



A Synoptic Survey of Select Wastewater Indicators and the Pesticide Imidacloprid in Florida's Ambient Freshwaters

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This presentation summarizes results provided in Silvanima, J., Woeber, A., Sunderman-Barnes, S. et al. *Environ Monit Assess* (2018) 190: 435.

<https://doi.org/10.1007/s10661-018-6782-4>.



Presentation Outline

- **Background Information**
- **2015 Sample Survey Objectives & Methods**
- **Sample Survey Results**
- **Summary**

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Emerging Substances of Concern

AKA Emerging Contaminants

‘How prevalent are substances of emerging concern in Florida’s ambient freshwaters?’

- **Chemicals and materials which are not included in routine monitoring that pose a real or perceived threat to the environment.**
- **Lack published human health or aquatic life criteria and their synergistic effects are largely unknown.**
- **Effects may include behavior modification, reduced fecundity, sterility and increased mutagenicity and toxicity**



How to Address the Question?

- **Can't sample for all of these compounds**
- **Need indicators to predict where they may be found**
- **FDEP's probability-based status monitoring network a good place to add indicators to estimate occurrence statewide**

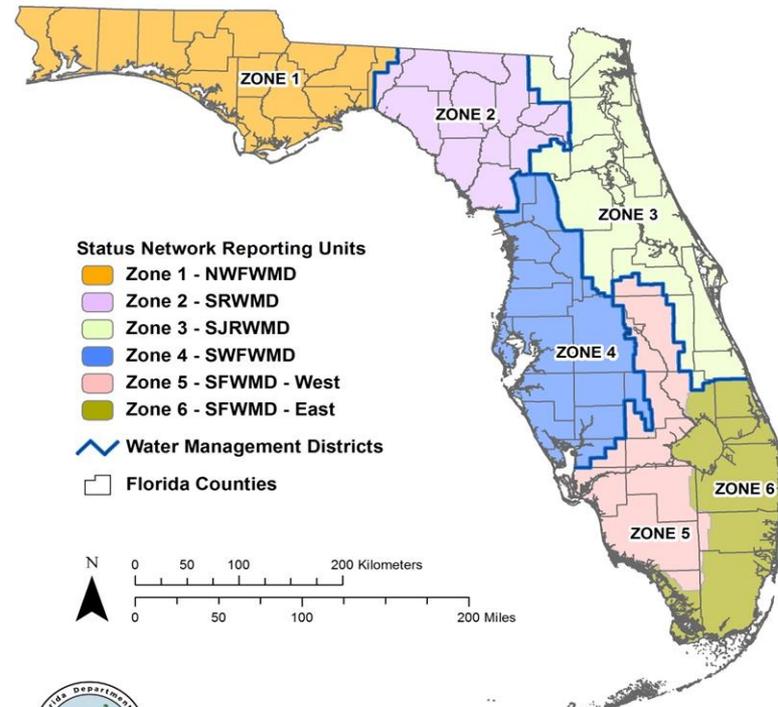


Status Network Design

Random Stratified

- 7 water resources
- 6 geographic areas
 - 15 random samples per surface water resource per zone per year
 - 20 randomly selected wells per ground water resource per zone per year

Watershed Monitoring Reporting Units



Created August 24, 2015 by Florida Department of Environmental Protection staff in the Division of Environmental Assessment and Restoration, Watershed Monitoring Section. This map is a representation of ground conditions and is not intended for further analysis. For more information contact (850)-245-8433.



Indicators, Study, Objectives, and Methods

- Standard Suit of WQ Analytes
- Wastewater Indicators
 - Sucralose
 - Select Pharmaceuticals
 - Acetaminophen
 - Carbamazepine
 - Primidone
 - Neonicotinoid Insecticide
 - Imidacloprid





Indicator Compounds

- **Sucralose** – Artificial Sweetener. Not metabolized by body and is not removed by wastewater treatment. Typical values found in receiving waters impacted by sewage treatment effluent 0.004 - 10 µg/L.
- **Acetaminophen** – Pain reliever. Removed by standard wastewater treatment.
- **Carbamazepine** – Anti-convulsant. Not effectively removed by standard wastewater treatment.
- **Primidone** – Anti-convulsant. Not effectively removed by standard wastewater treatment.
- **Imidacloprid** – Neonicotinoid insecticide. Most widely used insecticide in the world. Widespread use in agriculture, as a termiticide/ant killer, and for pet protection.



