

NBC PFAS Sampling – Developing a Protocol

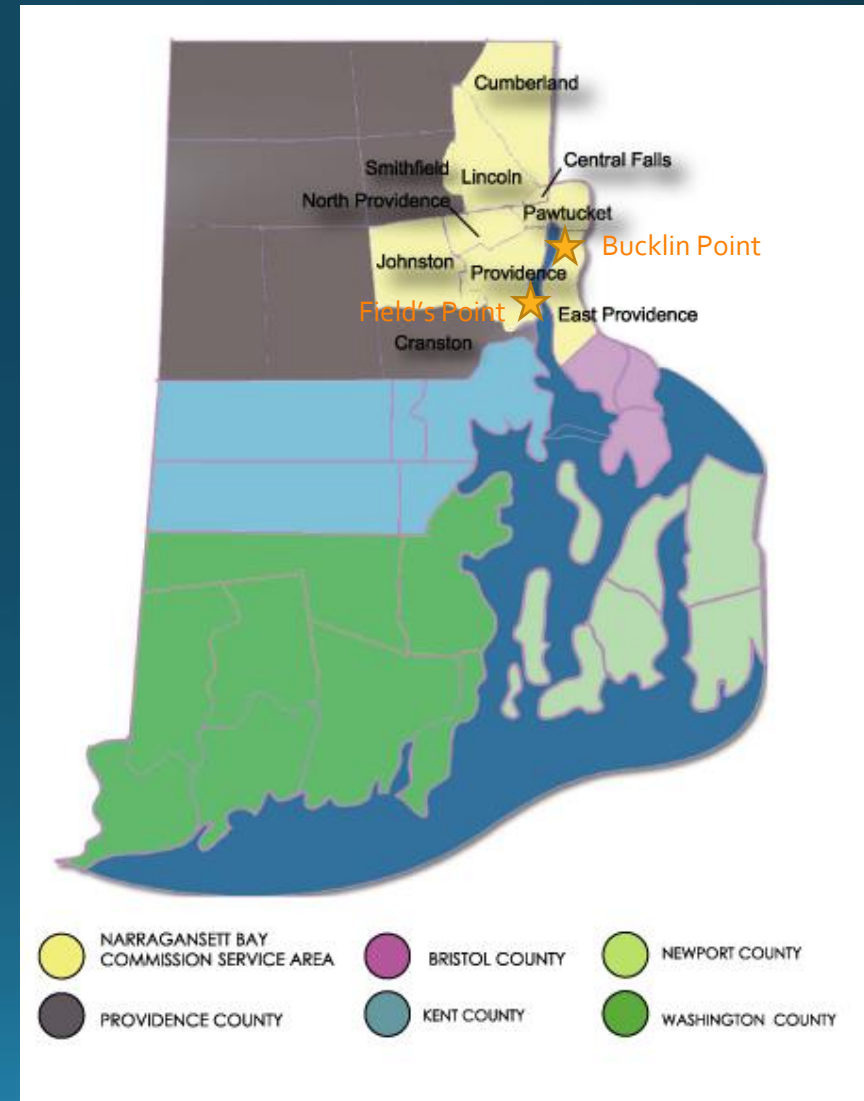
Eliza Moore – Environmental Scientist III, Narragansett Bay Commission
NEWEA PFAS Seminar May 3, 2023



The Narragansett Bay Commission



- Own and operate two largest WWTFs in Rhode Island, USA
- Serving Providence and surrounding towns
- Located at the headwaters of Narragansett Bay
- Current RIPDES permits in effect since 2017 – new permits due anytime



PFAS monitoring

- Monitoring requirements are expected with next permit draft
- **September 2020** – began proactively exploring PFAS
- Guidance on PFAS Sampling = *SCARY* intimidating given existing sampling routines
- Start simple, use blanks and other QC samples to evaluate potential for contamination



CBS News



Initial Protocol Development

- **Blanks**

- Reagent blank – grab sample directly from DI source
- Field blank (influent back-up autosampler) – DI water pumped through the sampler into a clean influent composite carboy, mix with stir bar, pour off via spigot into sample bottle
- Field blank (modified portable autosampler) – similar to above but using the “Modified” sampler.

All data shown today analyzed by contract lab using methods EPA 537m or 537.1m.

DISCLAIMER

“The NBC does not provide any certification concerning the precision or accuracy of such results and provides no assurance that such results are representative of the NBC’s influent, discharge, biosolids, or industrial user discharge.”

First Event

ng/L (ppt)	Direct from DI Unit	Qualifier
PFBA	7.0	U
PFPeA	4.1	U
PFHxA	6.4	U
PFHpA	7.1	U
PFOA	7.4	U
PFNA	4.9	U
PFDA	4.1	U
PFUnA	4.3	U
PFDoA	6.8	U
PFTRDA	6.9	U
PFTEDA	6.7	U
PFBS	5.1	U
PFPeS	7.4	U
PFHxS	5.2	U
PFHpS	3.3	U
PFOS	5.2	U
PFNS	7.0	U
PFDS	7.2	U
PFOSA	6.6	U
EtFOSA	9.0	U
MeFOSA	3.5	U
EtFOSE	9.4	U
MeFOSE	6.6	U
EtFOSAA	8.1	U
MeFOSAA	7.0	U
4:2 FSA	6.6	U
6:2 FSA	5.9	U
8:2 FSA	5.9	U
HFPO-DA	4.7	U
4,8-D-3H-PFNA	4.8	U
F-53B Major	9.3	U
F-53B Minor	5.3	U

