# Using tracers to infer potential extent of emerging contaminants in Florida's groundwater

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**Abstract** Current wastewater treatment technologies do not remove all potential contaminants of groundwater. Many of these contaminants, commonly referred to as emerging contaminants (ECs), are unregulated and there is concern these compounds may cause human health and environmental impacts. In an effort to infer statewide percentages of water resources affected, sucralose is employed as a human waste tracer. A 2012 statewide probabilistic survey of groundwater in wells provided detection rates of 18% in unconfined aquifers and 2% in confined aquifers. Trend monitoring of 47 wells and one spring shows unconfined aquifers consisting of both the Floridan aquifer system (FAS) and the surficial aquifer system (SAS) were more likely to have persistent detections. Three selected pharmaceuticals (acetaminophen, carbamazepine, and primidone) and sucralose were added as EC tracers to the unconfined aquifer status network in 2014. The 2014 status survey showed sucralose detections of 25% for wells tapping unconfined aquifers. Twelve percent of these wells had detections of the pharmaceuticals. All wells with carbamazepine detections were found to have sucralose detections; conversely, wells showing acetaminophen detections did not show detections of sucralose. These results highlight the vulnerability of Florida's unconfined aquifers and identify them as potential repositories for sucralose and other pharmaceutical compounds.

**Keywords** Aquifer, tracer, emerging contaminant, groundwater, unconfined

## Introduction

Detected in low concentrations in surface water bodies in the United States (US) and throughout the world, emerging contaminants (ECs) are compounds including pharmaceuticals, personal care products, hormones, pesticides and herbicides and their degradation products, detergents and their degradation products, plasticizers, flame retardants and polycyclic aromatic hydrocarbons (Kolpin et al. 2002, Barnes et al. 2008, Pal et al. 2010). Sources of these chemical compounds include, but are not restricted to, both human and animal waste-disposal activities. These include domestic wastewater (septage and treated municipal wastewater disposal), land application of bio-solids, and reclaimed wastewater. ECs also originate from agricultural activities including animal husbandry and crop production. In addition, aerosols generated from domestic, industrial, agricultural, and landfill activities, generate chemical dusts that are dispersed to soils through wet or dry deposition (Stuart et al. 2011).

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In 2000, the United States Geological Survey (USGS) collected water samples from a network of 47 groundwater sites in 18 states in areas known or thought to be susceptible to impacts from either human or animal wastewaters. ECs were detected at 81 percent of the sites and of these over 20 percent had detections for plasticizers, insect repellants, fire retardants, antibiotics, and solvents. Over ten percent had detections for detergent metabolites, disinfectants, combustion products, and non-prescription drugs. One of these non-prescription drugs, acetaminophen, was detected at a maximum concentration of 0.38 micrograms per Liter (μg/L) in 6.4 percent of the sites sampled. This study and others demonstrate that these compounds are present in low concentrations in the nation's groundwaters, and the potential exists for further detections of additional ECs (Barnes et al. 2008, Erickson et al. 2014).

The Florida Department of Environmental Protection (DEP) therefore created a workgroup to address ECs in 2008. The group recommended a series of actions, such as encouraging pharmaceutical collection to keep these ECs out of the waste stream and requested federal agencies such as the US Environmental Protection Agency (USEPA) research the impact of ECs in the environment (DEP 2008). With the exception of some pesticides and herbicides, the vast majority of ECs are unregulated by federal or state agencies. For instance, one study used provisional drinking water guidelines for selected ECs based on human toxicological information concluded that for the majority of these compounds, the maximum concentrations detected in real-world samples were well below the study's guideline values (Schriks et al. 2010). However, many studies document the ecological risks from ECs to aquatic organisms that reside in surface water (Guillette et al. 1996, Smital et al. 2004, Pal et al. 2010).

Unconfined aquifers can be distinguished from confined aquifers in that the upper phreatic zone is saturated with water that is exposed to the atmosphere and therefore water levels are free to rise or decline. Confined aquifers are characterized by having an overlying rock unit with very low hydraulic conductivity that restricts movement of groundwater into or out of the aquifer (Heath 1983). These physical properties make unconfined aquifers more vulnerable to contamination. Wells in this study are located in the Floridan aquifer system (FAS), the intermediate aquifer system (IAS), and the surficial aquifer system (SAS) including the Biscayne and Sand and gravel aquifers. Each of these aquifer units, with the exception of the Biscayne aquifer, shows areas of confinement. Wells tapping unconfined segments of aquifers are hereafter referred to as unconfined wells; and wells tapping confined segments of aquifers are hereafter referred to as confined wells.

