

PRI-SC[®] SULFIDE, PHOSPHORUS AND UV FOULING IMPROVEMENTS AT RALEIGH, NC

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ABSTRACT

The City of Raleigh has been using ferrous sulfate (FeSO₄) for years in their collection system for hydrogen sulfide and plant phosphorus control. Several years ago the Neuse River wastewater treatment plant upgraded their ultraviolet disinfection (UV) system to a higher intensity lamp technology. Although the UV system was equipped with mechanical wipers, manual cleaning by plant personnel was required due to the elevated iron levels carrying over to the disinfection stage coupled with the lamp sleeve's higher temperature. In 2008, the City of Raleigh implemented Peroxide Regenerated Iron Sulfide Control (PRI-SC[®]) as a means to improve collection system sulfide control and maintain plant phosphorus removal while reducing the amount of iron salts in the collection system. PRI-SC[®] chemical savings were found to be \$80,300 per year. Manual UV sleeve cleaning frequency was reduced from 2 weeks to 2 months, saving 32 man hours per cleaning or \$25,600 per year.

KEYWORDS: Hydrogen Sulfide, PRI-SC[®], Hydrogen Peroxide, Iron Salts, Alum, Odor Control, Phosphorus, Ultraviolet Disinfection

INTRODUCTION

The City of Raleigh Neuse River Wastewater Treatment Plant (Neuse River WWTP) is a tertiary wastewater treatment facility serving the City of Raleigh and surrounding communities. Its capacity is 157.7 m³/min (60 MGD) and it is treating an average of approximately 96.5 m³/min (36.7 MGD). Although the Neuse River WWTP is mainly surrounded by farmland and is fairly isolated from the community, the influent structure is near a neighborhood and odors at the plant are a concern. Figure 1 shows an aerial photo of the facility largely surrounded by farmland and identifies the raw influent chamber where the twin 1.83 m (72") diameter gravity lines enter the plant. These two 1.83 m gravity lines originate approximately 8 km (5 miles) upstream at the Walnut Creek Lift Station (WCLS).

The City of Raleigh has been adding FeSO₄ for years at three locations upstream of the WCLS in order to control odors and corrosion in the areas upstream of the WCLS through to the Neuse River WWTP. The FeSO₄ addition also provides phosphorus control at the Neuse River WWTP (Gutierrez, Park, Sharma and Yuan, 2010). A simplified collection system schematic identifying FeSO₄ feed locations is shown in Figure 2.



