Peracetic Acid as an Alternative Disinfection Technology for Wet Weather Flows

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ABSTRACT: Rain-induced wet weather flows (WWFs) consist of combined sewer overflows, sanitary sewer overflows, and stormwater, all of which introduce pathogens to surface waters when discharged. When people come into contact with the contaminated surface water, these pathogens can be transmitted resulting in severe health problems. As such, WWFs should be disinfected. Traditional disinfection technologies are typically cost-prohibitive, can yield toxic byproducts, and space for facilities is often limited, if available. More cost-effective alternative technologies, requiring less space and producing less harmful byproducts are currently being explored. Peracetic acid (PAA) was investigated as one such alternative and this research has confirmed the feasibility and applicability of using PAA as a disinfectant for WWFs. Peracetic acid doses ranging from 5 mg/L to 15 mg/L over contact times of 2 to 10 minutes were shown to be effective and directly applicable to WWF disinfection. *Water Environ. Res.*, **86,** 687 (2014).

KEYWORDS: peracetic acid, high-rate disinfection, wet weather flows, wastewater disinfection.

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Introduction

Problem Statement. Wet weather flows (WWFs) are discharges from aging and/or failing wastewater and stormwater sewer systems that can occur when there is a precipitation event. These WWFs can consist of combined sewer overflows (CSOs), sanitary sewer overflows (SSOs), and stormwater discharges, all of which typically discharge to surface waters and introduce pathogens to the nation's rivers, lakes, and streams in the process. These waterborne pathogens can include disease-causing bacteria, viruses, and protozoa and as such, there is a need to disinfect WWFs for the protection of human health while simultaneously protecting the environment to which these flows discharge.

Unfortunately, the traditional technologies used to address WWFs are often cost-prohibitive. According to a 2004 U.S. EPA Report to Congress, U.S. EPA has estimated that the number of CSO discharge events in 2002 was more than 9000, resulting in a volume of approximately 850 billion gal of combined wastewater (and stormwater) being discharged to surface waters from approximately 750 communities nationwide. Likewise, in 2002, it was estimated that between 23 000 and 75 000 SSO events occurred, discharging 3 to 10 billion gal of wastewater (diluted by infiltration and inflow) to the environment from thousands of SSO communities. The 2000 cost estimate to address CSOs was $50.6 billion and to address SSOs was $88.8 billion. Only $6 billion and $4 billion had been spent respectively through 2002, highlighting the magnitude of the cost to bring WWFs into compliance with water quality standards and the nationwide discrepancy between the cost to address the WWFs and the amount expended. Although more current information on national cost estimates and expenditures has not yet been made available by U.S. EPA, this discrepancy still exists and is exacerbated by the current economic climate. Based on over a dozen years of professional experience working with numerous communities trying to address wet weather flows, the authors have seen funding sources for infrastructure improvements decrease as costs continue to increase while the nation's infrastructure continues to age. Assuming expenditures remain the same (and are not reduced further due to the lack of funding), the only way to truly address WWFs and to bring them into compliance with water quality standards is through the use of emerging, innovative, cost-competitive solutions. One solution is to use a more cost-competitive disinfection technology for WWFs.

Traditional disinfection technologies used for wastewater disinfection, such as chlorination, ultraviolet radiation, and ozonation, have limitations and drawbacks, including high power consumption, safety issues, undesirable byproducts, large facility footprints due to high contact times, and so forth. In addition, because WWFs are highly variable in composition as compared to wastewater, are intermittent, and can have rapid increases of unconventionally large flow volumes, an easy to use, inexpensive, effective, and high-rate disinfectant is required. An alternative disinfectant, peracetic acid (PAA) has been identified as a possible candidate for use in treating wet weather discharges because it is stable, safe, easy to use, and reacts so quickly that there is normally very little residual left, particularly when the optimal dose is applied. Further, any residual that does remain is nontoxic and biodegradable in the environment.

The research that is discussed herein was undertaken to support the approval of PAA as a best available technology for the disinfection of WWFs in the United States. As such, the main objective of this research was to determine the feasibility of using PAA as a disinfectant for wet weather discharges. To address this objective, the research was designed to answer the question: Can PAA satisfy the existing regulatory requirements as an effective disinfectant for wet weather discharges? The research methodology to answer this question was broken down

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into three basic steps: (1) definition of technical requirements, (2) data collection and analysis, and (3) sample treatment and analysis.

Previous Research. Previous studies on PAA have primarily focused on the disinfection of wastewater with traditional disinfection times of 20 minutes or greater and PAA doses generally under 5 mg/L but often much lower than 1 or 2 mg/L (Constantine et al., 2009; Dell'Erba et al., 2004, 2007; Erie County Department of Environmental Services, 2002; Gehr et al. 2003; Lubello et al., 2002; Santoro et al., 2007; Veschetti et al., 2003; Wagner et al., 2002). In 1991, PAA was found to be effective in inactivating *E. coli* (Baldry et al., 1991) and in the early 2000s, a number of these studies documented the successful achievement of a 4-log reduction *E. coli* bacteria. Information from these studies indicated that PAA may be an appropriate disinfectant for WWFs (Meakim, et.al, 2007; Stinson, 1999; Wagner et al., 2002), and also noted that disinfection byproducts (DBPs) were "negligible" (Dell'Erba et al., 2007). Due to the lack of toxic DBPs, PAA has been explored for the disinfection of drinking water and it was suggested in one study that evaluation of PAA using higher concentrations be explored to further evaluate PAA disinfection performance (Monarca et al., 2004). The discussion that follows presents the performance results of PAA applied as a high-rate disinfectant for WWFs with shorter contact times from 2 to 10 minutes and PAA doses from 5 to 15 mg/L, generally higher than previously explored.

Technical Requirements to Address Problem. The first set of technical requirements involves the attainment of water quality standards (WQS) upon disinfection of WWFs. Until 1986, U.S. EPA had recommended the use of *fecal coliforms* as the preferred indicator organism to monitor for ambient water quality criteria; however, in 1986, it was determined that *E. coli* was a better predictor of waterborne illnesses and this became preferred pathogen to monitor (U.S. EPA, 1986). In the State of Kentucky, where this research was conducted, the Kentucky Division of Water has designated all surface waterbodies as being used for primary contact recreation (PCR). For PCR designated use, applicable from May 1 through October 31, the water quality criterion (WQC) in Kentucky Administrative Regulation 401 KAR 5:031 Section 7 (1)(a) requires that the *E. coli* geometric mean concentration computed from five samples taken during a 30-day period not exceed 130 col/100 mL and that the instantaneous concentration not exceed 240 col/100 mL in 20% or more of all samples taken during a 30-day period (Kentucky Administrative Regulations [KAR], 2012). Likewise, the allowable geometric mean for fecal coliforms is 200 col/100 mL and the allowable instantaneous concentration is 400 col/100 mL. The only secondary contact recreation (SCR) WQC, which is required to be met year round, is for fecal coliforms with an instantaneous concentration not to exceed 2000 col/100 mL. Because no secondary WQS exists for *E. coli*, the ratio for primary WQS of fecal coliforms to *E. coli* was used to estimate secondary WQS standards. Thus, the ratio of 240:400 is used in conjunction with the secondary WQS for fecal coliform of 2000 col/100 mL. The resulting estimated secondary WQS for *E. coli* would be 1200 col/100 mL [(240/400) $\times$ 2000] which was used to determine compliance with secondary WQS for this study. Kentucky Administrative Regulation 401 KAR 5:031 also requires both PCR- and SCR-designated waters have a pH ranging from 6.0 to 9.0 and a dissolved oxygen minimum daily average concentration above 6.0 mg/L with an instantaneous minimum of 5.0 mg/L (KAR, 2012).

