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Relation of Chlorine Demand to the Water Quality of Beaver Lake

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In drinking water treatment plants, source water quality can influence the chlorine demand of the raw water, affecting the amount of chlorine required for pre-treatment and to sustain free chlorine residuals throughout the distribution process. The current study evaluated the effect that a suite of water quality parameters had on four different chlorine concentration response variables, which identified the chlorine doses and demand required to either satisfy the chlorine demand of the water or for residuals to start accumulating. Results from simple linear regression analysis showed that iron (R^2 = 0.18 to 0.72), turbidity (R^2 = 0.13 to 0.67) and total organic carbon (TOC; R^2 = 0.24 to 0.31) were consistently the most important drivers of chlorine dose or demand, where increases in any of these parameters drove increases in chlorine dose and demand concentrations. When additional explanatory variables were included, but with fewer observations, UV_{254} and NH_3-N became important variables in explaining variation in chlorine dose and demand. Non-parametric change point analysis (NCPA) results showed that chlorine dose and demand concentrations of the raw water increased when iron was greater than 0.15 to 0.17 mg/L, TOC was greater than 1.60 to 1.96 mg/L, and turbidity was greater than 3 to 10 NTU. Interestingly, NCPA showed that chlorine demand was greater prior to May 9, 2014 and significantly decreased after this date, during the growing season for algae. UV_{254} and NH_3-N resulted in significant change points when additional explanatory variables were included. These results can be used to help guide water treatment managers with regard to the chlorine dosage required to meet the chlorine demand of the raw source water with changes in water quality characteristics.

INTRODUCTION

The Beaver Lake watershed covers 3,100 km^2 in northwest Arkansas and is the most upstream of the large reservoirs of the White River. The headwaters of the White River originate in the Boston Mountains and flows generally north through Franklin, Washington, Madison, Benton and Carroll counties. Land use and land cover in the Beaver Lake watershed is approximately 71% forest, 22% agriculture, 4% water and 3% urban (Davis and Shepard 2010). Beaver Water District (BWD) is one of four public water suppliers that withdraw water from Beaver Lake, which provides clean drinking water to over 400,000 Arkansans.

Chlorine is widely used as a disinfectant in drinking water treatment plants in order to ensure that the treated water is free of disease-causing pathogens. The amount of chlorine applied is related to the chlorine demand of the water, which is the amount of chlorine needed to satisfy all chemical reactions and leave a defined amount of free chlorine that is available for continuous disinfection. Source water quality has been shown to influence demand because chlorine readily reacts with metals and organic and inorganic matter (Barbeau et al. 2005, Clark et al. 1998, Yee et al. 2006). Reactions between chlorine and organic matter can lead to the formation of disinfection by-products (DBPs; Barbeau et al. 2005, Pifer and Fairey 2014), which can be harmful to human health and are regulated by the EPA (EPA 1998). Over supplying chlorine can lead to DBP formation, but undersupplying can result in too little residual to provide adequate disinfection. Understanding the relationships between source water quality and chlorine demand can help guide decisions regarding the disinfection process.

Beaver Water District is interested in understanding the relationships between the physical, chemical and biological characteristics of the raw source water and the amount of chlorine required for treatment. The objectives were to evaluate the chlorine demand of the raw water (response variable) and pair this data with measured water quality parameters (in-dependent, predictor variables) in order to statistically identify water quality drivers of chlorine demand.

METHODS

Daily chlorine demand analysis

Chlorine demand assays were conducted approximately three times per week from March through July 2013. Four L of raw water were collected from Beaver Lake each morning at approximately 6:00 am at the Beaver Water District (BWD) intake site by BWD personnel and returned to the lab where it was refrigerated at approximately 4°C. Chlorine demand assays were conducted within 3 hours of water collection. The collected raw water was used to fill 14-1 L amber bottles with 250 mL of water. A chlorine stock solution was made using household chlorine bleach and was added to the bottles at increasing dosage concentrations. Bottles were capped, inverted three times and allowed to incubate for 1.5 h.

After incubation, free chlorine residuals were analyzed using a Hach Pocket Colorimeter. Chlorine demand was calculated using the following equation:

$$\textit{chlorine demand} = \textit{chlorine dosage} - \textit{chlorine residual} \qquad \textit{(Eq. 1)}$$

This calculation provided chlorine demand values that correspond to each particular chlorine dosage concentration. Thus, further evaluation was conducted to generate a chlorine concentration value (or values) that could be related to water quality parameters. This evaluation is discussed in the "Statistical analysis" section of this report.

Water quality sampling and analysis

A variety of physicochemical properties were tested either daily, weekly or monthly by BWD personnel and results were shared with AWRC. Turbidity, temperature, pH, TOC (subsampled from the carboy collected at the intake site, hereafter TOC_{lab}) conductivity, manganese, iron, *Escherichia coli* (*E. coli*), and total coliforms were analyzed during each daily demand assay, while TOC, dissolved organic carbon (DOC), UV_{254}, nitrate-N (NO_3-N), ammonia-N (NH_3-N), and alkalinity were measured less frequently. This variation in measured parameters resulted in the separation of data into two datasets – the daily dataset includes all parameters measured during the daily chlorine demand assays and the weekly dataset includes more parameters, but fewer observation dates since these additional parameters were measured less frequently.

Statistical analysis

Dependent variable ("Chlorine concentration response variable (Y)") determination

Four different chlorine concentration response variables (CCRVs) were chosen from each daily chlorine demand assay by evaluating three relationships: 1) chlorine dosage versus the calculated chlorine demand, 2) chlorine dosage versus the measured chlorine residuals, and 3) calculated chlorine demand versus measured chlorine residuals. The response variables were statistically determined using either non-parametric change point analysis (NCPA; R software) or evaluating split linear regressions (Microsoft Excel). NCPA was used to estimate breakpoints in the data, and in constructing the models, a minimum of 5 observations were required on each side of the change point providing the best fit. Split linear regression was also used to evaluate a breakpoint in the data where the sum of squares from the regression on both sides of the point is smallest. (Figure 1).

Evaluating relationships between water quality and chlorine concentration response variables

As mentioned previously, due to variability in the occurrence of raw water quality sampling at the intake on Beaver Lake for different parameters, data was separated into daily and weekly datasets. The analyses described below were conducted on both datasets, except for the multiple linear regression analysis, which was only conducted on the daily dataset because there were too many missing observations in the weekly dataset.

Pearson correlation analyses were performed using R software to evaluate the univariate linear relationships between each response variable and the physicochemical properties of the raw water collected from the intake site at BWD. The 4 strongest Pearson correlation coefficients associated with each Y value in the daily dataset were further analyzed by simple linear regression (SLR) in SigmaPlot 13.0 (Systat Soft-are, Inc.). The single strongest Pearson correlation associated with each CCRV from the weekly dataset was further analyzed by SLR. To evaluate the potential interaction between multiple predictor variables, stepwise multiple linear regression (MLR) was performed using Statistix 10 software. Results from each of the linear relationship analyses were considered significant at alpha = 0.05.

Non-linear relationships were evaluated using regression tree (RT) analysis and NCPA. The MVPART library in R software was used for RT analyses. Each CCRV was evaluated separately as the dependent variable with the water quality parameters as multiple predictor variables. Regression tree analysis was used in order to determine the possible hierarchical nature of various water quality properties on the CCRVs. A minimum of 10 observations for a particular split were required to generate the model and at least 6 observations were required to occur on either side of the change point. Results from the RT analysis provided information about the 5 strongest predictor variables and guided the subsequent NCPA analyses. NCPA was performed on each of the top 5 primary splits provided by the RT analyses.