Half-Lives and Predicted No Effect Concentrations (PNECs)

Compound	Half-life Water	Aquatic Life PNEC	Reference
Sucralose	> year	930,000 ng/L	Tollefsen et al. 2012
Acetaminophen	days to weeks	9,200 ng/L	Kim et al. 2007, Table 3
Carbamazepine	days to weeks	31,600 ng/L	Kim et al. 2007, Table 3
Primidone	days to weeks	ND	ND
Imidacloprid	weeks to months	ND	ND

US EPA Pesticide Registration Program Aquatic Life Benchmarks^a

Compound	Fish (Acute)	Fish (Chronic)	Invert (Acute)	Invert (Chronic)
Imidacloprid	>114,500,000 ng/L	9,000,000 ng/L	385 ng/L	10 ng/L

Compounds' half-lives, predicted no effect concentrations (PNEC) and benchmarks for aquatic life. ND = Not determined. ^a U.S. EPA Office of Pesticide Program aquatic life benchmarks (<https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration>)



Indicator Study Objectives

- 1. Determine extent of water resources with detectable levels.**
- 2. Examine the relationship between unconfined aquifer well depth and the frequencies and magnitudes of these compounds.**
- 3. Examine spatial relationships of these compounds within and among Florida's drainage basins and the urban and agricultural land use found within them.**

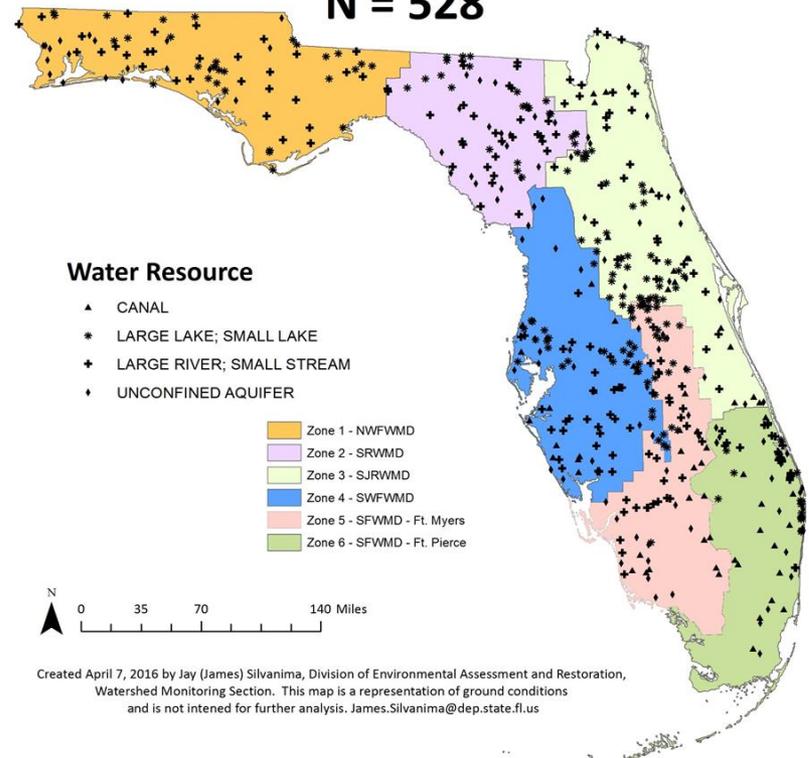


2015 Sample Surveys

- Sucralose, pharmaceuticals and Imidacloprid collected at 528 sites
 - 60 canal sites
 - 90 river sites
 - 90 stream sites
 - 90 large lake sites
 - 78 small lake sites
 - 120 unconfined wells

2015 Status Sites Sampled for Select Pharmas/Pesticides

N = 528





Spsurvey Used for Site Selections and Data Analysis

R package spsurvey:

- **Spatial Survey Design and Analysis**
- **Developed by US EPA for Aquatic Resource Monitoring.**
- **Ensures monitoring stations are representative of the target resources, spatially balanced, and their selection is unbiased.**
- **Utilizes a local neighborhood variance estimator that tends to produce smaller confidence limits compared to traditional variance estimates.**



Well Depth Comparisons

- **Categorized sampled unconfined aquifer wells by depth. Those less than 12.5 meters (~41 ft.) deep (58 wells) and those greater than 12.5 meters deep (60 wells).**
- **Developed contingency tables containing numbers of compound detections and non-detections for each well depth category.**
- **Utilized Fisher's exact test and the Mann-Whitney U test to determine if the two categories differed statistically with α set at 0.05.**

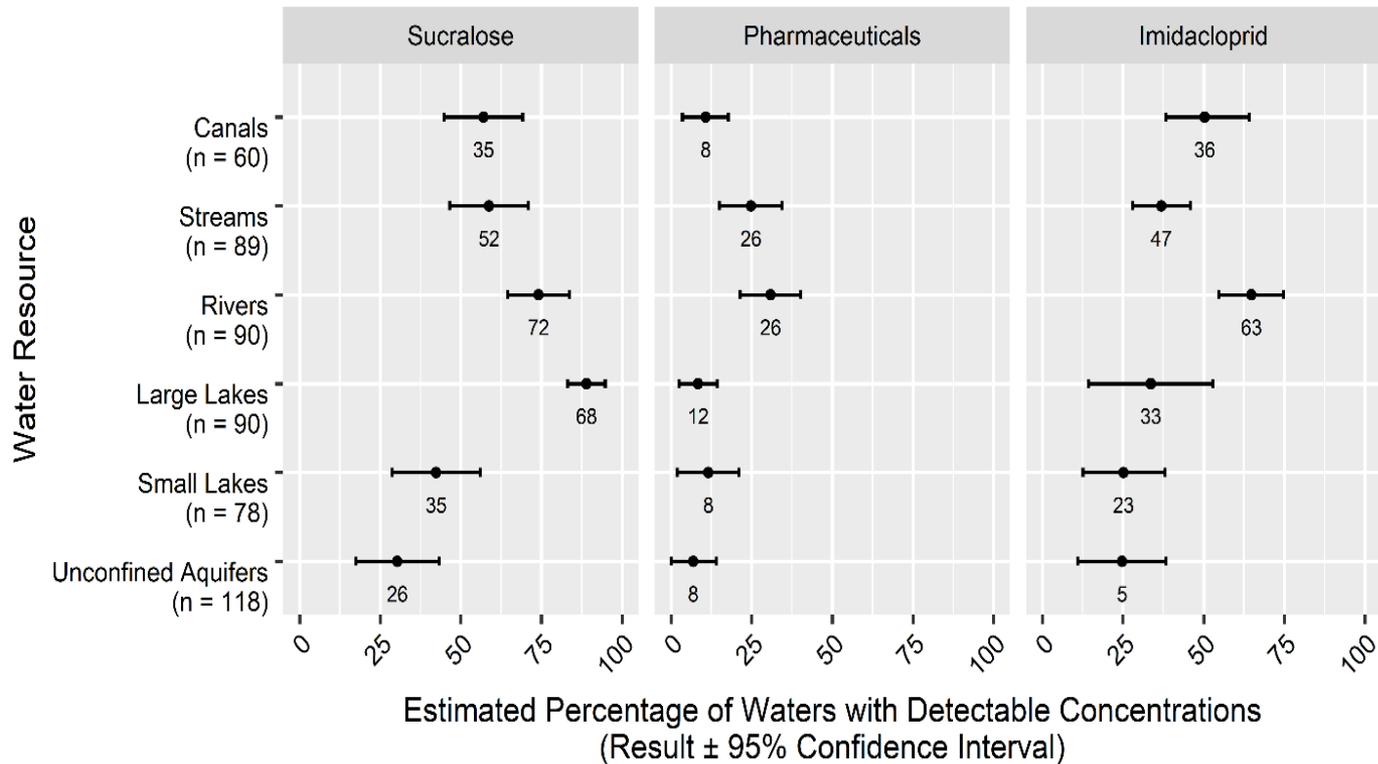


Geospatial Analyses

- **Estimated percentage urban and agricultural land use for Florida drainage basins using the land use and land cover system developed by the Florida Department of Transportation (FDOT 1999).**
- **Use R package micromap to visually compare number of detections and compound statistical summary per basin to land use categories and numbers of sites per basin.**
- **Developed weighted ordinary least square regression models to determine correlations between land use categories and percentage of detected compounds per basin.**



