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A Synoptic Survey of Select Wastewater-tracer Compounds and the Pesticide Imidacloprid in Florida's Ambient Freshwaters.

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Abstract

Current wastewater treatment technologies do not remove many unregulated hydrophilic compounds and there is growing interest that low levels of these compounds, referred to as emerging contaminants, may impact human health and the environment. A probabilistic-designed monitoring network was employed to infer the extent of Florida's ambient freshwaters containing the wastewater¹ indicators sucralose, acetaminophen, carbamazepine and primidone, and those containing the widely used pesticide imidacloprid. Extent estimates with 95% confidence bounds are provided for canals, rivers, streams, small and large lakes, and unconfined aquifers containing ultra-trace concentrations of these compounds as based on analyses of 2015 sample surveys utilizing 528 sites. Sucralose is estimated to occur in greater than 50 % of the canal, river, stream, and large lake resource extents. The pharmaceuticals acetaminophen, carbamazepine and primidone are most prevalent in rivers, with approximately 30 % of river kilometers estimated to contain at least one of these compounds. Imidacloprid is estimated to occur in 50 % or greater of the canal and river resource extents, and it is the only compound found to exceed published toxicity or environmental effects standards. Geospatial analyses show sucralose detection frequencies within Florida's drainage basins to be significantly related to the percentage of urban land use ($R^2 = 0.36$, $p < 0.001$), and imidacloprid detection frequencies to be significantly related to the percentage of urban and agricultural land use ($R^2 = 0.47$, $p < 0.001$). The extent of the presence of these compounds highlights the need for additional emerging contaminant studies especially those examining effects on aquatic biota.

¹ includes reuse water, septic systems leachate, and wastewater treatment effluent.

(KEY WORDS: ambient water resource; probabilistic monitoring; emerging contaminant; wastewater indicator; imidacloprid.)

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Supplemental Data

All data and R software code used for the analyses presented here can be found in the online version of this article.

Introduction

There is growing interest in the scientific community that unregulated contaminants and their degradants may be causing human health and ecological impacts as low levels of these compounds are increasingly being detected in water resources throughout the world. These contaminants are referred to as emerging contaminants by the United States Environmental Protection Agency (USEPA), their definition follows: “An emerging contaminant (EC) is a chemical or material characterized by a perceived, potential, or real threat to human health or the environment or by a lack of published health standards” (USEPA 2017a). They include food additives, pharmaceuticals, personal care products (PCPs), hormones, pesticides, detergents, plasticizers, flame retardants and polycyclic aromatic hydrocarbons (Barnes et al. 2008; Kolpin et al. 2002; Pal et al. 2010). Some of these

contaminants are being introduced into the aquatic environment through treated wastewaters, as standard wastewater treatment technologies are not optimized to remove many hydrophilic ECs (Petrie et al. 2015). Based on recommendations from an internal EC workgroup (FDEP 2008), the Florida Department of Environmental Protection (FDEP) began developing laboratory methodologies for ultra-trace level analyses of compounds to be used as tracers of wastewater and for pesticides in 2009 (Fitzpatrick et al. 2015; Seal et al. 2016). Compounds include the artificial sweetener sucralose; the pharmaceuticals acetaminophen, carbamazepine, and primidone; and the pesticide imidacloprid. These compounds are hydrophilic and therefore may be highly mobile in the freshwater environment (Bonmatin et al. 2015; Jenner 1989; Wishart 2006).

Wastewater indicators - sucralose

Sucralose is an artificial sweetener which is not effectively metabolized by the human body or removed by wastewater treatment processes (Labare and Alexander 1993; Soh et al. 2011). An unpublished 2011 study of 53 Florida domestic wastewater facility discharges measured detectable levels of sucralose in final effluent samples ranging from 1,000 to 40,000 ng/L (Dave Whiting FDEP, pers. comm.). Sucralose does not occur naturally, has low toxicity, is highly soluble and therefore mobile in water, has low sorption potential to soil and organic matter, has low bioaccumulation potential, persists in the environment with an environmental half-life greater than one year, and is easily detected at a concentration of 10 ng/L (Oppenhiemer et al. 2011; Tollefsen et al. 2012). These properties make sucralose an ideal domestic (treated and untreated) wastewater tracer (Oppenhiemer et al. 2011). Tollefsen et al. (2012) presented an environmental risk assessment of sucralose based on a review of available presence, fate, and environmental effects data. The review provided data showing that sucralose concentrations typical of those found in the environment should be benign. The assessment produced a no effect concentration on aquatic organisms of 930,000 ng/L. The review does note that several authors present behavioral and other non-traditional responses in aquatic organisms at lower concentrations but that relevance for assessing adverse effects on individuals and populations will require further investigation.

Wastewater indicators - pharmaceuticals (acetaminophen, carbamazepine, primidone)

The pharmaceuticals in this study have different uses; acetaminophen is an analgesic, while carbamazepine and primidone are anti-convulsant drugs. These pharmaceuticals have relatively short environmental half-lives, days as opposed to over a year for sucralose (Bu et al. 2016; Grice and Goldsmith 2000). Acetaminophen is effectively

removed by standard wastewater treatment; whereas carbamazepine and primidone are not (Drewes et al. 2002; Kostich et al. 2014; Rounds et al. 2009). Detections of acetaminophen provide evidence of untreated or poorly treated human wastewater. Kim et al. (2007) reported on the aquatic toxicity and potential ecological risks of the four most abundantly used pharmaceuticals in Korea: acetaminophen, carbamazepine, cimetidine, and diltiazem. They tested the aquatic toxicity of these compounds on a marine bacterium (*Vibrio fischeri*), a freshwater invertebrate (*Daphnia magna*), and the Japanese medaka fish (*Oryzias latipes*). Median lethal concentrations for the four chemicals were found to be relatively high, needing to be in the mg/L range. Additionally, they report predicted no effect concentrations (PNECs) of 9,200 ng/L for acetaminophen and 31,600 ng/L for carbamazepine.

The neonicotinoid insecticide imidacloprid

Imidacloprid is a neonicotinoid insecticide and, as of 2008, globally was the most applied agricultural insecticide by weight of active ingredient (Simon-Delso et al. 2015). It is used extensively in agricultural settings to protect seeds, plants and livestock and in urban settings for home, lawn, garden and pet protection. Annual agricultural use estimates in the United States increased from approximately 113,398 kg in the early 2000s to 340,194 kg in 2008, to 725,748 kg in 2010, and to 907,185 kg in 2014 (U.S. Geological Survey 2014). Imidacloprid is highly water soluble and has an environmental half-life that ranges from weeks to months; however, it does degrade relatively quickly through photolysis (Bonmatin et al. 2015). Imidacloprid is not effectively removed by standard wastewater treatment (Sadaria et al. 2016).

A review of the environmental risks posed by neonicotinoid pesticides (Goulson 2013) reports toxicity for target and non-target species. Imidacloprid concentrations that killed half of the test organisms (lethal concentration 50% = LC₅₀) were provided for aquatic insect and crustacean species. These ranged from 650 to 44,000 ng/L for individual insect species and from 7,100 to 361,000 ng/L for individual crustacean species. The author reported sub-lethal effects usually can be detected at 1/10th of the LC₅₀. Aquatic insects are more sensitive to exposure than other classes of aquatic arthropods or other aquatic phyla, and, in particular, Ephemeropterans (mayflies) are highly sensitive (Anderson et al. 2015; Morrissey et al. 2015). Doses 1 to 2 orders of magnitude lower than those producing lethal effects on aquatic insects have been shown to impair mobility and produce ataxia (inability to coordinate voluntary movements) in Ephemeropterans. These impairments are ecologically relevant since the organisms cannot feed or avoid predation. Morrissey et al. 2015 recommended ecological thresholds for water concentrations be below

200 ng/L and 35 ng/L for acute and chronic toxicity in their review of acute and chronic toxicity of 49 species of aquatic insects and arthropods.

Concerning terrestrial arthropods, a meta-analysis of 44 field and laboratory studies for the effect of neonicotinoids on 5 performance measures (abundance, behavior, condition, reproductive success, and survival) of non-target arthropods conducted by Main et al. 2018 concluded that all performance measures were negatively affected with arthropod behavior and survival the most negatively affected and abundance the least negatively affected. Hladik et al. 2018 report pollinators and aquatic insects appearing to be especially susceptible to chronic sublethal effects from exposure. Sublethal doses have been demonstrated to adversely impact pollinator behavior, fecundity, growth and longevity (Pisa et al. 2017). Nowell et al. 2018 used aquatic-life benchmarks and the Pesticide Toxicity Index (Munn et al. 2006, Nowell et al. 2014) to predict toxicity due to mixtures of dissolved pesticides, including imidacloprid, in Midwestern United States streams. Concerning community level effects, they report a significant inverse relationship between imidacloprid concentration and invertebrate community metrics (macroinvertebrate index, Ephemeroptera, Plecoptera and Trichoptera (EPT) abundance; EPT richness) found in 100 streams. They also conducted a mesocosm experiment indicating that a ten-day exposure of imidacloprid was toxic to EPT taxa at concentrations between 1,000 - 3,300 ng/L and to one Ephemeropteran taxon (*Baetis tricaudatus*) at concentrations as low as 60 ng/L. Due to this growing body of scientific evidence, the USEPA recommend lowering the imidacloprid aquatic life benchmarks for invertebrates in late 2016 and after public review did so in late 2017 from 34,500 ng/L to 385 ng/L for acute effects and from 1,050 to 10 ng/L for chronic effects (USEPA 2017b). The same review process led to the imidacloprid aquatic life benchmarks for fish being raised from 41,500,000 ng/L to 114,500,000 ng/L for acute effects and from 1,200,000 ng/L to 9,000,000 ng/L for chronic effects.

Objectives

Baseline data and inferential statistics providing estimates on the extent of ambient water resources affected by wastewater compounds and pesticides are lacking at the statewide/national scale. Most studies of ECs are watershed specific and focus on the sources of the contaminants. Examples include those being conducted by the United States Geological Survey (USGS) and published by Bradley et al. (2016, 2017) and Hladik et al. (2015). These USGS studies were based on a targeted monitoring design that selected 34 urban/agricultural-impacted stream

sites and four undeveloped (reference) stream sites dispersed throughout the United States in 24 states and Puerto Rico. Additionally, Batt et al. (2016) conducted a national probability-based survey of pharmaceuticals found in targeted United States rivers which were associated to urban areas. Their study utilized 182 sites sampled for the USEPA 2008 to 2009 National Rivers and Streams Assessment (USEPA 2016).

The FDEP utilized probability-based sample surveys to assess Florida's ambient flowing waters, lakes, and unconfined aquifers for the occurrence of the wastewater indicators sucralose, acetaminophen, carbamazepine and primidone, and the pesticide imidacloprid during 2015. The primary objectives of this study were to 1) determine the extent of Florida's ambient water resources with detectable levels of these compounds; 2) examine the relationship between unconfined aquifer well depth and the frequencies and magnitudes of detection of these compounds; and 3) examine the spatial relationships among the frequencies and magnitudes of detection of these compounds within Florida's 29 drainage basins, which are based on USGS's 8 digit hydrologic unit codes, and the urban and agricultural land use found within them.

Materials and methods

Quality assurance (QA) and quality control (QC)

A program-specific Quality Manual for the FDEP Water Quality Assessment Program Watershed Monitoring Section (FDEP 2016a) serves as the foundation of the Quality Assurance (QA) system used for the Status Monitoring Network. This document incorporates many elements of the program, including a sampling manual and a data management Standard Operating Procedures (SOP) manual. The program-specific Status and Trend Monitoring Networks Sampling Manual (FDEP 2016b) addresses all Status Monitoring sampling activities. The Status Monitoring Network uses Quality Control (QC) measures to assure that data collected meet the standards set forth in the department's SOPs. Some QC measures are required under departmental SOPs (e.g., equipment and/or field blanks), while others are program specific. Samplers collect equipment and/or field blanks, or samples of clean, deionized water, at a 20% frequency rate. This allows staff to monitor the on-site environment, equipment decontamination, container cleaning, suitability of preservatives and analyte-free water, and sample transport and

storage conditions. If analytes of interest are detected in both the blank and associated samples, the associated sample data are qualified per [Florida Administrative Code, Chapter 62-160, Quality Assurance](#).