RESULTS

Chlorine concentration response variables and raw water parameters

Figure 1 provides graphical representations of how each of the 4 chlorine concentration response variables (CCRVs) were statistically determined and Table 1 provides information about these dependent variable determinations and what the values represent regarding chlorine demand. The resulting dependent variables (CCRVs Y1, Y3, Y5, and Y7) were then used for all subsequent analyses relating chlorine demand to raw water quality.

CCRVs and raw water physicochemical characteristics are summarized in Table 2. The chlorine dose or demand for Y1, Y3, Y5, and Y7 ranged from 0.96 to 3.59, 0.81 to 3.30, 1.80 to 6.11 and 0.47 to 2.79 mg/L, respectively (Table 2). While all of these CCRVs represent essentially the same concept – the chlorine concentration where raw water demand is satisfied and chorine residuals start to increase in the pre-treated water – the different statistical determ-inations led to a large amount of variability among values, with chlorine dose (Y5) resulting

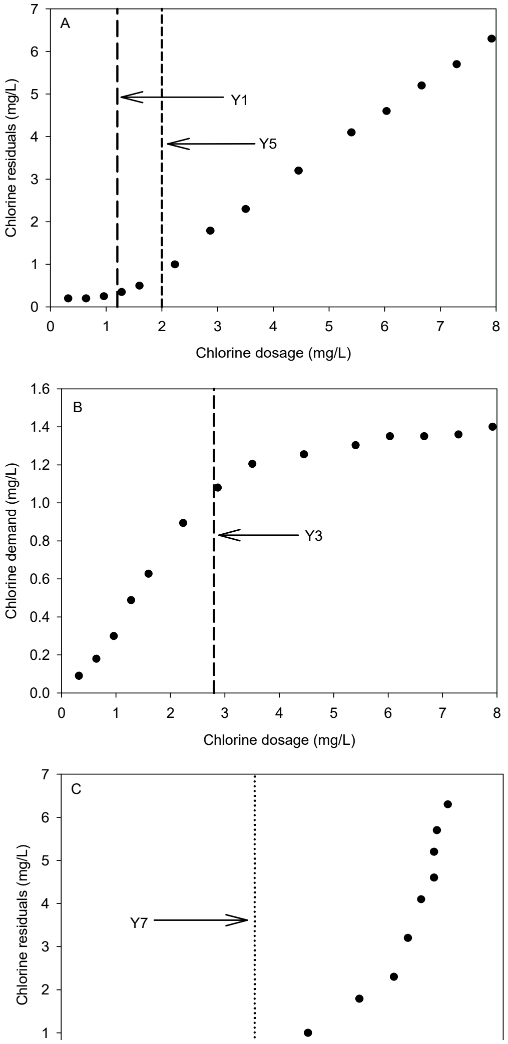

Figure 1. Theoretical representations of each of the chlorine concentration response variables estimated from each daily demand assay. (A) Chlorine dosage versus chlorine residuals where the long dashed vertical line represents the breakpoint concentration (Y1) statistically determined by split linear regression analysis and the short dashed vertical line represents the breakpoint concentration (Y5) statistically determined by non-parametric change point analysis (NCPA); (B) Chlorine dosage versus chlorine demand where the dashed vertical line represents the breakpoint concentration (Y3) statistically determined by NCPA; and (C) Chlorine demand versus chlorine residuals where the dotted vertical line represents the breakpoint concentration statistically determined by NCPA.

Table 1. For each of the 4 dependent variables, the description of the relationship produced from each daily demand assay, the statistical procedure used to determine each Y value and what these values represent. SLR = split linear regression analysis; NCPA = non-parametric change point analysis.

CCRV	Relationship	Statistical procedure	Representation
Y1	Dosage vs residuals	SLR	The chlorine dosage where chlorine residuals start accumulating
Y3	Dosage vs demand	NCPA	The chlorine dosage needed to satisfy the chlorine demand of the water
Y5	Dosage vs residuals	NCPA	The chlorine dosage where chlorine residuals start accumulating
Y7	Demand vs residuals	NCPA	The chlorine demand of the raw water after which chlorine residuals start accumulating

in relatively high concentrations (median = 3.97 mg/L) and chlorine demand (Y7 resulting in relatively low concentrations (median = 1.11 mg/L).

Some of the water quality parameters followed seasonal patterns, while others followed no apparent trend through time over this short study period. TOC (range TOC = 1.59 to 3.58 mg/L, TOC_{lab} = 1.37 to 3.87 mg/L) and DOC (range = 1.33 to 3.27 mg/L) increased in March and April, then decreased in May and June, then increased again in July, likely corre-sponding to shifts in primary production. Turbidity (range = 1.11 to 48.10 NTU), UV_{254} (range = 0.023 to 0.128 /cm), NO_3-N (range = 0.180 to 1.042 mg/L), and iron (range = 0 to 0.41mg/L) decreased through time while temperature (range = 5.6 to 27.8°C) and pH_{lab} (range = 7.06 to 9.22 SU) increased throughout the study period. Conductivity (range = 116 to 183 µS/cm), manganese (range = 0.009 to 0.088 mg/L), NH_3-N (range = 0.01 to 0.21 mg/L), alkalinity (range = 41 to 59 mg/L), *E. coli* (range = 0 to 373 CFU/100 mL), and total coliforms (range = 6 to 20,924 CFU/100 mL) were variable and showed little to no pattern with time.

Chlorine concentration response variable – Chlorine dose (Y1)

The chlorine dose (Y1) represents the dosage chlorine concentration required for residuals to begin accumulating, based on split linear regression analysis (Table 1, Figure 1 A). Linear relationships were found to exist between various raw water physicochemical parameters and chlorine dose (Y1) in the daily dataset. The Pearson correlation analysis showed significant positive relationships between chlorine dose (Y1) and TOC_{lab} (ρ = 0.42), iron (ρ = 0.32) and turbidity (ρ = 0.32) and a negative relationship with conductivity (ρ = -0.28) (Table 3). Simple linear regression analysis was performed with these 4 parameters and results showed that TOC_{lab}, iron, turbidity and conductivity explained 24, 18, 13 and 8% of the variation in the chlorine dose (Y1), respectively (Figure 2). Results from the multiple linear regression (MLR) analysis showed a significant relationship where TOC_{lab} explained 20% of the initial variation in the chlorine dose (Y1), and conductivity enhanced the model, where 29% of the variation was explained by TOC_{lab} and conductivity combined (Table 4).

