6PPDQ Stormwater Field Protocol Development

T. Clark and Dylan Ahearn

Stormwater Work Group 6PPD

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HERRERA
Science + Planning + Design


Tubing
Material
Carboy
Material &
Time of Contact

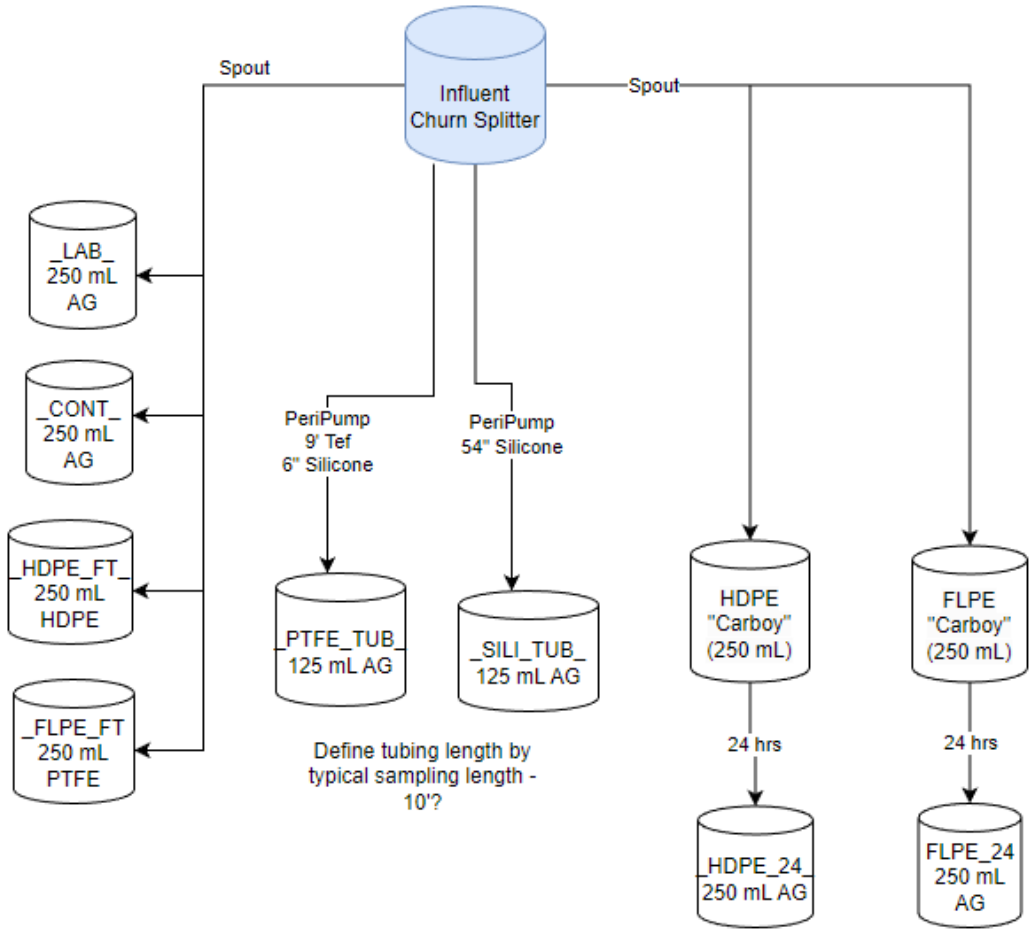
Experimental Groups

Code	Description	Purpose
CONT	**Control sample -** Amber glass bottle filled directly from churn splitter and **Field Duplicate**	Control + Field Duplicate
HDPE_FT	**HDPE bottle sample -** Bottle filled directly from churn splitter, held in bottle until analysis.	Evaluate 6PPD-q loss due to sorption to HDPE
HDPE_24	**HDPE "carboy" sample -** Bottle filled directly from churn splitter, held in bottle for 24 hours prior to transfer to amber glass bottle at laboratory.	Emulate typical HDPE exposure time for composite sampling and evaluate 6PPD-q loss due to sorption to HDPE.
FLPE_FT	**FLPE bottle sample -** Bottle filled directly from churn splitter, held in FLPE bottle until analysis.	Evaluate 6PPD-q loss due to sorption to FLPE
FLPE_24	**FLPE "carboy" sample -** Bottle filled directly from churn splitter, held in bottle for 24 hours prior to transfer to amber gloss bottle at laboratory.	Emulate typical FLPE exposure time for composite sampling and evaluate 6PPD-q loss due to sorption to FLPE.
PTFE_TUB	**PTFE Tubing -** PTFE tubing (10-feet) attached to silicone tubing (1-foot) within a peristaltic pump will be used to extract water from the churn splitter to fill sample bottle	Evaluate 6PPD-q loss due to use of a PTFE-to-Silicone tubing and peristaltic pump sampling method
SILI_TUB	**Silicone Tubing -** Silicone tubing (2-feet) within a peristaltic pump will be used to extract water from the churn splitter to fill sample bottle	Evaluate 6PPD-q loss due to use of a silicone tubing and peristaltic pump sampling method

Equipment and Lab Testing

SampleName Structure
EQUIP_[IN/OUT]_[GROUP]_[GRAB #]
(eg EQUIP_OUT_HOLD48_9)
Bottles can come come pre-labeled

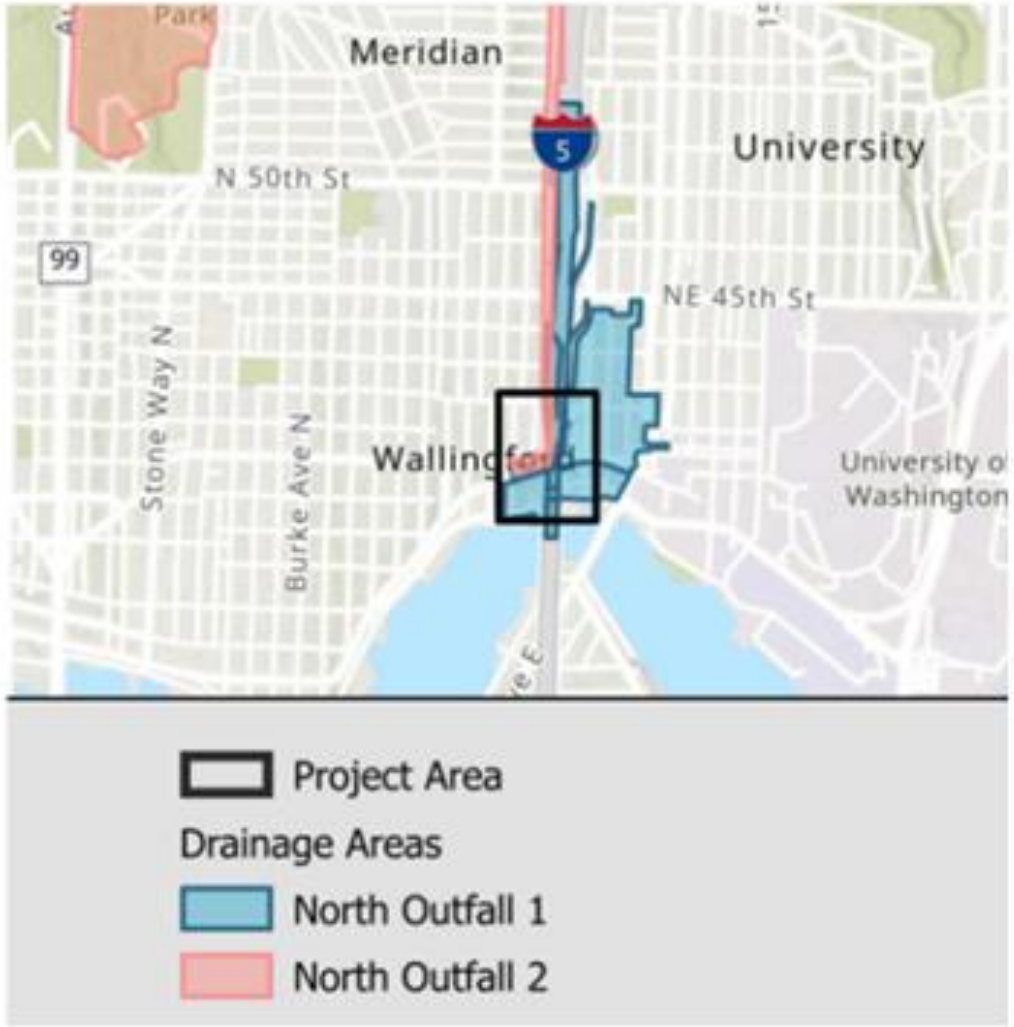
EACH SAMPLE = ~ **13 L into churn splitter**
Fresh Tubing?!?!
6 125-mL AGs direct
2 1.5-gal carboys (fresh?)
2 125-mL AGs (indirect from carboys)



