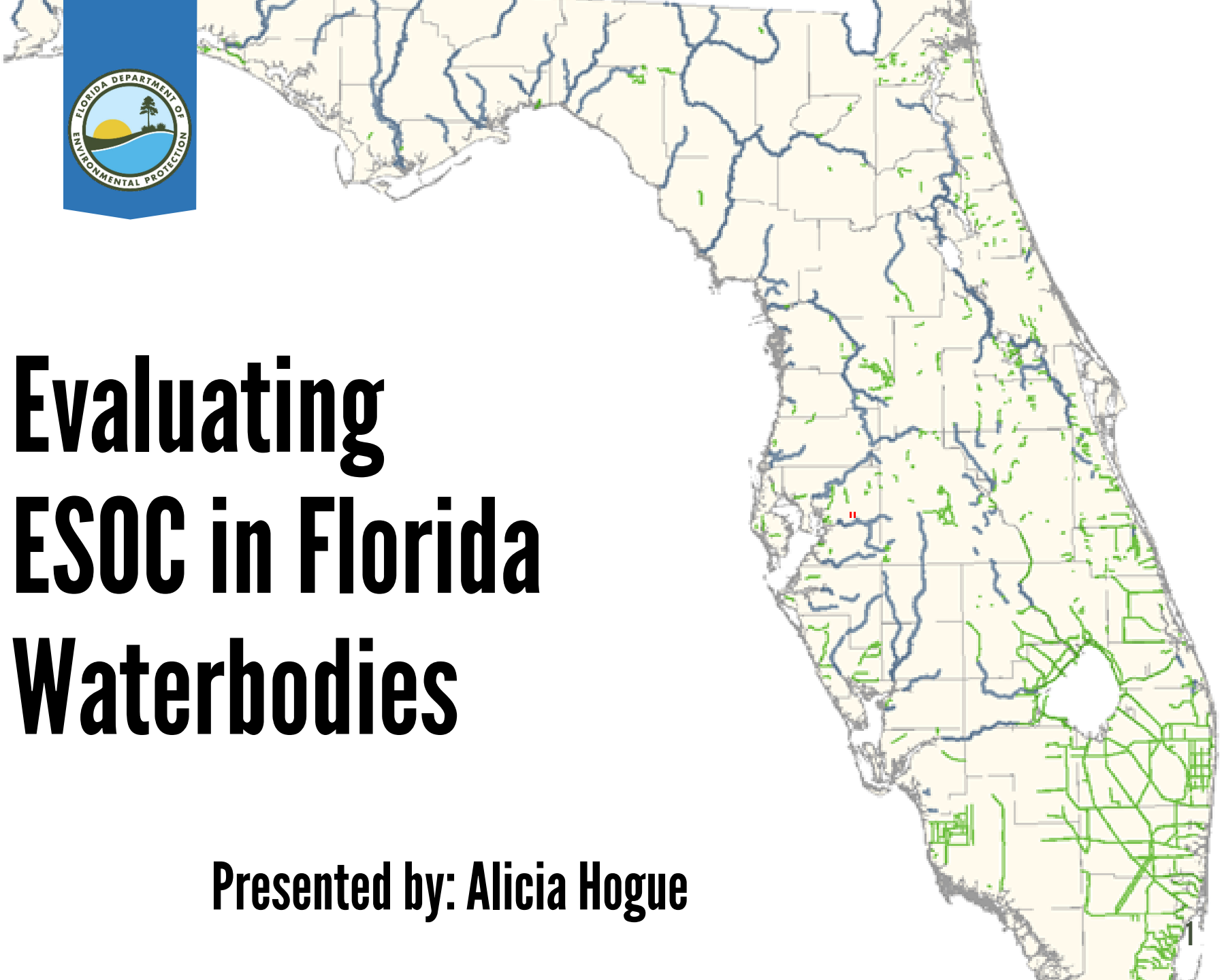


Evaluating ESOC in Florida Waterbodies

Presented by: Alicia Hogue

Overview

- 4 river sites chosen:
  - Ochlockonee, Withlacoochee, Apalachicola & Alafia
- 3 types of sample collection:
  - Semi-Permeable Membrane Device (SPMD)
  - Polar Organic Compound Integrative Sampler (POCIS)
  - Whole water samples (Grab)
- 6 Categories of compounds:
  - Pesticides, PPCPs, Hormones, PFCs, PBDEs, and Alkylphenols
- QA is discussed in each category.
- SGS Analytical data is presented, then DEP, UF, and lastly USGS.

