# Disinfection Performance of Peracetic Acid in Florida Wastewater Reuse Applications

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# DISINFECTION PERFORMANCE OF PERACETIC ACID IN FLORIDA WASTEWATER REUSE APPLICATIONS

by

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To my parents and Alissa, for your unwavering support

The thesis "Disinfection Performance of Peracetic Acid in Florida Wastewater Reuse Applications" submitted by Killian Paul Eckert in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering has been

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# ABSTRACT

As Florida's population continues to grow and urbanization increases, traditional freshwater sources are in danger of being exhausted. Wastewater reuse programs offer a way to create a potable offset in order to protect these freshwater sources and the environments in which they are found. Reuse regulations for the disinfection of wastewater are increasingly becoming more stringent. In addition to tough regulations, operating costs have also become a driving force behind a movement to assess new and potentially economical chemicals and processes for disinfection. The objective of this thesis is to assess the disinfection performance of peracetic acid (PAA), an alternative chemical that can be used for the disinfection of wastewater in reuse programs. A pilot study was conducted at the Miller St. Wastewater Treatment Plant (WWTP) located near Orange Park, Florida. The pilot study consisted of three phases that were designed to determine the dosage of PAA required to meet Florida's reuse regulations for treatment plants that provide high-level disinfection, quantify disinfection by-product (DBP) formation and aquatic toxicity, and investigate the effectiveness of utilizing multiple chemical injection points in series with smaller doses of acid. The results showed that the disinfection performance of PAA were comparable with the chlorination system currently in use at the plant when the proper dosage was used. In addition to its disinfection performance, the study showed that disinfection with PAA did not produce harmful amounts of DBP that are normally associated with chlorine-based disinfection.

# Chapter 1 - Introduction

A growing population and increased urbanization within Florida has led to an increase in the volume of wastewater that must be managed and treated. Treated wastewater is most often discharged into surface waters or utilized in reuse programs throughout Florida. One of the issues driving the implementation of reuse programs throughout Florida is the inability of most surface waters to assimilate large quantities of treated wastewater (York & Crook, 1990). Wastewater inputs can affect several water quality characteristics of a water body, such as dissolved oxygen and nutrient levels (UNF & JU, 2012). Additionally, discharging treated wastewater into a water body can have adverse effects on the aquatic life found within the discharge area such as impacting species' reproduction and growth rates. The beneficial use of treated wastewater would not only mitigate environmental impacts but would create a potable offset. The Florida Administrative Code (FAC) defines several uses for reuse wastewater including: landscape irrigation for places such as golf courses, cemeteries, highway medians, playgrounds, or residential properties; agricultural irrigation for food crops, nurseries, or pastures; aesthetic uses such as decorative ponds or fountains; groundwater recharge using slow-rate, rapid-rate, or absorption field land applications; industrial applications such as cooling and process water; wetlands restoration; or fire protection (FAC 62-600.200, 1996). In order to utilize this non-traditional source of water, it must be disinfected to appropriate levels to ensure public safety.

Chlorination is one of the most popular and cost effective chemicals for the disinfection of wastewater utilized around the world (Hammer & Hammer, 2003). While the use of chlorine has its advantages, when reacted with organic matter it has the potential to form DBPs. In order to mitigate the production of DBPs the Florida Department of Environmental Protection (FDEP) encourages the use of alternative disinfection methods (FAC 62-600.440, 1996). This has led some organizations to seek alternative chemicals or methods for the disinfection of wastewater. One such chemical, peracetic acid (PAA), has yet to be evaluated to determine if it is capable of providing a level of disinfection that is in accordance with the standards of Florida wastewater reuse regulations.

Prior to performing a full-scale trial at a treatment facility, the FDEP requires that pilot studies be performed for projects that provide disinfection (FAC 62-610.564, 1999). The pilot study for the evaluation of PAA was conducted at the Miller St. WWTP from January of 2012 through February of 2013. The Miller St. WWTP is located adjacent to the Town of Orange Park within the Jacksonville, Florida metro area and is operated by the Clay County Utility Authority (CCUA). The plant has an average design flow rate of 5.0 million gallons per day (mgd), with a peak capacity of 12.5 mgd. It provides primary and secondary wastewater treatment for the unincorporated area of Clay County near the Town of Orange Park and discharges wastewater effluent to the St. Johns River and to CCUA's reuse wastewater system. Where the facility discharges its effluent is dependent upon the demand for reuse water from neighboring areas. When demand is high, the facility operates in a reuse mode; diverting the treated effluent to adjacent neighborhoods and golf courses. During periods of low water demand within the CCUA service area, the treated effluent is discharged into a Class III marine portion of the St. Johns River. The Miller WWTP includes screens, equalization basins, clarifiers, sand filtration, chlorination/de-chlorination infrastructure, and sludge management facilities. The plant is permitted under the FDEP wastewater regulations and has an existing National Pollutant Discharge Elimination System (NPDES) operating permit (FL0025151). This permit has been amended six times, most recently in October of 2011. The latest permitted the Miller St. WWTP to begin providing its effluent for wastewater reuse purposes. Currently, the plant uses chlorination for pathogen inactivation. However, recent increases in the stringency of wastewater reuse regulations have resulted in a movement of system operators to find alternative non-chlorine based disinfection chemicals. An ideal disinfection system should guarantee the maximum efficiency in pathogenic microorganism inactivation without generating toxic and undesirable by-products (Veschetti, Cutilli, Bonadonna, Briancesco, Martini, Cecchini, Anastasi, & Ottaviani, 2003). Additionally, the disinfectant should be compatible with the current infrastructure in order to minimize conversion costs. PAA is an ideal candidate for those plants seeking a non-chlorine based disinfection chemical as it is compatible with the current infrastructure at most plants and does not produce the same harmful levels of DBPs that chlorination systems are associated with in the United States.

The pilot study was comprised of three phases, the primary objectives of this study were to: 1) determine the appropriate dose of PAA that would satisfy the disinfection standards as required by Florida reuse regulations for facilities providing high-level disinfection, 2) quantify the concentration of DBPs produced and aquatic toxicity, if any, after PAA had reacted with the waste stream, and 3) assess the potential benefits, if any, of utilizing multiple chemical injection points with smaller doses of PAA.  A secondary objective was also investigated, the possibility of inactivating emerging contaminants (e.g. personal care products, prescription drugs, industrial chemicals, etc.) using PAA. The details of this study can provide a framework for other plants throughout the country to assess the feasibility of utilizing PAA for purposes of disinfection.

## Chapter 2 - Literature Review

The disinfection of wastewater must be performed in order to protect the public from pathogenic microorganisms such as bacteria, viruses, and protozoans. The transmittance of these microorganisms and subsequently infectious diseases is proliferated by fecal wastes. Today there are a myriad of physical and chemical disinfection methods in use around the world. Common disinfection methods include: ultraviolet radiation, chlorination (gas and liquid), and ozone. Chlorination is currently one of the most common disinfection methods in the United States, with 98% of the systems using a chlorine-based disinfection system (Kutzing, 2011). Chlorine is an economical and widely used chemical for the disinfection of wastewater (Hammer & Hammer Jr., 2003). Chlorine was first used for the disinfection of wastewater in 1893 in Hamburg, Germany (Lofrano & Brown, 2010). The chlorine dosage needed for disinfection depends on the unique characteristics of the wastewater found at each WWTP including pH, temperature, contact time, and the presence of interfering substances (Hammer & Hammer Jr., 2003). Chlorine has many attractive features that contribute to its wide use in the water treatment industry. Four key attributes of chlorine are its effectiveness at inactivating a wide range of pathogens, the ability to measure and control the chlorine residual, cost-effective to employ, and its long track record of successful use (USEPA, 1999). Despite its advantages, the use of chlorine as a disinfection agent can result in the production of harmful levels of DBPs such as trihalomethanes (THMs) and haloacetic acids ($HAA_5$) (USEPA, 2012). Trihalomethanes and haloacetic acids are not formed instantaneously but continue to increase in concentration for an extended period of time following chlorination (Hammer & Hammer Jr., 2003). Thus, the THM and $HAA_5$ concentrations can increase in chlorinated water held in the distribution system (Hammer & Hammer Jr., 2003).

As an alternative to chlorination, PAA is a strong disinfectant with a wide range of disinfection uses. PAA has been widely used as a disinfectant and sterilant in many industries including food processing, beverage, medical, and pharmaceutical and as a de-coloring agent in textile and pulp and paper industries (Kitis, 2004). Due to the bactericidal, virucidal, fungicidal, and sporicidal effectiveness demonstrated in these industries the use of PAA as a disinfectant for wastewater effluents has been drawing more attention in recent years (Kitis, 2004). The use of PAA in various WWTPs has shown that doses between 1.0 and 10.0 ppm and contact times between 5 and 60 minutes can achieve 2.0 to 4.0-log reductions of fecal coliform (FC) (Falsanisi, Gehr, Santoro, Dell'Erba, Notarnicola, Liberti, 2006). PAA is an ideal candidate as a non-chlorine-based chemical disinfectant as it does not generate harmful levels of DBPs and is compatible with pre-existing chemical disinfection systems currently in operation throughout the world. The costs associated with converting existing treatment facilities to use PAA would be minimal due to the similarities between the chlorination and PAA disinfection systems. PAA disinfection formulations are available commercially as a mixture of peracetic acid, hydrogen peroxide, acetic acid, sulfuric acid, and water. Preparation of PAA typically involves a reaction of acetic acid and hydrogen peroxide with sulfuric acid acting as an acidic catalyst in order to facilitate the reaction to achieve equilibrium (Xue-bing, Ting, Yu-jie, De-hua, 2008). The formulation is an equilibrium mixture of peracetic acid ($CH_3CO_3H$), acetic acid ($CH_3CO_2H$), hydrogen peroxide ($H_2O_2$), and water ($H_2O$). This is presented in Equation 1.

$$CH_3CO_2H + H_2O_2 \overset{H_2SO_4}{\leftrightarrow} CH_3CO_3H + H_2O \qquad (1)$$

The breakdown of this formulation is highly biodegradable, forming acetic acid (vinegar) and water (FMC, 2012). Baldry and others first showed interest in the late 1980s using PAA for wastewater disinfection (Gehr, Wagner, Veerasubramanian, Payment, 2003). The disinfection effectiveness of PAA has been evaluated in several studies. Using a pilot-scale plant to compare the disinfection performance of PAA to chlorination with sodium hypochlorite, Veschetti et al. (2003) showed that 15% PAA doses between 0.5 and 4.0 ppm and contact times between 8 and 38 minutes yielded 0.9 to 3.5-log reduction in FC concentration. Additionally, their results showed that PAA has disinfection effectiveness similar to that of chlorination. Veschetti et al. (2003) advised future studies to include analysis of the effluent treated with PAA to investigate the presence of other by products in order to assess toxicity. Similar reductions in the concentration of FC were reported by a study performed at the City of Montreal WWTP, although the target disinfection was only achieved on two days during the study (Gehr et al., 2003). Using jar tests, 12% PAA doses of 4.5 to 6.0 ppm and a 1-hour contact time achieved a 2.2 to 4.1-log reduction in the concentration of FC. The cause of achieving the target disinfection on only two days of the study was attributed to the large presence of highly organic matter within the waste stream. At the time Gehr et al. (2003) concluded that PAA was not suited for the wastewater disinfection application as its use was not economical. A dose greater than 6 ppm was recommended in order to achieve proper disinfection while the economically viable range was between 1.5 to 2.0 ppm. The authors recommended further research into the disinfection mechanism of PAA in order to explain the wide variability of disinfection. The suitability of PAA for the disinfection of wastewater to be reused as agricultural irrigation was assessed at the Taranto WWTP in Taranto, Italy (Dell'Erba, Falsanisi, Liberti, Notarnicola, Santoro, 2004). Using a pilot-scale plant, Dell'Erba et al. (2004) found that 15% PAA doses of 4.0, 6.0, and 8.0 ppm with contact times between 31 and 46 minutes achieved a 1.8 to 2.1-log reduction in the concentration of total coliforms (TC). Slightly higher levels of disinfection were found to occur above doses of 6.0 ppm. The inactivation of TC was found to happen rapidly regardless of the dosage of PAA used. Kitis (2004) reviewed several studies in which the disinfection performance of PAA was investigated. Most studies reviewed found that PAA was able to achieve between 3.0 and 5-log reduction of TC, FC, and *Escherichia coli* (*E. coli)* using PAA doses of 5.0 to 10.0 ppm. Factors that were identified as affecting disinfection include: the nature and concentration of organic matter, temperature, pH, total suspended solids (TSS), and biochemical oxygen demand (BOD). The effects of organic matter on disinfection cited by Kitis (2004) agree with the results observed during the study conducted by Gehr et al. (2003) at the City of Montreal WWTP. A study conducted in 2005 at the Kuopio municipal WWTP was able to achieve 3.0-log reduction of TCs using 15% PAA doses of 2.0 to 7.0 ppm with a 22-minute contact time (Koivunen, Heinonen-Tanski, 2005). More recently, a study was conducted that investigated the efficiency of PAA and compared it to chlorine dioxide in the disinfection of secondary effluents from a WWTP located in Italy (De Luca, Sacchetti, Zanetti, Leoni, 2008). The comparison was made using PAA doses of 1.5 ppm and chloride dioxide doses of 1.5 and 2.0 ppm. Results from the study showed that both

PAA and chlorine dioxide led to a higher reduction in total and fecal coliforms than in the phages that were analyzed. PAA was, however, found to be more active than the chlorine dioxide and was not inhibited by the organic content found in the waste stream. This disagrees with the findings of Gehr et al. (2003) and Kitis (2004). The results of these studies indicated that the presence of highly organic matter does indeed have an effect on the disinfection capabilities of PAA. De Luca et al. (2008) found that both disinfectants did not produce significant quantities of DBPs; however, both disinfectants were not able to meet Italian wastewater reuse irrigation regulations. This is most likely due to the low doses used in the study. Figure 1 shows the relationship between CT (product of PAA dose and contact time) and log reduction of total coliform from some of the studies cited.

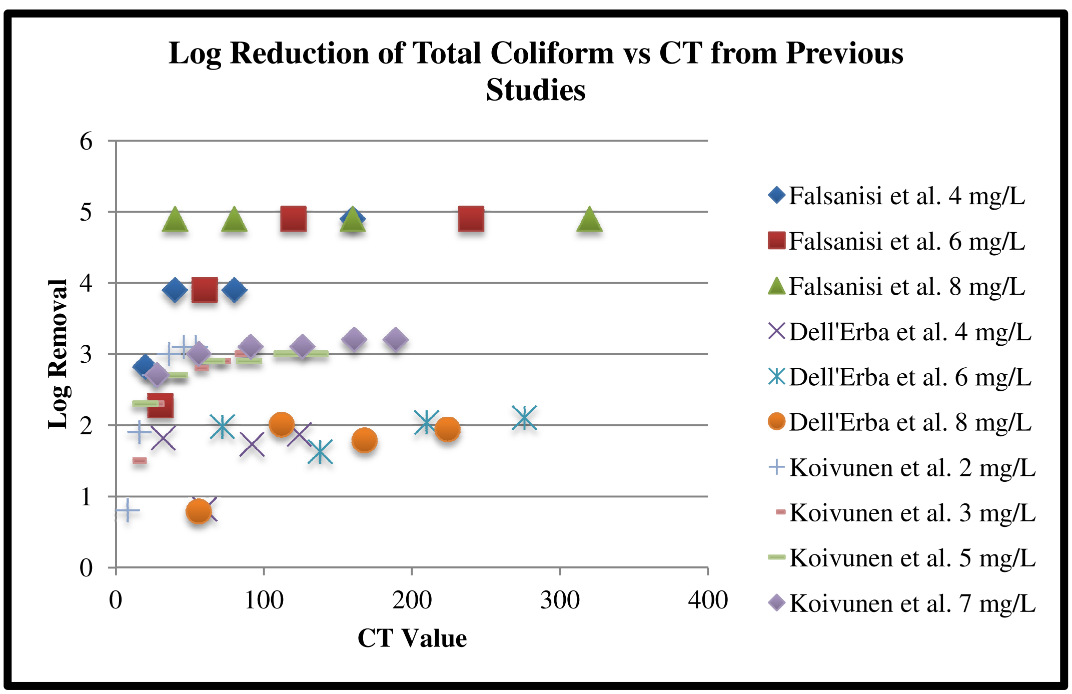


**Figure 1 - CT vs Log Reduction of Total Coliform**

Overall, PAA has been found to be an effective disinfectant with disinfection performance similar to other commonly used disinfection methods. Additional advantages of using PAA include reduced contact time requirements, an absence of significant and harmful levels of DBPs, and minimal infrastructure conversion costs for existing treatments facilities (Veschetti et al., 2003; Gehr et al., 2003; Kitis, 2004; Koivunen et al., 2005; Falsanisi et al., 2006; Santoro, Gehr, Bartrand, Liberti, Notarnicola, Dell'Erba, Falsanisi, & Haas, 2007). Negative aspects of PAA that have been identified are a lower disinfection efficiency for *Cryptosporidium* and *Giardia* (Gehr et al., 2003; Kitis 2004; Santoro et al., 2007) and the financial cost of buying PAA (Gehr et al., 2003; Kitis, 2004; Koivunen et al., 2005). It has been proposed, however, that if the use of PAA was to increase the production capacity and availability would increase (Koivunen et al., 2005), lowering the unit cost of the chemical. The applicability of using PAA may also be dependent upon the required level of treatment (Koivunen et al., 2005) and presence of highly organic material in the waste stream (Gehr et al, 2003; Kitis, 2004).

