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Dual-Disinfection of Wastewater Effluent with Combined Peracetic Acid (PAA) and Sodium Hypochlorite Treatment:

A FULL-SCALE PILOT STUDY AT MILL CREEK PLANT

Dual-Disinfection of Wastewater Effluent with Combined Peracetic Acid (PAA) and Sodium Hypochlorite Treatment: A Full-Scale Pilot Study at Mill Creek Plant

by

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Disclaimer

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

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This study report describes development of a practical dual-disinfection approach for municipal wastewater disinfection. This report summarizes the results from a wastewater treatment field study that was conducted at the Metropolitan Sewer District of Greater Cincinnati's Mill Creek Facility.

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Abbreviations

CFU	colony-forming unit
MSDGC	Metropolitan Sewer District of Greater Cincinnati
MCTP	Mill Creek Treatment Plant
MGD	million gallons per day
NaOCl	sodium hypochlorite
NPDES	National Pollutant Discharge Elimination System
OEPA	Ohio Environmental Protection Agency
ORD	Office of Research and Development
PAA	peracetic acid
TRO	total residual oxidants
EPA	United States Environmental Protection Agency

Executive Summary

Peracetic acid (PAA) in combination with chlorination was shown to provide effective bacterial reduction in secondary effluent during field study research conducted at the Mill Creek Treatment Plant of the Metropolitan Sewer District of Greater Cincinnati, located in Cincinnati, Ohio. This study compared PAA with sodium hypochlorite (NaOCl) chlorination and their combinations for the disinfection of *Escherichia coli* in the treatment plant's wastewater.

Key findings:

- This full-scale field study evaluated the effectiveness of PAA and NaOCl treatment for secondary effluent disinfection. The treatment data is then compared with sequential dual disinfection treatment using PAA followed by NaOCl. This treatment study showed that the PAA and chlorine combination is very effective for municipal wastewater disinfection. A major advantage of dual disinfection is the low residual oxidant content, better treatment efficiency, and low environmental impact compared to separate individual treatments.

- The field studies showed that the dual disinfection using PAA followed by chlorination provided better disinfection compared to individual disinfection steps. The disinfection mechanism is different for PAA and chlorination. For example, PAA is less effective in water with high oxygen demand where chlorine will be helpful to achieve the treatment goals.

- The sequential dual disinfection treatment using PAA followed by NaOCl has the potential to lower chlorine usage, which reduces chlorinated disinfection byproducts in the discharge and avoids the need for expensive dechlorination steps.

- The author's recent studies showed that the PAA addition to the existing municipal wastewater treatment train required very low capital investment. Economic savings can be expected from the reduction of capital and operational expenses needed for dechlorination and chlorination storage needs and consumption, respectively. In addition, PAA can be used to support facilities that use chlorination to achieve better compliance.

1. Introduction

In 2018, while renewing the National Pollutant Discharge Elimination System (NPDES) permit for Metropolitan Sewer District of Greater Cincinnati's (MSDGC) Mill Creek Treatment Plant (MCTP), the Ohio Environmental Protection Agency (OEPA) made key changes to the permit. Those changes included replacing fecal coliforms with *Escherichia coli* as the monitoring biomarker for secondary effluent disinfection during the recreational season (May 1– October 31). In addition, the weekly and monthly geometric mean of *E. coli* limits were set to 240 colony-forming units (CFU)/100mL and 126 CFU/100mL. By contrast, in the old permit, the weekly and monthly fecal coliform limits were 400 CFU/100mL and 200 CFU/100mL, respectively. The total maximum oxidant residual (0.33 mg/L) remained unchanged in the new permit. These changes in the permit prompted MSDGC to reevaluate its capabilities and assess challenges in meeting new permit requirements. A review of the *E. coli* data collected during the fall of 2018 at MCTP revealed that under current treatment conditions, MSDGC would consistently fail to meet the revised permit's weekly and monthly *E. coli* limits. One solution was to increase chlorination and dechlorinate after treatment to keep the total oxidant level below 0.33mg/L. The dechlorination step would need new contact tanks and sodium bisulphate addition (which could cause sodium pollution). The construction of new tanks would require large capital investments (20-30 million dollars). This prompted MSDGC to collaborate with ORD for developing cost-effective alternative disinfection methods (Jacangelo, 2019; Acher, 1997; Lazarova, 1998 and 1999), including the use of peracetic acid (PAA).

PAA is a chemical oxidizer that can be used as an alternative disinfectant for wastewater. The chemical formula for PAA is CH_3COOOH – essentially acetic acid with an extra oxygen molecule. Peracetic acid is used in parts of Europe as a replacement for chlorine disinfection in wastewater, and it is currently

used in North America in the food processing industry as a disinfectant for hard surfaces that have been in contact with fruits, vegetables, meats, and eggs (Basu and Gatchene, 2009). Recently, PAA has been evaluated as a replacement for chlorine to disinfect secondary effluent from wastewater treatment plants (Jacangelo, 2019). PAA is commercially available as an aqueous quaternary equilibrium mixture of acetic acid, hydrogen peroxide (H_2O_2), PAA, and water:

$$CH_3COOH + H_2O_2 \leftrightarrow CH_3CO_3H + H_2O$$

PAA is usually produced at concentrations of 5% -15%. Kitis (2004) reviewed the use of PAA as a disinfectant for wastewater effluents since the 1980s and reported it to be an efficient bactericidal, virucidal, fungicidal and sporicidal chemical. Typical PAA treatment concentrations for secondary effluent are 0.50-2.0 mg/L, and enhanced primary effluent typically requires a PAA concentration of 5-10 mg/L. PAA contact times are typically 10-30 minutes with most of the reaction occurring within the first 10 minutes (Dancey, 2008). Peragreen Solutions and Solvay Chemicals have treated between 5 and 8 MGD of secondary effluent with PAA dosages not exceeding 1.5 mg/L at the wastewater treatment plant in the City of Steubenville, Ohio (Maziuk et al., 2013). The disinfection action of PAA occurs through mechanisms such as the release of nascent oxygen, which could oxidize essential enzymes for cellular metabolism, disrupt cell membranes and transport mechanisms, and denature proteins in spores (Kitis, 2004). A major advantage of PAA as a disinfectant is that it is not known to produce any harmful disinfection byproducts (Liberti and Notarnicola, 1999; Namboodiri et al., 2016). Some limitations of using PAA as a disinfectant include lower disinfection efficiency against some viruses and parasitic oocysts as well as potential for regrowth of microbes since residual PAA contributes to organic carbon as a food source in the effluent (Kitis, 2004; Crebelli, 2005).

