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Abstract

Currently little is known of newer pesticide classes and their occurrence and persistence in recreational lakes. Therefore, the objectives of this study were to (1) assess average pesticide concentrations and loadings entering recreational lakes in three mixed land use watersheds throughout the growing season, (2) evaluate pesticide persistence longitudinally within the lakes, and (3) perform an ecotoxicity assessment. Six sampling campaigns were conducted at three lakes from April through October 2018 to measure the occurrence and persistence during pre, middle, and post growing season.

Polar organic chemical integrative samplers (POCIS) were placed in streams near lake inlets and monthly samples were collected for analysis of twelve pesticides. Additional monthly grab water samples were taken at each POCIS location and at the midpoint and outlet of each lake. All pesticide samples were analyzed using liquid chromatography/tandem mass spectrometry (LC/MS/MS) and individual pesticide loading rates were determined. Occurrence and persistence of specific pesticides were significantly different between lakes in varying watershed land uses. Specifically, the recreational lake receiving predominately urban runoff had the highest load of pesticides, likely in the form of biocides, entering the waterbody. Concentrations of imidacloprid exceeded acute and chronic invertebrate levels for 11% and 61% of the sampling periods, respectively, with the recreational lake receiving predominately urban runoff having the most occurrences. Findings from this study are critical for preventing and mitigating potential effects of pesticides, specifically applied as biocides in urban landscapes, from entering and persisting in recreational lakes.

Keywords: Neonicotinoids, Recreational lakes, Ecotoxicity, Fate and transport, Pesticides, Biocides

1. Introduction

Pesticides, which encompass insecticides, herbicides, and fungicides, are necessary to sustain food production demands worldwide (Grube et al., 2011). Over nine hundred million kilograms of pesticides were applied annually, in the United States (U.S.) alone, from 1992 to 2011, leading to chronic pollution in streams and rivers (Desneux et al., 2006; Weston et al., 2013). According to a U.S. Geological Survey national assessment conducted from 2002 to 2011, 61% of agricultural streams and 90% of urban streams had at least one pesticide exceeding aquatic-life benchmarks (Stone et al., 2014).Worldwide, detectable levels of pesticides in water resources continue to rise, which have significant human health and water security implications. After use, all pesticides encounter a range of variable environmental conditions that may result in the formation of both innocuous and potentially harmful byproducts. These pesticides and byproducts may produce significant ecological effects within agroecosystem food webs and negatively impact human health (e.g., potential honeybee colony collapse, reproductive and development disruption, carcinogens) (Anderson et al., 2015; Ueyamaet al., 2015).

This study aimed to assess the occurrence of commonly used pesticides such as organothiophosphate and neonicotinoid insecticides, as well as strobilurin and acylamino acid fungicides. Neonicotinoid

insecticides, in particular the chloropryidinyl compound imidacloprid and chlorothiazolyl compound clothianidin, have emerged as two of the most important neonicotinoids in agricultural and urban landscapes (as well as their associated adjacent and downstream aquatic ecosystems) (Main et al., 2014). Imidacloprid, introduced in 1992 as the first neo-nicotinoid on the U.S. market to control both turf grass and crop pests, is currently the most widely used insecticide in the world (Grube et al., 2011). Predominantly applied to soybeans, annual agricultural use of imidacloprid has grown exponentially from zero to one million kg per year between 1992 and 2014. The annual application of clothianidin, only registered for use within the U.S. since the early 2000s and pre-dominately applied to corn, has similarly increased to 1.7 million kg per year between 2003 and 2014. In contrast to imidacloprid, clothianidin is not only a registered insecticide, but also is a byproduct of another registered neonicotinoid, thiamethoxam (Uneme et al., 2006). Exposure to neonicotinoid and degradate residues have the potential to cause un-intended health effects in humans and non-target species (Anderson et al., 2015; Ueyamaet al., 2015; Louiset al., 2017; Wu-Smart and Spivak, 2016). Further, there is currently much concern over the potential tox-icity of imidacloprid exposure to honeybees as they are one of the non-target species possibly affected by chronic exposure to neonicotinoids (Mineau and Palmer, 2013; Žabar et al., 2011).

Unlike the increased use of insecticides, fungicide use has gener-ally remained constant from 1988 to 2007 around the world, includ-ing the U.S. (Grube et al., 2011). Strobilurin fungicides, such as azoxys-trobin and trifloxystrobin, were introduced to the fungicide market in 1996 (Bartlett et al., 2002) due to their effectiveness in limiting the pro-duction of adenosine triphosphate (ATP) in fungus. While quantities of fungicide use are generally much less than herbicides and insecticides across all markets (agricultural, home and garden, industry, etc.), resi-dues are still commonly found in surface waters across the U.S. (Stone et al., 2014). Non-target species negatively impacted by fungicides in-clude, but are not limited to, amphibians, algae, prokaryotes, and nitri-fying bacteria(Belden et al., 2010; Yang et al., 2011).

As of May 2018, the European Union completely banned the use of several pesticide classes, including neonicotinoids (European Commis-sion, 2018). In contrast, the U.S. Environmental Protection Agency's Of-fice Pesticide Programs records acute (toxicity value being usually the

lowest 48- or 96-h 50% effect concentration or 50% lethal concentration in a standardized test where the level of concern is 0.5) and chronic (toxicity value being usually the lowest no-observed-adverse-effects concentration from a invertebrate life-cycle test) toxicity for registered pesticides to identify areas of concern for registered pesticides. However, the prevalence of pesticides, specifically neonicotinoid insecticides and strobilurin fungicides, within U.S. waters and around the world elevates the importance of understanding their dynamic transport mechanisms into recreational lakes (which provide outdoor activities such as boating, kayaking, and fishing), persistence, and long-term fate.

While low concentrations of pesticides are known to be pervasive in both agricultural and urban streams (Beketov and Liess, 2008; Hansen et al., 2019), few studies have evaluated these 12 pesticides and their seasonal persistence in lakes. Recent reports have found pesticides in urban and agricultural lakes, including Midwestern national park lakes, as well as groundwater systems(Elliott and VanderMeulen, 2016)– (Spalding et al., 2003). However, to our knowledge, the occurrence and persistence of neonicotinoids and strobilurin fungicides have not been evaluated in the lacustrine environment. Therefore, the goal of this study was to provide one of the first evaluations of potential ecosystem exposure to pesticide contamination and persistence longitudinally in recreational lakes located in the Midwestern U.S. The primary objectives of the study were to (1) assess average neonicotinoid and strobilurin fungicide concentrations and loadings entering recreational lakes in three distinct watersheds comprised of varying land uses, (2) evaluate pesticide persistence longitudinally throughout the lakes, and (3) perform an ecotoxicity assessment. It was hypothesized the predominately agricultural watershed, compared to the predominately urban and herbaceous watersheds, would have the highest loading of pesticides and higher concentrations would be observed near the inlet of each lake.

2. Materials and methods

2.1. Site description

Three recreational lakes with varying predominant land uses within the watersheds were evaluated in the Lower Platte River Basin of Nebraska:

(1) herbaceous (Pawnee), (2) urban (Holmes) and (3) agricultural (Wagon Train) (**Fig. S1**). The lakes, each classified as reservoirs, will be referenced as "herbaceous", "urban", and "agricultural" based on predominant land cover for the remainder of this manuscript. Herbaceous refers to a watershed predominantly composed of grassy prairie, shrubs, and open vegetated areas, and excludes forested or woody areas. The urban watershed was primarily comprised of residentially developed areas. Lastly the agricultural watershed consisted of predominantly agricultural land use, specifically corn and soybeans.

The lacustrine ecosystems received runoff from diverse mixes of agricultural and urban land uses within each watershed. Specifically, the herbaceous watershed was comprised of 22.3% cultivated crop, 5.0% urban developed, 54.7% herbaceous, and 11.5% forested, while the urban watershed was comprised of 2.8% cultivated crop, 83.4% urban developed, 11.1% herbaceous, and 1.2% forested. Lastly, the agricultural watershed was comprised of 59.5% cultivated crop, 4.3% urban developed, 23.4% herbaceous, and 8.0% forested.

Each of the subwatersheds were located in the Salt Creek watershed (HUC 10200203) (USGS, 2018). The 0.45 km^2 urban lake had a drainage area of 7.4 km^2, predominantly from Antelope Creek. Hickman Branch drained a 33.9 km^2 watershed flowing into the agricultural lake (1.3 km^2), while the herbaceous lake was the largest of the three study sites with an area of 3.0 km^2 with the main source of water from Middle Creek with a drainage area of 70.3 km^2. Lake depths varied with the herbaceous lake having an average depth of ~3.7 m and a maximum depth of 5.5 m, the agricultural lake having an average depth of ~4.5 m and a maximum depth of 6.4 m, and the urban lake having an average depth of ~3 m and a maximum depth of 4.9 m (Nebraska Game & Parks Commission, 2020).

2.2. POCIS sampling

Concentrations measured in grab samples are dependent on sample timing and often result in samples missing peak flows and potentially the higher concentrations of pesticides (Noro et al., 2020). Passive samplers have been used to compliment grab sampling and provide a way to estimate time weighted average (TWA) concentrations at a given sampling point (Alvarez et al., 2004). Passive samplers, such as polar organic
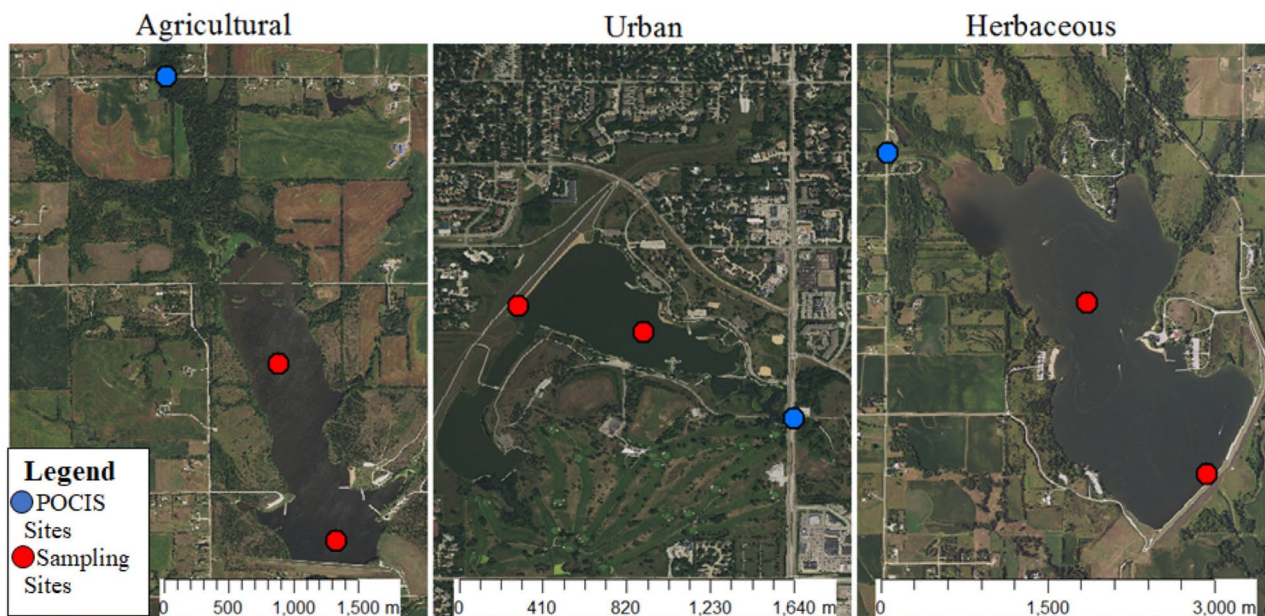
Fig. 1. Sampling locations for agricultural, urban, and herbaceous lakes. Blue dots represent locations where both grab samples and POCIS samples were collected.

