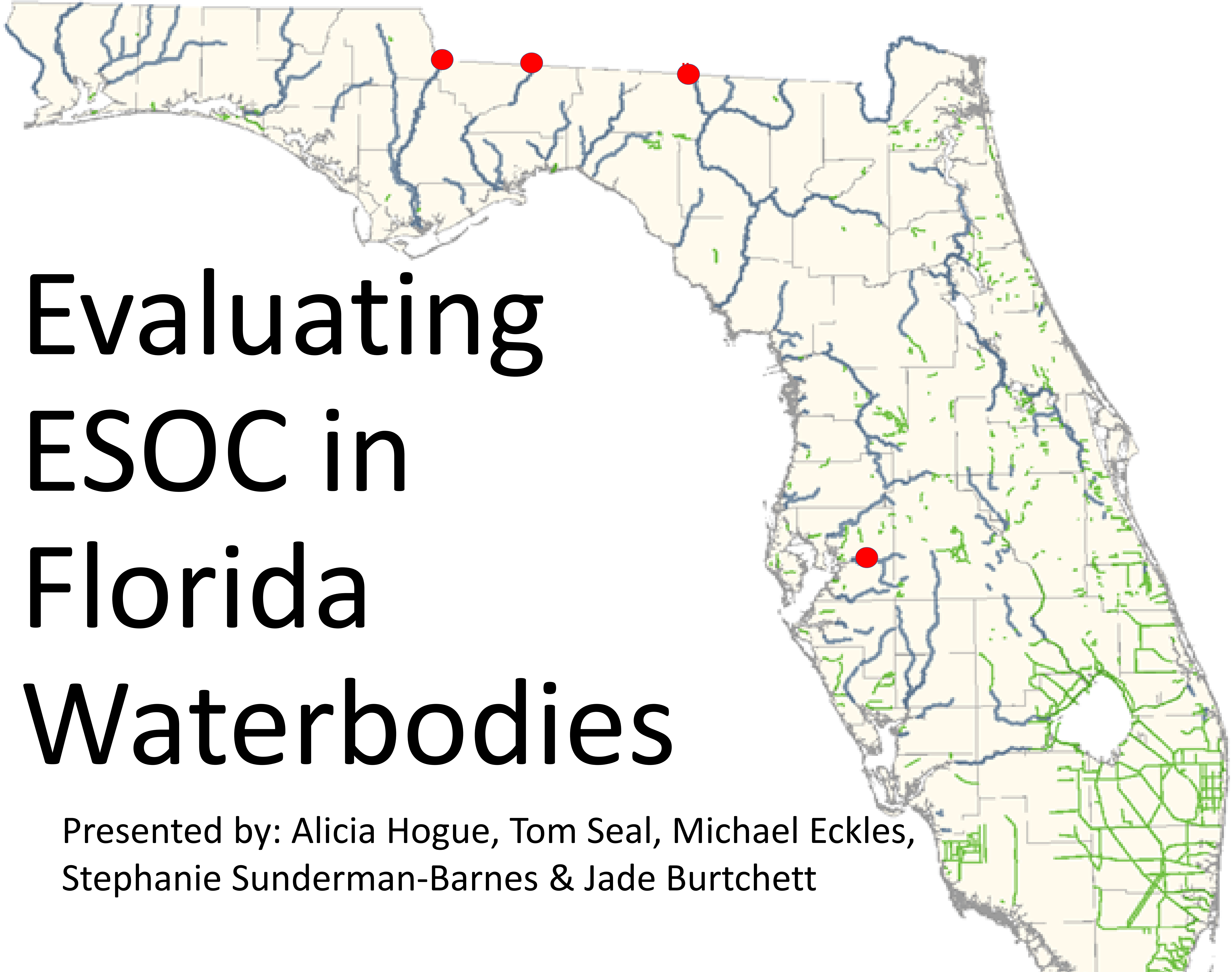


Evaluating ESOC in Florida Waterbodies

Presented by: Alicia Hogue, Tom Seal, Michael Eckles,
Stephanie Sunderman-Barnes & Jade Burtchett

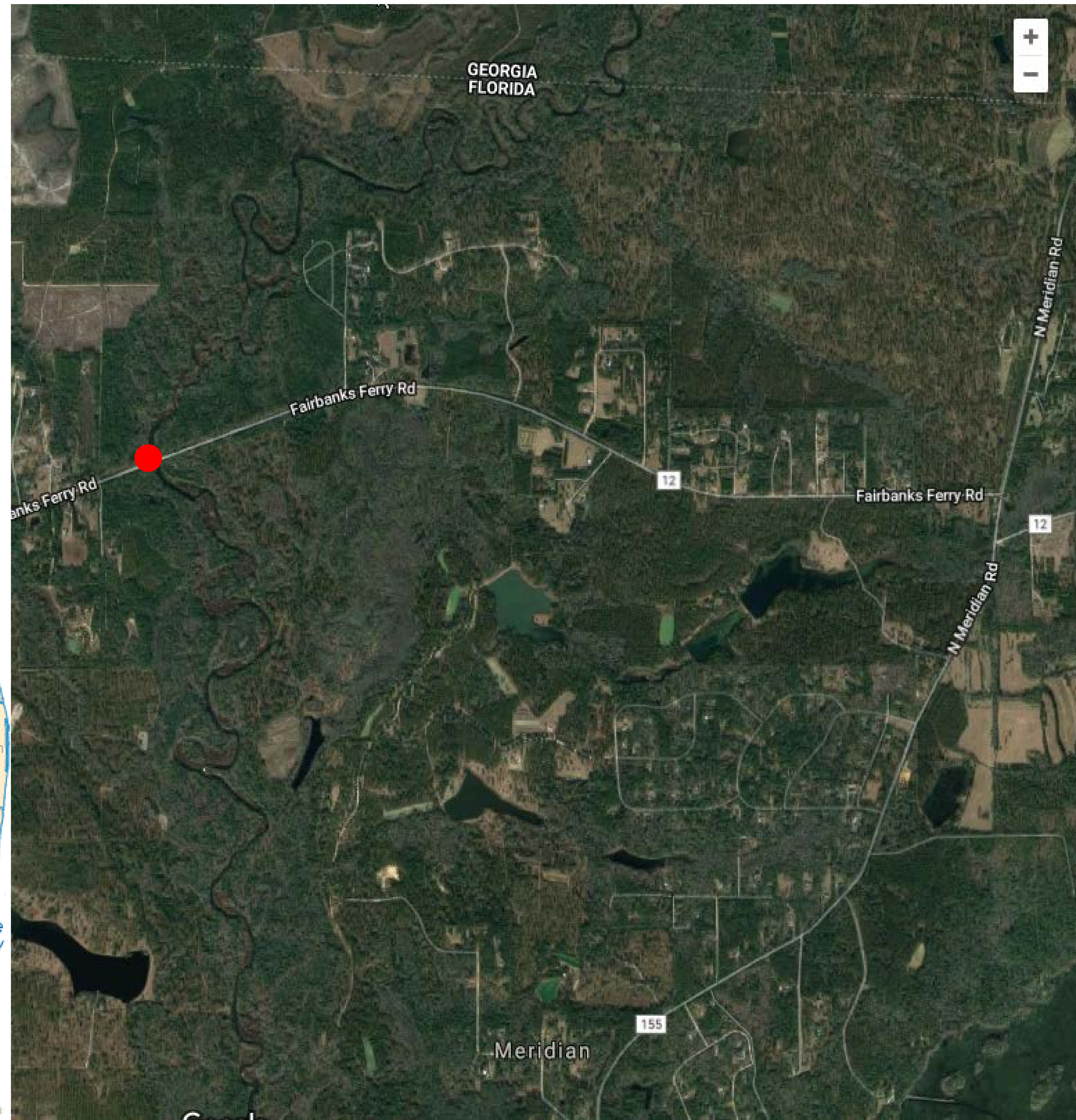


Overview

- 4 river sites chosen:
 - Ochlockonee, Withlacoochee, Apalachicola and Alafia
- 3 types of sample collection:
 - Semi-Permeable Membrane Device (SPMD)
 - Polar Organic Chemical Integrative Sampler (POCIS)
 - Whole water samples (Grab)
- 6 Categories of compounds:
 - Pesticides, PPCPs, Hormones, PFCs, PBDEs, and Alkylphenols
- Sample collection types were considered in up to 7 categories:
 - SPMD, POCIS, Grab (Pesticides)
 - SPMD & POCIS (Pesticides)
 - Grab & SPMD
 - Grab & POCIS
 - Grab only
 - SPMD only
 - POCIS only
- QA is discussed at the end of each category.
- SGS/Axys data are presented, then DEP data.

Ochlockonee River

500m



Ochlockonee River

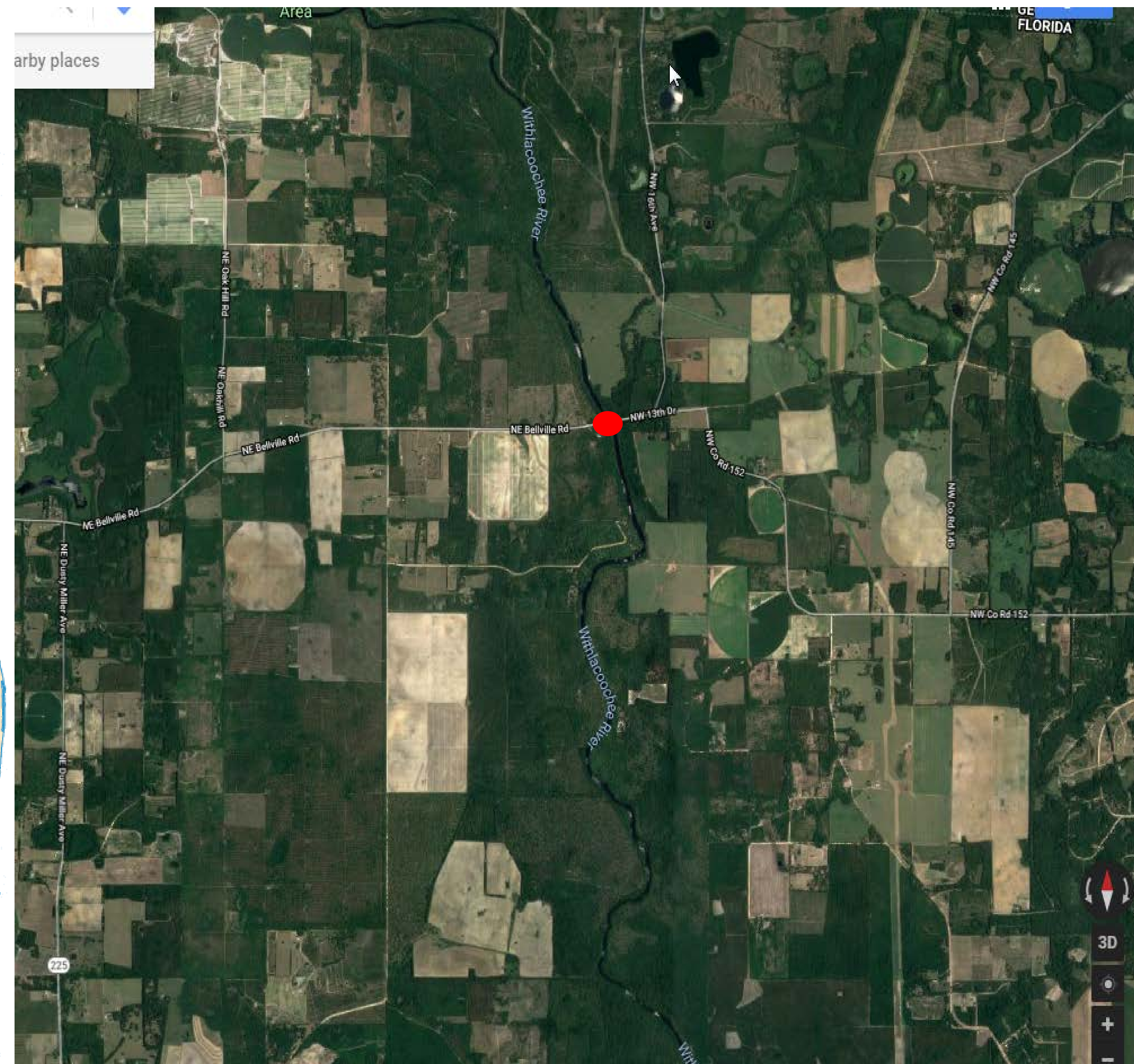
- 190 miles long
- The drainage basin is 1,002 square miles
- River discharge averages 1,870 cubic feet/second.
- Drainage basin receives sediments from the Coastal Plain province
- The river receives effluent from the Georgia cities of Cairo, Thomasville and Moultrie.
- Site is located just south of the FL-GA state line.
- Sucralose maximum value detected was 2.6 $\mu\text{g/L}$