Figure 1. City of Raleigh Neuse River WWTP

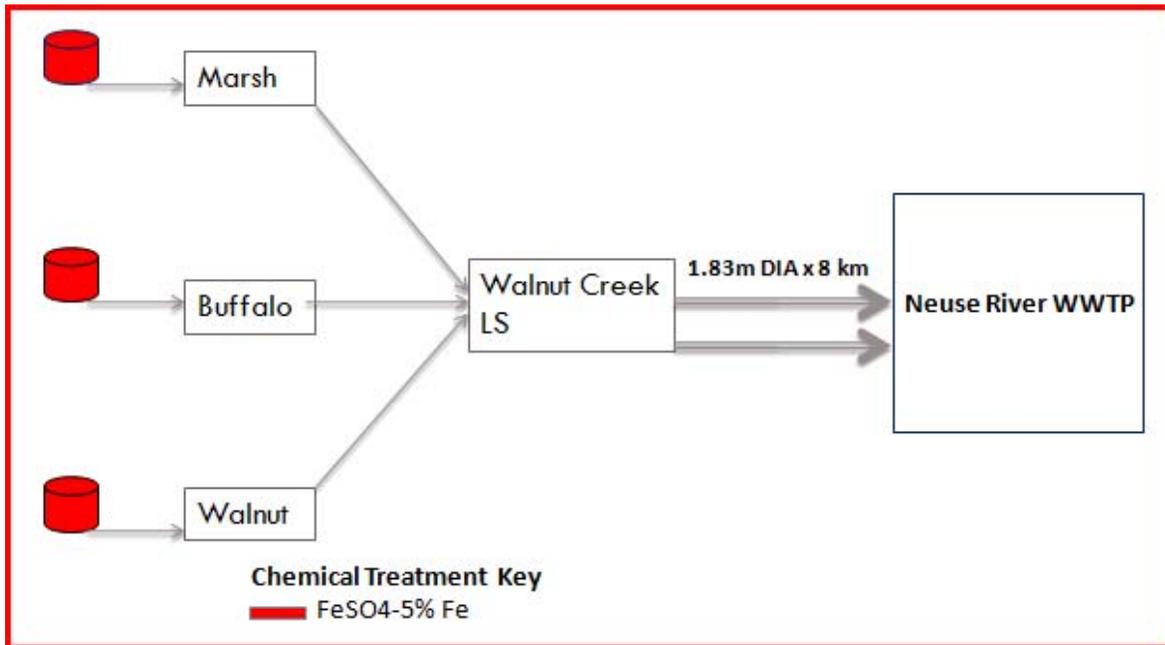


Figure 2. Simplified Collection System Schematic with FeSO₄ Feed Sites

The Neuse River WWTP upgraded their ultraviolet disinfection system to a higher intensity lamp technology several years ago. Although the UV system was equipped with mechanical wipers, manual cleaning by plant personnel was required due to the elevated iron levels carrying over to the disinfection stage coupled with the higher temperature of the lamp sleeves in the new system. Although fouling rates cannot be directly correlated to iron concentrations alone (Sehnaoui and Gehr, 2001), iron is still a part of the matrix of fouling materials. Heat from the UV lamps, also known as thermally-enhanced precipitation, increases the fouling rate of UV sleeves with iron being one of the predominant cations along with calcium and aluminum (Lin, Johnston and Blatchley III, 1999). The plant reduced collection system iron feed and implemented alum at the plant for phosphorus removal as a means to reduce manual UV system cleaning frequency. This had limited success but resulted in some increased levels of hydrogen sulfide in the collection system.

METHODOLOGY

In September 2008 the City of Raleigh contracted with US Peroxide (US Peroxide, LLC, Atlanta, Georgia, USA) to evaluate PRI-SC[®] technology (Walton, Velasco and Ratledge, 2003) as a way to improve upon the existing odor and phosphorus control program with the objective of also reducing manual UV sleeve cleaning frequency. US Peroxide provided the hydrogen peroxide, double walled chemical storage, dosing equipment, remote telemetry monitoring, data collection, dose rate adjustment, applications support and reporting. The City of Raleigh maintained their existing FeSO₄ sites, plant alum feed and collected data for raw and final phosphorus levels as required per their NPDES permit. The PRI-SC[®] technology was implemented by adding H₂O₂ at the WCLS to regenerate FeSO₄ fed from three upstream locations as shown in Figure 3.