Ochlockonee River

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.
- Sucralose maximum value detected was 2.6 µg/L.

Withlacoochee River

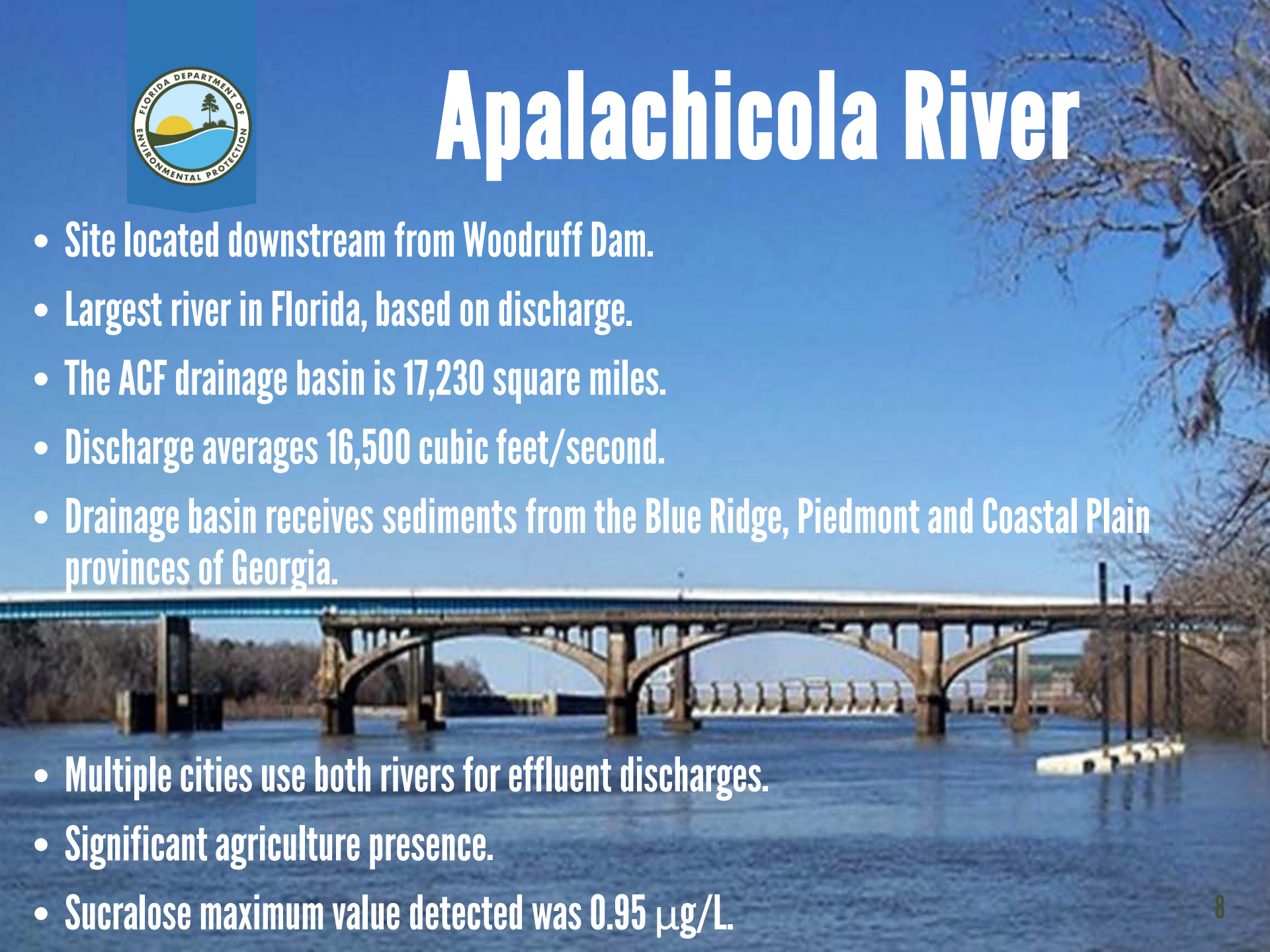
Withlacoochee River

- 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.
- Sucralose maximum value detected was 2.9 µg/L

