EWRI Pittsburgh Section
Meeting October 30, 2014

Comparing Peracetic Acid with Sodium Hypochlorite for Disinfection of Combined Sewer Overflows

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Today's Presentation

Peracetic Acid (PAA) Research

- EPA and Metropolitan Sewer District of Greater Cincinnati (MSDGC) jar test studies with peracetic acid on non-chlorinated secondary effluent at the U.S. EPA Test and Evaluation Facility in Cincinnati, Ohio.

- Case Study 1 - Comparison of chlorine/sodium bisulfite with peracetic acid at a WW Facility in Steubenville, OH

- Case Study 2 – Comparison of sodium hypochlorite and peracetic acid in disinfection of MSDGC Muddy Creek combined sewer overflow in Cincinnati, OH (Ongoing)

U.S. EPA Test & Evaluation Facility, Cincinnati, Ohio

Multi-faceted drinking water and wastewater research facility located on the grounds of the MSDGC

Disclaimer

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed, or partially funded and collaborated in, the research described herein. It has been subjected to the Agency's peer and administrative review and has been approved for external publication. Any opinions expressed are those of the author (s) and do not necessarily reflect the views of the Agency, therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Background

PAA Literature Review

- PAA is a strong disinfectant, as effective as Cl_2 against indicator bacteria in secondary and tertiary effluents
- Less effective than Cl_2 against viruses
- Synergistic with UV irradiation

M. Kitis, Disinfection of wastewater with peracetic acid: a review, Environment International, 3047-55 (2004).

- Does not form chlorinated DBPs but does form aldehyde, brominated organic DBPs due to reaction with spiked precursors in wastewater

Booth and Lester (1995), Crathorne et al. (1991).

Oxidation Potential

Oxidant	eV
Hydroxyl Radical	2.85
Ozone	2.08
Peracetic Acid	1.81
Hydrogen Peroxide	1.78
Permanganate	1.68
Hypochlorite Ion	1.64
Hypchlorous Acid	1.48
Monochloramine	1.4
Sodium Hypochlorite (Chlorine Bleach)	1.36
Dichloramine	1.34
Hypobromous Acid	1.33
Oxygen	1.23
Chlorine Dioxide	0.95

Lide (1995); AWWA (1990); Stumm and Morgan (1996)

Background

PAA Environmental Benefits

- Does not add conductivity (TDS)
- Does not form chlorinated disinfection byproducts (THMs and HAAs)
- Non persistent in the environment
- Breaks down into acetic acid, CO_2 and H_2O
- No RMP, SARA, or CERCLA requirements
- Degrades rapidly in soil (seconds) and seawater (minutes)

PAA Use Limitations

- Contributes TOC on a one to one basis.
- PAA is consumed by sulfites and sulfides.
- Reduced half life above pH 8.5.
- Cannot be stored in mild steel or contaminated containers.

PAA Suppliers

- Supplier information: FMC & Solvay
- FMC: VigorOX WWT II (PAA15%)
- Solvay: Proxitane WW-12 (PAA 12%)
- Manufacturing locations
  - FMC: Tonawanda, NY
  - Solvay: Joliet, IL
- Onsite PAA (>98%) generation:
  Eltron Research & Development, Inc.

MSDGC Jar Test Studies

What is in Solvay's Proxitane WW 12?

- PAA 12%
- Acetic Acid 15%
- Hydrogen Peroxide 18.5%
- $H_2O_2 + CH_3COOH \leftrightarrow CH_3COO\text{-}OH + H_2O$

Background

Advantages of PAA for WW Treatment

- Small footprint
- Feed in neat form
- Low freezing point
- Long shelf life (12 to 18 months)
- No extensive capital improvements required
- Minimal pH and temperature dependence

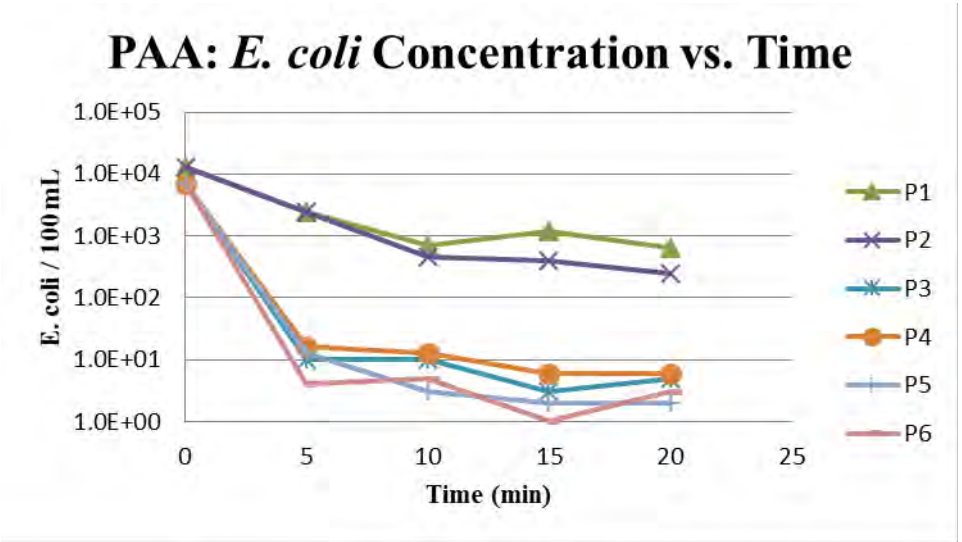
Disadvantages of PAA for WW Treatment

- Still requires State approval
- Cost? (site specific)
- Limited suppliers

MSDGC Jar Test Studies

E. Coli and PAA Concentrations in MSDGC Secondary Effluent vs. Time

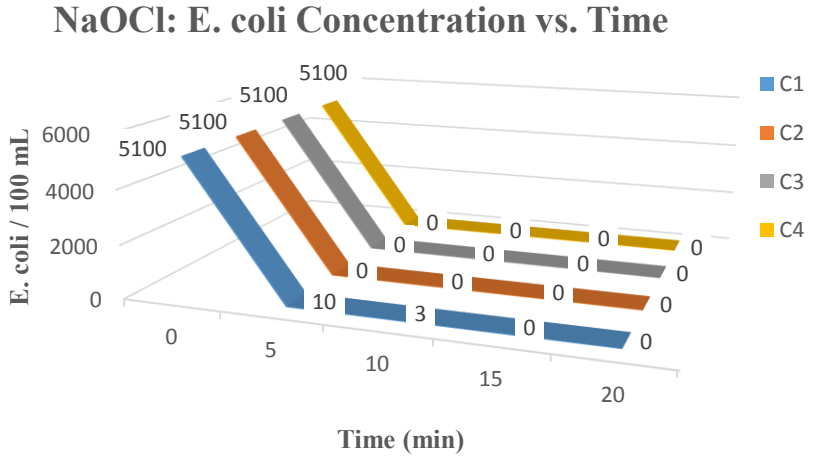
Time (min)	P1		P2		P3		P4		P5		P6	
	E. coli / 100 mL	PAA (mg/L)	*E. coli* / 100 mL	PAA (mg/L)	*E. coli* / 100 mL	PAA (mg/L)	*E. coli* / 100 mL	PAA (mg/L)	*E. coli* / 100 mL	PAA (mg/L)	*E. coli* / 100 mL	PAA (mg/L)
0	1.3 x EE4	4.4	1.3 x EE4	5.8	6.8 x EE3	5.9	6.8 x EE3	13.7	6.8 x EE3	20.3	6.8 x EE3	26.2
5	2.4 x EE3	3.3	>2.4 x EE3	4.7	10	5.6	16	12	13	18.2	4	26.2
10	687	2.6	457	4.1	10	5.1	13	11.6	3	18.2	5	25.7
15	1203	2.2	387	3.7	3	5.2	6	11.6	2	18.2	1	24.6
20	649	2	250	3.2	5	4.9	6	11.3	2	17.7	3	24.6