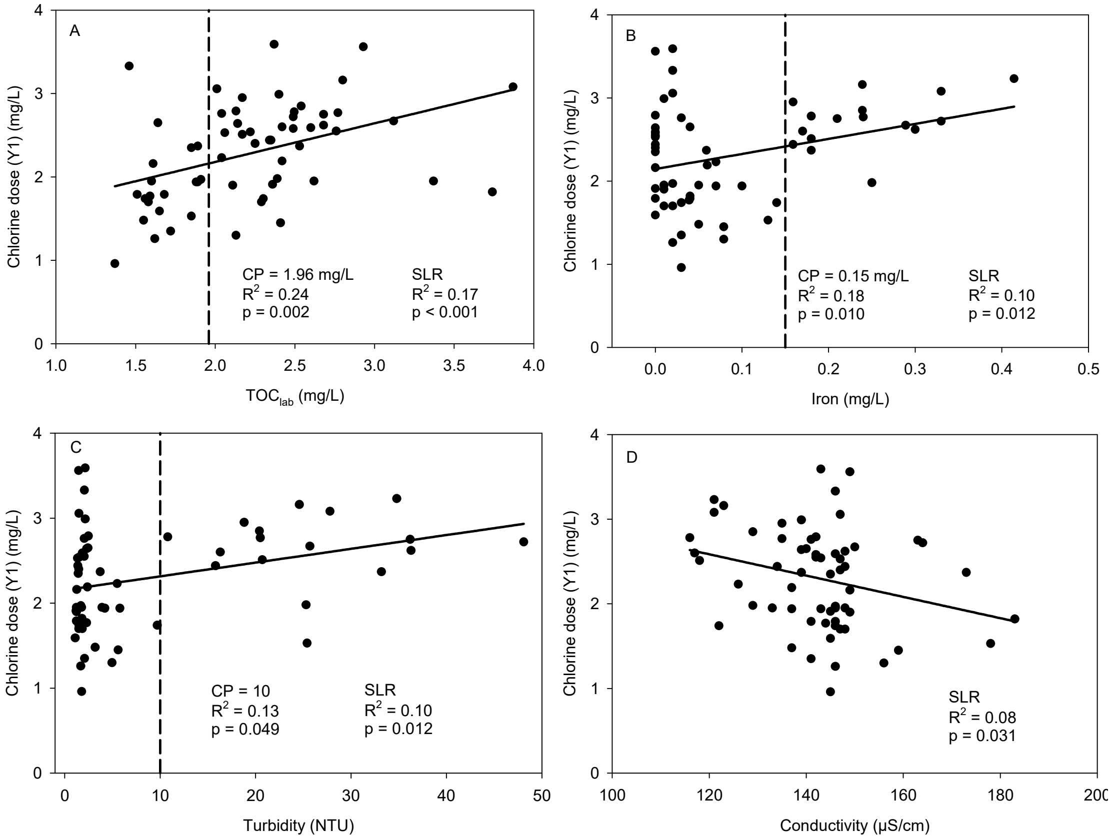

Figure 2. From the daily dataset, scatter plots of the relationships between chlorine dose (Y1) (response variable) and the top four explanatory variables from the Pearson correlation analysis and the regression tree with subsequent non-parametric change point analyses.

Manganese	mg/L	61	0.028	0.017	0.022	0.009	0.088
Iron	mg/L	61	0.09	0.11	0.04	0.00	0.41
Escherichia coli	CFU/100mL	55	25	77	1	0	373
Total coliforms	CFU/100mL	61	1425	3171	435	6	20924

When additional water quality parameters were included but with fewer observations (e.g. weekly dataset), TOC was the only significant relationship resulting from Pearson correlation analysis (ρ = 0.45; Table 5). Simple linear regression results showed that TOC explained 20% of the variation in chlorine dose (Y1) (Figure 3). Within this dataset, the number of observations among the water quality parameters ranged from 15 to 45, which was less than that in the daily dataset. Results from the regression tree and non-parametric change point analyses (NCPA) of the daily dataset showed that non-linear, threshold based relationships existed between chlorine dose (Y1) and various water quality parameters (Table 6, Figure 2). Table 6 shows the top 5 primary splits for chlorine dose (Y1), where the strongest threshold relationship was with TOC_{lab} ($R^2 = 0.24$, $p = 0.002$). The change point with TOC_{lab} was 1.96 mg/L, where when concen-trations were below 1.96 mg/L, mean chlorine dose (Y1) concentrations were 1.88 and when TOC_{lab} was greater than 1.96 mg/L, mean chlorine dose (Y1) concentration was 2.49 mg/L. Significant change points also existed with iron (CP = 0.15 mg/L), total coliforms (CP = 564 CFU/100 mL) and turbidity (CP = 10 NTU; Table 6; Figure 2). In the weekly dataset, the strongest change point occurred with TOC_{lab}, where the threshold TOC_{lab} concentration was 1.96 mg/L and mean chlorine dose (Y1) was 1.92 and 2.44 mg/L when TOC_{lab} was less than and greater than 1.96 mg/L, respectively (Figure 3B). A

significant change point also occurred with iron at a concentration of 0.15 mg/L (Table 7).

Chlorine concentration response variable – Chlorine dose (Y3)

The chlorine dose (Y3) represents the dosage chlorine concentration needed to satisfy the chlorine demand of the raw water, based on NCPA (Table 1, Figure 1B). Few linear or non-linear relationships were found between chlorine dose (Y3) and raw water quality. In the daily dataset, Pearson correlation coefficients were only significant for total coliforms, where there was a negative relationship with chlorine dose (Y3) ($\rho = -0.32$; Table 3). Simple linear regression analysis showed that 10% of the

Table 3. Pearson correlation coefficients comparing all the data collected during all chlorine demand assays (i.e. “daily dataset”), with only a few missing observations. These parameters included each of the 4 chlorine concentration response variables (CCRV) Y1, Y3, Y5, and Y7, and the predictor variables date, total organic carbon (TOC), turbidity, temperature, pH, conductivity, manganese (Mn), iron (Fe), *Escherichia coli* (EC), and total coliforms (TC). Asterisks (*) represent analyses conducted on samples collected from the carboy of water collected from the Beaver Water District intake site on Beaver Lake for the chlorine demand assays.

Daily dataset	Y1 n = 61	Y3 n = 61	Y5 n = 61	Y7 n = 61	Date n = 61	TOC$_{lab}$* n = 60	Turbidity n = 61	Temp. n = 60	pH$_{lab}$* n = 61	Cond. n = 61	Mn n = 61	Fe n = 61	*EC* n = 55	TC n = 61
Y1	1.00													
Y3	***0.33***	1.00												
Y5	***0.62***	0.25	1.00											
Y7	**0.29**	**0.26**	***0.59***	1.00										
Date	0.01	0.03	-0.12	***-0.70***	1.00									
TOC$_{lab}$*	***0.42***	0.16	***0.45***	***0.40***	-0.05	1.00								
Turbidity	**0.32**	0.18	***0.52***	***0.81***	***-0.74***	***0.40***	1.00							
Temp	-0.01	0.01	-0.14	***-0.72***	***0.97***	-0.13	***-0.75***	1.00						
pH$_{lab}$*	0.11	0.10	-0.03	***-0.62***	***0.89***	0.04	***-0.56***	***0.86***	1.00					
Cond.	**-0.28**	-0.04	***-0.34***	**-0.26**	0.08	0.05	-0.02	0.07	0.19	1.00				
Mn	0.11	0.08	0.19	***0.46***	***-0.47***	***0.46***	***0.65***	***-0.54***	**-0.34**	0.22	1.00			
Fe	**0.32**	0.12	***0.56***	***0.88***	***-0.77***	***0.45***	***0.93***	***-0.79***	***-0.65***	**-0.26**	***0.58***	1.00		
EC	0.02	0.15	0.08	**0.30**	***-0.43***	0.05	***0.66***	***-0.42***	**-0.31**	***0.50***	***0.50***	***0.39***	1.00	
TC	-0.20	**-0.32**	-0.22	-0.22	-0.02	***-0.37***	-0.12	0.00	-0.09	0.07	-0.10	-0.13	0.08	1.00

Note: Significant relationships are indicated by bold ($p < 0.05$), bold and italicized ($p < 0.01$), or bold, italicized and shaded ($p < 0.001$) coefficients. Refer to figure 1 and table 1 for explanation of CCRVs.

