confluence ENGINEERING GROUP LLC
517 NE 92nd Street, Seattle, WA 98115 ph (206) 527-6832 fx (206) 527-3148 confluence-engineering.com

To:	Jeff Cameron, Amy Blain – City of Longview	**Date:**	March 9, 2016
From:	Stephen Booth, Andrew Hill, Michael Hallett, and Melinda Friedman – Confluence	**Project:**	Softening Alternatives & Baltimore Street Water Quality Evaluation
Cc:		**Subject:**	Organic Nitrogen Removal – Coagulant and Peroxide Addition Technical Memorandum - FINAL

Introduction and Objectives

The City of Longview is investigating measures which could be implemented to mitigate on-going taste and odor (T&O) issues associated with the Mint Farm Regional Water Treatment Plant (MFRWTP) water supply. The City has received customer complaints related to sulfurous and chlorinous T&O. The cause of these has been attributed to two mechanisms: 1) loss of oxidizing conditions (and associated sulfate reversion to sulfides) within low flow areas of the distribution system and in-home plumbing systems; and 2) naturally-occurring organic nitrogen in the raw water, resulting in the formation of chlorinated compounds with objectionable T&O. This bench-scale testing evaluated the effectiveness of coagulant addition and hydrogen peroxide for removing organic nitrogen and reducing the formation of intermediate chloramine species in the MFRWTP water. These tests were performed as a proof-of-concept to determine if additional bench- or pilot-scale testing to further evaluate process performance was warranted.

Testing Approach

A standard jar testing apparatus was used for this testing. Additional details concerning the testing approach are provided below.

Coagulant Addition Testing Plan

For these tests coagulants and sodium hypochlorite were added to the jars. A no-coagulant control was also included. Mixing occurred for a specified time period after the addition of chemicals. The coagulant was added to facilitate removal of organic nitrogen from the water. The coagulated particles aggregated and formed pin-floc as the test progressed. Sodium hypochlorite was added at a dose similar to that currently used at the MFRWTP to oxidize iron and ammonia and produce a target free chlorine residual of 1.2 to 1.5 mg/L. For these tests, a bench-scale filtration apparatus was used to separate the coagulated/flocculated solids from the water. This bench-scale filtration did not adsorb and remove soluble manganese.

Chemical addition and mixing were performed as follows:

1. Add coagulant and rapid mix @ 100 RPM for 30 sec
2. Reduce mixing rate to 40 RPM for 2 minutes
3. Add hypochlorite and continue mixing @ 40 RPM for 5 min
4. Adjust the pH to a target of 7.5 to 8.0 by adding caustic soda (NaOH)
5. Filter the coagulant/flocculated water
6. Perform sampling, as described below

Three coagulants: 1) alum; 2) an aluminum chlorohydrate (ACH) product; and 3) a cationic polymer were included in this testing. Alum and ACH were included in previous bench-scale tests in which silica removal was investigated. Cationic polymer is often used as a coagulant aid and was used in conjunction with alum for one test condition. Chemical dosages are presented in Table 1. The jar numbering system used herein is consistent with the testing plan developed prior to conducting these tests (included as Attachment 1 to this Technical Memorandum). Some test conditions included in that plan were not performed, due to issues described below. Alum, and to a lesser degree ACH, consumes alkalinity and tends to reduce the pH of the water. It follows that more alkalinity is consumed as the coagulant dose is increased, so the pH of coagulation/flocculation varied for each jar, depending on the coagulant type and dose. Caustic soda was used to bring the pH of each jar to the current finished water pH target at the MFRWTP of 7.7.

Table 1. Chemical Dosing Strategy Coagulation Tests

Chemicals	Jar C1 (Control)	Jar C3	Jar C4	Jar C6
Alum dose (mg/L as $Al_2(SO_4)_3$-$14H_2O$)	-	58	58	-
Alum dose (mg/L as Al_2O_3)	-	10	10	-
Cationic Polymer Dose (mg/L as product)[1]	-	-	5	-
ACH Dose (mg/L as product)	-	-	-	17.1
ACH dose (mg/L as Al_2O_3)	-	-	-	10
Hypochlorite Dose (mg/L)[2]	5.5	6.5	5.5	5.5
Target pH	7.5 to 8.0			
NaOH dose (mg/L)	3.5	26.2	26.2	5.7

Notes:
1. Nalcolyte 8105.

Sampling and Analysis Plan for Coagulant Addition Tests

Water from each jar was sampled for the water quality parameters presented in Table 2.

Table 2. Sampling and Analysis Matrix for Coagulant Addition Jar Tests

Parameter	Location of Analysis	Sampling Times
Free and total chlorine residuals[1]	On-site	5 min, 15, min, 30 min, 1 hour, 2 hours, 24 hours, 4 days
Monochloramine	On-site	Periodic
TKN	AMTEST Laboratories	5 min, 30 min, 24 hour
Ammonia, total	AMTEST Laboratories	5 min, 30 min, 24 hour
TOC	AMTEST Laboratories	30 min

Notes:
1. One chlorine demand and decay (CDD) curve prepared for each jar.

Hydrogen Peroxide Testing Plan

A preliminary test to assess hydrogen peroxide reaction chemistry and dose response was performed (Test P1). The objectives of the test included determining hydrogen peroxide demand and decay characteristics and to assess peroxide reactivity with constituents of concern. For this test the following chemical dosing and mixing scheme was used:

1. Add peroxide and mix @ 100 RPM for 30 sec
2. Reduce mixing rate to 40 RPM for 3 hours

A single hydrogen peroxide dose of 12 mg/L was used. Sampling and analysis was performed as presented in Table 3.

Table 3. Sampling and Analysis Matrix for Peroxide Test

Parameter	Location of Analysis
pH	On-site
DO	On-site
Hydrogen peroxide residual	On-site
Hydrogen peroxide demand	On-site
Iron, total and dissolved	On-site
Manganese, total and dissolved	On-site
TKN	AMTEST Laboratories
Ammonia, total	AMTEST Laboratories
TOC	AMTEST Laboratories

Results and Discussion

Results from the bench-scale testing conducted in October, 2015 are discussed below.

Raw Water Characterization

A batch of raw PW3 well water was collected on each of the two days of testing at the MFRWTP (October 13 and 14, 2015). The raw water quality is presented in Table 4.