The author's previous bench, pilot, and field studies evaluated the effectiveness of PAA for treating combined sewer overflow (CSO) and dual disinfection by combining PAA/ultraviolet (UV) and PAA/chlorination for secondary effluent (Namboodiri et al., 2016 and 2020; Garg et al., 2017 and 2019). The current full-scale pilot study was based on data collected from several bench-scale studies conducted in the MSDGC laboratory with PAA and NaOCl. These laboratory studies indicated PAA alone was a better disinfectant than NaOCl and could meet permit limits for both *E. coli* and total residual oxidants (TRO). A third, potential dual disinfection treatment method, pre-treatment of secondary effluent with NaOCl followed by PAA, was evaluated in the laboratory but was found to be no more effective than NaOCl treatment alone at reducing *E. coli* numbers. Hence, this combination of NaOCl followed by PAA treatment was not evaluated in the field pilot study. Objectives of this full-scale plant-level pilot study were: 1) to determine if dual disinfection using PAA followed by NaOCl was better than individual PAA or NaOCl treatments in reducing *E. coli* concentrations, and 2) to find an optimal PAA followed by NaOCl dose combination in dual disinfection treatment to satisfy new permit limits for *E. coli* and total oxidant residuals during the recreational season.

2. Methodology

This section describes the treatment set-up, experimental, and analytical methods.

2.1. Treatment Set-up

This full-scale pilot study was conducted at MCTP from May to August 2019. During pilot study hours, the primary MCTP disinfection system (i.e., NaOCl) was shut off, while at the same time the PAA injection pump was activated to treat secondary effluent. At the conclusion of each day's testing, the primary NaOCl disinfection system was turned on prior to shutting off the PAA injection pump. This always ensured uninterrupted disinfection of secondary effluent.

The location for injecting NaOCl to disinfect secondary effluent during normal operation is designated as Location A in Figure 2.1. For the pilot study, however, Location A was selected to inject PAA using a separate Model M-6 chemical feed pump (Blue-White Industries, Ltd, Huntington Beach, California). Totes of PAA (PeroxyChem, Philadelphia, Pennsylvania) containing approximately 250 gallons of 15% PAA were stored near the injection site under a tent to provide protection from the weather. For dual disinfection tests, the NaOCl injection site was moved to Location B (Figure 2.1), with the Sampling Station at Location C.

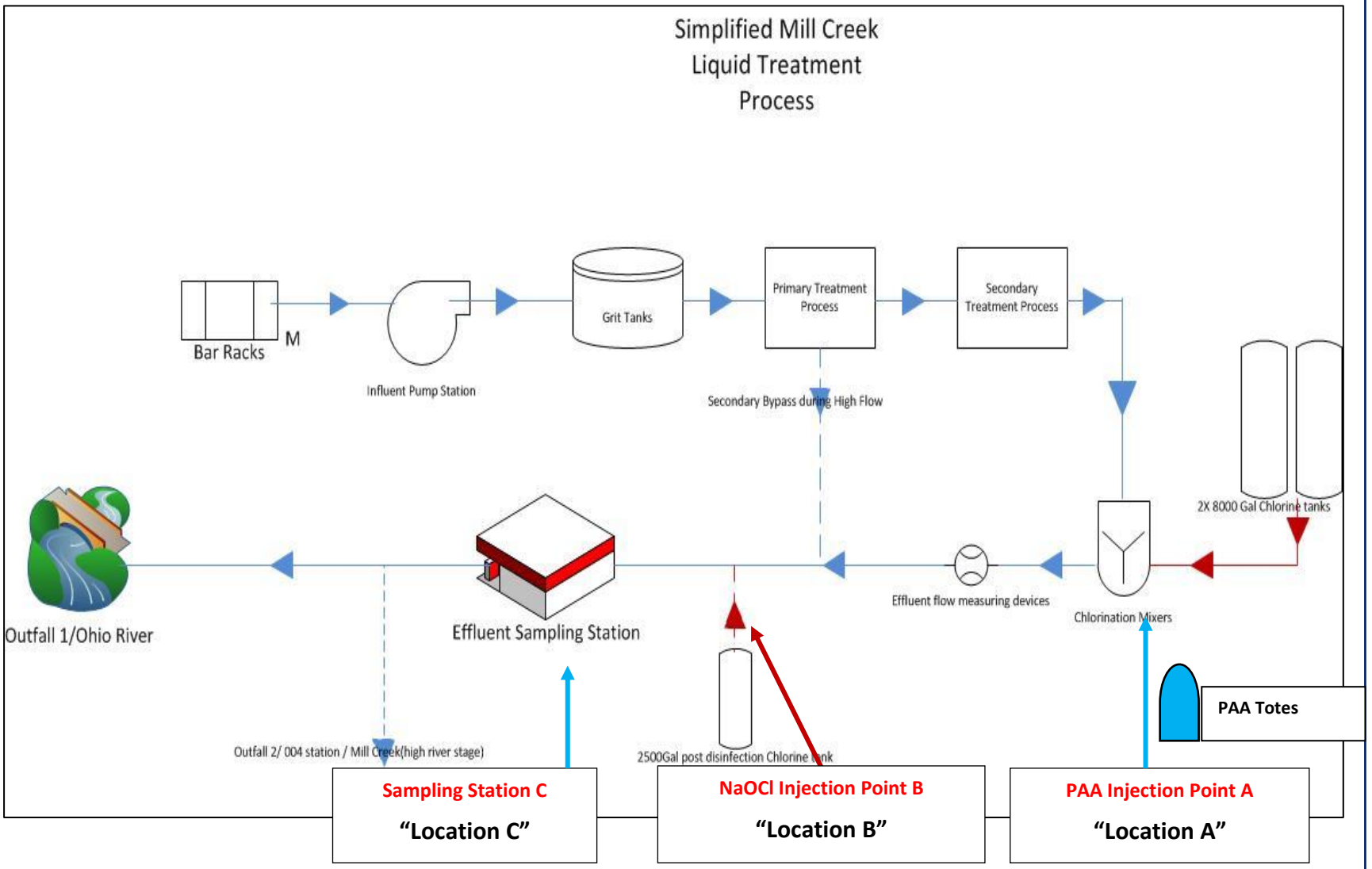

Figure 2.1. Simplified Mill Creek liquid treatment process. Treatment locations for injecting PAA ("A"), NaOCl ("B"), and sampling station ("C").

