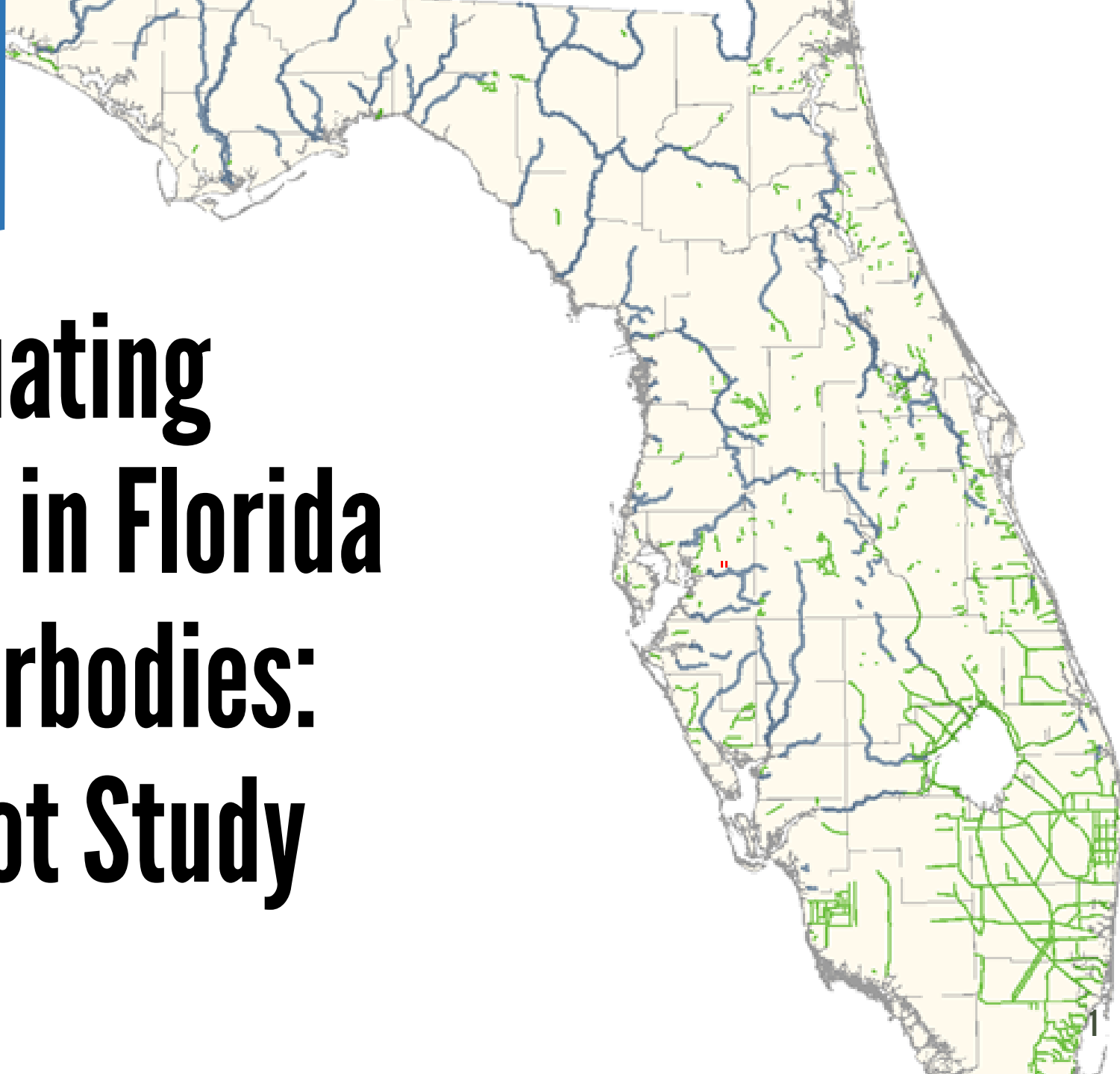




Evaluating ESOC in Florida Waterbodies: A Pilot Study



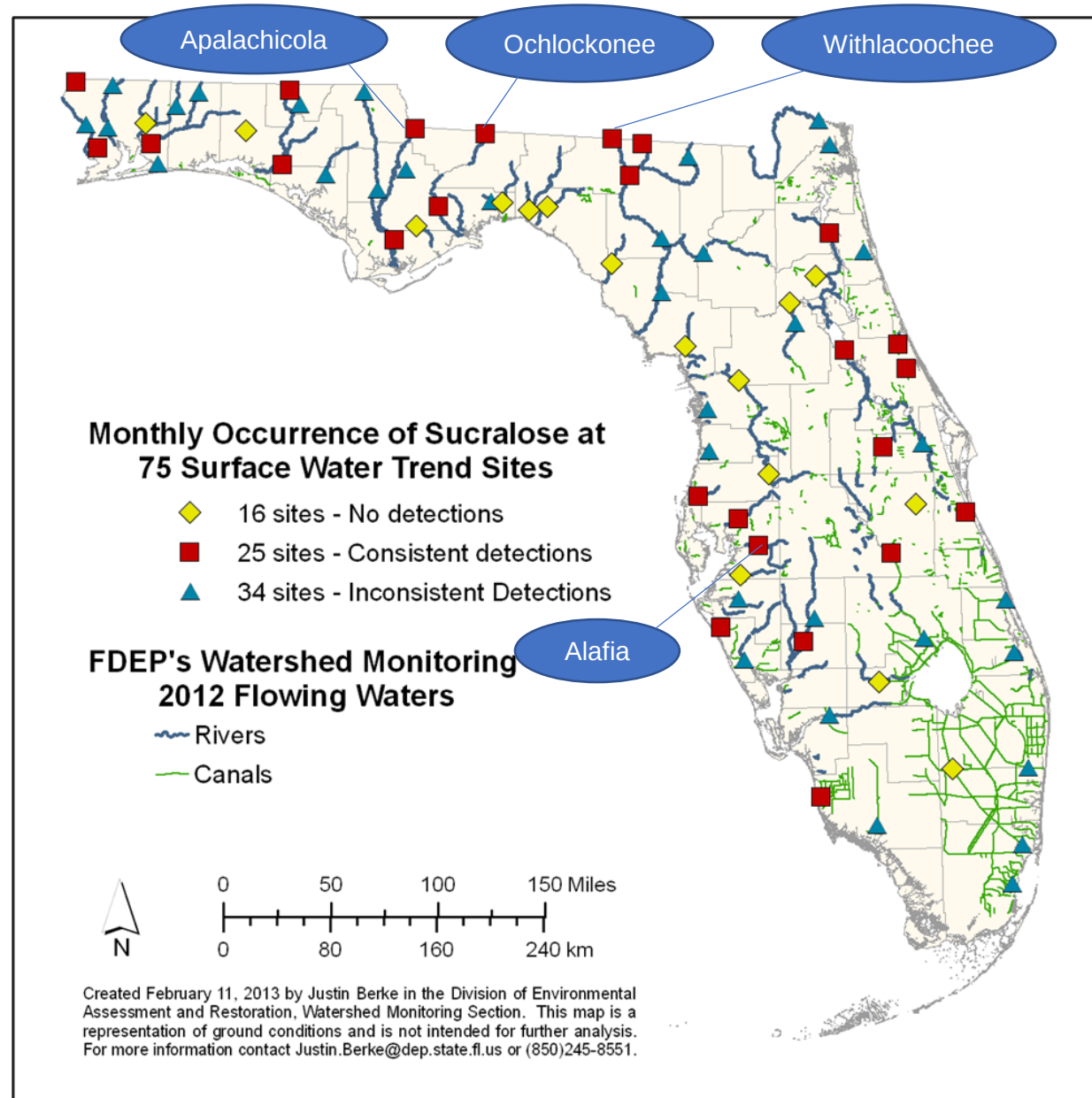


Overview

- **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.**



Surface Water Trend Stations' 2012 Sucralose Detection Frequency





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 $\mu\text{g/L}$.