Table 4. PW3 Raw Water Quality

Parameter	10/13	10/14
pH/Temperature (°C)[1]	7.3/12.6	7.3/12.4
Conductivity (µmho/cm)[1]	359	336
DO (mg/L)[1]	0.34	0.30
ORP (mV)[1]	-35	-
Alkalinity (mg/L as $CaCO_3$)[1]	100	-
Calcium (mg/L)[2]	39.1	39.1
Magnesium (mg/L)[2]	10.1	10.2
Hardness (mg/L as $CaCO_3$)	138	138
Total Kjeldahl Nitrogen – TKN (mg/L as N)[3]	< 0.2	0.426
Total Ammonia (mg/L as N)[3]	0.278	0.261
Organic Nitrogen (mg/L as N)	ND	0.165
Nitrate + Nitrite (mg/L as N)[3]	< 0.02	-
Arsenic, total (mg/L as As)[2]	0.0048	0.0047
Iron, total (mg/L as Fe)[2]	1.23	1.23
Iron, dissolved (mg/L as Fe)[2]	1.08	1.21
Manganese, total (mg/L as Mn)[2]	0.760	0.762
Manganese, dissolved (mg/L as Mn)[2]	0.768	0.760
Silica (mg/L as SiO_2)[2]	53.4	55.3
Total Organic Carbon (mg/L as C)[3]	0.89	0.82

Notes:

1. Measured in the field.
2. Analyzed at ALS. Filtrations performed in the field for dissolved metals.
3. Analyzed at AMTEST Laboratories. Organic nitrogen calculated from TKN and ammonia.

Water quality for PW3 was generally as anticipated from previous water quality monitoring with respect to pH, temperature, conductivity, DO, ORP, silica, and alkalinity. Calcium, magnesium, and hardness were higher than previously reported for this well, whereas, the concentrations of other metals were close to previous test results. TKN varied significantly between the two days of bench-scale testing.

The City has been performing sampling at the MFRWTP for several nitrogen-related parameters since the fall of 2014. Historical water quality data collected as part of that on-going nitrogen study sampling for PW3 (and analyzed at ALS) are presented in Table 5. Historical levels of TKN have been consistently greater than 0.4 mg/L. Total ammonia has varied somewhat and has averaged 0.326 mg/L. Organic nitrogen, which is calculated by subtracting total ammonia from the reported TKN value for a sample, has varied significantly. The average level of organic nitrogen found in PW3 water was 0.44 mg/L.

Table 5. Historical PW3 Raw Water Nitrogen Data (Analyzed at ALS)[1]

Parameter	Average	Maximum	Minimum
Total Kjeldahl Nitrogen – TKN (mg/L as N)	0.75	1.64	0.42
Total Ammonia (mg/L as N)	0.326	0.421	0.235
Organic Nitrogen (mg/L as N)	0.44	1.32	0.21

Notes:

1. Data collected between December, 2014 and October, 2015.

Sampling of the City's raw water for that nitrogen study was performed the day after bench-scale testing was completed. For this bench-scale testing, nitrogen-related parameters were analyzed at AMTEST Laboratories because their TKN method reporting limit is lower than that of ALS (0.2 mg/L at AMTEST compared to 0.4 mg/L at ALS). Since the date of the City's nitrogen study sampling occurred within one day of this bench-scale testing, a comparison of the data collected at both laboratories is presented in Table 6. TKN varied significantly, from undetectable to 0.79 mg/L, for the three days for which sampling occurred. Calculated organic nitrogen levels varied from less than 0.2 to 0.46 mg/L. Variations in water quality parameters to this extent are not normally expected for groundwaters. This degree of variability is likely attributable, in part, to the low levels of TKN, with some samples close to the method reporting limits. Some of the variability may also be attributable to contamination of samples during analysis at the laboratory. The TKN method is known to be susceptible to contamination from ambient gaseous nitrogen in the air during the aggressive acid digestion step of the method. Further testing would be required to determine if contamination of the samples during analysis is contributing to variability in the reported data.

Table 6. Comparison of Nitrogen Data for PW3 Raw Water

Parameter	10/13[1]	10/14[1]	10/15[2]
Total Kjeldahl Nitrogen – TKN (mg/L as N)	< 0.2	0.426	0.79
Total Ammonia (mg/L as N)	0.278	0.261	0.335
Organic Nitrogen (mg/L as N)	ND	0.165	0.46

Notes:

1. Analyzed at AMTEST Laboratories.
2. Analyzed at ALS.

Chlorine Demand and Decay Characteristics of POE Water

Figure 1 presents a comparison of CDD curves for two samples collected at the POE: one collected in May, 2015 during initial bench-scale tests to evaluate organic nitrogen; and another collected on October 14, 2015 during the bench-scale testing described herein. Raw water quality data for these two bench-scale tests are presented in Table 7. Based on these data, the CDD characteristics of the POE water have

changed significantly. In the spring sample, a persistent difference between free and total chlorine residuals was attributed to organic nitrogen found to be present in the raw water. This increase in organic nitrogen in May 2015 compared to pre-design and initial startup of the MFRWTP supply resulted in higher levels of combined chlorine species. In contrast, for the fall sample combined chlorine species were oxidized within the first few hours of holding time, indicating that the formation of undesirable combined chlorine species would likely be much less problematic. Both free and total residuals of the fall sample, remained well below the corresponding values measured in the spring throughout the range of holding times investigated. Also, in the fall sample, free and total residuals appear to be less stable compared to the spring sample and residuals continued to decline throughout the 48-hour duration of the test.

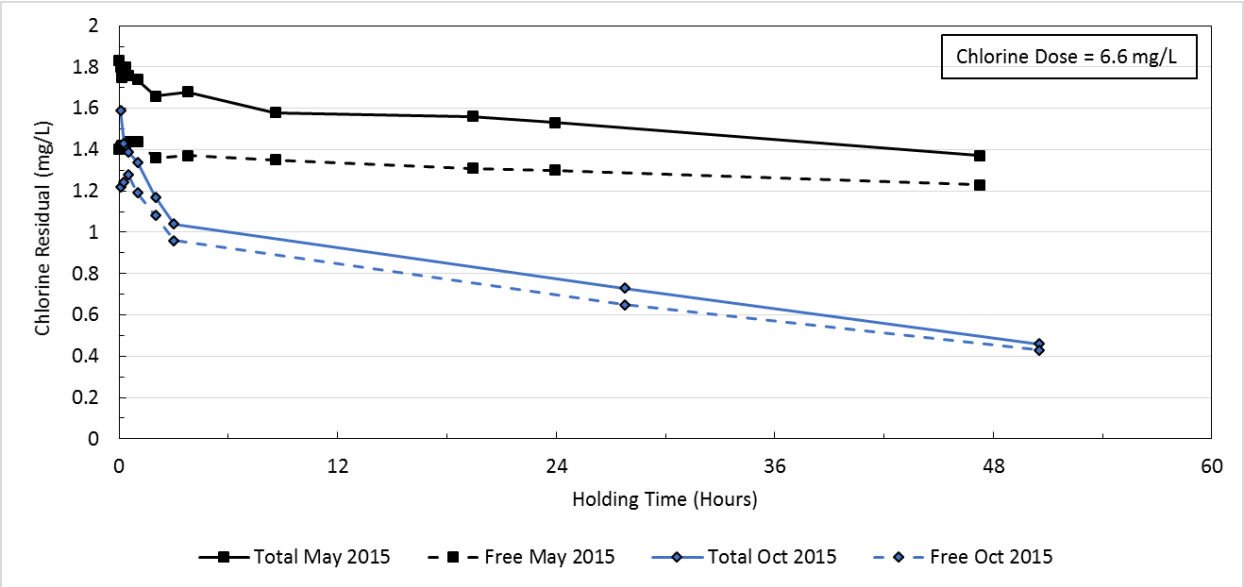

Figure 1. Comparison of CDD Curves for POE Water on Two Different Dates

Table 7. PW3 Raw Water Quality Comparison

Parameter	May 2015	October 14, 2015
TKN (mg/L as N)	0.51	0.426
Total Ammonia (mg/L as N)	0.295	0.261
Organic Nitrogen (mg/L as N)	0.22	0.165
Arsenic, total (mg/L as As)	0.0049	0.0047
Iron, total (mg/L as Fe)	1.24	1.23
Manganese, total (mg/L as Mn)	0.745	0.762
Silica (mg/L as SiO_2)	52.4	55.3