The second set of technical requirements is, in part, based on the U.S. EPA guidance document, "Combined Sewer Overflow Control", which discusses methods to achieve high-rate disinfection of WWFs (U.S. EPA, 1993). The guidance document indicates that an acceptable reduction in bacteria concentration of at least 4-log kills (99.99% removal) should be achieved at detention times less than the conventional values of 15 to 30 minutes. In addition to acceptable bacterial reduction, a desirable disinfectant should not produce toxic DBPs (Veschetti et al., 2003). Thus, alternative disinfectants for WWFs should meet the above requirements. However, a 10-minute contact time is now often used successfully for many of the leading alternative disinfectants, allowing smaller contact basins to handle the large flows that occur.

In summary, for PAA to be considered an effective disinfectant, appropriate for WWFs, the treated discharge should meet the following technical criteria:

- Log kill $\geq$ 4 logs
- Contact time $\leq$ 10 minutes
- No toxic byproducts
- 6.0 $<$ pH $<$ 9.0
- Instantaneous dissolved oxygen $>$ 5.0 mg/L
- Daily average dissolved oxygen $\geq$ 6.0 mg/L
- *E. coli* PCR WQS 240 col/100 mL maximum
- *E. coli* SCR WQS 1200 col/100 mL maximum

Chemistry and Disinfection Mechanism. To understand why PAA is effective, both the chemistry and microbiology should be understood. Peracetic acid is produced by combining acetic acid, hydrogen peroxide, and water with sulfuric acid added to catalyze the reaction. The equilibrium chemistry is as follows:

$$CH_3CO_2H + H_2O_2 \underset{\uparrow SO_4H_2}{\leftrightarrow} CH_3CO_3H + H_2O \quad (1)$$

Peracetic acid spontaneously decomposes into acetic acid, hydrogen peroxide, and oxygen. Acetic acid and hydrogen peroxide yield methane, carbon dioxide, water, and free oxygen.

$$CH_3CO_3H \rightarrow CH_3CO_2H + {}^1/_2O_2 \quad (2)$$

$$CH_3CO_2H \rightarrow CH_4 + CO_2 \quad (3)$$

$$H_2O_2 \rightarrow H_2O + {}^1/_2O_2 \quad (4)$$

Peracetic acid (CH_3CO_3H) is a relatively strong oxidant having an oxidation potential of 1.8 V. Further, PAA is a weak acid with a dissociation constant (pKa) of 8.2 (Santoro et al., 2005) and when introduced to water with a pH less than 8.2, spontaneous decomposition of PAA occurs and hydroxyl radicals with an oxidation potential of 2.8 V are formed. Table 1 compares oxidation potentials for various oxidative species, including PAA, the hydroxyl radical, and many common disinfectants.

The formation of hydroxyl radicals is pH dependent when PAA is in solution and at any given time there may be four disassociates. Spontaneous decomposition produces acetate and hydroxyl radicals ($CH_3CO_2^{\bullet}$ and $OH^{\bullet}$) and reaches its maximum at pH 8.2, while hydrolysis produces acetate ions ($CH_3CO_2^-$)

and peracetate ions ($CH_3CO_3^-$) and increases as the pH increases. At pH 10.5 and higher, the hydrolysis reactions become dominant (Pettas & Karayannis, 2004). These processes are described in eqs 5 through 7.

The relationship between pH, peracetic acid, and the peracetate ion are illustrated in Figure 1. As is common α notation in acid/base speciation, α0 is that fraction that is in the most protonated form and α*i* is that fraction that has lost *i* protons. Peracetic acid is a monoprotic acid and as such α0 represents the fraction of peracetic acid (CH_3CO_3H) and α1 represents that fraction that is the peracetate ion ($CH_3CO_3^-$). The arithmetic and logarithmic representations of α0 and α1 distribution as a function of the difference between pH and pKa and simply pH are shown in Figures 1(a) and 1(b). A plot of log α versus pH is shown in Figure 1(c). Finally, assuming that peracetic acid and the peracetate ion are both ideal solutes, the relationship as illustrated in Figure 2 can be generated (for various concentrations of PAA) to demonstrate changes in concentrations of the dissociates over many orders of magnitude of change in pH.

pH Dependent

Peracetate Ion

$CH_3CO_3H + H_2O \rightarrow CH_3CO_3^- + H_3O^+$ (5)

Hydrolysis

Acetate Ion

$CH_3CO_2H + H_2O \rightarrow CH_3CO_2^- + H_3O^+$ (6)

Hydroxyl Radical

Spontaneous Decomposition

$CH_3CO_3H \rightarrow CH_3CO_2^{\bullet} + OH^{\bullet}$ (7)

U.S. EPA has defined a broad pH range of 6 to 9 for WWFs in need of high-rate treatment. However the range of pH in this investigation fell below a pH of 8.2 when spontaneous decomposition governs and hydroxyl radicals are generated. As such it is believed that this is the mechanism of disinfection. Hydroxyl radicals have one unpaired electron and become electron "scavengers". For gram negative cells, such as *E. coli* with highly negatively charged cell walls, the scavenging of electrons can be quite damaging to cell wall structure as well as to cellular DNA (Madigan and Martinko, 2006).