# Chapter 3 - Testing and Results

## 3.1 Phase One Design and Testing

Phase One of the pilot study was designed by FMC. The objective for Phase One was to determine the dosage of PAA necessary to comply with wastewater reuse standards by disinfecting a constant side-stream of wastewater using a submersible pump placed in the effluent reservoir of the plant's sand filter and provide enough contact time for the PAA to react using a portable tank. The PAA dosage rate was adjusted over the course of the study in order to obtain a PAA residual that effectively reduced the concentration of FC to acceptable levels in order to comply with reuse standards. The chemical used during Phase One was FMC VigorOx® WWT II, a 15% PAA formulation which is approved by the U.S. Environmental Protection Agency (USEPA) (USEPA Reg. No 65402-8) for the disinfection of wastewater effluent streams. Two water samples were taken in order to assess the disinfection performance of PAA: 1) a pre-treatment wastewater sample (EFB-1) was taken in the effluent reservoir of the sand filter, and 2) a post-treatment wastewater sample (EFA-3) was taken at the discharge of the portable tank. The flow of the side-stream was monitored daily throughout Phase One using an inline flow meter; the average flow of the side-stream during Phase One was found to be 46.8 gpm. The side-stream was dosed with 7.5 mg/L of PAA using a single head adjustable output peristaltic pump and fed into the portable 2,500 gallon high-density plastic tank which provided a theoretical contact time of 53 minutes (the plant's actual chlorination contact time ranges between 125 to 160 minutes). It should be noted that the portable tank was not baffled and the mixing characteristics of the tank were not examined using a tracer study. Short-circuiting may have occurred during the mixing process, which could have been a source of error in Phase One. The discharge of the tank was diverted to an onsite lift station where the water was returned to the head of the plant for retreatment. A schematic for Phase One of the pilot study is shown in Figure 2. Detailed photos for Phase One are included in Appendix A.

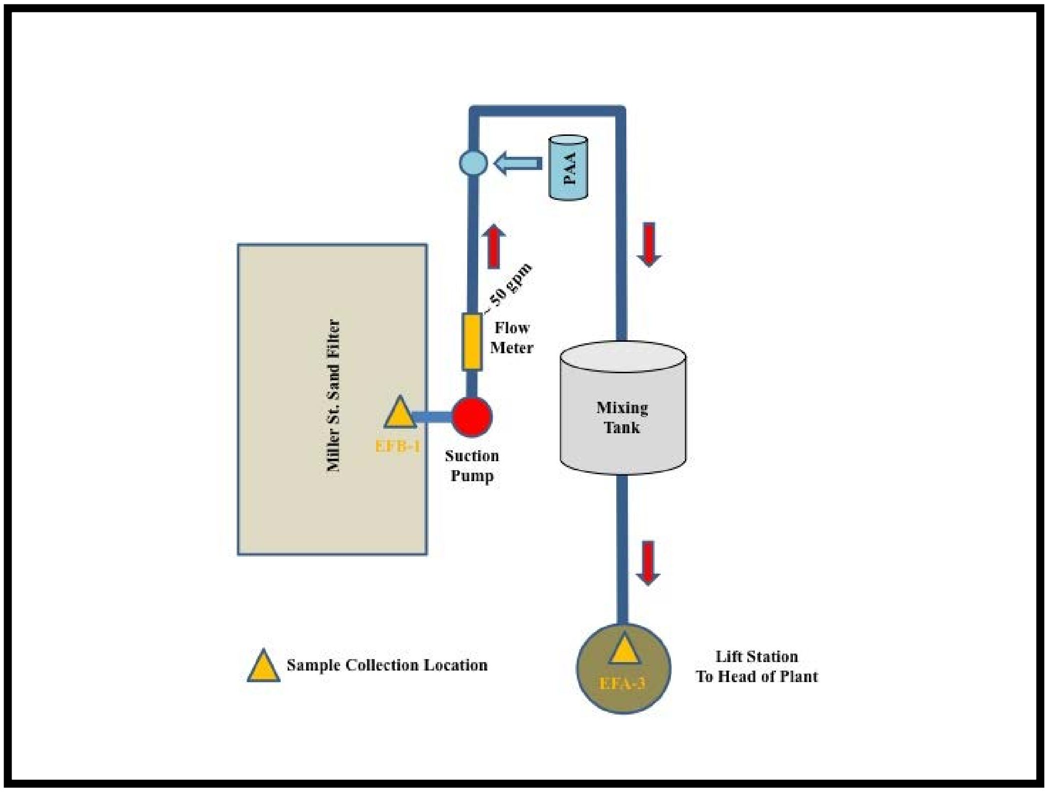


**Figure 2 - Phase One Schematic (Not to Scale)**

The overall disinfection performance of PAA during Phase One was measured using a number of analytes and indicator compounds including: FC, pH, total dissolved oxygen, chemical oxygen demand, flow, and the generation of undesirable DBPs (TTHM and $HAA_5$). These results were compared against the corresponding analytes and target compounds for the existing chlorination system currently in use at the plant. The test methods used to measure the levels of FC and DBPs present within each sample were

SM9222D (FC), USEPA method 524.2 (TTHM), and USEPA method 552.2 ($THAA_5$). Analysis of the samples was performed at CCUA's contract laboratory, Advanced Environmental Laboratories, Inc. located in Jacksonville, Florida. Field measurements of PAA residual and pH were taken hourly using a CHEMetrics V-2000 Multi-Analyte Photometer, and a Fisher Scientific Orion bench top pH meter. A number of other standard analytical parameters were also evaluated during Phase One including total suspended solids, nutrients, and primary/secondary drinking water parameters.

In addition to monitoring these analytes the aquatic toxicity of the wastewater treated with PAA was examined in order to determine if, when discharged into the environment, would the effluent adversely impact the aquatic life within the discharge area. While this test is not a requirement for wastewater reuse, this is an important consideration if the treated wastewater is to be discharged in a surface water body. The objective of the aquatic toxicity tests is to estimate the "safe" or "no effect" concentration of a substance, which is defined as the concentration that will permit normal propagation of fish and other aquatic life in the receiving waters (USEPA, 2002). The tests used to quantify the aquatic toxicity are called the 7-day Chronic Static Renewal Definitive Bioassays. The aquatic species used in the test is dependent on the location of the discharge area; for the Miller St. WWTP, the species used in the test are the water flea (*Ceriodaphnia dubia*) and the Fathead Minnow (*Pimephales promelas*). The effluent chronic toxicity test uses a multi-concentration test including a control and a minimum of five effluent concentrations. The test organisms are exposed to a fresh solution of the same concentration of sample every 24 hours or other prescribed interval, either by transferring the test organisms from one test chamber to another, or by replacing all or a portion of solution in the test chambers (USEPA, 2002). The aquatic toxicity tests are outlined in Table 1.

| Test Method | Species | Dilution Series (%) | USEPA Method |
|---|---|---|---|
| 7-day Chronic Static Renewal Definitive | Water Flea (*C. dubia*) | 0, 12.5, 25, 50, 75, 100 | USEPA-821-R-02-013 Method 1002.0 |
| 7-day Chronic Static Renewal Definitive | Fathead Minnow (*P. promelas*) | 0, 12.5, 25, 50, 75, 100 | USEPA-821-R-02-013 Method 1000.0 |

**Table 1 - Aquatic Toxicity Test Methods**

Testing for Phase One lasted from January 10, 2012 through February 19, 2012; however, it is believed that samples from EFB-1 and EFA-3 were switched at the lab from January 10, 2012 through January 16, 2012. Due to the uncertainty regarding the validity of these results, the data from these dates has been omitted from the analysis and results. The results from Phase One are discussed in Section 3.4.

## 3.2 Phase Two Design and Testing

Phase Two of the pilot study was designed to build upon Phase One. Phase Two was designed after Phase One was found to be unsuccessful in meeting all required treatment goals that will be discussed in Section 3.4. Phase Two provided an opportunity to address the shortcomings of Phase One and conduct a period of intensive sampling in order to gain insight into the disinfection kinetics of PAA; this type of sampling using PAA has not been performed anywhere else at the time of this writing. In order to address the shortcomings of Phase One, a model chlorine contact chamber (CCC) was designed and constructed in order to accurately simulate the hydraulic properties of the existing CCC in use at the plant. The model CCC was designed using a maximum detention time of 120 minutes at 3.5 gpm with an ability to simulate shorter contact times of 60 and 30 minutes using flow rates of 7 and 14 gpm, respectively. Alternatively, samples could be taken along the flow path at specific distances that correspond to desired contact times. The longitudinal-serpentine model CCC was sized based upon dynamic similarity between the model and prototype. The overall length to width (L/W) ratio of the model CCC's flow path was found to be 90 which corresponds to a $t_{10}/t_0$ ratio of 0.9 indicating that the system hydraulics approach "plug-flow" conditions (Davis, 2010). The $t_{10}/t_0$ ratio represents the ratio of the time necessary for 90 percent of the water to be exposed in the disinfection chamber ($t_{10}$) to the theoretical hydraulic detention time ($t_0$) (Davis, 2010). Figure 3 presents the impact of L/W on the $t_{10}/t_0$ ratio.

Graphic redacted, paper copy available upon request to home institution.

**Figure 3 - Impact of L/W on $t_{10}/t_0$ Ratio; Davis, 2010**

Due to this, the theoretical contact time should be similar to the actual hydraulic residence time. The influent for the model CCC was created in the same manner as it had been for Phase One, utilizing the same location within the sand filters effluent reservoir. The effluent of the model CCC was diverted to the onsite lift station to return the effluent to the head of the plant for retreatment. A schematic for Phase Two is shown in Figure 4. Detailed photos for Phase Two are included in Appendix A.

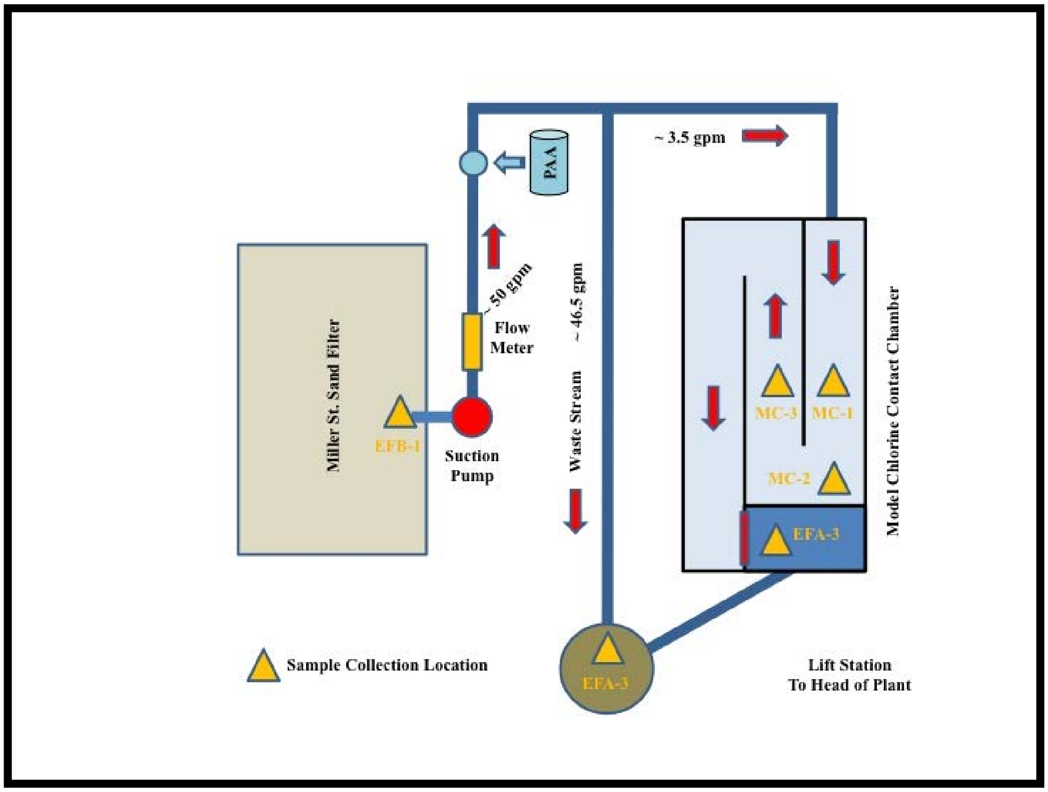


**Figure 4 - Phase Two Schematic (Not to Scale)**

Testing for Phase Two was completed over the summer of 2012. Phase Two consisted of a 10-day prove-out period followed by a 45-day testing period which focused on achieving successful pathogen inactivation in accordance with Florida wastewater reuse regulations. After the Florida wastewater reuse regulations had been met, a 6-day intensive sampling program was completed which focused on assessing pathogen inactivation using different contact times and dosages. The 10-day prove-out period was used to hone in on the most effective PAA dosage to assess during the 45-day reuse testing period. From the results of the 10-day period, a PAA dosage of 8.91 mg/L (approximately 9 mg/L) was found to be the most effective dosage; detailed results will be presented in Section 3.5. The 45-day testing period began on June 12, 2012 and lasted through August 3, 2012. During this time pre-treatment samples (EFB-1) and samples after disinfection (EFA-3) were taken within the effluent reservoir of the sand filter and the discharge of the model CCC, respectively. Analytes similar to those used in Phase One were monitored during the 45-day reuse testing period, these included: FC, pH, PAA residual, chemical oxygen demand, turbidity, and flow. Additionally the aquatic toxicity of the effluent was evaluated similarly to Phase One. Following the completion of the 45-day reuse testing period a 6-day intensive sampling program was completed. The 6-day intensive sampling program began on August 7, 2012 and lasted through August 15, 2012. The program was broken up into three, 2-day segments. During each 2-day segment a different PAA dose was evaluated at each contact time (20, 40, 60, and 120 minutes). Table 2 shows the dosages of PAA for each 2-day segment.

| Sampling Dates | PAA Dosage (mg/L) |
|---|---|
| August 7 and 8 | 8.91 |
| August 9 and 10 | 6.1 |
| August 14 and 15 | 2.5 |

**Table 2 - 6-day Intensive Sampling PAA Dosage Schedule**

During the program samples were taken before treatment (EFB-1) and at points within the model CCC that correspond to contact times of 20, 40, 60, and 120 minutes; these samples were designated as MC-1, MC-2, MC-3, and EFA-3 respectively. The contact times were kept consistent by collecting the samples at the same location within the model CCC while maintaining a constant flow rate. Samples were taken every 45 minutes beginning at 7 AM EST to measure: FC, pH, PAA residual, and total suspended solids.

3.3 Phase Three Design and Testing

Phase Two revealed that compliance with Florida wastewater reuse regulations using PAA is feasible, provided the correct dosage is used. Phase Two also revealed that at the correct dosage, conversion of the plant to PAA might not deliver the desired positive economic benefit that had been previously anticipated. This issue has been identified by previous studies as well (Gehr et al., 2003; Kitis, 2004; Koivunen et al., 2005). In an effort to increase the possibility of economic benefit by converting to PAA, the concept of utilizing smaller doses of PAA in series was evaluated. It had been noted previously in some studies (Falsanisi et al., 2006; Dell'Erba et al., 2004) that PAA reacts rapidly, which minimizes the overall contact time required for disinfection. Phase Three of the pilot study built upon Phase Two. Phase Three utilized the same model CCC, however, multiple chemical injection ports were installed. This differs from both Phases One and Two in which only one chemical injection port was used. The injection ports were named PAA SA #1 through 3. Table 3 shows the approximate location of each injection port within the system.

| Injection Port ID | Injection Port Location |
|---|---|
| PAA SA #1 | Before Model CCC |
| PAA SA #2 | 1/6$^{th}$ point of Model CCC |
| PAA SA #3 | 5/6$^{th}$ point of Model CCC |

**Table 3 - Location of Serial Injection Ports**

Field calibration of the previously used pump revealed that it would not be able to accurately inject the low doses of PAA that would be required. Therefore, two chemical metering pumps were used to dose the ports (one pump per port) within the contact chamber in order to use the lower doses desired. The smaller pumps were capable of delivering between 0.005 and 0.9 mL/minute depending on the speed and size of tubing used. In addition to the change in pump configuration, the flow through the model was increased from 3.5 gpm to 7 gpm to allow for lower PAA doses to be added. A schematic for Phase Three is shown in Figure 5. Detailed photos for Phase Three are included in Appendix A.