When the test plan was developed for this bench-scale test these significant changes in the nature and reactivity of organic nitrogen were not known. This testing was intended to address measures to remove elevated levels of organic nitrogen in the raw well water, as characterized during the May 2015 testing. The lower levels of organic nitrogen found in the October samples make determining organic nitrogen removals by coagulation or peroxide addition more challenging. Also, significant day-to-day variations in TKN levels were unexpected. For these reasons, the full test plan originally envisioned was not completed and an abbreviated set of conditions were included in this testing.

Coagulant Addition Tests

Jar testing was conducted using raw PW3 water. CDD curves for a control sample, to which no alum was added (Jar C1), and a jar with an alum dose of 58 mg/L (Jar C3) are presented in Figure 2. Clearly the addition of a coagulant resulted in lower chlorine residuals compared to the control and also higher levels of persistent combined chlorine species, as indicated by the significant difference between free and total CDD curves for Jar C3. The addition of alum is not expected to increase chlorine demand. The lower chlorine residuals for Jar C3 are likely, in part, due to the additional sample handling required during the filtration procedure which likely consumed a portion of the chlorine residual.

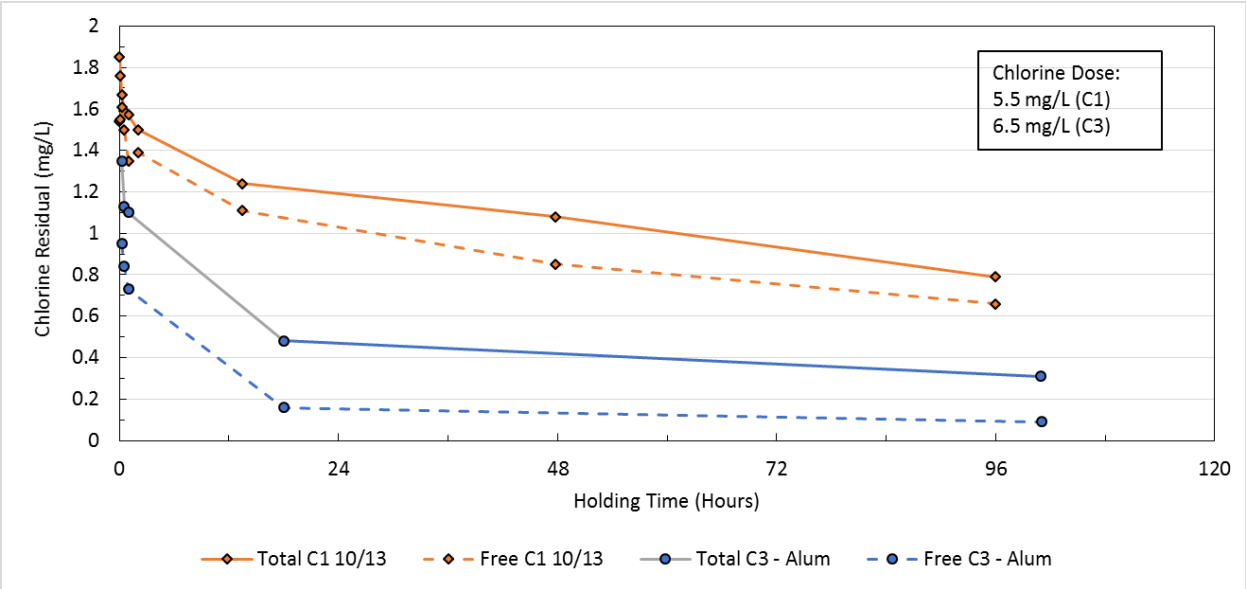

Figure 2. Effect of Alum on Treated Water CDD Curves

CDD curves for a raw PW3 sample treated with a combination of alum and cationic polymer (Jar C4) compared to a control (Jar C1) are presented in Figure 3. Jar C4 water had lower chlorine residuals compared to the control, although both Jars C1 and C4 had similar levels of combined chlorine. The overall CDD characteristics were similar for the control and Jar C4, although Jar C4 had somewhat lower chlorine residuals throughout the range of holding times. The lower chlorine residuals for Jar C4 are likely, in part, due to the additional sample handling required during the filtration procedure which likely consumed a portion of the chlorine residual. Based on these results, coagulation did not provide an improvement with respect to CDD characteristics.

