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Chlorine Demand Shows Thresholds and Hierarchy with Source Water Quality at Beaver Lake, Arkansas

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By

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Abstract

This study investigated the effects of source water quality in Beaver Lake on the amount of chlorine (Cl) needed to develop decision support system to help guide chlorination practices in pre-treatment of source water. Chlorine demand assays were performed on water samples from Beaver Lake collected from the intake structure at Beaver Water District from March 2014 through August 2015, and using data from these assays, the two points of interest in this study were the Cl dose at which Cl residuals began to accumulate and the mean Cl demand occurring after that dose. Three methods of analysis were used to characterize relationships between source water quality, Cl dose, and mean Cl demand: (1) Pearson correlation, (2) nonparametric change point analysis (nCPA), and (3) regression tree (RT) analysis. The Cl dose and mean Cl demand generally increased with increasing concentrations of natural organic matter (NOM), iron (Fe), turbidity, TSS, and bacterial counts and generally decreased with increasing pH, conductivity, and alkalinity. Nonlinear, threshold-based relationships were also identified between Cl dose, mean Cl demand, and source water quality parameters, where Cl dose and mean Cl demand increased with NOM properties, Fe, manganese (Mn), total nitrogen (TN), temperature, turbidity, and TSS and decreased with increasing conductivity, pH, and alkalinity. Additionally, RT analysis revealed hierarchical structure to exist between Cl dose, turbidity (16.2 NTU), and pH (8.15 SU) which explained 35% of the variation in Cl dose as well as between mean Cl demand, turbidity (7.93 NTU), conductivity (138 µS/cm), sample date (May 8th), and TOC (2.65 mg/L) which collectively explained 66% of the variation in mean Cl demand. The relationships identified previously were incorporated into decision trees to potentially guide chlorination used in pre-treatment, which identified multiple ranges for Cl dose and demand based on thresholds in source water quality parameters.

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Introduction

In the US, chlorine (Cl) is the most commonly used disinfectant and chlorination in drinking water disinfection has been in practice for over 100 years (Koechling, 1998; Harp, 2002). Much of its popularity stems from strong oxidizing capabilities and effectiveness in inactivation of pathogens (LeChevallier, 1999). The amount of Cl applied is related to the demand of the source water, which is the amount of Cl needed to satisfy all chemical reactions and leave a defined amount of free Cl that is available for continued disinfection.

While it remains the most prevalent form of disinfection in drinking water, several studies have provided evidence linking Cl use to formation of disinfection byproducts (DBPs; Rook, 1974; Bellar et al., 1974). Chlorine reacts with organic and inorganic compounds in source water to form DBPs such as total trihalomethanes, which have been suggested to be associated with occurrence of bladder, colon, and rectal cancer (Kohpaei and Sathasivan, 2011; Boorman et al., 1999; Gang et al., 2002). The US Environmental Protection Agency (USEPA) has established maximum contaminant levels (MCLs) for two major classes of DBPs specific to treatment with Cl known as Total Trihalomethanes (TTHMs) and Haloacetic Acids (HAA5) at 0.080 mg/L and 0.060 mg/L, respectively (USEPA, 2006). In addition, regulations have also been established under the Surface Water Treatment Rule, which require drinking water utilities to maintain a measurable disinfectant residual throughout the distribution system (USEPA, 2004a).

To meet more restrictive standards, drinking water utilities have started evaluating and optimizing disinfection practices (Gang et al., 2002). Drinking water utilities often add oxidants (e.g. Cl) when water is being pumped from the source to the plant to oxidize materials and improve clarification and filtration processes (LeChevallier and Au, 2004). However, source water quality can be variable affecting the amount of Cl needed for the demand. Furthermore, there is a need to understand the relationships between source water quality and Cl demand. This information can be used to optimize the amount of Cl applied in pre-treatment to quench the demand but not create residuals thereby also limiting the Cl residuals entering the plant.

Source water quality has been shown to influence demand because Cl readily reacts with many compounds, including ammonia (NH_3), nitrate (NO_3), natural organic matter (NOM), iron (Fe), manganese (Mn) and many others (Abdullah et al., 2009; Barbeau et al., 2005; Clark and Sivaganesan, 1998; Yee et al., 2006). Abdullah et al. (2009) showed that Cl demand increased with increased concentrations of NH_3-N, increased pH, and increased ultraviolet (UV) absorbance in the source water. Powell et al. (2000) also observed that as temperature, total organic carbon (TOC), and UV absorbance increased, Cl demand also increased. Observations also suggest that drinking water facilities using surface water sources experience seasonal variations in Cl usage, with increased usage in summer and early autumn (Casey et al., 2012).

Water quality in water supply reservoirs is largely determined by factors such as seasonal variation, quality of inflow water, and in-lake processes (Merz, 2013). Nutrients, sediments, and other contaminants can enter source water *via* point and nonpoint sources, contributing to potential impairment of lake quality (Parry, 1998). In-lake processes, such as seasonal lake stratification and turnover can also result in the seasonal release of inorganic constituents such as Mn , Fe, phosphorous (P), sulfides (S_2), and NH_3 from sediment (Kohpaei and Sathasivan, 2011; Merz, 2013). All of these factors both internal (reservoirs) and external (watershed and climate) will ultimately influence Cl demand of the source water during pre-treatment.

The goal of this study is to evaluate the effects of source water quality on the Cl demand of the water entering the treatment processes at Beaver Water District (BWD). Beaver Water

District, located on Beaver Lake, serves as the primary water supply for approximately 350,000 people and various industries in northwest Arkansas (Beaver Water District, Production Data. Accessed May, 2015, http://www.bwdh2o.org/). Beaver Lake and its watershed are considered regionally important, and BWD wants to quantify the relationship between source water components and drivers for Cl demand in order to forecast daily Cl demand at the intake. Specific objectives to meet this goal include (1) evaluating the correlation and seasonality between source water quality and Cl demand over different seasons, (2) identifying potential thresholds in source water quality components which relate to nonlinear responses in Cl demand, (3) evaluating hierarchical structure of source water quality components related to Cl demand, and (4) developing a decision support system to guide Cl dosage for pre-treatment at the intake based on source water quality.

Literature Review

Chlorine Chemistry

Chlorine is commonly used in water treatment in the form of chlorine gas (Cl_2), solutions of sodium hypochlorite (NaOCl), or solid calcium hypochlorite powder ($Ca(ClO)_2$) also referred to as high-test hypochlorite (HTH) (Pickard et al., 2006; Brown, 2009). These three forms of Cl will react in water *via* the following equations (Brown, 2009):

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl$$

$$NaOCl + H_2O \leftrightarrow HOCl + NaOH$$

$$Ca(OCl)_2 + 2H_2O \leftrightarrow Ca^+ + 2HOCl + 2OH^-$$

All three compounds react in water to form hypochlorous acid (HOCl), which is a weak acid with a pK_a of 7.6. It dissociates to form the hypochlorite (OCl^-) ion as follows (Rice and Gomez-Taylor, 1986; Brooks, 1999):

$$HOCl \leftrightarrow H^+ + OCl^-$$

The dissociation of HOCl is pH dependent, and both species (HOCl and OCl^-) have been shown to be present to some degree at pH values between 6.5 and 8.5 (Brooks, 1999). Several studies have shown HOCl, the more reactive species and stronger disinfectant, predominates at $pH < 8.0$ (Helmer et al., 1999; Connell, 1997). It has also been shown at $pH > 8.0$, OCl^- , the less effective oxidant, predominates (Larson and Weber, 1994; Brezonik and Arnold, 2011; Helmer et al., 1999; Connell, 1997; Brown, 2009).

Chlorine Treatment

Chlorine is a strong oxidant that is commonly used in both oxidation and disinfection processes such as pre-treatment oxidation and primary and secondary disinfection (USEPA, 2015a; LeChevallier and Au, 2004). Pre-treatment is generally considered to be any unit processes utilized prior to coagulation (Suffet et al., 1988). In this stage, oxidants such as Cl_2 are applied early in the treatment process to control taste and odor causing compounds as well as to oxidize Fe and Mn (Xie, 2004; Calabrese, 1989). Treatment plants also commonly use oxidants in pre-treatment to induce initial disinfection in source water and to control biological growth on intake structures and treatment basins (e.g. zebra mussels or algae) (LeChevallier and Au, 2004).

The pre-treatment process was almost entirely accomplished with Cl_2 until recent years when concerns were raised over DBP formation potential. Variable source water conditions were found to cause fluctuation in oxidant demand, and when increased concentrations of source water quality parameters such as NOM were present (e.g. in spring and summer), this could react with Cl *via* oxidation, addition, and substitution reactions to form DBPs (Gang et al., 2002). Abdullah et al. (2009) stated the formation of DBPs in pre-treatment was strongly influenced by reactions of Cl_2 with organic and inorganic compounds in source water.

Additional concerns regarding pre-treatment oxidation with Cl_2 include lysing of algal cells, which can result in the potential release of algal toxins (Yoo et al., 1995; Chorus and Bartram, 1999; City of Marion, 2014). These algal toxins, produced from certain species of algae referred to as cyanobacteria (or blue-green algae), can irritate skin as well affect the liver or brain (Burtle, 2015). For example, in 2014, the city of Toledo, Ohio was temporarily forced to shut down drinking water treatment operations as a result of high toxin levels from cyanobacteria blooms (Stow et al., 2015).

Chlorination of algal biomass in oxidation processes may also result in the production of DBPs (Plummer and Edzwald, 2001). Oxidation processes can cause disruption of algal cells, resulting in the release of intracellular organic matter (IOM) into water being treated (Wert, 2013; Mash et al., 2014). This IOM then can bind with oxidants being used to form DBPs (Huang et al., 2008).

To meet stricter regulations for DBP control as defined by the Stage 2 D/DBP Rule (USEPA, 2006), many treatment plants have modified or use nonconventional treatment processes (Richardson et al., 2007). An example of measures taken by many treatment plants include the use of alternative oxidants (e.g. chlorine dioxide (ClO_2) or potassium permanganate ($KMnO_4$)) in pre-treatment, which primarily serve as oxidizing agents for NOM and do not form chlorinated DBPs such as THMs and HAAs (Harris, 2001). Another approach taken to reduce DBP formation with Cl includes relocating the point of primary Cl_2 addition to locations within the plant where fewer precursors are present (Valenti, 2008). Several studies have investigated the use of ClO_2 as an alternative to Cl_2 in pre-treatment (Gordon, 2001; Rice and Gomez-Taylor, 1986; Clark et al., 1994). It was found that ClO_2, when used in pre-treatment, serves as a strong oxidant, and allows for delayed addition of Cl_2 until later in the treatment process. In addition, Clark et al. (1994) stated this allows for lowered Cl demand and potential for chlorinated DBPs.

Primary disinfection refers to the application of disinfectants typically after the filtration process to achieve a certain level microbial inactivation (Calabrese, 1989; Davis and Shepherd, 2010). This stage of disinfection is thought to be most effective following removal of particles by the preceding filtration, settling, and/or coagulation stages (Calabrese, 1989). In primary disinfection, Cl_2, or other commonly used primary disinfectants such as ClO_2, chloramines, ultraviolet (UV) radiation, and ozone are used to control microbial activity in treated water (Mobarak, 2002; USEPA 2015a; Richardson et al., 2007).

Following primary disinfection, a secondary disinfectant is often added to leave a residual in water leaving the plant for protection from harmful organisms in the distribution system (USEPA, 2015a). Chlorine remains the most widely used disinfectant in distribution systems, mainly due to its ability to maintain a residual (Bowden et al., 2006). However, it is also a non-selective oxidant, which can react with material in distribution pipe walls as well as sediment, resulting in consumption of Cl residual (Brown, 2009). Another concern when using Cl is the formation of DBPs in the distribution system to which customers can be exposed, depending on contact time and distance from the treatment plant (Mobarak, 2002).