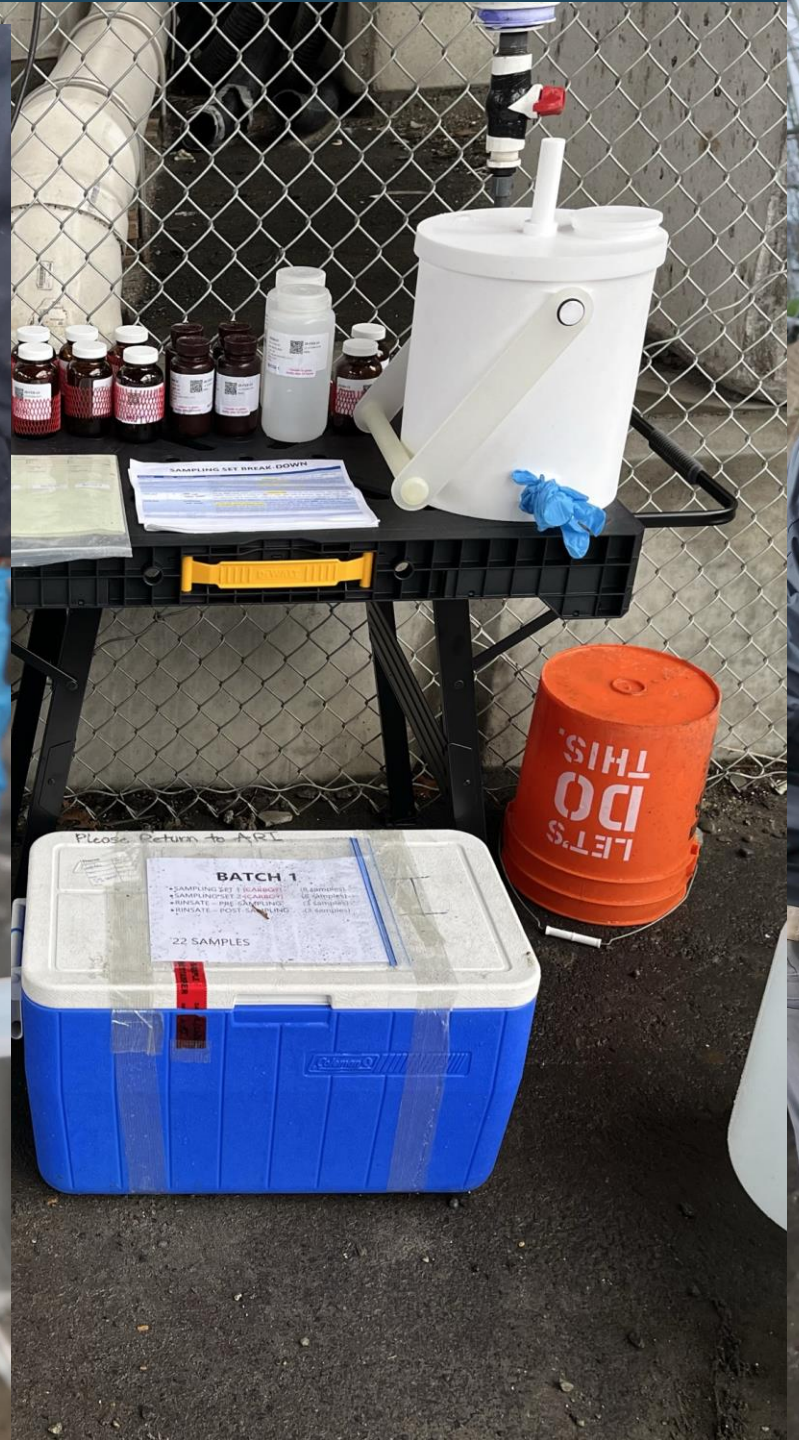
Field Sheet
Protocol Equipment Testing

table with columns:

- Influent/Effluent: (pre-fill
- Grab #: (pre-filled 1-10)
- Date:
- Time:
- Notes:
- Check Box for each gro

