

Near Real-Time Monitoring of Selenium and Mercury in FGD Wastewater for Process Control

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Acronyms

DL = Detection limit

ELG = Effluent Limitation Guidelines

FGD = Flue gas desulfurization

Hg = Mercury

HRTR = High Hydraulic Residence Time Biological Reduction

LRTR = Low Hydraulic Residence Time Biological Reduction

MS = Matrix spike

O&M = Operations and maintenance

ORSANCO = Ohio River Valley Water Sanitation Commission

RPD = Relative percent difference

RSD = Relative standard deviation

R&D = Research and Development

Se = Selenium

TDS = Total dissolved solids

TSS = Total suspended solids

VFC = Vertical Flow Cell

WCTS = Wood Chip Treatment System

WQBEL = Water Quality Based Effluent Limit

WW = Wastewater

Introduction

- Coal-fired power plants
- Biologically treated FGD WW
- Se and Hg



WW Treatment System Process Control

- Power industry need for rapid measurements
 - Off-site analysis can be relatively slow
 - Troubleshoot FGD and WW treatment systems
 - Comply with regulations; avoid permit violations



Ideal Attributes of a Near Real-Time Monitor

- Provides frequent results
- Produces precise and unbiased results
- Is easy to operate and maintain by plant staff
- Is rugged enough for intended operating conditions



Regulatory Limits and Targeted Detection Limits

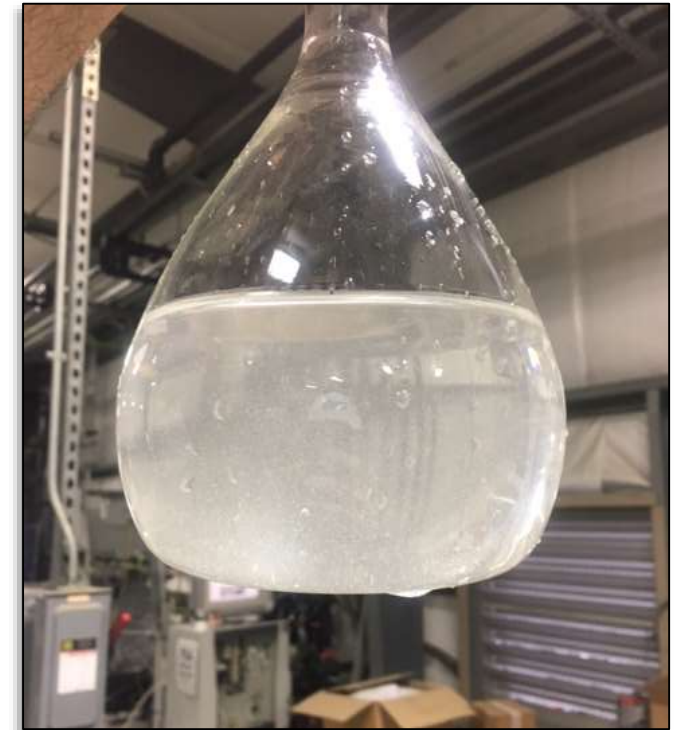
Parameter	2015 ELG Limits and Targets			WQBEL/ ORSANCO Limits	Targeted DLs for these Studies	2019 ELG (PROPOSED)	
	Daily Max	Monthly Average	LTA			LTA	LTA (VIP)
Mercury, total (ng/L)	788	356	159	12	2.4	13.5	5.1
Selenium, total (µg/L)	23	12	7.5	170	1.5	16.6	5.0

LTA = Long-term average

VIP = Voluntary Incentive Program

Measurement Challenges: Performance

- Trace levels of Hg (ng/L) and Se ($\mu\text{g/L}$)
- High TDS and TSS (mg/L), analytical interferences
- Reducing and reactive matrix
- Sample preparation



Monitor Challenges: Operability

- Dust, vibrations, humidity and temperature
- Operation and maintenance
 - Preparation and replacement of reagents
 - Replacement of filters or other routine components
 - Troubleshooting and repairs
 - Staffing
 - Chemists not always employed at power plants
 - Remote operation
 - Requirement is high for benchtop systems (20-40 hrs/wk vs 1-3 hrs/wk)

Technical Approach

- Different monitor types
 - Online and benchtop
 - Commercially available and prototype
- Lab and field studies
 - 2016 Lab and 2018 B Lab studies
 - Static water samples
 - Temperature- and humidity-controlled location
 - 2017, 2018 A, and 2018 B Field studies
 - Dynamic, real-time samples from treatment system outlets
 - Field environments at power plants

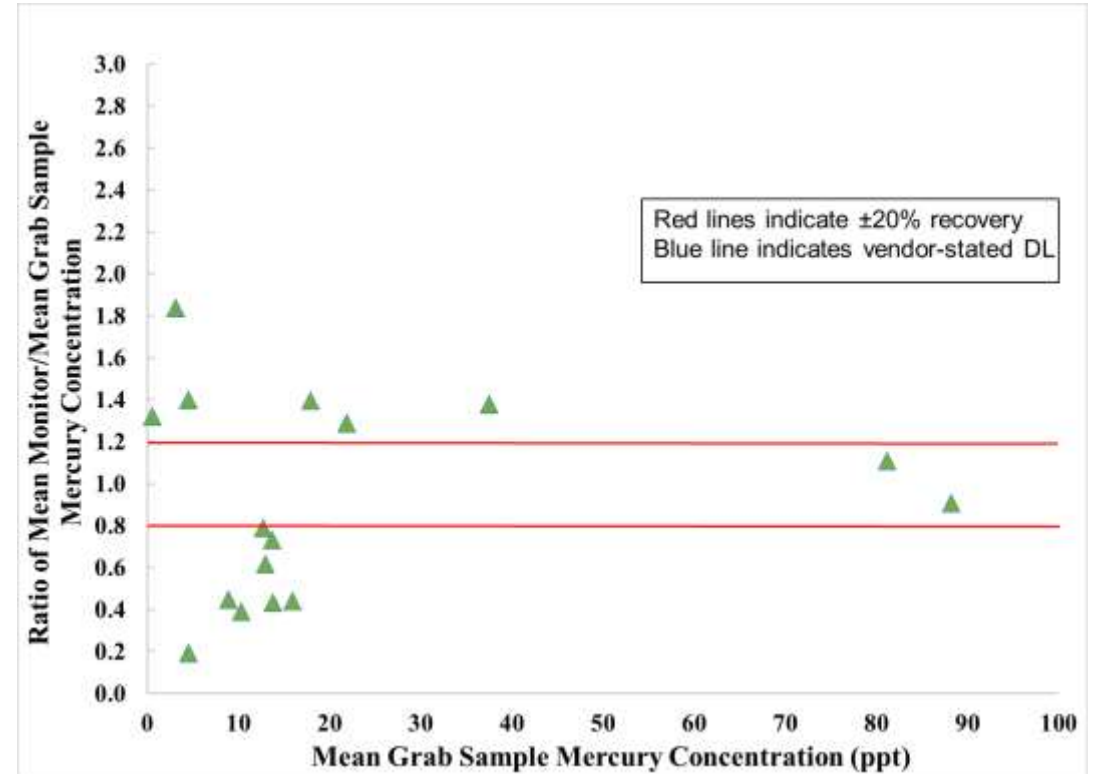


Technical Approach, continued

- **Fuels, treatment systems, and source water**
 - Most burned bituminous coal, one burned subbituminous coal
 - Most WWT systems had both phys/chem and bio treatment
 - Biotreatment processes included LRTR bioreactors, VFCs, and a WCTS
 - Included both pilot-scale and full-scale systems
 - Source water to the WWT systems included FGD blowdown and gypsum pond water
- **Data Gaps**
 - Tested at one sub-bituminous and no lignite coal plants
 - No HRTR biological systems tested
 - Limited field testing with ash pond wastewater (mercury only)

Technical Approach, continued

- Performance evaluation
 - Accuracy: $\pm 20\%$ recovery
 - Precision: $\leq 20\%$ RPD or RSD
 - DL is 5x lower than regulatory limit
 - Looser accuracy criteria may be acceptable
- Operability evaluation
- Feedback provided to monitor vendors