Sampler Location/Deployment



Withlacoochee River

1km



Withlacoochee River

- 112 miles long.
- The drainage basin is 2,120 square miles.
- Discharge average 1,870 cubic feet/second.
- Drainage basin receives sediments from only the Coastal Plain province.
- The river receives effluent from the city of Valdosta about 20 miles upstream of site.
- The Withlacoochee River joins with the Suwannee River downstream from the site.
- Site is located at state line.
- Sucralose maximum value detected was 2.9 $\mu\text{g/L}$

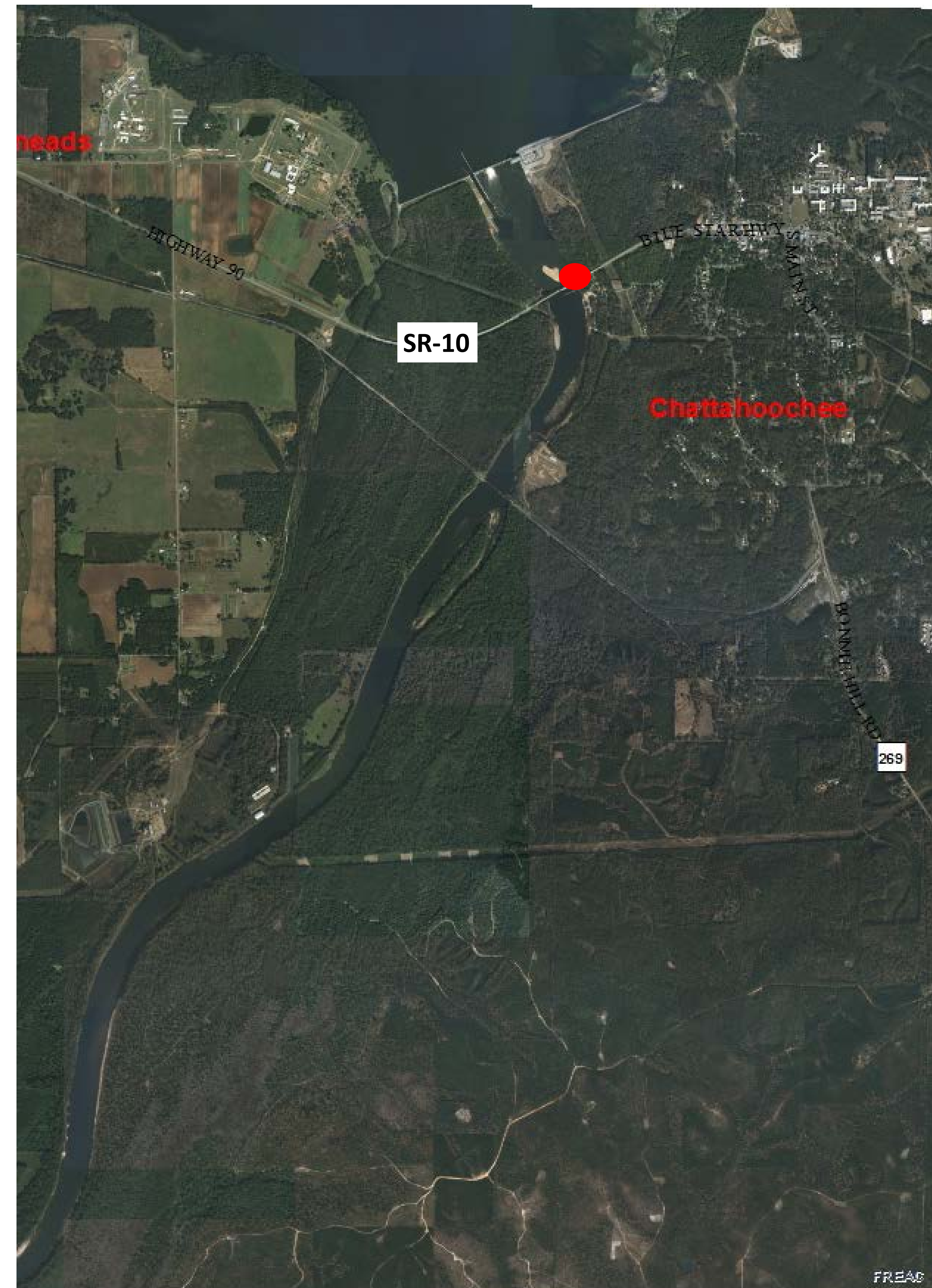
Sampler Location/Deployment



Apalachicola River

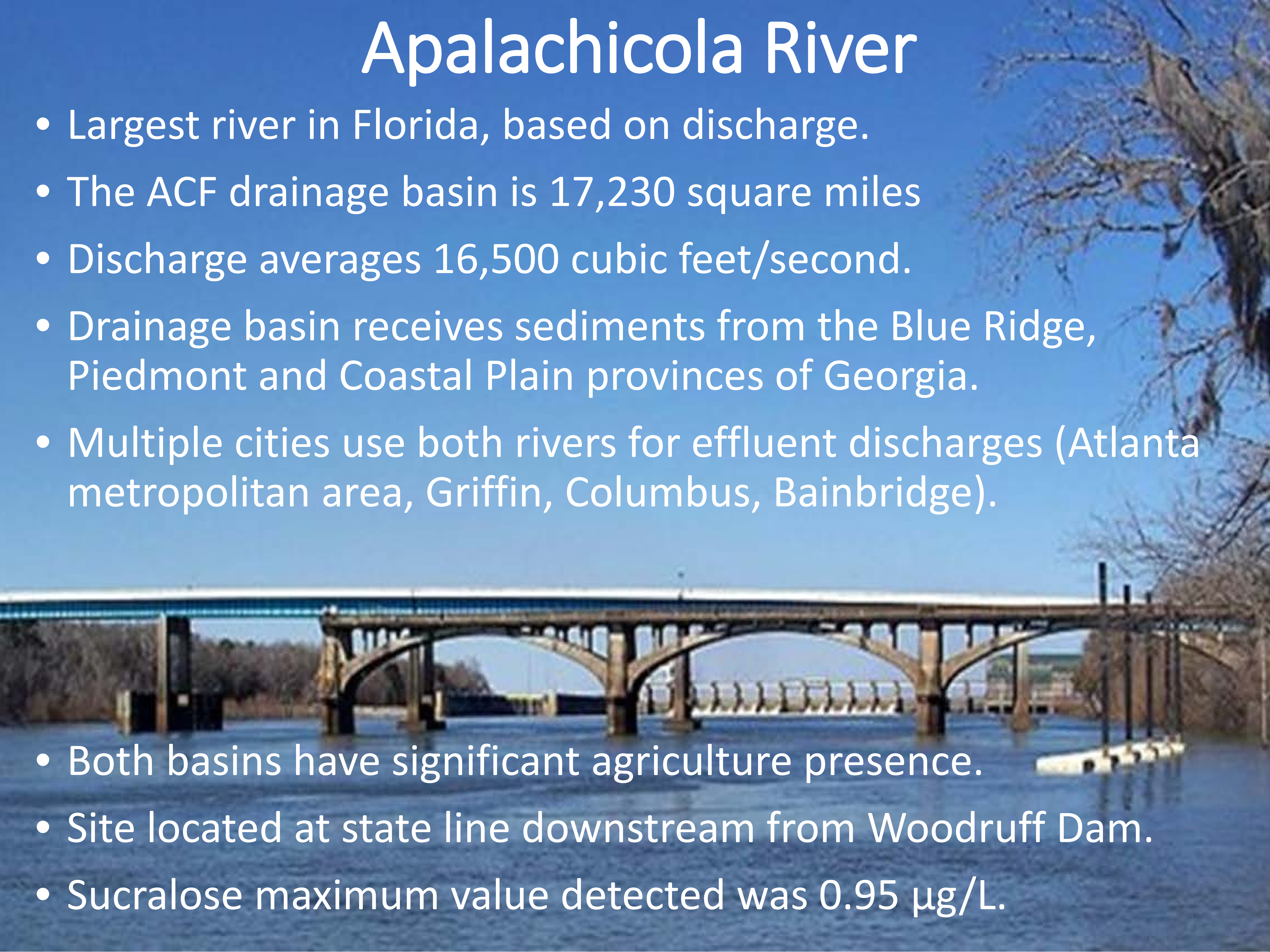


1km



Apalachicola River

- Largest river in Florida, based on discharge.
- The ACF drainage basin is 17,230 square miles
- Discharge averages 16,500 cubic feet/second.
- Drainage basin receives sediments from the Blue Ridge, Piedmont and Coastal Plain provinces of Georgia.
- Multiple cities use both rivers for effluent discharges (Atlanta metropolitan area, Griffin, Columbus, Bainbridge).

- 
- A photograph of a large, multi-arched concrete bridge spanning a wide river. The bridge has several tall, rectangular piers supporting the arches. In the background, a city skyline is visible under a clear blue sky. The water in the foreground is calm, reflecting the bridge and the sky. On the right side of the image, there are some bare trees and a small structure on the riverbank.
- Both basins have significant agriculture presence.
 - Site located at state line downstream from Woodruff Dam.
 - Sucralose maximum value detected was 0.95 $\mu\text{g/L}$.

Sampler Location/Deployment



Alafia River

200m



Alafia River

- 25 miles long, just a few feet above sea level for most of its length.
- Watershed is 335 square miles.
- Discharges an average of 200 cubic feet/second.
- Numerous land uses influence quality of the river, including the City of Lakeland WWTP, phosphate mine sites and phosphate ore processing sites, and agriculture.
- Salt water tidal influence occurs upstream from Tampa Bay.
- Sampling site is downstream of the confluence of the North & South Prongs of the river at Tampa Bay Water Authority (TBWA) withdrawal point.
- Sucralose maximum value detected was 7.3 $\mu\text{g/L}$

Sampler Location/Deployment



Sampler Deployment for Ochlockonee, Withlacoochee & Apalachicola



1. 60-80lb weight lowered using a 12volt ATV winch attached to a davit.

