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Collaborative Efforts to Implement On-Line Analyzer Technology for Regulatory Total Residual Chlorine Monitoring

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Topics

- Proposal
- Initial Data Review
- Improvements
- Recent Data
- Path Forward

Proposal

- Allow the WWTP to submit 2-hour TRC measurements collected by instrumentation in lieu of lab analysis. Reduce operator burden to parallel instrument verification (1x/day) for QC.

- Values contributing to the Discharge Monitoring Report submission would represent the minimum TRC measured by the Cl-17 during each 2-hour time period.

Comparison of Methods

- Lab analysis: operator collects grabs sample, zeros Hach Pocket Colorimeter using blank sample, then adds powdered DPD reagent and measures TRC

- Cl-17 analysis: instrument pumps sample into test chamber, zeros using blank sample, then adds liquid DPD reagent and measures TRC

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Current Nansemond TP Permit

B. ADDITIONAL TOTAL RESIDUAL CHLORINE (TRC) LIMITATIONS AND MONITORING REQUIREMENTS

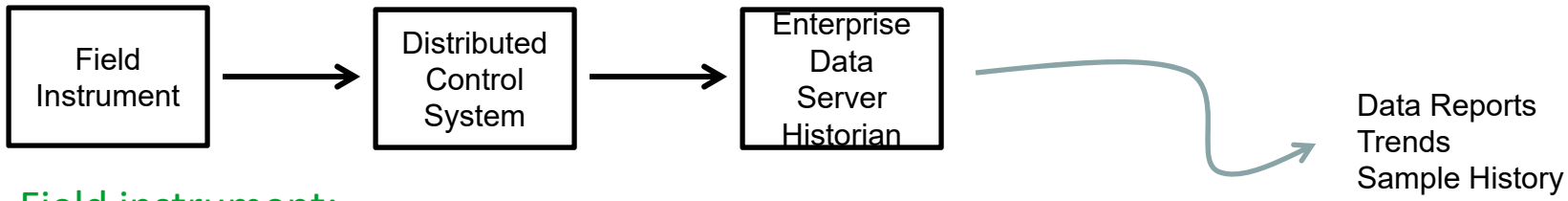
1. a. The permittee shall monitor the TRC at the outlet of the chlorine contact tank, prior to dechlorination, every two hours by grab sample.

b. No more than 36 of all samples taken after the chlorine contact tank, prior to dechlorination, shall be less than 1.5 mg/l for any one calendar month.

c. The facility shall operate the chlorination facilities in a manner, which will ensure continuous disinfection. The permittee shall notify the DEQ in the event TRC sample collected prior to dechlorination is less than 0.5 mg/l for 3 or more consecutive readings or the TRC sample collected is less than 0.1 mg/l. Reporting will be conducted in accordance with Part II.H. of the permit.

d. The limit in B.1.b.can be lowered to 0.5 mg/l based on a chlorine reduction study outlined in the permit special condition C.13.

CL17 Analyzer TRC Record Keeping and Data Retrieval



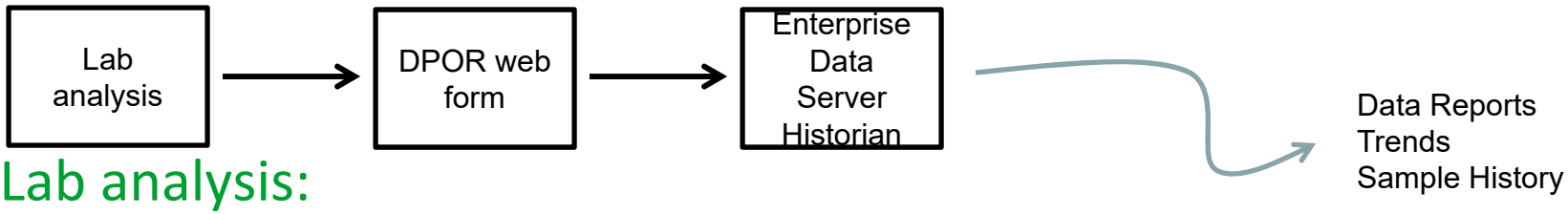
- Field instrument:
- draws from operator sample line with continuous flow
- 2.5 minute sample cycle

- Distributed Control System (DCS):
- scans for data every second
- "event" set at change of 0.001 mg/L

- Enterprise Data Server (EDS) Historian:
- compresses like data into time blocks
- interpolates data between saved values

Cl-17 data was retrieved every minute on the minute (HH:MM:00) for analysis, beginning 04/2016.