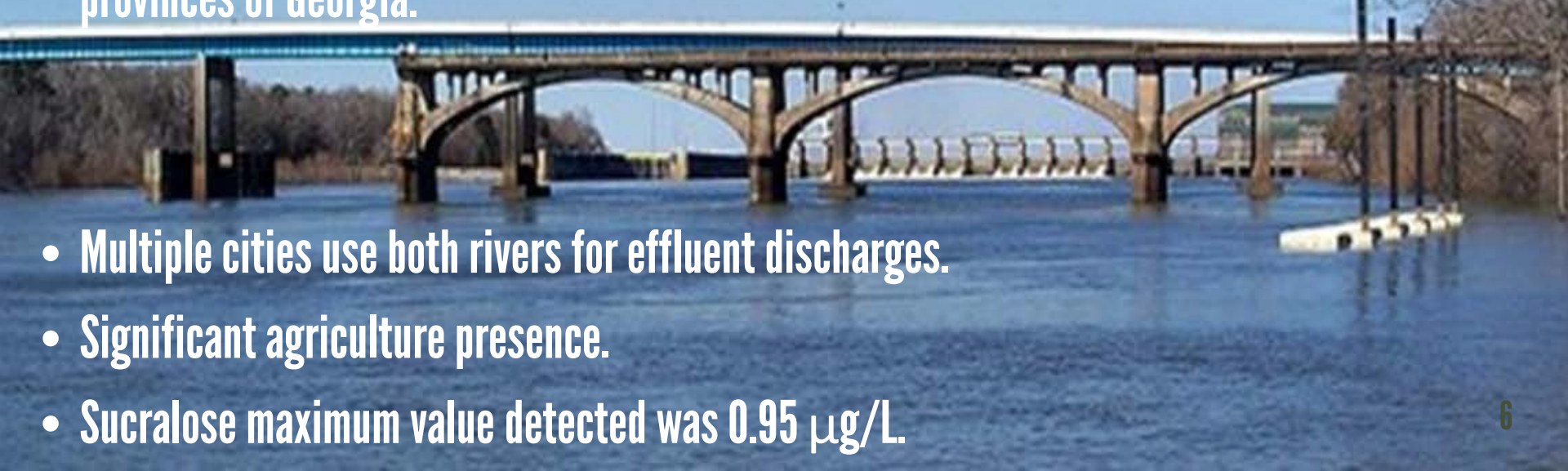


Withlacoochee River

- 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 $\mu\text{g/L}$



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.
- 
- A large concrete bridge with multiple arches spans a wide river. The bridge has several tall piers supporting the arches. In the background, a dam is visible. The river is calm, and the sky is clear.
- Multiple cities use both rivers for effluent discharges.
 - Significant agriculture presence.
 - Sucralose maximum value detected was 0.95 $\mu\text{g/L}$.



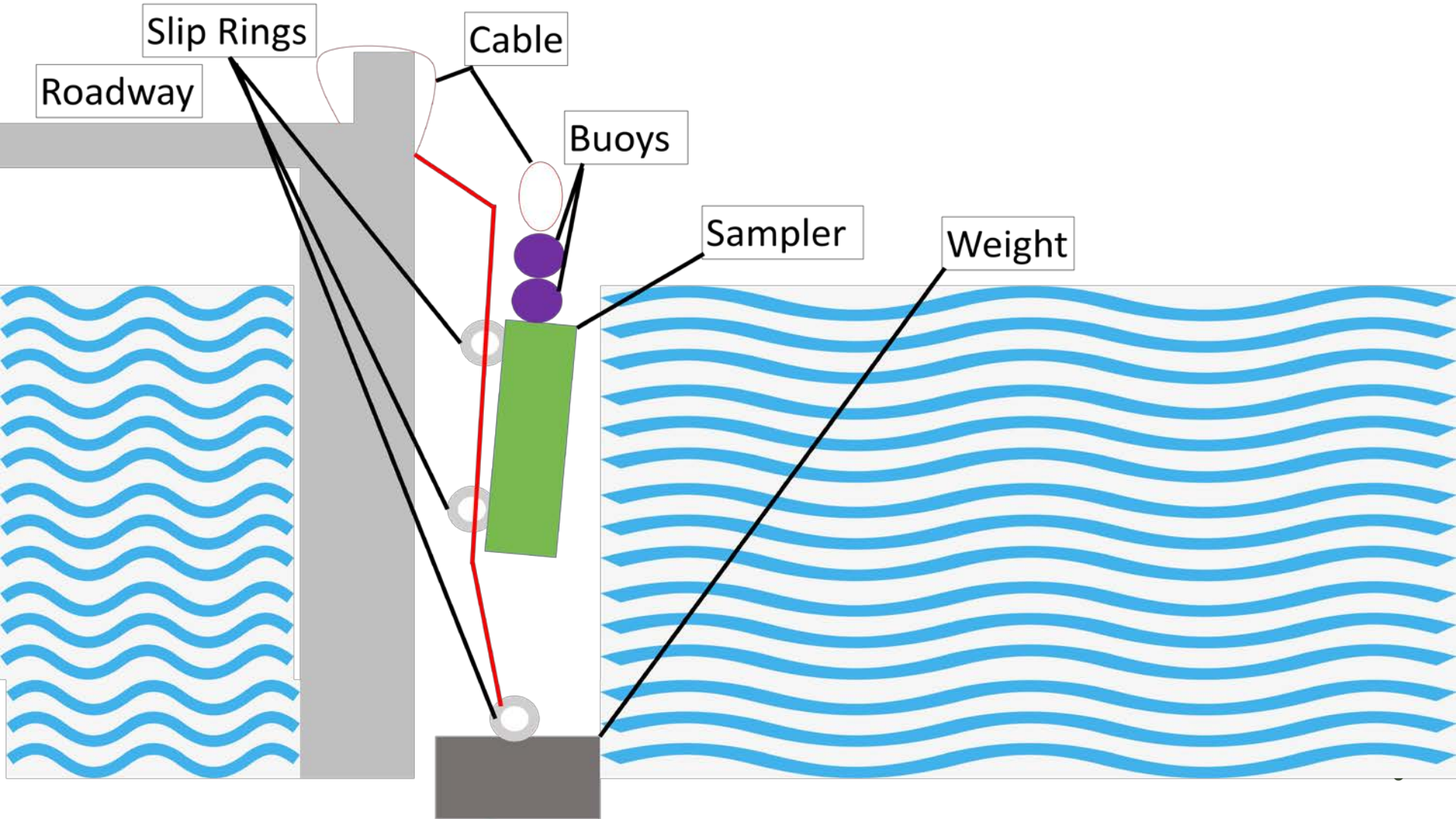
Alafia River

- 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 $\mu\text{g/L}$.



