



Regional extent, environmental relevance, and spatiotemporal variability of neonicotinoid insecticides detected in Florida's ambient flowing waters

James Silvanima · Stephanie Sunderman-Barnes · Rick Copeland · Andy Woeber · Elizabeth Miller

Received: 19 October 2021 / Accepted: 28 March 2022 / Published online: 10 May 2022
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Abstract The use of imidacloprid and, to a lesser degree, other neonicotinoid insecticides is widespread in FL (and globally). The moderate to high water solubility and environmental persistence of neonicotinoids allows these compounds to readily enter, and be retained in, water resources where they may harm nontarget organisms and impact biological communities and associated trophic structures negatively. To better understand imidacloprid's chronic long-term exposure potential to aquatic invertebrate communities in FL, grab water samples were collected monthly in 2015 at 77 monitoring stations statewide. Fifty-eight stations (75%), representing 24 of the 25 drainage basins sampled, had detectable concentrations of imidacloprid, with concentrations ranging from 2 to 660 nanograms per liter [ng/L]. Imidacloprid basin medians were found to be correlated with two of six land use categories (urban, transportation, agriculture, and three crop classes) examined; urban ($\rho=0.43$, p -value=0.03), and orchards and vineyards ($\rho=0.49$, p -value=0.01). The resampling of

12 select stations, representing eight basins, between August 2019 and July 2020, for the neonicotinoids acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam, showed that (1) median values of imidacloprid continued to exceed the US EPA chronic freshwater Invertebrate Aquatic Life Benchmark (IALB) (10 ng/L), (2) imidacloprid concentration was directly correlated with flow measurements, and (3) while median imidacloprid concentration decreased between the two sampling events (48.5 vs. 34.5 ng/L, p -value=0.01) differences in event 1 and 2 stream-flow regimes and disruptions due to the COVID-19 pandemic likely affected this outcome. Clothianidin was the only other neonicotinoid found to have values greater than a US EPA IALB, with detections at three stations exceeding the chronic IALB (50 ng/L). This study highlights the challenges associated with limiting neonicotinoids from entering water resources and identifies means to reduce their entry into and persistence within FL water resources.

Keywords Imidacloprid · Neonicotinoids · Environmental effects · Spatiotemporal variability

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10661-022-10000-3>.

J. Silvanima (✉) · S. Sunderman-Barnes · R. Copeland · A. Woeber · E. Miller
Florida Department of Environmental Protection, Division of Environmental Assessment and Restoration, 2600 Blair Stone Rd, Tallahassee, FL 32399-2400, USA
e-mail: James.Silvanima@dep.state.fl.us

Introduction

Neonicotinoid insecticides were introduced to the pesticide market in the mid-1990s and are now the most widely used class of insecticides in the world. The reasons for this dominance and the benefits of

their use are well documented in several review articles, including Borsuah et al., 2020; Simon-Delso et al., 2015; van Lexmond et al., 2015. They are predominant because they exhibit physicochemical properties that make them more useful than other classes of insecticides (Simon-Delso et al., 2015). These properties allow for a wide range of uses, including plant protection, urban pest control, and veterinary applications, and for a multitude of application techniques, including irrigation mixtures, sprays, coatings, soil drenching, stem and trunk injections, and topical applications for pets and livestock. While numbers on the relative use of these compounds are difficult to obtain, in North America, the largest use of these insecticides appears to be seed applications for row crops (Douglas & Tooker, 2015; Simon-Delso et al., 2015; Tooker et al., 2017). Imidacloprid, the first neonicotinoid to be developed, was approved for use in the USA in 1994 (Borsuah et al., 2020). As of 2008, it was the most applied agricultural insecticide by weight of active ingredient globally (Simon-Delso et al., 2015).

Neonicotinoids disrupt neural transmission in the central nervous system by binding to nicotinic acetylcholine receptors (Seifert, 2014). Due to differences in the number and structure of these receptors found between and within phyla, these pesticides are much more toxic to invertebrates compared with vertebrates and are particularly toxic to insects (Tomizawa & Casida, 2005). There is international concern that these compounds are harming nontarget organisms, including soil microbes, aquatic invertebrates, and insect pollinators, and that these effects may be impacting biological communities and their associated trophic structures negatively. Reviews by Hladik et al. (2018), van der Sluijs et al. (2015), and Wood and Goulson (2017) provide a synopsis of the

environmental risks and challenges associated with the continued use of neonicotinoid insecticides. Neonicotinoids have moderate-to-high water solubility and soil-leaching potentials and have environmental half-lives of weeks to months in water and months to years in soils (Bonmatin et al., 2015). These characteristics allow them to enter, be transported by, and be retained in water resources. The US Environmental Protection Agency (EPA) has developed individual freshwater Invertebrate Aquatic Life Benchmarks (IALBs) for acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam (US EPA, 2017a) (Table 1). Additionally, due to the potential for synergistic effects, Morrissey et al. (2015) have developed recommended freshwater aquatic invertebrate ecological thresholds for combined neonicotinoid concentrations (Table 1).

Many studies have documented that neonicotinoids are commonly detected in the flowing waters in the USA and Canada and that the potential for aquatic invertebrate toxicity is high (Bradley et al., 2017, 2019; Hladik & Kolpin, 2015; Metcalfe et al., 2019; Millemann et al. 2020; Nowell et al., 2021; Sandstrom et al. 2021; Silvanima et al., 2018). The occurrence and magnitude of imidacloprid detected values in freshwaters have been shown to be significantly correlated with the extent of urban and agricultural land uses in watersheds (Hladik & Kolpin, 2015; Silvanima et al., 2018) because of the multifaceted use of this insecticide to control insect pests. At the regional scale, examinations of the spatiotemporal variation in the concentrations of neonicotinoid insecticides found in inland waters have focused mainly on agricultural inputs associated with growing and/or wet/dry seasons (Cavallaro et al., 2019; Chen et al., 2019; Main et al., 2014; Metcalf et al. 2019; Sheedy et al., 2019). Spatiotemporal variation studies for neonicotinoids,

Table 1 Freshwater neonicotinoid invertebrate aquatic life benchmarks in ng/L per US EPA (2017a) and Morrissey et al. (2015)

Bench mark	Acetamiprid ^a	Clothianidin ^a	Dinotefuran ^{1*}	Imidacloprid ^a	Thiamethoxam ^a	Sum neonicotinoids ^b
Acute	10,500	11,000	484,150,000	385	17,500	200
Chronic	2100	50	95,300,000	10	740	35

^aUS EPA (2017a)

^bMorrissey et al. (2015)

*Dinotefuran pesticide review did not include insects, US EPA (2017b)

including multiple seasons and urban inputs at the regional scale, are more difficult to find. Two examples are those provided by Struger et al. (2017) and Hladik, Corsi, et al. (2018).

The Florida Department of Environmental Protection (FDEP) developed analytical methods for the determination of neonicotinoids in water and sediments beginning in 2014 and has incorporated sampling for these compounds in several FL monitoring networks. In 2015, FDEP conducted statewide surface water trend and probabilistic monitoring for imidacloprid. FDEP probabilistic assessments of flowing waters (Silvanima et al., 2018) show imidacloprid detection rates and ranges of reported values for canals, rivers, and streams (Table 2) similar to those reported nationally for streams by Hladik and Kolpin (2015) using comparable method detection limits. FDEP implemented managerial actions concerning neonicotinoids including (1) beginning in 2015, dialog with the Florida Department of Agriculture and Consumer Services (FDACS) and the Florida Fish and Wildlife Commission (FFWC) concerning the aquatic toxicity potential of imidacloprid in context to the ubiquity and persistence of imidacloprid detections recorded in state waters and (2) strategic statewide surface water monitoring beginning in July 2019 for acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam at waterbodies either suspected of, or failing, water quality standards for biologic metrics, nutrients, or bacteria.

Here we examine the potential for neonicotinoids to produce deleterious effects on the aquatic

invertebrate communities found in FL’s 25 flowing freshwater drainage basins. This study presents the findings of (1) monthly statewide FDEP surface water trend (SWT) sampling for imidacloprid during 2015 and the monthly resampling of 12 select SWT stations, representing 8 drainage basins, for acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam during 2019 and 2020 and (2) FDEP strategic monitoring program (SMP) statewide sampling of waterbodies either suspected of, or failing, water quality standards for biologic metrics, nutrients, or bacteria during 2019–2020 for the same five neonicotinoids. The objectives of this study were to (1) for each neonicotinoid compound sampled, determine each station’s and drainage basin’s numerical distribution of detected values and number of IALB exceedances, (2) determine if the imidacloprid median values and number of IALB exceedances for the 12 resampled SWT stations changed significantly between the two time periods, and (3) determine the correlations between the median values of detected neonicotinoids, streamflow, land use, and insecticide use, for determination of future managerial actions.