MSDGC Jar Test Studies

E. Coli and Chlorine Concentrations in MSDGC Secondary Effluent vs. Time

Time (min)	C1		C2		C3		C4	
	E. coli / 100 mL	Free Chlorine (mg/L)	*E. coli* / 100 mL	Free Chlorine (mg/L)	*E. coli* / 100 mL	Free Chlorine (mg/L)	*E. coli* / 100 mL	Free Chlorine (mg/L)
0	5.1 x EE3	0.8	5.1 x EE3	1.4	5.1 x EE3	1.8	5.1 x EE3	1.5
5	10	0.6	<1	1	<1	1.4	<1	1.3
10	3	0.6	<1	1	<1	0.9	<1	1.2
15	<1	0.8	<1	0.8	<1	0.7	<1	0.9
20	<1	0.5	<1		<1	0.5	<1	0.8



Results and Conclusions

- NaOCl with a concentration of 1.4 mg/L free chlorine resulted in complete inactivation of *E. coli* in less than 5 minutes
- PAA with a concentration of 14 mg/L resulted in significant inactivation of *E. coli* in 10 minutes.
- To achieve a log inactivation of greater than 3, PAA required a CT value greater than 150 mg*min/L, while NaOCl required a CT value of 8 mg*min/L.

Assumptions based on Results

- Sodium hypochlorite – For CES effluent, assume a NaOCl dose of 5 mg/L and dechlorination with sodium bisulfite at a dose of 2 mg/L.
- For raw or screened CSO, assume a NaOCl dose of 10 mg/L and dechlorination with sodium bisulfite at a dose of 4 mg/L.
- PAA – For raw or screened CES effluent, assume a PAA dose of 5 mg/L.
- For CSO, assume a PAA dose of 10 mg/L with no required dechlorinating facilities.

Case Study 1

Comparison of PAA and Chlorine/Sodium Bisulfite Disinfectants at a WW Facility in Steubenville, OH

PAA Totes and Injection Pump

Criteria for Success

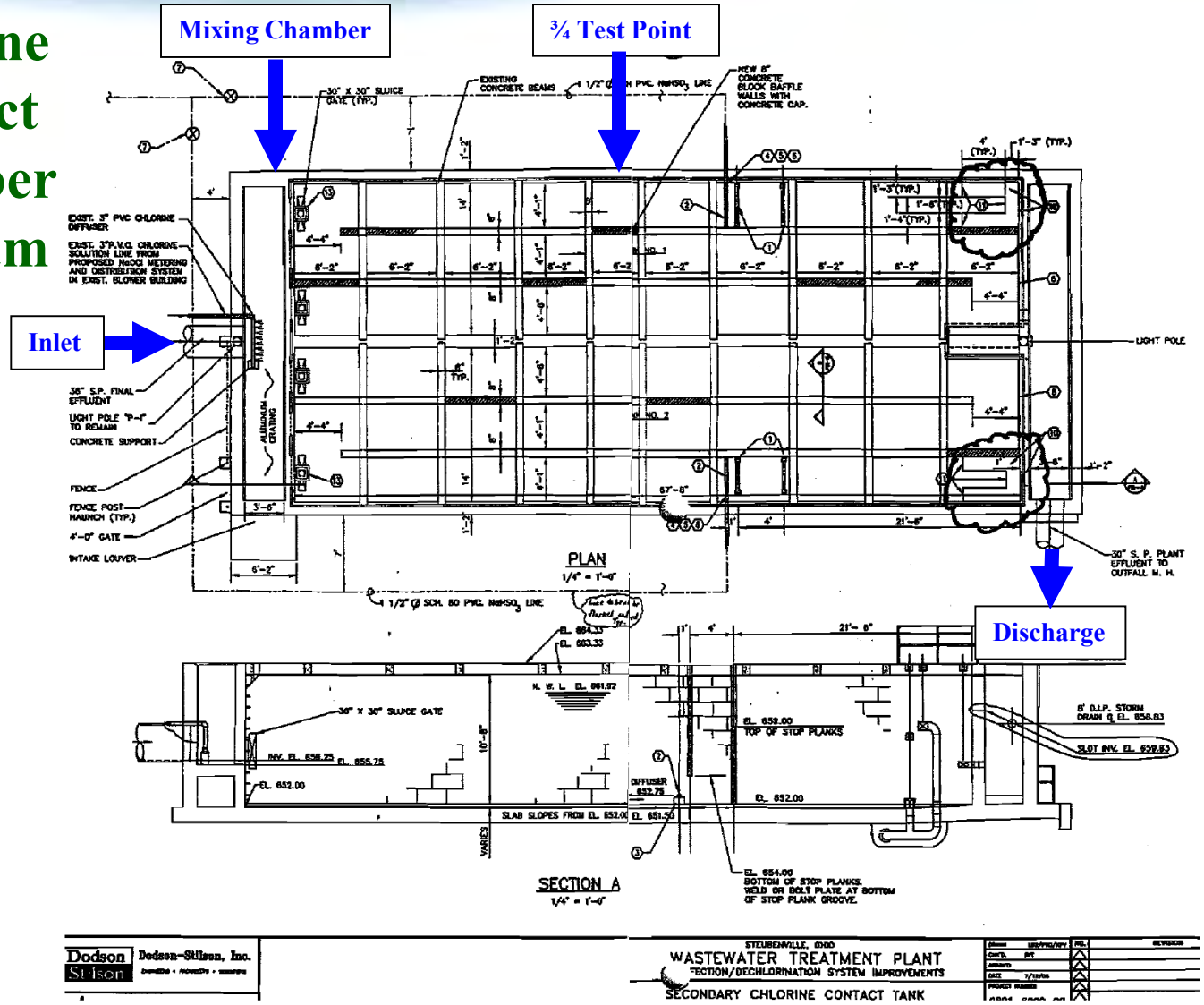
- Determine the lowest PAA levels required to meet the summer NPDES discharge fecal coliform limit of <200 CFU's/ml.
- Successfully pass the "WET" test (no acute affect on fresh water organisms) on the PAA treated discharge water with 0.4 ppm residual PAA.
- Determine that flow pacing is an adequate method of feeding Proxitane WW-12.
- Calculate cost effectiveness versus chlorine bleach and dechlorination using sodium bisulfite.