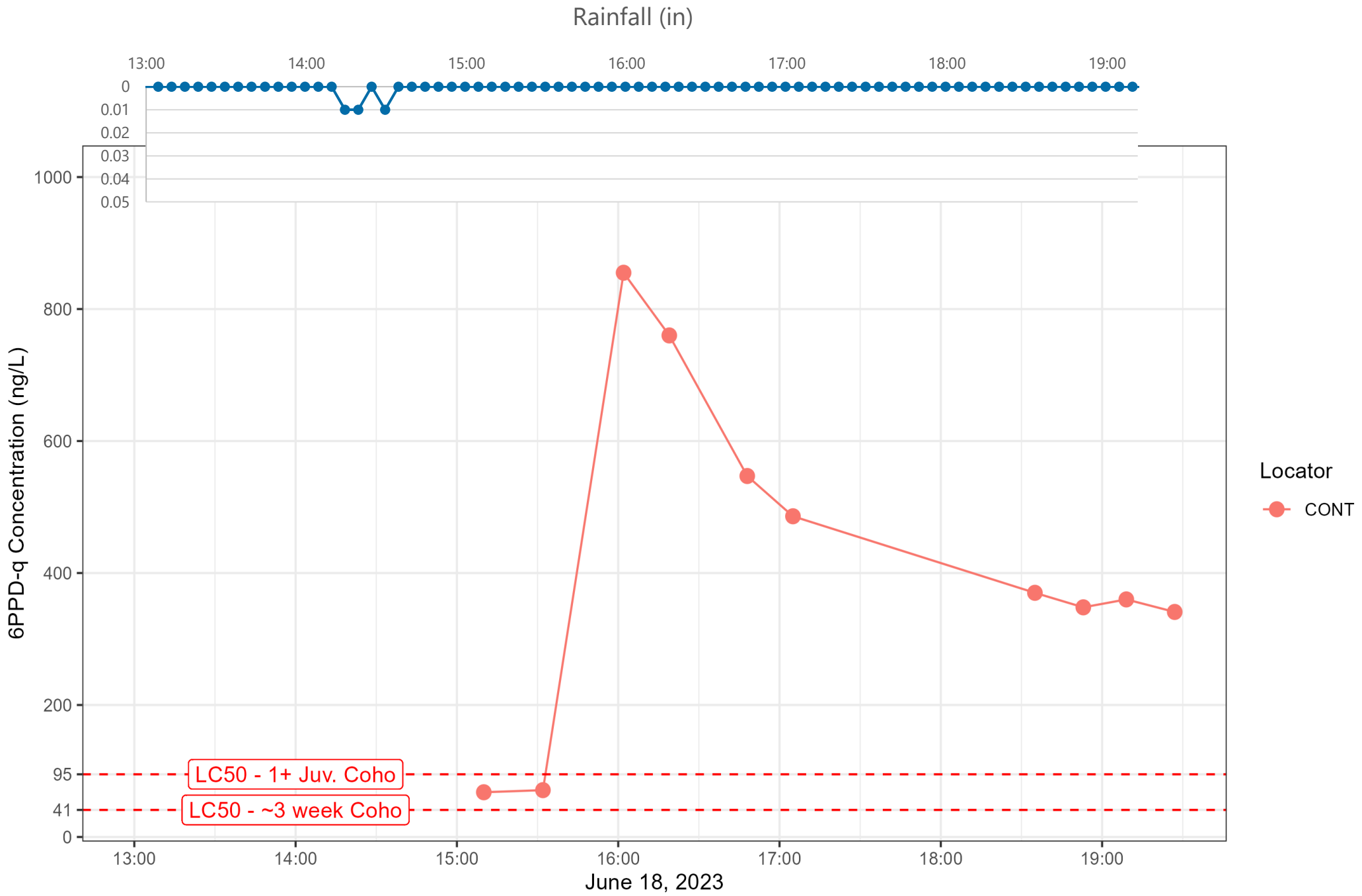


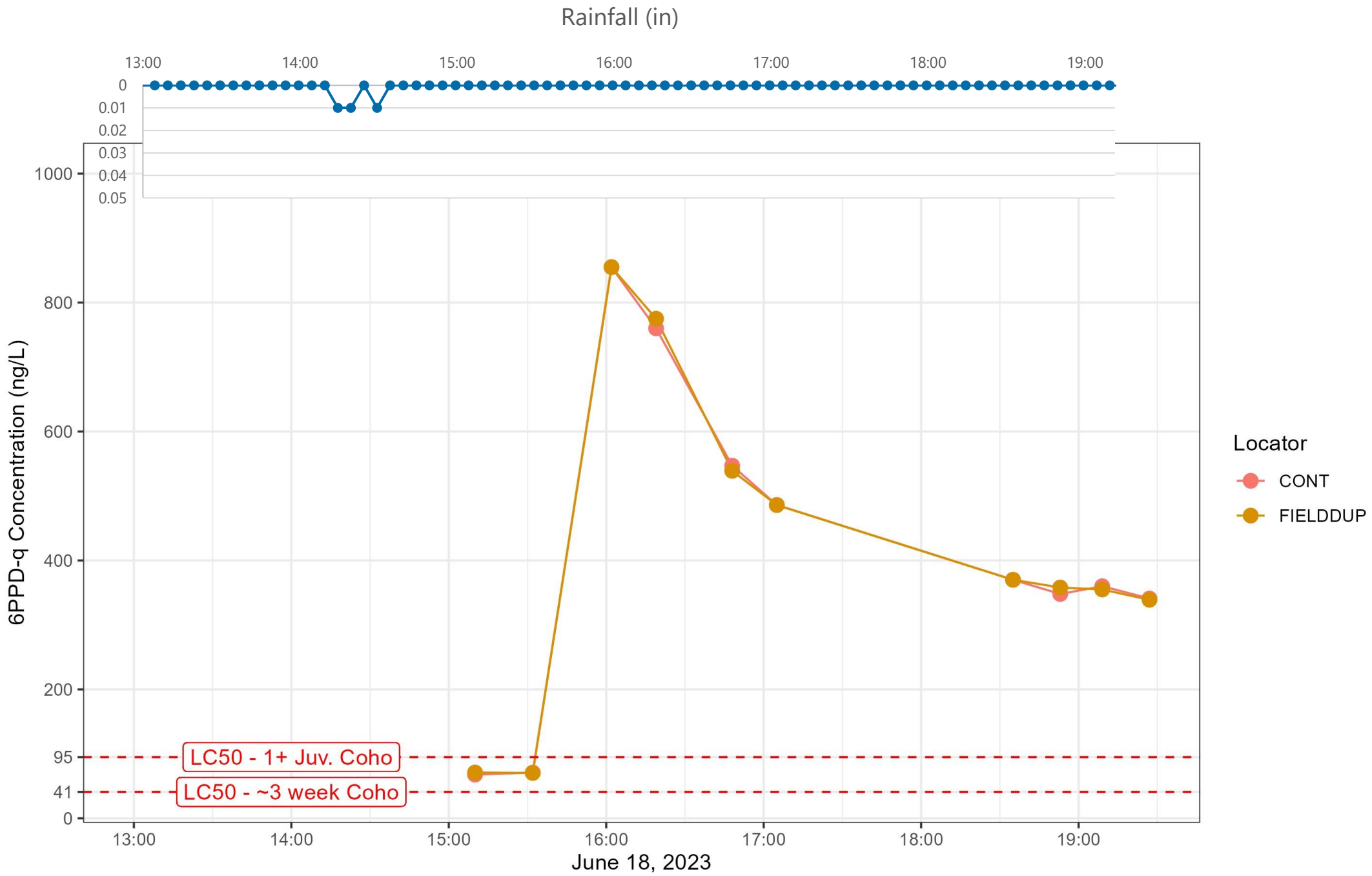
SCTF drainage area in blue. Seattle, Washington.


SAMPLING SET BREAK-DOWN
Please Return to ARL
BATCH 1
22 SAMPLES
LET'S DO THIS.


41
43


STOP


Rainfall (in)
13:00
14:00
15:00
16:00
17:00
18:00
19:00
0
0.01
0.02
0.03
0.04
0.05
1000
800
600
400
200
95
41
0
6PPD-q Concentration (ng/L)
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT


Rainfall (in)
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18:00
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0.05
1000
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600
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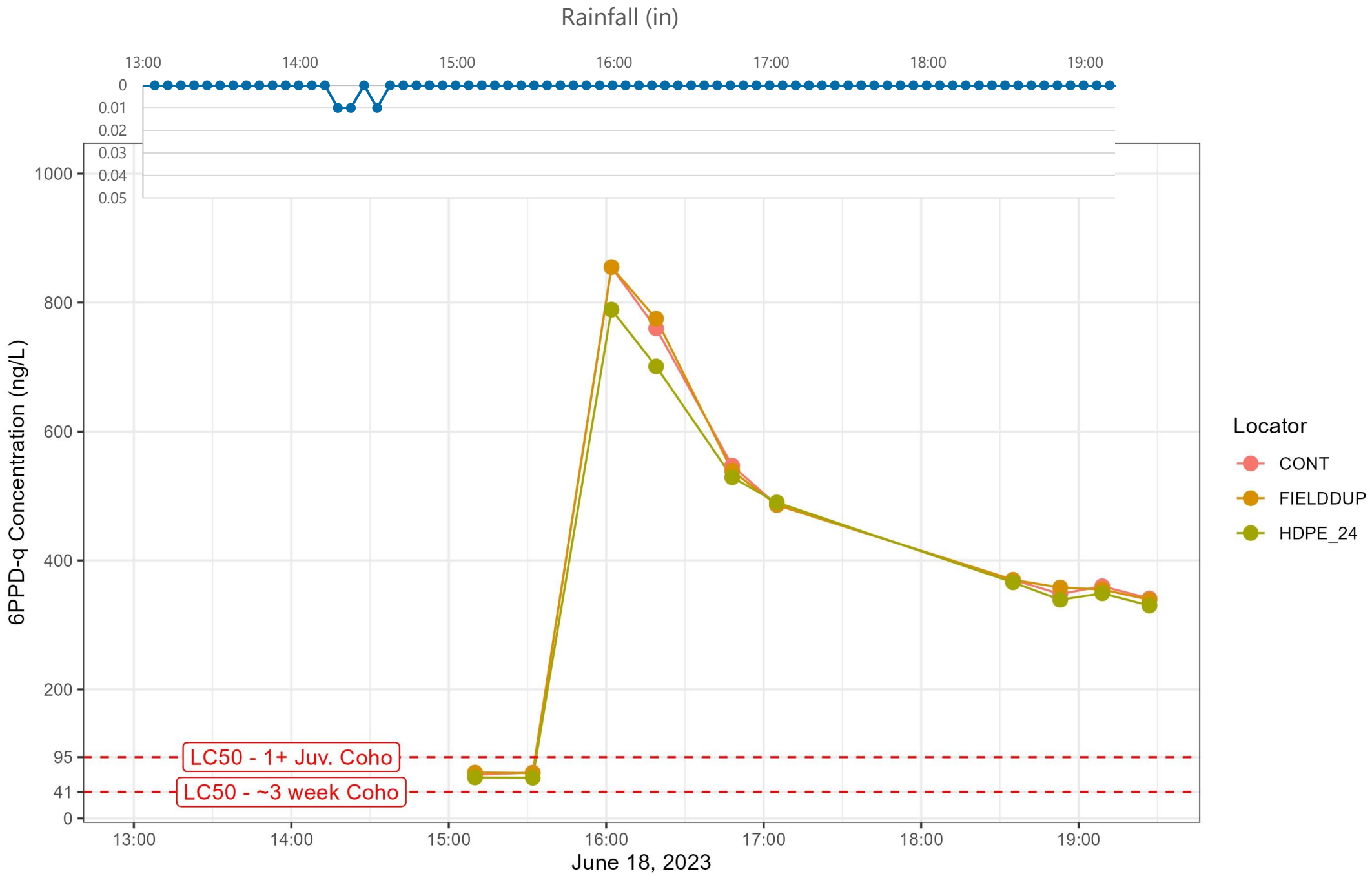
200
95
41
0
6PPD-q Concentration (ng/L)
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP