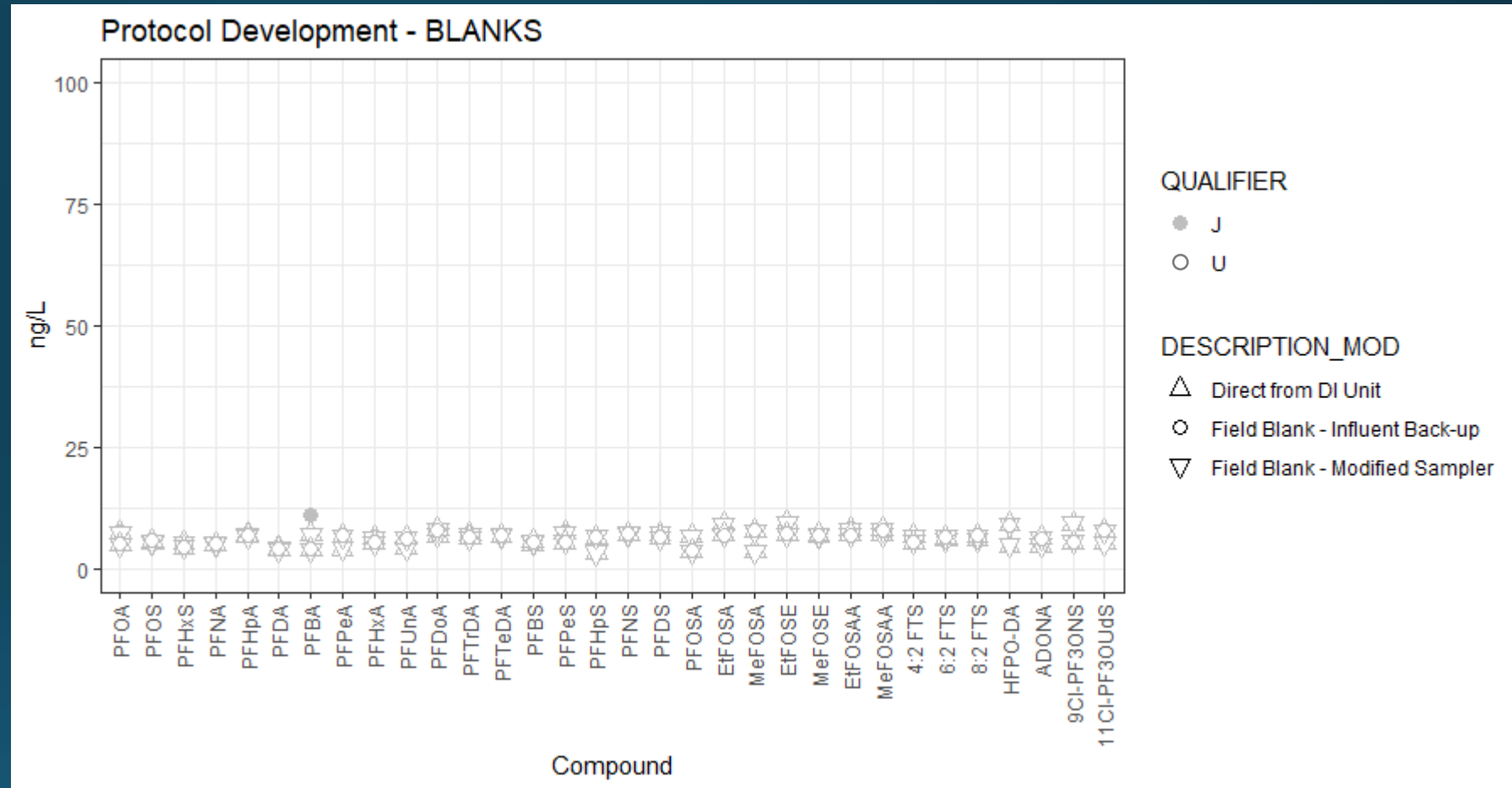
ng/L (ppt)	First Event			
	Direct from DI Unit	Qualifier	Field Blank: Influent Back-up	Qualifier
PFBA	7.0	U	11.0	J
PFPeA	4.1	U	6.0	J
PFHxA	6.4	U	6.4	U
PFHpA	7.1	U	7.1	U
PFOA	7.4	U	7.4	U
PFNA	4.9	U	4.9	U
PFDA	4.1	U	4.1	U
PFUnA	4.3	U	4.3	U
PFDoA	6.8	U	6.8	U
PFTRDA	6.9	U	6.9	U
PFTEDA	6.7	U	6.7	U
PFBS	5.1	U	5.1	U
PFPeS	7.4	U	7.4	U
PFHxS	5.2	U	5.2	U
PFHpS	3.3	U	3.3	U
PFOS	5.2	U	5.2	U
PFNS	7.0	U	7.0	U
PFDS	7.2	U	7.2	U
PFOSA	6.6	U	6.6	U
EtFOSA	9.0	U	9.0	U
MeFOSA	3.5	U	3.5	U
EtFOSE	9.4	U	9.4	U
MeFOSE	6.6	U	6.6	U
EtFOSAA	8.1	U	8.1	U
MeFOSAA	7.0	U	7.0	U
4:2 FSA	6.6	U	6.6	U
6:2 FSA	5.9	U	5.9	U
8:2 FSA	5.9	U	5.9	U
HFPO-DA	4.7	U	4.7	U
4,8-D-3H-PFNA	4.8	U	4.8	U
F-53B Major	9.3	U	9.3	U
F-53B Minor	5.3	U	5.3	U