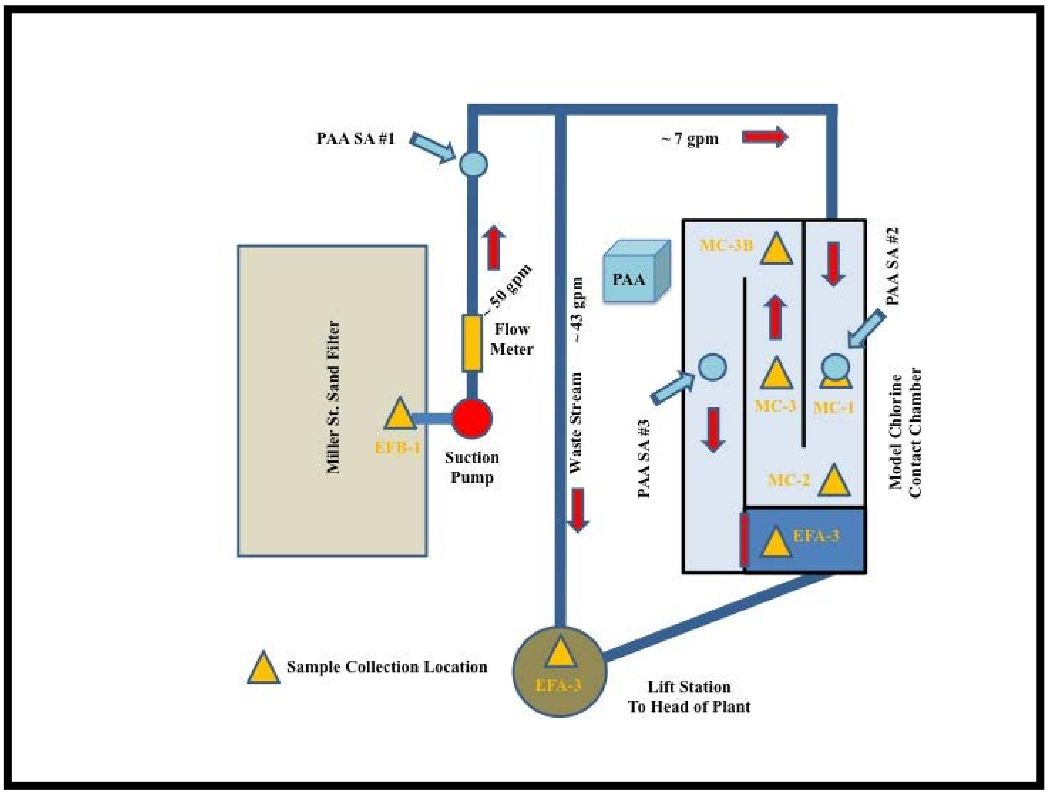


**Figure 5 - Phase Three Schematic (Not to Scale)**

Testing for Phase Three lasted from January 2, 2013 through February 15, 2013. Testing for Phase Three consisted of a 14-day prove-out period and an 11-day reuse sampling program. The 14-day prove-out period was used to determine the optimum combination of dosing and configuration for disinfection. The dosages and configurations used are shown in Table 4.

| Configuration | PAA SA #1 Dosage (mg/L) | PAA SA #2 Dosage (mg/L) | PAA SA #3 Dosage (mg/L) | Total PAA Dosage (mg/L) |
|---|---|---|---|---|
| 1 | 1.5 | Not Used | 1.5 | 3.0 |
| 2 | Not Used | 1.5 | 1.5 | 3.0 |
| 3 | 1.5 | Not Used | 3.0 | 4.5 |
| 4 | Not Used | 1.5 | 3.0 | 4.5 |
| 5 | 1.5 | Not Used | 4.5 | 6.0 |
| 6 | Not Used | 1.5 | 4.5 | 6.0 |
| 7 | 5.0 | Not Used | 4.0 | 9.0 |

**Table 4 - Dosage and Configurations for Intensive Sampling Program**

Since the injection of PAA now occurred within the model CCC in addition to prior to entering the model CCC, the contact times for each sampling point were altered. When injection points PAA SA #1 and #3 were in use the contact times for sample locations MC-1, MC-2, MC-3, MC-3B, and EFA-3 were 10, 20, 30, 40, and 60 minutes respectively. When injection points PAA SA #2 and #3 were in use the contact times for sample locations MC-1, MC-2, MC-3, MC-3B, and EFA-3 were approximately 1, 10, 20, 30, and 50 minutes respectively. Following the 14-day prove-out period, an 11-day reuse sampling program was conducted that mimicked the 45-day reuse sampling program from Phase Two. Samples were collected twice daily at locations EFB-1, MC-1, MC-2, MC-3B, and EFA-3 during the 11-day period. The samples were analyzed for FC, pH, PAA residual, and dissolved oxygen. Water quality samples were taken from both the influent and effluent of both the PAA treatment system and chlorination system and analyzed for emerging contaminants as well as *Cryptosporidium* and *Giardia*. This analysis was only completed once over the course of Phase Three due to the lab fees associated with testing for extremely low concentrations.

## 3.4 Bench Scale Experiment Design and Testing

The bench scale experiment was designed to assess the PAA demand in wastewater and deionized (DI) water using initial PAA doses of 4.5, 6, and 9 mg/L. Additionally, FC samples were collected for comparison purposes. The original scope of the bench scale experiment allotted enough FC samples for the 6 and 9 mg/L doses with 3 additional FC samples to be used if needed. The surplus samples were used to assess the 4.5 mg/L dose. The bench scale experiment was conducted using two plastic buckets that were filled with 5 gallons of DI water and wastewater obtained from the effluent of the sand filter, respectively. The samples were allowed to reach approximately the same temperature before testing began. The PAA dose was introduced into each of the two buckets using a burette. Once dosed, each bucket was stirred for 20 seconds to ensure adequate mixing. Measurements of the PAA residual, pH, and temperature as well as FC samples were taken at 0, 1, 10, 20, 40, 60, and 120 minutes; measurements using the 4.5 mg/L dose were taken at 0, 1, and 10 minutes. A longer contact time for the 4.5 mg/L dose was not thought to be beneficial given the fast-reacting behavior of PAA observed in the previous phases.

## 3.5 Phase One Results

The results of Phase One showed that the disinfection capabilities of PAA were comparable with the chlorination system currently in use at the plant. In addition to its disinfection capabilities, the tests showed that PAA does not produce harmful amounts of DBPs commonly associated with chlorine-based disinfection. The aquatic toxicity tests, however, showed that the effluent disinfected with PAA exhibited more toxicity to the water fleas (*Ceriodaphnia dubia*) used in the bioassay tests. In addition, the test was cut short by a few days due to the higher peracetic acid demand required during the test which resulted in the acid supply running out.

### 3.5.1 Disinfection Performance

The inflow of FC into the plant ranged from 1,000 to 7,000 CFU/100mL during Phase One. Figure 6 shows the relationship between plant flow and concentration of FC.

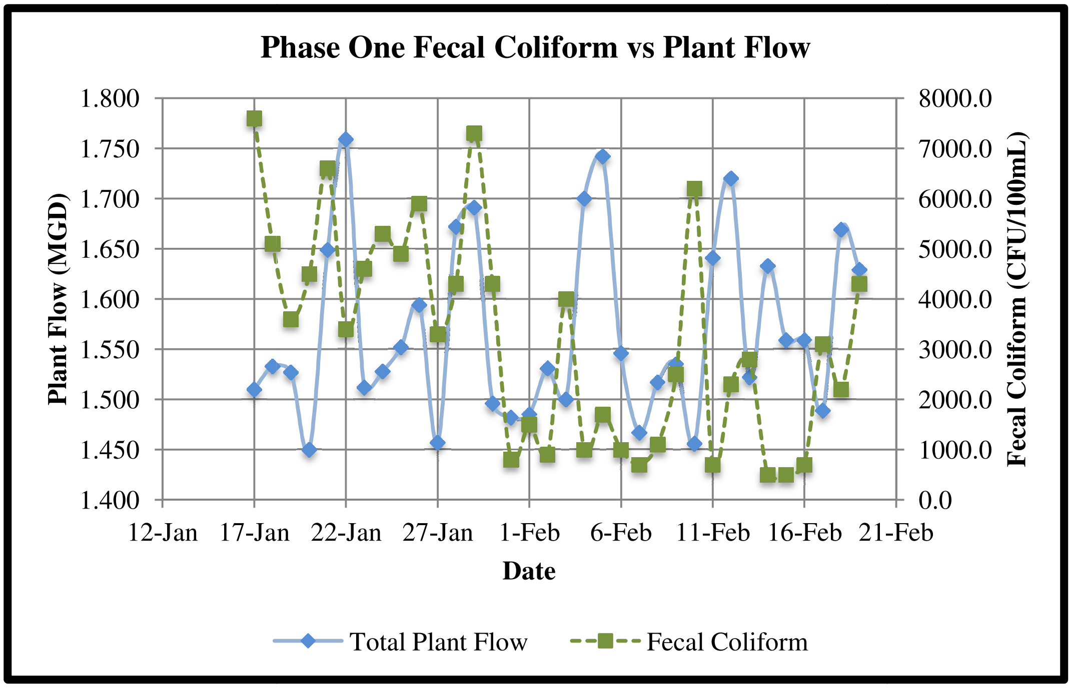


**Figure 6 - Relationship of Plant Flow to Fecal Coliform Concentrations for Phase One**

Although there is a slight lag in time, fluctuations in FC concentrations appear to correspond with increases and decreases in total plant flow. This is shown clearly between January 19th and January 31st. Using FC concentration as a metric of measuring disinfection performance, Figure 7 shows a comparison of the log removal results from the chlorination system to that of PAA.

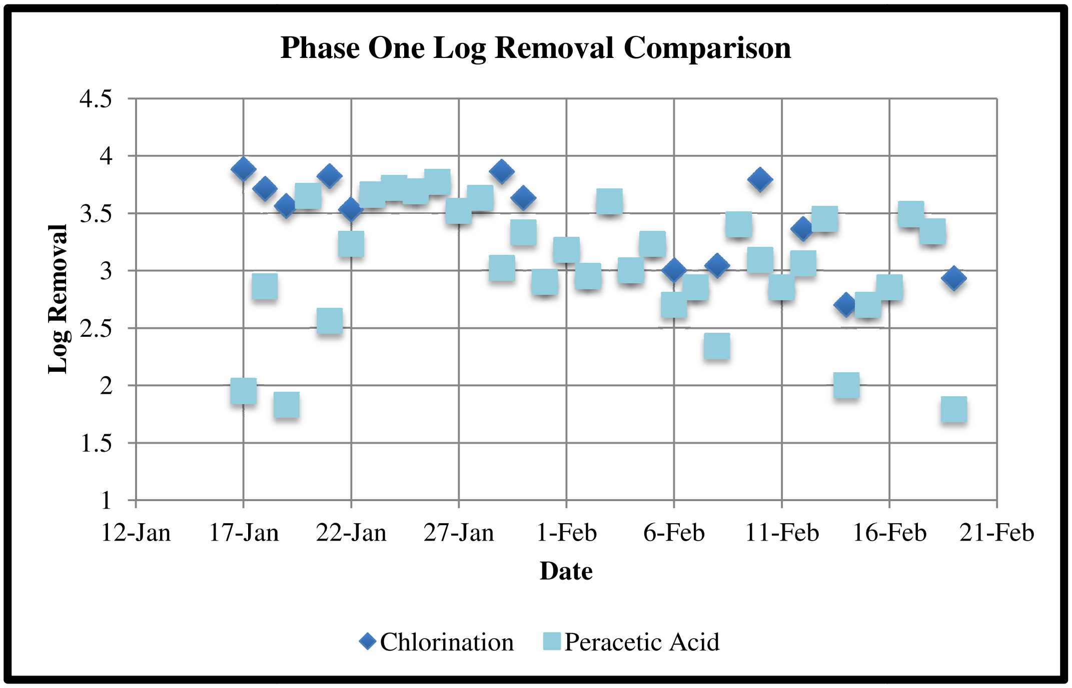


**Figure 7 – Comparison of Phase One Log Removal of Fecal Coliform**

The PAA dosage rate was adjusted over the course of Phase One in order to obtain a PAA residual that effectively reduced the presence of FC to acceptable levels. The low log removals observed for the PAA system from January 17$^{th}$ through January 21$^{st}$ are considered to be part of the study's adjustment period, and not a deficiency on part of PAA. Additionally the poor log removal observed on February 19$^{th}$ is attributed to the supply of PAA becoming depleted on that day. The comparison of disinfection between PAA and the chlorination system was therefore made using the data obtained between January 22$^{nd}$ and February 18$^{th}$. This was defined as Phase Ones "measurement period". Histograms showing the log removal by the PAA system and chlorination system are shown in Figures 8 and 9, respectively.

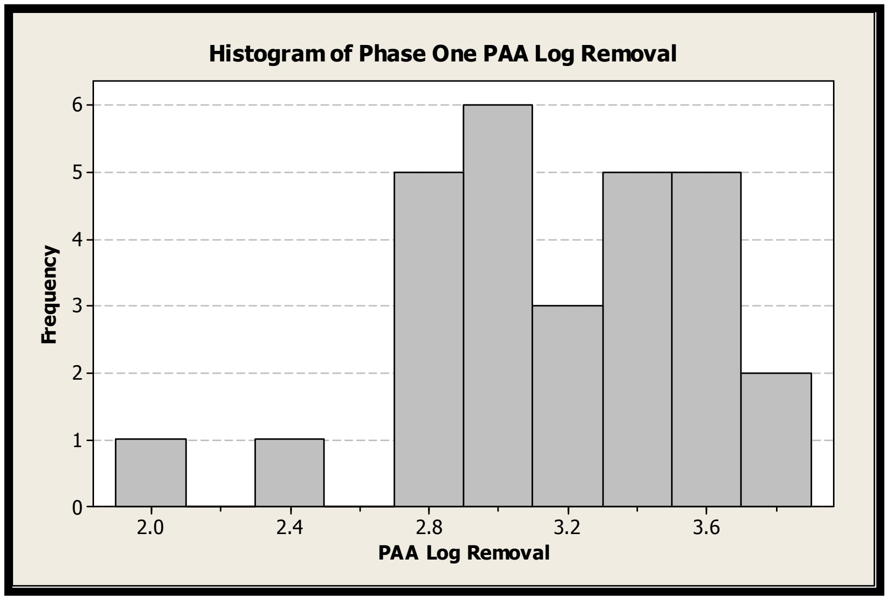


**Figure 8 - Phase One PAA Log Removal Histogram**

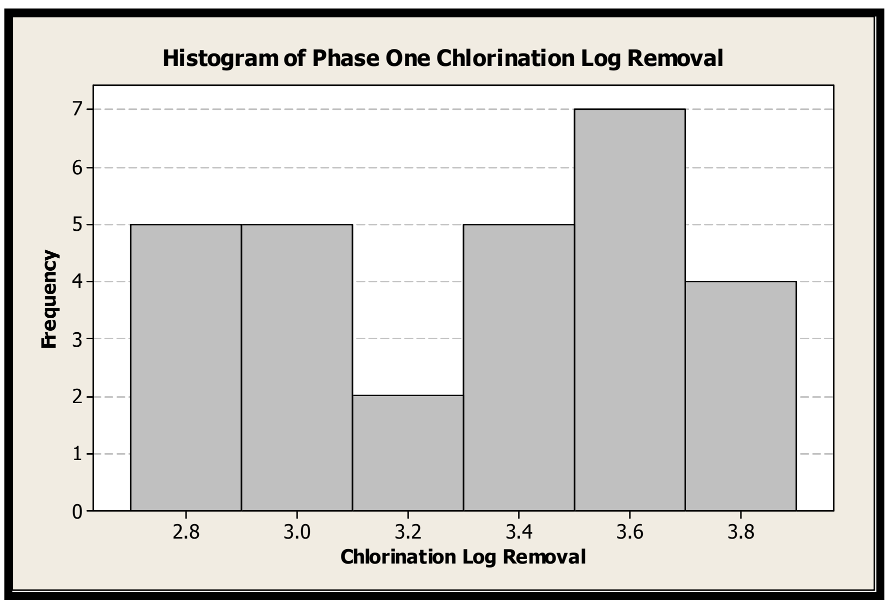


**Figure 9 - Phase One Chlorination Log Removal Histogram**

A comparison of the log removals from the PAA and chlorination systems are shown in the box plots using a 95% confidence level in Figure 10. The box plots display the values of the minimum, maximum, and median data values as well as the upper and lower quartiles.