Methodology

Data Collection and Analysis. Based on the range of water quality being investigated, information gained from similar research, and some preliminary bench testing, PAA doses of 5, 10, and 15 mg/L appeared to be adequate to achieve the required kill while meeting water quality standards. Comparable (if not higher) dosing levels of traditional disinfectants such as chlorine compounds are required to achieve the same disinfection targets. However, this in turn results in high levels of dangerous byproducts and often requires a secondary process such as dechlorination giving PAA disinfection an added economic advantage. The product chosen for PAA treatment was Proxitane WW-12, a 12% PAA solution, produced by Solvay Chemicals, Inc. of Houston, Texas, and registered by U.S. EPA for wastewater disinfection. In addition, contact times of 2, 5, and 10 minutes were used because shorter contact times are desired as reducing contact time may translate into additional cost savings by reducing the capital costs associated with larger contact chambers. Thus, nine possible treatment combinations were investigated based on the three PAA doses and three contact times. The matrix of treatments applied is shown on the right in Figure 3. The source of simulated WWFs used in experimentation was the primary effluent of the Lexington, Kentucky, Town Branch Wastewater Treatment Plant. By diluting primary effluent in varying amounts, 27 individual representative WWF samples, with a wide range of *E. coli* concentrations, were treated. If primary effluent is diluted a great deal, the water quality is more likely to be similar in nature to storm water quality, while diluting the primary effluent a moderate or minor amount (if any) would be representative of CSOs or SSOs, respectively.

A phosphate buffered saline (PBS) solution was chosen to dilute the primary effluent because it supports microbial life making up "what biochemists call the phosphate buffer present inside cells to maintain control over pH of the cell fluid" (Brady and Holum, 1988). In addition, wastewater is typically a phosphoric, salty, buffered solution ranging in pH from 6.5 to 7.5. As a result, the use of PBS for the dilution of the primary effluent was considered acceptable. However, a separate analysis to investigate the potential impact of the PBS solution on the

Table 1—Oxidation potential of various oxidative species.

Oxidative species	Chemical formula	Oxidation potential (Volts)
Hydroxyl radical (1)	$OH^{\bullet}$	2.8
Ozone (1)	O_3	2.1
Peracetic acid (2)	CH_3CO_3H	1.8
Hydrogen peroxide (1)	H_2O_2	1.8
Hypochlorite ion (1)	OCl^-	1.7
Chlorine dioxide (1)	ClO_2	1.5
Hypochloric acid (3)	HCl	1.5
Chlorine (3)	Cl_2	1.4
Oxygen (1)	O_2	1.2

[a] International Maritime Organization (2006).
[b] Madigan & Martinko, 2006.
[c] Wojtenko et al., 2002.

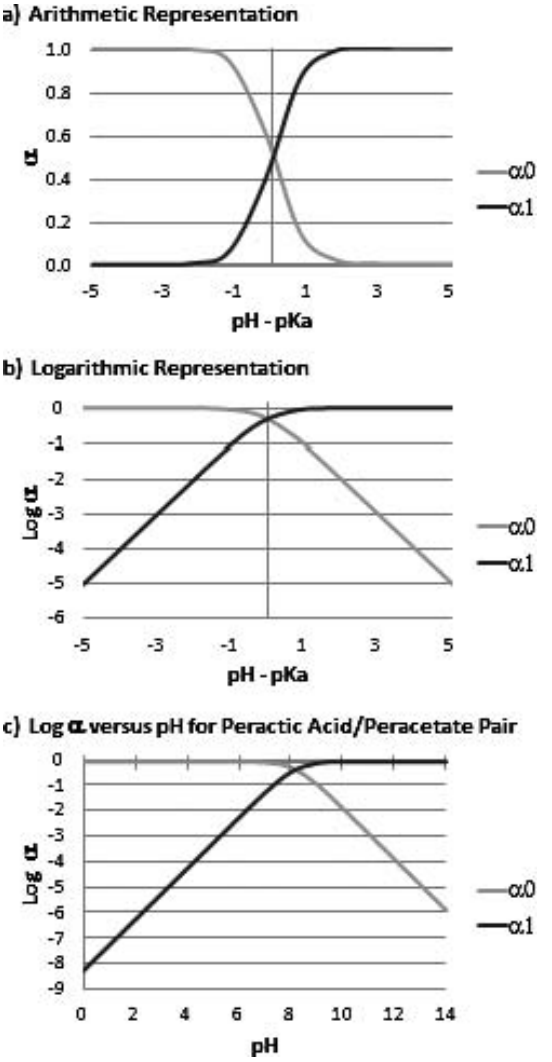

Figure 1—Relationship between pH, peracetic acid, and the peracetate ion.

disinfection process as was conducted and is further discussed in the Results and Discussion section.

Once the primary effluent sample was collected and the simulated WWFs were generated, the water quality characteristics of the samples were measured. The monitored parameters included the initial *E. coli* (E_o), final *E. coli* (E_f), ammonia (NH_3), total phosphorus, total suspended solids (TSS), chemical oxygen demand (COD), pH, specific electric conductance (SEC), and dissolved oxygen. This process is illustrated in Figure 3. The analysis to determine *E. coli* concentrations was done using IDEXX Colilert for growth media and IDEXX Quanti-Tray/2000 bubble packs for incubation (IDEXX Laboratories Inc., Westbrook, Maine). This is a U.S. EPA-approved method for the detection of *E. coli* for determining compliance with National Pollution Discharge Elimination System wastewater regulations and corresponds to Standard Methods 9223B (Clesceri et al., 1998) for *E. coli* analysis. The pH, SEC, and dissolved oxygen of samples was determined using a VWR SympHony SB90M5 bench probe (VWR International LLC, Radnor, Pennsylvania) in the same laboratory where the treatments were applied and E_o

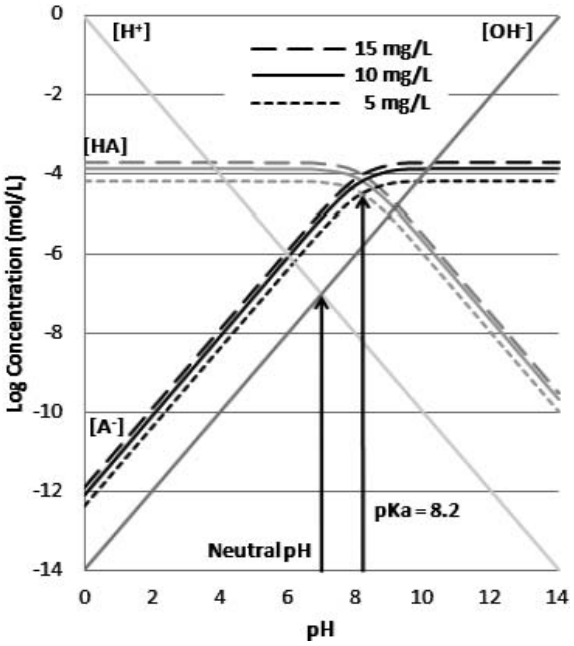

Figure 2—Peracetic acid speciation for concentrations of 5 mg/L, 10 mg/L, and 15 mg/L.

and E_f concentrations were determined. To determine the concentrations of the remaining parameters, all samples were packed in ice upon collection and delivered to the laboratories. Upon delivery to the laboratories, the samples were preserved according to the respective standard methods procedure. The TSS, NH_3, and total phosphorus analyses were conducted in the Kentucky Geological Survey laboratory at the University of Kentucky using standard methods 4500-NH3, 4500-P, and 2540-D, respectively (Clesceri et al., 1998). The chemical oxygen demand analysis was conducted by Microbac Laboratories in Lexington, Kentucky, and determined using standard method 5220-D (Clesceri et al., 1998).