Review of Deployment

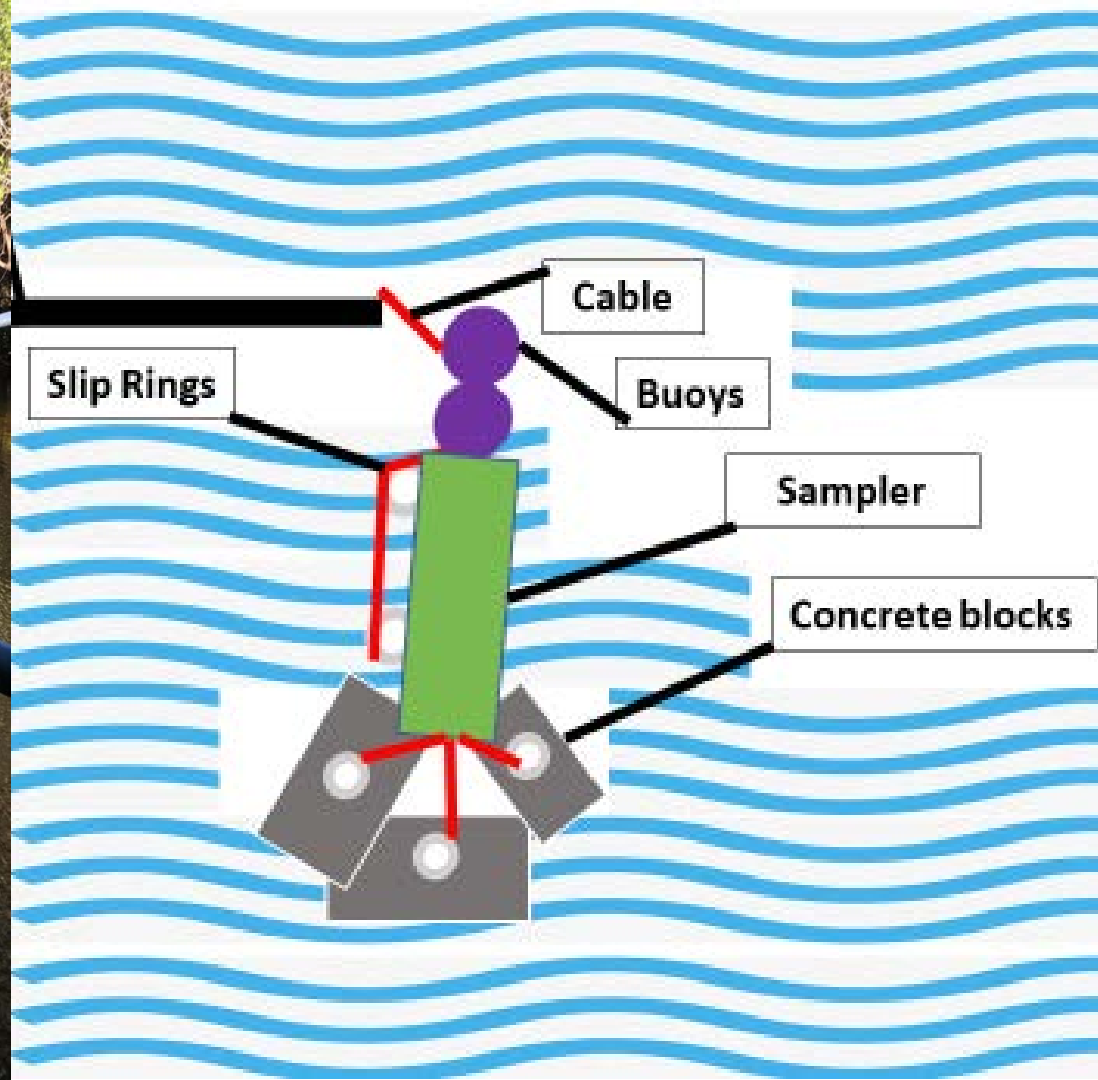
Ochlockonee, Withlacoochee & Apalachicola





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.



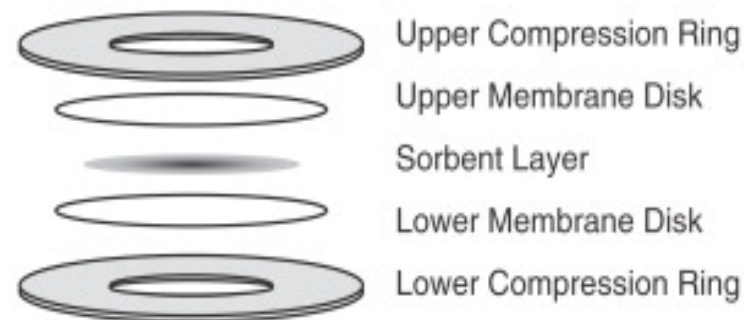
<http://www.est-lab.com/spmd.php>





Polar Organic Compound Integrative Sampler (POCIS)

- 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>





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.