ng/L (ppt)	First Event					
	Direct from DI Unit	Qualifier	Field Blank: Influent Back-up	Qualifier	Field Blank: Modified Sampler	Qualifier
PFBA	7.0	U	11.0	J	7.0	U
PFPeA	4.1	U	6.0	J	4.1	U
PFHxA	6.4	U	6.4	U	6.4	U
PFHpA	7.1	U	7.1	U	7.1	U
PFOA	7.4	U	7.4	U	7.4	U
PFNA	4.9	U	4.9	U	4.9	U
PFDA	4.1	U	4.1	U	4.1	U
PFUnA	4.3	U	4.3	U	4.3	U
PFDoA	6.8	U	6.8	U	6.8	U
PFTRDA	6.9	U	6.9	U	6.9	U
PFTEDA	6.7	U	6.7	U	6.7	U
PFBS	5.1	U	5.1	U	5.1	U
PFPeS	7.4	U	7.4	U	7.4	U
PFHxS	5.2	U	5.2	U	5.2	U
PFHpS	3.3	U	3.3	U	3.3	U
PFOS	5.2	U	5.2	U	5.2	U
PFNS	7.0	U	7.0	U	7.0	U
PFDS	7.2	U	7.2	U	7.2	U
PFOSA	6.6	U	6.6	U	6.6	U
EtFOSA	9.0	U	9.0	U	9.0	U
MeFOSA	3.5	U	3.5	U	3.5	U
EtFOSE	9.4	U	9.4	U	9.4	U
MeFOSE	6.6	U	6.6	U	6.6	U
EtFOSAA	8.1	U	8.1	U	8.1	U
MeFOSAA	7.0	U	7.0	U	7.0	U
4:2 FSA	6.6	U	6.6	U	6.6	U
6:2 FSA	5.9	U	5.9	U	5.9	U
8:2 FSA	5.9	U	5.9	U	5.9	U
HFPO-DA	4.7	U	4.7	U	4.7	U
4,8-D-3H-PFNA	4.8	U	4.8	U	4.8	U
F-53B Major	9.3	U	9.3	U	9.3	U
F-53B Minor	5.3	U	5.3	U	5.3	U

ng/L (ppt)	Second Event					
	Direct from DI Unit	Qualifier	Field Blank: Influent Back-up	Qualifier	Field Blank: Modified Sampler	Qualifier
PFBA	3.9	U	3.9	U	3.9	U
PFPeA	6.7	U	6.7	U	6.7	U
PFHxA	5.3	U	5.3	U	5.3	U
PFHpA	6.7	U	6.7	U	6.7	U
PFOA	5.0	U	5.0	U	5.0	U
PFNA	5.1	U	5.1	U	5.1	U
PFDA	3.9	U	3.9	U	3.9	U
PFUnA	6.2	U	6.2	U	6.2	U
PFDoA	8.0	U	8.0	U	8.0	U
PFTRDA	6.4	U	6.4	U	6.4	U
PFTEDA	6.8	U	6.8	U	6.8	U
PFBS	5.6	U	5.6	U	5.6	U
PFPeS	5.5	U	5.5	U	5.5	U
PFHxS	4.4	U	4.4	U	4.4	U
PFHpS	6.5	U	6.5	U	6.5	U
PFOS	5.7	U	5.7	U	5.7	U
PFNS	7.2	U	7.2	U	7.2	U
PFDS	6.4	U	6.4	U	6.4	U
PFOSA	3.6	U	3.6	U	3.6	U
EtFOSA	7.0	U	7.0	U	7.0	U
MeFOSA	7.8	U	7.8	U	7.8	U
EtFOSE	7.1	U	7.1	U	7.1	U
MeFOSE	7.0	U	7.0	U	7.0	U
EtFOSAA	7.0	U	7.0	U	7.0	U
MeFOSAA	8.0	U	8.0	U	8.0	U
4:2 FSA	5.4	U	5.4	U	5.4	U
6:2 FSA	6.5	U	6.5	U	6.5	U
8:2 FSA	6.7	U	6.7	U	6.7	U
HFPO-DA	9.0	U	9.0	U	9.0	U
4,8-D-3H-PFNA	6.3	U	6.3	U	6.3	U
F-53B Major	5.4	U	5.4	U	5.4	U
F-53B Minor	7.7	U	7.7	U	7.7	U

- Blanks

- All results <Reporting Limit
- MOST results <Detection Limit



Initial Protocol Development

- **Blanks**

- Reagent blank – grab sample directly from DI source
- Field blank (influent back-up autosampler) – DI water pumped through the sampler into a clean influent composite carboy, mix with stir bar, pour off via spigot into sample bottle
- Field blank (modified portable autosampler) – similar to above but using the “Modified” sampler.