Lab TRC Recording Keeping & Data Retrieval

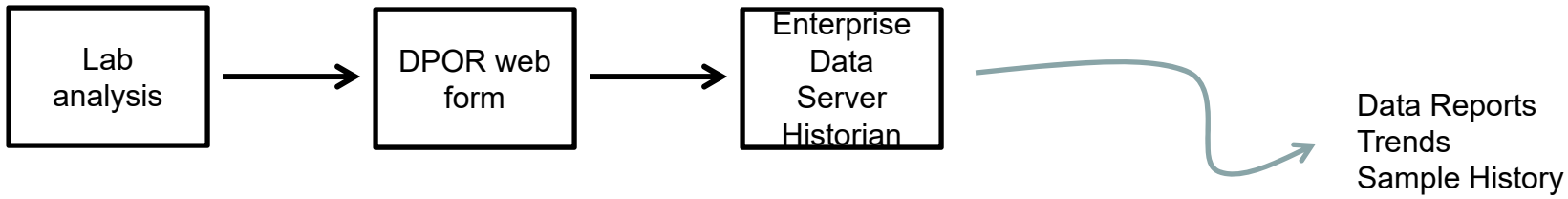


- Lab analysis:
  - grab sample every 2 hours from operator sample line
  - sample time recorded to the minute (HH:MM)

- Daily Plant Operation Report (DPOR), web form:
  - TRC value and sample time recorded as separate fields
  - Reference time of form is top of the hour (HH:00:00)

- Enterprise Data Server (EDS) Historian:
  - Saves form data twice, once with timestamp of form, second with timestamp of data submission

Lab TRC Recording Keeping & Data Retrieval



Colorimeter TRC values and sample times were retrieved from the EDS for analysis, beginning 04/2016. Corresponding DPOR forms provided a sample time in some instances where data could not be retrieved from the database - 00:00 placeholder was not replaced with a specific sampling time (no data saved) or invalid time format (no data saved).