Demonstration Criteria

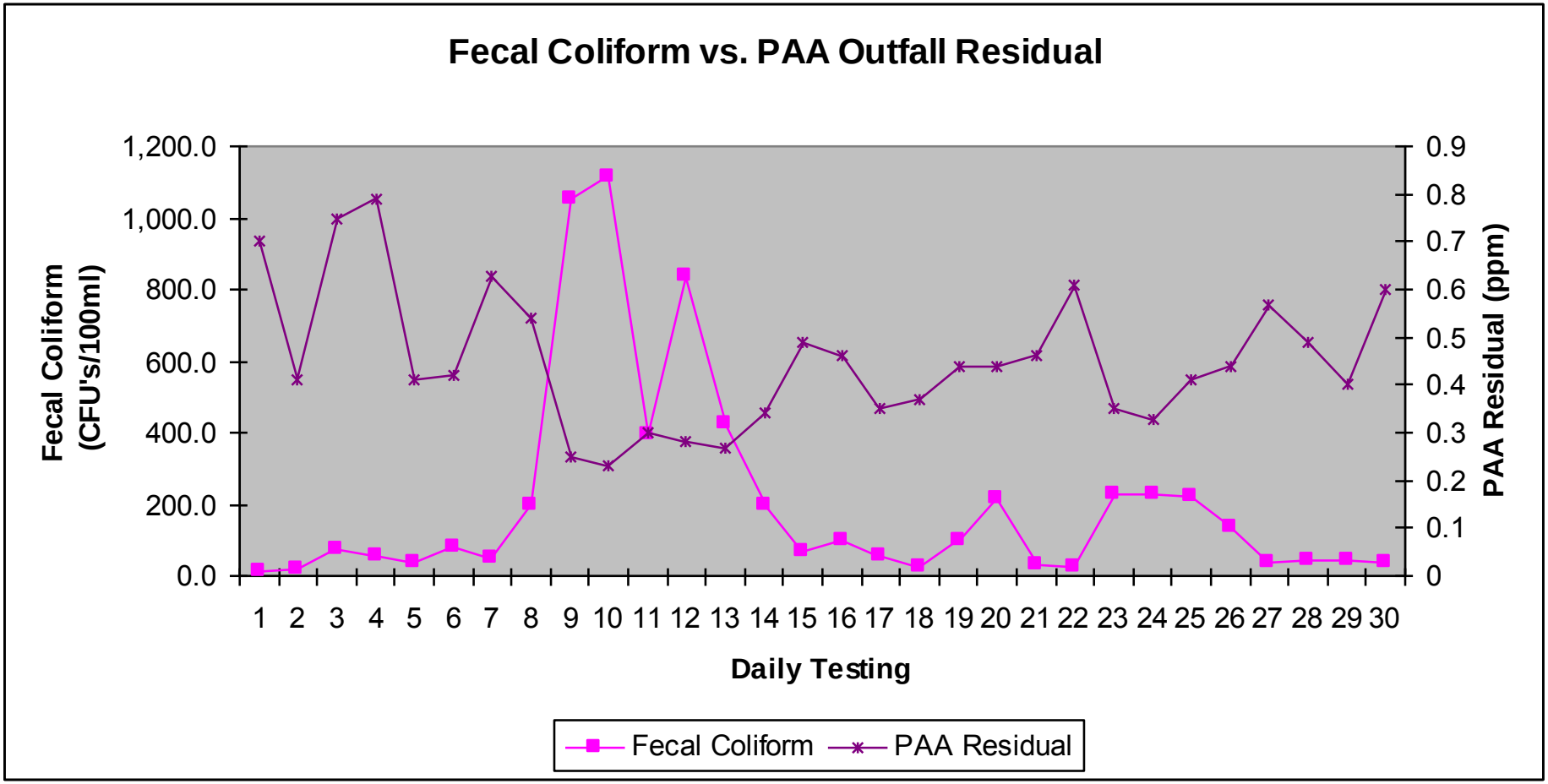
- Inject Peracetic Acid (Proxitane WW-12) neat, directly into the secondary clarifier combined discharge. At an initial feed rate of 1.5 mg/L active PAA based on total flow.
- Allow for adequate mixing in the contact chamber.
- Measure fecal coliform and PAA (indirectly through DPD Total Chlorine residual measurement). Sample mixing chamber and ¾ point PAA residuals once per day. Sample final effluent discharge every two hours and record PAA residual and total flow (see diagram on next slide).