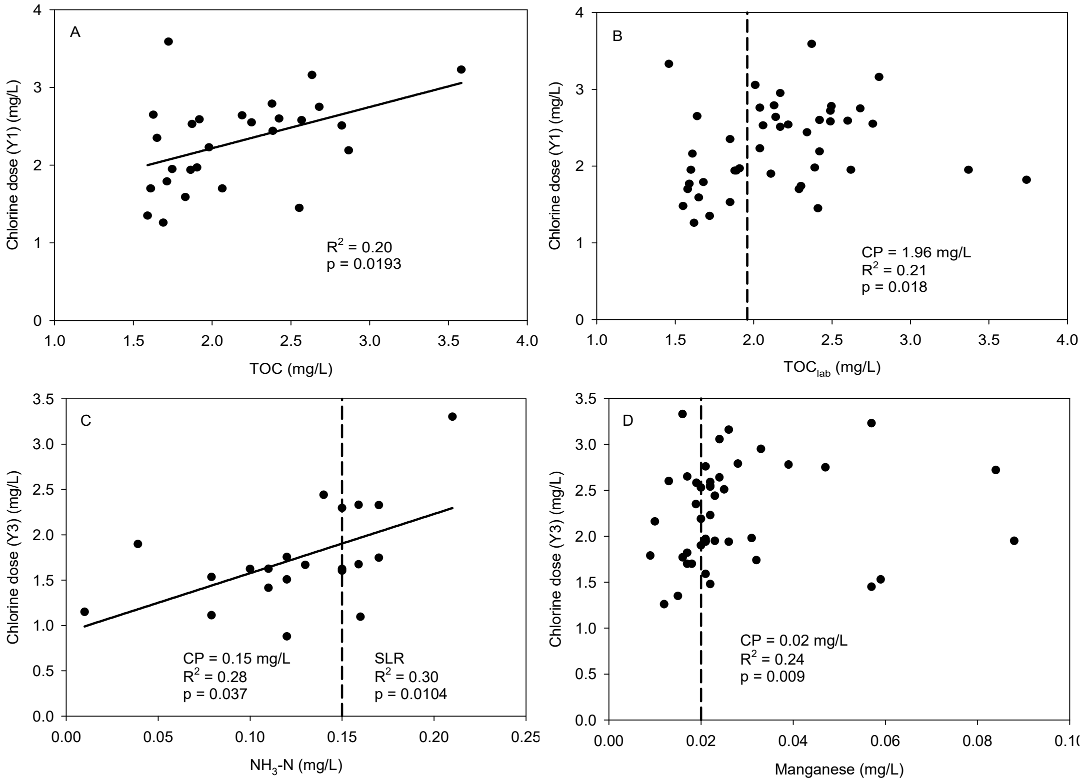

Figure 3. From the weekly dataset, scatter plots of the relationships between (A and B) The chlorine dose (Y1) (response variable) and (C and D) The chlorine dose (Y3) (response variable) with the top explanatory variable from the Pearson correlation analysis and the regression tree with subsequent non-parametric change point analyses.

variation in chlorine dose (Y3) was explained by total coliforms (Figure 4). There were no significant linear trends when data were analyzed by multiple linear regression. However, this could be an artifact of the statistical software regarding missing observa-tions.

Interestingly, Pearson correlation analysis of the weekly dataset showed a significant positive relationship with NH_3-N ($\rho = 0.55$; Table 5). There were only 21 observations available for NH_3-N and 30% of the variation in chlorine dose (Y3) was explained (Figure 3C). These data suggest that NH_3-N could be a useful predictor for chlorine demand, but more data is needed to understand this relationship.

There were no significant threshold relationships with chlorine dose (Y3) when the daily dataset was analyzed (Table 6). In the weekly dataset, NH_3-N was the strongest parameter associated with chlorine dose (Y3) in a non-linear, threshold type relationship. Mean chlorine dose (Y3) was 1.61 and 2.08 mg/L when NH_3-N concentrations were less than or greater than 0.15 mg/L, respectively (Table 7; Figure 3C). Regression tree analysis also showed a potential for a hierarchical split with NH_3-N, but this relationship was not significant. Again, these results suggest the potential importance of NH_3-N in driving chlorine not significant. Again, these results suggest the potential importance of NH_3-N in driving chlorine demand and further investigation is needed.

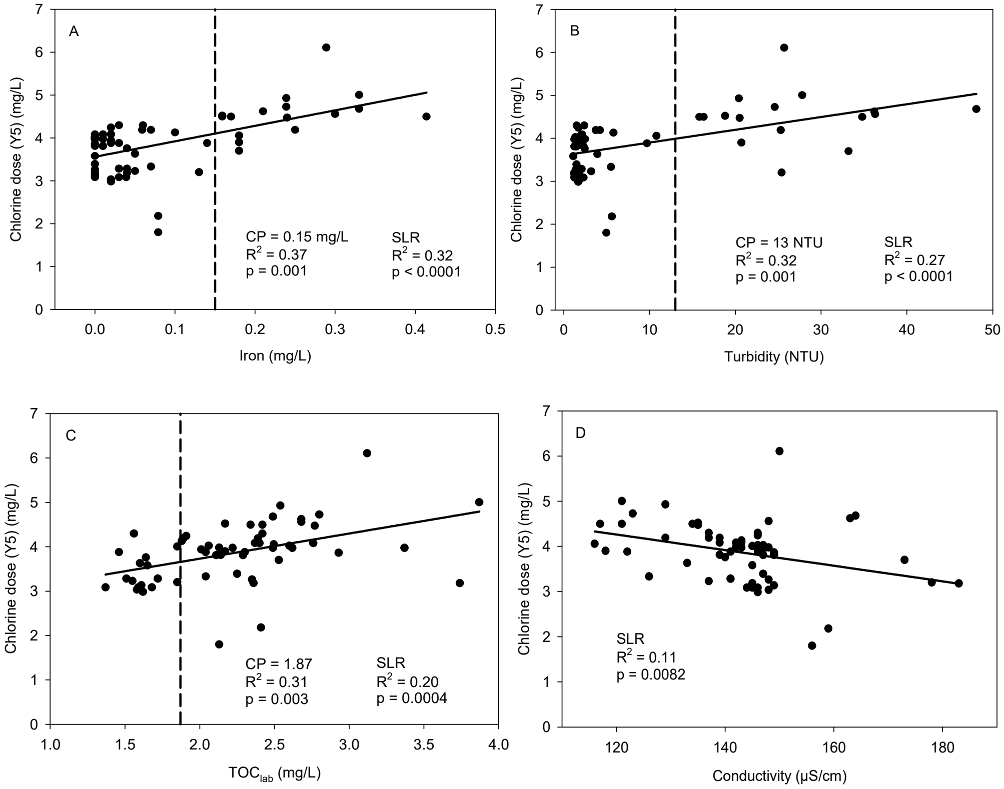

Figure 5. From the daily dataset, scatter plots of the relationships between chlorine dose (Y5) (response variable) and the top four explanatory variables from the Pearson correlation analysis and the regression tree with subsequent nonparametric change point analyses.