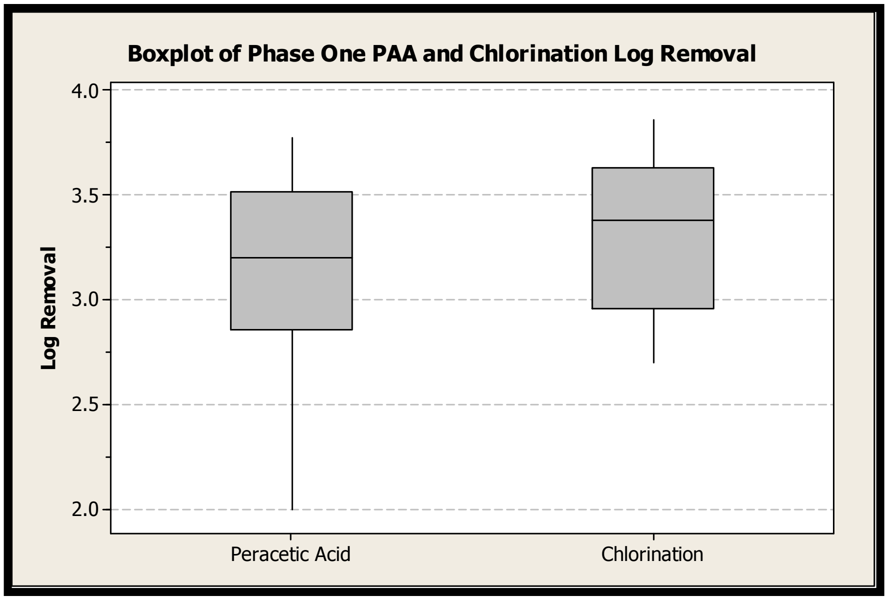


**Figure 10 - Box Plots for Phase One Log Removals from PAA and Chlorination Systems**

Figure 10 shows the spread of data obtained for the PAA system is slightly larger than that of the chlorination system, which indicates that the PAA system has greater variability in log removal than that of the chlorination system. A statistical summary for the PAA and chlorination system from Phase One is shown in Table 5.

| Statistics for Log Removal | PAA | Chlorination |
|---|---|---|
| No. of Data Points | 29 | 29 |
| Arithmetic Mean with 95% Confidence Interval | 3.12 ± 0.18 | 3.30 ± 0.13 |
| Median | 3.18 | 3.36 |
| Variance | 0.24 | 0.13 |
| Standard Deviation | 0.49 | 0.37 |

**Table 5 - Statistical Summary for Phase One**

The disinfection performance of the chlorination system and PAA side stream was also compared using a two-tailed paired T-test at the 95% confidence level. The result from the paired T-test is shown in Table 6.

| Category | No. of Data Points | Arithmetic Mean | Standard Deviation | Standard Error of the Mean | T-Value | P-Value |
|---|---|---|---|---|---|---|
| Chlorination | 29 | 3.30 | 0.37 | 0.07 | - | - |
| PAA | 29 | 3.12 | 0.49 | 0.09 | - | - |
| Difference | 29 | 0.18 | 0.32 | 0.06 | - | - |
| T-Test of Mean Difference = 0 (vs not = 0) | | | | | 3.06 | 0.005 |

**Table 6 - Phase One Paired T-Test Result**

From the data presented in Table 6 for the two-tailed paired T-test it is possible to see that there is significant difference between the disinfection performance of the chlorination and PAA systems at the 95% confidence level.

Figure 11 shows the relationship between log removal and CT values from Phase One.

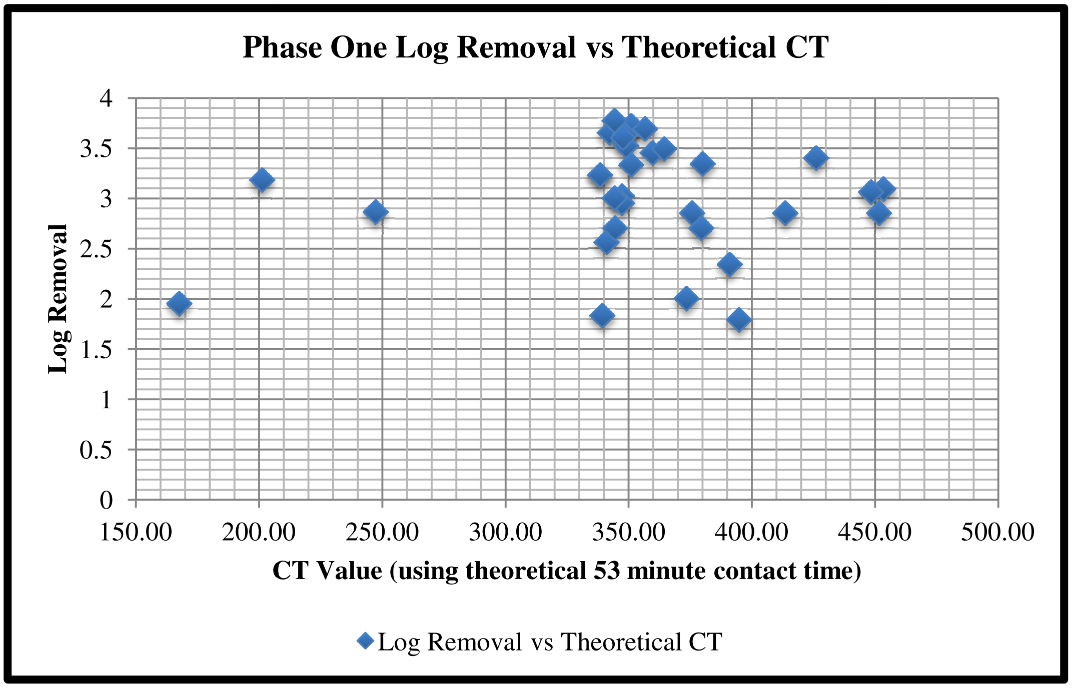


**Figure 11 – Phase One Log Removals vs Theoretical CT Value**

The CT values shown in Figure 11 were calculated using the PAA dosages tested during Phase One and the theoretical contact time of 53 minutes. PAA dosages of 6 mg/L and above were able to achieve at least 3-log reduction in FC.

When the Miller St. WWTP is operating in reuse mode, the FC requirements are subject to reuse requirements as detailed in the site operating permit and in parts 1 through 3 in FAC 62-600.440(5)f (1996). According to the standards, compliance of a domestic wastewater facility providing high-level disinfection level is dependent upon meeting the following criteria:

- Over a 30-day period, 75% of the FC values shall be below the detection limits; and,
- Any one sample shall not exceed 25 CFU/100mL.

While the log removal of FC was found to be at times comparable with the chlorination system, the percentage of samples from the PAA system that were found to be non-detectable for FC during the measurement period was found to be 39%; well below the required 75%. During the pilot study measurement period between January 22nd and February 18th, a 28-day period, all effluent samples were found to have FC concentrations below 25 CFU/100mL. Although the measurement period does not consist of the full 30 days, it is very close.

### 3.5.2 Disinfection By-Products

The DBPs that were measured during Phase One of this study were total trihalomethanes (TTHMs) and total haloacetic acids ($THAA_5$). The THMs and $HAA_5$ are listed in Table 7.

| Group | Compounds |
|---|---|
| THM | chloroform |
| | bromodichloromethane |
| | dibromochloromethane |
| | bromoform |
| $HAA_5$ | monochloroacetic acid |
| | dichloroacetic acid |
| | trichloroacetic acid |
| | monobromoacetic acid |
| | dibromoacetic acid |

**Table 7 - Disinfection By-Products**

Samples were taken nine times from the effluent of the PAA system during Phase One to assess the formation of DBPs. The results of the analyses are presented in Table 8.

| Date | TTHMs (μg/L) | $THAA_5$ (μg/L) |
|---|---|---|
| Jan 13, 2012 | 1.69 | 5.93 |
| Jan 17, 2012 | 2.12 | 5.75 |
| Jan 21, 2012 | 1.51 | 5.46 |
| Jan 25, 2012 | 1.60 | 5.69 |
| Jan 30, 2012 | 1.51 | 1.80 |
| Feb 2, 2012 | 1.70 | 2.59 |
| Feb 7, 2012 | 1.52 | 0.90 |
| Feb 10, 2012 | 1.27 | 4.06 |
| Feb 13, 2012 | 1.35 | 5.08 |

**Table 8 – PAA Disinfection By-Product Results**

The average concentrations for TTHMs and $THAA_5$ were found to be 1.59 and 4.14 μg/L, respectively. Both of these concentrations are well below the maximum allowable concentrations of 80 and 60 μg/L, respectively. TTHMs measured from the effluent of the chlorination system were found to have a concentration of 76.73 μg/L. While not exceeding the maximum allowable concentration, this concentration is much higher than that of the PAA system. Tests for $THAA_5$ were not performed on effluent from the chlorination system during the pilot study; however, results from previous testing indicate that the use of PAA produces considerably lower $THAA_5$.

### 3.5.3 Aquatic Toxicity

The results from the two sets of 7-day Chronic Static Renewal Definitive Bioassays show that the Fathead Minnow specimens exposed to the effluent from the PAA system maintained a 100% final survival for each concentration. This is slightly better than the results of the effluent from the chlorination system, as the final survival results for the 50 and 75% dilution series were 97.5% and 92.5% respectively. In terms of the $IC_{25}$ values, which estimates the concentration of the effluent that will cause a 25% reduction in growth and reproduction (Wisconsin State Laboratory of Hygiene, 2008), both sets of specimens did not exhibit chronic toxicity having $IC_{25}$ values of > 100%. The biggest difference in results was seen in the Water Flea. The Water Flea specimens exposed to effluent from the PAA system maintained similar final survival results to those exposed to effluent from the chlorination system until the dilutions were increased beyond 25 percent. At this point the final survival results for the specimens exposed to the PAA system effluent were much lower than those that had been exposed to chlorination effluent. In terms of $IC_{25}$ values, however, both sets of specimens exhibited chronic toxicity. The $IC_{25}$ values for the specimens exposed to chlorination and PAA effluent were found to be 83.68% and 26.89%, respectively. Summaries of the results from the aquatic toxicity tests are presented in Tables 9 and 10 for the chlorination and PAA systems, respectively.

| Percent Effluent | Water Flea (*C. dubia*) | | Fathead Minnow (*P. promelas*) | |
|---|---|---|---|---|
| | Final Survival (%) | Three Brood Totals (Average # of neonates/female) | Final Survival (%) | Average Dry Weight (mg/fish) |
| 0 | 90 | 33.0 | 100 | 0.631 |
| 12.5 | 80 | 24.1 | 100 | 0.607 |
| 25 | 100 | 28.4 | 100 | 0.716 |
| 50 | 100 | 26.6 | 97.5 | 0.706 |
| 75 | 100 | 26.0 | 92.5 | 0.650 |
| 100 | 100 | 22.4 | 100 | 0.626 |
| $IC_{25}$ | 83.68% | | > 100% | |

**Table 9 - Aquatic Toxicity Results from Chlorination System**

| Percent Effluent | Water Flea (*C. dubia*) | | Fathead Minnow (*P. promelas*) | |
|---|---|---|---|---|
| | Final Survival (%) | Three Brood Totals (Average # of neonates/female) | Final Survival (%) | Average Dry Weight (mg/fish) |
| 0 | 100 | 35.1 | 100 | 0.688 |
| 12.5 | 80 | 29.5 | 100 | 0.703 |
| 25 | 80 | 27.7 | 100 | 0.786 |
| 50 | 30 | 9.5 | 100 | 0.783 |
| 75 | 0 | 0 | 100 | 0.756 |
| 100 | 0 | 0 | 100 | 0.758 |
| $IC_{25}$ | 26.89% | | > 100% | |

**Table 10 - Aquatic Toxicity Results from PAA System**

The purpose of these tests is to ensure that the discharge from the WWTP does not have potential harmful effects on the aquatic life found within the discharge area. If the Miller St. WWTP were to divert all effluent to reuse applications 100% of the time bioassays would no longer need to be performed assuming that an additional operating permit modification is granted by FDEP for this purpose.

3.6 Phase Two Results

The results of Phase Two showed that the disinfection of wastewater with PAA in accordance with Florida reuse regulations is feasible using a PAA dose of at least 8.91 mg/L at most contact times. The aquatic toxicity tests showed that the effluent from the PAA system did not have the same effects that it had during Phase One, this may be due to a lower residual caused by an increased contact time.

3.6.1 Disinfection Performance

The inflow of FC into the plant during the reuse sampling program ranged from 837 to 44,000 CFU/100mL during Phase Two. Figure 12 shows the relationship between plant flow and concentration of FC during this period.

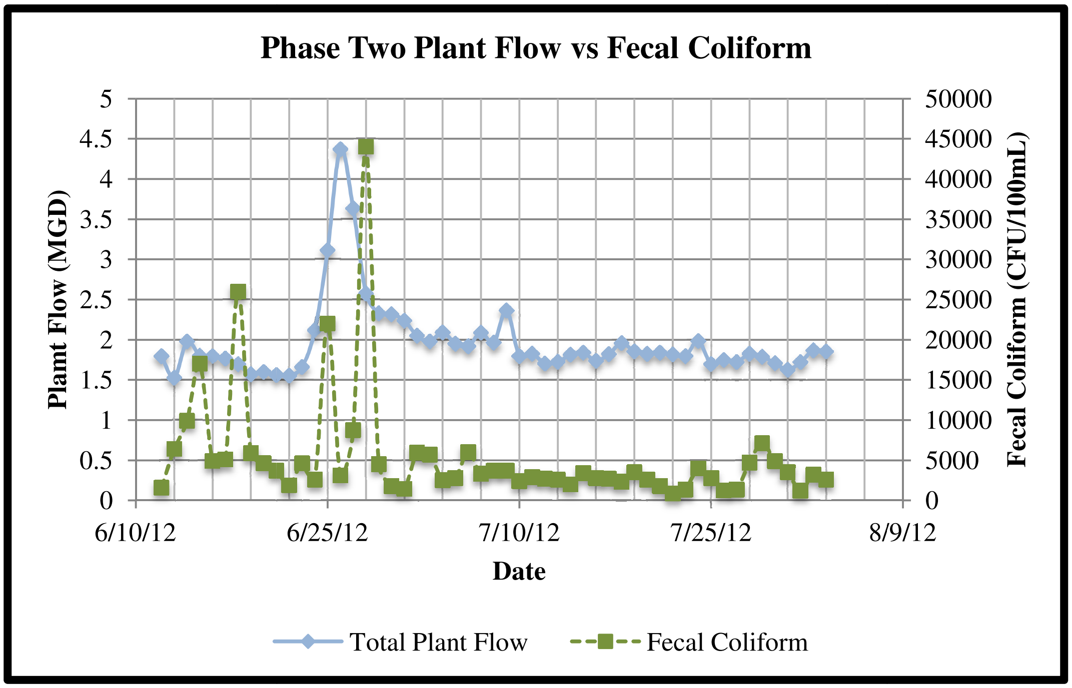


**Figure 12 - Relationship of Plant Flow to Fecal Coliform Concentrations for Phase Two**

The relationship between plant flow and FC concentrations previously observed in Phase One between plant flow and FC concentration does not seem to be as apparent in Phase Two. FC samples were not collected every day for the chlorination system. Additionally FC concentrations from the PAA system effluent that were too numerous to count were observed by the lab on two days during Phase Two, making an accurate assessment unlikely. A comparison between the two systems was therefore made using days in which accurate data was obtained from both systems, a period of 40 days. Figure 13 shows a comparison of the log removal results from the chlorination system to that of PAA during the reuse sampling program.

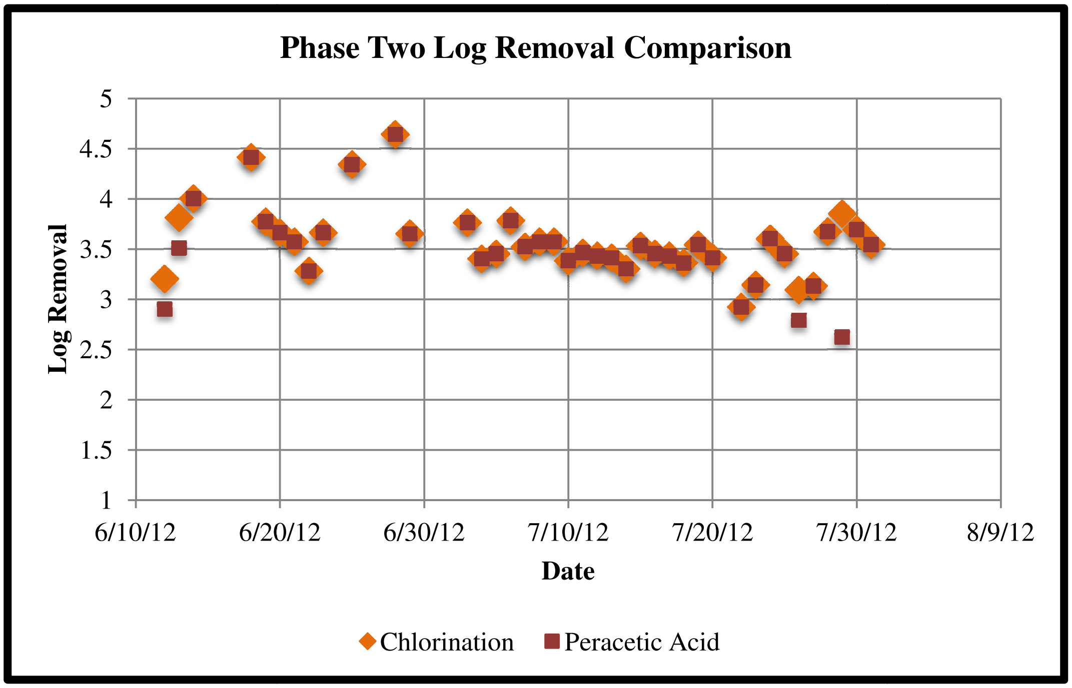


**Figure 13 - Comparison of Phase Two Log Removal of Fecal Coliform**

A PAA dosage of 8.91 mg/L was found to consistently produce almost identical log removals as the chlorination system currently in use at the plant. Histograms showing the log removal by the PAA and chlorination systems are shown in Figures 14 and 15, respectively.