chemical integrative samplers (POCIS), have been developed to trap and concentrate polar (water soluble) organic compounds from a moving water column (Alvarez et al., 2004). HLB-type (Hydrophilic-Lipophilic Balanced) POCIS were utilized for this study and placed at the inlet of each lake at the beginning of each sampling period in the center of the contributing stream (**Fig. 1**). Oasis HLB sorbent contained within two polyethersulfone filter membranes were deployed in a flow-through canister during the sampling period to compare with grab sample results. Unlike grab samples, POCIS samplers are deployed for longer periods of time, which allows for accumulation of analytes and provides an average concentration of pesticides entering each lake rather than a snapshot concentration (Alvarez et al., 2008).

POCIS were deployed at the beginning of six month long monitoring periods starting on April 25th, 2018. At the end of each period, the cages and membranes were replaced at each POCIS monitoring site. The final sampling period was completed on October 26th, 2018. POCIS were deployed to determine monthly concentrations of pesticides entering the waterbodies. Use of POCIS enabled determination of the average time-weighted concentrations of each individual pesticide detected.

Concentrations were then used with runoff volume estimates to calculate the total load of individual pesticides entering the monitored lake during each sampling period.

2.3. Grab samples

At the beginning of each sampling period, grab samples were taken at the POCIS deployment locations and from two additional locations within the lakes (Fig. 1). Samples were collected in 500-mL amber glass bottles, at approximately 15 cm below the air/water interface. The samples were transported on ice to the Nebraska Water Sciences Laboratory (Lincoln, NE), where they were stored frozen (–20 °C) until processing and analysis.

2.4. Pesticide extraction

Extraction, instrumental conditions, and validation results for pesticide analysis are provided in the supplementary materials and based on previously developed methods (Snow et al., 2020). Briefly, grabwater samples were divided into 100-mL portions, spiked with 50 ng of nitenpyram (surrogate), and extracted using preconditioned 200-mg Oasis HLB solid phase extraction (SPE) cartridges (Waters Corporation, MA, USA). Each SPE cartridge was preconditioned using 5 mL methanol followed by 5 mL ASTM Type I organic free reagent water. Each sample was slowly filtered under vacuum through a 25-mm pre-combusted 1-µm glass fiber filter in tandem with the SPE cartridge at a flow rate of 3–5 mL/min. After sample extraction, the cartridge was rinsed with 5 mL DI water and the analytes eluted with 4 mL of high purity methanol followed by 4 mL of acetonitrile (Optima, Fisher Scientific, St. Louis, MO). Eluate was concentrated by evaporation to near dryness under nitrogen gas and spiked with 50 ng stable isotope labelled internal standards (clothianidin-d3, imidacloprid-d4, metalaxyl-d6, thiamethoxam-d3, pyraclostrobin-d3). Residue was reconstituted with a mixture of 75% purified organic free reagent water (Nanopure, Thermo-Fisher, St. Louis, MO) and 25% methanol and transferred to an autosampler vial equipped with a salinized glass insert.

POCIS were removed from the deployment canister after retrieval, labelled and wrapped in aluminum foil and stored frozen until processing.

During processing, POCIS were brought to room temperature, disassembled and the HLB polymeric sorbent carefully transferred by rinsing with purified reagent water to silane-treated glass chromatography columns containing a plug of glass wool. After draining the water, three 20 mL portions of reagent grade acetonitrile were used to slowly extract and elute organic compounds from the sorbent into RapidVap tubes (Labconco, Kansas City, MO). The POCIS extracts were then spiked with nitenpyram surrogate and then evaporated under dry nitrogen at 40 °C to approximately 5 mL. The concentrated extract was then quantitatively transferred by rinsing with acetonitrile to a 10 mL borosilicate glass tubes, spiked with labelled internal standards listed above, and completely evaporated under dry nitrogen. Final residue was dissolved in 50 μL high purity methanol and mixed with 200 μL purified (distilled deionized, organic free) reagent water, transferred to a silane treated insert and autosampler vial, and analyzed for neonicotinoid insecticides and organophosphate insecticides, as well as strobilurin and acylamino acid fungicides, as described below.

2.5. Instrumentation

Quantification of target pesticides in POCIS and grab samples were performed by isotope-dilution using liquid chromatography tandem mass spectrometry (LC-MS-MS) at the University of Nebraska-Lincoln (UNL) Water Sciences Laboratory. Instrumentation used for this method was a Waters Quattro Micro triple quadrupole mass spectrometer with a Quattro-Micro API Mass Spectrometer (Waters Corporation, Milford, MA). Ionization was performed in the positive ion mode using atmospheric pressure chemical ionization (APCI). Tandem mass spectrometry was used for identification and quantitation. A pseudo-molecular ion $[M+H]^+$ was selected as the parent ion for fragmentation, and the corresponding fragment ion(s) was selected for identification and quantitation (**Table S1**). Instrument detection limits (POCIS = 0.2 ng, Grab = 0.01 μg/L) were determined by repeated injection of the lowest standard (3 × standard deviation) and method detection limit using 8–10 replicates of a fortified low-level blank (US EPA, 1986). Quality controls analyzed

with the grab samples and POCIS extracts included a laboratory reagent blank, fortified blank, laboratory duplicate and fortified matrix sample each processed and analyzed at a rate of not less than 5% of the field samples (1 in 20).

2.6. POCIS ambient water concentrations

Analysis of POCIS extracts provided a mass of each measured analyte per sampler. Recovered mass was converted using experimentally determined uptake rates for each evaluated analyte to determine time-weighted average concentrations (Equation (1)).

$$C_w = \frac{N}{R_s t} \qquad \text{(Eq. 1)}$$

where C_w was the ambient chemical concentration (ng/L), N was the mass accumulation in ng, R_s was the previously experimentally determined uptake rates for POCIS (L/d) (Noro et al., 2020; Ahrens et al., 2015), and t was the exposure time (sampling period, d).

2.7. Estimated loads

To estimate the flux or mass loading of pesticides entering the recreational lakes during the sampling periods, discharge was required. Unfortunately stream gages were absent along the evaluated streams of this study; therefore, the Soil Conservation Service Curve Number (SCSCN) method (Soulis and Valiantzas, 2012) was applied with the goal of calculating approximate runoff into each lake. Though there is uncertainty in assuming all runoff reached the watershed outlet, applying a complex uncalibrated hydrological model yields high uncertainty as well. For 11 watersheds in Nebraska, Van Liew and Mittelstet (2019) created models using the Soil and Water Assessment Tool (SWAT). The Nash-Sutcliffe Efficiency for the default SWAT models ranged from –5.69 to 0.69 with an average of –1.44 thus yielding poor results. The results improved significantly after models were calibrated with NSE values ranging from 0.51 to 0.84 with an average of 0.72. Therefore, applying uncalibrated complex hydrological models to a watershed may yield just as much or more uncertainty than a simple runoff method such as the curve number.

Runoff was computed using a combination of Equations (2)–(6). Equations (2) and (3) use CN (II) in order to calculate the wet or dry antecedent curve number (Boughton, 1989).

$$CN(I) = \frac{CN(II)}{2.334 - 0.01334*CN(II)} \qquad \text{(Eq. 2)}$$

$$CN(III) = \frac{CN(II)}{0.4036 + 0.0059*CN(II)} \qquad \text{(Eq. 3)}$$

$$S = \frac{1000}{CN} - 10 \qquad \text{(Eq. 4)}$$

$$Q = \frac{(P - 0.2S)^2}{(P + 0.8S)} \qquad \text{(Eq. 5)}$$

$$V = QA \qquad \text{(Eq. 6)}$$

where, CN (I) is the curve number for dry antecedent conditions (unit-less), CN (III) is the curve number for wet antecedent conditions (unit-less), CN (II) is the average curve number (unit-less) determined from available tables and charts (USDA, 1986), S is the potential maximum retention (unit-less), P was the rainfall (mm), Q is the runoff depth (mm), A was area (ha), and V is the volume of runoff (ha-mm).

Data from the High Plains Regional Climate Center were utilized to estimate precipitation during each rainfall event during the study (High Plains Regional Climate Center CLIMOD) (**Table S2**). The average precipitation was calculated from the four available rain gauge stations in the herbaceous (MALCOLM 0.3 SSE, PLEASANT DALE 2.5 NNW, RAYMOND 7.3 WNW, SEWARD 4.7 NE) and agricultural watersheds (HICKMAN 1.8 NNE, ROCA 5.0 NNE, LINCOLN 5.8 SSE, LINCOLN 7.7 SSE). However, for the urban watershed, only two rain gauge stations were within the watershed (LINCOLN 1.8 SE, LINCOLN 4.5 SE).

A rainfall event was determined to be any amount of rainfall; however, if the sum of the rainfall event was less than 20% of S, there was no runoff (Soulis and Valiantzas, 2012). Since each watershed consisted of multiple land uses and soil types, a weighted CN (CN (II)) was calculated (**Table S3**). CN (II) was then adjusted based on the antecedent moisture conditions at the time of a precipitation event. CN (I) was used for dry

conditions and CN (III) for saturated conditions. If there were five days or less between rainfall events, CN (III) was used, while periods with more than five days between rainfall events CN (I) was used for dry conditions, similar to past studies (Boughton, 1989). The limit of five days was chosen under the assumption that the vadose zone would drain during that period based on the local geology.