Apalachicola River

Apalachicola River

- Site located downstream from Woodruff Dam.
- 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.
- Significant agriculture presence.
- Sucralose maximum value detected was 0.95 µg/L.

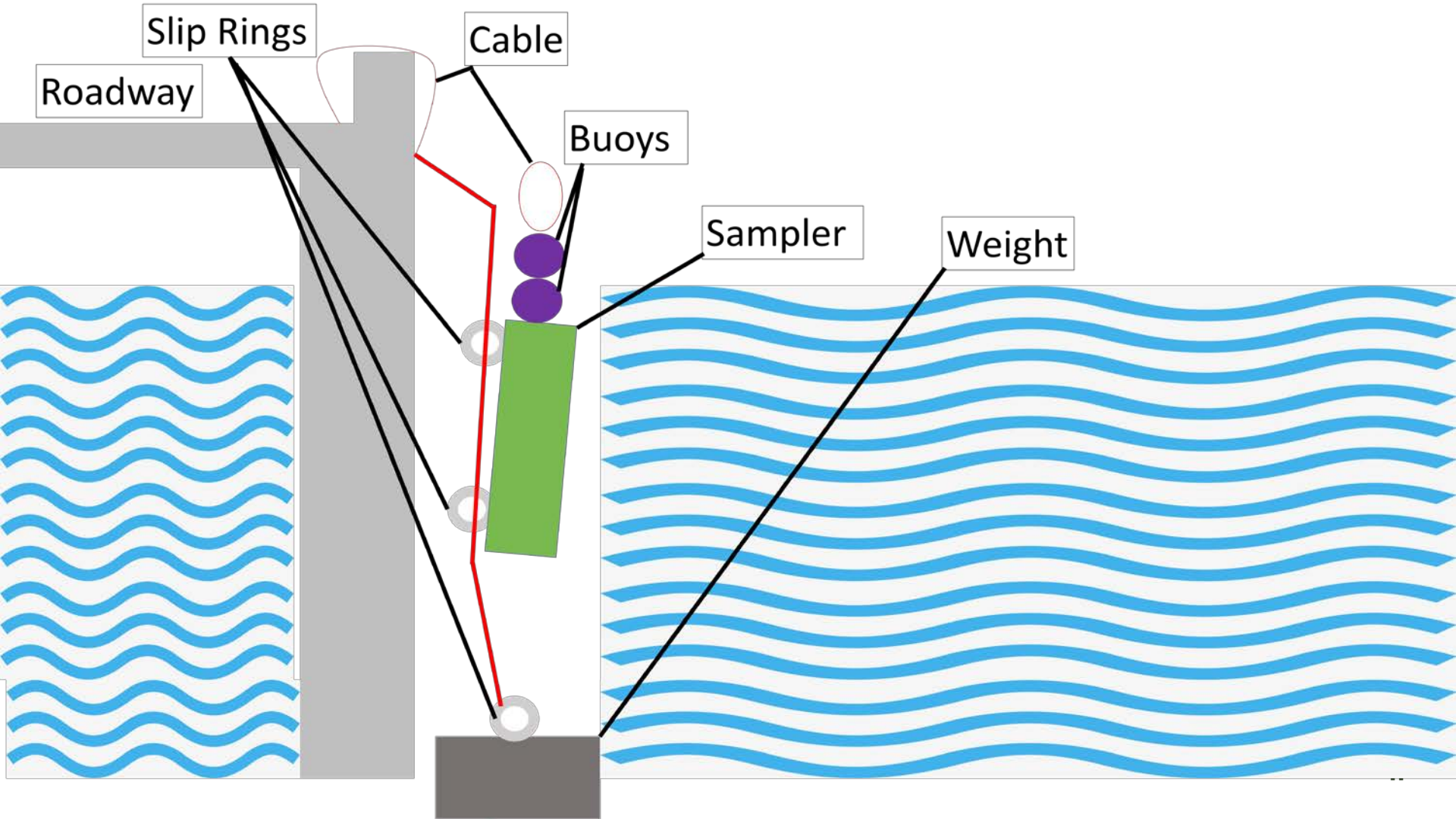
Alafia River

Alafia River

- Site is downstream of the confluence of the North & South Prongs of the river at Tampa Bay Water Authority (TBWA) withdrawal point.
- 25 miles long.
- 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.
- Sucralose maximum value detected was 7.3 µg/L.