Because Florida naturally has extensive exchange between surface and groundwater, a concern for the mobility of ECs to aquifers exists. More importantly, research now demonstrates that ECs are present in source groundwaters used for municipal drinking water systems (Focazio et al. 2008, Pal et al. 2014). According to Foster et al. (2012), USGS groundwater research identified the presence of ECs in the local surficial aquifers and canals located near outfalls of a wastewater treatment plant in southern Dade County, where the Biscayne aquifer is essentially at the surface. Pharmaceuticals, antibiotics, pesticides and pesticide degradation products, and the hormone 17-*beta*-estradiol (human birth control medication) were all detected in wells monitoring effluent discharge from the waste water treatment plant.

**Water Quality Monitoring Networks in Florida.** In 2000, the Florida Department of Environmental Protection's (DEP's) Watershed Monitoring Section (WMS) established two ambient water-quality monitoring networks. The Status network evaluates seven water resources: five surface-water categories (large lakes, small lakes, rivers, streams and canals) and two groundwater categories (confined aquifers and unconfined aquifers). Annually the network generates data for 680 distinct surface or groundwater stations. The Status network is based on a probabilistic assessment process that develops statistical estimates of the water quality for the entire state (Wayland 2001). A probabilistic stratified monitoring design can supply, with known confidence, an inference of the percentage of a water resource that is impaired due to exceedances of state water-quality criteria (Stevens and Olsen 1999). The use of probability assessments avoids bias and provides a survey of water-quality conditions in each resource statewide; thus reducing costs and increasing the effectiveness of Florida's water-quality monitoring programs.

The DEP WMS also maintains the Trend monitoring network, which currently consists of 78 surface-water and 48 groundwater sites, to monitor water-quality changes over time in rivers, streams, and aquifers (via wells and springs). Surface-water stations are sampled monthly and groundwater stations are sampled quarterly. The Trend network, which generates over 1,100 samples annually, complements the Status network by providing spatial and temporal information about surface and groundwater resources, and potential changes from anthropogenic sources or natural influences, including extreme hydrologic events (e.g., droughts, tropical weather systems).

**Sucralose a Tracer of Human Waste.** The stable chemical properties of sucralose promote its use as an ideal tracer to determine the influence of human activities. Johnson & Johnson, Inc. formed McNeil Specialty Products Company that marketed sucralose under the trade name Splenda® after a successful petition to the U.S. Food and Drug Administration (FDA) for sucralose to be used as a food additive in 1998 (see FDA Final Rule Docket Number 99F-0001; FDA 1999). Sucralose is made from real sugar using a substitution process of replacing three hydroxyl groups on the sugar molecule with three atoms of chlorine. Sucralose is used as an artificial sweetener in a wide variety of food products.

Studies show sucralose bypasses waste water treatment processes (Labare and Alexander 1993, Soh et al. 2011) and does not fraction out to bio-solids during water treatment. According to a study conducted by Torres et al.

(2011), seven samples of wastewater were collected from sewage treatment facilities in Arizona. The samples were run through both aerobic and anaerobic biological reactors. After 48 days of processing, no significant decrease was found in the amount of sucralose present in the water.

In a study conducted by Mawhinney et al. (2011), drinking water samples from 19 US drinking-water treatment plants serving more than 28 million people were analyzed for sucralose at the source, at the end of the water treatment process, and at distribution sampling points. Drinking water treatment plants whose source water was influenced by wastewater or recreational use of water were found to have levels of sucralose from 47 to 2,900 nanograms per Liter (parts per trillion). Little or no difference in sucralose reduction was observed between the samples taken from source water at the intake of the plants, samples taken at the end of water treatment, or samples taken within the water distribution systems.

Therefore sucralose resists breakdown and represents a marker compound to indicate water-quality conditions potentially impacted by human wastewater, treated or untreated. Sucralose has even been detected in the Gulf Stream off the coast of southeast Florida (Mead et al. 2009). Between 2011 and 2012, the DEP conducted laboratory analyses of 49 waste water treatment facilities in Florida and all of these facilities had detected sucralose between 10 and 40 μg/L in the effluent discharges.