2.2. Experimental Design

Secondary effluent was treated with the PAA alone, NaOCl alone, or various combinations of PAA followed by NaOCl (dual disinfection).

The following strategies were applied to achieve the desired treatments:

PAA only treatment. The plant's NaOCl (chlorine source) pump at Location A (Figure 2.1) was turned off and the PAA pump was turned on at this location. The pumping rate was set manually based on the flow rate of the secondary effluent. The post-treatment samples were collected at the Sampling Station (Location C) and kept for the time the flow reaches the discharge point. The holding time before quenching was calculated using NPDES permit approved flow rate discharge chart. The samples were then analyzed for residual oxidant content and microbiological analysis.

PAA followed by NaOCl Sequential Treatment (Dual Disinfection). Secondary effluent was treated first with PAA followed by NaOCl. With the plant's primary NaOCl dosing pump shut off, the PAA dosing pump was turned on at Location A. The NaOCl pump at Location B was turned on at the same time to inject the desired dose of NaOCl. It took between two to five minutes for PAA-treated secondary effluent from Location A to reach Location B where NaOCl was injected. The dual disinfection post-treatment samples were collected at the Sampling Station (Location C) for residual oxidant and microbiological analysis.

2.3. Analytical Methods

E. coli results were obtained using two analytical methods. For benchtop studies, the IDEXX Colilert®-18 method was used (IDEXX Laboratories, Inc., Westbrook, Maine) (Appendix A). For field studies, the membrane filtration method was applied (Standard Methods, method number 9222). Chlorine in samples was measured using total chlorine analysis by HACH® Method 8167 N, N-diethyl-p-phenylene-diamine

(DPD) colorimetric method (Hach, Loveland, Colorado) (Appendix B). Oxidant residuals were measured as TRO after PAA or dual disinfection combination treatments; samples were analyzed using an amperometric titrator. Analysis of PAA was carried out using PAA Vacu-Vials® ampoules and the I-2020 PAA single analyte meter (CHEMetrics, Midland, Virginia) (Appendix C).

Two sets of TRO data were collected during the study: intermediate and delayed. Intermediate TRO values represented the total oxidant levels in the secondary effluent three to five minutes (dependent on flow rate) after adding PAA at Location A. Delayed residual measurements were made after a predetermined holding period based upon the plant's flow rate. This predetermined delay represented the time it took treated secondary effluent to reach the outfall at the Ohio River. After holding the samples for the calculated delay time, one part of the sample was quenched for bacteriological analysis and the second part was used for TRO measurements. Samples for all analytes were collected at the Sampling Station (Location C).

3. Results and Discussion

This report only presents the details of the field study results. The secondary effluent treatment efficiency of PAA alone and with dual disinfection combinations was determined by measuring (Standard Methods, method number 9222) the reduction of *E. coli* after treatment. Treatment doses for PAA ranged from 0.5 mg/L to 1.2 mg/L. While multiple dual disinfection combinations were evaluated, only one combination is detailed in this report.

3.1. Treatments with PAA Alone

Although *E. coli* concentrations were significantly reduced with PAA doses between 0.5 mg/L and 0.65 mg/L, none of the 11 samples analyzed satisfied the permit limit of 126 CFU/100 mL (Figure 3.1). The

lowest number of *E. coli* observed after disinfection with doses between 0.5 mg/L and 0.65 mg/L was 160 CFU/100 mL. The geometric mean of these 11 samples was 889 CFU/100 mL (Figure 3.1).

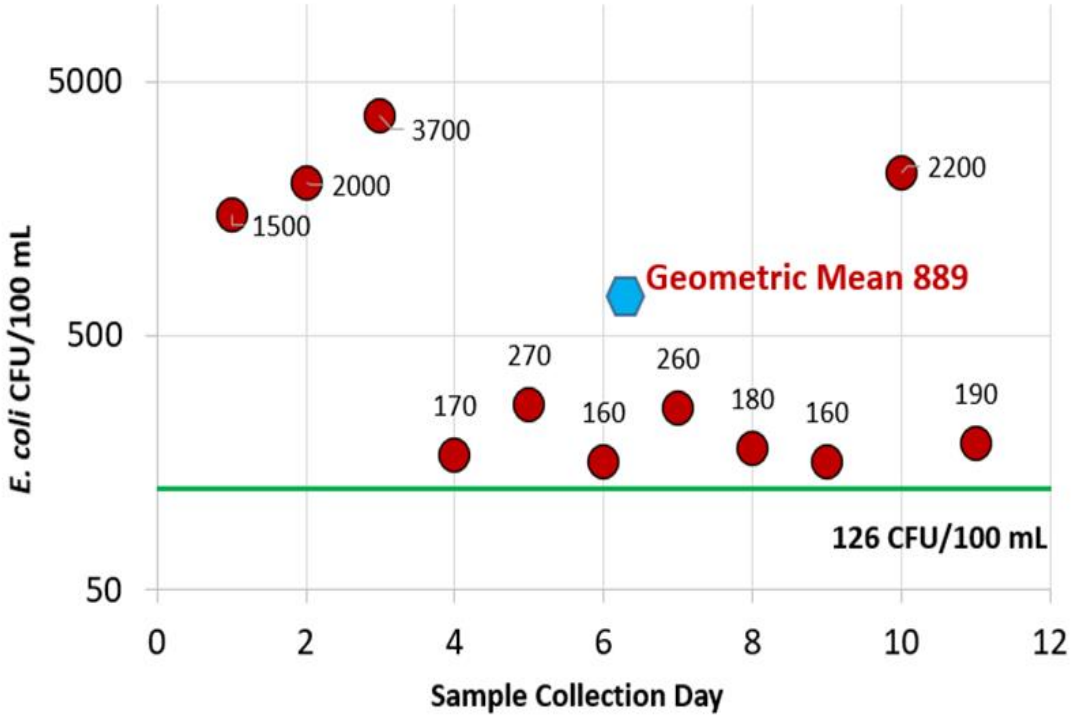

Figure 3.1 Treatment of secondary effluent with PAA doses ranging from 0.5mg/L to 0.65 mg/L. None of the samples satisfied permit limit. The treatment achieved a geometric mean of 889 CFU/100mL.

