Optimization of the Peace River/Manasota Conventional Coagulation Water Supply Facility

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TABLE 1: Historical Water Quality by Season for River, Reservoir, and Finished Waters

Parameter	**Units**	**Descriptive Statistic**	**Water Supply**				**Finished Water**	
			River		**Reservoir**			
			Wet Season	**Dry Season**	**Wet Season**	**Dry Season**	**Wet Season**	**Dry Season**
Color	CPU	95th Percentile	299	207	111	94	8	6
		75th Percentile	230	144	75	71	6	5
		50th Percentile	181	100	56	50	5	4
		25th Percentile	130	75	28	30	4	2
		n[*]	823	753	1144	1240	1112	1208
Turbidity	NTU	95th Percentile	12.1	11.4	15.6	5.7	0.22	0.31
		75th Percentile	6.2	6.5	5.9	3.5	0.16	0.19
		50th Percentile	4.6	4.6	3.6	2.6	0.13	0.14
		25th Percentile	1.8	1.8	0.6	0.8	0.10	0.05
		n	1113	1208	315	403	1112	1208
		50th Percentile	7.31	7.53	7.15	7.38	8.34	8.30
		25th Percentile	7.12	7.38	7.08	7.28	8.24	8.21
		n	823	753	319	406	1112	1108
NPDOC[†]	mg/L C	Average	22.1	22.1	16.2	16.2	6.6	6.6
TTHM[†]	g/L	Average	na[‡]	na	na	na	47	47
TDS	mg/L	Average	202	303	258	258	308	360
Conductivity	mohs/cm	Average	311	451	365	389	458	530
Total Hardness	mg/L $CaCO_3$	Average	113	148	118	133	114	152
Sulfate	mg/L	Average	8	10	8	8	115	125
Total Iron	mg/L	Average	0.05	0.03	0.01	0.01	0.02	0.03
Temperature	Deg. C	Average	25	22	23	23	26	23

* n represents number of observations.
• database not sufficient to determine seasonal variation.
, na indicates not available.

Peace River

Table 2: Optimized Coagulation Conditions and Resulting Water Quality

Parameter		River				Reservoir	
		Alum	Ferric Sulfate	PACl	Ferric Chloride	Alum	Ferric Sulfate
Dose (mg/L*)		150	175	100	175	90	130
pH		5.5	4.5	6	4.5	5.8	5.0
NPDOC (mg/L)	Untreated	14.5	14.5	14.5	14.5	13.1	13.1
	Treated	4.9	3.3	5.3	2.9	5.5	3.3
	% Removal	66	77	65	80	58	75
Color (CPU)	Untreated	110	110	110	110	55	55
	Treated	6	15.4	6	11	4.4	2.8
	% Removal	95	86	95	90	92	95

* as $Al_2(SO_4)_3$*14H_2O

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to confirm the selected treatment processe for the expansion.

The testing program was designed t verify that the existing treatment process provided optimal TOC removal as measured b non-purgeable dissolved organic carbo (NPDOC), or DBP precursor removal through conventional coagulation, flocculation, and sedimentation processes. A variet of coagulants were tested under a divers range of treatment conditions that allowed the process control variables primarily responsible for optimal coagulation/flocculation to be identified. Two of the objectives o the treatability evaluation were (1) to identify optimal coagulation conditions for NPDOC and turbidity removal, and (2) to compare resulting water quality to that produced by the other coagulants and the existing WSF treatment process.

Methods and Materials

Standardized jar-testing procedures were employed to mimic full-scale operating conditions. When administering the evaluation, the general jar-test procedures were adjusted to assess treatment under various coagulant doses and flocculation pH. All jar tests were performed in square acrylic 2-liter jars at ambient conditions (~22°C) with automated jar-test equipment (Phipps and Bird PB-900 & B-KER, Richmond, VA).

The coagulants used were aluminum sulfate (alum, $Al_2(SO_4)_3$*14H_2O), poly-aluminum chloride (PACl), ferric sulfate ($Fe_2(SO_4)_3$), and ferric chloride ($FeCl_3$) (Kemwater North America Co. Antioch, CA 94509). Each coagulant was diluted to equivalent strength as alum with 14 waters of hydration. Dilutions were intended to enhance coagulant distribution during coagulation and to provide greater experimental control. In order to establish performance over a broad range of coagulation and flocculation conditions, flocculation pH was varied independently of coagulant dose.

