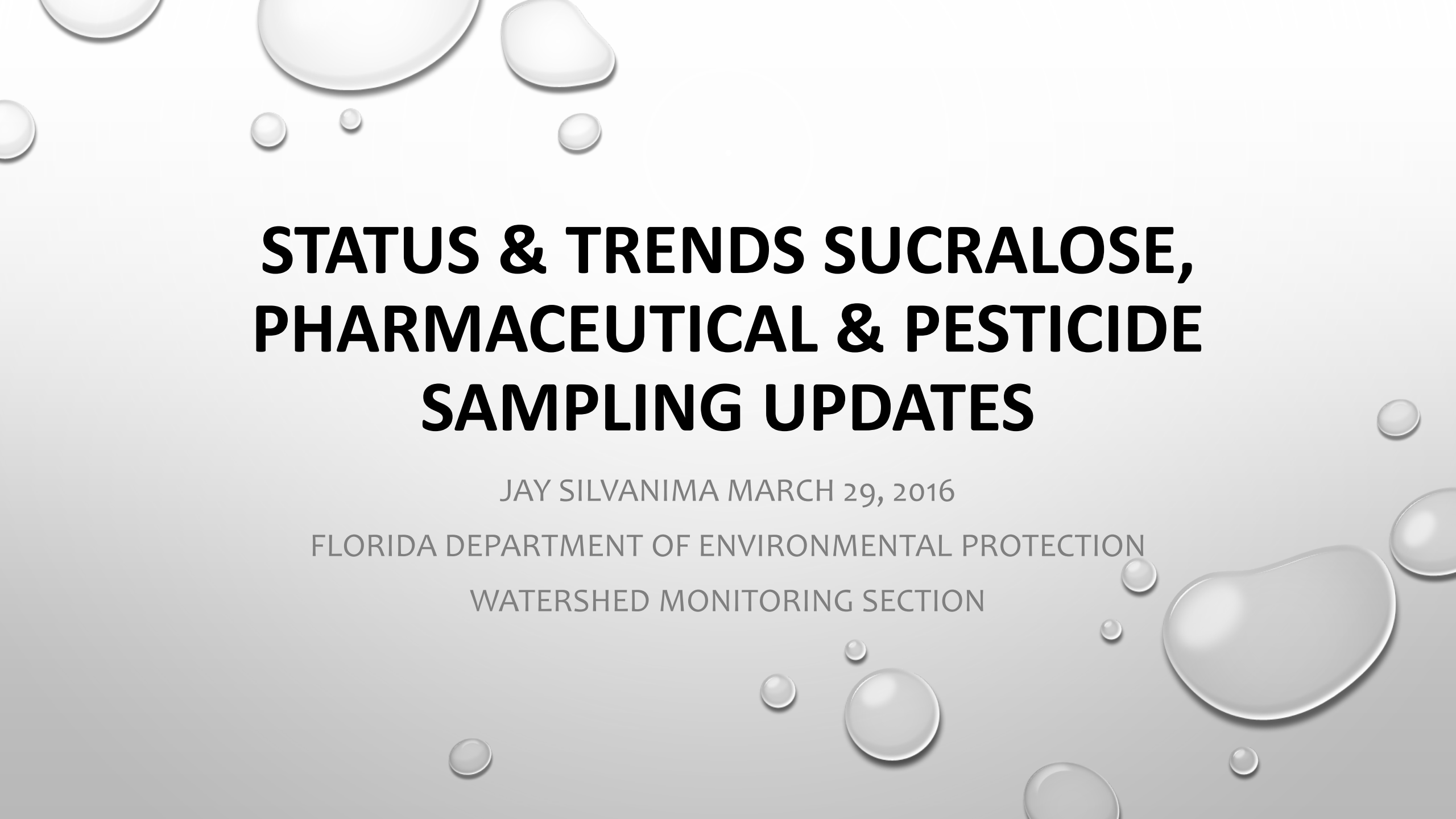


The background of the slide is a light gray gradient. It is decorated with numerous realistic water droplets of various sizes. Some droplets are at the top left, some are scattered in the middle, and a large, prominent one is on the right side. The droplets have highlights and shadows, giving them a three-dimensional appearance.

STATUS & TRENDS SUCRALOSE, PHARMACEUTICAL & PESTICIDE SAMPLING UPDATES

JAY SILVANIMA MARCH 29, 2016

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION
WATERSHED MONITORING SECTION

OVERVIEW OF STATUS AND TREND MONITORING NETWORKS

TREND NETWORK:

**LONG TERM TRENDS IN SURFACE AND GROUND WATER AT FIXED STATIONS. 78
SURFACE WATER, 49 GROUNDWATER STATIONS.**

STATUS NETWORK:

**ANNUAL STATEWIDE SURFACE AND GROUND WATER QUALITY CONDITION
'SNAPSHOT'. PROBABILISTIC DESIGN - STRATIFIED RANDOM SAMPLE SURVEY**

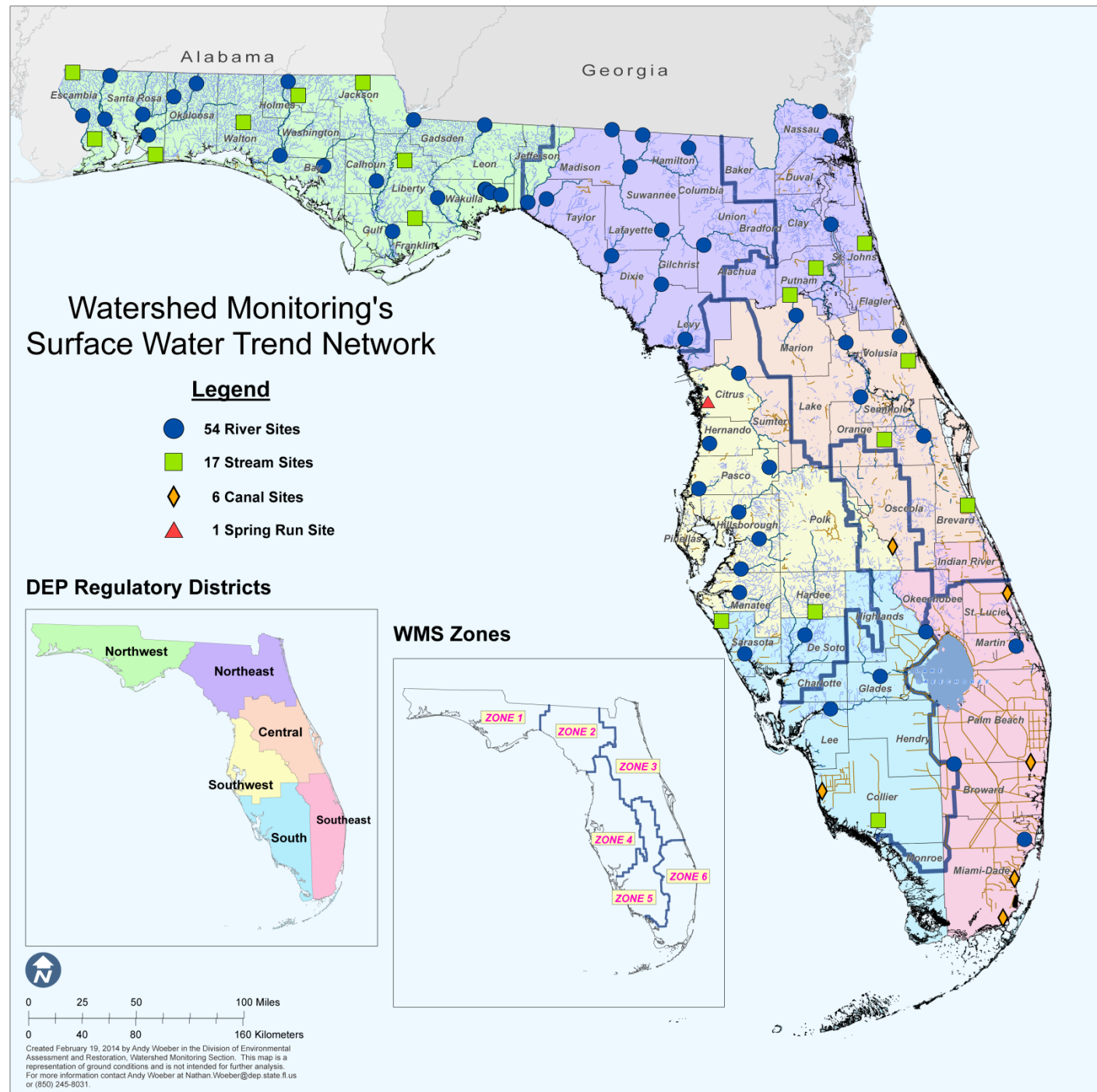
TREND MONITORING NETWORK

➤ GOALS:

- Make estimates of change in water quality at set stations over time
- Determine correlations with Status Network monitoring results in the same region
- Estimate general surface water basin-wide loading