3.1.1 PAA dose of 0.7mg/L

The lowest PAA dose to reduce *E. coli* below the new permit limit was found to be 0.7 mg/L. Of the ten samples treated with this PAA dosage, four were between 40 CFU /100 mL and 110 CFU /100 mL. The remaining six had a range of 140 CFU /100 mL to 300 CFU/100 mL. The geometric mean of these ten samples was 123 CFU /100 mL, just below the new permit limit of 126 CFU/100 mL (Figure 3.2). Earlier benchtop studies demonstrated a similar dose response and indicated that a minimum dose of 0.7 mg/L PAA would be required to meet new permit limits for *E. coli*.

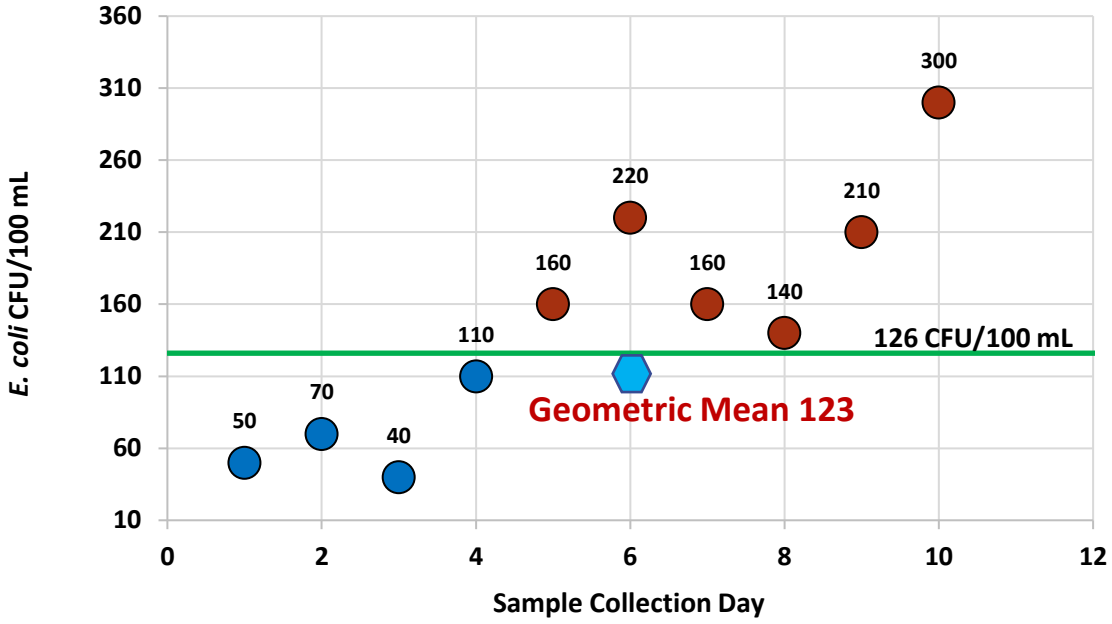

Figure 3.2. Treatment of secondary effluent with 0.7mg/L PAA. Of the ten samples analyzed, four were below the permit limit. This treatment achieved a geometric mean of 123 colony forming units (CFU)/100 mL, just below the permit limit.

3.1.2 PAA dose of 1 mg/L

When secondary effluent was treated with 1 mg/L PAA, the average number of *E. coli* was reduced to 61 CFU /100 mL (Figure 3.3). Two samples in the 1 mg/L PAA treatment group exceeded the new permit limit of 126 CFU/100 mL. These two samples (with 180 CFU /100 mL and 240 CFU /100 mL) were collected during rain events with very high plant flow; normal plant flow ranges between 80 MGD and 120 MGD. The flow rate was 200 MGD and 225 MGD during the first and second rain events, respectively. At these high flow rates, the contact time for PAA was reduced to 14-15 minutes from an average of 45 minutes during normal plant flow conditions. The reduced contact time was insufficient to bring the *E. coli* concentrations below the revised permit limit. The nine remaining samples were collected under normal flow conditions, and 1 mg/L PAA reduced the *E. coli* concentration to a geometric mean of 61 CFU /100 mL.