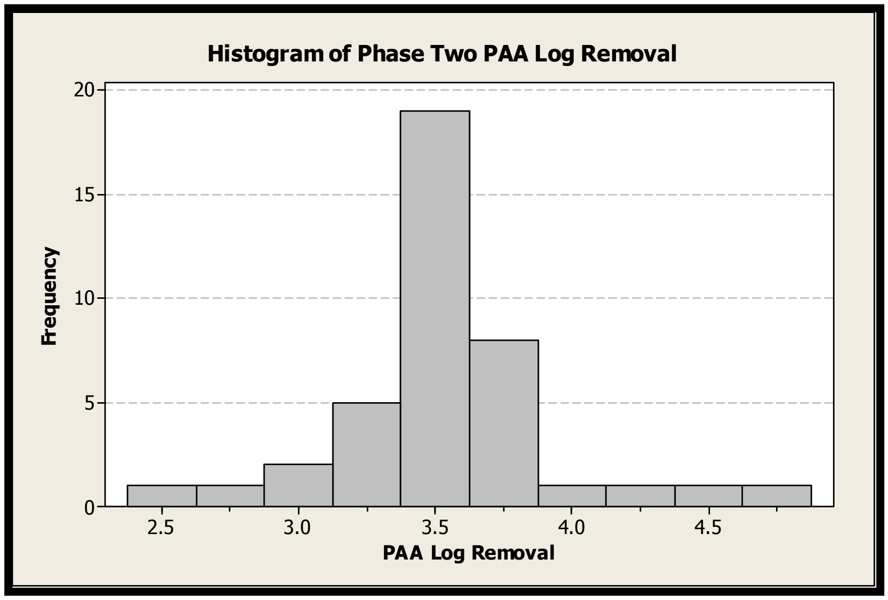


**Figure 14 - Phase Two PAA Log Removal Histogram**

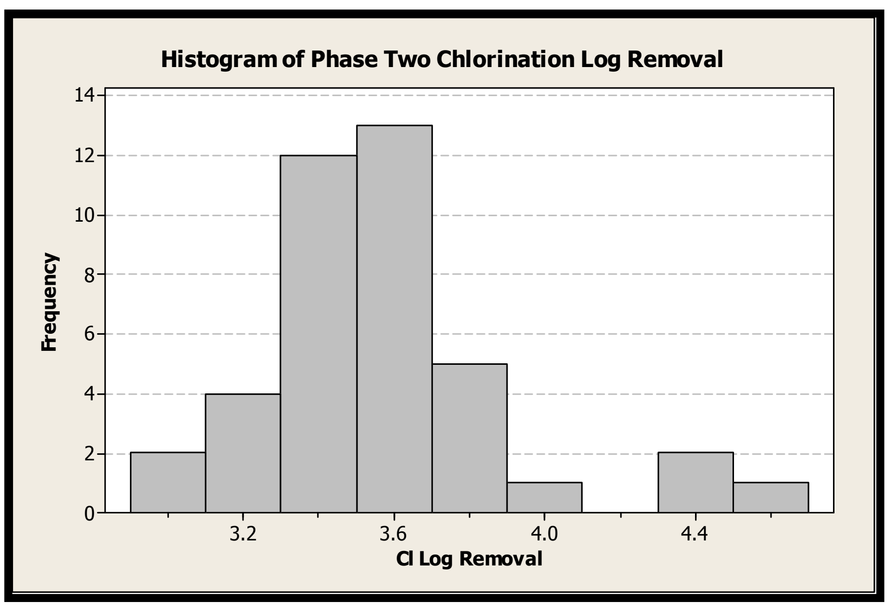


**Figure 15 - Phase Two Chlorination Log Removal Histogram**

A comparison of the log removals from the PAA and chlorination systems are shown in the box plots using a 95% confidence level in Figure 16. The asterisked values indicate outliers within the data sets.

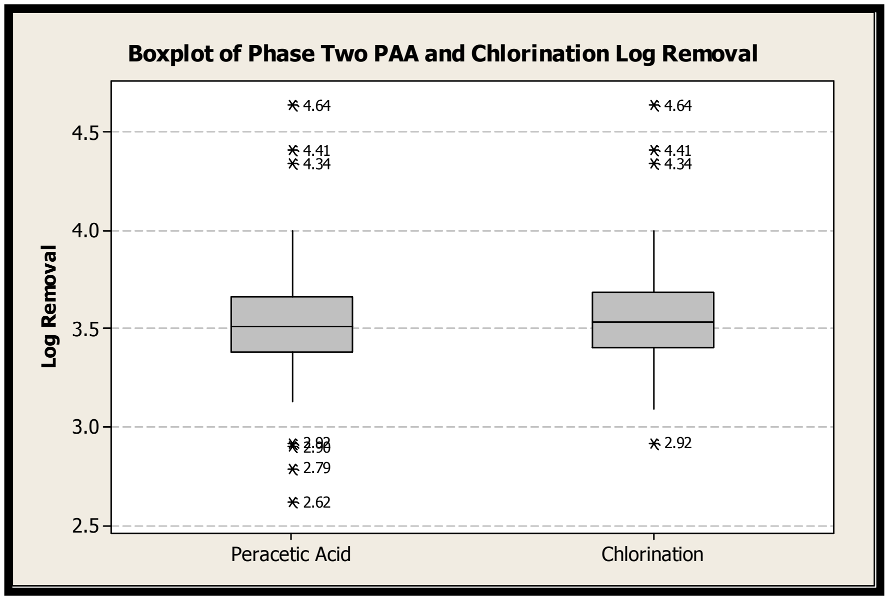


**Figure 16 - Box Plots for Phase Two Log Removals from PAA and Chlorination Systems**

The spread of the data obtained for the PAA system was found to be much less than it had been in Phase One, indicating the variability in log removal had decreased. The variance of the PAA systems log removal was, however, found to still be greater than the chlorination system. A statistical summary the PAA and chlorination system from Phase Two is shown in Table 11.

| Statistics for Log Removal | PAA | Chlorination |
|---|---|---|
| No. of Data Points | 39 | 39 |
| Arithmetic Mean with 95% Confidence Interval | 3.49 ± 0.11 | 3.54 ± 0.09 |
| Median | 3.51 | 3.53 |
| Variance | 0.12 | 0.09 |
| Standard Deviation | 0.35 | 0.30 |

**Table 11 - Statistical Summary for Phase Two**

The disinfection performance of the chlorination system and PAA side stream during the reuse sampling program was also compared using a two-tailed paired T-test at the 95% confidence level. The result from the paired T-test is shown in Table 12.

| Category | No. of Data Points | Arithmetic Mean | Standard Deviation | Standard Error of the Mean | T-Value | P-Value |
|---|---|---|---|---|---|---|
| Chlorination | 39 | 3.54 | 0.30 | 0.05 | - | - |
| PAA | 39 | 3.49 | 0.34 | 0.06 | - | - |
| Difference | 39 | 0.05 | 0.21 | 0.03 | - | - |
| T-Test of Mean Difference = 0 (vs not = 0) | | | | | 1.63 | 0.112 |

**Table 12 - Phase Two Paired T-Test Result**

From the data presented in Table 12 for the two-tailed paired T-test it is possible to see that there is no significant difference between the chlorination and PAA systems at the 95% confidence level, indicating the disinfection of wastewater with 8.91 mg/L of PAA was as effective as the chlorination system currently in use at the plant.

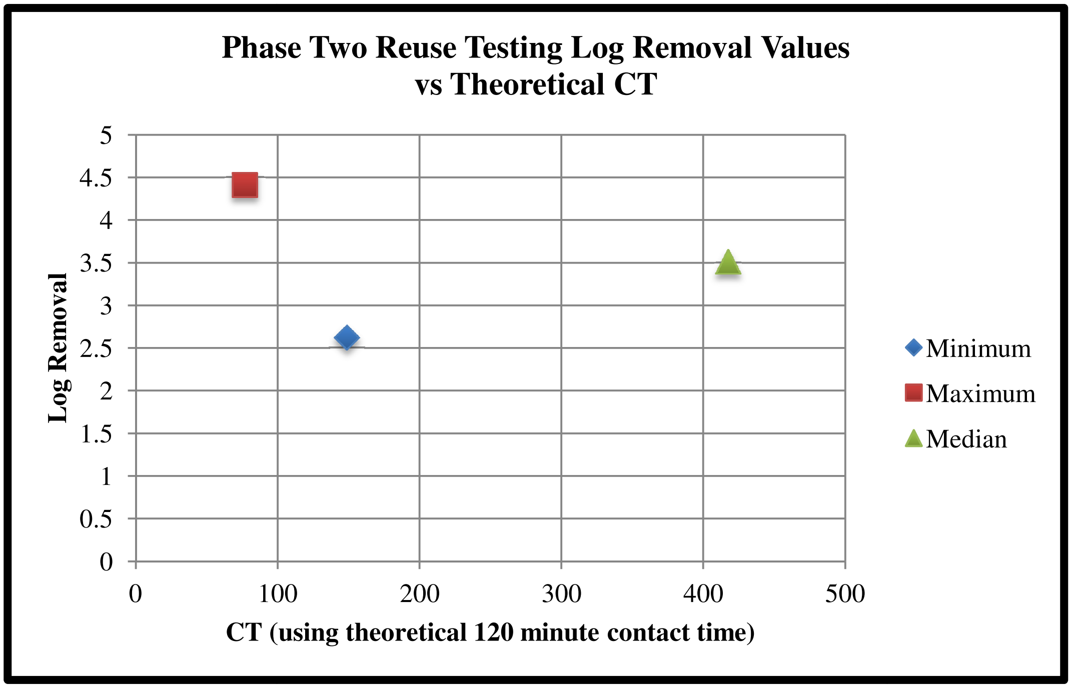


**Figure 17 - Phase Two Reuse Testing Log Removals vs Theoretical CT**

Figure 17 shows the corresponding CT values calculated for the minimum, maximum, and median values of FC log removal from the Phase Two reuse testing period. Ironically, the maximum log removal of FC was found to have a CT value lower than that of the minimum FC log removal. The PAA residual may have been taken at a different time than normal during this day.

As stated previously, the compliance of a wastewater treatment facility providing high-level disinfection is dependent upon meeting the following criteria:

- Over a 30-day period, 75% of the FC values shall be below the detection limits
- Any one sample shall not exceed 25 CFU/100mL

Over the course of the reuse sampling program, a 50-day period, effluent samples were taken daily in order to determine the reduction in FC concentration. Over the 50-day period 44 out of the 50, or 88%, of the samples were found to be non-detectable for FC. The remaining samples that were not found to be below detectable limits had concentrations of FC that were below 25 CFU/100mL. Two instances were noted in which the FC concentrations were too numerous to count. These instances are the result of a worn pump tube that caused a loss of chemical suction and ultimately a low PAA residual.

Following the successful completion of the reuse sampling program, the 6-day intensive sampling program began. The influent FC concentration ranged from 60 to 1,600 CFU/100mL, much lower than previous values observed during the pilot study. Over the course of the intensive sampling period samples were taken at locations EFB-1, MC-1, MC-2, MC-3, and EFA-3 every 45 minutes. A total of 11 sets of samples were taken daily. Table 13 presents a summary of the FC log removals at the associated sample locations observed during the intensive sampling period.

| 8.91 mg/L PAA Dose | | | | |
|---|---|---|---|---|
| Sampling Location | *MC-1* | *MC-2* | *MC-3* | *EFA-3* |
| Log Reduction | 3.01 | 2.91 | 2.88 | 2.30 |
| 6.1 mg/L PAA Dose | | | | |
| Sampling Location | *MC-1* | *MC-2* | *MC-3* | *EFA-3* |
| Log Reduction | 2.61 | 2.43 | 2.03 | 1.88 |
| 2.5 mg/L PAA Dose | | | | |
| Sampling Location | *MC-1* | *MC-2* | *MC-3* | *EFA-3* |
| Log Reduction | 2.00 | 2.11 | 1.71 | 1.44 |

**Table 13 – Intensive Sampling Log Removals**

The log removals in Table 11 were calculated using a geometric mean of the FC concentration at each sample location. The FC log removal is observed to decrease as the contact time is increased. This is believed to be due in part to the decrease in available PAA for inactivation as well as a decrease in amount of FC present. The relationship between PAA residual and theoretical contact time is presented in Figure 18.

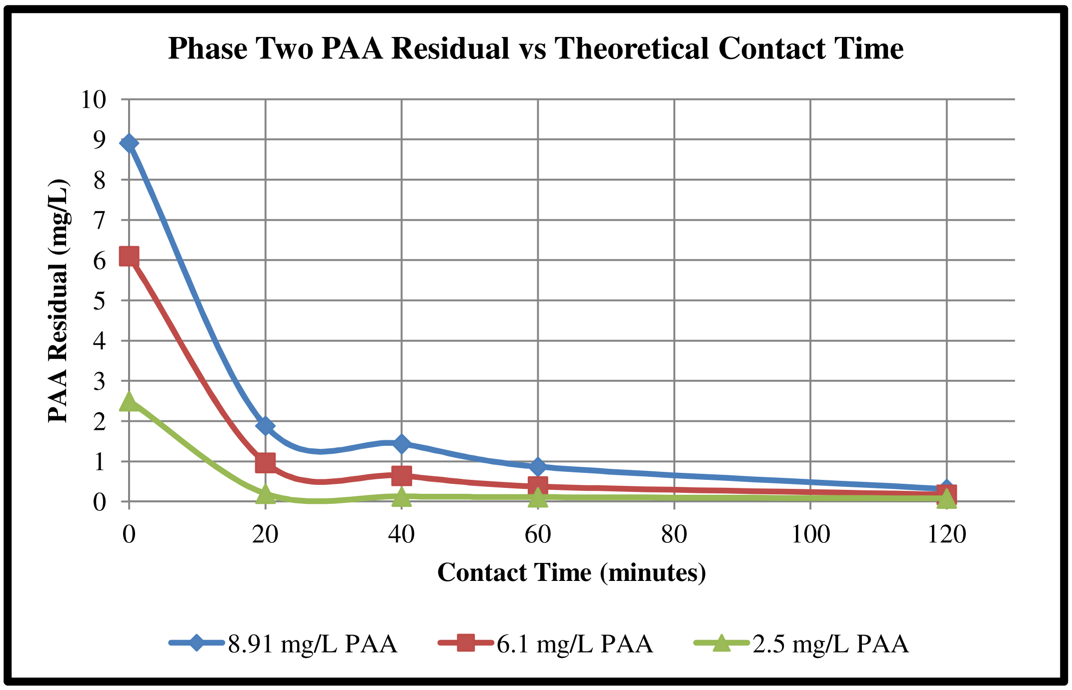


**Figure 18 - Relationship of PAA Residual and Theoretical Contact Time**

A steep reduction in PAA residual is noticed within the first 20 minutes of contact time regardless of initial PAA concentration. Residuals are less than 1 mg/L after 120 minutes of contact time for each dosage tested; this is an important consideration, as a residual of 1 mg/L will most likely need to be maintained within any distribution system. The reduction in available PAA is attributed to both the inactivation of FC and reaction with algae that was present within the model. The presence of algae will be reviewed further in the Discussion of Results.  The relationship between log removal and PAA residual at each sample location is shown in Figure 19.  As expected, higher reductions of FC were noted when there was a higher PAA residual measured.

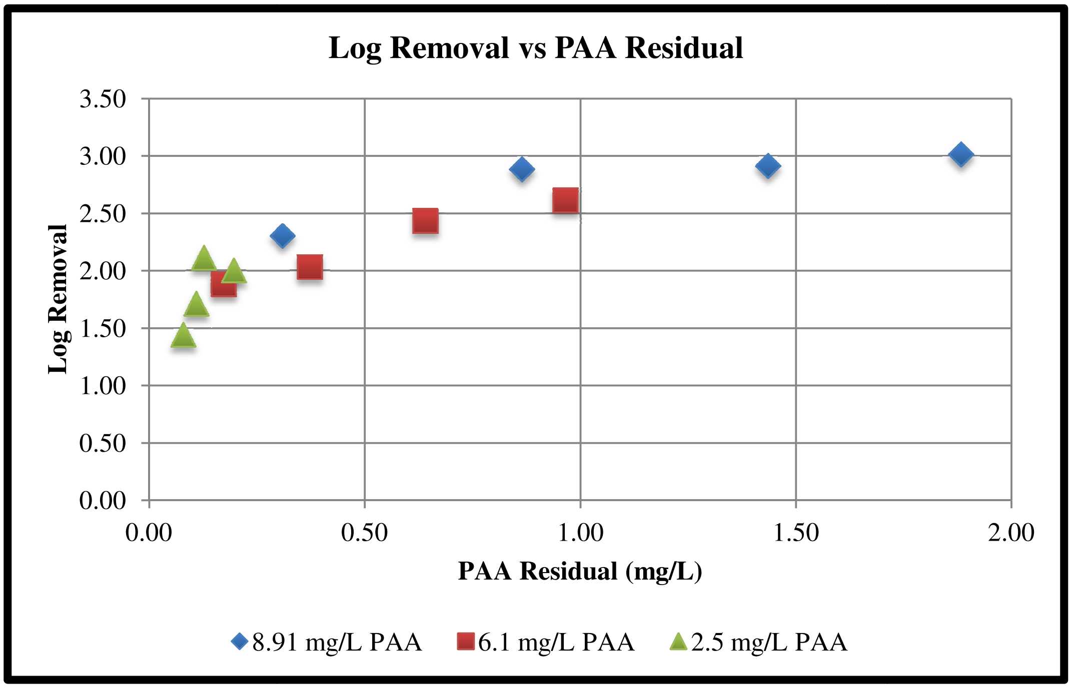


**Figure 19 - Relationship of Log Removal and PAA Residual**

The relationship between the pH of the wastewater and contact time is presented in Figure 20.

