Pesticide Occurrence and Persistence Entering Recreational Lakes Residing in Watersheds of Various Land Uses

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PESTICIDE OCCURRENCE AND PERSISTENCE ENTERING RECREATIONAL LAKES RESIDING IN WATERSHEDS OF VARIOUS LAND USES

by

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Across the United States, most streams and lakes are impaired in one way or another. Studies have shown pesticides are detected in finished drinking water and at high levels in surface water. In recent years, regular algal blooms and fish kills have created concern in affected communities. However, recent reports of pesticides impacting non-target species have emerged. As the population and food demand continues to grow, there is an increasing concern to quantify and reduce pesticide movement into streams and lakes.

Although there has been a great deal of research completed on older pesticides such as atrazine and DDT, newer pesticide classes, such as neonicotinoids, have limited information available. Therefore, the primary objectives of this Master's Project were to (1) assess average pesticide concentrations and loadings entering recreational lakes in three distinct watersheds and (2) evaluate pesticide persistence longitudinally throughout the lakes. It was hypothesized the agricultural watershed would have the highest loading of pesticides and higher concentrations would be observed near the inlet of each lake.

However, new insight was gained regarding neonicotinoid concentrations entering recreational lakes. Further, imidacloprid aquatic chronic and acute toxicity limits were exceeded at the urban and agricultural locations. Concentrations and loading of specific pesticides differed by watershed and sampling location within the lakes and was confirmed with statistical analysis (fully summarized in appendix A). Results from this study provide new knowledge for managing specifically neonicotinoid of pesticide usage as well implementation of best management practices around and within recreational waterbodies.

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CHAPTER 1: LITERATURE REVIEW

PESTICIDE OCCURRENCE AND PERSISTENCE ENTERING RECREATIONAL LAKES RESIDING IN WATERSHEDS OF VARIOUS LAND USES

Introduction

Common Use Pesticides (CUPs) are important for agricultural producers to sustain food production. As a result, regions with high rates of agricultural production, such as the Midwest, often have ubiquitous occurrences of pesticides in surface and groundwater [1]. Once pesticides are introduced into an ecosystem, pesticides have the potential for creating unwanted effects on non-target species and downstream environments [2,3]. However, pesticides do not come strictly from agricultural practices. Therefore, the research presented in this thesis focuses on the neonicotinoid and fungicide concentrations detected in recreational lakes as well as their persistence in these aquatic environments during the growing season in Eastern Nebraska.

Pesticides

Pesticides, which encompass insecticides, herbicides, fungicides, etc., are necessary to sustain growing food production demands worldwide. CUPs protect crops from pests, allowing agricultural producers to generate large product yields. In order to get the best protection, pesticides have underlying classes that affect pests differently. Neonicotinoids and botanical insecticides or amid fungicides are just a few examples of respective classes [4]. As our understanding of chemistry advances, so do the chemical makeup and effectiveness of pesticides.

Neonicotinoids are a fairly new class of insecticides and are widely used. They are a more selective insecticide as to who/what can be affected by them increasing their popularity. Neonicotinoids affect the endocrine system of insects flooding them with nicotine and effectively rendering them useless. However, they have the potential for un-desired effects on non-target species in terrestrial and aquatic environments [5].

Fungicides are used to prevent fungi and spore growth as well as molds and mildew in certain situations [6]. In the Midwest where the main crops are corn and soybeans, fungicides are applied to prevent and cure soybean wilt, north corn leaf spot, and northern corn leaf blight [7]. Herbicides are also applied to control broad-leaf weeds and some grasses. Therefore, they are applied to farms, lawns, golf courses, and edges of ponds or lakes. However, over time herbicides have become less effective, resulting in reduced performance, resistant weeds, and increased herbicide application to offset reduced performance [8,9]. For example, Giant Ragweed has become resistant to the herbicide glyphosate over the last decade, creating challenges for agricultural producers [8].

Pesticide Use

Insecticides and herbicides have been used for crop protection since before the introduction of dichlorodiphenyltrichloroethane (DDT) in 1945 [10]. DDT was one of the first synthetic pesticides introduced to the market. Before 1939 agricultural producers used organic pesticides such as sulfur, nicotine, arsenic, and other heavy metal compounds to increase crop production [11].

Four important CUP's (atrazine, glyphosate, imidacloprid, and thiamethoxam) are often found in aquatic agroecosystems due to surface water runoff from production fields. Subsequently, pesticide use has grown exponentially over time. In the U.S. for example; around 13 million kg of pesticides were applied to corn in 1960 and in 2008 approximately 93 million kg were applied [12]. Figures 1.1 and 1.2, from the United States Geological Survey (USGS), illustrate the increased use of the CUP imidacloprid across the United States from 2000 to 2014.