SURFACE WATER TREND NETWORK

78
SURFACE
WATER
FIXED SITES
SAMPLED
ON A
MONTHLY
BASIS



GROUND WATER TREND NETWORK

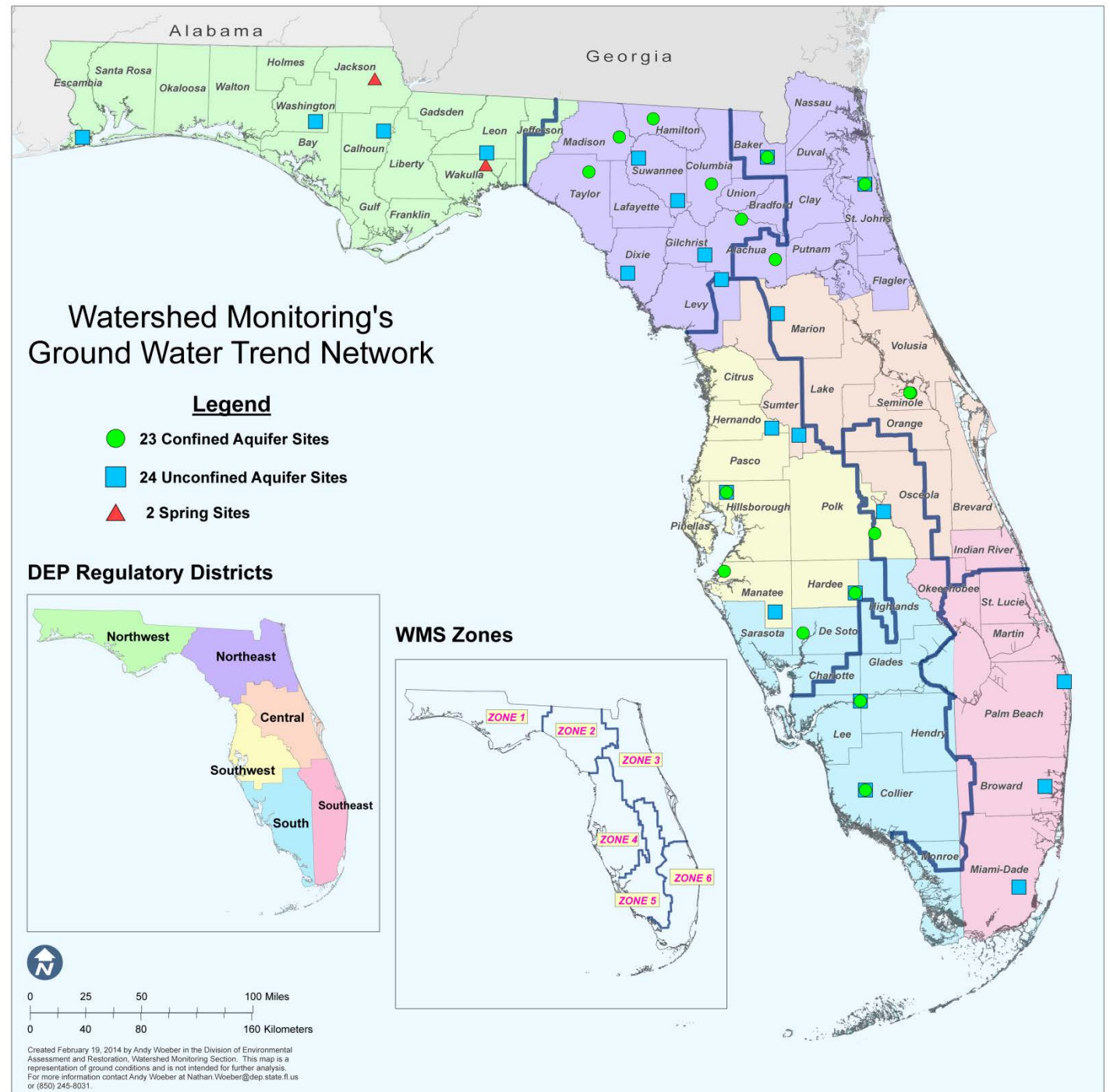
49 TREND STATIONS

- 23 CONFINED AQUIFER SITES

SAMPLED 4X YEAR
FIELD AND WQ

- 24 UNCONFINED SITES AND
TWO SPRINGS

SAMPLED 12X YEAR
FIELD PARAMETERS
4X PER YEAR COLLECT
WATER SAMPLES





STATUS MONITORING NETWORK

➤ GOALS:

- Characterize statewide water resource conditions
 - Infer percentage of each resource that meets standards or designated use (surface & ground water) with known confidence
- 

STATUS MONITORING NETWORK SAMPLE SURVEY DESIGN

- STRATIFIED RANDOM SAMPLE DESIGN
 - STRATA INCLUDE:
 1. Water resource type: rivers, streams, canals, large and small lakes, and confined and unconfined aquifers
 2. Geography: state divided into 6 regions by water management district boundaries

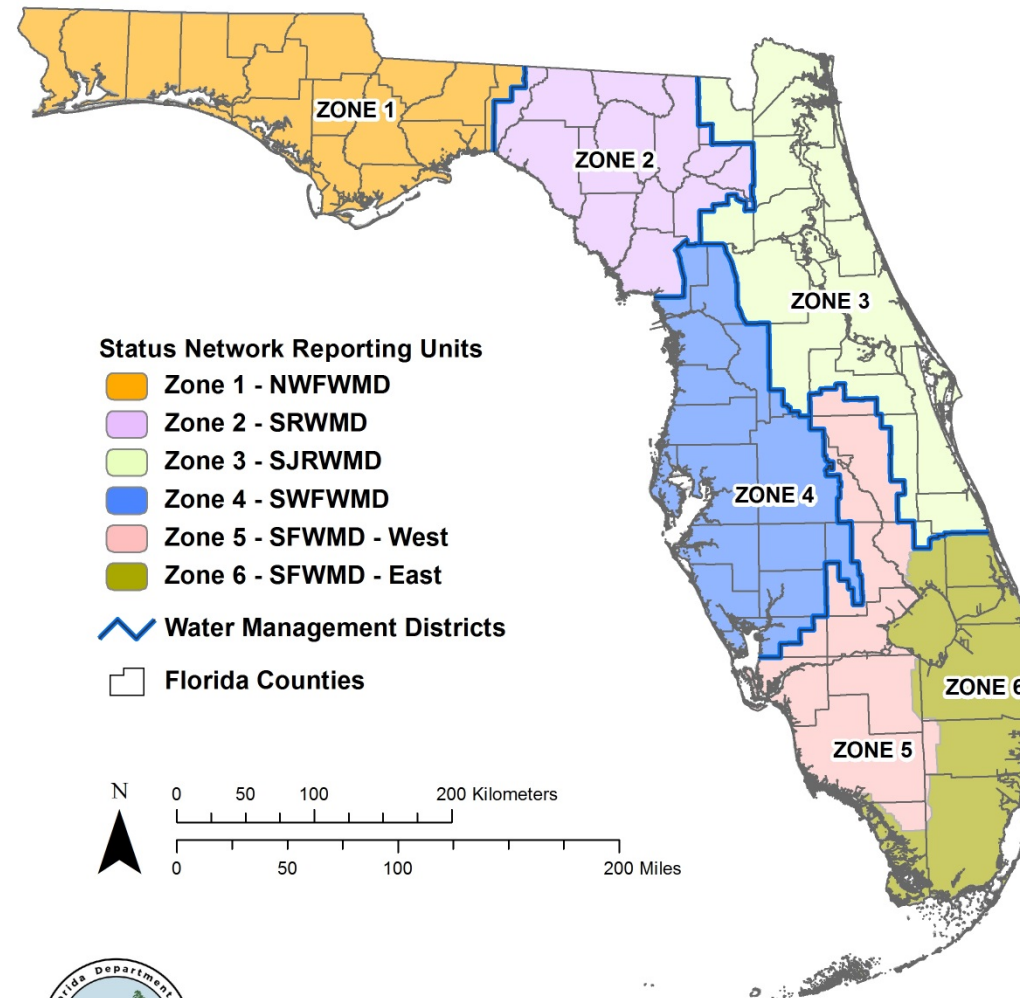
2015 Design Document found at

<http://www.dep.state.fl.us/water/monitoring/pubs.htm>

Status Network Sampling Design

- 6 zones
- 7 resources
- 90 samples per sw resource type per year (15 per zone)
- 60 samples for canals per year (15 per 4 zones)
- 120 samples for gw resources per year (20 per zone)

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.

In 2011 the WMS was asked by Drew Bartlett, then DEAR Director

- 'How prevalent are emerging contaminants in Florida's ambient freshwaters?'



EMERGING CONTAMINANTS (ECS)

- Chemicals that pose a real or perceived threat to the environment.
- The most common exposure route for all organisms, including humans, is through food ingestion.
- Published health or aquatic criteria for ECs is lacking, criteria development is still evolving.
- Some are endocrine disrupting compounds.
- New industrial and agricultural chemicals may be potential ECs.
- ECs are discharged in trace amounts in wastewater releases and in surface water runoff.

EMERGING CONTAMINANTS

- Organic Waste Water Compounds
 - Pharmaceuticals and Personal Care Products (PPCP), Synthetic Hormones, Disinfectant By-products
- Current Use Pesticides (over 20,000!)
- Brominated Flame Retardants (found in furniture, mattresses, carpet padding, insulation, & automobile seats)
- Akyphenolic Substances (additives for fuels, and lubricants)
- Perfluorinated Compounds (PFCs) (Surfactants including fire fighting foam. Used in the production of Teflon and other fluorinated polymers.)
- Chlorinated Paraffins (lubricants, plasticizers, flame retardants, plastic products including PVS pipe.)

HOW TO ADDRESS DREW'S Q???

- Can't sample for all of these compounds!
- Need indicators to infer where they may be found.
- Trend Monitoring Network may provide frequency of occurrence of specific groups of ECs
- Status Monitoring Network a good place to add indicators to estimate occurrence statewide

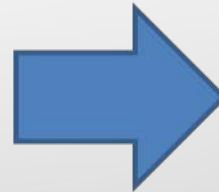


TRACERS AS INDICATORS OF EMERGING CONTAMINANTS

- Nitrogen isotopes
 - inorganic - fertilizers, organic - animal/human waste
- Sucralose (provided by DEP lab since 2010)
 - wastewater
- Pharmaceuticals (acetaminophen, carbamazepine, and primidone provided by DEP lab since 2014)
 - waste streams (acetaminophen is mostly removed by wastewater treatment)
- Pesticides at trace levels (provided by DEP lab since 2013)
 - Agricultural contaminants

SUCRALOSE

- Not metabolized by the body and comes out just as it went in!



SUCRALOSE

- Not metabolized by the body and comes out just as it went in!





SUCRALOSE

- Indicator of human waste water
 - Added to all Status and Trend projects for 2012
 - Produced some surprising results
 - Both in frequency of occurrence at trend sites
 - And in percentage of freshwaters showing detections as inferred from status monitoring
- 