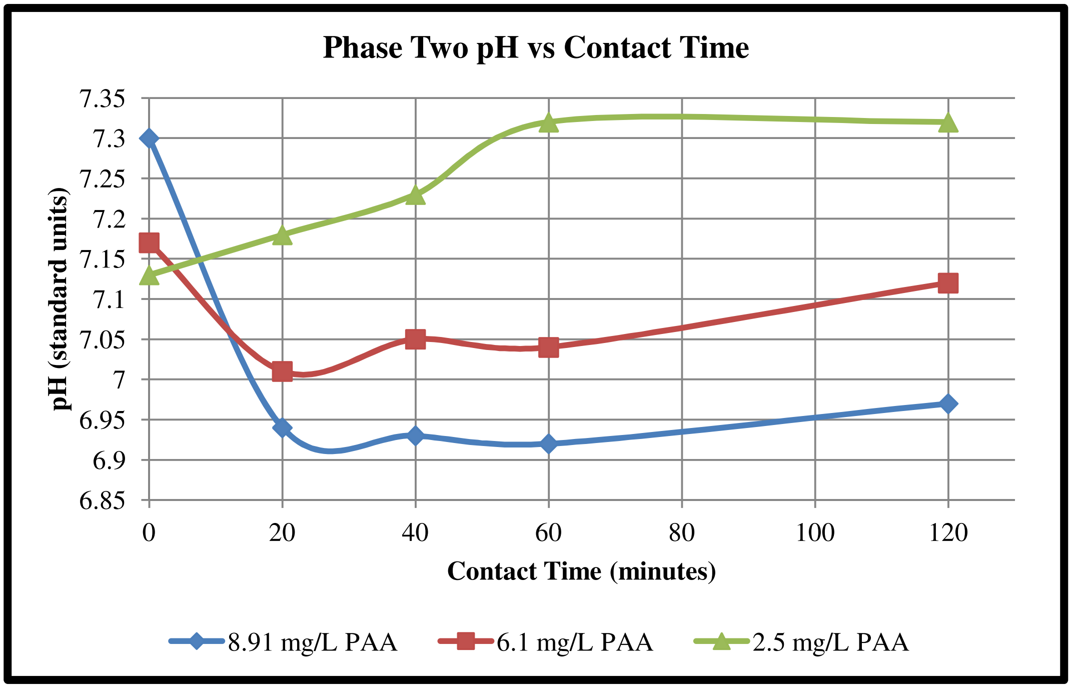


**Figure 20 - Relationship of pH to Contact Time**

The dosages of PAA each effect the pH similarly, however, as one might expect the magnitude of the decrease in pH is dependent on the initial dosage of PAA. By 120 minutes of contact time, the pH is observed to increase as a result of a loss in PAA residual. Figures 21 through 24 present the percentages of samples that were found to be non-detectable for FC at each contact time.

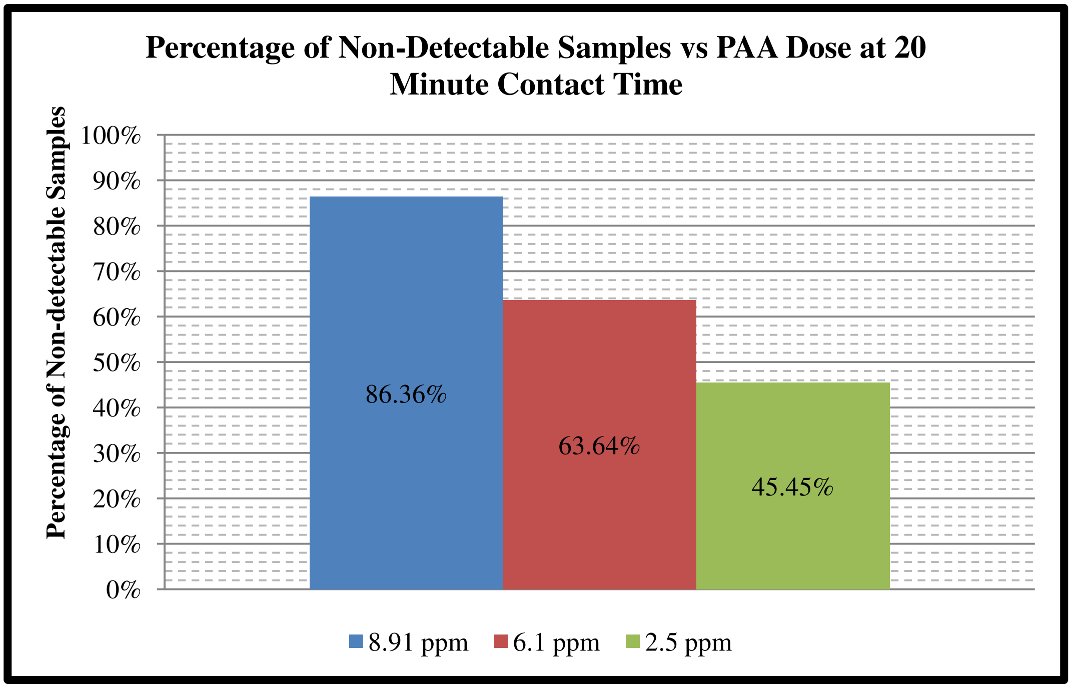


**Figure 21 - Non-Detectable Fecal Coliform Samples vs PAA Dose at 20 Minute Contact Time**

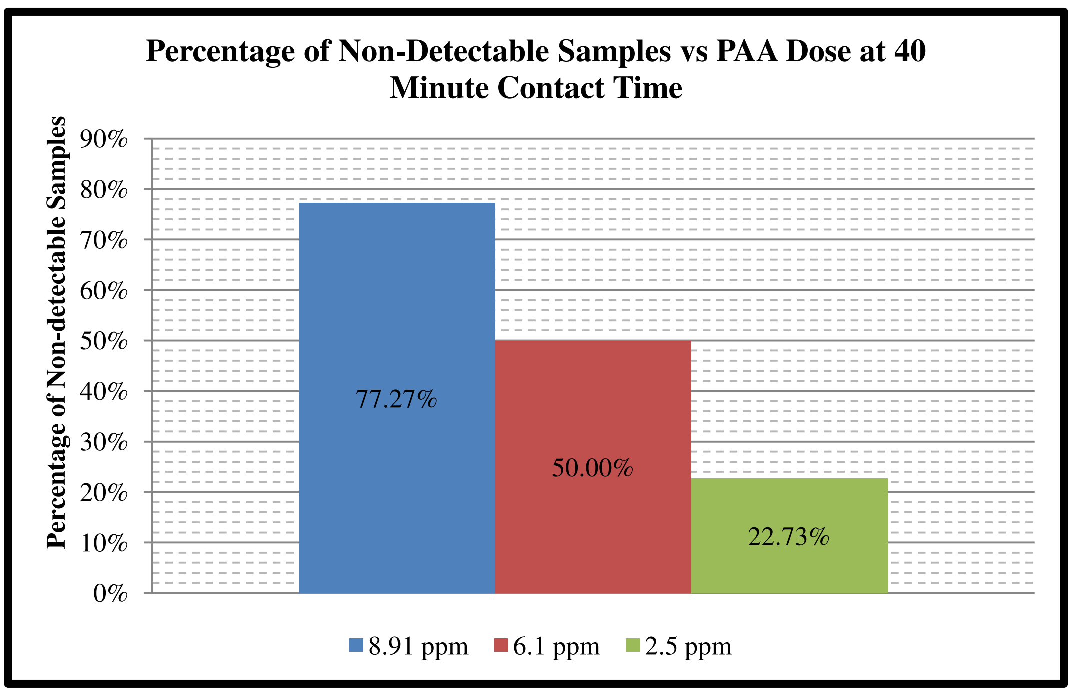


**Figure 22 - Non-Detectable Fecal Coliform Samples vs PAA Dose at 40 Minute Contact Time**

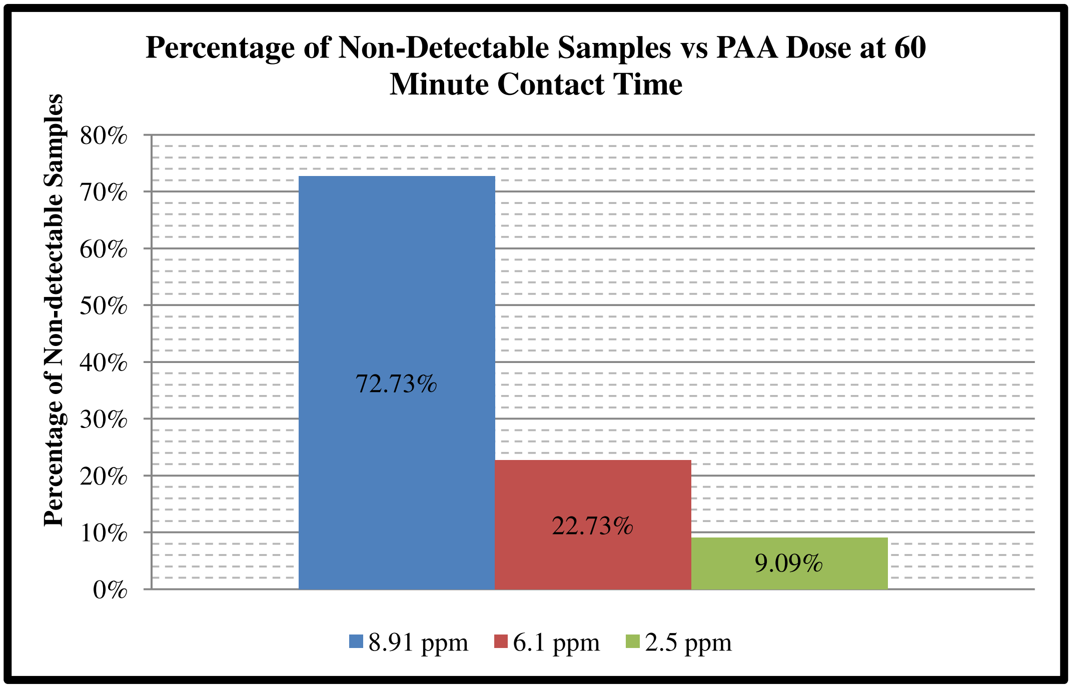


**Figure 23 - Non-Detectable Fecal Coliform Samples vs PAA Dose at 60 Minute Contact Time**

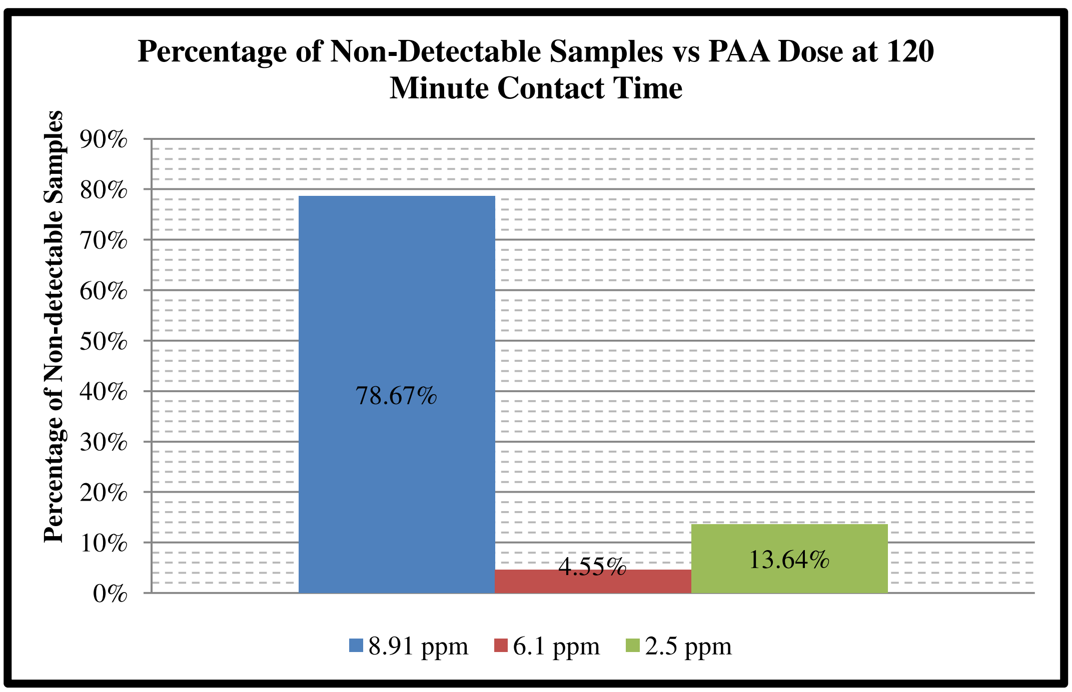


**Figure 24 - Non-Detectable Fecal Coliform Samples vs PAA Dose at 120 Minute Contact Time**

A PAA dose of 8.91 mg/L has shown to be the most effective at inactivating FC at all contact times tested. Compliance with Florida wastewater reuse regulations was met using this dosage at the contact times sampled with the exception of 60 minutes. While some of the samples taken at this contact time were detectable for FC, 91% of the samples were below 25 CFU/100mL. This is important because of the inherent changes in contact time experienced in the plants CCC due to fluctuations in plant flow (plant flow ranged from 1.526 MGD to 4.369 MGD during the reuse sampling program); this necessitates a disinfectant that will be effective at all contact times.

### 3.6.2 Aquatic Toxicity

Similar to Phase One, the aquatic toxicity of the effluent from the chlorination and PAA system was determined during Phase Two in order to assess potential adverse effects the discharge may have on aquatic life. Summaries of the results from the 7-day Chronic Static Renewal Definitive Bioassays are presented in Tables 14 and 15.

| Percent Effluent | *C. dubia* | | *P. promelas* | |
|---|---|---|---|---|
| | Final Survival (%) | Three Brood Totals (Average # of neonates/female) | Final Survival (%) | Average Dry Weight (mg/fish) |
| 0 | 100 | 35.3 | 100 | 0.503 |
| 12.5 | 100 | 32.4 | 100 | 0.495 |
| 25 | 100 | 30.3 | 100 | 0.540 |
| 50 | 100 | 31.2 | 97.5 | 0.522 |
| 75 | 100 | 27.2 | 100 | 0.580 |
| 100 | 100 | 25.2 | 97.5 | 0.576 |
| $IC_{25}$ | 84.06% | | > 100% | |

**Table 14: Chlorine Bioassay Results**

| Percent Effluent | *C. dubia* | | *P. promelas* | |
|---|---|---|---|---|
| | Final Survival (%) | Three Brood Totals (Average # of neonates/female) | Final Survival (%) | Average Dry Weight (mg/fish) |
| 0 | 100 | 33.2 | 100 | 0.634 |
| 12.5 | 100 | 31.7 | 97.5 | 0.643 |
| 25 | 90 | 29.6 | 100 | 0.600 |
| 50 | 90 | 27.9 | 100 | 0.582 |
| 75 | 100 | 34.0 | 100 | 0.633 |
| 100 | 100 | 32.2 | 100 | 0.633 |
| $IC_{25}$ | >100% | | >100% | |

**Table 15: PAA Bioassay Results**

The results from the 7-day Chronic Static Renewal Definitive Bioassays show that the Fathead Minnow specimens exposed to the effluent disinfected with PAA maintained a 100% final survival rate for each concentration except 12.5 percent. This is slightly better than the results of the effluent treated with chlorine, as the final survival results for the 50 and 100 percent concentrations were both 97.5%. In terms of the $IC_{25}$ values, which represents an estimate of the effluent concentration that causes a 25% reduction in growth and reproduction (Wisconsin State Laboratory of Hygiene, 2008), both sets of specimens did not exhibit chronic toxicity having $IC_{25}$ values of > 100%. The final survival for the Water Flea was similar for the chlorination and PAA effluents; however, the final survival percentages for the PAA effluent were slightly less than that of chlorine for the 25 and 50 percent concentrations. In terms of $IC_{25}$ values, however, the PAA effluent performed better than that of chlorination, having an $IC_{25}$ of >100% effluent compared to that of chlorine which was 84.06%. This was a substantial improvement over the bioassay previously conducted in Phase One using the PAA effluent.