Figure 3 also illustrates how the original sample was divided for treatment. Once the parameters for the initial sample were monitored, the sample was split into 11 subsamples and nine treatments were randomly assigned (from left to right) to nine of the subsamples (T1 to T9 in Figure 3). In addition, information regarding the quality of the data was collected by randomly selecting one of the nine treatments from each run to be done in

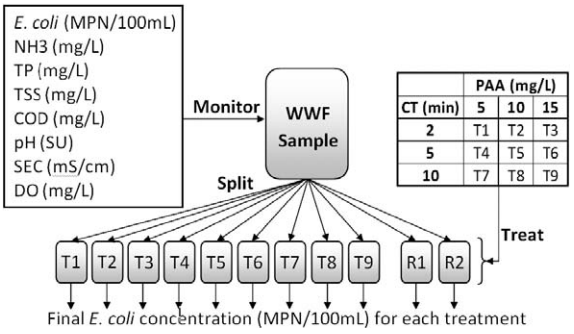

Figure 3—Method for data generation (TP = total phosphorus; DO = dissolved oxygen).

Table 2—Descriptive statistics of raw data.

	Initial values for samples to be treated							
Statistics	***E. coli***	**Ammonia**	**Total phosphorus**	**Total suspended solids**	**Chemical oxygen demand**	**Specific electric conductance**	**Dissolved oxygen**	**pH**
Minimum	72 000	1.0	3.2	3	7	1453	5.64	7.04
Maximum	2 419 000	20.0	40.5	41	130	2308	9.53	7.72
Mean	507 435	4.1	24.5	10	26	1939	7.86	7.45
Median	344 800	3.2	24.3	9	22	1987	8.13	7.43
Mode	241 960	3.2	19.8	10	22	2049	8.71	7.72
Range	2 347 600	19.0	37.3	38	123	855	3.89	0.68
St. deviation	415 488	2.8	8.4	6	19	202	1.18	0.20
Variance	1.73E+11	8.0	69.8	41	363	40 915	1.39	0.04
Count	255	144	144	144	144	144	166	166

triplicate (the original subsample treated plus two replicates, R1 and R2). Upon completion of the treatment contact time, each sample was quenched with 50 mg/L of sodium thiosulfate to remove the PAA from the solution and discontinue disinfection. The final *E. coli* (E_f) concentration was then determined for each of the treated subsamples as well as the other parameters originally monitored.

Results and Discussion

Raw Data. Data were collected from the fall of 2008 through the fall of 2009, during which time 27 lab runs were conducted on 27 individual representative WWF samples. This resulted in 290 data points. However, the first 2 days' runs were training days in which cross-contamination was noted to be a concern. Upon elimination of the practice runs done during training, 255 data points remained for analysis. Of the 255 data points, 144 had all monitored parameters measured successfully and an additional 22 had results for dissolved oxygen and pH only. The remaining 89 samples did not have additional parameters monitored for various reasons (e.g., broken probe, malfunctioning meter, etc.). Further, 101 samples were done in triplicate (one set had only two replicates) for use in determining the acceptability and quality of the data. A summary of the descriptive statistics of the raw data is in Table 2.

The E_o concentrations that were treated ranged from 72 000 MPN/100 mL to approximately 2.5 million MPN/100 mL providing a highly variable range of bacteria for disinfection purposes. In addition, the NH_3, TSS, and COD were quite variable and directly proportional to the E_o concentrations as shown in Figure 4. Figure 4 also shows the relative stability of pH and dissolved oxygen over the domain of the E_o concentrations considered. The stability of the pH results from the inherent buffering of the primary effluent as well as that of the PBS solution, while the stability of the dissolved oxygen results primarily from the consistent mixing of samples. Finally, Figure 4 shows the inversely proportional relationship between the E_o concentration and both SEC and total phosphorus. This is due to the PBS solution used for dilution purposes as explained previously. The more dilute the sample, the more phosphorus and saline (measured by ionic strength, i.e., SEC) introduced into the sample and the less the E_o concentration.

Statistical Analysis of Data. The precision of the bacteriologic data was evaluated using three different analyses: (1) a log difference test on the triplicates based on U.S. EPA criteria for *E. coli* densities (U.S. EPA, 1986), (2) a correlation and bias test on

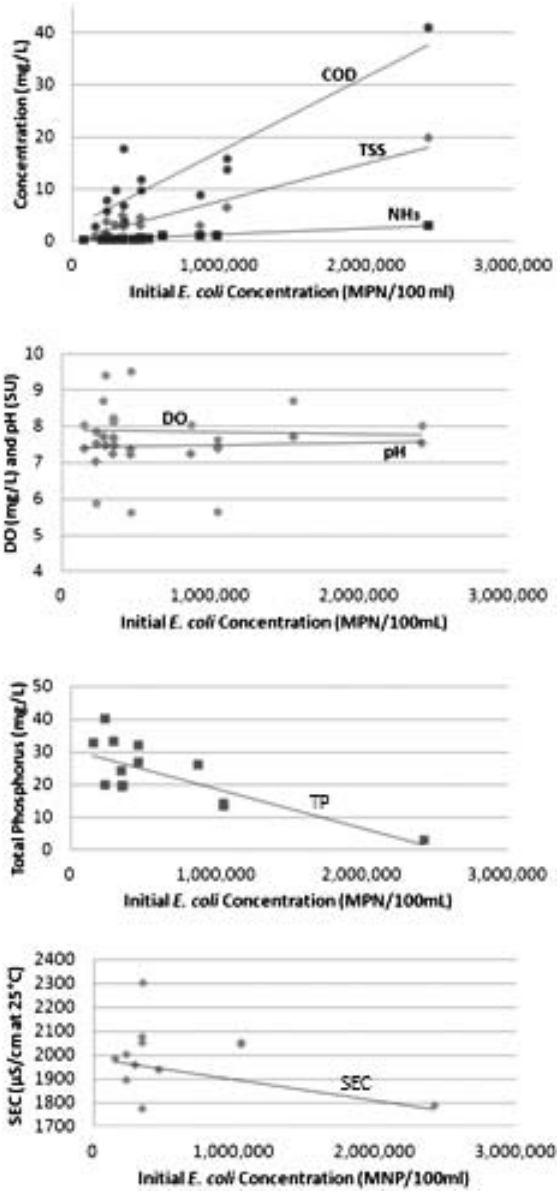

Figure 4—Water quality parameter correlations to initial *E. coli* concentrations.

Table 3—Results of one-way ANOVA on triplicate data set.