SELECT PHARMACEUTICALS



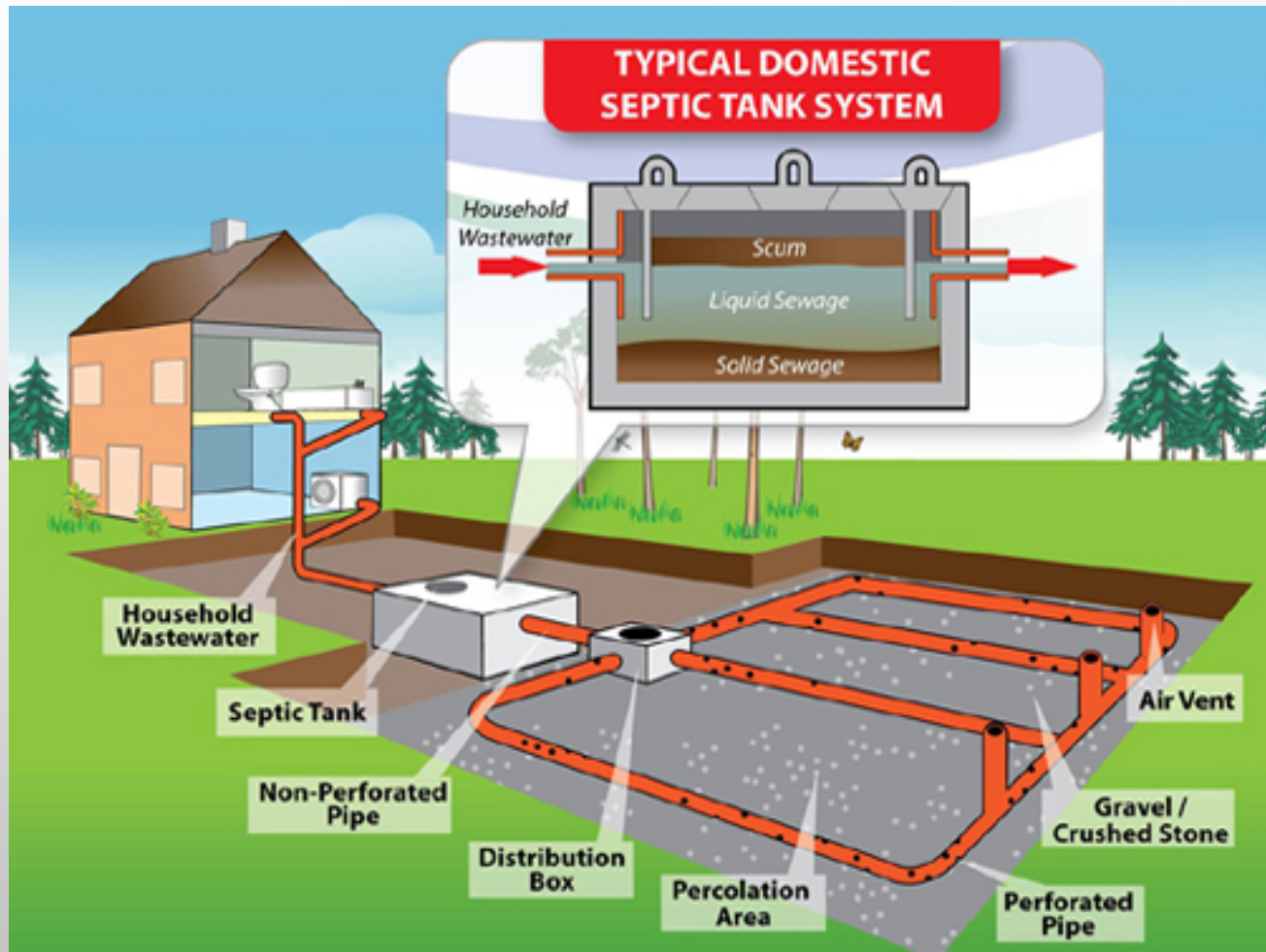
- Acetaminophen, Carbamazepine, Primidone, and Sucralose added for the sampling of
 - Status Unconfined Aquifers in Nov. – Dec. 2014
 - All status (except confined aquifer) and all trend projects 2015

SELECT PHARMACEUTICALS

- Acetaminophen
 - Analgesic - Common brand name, Tylenol
 - Removed by standard wastewater treatment
- Carbamazepine
 - Antiseizure medication – Common brand name, Tegretol
 - May be removed by standard wastewater treatment
- Primidone
 - Anticonvulsant –
 - Maybe removed by standard wastewater treatment

SELECT PHARMACEUTICALS

- Occurrence of these pharmaceuticals in the absence of sucralose may indicate an untreated wastewater stream



PESTICIDES

- Diuron, Linuron, Fluridone, & Imidacloprid added to all status and trend projects (except confined aquifers) for 2015.



PESTICIDES

- Organo nitrogen and phosphorous pesticides (43 compounds including degradates) added to Status unconfined aquifers Nov. – Dec. 2015, and all Status flowing waters for 2016.



PESTICIDES

- Organo nitrogen and phosphorous pesticides include:
 - Herbicides/Fungicides:
 - Acetochlor, Alachlor, Ametryn, Atrazine, Bromacil, Butylate, Cyanazine, EPTC (EPTAM), Metalaxyl, Metolachlor, Metribuzin, Molinate, Norflurazon, Prometon, Prometryn, Simazine, Terbutylazine
 - Insecticides/Arachnicides:
 - Chlorpyrifos, Demeton, Diazinon, Disulfoton, EPTC (EPTAM), Ethion, Fenamiphos, Fipronil, Fonofos, Malathion, Mevinphos, Parathion, Phorate

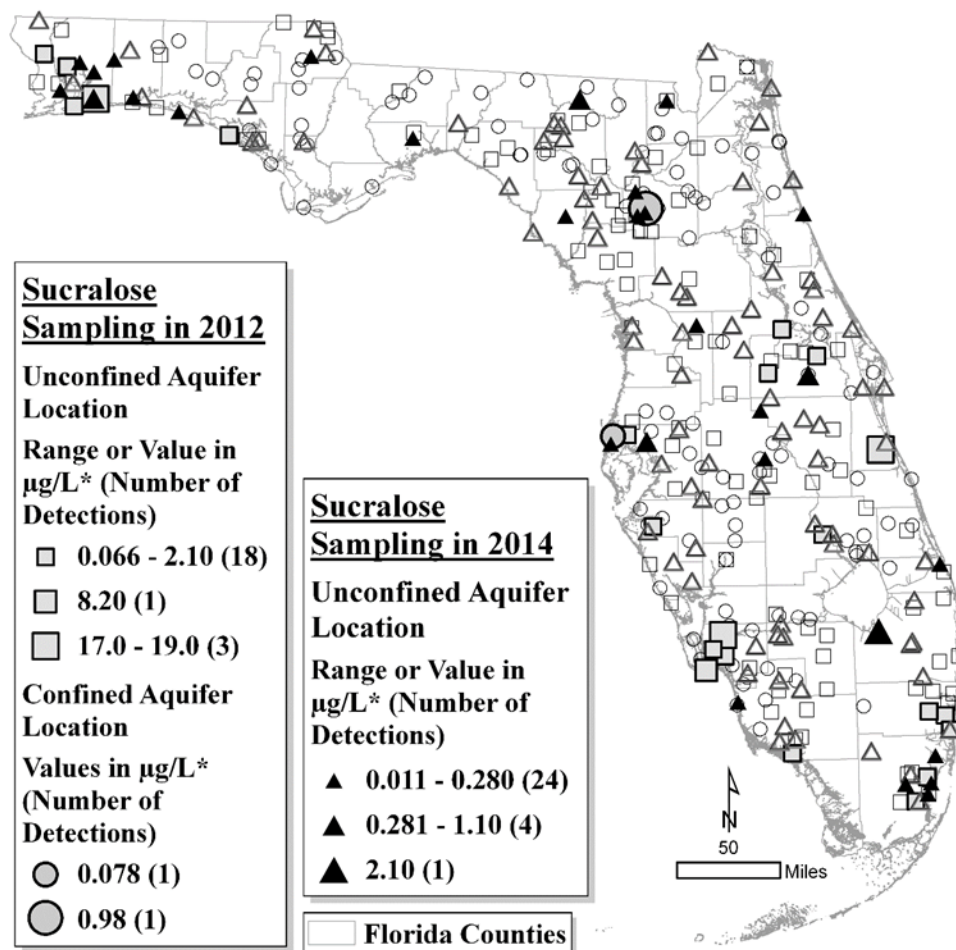
SO WE SAMPLED FOR THESE THINGS
WHAT DID WE FIND OUT???



STATUS AQUIFERS SUCRALOSE RESULTS

- 2012
 - Detections in 24/226 wells (~11%)
 - Unconfined 22/119 wells (~18%) at 0.066 µg/L to 19 µg/L
 - Confined 2/107 (~2%) wells at 0.078 µg/L to 0.98 µg/L
- 2014
 - Detections in 29/116 unconfined wells (~25%) at 0.011 µg/L to 2.1µg/L
- 2015
 - Detections in 28/120 unconfined wells (~23%) at 0.012 µg/L to 2.1µg/L

Sucralose Detections Within Florida's Status Monitoring Network (Aquifer Sampling in 2012 and 2014)



* $\mu\text{g/L}$ = micrograms per liter

Sucralose Not Detected

2012

- Unconfined Aquifer (97)
- Confined Aquifer (105)

2014

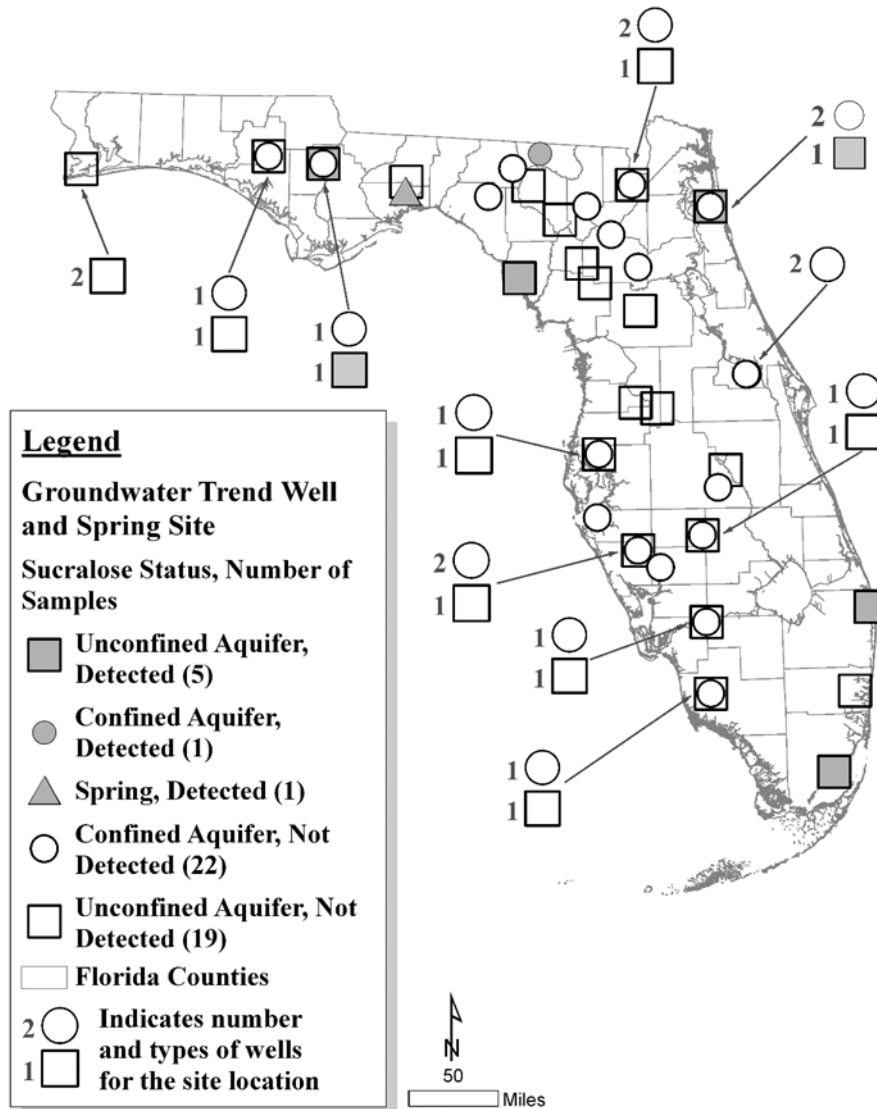
- △ Unconfined Aquifer (87)

(Number of non-detections)

GROUND WATER TREND SUCRALOSE SUMMARY

- 2012 Results
 - Confined wells 1/23 had detection (0.019 l $\mu\text{g/L}$)
 - Unconfined wells 5/24 had detections at (0.023 l $\mu\text{g/L}$ - 0.15 $\mu\text{g/L}$)
 - 3/24 wells had multiple detections, 2/24 wells had one detection
- 2015 Results
 - Confined wells 2/23 had detections (0.024 l $\mu\text{g/L}$ - 0.46 l $\mu\text{g/L}$)
 - Both wells had multiple detections, one well had detections for every sample event
 - Unconfined wells 5/24 had detections at (0.023 l $\mu\text{g/L}$ - 0.15 $\mu\text{g/L}$)
 - All had multiple detections. 4 wells had detections for every sample event.