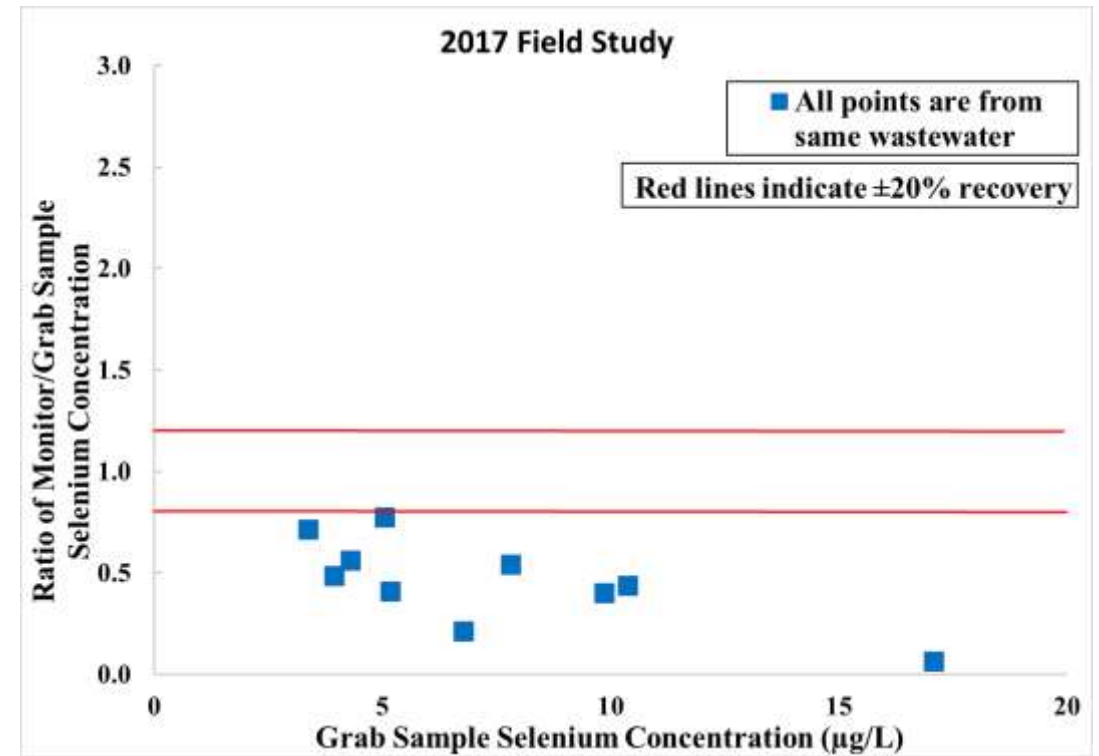
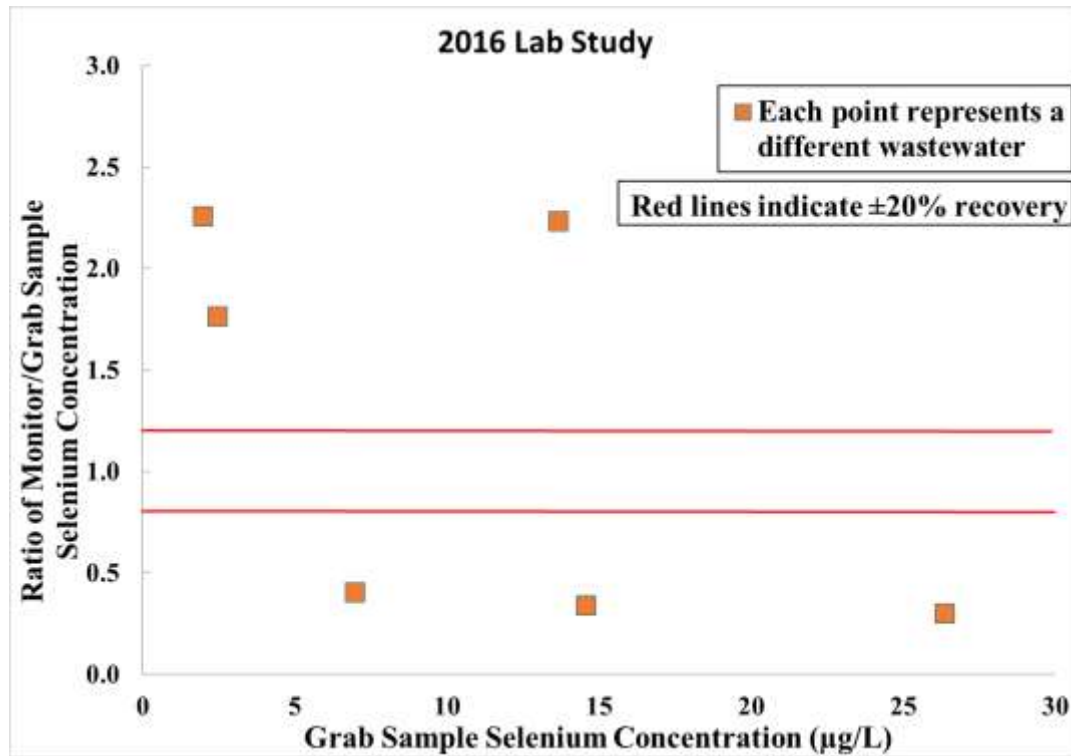
Example Graph

Selenium Monitors Tested

Vendor, Code	Technique	Availability, Type	Total Se DL* ($\mu\text{g/L}$)
Aqua Metrology Systems, A	Stripping voltammetry	Commercially available, online	5
PS Analytical, B	Hydride generation – flame atomic fluorescence spectroscopy	Commercially available, online	0.1
OndaVia, C	Surface enhanced Raman spectroscopy	Prototype, benchtop	5
Cooper Environmental, D	X-ray fluorescence spectroscopy	Prototype, online	0.1

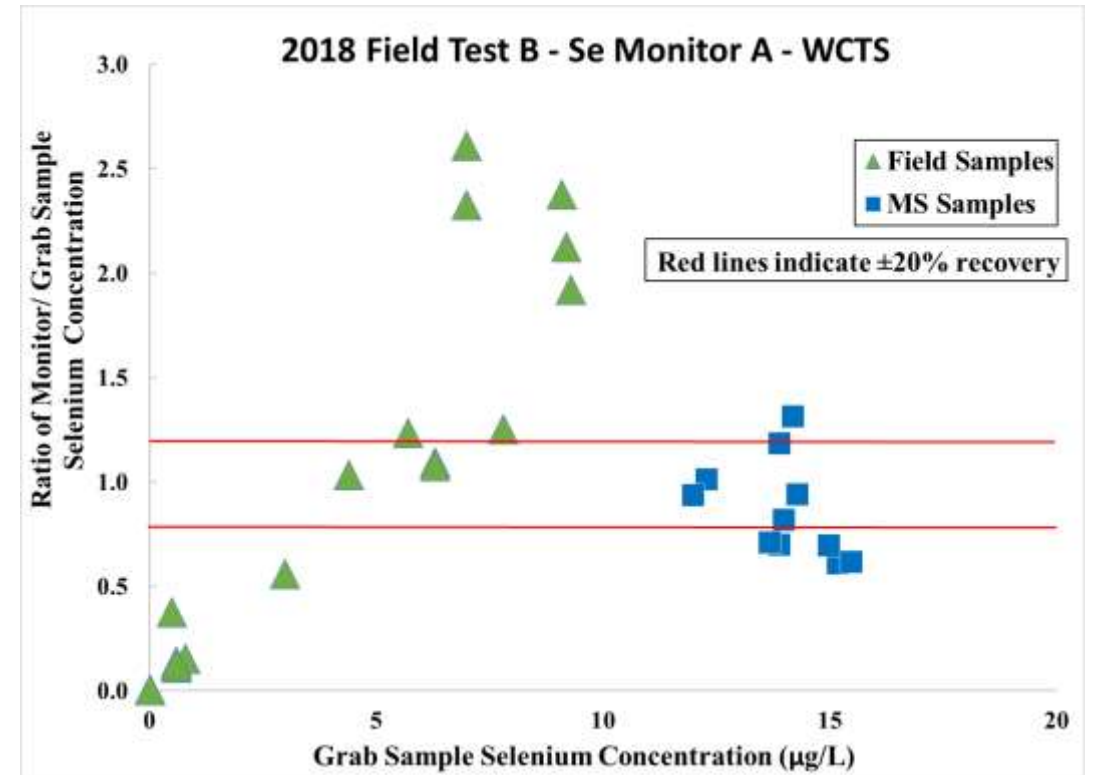
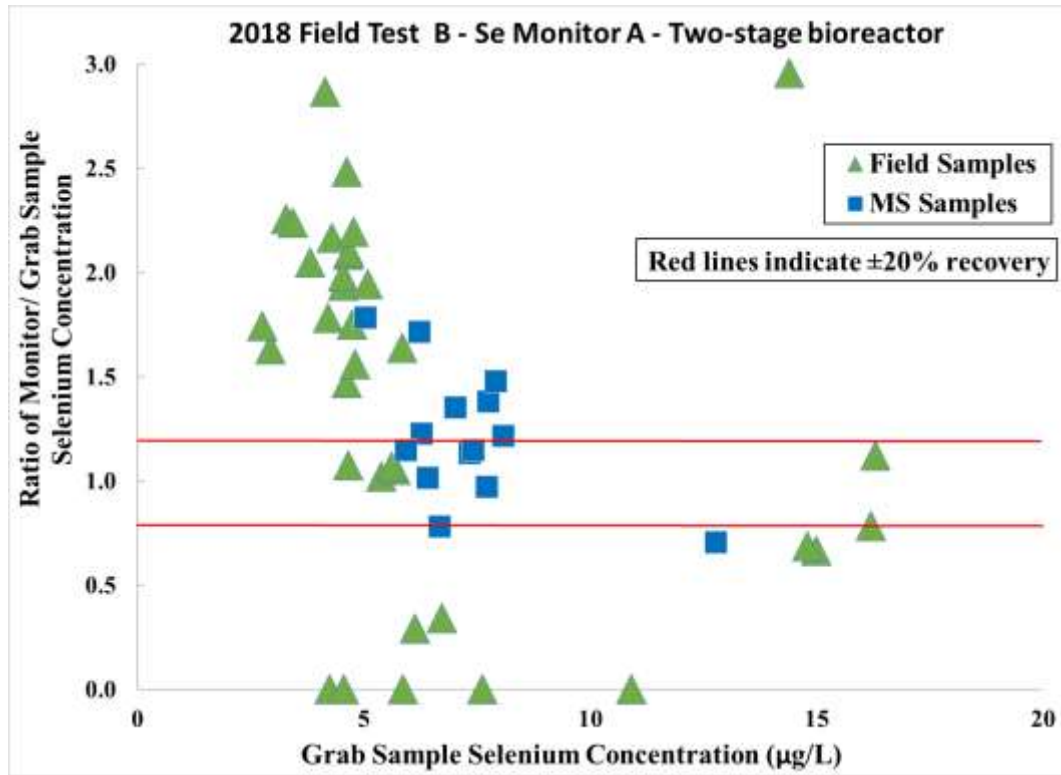
*DLs presented are vendor-stated in clean water, at time of study

Se Monitor A: Performance in 2016/2017



- Online, commercially available, stripping voltammetry
- Did not measure accurately at $7.5 \mu\text{g/L}$
- Method optimization recommended

Se Monitor A: Performance in 2018 B



- FGD WW DL = 8 - 9 $\mu\text{g/L}$
- Did not measure accurately at 7.5 $\mu\text{g/L}$
- May provide accurate results at higher Se concentrations