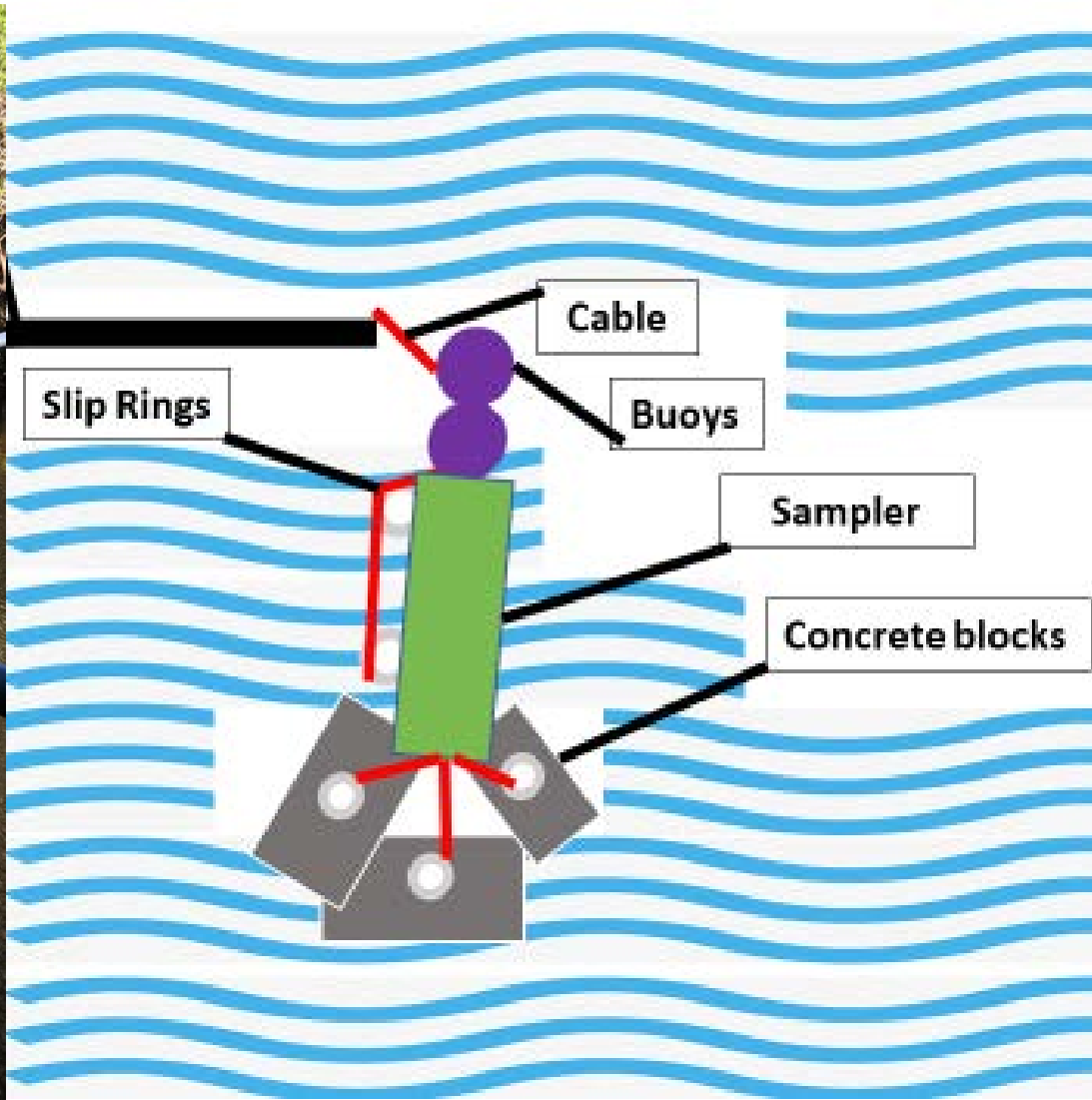
Review of Deployment

Ochlockonee, Withlacoochee & Apalachicola



Review of Deployment

Alafia



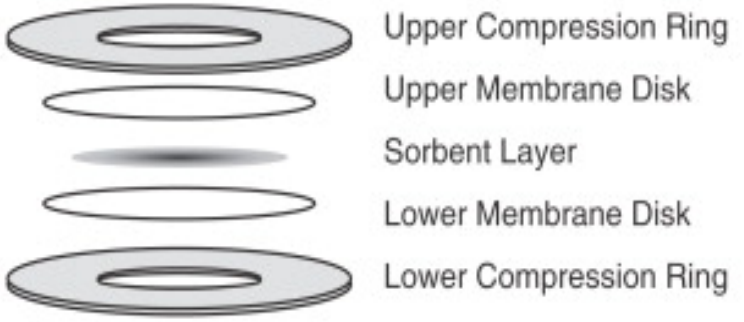
Semi-Permeable Membrane Device (SPMD)

- 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 POCs makes extraction & detection difficult.
- Monitors **hydrophilic** contaminants that could be potential EDs, or acutely toxic.
- Provides reproducible method for determining concentration of POCs in the ppt 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/POCIS (1)

- No PRC/spike addition.
- Extract split 1:3:
  - BLYES/BLYAS &SOS Chromotest analyses
  - ER/AR binding & transactivation assay
  - Pesticide analyses

SPMD/POCIS (2)

- PRCs/spikes added.
- Extract split 1:5:
  - Alkylphenols (SPMD Only)
  - MRES w/ ON
  - PBDEs
  - PRC analysis
  - Archive

Blank Collection

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 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 sample
   - Blank collected using DI water supplied from SGS.

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


SGS Data

Pesticides

- Analyzed samples for 76 compounds.
- 42 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.
- 18 of the 42 compounds detected were qualified.

https://www.nation.co.ke/business/seedsofgold/Bio-pesticides-in-focus-as-safety-concerns-reshape-export-trade-/2301238-2340128-9n3uwlz/index.html

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

Legend	
•	Data not qualified due to blank detections.
V	Lab blank result > 10% of sample result(s)
VG	Lab & field blank results > 10% of sample result(s).
G	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