2.8. Pesticide dissipation rate

Assuming dilution and evaporation effects are negligible between seasonal runoff and pesticide loading events, decreases in reservoir concentrations can be used to estimate persistence through modeling dissipation rates. Pesticide dissipation from aquatic systems is a function of chemical and biological transformation, volatilization, sorption, and other processes that remove a contaminant from a closed system. First-order dissipation rate constants (k) were estimated from the slope of the natural log of concentration change (C/C) versus time (t) via the following equation:

$$k = -\frac{\ln \frac{C}{C}}{t} \qquad \text{(Eq. 7)}$$

Reservoir dissipation half-life ($t_{1/2}$) was calculated from the rate constant (k) by the equation:

$$t_{1/2} = \frac{ln2}{k} \approx \frac{0.693}{k} \qquad \text{(Eq. 8)}$$

The dissipation half-life represents a maximum for each lake since additional pesticide laden runoff inputs and lake evaporation would result in longer half-lives.

2.9. Statistics

All pesticide data was normalized by log transformation and analyzed using one-way analysis of variance (ANOVA) with posthoc Tukey honest significance difference (HSD). This was completed to identify statistical differences between sample periods, individual pesticides, sampling method, and/or watersheds. All statistical analyses were completed in Minitab 17 (Minitab 17 Statistical Software, 2010).

3. Results and discussion

3.1. Mean pesticide concentrations

Both POCIS and grab samples were analyzed for the twelve pesticides. Four of the target pesticides, picoxystrobin, pyraclostrobin, thiacloprid, and trifloxystrobin, were not detected (<0.2 ng/ POCIS) in any of the POCIS extracts. Additionally, thiacloprid and trifloxystrobin were below the detection limit (0.005 μg/L) in all grab samples. The frequency of detection for each pesticide from POCIS and grab samples at the inlet sampling sites were summarized (**Fig. 2**). Azoxystrobin, clothianidin, and imidacloprid were detected most frequently for both sampling methods at all locations; however, concentrations were significantly different depending on land use and sampling method (**Fig. 3**; α = 0.05).
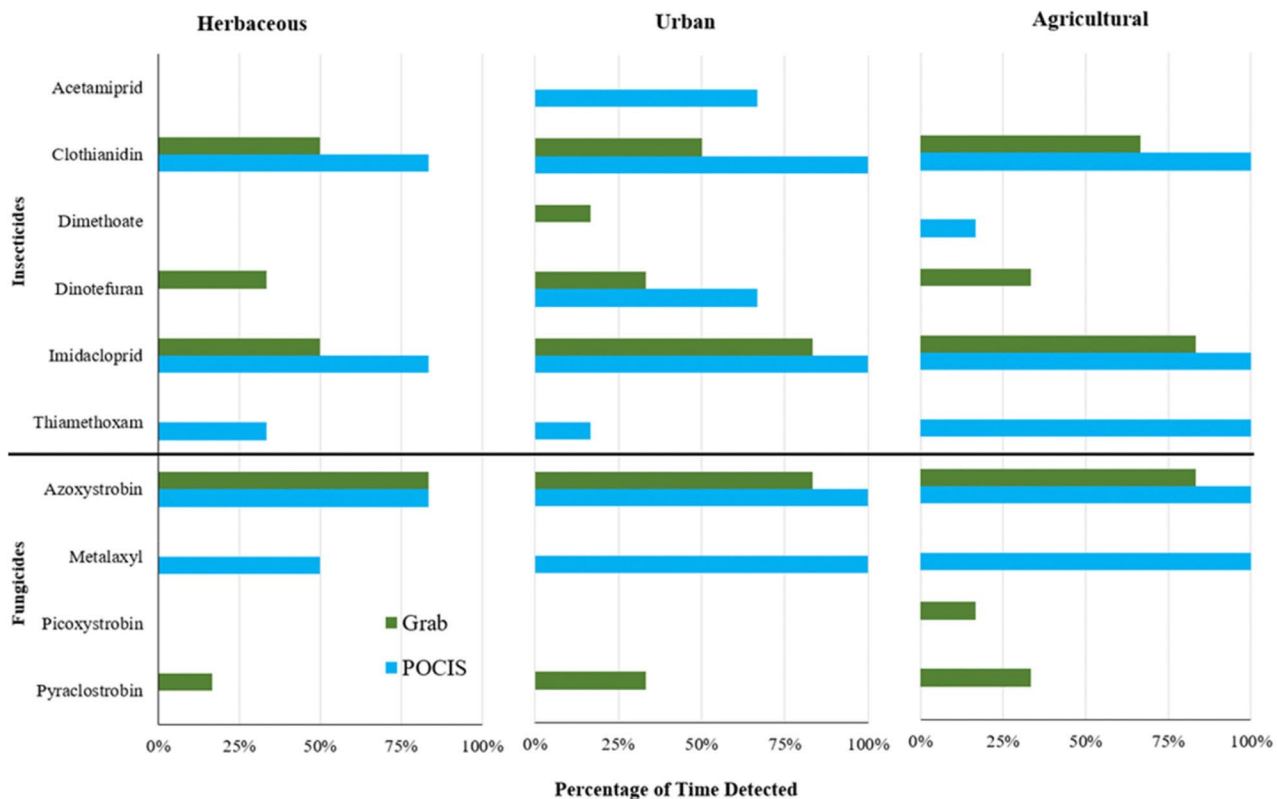
Fig. 2. Percentage of samples with pesticide concentrations above detection limit at the lake inlets for grab and POCIS samples.
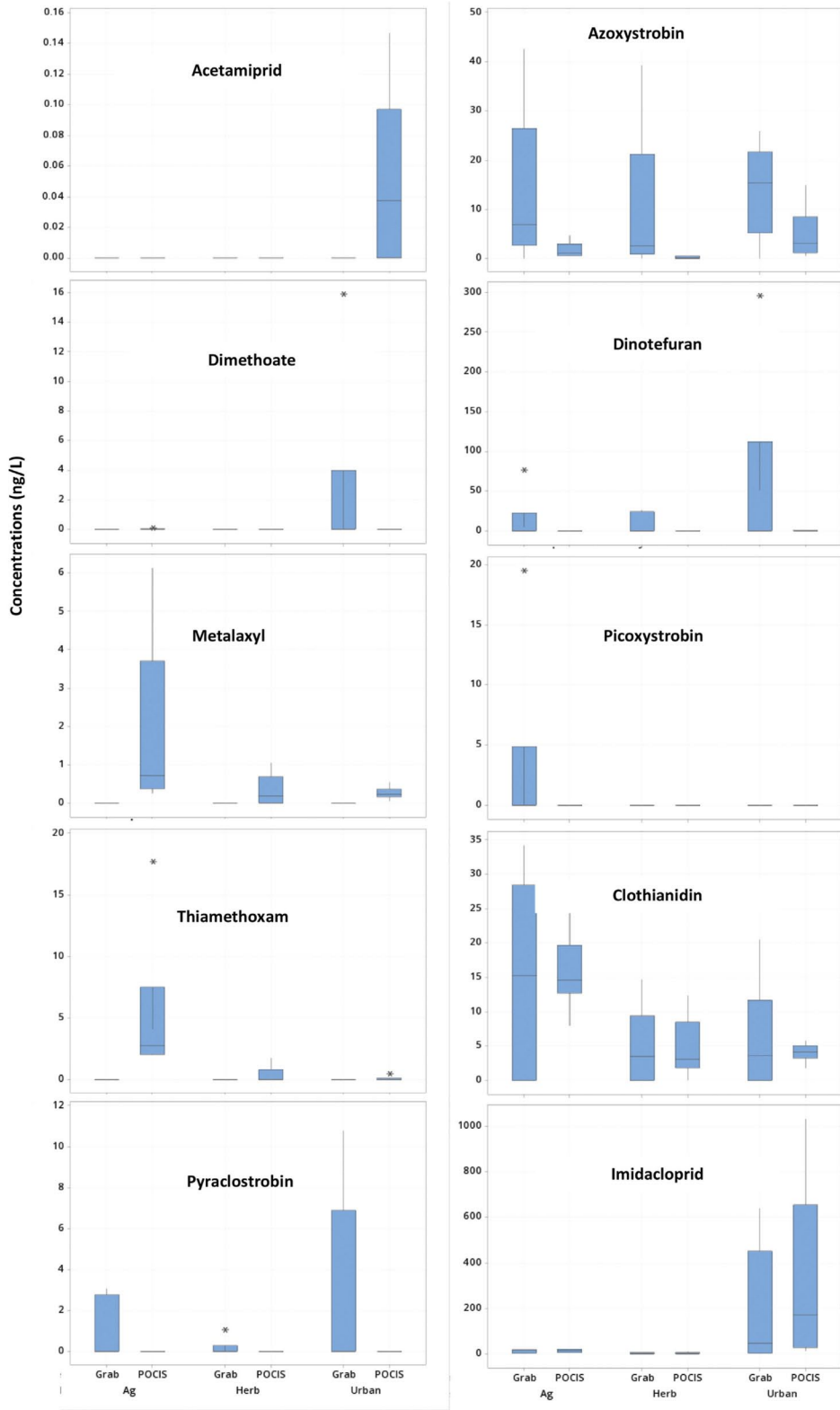
Fig. 3. Box plots for all pesticide concentrations throughout the study period for the agricultural (Ag), herbaceous (Herb) and urban watersheds at the lake inlets.

Significantly higher pesticide concentrations were observed in the urban watershed compared to the other two watersheds, particularly for imidacloprid (α = 0.05). Biocides, which can be chemically identical to a pesticide, are defined in Europe as pesticides used for non-plant protection purposes (i.e., domestic pets), with the regulation of pesticides and biocides being substantially different (Wittmer et al., 2011; McKnight et al., 2015). While agricultural usage of pesticides is highly regulated in both the U.S. and Europe (i.e., application amount, application timing), the domestic usage of biocides is minimally regulated in comparison.

Directly upstream to the urban lake was a dog park and next to the urban lake there was a golf course. Imidacloprid is used in flea prevention treatment for dogs, rapidly metabolized, and excreted primarily through urine (Sheets, 2014). Further, imidacloprid is often used to protect trees and shrubs from the insect species such as emerald ash borer (Herms et al., 2014), grasshoppers, and weevils (Eagle, 2014) and is commonly used in the region for insect prevention on residential lawns and golf courses (Kalisch et al., 2010). Therefore, the high concentrations of imidacloprid was suspected to be from biocide usage in the predominately urban watershed from contributions of domestic animals, lawn and tree care, and golf course maintenance.

