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To:	Amy Blain – City of Longview	**Date:**	June 25, 2015
From:	Stephen Booth, Michael Hallett – Confluence	**Project:**	Softening Alternatives & Baltimore Street Water Quality Evaluation
Cc:	Melinda Friedman, Andrew Hill – Confluence	**Subject:**	Bench-Scale CDD Study - Draft

Introduction and Objectives

The four production wells serving the Mint Farm Regional Water Treatment Plant (MFRWTP) contain various naturally-occurring constituents that exert different levels of chlorine demand and cause different rates of chlorine decay. Chlorine demand characteristics appear to have changed since plant startup, resulting in increased fractions of combined chlorine and intermediate constituents, which can cause taste and odor problems until reactions are complete. The objective of this evaluation was to compare chlorine demand and decay (CDD) characteristics of each production well and to assess the relative preference of wells with respect to minimizing combined chlorine species and producing the most stable free chlorine residual. This information may be used by the City to modify operations and preferentially use the production well(s) that produce the most aesthetically pleasing water and/or to determine if additional treatment should be considered for some or all of the wells to address taste and odor complaints.

Testing Approach

CDD curves were developed for each production well by collecting finished water samples from the MFRWTP with only one well in operation at a time. Free and total chlorine residuals were then tracked as a function of holding time with "T = 0" corresponding to the finished water as it enters the distribution system. Monochloramine analyses were performed in the field and at the Confluence laboratory and samples at selected holding times were also submitted to a certified laboratory (ALS Environmental) for total Kjeldahl nitrogen (TKN) and ammonia. Raw water samples were also collected (upstream of chlorination) to characterize water quality for each well. Applied chlorine doses for each well were determined from manufacturer specifications of the hypochlorite bulk solution and through calibration column drawdown measurements.

Results and Discussion

Raw Water Quality

Raw water quality for each of the production wells is presented in Table 1. Raw water samples were collected on May 5 (PW1 and PW2) and May 6 (PW3 and PW4), 2015. Organic nitrogen was calculated by subtracting ammonia from the corresponding TKN value for each well water. The well waters are similar in terms of TKN, organic nitrogen, and silica levels. PW2 has the highest level of ammonia, followed by PW3 and PW4, and PW1 with the lowest level of ammonia. PW2 also has the highest level of iron and PW1 the lowest level of iron.

Table 1. Raw Water Quality of Production Wells

Parameter	PW1	PW2	PW3	PW4
TKN (mg/L as N)	0.48	0.58	0.51	0.62
Total Ammonia (mg/L as N)	0.227	0.388	0.295	0.29
Organic Nitrogen (mg/L as N)	0.25	0.19	0.22	0.33
Arsenic (mg/L)	0.0044	0.0041	0.0049	0.0059
Iron (mg/L)	0.822	1.74	1.24	0.92
Manganese (mg/L)	0.563	0.585	0.745	0.557
Silica (mg/L as SiO_2)	53.3	52.7	52.4	51.6

Ammonia and Chlorine Demand

Ammonia and chlorine dose data for each production well are presented in Table 2. A reasonably consistent chlorine-to-ammonia ratio of between 21 and 23 is used for all production wells. A chlorine-to-ammonia ratio of 10 is often considered adequate to achieve breakpoint chlorination of ammonia. The higher chlorine-to-ammonia ratio used by the City is likely required due to the presence of organic nitrogen and, to a lesser extent, other naturally-occurring constituents in the well waters such as iron, manganese, sulfides, and other organics.

Table 2. Ammonia and Chlorine Dose of Production Well Waters

Well	Ammonia (mg/L as N)	Chlorine Dose (mg/L as Cl_2)	Chlorine:Ammonia Ratio
PW1	0.227	5.4	23.9
PW2	0.388	8.3	21.4
PW3	0.295	6.6	22.3
PW4	0.290	6.4	21.9

Tables 3 presents the chlorine demand for each production well water, calculated as the dose less the free chlorine residual measured at a given holding time. The vast majority of chlorine demand occurred during the contact time that occurred through the filters and associated piping to the system point-of-entry (shown as "initial" in Table 3). Subsequent chlorine decay was slower and lower in magnitude. PW1 had the lowest level of ammonia and the lowest chlorine demand. PW2 had the highest chlorine demand and also the highest level of ammonia. PW3 and PW4 had similar levels of ammonia, between that of PW1 and PW2, and have essentially the same chlorine demand.