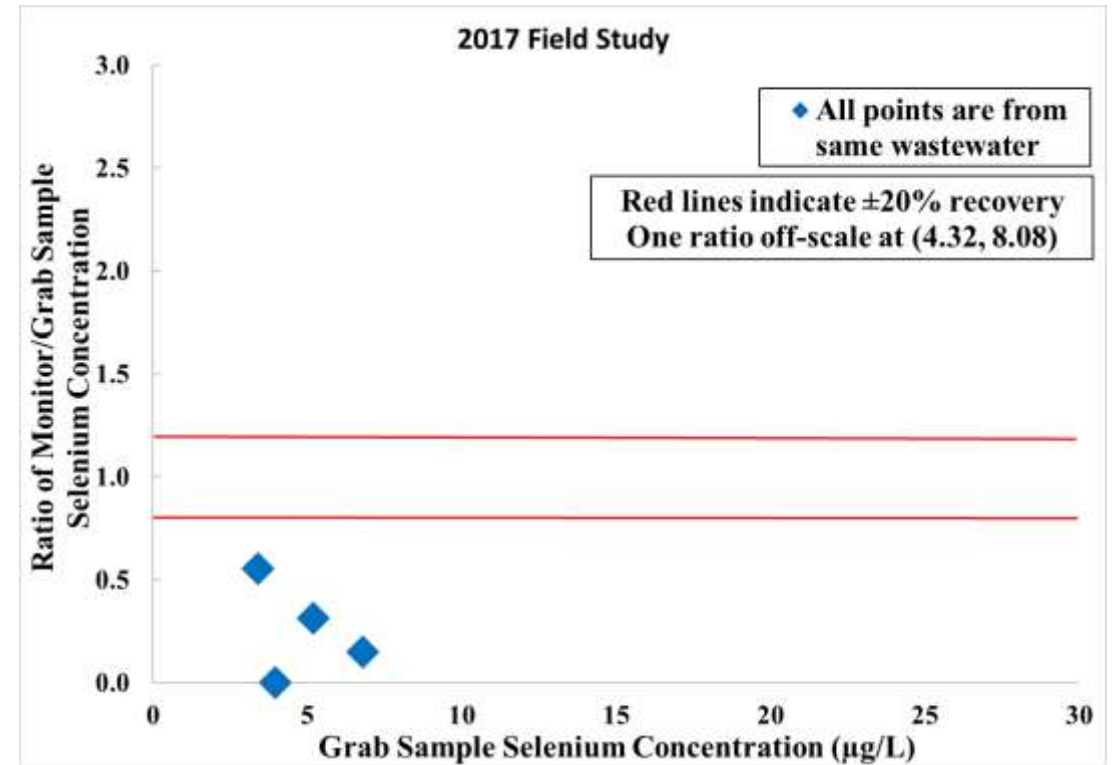
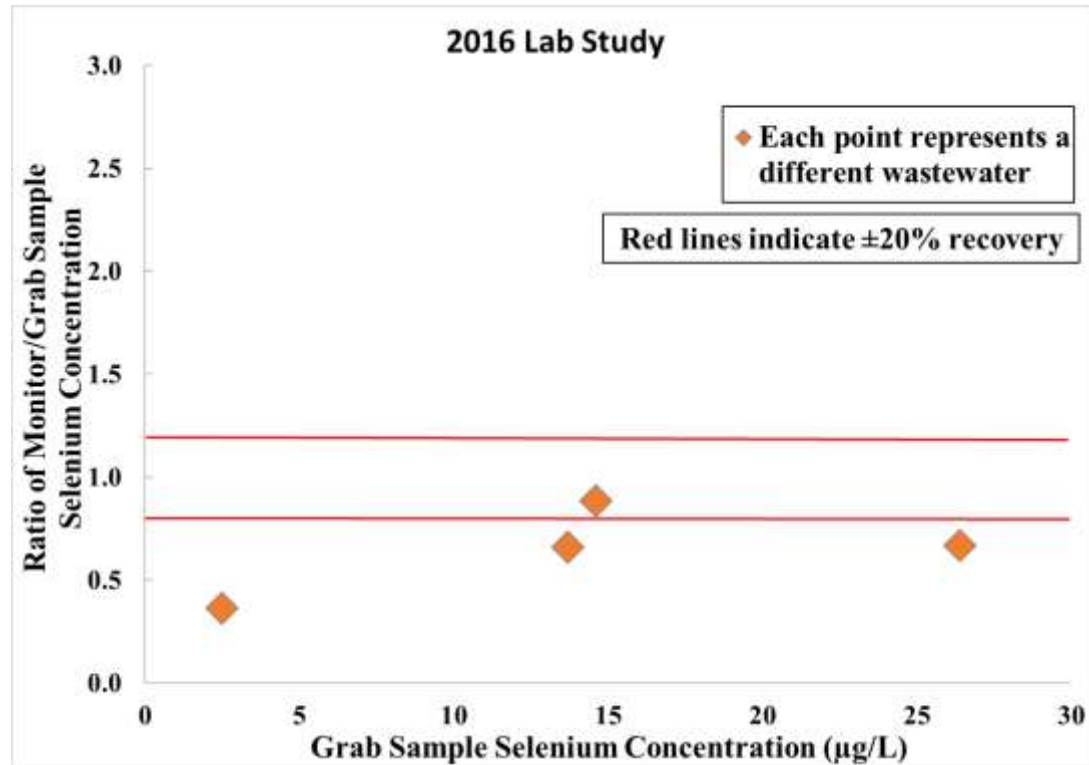
Se Monitor A: Operability

- Uptime varied
 - 2017 Field Study: 86%, no QC or hardware issues
 - 2018 Field Study B:
 - One monitor functional most of study
 - Other monitor not functional most of study
 - Increased ruggedness recommended
- Result generated every 120 min
- O&M ~ 1 hr/week
 - Replace reagents (come pre-made)
 - Dispose of waste



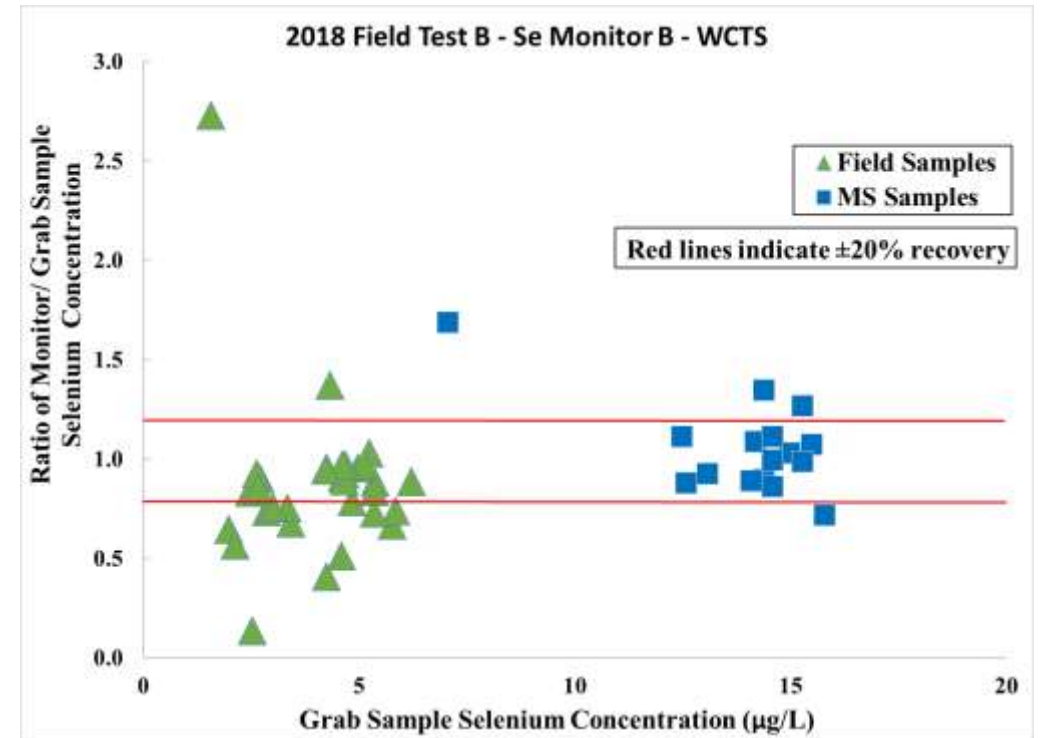
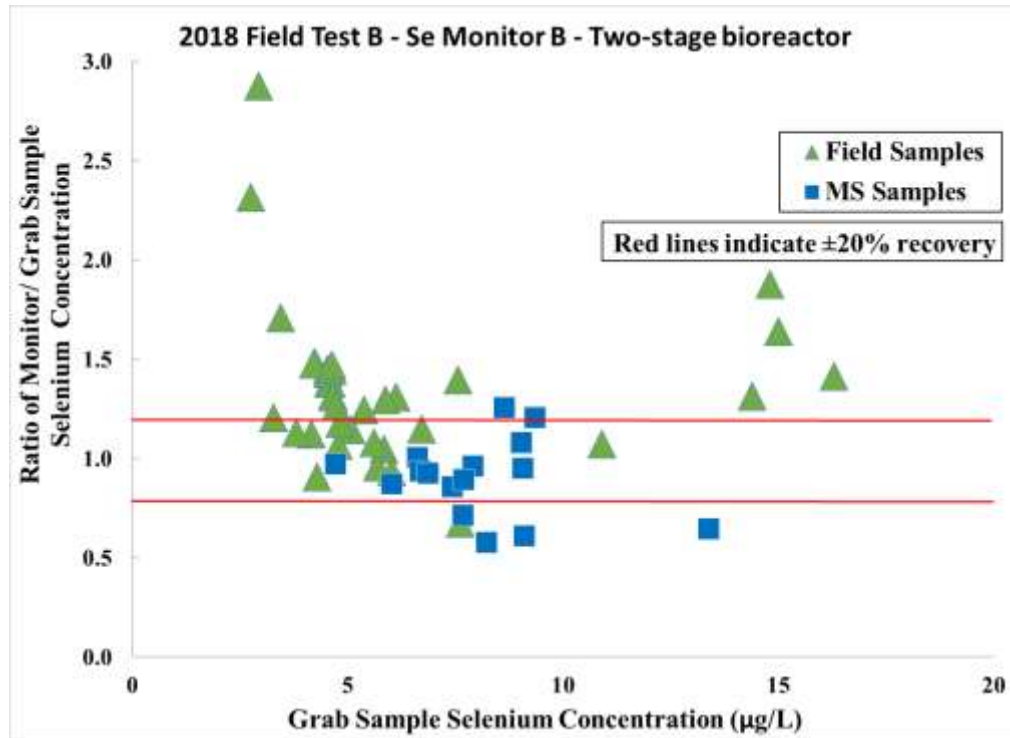
AMS MetalGuard