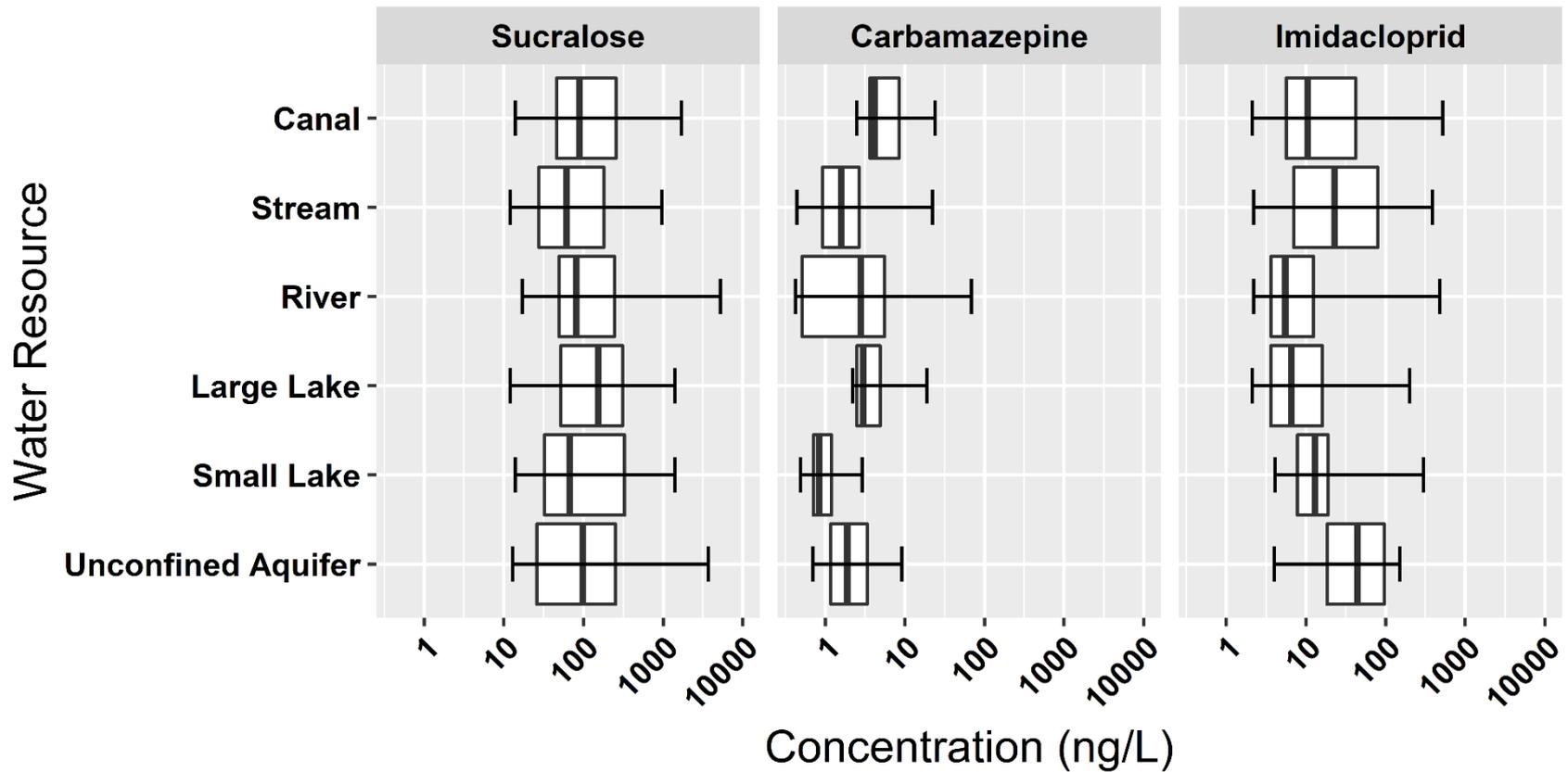
Results



Percentages of water resources expected to have detectable amounts of sucralose, pharmaceuticals, and imidacloprid. Dots represents estimates, whiskers are the 95% confidence bounds, n = total number of sites per resource, with number of detections per water resource / compound pair provided as inset.