In an effort to infer statewide percentages of ambient water resources affected by ECs, the WMS added DEP laboratory analysis for sucralose, starting with the 2012 Status and Trend networks sampling events. Between 2009 and 2010, the DEP laboratory was able to develop the methodology to analyze sucralose. With the knowledge that acetaminophen, primidone, and carbamazepine were more likely removed by standard sewage treatment than sucralose, the DEP laboratory developed the methodology to analyze them as additional tracers for human waste between 2012 and 2014.

## Methodology for Sample Collection and Laboratory Analyses

Samples are collected in one-liter brown glass bottles and transported on ice to the laboratory. Water samples are filtered using a specially dried 0.75 micrometer glass fiber filter from which an aliquot of 250 milliliters (mL) of filtered sample is passed through a solid phase cartridge consisting of a graphitized carbon-based solid-phase extraction (SPE) column. After extraction, the absorbed analytes are eluted from the SPE cartridge using 15 mL of 4:1 methylene chloride to methanol. Each extract is analyzed twice by High Performance Liquid Chromatography/Tandem Mass Spectrometer methods; one in negative ion mode for determination of sucralose and the other in positive ion mode for carbamazepine, primidone and acetaminophen determinations. The analytical procedure is based on USGS method O-2060-01, and its details are described in FDEP SOP LC-001/LC011 (Furlong et al. 2001).

The DEP laboratory determines a detection limit through the following process. Staff prepare a minimum of seven laboratory fortified blanks (LFB) at one to five times the estimated method detection limit (MDL) concentration and process each through the entire analytical method. The detection limit is derived using the Student's t-value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The MDL should be above the average lab blank level. The method detection limits and practical quantitation limits commonly provided by the laboratory are 0.01 μg/L and 0.05 μg/L for sucralose, 0.0004 μg/L and 0.002 μg/L for carbamazepine, 0.008 μg/L and 0.04 μg/L for primidone, and 0.004 μg/L and 0.016 μg/L for acetaminophen. For details, refer to FDEP SOP LB-007 (FDEP 2015).

## Results

The surface water results for the 2012 Status monitoring network samples show sucralose was detected at concentrations up to 27 micrograms per liter (μg/L) at 47 of 74 (63.5%) canal stations. For lakes, detections were found between 0.018 to 0.740 μg/L in 84 of 167 (50.3%) stations and for rivers and streams, the range was 0.023 to 4.70 μg/L in 81 of 180 (45.0%) stations. In the 2012 surface water Trend results (all river, stream, and canal stations), sucralose was detected in 59 of 78 (75.6%) stations at least once. Of these stations, the DEP ECs workgroup selected four sites with consistently high sucralose concentrations for water sampling using passive sampling devices containing specialized membranes designed to adsorb non-polar and polar compounds and subsequent bioassays to screen for biological effects. This study is a pilot project to evaluate the effectiveness of the sampling devices in surface waters for ECs and is ongoing.

Status groundwater sampling in 2012 shows sucralose was present in 24 of 226 wells (11%). The concentrations for unconfined-aquifer wells ranged from 0.066 to 19 μg/L in 22 of 119 wells (18%) and for confined-aquifer wells from 0.078 to 0.98 μg/L in 2 of 107 wells (~2%). In the 2014 Status network, 29 of 116 unconfined-aquifer wells (25%) sampled had detections of sucralose (Figure 1). In 2014, sucralose was detected in unconfined-aquifer wells from 0.011 to 2.10 μg/L. Figure 2 indicates quarterly trend monitoring of 47 wells and one spring in 2012 shows that 6 of the 47 wells (5 of 24 unconfined wells, 1 of the 23 confined) and the spring had detectable sucralose. Three of the unconfined Trend wells show detections in at least 3 of the 4 quarters (January to April 2012, April 2012 to July 2012, and July 2012 to October 2012), while two unconfined Trend wells produced a single detection (one well having a detection in January 2012 and the other having a detection in July 2012), a single confined aquifer had a detection in April 2012, and the spring had two detections in the following quarters, April 2012 and July 2012.