Results and Discussion

Raw-water quality: The raw water treated by the WSF genera ly has high organic content, moderate turbidity, low to moderate alkalinity, and moderate-to-high hardness content. Historical water-quality information is provided in **Table 1** for select parameters by wet and dry season fc river, reservoir, and finished waters. Untreated water varies by source, season, and parameter, making this a difficult water to coagulate. Disinfection byproduct precursors, as measured by NPDOC, were recorded as high as 27 mg/L C and averaged 20 mg/L C overall.

Treatment objectives are clear and include removal of turbidity and organic contaminants, though as in the case of many conventional coagulation facilities, particularly in the Southeast United States, organics removal is typically the component that limits finished-water quality. Despite the challenges presented by this water source, color in the finished water is relatively low, averaging 4 to 5 PCU with turbidity of approximately 0.1 nephelometric turbidity units (NTUs).

Coagulant screening evaluations: Initial testing was designed to establish conditions for optimized NPDOC or DBP precursor removal for each coagulant. Depending on the coagulant, 15 to 30 jar tests were conducted with raw Peace River water, which at the time of testing had an NPDOC of 14.5 mg/L C, true color of 110 PCU and UV-254 of 0.73 cm^{-1}. Optimal flocculation pH ranges were 5.5 to 6.5 for alum and PACl. Optimal pH ranges for ferric sulfate and ferric chloride were 3.5 to 4.5 and 4 to 5, respectively. Coagulant screening information is summarized in **Figure 1**, which shows NPDOC and color-removal efficiencies by coagulant, range of dose, and optimal flocculation pH range.

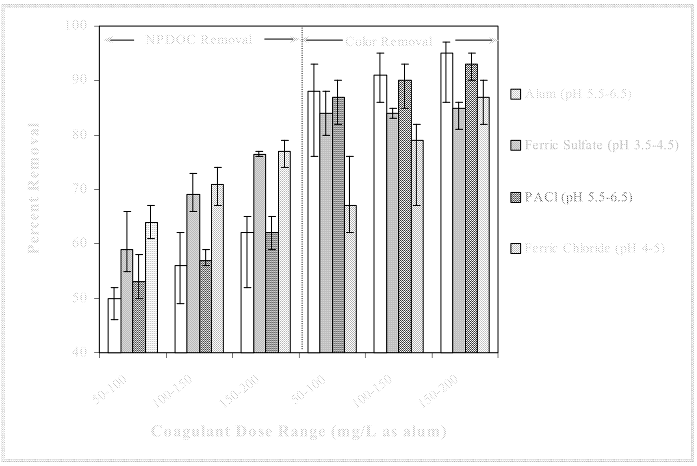

Figure 1: NPDOC and Color Removals by Coagulant, Dose and Optimized pH Range

Figure 1 reveals several key findings for the test conditions: NPDOC and color removal increased with increasing coagulant dose; percent color removals were significantly greater than corresponding NPDOC removals; ferric-based coagulants provided greater NPDOC removal than alum and PACl; and aluminum-based coagulants exceeded ferric-based color removals, particularly ferric chloride. Therefore, the use of alum or PACl is advantageous for color removal, and ferric sulfate or ferric chloride is advantageous for NPDOC removal.

The data also indicated that optimum color removal was similar to the optimum NPDOC removal by dose but not by pH. In order to achieve the greatest amount of NPDOC and color removal, almost twice the coagulant dose was typically required to achieve the final 10 percent of the highest NPDOC and color removals for each coagulant.

The iron-based salts were capable of removing at least 12 percent of NPDOC, or 1.4 mg/L C more than their aluminum-based counterparts. Chloride-based coagulants performed equal to or slightly better than the sulfate-based coagulants for NPDOC, UV-254, and color removal. Both alum and PACl reduced color the most effectively, representing at least a 5-to-9-percent improvement over ferric sulfate and ferric chloride, respectively.