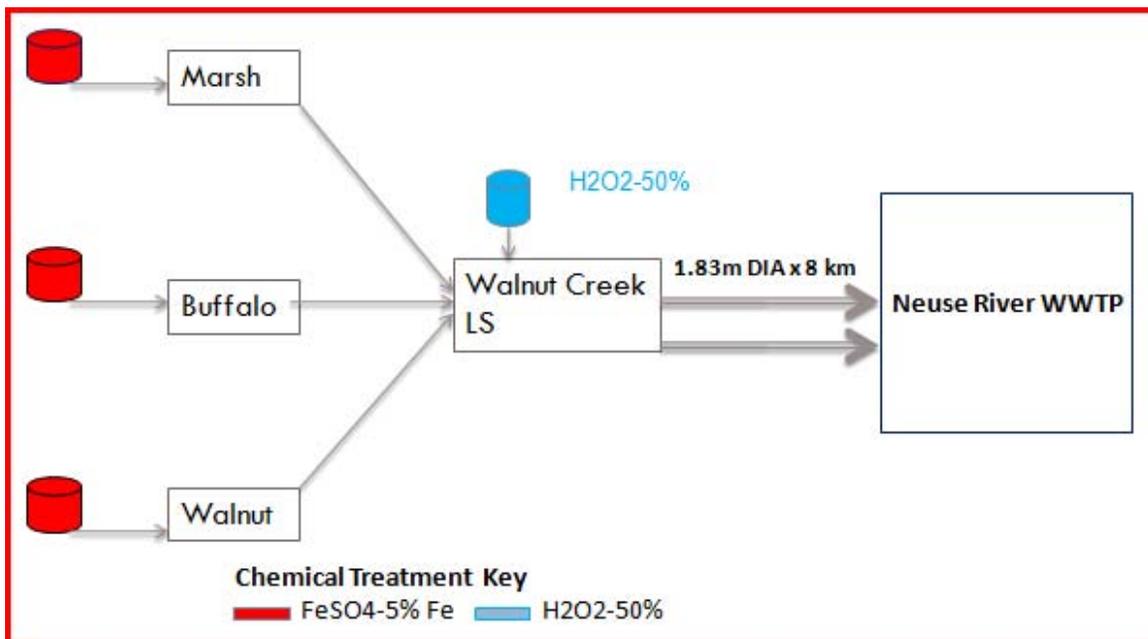


Figure 3. Simplified Collection System PRI-SC[®] Schematic

The PRI-SC[®] process is a patented technology that combines the use of iron salts (either FeCl₂, FeCl₃ or FeSO₄) and hydrogen peroxide or other oxidant in a unique fashion, whereby an iron salt is added as the primary sulfide control agent in the upper reaches of the collection system, and hydrogen peroxide is added at specific points downstream to “regenerate” the spent iron (FeS). The regeneration step effectively oxidizes the sulfide to elemental sulfur and in the process “frees up” the iron for subsequent sulfide and phosphorus control further downstream. PRI-SC[®] was chosen because it is a proven technology for long duration sulfide control (Walton, Nguyen and Hetherington, 2005; Neofotistos, Szczucki and Chau, 2006; Lynne, Grubb, Welle and Hausauer, 2009) that did not require a wholesale change of the City of Raleigh’s existing approach.

The H₂O₂ storage and dosing system was located at the WCLS at the base of the Archimedes screws as shown in Figure 4. The H₂O₂ was injected into the distribution channel feeding the



Figure 4. Hydrogen Peroxide System Installation at Walnut Creek Lift Station

bar screens located at the base of the Archimedes screws. The wastewater retention time is less than one minute from the H₂O₂ injection point to the top of the Archimedes screws.

The sampling locations used to compare the effectiveness of PRI-SC[®] versus the existing program are shown in Table 1. The goal was to provide equal or better performance for both

Table 1. Sampling and Monitoring Locations

Sampling Location	Time Frame	Analyses
Walnut Creek LS – Base of Archimedes screws	Throughout Demonstration	Total & Diss. Sulfide, pH, temp., Fe
Walnut Creek LS - Top of Archimedes screws	Throughout Demonstration	Vapor H ₂ S
Neuse River WWTP Raw Influent Chamber	Throughout Demonstration	Total & Diss. Sulfide, pH, temp., Fe, Vapor H ₂ S
Neuse River WWTP – Plant to Perform (Inlet and Outlet Phosphorus Levels)	Throughout Demonstration	Phosphorus

sulfide control and phosphorus control at an equal or lower cost and to observe any changes in the UV sleeve fouling rates. The sampling methods used during the evaluation period are outlined in Table 2. Liquid grab samples were taken on a regular basis throughout the test period. Vapor phase sulfide (H₂S) readings were continuously logged every five minutes using Odalogs.

Table 2. Sampling Methods

Liquid Grab Samples	Procedure
Total Sulfide	Std. Methods 4500-S ²⁻ D. Methylene Blue (LaMotte drop count kit)
Dissolved Sulfide	Std. Methods 4500-S ²⁻ D. Methylene Blue (LaMotte drop count kit) using pre-flocculation to remove insoluble sulfides
pH	Combination glass electrode
Temperature	NIST calibrated thermometer
Total Iron	Std. Methods 3500-Fe D. Phenanthroline (Hach colorimeter)
Ferrous Iron	Std. Methods 3500-Fe D. Phenanthroline (Hach colorimeter) without hydroxylamine reduction step
Residual H ₂ O ₂	DPD redox test strips (EM Quant)
Phosphorus	Acid Persulfate Digestion Method (Hach Method 8190)
Vapor Samples	
H ₂ S, ppm	App-Tek Odalog (monitor/datalogger)

A number of dosing scenarios were tested during the demonstration period. The scenarios tested included:

1. Baseline testing at existing FeSO₄ and alum feed rates.
 2. PRI-SC[®] dose scenarios with existing FeSO₄ feed rates and H₂O₂ dosing at WCLS with Neuse River WWTP alum dose rates reduced based on plant phosphorus levels.
 3. PRI-SC[®] dose scenarios with reduced FeSO₄ feed rates and H₂O₂ dosing at WCLS with Neuse River WWTP alum dose rates adjusted based on plant phosphorus levels.
- Detailed dose rates of FeSO₄ and H₂O₂ in liters per day (LPD) are outlined in Table 3.