Rainfall (in)
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15:00
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17:00
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1000
800
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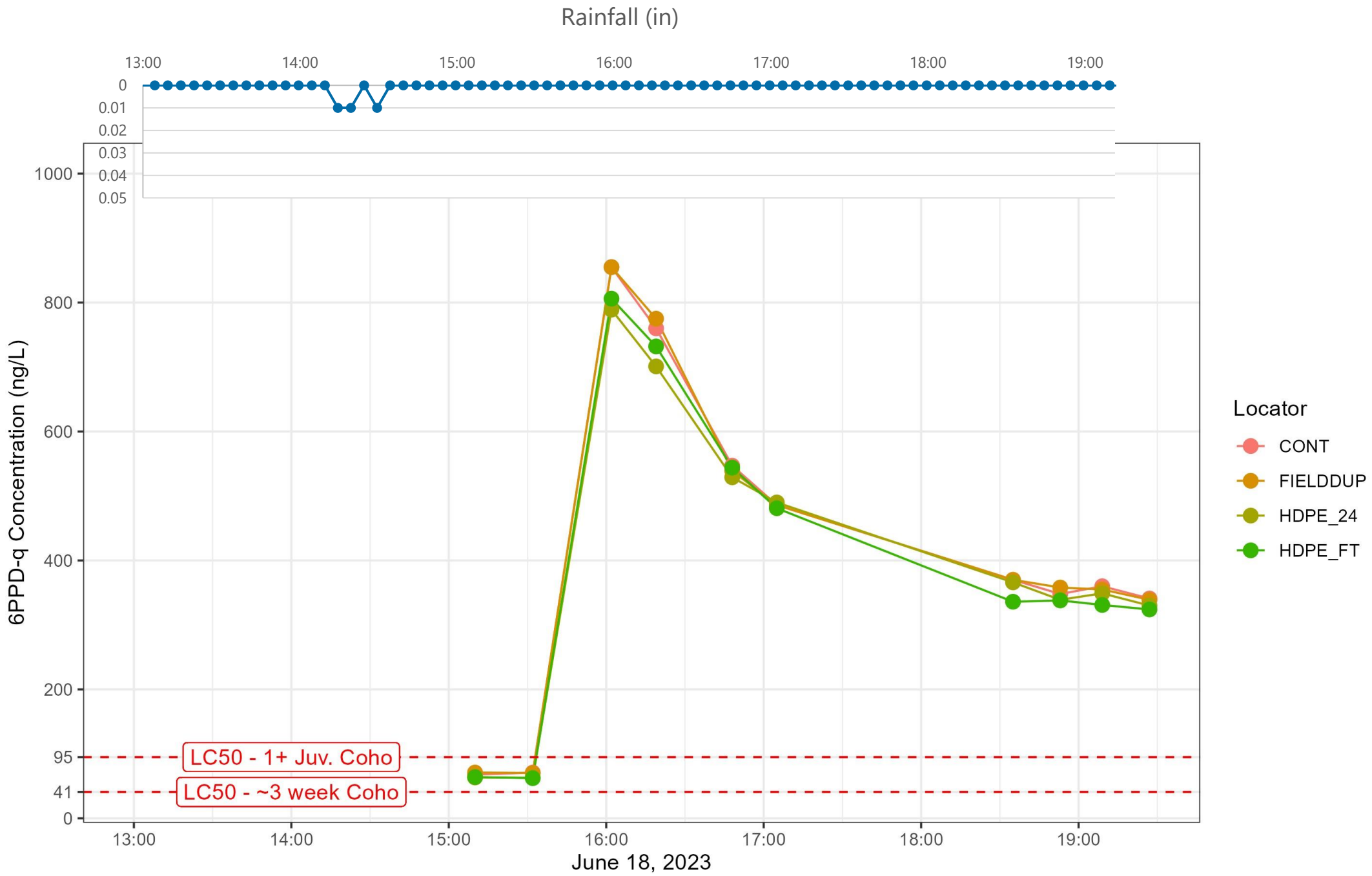
400
200
95
41
0
6PPD-q Concentration (ng/L)
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP
HDPE_24