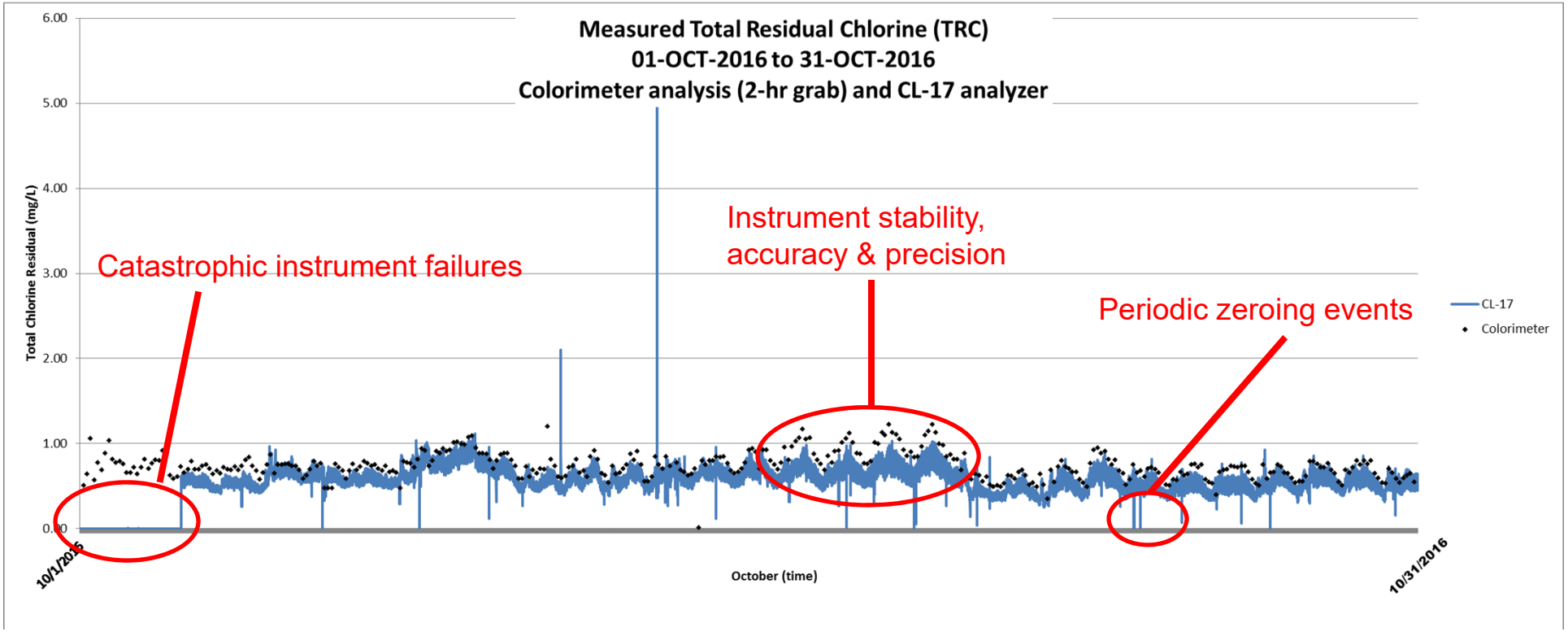
Initial Data Review

Cl-17 analyzer values were compared to colorimeter values from operator analysis over the period of 04/2016-02/2017 with the expectation that paired samples would agree (15% tolerance) and monthly exceptions would remain within the permitted allowance.

- Results indicated that operational and maintenance adjustments were required before the analyzer data would be acceptable.

  Example - October 2016

  TRC values from CL-17 analyzer (line) were plotted alongside lab analyses (points):



Initial Data Review

Cl-17 and colorimeter TRC values were paired at the grab sample time and tested for statistical relevance.

- Note: the analyzer was assumed to be offline when output dropped below 0.05 mg/L, offline data sets excluded from comparison

CL-17 values were consistently lower than lab values.

t-Test: Paired Two Sample for Means		
October 2016		
	Colorimeter	*CL-17*
Mean	0.734548	0.586661
Variance	0.024831	0.018909
Observations	343	343
Pearson Correlation	0.715882	
t Stat	**24.28908**	
P(T<=t) two-tail	1.93E-76	
t Critical two-tail	**1.966925**	