Range of Detected Values





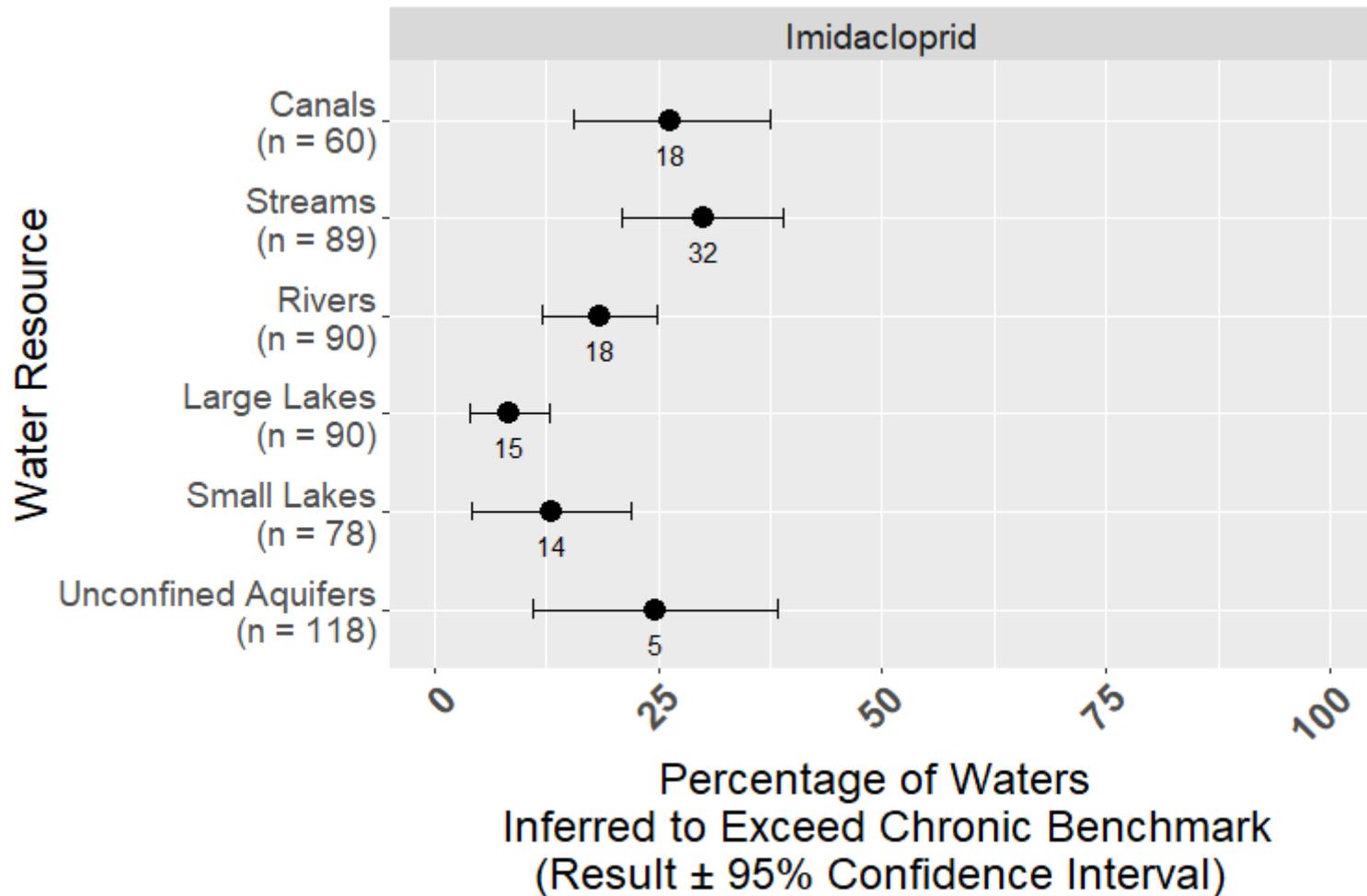
Toxicological Relevance

Range of Detected Values Versus Available Toxicology Guidance

- **Sucralose and pharmaceuticals – highest values are an order of magnitude lower than any known toxicology guidance.**
- **Imidacloprid – 26 of 408 surface water sites produced concentrations shown to impact mayfly species of the family Baetidae; 13 of these coming from the 90 stream sites sampled.**