Se Monitor B: Performance in 2016/2017



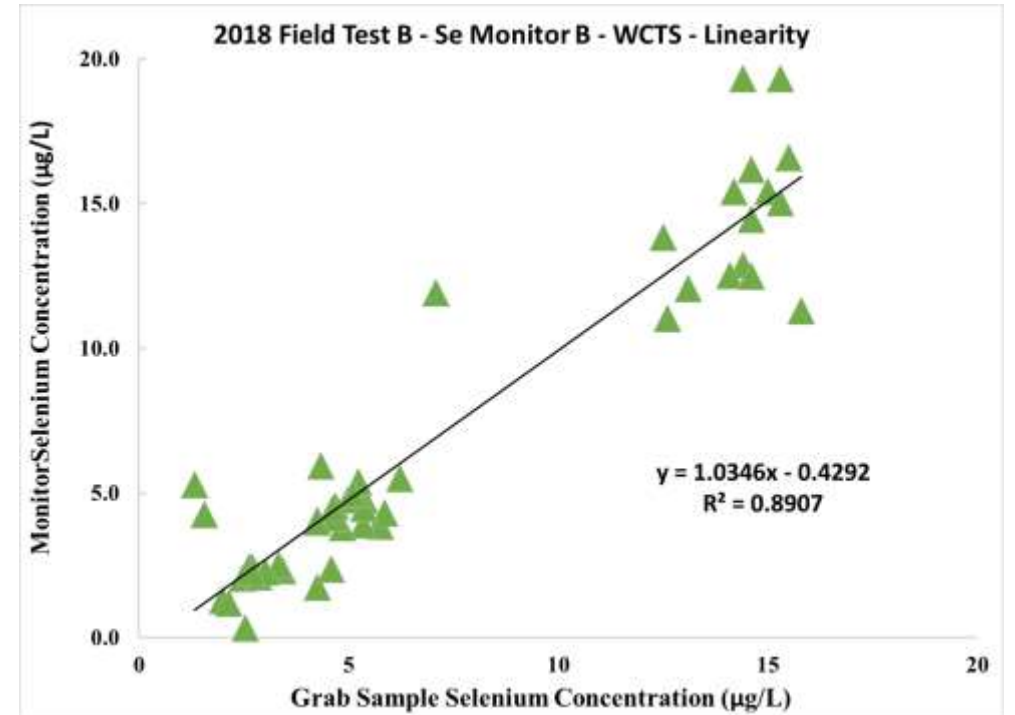
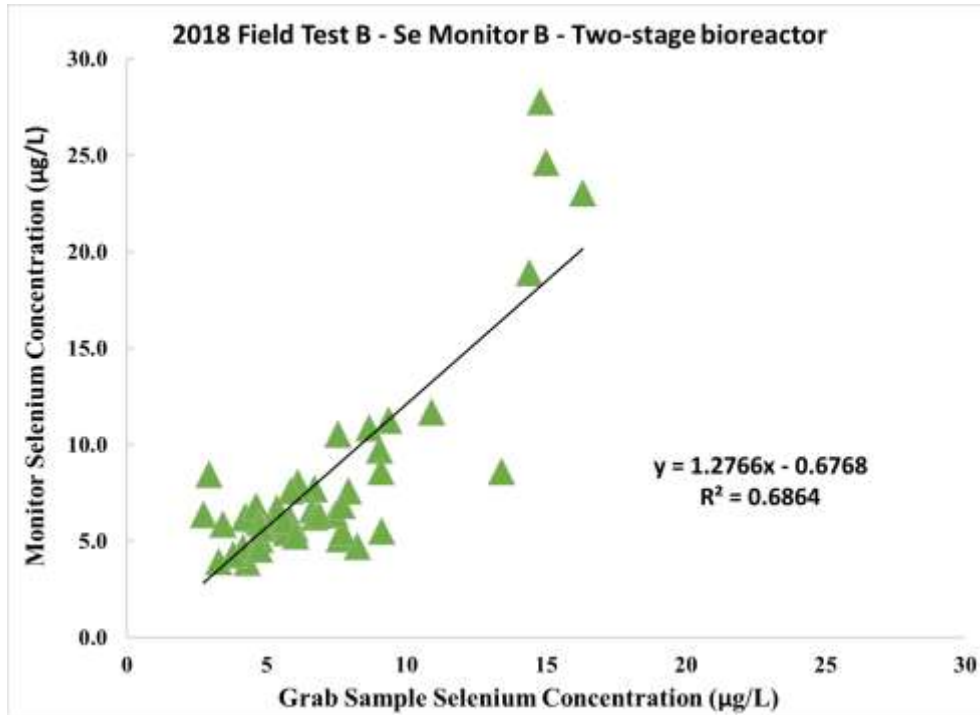
- Online, commercially available, HG – flame AFS
- Did not measure accurately at 7.5 $\mu\text{g/L}$
- Method optimization recommended

Se Monitor B: Performance in 2018 B



- FGD WW DL = 0.6 and 0.9 $\mu\text{g/L}$
- Did not measure accurately for a target DL of 7.5 $\mu\text{g/L}$
- May provide accurate results at higher Se concentrations

Se Monitor B: Performance in 2018 B



- Linearity assessed for all field and MS samples for each WW
- Correlation coefficients of 0.686 and 0.891
- Monitor may be useful in identifying trends

Se Monitor B: Operability

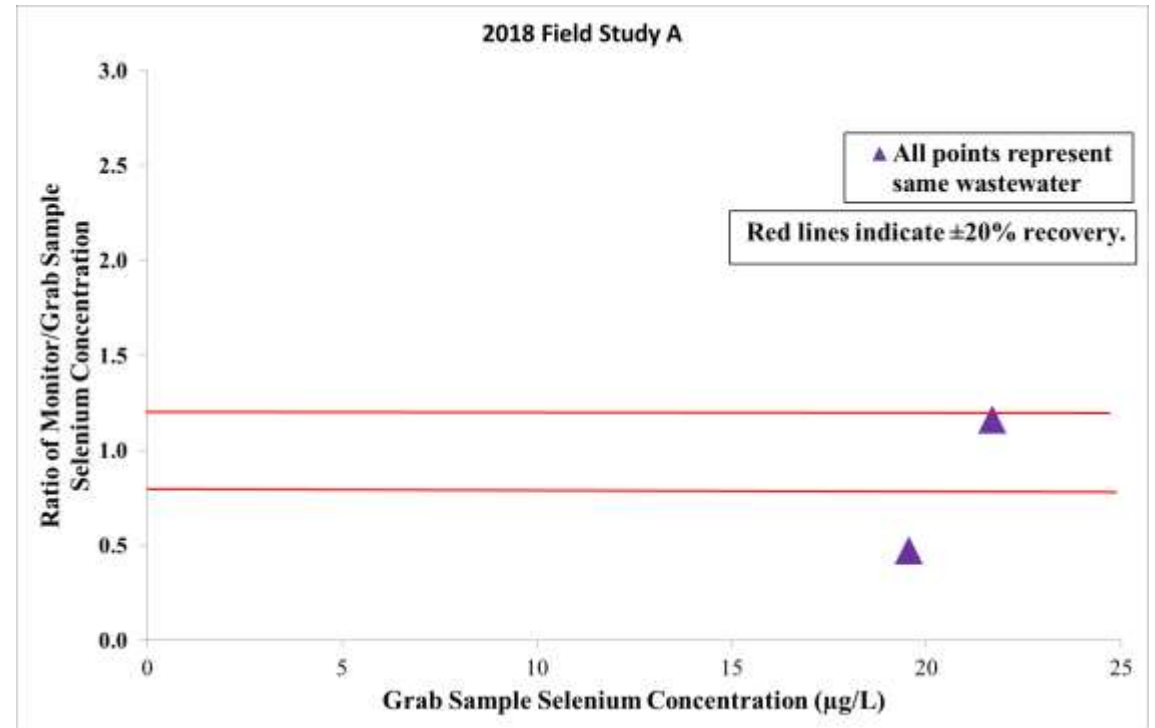
- Uptime
 - 2017 Field Study: 26%
 - 2018 Field Study B: 81%
- Result every 10 min
- O&M ~ 3 hr/week
 - Prepare and replace reagents
 - Dispose of waste
 - Reduced reagent consumption recommended



PSA 10.255

Se Monitor C: Performance in 2018 A

- Prototype, Benchtop
- Surface Enhanced Raman Spectroscopy
- FGD WW DL = 2.45 $\mu\text{g/L}$
- Insufficient data to evaluate; more testing recommended