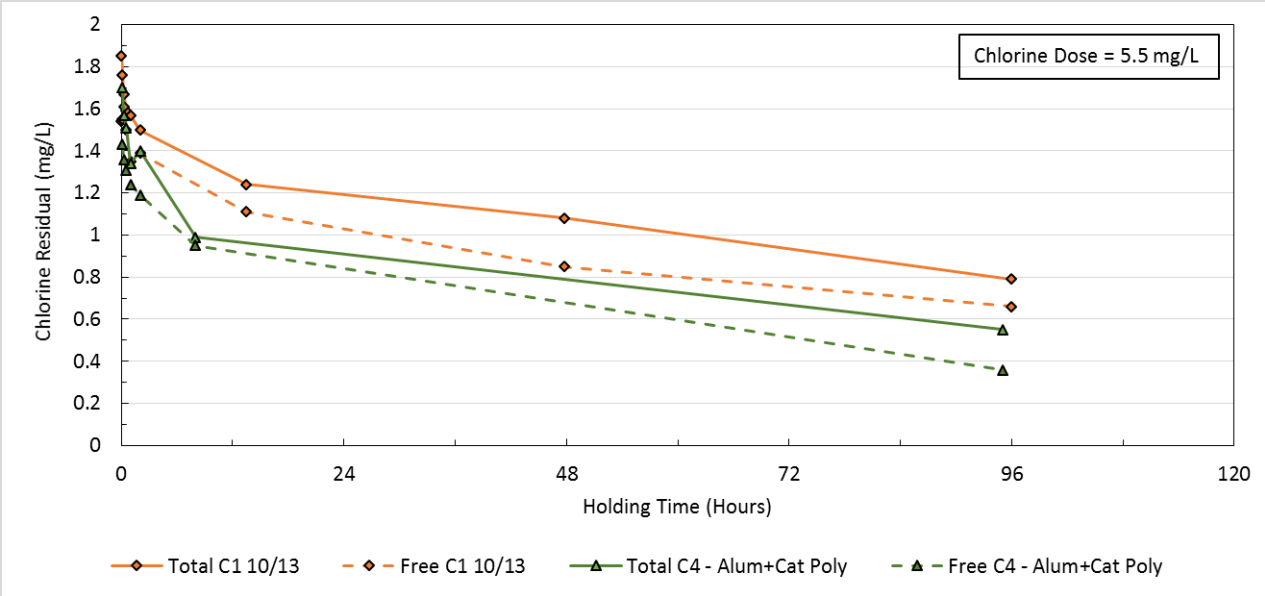

Figure 3. Effect of Alum and Cationic Polymer on Treated Water CDD Curves

TKN data collected during bench-scale testing are presented in Figure 4. TKN was detected in just four samples making it difficult to interpret the extent of organic nitrogen removal by coagulation. For the purposes of graphing these data, samples reported as less than the detection limit are shown as 0.1 mg/L, or one half the method reporting limit. There was more variability in the TKN data than expected, with one apparent outlier (Jar C6 treated with the coagulant ACH) with a TKN level approximately six times higher than the other samples. Also, the significant difference in raw water TKN levels for samples collected on consecutive days confounded data interpretation since the starting conditions were significantly different on each day testing was performed (Figure 4). Although interpreting this sparse data set is challenging, there does not appear to be an overall benefit of coagulant addition with respect to lowering TKN levels.

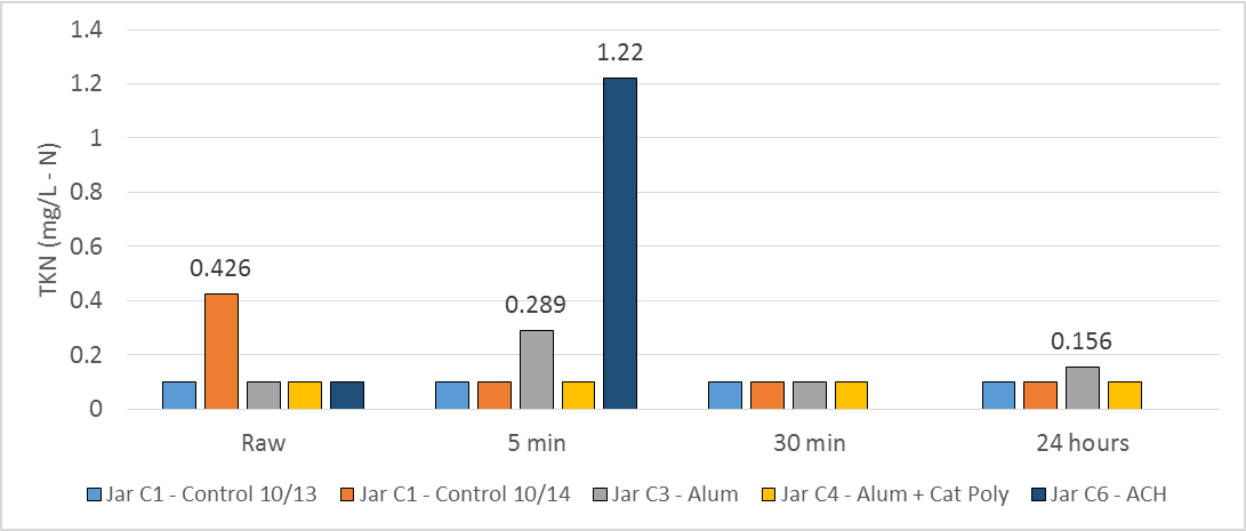

Figure 4. Effect of Coagulant Addition on TKN

Figure 5 presents organic nitrogen values calculated by subtracting ammonia from the corresponding TKN value for the coagulation addition tests. For the purposes of this calculation, the TKN values reported as below the detection limit were set at 0.1 mg/L, or half the detection limit of the method. The jars which included the addition of a coagulant did not appear to be significantly different from the control samples. Based on these data, coagulant addition did not appear to be beneficial in terms of removing organic nitrogen.

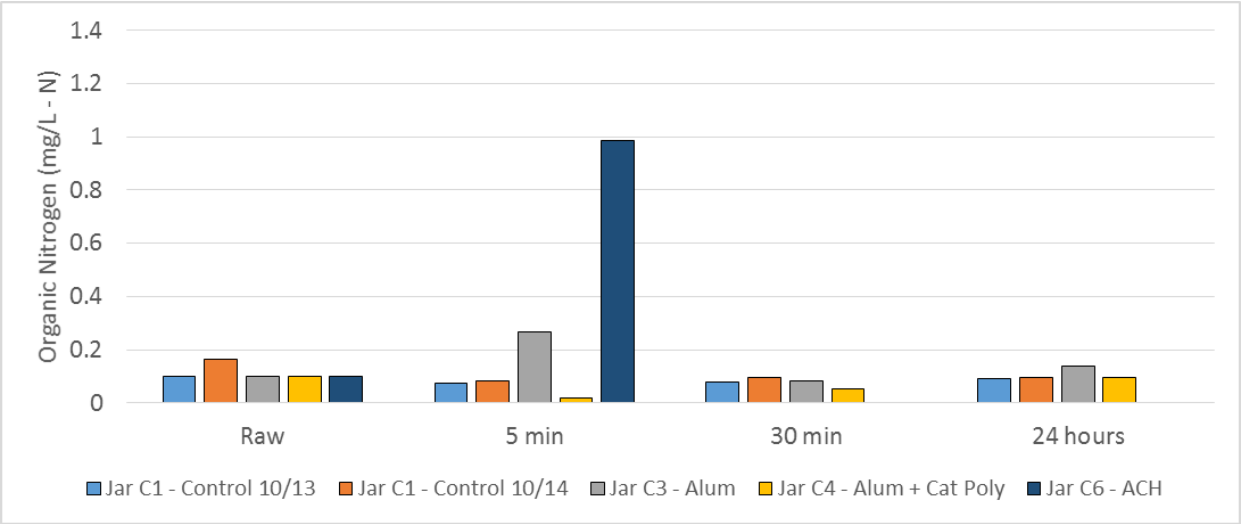

Figure 5. Effect of Coagulant Addition on Organic Nitrogen

Peroxide Addition Tests

Peroxide was added to raw PW3 water for this test. Table 8 presents water quality collected during the peroxide jar test.