Sampling design

The FDEP initiated the Status Monitoring Network (SMN) in January 2000 following USEPA monitoring network design guidelines (Copeland et al. 1999). The Spatial Survey Design and Analysis (spsurvey) package of the R statistical programming software is used for SMN sample survey designs and their analysis (Kincaid and Olsen 2012; R Core Team 2014). This methodology utilizes a stratified random approach which ensures monitoring stations are representative of the target resources, spatially balanced, and selection is unbiased. Additionally, the analysis of spatially balanced probabilistic surveys uses a local neighborhood variance estimator that tends to produce smaller confidence limits compared to traditional variance estimates (Stevens and Olsen 2004). Site locations are randomly generated from the geographic extent of each of seven water resources (canals, rivers, streams, small and large lakes, and confined, and unconfined aquifers) statewide based on Geographic Information Systems (GIS) data of those resources. During the annual statewide surveys, FDEP and contracted employees attempt to collect 120 samples statewide from each ground-water resource type, 90 samples from each of the stream, river and small and large lake resources, and 60 samples from canals found in Peninsular and Northeast Florida. Based on these sample sizes, the 95% confidence interval for estimates of annual statewide condition are approximately $\pm 12\%$ for surface water and $\pm 9\%$ for ground water. Factors such as periods of drought or landowner property access denials can reduce the number of stations sampled. For complete design information, refer to the Florida Watershed Monitoring Status and Trend Program Design Document, FDEP 2015a.

Target populations

Confined and Unconfined Aquifers

Florida has three major aquifer systems (Southeastern Geological Society 1986), all of which are sampled: the surficial aquifer system, the intermediate aquifer system, and the Floridan aquifer system. The ground-water resource is subdivided into two target populations for resource characterization: unconfined aquifers and confined aquifers. All three aquifer systems contain portions that are unconfined and confined. The confinement conditions

must be determined prior to sampling. Areas of industrialization and known ground-water contamination are avoided. Site selections are made from a list frame of existing unconfined and confined aquifer wells.

Rivers, Streams, and Canals

Flowing surface waters are divided into rivers, streams, and canals based on size and input from staff of FDEP and Florida's Water Management Districts (WMDs). Initially rivers were identified, and the remaining flowing surface waters were classified as streams or canals. Canals are treated as a separate altered resource because their biota and associated water quality may differ from that found in natural flowing systems (streams and rivers). Segments of impounded rivers, streams, and canals have been removed from their respective resource populations.

Large and Small Lakes

Lakes are subdivided into two populations: small lakes, 4 to less than 10 hectares; and large lakes, 10 hectares and larger. All lakes must include at least 1,000 square meters (m²) of open water, be at least 1-meter deep at the deepest point, and not be in direct contact with or influenced by oceanic waters. The differentiation based on size is intended to accommodate different design methodologies and to allow better representation of the resource types. Artificial lakes, such as agricultural ponds and borrow pits, have been removed from the targeted resource populations.

Sampling periods

Sucralose was added to the analyte lists for all water resources during the 2012 SMN sample surveys. Sucralose, acetaminophen, carbamazepine, primidone, and imidacloprid were included in the following sampling events: February – March 2015 canals, May – June 2015 rivers, July – September 2015 streams, April - May 2015 large lakes, September – October 2015 small lakes, November – December 2015 unconfined aquifers. The confined aquifer resource was not sampled for the wastewater indicators and imidacloprid during the 2015 sample surveys, as sucralose was only found in two of 107 confined wells sampled in the 2012 sample survey of that resource.

Sample collection and analytical methods

Samples were collected in one-liter brown glass bottles and transported on ice to the FDEP laboratory. Once at the laboratory water samples were filtered using a specially dried 0.75 micrometer glass fiber filter from which an

aliquot of 250 milliliters (mL) of filtered sample was passed through a solid phase cartridge consisting of a graphitized carbon-based solid-phase extraction (SPE) column. After extraction, the absorbed analytes were eluted from the SPE cartridge using 15 mL of 4:1 methylene chloride to methanol solution. Each extract was analyzed twice by High Performance Liquid Chromatography/Tandem Mass Spectrometer methods; once in negative ion mode for determination of sucralose and once in positive ion mode for acetaminophen, carbamazepine, primidone, and imidacloprid determinations. The analytical procedure is described in FDEP SOP LC011 (Reddy 2017). The FDEP laboratory determines a detection limit through the following process (Fitzpatrick et al. 2015). Staff prepare a minimum of seven laboratory-fortified blanks 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 laboratory blank level.

Data analysis methods

Structured query language (SQL) scripts were used to identify numbers of detections and non-detections, and the values of detections for sucralose, acetaminophen, carbamazepine, primidone, and imidacloprid per sample site. For this study, detections include those results which were between the MDL and the PQL ($MDL \leq \text{result} \leq PQL$). An R script, utilizing the Spatial Survey Design and Analysis (spsurvey) R package (Kincaid and Olsen 2016), was developed and used to determine the extent of each water resource having detectable amounts of sucralose, any of the three pharmaceuticals (acetaminophen, carbamazepine, primidone), any of the four wastewater indicators, and of imidacloprid. For determining the extent of waters with detectable levels of wastewater indicators, sites were grouped into four categories; sites with no detections, sites with only sucralose detections, sites with only pharmaceutical detections, and sites with detections of any of the four wastewater indicators. Data from two unconfined aquifer wells and one stream site were excluded from probabilistic analysis because their sampling violated the selection protocols for the SMN; however, the data from these sites are included in the summaries of detected values.

For the unconfined-aquifer resource we examined the effect of depth on the occurrence and the magnitude of any detected values of sucralose, any of the three pharmaceuticals, and of imidacloprid by categorizing the sampled wells into two depth categories of approximately equal size. The depths of sampled wells ranged from 2.7 meters to 100.6 meters deep, with only five greater than 60 meters deep. The well depth categories were comprised of wells

less than 12.5 meters deep (58 wells) and those greater than 12.5 meters deep (60 wells). To determine if compound detections were more frequent in shallow wells contingency tables were developed containing numbers of compound detections and non-detections for both well depth categories. Fisher's exact test was used, in lieu of Pearson's Chi-squared test, to determine statistical significance because of the small sample size ($n < 5$) found in some of the contingency table cells (McDonald 2014), with the null hypothesis being no difference between compound detections found in depth categories. The distributions of detected compound values per well depth category were compared visually. Low sample sizes of detected pharmaceuticals and imidacloprid prevented further analysis of these compounds. Because there was sufficient sample size for sucralose, the Mann-Whitney U test was used to determine if the distributions of detected values in the two depth categories differed, with the null hypothesis being no difference between median values found in depth categories. The significance level of all Fisher and Mann-Whitney tests was set at $\alpha = 0.05$.

Areal extent of urban and agricultural land was determined for each of Florida's 29 drainage basins by using a GIS layer created from data provided by the five Florida WMDs using the land use and land cover system developed by the Florida Department of Transportation (FDOT 1999). The FDOT land use and land cover system provides eight general levels of land use for the state: 1) urban and built-up, 2) agriculture, 3) rangeland, 4) upland forest, 5) water, 6) wetlands, 7) barren land, and 8) transportation/communication/utilities. For this study, 1) urban and built-up and 8) transportation/communication/utilities categories were combined and collectively referred to as urban. The period of record for the land use data is: Northwest Florida WMD 2012-2013, Suwannee River WMD 2013-2014, St. John's River WMD 2009, Southwest Florida WMD 2011, and South Florida WMD 2004-2005 and 2008-2009.

Geospatial relationships between compound occurrence and range of values and urban and agricultural land use within each of the 29 drainage basins were examined by pooling sites from all water resources to increase sample size. R software's micromap package (Payton et al. 2015), which allows one to view both statistical and geographic distributions of the data, was used to examine regional spatial distributions of sites with percent compound detections per basin. The size of the basins in hectares range from 104,703 (Perdido) to 2,147,948 (Suwannee) with the median size being 489,158 (Upper St. Johns). The Florida Keys basin was not sampled for any

water resource, and the remaining basins had between 3 and 77 sites sampled with a median value of 13 sites per basin (Tab. 1, Fig. 1).

To measure spatial autocorrelation among the variables the Spatial Dependence (spdep) R package (Bivand et al. 2008) was used to calculate the nearest neighbor rook weights for the 28 basins having sites and then Moran's Index (Moran 1950) tests were run for all dependent variables. Weighted Ordinary Least Square (OLS) linear regression models were developed to examine the relationship between percent of sites per basin having sucralose, pharmaceutical and imidacloprid detections to percent urban and agricultural land use per basin. Site density (sites per basin / area of basin) was used as a weighting factor due to the unequal number of sites per basin. The Global Validation of Linear Models Assumptions (gvlma) R package (Pena and Slate 2006) was used to validate all models. The significance level for all geospatial statistical tests was set at $\alpha = 0.05$.

Results

Quality assurance quality control findings

One hundred six QA/QC blanks were collected during this study: 12 canal field blanks, 18 stream field blanks, 18 river field blanks, 16 small lake field blanks, 18 large lake field blanks, and 14 field and 10 equipment unconfined aquifer well blanks. None of these blanks were found to contain detections for any of the five compounds examined. Concerning laboratory reporting limits, the MDLs reported by the FDEP laboratory were: 10 ng/L for sucralose, 2.0 and 4.0 ng/L for acetaminophen, 0.40 and 2.0 ng/L for carbamazepine, 4.0 and 8.0 ng/L for primidone, and 2.0 and 10 ng/L for imidacloprid. The reporting limits were reduced in May 2015 for all compounds except sucralose. Therefore, because of their respective sampling periods, rivers, streams, small lakes, and unconfined aquifers had lower reporting limits than those reported for canals and large lakes for the three pharmaceuticals and imidacloprid.

Summaries of detected values

Status Monitoring Network sampling in 2015 resulted in 528 sites being sampled: 60 canal sites, 90 stream sites, 90 river sites, 90 large lake sites, 78 small lake sites, 120 unconfined-aquifer wells (Fig. 1). Sucralose was detected in all water resources and found at 292/528 sites. The sucralose values ranged from 12 I² ng/L to 27,000

ng/L (Tab. 2, Fig. 2, Fig. 3) with 91 of the detections being between the MDL and PQL. At least one of the pharmaceuticals was detected at 90/528 sites (Tab. 3, Fig. 2, Fig. 3). Of the 292 sites having detections of sucralose, 202 did not show detections for any of the pharmaceuticals, while 89 did. One small stream site provided a non-detection for sucralose and a detection of a pharmaceutical (acetaminophen at 5.8 I ng/L). Acetaminophen was only found at 9 flowing water sites and ranged in value from 2.0 I ng/L to 11 ng/L with just one of the detections being between the MDL and PQL. Carbamazepine was detected at 82 sites representing all water resources and ranged in value from 0.44 I ng/L to 68 ng/L, with 22 values quantified. Primidone was detected at 11 sites representing all water resources, except for streams, and ranged in value from 5.8 I ng/L to 88 ng/L, with 2 values between the MDL and PQL. Concerning the pesticide imidacloprid, of the 528 sites sampled in the 2015 survey, there were detections at 208 sites (Tab. 4, Fig. 4). Values for the detections ranged from 2.1 I ng/L to 520 ng/L. Of these values 103 were between the MDL and PQL and the highest values came from flowing waters.