The potential for DBP formation in the distribution system has led to the evaluation of alternative secondary disinfectants (e.g. ozone, ClO_2, and UV). Dissolved ozone was found to be an effective oxidant and primary disinfectant, but it cannot maintain a residual in the distribution system (Hua and Reckhow, 2007). Ultraviolet radiation was also found to be effective as a primary disinfectant, but because it could not protect against re-growth in the distribution system, it was determined unfit to serve as a secondary disinfectant (Singer, 1994; Deininger et al., 1998; Dyksen et al., 2007). Chlorine dioxide, an oxidant shown to possess a strong disinfection capability was determined to be preferable for primary disinfection. However, Dyksen et al. (2007) stated the majority of ClO_2 is reduced to chlorite, a regulated inorganic byproduct, thus making it undesirable for secondary disinfection. Based on these limitations of alternative disinfectants, particularly for secondary disinfection, the use of Cl_2 remains a common method of disinfection to date.

Chlorine Reactions with Organic and Inorganic Species in Source Water

In addition to treatment practices, raw water constituents influence Cl demand (Clark and Sivaganesan, 2002). Being a non-selective oxidant, Cl will react with organic and inorganic species in source water (Warton et al., 2006). Natural organic matter (NOM), which is present in all source waters, has been shown to be especially reactive with oxidants such as Cl (Mobarak, 2002; Gang et al., 2003). Reactions between NOM and halogens such as Cl have been noted to occur mainly *via* oxidation and substitution pathways in which either Cl cleaves a double carbon-carbon bond (oxidation) or replaces a functional group (substitution) in NOM compounds (Westerhoff, et al., 2004).

Natural organic matter consists of a mixture of humic and non-humic materials and is commonly represented by surrogate parameters such as TOC and UV_{254} (Singer, 1994). Dissolved organic carbon (DOC) has also been identified as a surrogate for representing NOM in source water. Several studies have reported a ratio of UV_{254} to DOC to represent the aromatic character of NOM, and this ratio is referred to as specific ultraviolet (SUVA) (Amy 1993; Liang and Singer, 2003). Randtke (1988) stated the majority of Cl demand in source water can be attributed to NOM concentrations.

These concentrations also have also been shown to fluctuate with seasonal variation (Fabris et al., 2008). Seasonal events such as heavy precipitation, snowmelt, and production and decay of algal blooms can contribute to the increase in NOM content in source water (Chaulk, 2011). Higher concentrations of NOM can lead to higher Cl demand (Xie, 2004). It can also result in higher cost to treat the water and higher potential for DBP formation (Kornegay et al., 2000).

While NOM has been found to contribute to a majority of Cl demand, several studies have also observed reactions between inorganic compounds and Cl (Deborde and von Gunten, 2008; Valenti, 2008; White, 1992). Chlorine acts as an oxidizing agent for soluble Fe (II) and Mn (II) in source water to form insoluble Fe (III) and Mn (III; IV) (Brezonik and Arnold, 2011; Clark and Sivagenesan, 2002). The presence of Fe and Mn in source water can result from transport *via* surface and groundwater, and this also varies seasonally (Delfino and Lee, 1971). Typically, these constituents are found in soluble form under anoxic conditions and at lower pH (Brezonik and Arnold, 2011). Higher concentrations of soluble Fe (II) and Mn (II) have been reported during summer months when lakes have become stratified, producing anoxic conditions in the hypolimnion (Davison et al., 1982). Soluble Fe (II) and Mn (II) in raw water can contribute to coloring of waters and pipe corrosion, and these are typically removed by oxidation to insoluble Fe (III) and Mn (III, IV) forms, followed by filtration (Deborde and von Gunten, 2008; Wong, 1984). Valenti (2008) stated reactions of Cl with reduced species such as Fe (II) and Mn (II) can also create significant Cl demand. This could occur when using Cl for pre-treatment.

Fast reactions of Cl with other inorganic species in source water such as NH_3 have been documented (Rice and Gomez-Taylor, 1986; Van Hoof, 1992; Deborde and Gunten, 2008). During these reactions, Cl oxidizes NH_3 to form NO_3 and ultimately ending with products of free Cl and elemental N_2, also referred to as breakpoint chlorination (Deborde and Gunten, 2008). This oxidation process also includes intermediate products such as three types of chloramines (monochloramine, dichloramine, and trichloramine), and the distribution of these reaction products is pH dependent (Deborde and Gunten, 2008; Rice and Gomez-Taylor, 1986).

Chlorine Demand in Pre-treatment of Source Waters

Numerous studies have been conducted to better understand what is influencing Cl demand in source water and also how to more accurately predict how Cl demand will change, based on source water parameters (listed in Table 1). For example, Koechling (1998) evaluated samples from 11 different source waters from lakes for Cl demand, and its relationship to DOC, UV adsorption, bromide (Br^-), SUVA, and alkalinity. This study found at initial Cl doses ranging from 3.0 to 5.0 mg/L, and at reaction time intervals of 0.083 and 120 hours, average demands of 0.4 mg/L and 0.8 mg/L were determined, respectively (Koechling, 1998). Additionally, it was observed within this study, up to 20 percent of the 120 hour demand was generated within the first five minutes of the reaction time. This also correlated with a marked decrease in UV-absorbing compounds after the same period of time.

Fabris et al. (2008) found when investigating the relationship between 7 source waters and Cl demand, at initial Cl dosages of 20-30 mg/L, and after a reaction time of 24 hrs, Cl demand ranged from 5.6 to 29.0 mg/L, with an average of 17.6 mg/L. However, results from this study, in addition those from Koechling (1998) are based on short-term sampling regimes, and do not provide information on seasonal variation of Cl demand in source waters. This is similar to Casey et al. (2012) who evaluated Cl demand of Irish source waters in August 2012. In this study, it was found at an initial dosage of 1.51 mg/L, resulting demands of 0.91 and 1.39 mg/L were found at time intervals of five minutes and 120 hours, respectively. It was also reported at an initial dosage of 2.01 mg/L, a resulting demand of 1.07 and 1.66 mg/L was found after a five minute and 120 hour reaction time. However, this study only consisted of data generated from one grab sample collection, but it shows the majority of demand occurs quickly.

Limited research has been presented on the behavior of Cl demand levels over a long-term seasonal basis. Golfinopoulos and Arhonditsis (2002) found while investigating the effects of source water parameters on Cl dosage levels, dosage levels ranged from 0.4 to 3.8 mg/L, with higher values pertaining to summer and autumn months. However, this Cl dosage was representative of the sum of the Cl dosage applied prior to the coagulation process and the dosage applied before the distribution. This was not entirely representative of true demand in source water prior to entering the plant.

In another study by LeChevallier et al. (1981), Cl demand was found to fluctuate seasonally. Specifically, it was found at turbidity 0.1 to 16 NTU and TOC from 0.7 to 4.5 mg/L, Cl demand ranged from 0.2 to 2.4 mg/L. A strong positive linear correlation ($R^2 = 0.94$, $p<0.01$) was also found between Cl demand, TOC, and turbidity. Furthermore, these parameters were suggested to vary seasonally, and with TOC and turbidity following rainfall patterns. It was also explained TOC concentrations in source water typically increased in summer months and then again in November and December with stormwater bringing in organic debris from the watershed. Similar patterns were explained for turbidity within source water, where turbidity increased during periods of rainfall and storm event conditions (LeChevallier et al., 1981).

Methods

Sampling Site Description

Source water samples for the BWD treatment plant were collected from the intake structure at Beaver Lake. Construction of the reservoir was completed in 1963 by the Army Corps of Engineers with the initial purposes of flood control, hydroelectric power, and water supply (Haggard et al., 1999; Haggard and Green, 2002). Beaver Lake is also the most upstream reservoir in a series of large reservoirs on the White River, located within the Ozark Highlands of northwest Arkansas.

Beaver Lake has a surface area of 114 km^2 and average depth of 18 m (Haggard and Green, 2002). At the top of the current conservation pool, the lake contains 6,693 m^3 of water and has an average retention time of 1.5 years (Haggard and Green, 2002; Bolyard et al., 2010). The lake is a monomictic lake, with thermal stratification occurring annually in early June and persisting through mid-October (BWD, 2013; Galloway and Green, 2006).

Watershed land use for Beaver Lake is predominantly 71% forest and 22% agriculture, but also contains smaller areas of water (4%) and urban land use (3%) (Davis and Shepherd, 2010). The Beaver Lake Watershed has a drainage area of 3,087 km^2 (Haggard and Green, 2002), and the primary inflows include the White River, War Eagle Creek, and Richland Creek with drainage areas of 1,040 km^2, 681 km^2, and 356 km^2, respectively (Haggard and Green, 2002; Bolyard et al., 2010). The influence of inflow water quality on Beaver Lake has been studied by

Haggard et al. (1999); Haggard and Green, (2002); Hufhines et al., (2011); Bolyard et al., (2010). The influence of internal lake processes on water quality has been studied by Sen et al. (2006); Haggard et al. (1999).

The intake to BWD is located in the transitional zone of the reservoir, which is often considered the most productive zone in a reservoir (Thornton et al., 1990). However, Beaver Lake generally has a trophic gradient of eutrophic in the riverine zone to oligotrophic near the dam (Scott and Haggard, 2015). Water velocities also decrease in the transitional zone, which allows for settling of suspended particles out of the water column and increase in depth of light penetration, potentially leading to an increase in photosynthetic activity and resulting productivity (Galloway and Green, 2006). Galloway and Green (2006) also stated anoxic conditions develop typically early April in the hypolimnion during stratification of Beaver Lake, mainly because of greater sediment and biochemical oxygen demand.

Source Water Collection and Chlorine Demand Assays

Source water samples were collected weekly from the intake structure at BWD from March 2014 to August 2015. This sample period was chosen in order to capture two summers, as well as potential seasonal variation in Cl demand. A 5L sample of source water was collected from the intake site and transported to BWD water quality laboratory where it was stored in the dark at approximately 4° C until use, which was typically no longer than one hour storage time.

Temperature and pH were measured using a Hach HQ40d Multiparameter Meter (Hach Company, Loveland, CO) and using *Standard Method* 4500-H+ B (APHA, 2000). A 40 mL sub-sample was then taken from the carboy and analyzed for TOC by BWD personnel using a

Shimadzu TOC-VCSH TOC Analyzer (Shimadzu, Kyoto, Japan) and TOC high temperature combustion method as described in *Standard Methods* 5310 B (APHA, 2000).

Chlorine demand tests were performed by first preparing a stock solution of NaOCl using 2 mL of the 5% NaOCl solution (Clorox, Oakland, CA) in a 200 mL volumetric flask, filling to volume with deionized (DI) water, and inverting several times. The stock solution concentration of NaOCl was determined using *Standard Method* 4500-Cl G (APHA, 2000) and a pocket ii colorimeter (Hach Company, Loveland, OH). Next, 250 mL of raw source water were poured into 14 500 mL glass amber bottles, which were used to prevent degradation of samples during Cl demand assays. The dosing scheme for demand bottles was designed around general demand range previously observed by BWD (1.5-2 mg/L, M. Dearing, personal communication). Each bottle was spiked with a predetermined volume of NaOCl stock solution to measure demand at increasing dosages. The average range of Cl dose applied in Cl demand assays ranged from 0.3 to 6.6 mg/L Cl.