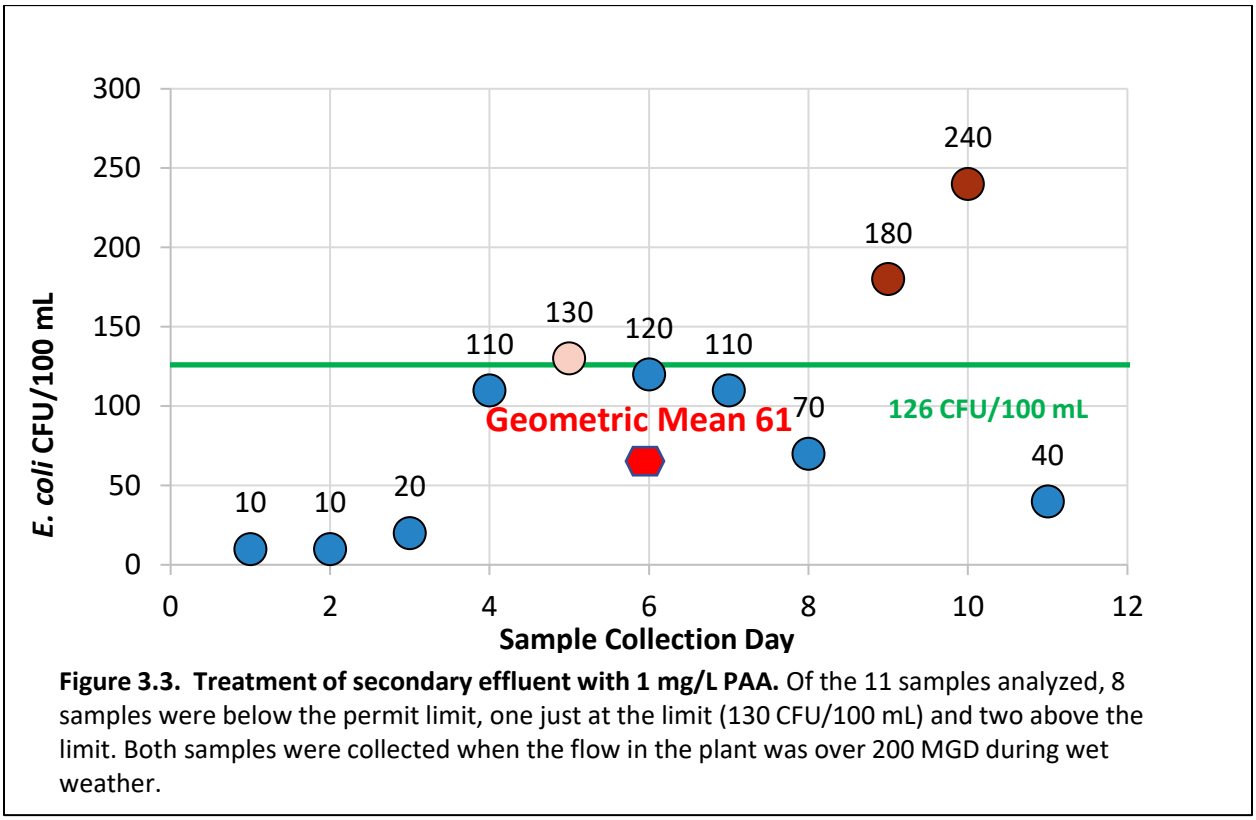

Figure 3.3. Treatment of secondary effluent with 1 mg/L PAA. Of the 11 samples analyzed, 8 samples were below the permit limit, one just at the limit (130 CFU/100 mL) and two above the limit. Both samples were collected when the flow in the plant was over 200 MGD during wet weather.

3.1.3 PAA dose of 1.1 mg/L

The most effective PAA dosage was found to be 1.1 mg/L (Figure 3.4). All seven samples, under normal flow rates, in this treatment group were between 40 CFU /100 mL and 90 CFU /100 mL *E. coli* with a geometric mean of 60 CFU /100 mL.

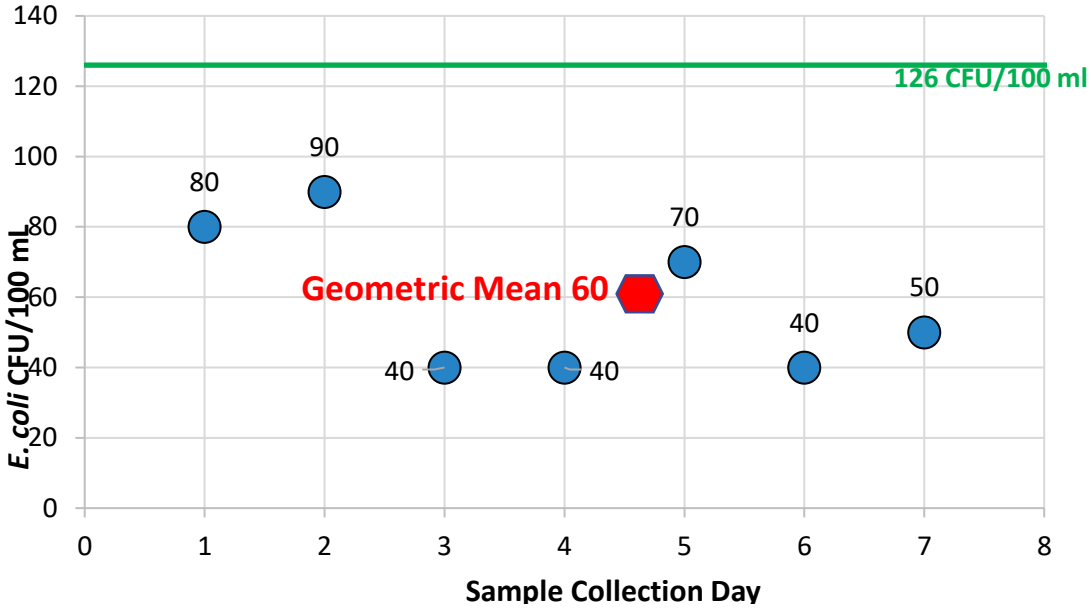

Figure 3.4. Treatment of secondary effluent with 1.1 mg/L PAA. All seven samples were found to be less than the new permit limit of 126 CFU/100 mL with a geometric mean of 60 CFU/100 mL.

3.2 Dual Disinfection Treatment

Bench scale studies showed combining PAA followed by NaOCl (dual disinfection) enhanced *E. coli* kills. These pilot study findings confirmed the results of laboratory studies. It is noteworthy that dual disinfection was most effective when NaOCl was added three to four minutes after PAA.

The combination of 0.7 mg/L PAA followed by 0.4 mg/L NaOCl was found to be the optimal dose to meet the new permit limit for *E. coli*. This combination achieved a geometric mean of 29 CFU /100 mL of *E. coli* (Figure 3.5). In comparison, 1.1 mg/L PAA alone achieved a geometric mean of 61 CFU /100 mL *E. coli* (Figure 3.4). This finding has significant implications for achieving higher treatment efficiency at lower cost. Although both treatment regimens (i.e., 1.1 mg/L PAA or 0.7 mg/L PAA + 0.4

mg/L NaOCl) used equal amounts of total oxidants (1.1 mg/L), the dual disinfection treatment was more effective. In the dual disinfection strategy, only 0.7 mg/L PAA was used compared with 1.1 mg/L PAA in the PAA-only treatment or about 38% less PAA. This reduction in the requirement for PAA can have a significant impact on the total cost of treatment. The use of dual disinfection did not increase the final total oxidant residuals, which remained at 0.2 mg/L or less.