Sucralose Detections From Florida's 2012 Trend Monitoring



SUCRALOSE STATEWIDE SUMMARY AQUIFERS

- Unconfined aquifers have detection rates of sucralose between 18 and 25% with a margin of error of $\sim 9\%$.
- Confined aquifers have a much lower detection, therefore we did not sample them for ECs in the 2014 & 2015 Status surveys.

STATUS FLOWING WATERS SUCRALOSE RESULTS

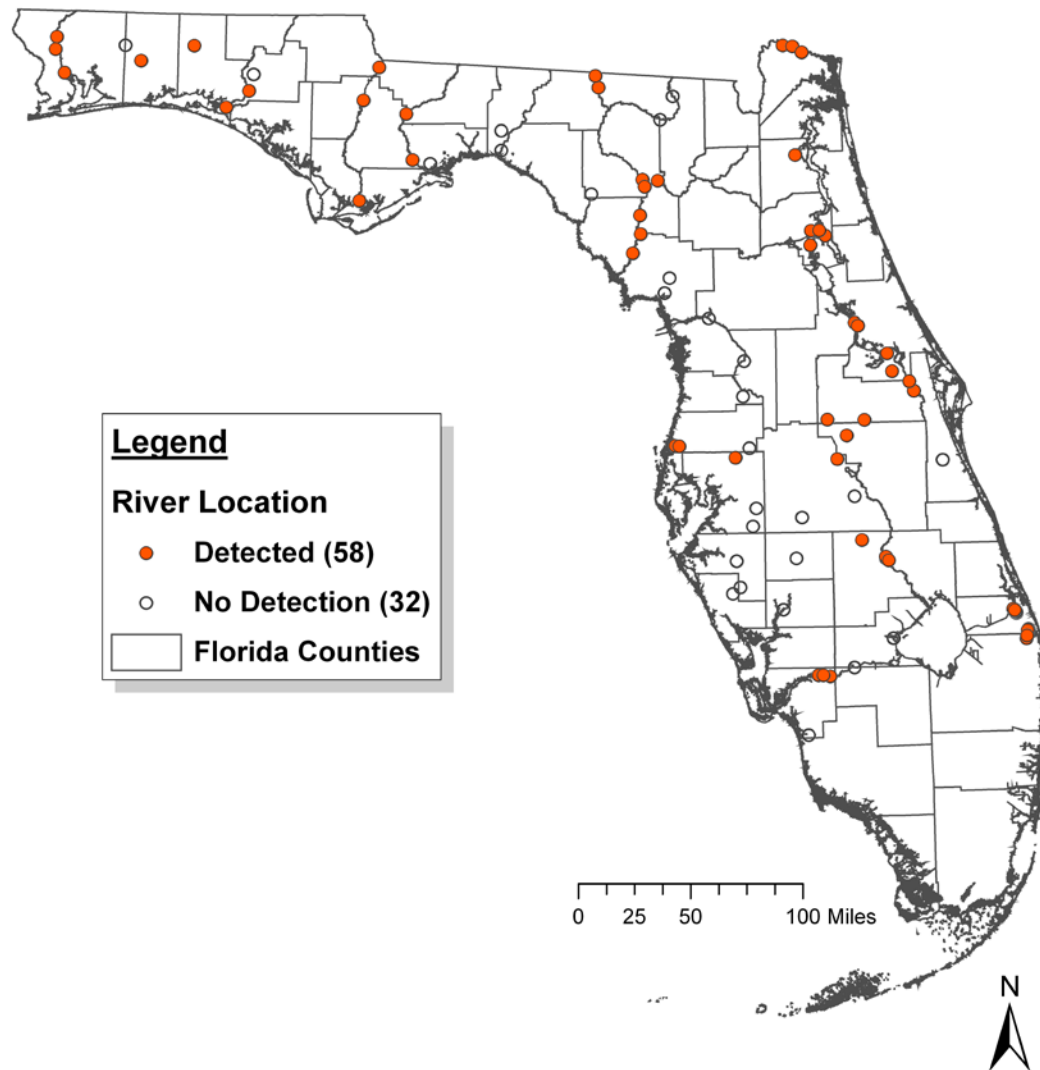
- 2012

- Rivers 58/90 sites (~64%) at 0.023 I $\mu\text{g/L}$ to 4.7 $\mu\text{g/L}$
- Streams 23/90 sites (~26%) at 0.027 I $\mu\text{g/L}$ to 1.4 $\mu\text{g/L}$
- Canals 47/74 sites (~64%) at 0.037 I $\mu\text{g/L}$ to 27 $\mu\text{g/L}$

- 2015

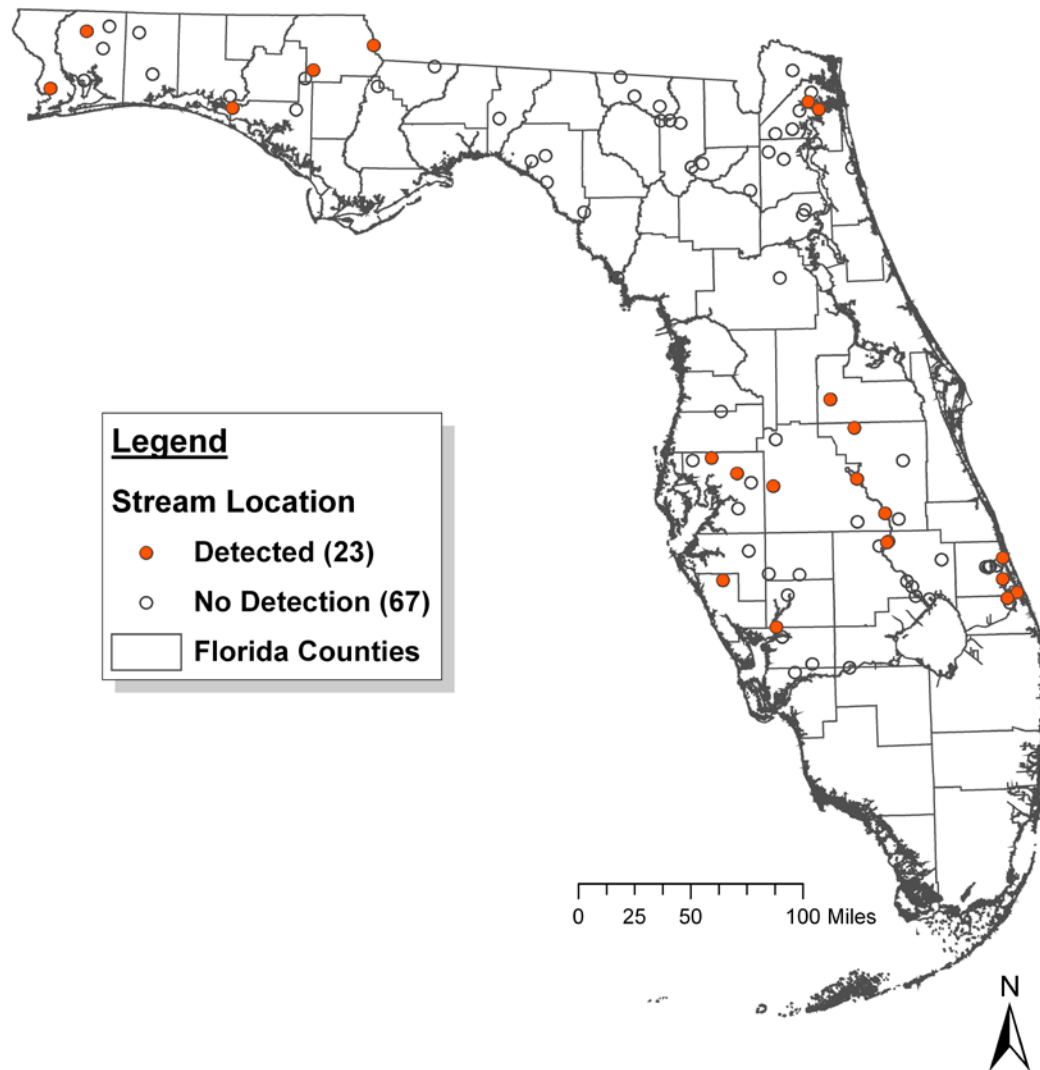
- Rivers 72/90 sites (80%) at 0.017 I $\mu\text{g/L}$ to 27 $\mu\text{g/L}$
- Streams 53/90 sites (~59%) at 0.012 I $\mu\text{g/L}$ to 0.96 $\mu\text{g/L}$
- Canals 35/60 sites (~58%) at 0.014 I $\mu\text{g/L}$ to 1.7 $\mu\text{g/L}$