Table 3. Chlorine Demand of Production Well Waters

	Chlorine Demand (mg/L as Cl_2)[1]			
Well	**Initial (T=0)**	**30 min**	**24 hrs**	**96 hrs**
PW1	4.2	4.2	4.4	4.5
PW2	6.9	6.9	7.1	7.2
PW3	5.2	5.1	5.3	5.4
PW4	5.1	5.1	5.2	5.4

Notes:

1. Chlorine dose less free chlorine residual measured at given holding time.

CDD Curves

CDD curves for production wells 1 through 4 are presented in Figures 1 through 4, respectively. The significant difference between free and total chlorine residuals, especially within the first few hours of holding time, indicates the formation of a significant quantity of combined chlorine. The combined chlorine species may include monochloramine, di- and tri-chloramine, and any organo-chloramines formed by the reaction between organic nitrogen and chlorine. In the absence of organic nitrogen the breakpoint reactions typically require several minutes to a couple of hours to essentially reach completion. One of the indications that the breakpoint reactions have completed is the convergence of the free and total chlorine residual curves, so that the difference is $\leq$ 0.1 mg/L. In the presence of organic nitrogen, organo-chloramine derivatives can be formed, contributing to combined chlorine. Chlorine oxidation of these intermediates occurs more slowly than with free ammonia, resulting in extended periods of combined chlorine in excess of 0.1 mg/L.

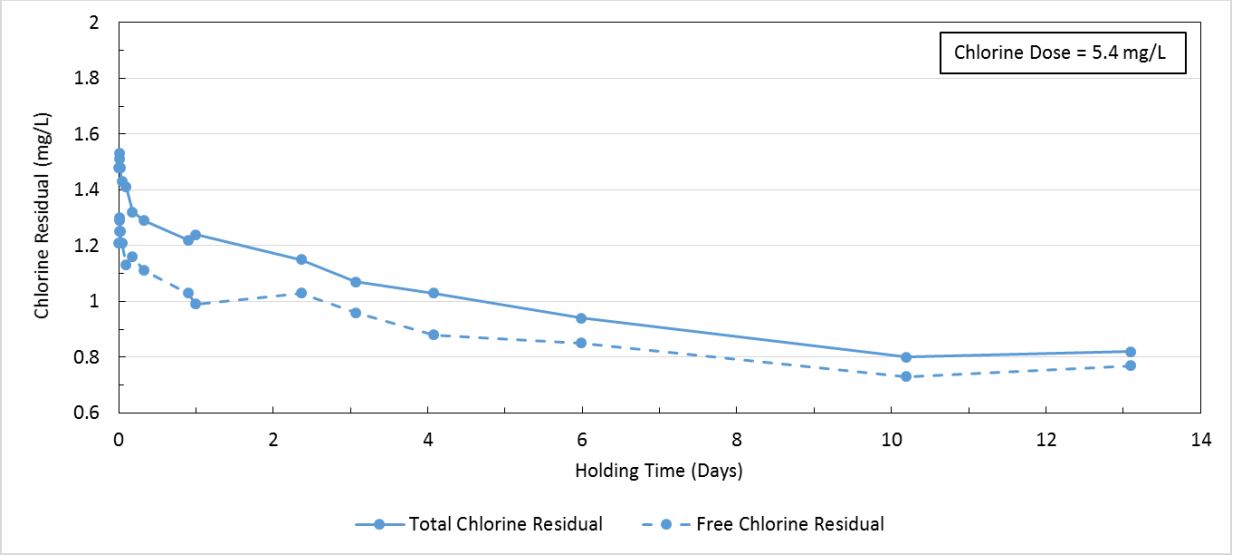


Figure 1. CDD curves for PW1.