Toxicological Relevance





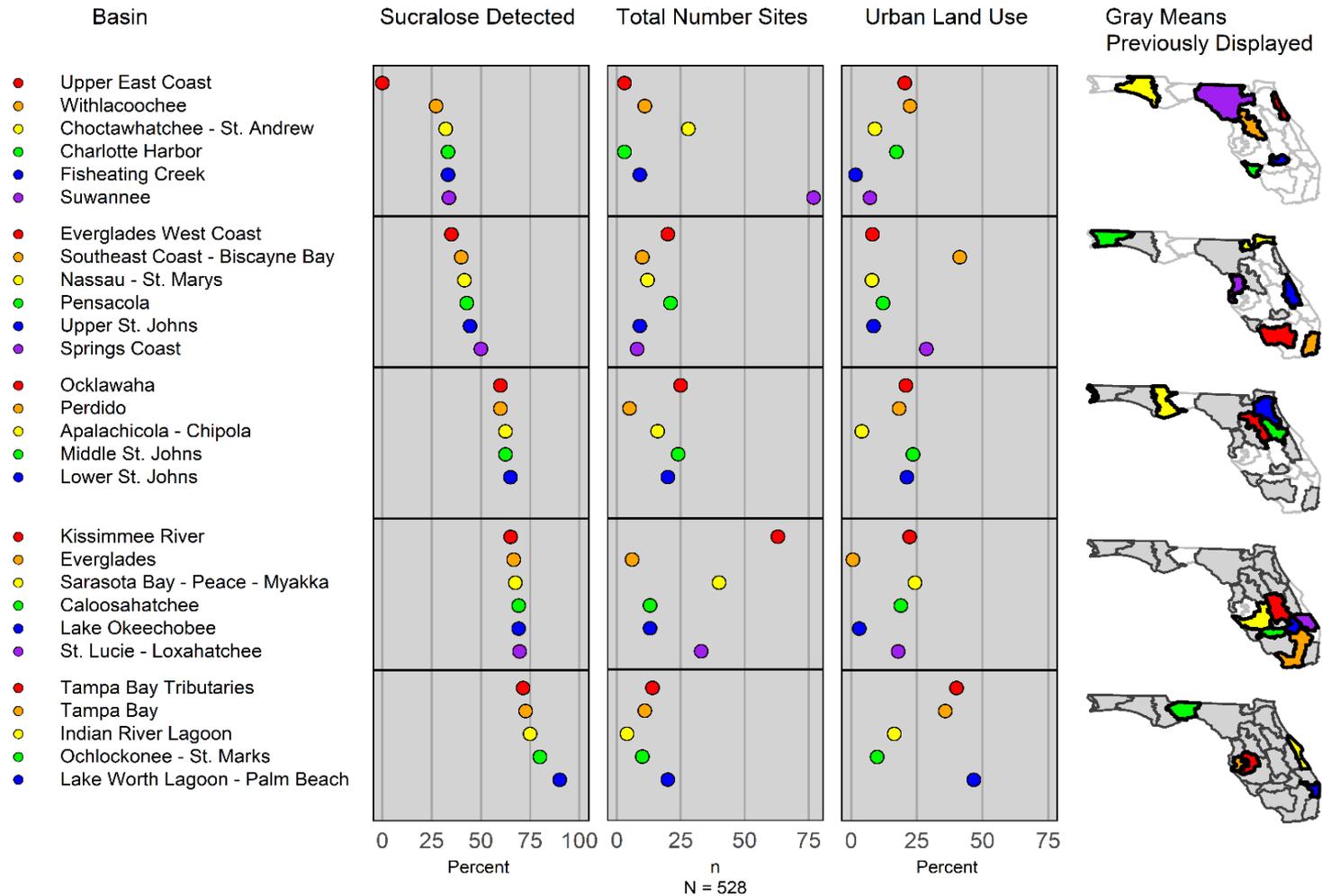
Well Depth Comparisons

**Number of Wells Having Detections
and Median Values (ng/L) of Detections by Well Depth**

Compound	Well Depth < 12.5 m, # Detects / # of Wells	Well Depth < 12.5 m, Median (ng/L)	Well Depth > 12.5 m, # Detects / # of Wells	Well Depth > 12.5 m, Median (ng/L)
Sucralose	13/58	140	13/60	96
Pharmaceuticals	6/58	8.6	2/60	1.6
Imidacloprid	3/58	86	3/60	23