Time Block	Comparison Time	Operator	CL-17		% Difference
10/3/2016 10:00	10/3/2016 9:59	0.65	0.48	-0.17	26%
10/3/2016 12:00	10/3/2016 12:01	0.69	0.64	-0.05	8%
10/3/2016 14:00	10/3/2016 14:03	0.78	0.60	-0.18	23%
10/3/2016 16:00	10/3/2016 16:00	0.69	0.52	-0.17	25%
10/3/2016 18:00	10/3/2016 18:03	0.69	0.54	-0.15	22%
10/3/2016 20:00	10/3/2016 20:02	0.73	0.66	-0.07	10%
10/3/2016 22:00	10/3/2016 22:00	0.74	0.57	-0.17	23%
10/4/2016 0:00	10/4/2016 0:05	0.7	0.45	-0.25	35%
10/4/2016 2:00	10/4/2016 2:00	0.63	0.47	-0.16	25%
10/4/2016 4:00	10/4/2016 3:59	0.67	0.45	-0.22	34%
10/4/2016 6:00	10/4/2016 6:02	0.64	0.46	-0.18	28%
10/4/2016 8:00	10/4/2016 8:00	0.71	0.58	-0.13	18%
10/4/2016 10:00	10/4/2016 9:59	0.69	0.56	-0.13	19%
10/4/2016 12:00	10/4/2016 12:00	0.68	0.59	-0.09	13%
10/4/2016 14:00	10/4/2016 14:01	0.72	0.48	-0.24	33%
10/4/2016 16:00	10/4/2016 16:00	0.68	0.56	-0.12	17%
10/4/2016 18:00	10/4/2016 18:03	0.73	0.26	-0.47	65%