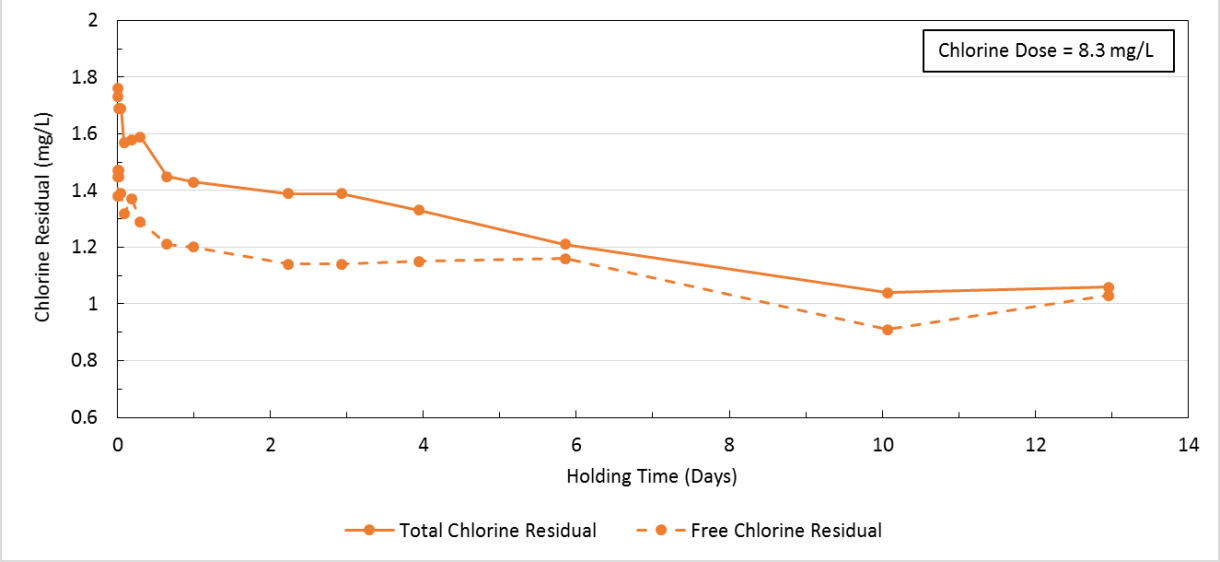


Figure 2. CDD curves for PW2.

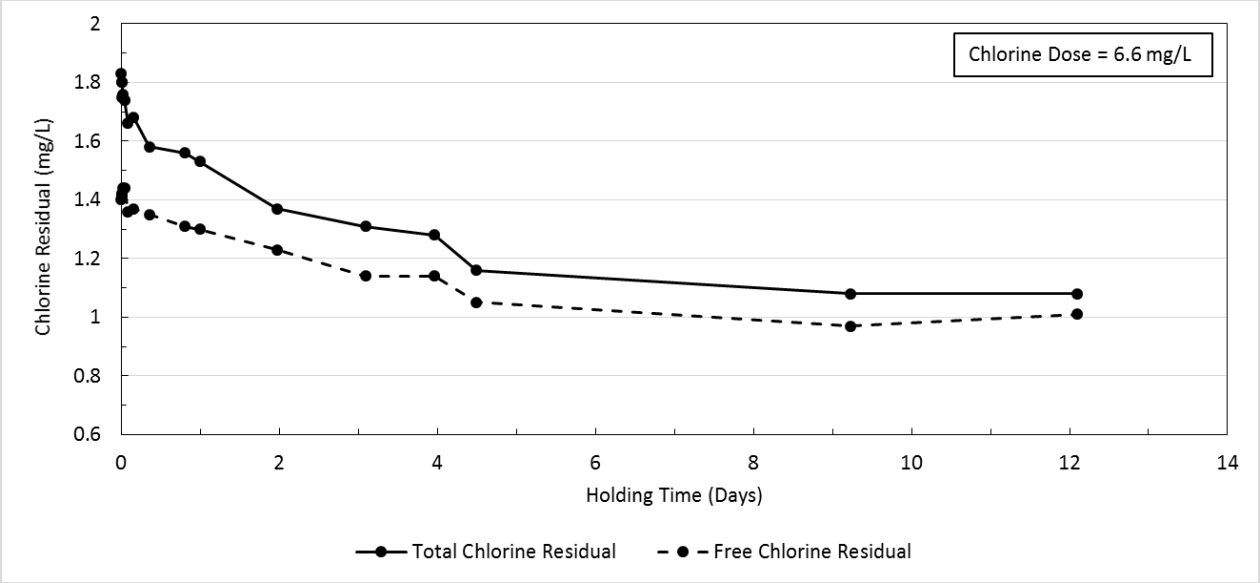


Figure 3. CDD curves for PW3.