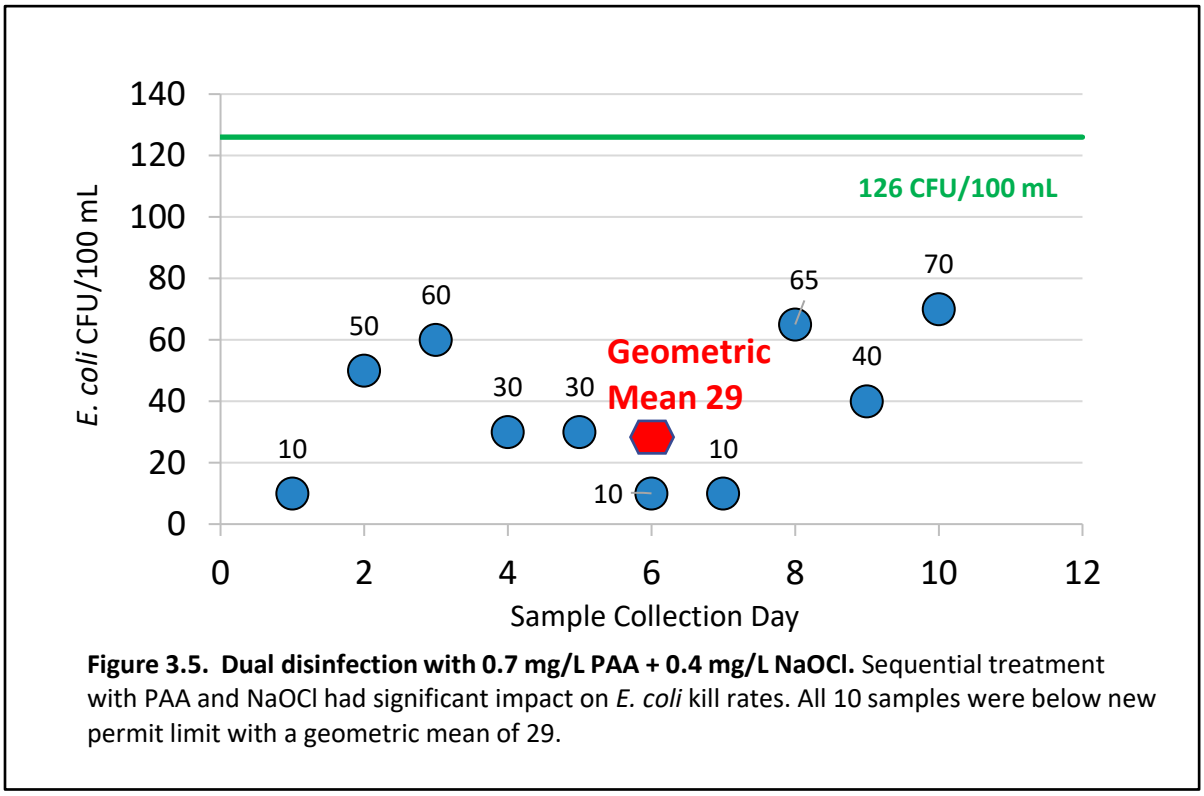

Figure 3.5. Dual disinfection with 0.7 mg/L PAA + 0.4 mg/L NaOCl. Sequential treatment with PAA and NaOCl had significant impact on *E. coli* kill rates. All 10 samples were below new permit limit with a geometric mean of 29.

Figure 3.6 presents a graphical comparison of geometric means from three of the different treatment schemes. The blue bar is the lowest dose of PAA alone to reduce *E. coli* below the new permit limit (0.7 mg/L). The orange bar is the most effective PAA alone dosage (1.1 mg/L). Finally, the grey bar is the optimal dual disinfection combination of 0.7 mg/L PAA followed by 0.4 mg/L NaOCl.

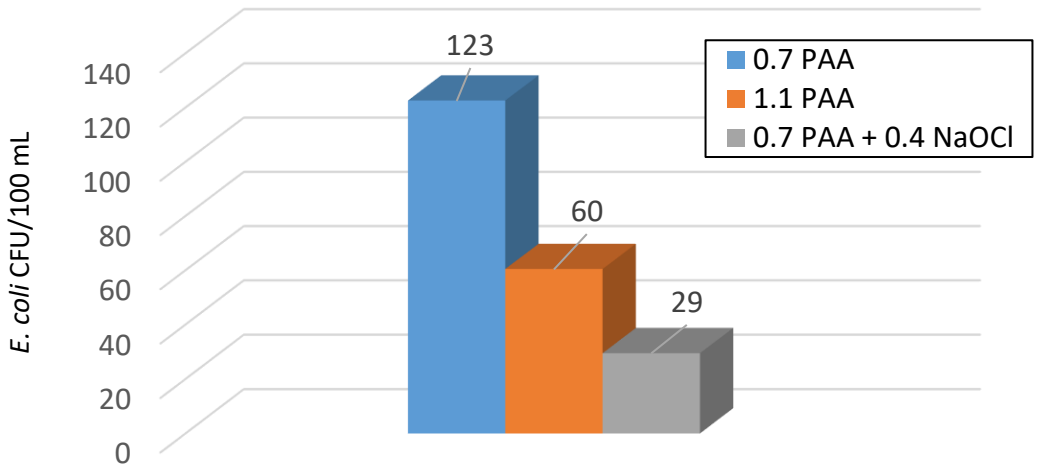

Figure 3.6. Comparing geometric means of different treatment schemes. Benchmark PAA concentrations compared with dual disinfection.

3.3 Total Residual Oxidants (TRO)

After collection at the sampling station (Location C, Figure 2.1), samples were analyzed for intermediate and delayed residuals. Intermediate residual measurements were made immediately. These TRO values represented the total oxidant levels in secondary effluent three to five minutes (dependent on flow rate) after adding PAA at Location A. Delayed residual measurements were made after a predetermined holding period based upon the plant's flow rate. This represented the time it took for treated secondary effluent to reach the outfall at the Ohio River, and the TRO levels being discharged therein.

Three delayed TRO samples, all from PAA only treatments, failed to meet the new permit's residual oxidant limit of 0.33 mg/L (Figure 3.7). Those three samples were collected during high flow conditions (between 200 MGD and 265 MGD), which resulted in delay times of 12-14 minutes. Normal plant flow is 80-120 MGD with an average delay time of 45 minutes. All TRO sample data from dual disinfection treatment (0.7 mg/L PAA + 0.4 mg/L NaOCl) was found to comply with the new permit's oxidant residual limit.