2. Buoys were attached to top of canister.



Sampler Deployment for Ochlockonee, Withlacoochee & Apalachicola



3. Canister was loaded with POCIS and SPMDs.

4. Cable was attached to canister through slip rings.



Sampler Deployment for Ochlockonee, Withlacoochee & Apalachicola



5. Sampler lowered with large weighted treble hook.

6. Looped & attached cable to bridge through drain hole.



Sampler Deployment for Ochlockonee, Withlacoochee & Apalachicola



7. Sampler deployed 30 -35 days; Initial water quality parameters collected.

8. Checked equipment & took field measurements halfway through.



Sampler Deployment for Ochlockonee, Withlacoochee & Apalachicola



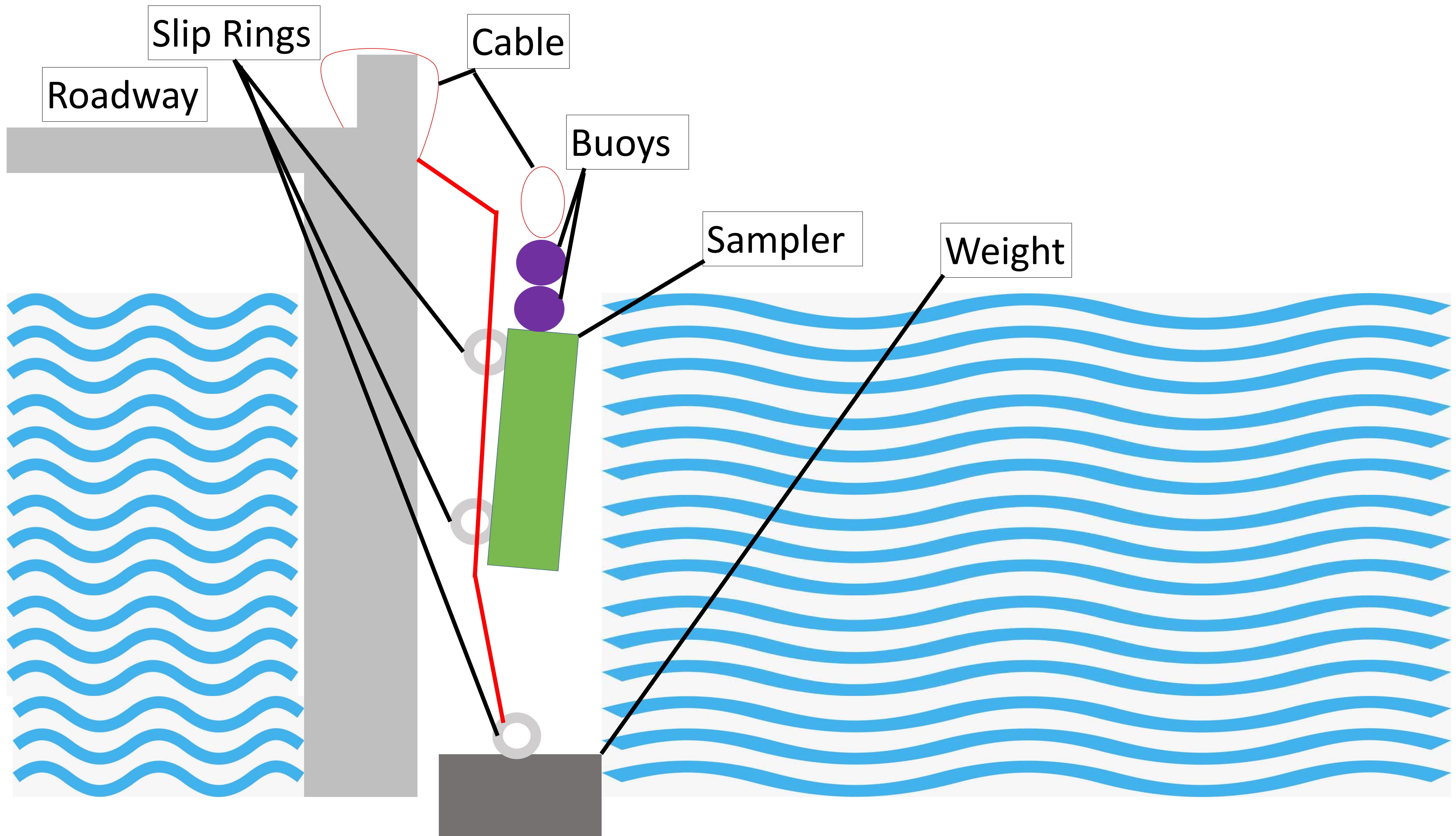
9. Grab samples collected. Sampler retrieved using treble hook. Weight raised using the winch & davit.



10. Canister contents (POCISs, SPMDs) loaded into cans. Cans sealed, stored in ice, and shipped to SGS/Axys for extraction.

Review of Deployment

Ochlockonee, Withlacoochee & Apalachicola



Sampler Deployment for Alafia

1. Metal pole was attached to TBWA withdrawal point control structure.

2. Concrete blocks placed in front of withdrawal point.



Sampler Deployment for Alafia



3. Buoys were attached to top of passive sampler.

4. Canister was loaded with POCIS and SPMDs.



Sampler Deployment for Alafia

5. Cable was attached to sampler through slip rings.



5. Sampler lowered into water, and positioned into place.



Sampler Deployment for Alafia



7. Initial water quality parameters were collected. Sampler deployed 30 -35 days.

8. Checked equipment & took field measurements halfway through.



Sampler Deployment for Alafia



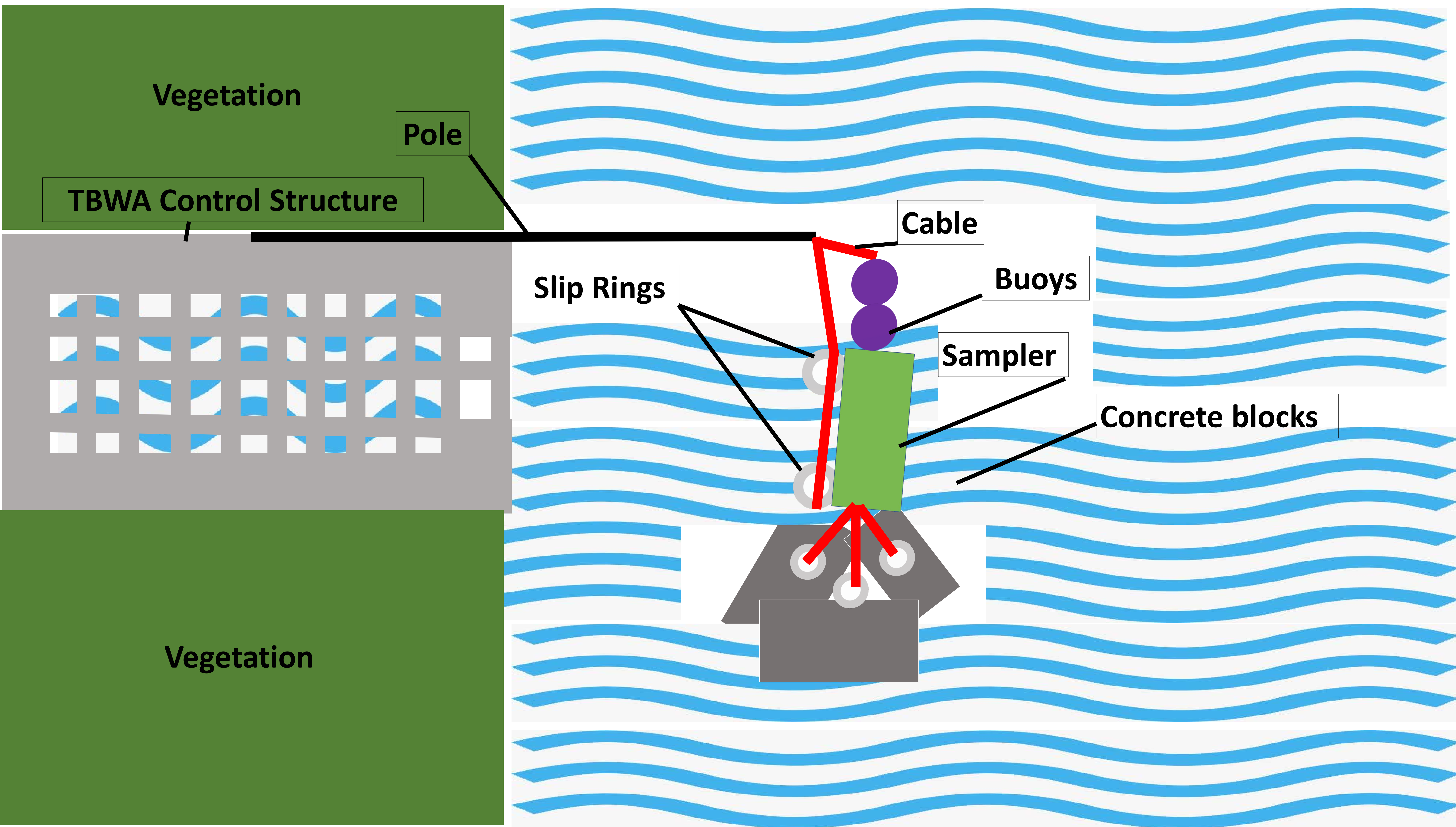
9. Grab samples collected.
Passive sampler retrieved.



10. Canister contents (POCISs,
SPMDs) loaded into cans. Cans
sealed, stored in ice, and shipped
to SGS/Axys for extraction.

Review of Deployment

Alafia



Semi-Permeable Membrane Device (SPMD)

- Mimics natural system to collect bioavailable pollutants in water.
- Passive transport similar to chemical transport through fish gills.
- Doesn't metabolize sequestered compounds, isn't affected by poor water quality conditions.
- Selective diffusion of **hydrophobic** organic chemicals through pores & stored in the lipid phase.