Se Monitor C: Operability

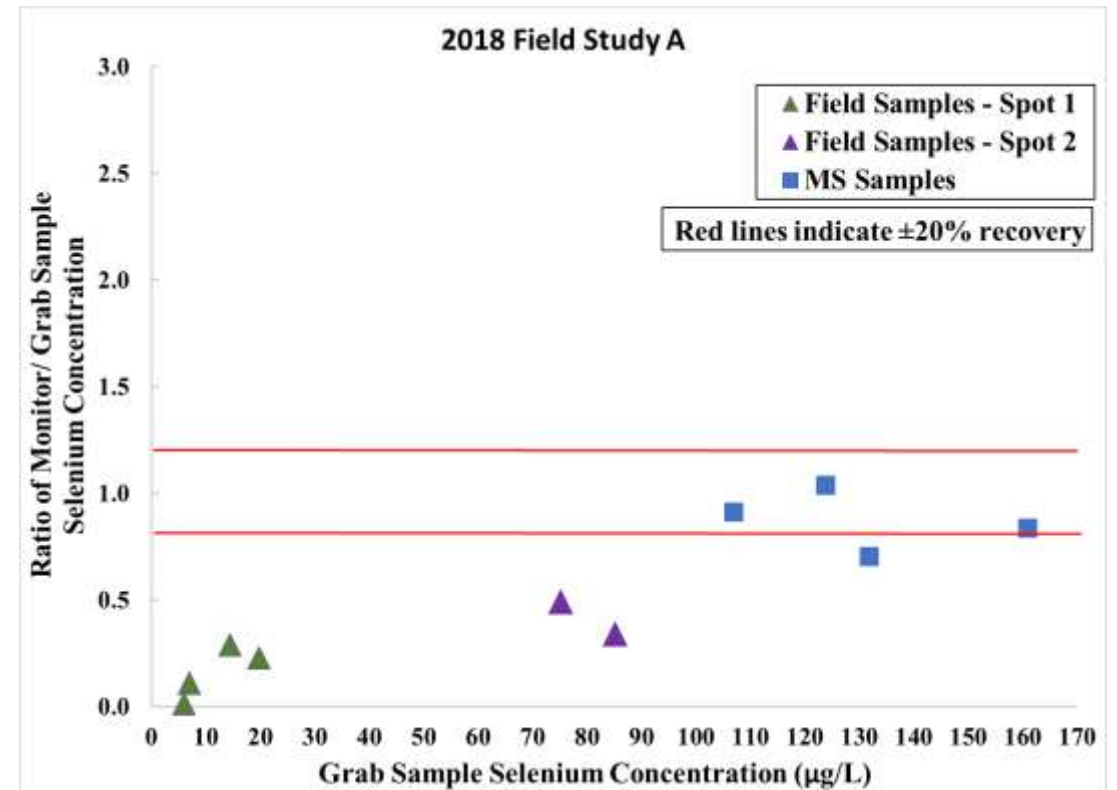
- Uptime not calculated
 - Improved ruggedness recommended
- Result every 1-3 hrs
- O&M ~15-30 hr/week currently
 - Vendor is working towards an online monitor



OndaVia Analysis System

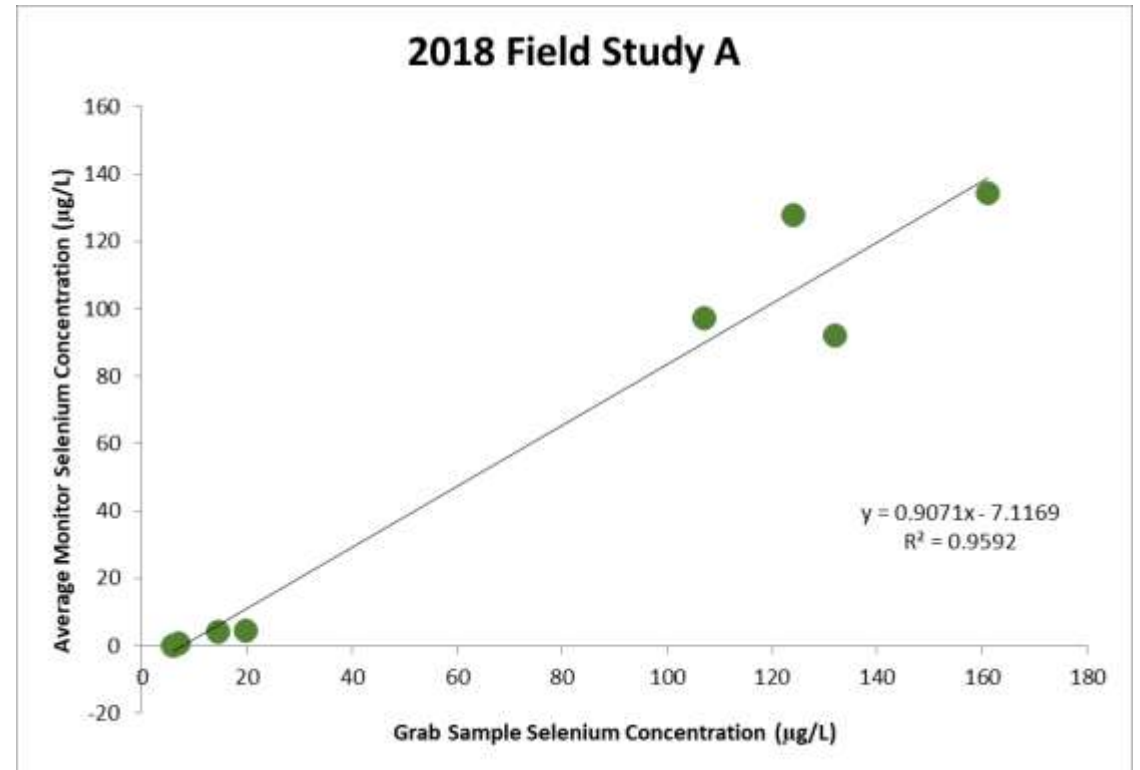
Se Monitor D: Performance in 2018 A

- Prototype, Online, XRF
- FGD WW DL = 9.15 $\mu\text{g/L}$
- Did not measure accurately at 7.5 $\mu\text{g/L}$
- Method optimization recommended



Se Monitor D: Performance in 2018 A

- Linearity assessed for all field and MS samples from one spot; correlation coefficient was 0.959
- Monitor may be useful in identifying trends



Se Monitor D: Operability

- Uptime was 46%
 - Vendor had to travel to site to troubleshoot
 - Improved ruggedness recommended
- Result every 60 min
- O&M ~ 1-2 hr/week



Cooper Xact 920

Selenium Monitor Summary

- Monitors show promise, but not ready for accurate detection at 7.5 $\mu\text{g}/\text{L}$
- Additional R&D needed
 - Method optimization for Se conversion
 - Reduce DLs
 - Improve ruggedness
 - Testing with additional WW

Mercury Monitors Tested

Vendor, Code	Technique	Availability, Type	Total Hg DL* (ng/L)
Mercury Instruments, E	SR-GA-CVAAS	Commercially available, continuous-flow, online	10
PS Analytical, F	SR-CVAFS	Commercially available, continuous-flow, online	<10
PS Analytical, G	SR-GA-CVAFS	Recently commercialized, batch-flow, online	1.5
Brooks Rand, H	SR-GA-CVAFS	Commercially available, benchtop	0.025

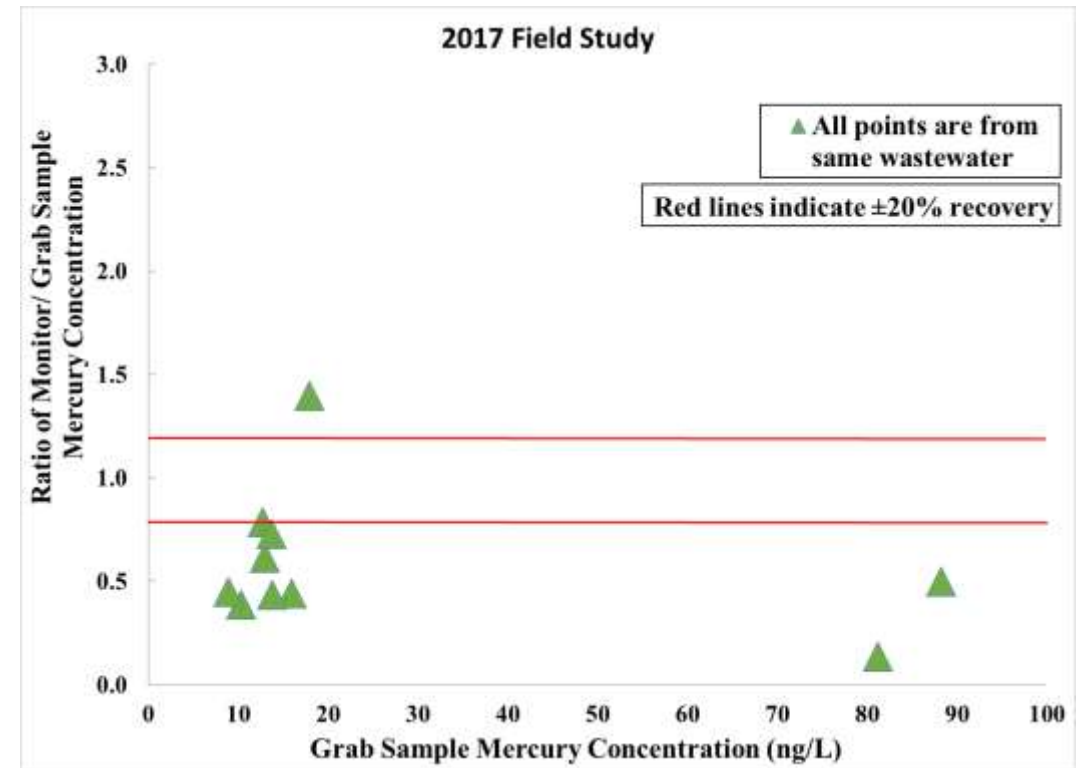
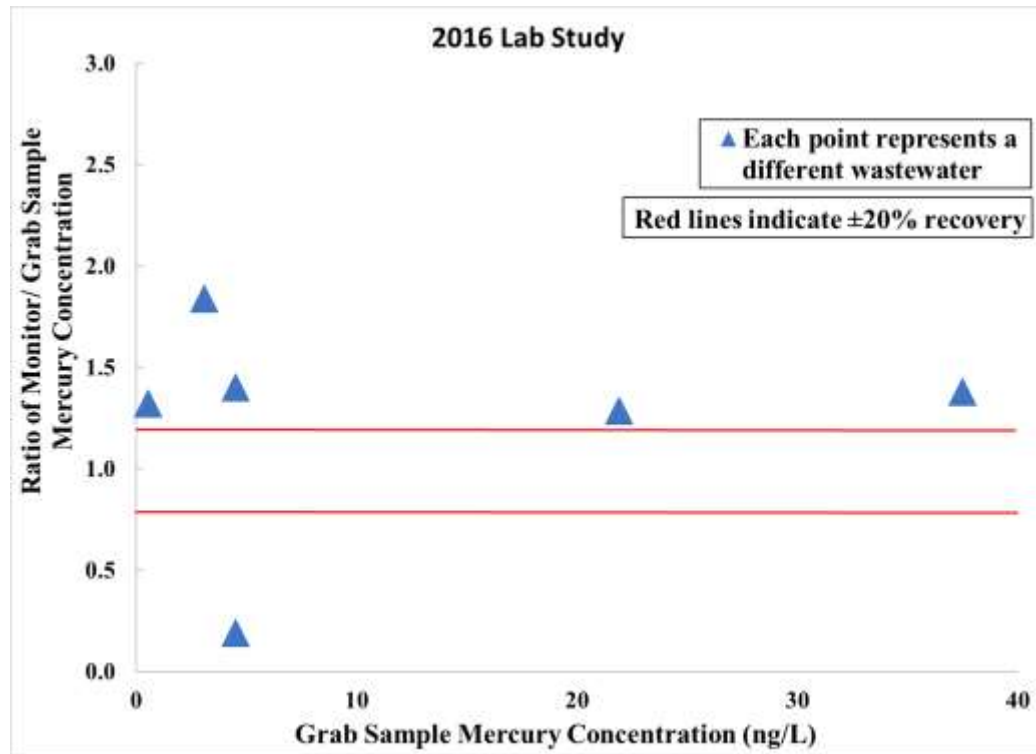
* DLs presented are vendor-stated in clean water, at time of study