Materials and methods

Quality assurance (QA) and quality control (QC)

The DEP Quality Assurance Program for Sect. 106 Funded Activities (FDEP, 2021) serves as the foundation of the quality assurance (QA) system used for

Table 2 Imidacloprid detections in the 2015 FDEP status monitoring network (from Silvanima et al., 2018). 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

Resource	Sites having imidacloprid detections	Total sites	Percent detected	Imidacloprid concentration range (ng/L) ^a	Sites having quantified values
Canal	36	60	60	<9–520	19
Stream	47	90	52.2	<9–390	32
River	63	90	70	<9–480	19
Large lake	33	90	36.7	<9–200	15
Small lake	23	78	29.5	<9–300	13
Unconfined aquifers	6	120	5	<9–150	5
All resources	208	528	39.4	<9–520	103

^aValues detected but not quantifiable by the analysis method are reported as <9 ng/L as the maximum quantification limit reported by the laboratory was 8 ng/L

SWT and SMP Monitoring. This document incorporates many elements of the program, including a sampling manual and a data management standard operating procedures (SOP) manual. Sample collection for this study followed the guidance presented in the status and trends monitoring networks sampling manual (FDEP, 2016) for 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. For example, field-generated blanks are collected for the SWT monitoring network at a 20% frequency rate, whereas field-generated blank collection for the SMP follows the departmental guidance of at least a 5% 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.

Monitoring design

The monitoring stations used for the determination of trends in this study comprise the FDEP SWT monitoring network, which was established in 1998 (FDEP, 2015). Stations for the network were selected to provide statewide coverage of flowing freshwaters based on FL's 52 eight-digit USGS hydrologic unit codes (HUCs). Many stations are located at or near existing USGS gauging stations and often are situated at the lower end of a watershed, enabling FDEP to obtain biology, chemistry, and loading data at a point that reflects multiple land use activities in the watershed. Some stations are located at or near the FL boundary with Alabama and Georgia to obtain chemistry and loading data for major streams entering FL. For managerial purposes, FDEP defined 29 drainage basins developed mainly from the aggregation of the state's eight-digit HUCs (Fig. 1). However, there are areas of the state where the basin boundaries do not align with the HUC boundaries. Four of the drainage basins have inadequate non-saline flowing waters to warrant fresh-water monitoring. The monitoring stations used to provide ancillary neonicotinoid data for this study were selected by the SMP. The sampling

methodology for the SMP, along with other ancillary data sources for this paper, are described in Supplementary information (SI) Sect. 4.

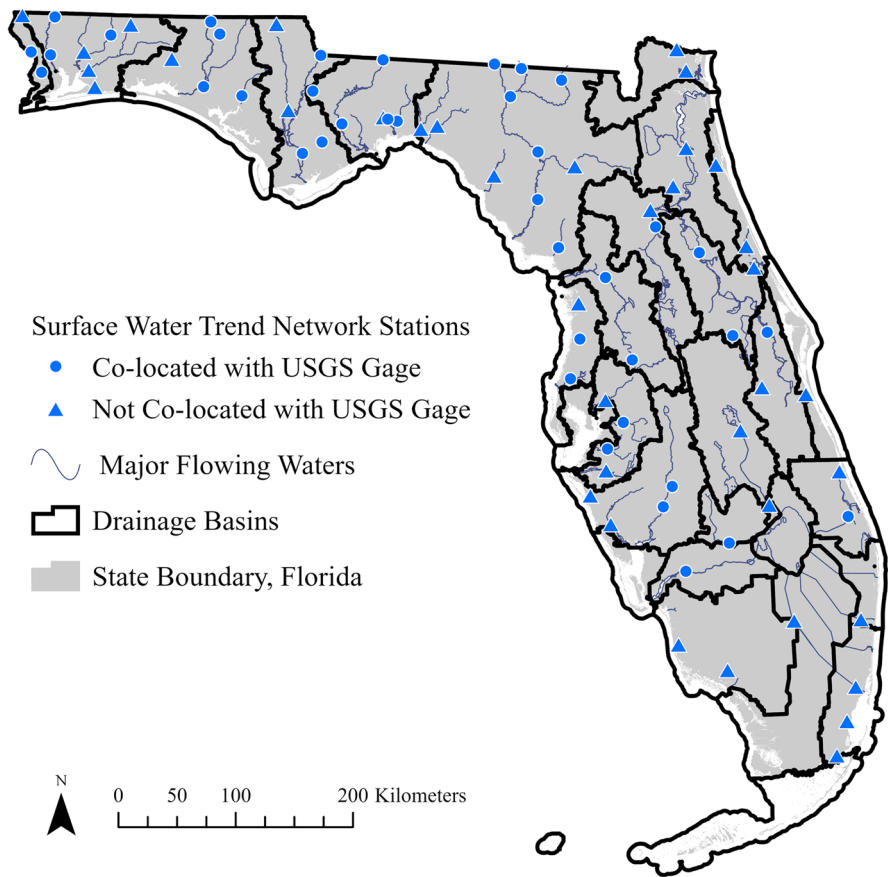
Sampling events

Imidacloprid was added to the analyte list for SWT in mid-January 2015, and the remaining neonicotinoids, acetamiprid, clothianidin, dinotefuran, and thiamethoxam were added in mid-July 2019. Monthly samples were collected from February to December 2015 at all 77 SWT stations and at 12 of the 77 SWT stations during August, September, October, November, and December 2019, and January, February, March, and July 2020. In January 2015, few stations were able to be sampled for imidacloprid, as the analytical method was not validated by the FDEP laboratory until late in the month. Most SWT sampling in April and all sampling in May and June of 2020 were canceled due to COVID-19 pandemic response restrictions. Concurrently from August 2019 through July 2020, neonicotinoid samples from 322 SMP stations were collected at varying frequencies. In addition to wastewater tracers and pesticides, all stations for both monitoring networks were sampled for a core list of surface-water quality indicators. For convenience, the 2015 data are referred to as event 1, and the 2019–2020 data are referred to as event 2.

Sample collection and analytical methods

The field sampling protocols used for the SWT Network are based on specific FDEP standard operating procedures. These protocols are found in the FDEP status and trend monitoring network sampling manual (FDEP, 2016). Sample collection and the analytical methods used for the 2015 sampling event for imidacloprid were the same as those reported by Silvanima et al. (2018), with the following exceptions. For the 2015 sampling event, samples were collected as either direct grabs into the sample container or using a horizontal Van Dorn (beta bottle) as an intermediate collection device. For the 2019–2020 sampling event, all samples were collected as direct grabs into the sample container. In 2015, samples were collected in 1-L brown glass bottles, whereas the 2019–2020 samples were collected in 500 mL brown glass bottles. All samples were transported on ice to the FDEP environmental laboratory in Tallahassee, FL, for analysis.

Fig. 1 FDEP SWT station locations with USGS stream gage co-location status and FDEP drainage basin boundaries



The laboratory methods used for the determination of imidacloprid from water samples collected in 2015 are the same as those reported by Silvanima et al. (2018). The analytical method developed for the determination of neonicotinoid compounds in the 2019–2020 samples is based on EPA Method 8321B and described in laboratory standard operating procedure SOP LC-001–3 (Reddy & Ware, 2021). A summary of the new method and associated laboratory quality control criteria is presented in SI Sect. 1.

Geospatial methodology

Streamflow and precipitation

Mean daily streamflow data collected during 2015 and 2019–2020 were retrieved from the USGS National Water Information System (NWIS; U.S. Geological Survey, 2022) for the 39 SWT stations co-located with

the USGS stream gages (Fig. 1). The daily streamflow data were summarized by sample event, week, month, and quarter and differences between the two SWT sampling events were analyzed. Precipitation data were obtained from the parameter-elevation regressions on independent slope model (PRISM) climate model (PRISM Climate Group Oregon State University, 2022). The daily precipitation data were obtained for the specific 4-km grid cells that each SMP station was located within, and these data were then summarized by week. The data preparation and analysis methods for the streamflow summaries and weekly estimates of precipitation are provided in SI Sect. 5.

Land use

The areal extent of urban, transportation, and agricultural land was determined for each of FL’s 29 basins using data provided by the five FL water management districts (WMDs) and the Florida Department

of Transportation (FDOT, 1999), as described by Silvanima et al. (2018). The period of record for the FDOT land use data is as follows: Northwest Florida WMD, 2019; Suwannee River WMD, 2016–2017; St. Johns River WMD, 2012–2016; Southwest Florida WMD, 2017; and South Florida WMD, 2017–2019. Additionally, the CropScape Cropland Data raster layer (USDA NASS, 2016) was used to produce areal extent of three categories of FL agricultural land use for each of the 29 basins based on the classification system provided in Table 3 of Nakagaki and Wolock (2005): (1) orchard and vineyard crops, (2) row and small grain crops and fallow land, and (3) pasture, hay, and sod crops. Further details on the geospatial methods used for land use are provided in SI Sect. 5.