Table 3. FeSO₄ and H₂O₂ Dose Rates Tested

Treatment Condition	Date	H ₂ O ₂ (LPD)	FeSO ₄ (LPD)
Baseline 2008	1/1-8/31	0	7297 (Avg.)
Baseline	9/3- 9/19	0	6404
PRI-SC [®] 1	9/19-9/24	749	6404
PRI-SC [®] 2	9/25-10/22	662	6404
PRI-SC [®] 3	10/22-10/31	662	4481
PRI-SC [®] 4	11/1-12/31	568	2214
PRI-SC [®] 2009	1/1-8/31	450 (Avg.)	2214 (Avg.)

RESULTS

Demonstration Period

The demonstration period started in September 2008 and went through December 2008. A summary of the total sulfide (TS) and dissolved sulfide (DS) results at both the WCLS and the Neuse River WWTP Raw Influent (NRRI) are shown in Table 4.

Table 4. Demonstration Period Liquid Sulfide Data

Treatment Condition	Date	H ₂ O ₂ (LPD)	FeSO ₄ (LPD)	WCLS Avg. Sulfide (mg/L) TS / DS	NRRI Avg. Sulfide (mg/L) TS / DS
Baseline	9/3- 9/19	0	6404	1.0 / 0.5	1.9 / 1.0
PRI-SC [®] 1	9/19-9/24	749	6404	0.3 / 0.1	1.3 / 0.3
PRI-SC [®] 2	9/25-10/22	662	6404	0.4 / <0.1	1.7 / 0.6
PRI-SC [®] 3	10/22-10/31	662	4481	0.3 / 0.3	1.1 / 0.5
PRI-SC [®] 4	11/1-12/31	568	2214	0.1 / <0.1	0.4 / 0.2

Baseline data was collected prior to the demonstration period and for several weeks in September 2008. Baseline FeSO₄ feed rates in September 2008 were 6404 LPD (1692 GPD) dosed at a constant rate over 24 hours. This level was a little lower than the prior 8 months average of 7297 LPD (1928 GPD). Baseline total and dissolved sulfide at the WCLS averaged 1.0 mg/L and 0.5 mg/L respectively. Baseline total and dissolved sulfide at the NRRI averaged 1.9 mg/L and 1.0 mg/L respectively. The dissolved sulfide is what was used for comparison purposes as this is the unbound portion that can be released into the gaseous phase under turbulent conditions.

The initial PRI-SC[®] test scenarios (PRI-SC[®] 1 & 2) were at the baseline collection system FeSO₄ feed rate (6404 LPD) with the addition of H₂O₂ at WCLS at a constant dose rate of 749 LPD (198 GPD) and then a subsequent profiled dose rate of 662 LPD (175 GPD). Under both PRI-SC[®] 1 & 2 rates, average dissolved sulfide levels at WCLS were reduced to 0.1 mg/L and below. The H₂O₂ PRI-SC[®] reaction time at WCLS is less than one minute, demonstrating the speed at which the catalytic oxidation of sulfide occurs. This is further demonstrated by observing the effect on the gaseous H₂S levels at the top of the highly turbulent Archimedes screws in Figure 5. Figure 5 compares the gaseous H₂S levels when the H₂O₂ was off (Baseline) for one day to the PRI-SC[®] 2 dose condition. Gaseous H₂S levels were reduced from an average of 21 ppm with peaks of 90 ppm to an average of 3 ppm with peaks of 16 ppm. Dissolved sulfide levels at the NRRI at PRI-SC[®] 1 & 2 conditions were reduced to 0.3 mg/L and 0.6 mg/L respectively. A corresponding gaseous H₂S reduction was seen in the Odalog files. Gaseous H₂S levels were reduced from an average of 10 ppm with peaks of 45 ppm to an average of 1 ppm with peaks of 8 ppm.