Extent estimates of 2015 sample surveys

Estimates of extent of water resources having detectable amounts of sucralose, pharmaceuticals, or imidacloprid are provided along with their 95% confidence bounds in Table 5. Given streams produced the only site found to have a pharmaceutical detection and a non-detection for sucralose (the site mentioned earlier having acetaminophen at 5.8 I ng/L), we have not included these results in Table 5. The 95% confidence bounds for streams expected to have this type of stand-alone detection is 0 – 3.4%. Figure 5 provides comparisons of extent of water resource affected by compound/compound group along with the number of detected values. For sucralose, the large-

² I = value not quantifiable by analysis method, between the MDL and PQL.

lake resource produced the largest extent estimate and smallest confidence interval of the six water resources sampled, while rivers produced the second highest extent estimate, yet have the highest sucralose detection rate and a larger confidence interval than large lakes. Rivers produced the highest extent estimates of waters expected to contain any of the pharmaceuticals or of imidacloprid.

Geospatial analysis - correlations with well depth

There were more detections of the pharmaceuticals in the shallow wells (6 in wells < 12.5 m vs. 2 in wells > 12.5 m) and the median values of detections for all three compound groups were higher in the shallow well category (sucralose 140 vs 96 ng/L, pharmaceuticals 8.6 vs. 1.6 ng/L, imidacloprid 86 vs 23 ng/L) (Tab. 6); however, no statistically significant differences were found between shallow and deep wells. The low number of pharmaceutical and imidacloprid detections presented problems with statistical test selection and an associated reduction of power for valid statistical tests. All Fisher's exact tests run to determine if proportions of wells with detections differ between well depth categories were insignificant. The low number of pharmaceutical and imidacloprid detections prevented the validity of any statistical test for the determination of differences between detected value distributions found in the two well depth categories. While the Mann-Whitney U test was used to test for differences in the distributions of sucralose detected values found in the two well groups, the result was insignificant.

Geospatial analysis – correlations with land-use activities among drainage basins

To investigate relationships between occurrence and magnitude of compounds detected in the 29 drainage basins and land use, the basins were ordered by percentage of sites with compound detections, and by median compound values, and the R package micromap was used to produce graphics (micromaps) for visual inspection. The panels in the micromaps show percentage of sites having detections, box plots of log $\mu\text{g/L}$ range of values, the total number of sites sampled, and percent urban and agricultural land use. Percentages of sites with sucralose and pharmaceutical detections per basin were compared to urban land use percentage (Figs. 6a, 6b) and sucralose's log $\mu\text{g/L}$ range of values were compared to carbamazepine log $\mu\text{g/L}$ range of values and to urban land use percentage per basin (Fig. 6c). Percentages of sites having imidacloprid detections were compared to percentage urban and percentage agricultural land use separately (Fig. 7a), and then with both land uses combined into a single panel with an additional panel providing box plots of the log $\mu\text{g/L}$ range of values (Fig. 7b). A scatterplot of percentage of sites

having imidacloprid detections by percentage of combined urban and agricultural land use was also prepared (Fig. 8).

Weighted OLS linear regression models were developed using percentage of sites having compound detections as dependent variables, the two land use categories as independent variables, and site density (number of sites per square kilometer of basin) as the weights. Moran's Index (Moran 1950) tests using nearest rook neighbors found no significant spatial autocorrelation for any of the dependent variables, which was visually confirmed by the lack of geographic patterning in the micromaps as neighboring basins did not show similar values of detection in the response variables. Additionally, the results from the weighted OLS regression models showed no evidence of spatial autocorrelation in the residuals in the series of models analyzed based on the Global Moran's I for regression residuals from the *spdep* R package (Bivand et al. 2008). All remaining model assumptions were evaluated and then validated via the *gvlma* R package (Pena and Slate 2006). The initial *gvlma* run on the sucralose model produced failures for skewness and heteroscedasticity. A scatter plot identified the Upper East Coast basin as a spatial outlier; therefore, it was removed from the OLS model and all model assumptions were then met.

Simple linear regression modeling provided significant results for relating the percentage of sites with sucralose detections per basin to percent of urban land use ($R^2 = 0.36$, $p < 0.001$) (Tab. 7). Whereas, the pharmaceuticals did not show a significant relationship between percentage of sites with detections per basin and percent urban land use ($R^2 = 0.07$, $p = 0.19$) (Tab. 7). Simple linear regression modeling of percentage of sites with imidacloprid detections per basin based on percent agricultural and urban land use show significant results for percent agricultural land use ($R^2 = 0.20$, $p = 0.017$) but not for percent urban land use ($R^2 = 0.13$, $p = 0.059$) (Tab. 8). A multiple linear regression model was developed for relating percent of sites with imidacloprid detections per basin to percent agricultural and percent urban land use. Collinearity of urban and agricultural land uses between basins was found to be insignificant by the Spearman's Rho test ($Rho = -0.1291735$, $p\text{-value} = 0.5108$). All remaining model assumptions were evaluated and then validated via the *gvlma* R package (Pena and Slate, 2006). The results of the regression indicate a significant direct relationship between the numbers of sites having imidacloprid per basin and percentage of agricultural and urban land use within the basin ($R^2 = 0.47$, $p < 0.001$) (Tab. 9).

Discussion

Wastewater indicators (sucralose, acetaminophen, carbamazepine, primidone)

Prior FDEP sample surveys reported by Seal et al. (2016) found similar numbers of sucralose detections to those reported here for all water resources. Additionally, for unconfined aquifers, they reported similar pharmaceutical detections, with detections in 14/116 wells sampled during the 2014 SMN unconfined aquifer survey versus the 9/120 detections presented here from the 2015 SMN unconfined aquifer survey. In the present study, while the number of detections found in shallow wells did not differ significantly from the deeper wells, the median values for sucralose, pharmaceuticals, and imidacloprid were all higher for the shallow well category (Tab. 6). These results are not surprising given the geologic composition of Florida's unconfined aquifers and associated karst topography within the state, allowing for relatively high rates of vertical and horizontal groundwater flow.

Ultra-trace level detections of sucralose were found at a large percentage of the SMN sample sites over the three years (2012, 2014, 2015) for which this wastewater indicator was collected. None of these detections were above published predicted no effect or acute toxicity concentrations for aquatic organisms (Seal et al. 2016) (Tab. 10, Fig. 9). While values were generally below what is found in receiving waters from wastewater treatment facilities, three unconfined aquifer wells sampled in 2014 and one river site sampled in 2015 show detections within the range found in domestic wastewater discharges (Labare and Alexander 1993; Soh et al. 2011). Probabilistic analyses show that large proportions (57.0 – 88.9 %) of Florida's canals, streams, and rivers, and large lakes can be expected to have detectable amounts of sucralose. Whereas, moderate proportions of small lakes (42.3 %) and unconfined aquifer wells (30.3 %) can be expected to have detectable amounts of sucralose.

While estimates of the percent of statewide and nationwide water resources having detectable concentrations of sucralose are lacking, studies of individual watersheds provide similar values (Spoelstra et al. 2013). The majority of available field generated occurrence data for sucralose comes from flowing waters. In a study of the occurrence of artificial sweeteners found in the Grand River Watershed in Ontario, Canada, Spoelstra et al. (2013) present the results of a literature review on sucralose concentration data coming from rivers, streams, and lakes. In 14 studies, including their own, the values range from below the method detection limit to 21,000 ng/L. The high value came from their study and at that time they reported the value as the highest concentration reported worldwide coming from a river. Coincidentally, our high value, 27,000 ng/L, also came from a river.

Ultra-trace levels of the three pharmaceuticals were found in low to moderate percentages in all water resource types in our 2015 sample surveys. None of these detections were above published PNECs or acute toxicity concentrations for aquatic organisms (Tab. 10). The highest detected values came from flowing water resources and the extent of waters containing these compounds was highest in rivers and streams. Carbamazepine (with an MDL much lower than the other pharmaceuticals) was found in all water resource types, primidone in all water resources except for small streams, and acetaminophen only in flowing waters for the 2015 sampling period. As noted earlier, acetaminophen was the only pharmaceutical detected at a site showing no detections for sucralose; therefore, the extent of waters expected to contain any of the three pharmaceuticals and not sucralose is very low.

These results are consistent with our understanding of these compounds' chemical properties (allowing three of our four wastewater indicators to travel through standard wastewater treatment processes), the increasing and widespread use of reclaimed water in Florida and elsewhere, and results of recent research. Bradley et al. (2016) report ultra-trace levels of metformin and other pharmaceuticals to be widespread in wadeable headwater streams in the Southeastern United States. Their study utilized the urban-gradient sites from the USGS' Southeast Stream Quality Assessment 2014 (Journey et al. 2015). These sites were selected within 5 urban centers (Atlanta, Charlotte, Greenville-Spartanburg, Raleigh-Durham-Greensboro, and Washington D.C.) and targeted to capture a gradient of urban land use. Fifty-nine wadeable streams were sampled for 108 pharmaceuticals and degradants and they found detections of at least one pharmaceutical, albeit at ultra-trace levels, in all sites. In a national study, Bradley et al. (2017) sampled 38 streams in 24 states and Puerto Rico once for organic contaminants coming from 14 target-organic methods (719 compounds) between November 2012 and June 2014. Their study was a targeted design that compared the results of 34 streams having a wide range of contaminant sources to four streams having fish and macroinvertebrate communities believed to be minimally disturbed by human development (reference sites). They report widespread ultra-trace levels of organic contaminants, with 8 pesticides (desulfinylfipronil, AMPA, chlorpyrifos, dieldrin, metolachlor, atrazine, CIAT, glyphosate) and two pharmaceuticals (caffeine, metformin) as the most frequently detected anthropogenic organics. Additionally, $\log_{10}$ values of galaxolide, triclosan, and carbamazepine were found to explain 71 - 82% of the variability in the total number of compounds detected.

Imidacloprid

Ultra-trace levels of imidacloprid were detected in 39.4% of the Florida ambient freshwater sites tested. Values for the detections ranged from 2.1 I to 520 ng/L (Fig. 9), with the highest value coming from a canal site. Probabilistic analyses show that 25.2 – 64.8 % of the surface water resource categories are expected to have detectable amounts of this pesticide; whereas, 24.7 % of unconfined aquifer wells are expected to have detectable amounts. Three detections (one site in each of the stream, river, and canal resources) were found to be above the USEPA acute pesticide registration benchmark for aquatic invertebrates and an additional 99 detections (5/118 aquifer, 31/89 small stream, 17/90 large river, 17/60 canal, 14/78 small lake, and 15/90 large lake sites) were found to be above the USEPA chronic pesticide registration benchmark for aquatic invertebrates (USEPA, 2017b) (Tab. 10, Fig. 9). FDEP probabilistic surface water sample surveys conducted in 2016 for flowing waters and in 2017 for lakes corroborate the imidacloprid results from this study. These more recent surveys produced two imidacloprid detections (one at a stream the other at a canal site) above the USEPA acute pesticide registration benchmark for aquatic invertebrates and an additional 106 detections (24/90 small stream, 30/90 large river, and 24/60 canal, 17/78 small lake and 11/90 large lake sites) were found to have detections above the USEPA chronic pesticide registration benchmark for aquatic invertebrates.

Some samples had concentrations that have been shown to produce detrimental effects to species of the Ephemeropteran family, Baetidae. For example, Nowell et al. (2018) determined concentrations of 60 ng/L to be chronically toxic to the North American Baetid *Baetis tricaudatus* in a mesocosm study; while Roessink et al. 2013 determined a chronic no-observed effect concentration (NOEC) of 41 ng/L for the European Baetid species *Cloeon dipterum* in the laboratory. While neither *Baetis tricaudatus* or *Cloeon dipterum* are found in Florida, this family of mayflies is well represented in the state, with at least 14 species present (Berner and Pescador 1988). Twenty-six (26) of our surface-water resource samples had concentrations of imidacloprid that were greater than 60 ng/L and one half of these came from stream sites (13 of 90 stream sites). Concerning effects on aquatic invertebrate communities, Whitefield-Ashlund et al. (2017) conducted a probabilistic risk assessment to determine potential effects of acute and chronic exposure to imidacloprid. They used data generated from mesocosm, semifield, and field studies to produce cumulative probabilities of exceedance versus the magnitude of community level effect

expressed as percent taxa affected. In doing so they derived chronic NOECs for 15 taxa of aquatic invertebrates with the family Baetidae producing the lowest chronic NOEC, 816 ng/L.