Watershed Monitoring Section
Status Rivers
Sucralose Sampling 2012



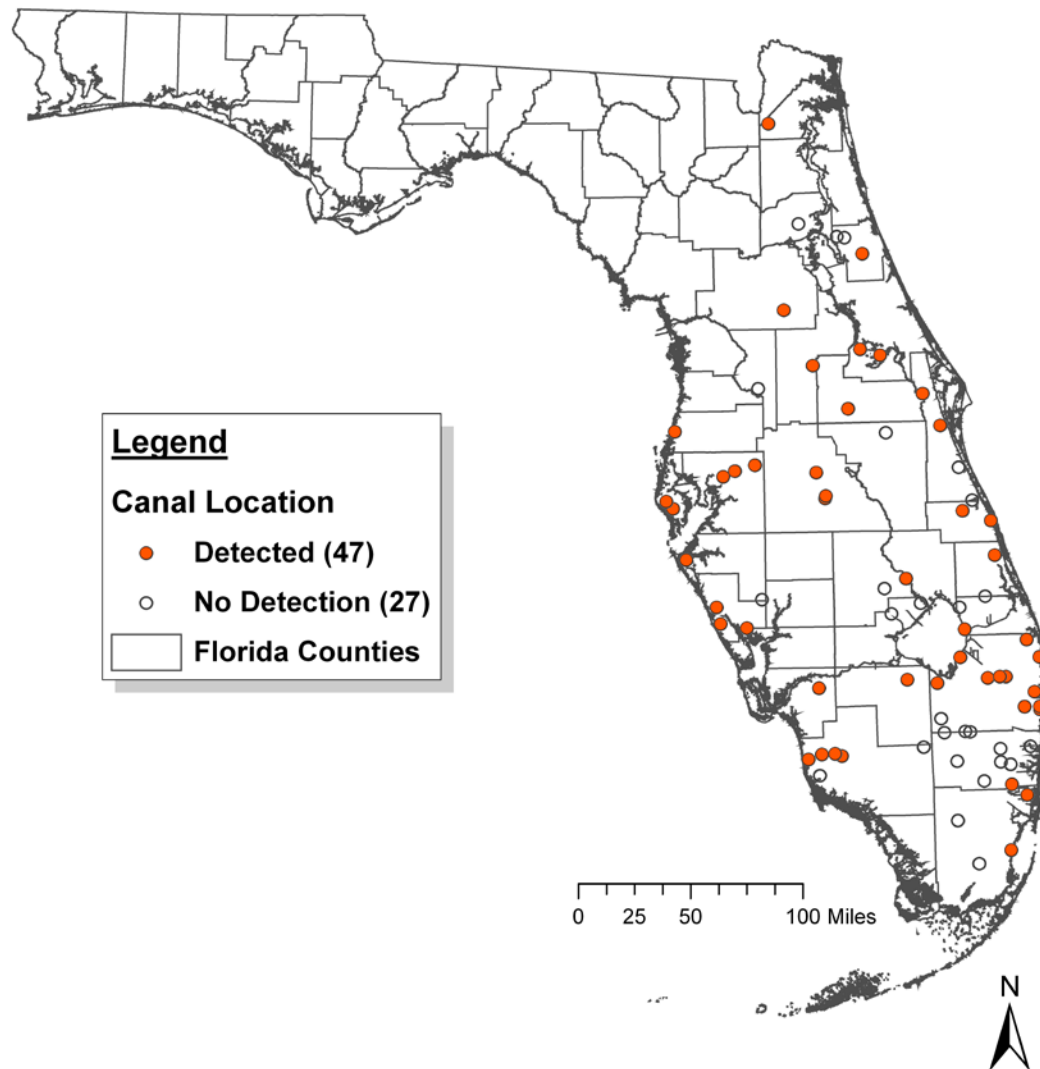
Map created by Andy Woeber, WMS, FDEP dated March 20, 2015
This is a cartographic representation and not intended for further analysis.

Watershed Monitoring Section
Status Streams
Sucralose Sampling 2012



Map created by Andy Woeber, WMS, FDEP dated March 20, 2015
This is a cartographic representation and not intended for further analysis.

Watershed Monitoring Section
Status Canals
Sucralose Sampling 2012



Map created by Andy Woeber, WMS, FDEP dated March 20, 2015
This is a cartographic representation and not intended for further analysis.

SURFACE WATER TREND SUCRALOSE SUMMARY

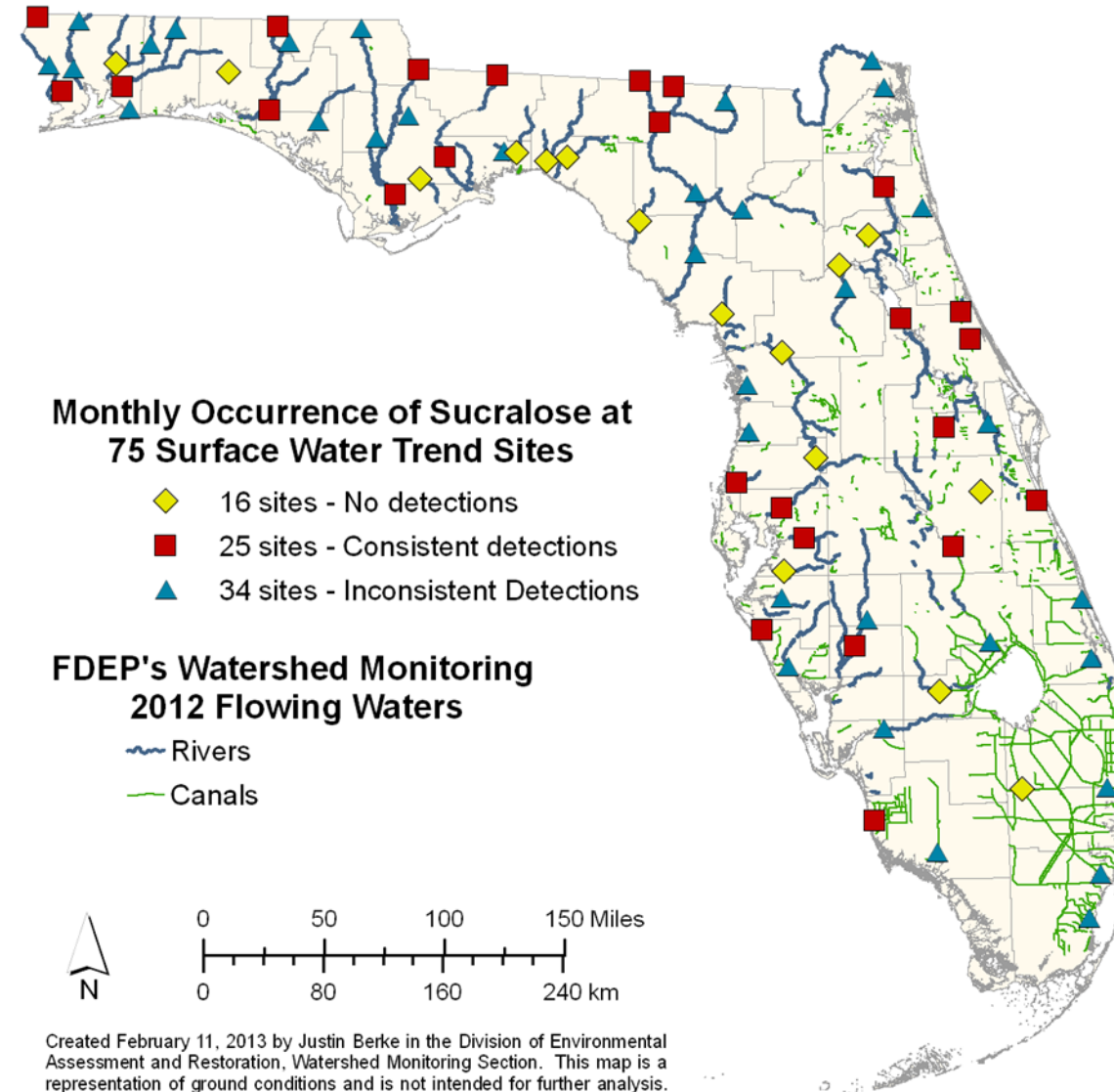
- 2012 Results

- Canal sites 5/5 detections (0.02 I $\mu\text{g/L}$ – .46 $\mu\text{g/L}$)
 - 2/5 sites had > 80%* detection rate
- River sites 40/51 detections (0.015 IJ $\mu\text{g/L}$ – 4.0 $\mu\text{g/L}$)
 - 16/40 sites had detections > 80% detection rate
- Stream sites 14/19 detections at (0.013 I $\mu\text{g/L}$ – 4.1 $\mu\text{g/L}$)
 - 6/19 sites had detections > 80% detection rate

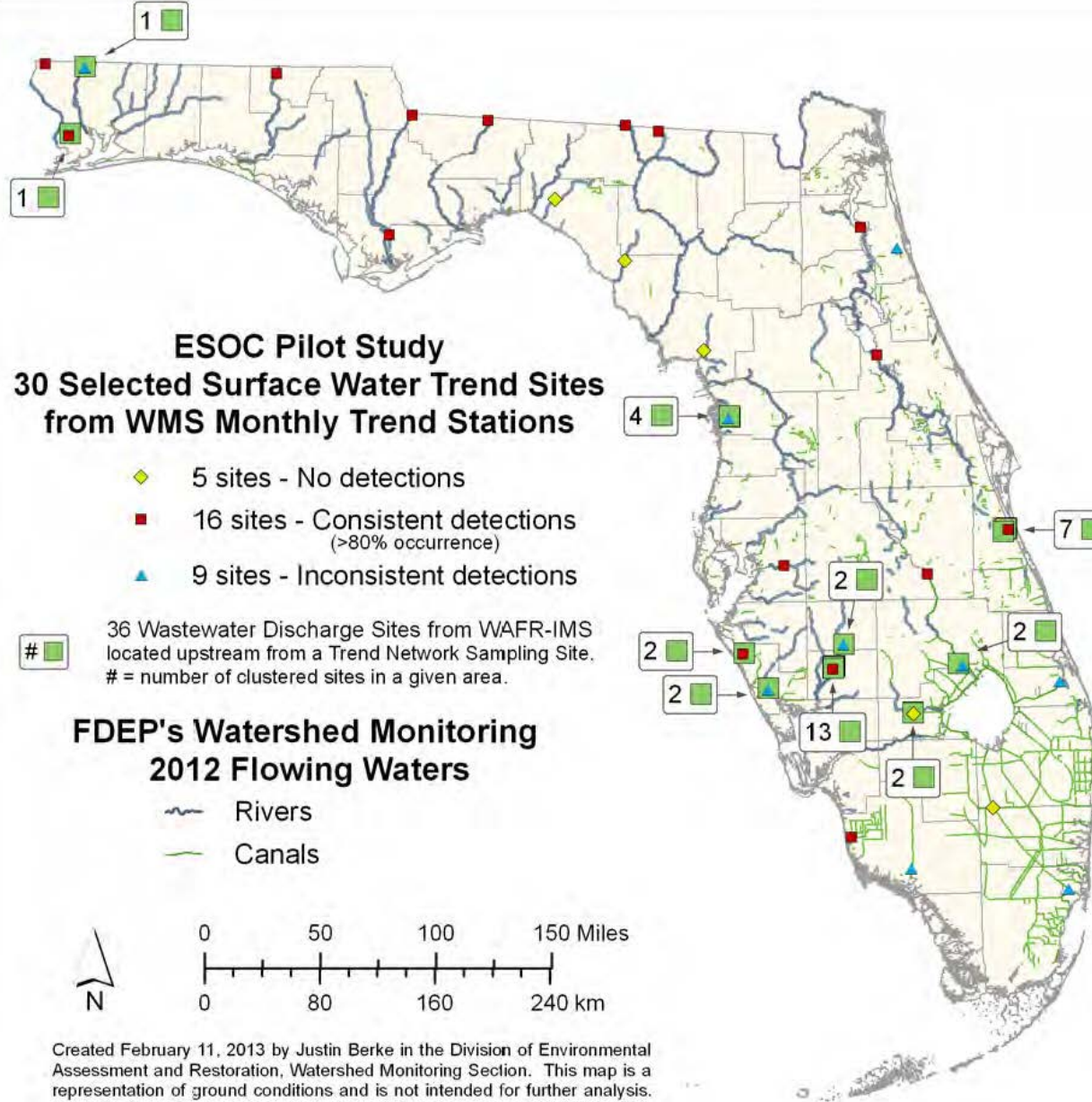
- 2015 Results

- Canal sites 5/6 detections (0.018 I $\mu\text{g/L}$ – .57 $\mu\text{g/L}$)
 - 2/5 sites had > 80% detection rate
- River sites 48/55 detections (0.011 IJ $\mu\text{g/L}$ – 8.5 $\mu\text{g/L}$)
 - 35/48 sites had detections > 80% detection rate
- Stream sites 15/19 detections at (0.010 I $\mu\text{g/L}$ – 4.8 $\mu\text{g/L}$)
 - 10/19 sites had detections > 80% detection

* 12 sample events annually therefore 80% = at least 10/12 detections per site



Created February 11, 2013 by Justin Berke 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 Justin.Berke@dep.state.fl.us or (850)245-8551.