Data analysis methods

Once all samples were analyzed, the field- and lab-generated measurements were reviewed and loaded into FDEP's Enterprise Oracle Database. All data manipulation and analyses were done in R (version 3.6.2) (RCore Team, 2019) using RStudio (version 1.2.5033) (RStudio Team, 2019). Two projects were created, one for SWT and one for SMP data, and scripts were developed to retrieve and manipulate the data for analyses and to provide summary statistics and graphics. R packages used include RODBC, RODM, dplyr, foreign, tidyr, sqldf, splitstackshape, stringr, EnvStats, ggplot, and micromap. The SWT sample data were binned by project month and may have included samples collected from the last full week of the prior month. The neonicotinoid data were converted from units of micrograms per liter ($\mu\text{g/L}$) to ng/L , and summary statistics were produced for each of the SWT and SMP stations and their associated FDEP drainage basins. If more than one SWT sample per station was collected during a single project month, a mean value was generated for each analyte prior to generating summary statistics. These statistics included the number of samples collected; minimum, median, and maximum values; interquartile range; the number of samples with below method detection limit (BDL) values; and the number of samples exceeding chronic and acute IALBs for values above the MDL and practical quantitation limit. Given a large number of BDL values for all neonicotinoids other than imidacloprid, BDL values were treated as if they were 0.00 ng/L . All statistical tests used in this study were

nonparametric tests and therefore do not rely on any assumption of data distribution. Where appropriate, the analyses were run as two-sided tests, as the null hypothesis was no difference. The significance level used in all statistical tests in this study was defined as one that produced a p -value ≤ 0.05 .

Tests for seasonality and comparison of the two events' imidacloprid values

The Kruskal–Wallis (KW) test (Conover, 1999), R Function `Kruskal.Test`, was used to determine if there were significant differences in streamflow regime between events and if seasonality was present in the event distributions of imidacloprid concentrations. The streamflow and imidacloprid data for both events were grouped into monthly and quarterly bins, with quarters defined as quarter 1, January–March; quarter 2, April–June; quarter 3, July–September; quarter 4, October–December. The KW test was used to determine if there were differences in the streamflow value distributions between sampling events, months, and quarters. For both events' imidacloprid datasets and for the combined event 1 and 2 imidacloprid dataset, the KW test was used to determine if seasonality was present by examining the distribution of imidacloprid values (seasonality) among the four quarters of the year. As there were few imidacloprid data available for the second quarter of 2020, this quarter was not able to be evaluated. The KW test was used to determine (1) if the quarterly values' distributions of the combined events' data differed, (2) if the event 1 quarterly distributions differed, and (3) if the event 2 quarterly distributions differed.

To compare the results of the two SWT events, four statistical tests were used: the Wilcoxon signed-rank (WSR) test, the Wilcoxon rank-sum test (also known as the Mann–Whitney [MW]) test, the binomial test, and the proportion test (Conover, 1999; Triola & Lossi, 2018). Any data collected during the months of January, April, May, and June were excluded from these comparative analyses due to the lack of data on one of the events. Two tests were used to compare the stations' imidacloprid median values between the two events, the WSR test, R Function `Kruskal.Test`, and the binomial test, R Function `Binom.Test`. Whereas the WSR uses the value generated from the differences between station medians, the binomial test uses the sign of the difference between the station

medians. The MW test, R Function *Kruskal.Test* was used to compare the results of each station’s monthly values between the two events. The MW allows the comparison of independent sampling events, while the WSR does not. MW tests were conducted for each station using the individual monthly values for the 2 events. The binomial test was also used to determine if the number of chronic IALB exceedances differed between the two events. The number of chronic IALB exceedances for each station during each event was compared, and the difference (positive or negative) was recorded. The test then compared the proportion of the differences between events. The proportion test, R Function *Binom.Test*, was used to determine if the proportion of the total number of samples having chronic IALBs differed between the two events.

Results and discussion

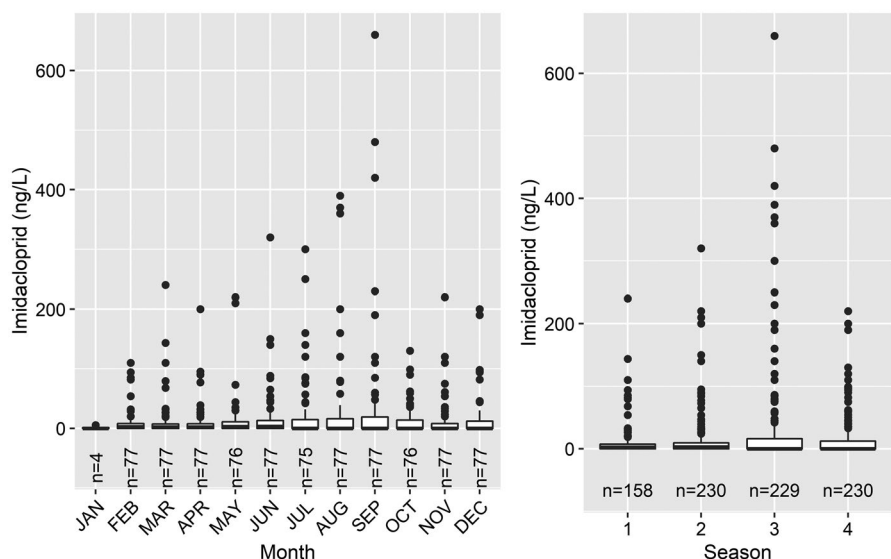
Summary of SWT sampling events for imidacloprid

No imidacloprid detections were noted from the 210 field and equipment blanks collected in event 1, and no detections for any of the five neonicotinoid insecticides were noted in the 48 field blanks collected during event 2 of this study. Concerning laboratory reporting limits, the MDLs reported by the FDEP laboratory were 2.0 and 4.0 ng/L for imidacloprid during event 1 and 2.0 ng/L for all five neonicotinoids

during event 2. Summary statistics of imidacloprid detections for all stations sampled in event 1 are provided in SI Table 2a. Of the 77 stations sampled, all but two were sampled monthly during the 11-month event. Nineteen of these stations produced no detections. Seasonal variation in the distribution of the stations’ imidacloprid values was examined by producing boxplots representing the monthly and quarterly ranges of the values for the calendar year (Fig. 2). No differences in the distributions of these monthly or quarterly data were noted from the KW test (monthly – chi-squared=5.8133, *df*=11, *p*-value=0.8855; quarterly – chi-squared=1.7571, *df*=3, *p*-value=0.6243). While no significant differences were found between the monthly or quarterly distributions, the third quarter of the year (July–September) produced the highest values of imidacloprid and all of the acute IALB exceedances (Fig. 2).

Imidacloprid comparative data summaries for the 12 SWT stations having event 1 median imidacloprid values greater than and minimum imidacloprid values near or above the chronic US EPA IALB are provided in SI Sect. 3. As mentioned in the Methods Section, the COVID-19 pandemic presented challenges during event 2 that prevented the collection of a full complement of samples in the second quarter of 2020. A total of 132 samples were obtained in event 1 and 114 in event 2 for a total of 246 samples (SI Fig. 3a). All samples contained detectable amounts of imidacloprid. Summaries of the individual station, month,

Fig. 2 Monthly and quarterly range of event 1 imidacloprid values for 77 stations. Boxes represent the 25th through 75th percentiles, heavy horizontal lines represent medians, whiskers represent 1.5 times the interquartile range, dots represent values greater than 1.5 times the interquartile range, and *n*= sample size. Season: 1=Jan, Feb, and March; 2=April, May, and June; 3=July, Aug, and Sept; 4=Oct, Nov, and Dec



and quarter median concentrations for each event are provided in Fig. 3 and SI Table 3a, b, and c. The median values for events 1 and 2 using all data are 44.0 and 30.5, respectively. These values are different from the event median values generated from the medians of station medians and exclude samples collected in the months of January, April, May, and June (48.5 and 34.5). For reasons mentioned in the methods section, any data collected during the months of January, April, May, and June were excluded from comparative analyses.

The WSR and binomial tests indicate there is significant evidence for a difference in the median concentrations the two events (WSR difference in medians = -14 ng/L, $V=70$, p -value = 0.01; binomial test: 10 of the 12 stations values decreasing, p -value = 0.04). Of the 10 stations having decreasing values, MW results show two stations' medians decreased significantly, Stations 3505 and 3556 (Manatee River and Peace River) (Table 3). Neither of the two stations with increasing median values showed significant differences via the MW tests. To evaluate the possibility of seasonality affecting the outcome of these analyses, we examined the data distributions for monthly and quarterly data of the combined quarterly data, and of the monthly and quarterly data by event (Figs. 2, 3b). Note that individual imidacloprid values are highest in the third quarter, as are their median values, suggesting there

may be seasonality in the data. The KW test results confirm that significant seasonality is present in (1) the combined data from both events, (2) event 1 data, and (3) the event 2 data (SI Table 3d). Therefore, the KW test results suggest that the statistical analyses provided by the WSR and binomial tests may have been affected by seasonal differences in imidacloprid values.