Source	Degrees of freedom	Sum of squares	Mean square error	*F* value
Between	2	0.1566	0.0783	0.0272
Within	99	285.0849	2.8796	
Total	101	285.2415		
F_{crit} (2,99)	3.07 ($p < 0.05$)		2.35 ($p < 0.1$)	

the triplicates, and (3) an analysis of variance (ANOVA) on the triplicates. The log difference test was conducted using the expected variances of freshwater *E. coli* samples as reported in Ambient Water Quality Criteria for Bacteria (U.S. EPA, 1986). This report provided the following equation for use in determining the expected variance for a single *E. coli* sample:

$$\text{Single sample limit} = \text{antilog}_{10}\text{abs}\{\log_{10}\text{IGMD}/100\text{ mL} + (\text{PF} \times \log_{10}\text{SD})\} \quad (8)$$

where

IGMD = indicator geometric mean density
PF = probability factor
SD = standard deviation

To determine the observed variance the following equation was used with the exception of the set with only two replicates:

$$\text{Observed variance} = \{\text{abs}(X1 - X2) + \text{abs}(X1 - X3) + \text{abs}(X2 - X3)\}/3 \quad (9)$$

For the sample with only two replicates, the observed variance was simply abs ($X2 - X3$). The expected variances for probability factors of 85, 90, and 95% were calculated to be 0.75, 1.02, and 1.32 (expressed in $\log_{10}$), respectively. When comparing replicate data, the observed frequency of data that was within the expected variances were 82, 94, and 97%, respectively. Thus, the analyzed data exceeded the expected frequency for the 90 and 95% confidence limits and closely approached the 85% expected frequency with an observed frequency of 82%, indicating that the analyses conducted were highly precise.

A second evaluation of the data quality was conducted using correlation and bias analysis. In this case the E_f concentrations were log transformed to normalize the bacteriologic data. Thus, the values of $\log(E_f)$ for each set of replicates was plotted against the remaining two sets using all the replicate data. An acceptable level of correlation was found between triplicates with R^2 values of 0.835, 0.815, and 0.904 for comparisons between replicates 1 versus 2, replicates 1 versus 3, and replicates 2 versus 3, respectively. A perfect correlation results in $R^2 = 1$ and the target for acceptability of this study was $R^2 > 0.7$, which is commonly used in water quality modeling and data collection. Based on 12 years of experience working with water quality models and data collection, an $R^2 > 0.7$ is often difficult, but possible to achieve. Furthermore, very little bias was indicated with slopes of 0.904, 0.946, and 1.007 for those same comparisons. No bias is indicated by a slope of 1. Finally, the y-intercepts of 0.209, 0.044, and –0.075 are closely approaching the theoretical value of zero for a perfect fit.

An ANOVA was the final analysis performed to determine the precision of the triplicate data set (and thus the entire data set as a whole). The null hypothesis is that triplicate means are the same and thus the data come from the same population. The alternative is that at least two of the three triplicate populations have different means and thus at least two populations are different. It is assumed that all samples are independent random samples, that $\log(E_f)$ is normally distributed for all three triplicate sets, and that there is a common unknown variance for all three triplicate sets. The results of the ANOVA are summarized in Table 3. The calculated value of F is much smaller than the critical values of F (F_{crit}) (Rosner, 2006) at different percentiles (i.e., $p = 0.05$ and $p = 0.10$, significance levels of 5 and 10%). Because F is very small relative to the critical value of F, the population means are roughly the same and the null hypothesis is not rejected. Thus, it can be assumed that triplicate data observations come from the same population and that the data are highly precise within the expected variance.

Influence of Water Quality Parameters. In addition to determining the quality and precision of the bacteriologic data, the influences of the monitored water quality parameters on the performance of PAA disinfection were also investigated. Ammonia, TSS, and COD were directly proportional to the E_o concentrations while dissolved oxygen and pH were fairly stable. Regardless of the relationship between NH_3, TSS, dissolved oxygen, pH, and E_o concentration, it was found that contact time and the applied dose of the disinfectant were the only two significant factors affecting the level of disinfection achieved. Initial range experiments showed that WQS could be met for various WWF strengths regardless of, and over the full range of, all the other water quality parameters. In addition, samples with the highest levels of disinfection were able to achieve these levels of kill even with very high E_o concentrations. These observations resulted in the conclusion that for the observed ranges, the water quality parameters NH_3, TSS, COD, dissolved oxygen, and pH did not strongly influence the performance of PAA in the matrices examined.

Influence of Phosphate Buffered Saline Used for Diluting Samples. The PBS buffering solution was observed to have an inverse effect on the values of total phosphorus and SEC (Figure 4). This relationship was further explored for any possible effect on the associated disinfection properties of the PAA.

Phosphate buffered saline contains a great deal of chloride ions (from sodium chloride [NaCl]) and potassium chloride [KCl]). Theoretically, the hydroxyl radical produced by the spontaneous decomposition of PAA (i.e., eq 7) will react with the Cl^- ions as follows:

$$OH^\bullet + Cl^- \rightarrow OCl^- \quad (10)$$

Further, the lower the pH, the more likely the protonation of $OC1^-$ will occur (bonding with an H^+ ion) to form HOCl as was observed in similar experiments with the oxidation of chloride ions by hydrogen peroxide (Hansen & Espenson, 1995). This reaction with Cl^- ions (regardless of reaction rate) is most likely to occur below a pH of 8.2 where the formation of hydroxyl radicals predominates and could theoretically consume hydroxyl radicals that would otherwise be consumed in the disinfection process, thus possibly affecting the disinfection efficiency of PAA.

This same phenomenon has been observed in another study in which the decay kinetics of PAA was explored for a variety of water matrices, with varying ionic strengths, had similar findings

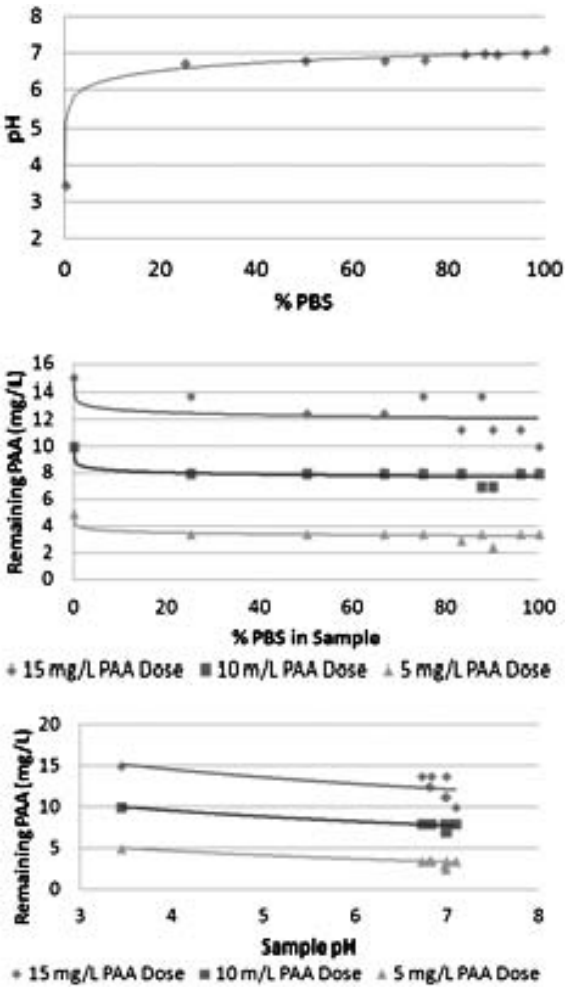

Figure 5—Relationships between percentage PBS, pH, and remaining PAA (TP = total phosphorus; DO = dissolved oxygen).