Steubenville WW Facility Study

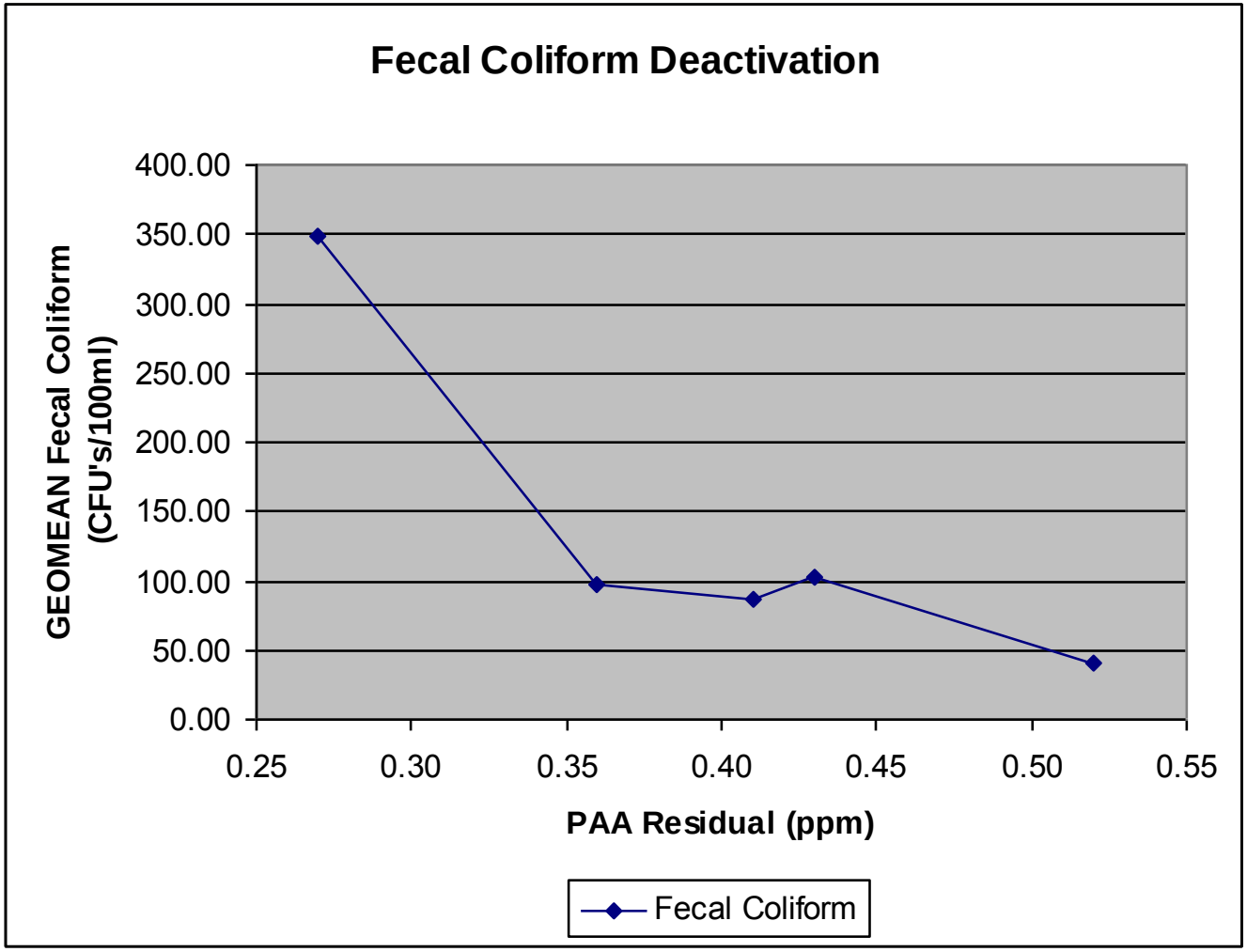
Chlorine Contact Chamber Diagram



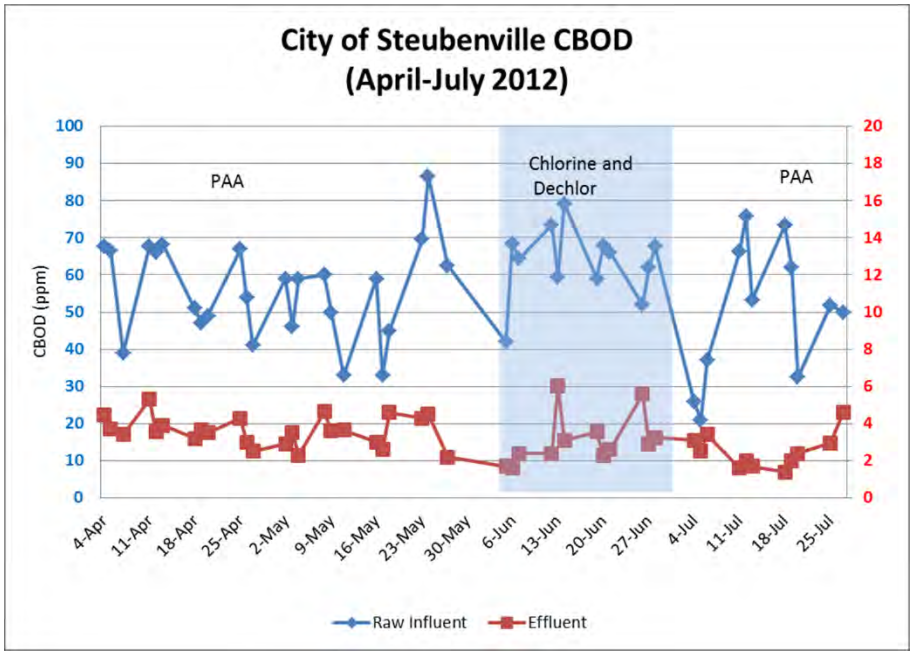
Steubenville WW Facility Study

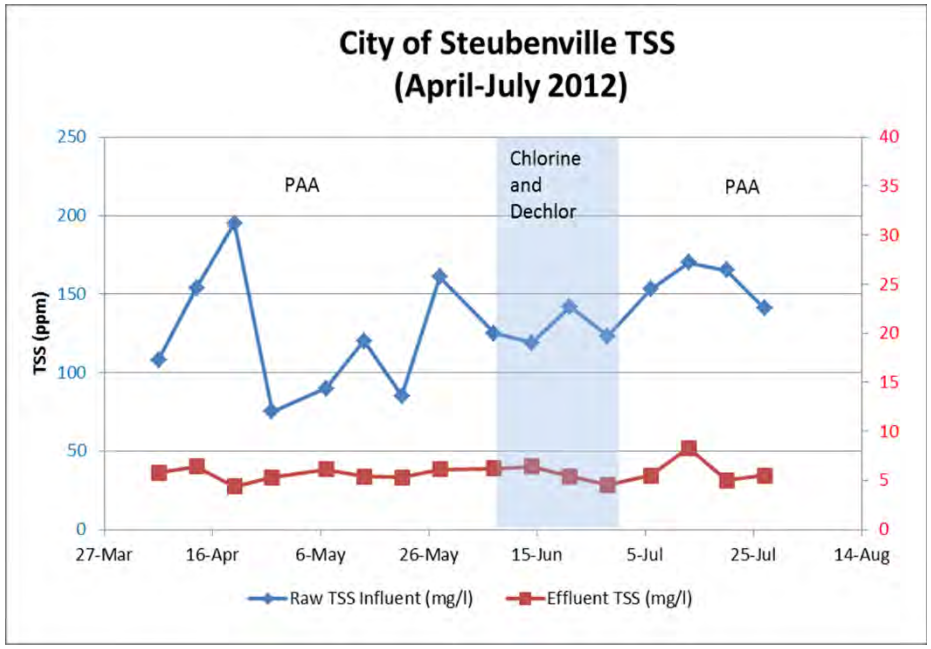


Steubenville WW Facility Study

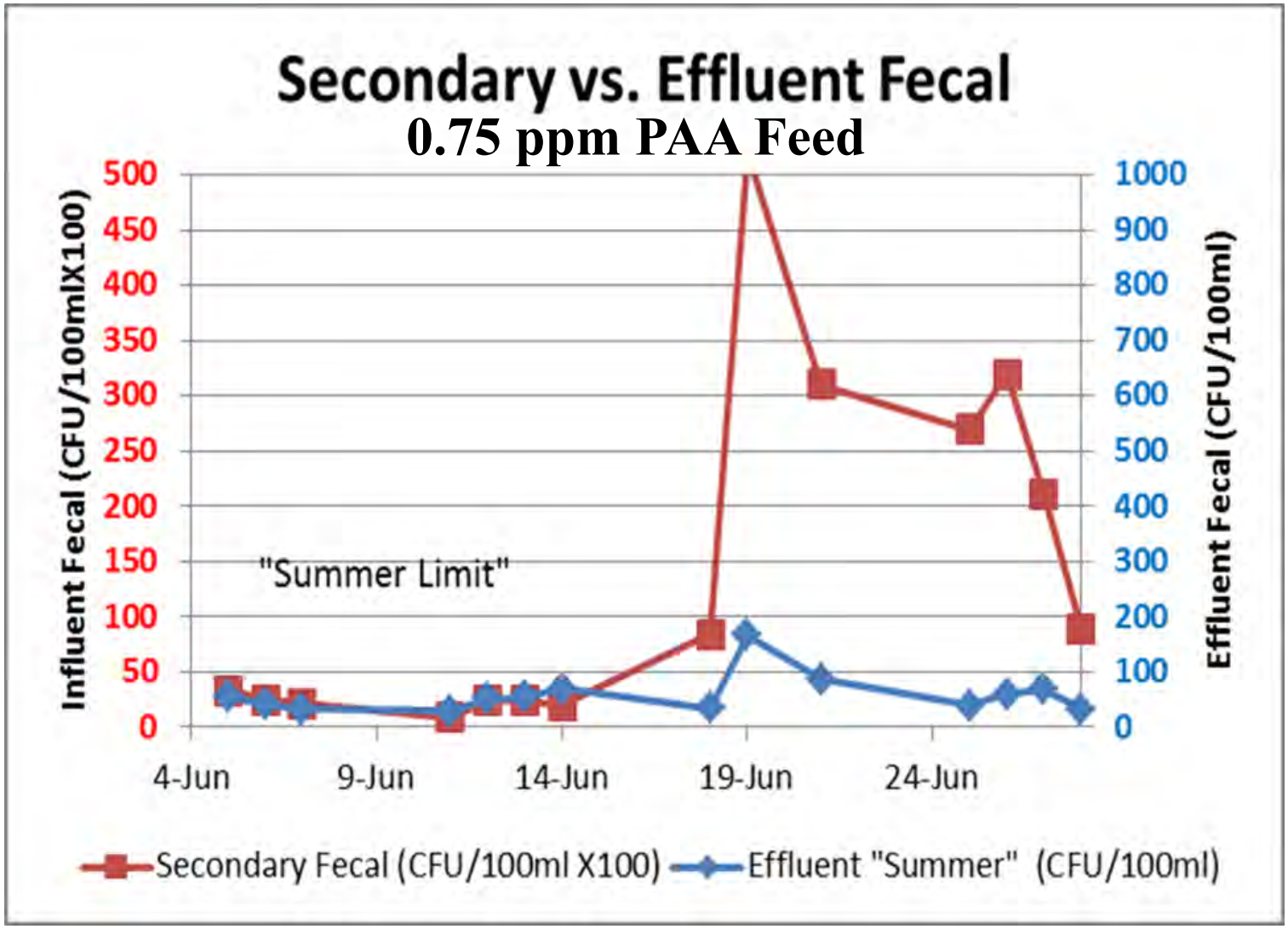


Steubenville WW Facility Study

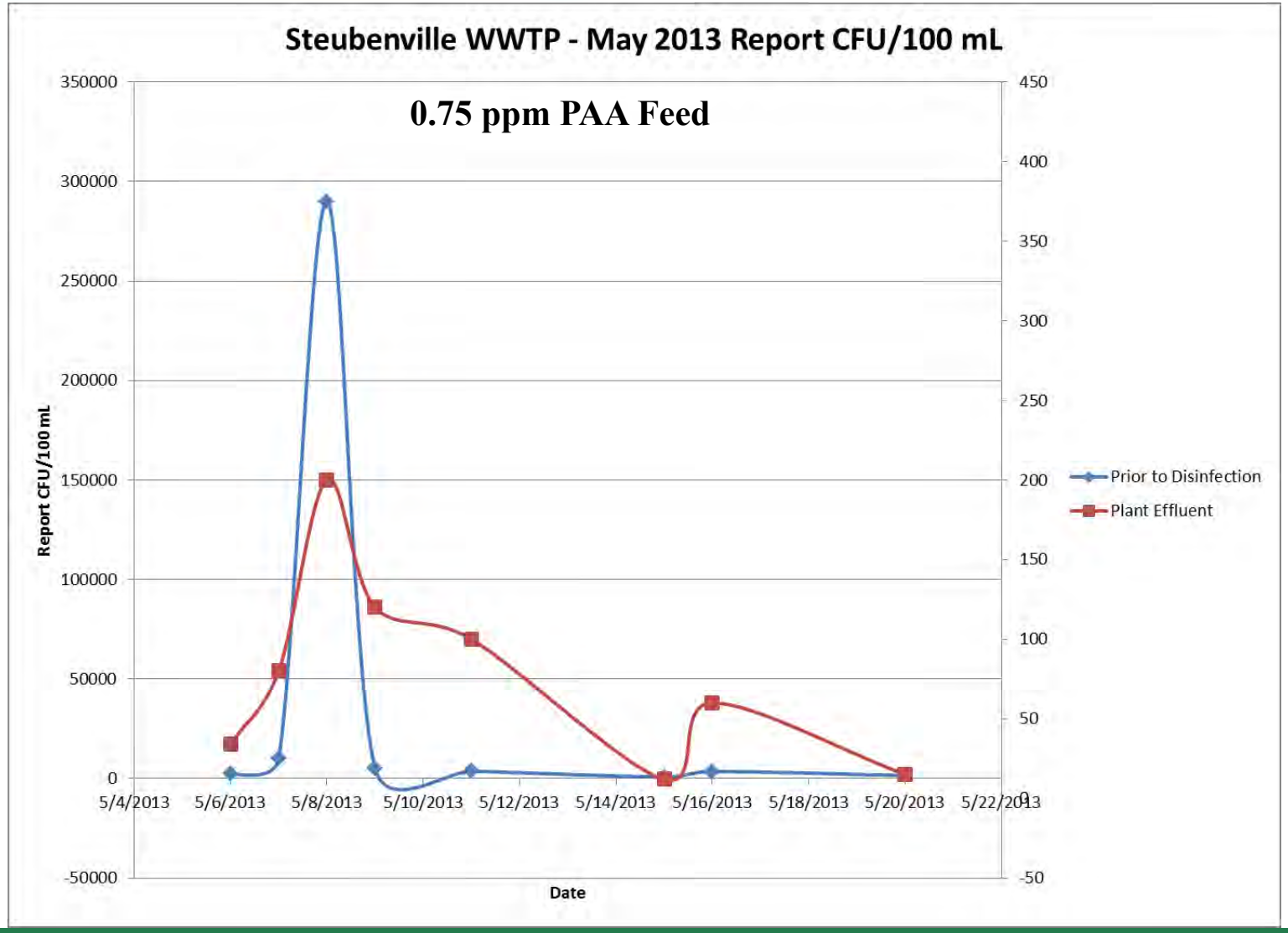




Steubenville WW Facility Study



Steubenville WW Facility Study



Results and Conclusions

- Proxitane WW-12 effectively controlled effluent fecal coliform at a 0.75 ppm PAA feed and 0.40 ppm PAA residual to meet both summer and winter NPDES permit requirements. PAA could achieve fecal coliform discharge limits even at PAA residual dosages of 0.32 ppm with improved chemical feed control.

- The "WET" test (Alloway Laboratories) at a 0.40 ppm PAA residual passed with no effect on selected organism survivability in the discharge stream. However, the Ohio EPA is establishing a PAA residual requirement of <0.1 ppm.

- Flow pacing is the desired method of Proxitane WW-12 feed and control.

Results and Conclusions

- Proxitane WW-12 reduced the operating costs for disinfection by 27% at the Steubenville WW Facility when compared to chlorine (bleach) and dechlorination (sodium bisulfite). However, with a PAA residual requirement of <0.1 ppm in Ohio these cost savings may no longer apply.