Rainfall (in)
13:00
14:00
15:00
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17:00
18:00
19:00
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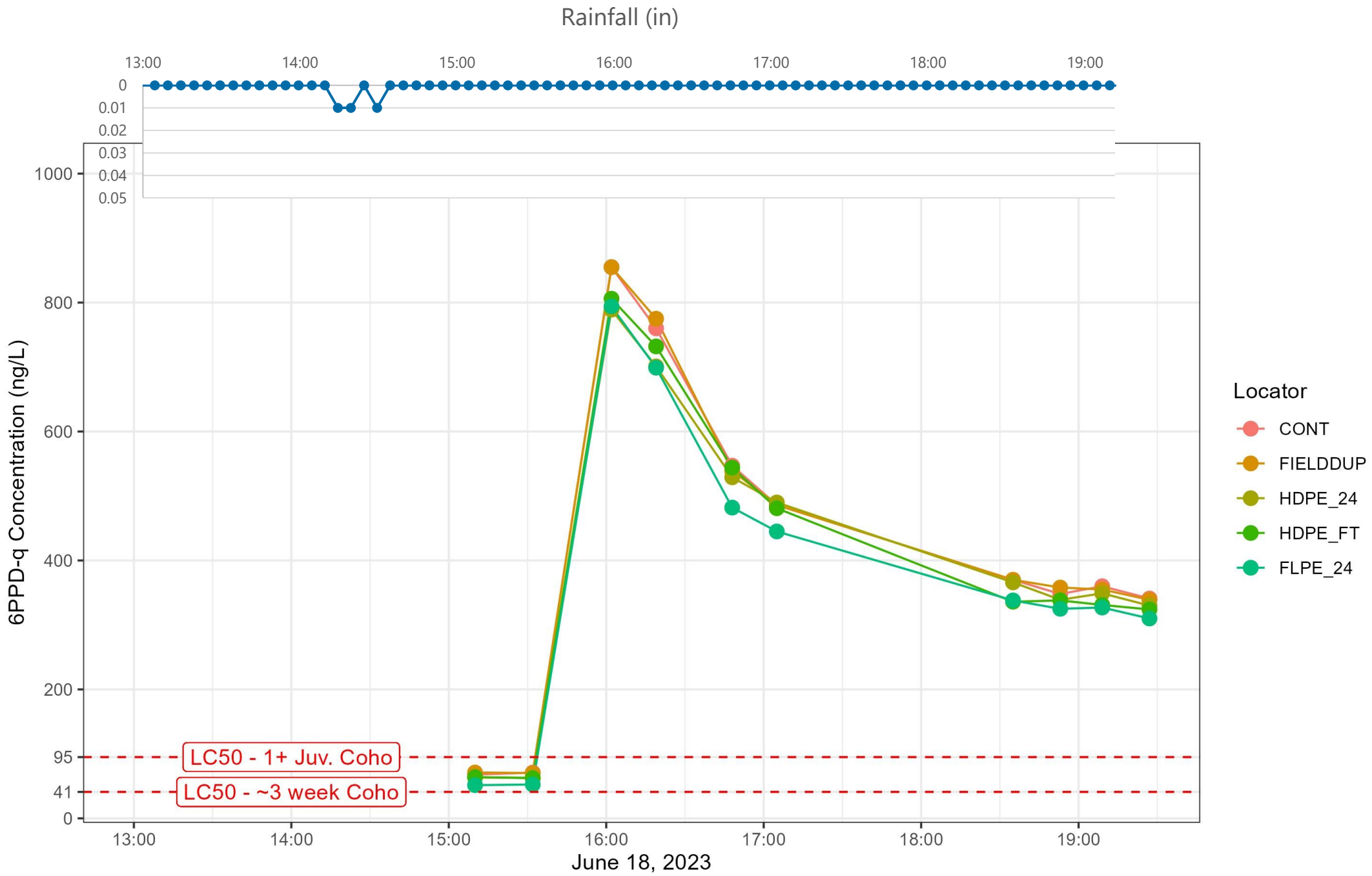
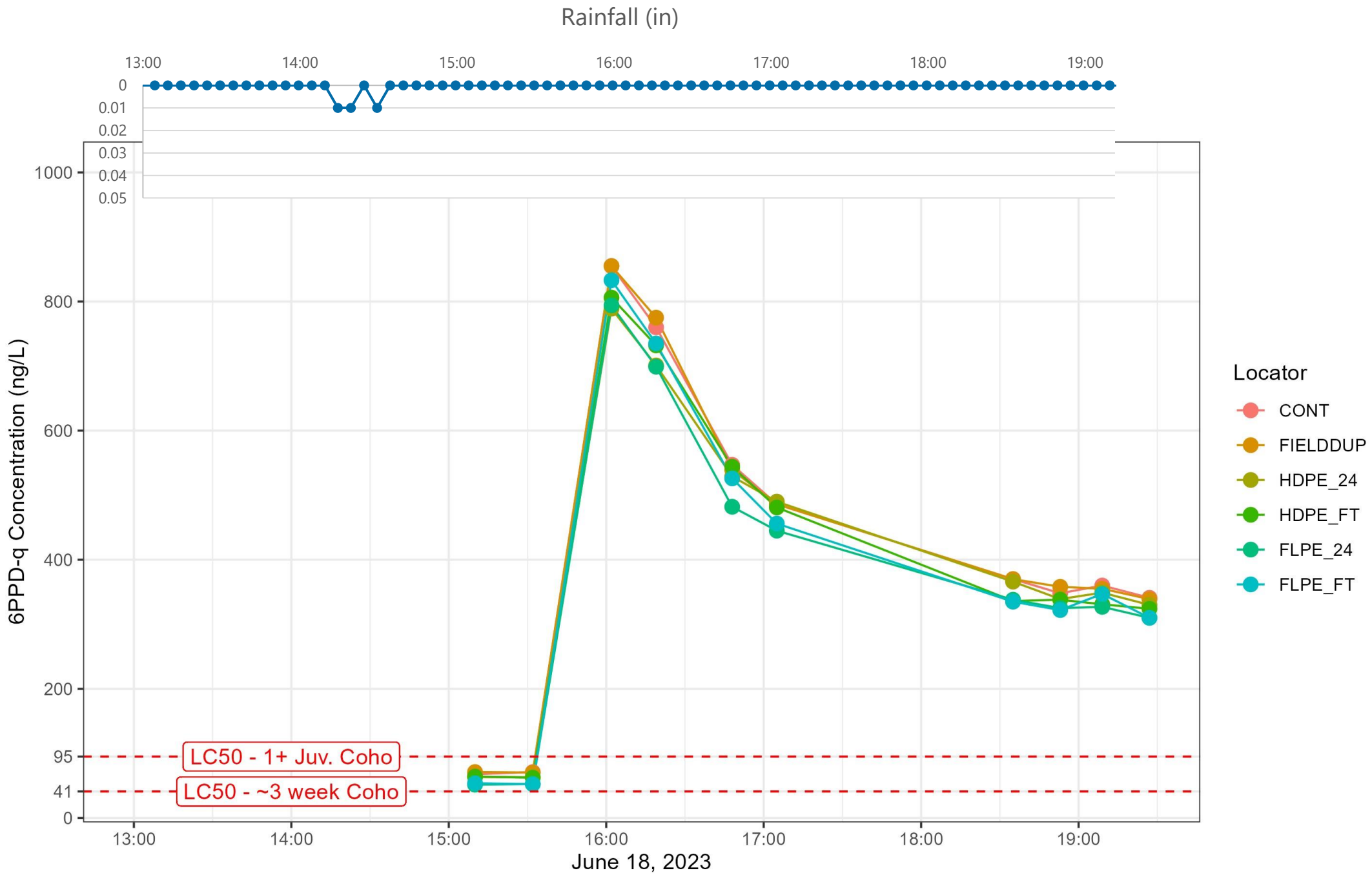