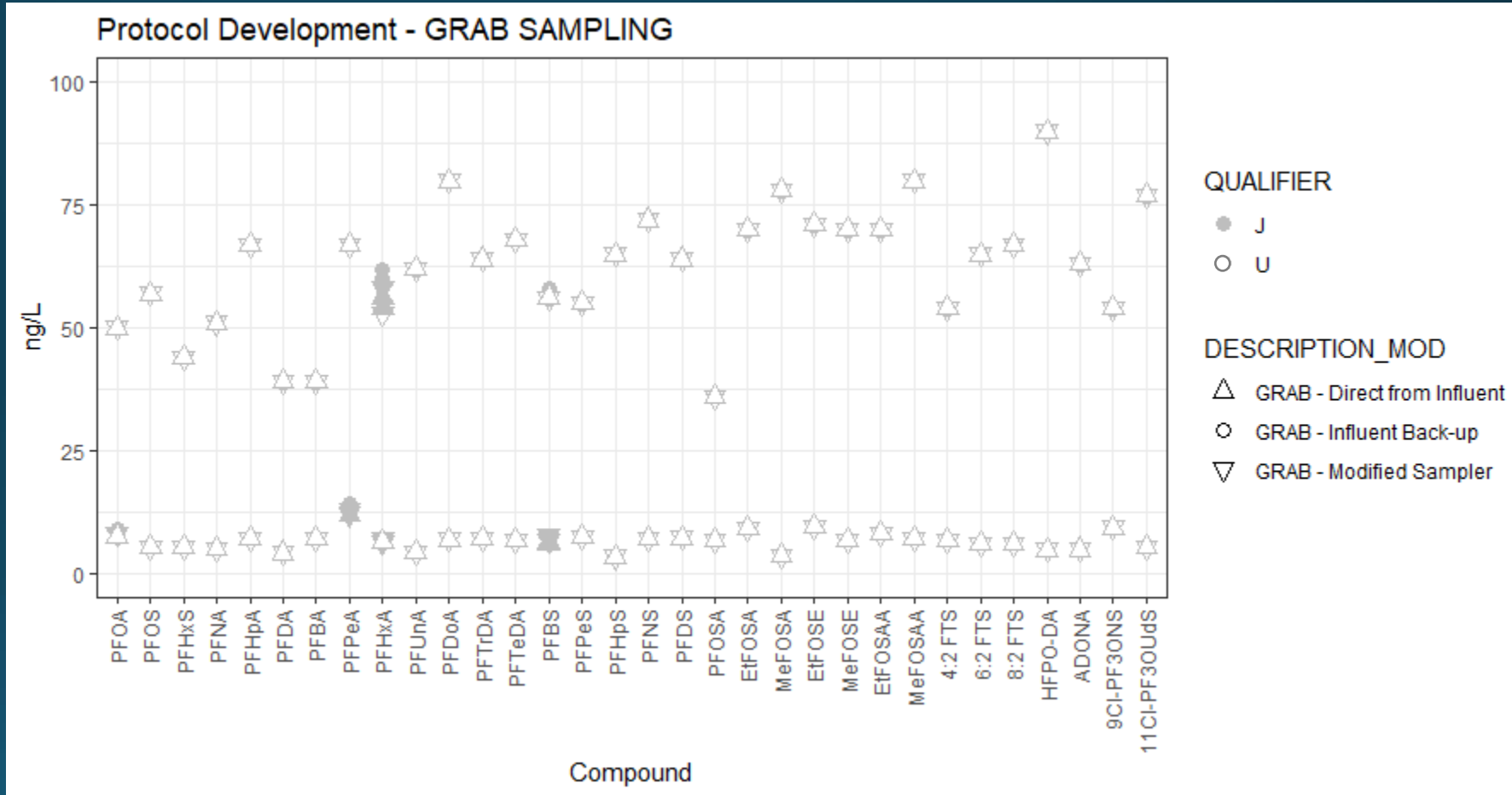
- Evaluate **sampling equipment and methods** (collected as concurrently as possible)

- Grab sample direct from influent (in duplicate)
- Pumped grab sample into 125 mL sample container using influent back-up autosampler
- Pumped grab sample into 125 mL sample container using modified portable autosampler

ng/L (ppt)	Direct grab from Influent	Qualifier	Direct grab from Influent DUP	Qualifier
PFBA	7.0	U	7.0	U
PFPeA	12.0	J	12.0	J
PFHxA	6.4	U	6.4	U
PFFHpA	7.1	U	7.1	U
PFOA	7.4	J	7.4	U
PFNA	4.9	U	4.9	U
PFDA	4.1	U	4.1	U
PFOUnA	4.3	U	4.3	U
PFDDoA	6.8	U	6.8	U
PFTRDA	6.9	U	6.9	U
PFTEDA	6.7	U	6.7	U
PFBS	6.0	J	6.2	J
PFPeS	7.4	U	7.4	U
PFHxS	5.2	U	5.2	U
PFFHpS	3.3	U	3.3	U
PFOS	5.2	U	5.2	U
PFNS	7.0	U	7.0	U
PFDS	7.2	U	7.2	U
PFOSA	6.6	U	6.6	U
EtFOSA	9.0	U	9.0	U
MeFOSA	3.5	U	3.5	U
EtFOSE	9.4	U	9.4	U
MeFOSE	6.6	U	6.6	U
EtFOSAA	8.1	U	8.1	U
MeFOSAA	7.0	U	7.0	U
4:2 FSA	6.6	U	6.6	U
6:2 FSA	5.9	U	5.9	U
8:2 FSA	5.9	U	5.9	U
HFPO-DA	4.7	U	4.7	U
4,8-D-3H-PFNA	4.8	U	4.8	U
F-53B Major	9.3	U	9.3	U
F-53B Minor	5.3	U	5.3	U