While CUP usage, particularly neonicotinoids, has appeared to decrease in recent years (2015-present), new studies have shown that this is not the case. Figure 1.3 shows this apparent decrease in the use of imidacloprid for soybeans. The reason for this deceptive decline in imidacloprid application is agricultural producers have started using seed treatment for insecticides, which remains unaccounted for in current application rates. As of 2015, USGS no longer attempts to quantify the amount of seed treated pesticides due to the uncertainty in translating the use to pounds [13]. Fungicides on the other hand do not all follow the same trend of use. Azoxystrobin and picoxystrobin have both increased the last few years while metalaxyl has decreased. On the other hand pyraclostrobin has stayed relatively the same [14].

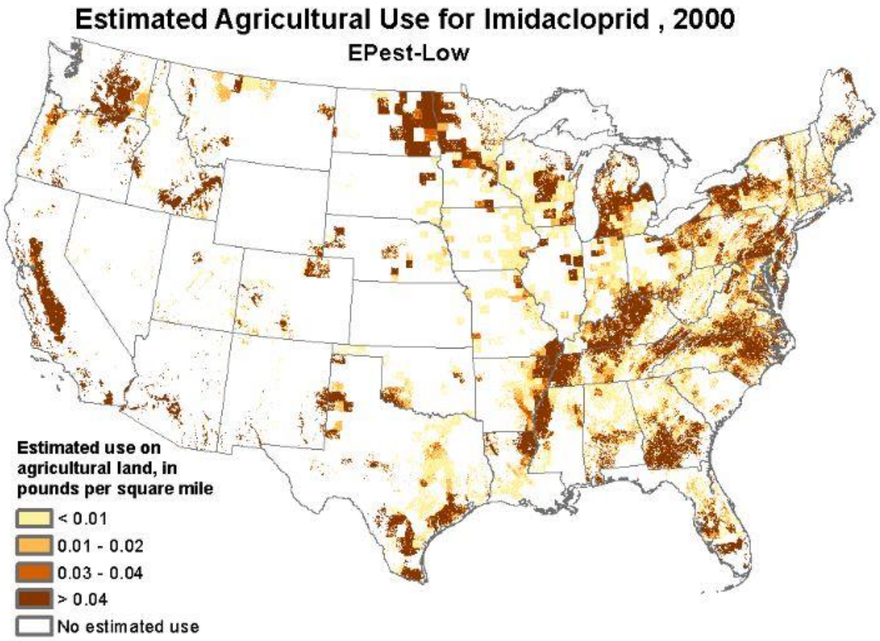

Figure 1.1: Estimated Agricultural Use of Imidacloprid for the United States in 2000 [13]

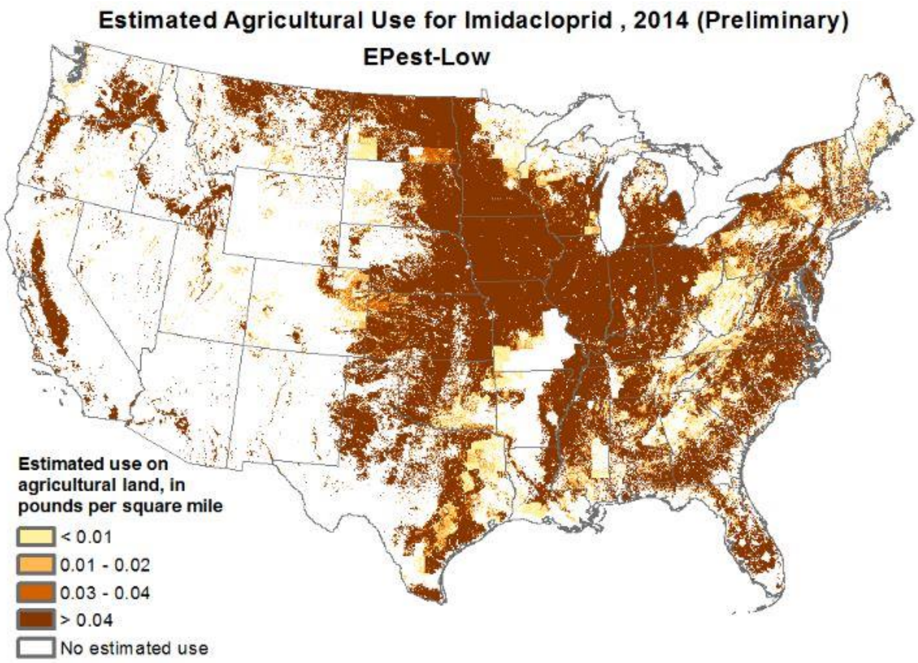

Figure 1.2: Estimated Agricultural Use of Imidacloprid for the United States in 2014 [13]