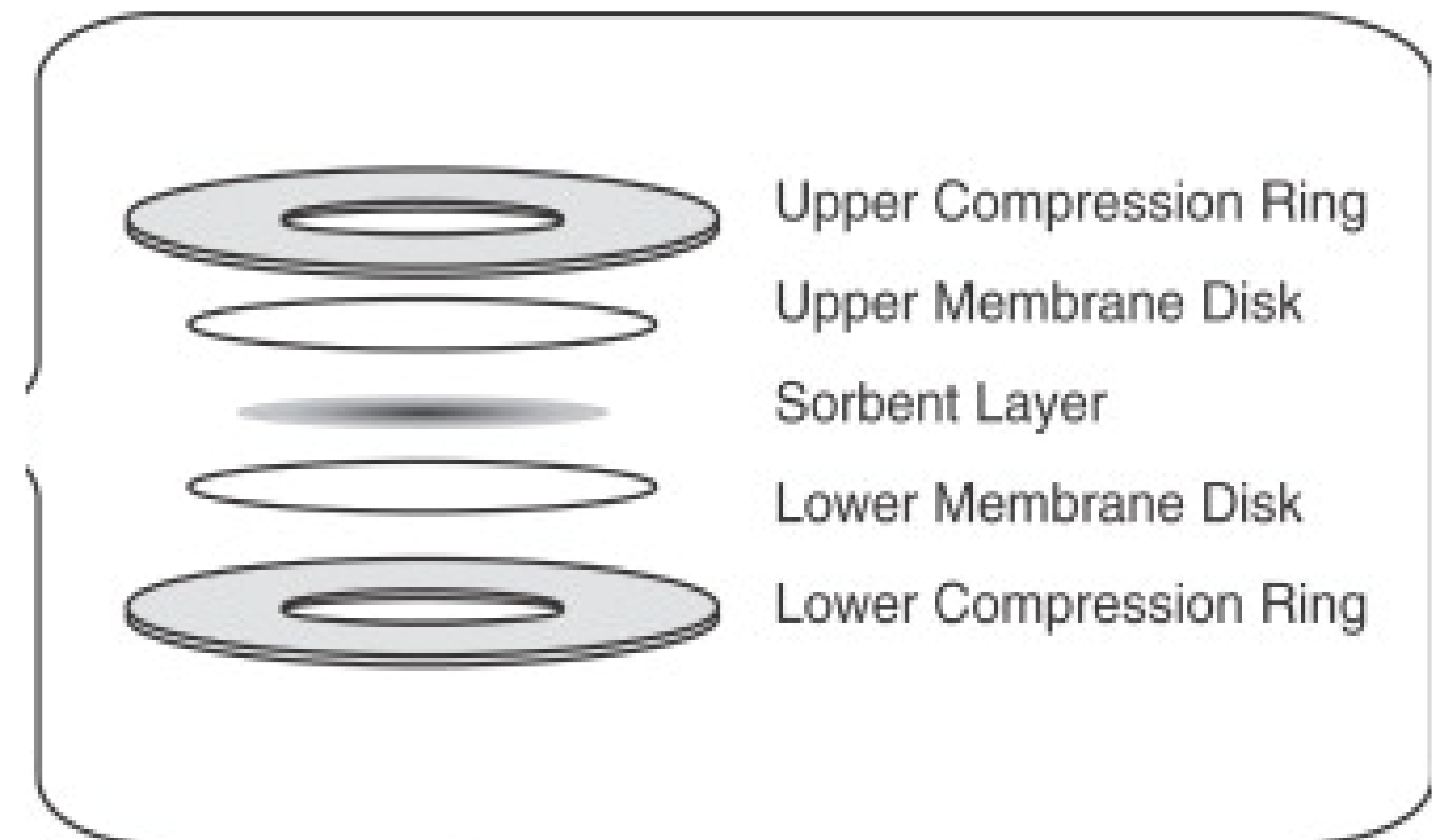


<http://www.est-lab.com/spmd.php>



Polar Organic Chemical Integrative Sampler (POCIS)

- High water solubility of polar organic chemicals (POCs) makes extraction & detection difficult.
- Monitors **hydrophilic** contaminants that could be potential EDs, or acutely toxic.
- POCIS provides reproducible method for the concentration of POCs in the ppt to ppq range



<https://www.sciencedirect.com/science/article/pii/S0166526X06480089>



Passive Sampler Collection

Canister (1)

- Holds 3 POCIS and 3 SPMD in water column during deployment.

SPMD (1)

- No PRC addition.
- No spike additions.
- Extract split 1:3.
 - BLYES & SOS Chromotest analysis by USGS
 - ER binding & transactivation assays by UF
 - Pesticide analyses by DEP lab

SPMD (2)

- PRCs added by EST.
- Spikes added by SGS/Axys.
- Extract split 1:5.
 - Alkylphenols by SGS/Axys
 - MRES w/ ON by SGS/Axys
 - PBDEs by SGS/Axys
 - PRC analysis by SGS/Axys
 - Archive



Passive Sampler Collection

POCIS-HLB (1)

- No spike additions.
- Extract split 1:3.
 - BLYES & SOS Chromotest analysis by USGS
 - ER binding & transactivation assays by UF
 - Pesticide analyses by DEP lab



POCIS-HLB (2)

- Spikes added by SGS/Axys.
- Extract from each disk split 1:4
 - MRES w/ ON by SGS/Axys
 - PPCP & hormones by SGS/Axys
 - PFC by SGS/Axys
 - Archive



Sample Container (Can)(2)

- Can #1 contains 3 SPMD (2 plates w/ PRCs or spikes, 1 plate marked w/ notch had no additions)
- Can #2 contains 3 POCIS (2 discs w/spikes, 1 marked w/ notch had no additions)

Blank Collections

2 field blanks were collected at Apalachicola

1. Passive sampling equipment

- The blank sample containers (cans) were opened twice; once when passive sampler was deployed, and again when recovered from the site.
- Blank cans stayed open while passive sampling devices (POCIS & SPMD) were exposed to air.
- Sealed blank cans were stored at -20°C during deployment period.

2. Grab samples

- Blank collected using DI water supplied from SGS/Axys.

Category Selection

This study separated analytes into 6 main categories

Category	Human exposure route	Aquatic life effects	Water Solubility	Sample device
Pesticides	Surface & ground water, sediment, food web	Toxic, potential endocrine disruptor (ED)	High	POCIS, SPMD & Grab
Pharmaceuticals & personal care products (PPCP)	Surface & ground water	Potential ED	High	POCIS & Grab
Synthetic hormones	Surface & ground water	Potential ED	High	POCIS & Grab
Perfluorinated compounds (PFC)	Food web, breast milk	Bioaccumulative, potential ED	Low	POCIS & Grab
Polybrominated diphenyl ethers (PBDE)	House dust, sediment, food web, breast milk, surface & ground water.	Bioaccumulative, potential ED, carcinogenic, toxic, persistent	Low	SPMD & Grab
Alkylphenols	Surface & ground water	Potential ED	High	SPMD & Grab

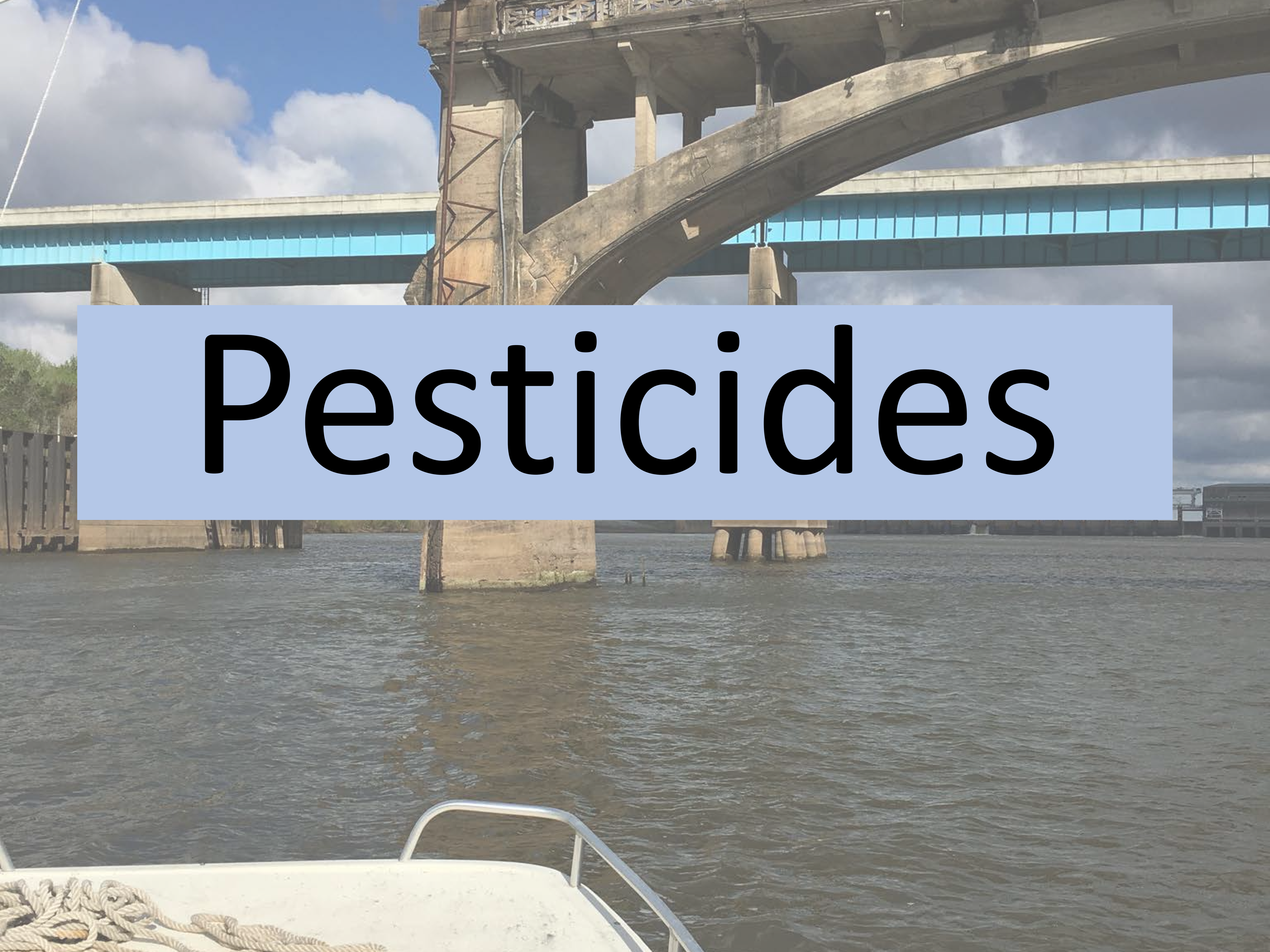
Analytical Strategy

Targeted analyses based on:

- Occurrence in published literature.
- Information gleaned from an RFI from SGS/Axys.
- Potential for adverse environmental effects.
- Availability of sampling methods.
- Capability of laboratories responding to an RFI.

The background image shows a body of water, possibly a river or lake, with a metal railing in the foreground. The railing is made of dark metal poles and horizontal bars. In the water, there is a white buoy with a spherical top. The water is calm, reflecting the surrounding greenery and the sky. The text "SGS/AXYS Data" is overlaid on the image in a large, black, sans-serif font, centered horizontally and partially obscured by a light blue rectangular background.

SGS/AXYS Data

A photograph of a large concrete dam with a blue bridge spanning across it. The view is from a boat on the water, with the boat's white railing and coiled rope visible in the foreground. The sky is blue with white clouds.

Pesticides

Pesticides

- Analyzed samples for 76 pesticide compounds
- **42** pesticide compounds detected at one or more sites, in at least one sample type (POCIS, SPMD, or Grab)
- 33% of detections from POCIS samples were qualified due to blank detections.
- 40% of detections from SPMD samples were qualified due to blank detections.
- 38% of detections from grab samples were qualified due to blank detections.