Available statewide and nationwide studies of water resources having detectable amounts of neonicotinoid pesticides tend to focus on the effects of land use within watersheds. Because of this most studies are targeted to focus on individual watersheds having large proportions of agricultural and/or urban lands. In the same national study previously described for Bradley et al. (2017), Hladik et al. (2015) report imidacloprid as the most frequently detected neonicotinoid with a 37% detection rate and a high value of 140 ng/L. In the Midwestern United States where neonicotinoid pesticide usage is widespread in association with agricultural activities Nowell et al. (2018) found imidacloprid to be the most frequently detected insecticide in a regional study utilizing 100 streams (50 randomly selected and 50 selected for agricultural and urban land use) sampled weekly May – August 2013, with 89 of the 100 stream sites having at least one detection and a high value of 2,154.9 ng/L. Imidacloprid, in addition to two other neonicotinoid insecticides (clothianidin, thiamethoxam), has been found in finished drinking water in the Midwestern United States (Klarich et al. 2017).

The FDEP, in cooperation with the Florida Department of Agriculture and Consumer Services (FDACS), collects samples for pesticides, including neonicotinoids during annual sampling of watersheds having water quality criteria failures for nutrients, copper, and aquatic biology metrics. During 2016 sampling, imidacloprid was detected in 37 of 75 water samples at values ranging from 4.9 to 1,400 ng/L (Brian Katz FDEP, pers. comm.). Beginning in November 2015, analysis suites of organo-nitrogen and phosphorous pesticides were added to the seven SMN water resource sample surveys. Unconfined aquifers were sampled in 2015, flowing waters in 2016, and lakes in 2017. The results will provide the FDEP a better understanding of the extent of detectable amounts of pesticides in Florida's freshwaters.

Geospatial relationships

Pooling all water resource sites to examine geospatial relationships between basins was a confounding factor in our analyses. Regardless, results from this study complement other published studies examining the occurrence and magnitude of detected values for these compounds and land use activities (Bradley et al. 2016; Hladik et al. 2015; Spoelstra et al. 2013). Sucralose provided a moderate positive correlation ($R^2 = 0.36$, $p < 0.001$) between percentages of sites having detectable sucralose and urban land use per basin. Given the chemical properties of

sucralose, most notably its relatively long half-life, hydrophilic nature, and relatively high usage rates, this is not surprising. Concerning the one basin, Upper East Coast, determined to be a spatial outlier for the relationship between sucralose detection frequency and urban land use, one possible explanation for this determination is that this basin may have a proportionately higher percentage of wastewater treatment facility outfalls directed into marine waters. This may also be the case for the Southeast Coast – Biscayne Bay basin, which ranks second in percentage of urban land of all basins, yet only ranked 21/28 for sucralose detection frequency. Five basins had median sucralose values greater than 100 ng/l, Charlotte Harbor (495), Tampa Bay (260), Middle St. Johns (195), Lake Worth Lagoon – Palm Beach Coast (120), and Tampa Bay Tributaries (110). Charlotte Harbor also had the highest median carbamazepine value (4.8 ng/L); while Tampa Bay Tributaries had the highest max value for combined pharmaceuticals (156 ng/L). These five basins rank as follows for urban land use percentage per basin: Charlotte Harbor 16/28, Tampa Bay 3/28, Middle St. Johns 7/28, Lake Worth Lagoon – Palm Beach Coast 1/28, and Tampa Bay Tributaries 2/28. For the pharmaceuticals, a very weak, insignificant positive relationship ($R^2 = 0.07$, $p = 0.19$) was found among percentage of sites having detections given urban land use coverage per basin. Perhaps an explanation for this insignificant result is that given the shorter half-lives of the pharmaceuticals they are less likely to travel very far from their sources. Therefore, the extent of water resource affected within any one basin may be limited.

Imidacloprid provides the strongest correlations with land use. The multiple regression using urban and agricultural land use as predictor variables shows a significant positive relationship ($R^2 = 0.47$, $p < 0.001$) between percentage of sites having detections of this neonicotinoid pesticide within basins and these land use categories. Imidacloprid's longer half-life, in comparison to the half-lives of the pharmaceuticals, and its high application rates in both agricultural and urban areas, are likely reasons for this strong correlation. Concerning the magnitude of imidacloprid values found in urban versus agricultural areas, visual examination of our imidacloprid detected values per basin, by use of linked micromaps, indicates that basins with proportionately more urban land use are no more likely to have higher median and maximum imidacloprid values than those with proportionately higher agricultural land use (Fig. 7). The highest median values were found in the following basins, Tampa Bay (16 ng/L), Caloosahatchee (14 ng/L), Indian River Lagoon (7 ng/L), Sarasota Bay – Peace – Myakka (6.35 ng/), and Springs Coast (6.25 ng/L). Of these five basins, Tampa Bay, Indian River Lagoon, and Springs Coast had more urban land coverage than agricultural, while Sarasota Bay – Peace – Myakka and Caloosahatchee had more agricultural land

coverage. This contrasts with results from Nowell et al.'s (2018) study of 100 Midwestern United States streams showing imidacloprid concentrations were significantly higher at urban sites than at agricultural sites (median values 52.2 and 8.8 ng/L respectively), and that maximum concentrations were directly related to the percentage of urban land within drainage basins, inversely related to percentage of cropland, and not related to agricultural pesticide use intensity. The differences between our results and Nowell et al.'s may be attributed to the localized nature of imidacloprid application and the study designs themselves, as our design did not directly assign a land use value to each site, but instead assigned one value for all sites within a basin. Each method has its own scientific merit, ours is focused toward determination of waters with detectable amounts, theirs towards determination of biological effects.

Conclusions

Sample survey results providing estimates for Florida's six surface-water resource types show that moderate to large proportions of Florida's surface waters are expected to contain ultra-trace concentrations of the wastewater tracer sucralose and low to moderate proportions of the examined pharmaceuticals (acetaminophen, carbamazepine, and primidone). Sucralose is found to be most prevalent in large lakes, with 88.9% of large lake area expected to contain ultra-trace concentrations, and least prevalent in small lakes, with 42.3 % of small lake area expected to contain this compound. The pharmaceuticals are most prevalent in rivers, with 30.9 % river kilometers expected to contain at least one of the three compounds, and least prevalent in large lakes, with 8.9 % of large lake area expected to contain at least one of them. Imidacloprid is estimated to be found in moderate to large proportions of Florida's surface waters. Imidacloprid is found to be most prevalent in rivers, with 64.8 % of river kilometers expected to contain ultra-trace concentrations, and least prevalent in small lakes, with 25.2 % of small lake area expected to contain this compound. These compounds are making their way into Florida's ground waters with estimates of unconfined aquifer wells containing these compounds at 30.9 % for sucralose, 24.7 % for imidacloprid, and 6.9 % for any of the pharmaceuticals. For the unconfined aquifer resource, compared to deeper wells, shallow wells provided more detections of the pharmaceuticals and had higher median values of the three compound groups (sucralose, pharmaceuticals, imidacloprid); however, no statistically significant differences were found between the two well categories. Pooling of sites from all water resource types (n = 528) for geospatial analysis shows detection frequency of sucralose and imidacloprid are significantly related to the percentage of urban land use, and to the percentage of urban and agricultural land use within basins, respectively; sucralose positively correlated with urban

land use ($R^2 = 0.36$, $p < 0.001$) and imidacloprid positively correlated with urban and agricultural land use ($R^2 = 0.47$, $p < 0.001$). While none of the studied pharmaceuticals or sucralose were found to exceed any published human health standards or no observed effects concentrations for aquatic organisms, 26 of 408 surface-water sites produced imidacloprid concentrations that have been shown to impact mayfly species of the family Baetidae; 13 of these coming from the 90 stream sites sampled. The extent of these compounds' presence highlights the need for additional emerging contaminant studies especially those examining effects on the aquatic biota.

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Drainage Basin	Id	Area (hectares)	Sample Size	% Urban	% Agriculture
Everglades West Coast	1	967,109	20	8.12	16.25
Lake Okeechobee	2	264,161	13	3.12	23.63
Ochlockonee - St. Marks	3	658,362	10	9.90	3.88
Ocklawaha	4	621,329	25	20.82	16.53
Suwannee	5	2,147,948	77	7.22	12.35
Tampa Bay	6	242,079	11	35.86	5.10
Apalachicola - Chipola	7	860,180	16	4.09	9.06
Charlotte Harbor	8	229,702	3	17.23	2.46
Lower St. Johns	9	731,251	20	21.22	7.41
Middle St. Johns	10	527,449	24	23.58	9.19
St. Lucie - Loxahatchee	11	396,492	33	17.93	40.23
Tampa Bay Tributaries	12	435,594	14	40.14	24.14
Caloosahatchee	13	356,722	13	18.91	43.38
Choctawhatchee - St. Andrew	14	1,023,566	28	9.05	6.15
Lake Worth Lagoon - Palm Beach Coast	15	228,413	20	46.71	8.46
Sarasota Bay - Peace - Myakka	16	879,448	40	24.29	33.19
Upper St. Johns	17	489,158	9	8.57	37.70
Fisheating Creek	18	219,880	9	1.67	65.59
Kissimmee River	19	759,833	63	22.25	33.42
Nassau - St. Marys	20	379,912	12	7.92	4.29
Pensacola	21	695,758	21	12.17	8.70
Southeast Coast - Biscayne Bay	22	456,531	10	41.35	6.69
Withlacoochee	23	645,700	11	22.42	27.14
Everglades	24	1,033,487	6	0.68	19.06
Florida Keys	25	644,921	0	1.34	0.00
Indian River Lagoon	26	365,064	4	16.44	5.75
Perdido	27	104,703	5	18.29	10.05
Springs Coast	28	415,130	8	28.67	5.73
Upper East Coast	29	254,494	3	20.45	1.97

Table 1. FDEP drainage basins with sample size and urban and agricultural land use percentages.

Resource	Sites Having Sucralose Detections	Total Sites Sampled	Percent Detected	Sucralose Concentration Range (ng/L)	Sites Having Quantified Values
Canal	35	60	58.3	14 I ^a – 1,700	25
Stream	53	90	60	12 I – 960	28
River	72	90	80	17 I – 27,000	54
Large lake	68	90	75.5	12 I – 1,400	53
Small lake	35	78	44.8	14 I – 1,400	20
Unconfined aquifers	28	120	23.3	12 I – 3,700	17
All Resources	292	528	55.3	12 I – 27,000	197

Table 2. Sucralose Detections in the Status Monitoring Network (2015). Number and percentage of sites having detections, range of detected values, and number of sites having quantifiable values for each water resource and for all resources. ^a I = value not quantifiable by the analysis method.

Resource	Acetaminophen Sites Having Detections	Acetaminophen Range (ng/L)	Carbamazepine Sites Having Detections	Carbamazepine Range (ng/L)	Primidone Sites Having Detections	Primidone Range (ng/L)
Canal	1 (1.7%)	3.1 I ^a	7 (11.7%)	2.5 I – 24	2 (3.3%)	12 I – 26
Stream	5 (5.6%)	2.0 I – 5.8 I	23 (25.6%)	0.44 I – 22	0	na ^b
River	3 (3.3%)	2.1 I – 11	25 (27.8%)	0.42 I – 68	3 (3.3%)	8.4 I – 88
Large lake	0	na	11 (12.2%)	2.2 I – 19	2 (2.2%)	5.8 I – 6.1
Small lake	0	na	7 (9.0%)	0.49 I – 2.9	1 (1.3%)	30 I
Unconfined aquifers	0	na	9 (7.5%)	0.7 I – 9.2	3 (2.5%)	9.7 I – 21 I
All Resources	9 (1.7%)	2.0 I – 11	82 (15.5%)	0.42 I – 68	11 (2.1%)	5.8 I – 88
Quantified Values	1 (< 0.5%)	11	22 (4.2%)	2 – 68	2 (0.4%)	26 – 88

Table 3. Pharmaceutical Detections in the Status Monitoring Network (2015). Number and percentage of sites having detections, and range of detected values for each of the pharmaceuticals for each water resource and for all water resources, and the number sites having quantified values for each pharmaceutical for all resources. ^a I = value not quantifiable by the analysis method. ^b na = not applicable.