- Proxitane WW-12 was extremely effective in handling upsets in secondary discharge fecal levels up to 290,000 CFUs/100ml without any change in the low PAA dosage of 0.75 ppm.

- Proxitane WW-12 was effective in treating wet weather flow with bypass flows up to and exceeding 22.66 MGD without deactivation.

Case Study 2

Comparison of Sodium Hypochlorite and Peracetic Acid in Disinfection of Muddy Creek Combined Sewer Overflow in Cincinnati, OH (Ongoing)

- EPA
  - NRMRL (Vasu Namboodiri, Craig Patterson)
  - NHSRC (Jeff Szabo)
  - CB&I (EPA Contractors, Don Schupp)
- Solvay Chemicals (John Maziuk)
  - Peragreen & Engineers Plus (Bob Freeborn)
- City of Cincinnati (MSDGC, Bruce Smith)
  - Wade Trim (MSDGC Contractor)
  - Muddy Creek Facility (field study)

Solvay CRADA Objectives

To evaluate the effectiveness of sodium hypochlorite and PAA in CSO wastewater using the following criteria:

- Effectiveness of the disinfectants in the inactivation of *E. coli*.
- Storage, shelf life, and application of the disinfectants.
- Formation of harmful byproducts by the disinfectants.
- Operation and maintenance costs, including the cost of the disinfectant, its storage, application, and neutralizing agent for the disinfectant to maintain the Ohio EPA guideline for residual disinfectant at the discharge point.