Optimized coagulation conditions are delineated for a sin-

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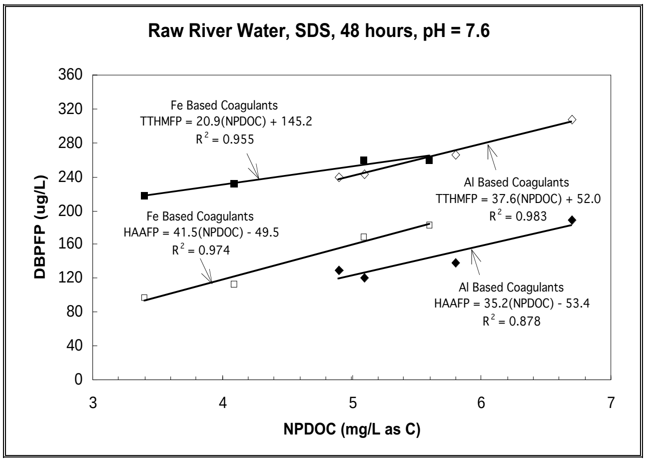
Figure 2: Disinfection Byproduct Formation Potential vs. NPDOC and Coagulant Type



Note: DBP data shown above reflects conditions used for baseline comparisons and is not representative of actual WSF effluent water-quality conditions.

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gle dose and flocculation pH combination for each coagulant. These results are summarized in **Table 2**. Note that in order to meet the WSF's multiple treatment objectives, optimal coagulation conditions were well in excess of the 50-percent minimum TOC removal required by the EPA. Minimization of acid or base addition, residual metals concentration, and diminishing treatment return comprise the criteria used to identify optimized conditions for concurrent NPDOC and color reductions.

Disinfection byproduct formation potential: The existing facility typically removes 60 to 70 percent of NPDOC, with the fraction remaining sufficient to form significant DBPs. As a result, primary disinfection of the coagulated and settled water with free chlorine is limited to approximately two minutes of contact time, with secondary disinfection provided by chloramines. For evaluation purposes, TTHM and HAA6 were formed in coagulated water by adding free-chlorine and maintaining free-chlorine residual for 48 hours. While not representative of the full-scale facility, the tests were used to compar DBPFP by coagulant and NPDOC level.

As shown in **Figure 2**, iron-based coagulants formed lowe DBP concentrations than the aluminum-based coagulants. The DBPs formed following iron- or aluminum-based coagulation increased directly with NPDOC, regardless of coagulant, as note by the overlap of the iron and aluminum DBP data sets. Both coagulants removed the same precursors; iron just removed more.

The use of either coagulant would require continued secondary disinfection with chloramines to avoid exceeding the Stage I D/DBP MCLs of 80 mg/L TTHM and 60 mg/L HAA5. A slight reduction in DBPs could be realized if ferric sulfate or ferric chloride were used at the WSF, but not enough to meet the D/DBP Rule requirements using free chlorine.

Coagulant titration evaluation: Acid strength is an important factor to consider when selecting a coagulant because the choice can dramatically affect the additional acid or base needed to achieve the desired flocculation pH. Under ideal conditions, the target flocculation pH is achieved by the coagulant, but raw-water alkalinity often varies by season, so the loss of pH control by coagulant alone is inevitable. Variations in untreated water quality at the WSF require the addition of supplemental hydroxide (OH) to increase alkalinity in the untreated water in order to maintain pH in the optimized coagulation zone.

Coagulant titrations were performed to determine the ratio of alkalinity destroyed to coagulant dose. The amount of each coagulant required to consume one milliequivalent (meq) of alkalinity were 2.5 meq PACl, 1.5 meq alum, 1.5 meq ferric sulfate, and 1.0 meq ferric chloride. The titrations indicated ferric sulfate had a significantly higher acid strength relative to alum and therefore had greater pH-reduction capability.

Based on a review of historical data, concurrent alum and sodium hydroxide addition was needed for approximately 66 days out of any given year, occurring primarily during the wet season when the buffer capacity of the raw water was low. This condition would favor the use of PACl, which had a lower acid strength and provided greater leeway for alkalinity swings in the untreated water. If PACl were used in lieu of alum, theoretical estimates indicate that the frequency of sodium hydroxide addition to the raw water could be decreased by half. However, the use of PACl instead of combined alum and sodium hydroxide addition was outweighed by cost.

Additional titrations performed in the absence of natural organic matter were used to assess possible metal-NOM interaction. Coagulant demand in synthetic water was unchanged, indicating metal-NOM interaction was not a dominant reaction mechanism. Reaction with bicarbonate alkalinity (i.e., metal hydroxide precipitation or sweep flocculation) in this water was apparently the favored coagulation reaction mechanism.