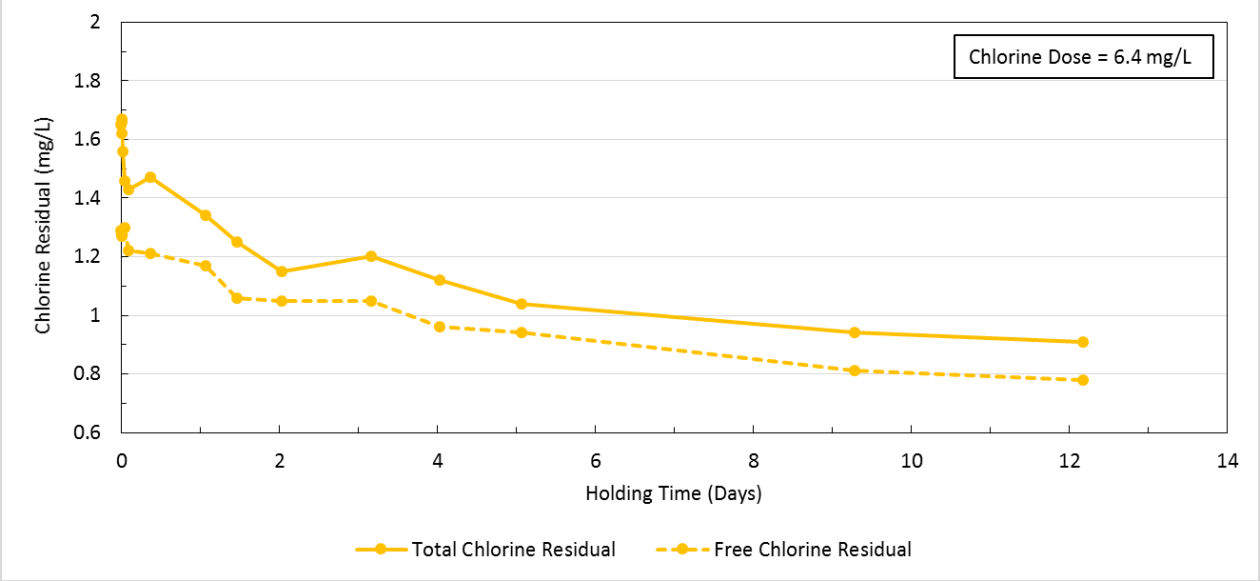


Figure 4. CDD curves for PW4.

First-order free chlorine decay coefficients calculated using the decay curves presented above are presented in Table 4. PW1 and PW4 appeared to have somewhat higher decay rates compared to PW2 and PW3, however, none of the decay coefficients were significantly different from the others and these decay coefficients are essentially the same at the 95% statistical confidence level. These decay coefficients reflect bulk water free chlorine reactions and higher rates of decay would be expected in the actual distribution system due to the contribution of inner pipe walls, scale and sediment, and biofilm, to the overall CDD.

Table 4. First Order Free Chlorine Decay Coefficients

Production Well	First-Order Decay Coefficient (1/hour)
PW1	0.89
PW2	0.67
PW3	0.77
PW4	0.91

Combined chlorine residuals for each production well are presented in Figure 5. In general, the highest levels of combined chlorine occurred within the half hour of holding time and then gradually decreased over time. Combined chlorine residuals generally decreased after one day, although significant levels of combined chlorine persisted for several days for all four well waters. PW2 had the highest levels of combined chlorine from approximately one day through four days of holding time. After four days of holding time, combined chlorine residuals were similar among the four production wells, although the combined chlorine residual for PW4 water remained consistently higher than that of the other well waters and PW1 had the lowest levels.

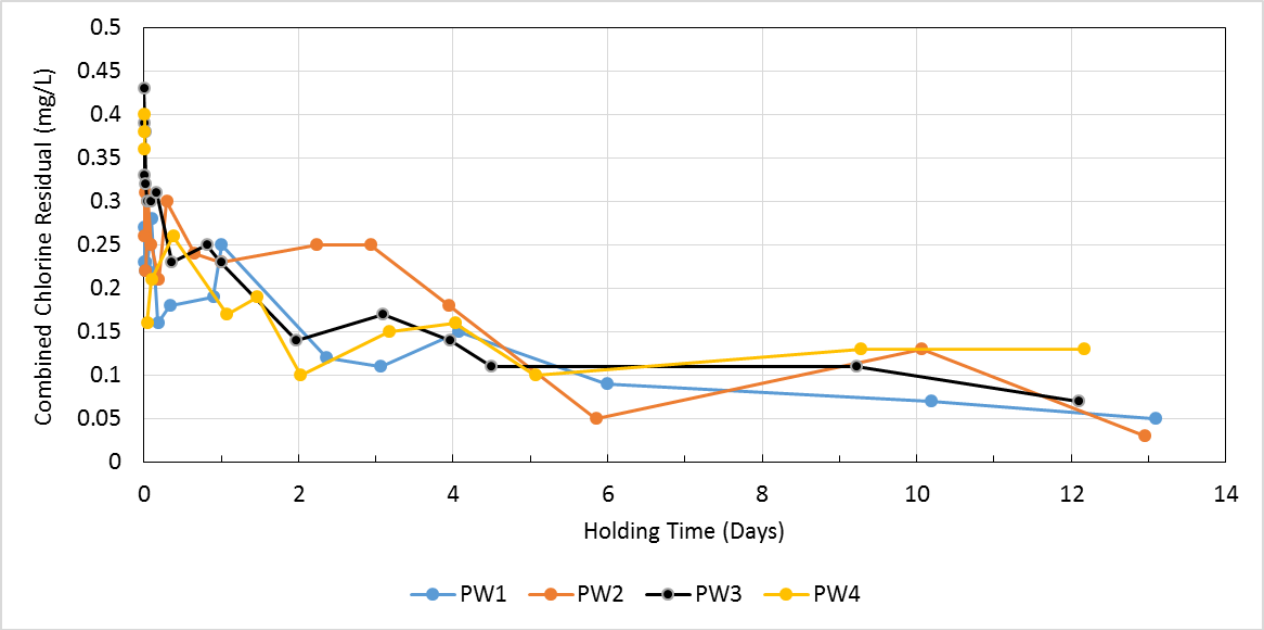


Figure 5. Combined chlorine residual profiles for the production wells.