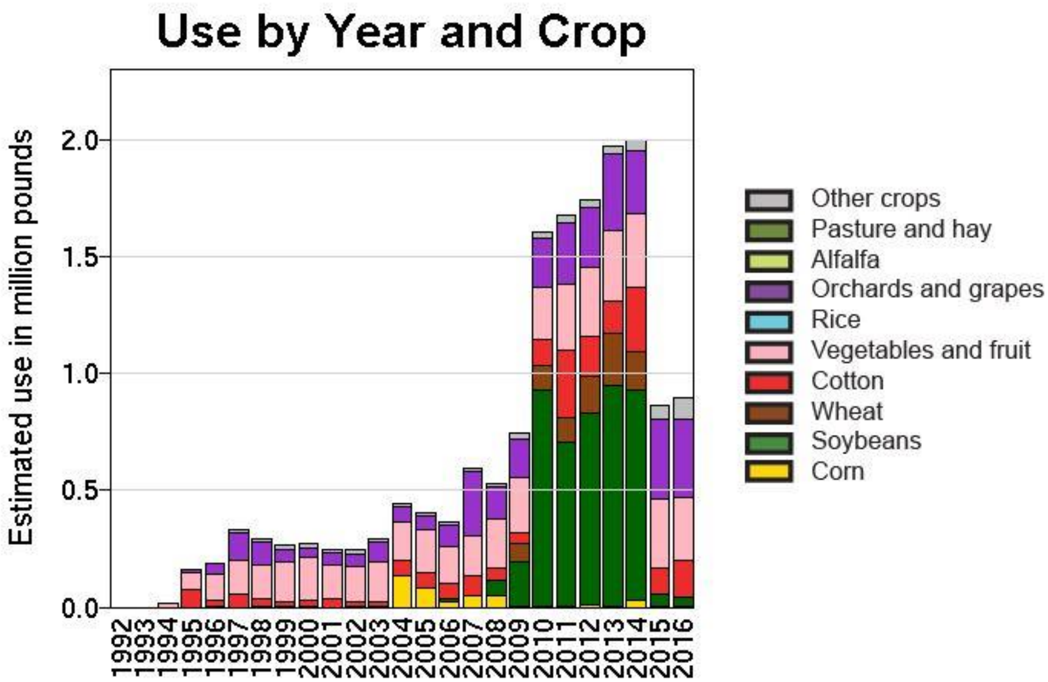

Figure 1.3: Estimated imidacloprid use from 1994-2016 [13] *Note seed treatment excluded from reports starting in 2015.

Toxicity

Before pesticides are ready for the market in the United States, they go through a registration process conducted by the Environmental Protection Agency (EPA). During this process, CUPs' environmental risks are assessed, including groundwater contamination, threats to endangered species, and the potential for endocrine disruption [15]. In spite of this, the environmental implications of potentially produced byproducts of CUPs in the natural environmental have not yet been evaluated. In 2003 a degradation study of thiamethoxam determined one of its byproducts was another commonly used pesticide, clothianidin [16].

Even though the effects of CUPs are not highly toxic at low concentrations in limited instances, CUPs have the potential to cause adverse effects as they degrade and move through the natural environment, thus resulting in the feminization of fish and death of non-target species [17–19].

One of the non-target species is honey bees which are essential to the environment. Wu-Smart *et al.* (2016) investigated the effects of neonicotinoids on honey bees and reported insecticides, specifically neonicotinoids, potentially were leading to honey bee collapse disorder. Imidacloprid caused decreases in queen egg laying; activity, mobility, as well as worker bees' foraging and hygienic behavior were all decreased. Honey bees are responsible for the pollination of many fruits and plants. Not only is this route for contamination, but it also means that if the honey bees die off, so do some of our favorite foods. The alternative would be to find another way to pollinate everything.

Other non-target species include aquatic life such as fish and invertebrates. In a statistical survey conducted across the United States, fish specimen were collected and examined. The fish species were analyzed together as a whole and not individually sampled. Through the experiment, it was determined that the insecticide dichlorodiphenyltrichloroethane (DDT) was detected in over half of the samples that were analyzed [20]. This means humans and other animals are consuming CUP's at unknown quantities. Pesticide consumption and exposure has led to cancer [20,21], a very common cause of death in the US.