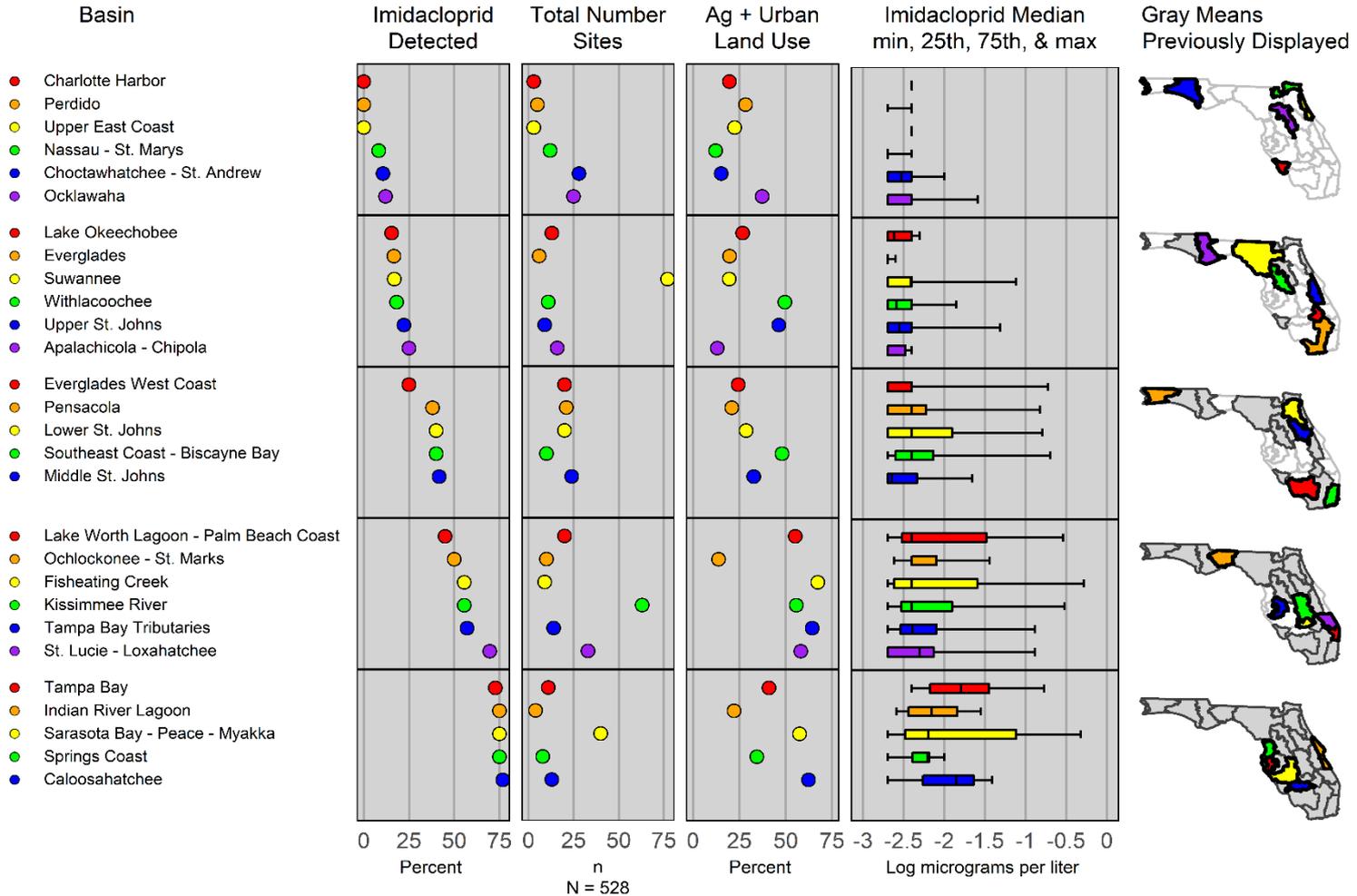


Micromap – Sucralose





Micromap - Imidacloprid





Weighted Ordinary Least Squares Regression Results

- Sucralose^a significantly related to the percentage of urban land use ($R^2 = 0.36$, $p < 0.001$).
- Pharms^b not significantly related to the percentage of urban land use ($R^2 = 0.07$, $p = 0.19$).
- Imidacloprid^{bc} significantly related to the percentage of urban and agricultural land use ($R^2 = 0.47$, $p < 0.001$). Independently agricultural land use ($R^2 = .20$, $p = 0.017$) and urban land use ($R^2 = 0.13$, $p = 0.059$).

^a 27 basins used in analysis, Upper East Coast Basin removed from analysis, ^b 28 Basins used in analyses, ^c Multiple regression analysis



Summary

- **Water resource extent estimates having ultra-trace concentrations of the wastewater indicators and imidacloprid are highest in the flowing water and large lake resources.**
- **Imidacloprid was the only compound found to exceed any recommended toxicology guidance, that for aquatic invertebrates. 26/408 surface water sites (~6 percent) had concentrations known to impact mayfly species of family Baetidae.**
- **Numbers and magnitude of sucralose are directly correlated with urban land use within drainage basins. While numbers and magnitude of imidacloprid detections are directly correlated with agricultural and urban land use within drainage basins.**



Questions

The screenshot shows the Florida Department of Environmental Protection (DEP) website. The main navigation bar includes links for A-Z Index, Forms, News, Events, Contact Us, and social media icons. Below this is a secondary navigation bar with links for About DEP, How Do I, Divisions, Air, Lands, Parks & Rec, Waste, and Water. The page title is "Watershed Monitoring" and the breadcrumb trail is "Home > Divisions > Division of Environmental Assessment and Restoration > Watershed Monitoring".