Figure 6 presents the maximum combined chlorine residual determined for each production well over the course of the 12-day CDD test. The holding time corresponding to that maximum is shown beside each production well number on the x-axis. PW1 had the lowest level of combined chlorine and PW2 water was only slightly higher. PW3 and PW4 had higher levels of maximum combined chlorine.

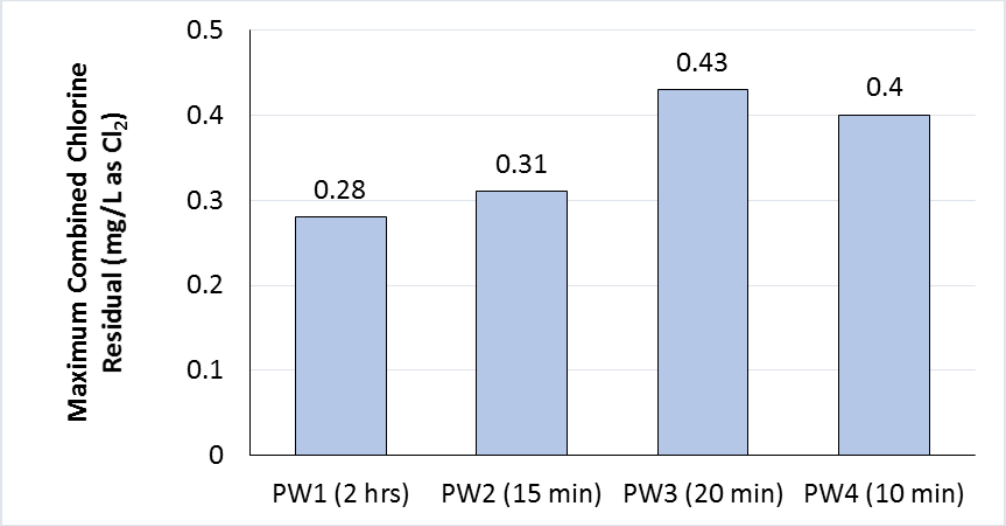


Figure 6. Maximum combined chlorine residuals determined during CDD tests.

Figure 7 presents the holding time required to achieve a combined chlorine residual of $\leq$ 0.1 mg/L, indicating the free and total chlorine residuals are essentially the same and the breakpoint reactions had completed. PW1 and PW2 had the lowest time, whereas, PW3 was higher and PW4 always remained slightly above 0.1 mg/L. While there are differences among the well waters, all of the wells required a relatively long time to complete the breakpoint reactions compared to the average water age of the City's system of approximately two to three days.

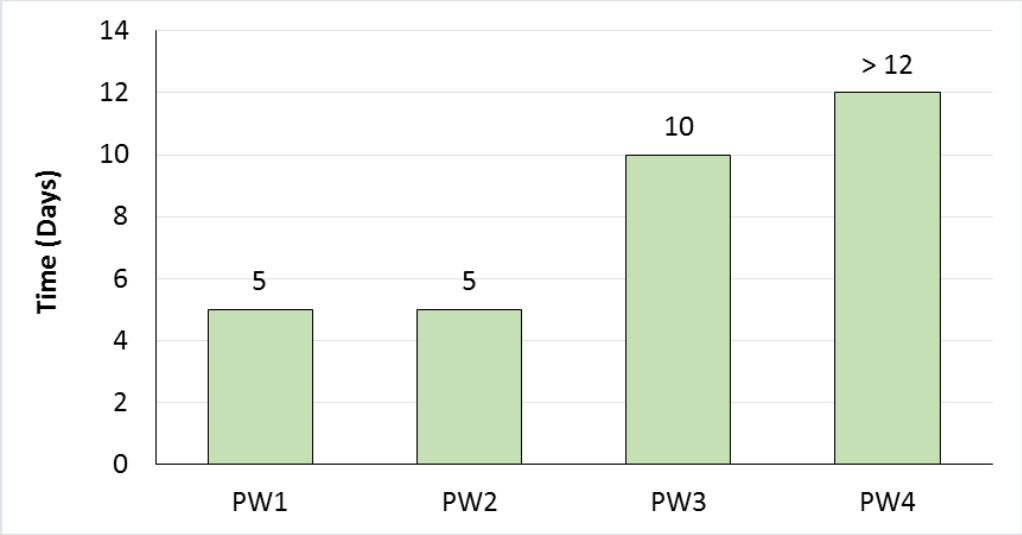


Figure 7. Time to achieve combined chlorine residual $\leq$ 0.1 mg/L during CDD tests.