10/4/2016 20:00	10/4/2016 20:02	0.8	0.51	-0.29	36%
10/4/2016 22:00	10/4/2016 22:00	0.83	0.60	-0.23	28%
10/5/2016 0:00	10/5/2016 0:00	0.73	0.46	-0.27	37%
10/5/2016 2:00	10/5/2016 2:01	0.67	0.44	-0.23	35%
10/5/2016 4:00	10/5/2016 4:00	0.57	0.43	-0.14	25%
10/5/2016 6:00	10/5/2016 5:57	0.65	0.49	-0.16	24%
10/5/2016 8:00	10/5/2016 8:01	0.74	0.50	-0.24	33%
10/5/2016 10:00	10/5/2016 10:01	0.86	0.82	-0.04	5%
10/5/2016 12:00	10/5/2016 12:02	0.64	0.60	-0.04	6%
10/5/2016 14:00	10/5/2016 14:01	0.74	0.76	0.02	-3%
10/5/2016 16:00	10/5/2016 16:04	0.74	0.64	-0.10	14%

- Combined effect produced exceptions well beyond the permitted allowance for Nansemond TP (36/month) …

	Exceptions	No Record	Total
Colorimeter	9	1	10
Cl-17 (2-hr Min)	222	36	258
Cl-17 (2-hr Avg)	66	36	102

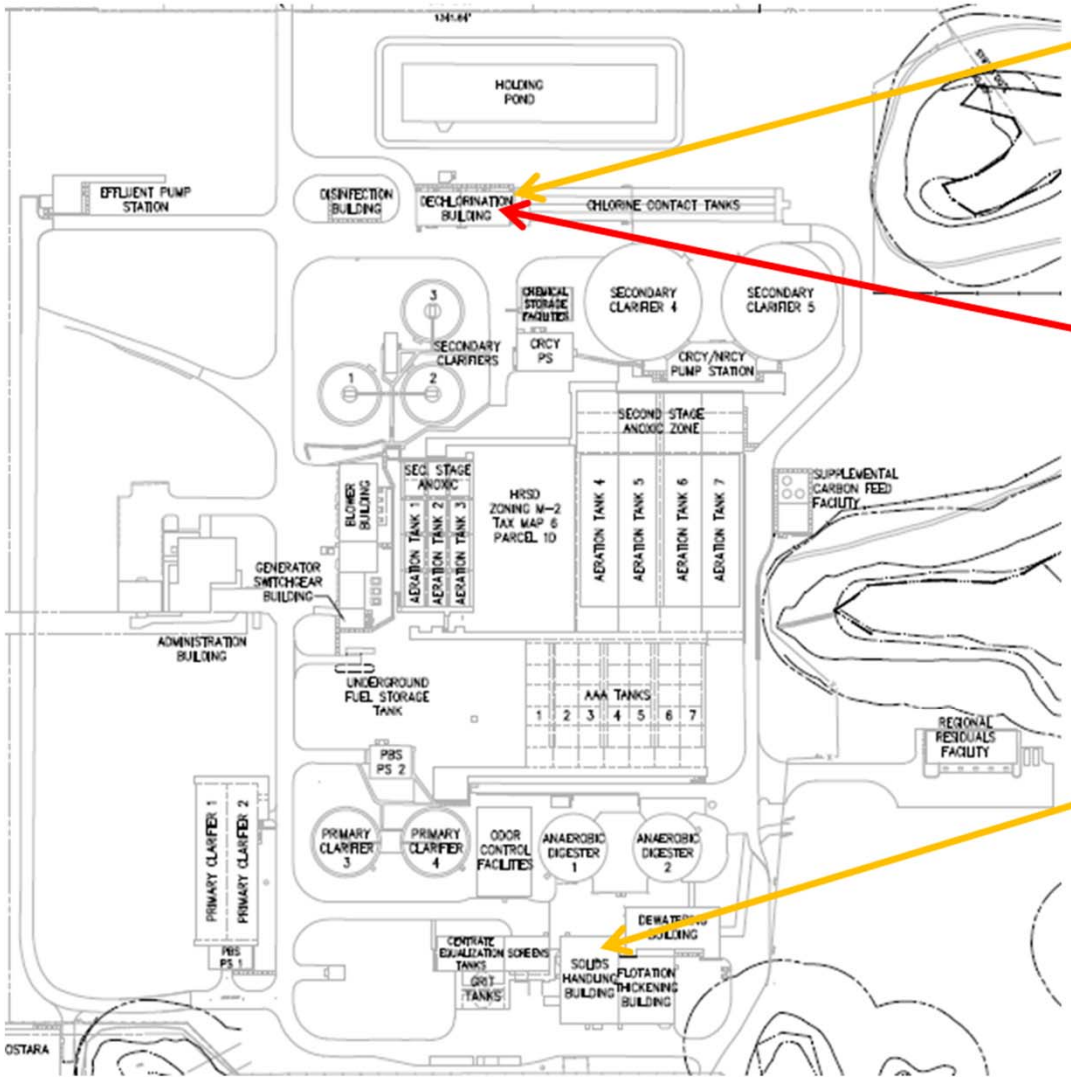
…prompting a review of equipment condition, maintenance standards, sampling procedures and record-keeping practices.