### 3.7 Phase Three Results

The results of Phase Three showed that a single dose of 8.91 mg/L ultimately provided the best dosage and configuration for the disinfection of wastewater at the Miller St. WWTP. Other doses and configurations that were tested did, however, result in promising results that should be investigated further in future studies with PAA.

#### 3.7.1 Disinfection Performance

The inflow of FC ranged from 1,290 to 114,000 CFU/100mL during the serial addition prove-out period of Phase Three. A plot showing the behavior of FC concentrations for each treatment configuration is presented in Figure 25. The data points were calculated using a geometric mean of the FC concentration at each sample location during each treatment configuration.

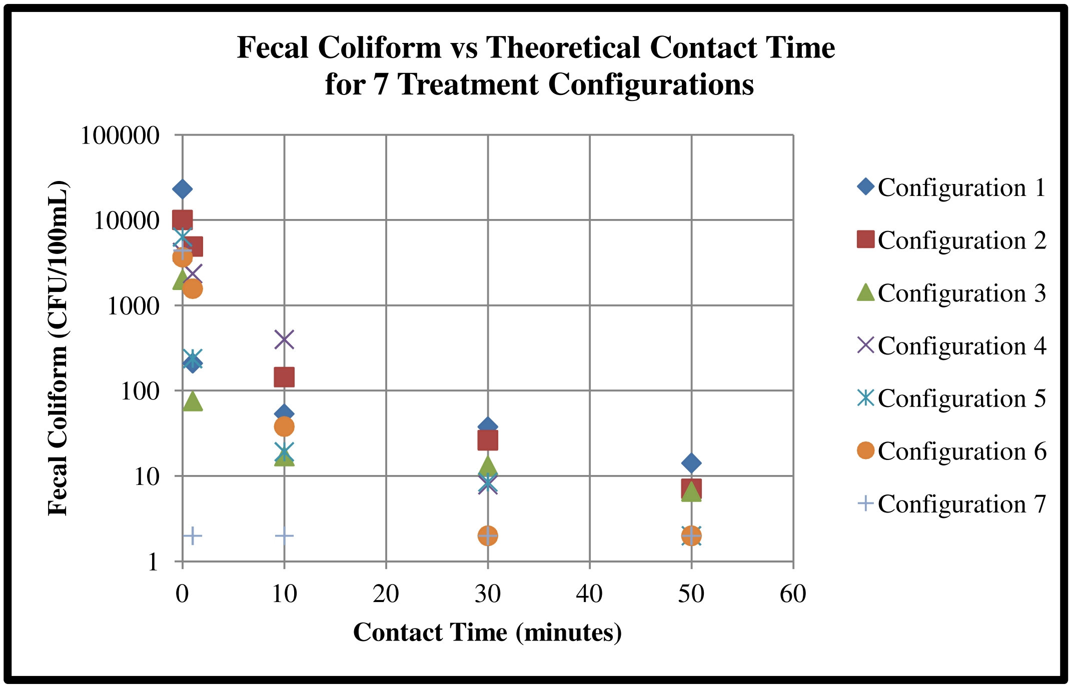


**Figure 25 - Fecal Coliform vs Theoretical Contact Time for 7 Treatment Configurations**

Treatment configuration refers to a specific combination of PAA dosage and chemical injection location; the configurations have been described previously in Table 4. The associated log reductions for each configuration are presented in Table 16.

| Configuration | Total PAA Dosage (mg/L) | Log Removal |
|---|---|---|
| 1 | 3.0 | 3.39 |
| 2 | 3.0 | 2.82 |
| 3 | 4.5 | 2.10 |
| 4 | 4.5 | 3.33 |
| 5 | 6.0 | 3.63 |
| 6 | 6.0 | 3.27 |
| 7 | 9.0 | 3.35 |

**Table 16 - Log Reductions for 7 Treatment Configurations**

For each configuration tested it appears that not only the total dosage of PAA effects removal, but the sequence by which it is injected into the system. Configurations in which the larger portion of the PAA dose was added at injection point PAA SA #1, with the remainder added at injection point PAA SA #3 appear do to slightly better. This holds true for every configuration except configuration 3. The majority of samples found to be non-detectable for FC were observed when the total dosage of PAA was above 4.5 mg/L.

Following the prove-out period of Phase Three, an 11-day reuse sampling program was completed. The program was similar to the prove-out period of Phase Three, having two sets of samples collected at locations EFB-1, MC-1, MC-2, MC-3B, and EFA-3 in the early morning and afternoon. Treatment configuration 6 was chosen for the reuse period of Phase Three. This configuration consisted of dosing injection points PAA SA #2 and #3 with 1.5 and 4.5 mg/L of PAA, respectively for a total dose of 6 mg/L. This configuration provided the most number of non-detectable FC samples after the previously used configuration that used a total PAA dosage of roughly 9 mg/L. The inflow FC concentration during this period ranged from 9 to 8820 CFU/100mL. A plot showing the FC concentration at each sample location is presented in Figure 26.

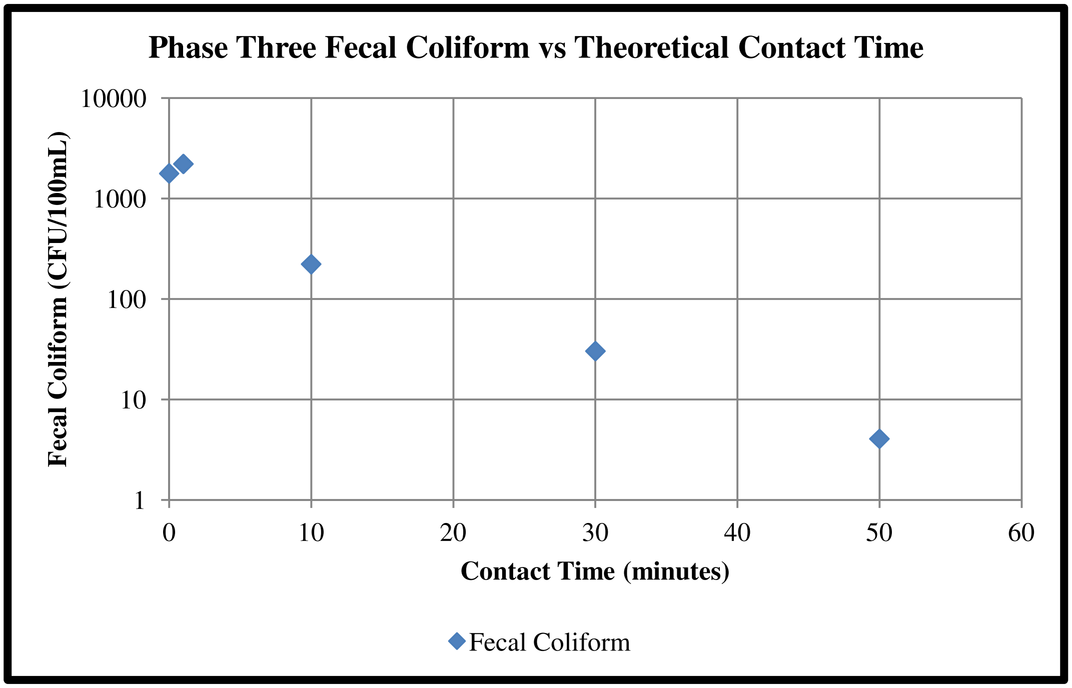


**Figure 26 - Phase Three Reuse Period Fecal Coliform vs Theoretical Contact Time**

A slight increase in FC was noted from sample locations EFB-1 to MC-1, this might be attributed to regrowth within the system before any disinfectant was added. FC concentrations were found to decrease throughout the model, however, only 7 out of 22 samples were found to be non-detectable for FC. This percentage (32%) is far below the regulatory required 75% non-detectable sample threshold. Dissolved oxygen (DO) measurements made within the system indicate that the level of DO actually increases between the inlet and discharge of the system. A small portion of this may be attributed to the dissolution of PAA during disinfection; however, it is suspected that the majority was caused by excessive algal growth within the model. Other possible effects of this algal growth will be covered in the Discussion of Results.

3.8 Bench Scale Experiment Results

The results from the bench scale experiment revealed that there is a large initial PAA demand when introduced to the wastewater. This is presented in Figure 27.

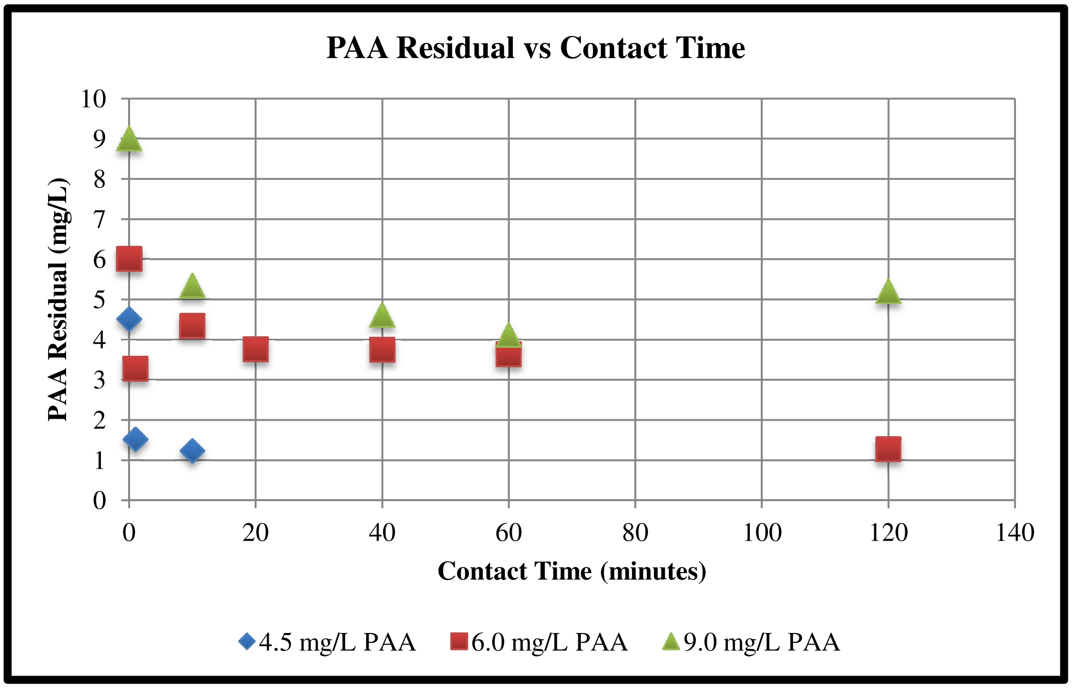


**Figure 27 - Bench Scale PAA Residual vs Contact Time in Wastewater**

From Figure 27 it is possible to see that there is an initial PAA demand of approximately half the initial dose when introduced to wastewater, even within the first minute of contact time. Residual measurements from the buckets filled with DI water indicate that there is a small initial clean water demand between 0.25 to 0.40 mg/L. Results from the FC samples taken from the buckets were analyzed using the wrong dilution at the lab and ultimately found to be unusable as the lowest detection limit was 9 CFU/100mL, which is above the regulatory limit of non-detectable.

## Chapter 4 - Discussion of Results

### 4.1 Florida Wastewater Reuse Regulations

The regulations outlining the required level of disinfection for various uses of reuse wastewater are outlined in Chapters 62-610.410 (1996), 460 (1999), 510 (199), 563 (1999), 610 (1996), and 652 (1999) of the FAC respectively. The four levels of wastewater disinfection are listed in Table 17 with their respective applications and FC limits as a basis for comparison.

| Disinfection Level | Fecal Coliform Limit | Application(s) |
|---|---|---|
| High-Level | Non-Detectable | Discharge to Class I[a] waters; underground injection; slow rate land application systems - public access areas; residential irrigation; and, edible crops |
| Intermediate | 14 CFU/100mL | Discharge to waters that are tributaries/contiguous to Class II[b] waters |
| Basic | 200 CFU/100mL | Slow rate land application systems - restricted public access areas |
| Low-Level | 2400 CFU/100mL | Overland flow systems and industrial use |

**Table 17 – Florida Reuse Wastewater Disinfection Levels**

[a]Class I – Potable water supplies

[b]Class II – Shellfish propagation or harvesting

Wastewater treatment facilities providing high-level disinfection, such as the Miller St. WWTP must meet certain design criteria and limits for FC concentrations. Currently plants that use chlorine must conform to the design criteria for total chlorine residuals (C) and contact time (T) presented in Table 18 (FAC 62-600.440, 1996). Where C and T are express in mg/L and minutes, respectively.

| Fecal Coliform Range (CFU/100mL) | C x T |
| --- | --- |
| < 1,000 | ≥ 25 |
| 1,000 to 10,000 | ≥ 40 |
| > 10,000 | ≥ 120 |

**Table 18 - Total Chlorine Design Criteria**

The compliance of a wastewater treatment facility with high-level disinfection is subject to the following criteria:

- Over a 30-day period, 75% of the samples analyzed shall be non-detectable for FC;
- Any one sample shall not have a FC concentration above 25 CFU/100mL; and,
- Any one sample shall not exceed 5 mg/L of TSS before application of disinfectant.

### 4.2 Comparison of Results to Florida Regulations

Each phase of the pilot study was unique in that generally each phase used different or multiple PAA dosages. The phases were compared using a common theoretical contact time of roughly 50 minutes from each study. Results from Phase Two were calculated by taking the arithmetic average of results from the 40 and 60 minute contact times. A comparison of the percentage of non-detectable FC samples from each of the phases of the pilot study is made in Figure 28.

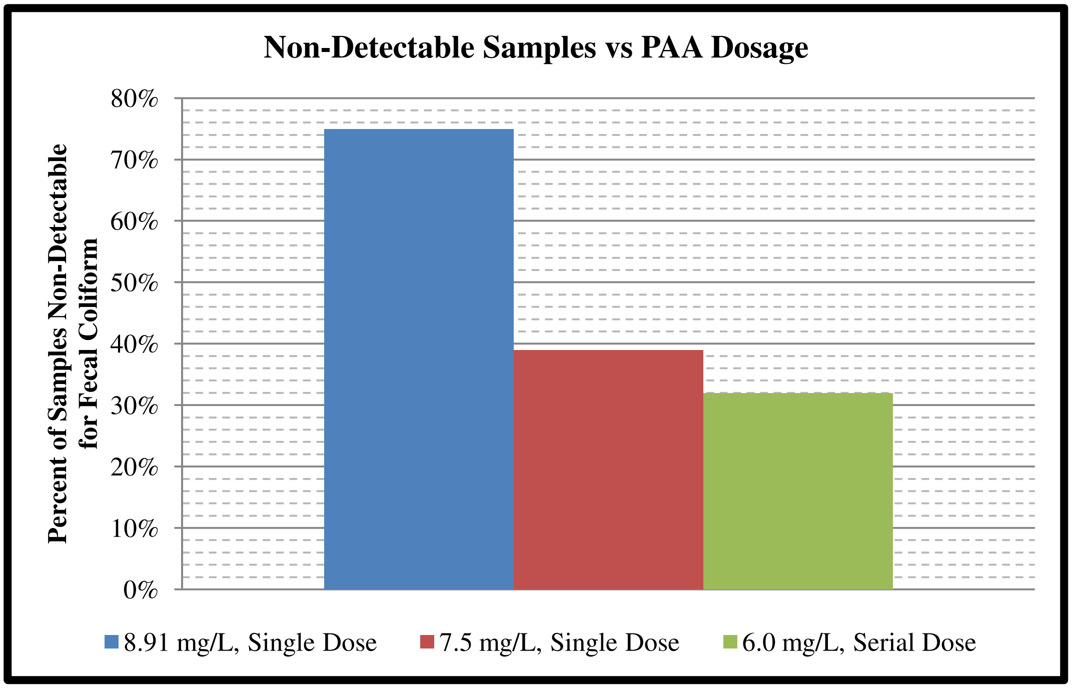


**Figure 28 - Comparison of Non-Detectable Fecal Coliform Samples from Pilot Study**

From Figure 28 it is possible to see that a single dose of PAA of roughly 9 mg/L was the only treatment configuration that was capable of providing the performance necessary in order to comply with Florida wastewater reuse regulations in terms of FC limits during a 30-day period. Using this dosage and a contact time of 120 minutes, a total of 53 samples were collected. Of these 53 samples 47 were found to be non-detectable for FC. The remaining samples ranged from 2 to 17 CFU/100mL, which still fall under the regulatory limit of 25 CFU/100mL. As discussed previously two samples were found to have FC concentrations that were too numerous to count. This breakdown in the trend is attributed to a worn pump tube that caused a loss of chemical suction and ultimately a low PAA residual (0.05 mg/L). Once this issue was resolved, the system performed as it had prior to becoming inoperative.