Resource	Sites Having Imidacloprid Detections	Total Sites	Percent Detected	Imidacloprid Concentration Range (ng/L)	Sites Having Quantified Values
Canal	36	60	60	2.1 I ^a – 520	19
Stream	47	90	52.2	2.2 I – 390	32
River	63	90	70	2.2 I – 480	19
Large lake	33	90	36.7	2.1 I – 200	15
Small lake	23	78	29.5	4.1 I – 300	13
Unconfined aquifers	6	120	5	4 I – 150	5
All Resources	208	528	39.4	2.1 I – 520	103

Table 4. Imidacloprid Detections in the Status Monitoring Network (2015). Number and percentage of sites having detections, range of detected values, and number of sites having quantifiable values for each water resource and for all resources. ^a I = value not quantifiable by the analysis method.

Water Resource (n)	Size ^a	Sucralose Estimate ± 95% CB ^b	Pharmas Estimate ± 95% CB	Imidacloprid Estimate ± 95% CB
Canals (60)	4,066	44.8 - 57.0 - 69.2	3.65 - 10.7 - 17.89	38.2 - 50.3 - 62.4
Streams (89)	26,175.1	46.5 - 58.7 - 70.9	13.95 - 24.86 - 33.11	27.9 - 36.9 - 45.9
Rivers (90)	4,308.3	64.6 - 74.1 - 83.6	21.51 - 30.86 - 40.20	54.7 - 64.8 - 74.8
Large Lakes (90)	408,378.3	83.1 - 88.9 - 94.7	2.50 - 8.41 - 14.32	14.4 - 33.6 - 52.8
Small Lakes (78)	9,521.5	28.6 - 42.3 - 56.0	2.00 - 11.56 - 21.12	12.6 - 25.2 - 37.9
Unconfined Wells (118)	15,559	17.5 - 30.3 - 43.2	0.00 - 6.90 - 14.05	11.1 - 24.7 - 38.4

Table 5. Estimated percentage of each statewide water resource having detectable amounts of sucralose, any of the pharmaceuticals (acetaminophen, carbamazepine, or primidone), and imidacloprid. Calculated using probabilistic monitoring design. ^a = Units are as follows: canals, streams, and rivers = kilometers; lakes = hectares, unconfined aquifers = number of wells. ^b = Confidence bounds.

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

Table 6. Comparison of detections and median values of detected compounds by well depth category (wells < 12.5 meters deep & wells > 12.5 meters deep).

Sucralose by Urban Land Use Model Summary

Multiple R-Squared	Adjusted R-Squared	Residual Standard Error	F-statistic	df1	df2	p-value
0.3608	0.3352	0.08307	14.11	1	25	0.0009238

Summary of Model Coefficients

Model Parameter	Coefficient	Estimated Standard Error	t-value	p-value
(Intercept)	44.2837	5.0967	8.689	5.05e-09
Percent Urban Land Use	0.7856	0.2091	3.756	0.000924

Pharmaceuticals by Urban Land Use Model Summary

Multiple R-Squared	Adjusted R-Squared	Residual Standard Error	F-statistic	df1	df2	p-value
0.06505	0.02909	0.06949	1.809	1	26	0.1903

Summary of Model Coefficients

Model Parameter	Coefficient	Estimated Standard Error	t-value	p-value
(Intercept)	12.9138	4.2555	3.035	0.00541
Percent Urban Land Use	0.2353	0.1749	1.345	0.19026

Table 7. Summaries of OLS linear regression models for sucralose and pharmaceuticals.

Imidacloprid by Urban Land Use Model Summary

Multiple R-Squared	Adjusted R-Squared	Akaike's Information Criterion	Residual Standard Error	F-statistic	df1	df2	p-value
0.1302	0.09676	266.2385	0.1396	3.892	1	26	0.05922

Summary of Model Coefficients

Model Parameter	Coefficient	Estimated Standard Error	t-value	p-value
(Intercept)	27.4689	8.5490	3.213	0.00349
Percent Urban Land Use	0.6933	0.3514	1.973	0.05922

Imidacloprid by Agricultural Land Use Model Summary

Multiple R-Squared	Adjusted R-Squared	Akaike's Information Criterion	Residual Standard Error	F-statistic	df1	df2	p-value
0.1999	0.1691	263.9016	0.1339	6.494	1	26	0.01707

Summary of Model Coefficients

Model Parameter	Coefficient	Estimated Standard Error	t-value	p-value
(Intercept)	27.7568	7.0029	3.964	0.000514
Agricultural Land Use	0.2353	0.1749	1.345	0.01707

Table 8. Summaries of OLS linear regression models for Imidacloprid.

Imidacloprid by Urban and Agricultural Land Use Multiple Regression Model Summary

Multiple R-Squared	Adjusted R-Squared	Akaike's Information Criterion	Residual Standard Error	F-statistic	df1	df2	p-value
0.4751	0.4332	254.0948	0.1106	11.32	2	25	0.0003166

Summary of Model Coefficients

Model Parameter	Coefficient	Estimated Standard Error	t-value	p-value
(Intercept)	0.4761	9.4980	0.0500	0.960419
Percent Agricultural Land Use	0.9439	0.2329	4.053	0.000432
Percent Urban Land Use	1.0600	0.2927	3.621	0.001301

Table 9. Summary of OLS multiple linear regression model relating percentage of sites expected to have detections of imidacloprid per drainage basin to agricultural and urban land use.

Compound	Half-life Water	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	10 ng/L	USEPA 2017b

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

Table 10. Compounds' half-lives and predicted no effect concentrations (PNEC) for aquatic invertebrates followed by imidacloprid's pesticide registration 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>).

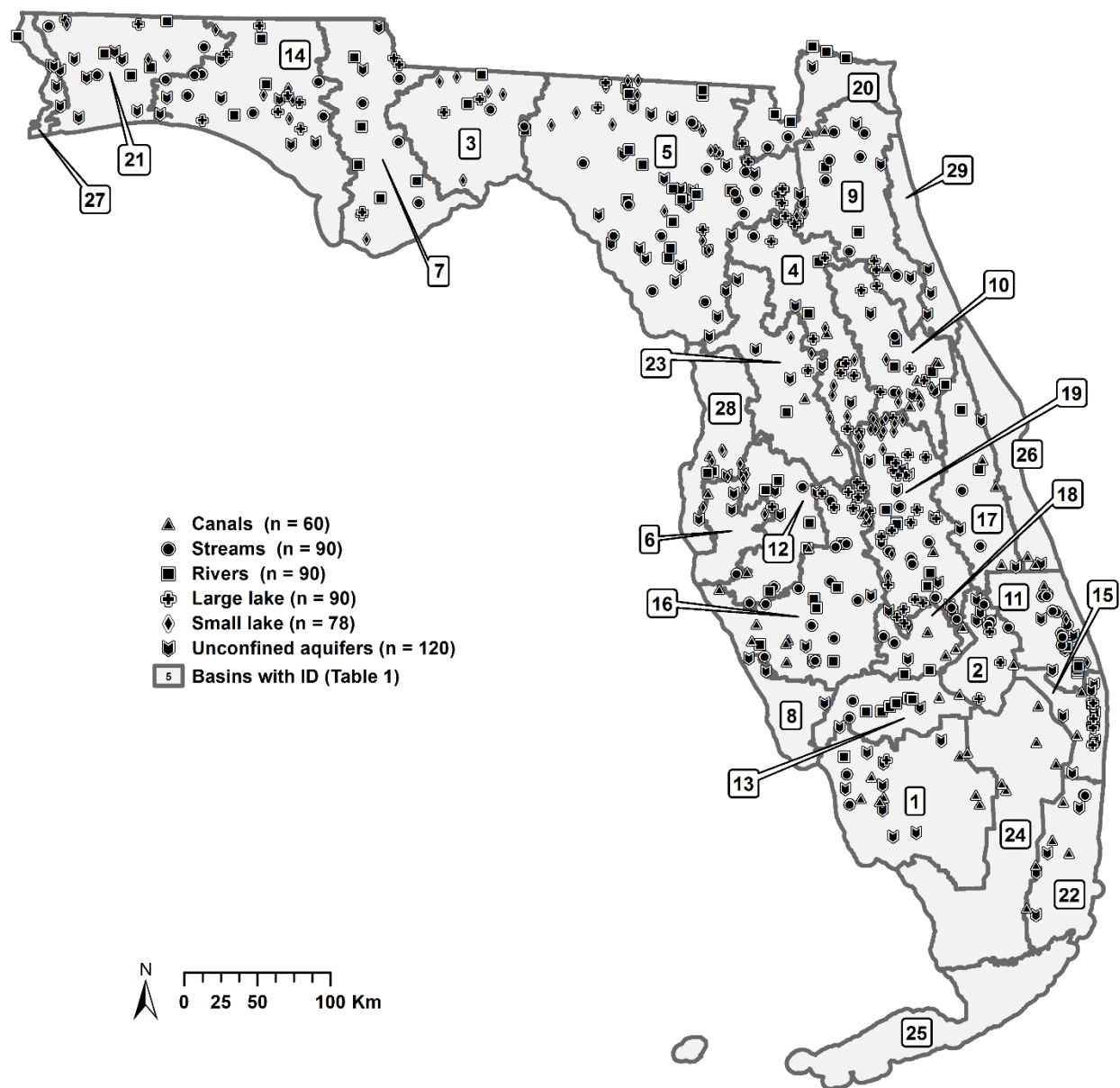


Fig. 1. Map of FDEP drainage basins with status monitoring locations sampled during 2015 (n = 528) symbolized by water resource type.