NPDOC equilibrium/adsorption isotherms: NPDOC removal was evaluated using adsorption isotherms. Isotherms represent defined distributions of NPDOC mass removed (X) per unit mass of coagulant added following coagulation (M), represented as X/M plotted versus the equilibrium NPDOC concentration following coagulation and flocculation. Shown as **Equations 1 and 2**, Freundlich and Langmuir isotherm models were applied to the alum and ferric-sulfate data sets.

$$\text{Log}\frac{X}{M} = \text{Log}(a) + \frac{1}{b}\,\text{Log}(C_e)$$

Equation 1

$$\frac{X}{M}^{1} = \frac{1}{c} + \frac{1}{cd}\,\frac{1}{C_e}$$

Equation 2

The physical-chemical constants a, b, c, and d were solved by performing a linear regression of the transformed models. Comparison of the models indicated the Freundlich model was slightly better than the Langmuir model, evident from higher coefficients of determination (r^2) of 0.82 to 0.91 versus 0.73 to 0.84 for alum, and 0.43 versus 0.33 for ferric sulfate.

The adsorption model results indicated NPDOC adsorption was better described with alum than ferric sulfate, as shown in **Figure 3**. The relationship between the solid (metal

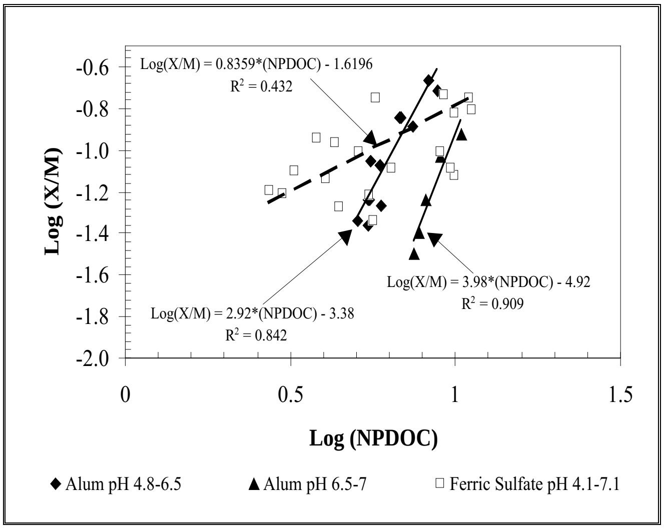

Figure 3: Freundlich NPDOC Adsorption Isotherm

hydroxide floc) and liquid phase (NPDOC) was significantly more variable for ferric sulfate than alum.

During the analysis, adsorption capacity was found to vary with flocculation pH, suggesting that removal mechanisms differ with pH. This prompted partitioning the alum jar-test data into two pH ranges: 4.8 to 6.5 and 6.5 to 7 Although not presented in the same manner, similar findings are reported by other investigators (e.g., White et al, 1997).

NPDOC modeling: NPDOC removal was shown previously to vary with coagulant dose and flocculation pH. Additional modeling was performed to predict NPDOC levels (mg/L C) as a function of coagulant dose, flocculation pH, and alkalinity. Given that alkalinity was artificially adjusted using sodium hydroxide and sulfuric acid, a wide range of initial alkalinities were represented. Coagulation with alum and ferric sulfate were modeled, based on the simple linear regression model presented as **Equation 3**. The resulting models for alum and ferric sulfate are shown as **Equations 4 and 5**, respectively, which were derived by applying a natural log (base e) transformation of Equation 3.