Pesticides Detections at All Sites by Sample Type

Total No. Detections, Qualified Detections, Non-detects & Not Quantifiable by Sample Type

Site	Detections			Qualified Detections (V,G)		
	SPMD	POCIS	Grab	SPMD	POCIS	Grab
Ochlockonee	19	16	13	11	7	7
Withlacoochee	20	14	10	12	6	4
Apalachicola	18	12	14	14	7	8
Alafia	18	12	8	14	6	8
Total	75	54	45	51	26	27

Site	Non-detects			Not Quantifiable		
	SPMD	POCIS	Grab	SPMD	POCIS	Grab
Ochlockonee	43	49	54	3	4	2
Withlacoochee	41	52	60	3	4	2
Apalachicola	41	53	52	3	4	2
Alafia	41	54	58	3	4	2
Total	166	208	224	12	16	8

Pesticides Detected at Every Site (n = 4) by Sample Type

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	SPMD	POCIS	Grab
alpha-Endosulphan	VG	VG	VG
Dieldrin	●	●	●
Hexachlorobenzene	G	VG	VG
Metolachlor	G	●	V
Chlordane, gamma (trans)	G	G	
Endosulphan Sulphate	●	●	
Heptachlor	G	G	
Heptachlor Epoxide	V	G	
Nonachlor, trans-	●	●	
beta-Endosulphan	VG		VG
Atrazine		●	●
Desethylatrazine		●	●
Simazine		●	●
Tebuconazol		●	●
2,4'-DDD	●		
4,4'-DDD	●		
4,4'-DDE	●		
4,4'-DDT	●		
Aldrin	V		
Chlordane, alpha (cis)	●		
Chlordane, oxy-	VG		
Chlorpyriphos	●		
Endrin	VG		
HCH, alpha	●		
HCH, beta	●		
HCH, gamma	G		
Mirex	VG		
Nonachlor, cis-	G		
Pendimethalin	●		
Trifluralin	●		
Total	26	13	9

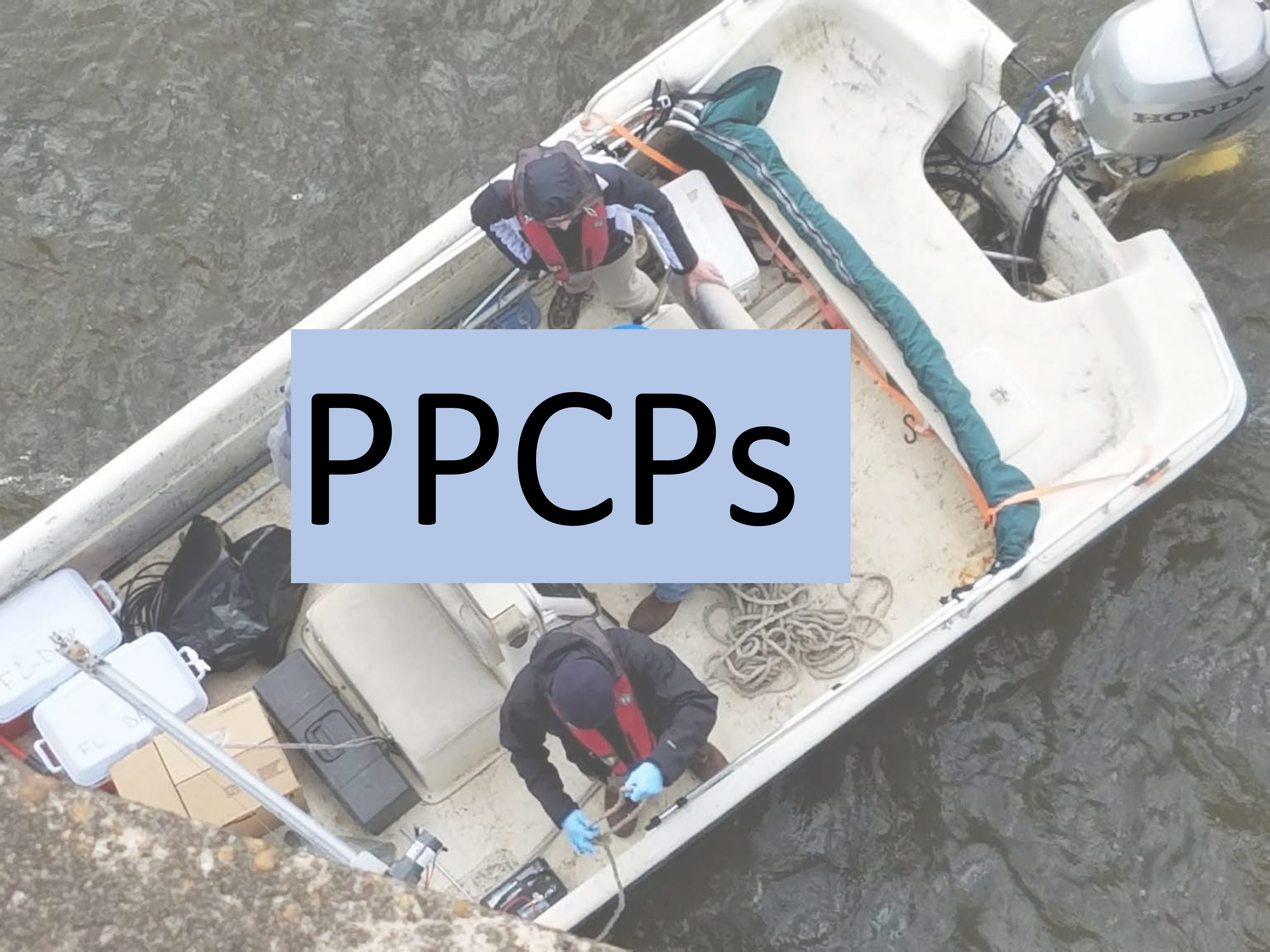
Quality Assurance

Summary - Pesticides

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	SPMD	POCIS	Grab
2,4'-DDD	●		
4,4'-DDD	●		
2,4'-DDE	●		
4,4'-DDE	●		●
4,4'-DDT	●		
Alachlor	●	●	VG
Aldrin	V	●	●
alpha-Endosulphan	VG	VG	VG
beta-Endosulphan	VG	VG	VG
Endosulphan Sulphate	●	●	●
Ametryn		●	
Atrazine	●	●	●
Desethylatrazine		●	●
Chlordane, alpha (cis)	●	●	
Chlordane, gamma (trans)	G	G	V
Chlordane, oxy-	VG		V
Chlorpyriphos	●		●
Diazinon	●	●	
Dieldrin	●	●	●
Dimethenamid	●	●	●
Endrin	VG		V

Compound	SPMD	POCIS	Grab
Endrin Ketone	●		G
Ethalfuralin	●		
Flufenacet	●		
Flutriafol		●	G
HCH, alpha	●	●	●
HCH, beta	●	●	●
HCH, delta	●	●	
HCH, gamma	G	●	●
Heptachlor	G	G	
Heptachlor Epoxide	V	G	VG
Hexachlorobenzene	G	VG	VG
Hexazinone		●	●
Metolachlor	G	●	V
Mirex	VG	●	●
Nonachlor, cis-	G		G
Nonachlor, trans-	●	●	●
Pendimethalin	●		
Quintozene	G	G	
Simazine		●	●
Tebuconazol	G	●	●
Trifluralin	●	●	



PPCPs

Analyzed Pilot Study Samples for 127 PPCP Compounds

39 PPCP Compounds Detected

At one or more sites, in at least one sample type (POCIS or Grab)

- Alprazolam
- Amitriptyline
- Amphetamine
- Atenolol
- Azithromycin
- Caffeine
- Carbamazepine
- Clarithromycin
- Cocaine
- Colchicine
- Cotinine
- DEET
- Dehydronifedipine
- Desmethyldiltiazem
- Diatrizoic acid
- Diazepam
- Diltiazem
- Diphenhydramine
- Erythromycin-H2O
- Furosemide
- Gemfibrozil
- Hydrochlorothiazide
- Hydrocodone
- Iopamidol
- Meprobamate
- Metformin
- Metoprolol
- Naproxen
- Oxolinic Acid
- Oxycodone
- Propoxyphene
- Sertraline
- Sulfadimethoxine
- Sulfamethazine
- Sulfamethoxazole
- Triamterene
- Trimethoprim
- Valsartan
- Venlafaxine

PPCP Detections at All Sites by Sample Type

Total No. Detections, Qualified Detections, Non-detects & Not Quantifiable by Sample Type

Site	Detections		Qualified Detections (V,G)	
	POCIS	GRAB	POCIS	Grab
Ochlockonee	24	17	1	2
Withlacoochee	23	11	1	3
Apalachicola	12	7	1	3
Alafia	9	9	1	1
Total	68	44	4	9

Site	Non-detects		Not Quantifiable	
	POCIS	GRAB	POCIS	Grab
Ochlockonee	102	100	0	8
Withlacoochee	95	106	8	7
Apalachicola	114	110	0	7
Alafia	117	117	0	0
Total	428	433	8	22

PPCPs Detections at All Sites by Sample Type

Total No. Undetects, Detects, Not Quantifiable
by Sample Type

Detections	POCIS	Grab
Ochlockonee	25	19
Alafia	10	10
Withlacoochee	24	14
Apalachicola	13	10
Total	72	53
Non-detects	POCIS	Grab
Ochlockonee	102	100
Alafia	117	117
Withlacoochee	95	106
Apalachicola	114	110
Total	428	433
Not Quantifiable	POCIS	Grab
Ochlockonee	0	8
Alafia	0	0
Withlacoochee	8	7
Apalachicola	0	7
Total	8	22