SR = Stannous reduction, GA = Gold amalgamation

CVAAS = Cold vapor atomic absorption spectroscopy

CVAFS = Cold vapor atomic fluorescence spectroscopy

Hg Monitor E: Performance in 2016/2017



- Online, commercially available, continuous-flow, SR-GA-CVAAS
- Did not measure accurately at 12 ng/L
- Method optimization recommended

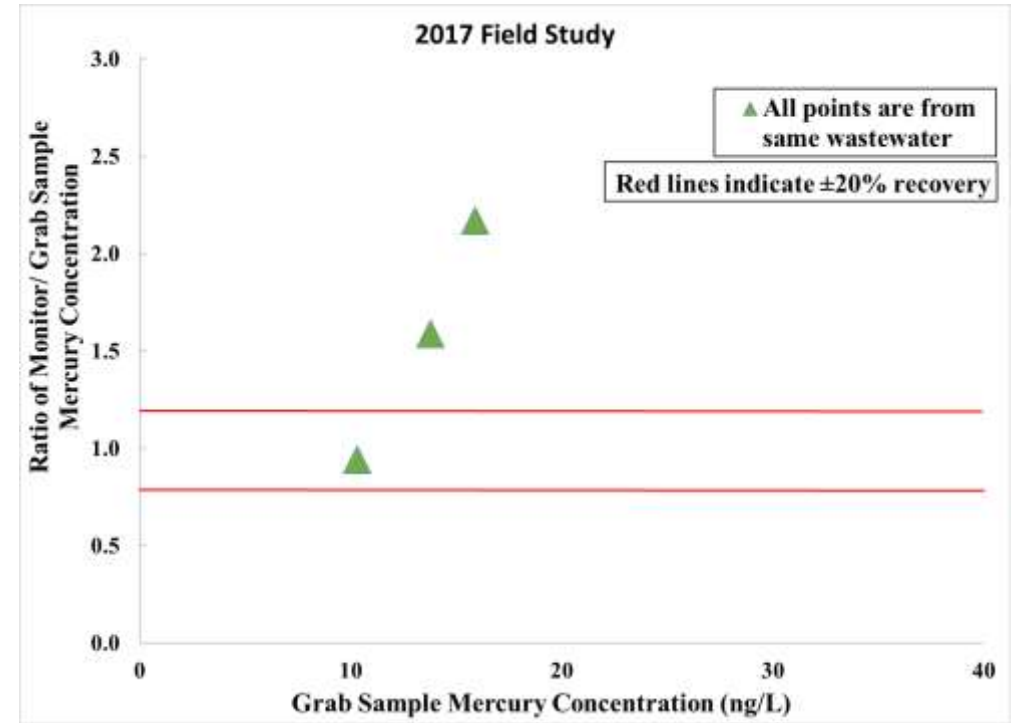
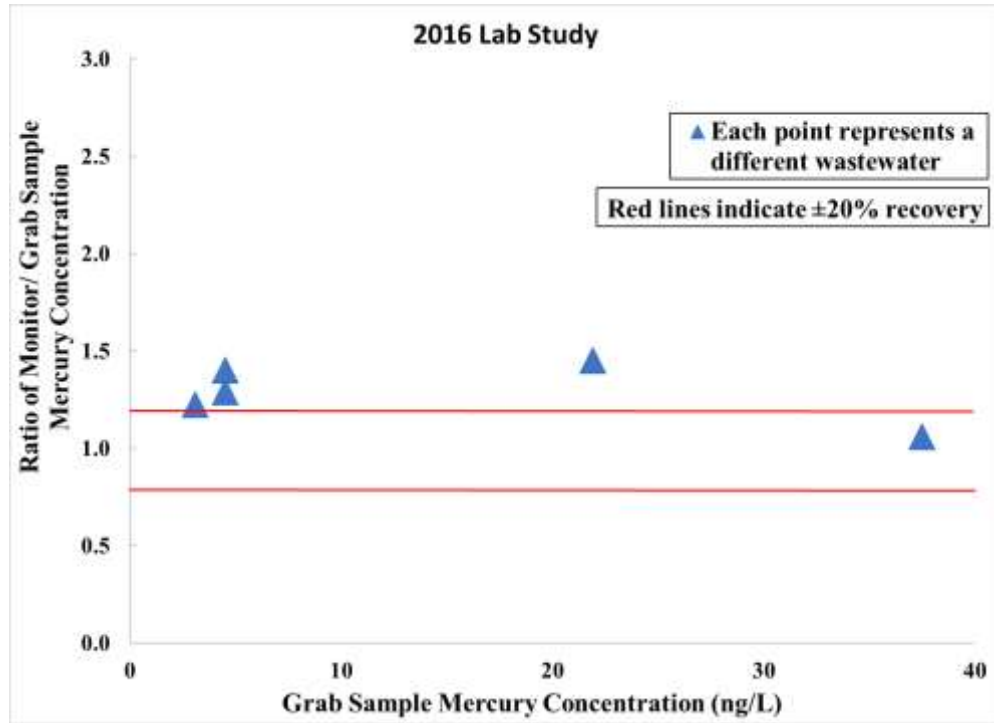
Hg Monitor E: Operability

- Uptime was 59%
- Result every 10 min
- O&M ~ 3 hr/week
- Reagent volume reduction recommended



Mercury Instruments PA-2/UT-3000

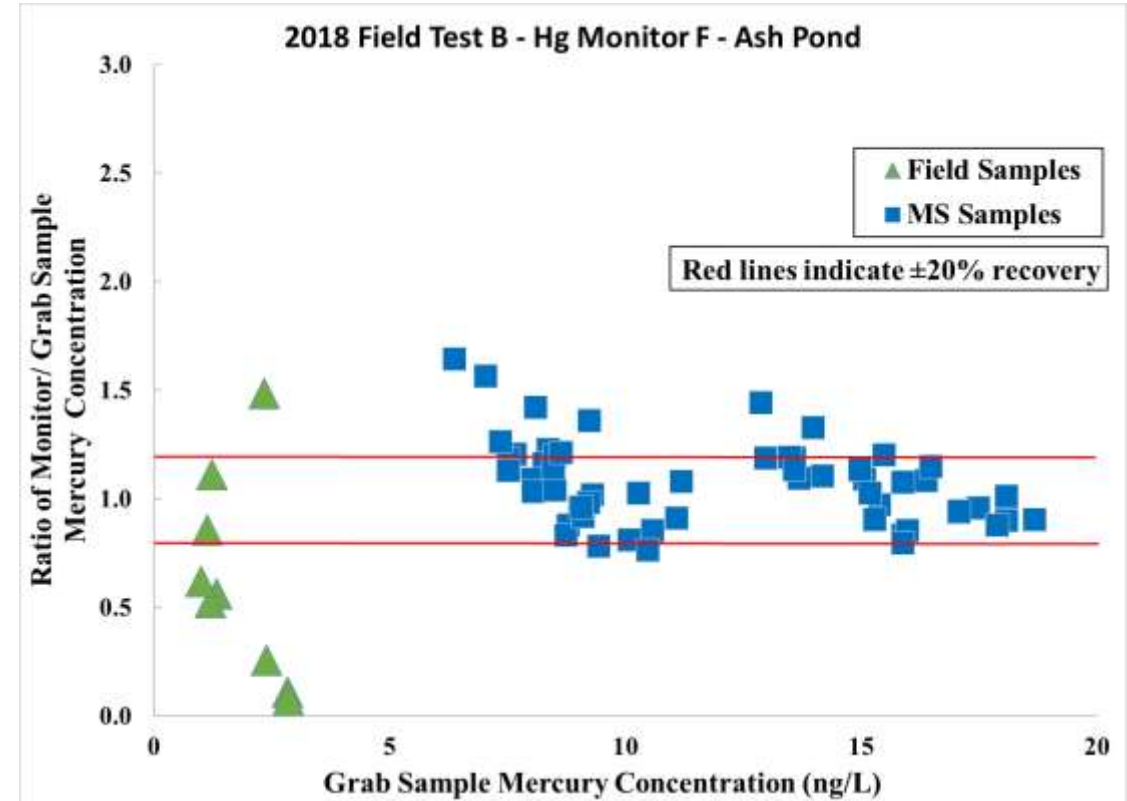
Hg Monitor F: Performance in 2016/2017



- Online, commercially available, continuous-flow, SR-CVAFS
- General high bias; did not measure accurately at 12 ng/L
- Method optimization recommended

