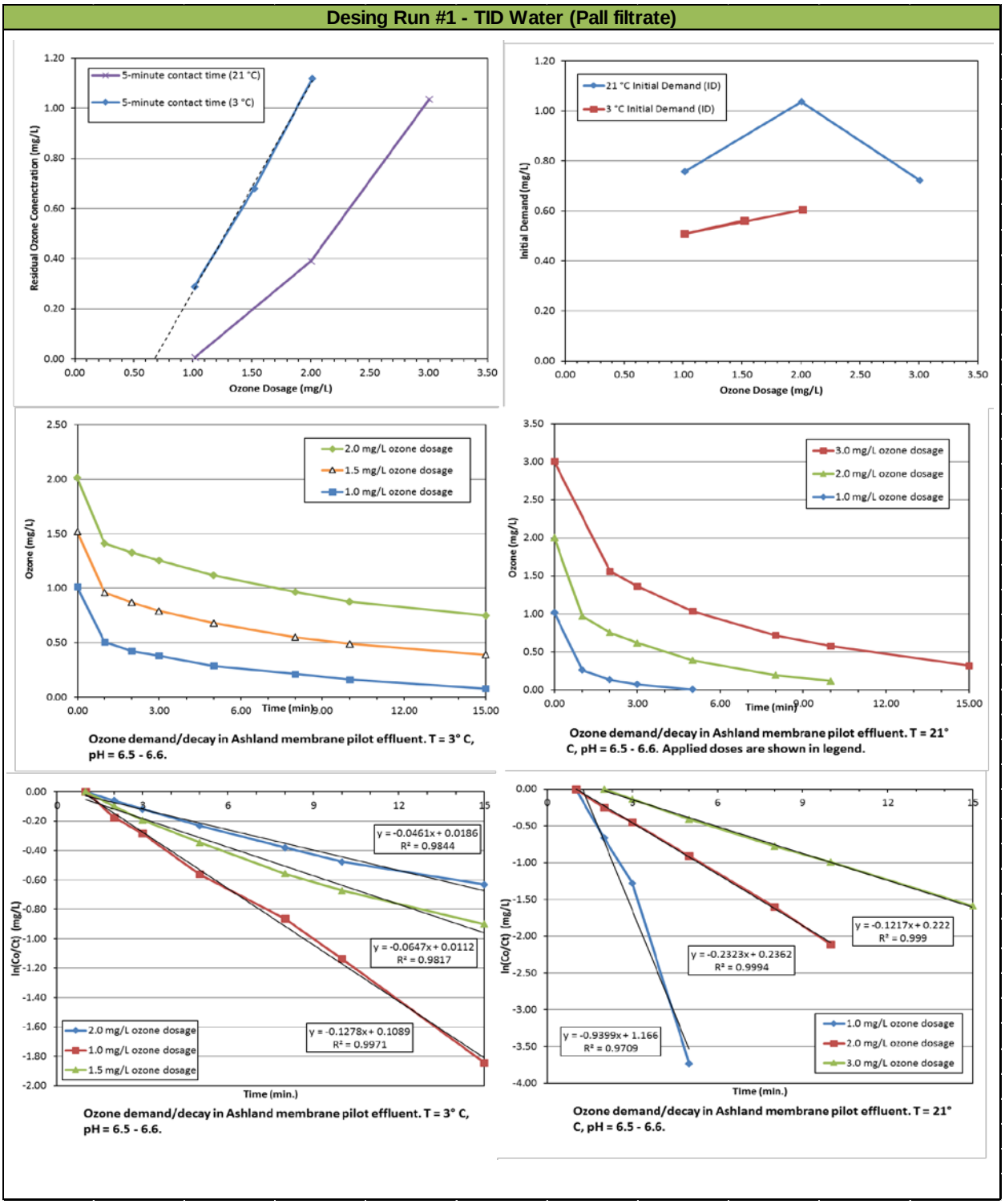

Figure 1. Design Run #1 – TID Water (Pall filtrate)

Table 2. Design Run #3 – Reeder Reservoir Water (Pall filtrate)

Desing Run #3 - Reeder Reservoir Water (Pall filtrate)								
Testing Conditions								
Variable	Unit	Run 1	Run 2	Run 3	Run 4	Run 6	Run 7	Run 8
Applied ozone dosage	mg/L	3.01	1.02	0.50	1.01	0.51	1.54	1.52
Temperature	°C	21	21	3	3	21	21	3
Water Quality Data of Sampled Water								
Constituent	Unit	Value						
TOC	mg/L	0.78						
DOC	mg/L	0.78						
pH	std. units	6.57						
Alkalinity	mg/L as $CaCO_3$	16						
Turbidity	NTU	0.11						
Color	std. Pt/Co units	-						
Estimated Values From Experimental Information								
Variable	Unit	Run 1	Run 2	Run 3	Run 4	Run 6	Run 7	Run 8
Ozone decay rate	$min.^{-1}$	-0.04559	-0.148	-0.0755	-0.0283	-0.507	-0.105	-0.0220
Ozone half life	min.	15.2	4.67	9.18	24.5	1.37	6.58	31.5
Initial Demand	mg/L	0.70	0.43	0.20	0.22	0.37	0.50	0.26
		5-minute HDT (21 °C)			5-minute HDT (3 °C)			
Ozone Demand	mg/L	0.71			0.26			