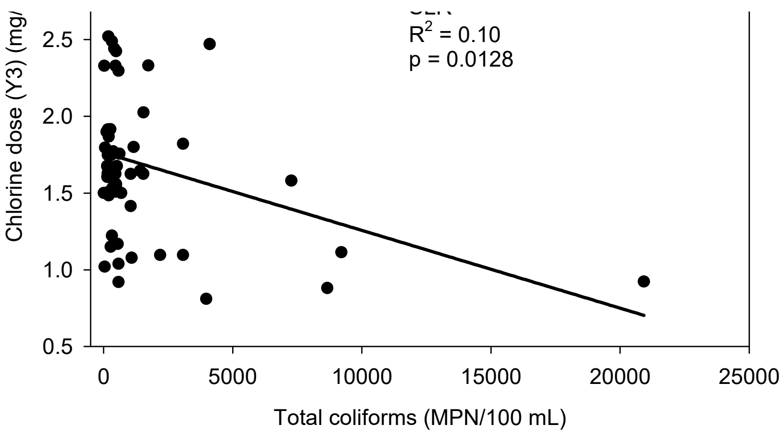

Figure 4. From the daily dataset, scatter plot of the relationship between chlorine dose (Y3) (response variable) and the only statistically significant explanatory variable from the Pearson correlation analysis.

Chlorine concentration response variable –

Chlorine dose (Y5)

Chlorine dose (Y5) represents the dosage chlorine concentration needed for residuals to begin accumulating, based on NCPA (Table 1; Figure 1A). In the daily dataset, Pearson correlation analysis showed significant positive relationships with iron (ρ = 0.56), turbidity (ρ = 0.52) and TOC_{lab} (ρ = 0.45) and a negative relationship with conductivity (ρ = -0.34; Table 3). Subsequent simple linear regression analyses showed that 37, 32, 31 and 11% of the variation in chlorine dose (Y5) was explained by iron, turbidity, TOC_{lab} and conductivity, re-spectively (Figure 5). Multiple linear regression analysis showed that iron explained 30% of the variation in chlorine dose (Y5) and that the model was enhanced when temperature was considered, explaining 62% of the overall variation (Table 4).

Analysis of the weekly dataset resulted in the inclusion of some of the water quality parameters that were sampled less frequently, in addition to those sampled daily. Pearson correlation analysis showed significant positive relationships with iron (ρ = 0.48) and turbidity (ρ = 0.48), but also with DOC (ρ = 0.48) and UV_{254} (ρ = 0.43; Table 5). Only 21 observations were available in the analyses with DOC and UV_{254}, but these results suggest the importance these water quality parameters may have on chlorine demand, and a more robust dataset

Table 5. Pearson correlation coefficients comparing the data tested approximately weekly during the chlorine demand assay study period (i.e. "weekly dataset"). These parameters included each of the 4 chlorine concentration response variables (CCRV) Y1, Y3, Y5, and Y7, and the predictor variables date, total organic carbon (TOC), dissolved organic carbon (DOC), turbidity, UV$_{254}$, temperature, pH, conductivity, NO3-N, NH$_3$-N, manganese, iron, alkalinity (Alk.), *Escherichia coli* (EC), and total coliforms (TC). Asterisks (*) represent analyses conducted on samples collected from the carboy of water collected from the Beaver Water District intake site on Beaver Lake for the chlorine demand assays. Table is continued on the next page.

Weekly dataset	Y1 n = 45	Y3 n = 45	Y5 n = 45	Y7 n = 45	Date n = 45	TOC n = 27	TOC$_{lab}$* n = 44	DOC n = 21	Turb. n= 45	UV$_{254}$ n = 21
Y1	1.00									
Y3	0.29	1.00								
Y5	***0.66***	***0.43***	1.00							
Y7	0.26	***0.45***	***0.49***	1.00						
Date	-0.04	-0.08	-0.01	***-0.65***	1.00					
TOC	**0.45**	0.16	**0.43**	***0.68***	-0.37	1.00				
TOC$_{lab}$*	0.21	0.06	**0.35**	0.23	0.17	***0.74***	1.00			
DOC	0.43	0.21	**0.48**	***0.86***	**-0.50**	***0.91***	***0.71***	1.00		
Turb.	0.29	0.25	***0.48***	***0.76***	***-0.71***	***0.73***	0.24	***0.91***	1.00	
UV$_{254}$	0.38	0.22	**0.43**	***0.93***	***-0.82***	***0.76***	0.39	***0.83***	***0.92***	1.00
Temp.	-0.02	-0.08	-0.08	***-0.68***	***0.94***	**-0.43**	0.03	**-0.53**	***-0.75***	***-0.80***
pH$_{lab}$*	0.10	0.04	0.06	***-0.58***	***0.83***	-0.13	0.20	-0.39	***-0.51***	***-0.78***
Cond.	-0.28	-0.11	**-0.36**	**-0.34**	0.20	-0.38	0.16	-0.34	-0.05	***-0.59***
NO$_3$-N	0.15	0.11	-0.01	**0.49**	***-0.90***	-0.28	-0.40	0.79	***0.67***	0.87
NH$_3$-N	-0.11	**0.55**	0.29	0.23	-0.23	-0.55	**-0.46**	-0.14	0.25	0.19
Mn	0.09	0.22	0.19	**0.37**	-0.33	***0.66***	***0.42***	***0.64***	***0.60***	**0.51**
Fe	0.29	0.22	***0.48***	***0.84***	***-0.75***	***0.76***	0.26	***0.89***	***0.93***	***0.97***
Alk.	0.01	0.13	-0.17	***-0.66***	**0.64**	-0.55	0.11	-0.76	-0.30	***-0.95***
EC	0.04	0.17	0.15	0.29	***-0.46***	0.29	0.04	**0.49**	***0.72***	0.40
TC	-0.11	**-0.35**	-0.24	-0.27	-0.11	-0.37	**-0.38**	-0.26	-0.07	-0.20

Note: Significant relationships are indicated by bold ($p < 0.05$), bold and italicized ($p < 0.01$), or bold, italicized and shaded ($p < 0.001$) coefficients. Refer to figure 1 and table 1 for explanation of CCRVs.

Table 5, continued.

Weekly dataset	Temp. n = 44	pH_{lab}* n = 45	Cond. n = 45	NO_3-N n = 20	NH_3-N n = 21	Mn n = 45	Fe n = 45	Alk. n = 15	*EC* n = 40	TC n = 45
Y1										
Y3										
Y5										
Y7										
Date										
TOC										
TOC_{lab}*										
DOC										
Turb.										
UV_{254}										
Temp.	1.00									
pH_{lab}*	***0.83***	1.00								
Cond.	0.14	0.25	1.00							
NO_3-N	***-0.93***	***-0.86***	-0.13	1.00						
NH_3-N	-0.24	0.01	-0.24	0.17	1.00					
Mn	***-0.45***	-0.21	0.22	-0.03	-0.03	1.00				
Fe	***-0.78***	***-0.62***	**-0.30**	***0.68***	0.09	***0.53***	1.00			
Alk.	0.46	***0.72***	***0.78***	-0.92	-0.38	0.15	-0.50	1.00		
EC	***-0.46***	-0.28	***0.46***	0.40	0.20	***0.61***	***0.47***	0.16	1.00	
TC	-0.01	-0.12	0.15	0.14	-0.15	-0.07	-0.11	0.12	0.28	1.00

Note: Significant relationships are indicated by bold ($p < 0.05$), bold and italicized ($p < 0.01$), or bold, italicized and shaded ($p < 0.001$) coefficients. Refer to figure 1 and table 1 for explanation of CCRVs.