(Howarth, 2003). The specific matrices investigated included moderately hard water, a very hard water, and seawater with conductivities of 341, 1280, and 45 000 and pHs of 7.7, 7.98, and 7.9, respectively. It was determined that PAA was most unstable in the seawater with the fastest decay rate while much more stable in the moderately hard water with significantly longer decay rate. This result supports a hypothesis that the hydroxyl radical produced by the spontaneous decomposition of PAA will react with the free Cl^- ions and that ionic strength (as measured by specific electric conductance in this study) can have a strong influence on PAA demand and thus performance. This hypothesis is further supported by the results of the current study in which samples containing different percentages of deionized water and PBS were treated with different concentrations of PAA. The pH associated with the deionized water alone was approximately 3.5, while the pH associated with the PBS alone is approximately 7.1. Figure 5 shows the pH associated with different percentages PBS as diluted with deionized water. The effect of different combinations of PBS (and deionized water) and pH on the final concentrations of PAA for different PAA doses (i.e., 5 mg/L, 10 mg/L, and 15 mg/L) are also shown in Figure 5 and the statistics for the final PAA concentrations are

Table 4—Statistics for final PAA concentrations for various PAA doses.

Final PAA concentration	Dose = 5 mg/L	Dose = 10 mg/L	Dose = 15 mg/L
Minimum	2.5	7	10
Maximum	3.5	8	13.75
Average	3.33	7.78	12.22
St. deviation	0.35	0.44	1.37
High range	3.69	8.22	13.59
Low range	2.98	7.34	10.86

summarized in Table 4. From inspection of Figure 5 the following observations were made:

- The pH approaches 7 with as little as 25% PBS and only goes as high as 7.1 with 100% PBS;
- The 5 and 10 mg/L doses of PAA resulted in approximately 1.7 and 2.2 mg/L of PAA being consumed respectively, regardless of pH (a narrow range) or percent PBS;
- The 15 mg/L dose of PAA resulted in an increased initial demand of PAA as the percentage of PBS in the solution increased; and
- A mixture of PAA and only deionized water (no Cl^- ions, 0% PBS) does not produce an initial demand, even though the pH is significantly reduced (i.e., pH = 3.45).

Based on the above observations and findings from other studies, it can be concluded that there is an initial "demand" for the PAA by the PBS and that while pH is slightly influential, the initial demand of PAA is more strongly related to the concentration of Cl^- ions and PAA dose.

The question remains, however, whether the same demand exists when the PBS and PAA are mixed with diluted concentrations of wastewater, as was the case in the disinfection studies conducted as part of this research. Comparisons of the treated PBS-only samples with the treated WWF samples having same percentage of PBS, were done in an attempt to answer the above question. Should the PBS-only samples and the WWF samples behave similarly, the same conclusions could be drawn about each of them. Some of those samples (both PBS-only and WWF samples made with the same percent PBS) are presented in Figures 6 and 7. For demonstration purposes PBS levels of 50 and 96% are shown, respectively.

From inspection of Figures 6 and 7 the following observations were made:

- With an increased PAA dose (a low pH solution made with deionized water—pH 3.45), the pH of the PBS-only samples drops significantly;
- The pH values associated with the samples that actually contained wastewater did not show such significant drops in pH;
- As the percentage of PBS increases, this drop in pH becomes less due to the buffering of the PBS; and
- The initial demand of PAA is accelerated in the PBS-only samples by low pHs.

As such, it is hypothesized that the loss of PAA resulting from reactions with the PBS chemical constituents in WWF samples would have been less than the situation in which only PBS was

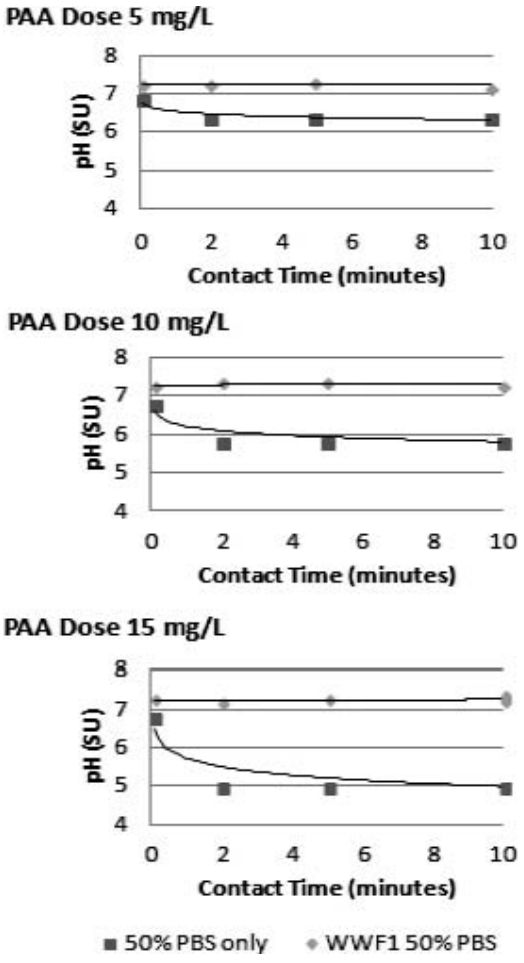

Figure 6—pH for PBS-only and WWF samples at PBS levels of 50%, by PAA dose.