Hg Monitor F: Performance in 2018 B

- WW from an ash pond
- WW DLs of 4.5, 8.2, and 3.8 ng/L
- Measured fairly accurately at 12 ng/L
- May provide accurate results at higher Hg concentrations



Hg Monitor F: Operability

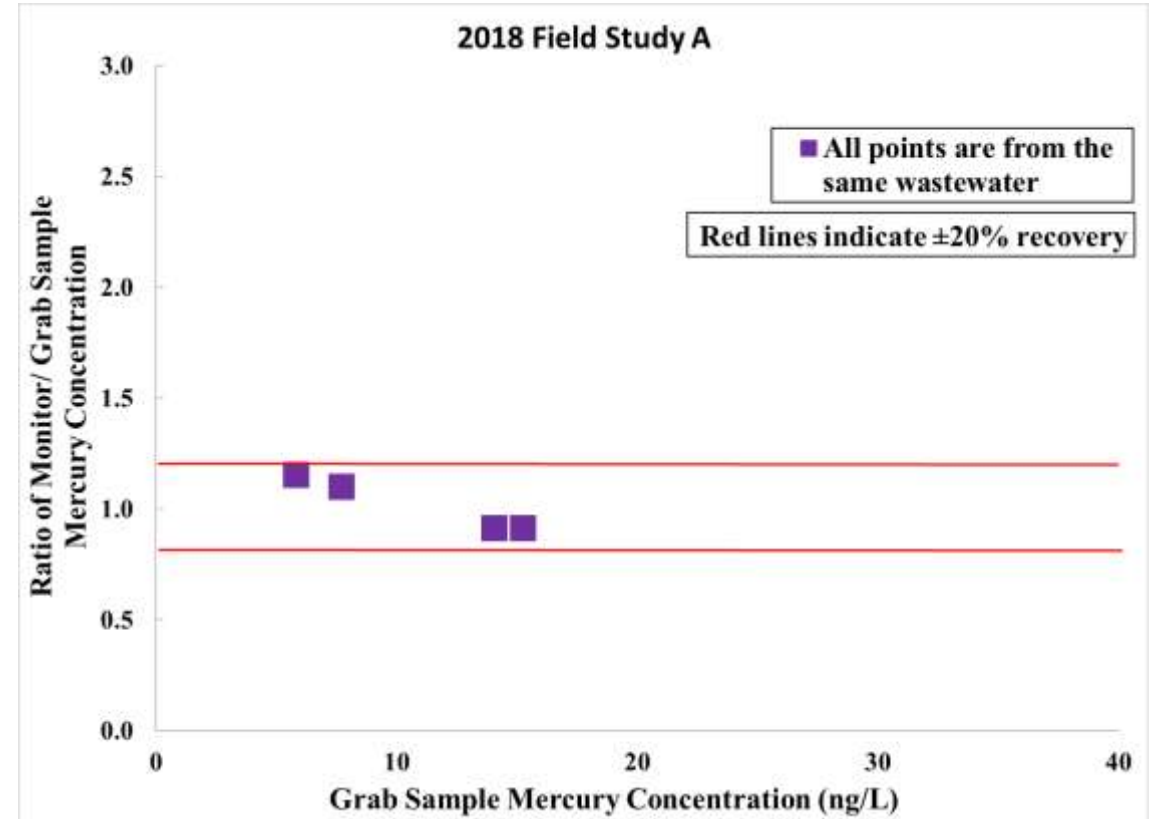
- Uptime
 - 2017 Field Study: 11%
 - 2018 Field Study: 45%
 - Improved ruggedness recommended
- Result every 10 min
- O&M ~ 3 hr/week
- Reagent volume reduction recommended



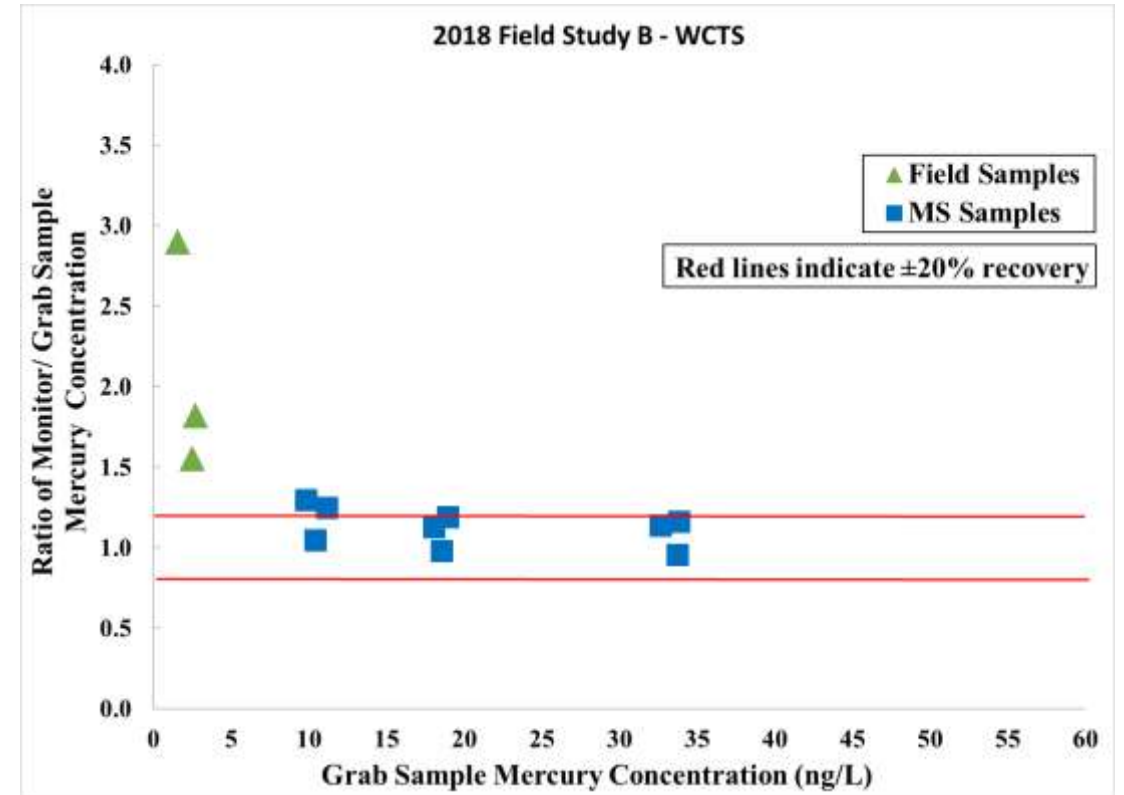
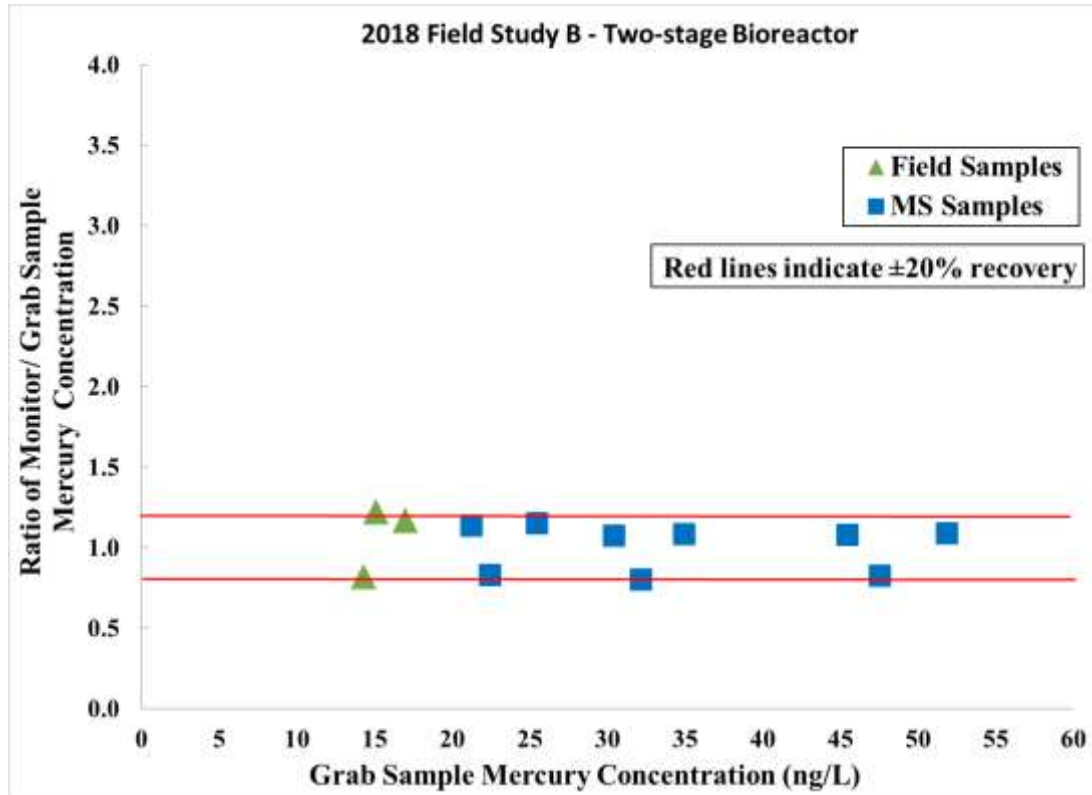
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Hg Monitor G: Performance in 2018 A Field Study

- Online, prototype, batch-flow, SR-GA-CVAFS
- FGD WW DL = 0.5 ng/L
- Met project criteria at 12 ng/L