Table 8. Water Quality Data for Peroxide Jar Test

Parameter	Raw PW3 Water	After 12 mg/L Peroxide Dose	
		T = 5 min	T = 3 hours
DO (mg/L)	4	4.5	4.5
Peroxide Residual (mg/L)	-	12	12
Peroxide Demand (mg/L)	-	< 0.2	< 0.2
Iron, total (mg/L as Fe)	1.2	1.2	-
Iron, dissolved (mg/L as Fe)	< 0.02	< 0.02	-
Manganese, total (mg/L as Mn)	0.970	0.932	-
Manganese, dissolved (mg/L as Mn)	0.924	0.942	-
Nitrate + Nitrite (mg/L as N)	ND	ND	-
Ammonia, total (mg/L as N)	0.261	-	0.269
TKN (mg/L as N)	0.426	-	0.342
Organic Nitrogen (mg/L as N)	0.165	-	0.073
TOC (mg/L as C)	0.82	-	0.96

The initial DO level of the raw water was higher than measured immediately following sample collection due to incidental aeration of the batch of raw water as samples were decanted into the jars for the tests. Peroxide appeared to be relatively unreactive, with the exception of perhaps oxidizing some dissolved

iron (incidental aeration after sample collection and during sample handling also oxidized some of the dissolved iron). The peroxide residual did not measurably decrease over the 3-hour contact time resulting in a negligible peroxide demand and peroxide had essentially no effect on manganese or ammonia concentrations in the raw water. Peroxide did appear to oxidize approximately 56% of the organic nitrogen in the raw water, as indicated by the decrease in TKN between raw and treated samples. The TKN and organic nitrogen results are presented graphically in Figure 6.

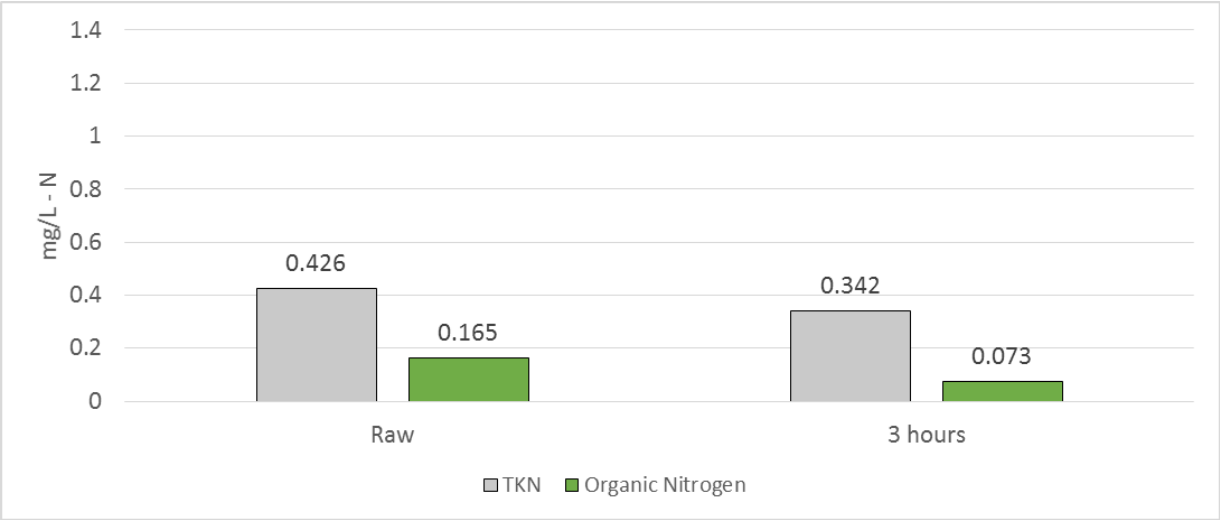

Figure 6. Effect of Peroxide on TKN and Organic Nitrogen

A high peroxide dose and long contact time were selected for this initial screening. Under the selected conditions, approximately a 20% reduction in TKN and approximately a 56% reduction in organic nitrogen were observed. While these results are promising, further testing is required to confirm the extent of organic nitrogen oxidation by peroxide, given the overall variability in this data set. A brief bench-scale test using a shorter contact time and lower range of peroxide doses is recommended to verify the efficiency of peroxide oxidation of organic nitrogen under more representative conditions.

Conclusions

Conclusions from this bench-scale testing are as follows:

1. The nature of the reactivity of organic nitrogen in the MFRWTP supply has changed between the previous bench-scale testing conducted in May, 2015 and the current study. The level of organic nitrogen in the PW3 water is somewhat lower and upon chlorination, combined chlorine residuals are oxidized within a few hours of contact time, compared to several days in the previous May test and conditions that have been observed in MFRWTP POE monitoring for the past 1.5 years. In the current test, free chlorine residuals were not as stable as in previous testing conducted in May, resulting in lower free and total chlorine residuals for a given holding time. The lower level of organic nitrogen in the water would tend to support lowering the chlorine dose at the MFRWTP since lower levels of combined chlorine species would be anticipated. However, the CDD of the October PW3 water are greater than measured in May. The instability of the chlorine residuals in the POE water suggest that lowering the chlorine dose would likely result in residuals below target levels in the distribution system.

2. The amount of organic nitrogen in the PW3 raw water appears to vary significantly, with significantly different results for TKN measurements on two consecutive days of bench-scale testing.

3. TKN and organic nitrogen have varied to a greater degree than expected, both in previous nitrogen study sampling and within this two-day bench-scale testing effort. It is possible that at least some of the variability in TKN, and organic nitrogen, is due to issues with the analytical methodology. TKN methods are known to be susceptible to contamination, especially at low levels, near the method detection limit. The aggressive acid digestion used in the method has a tendency to draw nitrogen out of the atmosphere and pull it into solution. It is not known if this type of contamination is occurring but the susceptibility of the method to this type of contamination may explain some of the unexpected variation in the results. Day-to-day variations in TKN, and hence organic nitrogen levels, for a given production well were not expected. Gradual changes in the nitrogen chemistry of the water over longer time periods and with increased production well pumping can occur.

4. Although the changing raw water quality conditions presented some challenges with respect to developing definitive conclusions, this testing did not demonstrate that coagulant addition could effectively remove organic nitrogen. Peroxide appeared to remove a moderate amount of TKN and a significant fraction of organic nitrogen when using a relatively high peroxide dose (12 mg/L) and long contact time for oxidation (3 hours).

Recommendations

Recommendations from this bench-scale testing are as follows:

1. The level of organic nitrogen in the raw water and its chemical reactivity appear to be changing significantly over time. Given these conditions, the pursuit of interim measures to remove organic nitrogen are less likely to be fruitful in terms of improving CDD characteristics, reducing chlorine demand, and improving the aesthetic character of the finished water. Although there is significant scatter in the data, possibly due to issues with the analytical methodology, coagulant addition for the purpose of removing organic nitrogen did not provide a measurable benefit and should therefore no longer be considered as a viable interim improvement at the MFRWTP.