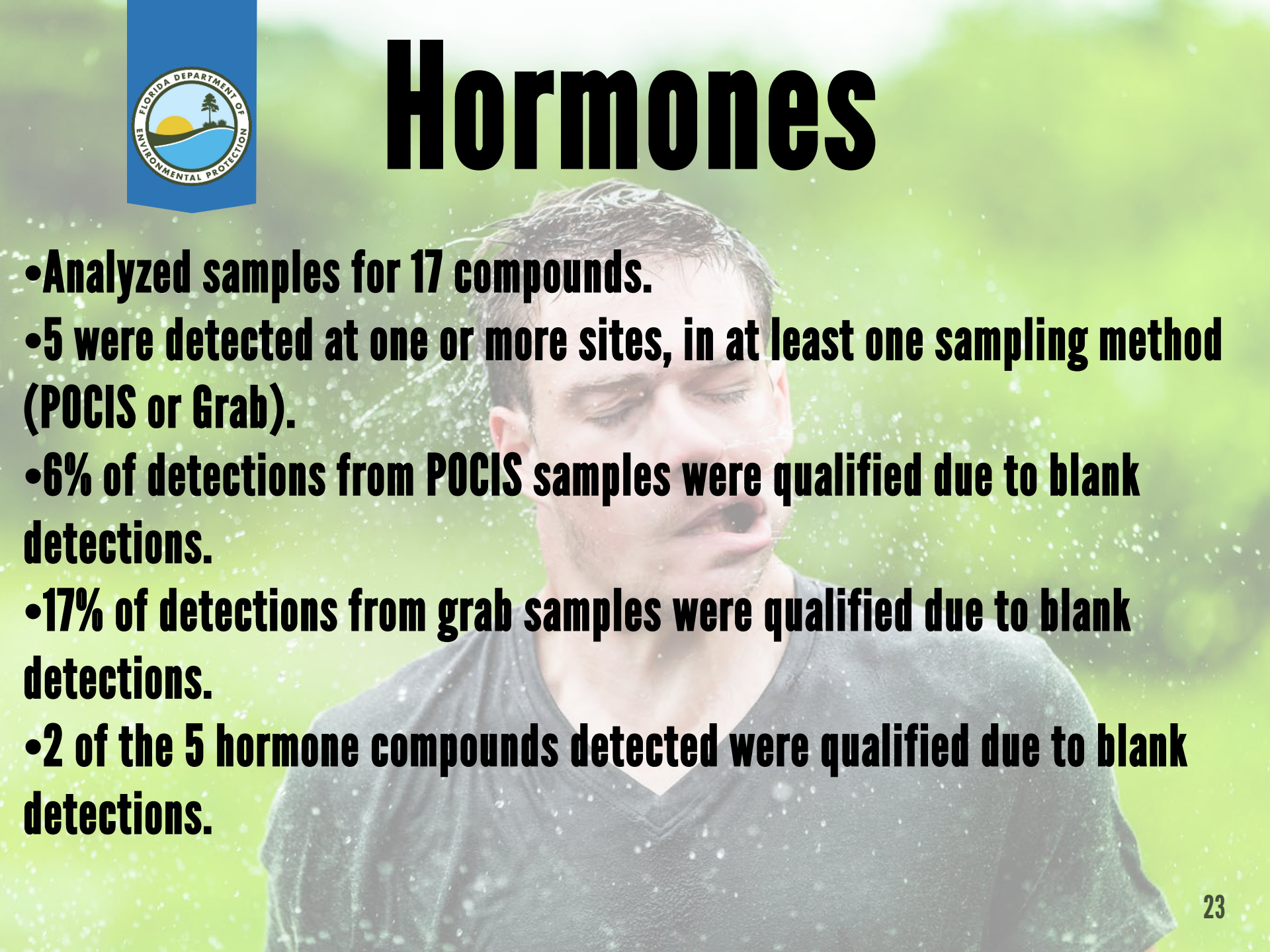
PPCPs

- Analyzed samples for 127 compounds.
- 39 were detected at one or more sites, in at least one sample type (POCIS or Grab).
- 6% of detections from POCIS samples were qualified due to blank detections.
- 17% of detections from grab samples were qualified due to blank detections.
- 3 of the 39 compounds detected were qualified.

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

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

Hormones



- Analyzed samples for 17 compounds.
- 5 were detected at one or more sites, in at least one sampling method (POCIS or Grab).
- 6% of detections from POCIS samples were qualified due to blank detections.
- 17% of detections from grab samples were qualified due to blank detections.
- 2 of the 5 hormone compounds detected were qualified due to blank detections.

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

Compound	POCIS	Grab
Mestranol		VG

Perfluorinated Compounds PFCs

- Analyzed samples for 13 compounds.
- 10 were detected at one or more sites, in at least one sampling method (POCIS or Grab).
- 0% of detections from POCIS & Grab samples were qualified due to blank detections.

https://www.google.com/search?q=perfluorinated+compounds&source=lnms&tbm=isch&sa=X&ved=0ahUKEwi4hcTa-qTdAhWmq1kKHcy7B0sQ_AUICygC&biw=1366&bih=620#imgrc=-vTOc9wh9VQc8M:

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

Compound	POCIS	Grab
PFOS	●	
PFHpA	●	
PFOA	●	

Polybrominated Diphenyl Ethers-PBDEs

- Analyzed samples for 8 compounds.
- All were detected at one or more sites, in at least one sampling method (SPMD or Grab).
- 100% of detections from SPMD samples were qualified due to blank detections.
- 92% of detections from grab samples were qualified due to blank detections.
- All of the PBDE compounds detected were qualified.