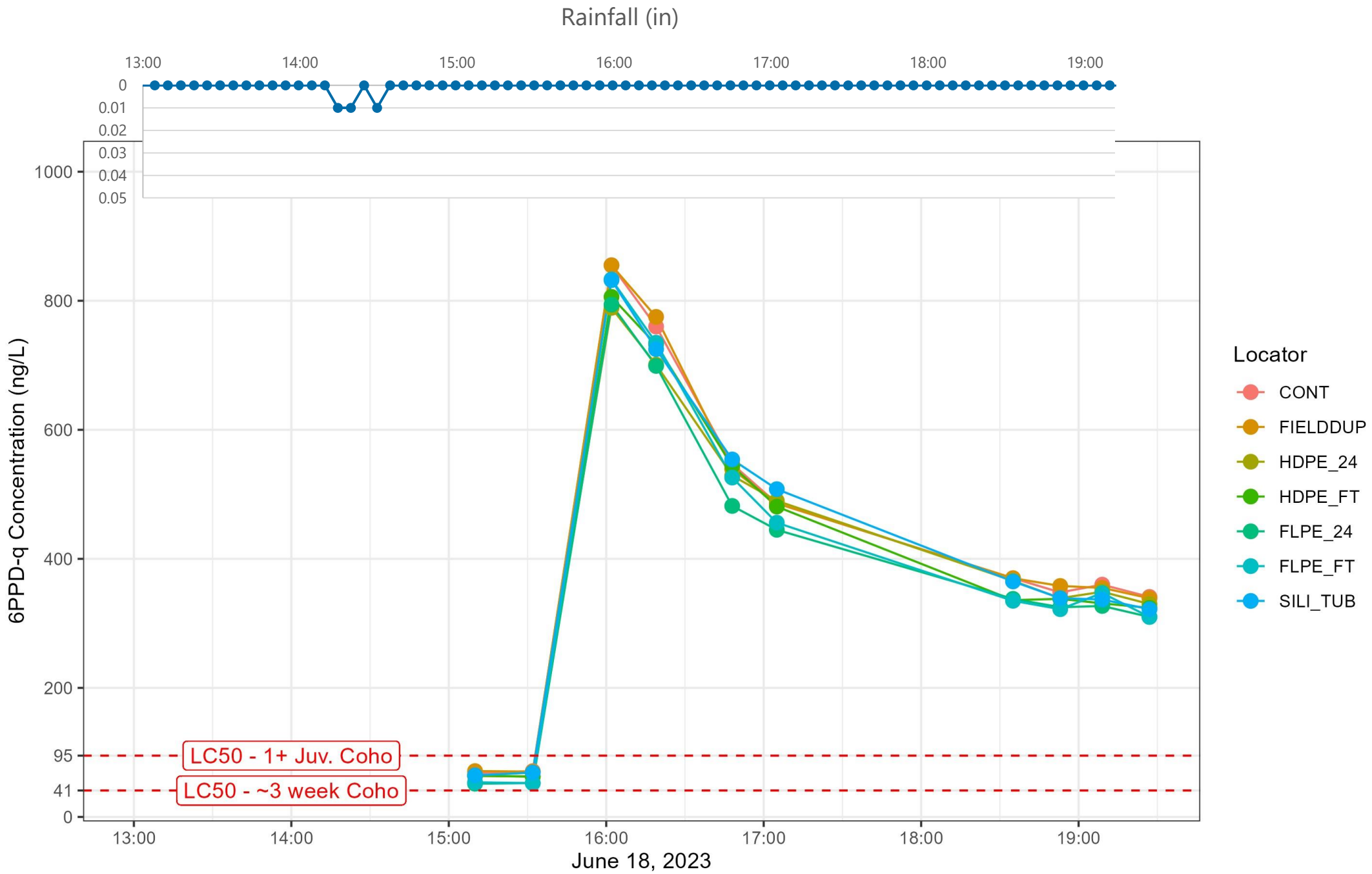
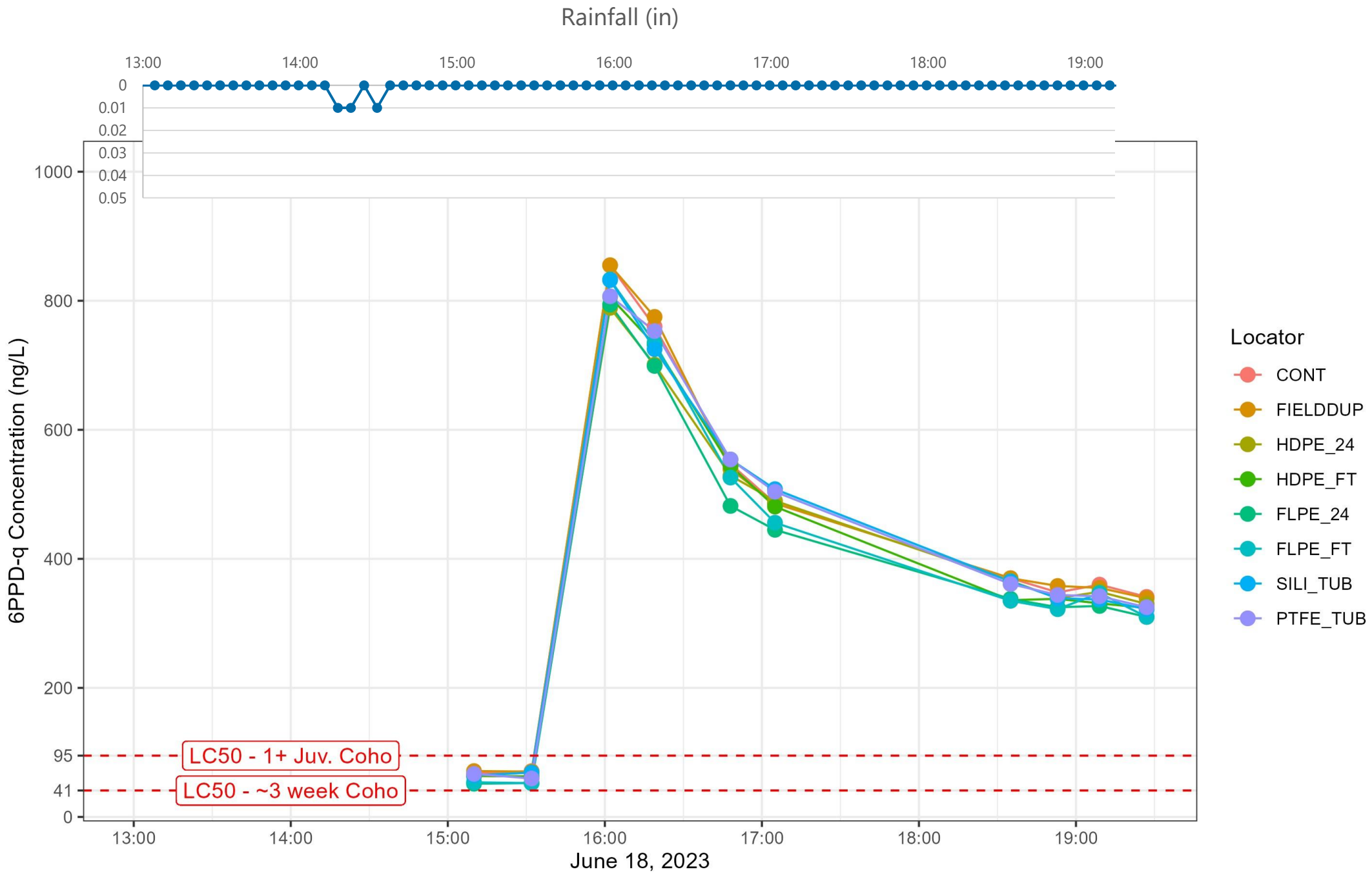
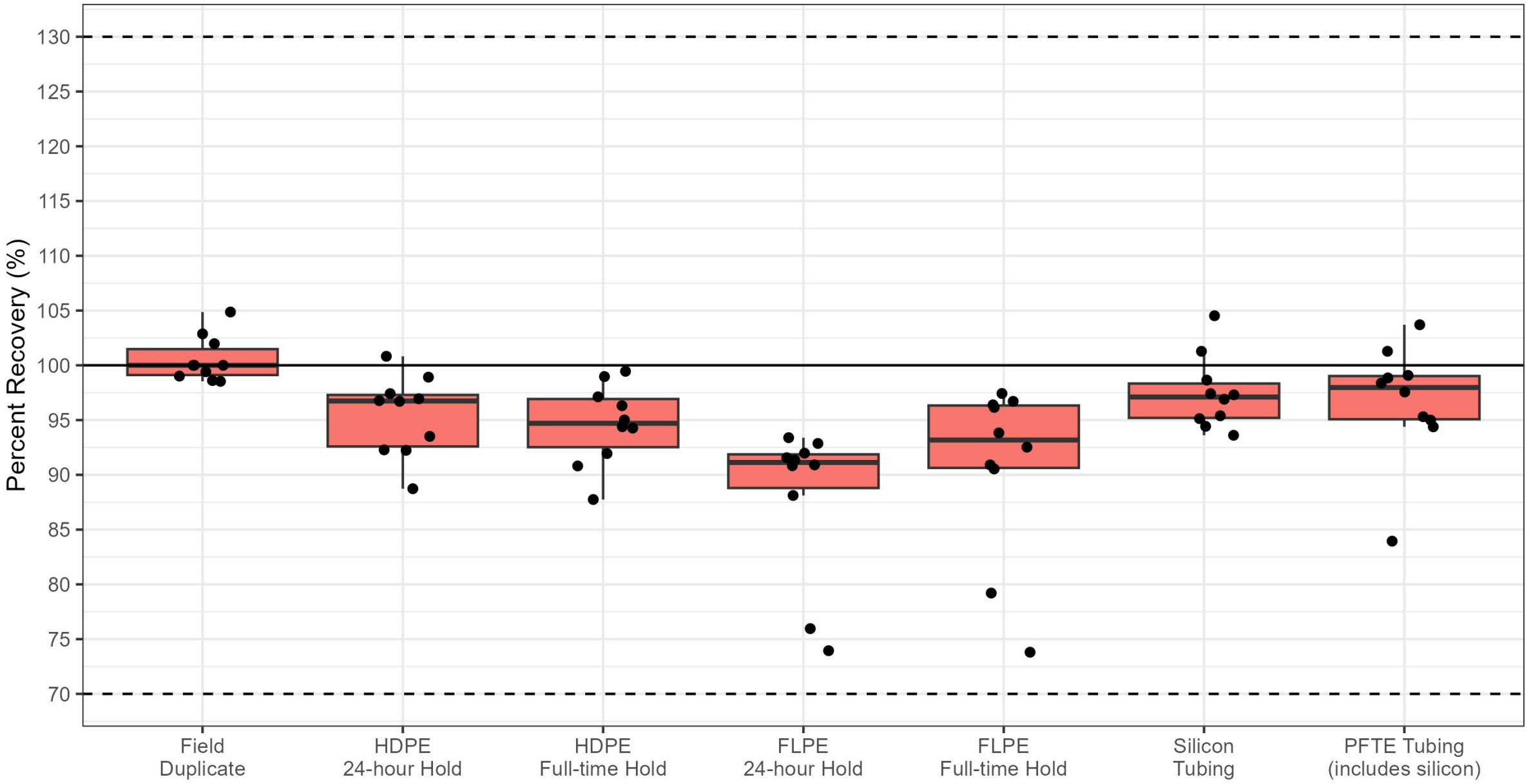
0.05
1000
800
600
400
200
95
41
0
6PPD-q Concentration (ng/L)
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP
HDPE_24
HDPE_FT