2. The addition of peroxide could possibly be a viable technique for removing organic nitrogen from the raw water supply. Changing raw water quality conditions and other challenges during this testing prevented a full analysis of peroxide addition. A brief set of additional bench-scale tests focused on evaluating a lower range of peroxide dosages at an achievable contact time is recommended in order to determine if an improvement in CDD characteristics is achievable with peroxide.

3. The nitrogen study sampling plan should be continued so that changes in raw water levels of TKN and organic nitrogen continue to be documented.

4. A series of split and duplicate samples should be sent to two or more different laboratories for the purpose of directly comparing measured levels of TKN, total ammonia, and calculated organic nitrogen. Modifications to existing methodologies could also be examined as part of such a labor-

atory comparison. This effort will help to determine the extent to which interferences in the analytical methods are contributing to the variability in the results of these nitrogen-related parameters and to better characterize actual levels of TKN and organic nitrogen in the source of supply.

5. Developing a CDD curve for a sample collected at the POE of the MFRWTP on a regular basis (perhaps every month or two), to include free and total chlorine residuals, is recommended to document changes in the CDD characteristics and changing reactivity of organic nitrogen species in the source of supply. A proposed Testing Plan is included as Attachment 2 to this Technical Memorandum. An Excel spreadsheet template for data entry has also been emailed to the City.

ATTACHMENT 1

Organic Nitrogen Removal – Coagulant Addition and Peroxide Oxidation Bench-Scale Testing Plan

confluence ENGINEERING GROUP LLC
517 NE 92nd Street, Seattle, WA 98115 ph (206) 527-6832 fx (206) 527-3148 confluence-engineering.com

To:	Jeff Cameron, Amy Blain – City of Longview	**Date:**	October 7, 2015
From:	Stephen Booth, Andrew Hill, and Michael Hallett – Confluence	**Project:**	Softening Alternatives & Baltimore Street Water Quality Evaluation
Cc:		**Subject:**	Organic Nitrogen Removal – Coagulant Addition and Peroxide Oxidation Bench-Scale Testing Plan - FINAL

Introduction and Objectives

The City of Longview is investigating measures which could be implemented to mitigate on-going taste and odor (T&O) issues associated with the Mint Farm Regional Water Treatment Plant (MFRWTP) water supply. The City has received customer complaints related to sulfurous and chlorinous T&O. The cause of these has been attributed to two mechanisms: 1) loss of oxidizing conditions (and associated sulfate reversion to sulfides) within low flow areas of the distribution system and in-home plumbing systems; and 2) naturally-occurring organic nitrogen in the raw water, resulting in the formation of chlorinated compounds with objectionable T&O. This plan describes bench-scale testing to be performed to address the second mechanism. Specifically, this testing will evaluate:

1. The effectiveness of coagulant addition for removing organic nitrogen
2. The effectiveness of hydrogen peroxide addition for oxidizing organic nitrogen

Both of these strategies are being investigated with the goal of minimizing the formation of intermediate chloramine species in the MFRWTP water and hence improving taste and odor. This initial bench-scale testing is being performed as a proof-of-concept and for screening purposes to determine if additional pilot-scale (or further bench-scale) testing is warranted, to better characterize process performance.

Raw Water Characterization

A batch of raw well water from a single well will be collected at the MFRWTP for this testing. The raw water quality will be characterized as presented in Table 1.

Table 1. Parameters to Characterize Raw Water Quality

Parameter	Units	Location of Analysis
pH/Temperature	°C	On-site
Conductivity	µmho/cm	On-site
DO	mg/L as O_2	On-site
Alkalinity	mg/L as $CaCO_3$	On-site
Hardness (Calcium and Magnesium)	mg/L as $CaCO_3$	ALS Environmental
Total Kjeldahl Nitrogen (TKN)[1]	mg/L as N	AMTEST Laboratories[1]
Ammonia, total[2]	mg/L as N	AMTEST Laboratories
Organic Nitrogen	mg/L as N	Calculated
Nitrate + Nitrite[2]	mg/L as N	AMTEST Laboratories

Parameter	Units	Location of Analysis
Arsenic, total	mg/L as As	ALS Environmental
Iron, total and dissolved	mg/L as Fe	On-site and ALS Environmental
Manganese, total and dissolved	mg/L as Mn	On-site and ALS Environmental
Silica	mg/L as SiO_2	ALS Environmental
Total Organic Carbon	mg/L as C	AMTEST Laboratories

Notes:

1. AMTEST in Kirkland, WA offers a lower method reporting limit for TKN which is more appropriate for this testing compared to the method used by ALS Environmental.
2. Selected samples will be analyzed on-site using the Hach® TNT method.

Testing Plan

A standard jar testing apparatus will be used for this testing.

Coagulant Addition Testing Plan

A coagulant and sodium hypochlorite will be added to each jar for these tests, plus a no-coagulant control. Mixing will occur for a specified time period after the addition of chemicals. The coagulant will be added to attempt coagulation and removal of organic nitrogen from the water. The coagulated particles may aggregate and begin to form pin-floc as the test progresses. Sodium hypochlorite will be added at a dose similar to that currently used at the MFRWTP to oxidize iron and ammonia and produce a target free chlorine residual of 1.2 to 1.5 mg/L. For these tests, a bench-scale filtration apparatus will be used to separate the coagulated/flocculated solids from the water. This bench-scale filtration does not adsorb and remove soluble manganese, and as such, manganese will likely pass through the filters because adequate time for manganese oxidation will not be provided. Subsequent pilot-scale testing may be performed, which will better mimic the full-scale filtration process and remove manganese, and allow a better approximation of full-scale performance. The proposed bench-scale testing approach will be adequate to determine if sufficient organic nitrogen can be removed to warrant subsequent pilot-scale testing.

Chemical addition and mixing will be performed as follows:

1. Add coagulant and rapid mix @ 100 RPM for 30 sec
2. Reduce mixing rate to 40 RPM for 2 minutes
3. Add hypochlorite and continue mixing @ 40 RPM for 5 min
4. Adjust the pH to a target of 7.5 to 8.0 by adding caustic soda (NaOH)
5. Filter the coagulated/flocculated water
6. Perform sampling, as described in Table 4, below

The mixing rates have been selected to provide adequate dispersion of chemicals and coagulation in the batch system under investigation. If the results of this testing are promising, chemical mixing conditions (time and energy) achievable at the full-scale will be further evaluated during subsequent pilot-scale testing.

Three coagulants: alum; an aluminum chlorohydrate (ACH) product; and a cationic polymer will be included in this testing. Alum and ACH were included in previous bench-scale tests in which silica removal was investigated. Cationic polymer is often used as a coagulant aid and will be used in conjunction with alum for one test condition. Chemical dosages to be used in tests C-1 (alum) and C-2 (ACH) are provided in Tables 2 and 3, respectively. Alum, and to a lesser degree ACH, consumes alkalinity and tends to reduce the pH of the water. More alkalinity is consumed as the coagulant dose is increased, so the pH of coagulation/flocculation will vary for each jar, depending on the coagulant type and dose. At the conclu-

sion of each test, caustic soda will be added to bring the pH of each jar to the current finished water pH target of 7.7 (range of 7.5 to 8.0) at the MFRWTP. A single control jar will be included and no coagulant will be added to that jar (as shown in Table 2).