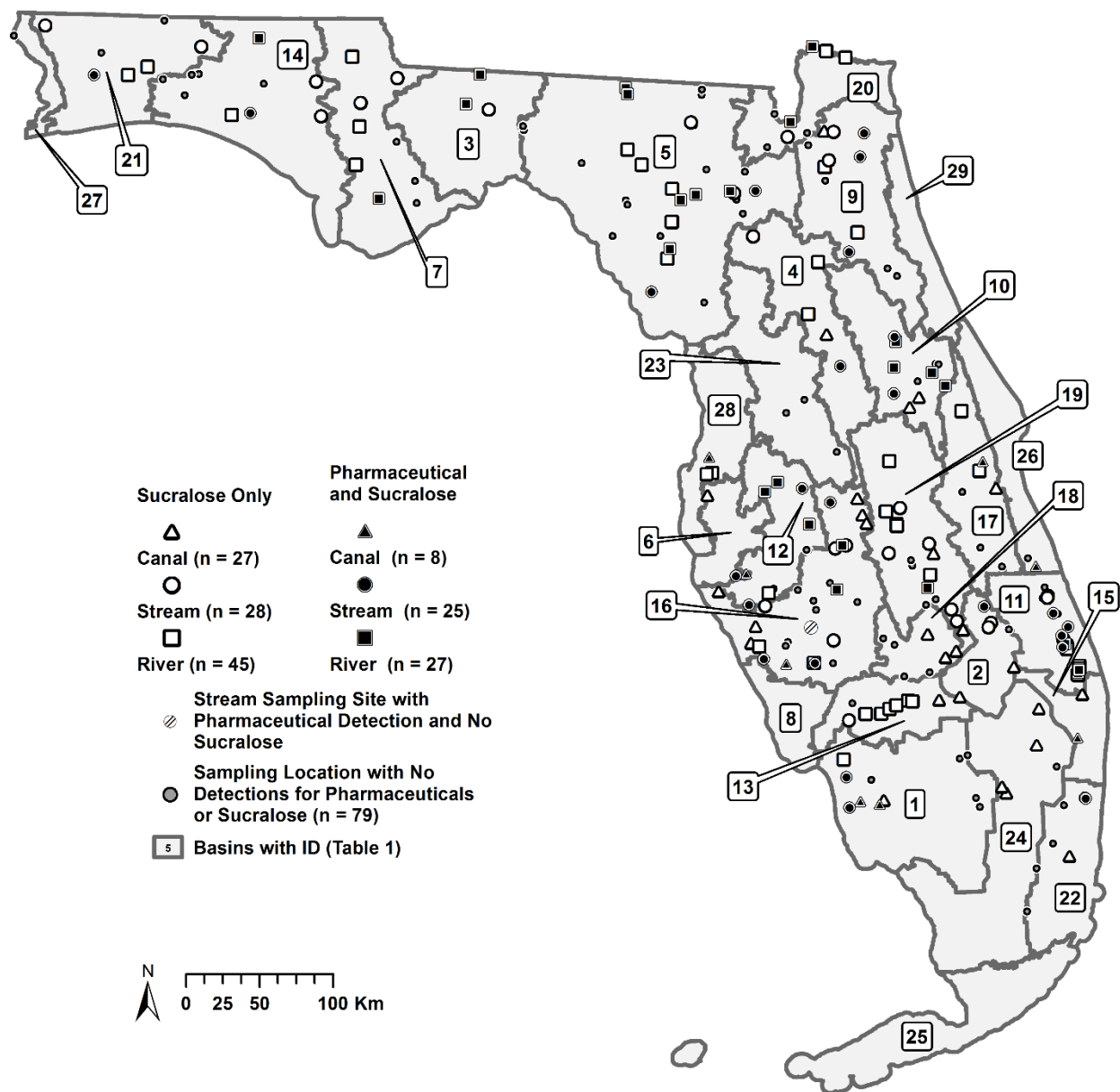


Fig. 2. Map of FDEP drainage basins with status monitoring network flowing waters 2015 sample locations (n = 240) symbolized by water resource type and wastewater indicator non-detections / detections.

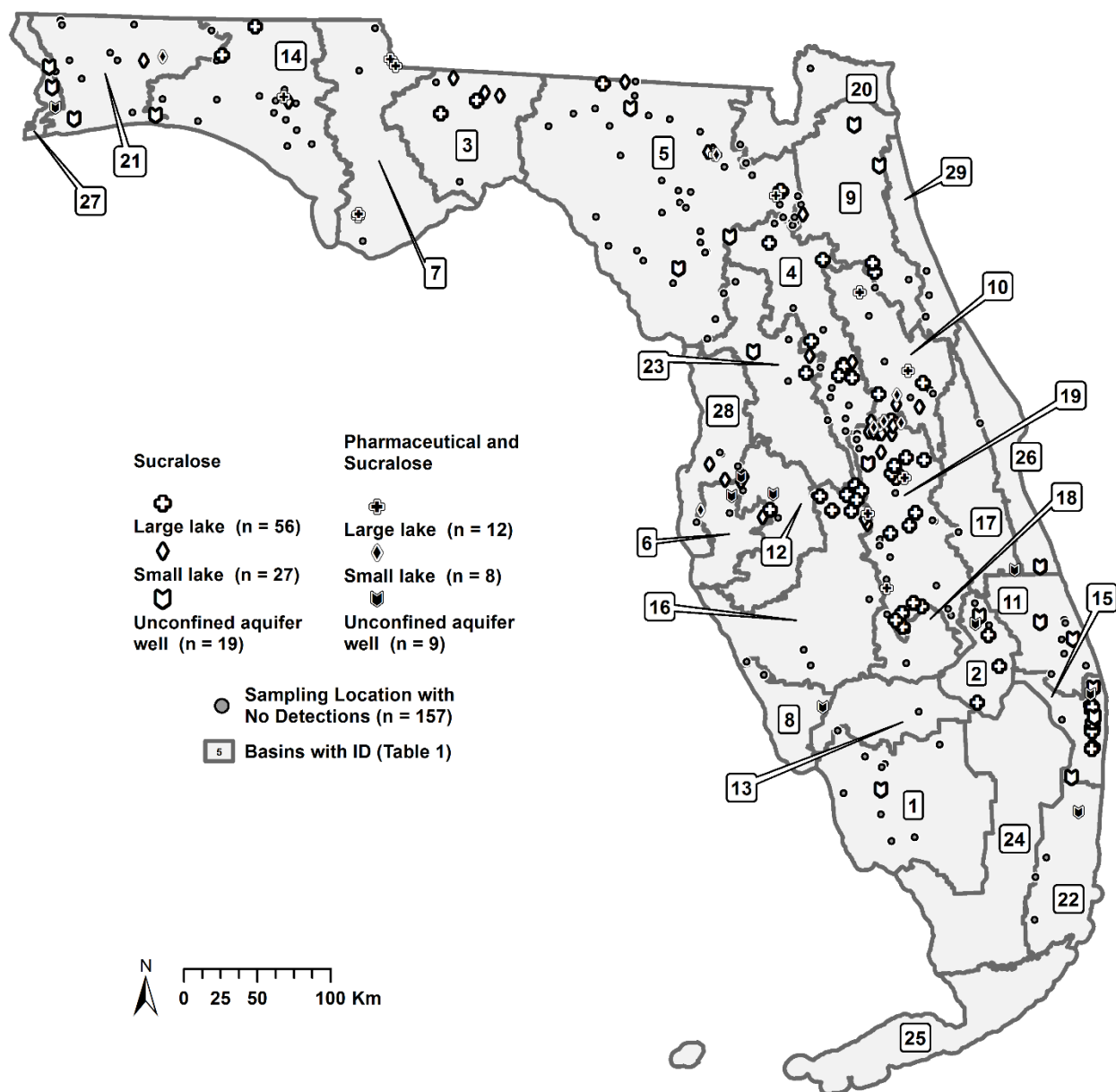


Fig. 3. Map of FDEP drainage basins with status monitoring network lakes and unconfined wells 2015 sample locations (n = 168 and 120 respectively) symbolized for wastewater indicator non-detections / detections.

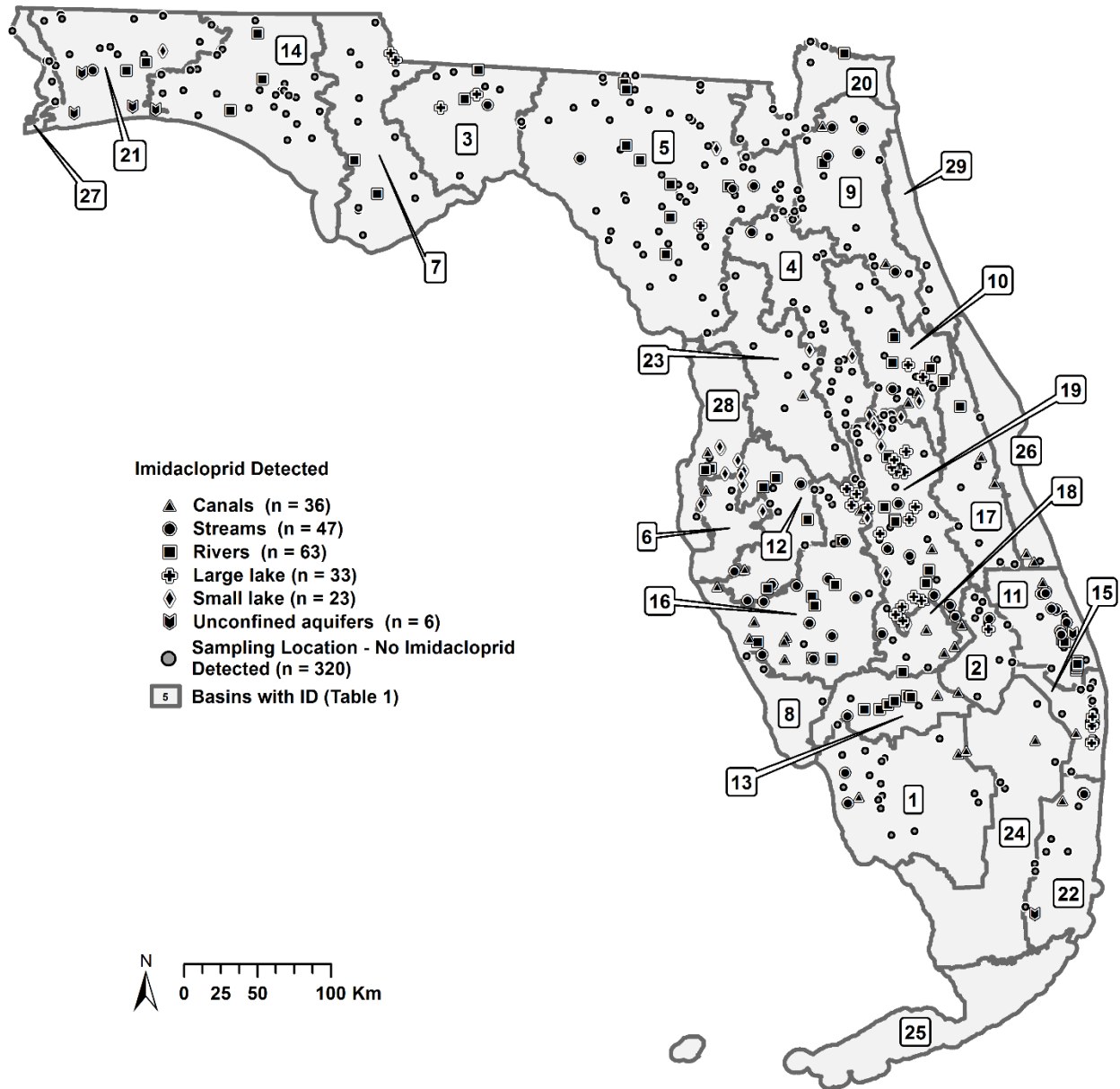


Fig. 4. Map of FDEP drainage basins with status monitoring locations sampled during 2015 (n=528) symbolized by water resource and imidacloprid non-detections / detections.