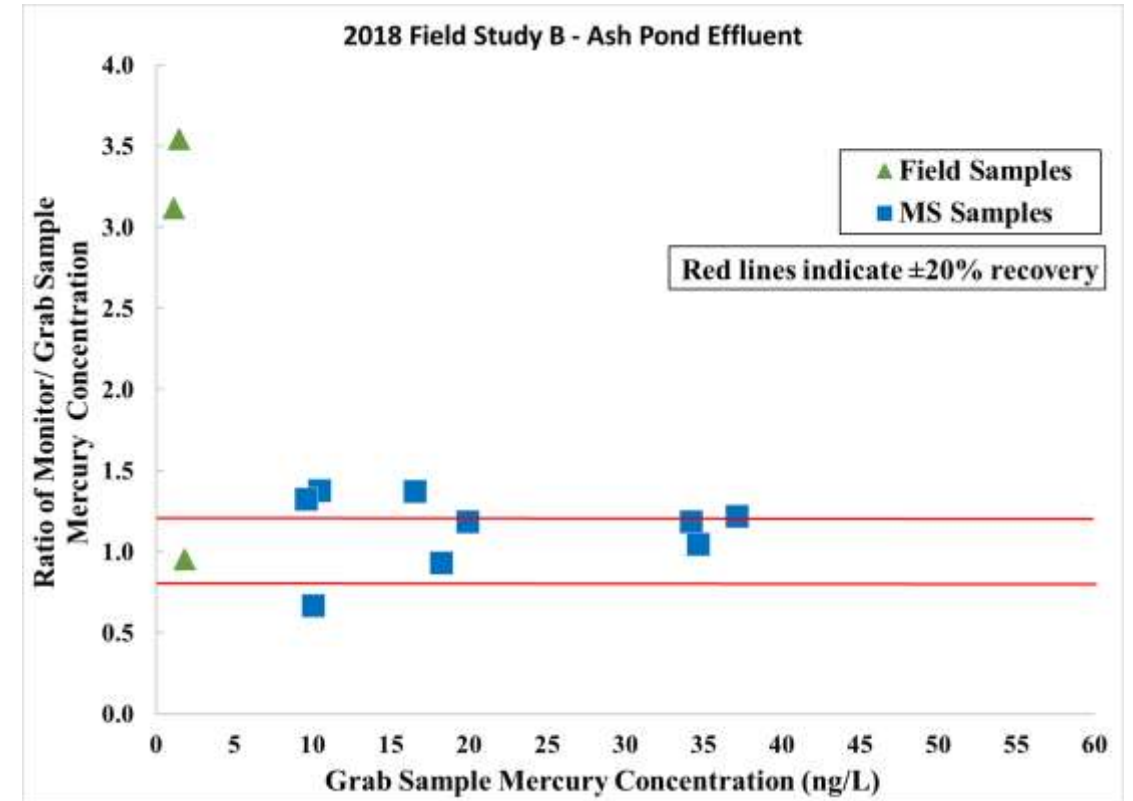
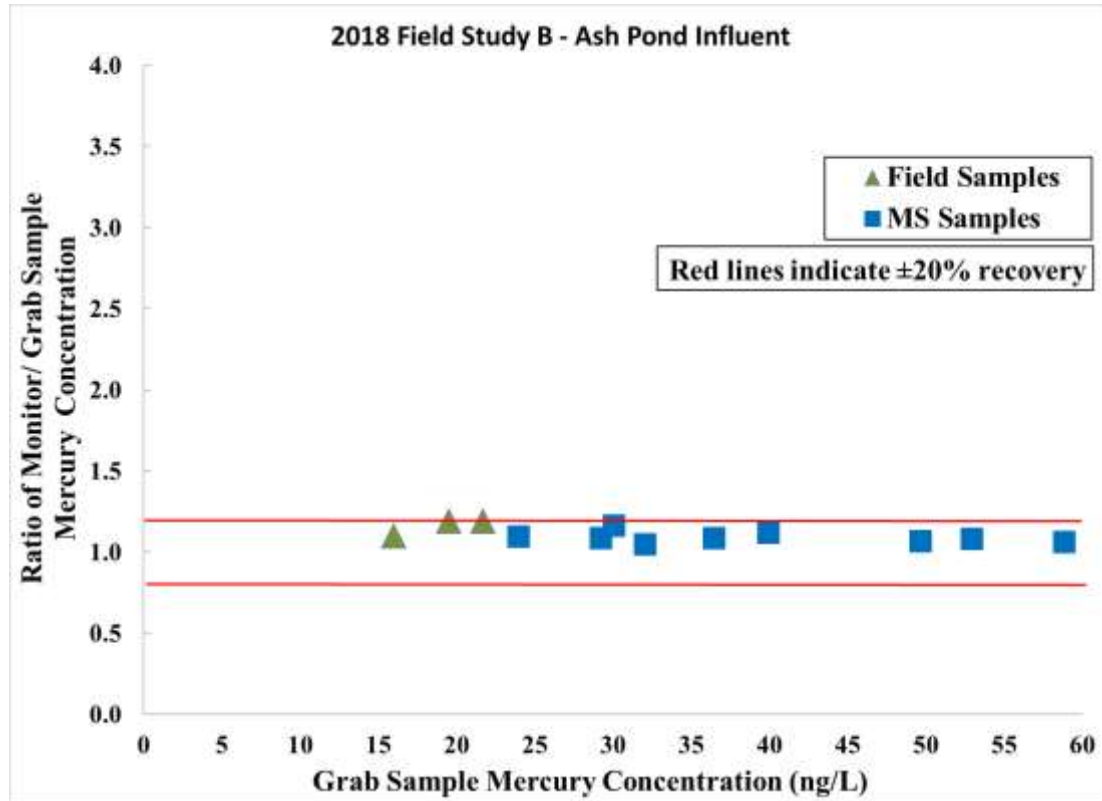


Hg Monitor G: Performance in 2018 B Lab Study



- FGD WW
- Nearly all results met project criteria at 12 ng/L

Hg Monitor G: Performance in 2018 B Lab Study



- Ash pond WW; influent and effluent
- Nearly all results met project criteria at 12 ng/L

Hg Monitor G: Operability

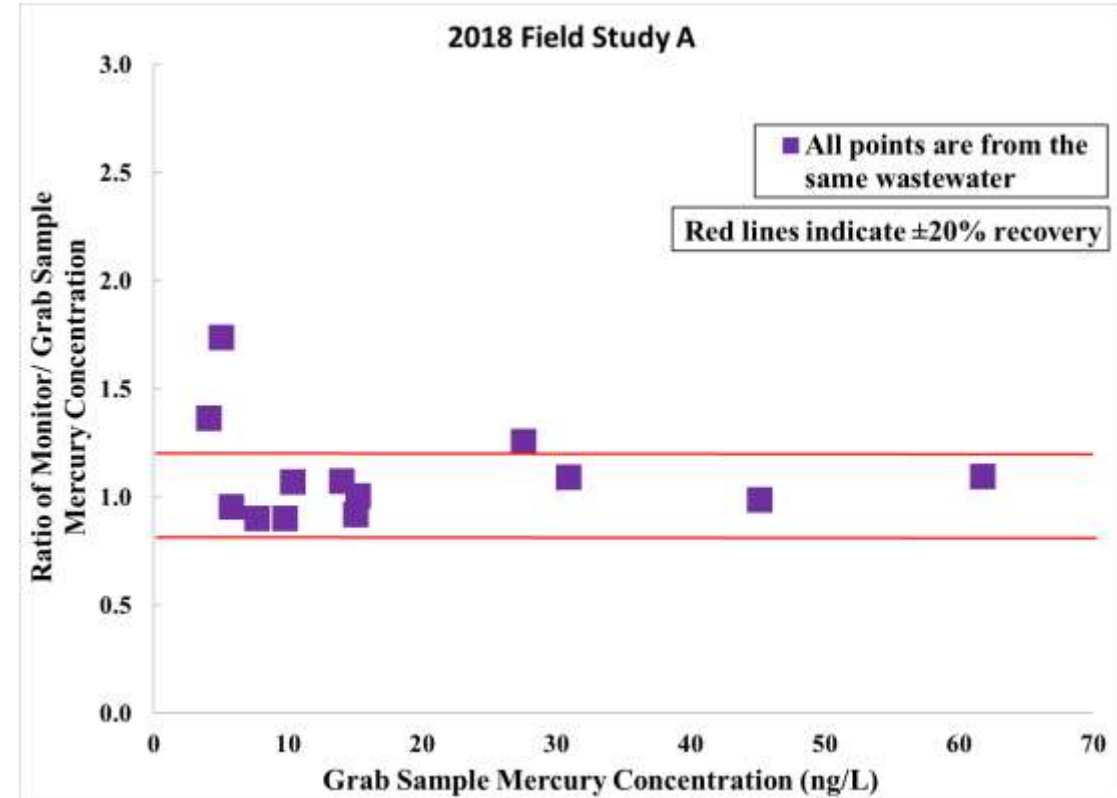
- Uptime
 - 2018 Field Study A: 70%
 - Additional field evaluation needed
- Result every 10 min
- O&M ~ 2 hr/week



PSA 10.226

Hg Monitor H: Performance

- Benchtop, commercially available, SR-GA-CVAFS
- FGD WW DL = 1.48 ng/L
- Met project criteria at 12 ng/L, when contamination controlled
- Clean laminar flow hood recommended



Hg Monitor H: Operability

- Uptime: No hardware or software issues
- Result generated every 1-2 hr
- O&M 20-40 hr/week



Brooks Rand MERX-T

Mercury Monitor Summary

- Some monitors are promising for this application, but further evaluation is recommended
 - Produce frequent results, have DLs < 5x regulatory limit, meet performance and operability requirements
 - Longer-term field testing
 - Testing with additional WW
- Other monitors require additional R&D
 - Reduce DLs
 - Reduce reagent volumes

General Monitor Summary

- Some Hg monitors are promising
- Se monitors require more development, lower DLs
- Benchtop analyzers require significant O&M time
- Prototype monitors require improved ruggedness
- Additional R&D needed
 - Perform longer-term testing
 - Perform testing in additional WW sources

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