Initial Data Review

Potential contributing factors were investigated/mitigated:

- Up to 3 minutes difference between grab sample and analyzer value with same time stamp (Cl-17 cycle + recording uncertainty)
- Lack of calibration/maintenance records
- Failure to hold output during maintenance activity
- Previous analyzer
- Air in Cl-17 test chamber
- False blank/failure to flush spent sample from test chamber
- Plant flow/turbidity/chemistry (investigated - no correlation to zeroing events)

Establish Satellite Laboratory for Rapid TRC Analysis

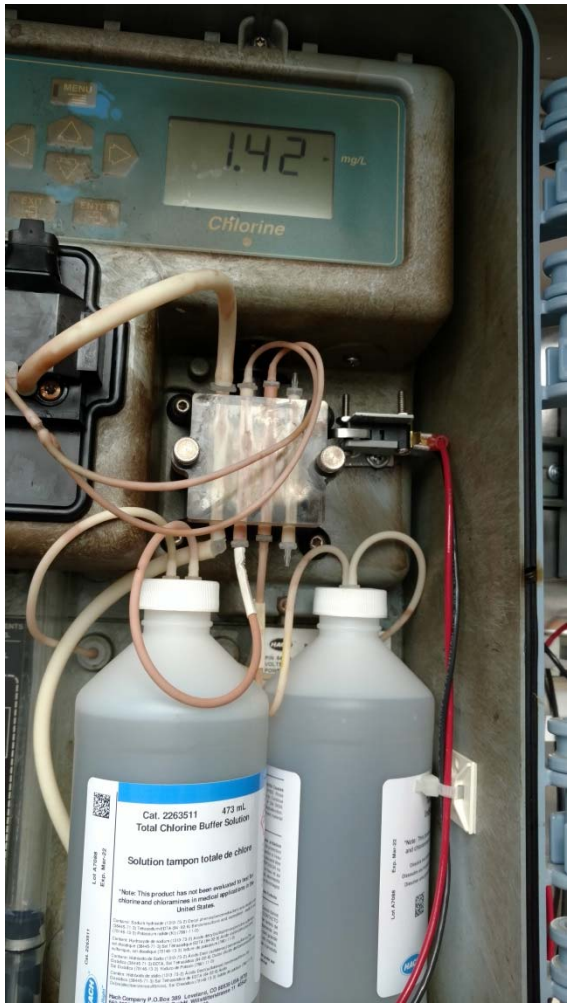


Sample Location at end of Contact Tanks

New Satellite Lab in Dechlorination Building

Plant Lab (2nd floor)