Watershed Monitoring Section Quick Links

- Status Network
- Trend Network
- Status and Trend Networks Brochure
- Interactive Water Quality Report Cards
- Reports, Standard Operating Procedures, Documents, and Links
- Sediment Guidelines
- Contacts
- Florida Water Resources

One of DEP's top priorities is watershed and ecosystem restoration. The process begins with collecting reliable data. DEP's Watershed Monitoring Program (WMP) fills this role by taking water samples from rivers, streams, lakes, canals, and wells around the state. Laboratory scientists measure the levels of certain "indicator" substances in each sample. Dissolved oxygen, nutrients, and bacteria are examples of these water quality indicators. Other sections in DEP use the measurements to determine which waters are impaired and what should be done to restore them. The success of these plans is dependent upon accurate and representative data. In 1996, DEP updated its water monitoring strategy to increase efficiency and save money. The new program, called the Integrated Water Resource Monitoring Network (IWRM), monitors Florida's water at three spatial scales or "tiers." Tier I relates to the state as a whole. Tier II includes basin-scale monitoring to identify and confirm impaired waters. Tier III consists of site-specific monitoring to determine regulatory compliance. Results from IWRM are used in the state's [Integrated 303\(d\) / 305\(b\) Report](#) to the U.S. Environmental Protection Agency.

<https://floridadep.gov/dear/watershed-monitoring-section>