Recently DEP Central Laboratory developed the capability to perform ultra-trace level analyses of other EC compounds, including the pharmaceutical compounds acetaminophen (analgesic and antipyretic medication), carbamazepine (anti-epileptic medication) and primidone (anti-convulsing medication). Due to the few sucralose detections found in confined aquifers they were not selected for any additional study. The above pharmaceuticals occurred in

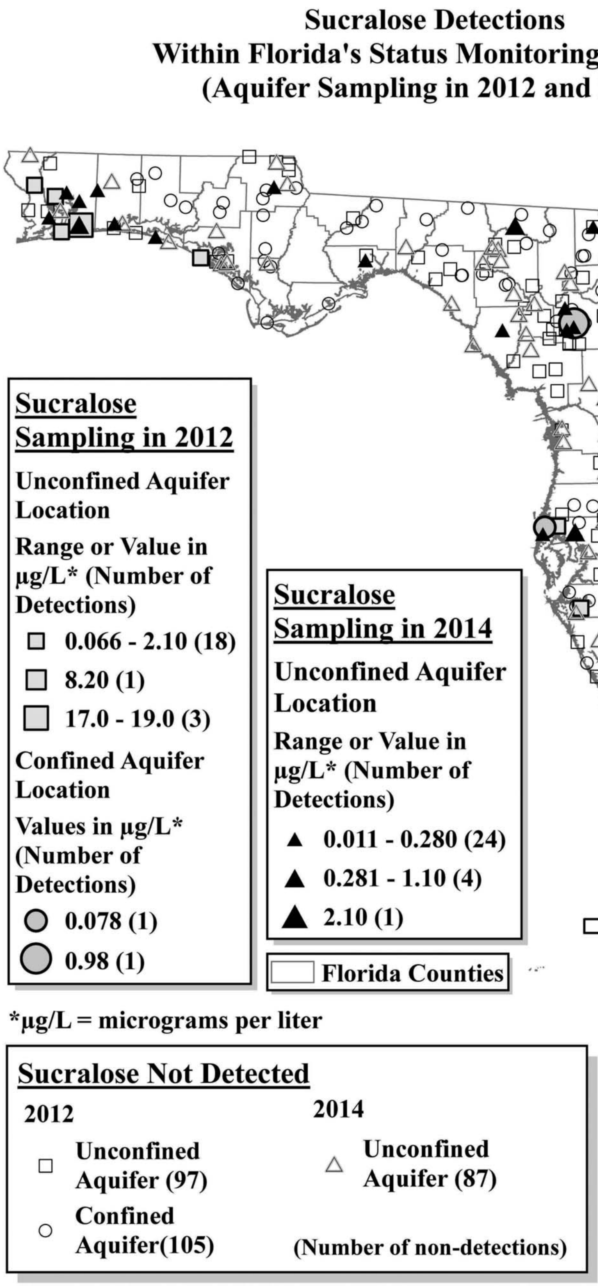


Figure 1. Sucralose Detections within Florida's Status Monitoring Network (Aquifer Sampling in 2012 and 2014).