Comparing pesticide concentrations between varying geographical locations is challenging due to contrasts in watershed size and land use differences. However, three studies recently evaluated pesticide concentrations using similar methodology in waterbodies (Xiong et al., 2019; Metcalfe et al., 2019). Xiong et al. (2019) evaluated pesticides at 22 different sites along the Guangzhou reach of the Pearl River and its tributaries in Southern China during the growing season (November and December). The sites were adjacent to areas with both agricultural and residential land uses. Xiong et al. (2019) observed thiamethoxam concentrations of 53 ng/L from POCIS samples receiving runoff from agricultural areas draining vegetable crops, which were significantly higher in comparison to average concentrations of 5.2 ng/L observed in our study. However, imidacloprid concentrations were 249 ng/L in the Chinese residential (urban) system compared to similar average concentrations of 324 ng/L in our study. The differences in concentrations in the agricultural regions between Xiong et al. (2019) and our study were likely attributed to differences in pest management and regulatory

application requirements, specifically regulated agricultural usage of pesticides in the U.S.

Metcalfe et al. (2016) investigated six Canadian streams and classified the contributing watersheds based on forest, urban, and agricultural land uses. The number of golf courses was also evaluated in each of the six assessed watersheds to help determine pesticide loading source areas. POCIS were deployed in streams entering the lakes for approximately 33 days between September and October and tested for 22 pesticides. Of the 22 pesticides analyzed, only azoxystrobin was also assessed in our study, which was not detected in any of their samples. Similarly, Metcalfe et al. (2019) observed undetectable azoxystrobin concentrations in the Great Lakes region (Metcalfe et al., 2019).

Metcalfe et al. (2019) assessed the occurrence of 29 pesticides in watersheds during May and June, including eight of the same pesticides that were evaluated in our study. Like our study, Metcalfe et al. (2019) evaluated results from both POCIS and grab samples from the same locations. The study evaluated runoff inputs using data from 18 monitoring sites with land uses ranging from urban, wetland, pasture, orchards, etc. and watershed areas varying from 1900 to 671,200 ha. In comparison to our study, Metcalfe et al. (2019) often reported higher grab sample concentrations compared to POCIS time-weighted averages. **Table S4** summarizes comparisons between these maximum concentrations observed in this study and Metcalfe et al. (2019) using the two sampling methods (POCIS and grab sampling).

3.2. Ecotoxicity concerns

Chronic toxicity occurs when an organism is exposed to a contaminant over a long period of time, while acute toxicity occurs from a single exposure over a short duration (**Table S5**) (United States Environment, 2016). Neonicotinoids have been reported to affect non-targeted aquatic invertebrates, which negatively impact aquatic food webs (Gibbons et al., 2015). Pesticide concentrations exceeding acute aquatic toxicity benchmarks for aquatic invertebrates were observed only for imidacloprid in the urban lake during the third and fourth periods (Fig. 4). Similarly, chronic aquatic toxicity benchmarks for aquatic invertebrates were observed for imidacloprid in the urban lake for every sampling period and in the agricultural lake in second through fifth sampling periods for the
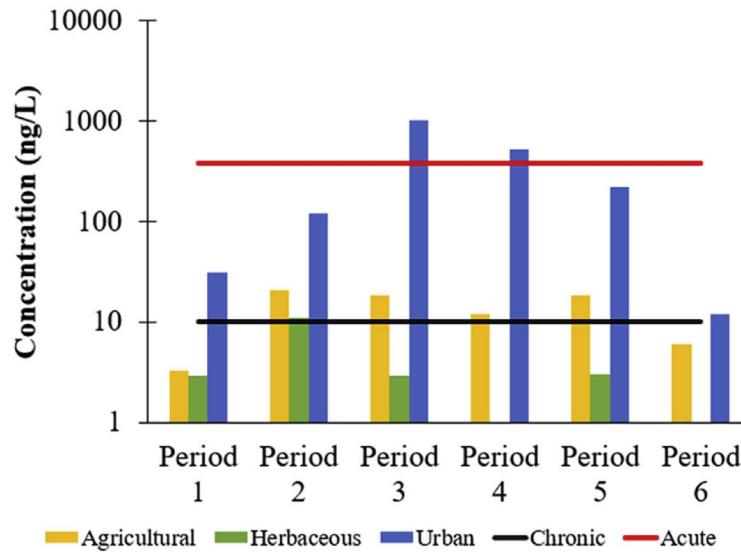
Fig. 4. Imidacloprid POCIS concentrations at each lake throughout the length of the experiment. * POCIS membranes for the herbaceous lake were not viable due to storage complications during Period 4. The red and black lines represent acute and chronic aquatic invertebrate toxicity, respectively.

POCIS samples (Fig. 4). While clothianidin and thiamethoxam at the agricultural site displayed the highest concentrations, they remained well below the chronic and acute toxicity limits for both pesticides (**Figs. 4 and 5A**). In comparison, Metcalfe et al. (2019) observed toxicity limit exceedances for imidacloprid, thiamethoxam, and clothianidin in the Great Lakes region.

Similar pesticide concentration trends were observed from the grab samples (**Fig. 5**B). Since thiamethoxam was not detected at any of the inlet grab samples, Fig. 5B only compares clothianidin and imidacloprid between the three watersheds. Like the result from POCIS samples, imidacloprid concentrations in grab samples exceeded chronic toxicity limits in both the agricultural and urban sites. Similar to the POCIS samples, clothianidin concentrations at each inlet fell below toxicity limits.

Williams and Sweetman (2018), who evaluated pesticide concentrations in 40 wetlands in west central Minnesota near agricultural landscapes, reported similar findings to our study, where grab samples were collected in April, May, and June. However, Williams and Sweetmans'
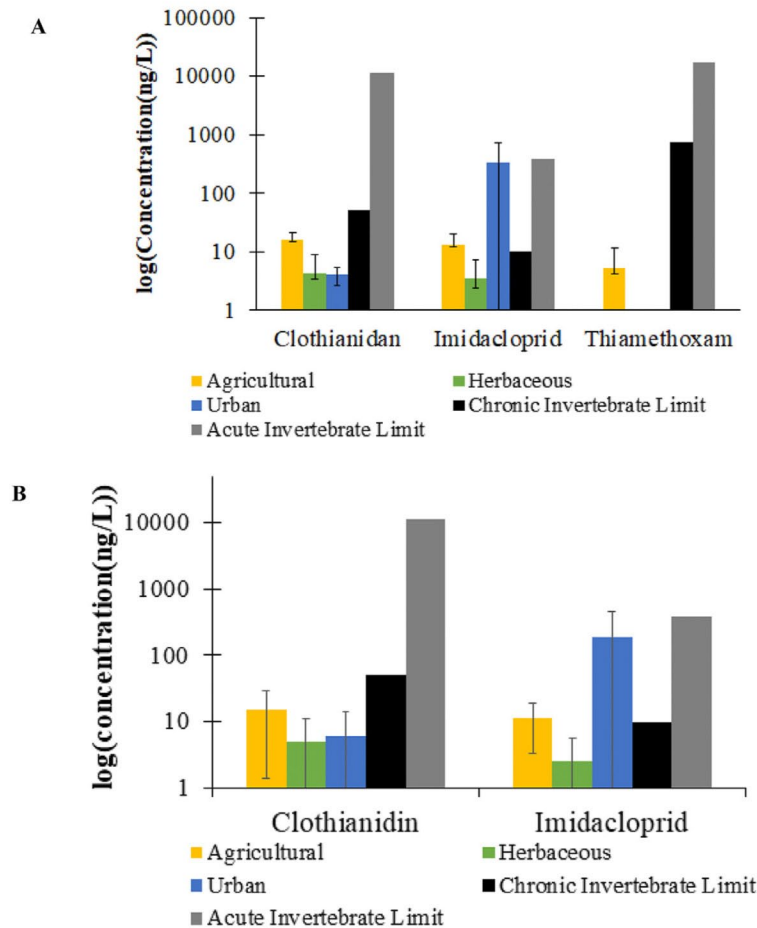
Fig. 5. (A) POCIS pesticide concentrations averaged over the six sampling periods at each lake. Chronic and acute aquatic invertebrate limits were added for comparison. Error bars represent the standard deviation of the means for each pesticide within each watershed. (B) Average inlet grab concentrations for the six sampling periods at each lake. Chronic and acute invertebrate limits were added for comparison. Error bars represent the standard deviation of the means for each pesticide within each watershed. * Note imidacloprid is the only pesticide to exceed toxicity limits for this study.

(2018) study sites ranged from 1 to 10 ha, while we evaluated 530–6880 ha watersheds. Average clothianidin, imidacloprid, and thiamethoxam were found to be similar to concentrations in our study with observed agricultural concentrations of 8.6, 13.1, and 10.6 ng/L respectively (Williams and Sweetman, 2018), while we observed concentrations of 25.7, 16.4, and 8.9 ng/L, respectively.

3.3. Comparison of POCIS and grab samples

POCIS are widely used as a monitoring tool for a wide variety of water-soluble organic contaminants such as modern insecticides and fungicides. Estimation of representative time weighted average concentrations using these samplers is dependent on a variety of environmental, chemical, and physical factors (Alvarez et al., 2004). There are considerable variations in reported experimentally determined uptake rates for some compounds that may due to differences in calibration design, water temperature, and flow rates (Harman et al., 2012). Differences between average grab sample chemical concentrations and POCIS-determined time weighted average may be due to fluctuations in water temperature, flow rates, dissolved solids content, pH, and membrane fouling and these effects may be compound-dependent (Harman et al., 2012). On the other hand, mean concentrations estimated from too few grab samples collected during a synoptic run-off event grab samples may overestimate or underestimate actual chemical loading in a stream from incomplete sampling of a rapidly changing concentration profile.

The two sampling methods (POCIS vs. grab) showed similar trends; however, there were some differences between the pesticides detected. As mentioned above, picoxystrobin and pyraclostrobin were both detected in the grab samples but not in the POCIS samples. These pesticides have low uptake rates to the POCIS membranes compared to neonicotinoid compounds. Further, grab sampling can miss important pesticide pulses that may be measured using POCIS sampling. For example, thiamethoxam grab samples at the inlet vs. the POCIS samples (Fig. 3) varied between each site. Further, while POCIS sampling was more costly, samples overall better represent pesticide concentrations entering a waterbody through time(Sellin et al., 2009; Jaimes-Correa et al., 2015). For example, POCIS samples detected thiamethoxam while the inlet grab samples did not. Differences in reported uptake rates for specific compounds such as picoxystrobin noted earlier are likely due to a variety of factors, including design of uptake experiment and affinity for sorbent (Alvarez et al., 2008; Harman et al., 2012). Because complete sampling of rapidly changing concentrations in stream runoff is also quite difficult and costly, use of POCIS should be considered complementary to grab sampling and their limitations considered when evaluating the results.