The number of observations per station exceeding the imidacloprid US EPA chronic and acute IALBs (10 and 385 ng/L, respectively) for individual values from each station is provided in SI Table 3e. Two stations had at least one imidacloprid value < 10 ng/L during event 1. The number of stations having at least one imidacloprid value < 10 ng/L increased to seven during event 2. All stations included in this study had at least five imidacloprid values ≥ 10 ng/L for each event. Three stations had at least one imidacloprid value ≥ 385 ng/L in event 1, while two stations had at least one imidacloprid value ≥ 385 ng/L in event 2. The total number of imidacloprid detections ≥ 10 ng/L for event 1 was 130 out of a total of 132 samples, and for event 2 was 98 out of a total of 114 samples. The results of the two-sample proportion test excluding the data from the months with missing data (chi-square of 7.304, $df=1$, p -value < 0.01) indicate this is a significant difference. There were proportionally fewer exceedances of the chronic benchmark during event 2.

Table 3 Mann–Whitney test results of comparison of individual stations' event median imidacloprid concentrations. Median value units are ng/L

Station	Station name	Median event 1	Event 1 <i>n</i>	Median event 2	Event 2 <i>n</i>	Difference in medians	<i>U</i> -statistic	<i>P</i> -value
3495	Golden Gate Canal	13.5	8	11.5	8	-2	33	0.96
3497	Fisheating Creek	17.5	8	37	8	19.5	14	0.06
3502	Phillippe Creek	47	8	40	8	-7	36	0.71
3504	Belcher Canal	145	8	41.5	8	-103.5	47	0.13
3505	Manatee River	49	8	22	8	-27	54.5	0.02
3554	Alafia River	20	8	15.5	8	-4.5	42	0.32
3555	Little Manatee River	92	8	68.5	8	-23.5	47	0.13
3556	Peace River	109.5	8	75	8	-34.5	47	0.03
3561	Charlie Creek	166.75	8	150	8	-16.75	35	0.79
3565	Elevenmile Creek	29	8	32	8	3	27	0.64
3568	Caloosahatchee River	78.5	8	28	8	-50.5	50	0.07
3569	Little Econlockhatchee River	48	8	21.5	8	-26.5	47	0.13

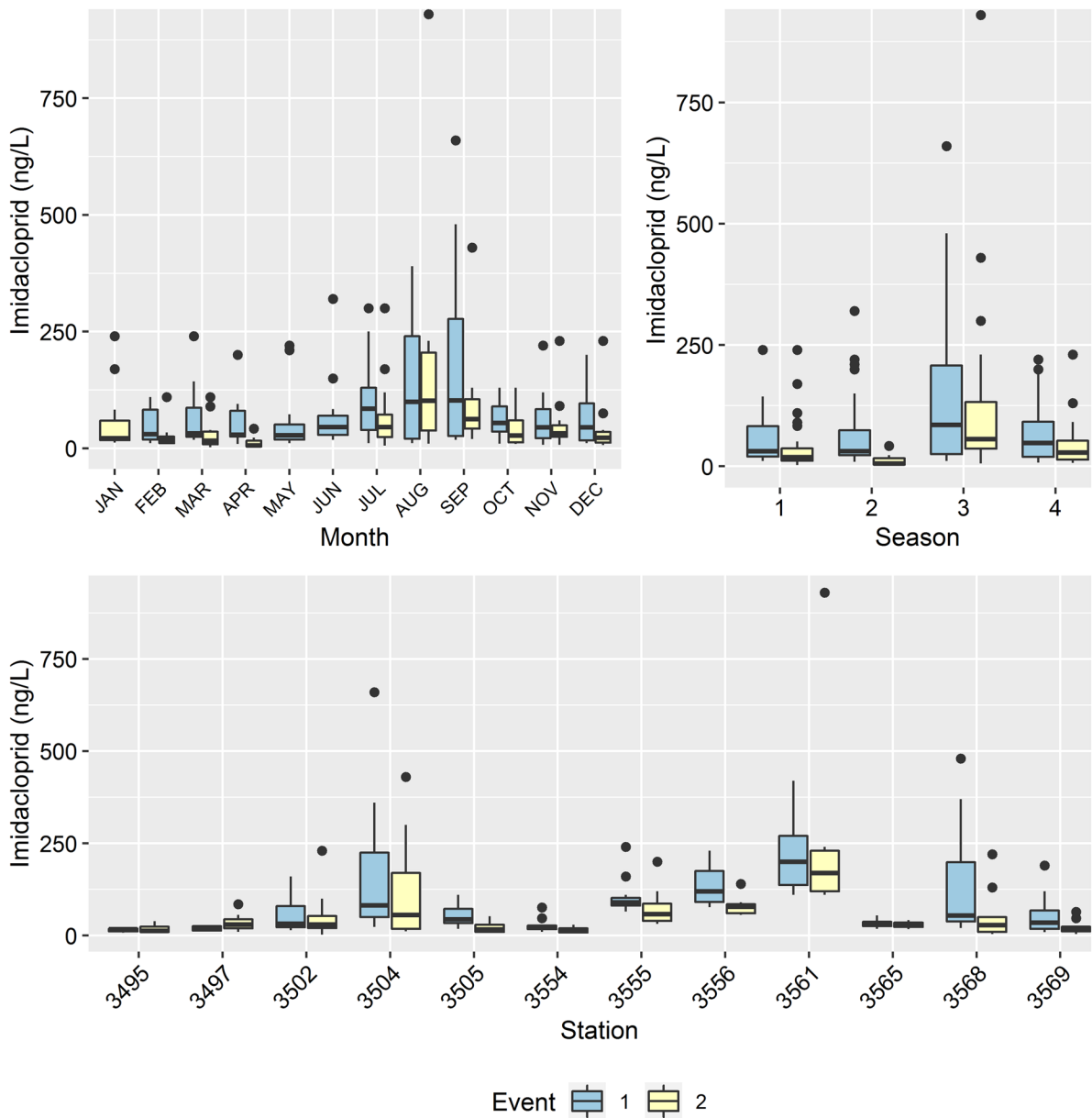


Fig. 3 Imidacloprid concentration (ng/L) distributions per month, season, and station for events 1 and 2. Boxes represent the 25th through 75th percentiles, heavy horizontal lines represent medians, whiskers represent 1.5 times the interquar-

tile range, and dots represent values greater than 1.5 times the interquartile range. Season: 1 = Jan, Feb, and March; 2 = April, May, and June; 3 = July, Aug, and Sept; 4 = Oct, Nov, and Dec

Additional neonicotinoids from event 2

For each SWT station sampled for event 2, median values were calculated for acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam and for the sum of the five compounds' values. (Table 4).

Given a large number of BDL values for all neonicotinoids other than imidacloprid, BDL values were treated as if they were 0.00 ng/L. Thus, the reported median values may be lower than the actual median. Of note, all samples collected for SWT event 2 produced detectable concentrations of imidacloprid.

Table 4 Median concentrations and the number of samples (*n*) by station of neonicotinoid pesticide concentrations in ng/L during event 2. Concentrations below method detection limit (2 ng/L) treated as 0.0

Station	Station name	<i>n</i>	Median acetamiprid	Median clothianidin	Median dinotefuran	Median imidacloprid	Median thiamethoxam	Total of medians
3495	Golden Gate Canal	9	0	2.5	2.6	13	0	17.3
3497	Fisheating Creek	10	0	0	1.6	30.5	1	36.2
3502	Phillippe Creek	10	0	2.4	1.7	29.5	2.35	34
3504	Belcher Canal	9	0	20	0	56	7.3	81.3
3505	Manatee River	10	0	3.7	6.8	16.6	12	45.9
3554	Alafia River	10	0	5.6	4.6	15.5	7.1	34.1
3555	Little Manatee River	10	0	30.5	17.5	58	76	202
3556	Peace River	8	0	15	1.6	78.6	43.5	151.4
3561	Charlie Creek	9	0	26	0	170	41	223
3565	Elevenmile Creek	9	0	0	0	30	0	30
3568	Caloosahatchee River	10	0	6.9	10.5	28	12.4	52.7
3569	Little Econlockhatchee River	10	0	3.1	2.3	20	0	26.1
Medians		114	0	6.275	2	29.5	7.2	41.1

Thiamethoxam was detected at all but two stations: 3495-Golden Gate Canal and 3565-Elevenmile Creek. Acetamiprid was detected at one station, 3554-Alafia River, in four out of 10 samples. Clothianidin and dinotefuran were detected at all stations except for 3565-Elevenmile Creek. Detection percentages are as follows for the 114 samples coming from these select 12 SWT stations: acetamiprid 3.5%, clothianidin 73.7%, dinotefuran 59.6%, imidacloprid 100%, and thiamethoxam 68.4%. The median concentrations of acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam were 0.0, 5, 2.55, 30.5, and 6.3 ng/L, respectively. The sum of the medians for these five compounds was 44.98 ng/L.