After the initial NaOCl spike was applied, each bottle was capped, inverted three times and left to react for 1.5 hours. A reaction time of 1.5 hours was chosen to simulate the approximate hydraulic retention time of travel of source water from the intake to the flash mixers in the BWD treatment facility. Following reaction time of 1.5 hours, sub-samples were poured from each amber bottle into clear, 10 mL glass vials. Chlorine residuals were determined using *Standard Method* 4500-Cl G (APHA, 2000), and the demand for each bottle was determined by the following equation:

$$\mathrm{Cl_2\ demand}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) = \mathrm{Cl_2\ dose}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) - \mathrm{Cl_2\ residuals}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right)$$

where Cl_2 demand is the concentration of Cl_2 necessary to satisfy chemical reactions within the source water during 1.5 hour reaction time, Cl_2 dose is the initial concentration of Cl_2 applied to each bottle at the start of the assay experiment, and Cl_2 residuals is the concentration of Cl_2 remaining after a reaction period of 1.5 hours.

The two points of interest for this study were the Cl dose where residuals begin to accumulate (critical Cl dose) (Figure 1A) and the mean Cl demand that occurred after that dose (Figure 1B). These points were determined for each daily assay using nonparametric change point analysis (nCPA). These two points were then used to relate to source water quality parameters collected at the time of Cl demand assays.

Beaver Water District Treatment Plant

A suite of physico-chemical parameters were measured and shared by BWD on source water water samples used in the Cl demand assays. BWD is a state-certified laboratory by the Arkansas Department of Environmental Quality (ADEQ) for analysis of multiple constituents and also falls in compliance with national standards outlined in the Safe Drinking Water Act by the United States Environmental Protection Agency (USEPA, 2004b). For parameters measured and standard methods used, see Table 1. However, the number of observations varied for each parameter. Each parameter with at least 50 observations and that exceeded the method detection limit (MDL) was included in subsequent analyses (Table 1). Additional parameters with less than 50 observations (TN, TP, UV_{254}, and DOC) were also included in correlation analysis, if reported by previous studies as being related to Cl demand in source water (Granderson et al., 2013; Mash et al., 2014).

Statistical Analysis

Linear Regression Models

Linear regression can be used to relate a single dependent variable (critical Cl dose or mean demand) to any number of independent predictor variables, given that the assumptions for regression are satisfied (i.e. data are normally and independently distributed) (Helsel and Hirsch, 2002). Linear associations between critical Cl dose, mean Cl demand, and source water quality parameters were first identified using Pearson's correlation ($P<0.05$) and then simple linear regression (SLR) was used to evaluate predictive relationships when desired in SigmaPlot 13.0 (Systat Software, San Jose, CA). Regression techniques have been widely used to depict linear relationships between Cl demand and source water quality parameters (Abdullah et al., 2009; LeChevallier et al., 1981; Koechling, 1998). However, it does not provide information about specific thresholds in source water parameters which may produce abrupt changes in critical Cl dose or mean demand.

Nonparametric Change point Analysis

Potential thresholds in source water quality variables producing a nonlinear response in critical Cl dose or demand were identified using nonparametric change point analysis (nCPA) in R 3.2.1 software (R Core Team, 2015). Nonparametric tests such as nCPA have been found to be more robust for analyzing nonlinear relationships (Evans-White et al., 2009) and can provide more information regarding specific concentrations in source water quality where Cl response changes, aiding in development of more targeted Cl dosing schemes. This method examines relationships between a single predictor (source water quality parameters) and single response variable (critical Cl dose or demand) and splits the dataset into two groups, producing the greatest reduction in deviance from the mean of the response variable (King and Richardson, 2003; Qian et al., 2003). Confidence intervals can also be determined to express uncertainty around a potential change point.

Regression Tree

Regression tree analysis (RT) was used to evaluate hierarchical structures present in source water quality parameters influencing critical Cl dose and demand using the RPART library (Thernau et al., 2015) in R 3.2.1 (R Core Team, 2015). Regression tree analysis uses recursive partitioning to separate data into more homogenous sub-groups (Prasad et al., 2006). The initial split is chosen after reviewing the entire data set and selects the independent variable (source water quality parameter) to split the data into two sub-groups, which produce the maximum homogeneity in terms of the response variable (Gu et al., 2014; Prasad et al., 2006). Secondary splits continue to be made until a terminal node is reached, and these are based on user specifications. The end product of RT analysis is a tree-like structure containing multiple change points with increasingly more homogeneous sub-groups (e.g., see Haggard et al., 2013). To avoid overfitting of the data, cross validation was performed to prune the tree to an appropriate size as described by Thernaeu and Atkinson (1997). Nonparametric change point analysis was used to verify and provide a confidence interval for each change point determined from RT analysis.

Results and Discussion

Critical Chlorine Dose

Source Water Quality Correlations

The critical Cl dose where residuals started to accumulate (based on nCPA) varied from 1.80 to 6.11 mg/L across the assays performed on the source water from Beaver Lake. The mean critical Cl dose was 3.65 mg/L (Table 2), and the dose was less than 4 mg/L in almost 75% of the assays performed. The mean critical Cl dose identified in these assays was actually higher than the typical pre-treatment dose historically used by BWD, when Cl was the primary chemical used at the intake (0.5-0.9 mg/L, R. Avery, personal communication). The range of critical Cl dose observed (1.80-6.11 mg/L) was within the range generally applied in pre-treatment of source waters in the literature (0.34-5.78 mg/L; Koechling, 1998; Golfinopoulous, et al., 2002).

Interestingly, the critical Cl dose where residuals started to accumulate showed no discernable seasonal pattern from March 2014 to August 2015. However, this is in contrast with previous studies which have suggested higher Cl doses are necessary in warmer months due to rapid depletion of residuals (Garcia-V. et al., 1997; Rodriguez and Serodes, 2001; Mobarak, 2002). The increased Cl doses in the literature were largely influenced by presence of organic matter present in source water as well as higher temperatures, suggesting temporal variations in source water quality influenced Cl dosing and demand.

The critical Cl dose was positively correlated with many source water quality parameters (Table 3), which had quite variable ranges in measured values (Table 2). As expected, critical Cl dose was found to increase with increasing concentrations of NOM properties, showing positive correlations with TOC (r=0.20, p=0.033), DOC (*r*=0.46, p=0.013) and UV_{254} (*r*=0.44, p=0.019) in the source water (Table 3; Figure 2). This was in agreement with previous research which suggested the importance of DOC and UV_{254} in driving Cl dosing strategies (Yee et al., 2006; Gang et al., 2003; Abdullah, et al., 2009). This also reflects what was found previously with TOC (Rodriguez and Serodes, 2001; LeChevallier et al., 1981), showing that higher Cl doses were needed for oxidation with increases in TOC.

The critical Cl dose showed variable relationships with inorganic species measured in the water samples collected from the intake at Beaver Lake. Shown in Figure 2, critical Cl dose and Fe were found to be positively correlated (*r*=0.34, p<0.001). This was expected due to many studies that reported rapid oxidation rates of soluble Fe, typically found in a reduced valence state in the water column, to a less soluble form by Cl (Warton et al., 2006; Brezonik and Arnold, 2011; Deborde and von Gunten, 2008). Thus, when anaerobic conditions are present in the hypolimnion during stratification, this could lead to an increase in soluble Fe present and higher Cl dose required for oxidation (Davison et al., 1982; Valenti, 2008).

However, critical Cl dose was negatively correlated with Mn (*r*=-0.23, p=0.013) which contrasted that previously described in the literature (Deborde and Gunten, 2008; Zogo et al., 2011). It would be expected at greater concentrations of Mn that there would be a higher critical Cl dose necessary for oxidation. In general, Fe and Mn concentrations expressed similar seasonal patterns with higher concentrations observed during spring and fall, coinciding with typical periods seen for stratification and turnover where anoxic conditions develop in the hypolimnion. However, Mn concentrations in the source water were higher when Fe concentrations were low, and when Fe peaked, lower Mn concentrations were observed. This follows typical patterns seen with electron acceptors where Mn is utilized before Fe under anaerobic conditions in the hypolimnion.

Some physico-chemical properties were also related to critical Cl dose, while others (e.g., temperature, pH) were not as previously reported in the literature (Brown, 2009; Brezonik and Arnold, 2011; Work, 2006). As expected, critical Cl dose and turbidity (r=0.40, p<0.001) were positively correlated (Figure 2). LeChevallier et al. (1981) found as turbidity increased, the critical Cl dose required for oxidation also increased. Furthermore, LeChevallier et al. (1981) also explained elevated turbidity can contain higher concentrations of organic and inorganic matter, as well as bacteria adsorbed onto the surface of particulate matter. As a result, this can slow the oxidation process, creating need for a higher critical Cl dose.

Source Water Quality Thresholds

Examining the significant correlations observed between critical Cl dose and source water quality parameters, thresholds of each parameter where nonlinear response began using nCPA were identified with source water quality parameters in (Table 4). Specifically, NOM properties showed thresholds with critical Cl dose, including UV_{254} (0.08 cm^{-1}, r^2=0.39), DOC (1.77 mg/L, r^2=0.31), and TOC (2.15 mg/L, r^2=0.08). The mean critical Cl dose observed increased from 3.5 to almost 4.5 mg/L, when NOM property concentrations exceeded the threshold values determined by nCPA, suggesting that these concentrations could serve as indicators where there will be change in response for critical Cl dose where residuals begin to accumulate.

While the use of nonparametric statistical techniques to evaluate the effects of NOM on treatment of source water have been documented (Towler et al., 2009; Amy et al., 1987; Gibbs et al., 2006), these have mostly focused on traditional nonlinear regression methods and do not provide information regarding threshold responses between critical Cl dose and NOM properties. However, the threshold found for TOC (2.15 mg/L) was similar to ranges reported by Concerty et al. (2004) where DBP concentrations were found to noticeably increase in a study of several chlorinated surface waters. This threshold also reflected TOC concentrations (2 mg/L) where required reduction prior to Cl disinfection becomes necessary for prevention of DBPs in surface water treatment as specified in the Stage 2 D/DBP Rule (USEPA, 2006).

Inorganic species also showed significant thresholds with critical Cl dose (Table 4), including Fe (0.23 mg/L, r^2=0.18) and Mn (0.07 mg/L, r^2=0.08). The Fe threshold showed an increase in mean critical Cl dose from 3.6 to 4.3 mg/L, whereas the Mn threshold showed a decrease from 3.7 to 3.3 mg/L in critical Cl dose. The coefficient of variation (CV) determined for data on either side of the threshold identified by nCPA revealed higher variation in critical Cl dose at lower Mn concentrations (<0.07 mg/L). This also corresponded with sample dates when higher Fe concentrations were observed, which may have contributed to the higher critical Cl dose observed at Mn less than 0.07 mg/L. Furthermore, higher mean critical Cl dose was observed at Fe concentrations greater than 0.23 mg/L (Table 4), which also coincided with periods when greater NOM property concentrations were observed. Knocke et al. (1991) suggested raw waters containing high levels of NOM can result in competing reactions between NOM properties and inorganic species such as Fe and Mn, therefore requiring a higher critical Cl dose for oxidation. This may contribute to increased variation in critical Cl dose observed with the trace metal concentrations.