Chloramine Species

Combined chlorine represents a variety of chlorinated nitrogen compounds, including monochloramine, di-chloramine, tri-chloramine, and various organo-chloramine species. The di- and tri-chloramine compounds are responsible for objectionable taste and odor. The monochloramine portion of the combined chlorine residual was measured at selected times during this evaluation. Subtracting these measurements

from the same-sample combined chlorine results in the sum of the di-, tri-, and organo-chloramines. Further distinction among these "other chloramine" compounds (e.g., their relative concentration and contribution to taste and odor) cannot be performed; however, all three are considered undesirable.

The concentration of monochloramine and the other chloramine species at selected holding times is presented in Figure 8. Figure 8a presents these data at a holding time of approximately 15 minutes. PW1 water had the lowest concentration of both monochloramine and the other chloramines, whereas, PW4 had the highest level of the other chloramines. At a holding time of four hours, the level of the other chloramines had been significantly reduced for PW1 and PW2. On the other hand, similar levels of these other chloramine species continued to persist for PW3 and PW4. After two days of holding time PW1 had a similar level of combined chlorine, PW2 had a higher level, whereas, PW3 and PW4 had much lower levels of the other chloramine species, all compared to the 4-hour holding time. After four days of holding time, the composition of chloramine species and the overall level of combined chlorine residuals were relatively similar for all four production wells. The production of objectionable chloramine species appears to be highest in the first few hours following chlorination and the chloramine profile becomes more similar for all of the production wells after an extended holding time (i.e. 2 to 4 days).