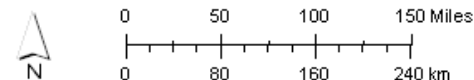
Four of the SW Trend sites with consistent detections were selected for an EC pilot Study.

ESOC Pilot Study Selected Surface Water Stations from WMS Trend Network

■ Selected sites with highest sucralose concentrations

FDEP's Watershed Monitoring
2012 Flowing Waters

— Rivers
— Canals



Created October 14, 2013 by Andy Woeber 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 Andy Woeber at
nathan.woeber@dep.state.fl.us or (850) 245-8031

STATUS LAKES SUCRALOSE RESULTS

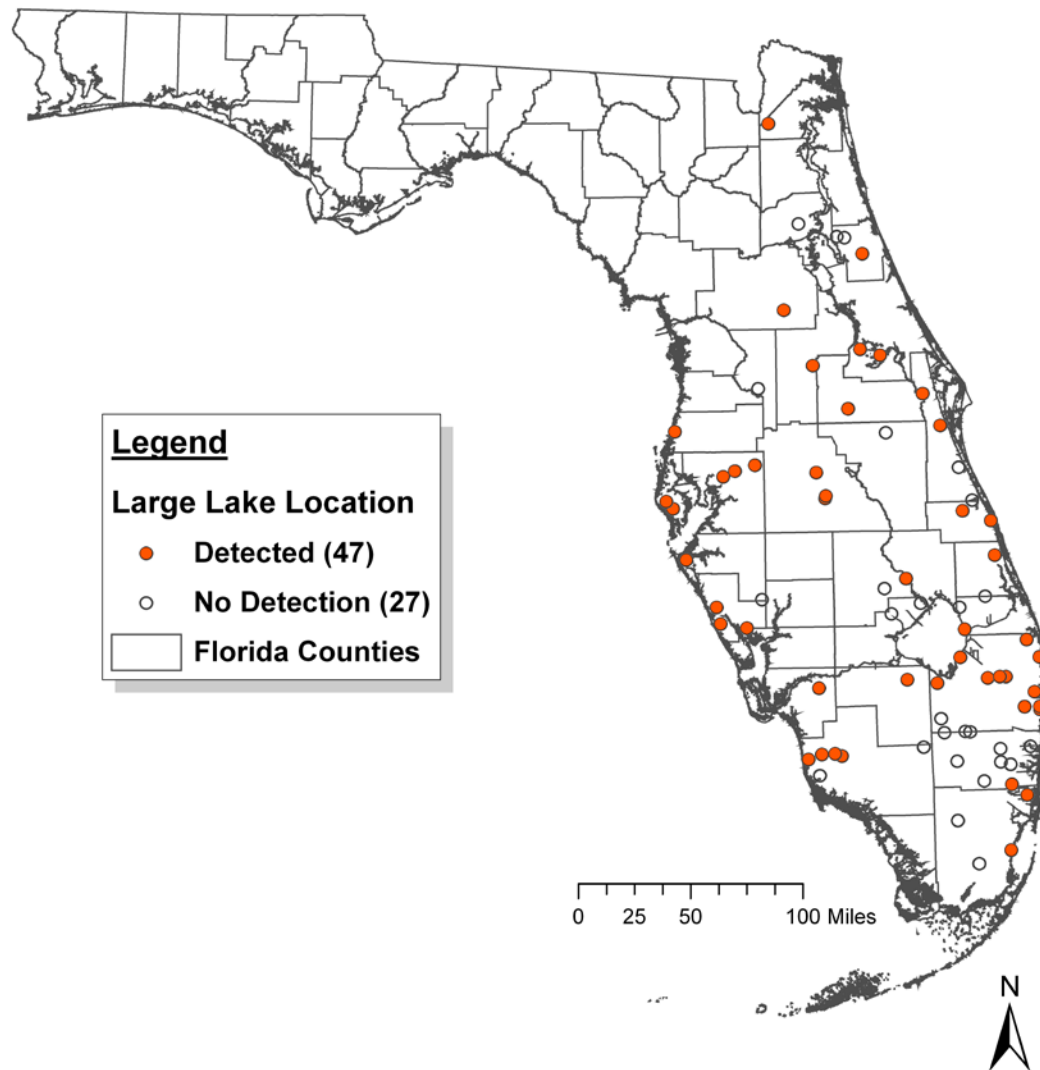
- 2012

- Large Lakes 59/90 sites (~66%) at 0.018 I $\mu\text{g/L}$ to 0.74 $\mu\text{g/L}$
- Small Lakes 25/77 sites (~32%) at 0.028 I $\mu\text{g/L}$ to 0.58 $\mu\text{g/L}$

- 2015

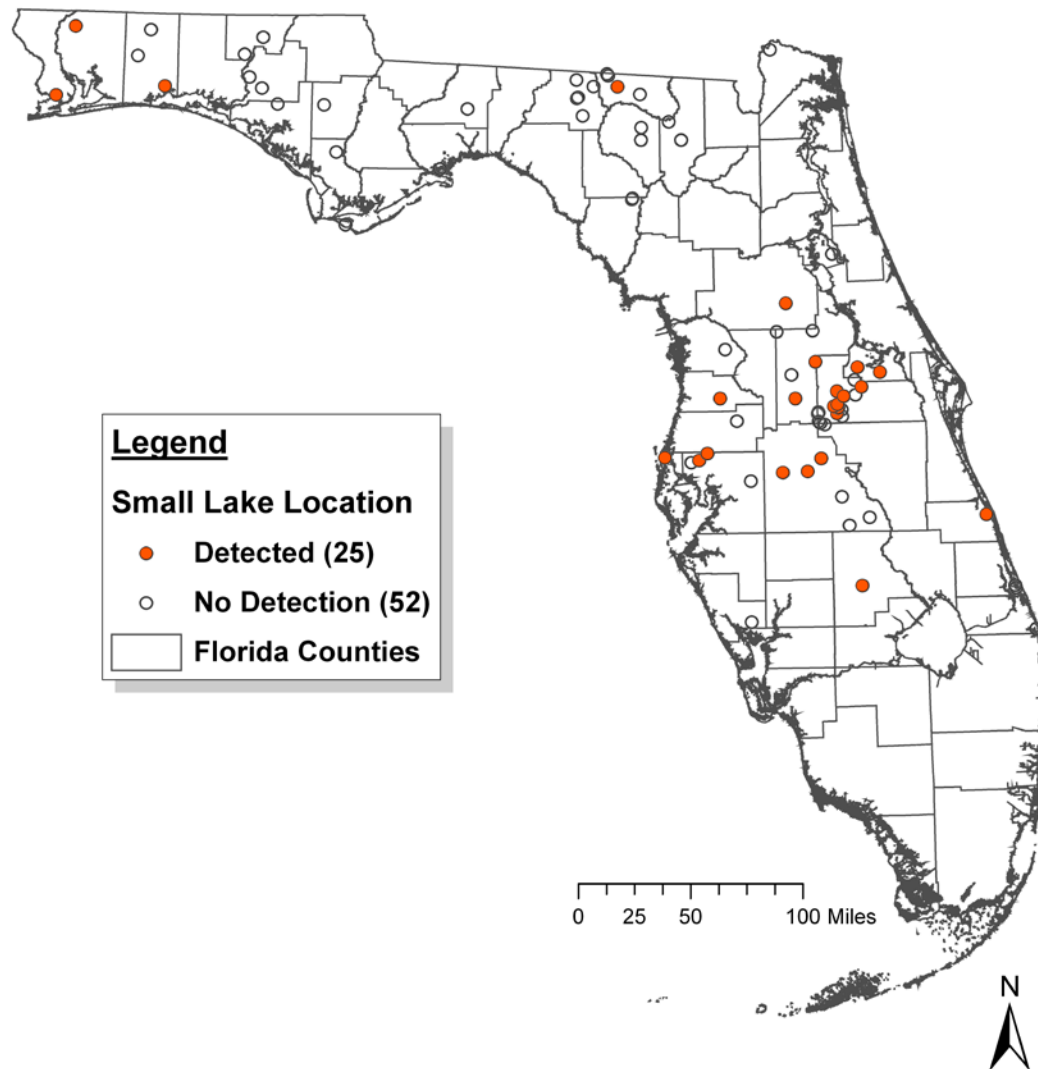
- Large Lakes 68/90 sites (~76%) at 0.012 I $\mu\text{g/L}$ to 1.4 $\mu\text{g/L}$
- Small Lakes 35/78 sites (~45%) at 0.014 I $\mu\text{g/L}$ to 1.4 $\mu\text{g/L}$