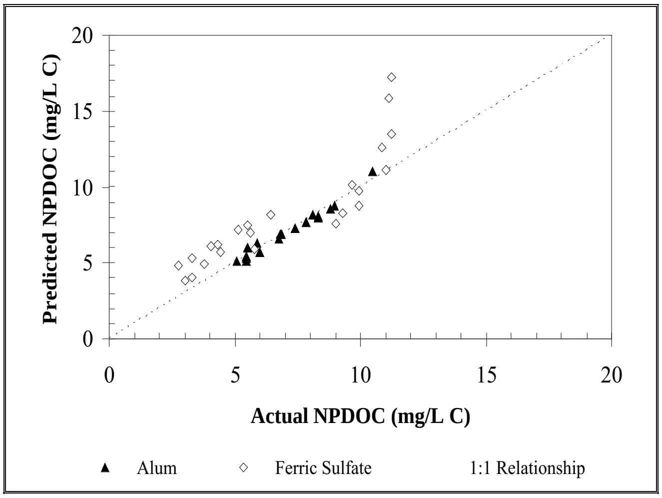

Figure 4: Alum and Ferric Sulfate NPDOC Modeling Results

$$NPDOC_{Effluent} = K_a + K_b(Dose) + K_c(pH) + K_d(Alkalinity)$$

Equation 3

$$NPDOC_{Effluent} = 3.48\ (Alum\ Dose)^{0.21}(pH)^{0.89}$$

Equation 4

$$NPDOC_{Effluent} = 3.75\ (Ferric\ Sulfate\ Dose)^{0.32}(pH)^{1.16}$$

Equation 5

For both coagulants, coagulant dose (mg/L as alum) and flocculation pH were good predictors of the amount of NPDOC removal following coagulation/flocculation. Both independent variables were significant to greater than 99-percent confidence. Alkalinity before coagulation did not contribute significantly for either coagulant (i.e., $p>0.05$).

Predicted versus actual NPDOC concentrations were in good agreement, as illustrated in **Figure 4.** Similar to that indicated in the adsorption isotherm data, less variation was apparent for alum than ferric sulfate. With a mean square error (MSE) of 1.54 mg/L C, greater error was indicated for ferric sulfate than alum, which had an MSE of 0.39 mg/L C. Over prediction of NPDOC following ferric sulfate coagulation occurred predominantly for low chemical dosages (i.e., below 13 mg/L as alum).

Coagulant selection: Alum was identified as the most advantageous coagulant for use at the WSF. This selection was based upon treatment performance, associated chemical cost, evaluation of advantages and disadvantages, and demonstrated history at the WSF. Ferric sulfate and PACl were not chosen because of higher chemical cost (roughly four times greater than alum). Corrosivity, difficulty in handling, and higher chemical costs precluded a recommendation favoring use of ferric chloride.

Conclusions and Recommendations

Alum, ferric sulfate, PACl and ferric chloride were each capable of meeting the D/DBP Rule requirement of 50-percent NPDOC removal for this water. Depending on the specific coagulant/raw-water combination, the iron-based coagulants removed approximately 10 to 15 percent more NPDOC than did the aluminum-based coagulants, with maximum NPDOC values reaching 77 percent for ferric sulfate and 65 percent for alum. Even with maximum NPDOC removal, the use of chloramines will still be required to meet Stage 1 DBP regulations. As for color removal, the sulfate-based coagulants were generally superior to the chloride-based coagulants. Overall, alum was the least-expensive coagulant for use at the WSF and was recommended for continued use because it met critical operational, aesthetic, and regulatory requirements for treatment.

The alum, PACl, ferric-sulfate and ferric-chloride coagulants offered a wide range of acid strengths. Each coagulant except ferric chloride was partially hydrolyzed. At acid strengths ranging from 2.5 meq PACl (as alum) per meq alkalinity and 1.0 meq ferric chloride (as alum) had the least and greatest alkalinity demand, respectively. Optimized coagulation with the iron-based coagulants in the pH range of 3.5 to 5 produced significantly less buffered clarified water.

NPDOC adsorption was characterized using isotherms. Alum coagulation-flocculation was well described by the Freundlich isotherm. The alum isotherm data also indicated NPDOC removal mechanisms varied consistently by flocculation pH region. NPDOC adsorption behavior was more varied and poorly described by both the Freudlich and Langmuir isotherm.

Empirical modeling confirmed that NPDOC removal was significantly related to coagulant dose (alum and ferric sulfate dose) and pH, but was not significantly related to alkalinity prior to coagulation over the experimental range for dose and pH. Resulting models indicated the relationships were nonlinear and well described using a natural log transformation of a simple linear regression model. Comparison of the mean square error for each coagulant led to the conclusion that NPDOC removal via alum was more predictable than that of ferric sulfate.

Finally, it was concluded that the off-stream reservoir could be used for continuous pre-sedimentation of raw river water. Conceptual advantages associated with this process configuration included reduced raw-water quality fluctuation at the plant and improved taste and odor control.

Acknowledgments

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