For the 322 SMP stations sampled statewide during event 2 (SI Fig. 4), basin-wide data summaries for acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam are provided in SI Table 4a. Detection percentages are as follows for these stations: acetamiprid 5.7%, clothianidin 47.5%, dinotefuran 35.8%, imidacloprid 80.4%, and thiamethoxam 32.0%. Two hundred fifty-eight of the 322 stations had at least one neonicotinoid detection. Of the 254 stations having imidacloprid detections, 149 produced values exceeding the US EPA chronic IALB and 6 produced values exceeding the US EPA acute IALB. The six stations having acute exceedances were located in four basins; Indian River Lagoon, Lake Worth Lagoon–Palm Beach Coast, Sarasota

Bay–Peace–Myakka, and Tampa Bay Tributaries. Thirteen basins produced imidacloprid median values exceeding the US EPA chronic IALB include Everglades West Coast, Fisheating Creek, Indian River Lagoon, Lake Worth Lagoon–Palm Beach Coast, Lower St. Johns, Middle St. Johns, Ocklawaha, Perdido, Sarasota Bay–Peace–Myakka, Southeast Coast–Biscayne Bay, Springs Coast, Tampa Bay, and Tampa Bay Tributaries. The only other neonicotinoid to have station median or maximum values exceeding a US EPA IALB is clothianidin. Four stations within the Sarasota Bay–Peace–Myakka basin and three stations within Tampa Bay Tributaries basin produced median values greater than the chronic IALB.

In summary, for the combined dataset of 12 SWT and 322 SMP monitoring stations sampled during July 2019–August 2020; (1) two hundred seventy of the 334 stations had at least one neonicotinoid detection and (2) station detection frequencies of the five compounds were as follows: acetamiprid 18 of 328 [5.5%], clothianidin 156 of 328 stations [46.7%], dinotefuran 122 of 328 [37.2%], imidacloprid 266 of 334 [80.0%], and thiamethoxam 101 of 328 [34.8%].

Environmental relevance

Of the 77 SWT stations sampled for imidacloprid during event 1, 58 (75%) produced detections, and 35 (45%) produced at least one value exceeding the

chronic IALB for imidacloprid. Of these 35 stations, 19 (25%) had event median values exceeding the chronic IALB (SI Table 2a). The only acute IALB exceedances came from three stations also having median event values greater than the chronic IALB. Twenty-five of the 29 FDEP drainage basins had associated SWT stations (SI Table 2b). Of these 25 basins, eight (32%) had median imidacloprid values meeting or exceeding the chronic IALB of 10 ng/L: Caloosahatchee, Fisheating Creek, Indian River Lagoon, Middle St. Johns, Perdido, Sarasota Bay–Peace–Myakka, Tampa Bay Tributaries, and Upper East Coast. Concerning the resampling of the twelve SWT stations for event 2, imidacloprid was detected at all stations, and its median values continued to exceed the chronic IALB for all stations. Of all five compounds, the only one with station median values failing a US EPA chronic IALB was imidacloprid. For acetamiprid, clothianidin, dinotefuran, and thiamethoxam, the only compound to have individual values exceeding a chronic IALB was clothianidin (Fig. 4, SI Fig. 3c). Three stations produced at least one clothianidin value greater than the chronic IALB of 50 ng/L: 3504–Belcher Canal, 3555–Little Manatee River, 3561–Charlie Creek. For comparative purposes, the number of observations per station exceeding Morrissey et al.’s (2015) recommended guidance for the total concentration of neonicotinoid compounds (chronic 35 ng/L; acute 200 ng/L) is provided in SI Table 3e.

Data summaries based on SWT monitoring show that 8 of the 25 drainage basins sampled for this study have median values of imidacloprid above the chronic IALB (Figs. 5, 6, SI Table 2b). These basins also produced the highest median values of imidacloprid from the 2015 statewide probabilistic survey for combined water resources (Silvanima et al., 2018). Four of these basins—Fisheating Creek, Tampa Bay Tributaries, Caloosahatchee, and Sarasota–Peace–Myakka have large percentages of combined agricultural + urban + transportation land use, ranking 1st, 2nd, 3rd, and 5th, respectively, while Middle St. Johns, Perdido, Upper East Coast, and the Indian River Lagoon rank 14th, 16th, 19th, and 20th, respectively, of the 29 basins (SI Table 5a). Except for Perdido, these basins have some of the higher insecticide use estimates, as determined by Woeber (2018) (Fig. 7). Perdido is a small, narrow (east to

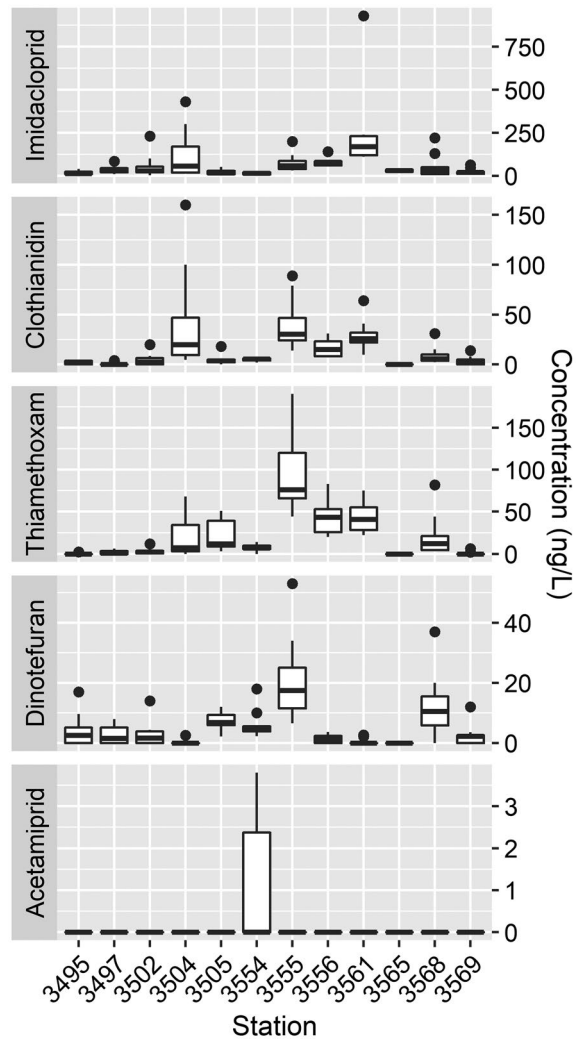


Fig. 4 Box plots of neonicotinoid concentration (ng/L) distributions from event 2 by station and an individual neonicotinoid. Boxes represent the 25th through 75th percentiles, heavy horizontal lines represent medians, whiskers represent 1.5 times the interquartile range, and dots represent values greater than 1.5 times the interquartile range

west), mainly riparian basin that is densely populated in the south (Pensacola) and receives the majority of its flowing water from a predominantly agricultural drainage basin in Alabama via the Perdido River. These results support the outcomes of the geospatial analyses done on FDEP’s 2015 probabilistic survey data that show significant correlations between agricultural and combined agricultural + urban + transportation land use percentages and the percentage of