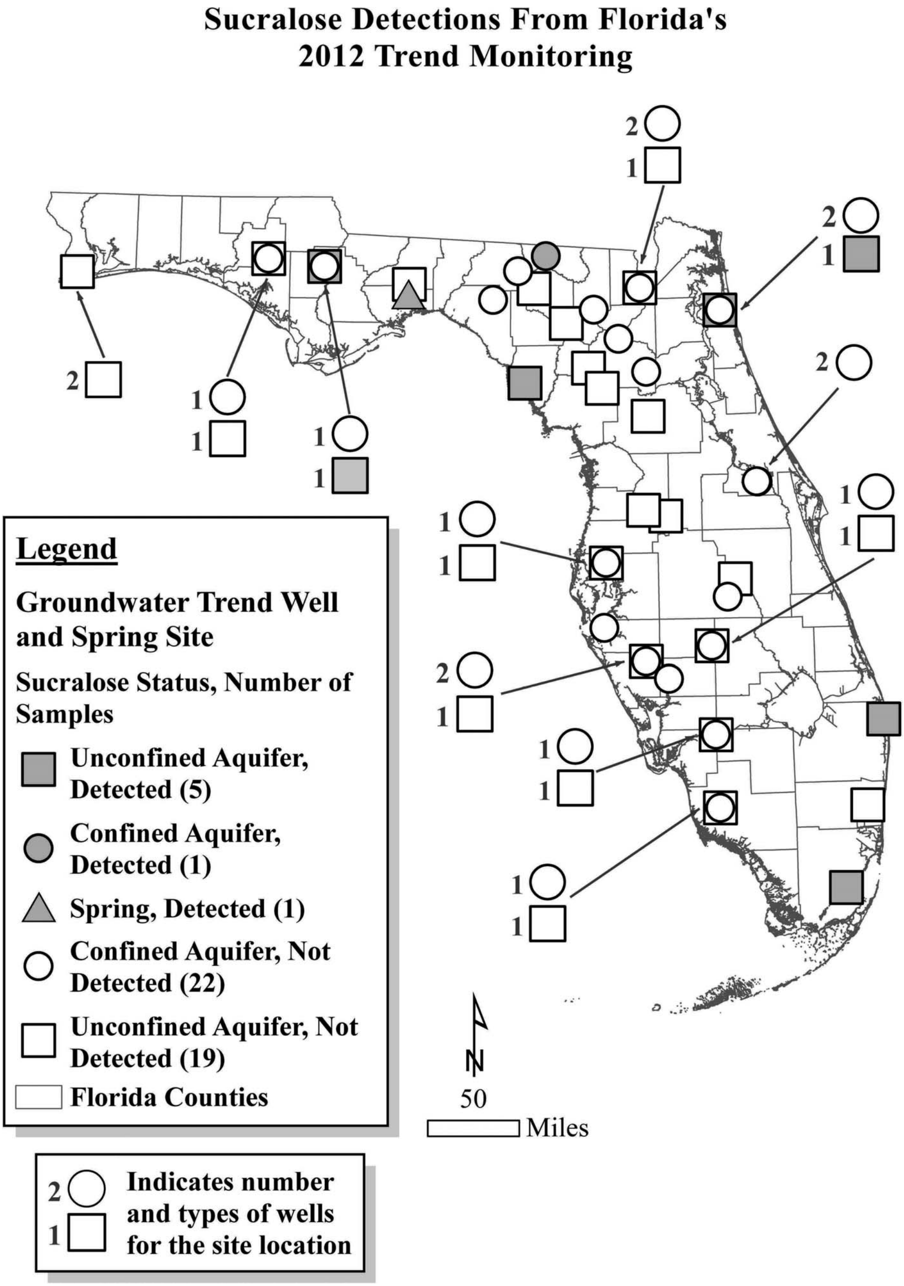


Figure 2. Sucralose Detections within Florida's Trend Monitoring Network; Confined and Unconfined Aquifers and Springs Sampling (2012).

14 out of 116 unconfined-aquifer wells (12%) sampled for the 2014 Status network. Four detections of carbamazepine occurred (3.4% of 116 wells). Three detections of acetaminophen occurred (2.6% of 116 wells). Eight detections of primidone occurred (6.9% of 116 wells). Sucralose detections were found in conjunction with all of the carbamazepine detections and with 4 of the 8 primidone detections. Whereas, none of the wells having acetaminophen detections showed sucralose detections. See Figure 3 for the concentrations of pharmaceuticals detected and their locations.

## Future Monitoring Plans

To develop the best strategies for understanding the distribution of ECs in Florida's ambient waters, future monitoring plans will need to take into account the sources and fates of these compounds. In the fall of 2015, organonitrogen and organophosphorus pesticide analyses were added to the Status unconfined aquifer sampling event, these in addition to analyses for sucralose, acetaminophen, primidone, and carbamazepine. For the calendar year 2016 the same suites of pesticides and pharmaceuticals were added to all Status flowing waters (rivers, streams, canals).

The pesticide analyses include the insecticides imidacloprid, parathion methyl and parathion ethyl, and the herbicides diuron, linuron, and fluridone. Imidacloprid is the most widely used agricultural insecticide in the world and is used on over 400 types of crops and tree species. In animal husbandry, it is applied to livestock to control insect pests. Commercially, it is also sold as Advantage® for flea control on household pets. The insecticide has been implicated in adversely impacting economically important pollinator species such as *Apis mellifera*, the European honey bee (Dively et al. 2015, Lu et al., 2012 Lu et al. 2014). Diuron and linuron are agricultural herbicides, whereas fluridone (trade name Sonar®) is a widely used aquatic herbicide in Florida for control of hydrilla and other nuisance aquatic vegetation.

## Conclusion

The DEP WMS identified sucralose in both surface and groundwater. Sucralose was found to be ubiquitous in all ambient surface-water resources monitored in 2012. For groundwater probabilistic monitoring of confined-aquifer wells in 2012 provided a detection rate of $\sim$ 2%. Probabilistic monitoring of unconfined-aquifer wells in 2012 and 2014 provided detection rates of 18% and 25%, respectively, showing shallow aquifers are particularly vulnerable to contamination by emerging contaminants. The pharmaceuticals carbamazepine, primidone, and acetaminophen were detected in 14 out of 116 unconfined-aquifer wells (12%) sampled during the 2014 probabilistic survey of unconfined-aquifer wells. Seven of the wells with pharmaceuticals detections (50%) show detections for sucralose. All wells with carbamazepine detections were found to have sucralose detections; conversely, wells showing acetaminophen detections did not show detections of sucralose.