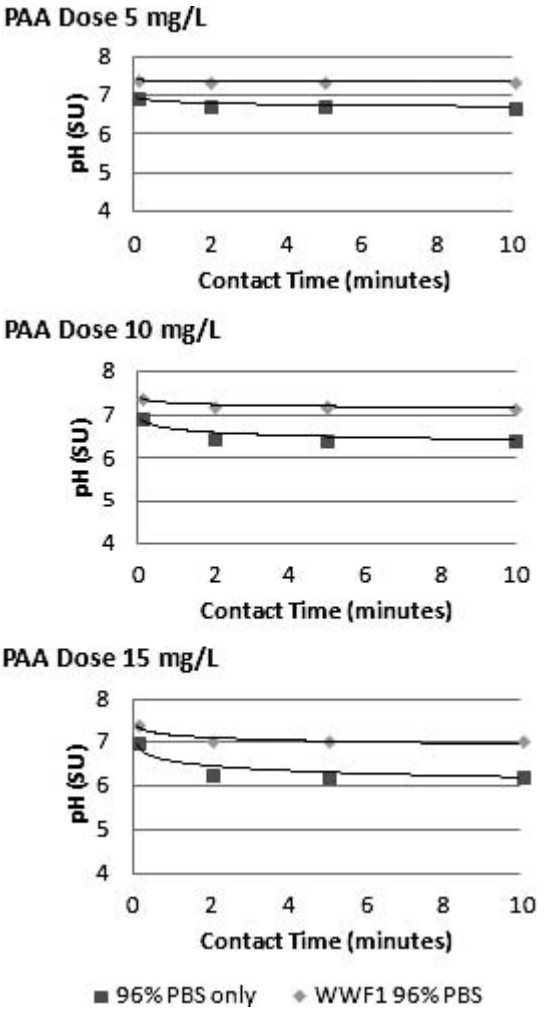

Figure 7—pH for PBS-only and WWF samples at PBS levels of 96%, by PAA dose.

present. The WWF samples are diluted with PBS as the first step after collecting the primary effluent and it is quite probable that some of the excess Cl^- in the PBS would have reacted with the constituents in the wastewater to such an extent that the concentration of the Cl^- would most likely be significantly less than in a solution with PBS only. Thus, there is most likely little Cl^- left to react with PAA by the time the actual treatments are applied to the WWF samples.

While there obviously exists some potential effect of the PBS on the available PAA for actual disinfection, in the end, this effect was not explicitly considered for the following reasons: (1) the pH values associated with the treated wastewater were fairly consistent and thus the influence of the rate of spontaneous decomposition of PAA is thought to be minimized, (2) it is hypothesized that a significant amount of the PAA demand associated with the Cl^- in the PBS would be reduced by reactions between PBS constituents and constituents in the wastewater, (3) any minor influence of PBS in the representative WWF samples results in conservative estimates of PAA performance, and (4) prior disinfection kinetic studies have consistently ignored the initial demand that is observed at the beginning of the disinfection process and have lumped that effect with the aggregate disinfection demand (Chick, 1908; Gyurek & Finch, 1998; Hom, 1972; Santoro et al., 2007; Tchobanoglous & Schroeder, 1985; Watson, 1908). Thus, such studies, as well as disinfection studies with other disinfection agents (e.g., chlorine), always develop their disinfection kinetic models based on dose applied as opposed to the amount consumed. As a consequence, this protocol has been observed in this research to provide a basis for comparison with prior research. Finally, in the context of an actual application of such technology, use of the applied dose as opposed to the amount consumed will yield a conservative estimate of dose required, which can be further refined through in situ calibration of the system to the specific wastewater.

Performance of Peracetic Acid Disinfectant. Strong WWFs were considered those with E_o concentrations greater than 1 million MPN/100 mL and the strongest treatment explored in this research was a PPA dose of 15 mg/L and contact time of 10 minutes. Using this treatment, PCR WQS (i.e., <240 MPN/100 mL) were achieved consistently in those samples having an E_o concentration from 1 million MPN/100 mL up to 1.5 million MPN/100 mL. Further, estimated SCR WQS (i.e., 1200 MPN/100 mL) were achieved with this treatment in samples having an E_o concentration from 1 million MPN/100 mL up to 2.5 million MPN/100 mL. In general, as E_o concentrations approached 1

million MPN/100 mL, lower PAA doses and shorter contact times were sufficient to meet PCR and SCR WQS, with a 5-minute contact time and 10 mg/L PAA dose achieving these goals in some of the laboratory runs. However, in two runs on November 12, 2008, and in one run on August 29, 2009, with E_o concentrations of approximately 1 million MPN/100 mL, WQS were only barely achieved with the strongest treatment of a PAA dose of 15 mg/L and a contact time of 10 minutes. Thus, because of the length of time required to achieve acceptable disinfection with generous margins of safety for WWFs with E_o concentrations near or above 1 million MPN/100 mL, this was considered the E_o limit for reliable performance using the PAA treatments explored. The most interesting observation for these strong WWFs is that the majority of the kill occurred in the first 5 minutes with 10 and 15 mg/L PAA. This is one-third the contact time traditionally used in chlorinated disinfection processes, a fact in favor of using PAA in smaller contact structures.

Moderate WWFs were considered those with E_o concentrations between 1 million and 100 000 MPN/100 mL. The E_o concentrations associated with the moderate WWF data ranged from 214 300 to 866 400 MPN/100 mL. The results showed that with PAA doses of 10 and 15 mg/L, primary WQS were typically met, and very closely approached using 5 mg/L PAA. Again, contact times were rapid with primary WQS often being met in 2 minutes using a 15 mg/L PAA dose and the majority of the kill typically occurring in the first 5 minutes with all doses.

Weak WWFs were considered those with E_o concentrations under 100 000 MPN/100 mL. The weakest WWF treated had an E_o concentration of 72 000 MPN/100 mL. The laboratory results for the sample for this date revealed that both PCR and the estimated SCR WQS could be met with all contact times (using 15 mg/L PAA with a 2-minute contact time, 10 mg/L PAA with a 5-minute contact time, and 5 mg/L PAA with a 10-minute contact time). Again, the majority of kill occurred in the first 5 minutes. Based on this and the above information, it has been demonstrated that PAA could be used to disinfect WWFs with E_o concentrations ranging from 72 000 to approximately 1 million MPN/100 mL to PCR WQS (i.e., 240 MPN/100 mL) with PAA doses between 5 and 15 mg/L and contact times between 2 and 10 minutes.

In addition to evaluating the performance of PAA based on WQS, it was evaluated based on a statistic referred to as the kill ratio $\ln(E_f/E_o)$, the natural log of the ratio of the final *E. coli* concentration (E_f) to the initial *E. coli* concentration (E_o). This was done for a number of reasons. First, the relationship between E_f and E_o concentration is preserved. Secondly, this statistic is commonly used in traditional disinfection kinetics (i.e., Chick, Chick-Watson, and Hom models) and can be compared to other disinfectants and studies. Finally, it is easy to relate the kill ratio to the technical requirement for a high-rate disinfectant to achieve a kill of 4 logs, or 99.99% kill. To achieve this level of disinfection the ratio of E_f/E_o is equal to 1/10 000. Thus, a kill ratio $\ln(E_f/E_o)$ of $\ln(1/10\ 000) = -9.21$ must be achieved.