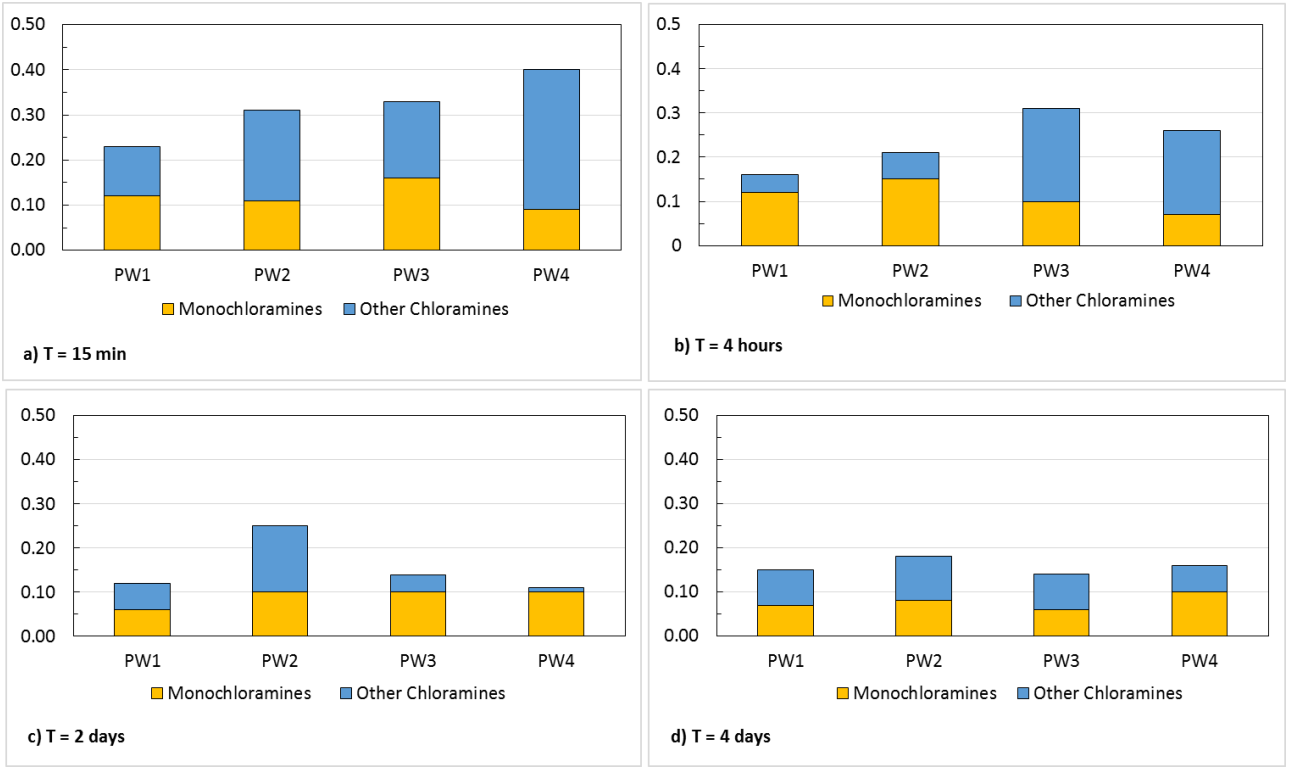
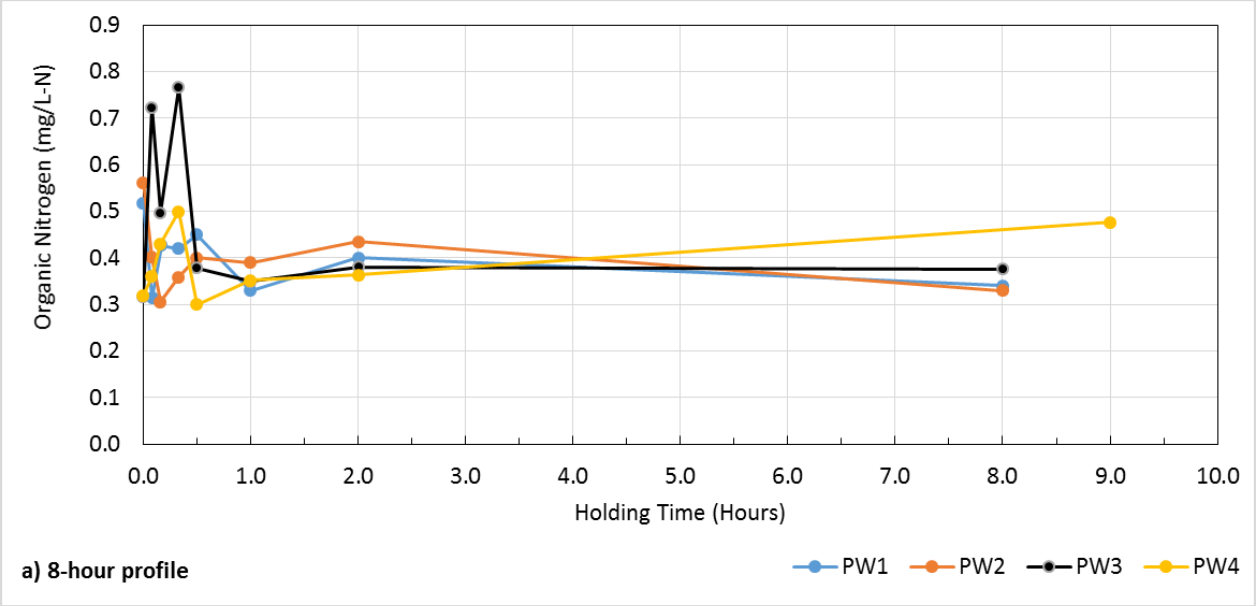


Figure 8. Chloramines species (in mg/L) at selected holding times for each production well.

Organic Nitrogen

The organic nitrogen profiles for each of the production wells is presented in Figure 9.