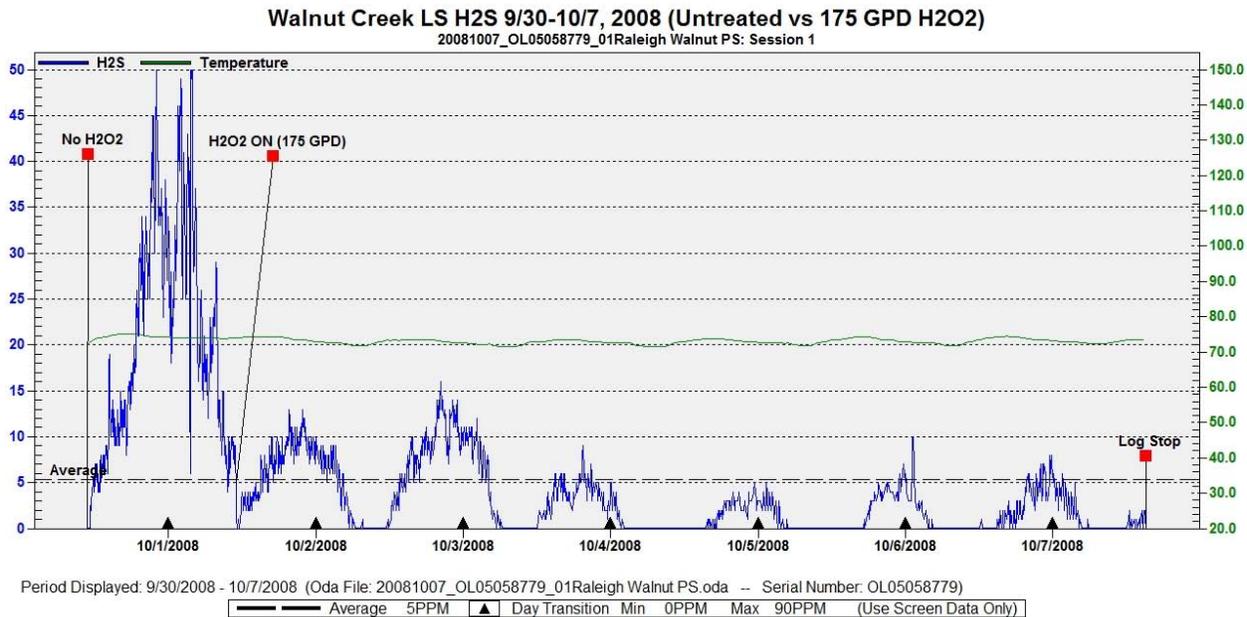


Figure 5. Walnut Creek Lift Station Gaseous H₂S Baseline versus PRI-SC[®] 2

PRI-SC[®] test condition 3 was at both reduced FeSO₄ (4481 LPD) and H₂O₂ (662 LPD) feed rates as detailed in Table 3. Under this test condition, average dissolved sulfide levels at WCLS were reduced to 0.3 mg/L. Dissolved sulfide levels at the NRRI at PRI-SC[®] 3 condition were reduced to 0.5 mg/L. PRI-SC[®] test condition 4 was at further reduced FeSO₄ (2214 LPD) and H₂O₂ (568 LPD) feed rates. Under this test condition, average dissolved sulfide levels at WCLS were reduced to less than 0.1 mg/L. Dissolved sulfide levels at the NRRI at PRI-SC[®] 4 condition was reduced to 0.2 mg/L. Some of the PRI-SC[®] 4 condition probably captured sulfide level reduction due to seasonal factors although the typical seasonal reductions in North Carolina are not as pronounced due to the warmer climate. From a sulfide odor control perspective, PRI-SC[®] provided better performance at both the WCLS and the Neuse River WWTP under all conditions tested during the demonstration period.

At the reduced FeSO₄ feed rates, the plant was able to maintain phosphorus levels below their 2.0 mg/L NPDES permit limit with adjustments to the plant alum. Since it was demonstrated that PRI-SC[®] could reduce the FeSO₄ feed rates significantly while providing equal or better performance for both hydrogen sulfide and phosphorus control, the City of Raleigh decided to move into an extended optimization period where the longer term performance and cost for hydrogen sulfide, phosphorus and UV sleeve fouling could be measured.

Extended Optimization Period

The Extended Optimization Period started in January 2009 and went until August 2009. The extended optimization period allowed for long, steady state operation of the PRI-SC[®] program. Goals of the extended optimization period were as follows:

1. Compare average phosphorus removal efficiency over the three seasons of the existing program versus the PRI-SC[®] program.
2. Compare hydrogen sulfide control at WCLS and the Neuse River WWTP over the three seasons with PRI-SC[®] versus the existing program.