Improvements – Cabinet Overview



Improvements – Operator Sampling

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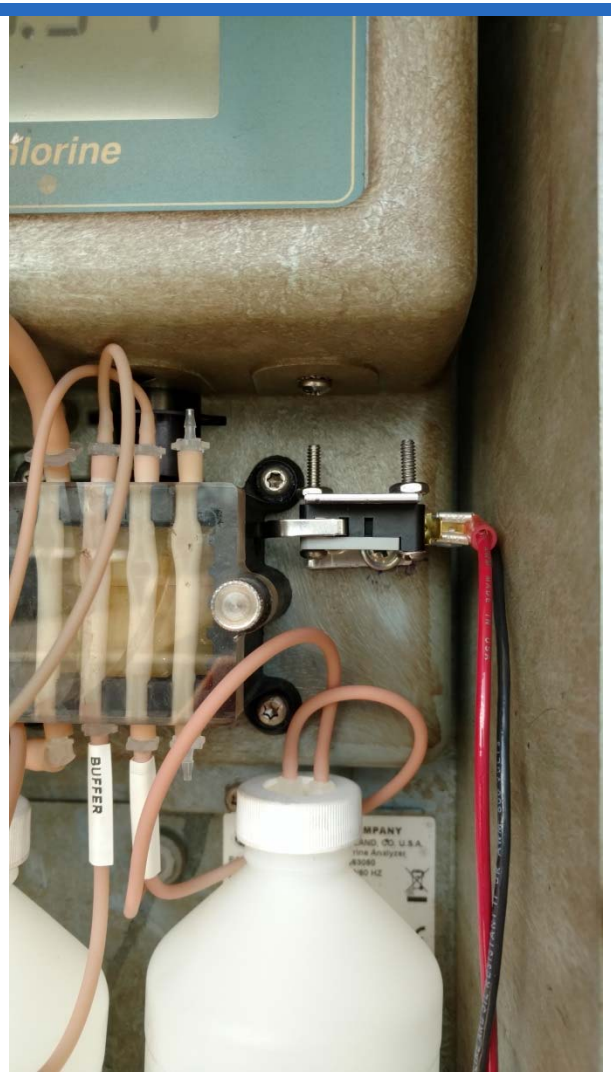
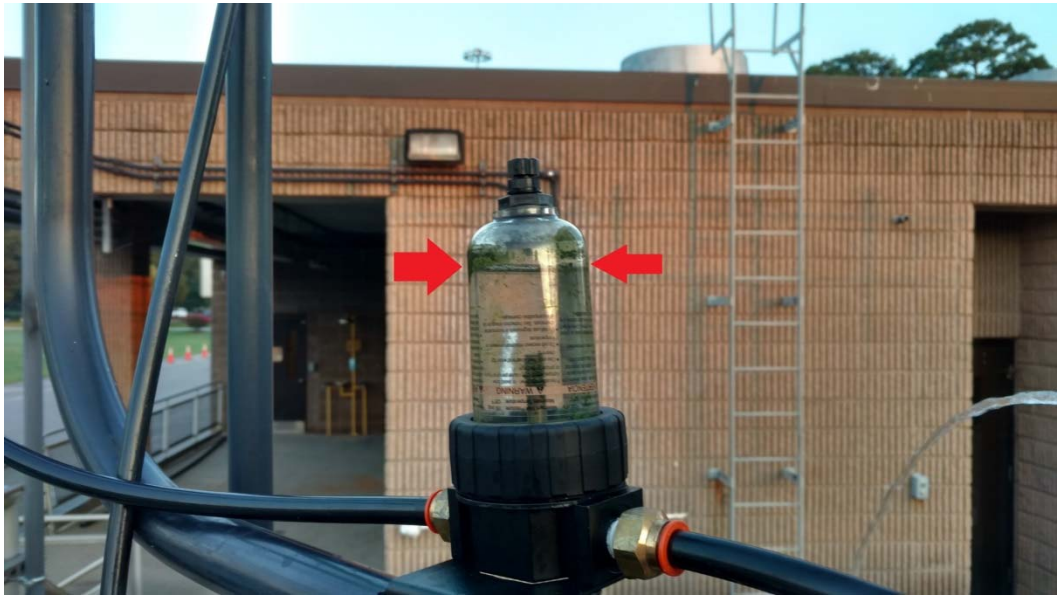
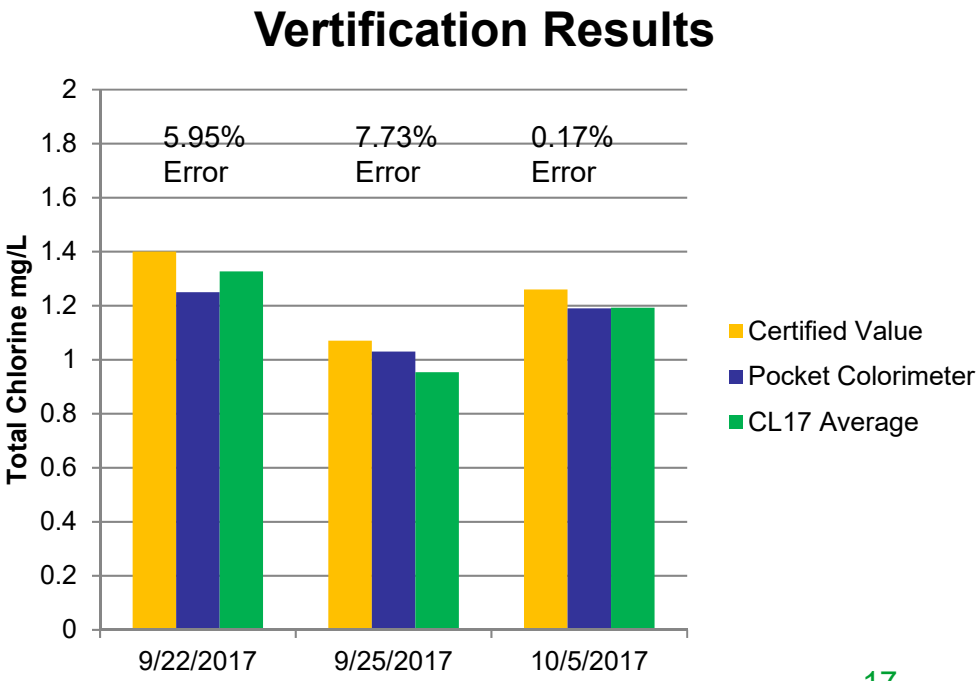