Table 2. Chemical Dosing Strategy for Test C1 - Alum

Chemicals	Jar C1 (Control)	Jar C2	Jar C3	Jar C4
Alum dose (mg/L as $Al_2(SO_4)_3$-$14H_2O$)	-	29	58	58
Alum dose (mg/L as Al_2O_3)	-	5	10	10
Cationic Polymer Dose (mg/L as product)[1]	-	-	-	5
Hypochlorite Dose (mg/L)[2]	6.5	6.5	6.5	6.5
Target pH	7.5 to 8.0			
NaOH dose (mg/L)	3.5	14.9	26.2	26.2

Notes:

1. Nalcolyte 8105.
2. The hypochlorite dose used at the full-scale for the particular well water used for this testing will be applied in this bench-scale test (dose for PW3 water is shown).

Table 3. Chemical Dosing Strategy for Test C2 - ACH

Chemicals	Jar C5	Jar C6
ACH Dose (mg/L as product)	8.6	17.1
ACH dose (mg/L as Al_2O_3)	5	10
Hypochlorite Dose (mg/L)[1]	6.5	6.5
Target pH	7.5 to 8.0	
NaOH dose (mg/L)	4.6	5.7

Notes:

1. The hypochlorite dose used at the full-scale for the particular well water used for this testing will be applied in this bench-scale test (dose for PW3 water is shown).

Sampling and Analysis Plan for Coagulant Addition Tests

Water from each jar in each test will be sampled for the water quality parameters presented in Table 4.

Table 4. Sampling and Analysis Matrix for Coagulant Addition Jar Tests

Parameter	Location of Analysis	Sampling Times
Free and total chlorine residuals (mg/L as Cl_2)[1]	On-site	5 min, 15, min, 30 min, 1 hour, 2 hours, 24 hours, 4 days
Monochloramine (mg/L as Cl_2)	On-site	5 min, 15, min, 30 min, 1 hour, 2 hours, 24 hours, 4 days
TKN (mg/L)	AMTEST Laboratories	5 min, 30 min, 24 hour
Ammonia, total (mg/L)[2]	AMTEST Laboratories	5 min, 30 min, 24 hour
TOC (mg/L)	AMTEST Laboratories	30 min
Flavor Profile Analysis	SPU Laboratory	Highest coagulant dose for each test plus control (4 samples)

Notes:

1. To be used to prepare one chlorine demand and decay (CDD) curve for each jar.
2. Selected samples will be analyzed on-site using the Hach® TNT method.

Hydrogen Peroxide Testing Plan

The hydrogen peroxide bench-scale tests will be performed using the following steps:

- **Test P1**. A preliminary test to assess hydrogen peroxide reaction chemistry and dose response.
- **Test P2**. A preliminary test to determine the required chlorination doses for a range of hydrogen peroxide doses and pH adjustment requirements.
- **Test P3**. Conduct final hydrogen peroxide test using chemical dosages established in previous tests and collect samples for CDD curves.

Test P1

The objectives of this test include determining hydrogen peroxide demand and decay characteristics for the target contact time and to assess peroxide reactivity with constituents of concern. For this test the following chemical dosing and mixing scheme will be used:

1. Add peroxide and mix @ 100 RPM for 30 sec
2. Reduce mixing rate to 40 RPM for 2 minutes

Hydrogen peroxide doses will be as presented in Table 5.

Table 5. Test P1 - Hydrogen Peroxide Dosages

Chemical	Jar P1	Jar P2	Jar P3	Jar P4
Hydrogen Peroxide Dose (mg/L)	0.5	2	5	10

For each jar a sample of the parameters listed in Table 6 will be collected and analyzed.

Table 6. Test P1 - Sampling and Analysis Matrix

Parameter	Location of Analysis
pH	On-site
DO (mg/L)	On-site
Hydrogen peroxide residual (mg/L)	On-site
Hydrogen peroxide demand (mg/L)	On-site
Iron, total and dissolved (mg/L)	On-site
Manganese, total and dissolved (mg/L)	On-site
Ammonia, total (mg/L)	On-site
Nitrite and nitrate (mg/L)	On-site

Test P2

The objectives of this test include determining the hypochlorite (chlorine) demand as a function of peroxide dose and determining the acid or base needed as a function of residual hydrogen peroxide level and hypochlorite dose.

Based on Test P1, three hydrogen peroxide dosages will be selected to target residual hydrogen peroxide levels of 1, 4, and 8 mg/L at the conclusion on the mixing time. Following the addition of hydrogen peroxide the residual hydrogen peroxide will be measured to confirm it is reasonably close to the target. The same hydrogen peroxide mixing conditions as used for Test P1 will be used for this test.

Hydrogen peroxide reacts with chlorine residual so the required hypochlorite dose to achieve the desired free chlorine residual will vary for each jar. An initial hypochlorite dose for each jar will be calculated based upon the dose used at the MFRWTP and the residual hydrogen peroxide for that jar. If neces-

sary, the dose will then be adjusted incrementally to achieve the target final free chlorine residual of 1.2 to 1.5 mg/L. Caustic soda will be added to the control jar at the same dose as used at the MFRWTP, to produce a target final pH between 7.5 and 8.0. A lower dose of caustic soda will likely be required in the remaining jars since a significantly higher hypochlorite dose will be used due to the presence of residual hydrogen peroxide. For the higher hypochlorite doses, the pH may be above the target range and an acid may be required to bring the pH of that jar down to the target range. The chemical dosing scheme for Test P2 is presented in Table 7.

Table 7. Test P2 – Chemical Dosing Scheme

Chemical	Jar P5	Jar P6	Jar P7
Hydrogen peroxide dose (mg/L)	*Based on results of Test P1*		
Hydrogen peroxide target residual (mg/L)	1	4	8
Hypochlorite dose (mg/L)	*Add incrementally to target free residual*		
pH Target	7.5 to 8.0		
Caustic Dose (mg/L)	*To be determined*		
Sulfuric Acid Dose (mg/L)	*To be determined*		

Test P3

The objectives of this test are to assess organic nitrogen removal and develop CDD curves for the selected hydrogen peroxide doses to provide hydrogen peroxide residuals of 1, 4, and 8 mg/L. The hypochlorite doses and pH adjustment scheme determined in Test P2 will be used for this test. This test will also include a control jar which will not be dosed with hydrogen peroxide. The following chemical dosing and mixing scheme will be used:

1. Add peroxide and mix @ 100 RPM for 30 sec
2. Reduce mixing rate to 40 RPM for 2 minutes
3. Collect pre-chlorination samples, as described in Table 9, below
4. Add hypochlorite to achieve target free chlorine residual of 1.2 to 1.5 mg/L
5. Adjust pH so that it is in the target range of 7.5 to 8.0
6. Perform post-chlorination sampling, as described in Table 9, below.