3.4. Occurrence and persistence of pesticides entering recreational lakes

Pesticide concentrations occurring in these lakes were assessed between sampling periods and throughout the lakes to gain an improved understanding of pesticide transport and persistence within these systems. For example, imidacloprid exceeded acute and chronic invertebrate levels in 11% and 61% of the POCIS sampling periods, respectively (Fig. 4). However, as already discussed, the higher concentrations and occurrences of specifically imidacloprid was likely due to biocide usage.

Imidacloprid TWA concentrations observed during July (Period 3) had significantly greater imidacloprid concentrations then the lowest concentrations collected in October (Period 6; α = 0.05). Similarly, clothianidin TWA concentrations were highest in July (Period 3) and significantly lower in October (Period 6; α = 0.05). Acetamiprid and azoxystrobin TWA concentrations were highest in August (Period 4), while metalaxyl concentrations were highest in June (Period 2) in the urban lake. In contrast, the lake receiving runoff from the agriculturally watershed had azoxystrobin TWA concentrations highest in October (Period 6), while metalaxyl was highest in July (Period 3). See supplementary materials for a full list of statistical significances (**Tables S6–S13**). There are few comparative studies of application timing of these specific pesticides (Elliott and VanderMeulen, 2016; Metcalfe et al., 2016; 2019; Fernandez-Cornejo et al., 2014). However, our observations validate the need for further field-scale studies on the occurrence, persistence, and ecological impact of these pesticides in recreational lakes (Spalding et al., 2003; Stammet al., 2013).

Pesticide transport from the lakes' inlets to outlets was also evaluated to assess transport and persistence of each pesticide. **Fig. S2** illustrates pesticide concentrations at each of the nine grab sampling locations. Slight trends were observed for clothianidin and imidacloprid at the agricultural site throughout the entire study period (April [Period 1] through October [Period 6]); the pesticide concentrations appeared to change slowly over time. The lake inlets peaked in the middle of the growing season (Periods 3 [July] and 4 [August]), while the middle of the lakes and outlets increased throughout the end of the growing season (Periods 5 [September] and 6 [October]) in all three lakes. Note that before the growing season application and spring flush, agricultural pesticides were not observed in the middle or outlet of the lakes.

Of the three insecticides presented in Fig. S2, only clothiandin and imidacloprid grab sample concentrations varied based on location within the lake (inlet, middle, outlet). Clothiandan concentrations from grab samples in the agricultural watershed were highest at the middle and outlet of the lake in September (Period 5) and October (Period 6) and lowest in May (Period 1) and June (Period 2), with significant differences between September (Period 5) and October (Period 6) compared to April (Period 1) and May (Period 2) ($\alpha = 0.05$). In contrast, imidacloprid concentrations from grab samples at the urban watershed had higher concentrations at all locations in the lake during July (Period 3) and similar values in August (Period 4). However, inlet concentrations began to decline in September (Period 5) and October (Period 6), while they remained constant at the middle and outlet of the lakes throughout the end of the growing season. The lowest imidacloprid concentrations were measured in May (Period 1) and June (Period 2) at the urban lake at all locations within the waterbody.

Thiamethoxam concentrations in grab samples exhibited no trends at any of the sites and was not detected at the inlet during any of the monitoring periods. It is hypothesized that a golf course, located next to the lake at the urban site, was the primary source of thiamethoxam, which would bypass the inlet and go directly into the lake as runoff. Another potential explanation is that thiamethoxam is known to photolyse into clothianidin, which could have led to higher observed concentrations of clothiandin in the urban lake(Nauen et al., 2003). Lastly, park management may have applied pesticides around the edges of lakes, likely directly introducing them to the water.

Reductions in pesticide concentrations in the lakes were attributed to dilution and/or degradation (Spalding et al., 1994). Therefore, dissipation rate constants and half-lives were estimated for pesticides using apparent peaks followed by decreases in concentrations through time at grab sample lake locations. First order dissipation rates and half-lives were calculated using equations (7) and (8).

The best agreements were for clothianidin, imidacloprid, and pyraclostrobin in the agricultural lake inlet sampling location, while imidacloprid, pyraclostrobin, and metalaxyl had the best agreements in the urban lake at both the inlet and middle of the lake ($r^2 = 0.98$ (middle), 0.86 (inlet); 0.78 (middle), 0.78 (inlet); 0.98 (middle), 0.83(inlet), respectively). Dissipation rates and half-lives can be found in **Table 1** and

Table 1 Average estimated half-lives in days using pseudo first order reaction kinetics with published water and soil half-lives (days). Values in parentheses indicates linear least squares coefficient of determination (r^2).

Pesticide	Urban Inlet	Urban Middle	Agricultural Inlet	Water Half-Lives	Soil Half-Lives
Imidacloprid	15 (0.86)	53 (0.98)	14 (0.62)	2 (Phong et al., 2009)	36–116 (Mahapatra et al., 2017)
Metalaxyl	46 (0.83)	37 (0.98)	N/A	0.1–0.25 (Topalov et al., 1999)	36-73 (Sukul and Spiteller, 2001)
Clothianidin	N/A	N/A	46 (0.93)	15 - 19 (Mulligan et al., 2016)	90 - 280 (Li et al., 2018)
Pyraclostrobin	11 (0.79)	12 (0.78)	15 (0.71)	7–12 (Guo et al., 2017)	13 - 17 (Zhang et al., 2012)

are compared to previously reported soil half-lives and water half-lives in other field and laboratory studies.

Half-lives observed in our study were longer for imidacloprid, metalaxyl, and clothianidin compared to aquatic half-lives likely due to most aquatic half-lives using photolysis experiments in the laboratory. However, the aquatic half-lives reported for pyraclostrobin were observed in field-scale paddy water and were similar to our observed half-lives in the lakes. Overall, these pesticides appear to be persistent, particularly in the middle of the lake, where dilution would be minimal compared to the inlet. Further research is needed to monitor the persistence of the pesticides throughout the year and for multiple years.

3.5. Watershed pesticide contributions into lakes

Pesticide loads entering each lake was estimated for the eight pesticides with the highest concentrations for each watershed (**Fig. 6**). Strictly assessing pesticide load, the agricultural watershed contributed the most azoxystrobin, clothianidin, and thiamethoxam. However, if watershed areas were considered to normalize the dataset, the urban watershed delivered the largest pesticide load per unit area. This was due to the herbaceous watershed being nearly ten times the size of the urban watershed and two times larger than the agricultural watershed. Overall, the urban watershed was the primary pesticide contributor per unit area. We hypothesize that this is likely due to limited pesticide outreach programs for homeowners regarding ideal timing and quantity of biocide applications along with absent regulations for pesticide applications in nonagricultural areas.
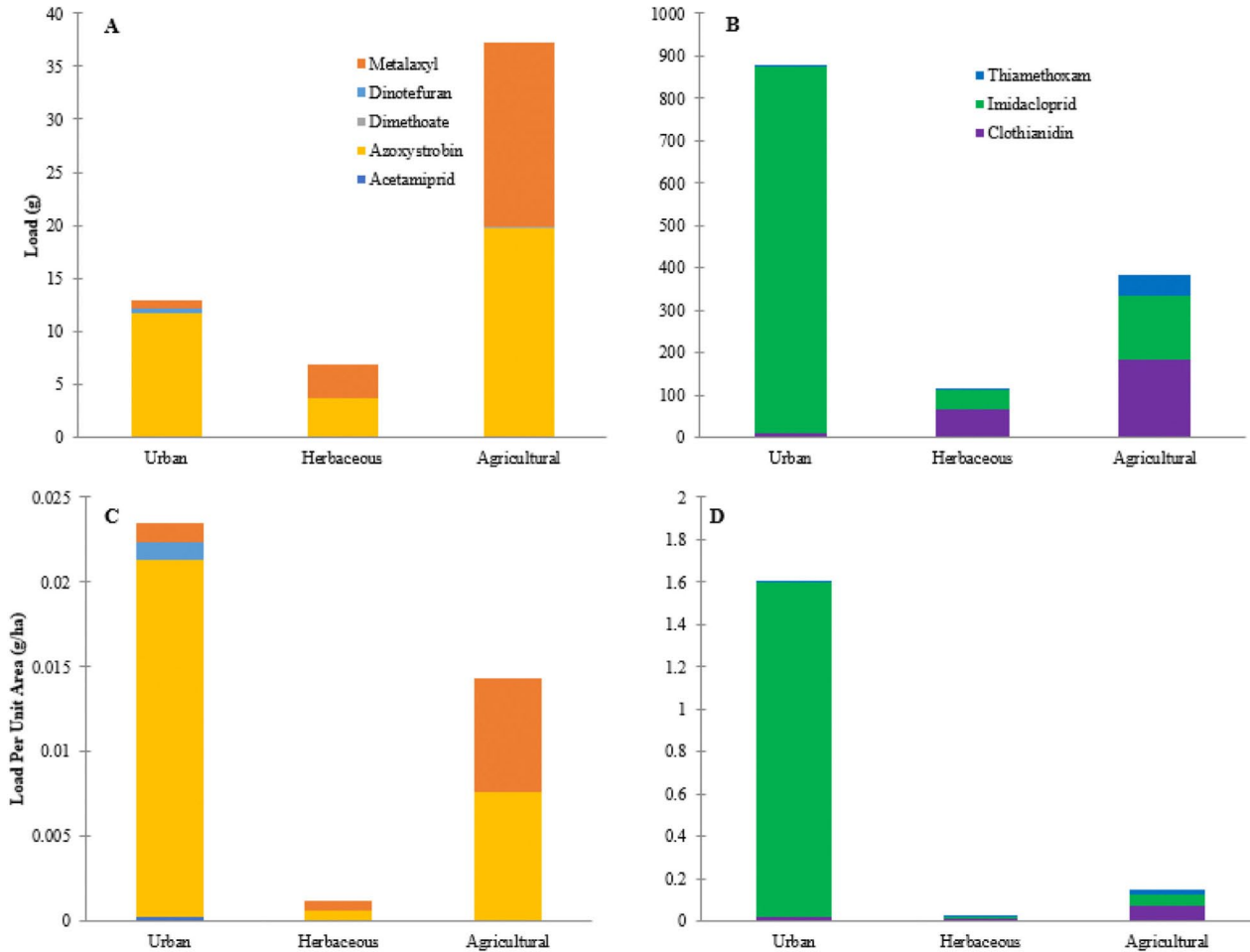
Fig. 6. Comparison of pesticide load and watershed size for each lake. A and B) Total load of pesticides entering each lake. C and D) Total load entering each lake divided by the respective watershed size. *Note scales and units.