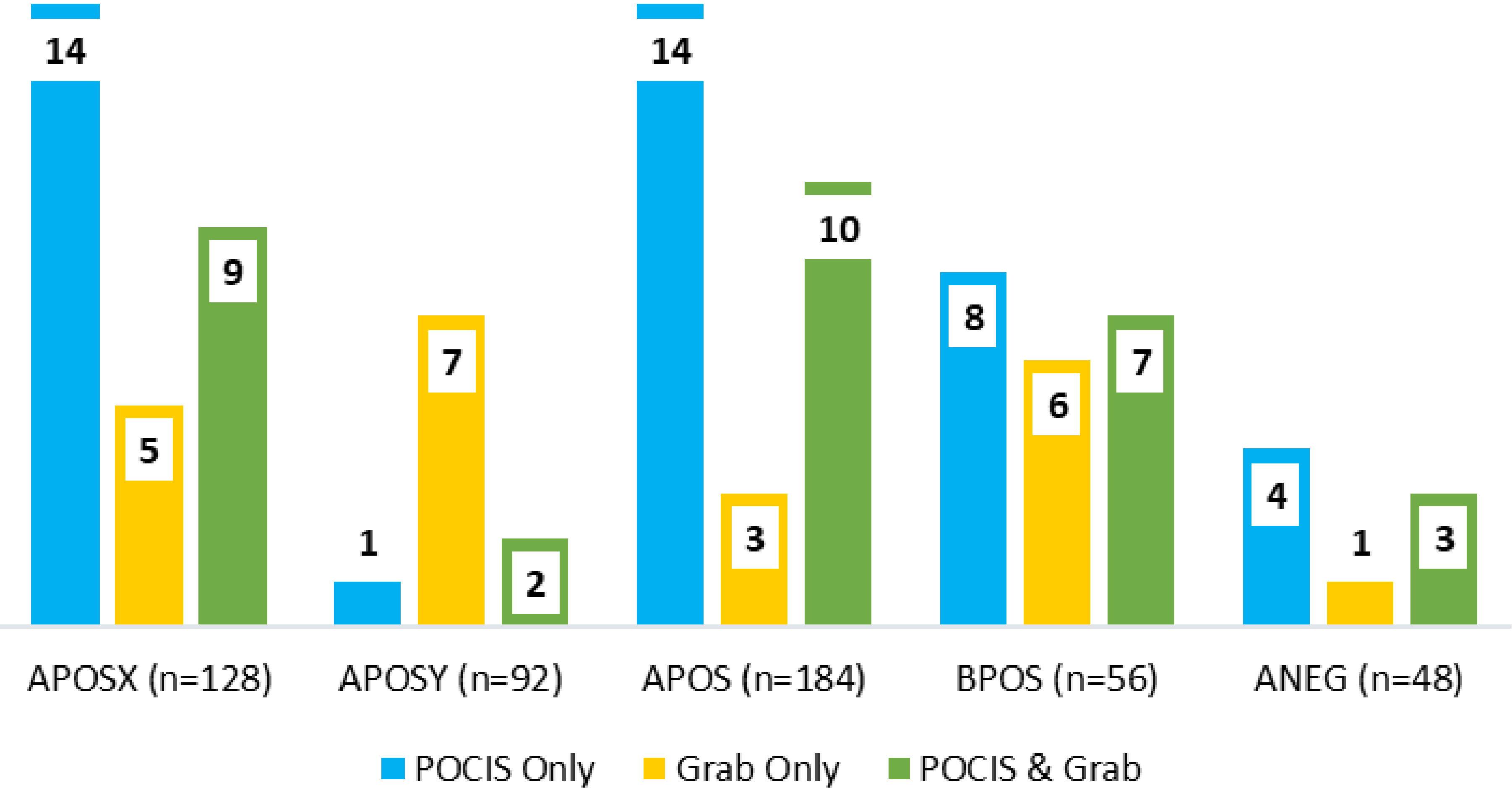
No. PPCPs Detected by Sample Type

	POCIS &Grab	POCIS Only	Grab Only
OCHLOCK	10	15	9
ALAFIA	7	3	3
WITHLAC	10	14	4
APALACH	4	9	6
Total - All Sites	31	41	22

PPCPs Detected at Every Site (n = 4)
by Matrix

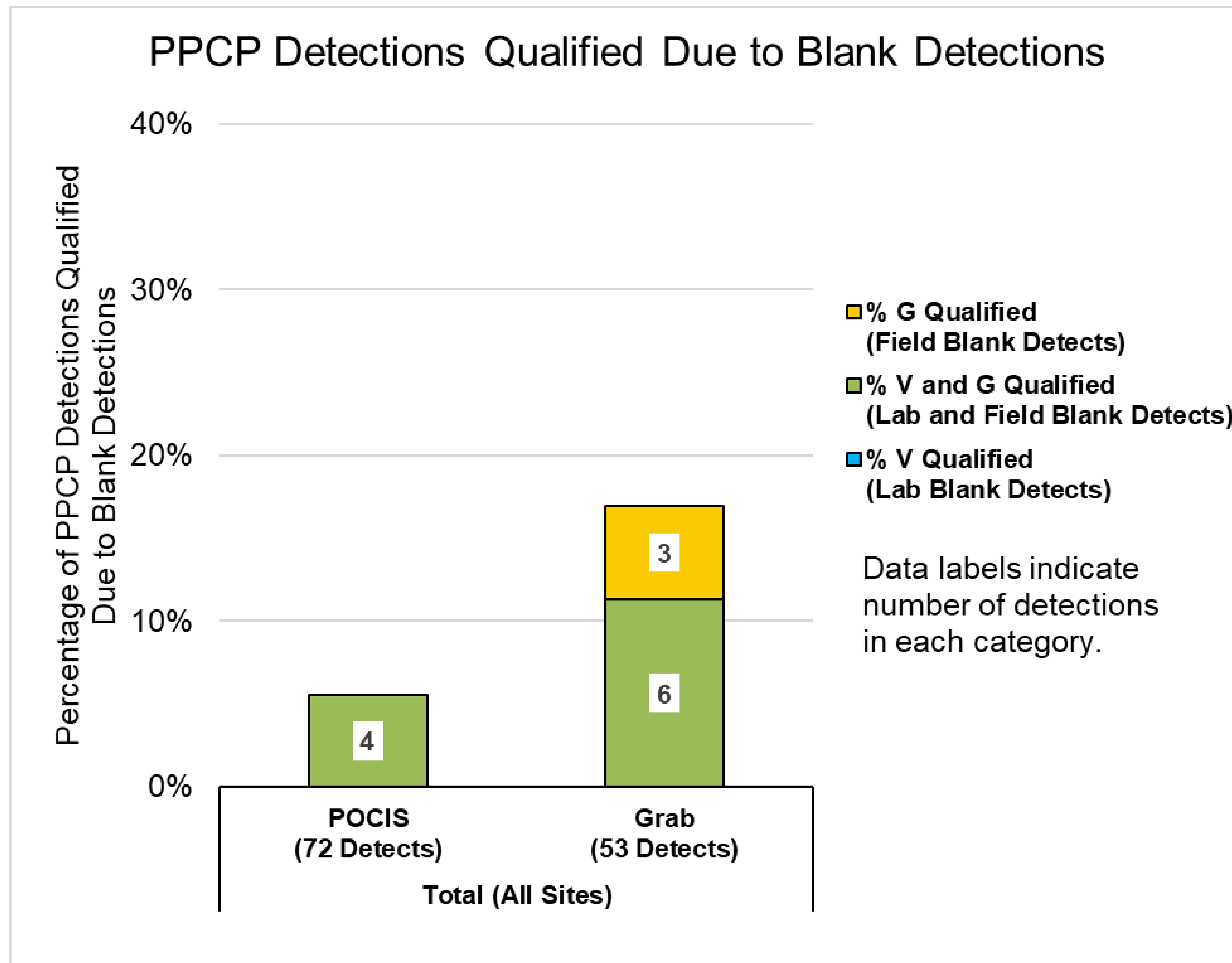
Compound	POCIS	Grab
Amphetamine	Y	Y
DEET	Y	Y
Sulfamethoxazole	Y	Y
Alprazolam	Y	
Carbamazepine	Y	
Erythromycin-H2O	Y	
Amitriptyline		Y
Total	6	4

Detects per List at All Sites by Sample Type



Quality Assurance Summary - PPCPs

- 6% of detections from POCIS samples were qualified due to blank detections.
- 17% of detections from grab samples were qualified due to blank detections.



Quality Assurance Summary - PPCPs

3 of the 39 PPCP compounds detected were also detected in lab blanks or field blanks at concentrations that required data from at least one site to be qualified.

Compound	POCIS	Grab		Compound	POCIS	Grab
Alprazolam	●			Gemfibrozil	●	
Amitriptyline	●	●		Hydrochlorothiazide	●	
Amphetamine	VG	VG		Hydrocodone	●	
Atenolol	●	●		Iopamidol		●
Azithromycin	●			Meprobamate		●
Caffeine		●		Metformin		G
Carbamazepine	●	●		Metoprolol	●	
Clarithromycin	●			Naproxen	●	●
Cocaine	●	●		Oxolinic Acid	●	●
Colchicine		●		Oxycodone	●	
Cotinine		●		Propoxyphene	●	
DEET	●	VG		Sertraline	●	●
Dehydronifedipine	●	●		Sulfadimethoxine	●	
Desmethyldiltiazem	●			Sulfamethazine	●	
Diatrizoic acid		●		Sulfamethoxazole	●	●
Diazepam	●			Triamterene	●	●
Diltiazem	●	●		Trimethoprim	●	
Diphenhydramine	●	●		Valsartan	●	●
Erythromycin-H2O	●			Venlafaxine	●	●
Furosemide		●				

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Hormones



Analyzed Pilot Study Samples for 17 Hormone Compounds

5 Hormone Compounds Detected

At one or more sites, in at least one sampling method (POCIS or Grab)

- Allyl Trenbolone
- Androstenedione
- Androsterone
- Mestranol
- Testosterone

Hormones Detections at All Sites by Sample Type

Total No. Undetects, Detects, Not Quantifiable by Sample Type

Detections	POCIS	Grab
Ochlockonee	4	2
Alafia	0	1
Withlacoochee	3	2
Apalachicola	3	1
Total	10	6
Non-detects	POCIS	Grab
Ochlockonee	13	15
Alafia	17	16
Withlacoochee	14	15
Apalachicola	14	16
Total	58	62
Not Quantifiable	POCIS	Grab
Ochlockonee	0	0
Alafia	0	0
Withlacoochee	0	0
Apalachicola	0	0
Total	0	0

Hormones Detected at Every Site (n = 4)
by Matrix

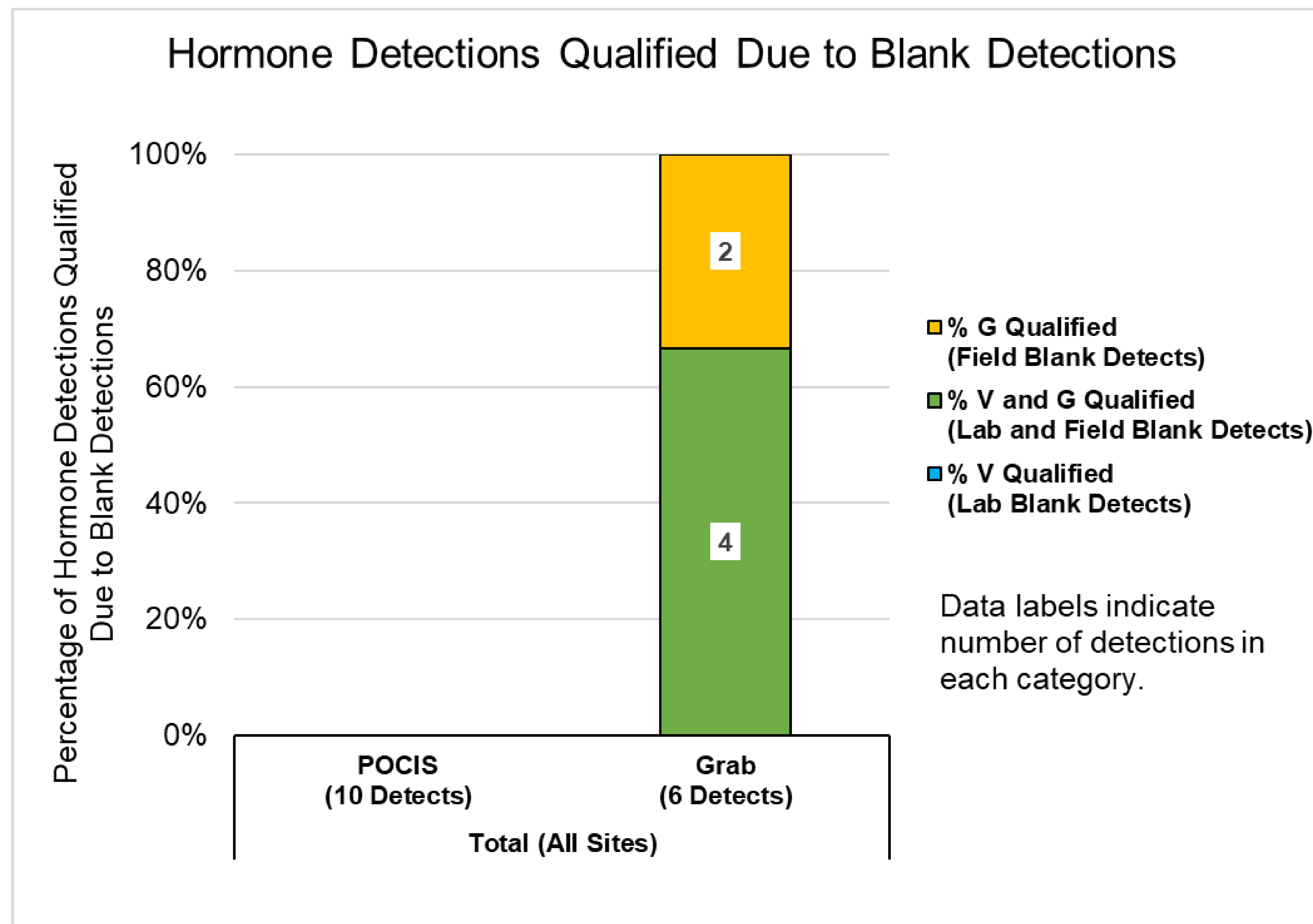
Compound	POCIS	Grab
Mestranol		Y
Total	0	1