Some physico-chemical properties also showed significant thresholds with critical Cl dose (Table 3), including turbidity (16.2 NTU, r^2=0.25), conductivity (153 µs/cm, r^2=0.11), and temperature (8.0 °C, r^2=0.08). The turbidity threshold showed an increase in mean critical Cl dose from 3.5 to 4.3 mg/L. Additionally, the turbidity was generally under 5 NTU for over 60% of sample dates, and therefore suggests the critical Cl dose observed at turbidity greater than 16.2 NTU likely represents more episodic storm events. This was also supported by positive relationships identified between turbidity and TSS (r=0.72, p<0.001), TOC (r=0.37, p<0.001) and DOC (r=0.80, p<0.001). LeChevallier et al. (1981) explained greater amounts of sediment as well as various forms of NOM can be carried into the reservoir from the watershed during these events, thus increasing the required Cl dose for oxidation.

Interestingly, mean critical Cl dose decreased when conductivity exceeded 153 µS/cm (Table 4). One possible explanation is that the conductivity in Beaver Lake decreases during storm events. Brezonik and Arnold (2011) also explained rainfall with lower ionic composition in comparison to surface waters can result in temporary dilution of conductivity in lake. Additionally, when conductivity was low in the lake, higher concentrations of turbidity and NOM properties were also observed, which could contribute to increasing the critical Cl dose required before residuals begin to accumulate.

The mean critical Cl dose also increased when temperature was greater than 8.0°C, from 3.2 to 3.7 mg/L. However, temperature was also positively correlated with TOC (*r*=0.34, p<0.001) as well as total coliforms (*r*=0.73, p<0.001), which is similar to previous findings in the literature (Chaulk, 2011; Fabris et al., 2008). Furthermore, this indicates that NOM property concentrations and bacterial numbers could influence the mean critical Cl dose observed.

Bacterial counts showed significant thresholds with critical Cl dose (Table 4), including *E. coli* (21 MPN, r^2=0.12) and total coliforms (101 MPN, r^2=0.09). The mean critical Cl dose observed increased from 3.3 to above 4.1 mg/L when bacterial numbers exceeded the threshold values. Bacterial counts were positively correlated to turbidity (*r*=0.91, p<0.001) as well as TSS (*r*=0.83, p<0.001). These results are similar to those found previously (Karikari and Ampofo, 2013; LeChevallier et al., 1981) which suggest elevated turbidity can indicate higher bacterial numbers due to increased attachment surfaces from particulate matter. It was also suggested that increased turbidity as well as bacterial numbers can greatly affect dose necessary for oxidation (LeChevallier et al., 1981).

Hierarchical Structure with Water Quality Variables

Hierarchical structure was found to exist between critical Cl dose, turbidity, and pH in the RT analysis (Figure 3). When evaluating the entire dataset, turbidity (16.2 NTU) was the first predictor and explained 23% of the variation in critical Cl dose. When turbidity was less than 16.2 NTU, then pH (8.15 SU) became an important predictor of critical Cl dose and explained an additional 12% of the variation in critical Cl dose. Collectively, the overall RT model explained 35% of the variation in critical Cl dose and identified three sub-groups of data for mean critical Cl dose observed. These sub-groups included (1) the lower mean (±2 standard deviations) critical Cl dose (3.4±1.0 mg/L) observed when turbidity and pH were less than 16.2 NTU and 8.15 SU, respectively, (2) moderate mean critical Cl dose (3.8±0.7 mg/L) observed when turbidity was less than 16.2 NTU but pH exceeded 8.15 SU, and (3) higher critical Cl dose (4.3±1.4 mg/L) observed when turbidity exceeded 16.2 NTU (Figure 3).

Decision Tree for Critical Cl Dose (Where Residuals Started to Accumulate)

From the myriad of statistical analyses, a decision tree was developed which could help guide Cl dosing strategies at Beaver Lake (Figure 4) if the dose required before residuals start to accumulate was of interest. This tree identifies two key water quality parameters, turbidity and pH, which were found previously in RT and nCPA to be important predictors in critical Cl dose. An operator could walk through a series of questions regarding typically daily monitored parameters (e.g., turbidity and pH) to determine what range of critical Cl dose to apply. As shown in Figure 4, the operator would first determine:

- What is the turbidity for the day, and is it greater than or less than 16 NTU?
- What is the pH, and is it greater than or less than 8.2 SU?

If the turbidity was less than 16 NTU and pH was less than 8.2 SU, the mean critical Cl dose was 3.4 mg/L, but the operator could expect the critical Cl dose before residuals begin to accumulate to be from 2.4 to 4.4 mg/L Cl. For turbidity greater than 16 NTU and pH greater than 8.2 SU, critical Cl dose increased with increasing pH (r^2=0.26, p=0.002), which the operator could then use this relationship to estimate what the necessary critical Cl dose using the following equation:

$$\text{Critical Cl Dose (mg/L)} = (0.61*\text{pH}-1.48)$$

Additionally, if turbidity was elevated, such as during a storm event where turbidity was greater than 16 NTU, the operator could expect an increase in the mean critical Cl dose to 4.3 mg/L. However, the critical Cl dose where residuals begin to accumulate could range from 2.9 to 5.7 mg/L Cl.

Mean Cl Demand

Source Water Quality Correlations

The mean Cl demand after the dose where residuals started to accumulate (based on nCPA) varied from 0.60 to 3.48 mg/L across the assays performed on the source water from Beaver Lake (Table 2). The mean Cl demand was less than 2 mg/L in almost 80% of the assays performed, and was similar to the range previously reported by BWD (1.5-2 mg/L, M. Dearing, personal communication). The range of mean Cl demand observed (0.60-3.48 mg/L) was also well within the range generally reported in pre-treatment of source waters in the literature (0.2-5.0 mg/L; Warton et al., 2006; Koechling et al., 1998; LeChevallier et al., 1981)

As expected, the mean Cl demand after the critical Cl dose where residuals started to accumulate showed seasonal variation from March 2014 to August 2015 with generally higher demand observed in spring and summer months. Similar behavior has also been noted in the literature (Golfinopoulous et al., 2002; Gallard and Gunten, 2002). The fluctuation in demand was largely influenced by presence of organic matter as a well as increased temperatures, further suggesting the temporal variations in source water quality influenced Cl demand.

The mean Cl demand was positively correlated with many source water quality parameters (Table 3), which had quite variable ranges in measured values (Table 2). As expected, mean Cl demand was found to increase with increasing concentrations of NOM properties, showing positive correlations with TOC (r=0.58, p<0.001), DOC (r=0.82, p<0.001), and UV_{254} (r=0.82, p<0.001) in the source water (Table 3; Figure 5). These relationships agreed with previous studies (Abdullah et al., 2009; Fabris et al., 2008; Gang et al., 2003) and further suggest higher concentrations of organic matter can significantly influence demand in source waters, like Beaver Lake.

The mean Cl demand showed variable relationships with inorganic species measured in the source water samples collected from the intake at Beaver Lake. As expected, the mean Cl demand and Fe (*r*=0.69, p<0.001) were found to be positively correlated (Figure 3). These findings are supported by those found in the literature (Warton et al., 2006; Brezonik and Arnold, 2011; Deborde and Gunten, 2008) which describe rapid oxidation rates of Fe by Cl from its generally highly reactive, soluble, and reduced valence state to its fully oxidized, less soluble state. Therefore, in anaerobic conditions, such as those produced in the hypolimnion during summer months, this can foster an increased presence of soluble Fe in the water column, therefore increasing the Cl demand (Valenti, 2008; Knocke et al., 1991; Davison et al., 1982).

The mean Cl demand showed variable relationships with nutrients within source water (Table 3). As expected, mean Cl demand showed positive relationships with total nitrogen (TN) (*r*=0.71, p=0.001) which is in agreement with previous studies that express rapid rates of oxidation of nitrogenous compounds with Cl (Rice and Gomez-Taylor, 1986; Deborde and Gunten, 2008, Brooks, 2009). Additionally, mean Cl demand was positively correlated with SiO_2 (*r* = 0.50, p<0.001) and chlorophyll (*r*=0.23, p=0.05). While not considered directly reactive with Cl (Brezonik and Arnold, 2011), SiO_2 and chlorophyll-a have been identified in previous studies as indicators of algal biomass in source water (Mash et al., 2014; Lewis, 1966), which can influence demand. It was also stated by Lewin (1966) that higher concentrations of SiO_2 can contribute to diatom algal growth due it being a necessary component for shell development. Furthermore, these relationships suggest that mean Cl demand is moderately influenced by algal presence on Beaver Lake.

Some physico-chemical properties were also related to mean Cl demand, while others (e.g., temperature) were not as previously reported in the literature (Brown, 2009; Brezonik and

Arnold, 2011; Work, 2006). As expected, mean Cl demand was positively related to turbidity (Figure 2; *r*=0.64, p<0.001) and TSS (*r*=0.28, p=0.013) which reflects previous findings (LeChevallier, et al., 1981) and further indicates that increased sediment in the water column will also yield an increase in mean Cl demand.

Unexpectedly, mean Cl demand was found to decrease with increasing pH (*r*=-0.41, p<0.001), conductivity (r=-0.49, p<0.001), and alkalinity (*r*=-0.46, p=0.001). This contrasts previous studies (Helmer et al., 1999; Connell, 1997) where it was suggested the more effective species of Cl (HOCl) prevails at pH less than 8 SU. It would be expected that the mean Cl demand would have a positive relationships with pH. Also, it would be expected at greater conductivity, this would result in greater mean Cl demand as Marzio et al. (2005) suggested conductivity can be used to characterize changes in dissolve solids as well as nutrient content within source water. However, one explanation is that conductivity in Beaver Lake decreases during storm events. Furthermore, Brezonik and Arnold (2011) explained rainfall with lower ionic composition in comparison to source water can result in temporary dilution of conductivity in the lake. Additionally, when conductivity was lower in the lake, higher concentrations of turbidity as well as NOM property concentrations were also observed, which could contribute to the demand in the source water.

Additionally, some bacterial counts showed positive relationships with mean Cl demand (Table 3). As expected, *E. coli* and mean Cl demand (*r*=0.28, p=0.003) were positively correlated which is in accordance with previous findings (LeChevallier et al., 1981; Helbling and VanBriesen, 2007). Furthermore, it was explained by Helbling and VanBriessen (2007) that depending on the concentration of coliforms present and potential resistance mechanisms, this can greatly impact Cl demand.

Source Water Quality Thresholds

While several correlations were observed between mean Cl demand and source water quality parameters, thresholds using nCPA were also identified with source water quality (Table 5). Specifically, NOM properties showed significant thresholds with mean Cl demand, including UV_{254} (0.07 cm^{-1}, r^2=0.63), DOC (2.0 mg/L, r^2=0.63), and TOC (2.45 mg/L, r^2=0.33). The mean Cl demand observed increased from 1.2 to almost 2.4 mg/L when NOM property concentrations exceeded the CP values determined by nCPA. These thresholds were also similar to thresholds identified between NOM properties and critical Cl dose where residuals began to accumulate.

The use of nonparametric statistical techniques to evaluate the effects of NOM properties on source water have been documented (Towler et al., 2009; Amy et al., 1987; Gibbs et al., 2006). However, these studies have been more focused on traditional nonlinear regression and do not provide information regarding threshold based responses between Cl demand and NOM properties. However, the threshold for TOC (2.5 mg/L) was similar to values found in the literature (Concerty et al., 2004) where DBP formation potential was found to significantly increase. Additionally, this CP also is similar to TOC concentrations (2 mg/L) where required removal prior to disinfection becomes necessary to limit the potential for DBP formation Stage (USEPA, 2006).