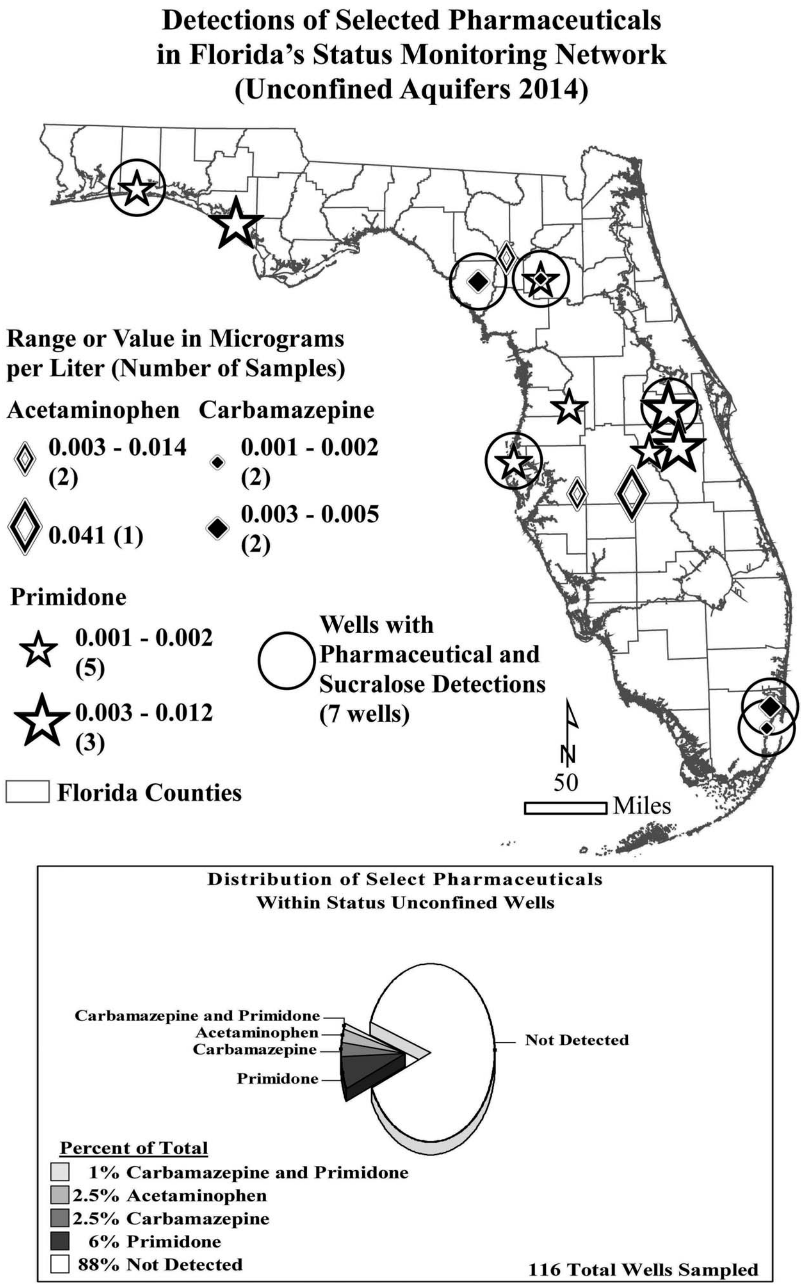


Figure 3. Detections of Selected Pharmaceuticals in Florida's Status Monitoring Network (Unconfined Aquifers 2014).

While the human and ecological effects for low-level detections of the above pharmaceuticals may yet to be documented, those for several of the pesticides recently added to the DEP WMS groundwater monitoring networks are documented. Continued monitoring for emerging contaminant compounds can produce valuable data which may be used by the scientific community to determine human and ecological effects and by water resource managers to protect Florida's surface and groundwater resources.

Florida's groundwater resources are a part of its ecological and environmental heritage and serve as a foundation on which our state's economy rests (Fernald and Purdum 1998). Protecting Florida's groundwater is a paramount responsibility of elected officials in both state and local governments. Because the number and types of various emerging contaminant compounds are expected to grow and the sources and fates for these compounds are not well understood or identified, it is important to remain focused on monitoring efforts for emerging contaminants.

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