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.**



Compound Priority List

Workgroup determined priority pollutant list

- 141 compounds selected

Pesticides	PPCPs	Hormones	PCFs	PBDEs	Alkyl Phenols
72	21	15	15	8	10



SGS Data



Pesticides

- Analyzed samples for 76 compounds (72 on DEP priority list).
- 42 compounds (39 on priority list) detected at one or more sites, in at least one sample type (POCIS, SPMD, or Grab).
- 38 / 39 priority compounds detected using combo. of Grab & SPMD.
- 30 compounds (28 on priority list) detected at all sites (N = 4), using a single sampling method.
- 17 priority & 1 non-priority compounds detected had data qualified due to lab/field blank detections (37% of all detects qualified).

Compound (* = DEP Priority)	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects	Compound (* = DEP Priority)	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
2,4'-DDD*	4			Endrin Ketone*	2		1 (100% G**)
2,4'-DDE*	3			Ethalfuralin*	3		
4,4'-DDD*	4			Flufenacet	1		
4,4'-DDE*	4		1	Flutriafol*		1	1 (100% G)
4,4'-DDT*	4			HCH, alpha*	4	2	1
Alachlor*	1	1	1 (100% VG)	HCH, beta*	4	3	3
Aldrin*	4 (75% V)	1	2	HCH, delta*	2	1	
alpha-Endosulphan*	4 (100% VG**)	4 (100% VG**)	4 (100% VG)	HCH, gamma	4 (100% G)	3	1
Ametryn*		1		Heptachlor*	4 (100% G)	4 (100% G)	
Atrazine*	2	4	4	Heptachlor Epoxide*	4 (50% V)	4 (100% G)	3 (100% VG**)
beta-Endosulphan*	4 (100% VG)	3 (100% VG**)	4 (100% VG**)	Hexachlorobenzene*	4 (100% G)	4 (100% VG)	4 (100% VG**)
Chlordane, alpha (cis)*	4	2		Hexazinone*		1	2
Chlordane, gamma (trans)*	4 (75% G)	4 (100% G)	3 (100% V)	Metolachlor*	4 (100% G)	4	4 (25% V)
Chlordane, oxy-*	4 (100% VG)		2 (100% V)	Mirex*	4 (100% VG)	1	3
Chlorpyrifos*	4		1	Nonachlor, cis-*	4 (25% G)		1 (100% G)
Desethylatrazine*		4	4	Nonachlor, trans-*	4	4	2
Diazinon*	1	1		Pendimethalin*	4		
Dieldrin*	4	4	4	Quintozene*	3 (100% G**)	3 (100% G**)	
Dimethenamid*	1	3	3	Simazine*		4	4
Endosulphan Sulphate*	4	4	3	Tebuconazol*	3 (100% G)	4	4
Endrin*	4 (75% V, 100% G)		2 (100% V**)	Trifluralin	4	1	

	Compound detected at all sites (N = 4).	V	Data qualified due to lab blank detection.
	Compound not detected at any sites.	G	Data qualified due to field blank detection.
*	DEP Priority Compound	**	Presence uncertain due to high analyte concentration in blanks.



PPCPs

- **Analyzed samples for 127 compounds (21 on DEP priority list).**
- **Compounds divided into 5 analytical lists. ANEG had most priority compounds. APOS had most priority compounds detected.**
- **39 compounds (15 on priority list) were detected at one or more sites, in at least one sample type (POCIS or Grab).**
- **14 / 15 priority compounds detected in POCIS; 10 / 15 detected in Grab**
- **7 compounds (2 on priority list) detected at all sites (N = 4), using a single sampling method.**
- **3 non-priority compounds detected had data qualified due to lab/field blank detections (10% of all detects qualified).**

Compound (* = DEP Priority)	List	POCIS # Sites with Detects	Grab # Sites with Detects
Alprazolam	APOSX	4	
Amitriptyline	APOSX	2	4
Amphetamine	BPOS	4 (100% VG**)	4 (100% VG**)
Atenolol*	BPOS	2	3
Azithromycin	APOS	1	
Caffeine	APOS		2
Carbamazepine*	APOS	4	3
Clarithromycin	APOS	1	
Cocaine	APOSX	3	2
Colchicine	APOSY		2
Cotinine	BPOS		2
DEET	APOSX	4	4 (50% VG)
Dehydronifedipine	APOS	1	1
Desmethyldiltiazem	APOSX	2	
Diatrizoic acid	APOSY		2
Diazepam	APOSX	1	
Diltiazem*	APOS	2	1
Diphenhydramine*	APOS	1	1
Erythromycin-H2O	APOS	4	
Furosemide*	ANEG		1