Inorganic species also showed significant thresholds with mean Cl demand (Table 5), including Fe (0.15 mg/L, r^2=0.43) and Mn (0.03 mg/L, r^2=0.10). The mean Cl demand observed noticeably increased from 1.3 to 2.3 mg/L when Fe concentrations exceeded the threshold values determined by nCPA, which was also seen when threshold concentrations for Mn were exceeded and mean Cl demand increased from 1.4 to 1.7 mg/L. This actually contradicts behavior seen for critical Cl dose with increasing Mn concentrations, where there was a decrease in mean critical

Cl dose observed. However, the coefficient of variance (CV) determined for data on either side of the threshold identified by nCPA revealed higher variation at lower Mn concentrations (<0.03 mg/L). This also corresponded with sample dates where higher Fe concentrations were measured. Higher mean critical Cl dose was observed at Fe concentrations > 0.15 mg/L (Table 3), which also coincided with periods when increased concentrations of NOM properties were observed, and Knocke et al. (1991) suggested raw waters containing high levels of NOM in addition to higher Fe and Mn concentrations can greatly contribute to the overall demand of the source water.

Nutrients as well as anions showed significant thresholds with mean Cl demand (Table 4) including TN (0.95 mg/L, r^2=0.61) and SiO_2 (3.50 mg/L, r^2=0.28). The TN threshold showed an increase in mean Cl demand from 1.16 to 1.82 mg/L, whereas the SiO_2 threshold resulted in an increase in mean Cl demand from 1.25 to 1.88 mg/L. While limited studies have been provided which specifically investigate the threshold-based relationships between Cl demand and nutrient content, the TN threshold is actually higher than the values reported previously for TN nutrient targets at Beaver lake (0.4 mg/L) (FTN Associates, 2008).

Some physico-chemical properties showed significant thresholds with mean Cl demand (Table 5), including turbidity (7.9 NTU, r^2=0.49) and TSS (5.5 mg/L, r^2=0.18) as well as pH (7.66, r^2=0.22), conductivity (136 µS/cm, r^2=0.35), and alkalinity (51 mg/L, r^2=0.33). The turbidity and TSS thresholds showed an increase in mean Cl demand from 1.3 to 2.3 mg/L, which was in accordance with previous studies (LeChevallier et al., 1981, Helbling and VanBriesen, 2007). However, the pH, conductivity, and alkalinity thresholds showed a decrease in mean Cl demand from 2.1 to 1.3 mg/L. This could be attributed to storm events, as described previously. Furthermore, higher concentrations of turbidity, TSS, and NOM properties, such as those seen during times when conductivity was lower, could contribute to the higher Cl demand observed.

The sample date also showed a significant threshold with mean Cl demand (189, r^2=0.14) where this threshold value represented early July. The mean Cl demand was shown to decrease from 1.7 to 1.2 mg/L when the threshold value was exceeded, or when the sample date occurred after the beginning of July. Higher mean Cl demand was observed in spring and early summer compared to fall and winter, which is in agreement with previous studies (Golfinopoulous et al., 2002; Gallard and Gunten, 2002) where higher NOM property concentrations occurred during spring and summer, which further contribute to increase in Cl demand.

Bacterial numbers also possessed significant thresholds with mean Cl demand (Table 4), such as *E. coli* (4 MPN, R^2=0.31). The mean Cl demand increased from 1.4 to 2.1 mg/L when bacterial numbers exceeded the threshold value from nCPA. *E. coli* was also positively correlated with TSS (r=0.83, $p<0.001$). This echoes previous statements where with higher turbidity, TSS, and NOM property concentrations, such as those seen during storm events, can also contain greater presence of coliforms, which all collectively can increase the amount of Cl necessary to satisfy demand in source water.

Hierarchical Structure with Water Quality Variables

Hierarchical structure was found to exist between mean Cl demand, turbidity, conductivity, sample date, and TOC in the RT analysis (Figure 6). When evaluating the entire dataset, turbidity (7.9 NTU) was the first predictor and explained 49% of the variation in mean Cl demand. When turbidity was less than 7.9 NTU, then conductivity (138 µS/cm) became an important predictor of mean Cl demand and explained an additional 8% of the variation in mean

Cl demand. Furthermore, if turbidity was less than 7.9 NTU, and conductivity was ≥ 138 μS/cm, then time of year (May) became another important predictor and explained an additional 2% of the variation for mean Cl demand. As shown in figure 6, if turbidity was greater than 7.9 NTU, then TOC (2.65 mg/L) became another important predictor and explained an additional 7% of the variation in mean Cl demand. Collectively, the overall RT model explained 66% of the variation in mean Cl demand and identified five sub-groups of data for mean Cl demand observed, including (1) moderate mean (±2 standard deviations) Cl demand (1.8±0.9 mg/L) observed when turbidity was less than 7.9 NTU and conductivity was less than 138 μS/cm, (2) lower mean Cl demand (1.4±0.8 mg/L) observed when turbidity was less than 7.9 NTU, conductivity was greater than or equal to 138 μS/cm, and time of year was prior to May (3) lower mean Cl demand (1.1±0.6 mg/L) observed when turbidity was less than 7.9 NTU, conductivity was greater than or equal to 138 μS/cm, and time of year was after the first week of May, (4) higher mean Cl demand (2.0±0.8 mg/L) observed when turbidity was greater than 7.9 NTU and TOC was less than 2.65 mg/L and (5) even higher mean Cl demand (2.6±0.9 mg/L) observed when turbidity was greater than 7.9 NTU and TOC was greater than 2.65 mg/L (Figure 6).

Decision Tree for Mean Cl Demand (After the Dose Where Residuals Started to Accumulate)

From the previous analyses, a decision tree was developed which could help assess expected mean Cl demand at Beaver Lake (Figure 7). This tree identifies four key water quality parameters, turbidity, conductivity, sample date, and TOC, which were found previously in RT and nCPA to be important predictors in mean Cl demand. An operator could walk through a series of questions regarding typically daily monitored parameters (e.g., turbidity, conductivity, and TOC) to determine what the general mean Cl demand would be in the source water at Beaver Lake. As shown in Figure 7, the operator would first determine:

- What is the turbidity for the day, and is it greater than 8 NTU?
    1) If yes, what is the TOC for the day, and is it greater than 2.65 mg/L?
    2) If no, proceed to subsequent questions below:
- What is the conductivity for the day, and is it ≥ 138 µS/cm?
- What is the date, and is it before or after the beginning of May?

If the turbidity was less than 8 NTU and conductivity was less than 138 µS/cm, the mean Cl demand was 1.8 mg/L, but the operator could expect the mean Cl demand to be from 0.9 to 2.7 mg/L Cl. For turbidity less than 8 NTU, conductivity greater than or equal to 138 µS/cm, and date occurring before the beginning of May, the mean Cl demand would be 1.4 mg/L, but could range from 0.6 to 2.2 mg/L Cl. If the same conditions were present except for the date occurring after the beginning of May, the operator could expect a mean Cl demand of 1.1 mg/L, but this could range from 0.5 to 1.7 mg/L. Conversely, if the turbidity was greater than 8 NTU, but TOC was less than 2.65 mg/L, the mean Cl demand was 2.0 but ranged from 1.2 to 2.8 mg/L Cl. If the turbidity was greater than 8 and also greater than 2.65 mg/L, the operator could expect a mean Cl demand of 2.6 mg/L, but this could range from 1.7 to 3.5 mg/L Cl.

Conclusions

This study has demonstrated the application of parametric (Pearson correlation) and nonparametric statistical techniques (nCPA, RT analysis) when evaluating relationships between the critical Cl dose where residuals begin to accumulate, the mean Cl demand, and source water quality at the intake to Beaver Water District on Beaver Lake. This information was then used in development of a decision tree, a user-friendly tool, to guide chlorination practices in the pre-treatment of drinking water.

The critical Cl dose and mean Cl demand were observed to be positively correlated with NOM properties (TOC, DOC, and UV_{254}), inorganic species (Fe), and physico-chemical properties (turbidity, TSS). This is similar to what has been seen previously in the literature, suggesting these parameters contribute to the demand of source water at Beaver Lake. Conversely, the critical Cl dose decreased with increasing Mn concentrations, whereas mean Cl demand was not linearly associated. This was thought to be resultant of higher NOM and Fe concentrations present in source water when lower Mn concentrations were observed, possibly explaining the increased critical Cl dose observed during these periods.

The critical Cl dose and mean Cl demand decreased with increasing conductivity, and this is considered to be attributed to storm event conditions were present, possibly diluting ionic composition in source water from rainfall. Also, these periods also coincided with sample dates where higher concentrations of turbidity, TSS, NOM properties, and bacterial counts were present, possibly driving critical Cl dose and mean demand to increase. Furthermore, these observations collectively suggest that critical Cl dose and mean Cl demand are moderately impacted by storm events at Beaver Lake

The critical Cl dose and mean Cl demand also possessed several nonlinear, threshold-based relationships with source water quality. The threshold-based relationships explored in this study indicate that NOM property concentrations ranging from 2.0 to 3.0 mg/L TOC, 1.8 to 2.0 mg/L DOC, and 0.07 to 0.08 cm^{-1} UV_{254} were threshold concentrations after which a change in response occurred for critical Cl dose and mean Cl demand, which also reflect values established in the literature for DBP control in drinking water (USEPA, 2006). These results suggest these concentrations could be used as indicators for assessing Cl dosing strategies in pre-treatment of source waters.

Additionally, critical Cl dose and mean Cl demand exhibited changes in response with inorganic species concentrations ranging from 0.15 to 0.23 mg/L Fe and 0.03 to 0.07 mg/L Mn, respectively. The critical Cl dose decreased after this concentration, whereas mean Cl demand increased minimally. The decrease in critical Cl dose could be attributed to reasons stated previously regarding increased Fe and NOM concentrations present during periods of lower Mn (<0.07 mg/L), possibly affecting Mn oxidation.

Physico-chemical property concentrations ranging from 7.9 to 16.2 NTU turbidity and 136 to 153 μS/cm conductivity were significant thresholds, where critical Cl dose and mean Cl demand increased after this range of turbidity, which was expected, but decreased after this range for conductivity. The lower conductivity concentrations where after exceedance the critical Cl dose and mean Cl demand were higher were considered to be representative of more episodic storm events. Therefore, this should be taken into consideration in determining Cl dosing strategies.

According to RT analysis for data collected from March 2014 through August 2015, the strongest contributing factors to the critical Cl dose where residuals began to accumulate, in order of importance, were turbidity (16.2 NTU) and pH (8.15 SU), which explained roughly 35% of the variation in critical Cl dose. This is interesting, considering pH did not become important until turbidity concentrations less than 16 NTU; however, this reflects previous descriptions where critical Cl dose will increase with increasing pH (Brezonik and Arnold, 2011; Work, 2006, Brown, 2009) and furthermore demonstrates that RT can be effective in revealing underlying relationships between source water quality and critical Cl dose.

The strongest predictors of mean Cl demand were turbidity (7.93 NTU), conductivity (138 μS/cm), sample date (May 8th), and TOC (2.65 mg/L), explaining 66% of the variation in mean Cl demand. The thresholds identified by RT were also similar to the thresholds identified individually with nCPA. Interestingly, there was lower mean Cl demand observed after the first week of May; however, this follows general patterns described where higher Cl demand was observed in spring and early summer months (Golfinopoulous, et al., 2002; Gallard and Gunten, 2002) mainly due to increase in NOM property concentrations.

The decision trees developed in this study for critical Cl dose suggested that turbidity and pH are important parameters which should be considered when developing daily dosing strategies for pre-treatment of source water if the critical Cl dose where residuals begin to accumulate was of interest. Additionally, it identified three categories for critical Cl dose ranges which could be applied based on where daily parameter concentrations for turbidity and pH thresholds fell in relation to thresholds determined from RT analysis. This information could then be used by the operator to make more informed estimations for Cl dosing strategies for that day.