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

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

Alkylphenols

- Analyzed samples for 4 compounds.
- 2 were detected at one or more sites, in at least one sampling method (SPMD or Grab).
- All compounds detected in SPMD & Grab were also detected in blanks at concentrations that required data from all sites to be qualified.

https://www.google.com/search?q=laundry+detergent+alkylphenols&rlz=1C1GCEA_enUS757US757&source=lnms&tbm=isch&sa=X&ved=0ahUKEwjbn86M8bDdAhWJyVMKHfMlCmIQ_AUIDygC&biw=1280&bih=887#imgrc=wdzaBL1XIfCGfM:

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

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

DEP Data

DEP Data

- Analyzed samples for 92 compounds.
- 32 compounds detected at one or more sites, in at least one sampling method (POCIS, SPMD, or Grab).
- 0% of detections from POCIS & Grab samples were qualified due to blank detections.

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

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

Review SGS Data

Pesticides

- 42 compounds detected of 76 analyzed; most found in the SPMD.

PPCPs

- 39 compounds detected of 127 analyzed; most found in POCIS.

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 Data

PFCs

- 10 compounds detected of 13 analyzed; most found in POCIS.

PBDEs

- All compounds analyzed were detected in SPMD & Grab samples at one or more sites, but blank interference caused all SPMD data & > 90% of Grab sample data to be qualified.

Alkylphenols

- 2 compounds detected of 4 analyzed, but blank interference caused all SPMD and Grab sample data to be qualified.

Review DEP Data

Pesticides

- 29 compounds detected of 88 analyzed; most found in Grab.

PPCPs

- 3 compounds detected of 4 analyzed; most found in Grab & SPMD.
- Acetaminophen was detected in Grab samples analyzed by DEP, but not in those analyzed by SGS.


University of
Florida

ER and AR Transactivation Assay

Tests for the ability of the activated receptor to turn on gene transcription

Estrogen Receptor Results

- **Grab**
  - Estrogenic activity found only at Ochlockonee.
  - Interference at Apalachicola.
- **POCIS & SPMD**
  - Variable results indicated interference with the assay.
  - POCIS sample from Apalachicola was only one that conclusively showed no estrogenic activity.

Androgen Receptor Results

- **Grab**
  - Low level of androgenic activity found in the field blank.
    - May be due to androsterone contamination in the sample (analyzed by SGS-Axys).
  - Low level of androgenic activity found in the grab sample for Ochlockonee.
  - Interferences were found in the Apalachicola sample.
- **POCIS & SPMD**
  - No activity.