No. Hormones Detections by Sample Type

	POCIS &Grab	POCIS Only	Grab Only
Ochlockonee	2	2	0
Alafia	0	0	1
Withlacoochee	1	2	1
Apalachicola	1	2	0
Total (All Sites)	4	6	2

Quality Assurance Summary - Hormones

- 0% of detections from POCIS samples were qualified due to blank detections.
- 100% of detections from grab samples were qualified due to blank detections.



Quality Assurance Summary - Hormones

2 of the 5 hormone compounds detected were also detected in lab blanks or field blanks at concentrations that required data from at least one site to be qualified.

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	POCIS	Grab
Allyl Trenbolone	●	
Androstenedione	●	
Androsterone	●	G
Mestranol	●	VG
Testosterone	●	

PFCs

Analyzed Pilot Study Samples for 13 PFC Compounds

10 PFC Compounds Detected

At one or more sites, in at least one sampling method (POCIS or Grab)

- PFBA
- PFBS
- PFDA
- PFHpA
- PFHxA
- PFHxS
- PFNA
- PFOA
- PFOS
- PFPeA

PFC Detections at All Sites by Sample Type

Total No. Undetects, Detects, Not Quantifiable by Sample Type

Detections	POCIS	Grab
Ochlockonee	3	1
Alafia	7	7
Withlacoochee	5	0
Apalachicola	6	4
Total	21	12
Non-detects	POCIS	Grab
Ochlockonee	14	16
Alafia	10	10
Withlacoochee	12	17
Apalachicola	11	13
Total	47	56
Not Quantifiable	POCIS	Grab
Ochlockonee	0	0
Alafia	0	0
Withlacoochee	0	0
Apalachicola	0	0
Total	0	0

PFCs Detected at Every Site (n = 4)
by Matrix

Compound	POCIS	Grab
PFOS	Y	
PFHpA	Y	
PFOA	Y	
Total	3	0

No. of Detections by Sample Type

	POCIS &Grab	POCIS Only	Grab Only
Ochlockonee	0	3	1
Alafia	5	2	2
Withlacoochee	5	0	0
Apalachicola	2	4	2
Total (All Sites)	12	9	5

Quality Assurance Summary - PFCs

No PFC compounds were detected in lab blanks or field blanks at concentrations that required data from at least one site to be qualified.

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	POCIS	Grab
PFBS	●	●
PFHpA	●	●
PFHxA	●	●
PFOA	●	●
PFOS	●	●
PFDA	●	
PFHxS	●	
PFNA	●	
PFBA		●
PFPeA		●



PBDES

Analyzed Pilot Study Samples for 8 PBDE Compounds

8 PBDE Compounds Detected

At one or more sites, in at least one sampling method (SPMD or Grab)

- 2,2',3,3',4,4',5,5',6,6'-DeBDE
- 2,2',3,4,4',5',6-HpBDE
- 2,2',4,4',5,5'-HxBDE
- 2,2',4,4',5,6'-HxBDE
- 2,2',4,4',5-PeBDE
- 2,2',4,4',6-PeBDE
- 2,2',4,4'-TeBDE
- 2,4,4'-TriBDE

PBDE Detections at All Sites by Sample Type

Non-detects, Detects, Not Quantifiable by Sample Type

Detections	SPMD	Grab
Ochlockonee	8	8
Alafia	8	7
Withlacoochee	8	7
Apalachicola	8	4
Total	32	26
Non-detects	SPMD	Grab
Ochlockonee	0	0
Alafia	0	1
Withlacoochee	0	1
Apalachicola	0	4
Total	0	6
Not Quantifiable	SPMD	Grab
Ochlockonee	0	0
Alafia	0	0
Withlacoochee	0	0
Apalachicola	0	0
Total	0	0

PBDEs Detected at Every Site (n = 4) by Matrix

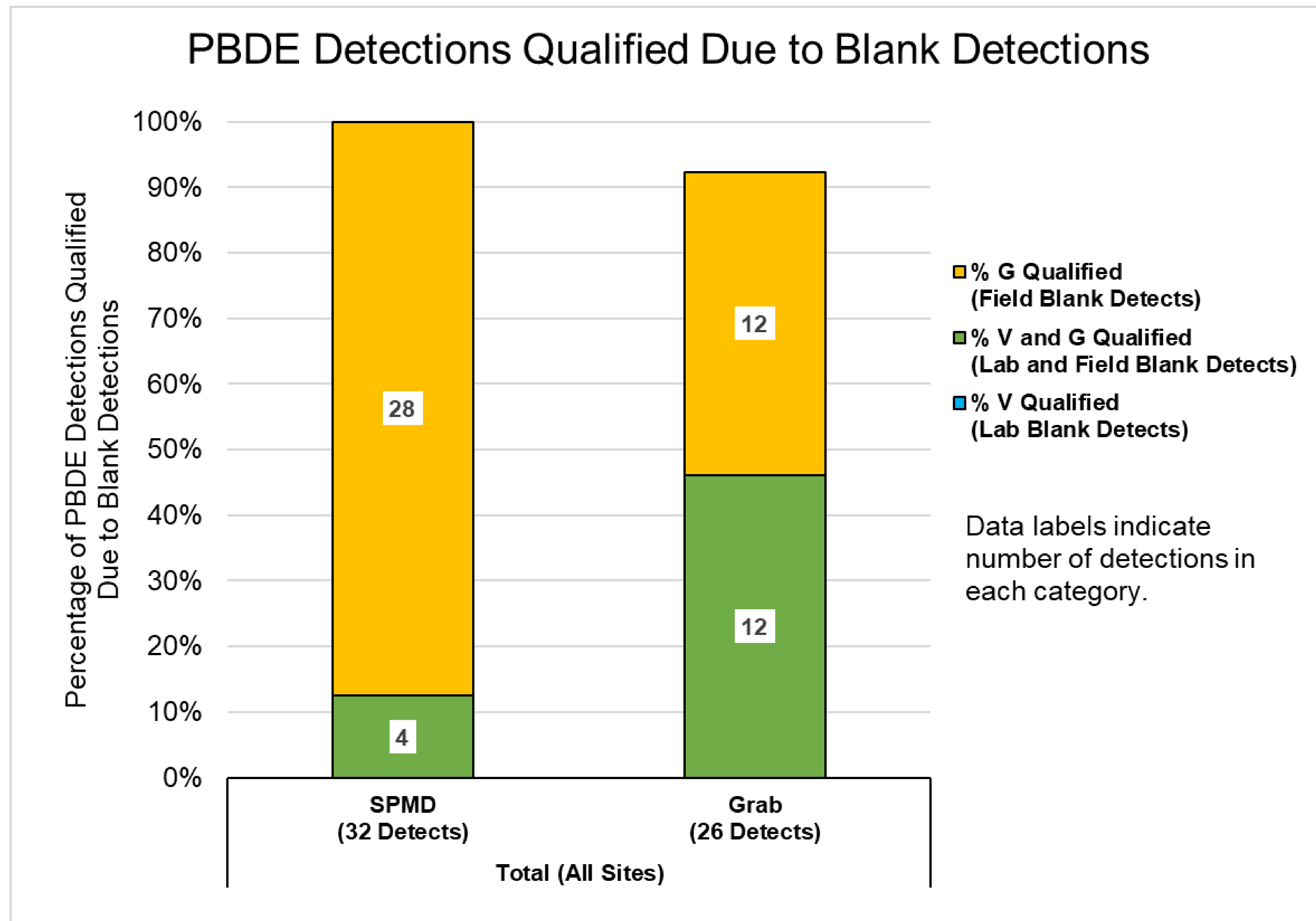
Compound	SPMD	Grab
2,2',3,3',4,4',5,5',6,6'-DeBDE	Y	Y
2,2',4,4',5-PeBDE	Y	Y
2,2',4,4',6-PeBDE	Y	Y
2,2',4,4'-TeBDE	Y	Y
2,2',3,4,4',5',6-HpBDE	Y	
2,2',4,4',5,5'-HxBDE	Y	
2,2',4,4',5,6'-HxBDE	Y	
2,4,4'-TriBDE	Y	
Total	8	4

No. PBDEs Detected by Sample Type

	SPMD & Grab	SPMD Only	Grab Only
OCHLOCK	8	0	0
ALAFIA	7	1	0
WITHLAC	7	1	0
APALACH	4	4	0
Total (All Sites)	26	6	0

Quality Assurance Summary - PBDEs

- 100% of detections from SPMD samples were qualified due to blank detections.
- 92% of detections from grab samples were qualified due to blank detections.



Quality Assurance Summary - PBDEs

All of the PBDE compounds detected, were also detected in lab blanks or field blanks at concentrations that required data from at least one site to be qualified.