Compound (* = DEP Priority)	List	POCIS # Sites with Detects	Grab # Sites with Detects
Gemfibrozil*	ANEG	3	
Hydrochlorothiazide*	ANEG	1	
Hydrocodone	BPOS	3	
Iopamidol	APOSY		3
Meprobamate	APOSX		2
Metformin	BPOS		3 (100% G)
Metoprolol*	APOSX	3	
Naproxen*	ANEG	3	3
Oxolinic Acid	APOS	1	1
Oxycodone*	BPOS	3	
Propoxyphene	APOSX	1	
Sertraline*	APOSX	1	1
Sulfadimethoxine	APOS	1	
Sulfamethazine	APOS	1	
Sulfamethoxazole*	APOS	4	4
Triamterene*	BPOS	3	1
Trimethoprim*	APOS	3	
Valsartan*	APOSX	2	1
Venlafaxine	APOSY	3	2

	Compound detected at all sites (N = 4).
	Compound not detected at any sites.
*	DEP Priority Compound

V	Data qualified due to lab blank detection.
G	Data qualified due to field blank detection.
**	Presence uncertain due to high analyte concentration in blanks.



Hormones

- Analyzed samples for 17 compounds (15 on DEP priority list).
- 5 compounds (3 on priority list) detected at one or more sites, in at least one sample type (POCIS or Grab).
- 3 / 3 priority compounds detected using POCIS.
2 / 3 priority compounds detected using Grab.
- 100% of Grab detects and 0% of POCIS detects qualified due to lab/field blank detections
- 1 priority compound detected at all sites ($N = 4$), using a single sampling method.



Compound (* = DEP Priority)	POCIS # Sites with Detects	Grab # Sites with Detects
Allyl Trenbolone	2	
Androstenedione*	3	
Androsterone*	2	2 (100% G)
Mestranol*	2	4 (100% VG)
Testosterone	1	

	Compound detected at all sites (N = 4).	V	Data qualified due to lab blank detection.
	Compound not detected at any sites.	G	Data qualified due to field blank detection.
*	DEP Priority Compound	**	Presence uncertain due to high analyte concentration in blanks.



Perfluorinated Compounds

PFCs

- Analyzed samples for 13 compounds (10 on DEP priority list).**
- 10 compounds (8 on priority list) detected at one or more sites, in at least one sample type (POCIS or Grab).**
- 8 / 8 priority compounds detected using POCIS.**
- 5 / 8 priority compounds detected using Grab.**
- No data qualified due to lab/field blank detections.**
- 3 priority compounds detected at all sites (N = 4), using a single sampling method.**

Compound (* = DEP Priority)	Acronym	POCIS # Sites with Detects	Grab # Sites with Detects
Perfluorobutanoate	PFBA		2
Perfluorobutanesulfonic acid*	PFBS*	1	1
Perfluorodecanoic acid*	PFDA*	2	
Perfluoroheptanoic acid*	PFHpA*	4	2
Perfluorohexanoic acid*	PFHxA*	1	2
Perfluorohexanesulfonic acid*	PFHxS*	3	
Perfluorononanoic acid*	PFNA*	2	
Perfluorooctanoic acid*	PFOA*	4	2
Perfluorooctanesulfonic acid*	PFOS*	4	1
Perfluoropentanoate	PFPeA		2

	Compound detected at all sites (N = 4).	V	Data qualified due to lab blank detection.
	Compound not detected at any sites.	G	Data qualified due to field blank detection.
*	DEP Priority Compound	**	Presence uncertain due to high analyte concentration in blanks.



Polybrominated Diphenyl Ethers PBDEs

- **Analyzed samples for 8 compounds (all on DEP priority list).**
- **All compounds detected at one or more sites, in both sample types (SPMD and Grab).**
- **All SPMD detects and 92% of Grab detects qualified due to lab/field blank detections.**
- **All priority compounds detected at all sites ($N = 4$), using a single sampling method.**



Compound	SPMD # Sites with Detects	Grab # Sites with Detects
2,2',3,3',4,4',5,5',6,6'-DeBDE	4 (100% VG**)	4 (100% G)
2,2',3,4,4',5',6-HpBDE	4 (100% G)	3 (100% G)
2,2',4,4',5,5'-HxBDE	4 (100% G)	2
2,2',4,4',5,6'-HxBDE	4 (100% G)	3 (100% G)
2,2',4,4',5-PeBDE	4 (100% G)	4 (100% VG)
2,2',4,4',6-PeBDE	4 (100% G)	4 (100% VG)
2,2',4,4'-TeBDE	4 (100% G)	4 (100% VG)
2,4,4'-TriBDE	4 (100% G)	2 (100% G**)

	Compound detected at all sites (N = 4).	V	Data qualified due to lab blank detection.
	Compound not detected at any sites.	G	Data qualified due to field blank detection.
*	DEP Priority Compound	**	Presence uncertain due to high analyte concentration in blanks.