ng/L (ppt)	First Event							
	Direct grab from Influent	Qualifier	Direct grab from Influent DUP	Qualifier	Grab - Influent Back-up Sampler	Qualifier	Grab - Influent Back-up Sampler DUP	Qualifier
PFBA	7.0	U	7.0	U	7.1	J	7.0	U
PFPeA	12.0	J	12.0	J	14.0	J	14.0	J
PFHxA	6.4	U	6.4	U	7.0	J	7.1	J
PFHpA	7.1	U	7.1	U	7.1	U	7.1	U
PFOA	7.4	J	7.4	U	8.8	J	8.6	J
PFNA	4.9	U	4.9	U	4.9	U	4.9	U
PFDA	4.1	U	4.1	U	4.1	U	4.1	U
PFUnA	4.3	U	4.3	U	4.3	U	4.3	U
PFDoA	6.8	U	6.8	U	6.8	U	6.8	U
PFTRDA	6.9	U	6.9	U	6.9	U	6.9	U
PFTEDA	6.7	U	6.7	U	6.7	U	6.7	U
PFBS	6.0	J	6.2	J	6.5	J	6.7	J
PFPeS	7.4	U	7.4	U	7.4	U	7.4	U
PFHxS	5.2	U	5.2	U	5.2	U	5.2	U
PFHpS	3.3	U	3.3	U	3.3	U	3.3	U
PFOS	5.2	U	5.2	U	5.2	U	5.2	U
PFNS	7.0	U	7.0	U	7.0	U	7.0	U
PFDS	7.2	U	7.2	U	7.2	U	7.2	U
PFOSA	6.6	U	6.6	U	6.6	U	6.6	U
EtFOSA	9.0	U	9.0	U	9.0	U	9.0	U
MeFOSA	3.5	U	3.5	U	3.5	U	3.5	U
EtFOSE	9.4	U	9.4	U	9.4	U	9.4	U
MeFOSE	6.6	U	6.6	U	6.6	U	6.6	U
EtFOSAA	8.1	U	8.1	U	8.1	U	8.1	U
MeFOSAA	7.0	U	7.0	U	7.0	U	7.0	U
4:2 FSA	6.6	U	6.6	U	6.6	U	6.6	U
6:2 FSA	5.9	U	5.9	U	5.9	U	5.9	U
8:2 FSA	5.9	U	5.9	U	5.9	U	5.9	U
HFPO-DA	4.7	U	4.7	U	4.7	U	4.7	U
4,8-D-3H-PFNA	4.8	U	4.8	U	4.8	U	4.8	U
F-53B Major	9.3	U	9.3	U	9.3	U	9.3	U
F-53B Minor	5.3	U	5.3	U	5.3	U	5.3	U

- Influent Grab Samples
 - MOST results <Detection limit
 - PFOA, PFPeA, PFHxA, PFBS detected (J-qualified)



Initial Protocol Development

- **Blanks**

- Reagent blank – grab sample directly from DI source
- Field blank (influent back-up autosampler) – DI water pumped through the sampler into a clean influent composite carboy, mix with stir bar, pour off via spigot into sample bottle
- Field blank (modified portable autosampler) – similar to above but using the “Modified” sampler.

- **Evaluate sampling equipment and methods** (collected as concurrently as possible)

- Grab sample direct from influent (in duplicate)
- Pumped grab sample into 125 mL sample container using influent back-up autosampler
- Pumped grab sample into 125 mL sample container using modified portable autosampler