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	SPMD	Grab
2,2',3,3',4,4',5,5',6,6'-DeBDE	VG	G
2,2',3,4,4',5',6-HpBDE	G	G
2,2',4,4',5,5'-HxBDE	G	●
2,2',4,4',5,6'-HxBDE	G	G
2,2',4,4',5-PeBDE	G	VG
2,2',4,4',6-PeBDE	G	VG
2,2',4,4'-TeBDE	G	VG
2,4,4'-TriBDE	G	G

Alkylphenols



Analyzed Pilot Study Samples for 4 Alkylphenol Compounds

2 Alkylphenol Compounds Detected

At one or more sites, in at least one sampling method (SPMD or Grab)

- 4-Nonylphenols
- 4-Nonylphenol diethoxylates

Alkylphenol Detections at All Sites by Sample Type

Total No. Undetects, Detects, Not Quantifiable
by Sample Type

Detections	SPMD	Grab
Ochlockonee	2	1
Alafia	2	1
Withlacoochee	2	1
Apalachicola	2	1
Totals	8	4
Undetects	SPMD	Grab
Ochlockonee	2	3
Alafia	2	3
Withlacoochee	2	3
Apalachicola	2	3
Totals	8	12
Not Quantifiable	SPMD	Grab
Ochlockonee	0	0
Alafia	0	0
Withlacoochee	0	0
Apalachicola	0	0
Totals	0	0

Alkylphenols Detected at Every Site (n = 4)
by Matrix

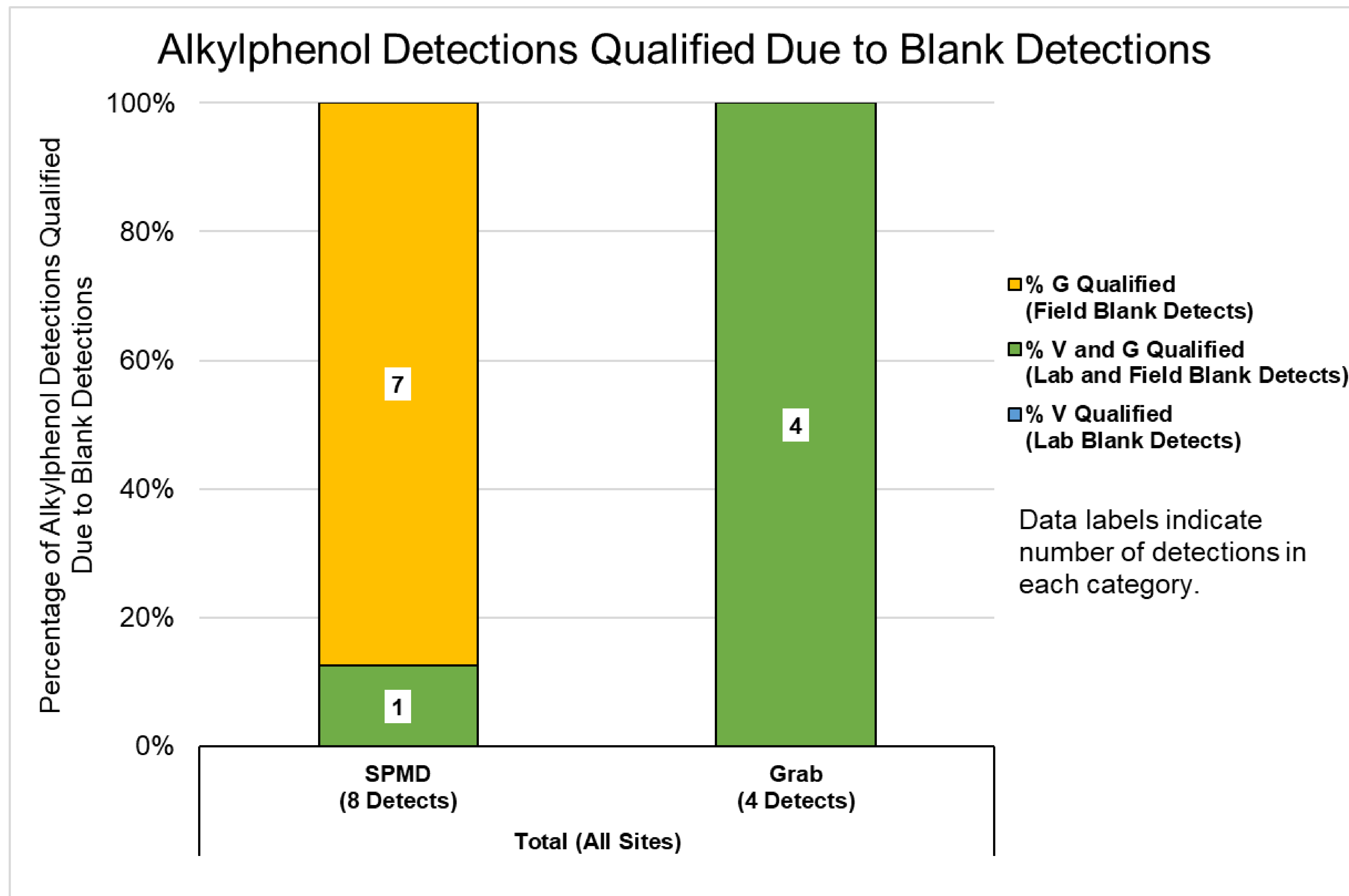
Compound	SPMD	Grab
4-Nonylphenols	Y	Y
4-Nonylphenol diethoxylates	Y	
Total	2	1

No. Alkylphenols Detected by Sample Type

	SPMD only	Grab only	SPMD&Grab
Ochlockonee	1	0	1
Alafia	1	0	1
Withlacoochee	1	0	1
Apalachicola	1	0	1
Total-All Sites	4	0	4

Quality Assurance Summary - Alkylphenols

100% of detections from SPMD & grab samples were qualified due to blank detections.



Quality Assurance Summary

All alkylphenol compounds detected, were also detected in lab blanks or field blanks at concentrations that required data from all sites to be qualified.

All detections from SPMD & grab samples were qualified due to blank detections.

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	SPMD	Grab
4-Nonylphenols	VG	VG
4-Nonylphenol diethoxylates	G	

DEP Data



Analyzed Pilot Study Samples for 92 Compounds

32 Compounds Detected

At one or more sites, in at least one sampling method (POCIS, SPMD, or Grab)

* Indicates compounds where analysis not performed on POCIS samples

- | | | |
|--------------------|---------------------|----------------|
| ●2,4-D | ●Chlorpyrifos Ethyl | ●Imidacloprid |
| ●Acetaminophen | ●DDD-p,p'* | ●Metalaxyl |
| ●Acetochlor | ●DDE-p,p'* | ●Metolachlor |
| ●Alpha-Chlordane* | ●Dieldrin* | ●Norflurazon |
| ●Ametryn | ●Diuron | ●Pendimethalin |
| ●Atrazine | ●Fipronil | ●Prometon |
| ●Atrazine Desethyl | ●Fipronil Sulfide | ●Simazine |
| ●Bentazon | ●Fipronil Sulfone | ●Sucralose |
| ●Bromacil | ●Fluridone | ●Toxaphene* |
| ●Carbamazepine | ●Gamma-Chlordane* | ●Trifluralin* |
| ●Chlordane* | ●Hexazinone | |

Compound Detections at All Sites by Sample Type

Total No. Detects & Non-detects by Sample Type

Detections	SPMD	POCIS	Grab
Ochlockonee	10	11	20
Alafia	1	12	16
Withlacoochee	7	14	20
Apalachicola	10	12	17
Total	28	49	73
Undetects	SPMD	POCIS	Grab
Ochlockonee	81	52	72
Alafia	90	51	76
Withlacoochee	84	49	72
Apalachicola	81	51	75
Total	336	203	295

Compounds Detected at Every Site (n = 4) by Matrix

Compound	SPMD	POCIS	Grab
Chlorpyrifos Ethyl	Y		
Atrazine		Y	Y
Bromacil		Y	Y
Carbamazepine		Y	Y
Diuron		Y	Y
Imidacloprid		Y	Y
Metalaxyl		Y	Y
Metolachlor		Y	Y
Simazine		Y	Y
Sucralose		Y	Y
Atrazine Desethyl			Y
Bentazon			Y
Fipronil Sulfone			Y
Hexazinone			Y
Total	1	9	13

No. Compounds Detected by Sample Type

	POCIS, SPMD, Grab	SPMD only	Grab only	Grab & SPMD	Grab & POCIS
OCHLOCK	1	9	9	0	10
ALAFIA	0	1	4	0	12
WITHLAC	2	5	6	0	12
APALACH	0	9	4	1	12
Total - All Sites	3	24	23	1	46

Quality Assurance

Summary – DEP

Data

Legend	
●	Compound detected at one or more sites. Data not qualified due to blank detections.
V	Compound detected at one or more sites. Lab blank result > 10% of sample result(s)
VG	Compound detected at one or more sites. Lab blank and field blank results > 10% of sample result(s).
G	Compound detected at one or more sites. Field blank result > 10% of sample result(s).
	Compound not detected at any sites.

Compound	SPMD	POCIS	Grab
Metolachlor	●	●	●
Sucralose	●	●	●
Chlorpyrifos Ethyl	●		●
2,4-D		●	●
Acetochlor		●	●
Atrazine		●	●
Bentazon		●	●
Bromacil		●	●
Carbamazepine		●	●
Diuron		●	●
Fipronil		●	●
Fluridone		●	●
Imidacloprid		●	●
Metalaxyl		●	●
Norflurazon		●	●
Prometon		●	●
Simazine		●	●
Alpha-Chlordane	●		
Chlordane	●		
DDD-p,p'	●		
DDE-p,p'	●		
Dieldrin	●		
Gamma-Chlordane	●		
Pendimethalin	●		
Toxaphene	●		
Trifluralin	●		
Acetaminophen			●
Ametryn			●
Atrazine Desethyl			●
Fipronil Sulfide			●
Fipronil Sulfone			●
Hexazinone			●

Review

SGS/Axys Data

- Pesticides
 - 42 compounds detected of 76 analyzed.
 - Most compounds were found in the SPMD only.
- PPCPs
 - 39 compounds detected of 127 analyzed.
 - Most compounds were found in POCIS only; there was a widespread distribution of compounds also found in the Grab.
- Hormones
 - 5 compounds detected of 17 analyzed.
 - Blank interference caused all grab sample data to be qualified, but did not affect POCIS sample data.

Review

SGS/Axys Data

- PFCs
 - 10 compounds detected of 13 analyzed.
 - Most compounds found in POCIS only or POCIS & Grab.
- PBDEs
 - All compounds analyzed (n = 8) were detected in SPMD & Grab samples at one or more sites.
 - Blank interference caused all SPMD data & > 90% of Grab sample data to be qualified.
- Alkylphenols
 - 2 of the 4 compounds analyzed were found in SPMD only or SPMD & Grab.
 - Blank interference caused all SPMD and Grab sample data to be qualified.

Review DEP Data

- Pesticides
 - 29 compounds detected of 88 analyzed.
 - Most compounds were found in Grab & POCIS.
 - Several compounds were found in SPMD only.
- PPCPs
 - 3 compounds detected of 4 analyzed.
 - Most compounds were found in Grab and SPMD.
 - Acetaminophen was detected in Grab samples analyzed by DEP, but not in those analyzed by SGS/Axys.

Looking Ahead

- Awaiting results from the USGS .
- Working with the University of Florida on analyzing final report.
- Interpreting results and compiling information to finalize report.

Further Discussion

- Analytes that should be added or removed if the project was expanded? Are there analyte groups that are of higher priority?
- Intensity of sample collection and analysis vs. the results.
- Discussion about data and QA/QC.
- Take home messages that can be extracted from this project, and how they construct our path forward.

References

- Alvarez, D et al. (2007) Chapter 8 Tool for monitoring hydrophilic contaminants in water: polar organic chemical integrative sampler (POCIS). Comprehensive Analytical Chemistry. 48, 171-197. doi:10.1016/S0166-526X(06)48008-9
- Smith, R. (2018) Product: Semipermeable Membrane Device (SPMD) and its Deployment. <http://www.est-lab.com/spmd.php>