Watershed Monitoring Section
Status Large Lakes
Sucralose Sampling 2012



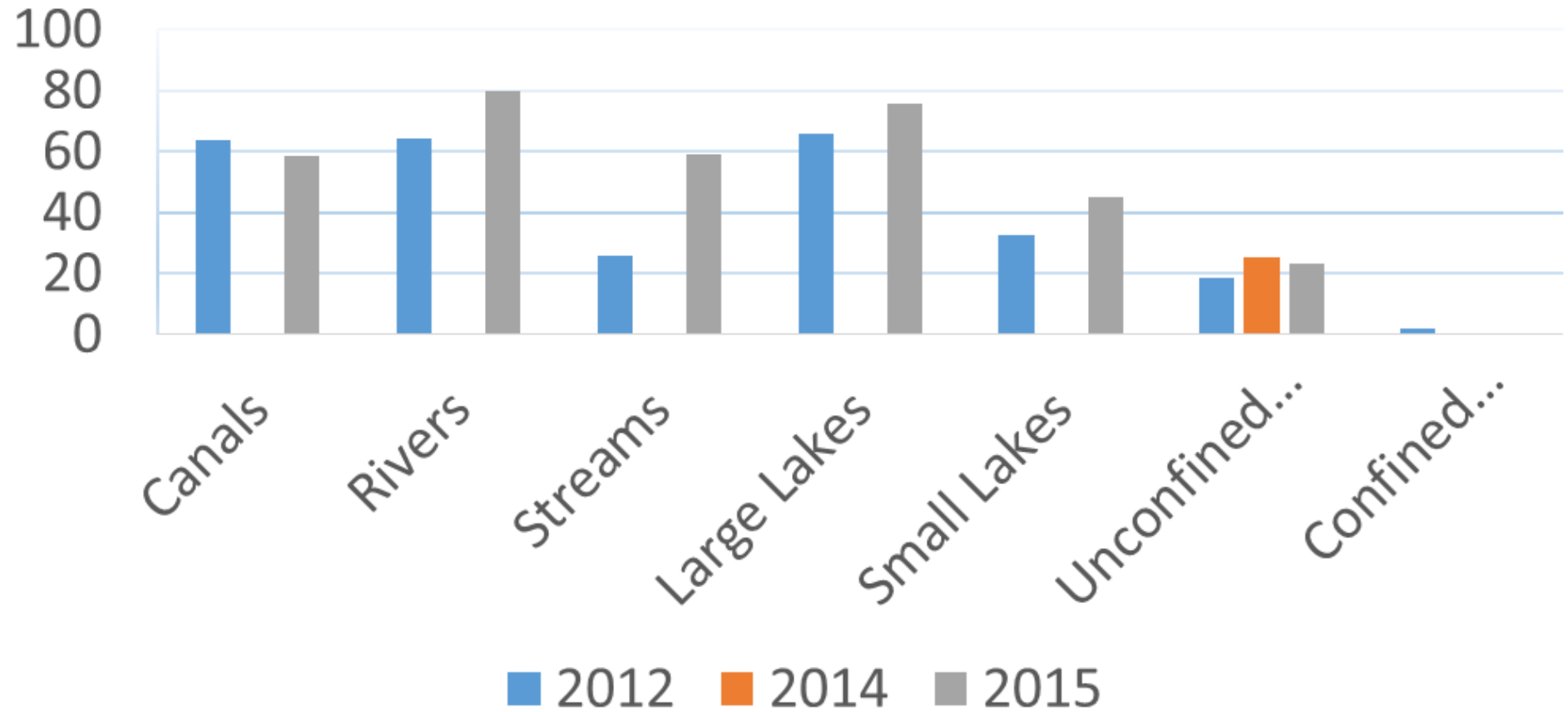
Map created by Andy Woeber, WMS, FDEP dated March 20, 2015
This is a cartographic representation and not intended for further analysis.

Watershed Monitoring Section
Status Small Lakes
Sucralose Sampling 2012



Map created by Andy Woeber, WMS, FDEP dated March 20, 2015
This is a cartographic representation and not intended for further analysis.

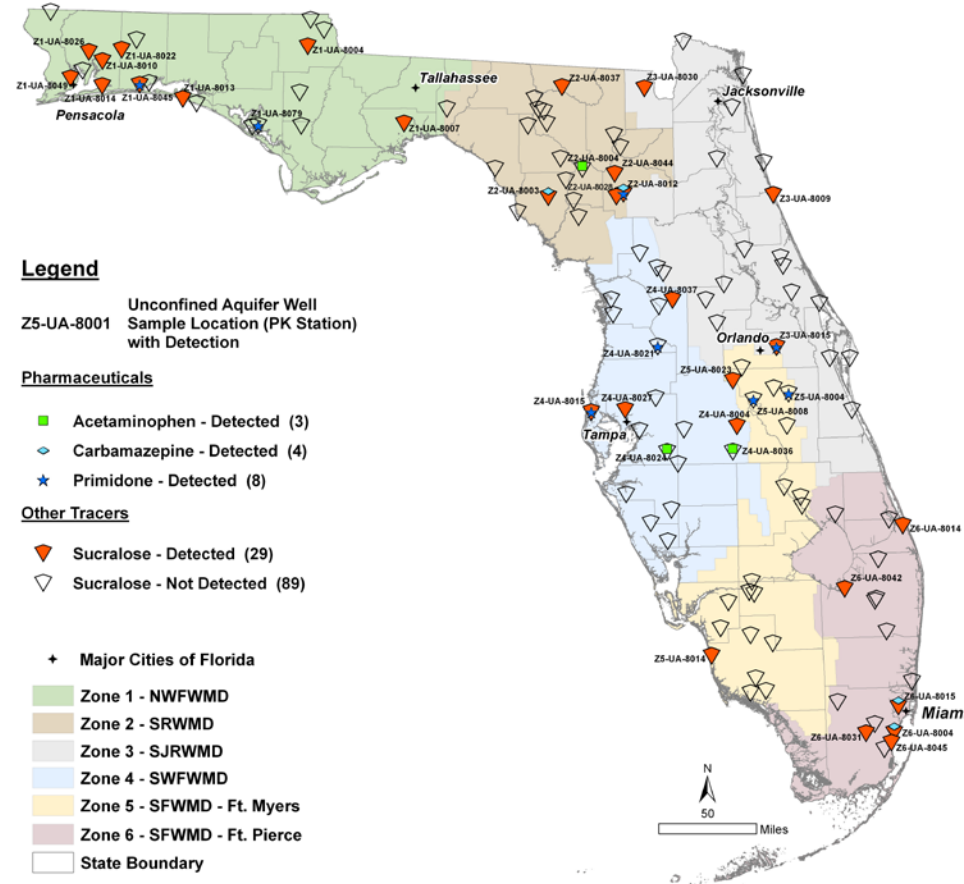
% Status Resource with Detectable Sucralose



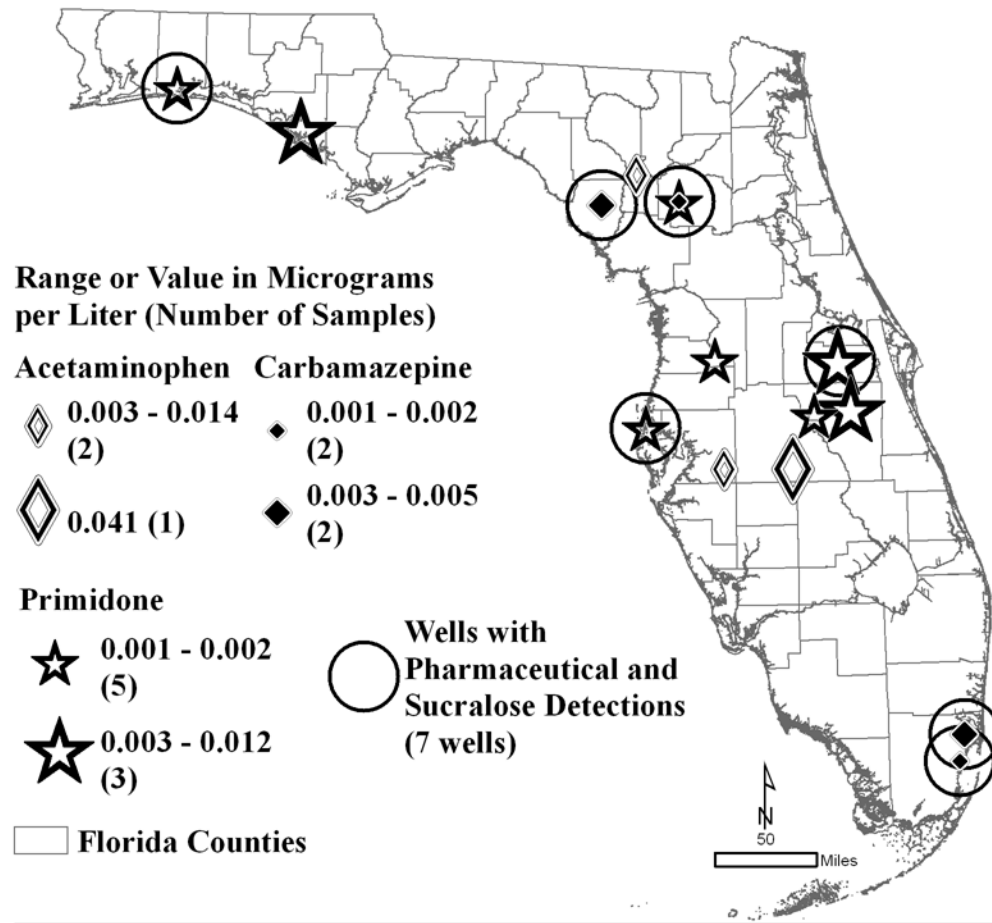
2014 & 2015 STATUS UNCONFINED AQUIFERS PHARMA RESULTS

- Acetaminophen detections
 - 2014 - 3/116 wells (0.003 µg/L - 0.041 µg/L)
 - 2015 - 0/120 wells no detections
- Carbamazepine detections
 - 2014 - 4/116 wells (0.0007 I µg/L - 0.0056 I µg/L)
 - 2015 - 9/120 wells (0.00082 I µg/L - 0.0092 µg/L)
- Primidone detections
 - 2014 - 8/116 wells 0.0012 I µg/L & 0.012 µg/L
 - 2015 - 3/120 wells (0.0097 I µg/L - 0.021 I µg/L)

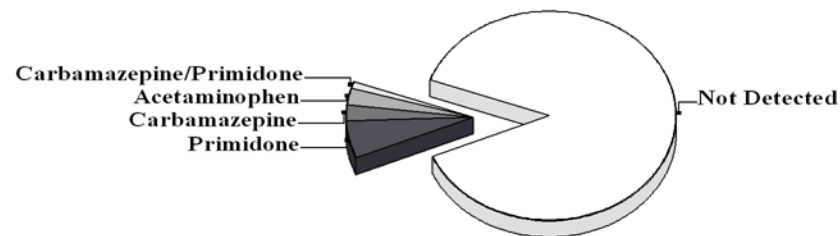
Comparison of Sucralose with Detected Pharmaceutical Compounds 2014 Status Network - Unconfined Aquifers



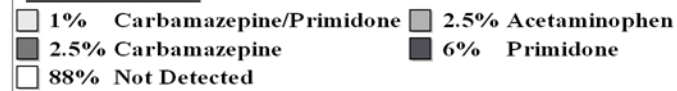
(Unconfined Aquifers 2014)