Table 6. For the daily dataset, resulting splits from the regression tree analysis and subsequent non-parametric change point analyses (NCPA). For each chlorine concentration response variable (CCRV), the constituent forming the breakpoint is shown. Total organic carbon is shown as “TOC”, total coliforms as “TC”, *Eschericia coli* as “EC” and temperature as “Temp”. Also shown are the units, the change point CCRV values (CP), the amount of variability explained by the constituent (R^2), the level of significance (p, bolded if significant), the 5% and 95% confidence intervals, the mean CCRVs to the left and right of the split, and the number of observations to the left and right of the splits and the total number of observations.

Daily dataset

Response variable	Constituent	Units	CP	R^2	p	5%	95%	Mean Left	Mean Right	n left	n right	n total
Y1 Primary split	TOC$_{lab}$	mg/L	1.96	0.24	**0.002**	1.63	2.46	1.88	2.49	20	40	60
	Iron	mg/L	0.15	0.18	**0.010**	0.03	0.20	2.15	2.72	45	16	61
	TC	CFU/100 mL	564	0.13	**0.045**	49	3593	2.46	2.02	39	19	58
	Turbidity	NTU	10	0.13	**0.049**	1	26	2.16	2.65	44	17	61
	Conductivity	uS/cm	144	0.09	0.143	122	153	2.48	2.12	30	31	61
Y3 Primary split	pH$_{lab}$	SU	8.86	0.15	0.082	7.30	8.95	1.63	2.27	55	6	61
	TOC$_{lab}$	mg/L	1.65	0.13	0.112	1.44	2.35	1.30	1.77	11	49	60
	TC	CFU/100 mL	533	0.11	0.115	403	7270	1.82	1.48	38	20	58
	Manganese	mg/L	0.02	0.09	0.161	0.01	0.03	1.43	1.78	19	42	61
	Date		6/10/2014	0.06	0.469	14076	14200	1.60	1.86	38	23	61
Y5 Primary split	Iron	mg/L	0.15	0.37	**0.001**	0.09	0.21	3.62	4.56	45	16	61
	Turbidity	NTU	13	0.32	**0.001**	6	26	3.64	4.51	45	16	61
	TOC$_{lab}$	mg/L	1.87	0.31	**0.003**	1.77	2.42	3.37	4.02	41	19	60
	EC	CFU/100 mL	17	0.16	**0.012**	2	18	3.79	4.47	44	14	58
	Date		5/6/2014	0.12	0.055	14085	14130	4.16	3.68	24	37	61
Y7 Primary split	Iron	mg/L	0.17	0.72	**0.001**	0.06	0.17	1.05	2.21	47	14	61
	Turbidity	NTU	10	0.67	**0.001**	3	20	1.03	2.08	44	17	61
	pH$_{lab}$	SU	7.65	0.62	**0.001**	7.63	7.69	1.88	0.95	24	37	61
	Date		5/8/2014	0.61	**0.001**	14113	14131	1.86	0.94	25	36	61
	Temp.	°C	16	0.58	**0.001**	16	19	1.90	0.99	22	38	60

could strengthen our understanding of these relationships. Simple linear regression analysis showed that 23 and 19% of the variation in chlorine dose (Y5) was explained by iron and UV$_{254}$, respectively (Figure 6).

Regression tree and NCPA of the daily dataset showed that significant non-linear relationships exist between chlorine dose (Y5) and water quality constituents. Again, the strongest change point relationship occurred with iron, where mean chlorine dose (Y5) was 3.62 and 4.56 mg/L when iron was less than or greater than 0.15 mg/L (Table 6; Figure 5A). Significant change points also existed for turbidity (CP = 13 NTU),

Table 7. For the weekly dataset, resulting splits from the regression tree analysis and subsequent non-parametric change point analyses (NCPA). For each chlorine concentration response variable (CCRV), the constituent forming the breakpoint is shown. Total organic carbon is shown as "TOC", total coliforms as "TC", *Eschericia coli* as "EC" and temperature as "Temp". Also shown are the units, the change point CCRV values (CP), the amount of variability explained by the constituent (R^2), the level of significance (p, bolded if significant), the 5% and 95% confidence intervals, the mean CCRVs to the left and right of the split, and the number of observations to the left and right of the splits and the total number of observations.

Weekly dataset

Response variable	Constituent	Units	CP	R^2	p	5%	95%	Mean Left	Mean Right	n left	n right	n total
Y1 Primary split	TOC_{lab}	mg/L	1.96	0.21	**0.018**	1.52	2.34	1.92	2.44	16	28	44
	Iron	mg/L	0.15	0.17	**0.032**	0.03	0.17	2.15	2.71	35	10	45
	TOC	mg/L	2.13	0.18	0.177	1.62	2.59	2.08	2.57	15	12	27
	Turbidity	NTU	10	0.11	0.232	1	30	2.17	2.60	34	11	45
	Manganese	mg/L	0.02	0.11	0.169	0.01	0.02	2.13	2.52	13	32	45
Y3 Primary split	NH_3-N	mg/L	0.15	0.28	**0.037**	0.12	0.17	1.61	2.08	12	9	21
	Manganese	mg/L	0.02	0.24	**0.010**	0.02	0.02	1.27	1.79	13	32	45
	TOC_{lab}	mg/L	1.60	0.19	**0.044**	1.59	1.98	0.98	1.69	4	40	44
	TOC	mg/L	1.72	0.22	0.101	1.69	2.30	1.25	1.82	6	21	27
	TC	CFU/100 mL	468	0.13	0.098	206	1315	1.81	1.47	22	23	45
Y5 Primary split	UV_{254}	/cm	0.070	0.36	**0.041**	0.045	0.089	3.66	4.46	15	6	21
	Iron	mg/L	0.12	0.34	**0.001**	0.06	0.17	3.68	4.42	35	10	45
	TOC_{lab}	mg/L	1.87	0.31	**0.001**	1.75	2.42	3.37	4.02	13	31	44
	Turbidity	NTU	6	0.26	**0.007**	2	18	3.67	4.26	33	12	45
	Manganese	mg/L	0.02	0.20	**0.044**	0.01	0.05	3.43	3.97	13	32	45
Y7 Primary split	Iron	mg/L	0.17	0.59	**0.001**	0.05	19.75	1.08	2.06	37	8	45
	pH_{lab}	SU	7.64	0.58	**0.001**	7.58	7.68	1.76	0.98	16	29	45
	Date		5/8/2014	0.58	**0.001**	14114	14131	1.73	0.97	17	28	45
	Turbidity	NTU	4	0.58	**0.001**	2	20	0.97	1.73	29	16	45
	Temp.	°C	19	0.57	**0.001**	16	20	1.73	0.97	17	27	44

TOC_{lab} (CP = 1.87 mg/L) and *E. coli* (CP = 17 CFU/100 mL; Table 6; Figure 5).