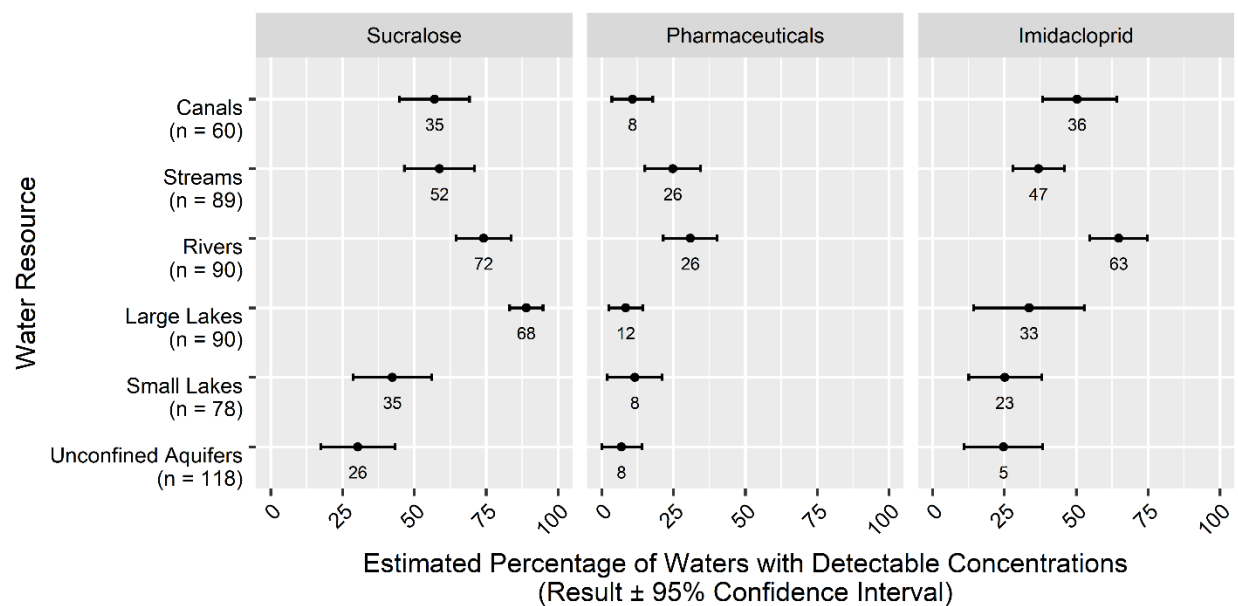
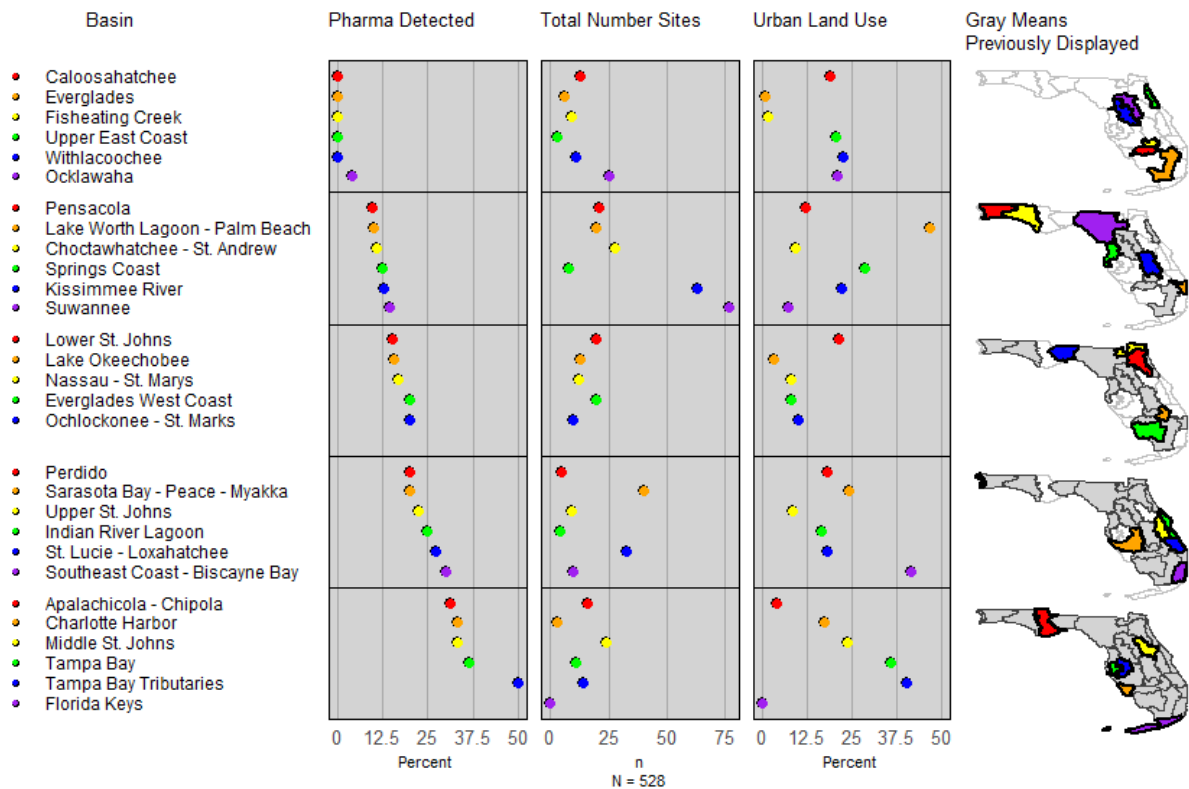
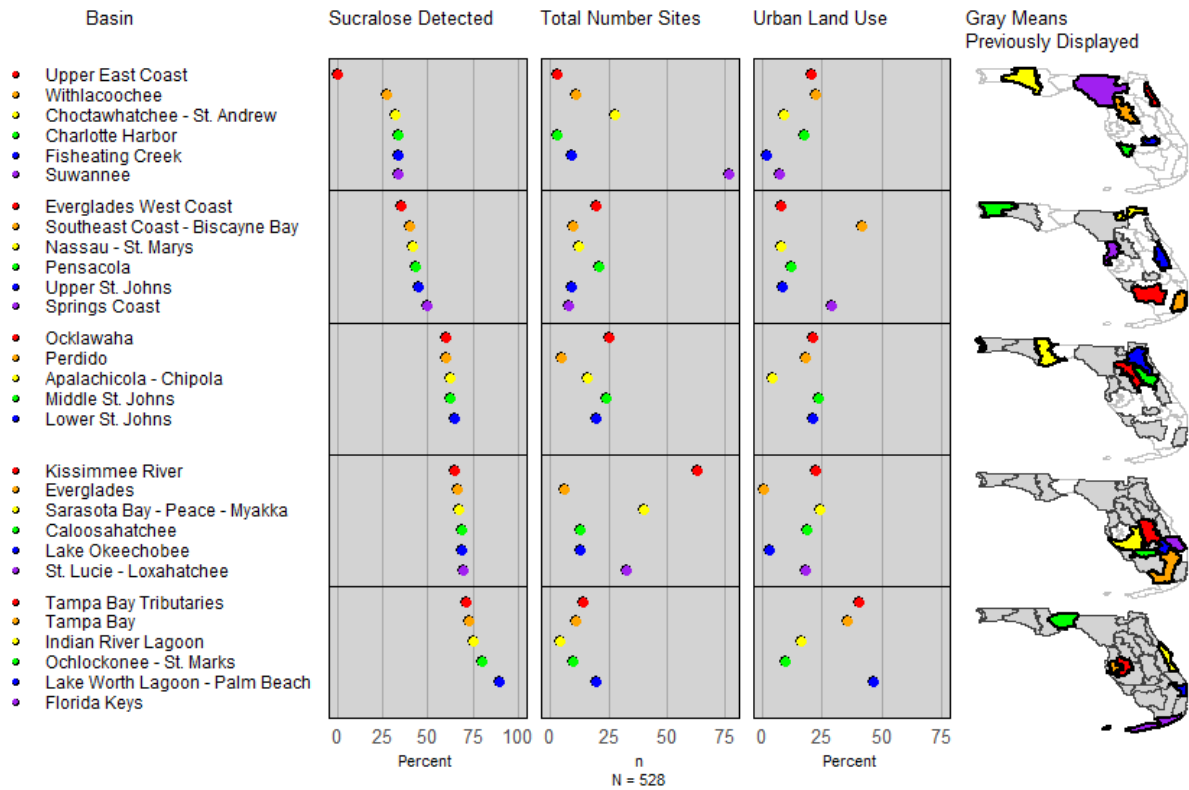


Fig. 5. Percentages of water resources expected to have detectable amounts of sucralose, pharmaceuticals, and imidacloprid. Dots represents estimates, whiskers are the 95% confidence bounds, n = total number of sites per resource, with number of detections per water resource / compound pair provided as inset.



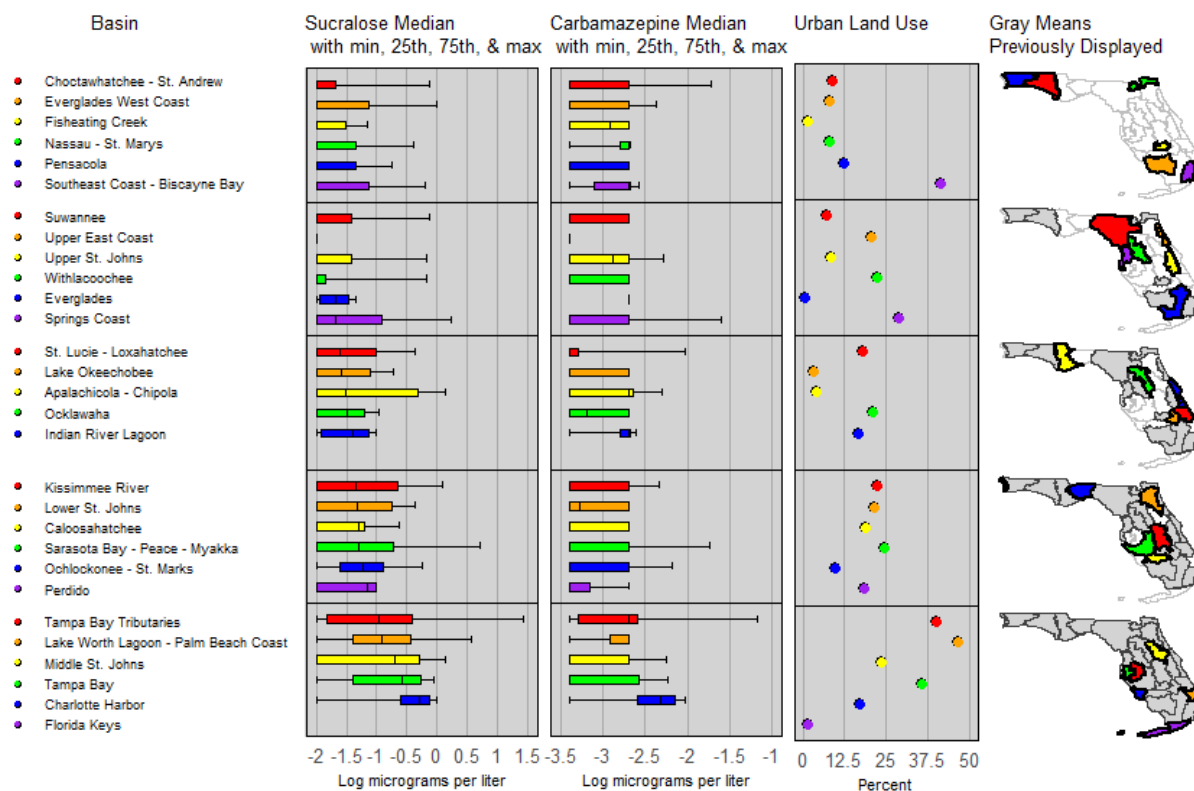


Fig. 6. (A, B, & C) Linked micromaps of percentage of sites within FDEP drainage basins having detections for (A) sucralose, total number of sites, percent urban land use, and (B) any pharmaceutical, total number of sites, percent urban land use, and (C) for range of sucralose and the most frequently detected pharmaceutical, carbamazepine values. The incremental gray shading of basins indicates which basins appeared in the previous grouping within each map.