Alkylphenols

- **Analyzed samples for 4 compounds (all on DEP priority list).**
- **2 compounds detected at one or more sites, in at least one sample type (SPMD or Grab).**
- **2 / 2 priority compounds detected using SPMD.**
1 / 2 priority compounds detected using Grab.
- **All data qualified due to lab/field blank detections.**
- **Both compounds detected at all sites (N = 4), using a single sampling method.**



Compound (* = DEP Priority)	SPMD # Sites with Detects	Grab # Sites with Detects
4-Nonylphenol diethoxylates*	4 (100% G)	
4-Nonylphenols*	4 (100% G, 25% V)	4 (100% VG)

	Compound detected at all sites (N = 4).	V	Data qualified due to lab blank detection.
	Compound not detected at any sites.	G	Data qualified due to field blank detection.
*	DEP Priority Compound	**	Presence uncertain due to high analyte concentration in blanks.



DEP Data



DEP Data

- **Analyzed samples for 92 compounds (5 PPCPs, 87 pesticides).
44 (1 PPCP, 43 pesticides) on priority list**
- **32 compounds (3 PPCPs, 29 pesticides) detected at one or more sites, in at least one sampling method (SPMD, POCIS, or Grab).
13 (1 PPCP, 12 pesticides) on priority list.**
- **No data qualified due to lab / field blank detections.**

Compound (* = DEP Priority)	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
2,4-D		2	3
Acetaminophen			2
Acetochlor		3	3
Ametryn*			1
Atrazine*		4	4
Atrazine Desethyl*			4
Bentazon		1	4
Bromacil		4	4
Carbamazepine*		4	4
Chlordane	3	N/A	
Chlordane (alpha)*	3	N/A	
Chlordane (gamma)*	2	N/A	
Chlorpyrifos Ethyl*	4		1
DDD-p,p' *	2	N/A	
DDE-p,p'*	3	N/A	
Dieldrin*	2	N/A	

Compound (* = DEP Priority)	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
Fipronil		1	3
Fipronil Sulfide			1
Fipronil Sulfone			4
Fluridone		3	3
Diuron		4	4
Hexazinone*			4
Imidacloprid		4	4
Metolachlor	2	4	4
Norflurazon		1	2
Pendimethalin*	2		
Prometon		2	2
Simazine*		4	4
Sucralose	1	4	4
Toxaphene	2	N/A	
Trifluralin	2	N/A	

	Compound detected at all sites (N = 4).	V	Data qualified due to lab blank detection.
	Compound not detected at any sites.	G	Data qualified due to field blank detection.
*	DEP Priority Compound	**	Presence uncertain due to high analyte concentration in blanks.



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).
- 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

- **Grab**

- All sites had presence of estrogenic/androgenic activity
- Highest concentration at Withlacoochee
- Background fluorescence detected
 - High color water an issue

- **SPMD**

- All sites had presence of estrogenic/androgenic activity

- **POCIS**

- Results variable due to background fluorescence
- No androgenic activity at Apalachicola