In the weekly dataset, UV_{254} showed the strongest change point with chlorine dose (Y5), where mean chlorine dose (Y5) was 3.66 and 4.46 mg/L when UV_{254} was less than and greater than 0.070 /cm, respectively (Table 7; Figure 6B). Significant change points also existed for iron (CP = 0.12 mg/L), TOC_{lab} (1.87 mg/L), turb-idity (CP = 6 NTU) and manganese (CP = 0.02 mg/L; Table 7).

Chlorine concentration response variable – Chlorine demand (Y7)

Chlorine demand (Y7) represents the chlorine demand concentration of the raw water after which residuals begin accumulating, based on NCPA (Table 1; Figure 1). Analyses relating chlorine demand (Y7) with water quality parameters consistently yielded the strongest statistical relationships compared to the other chlorine concentration response variables (Y1, Y3 and Y5). In the daily dataset, Pearson correlation analysis showed significant positive relationships with all of the water quality parameters except for total coliforms (Table 3).

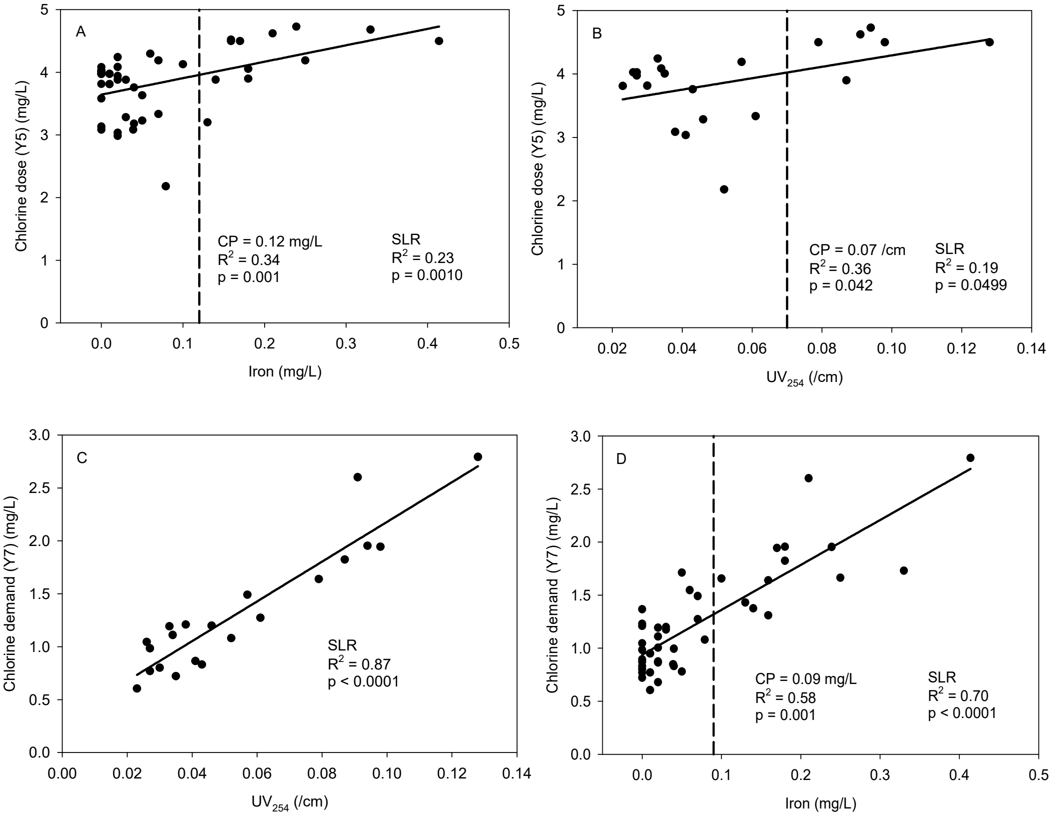

Figure 6. From the weekly dataset, scatter plots of the relationships between (A and B) The chlorine dose (Y5) (response variable) and (C and D) The chlorine demand (Y7) (response variable) with the top explanatory variable from the Pearson correlation analysis and the regression tree with subsequent non-parametric change point analyses.

The 4 most important predictor variables were iron (ρ = 0.88), turbidity (ρ = 0.81), temperature (ρ = -0.72) and date (ρ = -0.70), where iron and turbidity were positively correlated and temperature and date were correlated with chlorine demand (Y7) (Table 3).

Subsequent simple linear regression analyses showed that 72, 67, 58 and 61% of the variation in chlorine demand (Y7) was explained by iron, turbidity, temperature and date, respectively (Figure 7). Multiple linear regression analysis resulted in a single predictor variable, iron, which explained over 70% of the variation (Table

6).

Analysis of the weekly dataset demonstrated the importance of raw water physicochemical parameters not available in the daily dataset. For example, Pearson correlation analysis showed the strongest relationship with UV_{254} (ρ = 0.93), followed by DOC (ρ = 0.86), where chlorine demand (Y7) increased with increasing UV_{254} and DOC concentrations (Table 5). Iron (ρ = 0.84) and turbidity (ρ = 0.76) were also highly positively correlated with chlorine demand (Y7) (Table 5). Simple linear regression analyses showed that 87 was explained by UV_{254} and iron, respectively and 58% of the variation in chlorine demand (Y7) was explained by UV_{254} and iron, respectively (Figure 6).

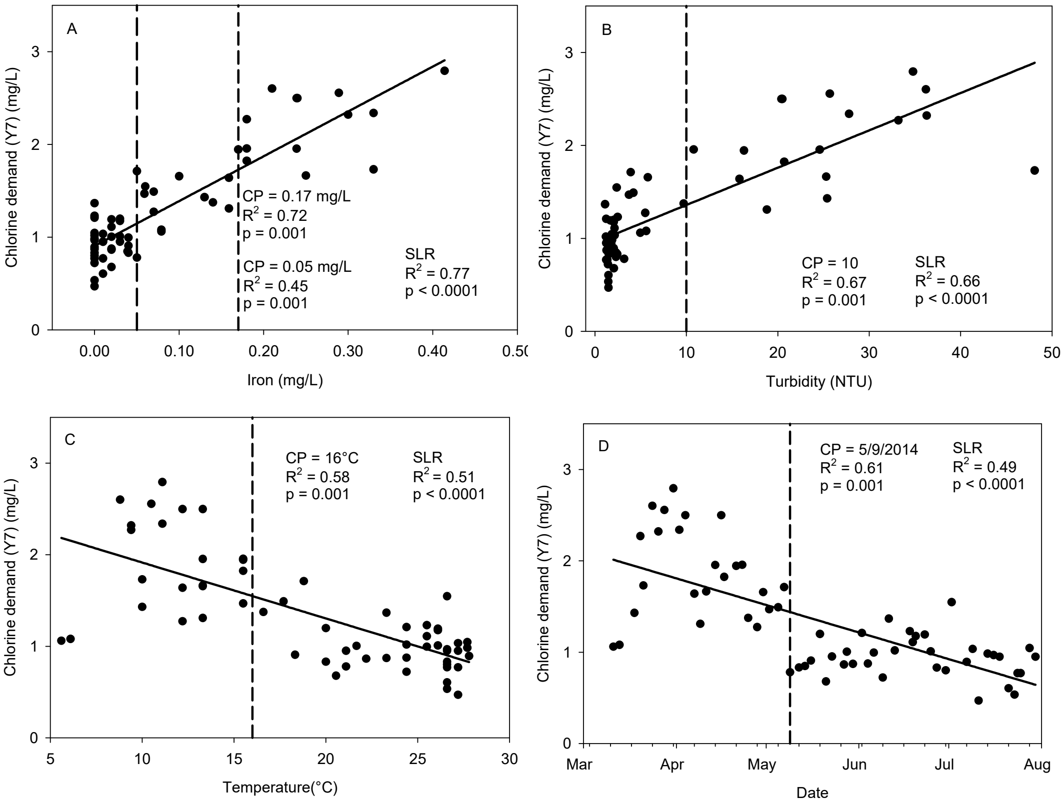

Figure 7. From the daily dataset, scatter plots of the relationships between chlorine demand (Y7) (response variable) and the top four explanatory variables from the Pearson correlation analysis and the regression tree with subsequent non-parametric change point analyses.