## 4.3 Comparison of Results to Previous Studies

Phase Two of the study demonstrated that PAA is capable of disinfection similar to the chlorination system currently in place at the plant, having an arithmetic mean log reduction of 3.49 in FC concentration. The results obtained during this study also compare favorably with other studies that assessed the disinfection performance of PAA. Figure 29 shows graphically the relationship between the results obtained during the intensive sampling portion this study and the results of two previous studies performed by Dell'Erba et al. (2004) and Koivunen and Heinonen-Tanski (2005). These two studies assessed the disinfection performance of PAA in wastewaters from secondary treatment; similar to the setup used in Phase Two, however the target for reduction was TC. While the theoretical contact times used varied between each study, the PAA dosages used are relatively close.

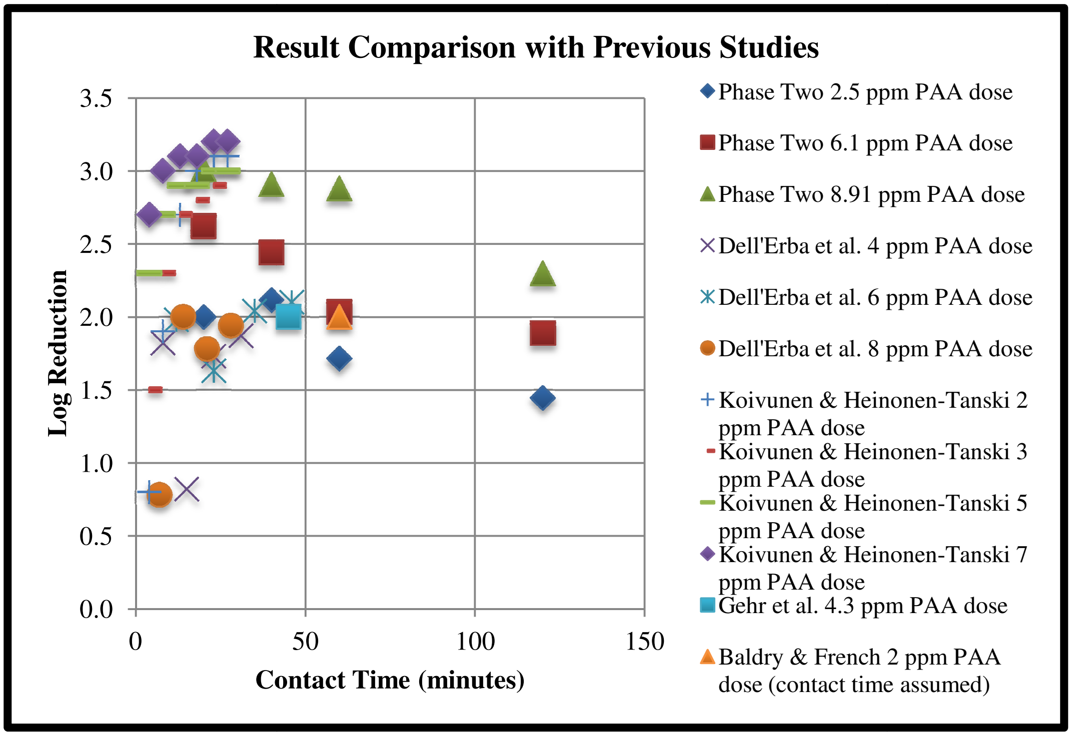


**Figure 29 - Comparison of Phase Two Data with Previous Studies**

The reductions in TCs noted in the study performed in Tarnato, Italy by Dell'Erba et al. (2004) were found to be slightly less than the reductions in FC noted during Phase Two. For a PAA dose around 6 ppm and roughly 20 minutes of contact time Phase Two produced a 2.6-log reduction in FC; Dell'Erba et al. (2004) reported a 1.63-log reduction in TC. Similarly for a PAA dose between 8 and 9 ppm and roughly 20 minutes of contact time Phase Two produced a 3.0-log reduction in FC; Dell'Erba et al. (2004) reported a 0.78-log reduction in TC. The pathogen levels coming into the model CCCs may explain the variation in reductions between the two studies. Dell'Erba et al. (2004) reported an arithmetic average TC concentration of 10,700 colony forming units (CFU)/100mL coming into their model CCC; the arithmetic average of the FC concentration for the intensive sampling portion of this study was found to be 654 CFU/100mL.

The study performed by Koivunen and Heinonen-Tanski (2005) reported reductions in TC that are greater than the reductions in FC noted in this study. For a PAA dose of 2.5 ppm and contact time of roughly 20 minutes, Phase Two produced a 2-log reduction in FC; Koivunen and Heinonen-Tanski (2005) reported a 3-log reduction in TC using a PAA dose of 2 ppm and 18 minutes of contact time. Similarly for a PAA dose of 6.1 ppm and contact time of roughly 20 minutes, Phase Two produced a 2.6-log reduction in FC; Koivunen and Heinonen-Tanski (2005) reported a 2.9-log reduction in TC using a PAA dose of 5 ppm and contact time of 18 minutes. The largest difference noted between the study performed by Koivunen and Heinonen-Tanski and Phase Two were the pilot study setups. Koivunen and Heinonen-Tanski (2005) utilized a 0.4 $m^3$ chicane tank that mixed the disinfectant hydraulically. The influent pathogen levels noted by Koivunen and Heinonen-Tanski (2005) were found to be greater than those observed in Phase Two, having a geometric mean of 480,000 CFU/100mL.

The pilot study has also demonstrated that disinfecting wastewater with PAA did not result in the production of harmful levels of toxic DBPs, which is the most common concern when disinfecting water with highly organic wastewater with traditional chlorine. The effluent was also found not to exhibit aquatic toxicity when exposed to the water flea and Fathead Minnow.

4.4 Algae

Over the course of the pilot study algal growth was found to be an issue, especially during Phase Three. Figures 30 and 31 show the growth of algae within the contact chamber taken one week after cleaning during Phase Three.

**Figure 30 - Algal Growth in Contact Chamber**

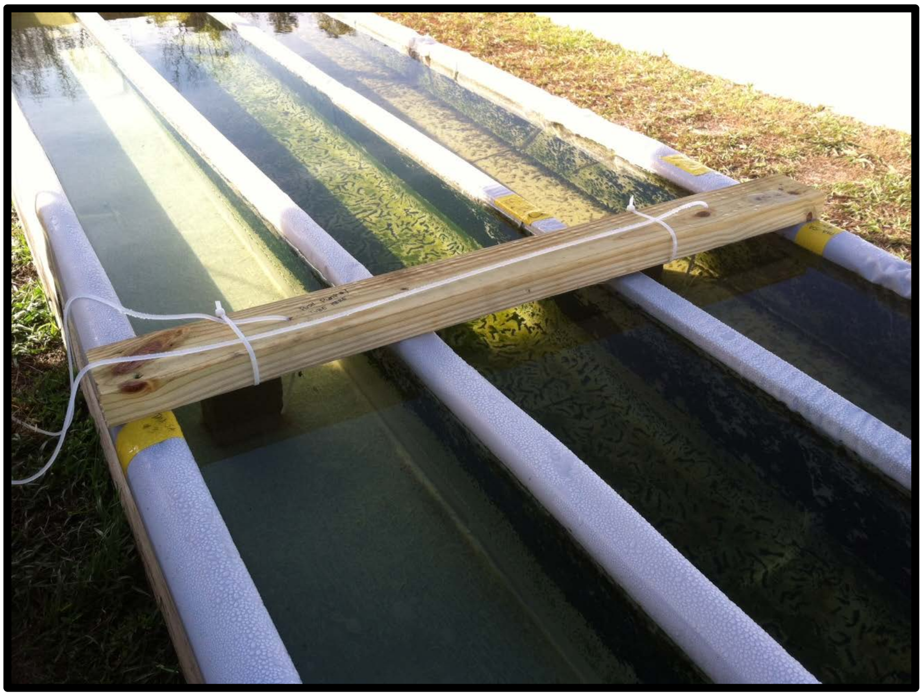

**Figure 31 - Closer View of Algal Growth**

Algae would develop at the influent of the model and progress throughout the rest with time. Similarly the effluent reservoir of the model, shown in the bottom right corner of Figure 30, developed what can be described as tree-like algae that would sprout up from the bottom. The full-size contact chamber supports algae growth but on a much smaller scale that what was observed within the model. This may be attributed to the obvious difference in channel depth. The shallower channel of the model may have allowed a larger amount of sunlight to penetrate all the way to the bottom as opposed to the deeper channel in the full-size contact chamber. The presence of algae was also noted in Phase Three by measurement of DO. The concentration of DO was found to increase between the inlet and discharge of the model. This is attributed to both the dissolution of PAA and respiration of algae within the model. It is possible that this large amount of algae may have affected the disinfection results of this study by providing another disinfection target for the PAA, reducing the amount of PAA available for inactivating the FC present within the wastewater.

## Chapter 5 - Conclusions and Recommendations

A pilot study assessing the disinfection performance of PAA was conducted at the Miller St. WWTP near the Town of Orange Park, Florida. The study consisted of three phases and focused on determining if the new non-chlorine based disinfectant was capable of disinfection in compliance with Florida wastewater reuse regulations. Phase One consisted of dosing a side stream of wastewater withdrawn from the effluent reservoir of the plants sand filter with a PAA dose of 7.5 mg/L and providing a theoretical contact time of 53 minutes. Samples were taken before and after disinfection and analyzed to determine the reduction in FC. Based on the results from Phase One a second phase was planned that built upon the knowledge gained. Phase Two followed the same methodology that had been previously used in Phase One; however, a scaled model chlorine contact chamber was constructed in order to more accurately simulate the hydraulics of the disinfection system installed at the plant. A PAA dosage of 8.91 mg/L was used in order to improve the disinfection results enough to comply with Florida wastewater reuse regulations. After successful completion of Phase Two, a final experimental phase was planned that investigated the possibility of using multiple injection points in series with smaller doses of PAA. Phase Three used the same methodology that had been used in Phase Two; however, multiple treatment configurations were tested that alternated dosing magnitude and location. A dosage of roughly 9 mg/L was found to have the best performance for the disinfection of wastewater at the Miller St. WWTP. This dosage provided adequate levels of disinfection at almost all contact times simulated. This is an important characteristic due to the inherit variation in a treatment facility's loading; the plants flow ranged from 1.35

to 4.37 mgd over the course of the pilot study. While this dosage was not found to be economical at this time, lower doses were also found capable of some inactivation of FC. The use of PAA may be dependent upon the required level of disinfection. A lower dosage of PAA could be used in combination with other treatment methods such as ultraviolet disinfection as a pretreatment. If the use of PAA were to become widespread, an inherit increase in manufacturing may provide a catalyst to reduce the unit cost.

Over the course of the pilot study, ideas for further research and ways to improve upon this study were crafted. These ideas include tracer study implementation, serial addition, and disinfection variability. Future studies using a similar model contact chamber could confirm the hydraulic residence times within the model by using a tracer study to ensure they are similar to the theoretical contact times. Although this study did not complete a tracer study it is believed that the system exhibits close to perfect plug flow conditions due to the length to width ratio as cited by Davis (2010). Although not successful in meeting Florida wastewater reuse regulations, the serial addition of PAA did prove to have some merit. Future studies should include a computer-modeling program that focuses on optimizing the PAA dosage and injection location in order to maximize the kill power of each dose. Throughout the course of the pilot study a disinfection performance variation greater than that of the plants chlorination system was noted. The characteristics that affect the disinfection performance of PAA should be further investigated in order to determine the applicability of PAA for use in other facilities. The greater variability in PAA disinfection at dosages less than 9 mg/L warrants further research.

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## APPENDIX A

Phase One Site Pictures

**Figure 32 - PAA Barrels on Containment System**

**Figure 33 - PAA Injection Point with Inline Flowmeter**

**Figure 34 - Effluent Reservoir of Sand Filter**

**Figure 35 - Portable Tank Used for PAA Contact Chamber Discharging to Lift Station**

Phase Two Site Pictures

**Figure 36 - Leveling and Construction of Model CCC**

**Figure 37 - Completed Framework of Model CCC**

**Figure 38 - Vinyl-Lined CCC with V-Notch Weirs and Discharge Line**

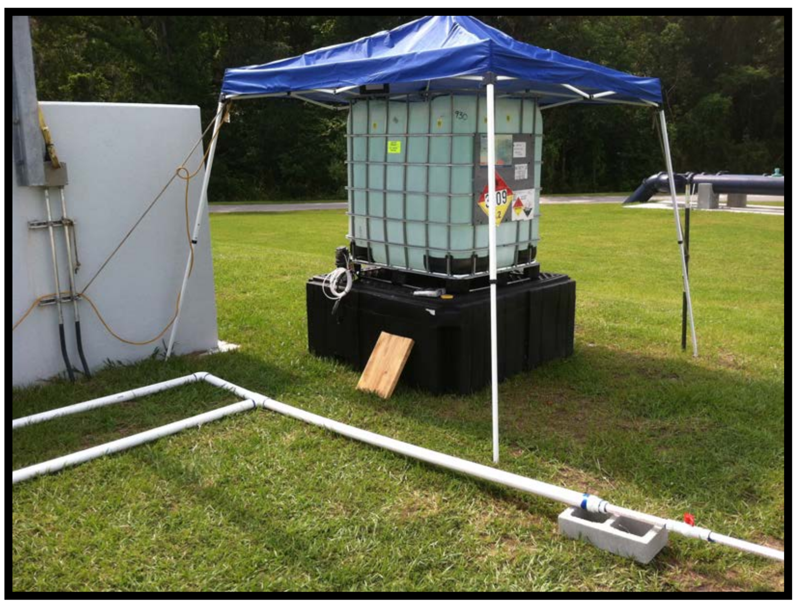

**Figure 39 - PAA Tote on Containment System**

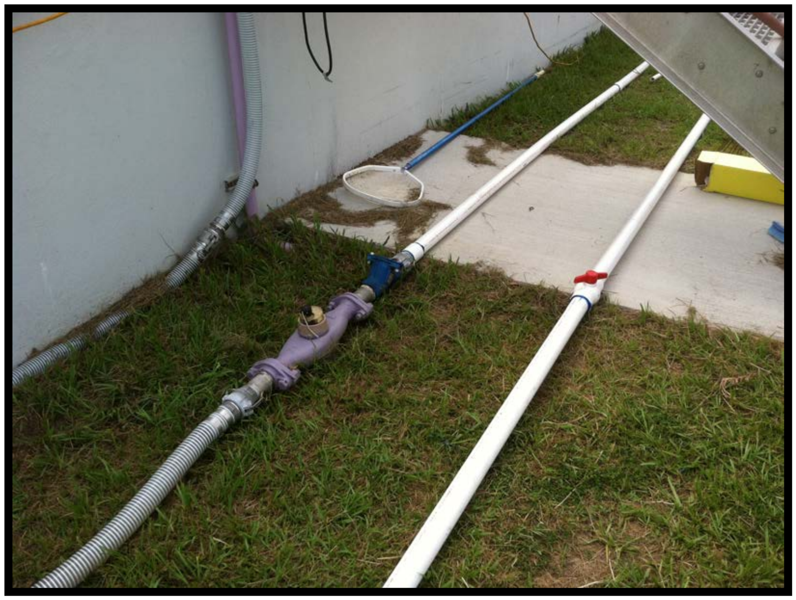

**Figure 40 - Inline Flowmeter and Waste Discharge with Ball Valve**


**Figure 41 - PAA Injection Point**

Phase Three Site Pictures

**Figure 42 - Phase Three Site Configuration**

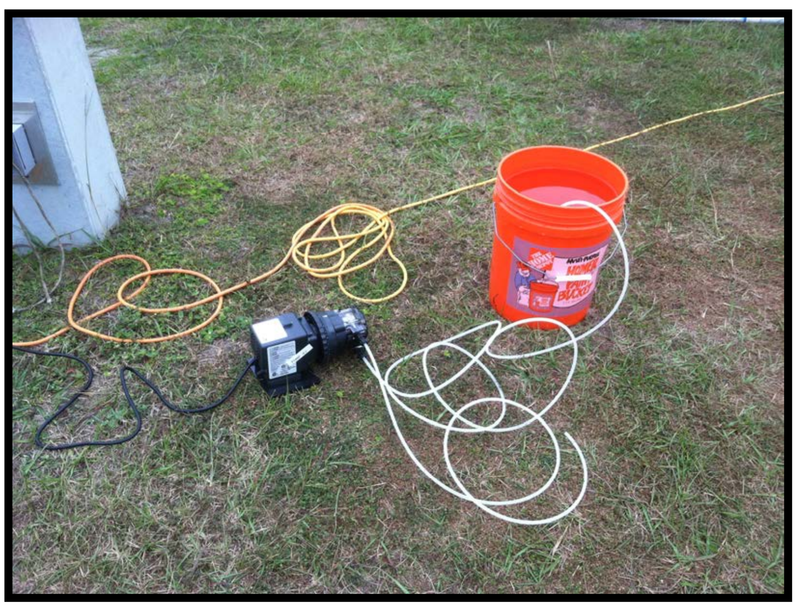

**Figure 43 - Chemical Dosing Pump Calibration**