- **Evaluate composite sampling**

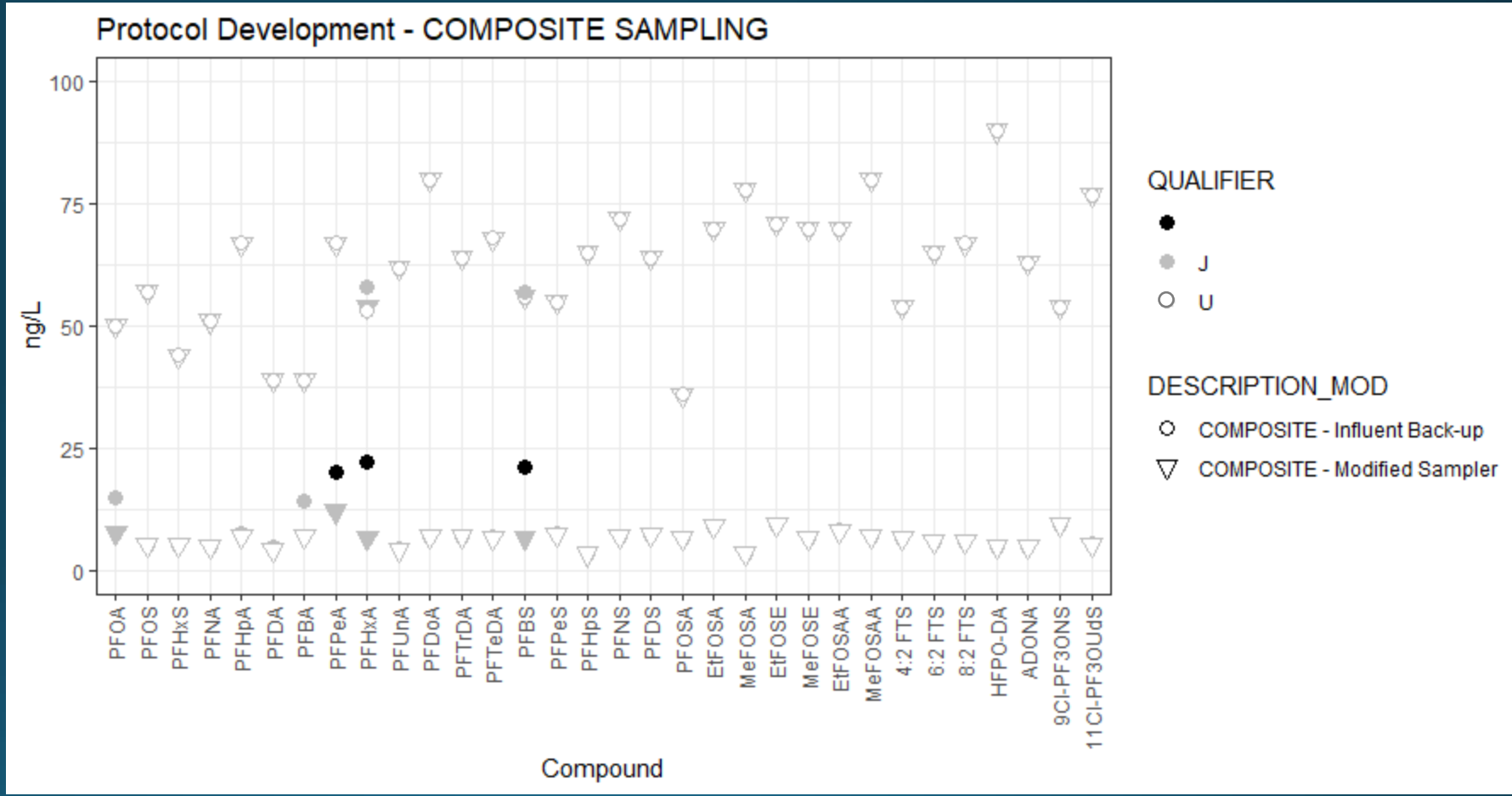
- Poured-off sample direct from influent back-up composite carboy (non-Teflon)
- Poured-off sample from 250 mL composite, collected over same time period as above using modified portable autosampler

ng/L (ppt)	First Event			
	24-hr Composite - Influent Back-up Sampler	Qualifier	24-hr Composite Modified Sampler	Qualifier
PFBA	14.0	J	7.0	U
PFPeA	20.0		12.0	J
PFHxA	22.0		6.5	J
PFHpA	7.4	J	7.1	U
PFOA	15.0	J	7.8	J
PFNA	4.9	U	4.9	U
PFDA	4.6	J	4.1	U
PFUnA	4.3	U	4.3	U
PFDoA	6.8	U	6.8	U
PFTRDA	6.9	U	6.9	U
PFTEDA	6.7	U	6.7	U
PFBS	21.0		6.7	J
PFPeS	7.4	U	7.4	U
PFHxS	5.2	U	5.2	U
PFHpS	3.3	U	3.3	U
PFOS	5.2	U	5.2	U
PFNS	7.0	U	7.0	U
PFDS	7.2	U	7.2	U
PFOSA	6.6	U	6.6	U
EtFOSA	9.0	U	9.0	U
MeFOSA	3.5	U	3.5	U
EtFOSE	9.4	U	9.4	U
MeFOSE	6.6	U	6.6	U
EtFOSAA	8.1	U	8.1	U
MeFOSAA	7.0	U	7.0	U
4:2 FSA	6.6	U	6.6	U
6:2 FSA	5.9	U	5.9	U
8:2 FSA	5.9	U	5.9	U
HFPO-DA	4.7	U	4.7	U
4,8-D-3H-PFNA	4.8	U	4.8	U
F-53B Major	9.3	U	9.3	U
F-53B Minor	5.3	U	5.3	U