Regression tree and NCPA of the daily dataset showed the strongest change point with iron, where mean chlorine demand (Y7) was 1.05 and 2.21 mg/L when iron was less than and greater than 0.17 mg/L, respectively (Table 6; Figure 7). Additionally, regression tree analysis resulted in a hierarchical split with iron, where when iron was less than 0.17 mg/L, another split occurred at an iron concentration of 0.05 mg/L. Here, mean chlorine demand (Y7) was 0.93 and 1.37mg/L when iron was less than and greater than 0.05 mg/L. (Table 6). Significant change points also existed for turbidity (CP = 10 NTU), pH (CP = 7.65), date (CP = May 8, 2014) and temperature (CP = 16°C; Table 6; Figure 7).

In the weekly dataset, iron showed the strongest change point with chlorine demand (Y7) at a concentration of 0.17 mg/L, where mean chlorine demand (Y7) was 1.08 and 2.06 mg/L below and above 0.17 mg/L iron, respectively (Table 7; Figure 7A). Significant change points also existed for pH (CP = 7.64), date (CP = May 8, 2014), turbidity (CP = 4 NTU) and temperature (CP = 19°C; Table 7).

DISCUSSION

The chlorine demand of source water for drinking water treatment is a measure of the amount of chlorine disinfectant consumed by reactions before free chlorine residuals accumulate in the water. Raw water quality can greatly influence chlorine demand by reactions between free chlorine and reduced organic and inorganic compounds like ammonia, nitrate, organic matter, iron, manganese and others, and these reactions can be influenced by temperature and pH (Barbeau et al. 2005, Abdullah et al. 2009). In the current study, results consistently demonstrated the importance of iron to chlorine dose and demand concentrations. Iron was positively linearly correlated with almost all the CCRVs in both the daily and weekly datasets. Non-linear relationships also existed with iron and most of the CCRVs in both datasets, where significant increases in chlorine dose and demand concentrations occurred at either 0.15 or 0.17 mg iron/L. Iron is a reducing agent that readily combines with free chlorine, thus increases in iron concentrations should be expected to influence the chlorine demand of source water.

Turbidity was also consistently important in driving most of the CCRVs investigated in the current study. Turbidity was positively linearly related to CCRVs in both the daily and weekly datasets and showed significant change points where chlorine dose and demand concentrations increased when turbidity was greater than 4 to 13 NTU. As a measure of water clarity, turbidity can be influenced by organic and inorganic matter, among other things. Organic matter as a measure of DOC, TOC, UV_{254} and turbidity has been shown to influence chlorine demand as well as disinfection by-product formation (LeChavallier et al. 1981, Clark et al. 1998, Yee et al. 2006, Pifer and Fairey 2014). In a study of surface water from 6 lakes in Oregon, turbidity (range = 0.2 to 15 NTU) was positively correlated with chlorine demand and was an important predictor for disinfection efficiency (LeChavallier et al, 1981).

TOC was often an important predictor and was positively correlated with many of the CCRVs. When TOC was greater than 1.60 to 1.96 mg/L, increased concentrations of chlorine were required to satisfy raw water chlorine demand and for residuals to begin accumulating. Yee et al. (2006) isolated DOM from samples collected at a drinking water treatment plant and found that increases in DOM resulted in increased chlorine demand as well as THM formation. DOC was found to be an important predictor for DBP formation when water samples from several drinking water treatment plants were analyzed (Pifer and Fairey 2014), and this increase in DBP formation is likely concomitant with increases in chlorine demand (Yee et al. 2006).

Interestingly, temperature and date weren't generally important predictors, linearly or non-linearly, for CCRV Y1, Y3 and Y5 and only showed significant negative relationships and change points with CCRV Y7. Specifically, the chlorine demand (Y7) of the raw intake water was greater prior to May 9th and then decreased after May

9th. Lakes and reservoirs often show a bimodal peak in primary production (measured as chlorophyll *a* concentrations), where productivity is greatest in late spring and summer; In fact, water quality criteria for chlorophyll *a* in Beaver Lake apply during the growing season, a time when chlorine demand (Y7) significantly decreased. These results demonstrate the complex relationships that may drive chlorine demand and the need for further investigation and data collection in order to capture seasonal variability and better understand these relationships.

When additional predictor variables were evaluated in the weekly dataset, NH_3-N and UV_{254} became important and significant variables, both in linear and non-linear analyses. In a study of the source water in a drinking water treatment plant, Abdullah et al. (2009) found that NH_3-N and UV_{254} were significantly related to chlorine demand with Pearson correlation coefficients of 0.86 and 0.84, respectively. UV_{254} was the strongest predictor variable tested as a DBP precursor in a study of the source water from several drinking water treatment plants (Pifer and Fairey 2014). These data suggest the potential importance of NH_3-N and UV_{254}, which are typically measured less frequently at BWD, in predicting chlorine demand of source water. While results from the current study should be interpreted cautiously given data limitations, they do demonstrate the importance of continuing to develop a long term, robust dataset.

SUMMARY

Source water quality of Beaver Lake at the intake of Beaver Water District drove changes in the 4 chlorine concentration response variables (CCRVs), with the following major findings:

- Iron concentrations, turbidity and TOC concentrations were the most important and strongly related water quality parameters that drove changes in chlorine dose and demand concentrations that were required to either satisfy chlorine demand or for chlorine residuals to begin accumulating. Both linear and threshold relationships occurred where higher concentrations of iron, turbidity and TOC resulted in higher chlorine dose and demand concentrations. Change points occurred between 0.09 to 0.17 mg/L for iron, between 4 to 13 NTU for turbidity, and between 1.60 to 1.96 mg/L for TOC.
- NH_3-N and UV_{254} became important explanatory variables when analyzing the weekly dataset, where they were both positively related to chlorine dose and demand concentrations required to either satisfy chlorine demand or for residuals to begin accumulating in the water.
- To address the influence of all the potentially important water quality drivers of chlorine demand, including seasonal variation, continuation of chlorine demand assays coinciding with analysis of a more robust set of water quality physico-chemical parameters could be useful.
- The chlorine demand concentration where residuals begin accumulating (Y7) could be a useful metric to evaluate the chlorine demand of raw water because it showed consistently strong relationships with water quality data. Chlorine demand concentration (Y7) is easy to statistically determine – non-parametric change point analysis of the daily demand assays using the relationship between chlorine demand and chlorine residuals was used – and it represents the chlorine demand concentration at which point residuals begin accumulate.

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