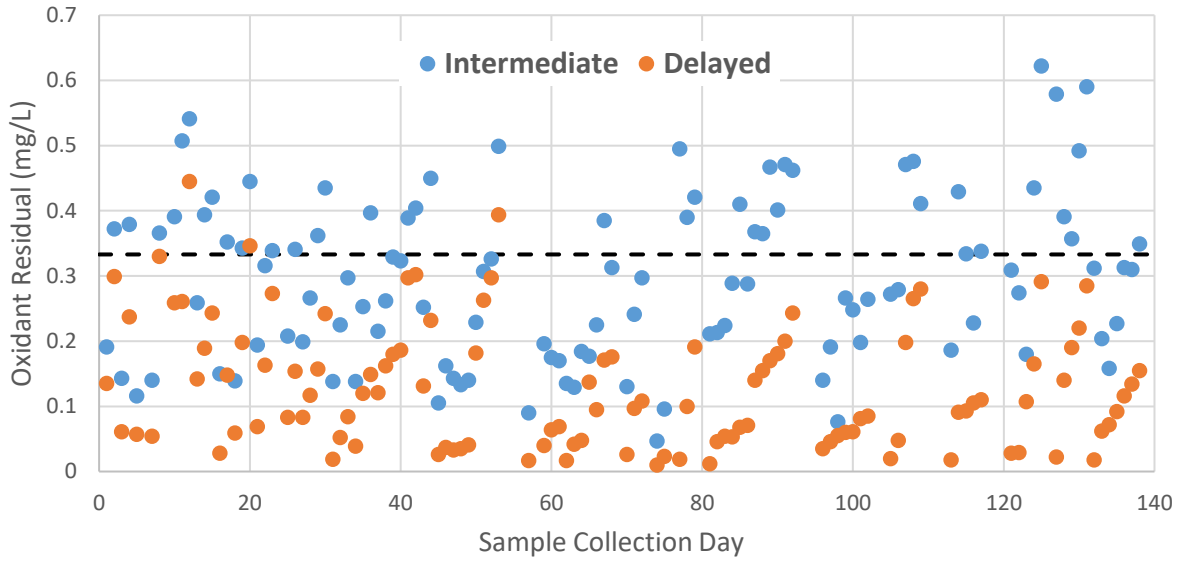

Figure 3.7. Intermediate and delayed oxidant residual data. Only three delayed TRO measurements failed to meet the new permit limit of 0.33 mg/L.

4. Conclusions

This full-scale pilot study evaluated the effectiveness of individual PAA and NaOCl treatments for secondary effluent disinfection and compared them to sequential dual disinfection using PAA followed by NaOCl. The study optimized PAA and NaOCl dose combination to satisfy new OEPA permit limits for *E. coli* and total oxidant residuals during the recreational season.

- Dual disinfection with PAA followed by sodium hypochlorite is significantly more effective than individual PAA or sodium hypochlorite treatments.
- Treatment with 0.7 mg/L PAA followed by addition of 0.4 mg/L NaOCl three to four minutes later was found to be the optimal dose combination.
- The above dual disinfection combination achieved a post-treatment geometric mean *E. coli* concentration of 29 CFU/100mL with total oxidant residuals <0.2 mg/L.

- The sequential disinfection using PAA followed by NaOCl treatment satisfied both *E. coli* and residual oxidant NPDES permit limits for the MCTP. Therefore, PAA can be used to support facilities that use chlorination to achieve better disinfection compliance.

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Appendices

Table A-1. ATPTIM and EPA's Testing and Evaluation (T&E) Facility's Standard Operating Procedures (SOPs)

APPENDIX A	APTIM T&E SOP 310 ("Total Coliform and E. *coli* Analysis Using IDEXX Colilert® 18 Method")	T&E SOP 310 TotalColiform & Ecoli
APPENDIX B	APTIM T&E SOP 504 (FREE CHLORINE & TOTAL CHLORINE ANALYSIS, "Free Chlorine Analysis by HACH® Method 8021 And Total Chlorine Analysis by HACH®: Method 8167 N.N-diethyl-p-phenylene-diamine (DPD) Colorimetric Method; 0.02 to 2.00 mg/L Cl*2*")	T&E SOP 504 Free Chlorine And Total Ch
APPENDIX C	APTIM T&E SOP 511 (PERACETIC ACID BY CHEMETRICS, "Peracetic Acid (PAA) by CHEMetrics® DPD Method")	T&E SOP 511 Peracetic Acid By CHE

T&E, EPA's Testing and Evaluation Facility, Cincinnati, Ohio; SOP, standard operating procedure

Appendix D - Quality Assurance/Quality Control (QA/QC) Measures

D.1 Introduction

An important aspect of technology testing is the quality assurance/quality control (QA/QC) procedures and requirements developed. Careful adherence to the procedures detailed in the quality assurance project plan (QAPP) enables researchers to evaluate the performance of dual disinfection treatment using peracetic acid (PAA) followed by NaOCl to disinfect secondary wastewater and present the data in this report. The primary measures of evaluation for data quality were representativeness, accuracy, and precision.

D.2 Analytical Procedures

The Metropolitan Sewer District of Greater Cincinnati (MSDGC) staff conducted the full-scale field study that was created specifically for these evaluations and performed any sample analyses on site that needed to be made immediately. APTIM staff conducted the *E. coli* analyses following Aptim T&E standard operating procedure (SOP) 310 "Total Coliform and *E. coli* Analysis Using IDEXX Colilert®18 Method" (Appendix A). Analytical methods for the laboratory analyses are presented in Table D-1.

D.3 Sample Handling

Samples were collected by MSDGC and were labeled with unique sample names in the format specified in the EPA-approved QAPPs. Samples were transferred by MSDGC from the study location to APTIM at EPA's Test and Evaluation (T&E) Facility in Cincinnati, Ohio, for *E. coli* analyses within 6 hours of sample collection in hard-sided coolers with ice. All samples were analyzed within the sample holding time specified in the QAPP.