ng/L (ppt)	Second Event					
	24-hr Composite - Influent Back-up Sampler	Qualifier	24-hr Composite - Influent Back-up Sampler DUP	Qualifier	24-hr Composite - Modified Sampler	Qualifier
PFBA	39	U	39	U	39	U
PFPeA	67	U	67	U	67	U
PFHxA	58	J	53	U	54	J
PFHpA	67	U	67	U	67	U
PFOA	50	U	50	U	50	U
PFNA	51	U	51	U	51	U
PFDA	39	U	39	U	39	U
PFUnA	62	U	62	U	62	U
PFDoA	80	U	80	U	80	U
PFTRDA	64	U	64	U	64	U
PFTEDA	68	U	68	U	68	U
PFBS	56	U	57	J	56	U
PFPeS	55	U	55	U	55	U
PFHxS	44	U	44	U	44	U
PFHpS	65	U	65	U	65	U
PFOS	57	U	57	U	57	U
PFNS	72	U	72	U	72	U
PFDS	64	U	64	U	64	U
PFOSA	36	U	36	U	36	U
EtFOSA	70	U	70	U	70	U
MeFOSA	78	U	78	U	78	U
EtFOSE	71	U	71	U	71	U
MeFOSE	70	U	70	U	70	U
EtFOSAA	70	U	70	U	70	U
MeFOSAA	80	U	80	U	80	U
4:2 FSA	54	U	54	U	54	U
6:2 FSA	65	U	65	U	65	U
8:2 FSA	67	U	67	U	67	U
HFPO-DA	90	U	90	U	90	U
4,8-D-3H-PFNA	63	U	63	U	63	U
F-53B Major	54	U	54	U	54	U
F-53B Minor	77	U	77	U	77	U

- Influent Composite Samples

- MOST results <Detection limit
- Actual detections of PFPeA, PFHxA, PFBS



Protocol Development QC Samples

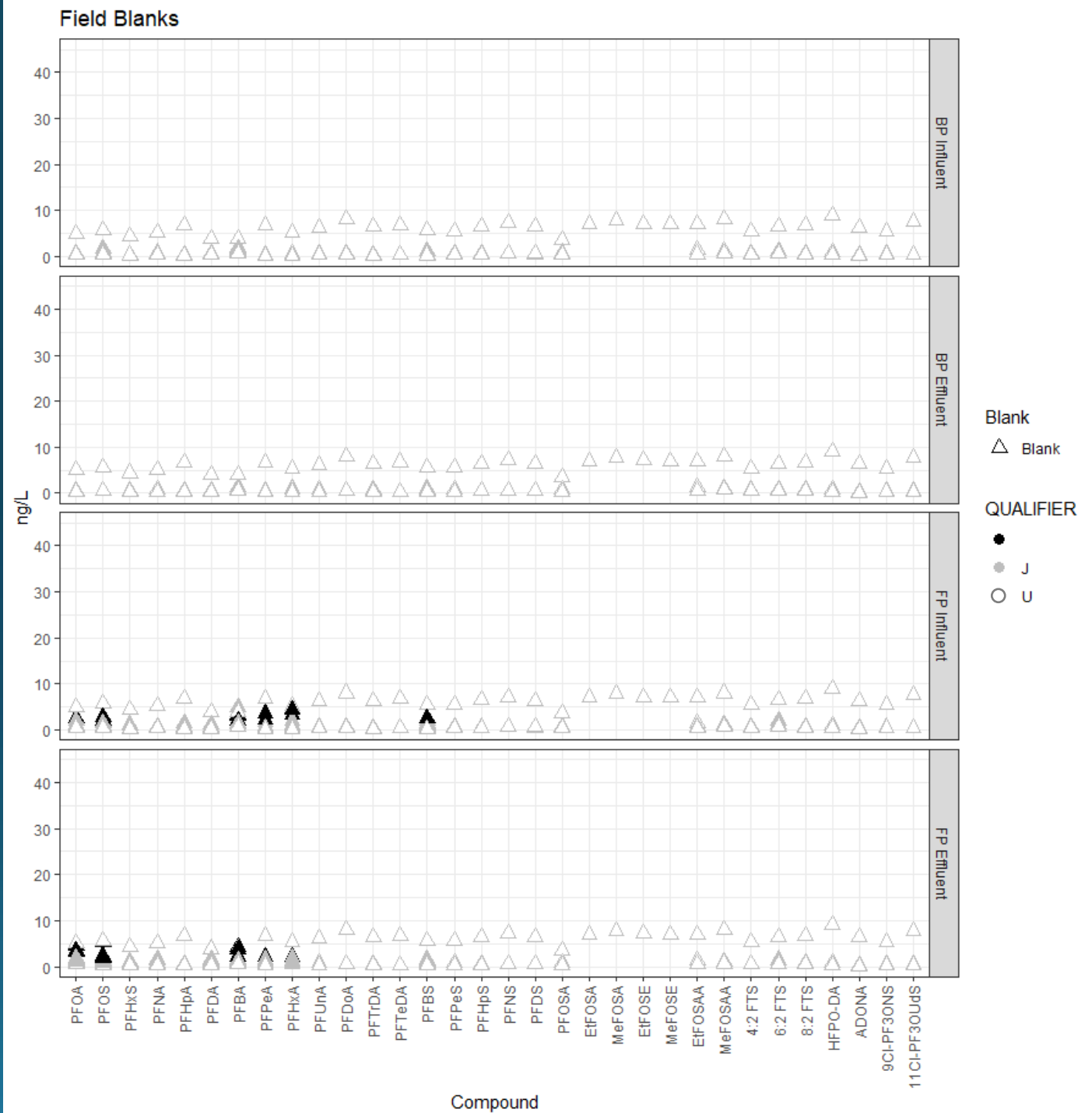
- No evidence of blank contamination in DI water source
- Limited evidence of blank contamination using autosamplers (influent back-up or modified)
- Limited evidence of contamination by autosampler use
- Final selection - **Influent back-up sampler** – pour-off of 24-hour composite sample selected for protocol
 - Potential contamination appeared low
 - Allows minimal disruption to existing sampling routine
 - More representative than a grab sample

Commence sampling...