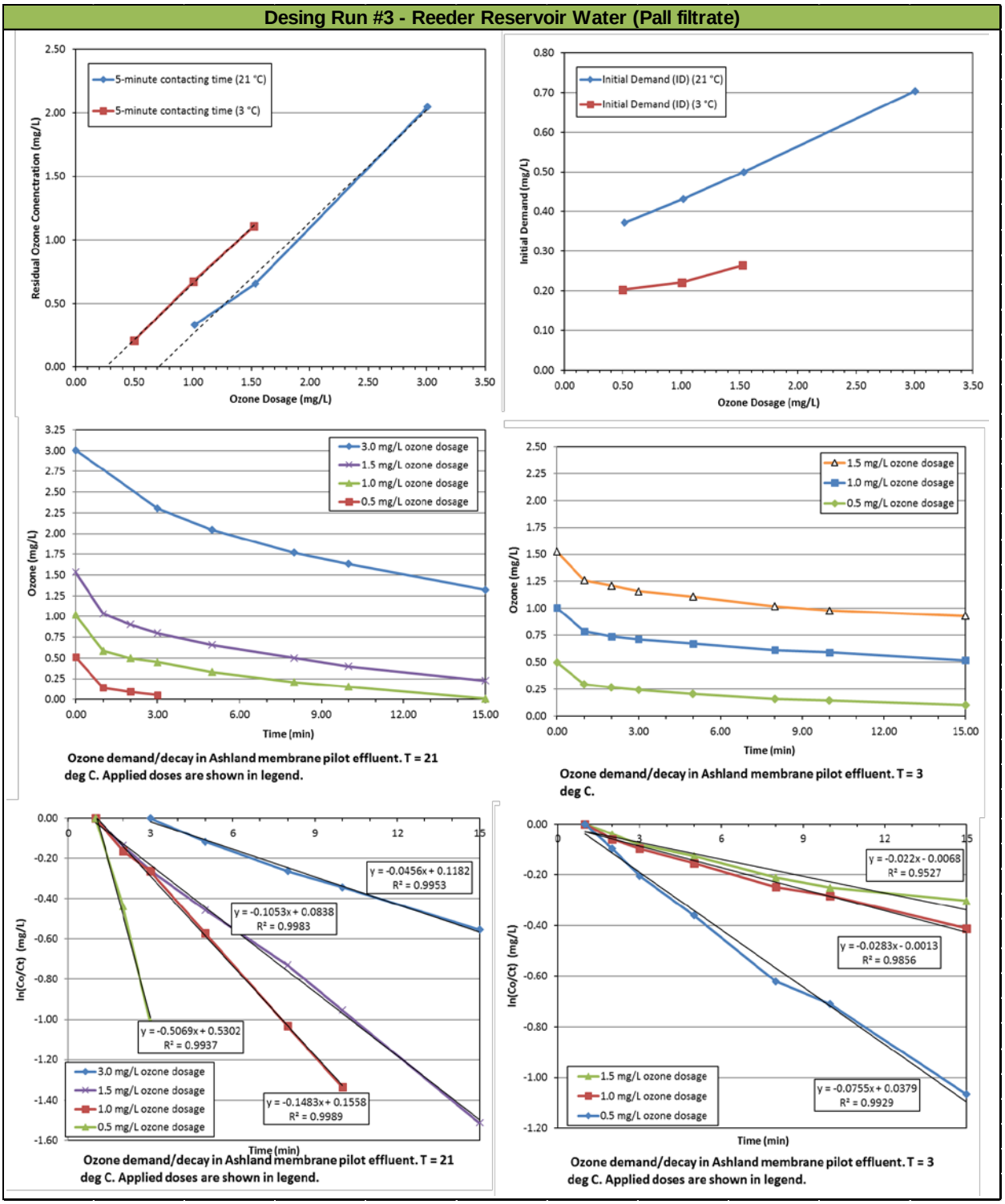

Figure 2. Design Run #3 – Reeder Reservoir Water (Pall filtrate)

Table 3. Geosmin Results

Geosmin Results				
Desing Run #1 - TID Water (Pall filtrate)				
Variable	Unit	Value	Value	Value
Applied ozone dosage	mg/L	0	1	2
Desing Run #1 (21 °C)	ng/L	65	29	6.4
Desing Run #3 - Reeder Reservoir Water (Pall filtrate)				
Variable	Unit	Value	Value	Value
Applied ozone dosage	mg/L	0	0.5	1
Desing Run #3 (21 °C)	ng/L	85	55	30

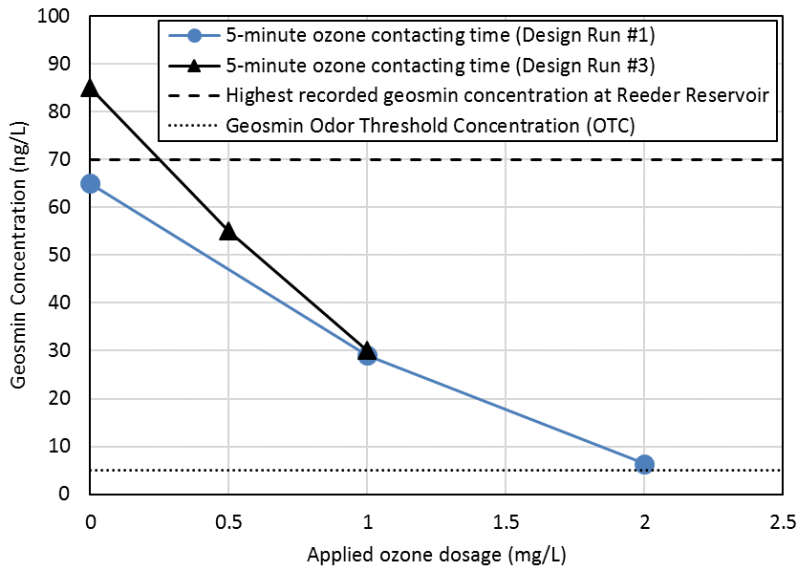

Figure 3. Geosmin Results

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