3. Determine the UV sleeve manual cleaning frequency under the PRI-SC[®] program.
4. Compare the overall costs of the PRI-SC[®] program versus the existing program over the three seasons.

The average FeSO₄ and alum feed rates from January 2008 through the end of August 2008 were 7297 LPD (1928 GPD) and 2048 LPD (541 GPD) respectively. The average FeSO₄, H₂O₂ and alum feed rates from January 2009 through the end of August 2009 were 2214 LPD (585 GPD), 450 LPD (119 GPD) and 2198 LPD (581 GPD) respectively. The City of Raleigh had extensive influent and effluent phosphorus data collected as part of their NPDES permit requirements. This allowed for a detailed comparison of the FeSO₄ and alum only program in 2008 versus the PRI-SC[®] and alum program in 2009. Table 5 details the influent and effluent phosphorus data from January through August 2008. Table 6 details the influent and effluent phosphorus data from January through August 2009. In the 2008 period, the influent and effluent phosphorus levels averaged 6.47 mg/L and 1.24 mg/L respectively. This calculates to 80.8% removal efficiency with their FeSO₄ and alum program. In the 2009 period, the influent and effluent phosphorus levels averaged 6.41 mg/L and 1.43 mg/L respectively. This calculates to 77.7% removal efficiency with the PRI-SC[®] and alum program. This longer term operational history demonstrated that the PRI-SC[®] program could provide equivalent phosphorus removal efficiency with the reduced FeSO₄ rates in the collection system and similar alum feed rates at the plant.

Table 5. Neuse River WWTP Phosphorus Data 2008 FeSO₄ and Alum Program

Month	Influent T-P (Avg. mg/L)	Effluent T-P (Avg. mg/L)	T-P Removed (Avg. %)
January	6.91	1.72	75.73
February	6.38	1.77	77.88
March	6.60	1.12	83.21
April	6.73	0.39	93.95
May	6.87	0.48	92.71
June	6.17	1.34	78.24
July	6.00	1.72	72.11
August	6.09	1.37	76.17
Average	6.47	1.24	80.83

Table 6. Neuse River WWTP Phosphorus Data 2009 PRI-SC® and Alum Program

Month	Influent T-P (Avg. mg/L)	Effluent T-P (Avg. mg/L)	T-P Removed (Avg. %)
January	6.91	1.58	76.34
February	7.51	1.42	81.32
March	6.44	0.98	84.80
April	5.90	0.88	85.15
May	5.60	1.97	65.64
June	5.69	1.95	63.80
July	6.94	1.67	75.97
August	6.75	1.03	83.69
Average	6.41	1.43	77.69

Hydrogen sulfide data collected throughout 2009 continued to demonstrate improved performance versus the FeSO₄ only program in place in 2008. Table 7 shows the average liquid sulfide values over the January through August period in 2008 when the city was running FeSO₄ only versus 2009 when PRI-SC® was operational. Dissolved sulfide data at the WCLS were

Table 7. Extended Optimization Period Liquid Sulfide Data

Treatment Condition	Date	H ₂ O ₂ (LPD)	FeSO ₄ (LPD)	WCLS Avg. Sulfide (mg/L) TS / DS	NRRI Avg. Sulfide (mg/L) TS / DS
Baseline	2008	0	7297	1.9 / 0.5	1.0 / 1.0
PRI-SC®	2009	450	2214	1.2 / <0.1	0.5 / 0.3

reduced from an average of 0.5 mg/L to less than 0.1 mg/L. Dissolved sulfide data at the NRRI were reduced from an average of 1 mg/L to 0.3 mg/L. The data collected over the 2009 period plus the extensive data collected during the Demonstration Period showed that consistent improvements in hydrogen sulfide control could be achieved with the PRI-SC® program.

During the operation of the existing FeSO₄ and alum program in 2008, it was estimated that the plant operators manually cleaned the UV lamp sleeves every two weeks. Each manual UV sleeve cleaning takes two operators two days to perform or 32 total man-hours. The cleaning process requires the operators to remove the UV lamp modules from the channel and to manually wipe each quartz sleeve in order to remove the deposits on the surface that can inhibit the disinfection performance of the system. During the 2009 PRI-SC[®] operation period, manual UV sleeve cleaning frequency was reduced from every two weeks to every two months. This 77% reduction in cleaning frequency correlates pretty closely to the 70% reduction in FeSO₄ feed rate over the comparison period.