Background

Comparison of PAA and NaOCl

	PAA	NaOCl
Efficacy	High	High
Efficacy > pH8	High	Low
Oxidation Capacity	1.81 eV	1.36 eV
Oxidizes H_2S	Yes	Yes
Degraded by UV	No	Yes, T1/2 45 mins
Contributes Na^+	No	1.8 lb NaCl/gallon
Aquatic toxicity	Very Low	High
Field test kit	Yes	Yes

Muddy Creek Facility Study

The Muddy Creek CSO treatment facility was constructed to provide disinfection using sodium hypochlorite for two CSOs from the Westwood Trunk sewer.

Baseline Study

A 2 hour baseline study was performed to determine the current operating conditions. Samples were collected every 15 minutes for the duration of the wet-weather event:

- Tank 1 Access (beginning) – TSS and VSS
- Tank 1 Access (end) – TSS, VSS, free and total chlorine, pH, temperature, *E. coli*, *Enterococci*, and fecal coliform
- Tank 2 Access (beginning) – Free and total chlorine, pH, temperature, *E. coli*, *Enterococci*, and fecal coliform
- Tank 2 Access (end) – Free and total chlorine, pH, temperature, *E. coli*, *Enterococci*, and fecal coliform
- Treated Effluent – *E. coli*, *Enterococci*, and fecal coliform

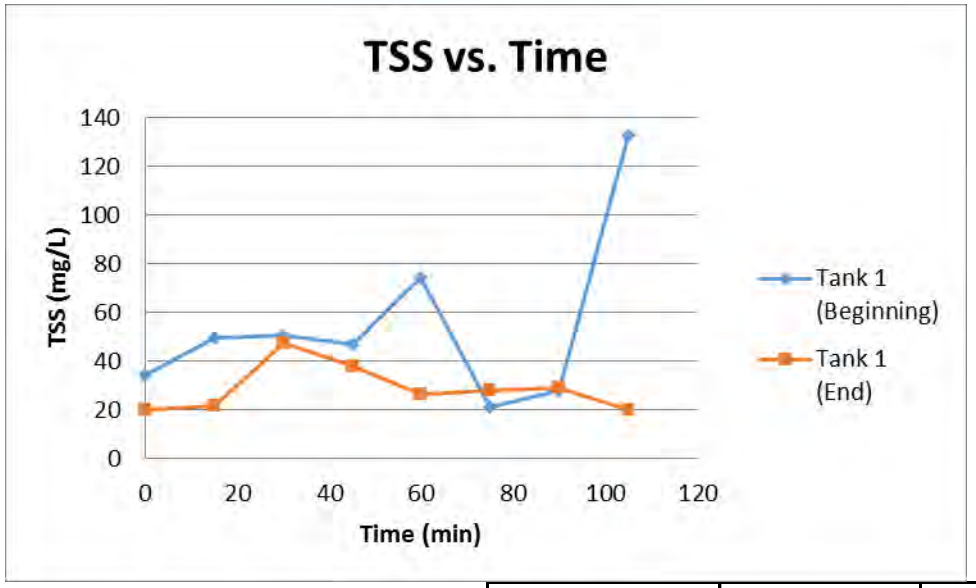
Muddy Creek Facility Study

Baseline Study Sampling Locations

Baseline Study (Sodium Hypochlorite Addition)

Chlorine is added between Tanks 1 and 2. Tank 1 is designed to settle out solids while Tank 2 is for chlorine treatment.

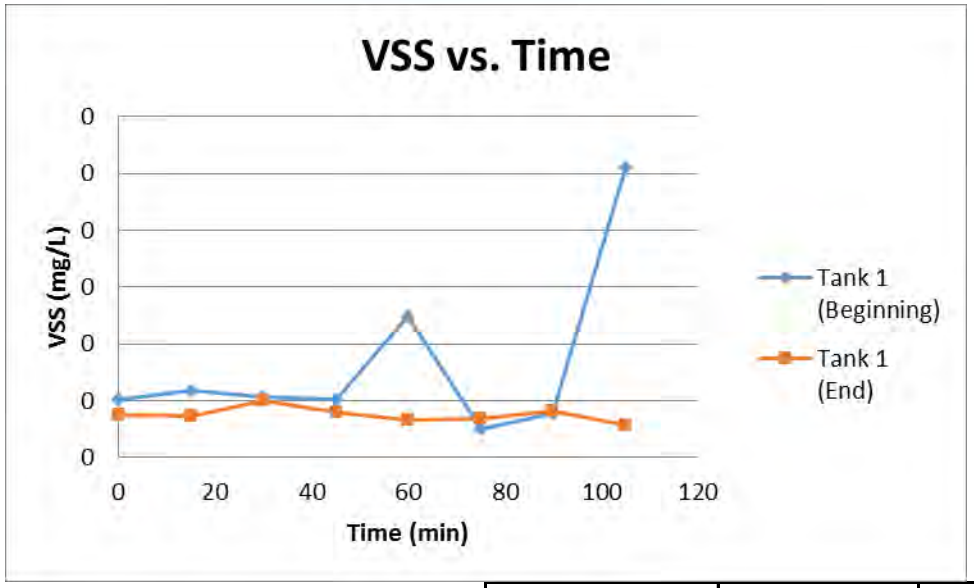
TSS Results



Baseline Study Results

		TSS, mg/L				
Sample Time	Time (min)	Tank 1 (Beginning)	Tank 1 (End)	Tank 2 (Beginning)	Tank 2 (End)	Final Effluent
8:15	0	34.14	20.00	NA	NA	NA
8:30	15	49.43	21.83	NA	NA	NA
8:45	30	50.81	47.41	NA	NA	NA
9:00	45	46.64	38.20	NA	NA	NA
9:15	60	74.18	26.42	NA	NA	NA
9:30	75	20.85	28.17	NA	NA	NA
9:45	90	28.17	29.07	NA	NA	NA
10:00	105	132.69	19.83	NA	NA	NA