4. Conclusions

Findings of this study provide a novel investigation of pesticides entering and residing in recreational lakes and increase the overall knowledge of their fate and transport in these ecosystems. Imidacloprid concentrations were observed at levels exceeding ecotoxicity limits for aquatic invertebrates, specifically in the recreational lake receiving predominately urban runoff. Pesticides were persistent within recreational lakes throughout the growing season. Our findings reiterate the importance of varying sampling techniques as well as replicate samples

in order to provide a holistic image of fate, transport, and persistence of pesticides in lakes. Further, our findings emphasize the importance of implementing and/or expanding biocide education outreach and exploring stricter biocide usage regulations. Future research is needed to identify pesticide concentrations latitudinally and their long-term persistence and fate in recreational lakes to improve mitigation efforts for lake managers.

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Abbreviations

CN (I)	Curve Number for dry conditions
CN (II)	Curve Number for average conditions
CN (III)	Curve Number for wet conditions
HLB	Hydrophilic-Lipophilic-Balanced
POCIS	Polar Organic Integrative Sampler
TWA	Time Weighted Average
USGS	United States Geological Survey
USEPA	United States Environmental Protection Agency

References

Ahrens, L., Daneshvar, A., Lau, A.E., Kreuger, J., 2015. Characterization of five passive sampling devices for monitoring of pesticides in water. J. Chromatogr. A 1405, 1–11. https://doi.org/10.1016/j.chroma.2015.05.044

Alvarez, D.A., Cranor, W.L., Perkins, S.D., Clark, R.C., Smith, S.B., 2008. Chemical and toxicologic assessment of organic contaminants in surface water using passive samplers. J. Environ. Qual. 37 (3), 1024–1033. https://doi.org/10.2134/jeq2006.0463

Alvarez, D.A., et al., 2004. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ. Toxicol. Chem. 23 (7), 1640–1648. https://doi.org/10.1897/03-603

Anderson, J.C., Dubetz, C., Palace, V.P., 2015. Neonicotinoids in the Canadian aquatic environment: a literature review on current use products with a focus on fate, exposure, and biological effects. Sci. Total Environ. 505, 409–422. https://doi.org/10.1016/j.scitotenv.2014.09.090

Bartlett, D.W., Clough, J.M., Godwin, J.R., Hall, A.A., Hamer, M., Parr-Dobrzanski, B., 2002. The strobilurin fungicides. Pest Manag. Sci. 58 (7), 649–662. https://doi.org/10.1002/ps.520

Beketov, M.A., Liess, M., 2008. Potential of 11 pesticides to initiate downstream drift of stream macroinvertebrates. Arch. Environ. Contam. Toxicol. 55 (2), 247–253. https://doi.org/10.1007/s00244-007-9104-3

Belden, J., McMurry, S., Smith, L., Reilley, P., 2010. Acute toxicity of fungicide formulations to amphibians at environmentally relevant concentrations. Environ. Toxicol. Chem. 29 (11), 2477–2480. https://doi.org/10.1002/etc.297

Boughton, W.C., 1989. A review of the USDA SCS curve number method. Soil Water Manag. Conserv. 13.

Desneux, N., Decourtye, A., Delpuech, J.-M., 2006. The sublethal effects of pesticides on beneficial arthropods. Annu. Rev. Entomol. 52 (1), 81–106. https://doi.org/10.1146/annurev.ento.52.110405.091440

Eagle, V., 2014. Amended Label Adding Pollinator Protection Language, Washington.

Elliott, S.M., VanderMeulen, D.D., 2016. A regional assessment of chemicals of concern in surface waters of four Midwestern United States national parks. Sci. Total Environ. 579, 1726–1735. https://doi.org/10.1016/j.scitotenv.2016.11.114

European Commission, 2018. Legislation 132. Off. Journal Eur. Union 61.

Fernandez-Cornejo, J., Nehring, R., Osteen, C., Wechsler, S., Martin, A., Vialou, A., 2014. Pesticide Use in U.S. Agriculture : 21 Selected Crops, 1960-2008.

Gibbons, D., Morrissey, C., Mineau, P., 2015. A review of the direct and indirect effects of neonicotinoids and fipronil on vertebrate wildlife. Environ. Sci. Pollut. Res. 22 (1), 103–118. https://doi.org/10.1007/s11356-014-3180-5

Grube, A., Donaldson, D., Kiely, T., Wu, L., 2011. Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates.

Guo, X., et al., 2017. Residue dynamics and risk assessment of pyraclostrobin in rice, plants, hulls, field soil, and paddy water. Hum. Ecol. Risk Assess. 23 (1), 67–81. https://doi.org/10.1080/10807039.2016.1222579

Hansen, S.P., Messer, T.L., Mittelstet, A.R., 2019. Mitigating the risk of atrazine exposure: identifying hot spots and hot times in surface waters across Nebraska, USA. J. Environ. Manage. 250 (August), 109424. https://doi.org/10.1016/j.jenvman.2019.109424

Harman, C., Allan, I.J., Vermeirssen, E.L.M., 2012. Calibration and use of the polar organic chemical integrative sampler-a critical review. Environ. Toxicol. Chem. 31 (12), 2724–2738. https://doi.org/10.1002/etc.2011

Herms, D., McCullough, D.G., Smitley, D.R., Clifford, C.S., Cranshaw, W., 2014. Insecticide Options for Protecting Ash Trees from Emerald Ash Borer Insecticide, second ed. North Cent. Cent. Bull., pp. 1–16

High Plains Regional Climate Center CLIMOD. https://hprcc.unl.edu/index.php

Jaimes-Correa, J.C., Snow, D.D., Bartelt-Hunt, S.L., 2015. Seasonal occurrence of antibiotics and a beta agonist in an agriculturally-intensive watershed. Environ. Pollut. 205, 87–96. https://doi.org/10.1016/j.envpol.2015.05.023

Kalisch, J.A., Associate-entomology, E., Baxendale, F.P., Specialist-entomology, E., 2010. Insect Borers of Shade Trees and Woody Ornamentals.

Li, Y., Su, P., Li, Y., Wen, K., Bi, G., Cox, M., 2018. Adsorption-desorption and degradation of insecticides clothianidin and thiamethoxam in agricultural soils. Chemosphere 207, 708–714. https://doi.org/10.1016/j.chemosphere.2018.05.139

Louis, L.M., et al., 2017. A prospective study of cancer risk among Agricultural Health Study farm spouses associated with personal use of organochlorine insecticides. Environ. Heal. A Glob. Access Sci. Source 16 (1), 1–11. https://doi.org/10.1186/s12940-017-0298-1

Mahapatra, B., et al., 2017. Effect of abiotic factors on degradation of imidacloprid. Bull. Environ. Contam. Toxicol. 99 (4), 475–480. https://doi.org/10.1007/s00128-017-2159-6

Main, A.R., Headley, J.V., Peru, K.M., Michel, N.L., Cessna, A.J., Morrissey, C.A., 2014. Widespread use and frequent detection of neonicotinoid insecticides in wetlands of Canada's prairie pothole region. PloS One 9 (3). https://doi.org/10.1371/journal.pone.0092821

McKnight, U.S., Rasmussen, J.J., Kronvang, B., Binning, P.J., Bjerg, P.L., 2015. Sources, occurrence and predicted aquatic impact of legacy and contemporary pesticides in streams. Environ. Pollut. 200, 64–76. https://doi.org/10.1016/j.envpol.2015.02.015

Metcalfe, C.D., et al., 2019. Pesticides related to land use in watersheds of the Great Lakes basin. Sci. Total Environ. 648, 681–692. https://doi.org/10.1016/j.scitotenv.2018.08.169

Metcalfe, C.D., Sultana, T., Li, H., Helm, P.A., 2016. Current-use pesticides in urban watersheds and receiving waters of western Lake Ontario measured using polar organic chemical integrative samplers (POCIS). J. Great Lake. Res. 42 (6), 1432–1442. https://doi.org/10.1016/j.jglr.2016.08.004

Mineau, P., Palmer, C., 2013. Neonicotinoid insecticides and birds the impact of the nation's most widely used insecticides on birds. Am. Bird Conserv. http://www.abcbirds.org/abcprograms/policy/toxins/Neonic_FINAL.pdf

Minitab 17 Statistical Software, 2010 [Online]. Available. Minitab, Inc., State College, PA. www.minitab.com

Mulligan, R.A., Redman, Z.C., Keener, M.R., Ball, D.B., Tjeerdema, R.S., 2016. Photodegradation of clothianidin under simulated California rice field conditions. Pest Manag. Sci. 72 (7), 1322–1327. https://doi.org/10.1002/ps.4150

Nauen, R., Ebbinghaus-Kintscher, U., Salgado, V.L., Kaussmann, M., 2003. Thiamethoxam is a neonicotinoid precursor converted to clothianidin in insects and plants. Pestic. Biochem. Physiol. 76 (2), 55–69. https://doi.org/10.1016/S0048-3575(03)00065-8

Nebraska Game & Parks Commission, 2020. Lake Contour Maps. https://maps.outdoornebraska.gov/lakemaps/

Noro, K., Endo, S., Shikano, Y., Banno, A., Yabuki, Y., 2020. Development and calibration of the polar organic chemical integrative sampler (POCIS) for neonicotinoid pesticides. Environ. Toxicol. Chem. (1) https://doi.org/10.1002/etc.4729

Phong, T.K., Nhung, D.T.T., Motobayashi, T., Thuyet, D.Q., Watanabe, H., 2009. Fate and transport of nursery-box-applied tricyclazole and imidacloprid in paddy fields. Water Air. Soil Pollut. 202 (1–4), 3–12. https://doi.org/10.1007/s11270-008-9953-z

Sellin, M.K., Snow, D.D., Schwarz, M., Carter, B.J., Kolok, A.S., 2009. Agrichemicals in Nebraska, USA, watersheds: occurrence and endocrine effects. Environ. Toxicol. Chem. 28 (11), 2443–2448. https://doi.org/10.1897/09-135.1

Sheets, L.P., 2014. Imidacloprid. Encycl. Toxicol 2, 1000–1003 third ed. https://doi.org/10.1016/B978-0-12-386454-3.00153-6

Snow, D.D., et al., 2020. Legacy and current pesticide residues in Syr Darya, Kazakhstan: contamination status, seasonal variation and preliminary ecological risk assessment. Water Res. 184, 116141. https://doi.org/10.1016/j.watres.2020.116141

Soulis, K.X., Valiantzas, J.D., 2012. SCS-CN parameter determination using rainfall runoff data in heterogeneous watersheds-the two-CN system approach. Hydrol. Earth Syst. Sci. 16 (3), 1001–1015. https://doi.org/10.5194/hess-16-1001-2012

Spalding, R.F., Snow, D.D., Cassada, D.A., Burbach, M.E., 1994. Study of pesticide occurrence in two closely spaced lakes in Northeastern Nebraska. J. Environ. Qual. 23, 571–578.