D.4 Sample QA/QC

The calibration of analytical instruments and the analyses of parameters complied with the QA/QC provisions of the EPA-approved QAPP used in this evaluation. Sample volumes, preservation, and holding times are shown in Table D-2. Laboratory QA/QC checks for the chemical and microbiological analyses are shown in Table D-3.

The APTIM QA/QC requirements specified in the referenced T&E SOP (Table A-1, following the Appendices heading, above) were compliant with those stated in the EPA-approved QAPPs for each respective parameter. The SOPs implemented at the T&E Facility for the chemical and microbiological analyses conducted for this evaluation are provided as attachments in the EPA-approved QAPP.

Table D-1. Measurements and Analytical Methods

Measurement	Analytical Method/ SOP
PAA	Chemetrics, Inc. K-7913
Total Chlorine	Total Chlorine Analysis by HACH® Method 8167 DPD Colorimetric Method
E. coli	APTIM SOP 310 and Standard Methods #9222
Total Residual Oxidants	Hach Amperometric titrator Model AT1000
Temperature	Thermometer
Flow rate	Non-Contact LaserFlow® Velocity Sensor

DPD = N,N-diethyl-p-phenylene-diamine, SOP = standard operating procedure

Table D-2. Sample Volumes, Preservation, and Holding Times

Measurement	Sample Container	Volume of sample	Preservation	Holding Time
PAA	Glass beaker	100 mL	None	None. Analyze immediately after sampling.
Total Chlorine	Glass beaker	100 mL	None	None. Analyze immediately after sampling.
E. coli	Plastic	100 mL	Sodium thiosulfate, 4°C	24 hours
Total Residual Oxidants	Glass beaker	100 mL	None	None. Analyze immediately after sampling.

Measurement	Sample Container	Volume of sample	Preservation	Holding Time
Temperature	Glass beaker	50 mL	None	None. Analyze immediately after sampling.

D.5 Documentation

Laboratory activities were documented using standardized datasheets, logbooks, and laboratory notebooks. Laboratory data reports were entered into Microsoft™ Excel® spreadsheets. These spreadsheets were used to calculate the mean, standard deviation, and ranges, as applicable.

D.6 Data Review

Calculations performed on a computer were checked initially by the analyst for gross error and miscalculation. The calculations and data entered into computer spreadsheets were checked by a peer reviewer for accuracy by printing out the calculation or data spreadsheet and checking the calculation by hand or comparing each entry of data with the original.

Table D-3. QA/QC Checks

Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
PAA	Check Standard (2.5 mg/L)	Before analysis, after every 10 samples, and at the end of batch analysis	±10% of acceptance criteria	Discard data point, repeat experiment if insufficient data points
	Duplicate	Once per batch of 10	RPD[a]<30%	Repeat analysis on the same sample; if sample volume does not allow, choose another sample and document accordingly
Total Chlorine	Check Standard (2.5 mg/L)	Before analysis, after every 10 samples, and at the end of batch analysis	±10% of acceptance criteria	Discard data point, repeat experiment if insufficient data points
	Duplicate	Once per batch of 10	RPD[a]<30%	Repeat analysis on the same sample; if sample volume does not allow, choose another sample and document accordingly
E. coli	Lab blank	Once per counting session	0 MPN[b]/tray	Investigate lab technique Reanalyze blank
	Positive control	Once per counting session	±10 fold of the spiking suspension	Investigate lab technique Re-analyze the spiking suspension and change it if necessary
	Negative control	Once per counting session	0 MPN/tray	Investigate lab technique Reanalyze buffer and change it if necessary
Total Residual Oxidants	Check Standard (2.5 mg/L)	Before analysis, after every 10 samples, and at the end of batch analysis	±10% of acceptance criteria	Discard data point, repeat experiment if insufficient data points
	Duplicate	Once per batch of 10	RPD[a]<30%	Repeat analysis on the same sample; if sample volume does not allow, choose another sample and document accordingly
Temperature	Calibration verification	Beginning of project	±1°C	Verify accuracy against NIST or NIST-traceable thermometer
Flow Rate	Calibration verification	Beginning of project	Full-scale factory-calibrated accuracy of ±1%	Initially at the factory; checked by measuring volume and time prior to testing

a: Relative Percent Difference (RPD)
b: Most Probable Number (MPN)

D.7 Data Quality Indicators

The quality of data generated for this system performance evaluation is established through three indicators of data quality: representativeness, accuracy, and precision.

D.7.1 Representativeness

Representativeness is a qualitative term that expresses "the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition." Representativeness was ensured by consistent execution of the test protocol for each challenge, including timing of sample collection, sampling procedures, and sample preservation. Representativeness was ensured by following standard operating procedures and published methods to provide reproducible results and represents the most accurate and precise measurement the analytical method is capable of achieving.

D.7.2 Accuracy

Accuracy was quantified as the percent recovery of the parameter in a sample of known quantity. Accuracy was measured through use of certified standards during calibration of an instrument.

The following equation was used to calculate percent recovery:

$$\text{Percent Recovery} = 100 \times [(X_{known} - X_{measured})/X_{known}]$$

Where:

X_{known} = known concentration of the measured parameter

$X_{measured}$ = measured concentration of parameter

The EPA-approved QAPP specifies the frequency of calibration checks as well as the accuracy acceptance criteria for the chemical analyses. Calibration and calibration check requirements specified in the QAPP were achieved for all analyses.

D.7.3 Precision

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. At least one out of every ten samples for THMs, HAAs, sodium, pH, PAA, chlorine, and solids were analyzed in duplicate as part of the analysis batch. Precision of duplicate analyses was measured using the following equation to calculate RPD:

$$RPD = \left| \frac{S_1 - S_2}{S_1 + S_2} \right| \times 200$$

Where:

S_1 = sample analysis result; and

S_2 = sample duplicate analysis result.

Because the microbiological analyses (*E. coli*, fecal coliform, and *Enterococci*) are measured on a logarithmic scale, typical RPD calculations might result in higher than the expected RPD values. For this reason, the RPD was calculated after transforming the concentrations with a common logarithm (base 10):

$$RPD = \left| \frac{\log S_1 - \log S_2}{\log S_1 + \log S_2} \right| \times 200$$

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