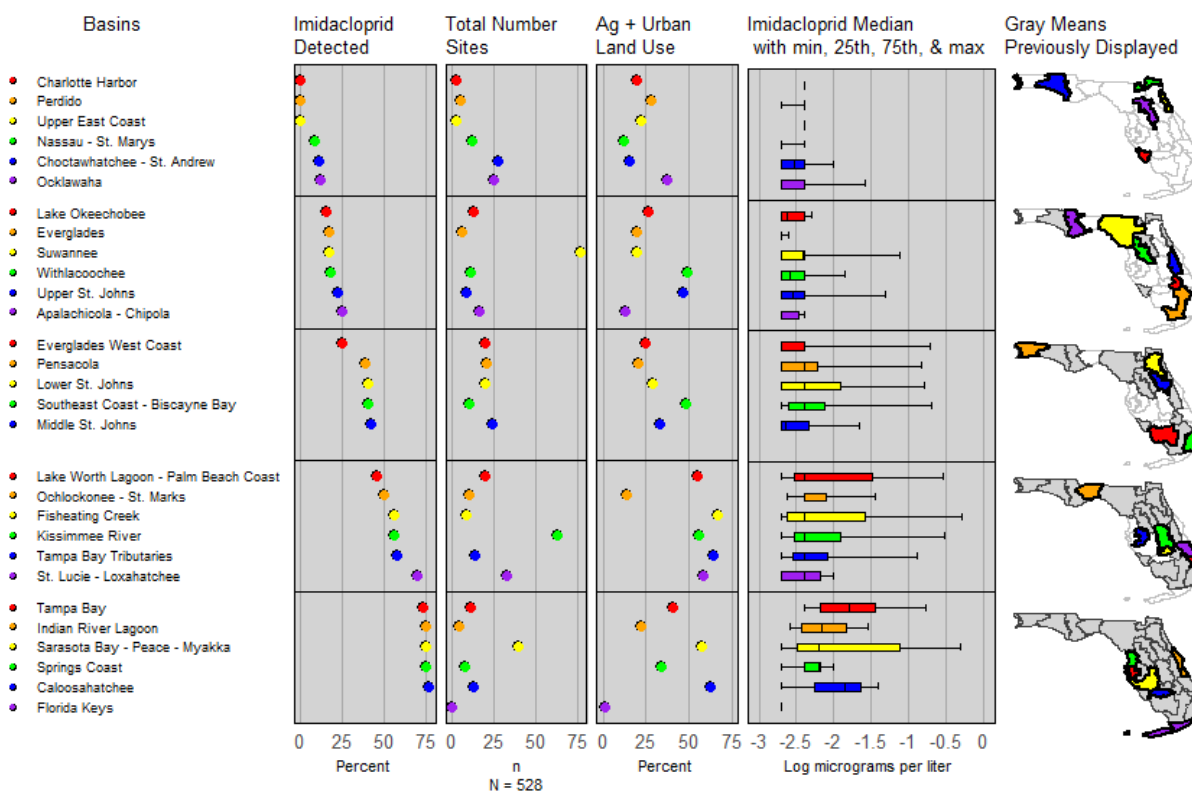
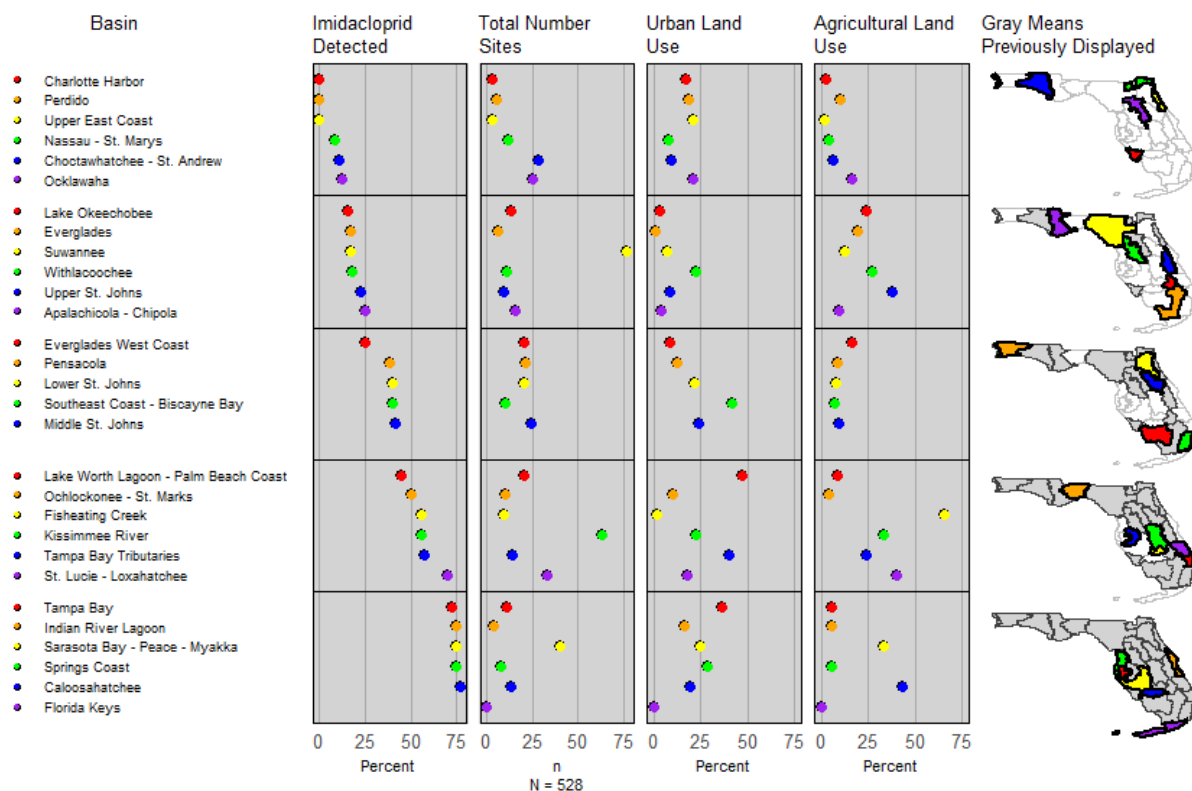


Fig. 7. (A&B) Linked micromap of FDEP drainage basins having detections for imidacloprid with, (A) total number of sites, percent urban and agricultural land use, (B) total number of sites, percentage of urban and agricultural land, median value (log $\mu\text{g/L}$) with upper and lower quartiles and minimum and maximum values (log $\mu\text{g/L}$). The incremental gray shading of basins indicates which basins appeared in the previous grouping within each map.

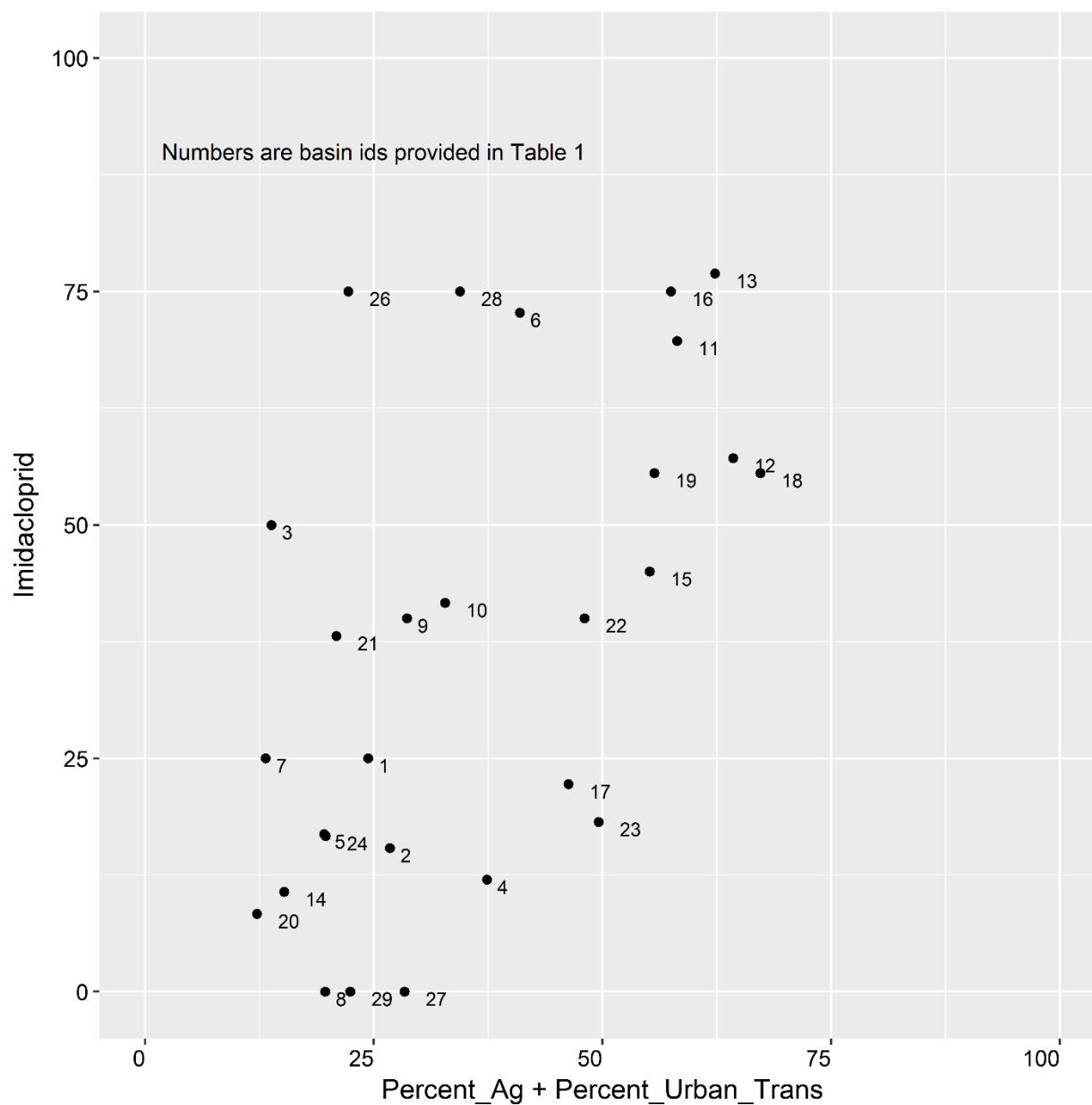


Fig. 8. Scatter plot of number of imidacloprid detections per FDEP drainage basin versus percentage of urban and agricultural land use within basin. Point labels within plot are basin identifiers given in Table 1.

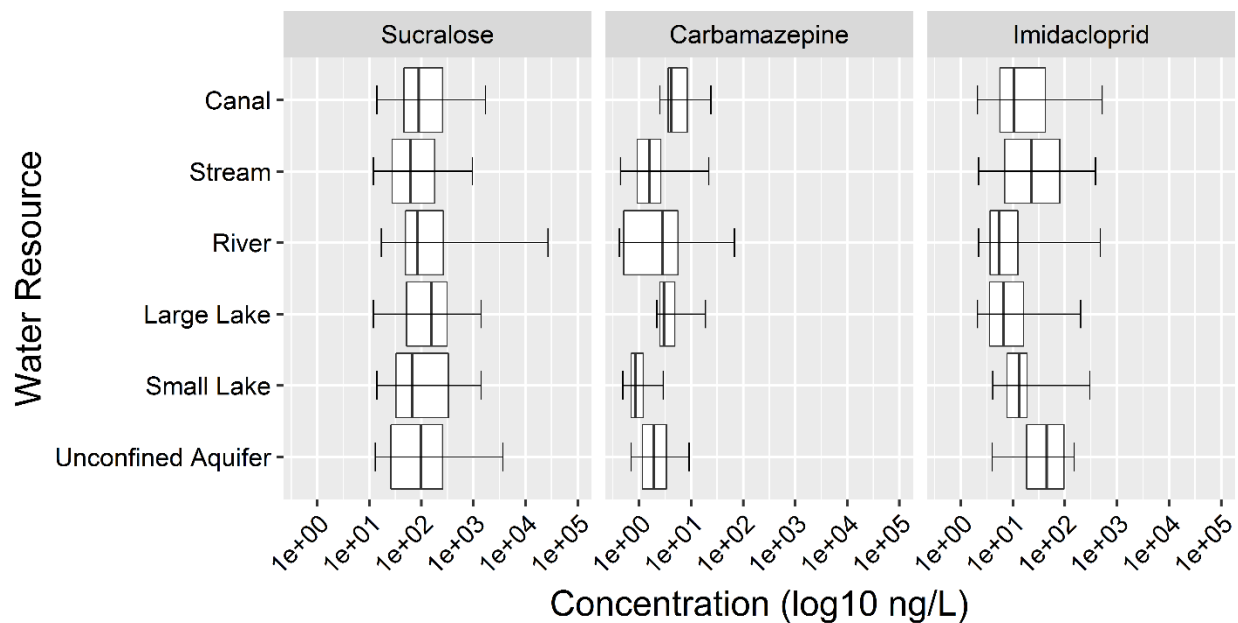


Fig. 9. Concentrations of detected values of sucralose, carbamazepine and imidacloprid by water resource. Boxplots represent 25th to 75th percentiles with imbedded median represented by vertical black line, whiskers represent minimum and maximum detected values.