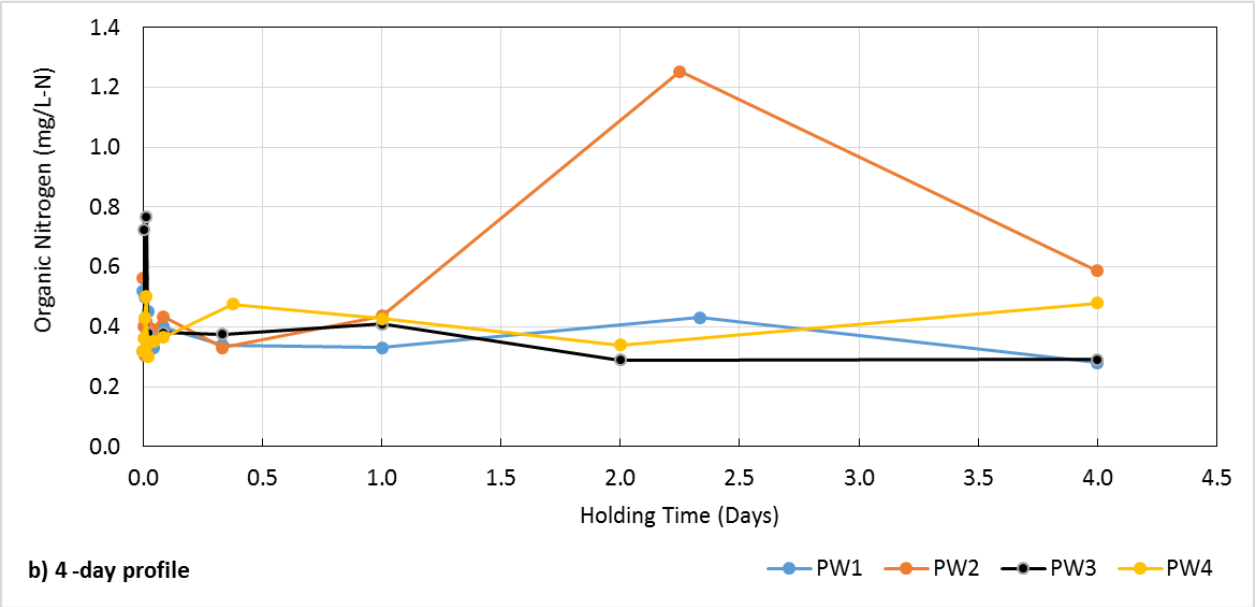


Figure 9. Organic nitrogen profiles for the production wells.

Organic nitrogen was calculated by subtracting the ammonia concentration from the corresponding TKN value. In the finished water the concentration of ammonia for all four production wells was below the method reporting limit and would normally have been reported as not detected. The laboratory provided estimates of the ammonia concentration when it was detected between the method detection limit of 0.02 mg/L and the minimum reporting level of 0.05 mg/L. This approach allowed estimates of the ammonia concentration to be included in the calculations but introduced a higher level of variability in these data because they were lower than normally reported by the lab. The same approach was used for the TKN data when its concentration was between the method detection limit of 0.08 mg/L and the minimum reporting level of 0.4 mg/L. Approximately half of the TKN data were between these two levels and hence exhibit an increased degree of variability.

The variability in the organic nitrogen data, particularly within the first hour of holding time, may be due to the reduced analytical accuracy at these low levels of organic nitrogen. Given the analytical limitations, it was not possible to determine the extent of any meaningful differences in the organic nitrogen profiles among the four production wells. The data point for PW2 at a holding time of 2.25 days is an outlier (Figure 9b). While organic nitrogen significantly interferes with rapid completion of the breakpoint reactions it is not significantly oxidized or degraded by chlorine and remained essentially unchanged after four days of holding time (Figure 9b).

Conclusions

The overall CDD characteristics are generally similar for the four production wells with regard to free chlorine decay rates, the level of TKN and organic nitrogen, and each of the wells forms some level of combined chlorine, likely including the di- and tri-chloramine species. The production well waters do differ with respect to chlorine demand and ammonia concentrations, and the extent of combined chlorine residuals formed. Table 5 presents a summary of key CDD characteristics of the production wells and ranks the wells in order of preference based on these data.

Table 5. Comparison of Key CDD Characteristics among Production Wells

CDD Characteristic	PW1	PW2	PW3	PW4	Ranking[1]
Initial chlorine demand (mg/L)	4.2	6.9	5.2	5.1	PW1, PW4, PW3, PW2
24-hour chlorine demand (mg/L)	4.4	7.1	5.3	5.2	PW1, PW4, PW3, PW2
Chlorine decay rate (1/hr)	0.89	0.67	0.77	0.91	None[2]
Max. combined chlorine residual (mg/L)	0.28	0.31	0.43	0.40	PW1, PW2, PW4, PW3
Time to complete breakpoint[3] (days)	5	5	10	>12	PW1/PW2, PW3, PW4
Max. other chloramines formed[4] (mg/L)	0.13	0.20	0.21	0.31	PW1, PW2, PW3, PW4

Notes:

1. Ranked in order of preference from left to right.
2. The free chlorine decay rates were not statistically significantly different.
3. Holding time required to achieve combined chlorine residual $\leq$ 0.1 mg/L as Cl_2.
4. Calculated as combined chlorine residual minus same-sample monochloramine residual.

PW1 had the lowest chlorine demand and as such, requires the lowest chlorine dose to achieve the target free chlorine residual. PW1 also formed slightly lower levels of combined chlorine and problematic chloramine species which are a likely cause of consumer dissatisfaction and objectionable taste and odors. For these reasons PW1 is preferred to the other well waters, with regard to CDD characteristics. Despite a higher chlorine demand and corresponding higher required chlorine dose, PW2 is the next most preferred well because of its lower level of combined chlorine residual and slightly lower level of other chloramine species. PW3 is slightly preferred over PW4 due to its lower level of other chloramine species and slightly better time to complete breakpoint reactions. PW3 and PW4 waters were similar with regard to CDD characteristics in this testing.

Operating the production wells in the following order of preference will help to minimize the extent of the formation of undesirable chloramine species and provide the most stable free chlorine residual in the system:

PW1 > PW2 > PW3 > PW4