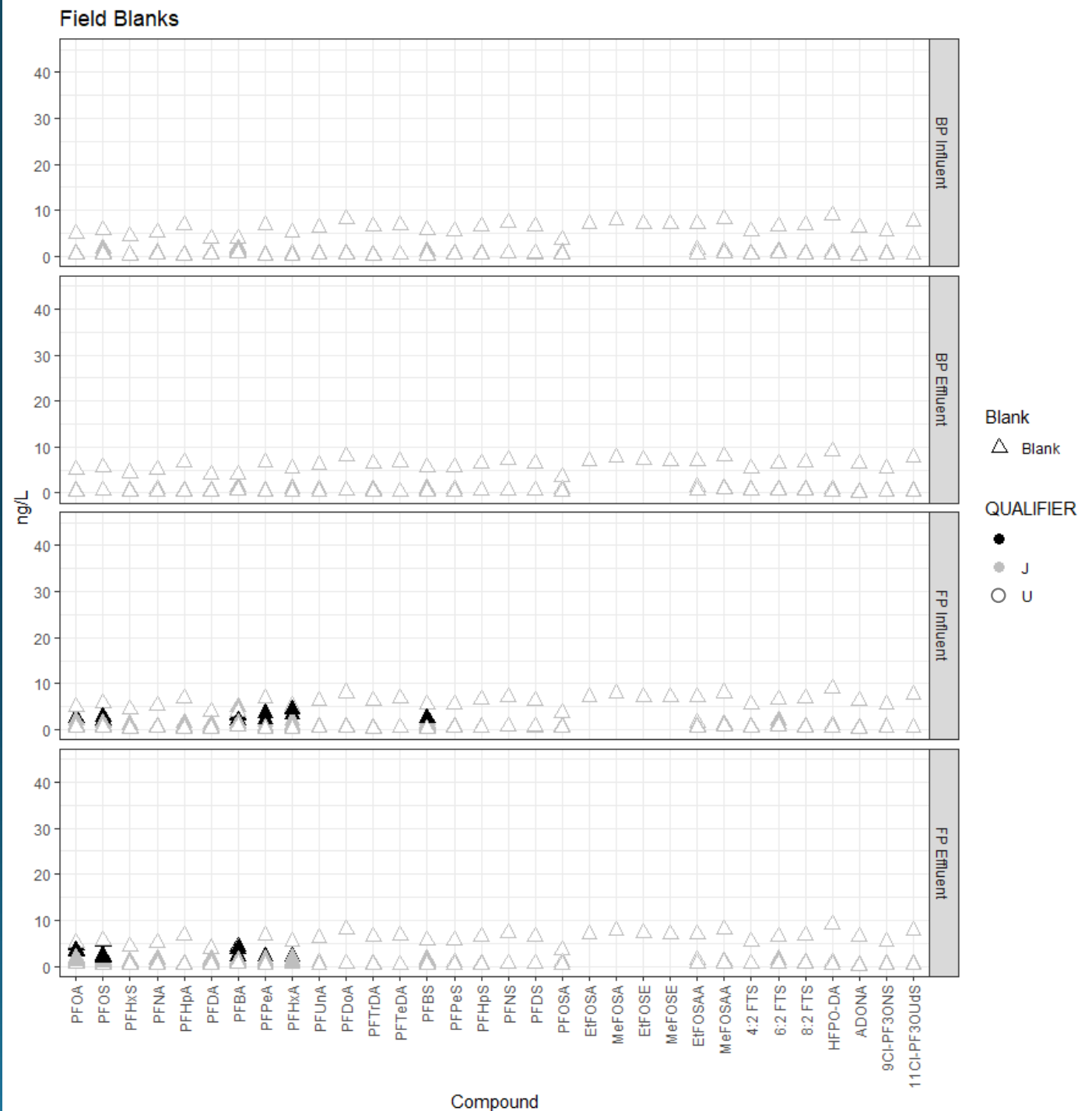
- Influent and effluent samples collected ~monthly at Bucklin Point and Field's Point WWTFs
- Field blanks collected with each monthly event
- All data considered exploratory and non-reportable



- Field Blanks collected 2020-present
 - Field's Point detections generally <5 ng/L
 - Bucklin Point < Reporting Limit



- Field Blanks collected 2020-present
 - Field's Point detections generally <5 ng/L
 - Bucklin Point < Reporting Limit
- Detections in blanks are low relative to true sample results



Conclusions

- Minimal evidence of sample contamination using routine sample collection methods



- Potential interference of very small magnitude may be important for compliance
- Need to reevaluate methodology as EPA-approved method implemented

Thank you!

- Eliza Moore - Environmental Scientist III emoore@narrabay.com
- Appreciations to NBC Environmental Monitoring, Technical Analysis and Compliance, and Laboratory staff for their support and sample handling.

The Narragansett Bay Commission's mission is to maintain a leadership role in the protection and enhancement of water quality in Narragansett Bay and its tributaries by providing safe and reliable wastewater collection and treatment services to its customers at a reasonable cost.