Furthermore, the decision tree developed for mean Cl demand suggested that turbidity, conductivity, sample date, and TOC were important parameters which should be considered if mean Cl demand for that day were of interest. Additionally, it identified five categories for mean Cl demand ranges, which could be applied based on where concentrations for these parameters fell in relation to threshold values from RT. Overall, the decision trees developed in this study help to elucidate relationships present which can drive critical Cl dose and mean Cl demand, as well as help provide easy to interpret guidance for operators in determining Cl dosing strategies for source water at Beaver Lake.

Suggestions for Future Work

Initially, this project was focused on evaluating the effects of source water quality on Cl demand at the intake to Beaver Water District, given until 2013, the primary pre-treatment agent for the plant was Cl. However, after 2013, Cl was replaced with ClO_2 in order to reduce the potential for DBP formation and was supplemented with additional Cl when higher demand occurred. Using data collected for Cl demand from March 2014 through August 2015, this was paired with the ClO_2 that was consumed from the pre-treatment point to the front of the plant where residuals were quenched. A positive relationship was revealed between mean Cl demand and ClO_2 consumed (Figure 8) ($R^2=0.22$, $p<0.001$), suggesting there may be similarities in the way these oxidants react with source water. Therefore, using the information from this study, this can be applied to further analysis with ClO_2 data from pre-treatment at BWD, which can be utilized in the development of a decision support system to guide chlorination practices in pre-treatment.

Table 1. Summary of parameters measured in source water samples by Beaver Water District where n represents the number of paired observations between critical Cl dose, mean Cl demand, and source water parameters.

Parameter	Units	n	MDL #	Method	Reference
TOC	mg/L	114	0.2	SM5310B	APHA (2000)
DOC	mg/L	29	0.2	SM5310B	APHA (2000)
UV_{254}	/cm	28	NA	SM 5910	APHA (2000)
Chl-a	µg/L	72	NA	SM 10200 H	APHA (2000)
Temperature	C	116	NA	SM 2550 B	APHA (2000)
pH	SU	116	NA	SM 4500 H+B	APHA (2000)
Conductivity	µs/cm	116	0.38	SM 2510 B	APHA (2000)
Alkalinity	mg/L	49	2	SM 2320 B	APHA (2000)
TN	mg/L	13	0.1	SM 4500-N/ HACH 8075	APHA (2000); HACH (2013)
NH_3-N	mg/L	76	0.08	HACH 8038	HACH (2013)
NO_3-N	mg/L	75	0.016	EPA 300.0	USEPA (1983)
NO_2-N	mg/L	75	0.03	EPA 300.0	USEPA (1983)
TP	mg/L	13	0.01	SM4500-P/ HACH 8048	APHA (2013); HACH (2013)
PO_4-P	mg/L	75	0.04	HACH 8048	HACH (2013)
Mn	mg/L	116	0.02	HACH 8149	HACH (2013)
Fe	mg/L	116	0.01	HACH 8012	HACH (2013)
SiO_2	mg/L	72	1	HACH 8185	HACH (2013)
Cl^-	mg/L	74	0.03	EPA 300.0	USEPA (1983)
F^-	mg/L	72	0.03	SM 4500-F C	APHA (2013)
SO_4^{2-}	mg/L	75	0.17	EPA 300.0	USEPA (1983)
Escherichia coli	MPN	110	1	SM 92223 B	APHA (2013)
Total Coliforms	MPN	115	1	SM 92223 B	APHA (2013)
Turbidity	NTU	116	0.05	SM 2130B	APHA (2013)
TSS	mg/L	76	1	SM 2540 D	APHA (2013)
TDS	mg/L	45	2.2	SM 2540 C	APHA (2013)

Table 2. Summary statistics for critical chlorine (Cl) dose, mean Cl demand, and source water quality parameters collected at times when Cl demand assays were conducted.

Parameter	Units	Min.	Max.	Median	Mean	Std. Dev.
Critical Cl Dose	mg/L	1.80	6.11	3.62	3.65	0.61
Mean Cl Demand	mg/L	0.60	3.48	1.39	1.55	0.63
TOC	mg/L	1.03	3.92	2.18	2.28	0.66
DOC	mg/L	1.33	3.27	1.77	1.90	0.50
UV_{254}	cm-1	0.02	0.13	0.04	0.05	0.03
Chl-a	µg/L	2.53	26.19	8.78	8.79	4.18
Temperature	C	4.44	30.60	20.00	18.83	7.58
pH	SU	6.88	9.22	7.68	7.87	0.59
Conductivity	µs/cm	111	183	146	145	17
Alkalinity	mg/L	35	68	51	51	7
TN	mg/L	0.41	1.11	0.98	0.89	0.23
NH_3-N	mg/L	0.01	0.24	0.13	0.13	0.03
NO_3-N	mg/L	0.00	1.04	0.38	0.43	0.30
NO_2-N	mg/L	0.00	0.02	0.00	0.00	0.00
TP	mg/L	0.00	0.08	0.02	0.03	0.02
Mn	mg/L	0.01	0.20	0.03	0.04	0.04
Fe	mg/L	0.00	0.41	0.05	0.09	0.10
SiO_2	mg/L	0.00	6.00	3.00	3.31	1.85
Cl^-	mg/L	1.88	6.38	3.56	3.57	0.83
F^-	mg/L	0.04	0.10	0.05	0.05	0.01
SO_4^{2-}	mg/L	4.72	14.06	7.54	7.77	1.74
Esherichia coli	MPN	0	373	1	21	66
Total Coliforms	MPN	6	30655	461	1780	4545
Turbidity	NTU	1.11	48.10	3.20	8.30	10.53
TSS	mg/L	1.15	21.60	3.36	4.30	3.37
TDS	mg/L	69	1007	91	112	136.93

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Table 3. Pearson correlation coefficients (r) and level of significance (P) for correlations between source water quality parameters and critical chlorine (Cl) dose and mean Cl demand.

	Cl Dose n=116		Mean Cl Demand n=116	
	r	*P*	*r*	*P*
Sample Date	-0.16	0.085	-0.30	0.001*
TOC	0.20	0.033*	0.58	<0.001*
DOC	0.46	0.013*	0.82	<0.001*
UV_{254}	0.44	0.019*	0.82	<0.001*
Chl-a	0.04	0.722	0.23	0.052
Temperature	0.04	0.703	-0.17	0.074
pH	0.14	0.145	-0.41	<0.001*
Conductivity	-0.26	0.005*	-0.49	<0.001*
Alkalinity	-0.03	0.842	-0.46	0.001*
TN	0.33	0.266	0.71	0.006*
NH_3-N	0.03	0.807	0.16	0.173
NO_3-N	0.04	0.754	0.12	0.297
TP	-0.22	0.463	-0.07	0.809
Mn	-0.23	0.013*	-0.09	0.323
Fe	0.34	<0.001*	0.69	<0.001*
SiO_2	-0.11	0.361	0.50	<0.001*
SO_4^{2-}	-0.09	0.434	-0.39	<0.001*
Esherichia coli	0.14	0.144	0.28	0.003*
Total Coliforms	-0.13	0.167	0.07	0.448
Turbidity	0.40	<0.001*	0.64	<0.001*
TSS	0.05	0.657	0.28	0.013*
TDS	-0.16	0.289	-0.06	0.672

Note: * indicates significant relationships (P<0.05).

Table 4. Thresholds determined by nonparametric change point analysis (nCPA) for source water quality parameters in relation to critical chlorine (Cl) dose where residuals begin to accumulate.

Parameter	Units	Threshold	R^2	*P*	Confidence Interval		Mean Critical Cl Dose	
					5%	95%	Below threshold	Above threshold
TOC	mg/L	2.15	0.08	0.028	1.85	3.25	3.46	3.81
DOC	mg/L	1.77	0.31	0.020	1.73	2.33	3.53	4.13
UV_{254}	/cm	0.08	0.39	0.002	0.06	0.08	3.61	4.46
Temperature	°C	8.0	0.08	0.026	6.7	25.3	3.16	3.71
Conductivity	µS/cm	153	0.11	0.010	144	168	3.78	3.35
Mn	mg/L	0.07	0.08	0.019	0.05	0.10	3.73	3.31
Fe	mg/L	0.23	0.18	0.001	0.14	0.28	3.55	4.32
Esherichia coli	MPN	21	0.12	0.005	3	33	3.57	4.14
Total Coliforms	MPN	101	0.09	0.038	10	7159	3.27	3.74
Turbidity	NTU	16.2	0.25	0.001	14.4	25.6	3.51	4.31

Table 5. Thresholds determined by nonparametric change point analysis (nCPA) for source water quality parameters in relation to mean Cl demand after the dose where residuals begin to accumulate.

					Confidence Interval		Mean Cl Demand	
Parameter	Units	Threshold	R^2	*P*	5%	95%	Below threshold	After threshold
Sample Date		189	0.14	0.002	124	197	1.71	1.22
TOC	mg/L	2.45	0.33	0.001	2.45	3.75	1.31	2.06
DOC	mg/L	2.0	0.63	0.001	1.94	2.60	1.23	2.39
UV_{254}	/cm	0.07	0.63	0.001	0.06	0.08	1.23	2.26
pH	SU	7.66	0.22	0.001	7.60	8.09	1.85	1.26
Conductivity	µS/cm	136	0.35	0.001	122	138	2.14	1.32
Alkalinity	mg/L	51	0.33	0.001	45	51	2.14	1.41
TN	mg/L	0.95	0.61	0.012	0.82	1.08	1.16	1.82
Mn	mg/L	0.03	0.10	0.029	0.03	0.10	1.35	1.73
Fe	mg/L	0.15	0.43	0.001	0.13	0.23	1.32	2.29
SiO_2	mg/L	3.50	0.28	0.001	3.50	5.50	1.25	1.88
Esherichia coli	MPN	4	0.31	0.001	4	23	1.36	2.12
Turbidity	NTU	7.9	0.49	0.001	7.8	11.3	1.29	2.29
TSS	mg/L	5.5	0.18	0.003	3.5	7.0	1.42	2.08

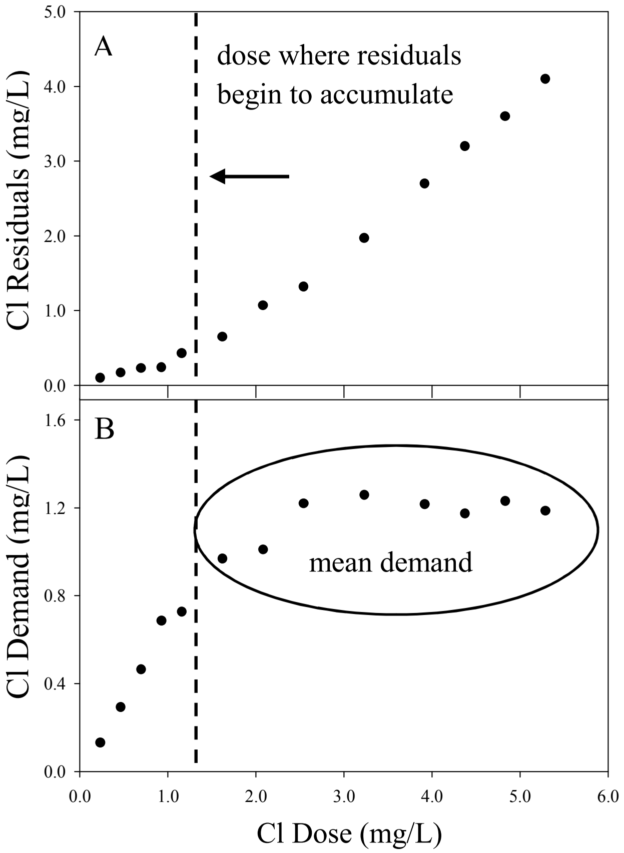

Figure 1. (A) Chlorine (Cl) dose versus residuals where the dashed line represents the dose at which Cl residuals begin to form and accumulate as determined by nonparametric change point analysis (nCPA). (B) Chlorine dose versus demand where the mean demand was determined after the dose where residuals begin to accumulate as determined by nCPA.