Operation over similar eight month periods in 2008 and 2009 allowed for a more accurate cost comparison between the existing program and PRI-SC[®]. Day to day fluctuations and one-time events spread out over three seasons were not expected to materially impact the cost analysis. Table 8 has the average daily feed rates of H₂O₂, FeSO₄ and alum over the January to August comparison periods with the average daily cost calculated for both conditions. The daily cost

Table 8. Extended Optimization Period Cost Comparison

Condition	Period	H ₂ O ₂ (LPD)	FeSO ₄ (LPD)	Alum (LPD)	Cost/day (\$)
Baseline	2008	0	7297	2048	2344
PRI-SC [®]	2009	450	2214	2198	2124

savings were calculated to be \$220 per day or \$80,300 per year. The PRI-SC[®] program reduced the number of UV sleeve cleanings from 26 per year down to 6 per year. This resulted in a savings of 640 man-hours per year or approximately \$25,600 per City of Raleigh calculations. Total annual savings by implementing PRI-SC[®] long-term are estimated to be \$105,900.

DISCUSSION

FeSO₄ feed rates in the collection system were reduced by 70% on average, which led to a reduction in UV sleeve manual cleaning frequency of 77%. Although the literature suggests that UV sleeve fouling rates cannot be directly correlated to iron concentrations alone, in this particular instance they correlated closely. Each wastewater treatment plant is unique in the wastewater make-up, process equipment and process configuration. Depending on the set-up, iron may be more or less likely to carry over into the disinfection stage. In the case of the Neuse River WWTP, the initial iron concentration of 3.2 mg/L entering the plant may have been high enough to allow a portion of it to make it past both the primary clarifiers and the aeration basins. The primary clarifiers will typically remove a large portion of the spent iron with the aeration basins taking care of the rest by converting both the spent iron and any free iron into ferric. The majority of the ferric in an aeration basin will bind with orthophosphate or organic material and find its way into the waste activated sludge. 2009 PRI-SC[®] iron concentrations entering the Neuse River WWTP were 1.0 mg/L. Assuming similar percent removal of the iron through the combined plant process steps would result in the reduced fouling rates observed during the extended demonstration period.

The regeneration of iron at the WCLS allowed for similar levels of phosphorus removal at the Neuse River WWTP with a minimal 7% increase in alum feed rates. This demonstrates that the regenerated iron is providing similar phosphorus control benefit at the Neuse River WWTP versus the previous program dosing FeSO₄ only at much higher rates. As discussed in the previous paragraph, a majority of the spent iron entering the Neuse River WWTP settles out in the primary clarifiers and will not carry over into the aeration basins where it can be converted to ferric and remove phosphorus. Therefore, for phosphorus removal what is important is how much free iron is carried over into the aeration basins. Based on the phosphorus removal results during the extended demonstration period, the amount of free iron provided to the aeration basins was similar for both the FeSO₄ only program and PRI-SC[®]. This finding supports the proposition that regenerated Fe from PRI-SC[®] is available for phosphorus control as well as for sulfide control.

CONCLUSIONS

When compared to the FeSO₄ program alone, PRI-SC[®] was able to provide improved hydrogen sulfide control at both the WCLS and the Neuse River WWTP. Even though the FeSO₄ levels were reduced by 70% in the collection system, equivalent levels of phosphorus removal were achieved at the Neuse River WWTP with similar levels of alum feed. By reducing the amount of iron entering the Neuse River WWTP, UV sleeve fouling rates were significantly reduced, resulting in 77% fewer manual sleeve cleanings per year. By implementing PRI-SC[®], the City of Raleigh achieved annual chemical cost savings of \$80,300 plus an additional \$25,600 per year in labor savings from the reduced frequency of manual UV sleeve cleanings. The City of Raleigh continues to utilize PRI-SC[®] in their collection system. The PRI-SC[®] program has allowed the city to address both collection system and treatment plant issues in a more holistic manner.

In the future, further work may be done to better quantify the iron concentrations at each stage throughout the Neuse River WWTP. This would allow for confirmation of the free iron concentration entering the aeration basins for phosphorus removal and the iron levels carrying over into the UV disinfection process.

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