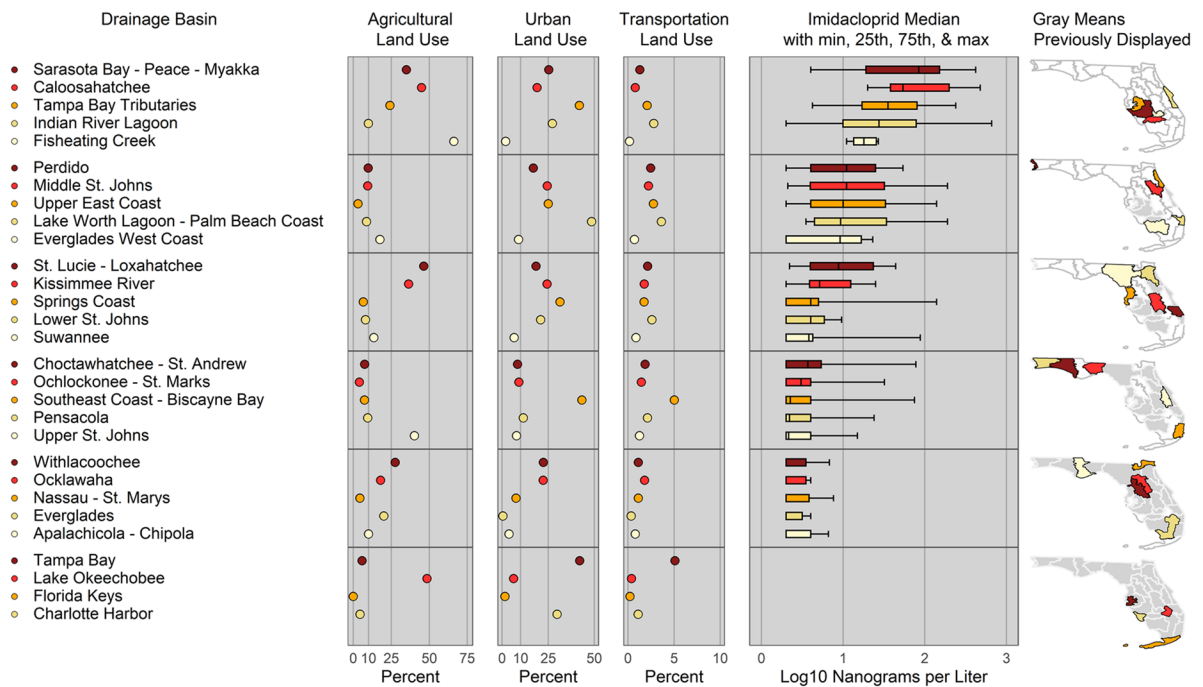


Fig. 5 Linked micromap of FDEP drainage basins, percentage of agricultural, urban, and transportation land, and imidacloprid summary statistics (median with upper and lower quartiles and minimum and maximum values) from event 1. Basins are

ordered by the median value of imidacloprid. The incremental gray shading of basins indicates which basins appeared in the previous grouping within each map

samples with imidacloprid detections for combined water resources (streams, lakes, and unconfined aquifers) (Silvanima et al., 2018).

There were proportionally fewer chronic IALB exceedances found in event 2. In event 1, three stations produced acute IALB exceedances for imidacloprid—Belcher Canal, Charlie Creek, and the Caloosahatchee River. Belcher Canal and Charlie Creek produced acute invertebrate exceedances again during event 2, and the Caloosahatchee River did not. Excluding imidacloprid, the only IALB exceedances coming from event 2 were for clothianidin (Fig. 4). These came from individual samples collected in Belcher Canal, the Little Manatee River, and Charlie Creek. The highest detected values for dinotefuran (53 ng/L) and thiamethoxam (190 ng/L) came from the Little Manatee River. Acetamiprid was only detected in the Alafia River. Summing the five neonicotinoids detected values for each station’s sample data produced 69 out of 114 results above the Morrissey et al. (2015) recommended chronic guidance of 35 ng/L, and 17 out of the 114 results above

the Morrissey et al. (2015) recommended acute guidance of 200 ng/L (Fig. 8). Stations, where at least one sample data’s results exceeded the acute guidance of 200 ng/L, were Phillippe Creek, Belcher Canal, the Little Manatee River, the Peace River, Charlie Creek, and the Caloosahatchee River. The highest total concentration of the combined five neonicotinoid values (1018 ng/L) came from the August 2019 sampling of Charlie Creek.

While it is important to understand that the data collection for the SMP sampling event was focused on waterbodies either known to be or suspected of being impaired due to other water quality metrics, the general patterns of neonicotinoid detection rate and IALBs exceedances mirror those provided from the SWT event 2 monitoring. That is, for the five neonicotinoids examined, (1) imidacloprid is ubiquitously detected and has the highest number of IALB exceedances by far, (2) clothianidin is the only other compound found to exceed current IALBs, and (3) clothianidin follows imidacloprid in detection rate, with dinotefuran and thiamethoxam closely following,

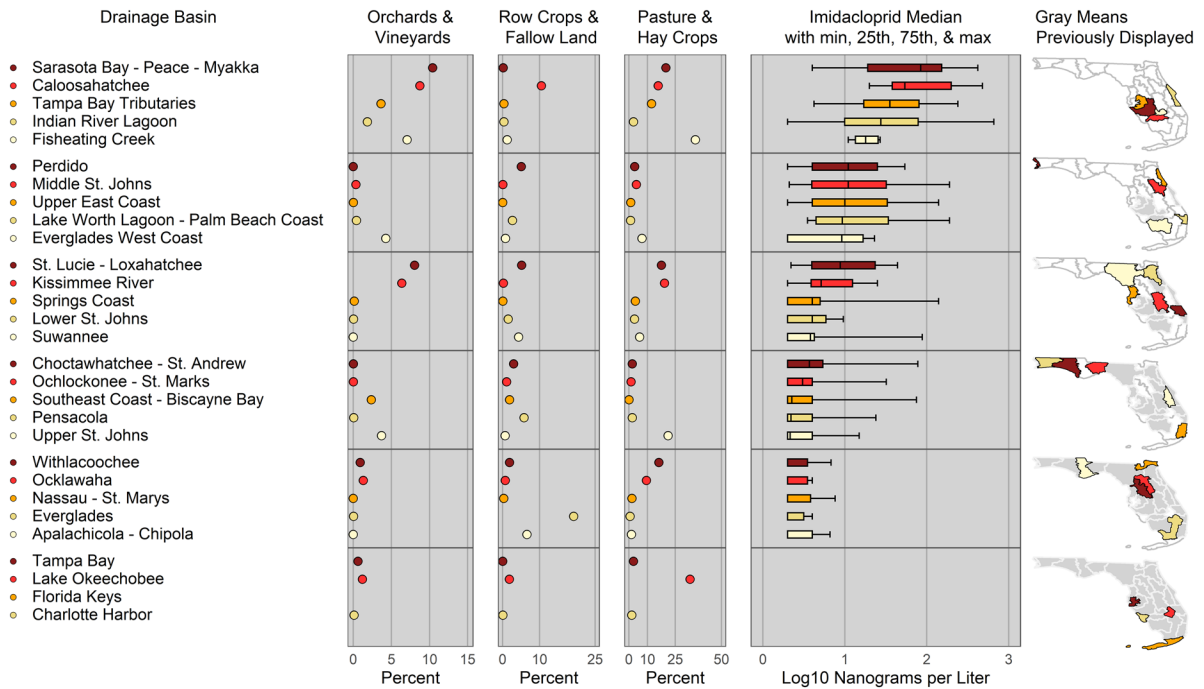


Fig. 6 Linked micromap of FDEP drainage basins, percentage of three crop classes, and imidacloprid summary statistics (median with upper and lower quartiles and minimum and

maximum values) from event 1. The incremental gray shading of basins indicates which basins appeared in the previous grouping within each map

and acetamiprid providing the least detections. The additional information provided from SMP event 2 also hints that the potential for imidacloprid to produce chronic level effects on aquatic invertebrates has increased in some basins. This is because, as compared to the DEP 2015 probabilistic and trend statewide sampling events for imidacloprid, the basin-wide data summaries of SMP event 2 data (SI Table 4a) show additional basins having median values exceeding the chronic IALB.

Aquatic insects receiving chronic doses of neonicotinoids have been shown to have impaired mobility, ataxia, and feeding inhibition, all of which may lead to increased mortality due to predation and reductions in fecundity, growth, and longevity (Anderson et al., 2015; Hladik et al., 2018; Morrisey et al., 2015; Pisa et al., 2017). These impairments are ecologically relevant as they impact survival and population size and therefore, potentially affect ecological community dynamics (Sánchez-Bayo et al., 2016). Mesocosm experiments have documented aquatic invertebrate community composition changes caused by exposure to chronic levels of neonicotinoids (Alexander

et al., 2016; Barmiento et al., 2021; Chará-Serna et al., 2019; Dimitri et al., 2021; Merga and Van den Brink 2021; Sumon et al., 2018). While field studies are fewer, Cavallaro et al. (2019) documented how multiple stressors, including neonicotinoid concentration, affected emerging aquatic insects from wetlands impacted by intensive agricultural practices. They determined that mean neonicotinoid concentration and turbidity were influencing the emerging insect community composition significantly. Insect taxa were more diverse in wetlands receiving lower concentrations of neonicotinoids, while wetlands receiving higher concentrations had a higher abundance of tolerant species.