Spalding, R.F., Exner, M.E., Snow, D.D., Cassada, D.A., Burbach, M.E., Monson, S.J., 2003. Herbicides in ground water beneath Nebraska's management systems evaluation area. J. Environ. Qual. 32 (1), 92–99. http://digitalcommons.unl.edu/watercenterpubs/11

Stamm, M.D., et al., 2013. Effect of distribution and concentration of topically applied neonicotinoid insecticides in buffalograss, *Buchloe dactyloides*, leaf tissues on the differential mortality of *Blissus occiduus* under field conditions. Pest Manag. Sci. 69 (2), 285–291. https://doi.org/10.1002/ps.3387

Stone, W.W., Gilliom, R.J., Ryberg, K.R., 2014. Pesticides in U.S. streams and rivers: occurrence and trends during 1992-2011. Environ. Sci. Technol. 48 (19), 11025–11030. https://doi.org/10.1021/es5025367

Sukul, P., Spiteller, M., 2001. Influence of biotic and abiotic factors on dissipating metalaxyl in soil. Chemosphere 45 (6–7), 941–947. https://doi.org/10.1016/S0045-6535(01)00010-8

Topalov, A., Molnár-Gábor, D., Csanádi, J., 1999. Photocatalytic oxidation of the fungicide metalaxyl dissolved in water over TiO_2. Water Res. 33 (6), 1371–1376. https://doi.org/10.1016/S0043-1354(98)00351-0

Ueyama, J., et al., 2015. Temporal levels of urinary neonicotinoid and dialkylphosphate concentrations in Japanese women between 1994 and 2011. Environ. Sci. Technol. 49 (24), 14522–14528. https://doi.org/10.1021/acs.est.5b03062

US EPA, 1986. Guidelines for Establishing Test Procedures for the Analysis of Pollutants —Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11. Electronic Code of Federal Regulations Title 40: Protection of Environment(Part 136), A.

Uneme, H., Konobe, M., Akayama, A., Yokota, T., Mizuta, K., 2006. Discovery and Development of a Novel Insecticide Clothianidin. April 2002. Sumitomo Chem. Co., Ltd., pp. 1–15

United States Environmental Protection Agency, 2016. Aquatic life benchmarks and ecological risk assessments for registered pesticides, 35.

USDA, 1986. Urban Hydrology for Small Watersheds.

USGS, 2018. Science in Your Watershed.

Weston, D.P., Ramil, H.L., Lydy, M.J., 2013. Pyrethroid insecticides in municipal wastewater. Environ. Toxicol. Chem. 32 (11), 2460–2468. https://doi.org/10.1002/etc.2338

Williams, N., Sweetman, J., 2018. Distribution and concentration of neonicotinoid insecticides on waterfowl production areas in west central Minnesota. Wetlands 39 (2), 311–319. https://doi.org/10.1007/s13157-018-1090-x

Wittmer, I.K., Scheidegger, R., Bader, H.P., Singer, H., Stamm, C., 2011. Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409 (5), 920–932. https://doi.org/10.1016/j.scitotenv.2010.11.031

Wu-Smart, J., Spivak, M., 2016. Sub-lethal effects of dietary neonicotinoid insecticide exposure on honey bee queen fecundity and colony development. Nat. Publ. Gr. (August), 1–11. https://doi.org/10.1038/srep32108

Xiong, J., Wang, Z., Ma, X., Li, H., You, J., 2019. Occurrence and risk of neonicotinoid insecticides in surface water in a rapidly developing region: application of polar organic chemical integrative samplers. Sci. Total Environ. 648, 1305–1312. https://doi.org/10.1016/j.scitotenv.2018.08.256

Yang, C., Hamel, C., Vujanovic, V., Gan, Y., 2011. Fungicide: modes of action and possible impact on nontarget microorganisms, 2011 ISRN Ecol. 1–8. https://doi.org/10.5402/2011/130289

Žabar, R., Dolenc, D., Jerman, T., Franko, M., Trebše, P., 2011. Photolytic and photocatalytic degradation of 6-chloronicotinic acid. Chemosphere 85 (5), 861–868. https://doi.org/10.1016/j.chemosphere.2011.06.107

Zhang, F., Wang, L., Zhou, L., Wu, D., Pan, H., Pan, C., 2012. Residue dynamics of pyraclostrobin in peanut and field soil by QuEChERS and LC-MS/MS. Ecotoxicol. Environ. Saf. 78, 116–122. https://doi.org/10.1016/j.ecoenv.2011.11.003.

Supplemental Information

Table S1: LC-MS-MS settings for cone voltage, collision energy, and retention time pertaining to standards and analytes of specific pesticides analyzed.

Compound	Parent Ion (m/z)	Product Ion (m/z)	Cone Voltage (V)	Collision Energy (eV)	Retention Time (min)	R_S (L/d)[30,35]
Acetamiprid	223.1	126.1	27	18	6.88	0.38
Azoxystrobin	404.0	372.0	20	20	9.96	0.18
Clothianidin	250.1	169.0	19	18	6.63	0.22
Clothianidin-d3*	253.1	172.0	19	18	6.63	-
Dimethoate	229.8	124.7	18	17	6.88	0.40
Dinotefuran	203.1	129.0	12	12	5.89	0.16
Imidacloprid	256.0	209.3	27	18	6.55	0.18
Imidacloprid-d4*	260.0	213.1	27	18	6.55	-
Metalaxyl	280.1	220.2	20	13	9.03	0.45
Metalaxyl-d6*	286.1	226.2	20	13	9.03	-
Nitenpyram**	271.0	126.0	15	27	5.97	-
Picoxystrobin	368.0	145.0	20	30	12.99	0.08
Pyraclostrobin	388.0	163.0	20	20	14.39	0.03
Pyraclostrobin-d3*	391.0	163.0	20	20	14.34	-
Terbuthylazine**	230.0	174.0	33	17	10.35	-
Thiacloprid	253.0	126.0	28	22	7.04	0.39
Thiamethoxam	292.1	211.0	27	18	6.30	0.25
Thiamethoxam-d3*	295.1	214.0	27	18	6.30	-
Trifloxystrobin	409.0	186.0	15	30	15.28	0.43

*Internal Standard; **Surrogate*

Table S2: Precipitation data for each of the lakes' watersheds, used to determine *P*.

Sampling Dates	Period	Days Between Sampling Events	Number of Rainfall Events			Total Precipitation (cm)		
			Herb	Ag	Urban	Herb	Ag	Urban
5/23/2018	1	28	6	6	6	0.28	0.38	0.38
6/26/2018	2	34	5	8	9	5.84	4.09	6.63
7/27/2018	3	31	5	5	7	1.32	2.93	6.16
8/24/2018	4	28	7	7	8	1.68	4.90	2.38
9/27/2018	5	34	4	6	7	6.41	10.66	8.98
10/26/2018	6	29	4	5	5	1.45	5.16	4.60
Total			**31**	**37**	**42**	**16.98**	**28.11**	**29.14**

Table S3: Weighted Curve numbers based on soil type, area, and CN(II) for each watershed. CN (II) values were an average of each land use classification (developed, open, forrested, etc.). Weighted Curve Numbers were the average of CN (II) based on perentage of soil type.
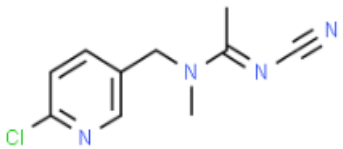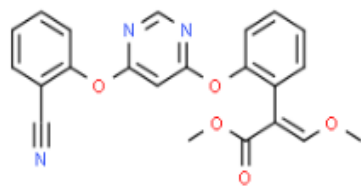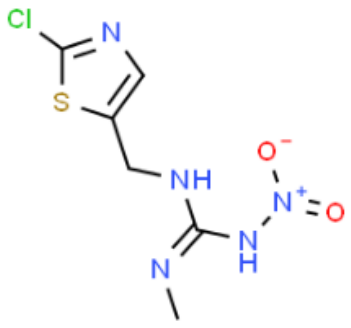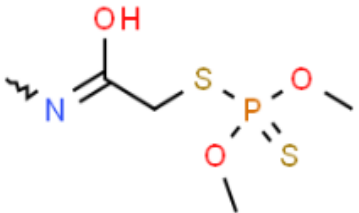
Site	Soil Type	Area (ha)	CN (II) [38]	Weighted Curve Number
Ag	C	494.8	83	83
	D	2103.5	87	
Herb	B	1136.8	75	81
	C	3258.5	83	
	D	2343.5	87	
Urban	C	302.3	83	84
	D	246.5	87	

Table S4: Comparison of maximum observed pesticide concentrations and sampling methods between Metcalfe et al. (2019) and this study.

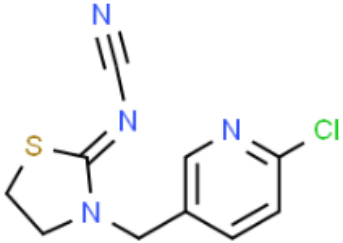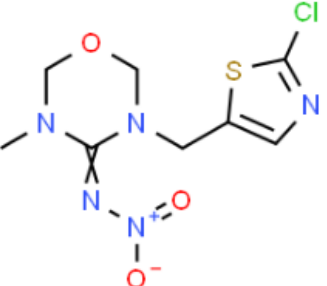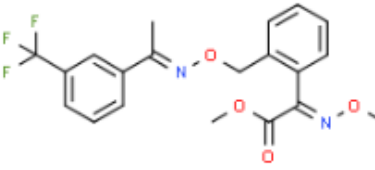| Pesticide	Max POCIS	Max Grab	Max POCIS	Max Grab
	Ontario (ng/L)		Nebraska (ng/L)	
Acetamiprid	249	109	0.15	0
Clothianidin	740**	778**	25	40
Imidacloprid	972*	1,333*	1,033*	640*
Pyraclostrobin	43	14	0	11
Thiacloprid	4	7	0	0
Thiamethoxam	914**	1,607**	17	79

*Indicates values exceeding acute aquatic invertebrate toxicity. ** Indicates values exceeding chronic aquatic invertebrate toxicity.*

Table S5: Physical properties and usage of evaluated pesticides. A=Acute toxicity; C=Chronic toxicity