The chemical dosing scheme for Test P3 is presented in Table 8.

Table 8. Test P3 – Chemical Dosing Scheme

Chemical	Jar P8	Jar P9	Jar P10	Jar P11
Hydrogen peroxide dose (mg/L)	0	*Based on results of Test P1*		
Hydrogen peroxide target residual (mg/L)	*0*	*1*	*4*	*8*
Hypochlorite dose (mg/L)	6.5	*Based on results of Test P2*		
pH Target	7.5 to 8.0			
Caustic Dose (mg/L)	3.5	*Based on results of Test P2*		
Sulfuric Acid Dose (mg/L)	0	*Based on results of Test P2*		

The sampling and analysis plan is as presented in Table 9.

Table 9. Sampling and Analysis Matrix for Test P3

Parameter	Location of Analysis	Sampling Times
Pre-Chlorination Samples		
TKN (mg/L)	AMTEST Laboratories	One sample at conclusion of peroxide mixing and prior to hypochlorite addition
Ammonia, total (mg/L)[1]	AMTEST Laboratories	
Nitrite + Nitrate (mg/L)	AMTEST Laboratories	
TOC (mg/L)	AMTEST Laboratories	
Post-Chlorination/pH adjustment Samples		
Free and total chlorine residuals (mg/L as Cl_2)[2]	On-site	5 min, 15, min, 30 min, 1 hour, 2 hours, 24 hours, 4 days
Monochloramine (mg/L as Cl_2)	On-site	5 min, 15, min, 30 min, 1 hour, 2 hours, 24 hours, 4 days
TKN (mg/L)	AMTEST Laboratories	5 min, 30 min, 24 hour
Ammonia, total (mg/L)[1]	AMTEST Laboratories	5 min, 30 min, 24 hour
Nitrite + Nitrate (mg/L)	AMTEST Laboratories	5 min, 30 min, 24 hour
Flavor Profile Analysis[3]	SPU Laboratory	Select 3 samples plus one control (4 samples)

Notes:

1. Selected samples will be analyzed on-site using the Hach® TNT method.
2. To be used to prepare one chlorine demand and decay (CDD) curve for each jar.
3. Samples for Flavor Profile Analysis will be filtered.

ATTACHMENT 2

Chlorine Demand and Decay Curve Test Plan

confluence ENGINEERING GROUP LLC
517 NE 92nd Street, Seattle, WA 98115 ph (206) 527-6832 fx (206) 527-3148 confluence-engineering.com

To:	Jeff Cameron, Amy Blain – City of Longview	**Date:**	February 3, 2016
From:	Stephen Booth, Michael Hallett, and Melinda Friedman – Confluence	**Project:**	Softening Alternatives & Baltimore Street Water Quality Evaluation
Cc:		**Subject:**	Chlorine Demand and Decay Curve Test Plan

Introduction and Objectives

Bench-scale testing was recently performed to evaluate coagulation for removing organic nitrogen and hydrogen peroxide for oxidizing organic nitrogen in the Mint Farm Regional Water Treatment Plant (MFRWTP) ground water supply. The results of that testing were inconclusive due to apparent rapid variations in Total Kjehldahl Nitrogen (TKN) and organic nitrogen in the source of supply and also due to suspected issues with the analytical methodology which may have increased the variability and inconsistency of the results.

The effect of organic nitrogen on chlorine demand and decay (CDD) characteristics remains of concern. This testing plan outlines additional bench-scale tests to track CDD characteristics and the collection of corresponding data for nitrogen-related parameters, on a regular basis. The goal of this testing is to develop a more robust data set to allow a better understanding of the interrelationships among these water quality parameters. It is suggested this testing be performed every week or every two weeks. City staff will determine the most feasible frequency based on existing workloads.

Testing Approach

Samples used to generate the CDD curves will be collected in 1-liter, pre-cleaned, amber glass bottles with Teflon®-lined caps. (The cleaning procedure is described below). Two amber glass bottles should be filled each time this testing is performed, from the finished water tap at the MFRWTP. Chlorine residuals will be tracked as a function of time and additional water quality sampling will be performed, as described below. The following information should be recorded at the time of sample collection:

- The production well(s) being operated
- Finished water free and total chlorine residuals
- Finished water pH

Sampling and Analysis Plan for CDD Tests

Two amber glass bottles will be filled with finished water. The first bottle (Jar #1) will be used to collect chlorine decay data. The time at which the sample is drawn from the finished water tap should be considered T = 0 hours. Sampling for chlorine residuals will proceed as presented in Table 1. These times can be modified, as required to accommodate other duties to be performed during the test.

Table 1. Sampling Times for Chlorine Residual Testing from Jar #1

Sampling Time (hours)	Parameters
	Free and Total Chlorine Residual
0.25	✓
0.5	✓
1	✓
2	✓
4	✓
12	✓
24	✓
48	✓
72	✓

Samples for laboratory analysis will also be collected in conjunction with the chlorine residual testing being performed on-site. The water quality parameters included are presented in Table 2. The raw and finished water samples should be collected on the same day and at the same time as the amber glass bottles are filled. To better understand laboratory variability, split samples will be collected for both TKN and ammonia, so that two laboratories will receive essentially identical samples for analysis. Spilt-sampling is as presented in Table 2.

Table 2. Laboratory Sampling and Analysis Plan

Sample Location	**Number of Samples**		
	TKN	**Total Ammonia**[a,b]	**TOC**
Raw Water Tap	2[c]	2[c]	1
Finished Water Tap	2[c]	2[c]	1
Jar #2 @ 72-hour holding time	2[c]	2[c]	1

Notes:

a. Total ammonia may also be measured on-site using an appropriate test method (e.g. Hach® Method 10205, salicylate method, TNT plus™, ultra-low range: 0.015 – 2.00 mg/L).

b. Ammonia may be analyzed from the same sample bottle as TKN, depending on the laboratory.

c. Two samples are to be collected and each sample is to be sent to a different laboratory for analysis. Suggested laboratories are: ALS Environmental and AMTEST.

Procedure for Pre-Cleaning Amber Glass Bottles

The procedure for pre-cleaning the amber glass bottles is as follows:

- Partially fill and rinse each bottle three times with deionized (DI) water
- Fill each bottle approximately three-quarters full with DI water
- Add 10-mL of standard bleach, cap, and mix by inverting several times
- Fill each bottle with DI headspace-free and cap
- Place each bottle in the dark overnight to render the glassware chlorine demand-free
- The following day, empty each bottle and rinse at least three times with DI water
- Oven dry the bottles and caps
- At the time of sample collection rinse each bottle three additional times with sample prior to filling the bottle headspace-free with sample