VSS Results

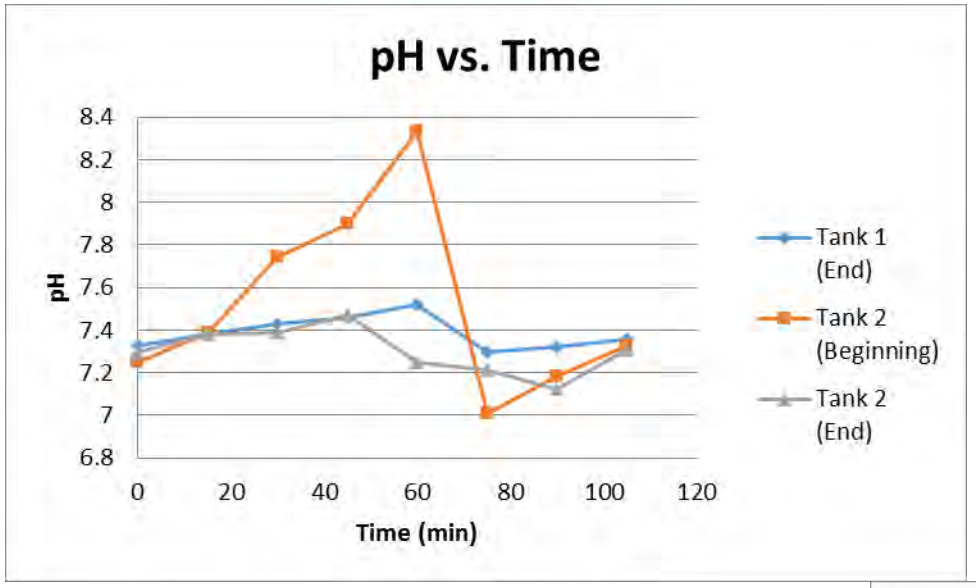


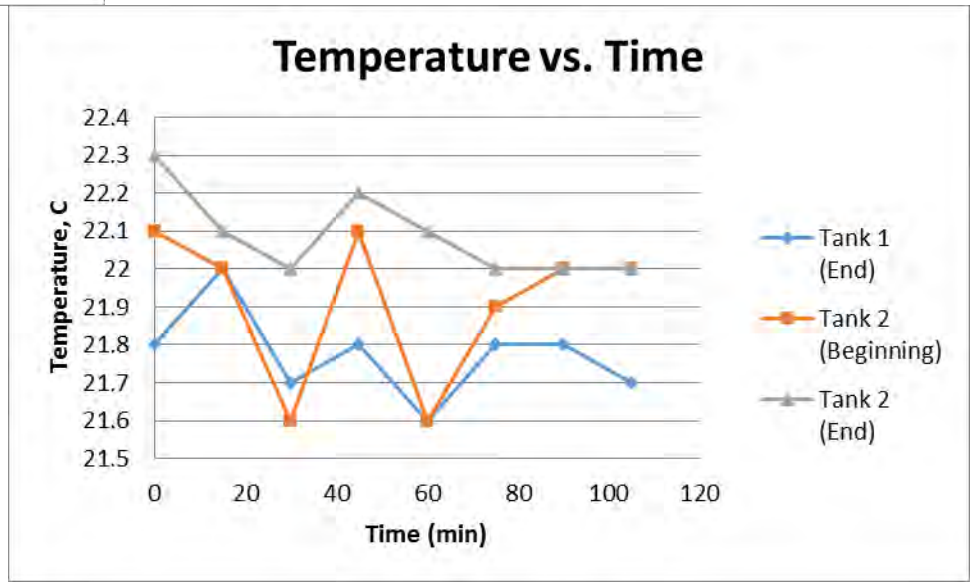
Baseline Study Results

		VSS, mg/L				
Sample Time	Time (min)	Tank 1 (Beginning)	Tank 1 (End)	Tank 2 (Beginning)	Tank 2 (End)	Final Effluent
8:15	0	0.0205	0.0152	NA	NA	NA
8:30	15	0.0236	0.0147	NA	NA	NA
8:45	30	0.0214	0.0200	NA	NA	NA
9:00	45	0.0205	0.0161	NA	NA	NA
9:15	60	0.0500	0.0134	NA	NA	NA
9:30	75	0.0102	0.0139	NA	NA	NA
9:45	90	0.0155	0.0163	NA	NA	NA
10:00	105	0.1023	0.0116	NA	NA	NA

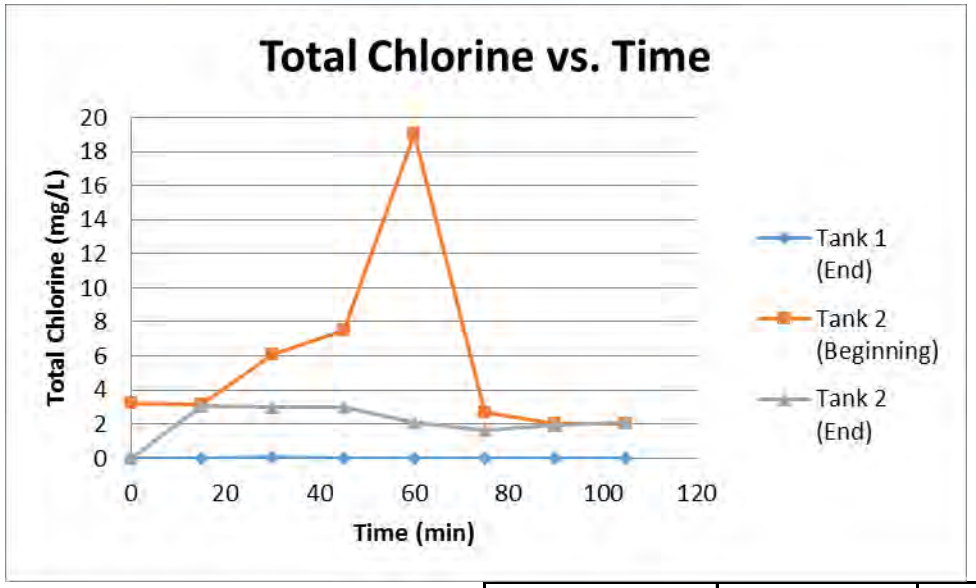
pH and Temperature Results

Baseline Study Results





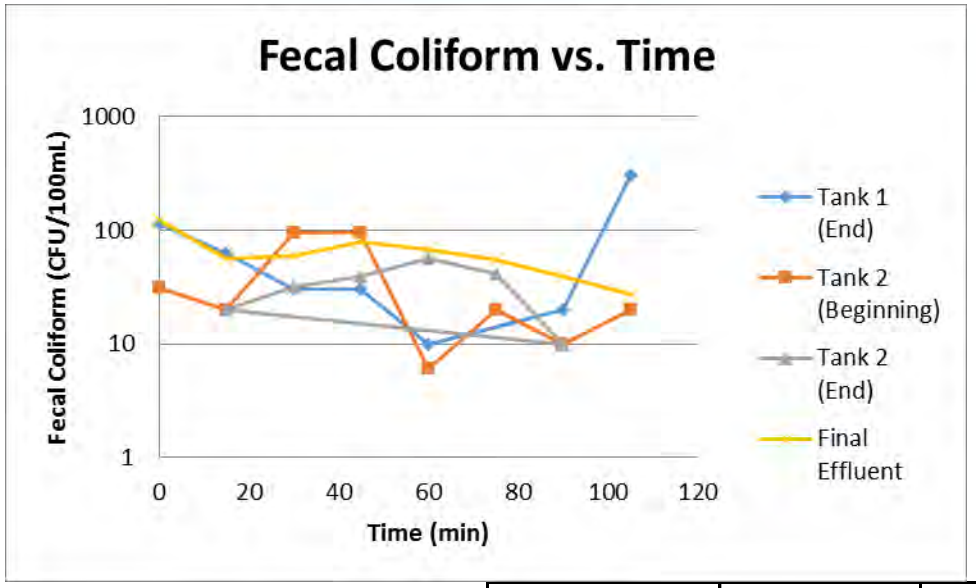
Total Chlorine Results



Baseline Study Results

		Total Chlorine, mg/L				
Sample Time	Time (min)	Tank 1 (Beginning)	Tank 1 (End)	Tank 2 (Beginning)	Tank 2 (End)	Final Effluent
8:15	0	NA	0	3.26	0.01	NA
8:30	15	NA	0	3.16	3.08	NA
8:45	30	NA	0.09	6.1	2.98	NA
9:00	45	NA	0	7.5	3	NA
9:15	60	NA	0	19	2.08	NA
9:30	75	NA	0	2.7	1.66	NA
9:45	90	NA	0	2	1.97	NA
10:00	105	NA	0	2.01	2.06	NA