Pesticide (Trade Name)	Atomic Structure	Molar Mass (g/mol)	Class (Wood, 2020)	Usage	Aquatic Invertebrate Toxicity (ng/L) (United States Environmental Protection Agency, 2016)
Acetamiprid (Assail™, Pristine™, and Chipco™) (EPA, 2002)		223	Pyridylmethylamine neonicotinoid insecticide	Controls sucking insects for cotton, leafy vegetables, citrus	A:10,500 C:2,100
Azoxystrobin (Heritage™ Fungicide) (EPA, 1997)		403	Methoxyacrylate strobilurin fungicide	Golf courses and commercial turf farms	A:130,000 C:44,000
Clothianidin (Poncho 600) (EPA, 2003)		250	Nitroguanidine neonicotinoid and thiazole insecticide	Emerald Ash Borer

Commercially for corn and canola | A:11,000 C: 50 |
| Dimethoate (Dimethoate 400) (Eagle, 2013) | | 229 | Aliphatic amide organothiophosphate insecticide | Aphids, thrips, mites, grasshoppers | A: 21,500 C: 500 |

Name	Structure	Molecular Weight	Class	Use	Amount
Dinotefuran (Dinotefuran, MTI-446) (EPA, 2004)		202	Nitroguanidine neonicotinoid insecticide	Emerald Ash Borer Golf courses, lawns and gardens	A: >484,150,000 C: >95,300,000
Imidacloprid		256	Nitroguanidine neonicotinoid and pyridylmethylamine neonicotinoid insecticide	Emerald Ash Borer	A: 385 C: 10
Metalaxyl		279	Acylamino acid and anilide fungicide		A: 14,000,000 C: 1,200,000
Picoxystrobin		367	Carbanilate, phenylpyrazole, and methoxycarbanilate strobilurin fungicide		A: 12,000 C: 1,000
Pyraclostrobin		388	Phenylpyrazole and methoxyacrylate strobilurin fungicide		A:7,850 C: 4,000

Thiacloprid		253	Pyridylmethylamine neonicotinoid and thiazolidine insecticide	A: 18,900 C: 970
Thiamethoxam		292	Nitroguanidine neonicotinoid and thiazole insecticide	A: 17,500 C: 740
Trifloxystrobin		408	Methoxyimino acetate strobilurin fungicide	A: 12.650 C: 2,760

Table S6.: Tukey significance grouping for urban POCIS samples by date for the predominately urban land use watershed.

		Urban POCIS				
Date	Period	Acetamiprid	Azoxystrobin	Clothianidin	Imidacloprid	Metalaxyl
5/23/18	1	B	E	A	E	AB
6/26/18	2	AB	CD	A	D	A
7/27/18	3	B	AB	A	A	AB
8/24/18	4	A	A	A	B	AB
9/27/18	5	B	BC	A	C	AB
10/26/18	6	B	DE	B	F	B

Table S7: Tukey significance grouping for agricultural POCIS samples by date for the predominately agricultural land use watershed.

	Agricultural POCIS		
Date	Period	Azoxystrobin	Metalaxyl
5/23/18	1	AB	AB
6/26/18	2	B	B
7/27/18	3	AB	AB
8/24/18	4	AB	A
9/27/18	5	AB	AB
10/26/18	6	A	AB

Table S8: Tukey significance grouping for urban samples by sampling method.

Urban POCIS vs. Grab	
Sample Site	Metalaxyl
POCIS	A
Grab	B

Table S9: Tukey significance grouping for herbaceous samples by sampling method.

Herbaceous POCIS vs. Grab		
Sample Site	Azoxystrobin	Dimethoate	Metalaxyl
POCIS	B	B	A
Grab	A	A	B

Table S10: Tukey significance grouping for agricultural samples by sampling method.

Sample Site	Dimethoate	Metalaxyl	Pyraclostrobin	Thiamethoxam
Agricultural POCIS vs. Grab				
POCIS	B	A	B	A
Grab	A	B	A	B

Table S11: Tukey significance grouping for all urban grab samples by date.

Date	Period	Dimethoate	Imidacloprid	Pyraclostrobin
Urban Grab				
5/23/18	1	A	B	B
6/26/18	2	A	C	B
7/27/18	3	B	A	A
8/24/18	4	B	A	B
9/27/18	5	B	A	B
10/26/18	6	B	A	B

Table S12: Significance grouping for all herbaceous grab samples by date.

Date	Period	Dimethoate	Pyraclostrobin
Herbaceous Grab			
5/23/18	1	A	A
6/26/18	2	A	B
7/27/18	3	B	B
8/24/18	4	B	B
9/27/18	5	B	B
10/26/18	6	B	B

Table S13: Significance grouping for all agricultural grab samples by date.

Date	Period	Clothianidin	Picoxystrobin	Pyraclostrobin
Agricultural Grab				
5/23/18	1	B	B	A
6/26/18	2	B	A	A
7/27/18	3	AB	B	B
8/24/18	4	AB	B	B
9/27/18	5	A	B	B
10/26/18	6	A	B	B
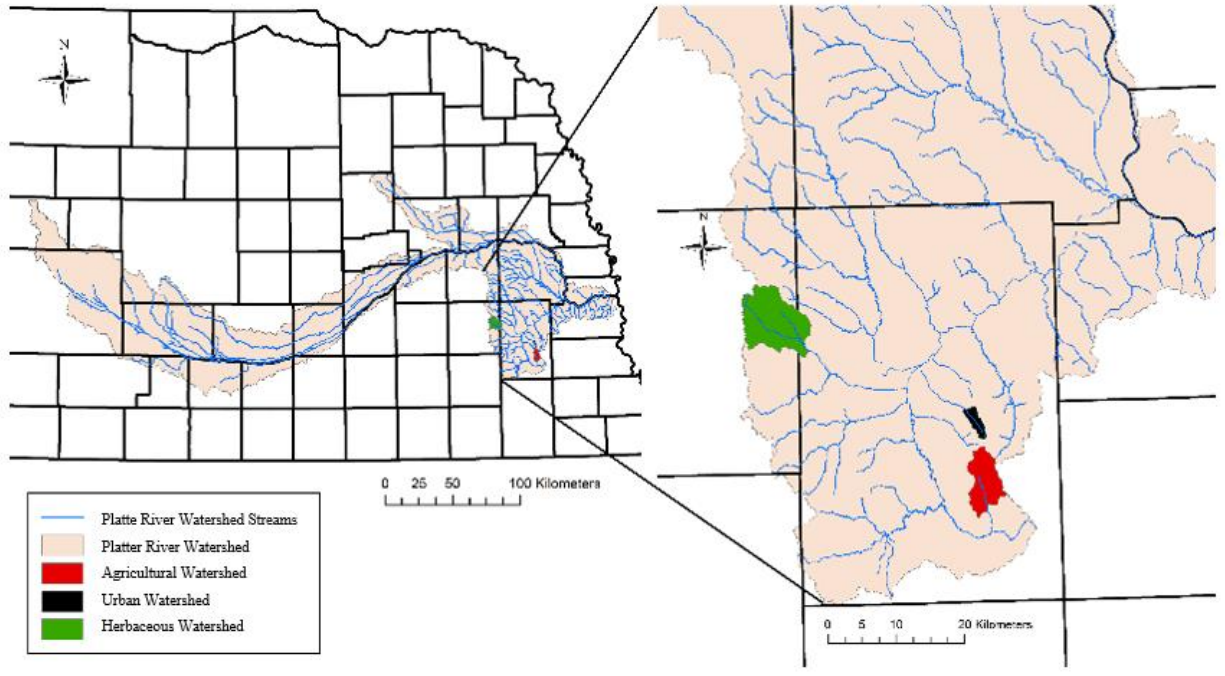
Figure S1: Location of the three study watersheds (urban, agriculture, herbaceous predominant land uses) within the Platte River watershed.
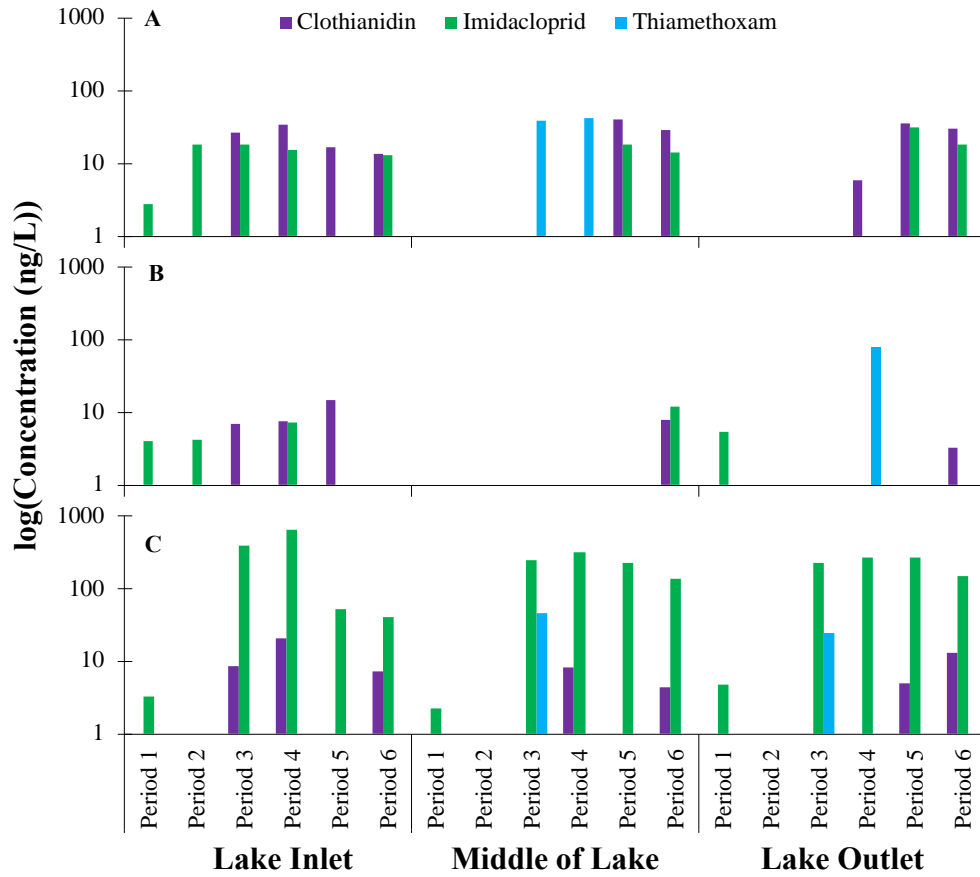
Figure S2: Grab pesticide concentrations of clothianidin, imidacloprid, and thiamethoxam at each sampling location in the agricultural (A), herbaceous (B), and urban (C).