While it is unclear which aquatic invertebrates may be impacted by neonicotinoid loads determined in this study or what ecological community dynamics these impacts may be interrupted, it is clear that at least eight FDEP drainage basins are receiving neonicotinoid loads with the potential to cause chronic effects to freshwater invertebrates. In addition, based on sampled concentrations, Tampa Bay, Sarasota Bay, Charlotte Harbor, and the Indian River Lagoon

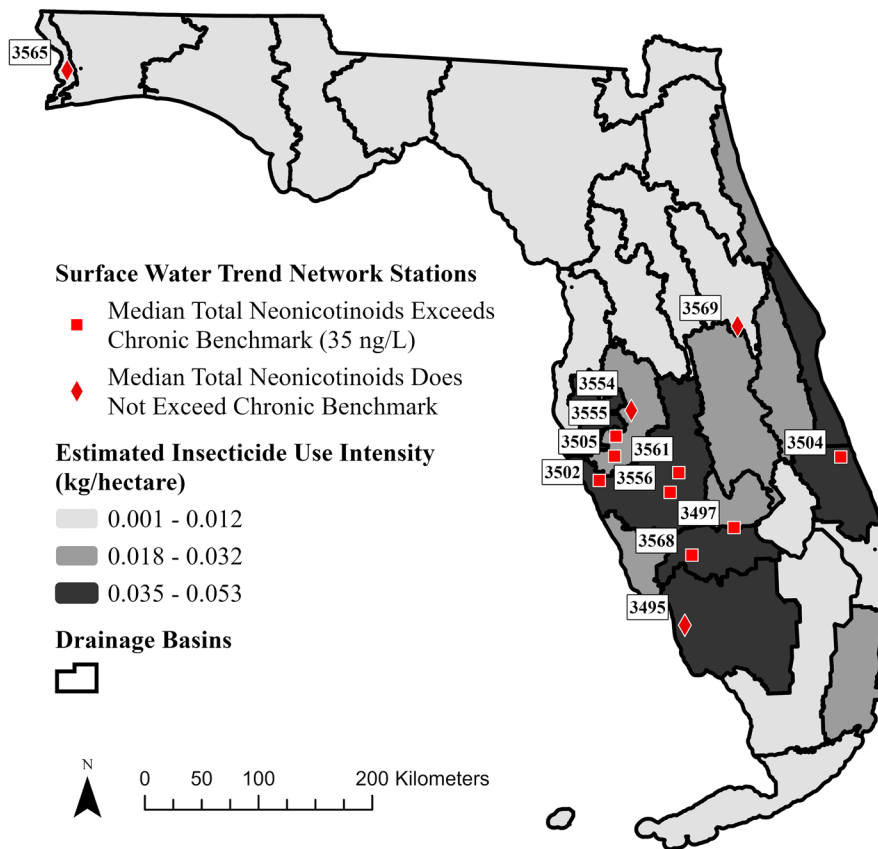


Fig. 7 Map of estimated insecticide use per drainage basin with station median values from event 2 exceeding Morrissey et al., 2015's recommended chronic IALB for total concentration of neonicotinoid compounds. Insecticide use intensity estimates from Woeber (2018)

consistently receive neonicotinoid loads above the US EPA chronic freshwater IALBs. It is unclear whether the loads flowing from these basins have the potential to cause impacts on marine organisms and their associated trophic structures since neonicotinoid aquatic life benchmarks for marine invertebrates to have yet to be developed.

Spatiotemporal relationships

The ubiquitous uses of neonicotinoids allow them to be released into the environment from both agricultural and urban uses, where they may then enter waterways through surface runoff, aerial drift, atmospheric deposition, and seepage into unconfined groundwater (Borsuah et al., 2020; van Lexmond et al., 2015). Historically the development of estimates for insecticide use rate for determining inputs into waterways relied heavily on agricultural data. More recent studies have focused on the contributions

from urban areas (Batikian et al., 2019; Nowell et al., 2018, 2021; Sadaria et al., 2016; Silvanima et al., 2018; Stehle et al., 2019; Webb et al., 2021; Xie et al., 2021). Hydrologic functions in urban areas differ from those found in rural and agricultural areas mainly because impervious surface runoff causes sporadic high-flow stormwater events. Additionally, conventional wastewater treatment systems are not maximized to remove many hydrophilic emerging substances of concern (Petrie, 2015), and many studies have documented wastewater effluent as a source of neonicotinoid insecticides in flowing waters (FDEP, 2018; Hope et al., 2012; Campo et al., 2013; Qi et al., 2015; Sadaria et al., 2016; Sutton et al., 2019; Webb et al., 2021). In fact, imidacloprid and clothianidin detections in the US receiving waters commonly exceed US EPA IALBs (FDEP, 2018; Sadaria et al., 2016, 2017; Sutton et al., 2019; Webb et al., 2021). These outcomes clearly show that urban surface runoff and wastewater may be significant

sources of imidacloprid and, perhaps to a lesser degree, other neonicotinoids in flowing waters.

In this study, we examined the potential effects of streamflow, precipitation, land use, and agricultural insecticide use intensity on the occurrence and magnitude of imidacloprid, and to a lesser extent, the other neonicotinoids, in FL’s flowing waters (SI Sect. 4). For the 8 resampled SWT stations co-located with USGS gage stations, streamflow regimes of the events differed significantly ($\chi^2=93.65$, $p\text{-value} < 0.01$), with event 1 having higher flows than event 2. (Fig. 9, SI Tables 5d1–3). Additionally, a significant overall correlation was found between imidacloprid concentration and the weekly mean streamflow measurements generated from the weeks individual samples were collected ($\rho=0.24$, $p\text{-value} < 0.01$) for these 8 stations. We used the 322-station statewide SMP event 2 datasets to examine the potential effects of rainfall on neonicotinoid concentration by obtaining daily precipitation values for the specific PRISM 4 km grid cell for which each SMP station was located and then running Spearman rank sum correlations for each neonicotinoid’s concentration and mean weekly precipitation per sample date. For this statewide dataset, correlations between rainfall and concentration were found for clothianidin ($\rho=0.087$, $p\text{-value}=0.02$) and imidacloprid ($\rho=0.127$, $p\text{-value} < 0.01$) (SI Table 5c). The highest monthly individual and median values of these insecticides coincide with the portion of the hurricane season most likely to impact FL: the third quarter of the calendar year (July–September), which receives the most annual statewide rainfall (SERCC, 2021) (SI Table 5b). These results suggest that the significant decrease in median imidacloprid values at these 12 stations, as provided by the WSR test, was likely influenced by flow and associated precipitation.

Concerning land use, the areal extent of urban, transportation, agricultural, and 3 crop classes per basin was determined using the methods provided in SI Sect. 5 (SI Fig. 5). The area of each basin represented by water was removed, as this is unlikely to be a source of imidacloprid, prior to calculating land use percentages per basin. Figures 5 and 6 provide a visual examination of the percentages of these respective land uses plotted beside the range of imidacloprid values determined for each basin as ordered by median imidacloprid values. For the SWT event 1

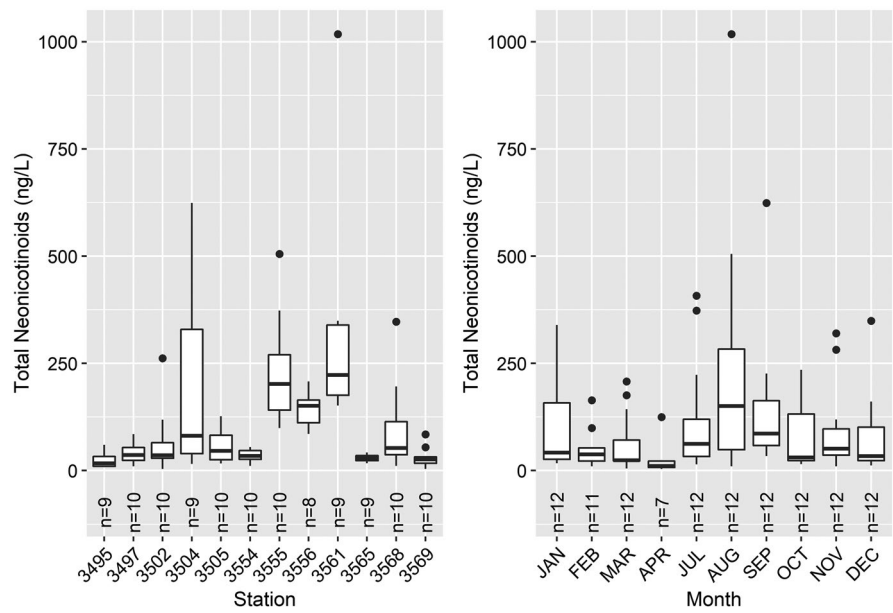
dataset direct correlations were found between imidacloprid concentration and the percentages of urban land use and the crop class orchards and vineyards land use (Table 5). These results are similar to those reported from the FDEP probabilistic assessment for combined water resources (Silvanima et al., 2018). The 2018 study included the extent of water in the total basin area and used general linear model regression analysis for combined urban + transportation and agricultural land uses. Additionally, the 2018 study only ran a regression on combined urban + transportation land use. It did not separate urban from transportation land uses.