Distribution of Select Pharmaceuticals Within Status Unconfined Wells



Percent of Total



2015 STATUS SURFACE WATER PHARMA RESULTS

- Acetaminophen detections
 - Canals 1/60 sites at 0.0031 I $\mu\text{g/L}$ (Z6-CN-9015)
 - Rivers 3/90 sites (0.0021 I $\mu\text{g/L}$ - 0.011 $\mu\text{g/L}$)
 - Streams 5/90 sites (0.002 I $\mu\text{g/L}$ - 0.0058 I $\mu\text{g/L}$)
 - Large Lakes 0/90 sites no detections
 - Small Lakes 0/78 sites no detections

2015 STATUS SURFACE WATER PHARMA RESULTS

- Carbamazepine detections
 - Canals 7/60 sites (0.0025 I $\mu\text{g/L}$ & 0.024 $\mu\text{g/L}$)
 - Rivers 25/90 sites (0.00042 I $\mu\text{g/L}$ - 0.068 $\mu\text{g/L}$)
 - Streams 23/90 sites (0.00044 I $\mu\text{g/L}$ - 0.022 $\mu\text{g/L}$)
 - Large Lakes 11/90 sites (0.0022 I $\mu\text{g/L}$ - 0.019 $\mu\text{g/L}$)
 - Small Lakes 7/78 sites (0.00049 I $\mu\text{g/L}$ - 0.0029 $\mu\text{g/L}$)

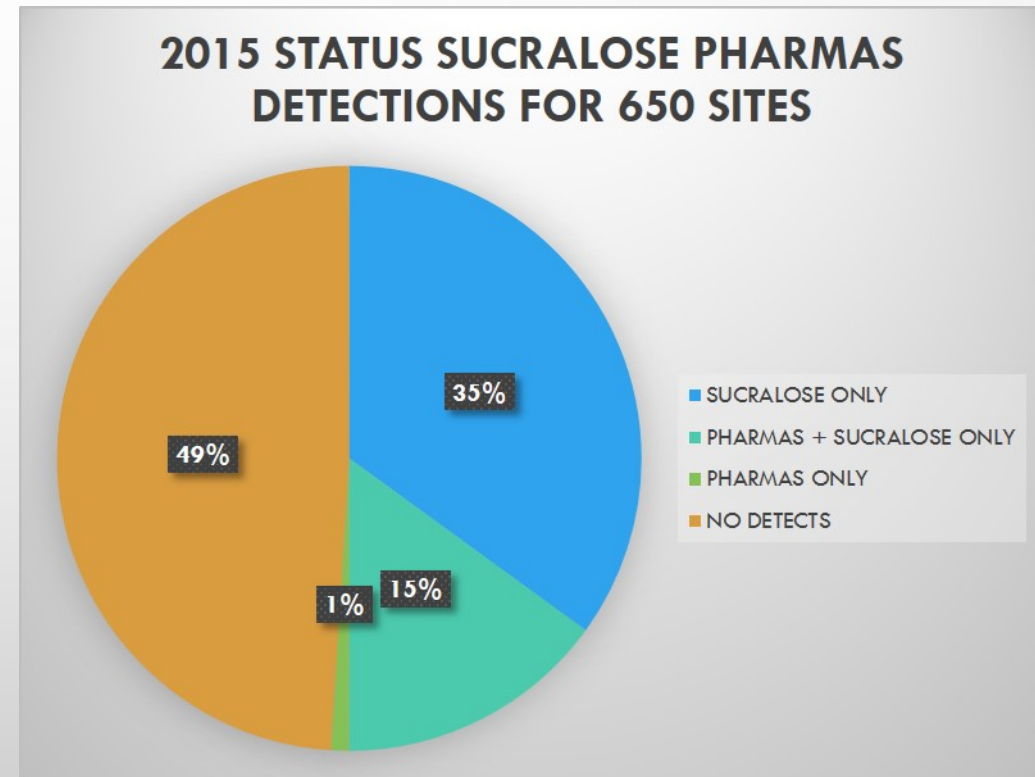
2015 STATUS SURFACE WATER PHARMA RESULTS

- Primidone detections
 - Canals 2/60 sites 0.012 I $\mu\text{g/L}$ & 0.026 $\mu\text{g/L}$
 - Rivers 3/90 sites (0.0084 I $\mu\text{g/L}$ – 0.088 $\mu\text{g/L}$)
 - Streams 0/90 sites no detections
 - Large Lakes 2/90 sites (0.0058 I $\mu\text{g/L}$ & 0.0061 $\mu\text{g/L}$)
 - Small Lakes 1/78 sites at 0.030 I $\mu\text{g/L}$

SUMMARY STATUS NETWORK

2015 SUCRALOSE/PHARMACEUTICALS

- SUCRALOSE DETECTED IN 325/650 OF STATUS SITES SAMPLED
 - 227 SITES WITH DETECTIONS OF SUCRALOSE ALONE, NO PHARMAS
- AT LEAST ONE OF THE THREE PHARMAS DETECTED IN 104/650 STATUS SITES SAMPLED
 - OF THESE SITES 8 SHOWED NO SUCRALOSE DETECTIONS.





2015 STATUS UNCONFINED AQUIFER PESTICIDE RESULTS

- 60/120 Unconfined wells produced detections for 18 of the 43 pesticides and degradates analyzed.
- 

2015 STATUS UNCONFINED AQUIFER PESTICIDE DETECTONS

PARAMETER	# DETECTIONS
Alachlor	3
Ametryn	4
Atrazine	21
Atrazine Desethyl	12
Bromacil	7
Diuron	4
Fipronil	3
Fipronil Sulfide	5
Fipronil Sulfone	15
Fluridone	8
Hexazinone	32
Imidacloprid	6
Metalaxyl	5
Metolachlor	4
Metribuzin	1
Norflurazon	10
Prometon	2
Simazine	6

2015 STATUS

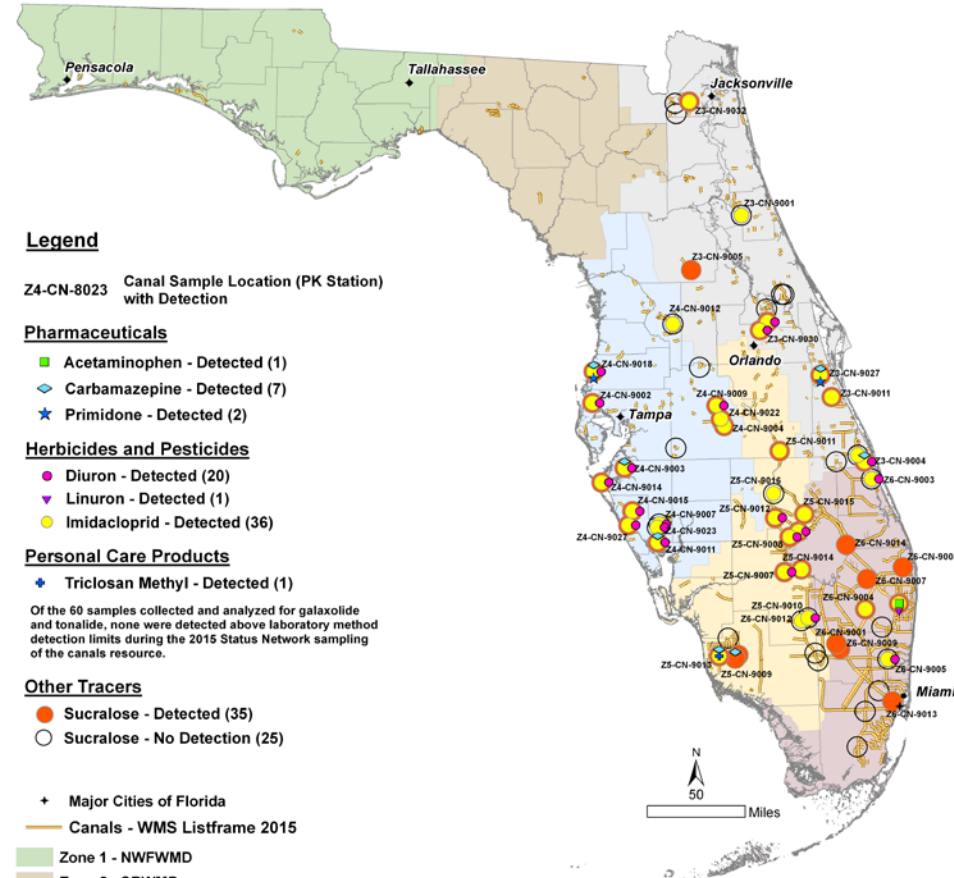
UNCONFINED AQUIFER PESTICIDE RESULTS

- 15/43 of the pesticides we analyzed for have Primary Drinking Water Std. or a Health Advisory Level.
- No Primary Drinking Water standards or Health Advisory Levels were exceeded for 15/43 pesticides we analyzed for.

Name	PDW STD ug/L	HAL ug/L
Alachlor	2	N/A
Ametryn	N/A	63
Atrazine	3	N/A
Bromacil	N/A	90
Butylate	N/A	350
Chlorpyrifos	N/A	21
EPTC (EPTAM)	N/A	180
Ethoprop	N/A	0.7
Fluridone	N/A	560
Hexazinone	N/A	230
Metribuzin	N/A	180
Mevinphos	N/A	1.8
Norflurazon	N/A	280
Prometryn	N/A	28
Simazine	4	N/A

Comparison of Sucralose with Detected Compounds; Pharmaceuticals, Herbicides, Pesticides and Personal Care Products

2015 Status Network - Canals



Legend

Z4-CN-8023 Canal Sample Location (PK Station) with Detection

Pharmaceuticals

- Acetaminophen - Detected (1)
- ◇ Carbamazepine - Detected (7)
- ★ Primidone - Detected (2)

Herbicides and Pesticides

- Diuron - Detected (20)
- ▼ Linuron - Detected (1)
- Imidacloprid - Detected (36)

Personal Care Products

- ◆ Triclosan Methyl - Detected (1)

Of the 60 samples collected and analyzed for galaxolide and tonalide, none were detected above laboratory method detection limits during the 2015 Status Network sampling of the canals resource.

Other Tracers

- Sucralose - Detected (35)
- Sucralose - No Detection (25)

- + Major Cities of Florida
- Canals - WMS Listframe 2015
- Zone 1 - NWFWMD
- Zone 2 - SRWMD
- Zone 3 - SJRWMD
- Zone 4 - SWFWMD
- Zone 5 - SFWMD - Ft. Myers
- Zone 6 - SFWMD - Ft. Pierce
- State Boundary

Map created by Andy Woelber, WMS, FDEP and dated March 28, 2016.

The map is a cartographic representation and not intended for further analysis.



WRAP UP

- Our data indicate that between 20-80% of the all status resources (with the exception of confined aquifers) show low levels of the emerging contaminant indicators.
- Next step is to address the question 'so what does this mean, are the biota effected by this? Hopefully the EC Pilot Study will provide some clues.



Conclusion: if we
continue to ignore
ECs, even at low
levels we all could
end up looking
like this guy!