Improvements – Bubble Trap



Improvements – Verification

- Hold outputs from DCS
- Training on Verification Process
- Record Keeping



Additional Instrument

- Sample Intake design closely matches HACH recommendation
- Dramatic reduction in zeroes attributed to sample introduction issues
- Intake plumbing designed to handle high flow of contact tank
  - Strainers
  - Reject line

Additional Instrument

Continuing Efforts

Items that are currently under evaluation:

- Prevention of zeroing events
- Maintenance Schedule
- Strainer cleaning
- Calibration Verification
- Data evaluation

Path Forward

- Ensuring HRSD developed protocols can translate to EPA method
  - Intake plumbing non-manufacturer specific
  - Daily Instrument Verification
  - Data handling to ensure appropriate for DMR reporting
  - 12 QA/QC Elements included in 40 CFR Part 136.7

Protocol Development

- Ensuring HRSD developed protocols can be used to potentially develop a method that can be approved for regulatory analysis
  - Intake plumbing non-manufacturer specific
  - Daily instrument verification
  - Data handling to ensure appropriate for DMR reporting
  - 12 QA/QC Elements included in 40 CFR Part 136.7

Quality Assurance and Quality Control

i. Demonstration of Capability (DOC)	vii. Calibration (initial and continuing)
ii. Method Detection Limit (MDL)	viii. Control Charts
iii. Laboratory Reagent Blank (LRB)	ix. Corrective Action
iv. Laboratory Fortified Blank (LFB)	x. QC Acceptance Criteria
v. Matrix Spike and Matrix Spike Duplicate (MS and MSD)	xi. Definitions of Preparation and Analytical Batches that may drive QC Frequency
vi. Internal Standard	xii. Minimum frequency for conducting all QC elements

40 CFR Part 136.7

- On-line technology makes direct implementation of these 12 QA/QC elements difficult, and some elements not appropriate
- Relevant QA/QC elements will be addressed on the hand held colorimeter used for daily verification if not possible directly on the on-line analyzer

40 CFR Part 136.7

- Demonstration of Capability (DOC)
  - Annual Operator Certification
    - Completion of written test
    - Duplicate analysis of total residual chlorine certified reference material meeting both precision and accuracy limits.
  - Indirect demonstration of capability for on-line method

40 CFR Part 136.7

- Method Detection Limit (MDL)
  - Not appropriate for on-line analyzer
  - Manufacturer specifies working range of instrumentation
  - Permits specify limits for chlorination and/or limits required sensitivity for dechlorination
  - Appropriate reagents and working ranges should be used to quantify in regulatory range

- Laboratory Reagent Blank (LRB)
  - Not appropriate for on-line analyzer
  - Analyzer performs a “zeroing” step before adding reagents to quantify TRC.
  - Same procedure is used for handheld colorimeter used to perform daily verification

- Laboratory Fortified Blank (LRB)
  - Quarterly analysis of certified reference material to verify acceptable results are obtained
  - Quarterly analysis of same certified reference material on handheld colorimeter to validate proper function and validate daily comparative analysis used for daily verification
  - Values compared to ensure on-line analyzer system is functioning in a manner to not introduce bias beyond inherent uncertainty

40 CFR Part 136.7

- Matrix Spike and Matrix Spike Duplicate (MS and MSD)
  - Not appropriate for on-line analyzer
  - Not performed for handheld colorimeter
- Internal Standard
  - Not applicable for TRC analysis by on-line analyzer or colorimeter

40 CFR Part 136.7

- Calibration (initial and continuing)
  - Manufacturer's internal calibration used for on-line instrument
    - Recommend any manual calibration verified periodically according to manufacturers instructions
  - Handheld colorimeter internal calibration verified quarterly with gel standards
    - Recommend any manual calibration verified periodically according to manufacturers instructions

- Control Charts
  - Results obtained through daily verification should be compared to results obtained from on-line analyzer to determine any drift of the on-line analyzer
  - The difference between the on-line analyzer result and the verification must be ≤30%
  - Trending is key to determine needs for preventative maintenance or troubleshooting

- QC Acceptance Criteria
  - Not directly applicable to on-line analyzer
  - Certified Reference Materials analyzed on the handheld colorimeter must meet manufacturers acceptance range for accuracy and in-house limits for precision if analyzed in duplicate
  - Acceptance criteria for verification using gel standards must be documented and met

40 CFR Part 136.7

- Definitions of Preparation and Analytical Batches that may drive QC Frequency
  - Not applicable to on-line analyzer or handheld colorimeter
- Minimum frequency for conducting all QC elements
  - Daily Verification of the on-line analyzer using the handheld colorimeter
  - Quarterly analysis of Certified Reference Materials
  - Quarterly verification of calibration by analysis of gel standards

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Summary

- On-line analysis of total residual chlorine for NPDES Compliance is possible
- Daily verification of on-line instrumentation using a handheld colorimeter is ideal to ensure the on-line analytical system is meeting data quality objectives for NPDES analysis.
- Additional development on overcoming sample intake issues specific to wastewater is necessary to optimize technology application

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Questions?

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