ER and AR Binding Assay

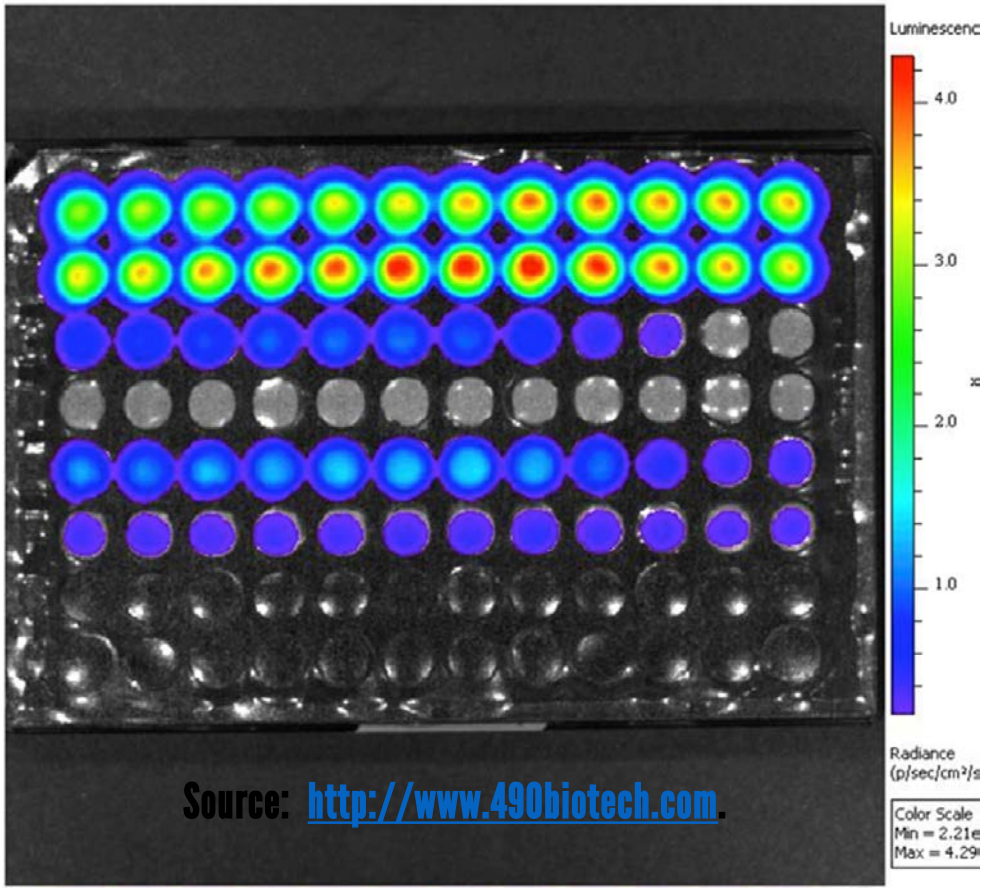
Tests the ability of estrogen or an estrogen mimic to bind directly to the estrogen receptor, or an androgen mimic to bind directly to the androgen receptor

USGS

science for a changing world

Bioluminescent Yeast Estrogen & Androgen Screen

Used to detect water's estrogenic and androgenic activity by promoting a light-generating or bioluminescent response in the yeast strain



Source: http://www.490biotech.com.

Bioluminescent Yeast Estrogen & Androgen Screen Results

BLYES Results

- Grab
  - Alafia, Apalachicola, Withlacoochee Rivers had estrogenic samples
- POCIS
  - All sites had estrogenic samples

BLYAS results

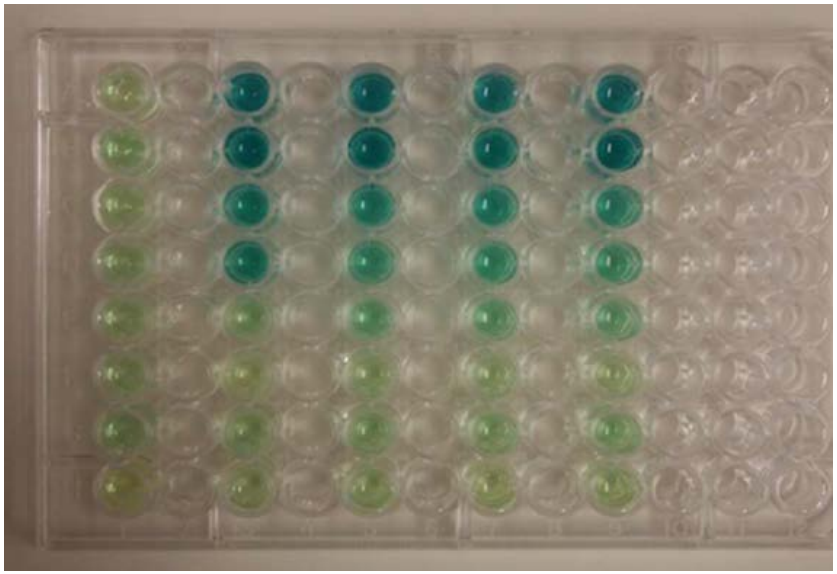
- No androgenic activity

SOS Chromotest

The SOS Chromotest is a colorimetric test that measures the reaction of E. coli bacteria to DNA damaging compounds in water samples.

Results

- POCIS & SPMD
  - Presence of DNA damaging compounds at the Alafia River site.



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