Rainfall (in)
13:00
14:00
15:00
16:00
17:00
18:00
19:00
0
0.01
0.02
0.03
0.04
0.05
6PPD-q Concentration (ng/L)
1000
800
600
400
200
95
41
0
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP
HDPE_24
HDPE_FT
FLPE_24


Rainfall (in)
13:00
14:00
15:00
16:00
17:00
18:00
19:00
0
0.01
0.02
0.03
0.04
0.05
1000
800
600
400
200
95
41
0
6PPD-q Concentration (ng/L)
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP
HDPE_24
HDPE_FT
FLPE_24
FLPE_FT


Rainfall (in)
13:00
14:00
15:00
16:00
17:00
18:00
19:00
0
0.01
0.02
0.03
0.04
0.05
6PPD-q Concentration (ng/L)
1000
800
600
400
200
95
41
0
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP
HDPE_24
HDPE_FT
FLPE_24
FLPE_FT
SILI_TUB


Rainfall (in)
13:00
14:00
15:00
16:00
17:00
18:00
19:00
0
0.01
0.02
0.03
0.04
0.05
6PPD-q Concentration (ng/L)
1000
800
600
400
200
95
41
0
LC50 - 1+ Juv. Coho
LC50 - ~3 week Coho
June 18, 2023
Locator
CONT
FIELDDUP
HDPE_24
HDPE_FT
FLPE_24
FLPE_FT
SILI_TUB
PTFE_TUB


Percent Recovery (%)
130
125
120
115
110
105
100
95
90
85
80
75
70
Field Duplicate
HDPE 24-hour Hold
HDPE Full-time Hold
FLPE 24-hour Hold
FLPE Full-time Hold
Silicon Tubing
PFTE Tubing (includes silicon)

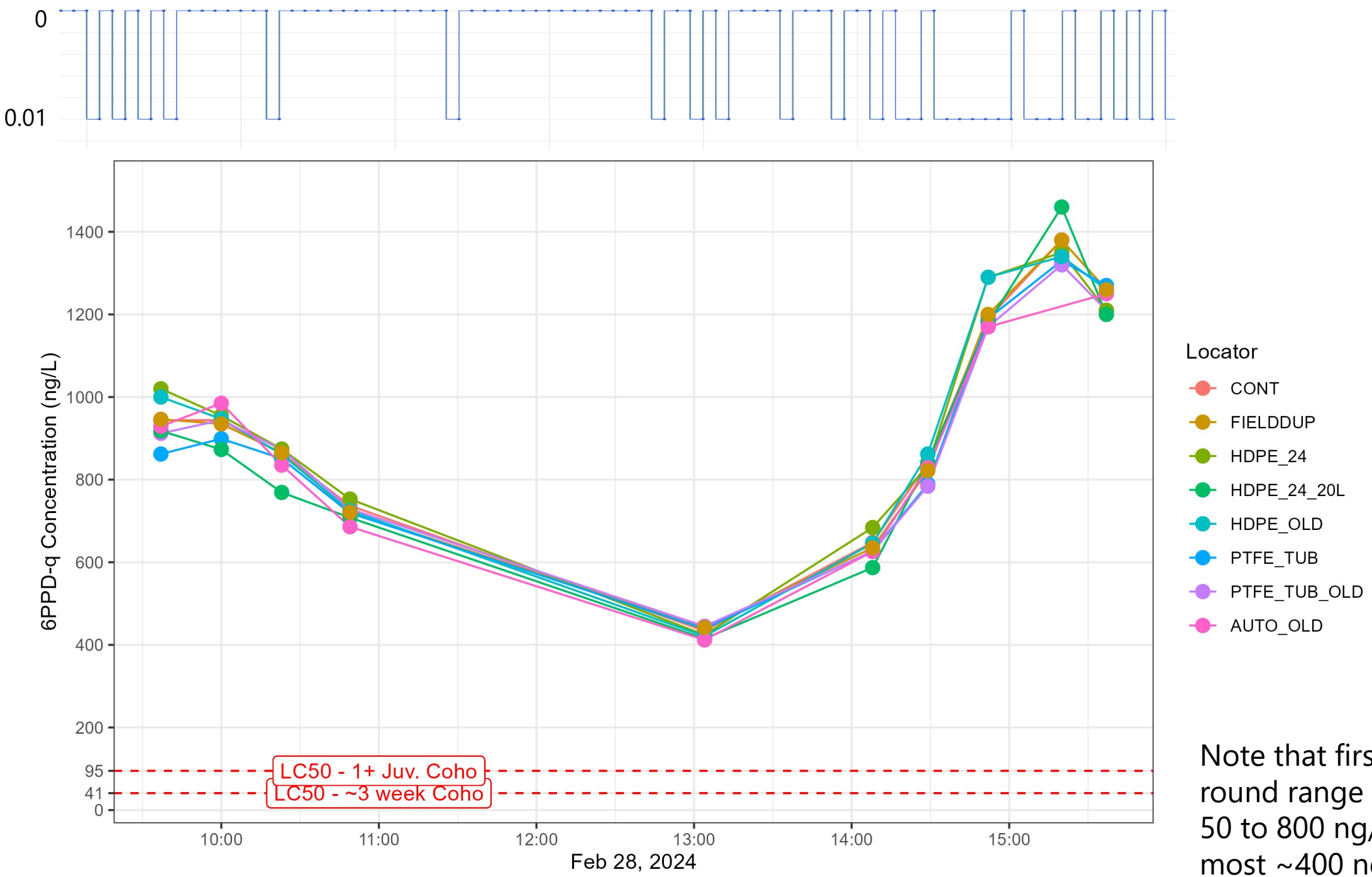
Field Protocol and Lab Results

Group Code	Test Group	Mean Percent Difference	Mean Percent Recovery	Wilcoxon Paired p-value	Permutation Paired Test p-value
FIELDDUP	Field Duplication (FIELDDUP)	0.5%	101%	0.80	0.57
PTFE_TUB	PTFE (Teflon) Tubing	-3.3%	97%	0.14	0.13
SILI_TUB	Silicone Tubing	-2.5%	98%	0.11	0.11
HDPE_24	**HDPE Bottle (24 hours)**	-4.6%	95%	**<0.01**	**<0.01**
HDPE_FT	**HDPE Bottle (until extraction)**	-5.4%	95%	**<0.01**	**<0.01**
FLPE_24	**FLPE Bottle (24 hours)**	-11.9%	**88%**	**<0.01**	**<0.01**
FLFE_FT	**FLPE Bottle (until extraction)**	-9.3%	**91%**	**<0.01**	**<0.01**