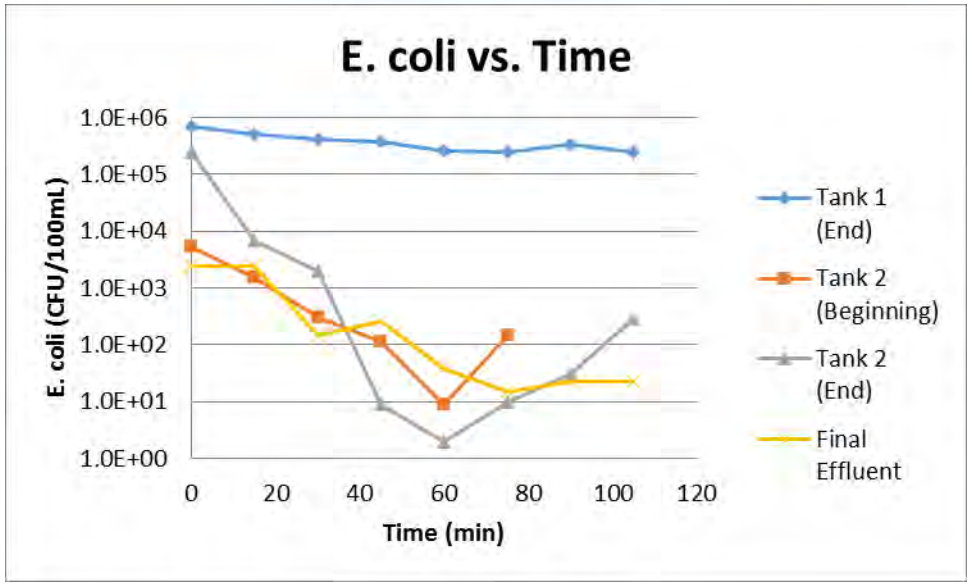
Fecal Coliform Results



Baseline Study Results

		Fecal Coliform, CFU/100 mL				
Sample Time	Time (min)	Tank 1 (Beginning)	Tank 1 (End)	Tank 2 (Beginning)	Tank 2 (End)	Final Effluent
8:15	0	NA	113	31	0*	122
8:30	15	NA	62	20	20	57
8:45	30	NA	30	96	32	60
9:00	45	NA	30	96	39	80
9:15	60	NA	10	6	57	68
9:30	75	NA	0*	20	41	55
9:45	90	NA	20	10	10	39
10:00	105	NA	307	20	0*	27

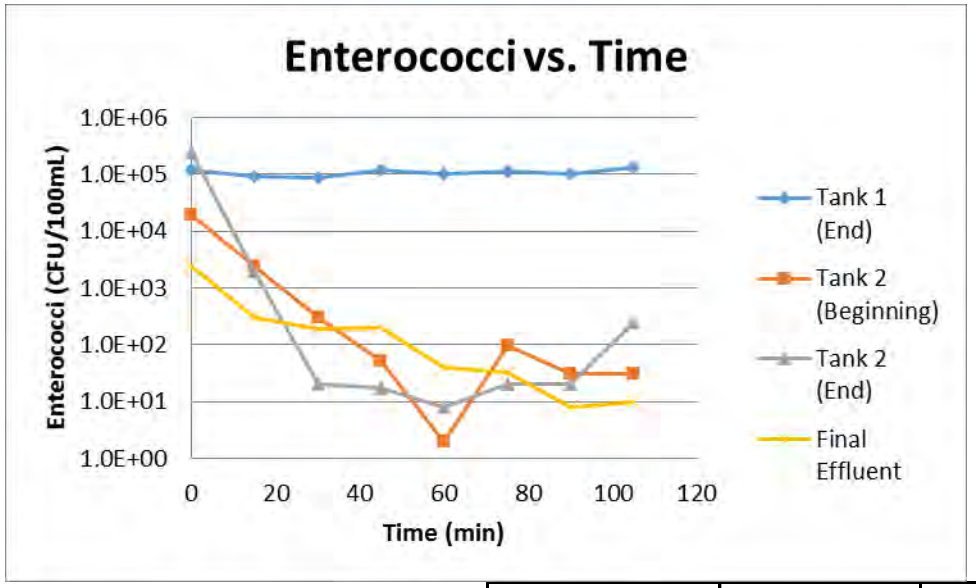
E. coli Results



Baseline Study Results

		E. coli, CFU/100 mL				
Sample Time	Time (min)	Tank 1 (Beginning)	Tank 1 (End)	Tank 2 (Beginning)	Tank 2 (End)	Final Effluent
8:15	0	NA	6.9E+05	5.2E+03	>2.4E+05	>2.4E+03
8:30	15	NA	5.2E+05	1.5E+03	6.9E+03	>2.4E+03
8:45	30	NA	4.1E+05	295	2.0E+03	147
9:00	45	NA	3.7E+05	110	9	261
9:15	60	NA	2.6E+05	9	2	38
9:30	75	NA	2.4E+05	145	10	15
9:45	90	NA	3.3E+05	0*	31	22
10:00	105	NA	2.4E+05	0*	279	22

Enterococci Results



Baseline Study Results

		Enterococci, CFU/100 mL				
Sample Time	Time (min)	Tank 1 (Beginning)	Tank 1 (End)	Tank 2 (Beginning)	Tank 2 (End)	Final Effluent
8:15	0	NA	1.2E+05	1.9E+04	>2.4E+05	>2.4E+03
8:30	15	NA	9.3E+04	2.4E+03	2.0E+03	299
8:45	30	NA	8.8E+04	309	20	188
9:00	45	NA	1.2E+05	52	17	199
9:15	60	NA	9.9E+04	2	8	39
9:30	75	NA	1.1E+05	97	20	32
9:45	90	NA	9.9E+04	30	20	8
10:00	105	NA	1.3E+05	31	241	10

Field Study Parameters

The following field study parameters will be measured or analyzed:

- Sodium Hypochlorite Level (height or volume) in the Storage Tank
- PAA Level (height or volume) in the container
- PAA and Chlorine concentration (chlorine is a measure of sodium hypochlorite concentration)
- *E. coli*, *Enterococci*, and fecal coliform
- Temperature
- pH
- TSS and VSS
- Total Dissolved Solids (TDS) (effluent only)
- Trihalomethanes (THMs) and Haloacetic Acids (HAAs) disinfection byproducts (effluent only)
- Chemical Oxygen Demand (COD) (effluent only)

Measurement	Units
Free and total chlorine	mg/L
PAA	mg/L
E. coli	CFU/100 mL
Enterococci	CFU/100 mL
Fecal coliform	CFU/100 mL
TSS	mg/L
VSS	mg/L
TDS	mg/L
pH	S.U.
Temperature	ºC
THM	µg/L
HAA	µg/L
COD	mg/L

Field Study Sampling Plan

Influent samples will be collected just upstream of the application of PAA and sodium hypochlorite, and the effluent samples will be collected from the pit used for bi-sulfite sampling based on the following schedule:

Sample	Time after rainfall begins
1	15 minutes
2	30 minutes
3	45 minutes
4	1 hour
5	1.5 hours
6	2 hours
7	3 hours
8	4 hours

Conclusions

- The Muddy Creek Facility Baseline Study was completed this year during wet weather flow events (September 2, 2014).
- The Muddy Creek PAA Comparison Study will be completed next year during wet weather flow events (May 1-September 30, 2015).
- Results will be useful in WW treatment decision making.
- Many wastewater treatment facilities are conducting PAA pilot and field studies:
  - Storage, handling and security issues, to reduce toxic DBPs, TDS & sodium pollution (chlorination & dechlorination).
  - Hydraulic fracturing businesses are using PAA in the field.
- Other applications of PAA (prevent biofilm growth, membrane cleaning, decontamination studies & chlorine resistant pathogens).

Questions?

Craig Patterson
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