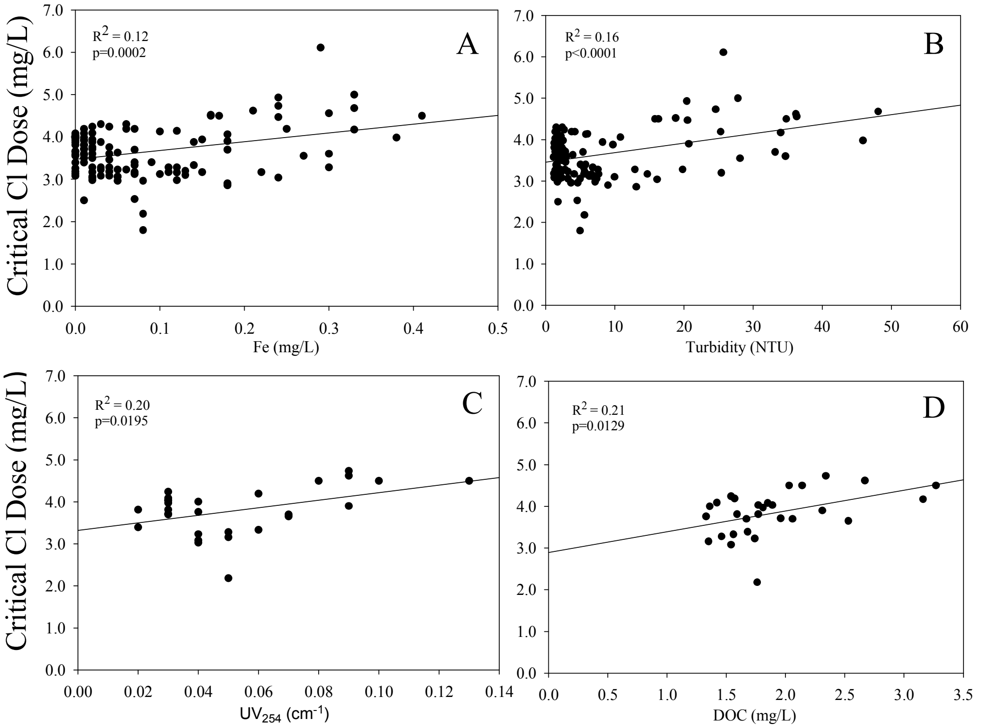

Figure 2. The relation between critical chlorine (Cl) dose and various source water quality parameters at Beaver Lake, including iron (Fe) (A) turbidity (B), ultraviolet absorbance (UV_{254}) (C) and dissolved organic carbon (DOC) (D).

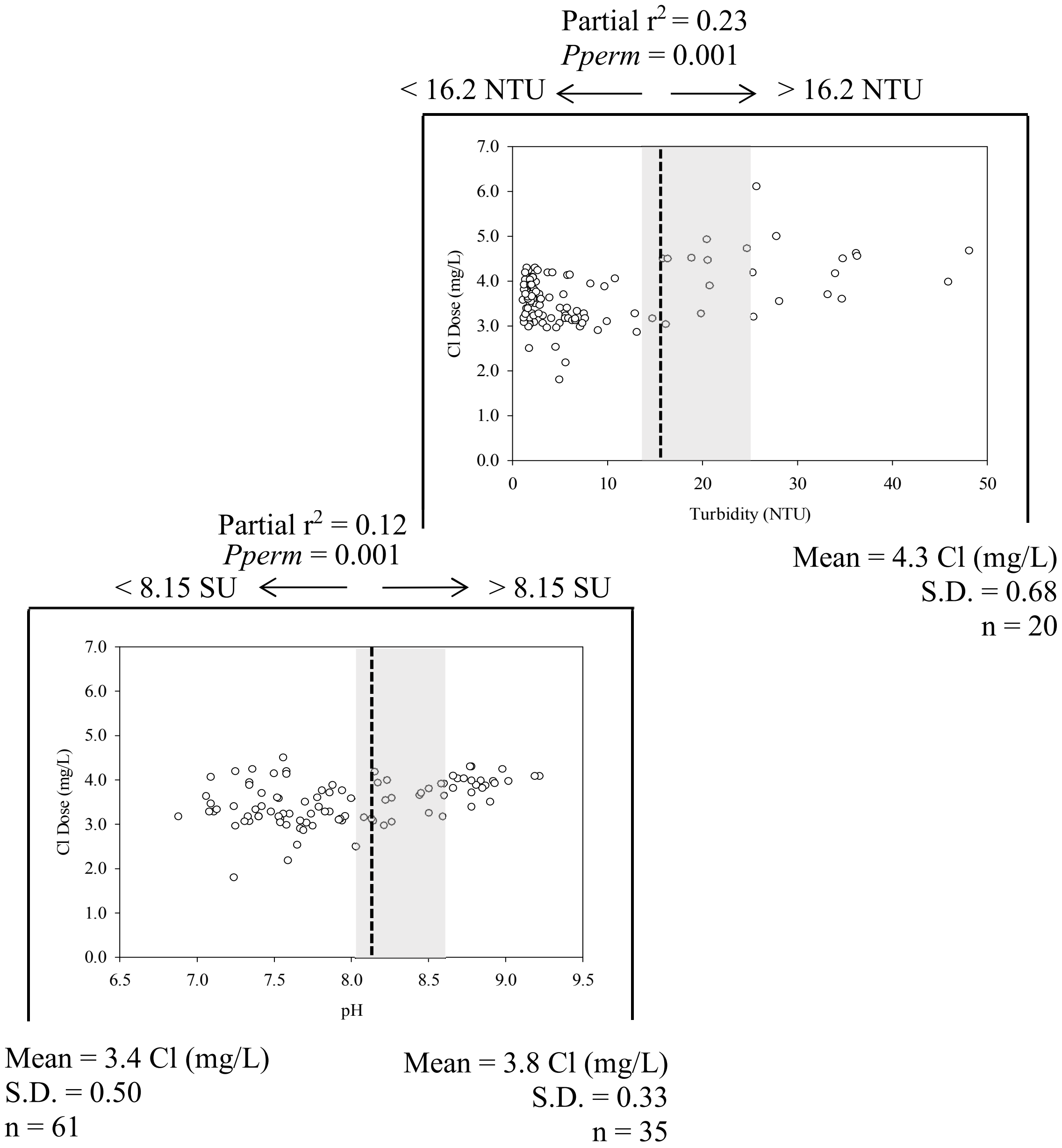

Figure 3. Regression Tree analysis showing hierarchical structure and threshold for turbidity and pH in relation to critical chlorine (Cl) dose. The dashed line represents the threshold, and the grey shaded area represents the 95% confidence intervals around the thresholds as determined by nCPA.

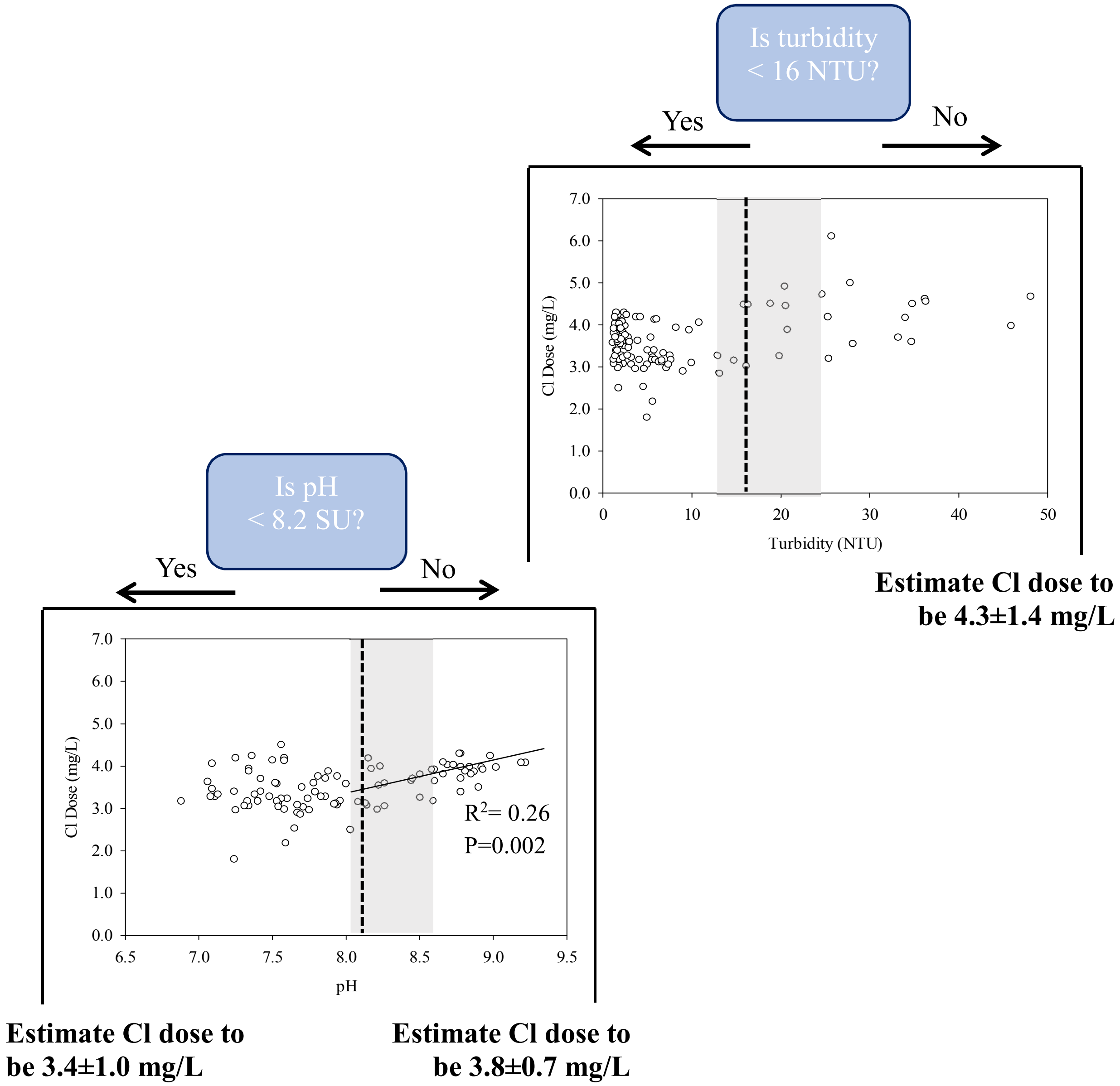

Figure 4. Decision tree which indicates principal water quality parameters and steps in guiding chlorine (Cl) dosing strategies at Beaver Lake. The endpoints represent the suggested range for Cl within a 95% confidence interval.