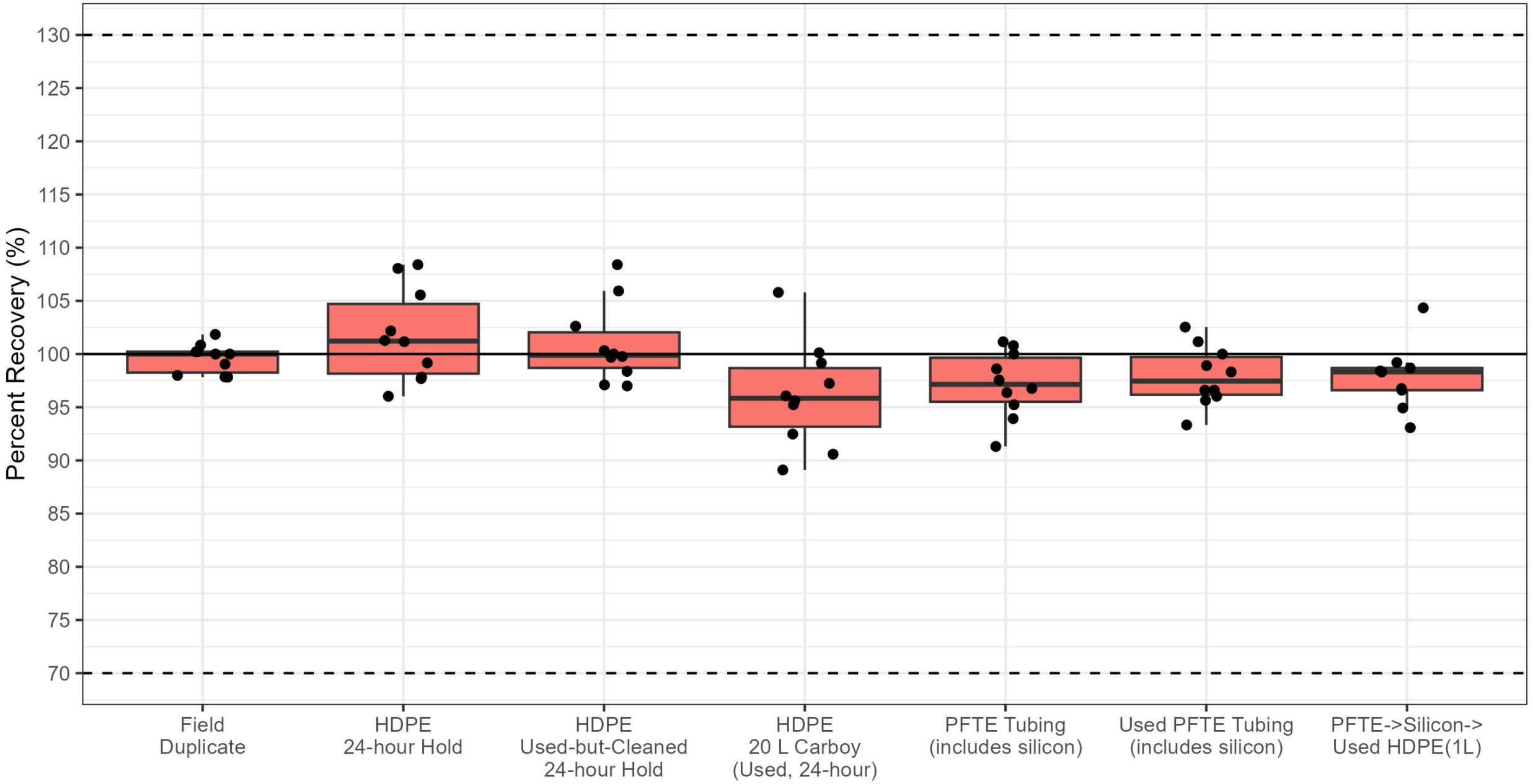
ROUND 2!

Field Protocol and Lab Results – Round 2

Group Code	Test Group
Control	**250mL Amber Glass**
FieldDup	**250mL Amber Glass -** *Field Duplication*
HDPE_24	**250mL HDPE** *(24-hour hold -> amber glass)*
HDPE_24_20L	**20 L HDPE Carboy** filled to 2 L *(used-but-cleaned at lab)* *(24-hour hold -> amber glass)*
HDPE_OLD	**250mL USED HDPE** *(used-but-cleaned at lab)* *(24-hour hold -> amber glass)*
PTFE_TUB	**PTFE (Teflon) Tubing -> Amber Glass**
PTFE_TUB_OLD	**PTFE (Teflon) Tubing -> Silicon -> Amber Glass** *(previously used for stormwater sampling)*
AUTO_OLD (Full Meal Deal)	**PTFE-> Silicon** *(tubing previously used for stormwater sampling)* **-> 1L HDPE** *(used-but-cleaned at lab, filled to 250 mL)* *(24-hour hold -> amber glass)*



Note that first round range from 50 to 800 ng/L, most ~400 ng/L


Percent Recovery (%)
130
125
120
115
110
105
100
95
90
85
80
75
70
Field Duplicate
HDPE 24-hour Hold
HDPE Used-but-Cleaned 24-hour Hold
HDPE 20 L Carboy (Used, 24-hour)
PFTE Tubing (includes silicon)
Used PFTE Tubing (includes silicon)
PFTE->Silicon-> Used HDPE(1L)

Field Protocol and Lab Results – Round 2

Group Code	Test Group	Second Round (2/28/2024)			First Round (6/18/2023)		
		Mean RPD (%)	Mean Recovery (%)	Permutation Paired Test p-value	Mean RPD (%)	Mean Recovery (%)	Permutation Paired Test p-value
FieldDup	Field Duplication (FIELDDUP)	0.4%	99.6%	0.3190	-0.5%	101%	0.6090
HDPE_24	HDPE (24-hour hold)	-1.7%	102%	0.3190	**4.6%**	**95.4%**	**0.0059**
HDPE_24_20L	HDPE (20 L carboy, used-but-cleaned)	*3.9%*	*96.1%*	*0.0913*	Not Assessed		
HDPE_OLD	HDPE (used-but-cleaned)	-0.9%	101%	0.4310	Not Assessed		
PTFE_TUB	PTFE (Teflon) Tubing	**2.8%**	**97.2%**	**0.0194**	3.2%	96.7%	0.1290
PTFE_TUB_OLD	PTFE (Teflon) Tubing ->Silicon (previously used)	**2.1%**	**97.9%**	**0.0310**	Not Assessed		
AUTO_OLD (FullMealDeal)	PTFE->Silicon (used) -> 1L HDPE (used-but-cleaned	2.2%	97.8%	0.0968	Not Assessed		

Recommended Field Protocol

Table 2. Summary of 6PPDQ Stormwater Composite Sampling Recommendations.

Component	Recommendation
Carboy Material	Use amber glass or clear glass with protection from light.
	HDPE can be used with minimal 6PPDQ loss.
	Avoid silicone or rubber gaskets on carboy lids where possible.
Carboy Size	Select the smallest feasible size to minimize headspace and surface area to volume ratio.
Sample Tubing	Use PTFE-lined sample intake tubing.
	Short sections of silicone tubing may be used if necessary to operate peristaltic pumps.
Tubing Installation	Use the minimum necessary length of all tubing to minimize contact with sorptive materials.
	Intake tubing should be installed in conduit or otherwise out of direct sunlight.
Sampler Installation	Automated samplers should be programmed to fully rinse and flush sample intake lines for each aliquot.
	Intake tubing should be rinsed with deionized water prior to target storm events.
	Sample aliquot volume should be calculated to ensure minimal headspace in the final sample volume.
Sample Handling	Keep samples on ice and out of direct sunlight as required by EPA Method 1634[a].
	During field handling and transportation to the laboratory, avoid agitating the carboy to prevent unnecessary contact between sample volume and carboy materials.
Quality Control Samples	Collect equipment rinsate blanks prior to sample collection, upon conclusion of the monitoring period, and in the middle of extended monitoring periods to identify potential contamination
	Collect field duplicate samples for every ten primary samples collected.

Links to Documents

Memo: 6PPDQ Roadway Runoff Stormwater Composite Sampling Protocol Recommendations

2023-2024 Summary Report 6PPDQ in Highway Runoff and BMP Effectiveness
Seattle, Washington and Portland, Oregon

https://www.herrerainc.com/publications/

Conclusions and Remaining Questions

Conclusion:

- The typical auto-sampling configuration is appropriate for sampling 6PPDQ in highway runoff and other stormwater with higher concentrations.

Questions:

- What about contamination/loss when the source water has low(er) 6PPDQ levels (e.g., streams, lakes)?
- How does 6PPDQ gains/losses compare to other parameters (e.g., zinc, phosphorus)?
- Why was there higher loses for FLPE?

Acknowledgements

King County Environmental Laboratory
Meghan Elkey, Francis Sweeney, and Elizabeth Frame

Herrera Team
Nicholas Harris, Scott Shumway, and Sam Nilsson

Ecology Project Manager
Morgan Baker

Questions?

Are you lost?

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