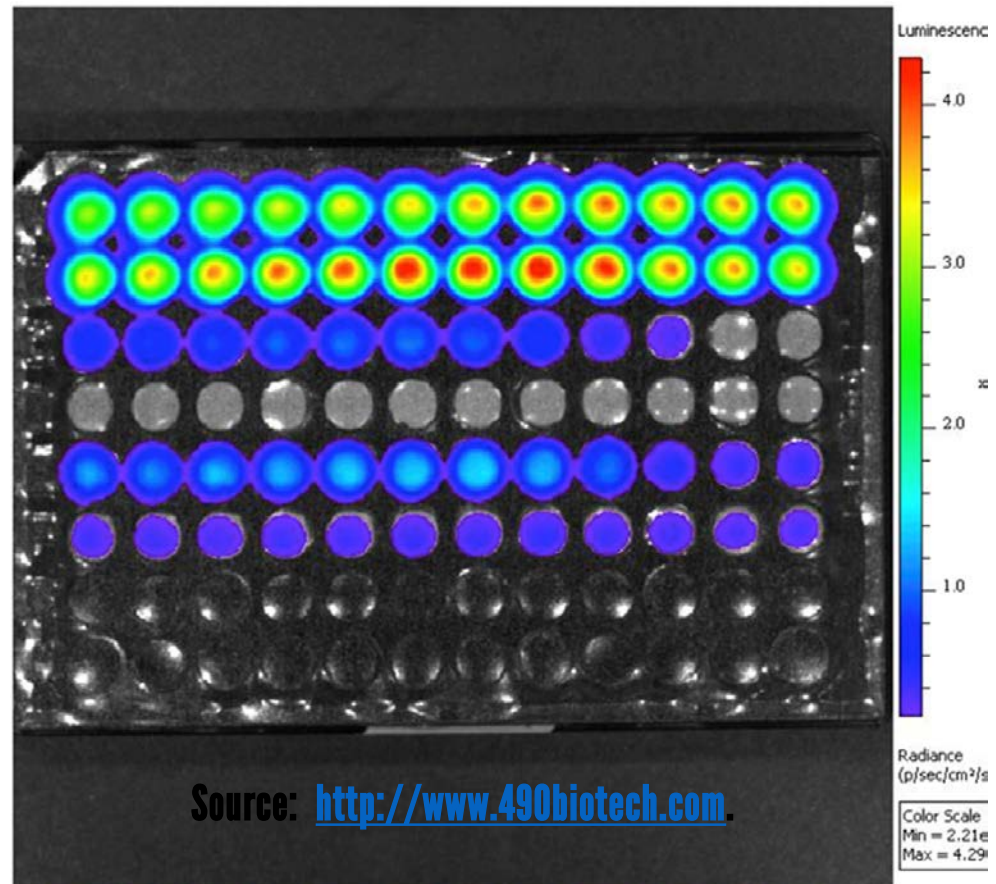
USGS

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





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**

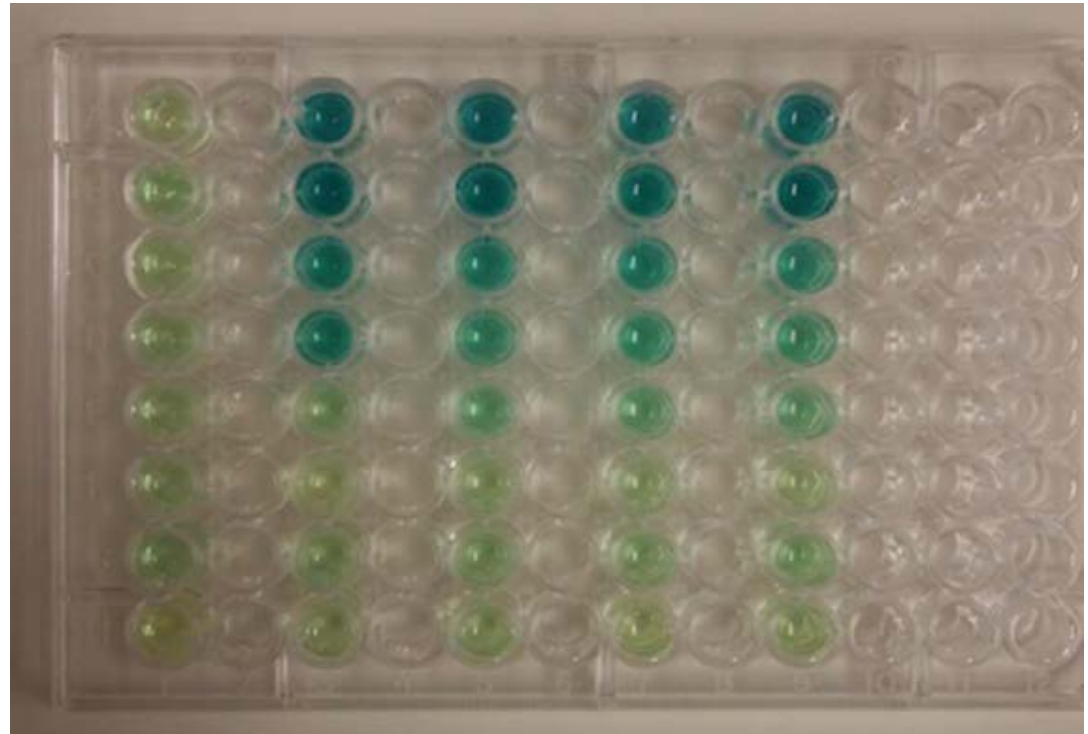


SOS Chromotest

*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.





Take Home Messages

Water Chemistry

- **Advantages of using passive sampling devices is that they pick up periodic discharges of the compounds whereas grab samples may miss them.**
- **Odds are if you're seeing the compounds in grab samples they are likely to be continually present in the water column .**
- **Some pesticides, the PBDEs, and the alkyl phenols are hydrophobic. Therefore we need to use SPMDs and/or collect sediment samples to determine their presence.**
- **The vast majority of the remaining compounds may be collected by grab samples, reducing the need for POCIS sampling to the first bullet above.**



Take Home Messages

Ecotoxicology

- **The BLYES and SOS Chromotest provided information corroborating our water chemistry results.**
- **ER & AR transactivation and binding assays protocols need to be revisited to make sure that they are applicable to highly colored water.**



Questions?



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.
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- **Smith, R. (2018) Product: Semipermeable Membrane Device (SPMD) and its Deployment. <http://www.est-lab.com/spmd.php>**