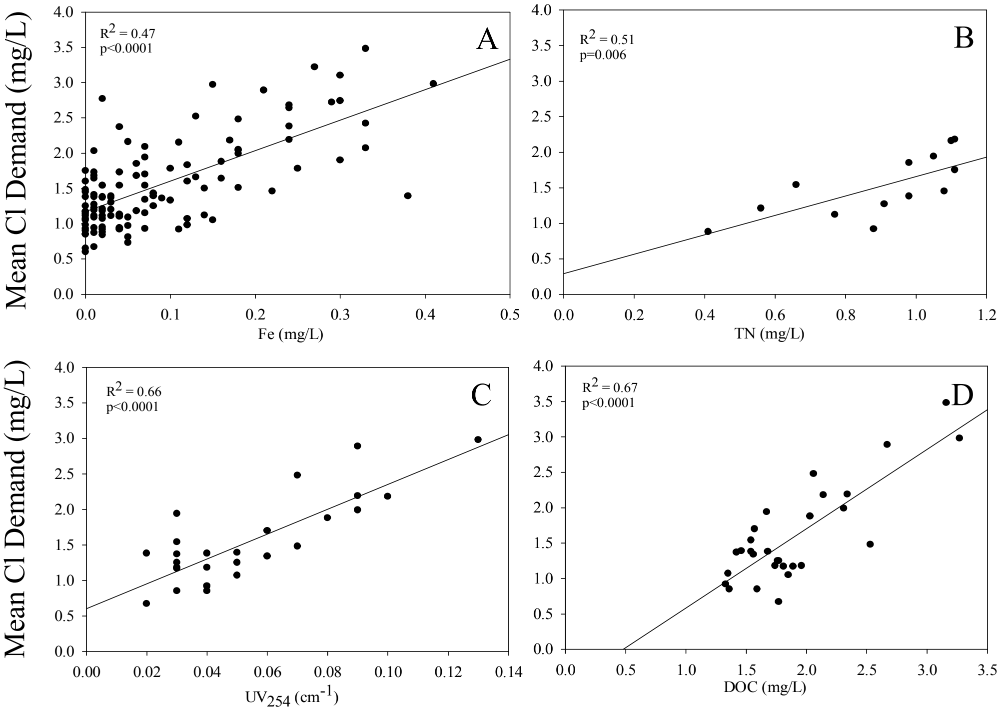

Figure 5. The relation between mean chlorine (Cl) demand and various source water quality parameters at Beaver Lake, including iron (Fe) (A), total nitrogen (TN) (B), ultraviolet absorbance (UV_{254}) (C), and dissolved organic carbon (DOC) (D).

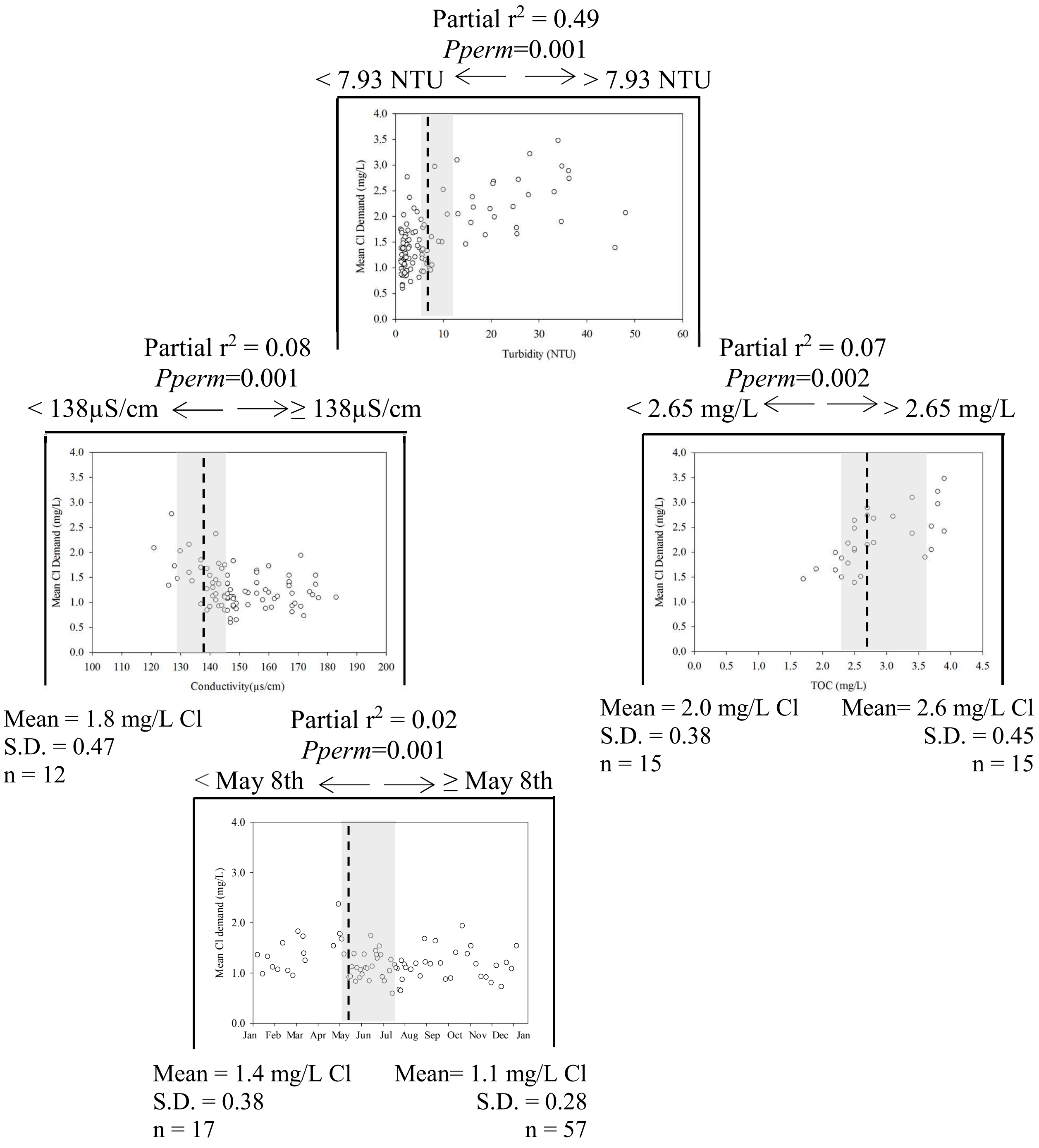

Figure 6. Regression Tree analysis and thresholds for turbidity, conductivity, date, and total organic carbon (TOC) in relation to mean chlorine (Cl) demand. The dashed line represents the threshold and the grey shaded area represents the 95% confidence intervals around the thresholds as determined by nCPA.

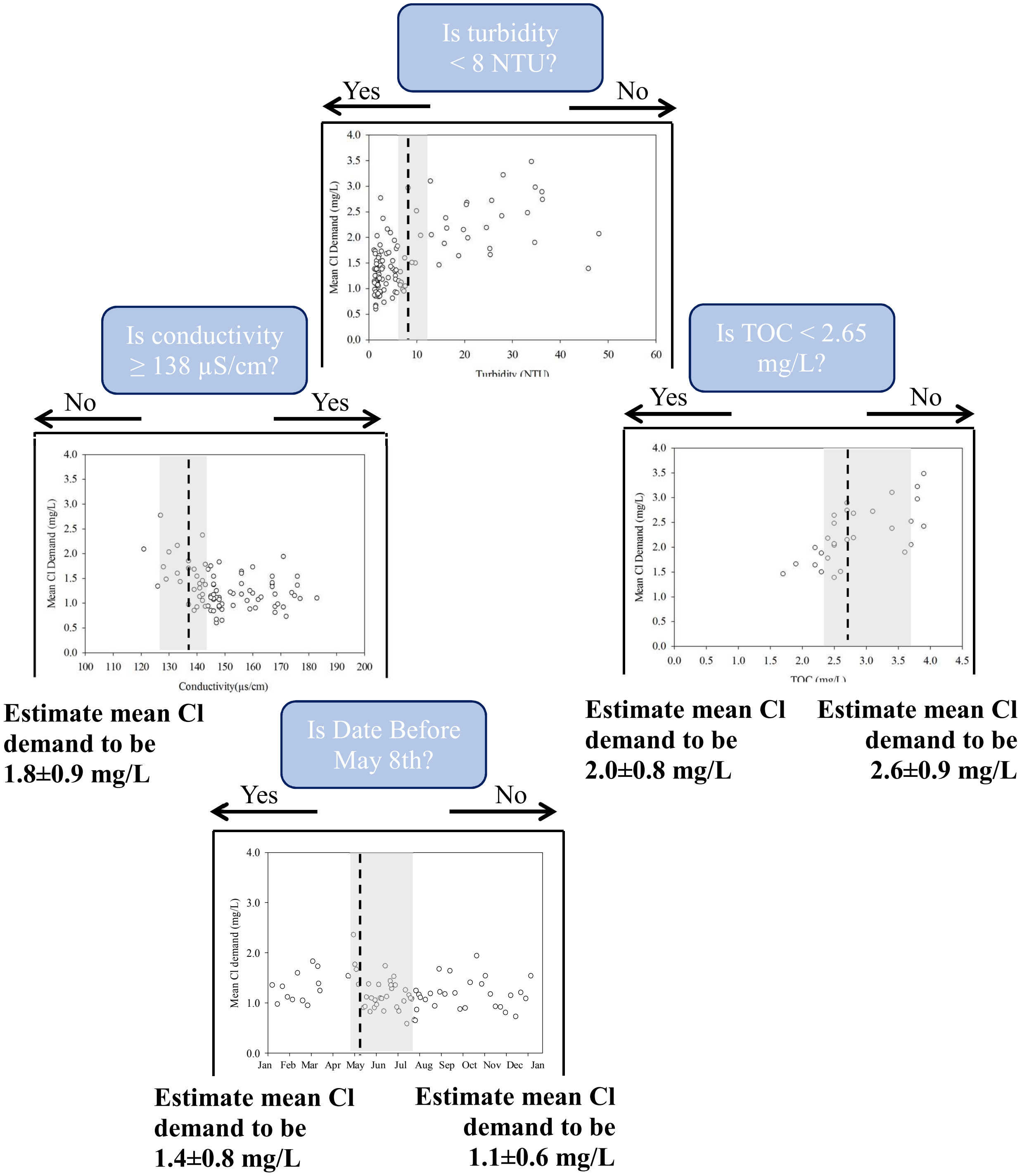

Figure 7. Decision tree which indicates principal water quality parameters in assessing expected mean chlorine (Cl) demand at Beaver Lake. The endpoints represent the suggested range for Cl within a 95% confidence interval.

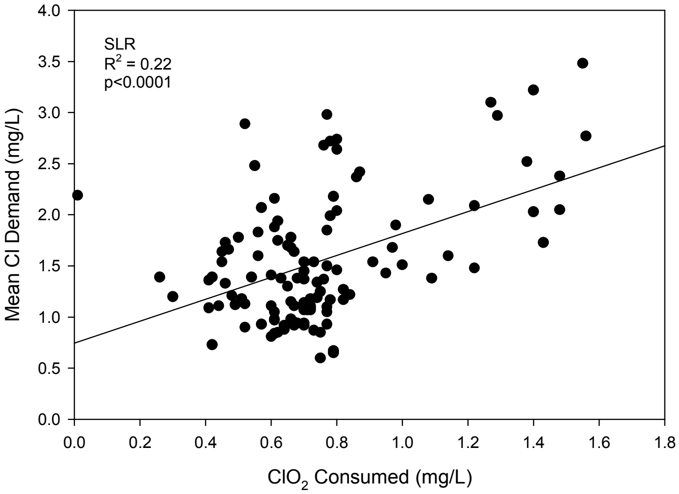

Figure 8. The relation between mean chlorine (Cl) demand observed and chlorine dioxide (ClO_2) consumed from the pre-treatment building to the front of the treatment plant at Beaver Water District from March 2014 to August 2015.

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