Determining insecticide use estimates in general, and specifically for neonicotinoids, presents challenges. Their usage generally is considered confidential, and estimates typically are made through voluntary surveys, were available from purchasing data, and/or by estimating application rates based on manufacturer-recommended product guidance (Main et al., 2014). In urban areas, sales estimates for products containing these compounds are not tracked for residential and veterinary uses. These products are readily available for sale in home and garden centers and veterinary services throughout the USA and globally. As these products are used to protect homes, lawns, right of way, golf courses, gardens, shrubs, trees, and pets, their contribution to what is seen in water resources is expected to be high. Our results corroborate this assumption with urban land use producing the strongest land-use correlation with the imidacloprid concentrations found in this study. Concerning agricultural usage, the USGS, as part of the National Pesticide Synthesis Project (USGS, 2017), reports estimated annual agricultural

Table 5 Spearman rank sum correlations for event 1 imidacloprid basin median values and land use

Land use	S	Rho	P-value
Transportation	1977.4	0.24	0.25
Urban	1472.2	0.43	0.03
Transportation + urban	1508.5	0.42	0.04
Agriculture	2005.5	0.23	0.27
Orchards and vineyards	1327.6	0.49	0.01
Row crops and fallow land	3308	−0.27	0.19
Pasture and hay crops	1726.3	0.34	0.10
Other agriculture	1725.3	0.34	0.10

Fig. 8 Sum of the total concentration of neonicotinoids for event 2 by station and month



pesticide use for the US-based on-farm surveys of pesticide use and estimates of harvested crop acres. It creates maps showing agricultural pesticide use by allocating the county-level estimates to agricultural land in each county nationwide. The low estimates for annual agricultural use show imidacloprid use in the US increased from 113,398 kg (kg) in the early

2000s to 340,194 kg in 2008, to 725,748 kg in 2010, and to 907,185 kg in 2014 (USGS, 2020). However, in 2015 the agency discontinued making estimates for the seed treatment application of pesticides because of uncertainty; therefore, the most recent estimates are lower than those provided prior to 2015. Even so, as of this writing, the most recent USGS estimates

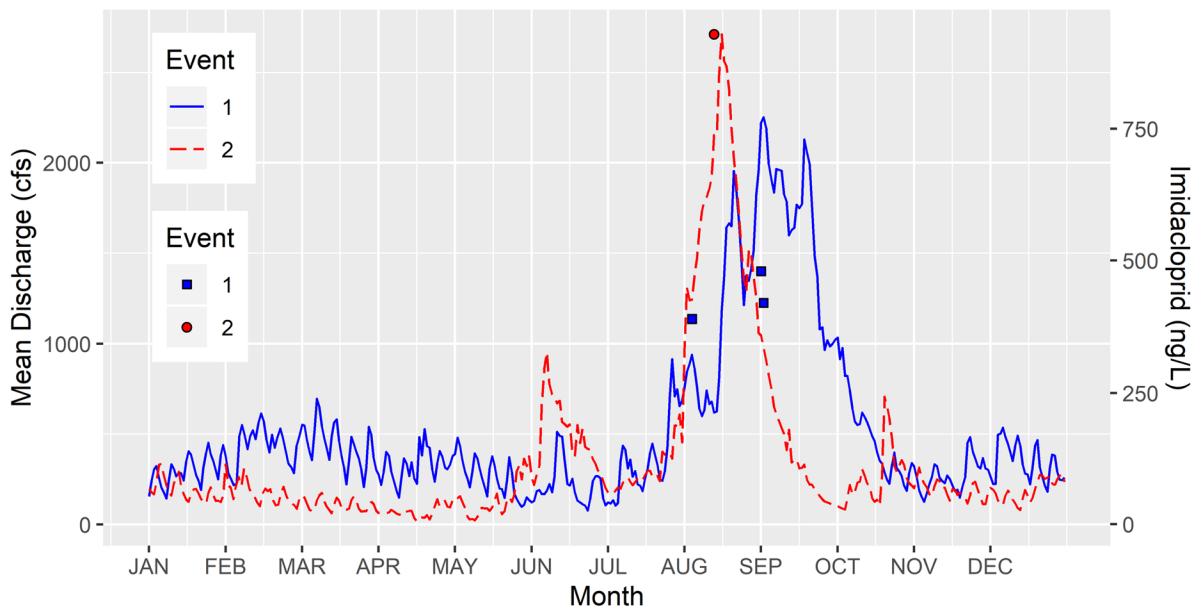


Fig. 9 Imidacloprid sample values exceeding the US EPA Acute IALB plotted with mean daily streamflow values for the 8 stations collocated with USGS stream gages by event

(2020) show annual increases from 396,893 kg in 2015 to 408,233 kg in 2016 and to 580,598 kg in 2017.

For agriculturally related seasonal effects, neonicotinoid insecticides are liberated into the environment as seeds coated with them are disbursed during planting and during periodic aerial and stem application to control insects during the plants' growth (Borsuah et al., 2020). Concerning agriculture in FL, the panhandle and northern peninsula are dominated by 2 crop categories: (1) row and small-grain, and (2) pasture, hay, and sod crops, whereas the rest of the state has more of a mix of the three crop categories presented here (Fig. 6). Due to differences in climate and associated growing season, neonicotinoid use in these two regions of the state differs. In the panhandle and northern peninsular FL, these neonicotinoids are used mainly in the spring through summer. In the rest of the state, where the growing season is year-round, there are generally two planting/application seasons (late fall through winter and spring through summer), and neonicotinoids are used year-round. An examination of imidacloprid and fipronil use intensity estimates provided by Woeber (2018) indicates that southwest FL and the Indian River Lagoon areas of the state have the highest statewide use intensity estimates. These areas produced the highest total concentrations of the neonicotinoid insecticides examined in this study (Fig. 7).

Conclusions

The results of the 2015 FDEP monthly statewide sampling of 77 surface water trend monitoring stations show that imidacloprid is ubiquitous throughout FL's flowing surface waters, with 24 of the 25 FDEP drainage basins sampled producing detections ranging from 2 to 660 ng/L. Additionally, significant direct correlations between imidacloprid and the percentages of two specific land use classes per basin were noted: urban ($\rho=0.43$, p -value=0.03), orchard and vineyards ($\rho=0.49$, p -value=0.01). Eight of the 25 basins represented had median values of imidacloprid greater than the US EPA chronic IALB (10 ng/L). Twelve stations representing these eight basins were resampled for the neonicotinoids acetamiprid, clothianidin, dinotefuran, imidacloprid, and thiamethoxam from August 2019 to July 2020. Imidacloprid

was detected in all samples. Of the remaining 4 compounds, clothianidin was detected most frequently (73.7%), followed by thiamethoxam (68.4%), dinotefuran (59.6%), and acetamiprid (3.5%). Streamflow examinations showed that the streamflow regimes differed between the events' water years for the stations represented (KW p -value < 0.01) and that imidacloprid concentrations were directly correlated with the weekly mean streamflow measurements generated from the week's individual samples were collected ($\rho=0.24$, p -value = < 0.01). And while median event values of imidacloprid were found to decrease from 48.5 to 34.5 ng/L (p -value=0.011), we conclude that streamflow influences, in conjunction with missing data due to the COVID-19 pandemic, likely impacted the WSR test used to determine statistical significance. Imidacloprid was the only compound found to exceed an acute US EPA IALB, and these acute values coincided with hurricane season, associated rainfall, and peak agricultural activities for both events. Clothianidin was the only other compound found at levels exceeding a US EPA IALB, that for chronic exposure (50 ng/L). During both events, neonicotinoids were found at concentrations known to produce deleterious, and in some cases fatal, effects on aquatic invertebrates at these 12 monitoring stations representing eight drainage basins. Furthermore, based on sampled concentrations, Tampa Bay, Sarasota Bay, Charlotte Harbor, and the Indian River Lagoon are receiving consistent neonicotinoid loads above the US EPA chronic freshwater IALBs. As no marine IALBs are available, the extent to which marine organisms are being affected is not clear. This FL study adds to the body of literature documenting the regional extent of imidacloprid's chronic long-term exposure potential to aquatic insect communities in North American waters and highlights the challenges associated with limiting the entry of neonicotinoid compounds into water resources. Reduction of these compounds' entry into, and persistence within, FL water resources could be achieved by (1) restricting sales of products containing imidacloprid and other neonicotinoids for non-agricultural usage and (2) limiting agricultural usage through the development of integrated pest management strategies utilizing scouting services to dictate what type of neonicotinoid applications are appropriate and when to apply them.

Acknowledgements We thank the numerous field and laboratory staff responsible for sample collection, data entry, chemical analysis, and analytical method development. Reviews provided by two anonymous referees and several Florida Department of Environmental Protection staff significantly increased the quality of this manuscript. Ongoing financial support for the Trend Monitoring Network is provided by the US EPA Office of Water through 604 monitoring grants.

Declarations

Competing interest The authors declare no competing interests.

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