Using triplicate data points, the contact time was plotted against the average and range of $\ln(E_f/E_o)$ for each PAA dose as shown in Figure 8. The target kill ratio of 9.21 is also shown on each graph. Upon inspection of the plot for a PAA dose = 5 mg/L (top plot in Figure 8), minimal disinfection was observed at the 2-minute contact time. However, in 5 minutes, a minimum kill ratio [i.e., $\ln(E_f/E_o)$] of 3 was achieved with an average of kill ratio of 5. Further, at the 10-minute contact time, a kill ratio

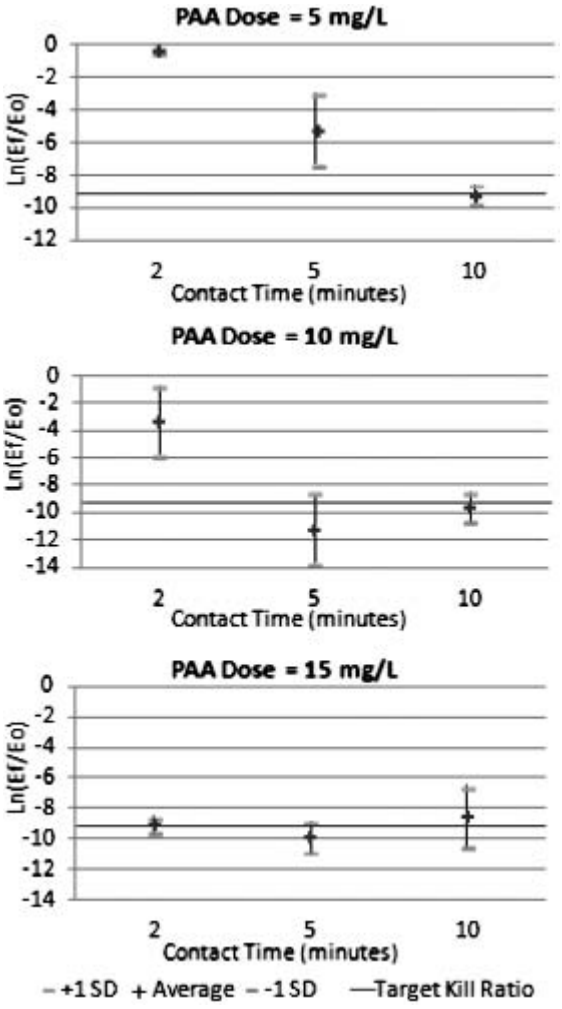

Figure 8—Contact time versus $\ln(E_f/E_o)$ by PAA dose.

greater than 9 was achieved. In addition, there was a distinct linear relationship such that, as time increases, kill increases over the complete range of contact time. The same relationship is observed from the plot for PAA dose of 10 mg/L (middle plot in Figure 8), but only for the 2- and 5-minute contact times and not over the full range of contact time. At 2 minutes, the 10 mg/L dose resulted in a kill ratio of approximately 3, and at 5 minutes, the kill ratio was more than 8 with an average of 11 observed.

The 5- and 10-minute contact times did not show any statistically significant difference for a PAA dose of 10 mg/L. It can be assumed that the majority of disinfection that occurred using the 10 mg/L dose was accomplished in the first 5 minutes. The same holds for the plot for PAA dose of 15 mg/L (bottom plot in Figure 8) across all contact times. It appears that for a PAA dose = 15 mg/L, most of the kill occurred within the first 2 minutes. Further, the level of disinfection achieved with the 15 mg/L dose that was recorded at 2 minutes may have occurred sooner, but no data points exist between zero and 2-minute contact times.

Conclusions

The main objective of this research was to determine the feasibility of using PAA as a disinfectant for wet weather

discharges of diluted wastewater. Thus, this research attempted to answer the question: Can PAA satisfy the regulatory requirements as an effective, high-rate disinfectant for wet weather discharges? The research supports an affirmative answer. Water quality standards were met with reasonable PAA doses within contact times less than normal design parameters.

The established criteria for an effective high-rate disinfectant, appropriate for WWFs were met. Within the range of treatments explored (i.e., PAA dose range from 5 to 15 mg/L and contact times ranging from 2 to 10 minutes) with a range of E_o concentrations to be treated (from approximately 100 000 MPN/100 mL to 1 million MPN/100 mL), PCR WQS were reliably achieved via disinfection with PAA. Furthermore, this level of disinfection by PAA was fast, with the majority of the kill occurring in the first 5 minutes regardless of dose applied or E_o concentration. In addition, PAA has shown to be able to achieve a 99.99% disinfection level (or a 4-$\log_{10}$ kill) with the treatments applied. The criteria regarding dissolved oxygen and pH have been met although the range of pH was narrower in this study (and more representative of WWF water quality) being between approximately 6.5 and 7.5. It should be noted that the levels of PAA used did not significantly affect pH. Dissolved oxygen was predominantly a function of mixing. PAA does release some free oxygen and will not reduce oxygen levels. Finally, U.S. EPA has recommended PAA as a possible alternative disinfectant because there are no known, toxic DBPs (Manarca et al., 2004; Stinson, 1999). Meeting each of these high-rate disinfection criteria supports the conclusion that PAA is an appropriate alternative disinfectant for WWFs.

Based on the results of this research, it would seem that PAA could successfully be applied to drop *E. coli* concentrations in WWFs to levels that would not negatively affect receiving waters. Areas where traditional disinfectants cannot be used due to limited space, such as in inner cities and highly developed urban areas (where many WWFs traditionally occur), could take advantage of high-rate PAA disinfection with smaller footprints at more affordable capital costs. Further, it may be possible to drip feed PAA into manholes upstream of the WWF discharge locations as long as the contact time in-line exceeds 2 minutes, particularly for WWFs that are predominantly stormwater where end-of-pipe removal of litter can be implemented. This would simply require a small equipment storage chamber (above or below ground) in the vicinity of the manhole. Many times, there are long dry periods between WWF events, and PAA is stable in storage for use with intermittent flows. In addition, reduced initial capital costs can be realized due to quicker contact times, but also because the nontoxic nature of PAA residuals negates the need for dechlorination or residual removal (requiring a second pumping system and second contact chamber as well as additional chemicals) particularly when the optimal dose of PAA is applied. It is also possible to retrofit existing wastewater treatment facilities that are periodically inundated with infiltration and inflow and no longer have the contact times for which they were designed. Other factors to consider are that PAA has a smaller carbon footprint and energy costs for manufacturing and application as compared to energy-intensive disinfectants such as ultraviolet and ozone disinfection or as compared to the two chemical feed systems needed for chlorination and dechlorination. Finally, PAA application is safer as compared to other chlorine-based products as it has no known toxic DBPs. In summary, there are a number of practical applications for PAA as a high-rate disinfectant with a great deal of added benefits when compared to traditional technology.

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