In light of this information, some countries are taking action. As of May, 2018, the European Union (EU) has completely banned the use of imidacloprid, clothianidin, and thiamethoxam. Not only can these CUP's not be used as spray treatment, but they are also banned for seed treatment barring some exceptions [22]. However, bans have yet to be established in the United States.

Objectives

The type and quantity of pesticides entering lakes is unknown and is causing impaired water quality as well as adverse effects on the aquatic environment. Therefore the primary objectives of this project were to (1) assess average neonicotinoid concentrations and loadings entering recreational lakes in three distinct watersheds and (2) evaluate pesticide persistence longitudinally throughout the lakes. It was hypothesized the agricultural watershed (Wagon Train) would have the highest loading of pesticides and higher concentrations would be observed near the inlet of each lake.

CHAPTER 2: PESTICIDE OCCURRENCE AND PERISTENCE ENTERING RECREATIONAL LAKES IN WATERSHED OF VARYING LAND USES

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Abstract

Over the past 50 years, low levels of pesticide residues have become ubiquitous in agricultural and urban aquatic ecosystems. Currently, little is known of their occurrence and persistence in recreational lakes. Therefore, the objectives of this study were to (1) assess average neonicotinoid concentrations and loadings entering recreational lakes in three distinct watersheds throughout the growing season and (2) evaluate pesticide persistence longitudinally within the lakes. Six sampling campaigns were conducted at three lake sites from April through October in 2018. Polar organic chemical integrative samplers (POCIS) were placed at each lake inlet and monthly samples were assessed for twelve pesticides: acetamiprid, azoxystrobin, clothianidin, dimethoate, dinotefuran, imidacloprid, metalaxyl, picoxystrobin, pyraclostrobin, thiacloprid, thiamethoxam, and trifloxystrobin. Monthly grab water-quality samples were also taken at the POCIS location, midpoint of each lake, and near the outlet of each lake. All pesticide samples were analyzed using LC MS/MS analysis and individual pesticide loading rates were determined. The occurrence and persistence of specific pesticides were significantly different between lakes in varying watershed land uses. Imidacloprid exceeded acute and chronic invertebrate levels 11% and 61% of the POCIS sampling periods, respectively. All other pesticides were below toxicity limits. Findings from this project are critical for preventing and mitigating pesticides entering and residing in recreational waters.

Keywords: Neonicotinoids, recreational lakes; ecotoxicity; fate and transport; pesticides

Introduction

Pesticides, which encompass insecticides, herbicides, and fungicides, are necessary to sustain food production demands worldwide [23]. 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 [24–27]. According to a U.S. Geological Survey (USGS) national assessment conducted from 2002 to 2011, 61% of agricultural streams and 90% of urban streams contained chronic levels of pesticides [26]. Worldwide chronic levels of pesticides in water resources continue to rise, which have significant human health and water security implications. Specifically, once exposed to the environment, pesticides encounter a range of different environmental conditions resulting in the formation of potentially harmful byproducts, which produce significant ecological effects within agroecosystem food webs and negatively impact human health (e.g., honey bee colony collapse, reproductive and development disruption, carcinogens) [18,28–33].

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) [34]. Imidacloprid, introduced in 1992 as the first neonicotinoid on the American market to control both turf grass and crop pests, is currently the most widely used insecticide in the world [23]. Predominantly applied to soybeans, agricultural use of imidacloprid has grown exponentially from zero to one million kg between 1992 and 2014. Imidacloprid degrades in the aquatic environment primarily through photochemical mechanisms [35–38], although biodegradation through microbial transformation also plays an important role [39]. Clothianidin, only registered for use within the United States since the early 2000s and predominately applied to corn, has similarly grown to 1.7 million kg 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) [40]. Furthermore, neonicotinoids have the potential to cause unintended effects as they degrade in the natural environment, resulting in the feminization of fish, cancer in humans, and death of non-target species [17–19,21]. There is currently much concern over the toxicity of imidacloprid to honeybees as they are one of the non-target species potentially affected by neonicotinoids [41,42].

Unlike the increased use of insecticides, fungicide use has generally remained constant from 1988-2007 around the world and the U.S.[23]. When strobilurin fungicides, such as azoxystrobin trifloxystrobin, were introduced in 1996[43] they dominated the fungicide market due to the way they stop the production of adenosine triphosphate (ATP) in the fungus. Even so, fungicides are used less than herbicides and insecticides across all markets (agricultural, home and garden, industry, etc.), and yet they are still being found in surface waters across the U.S.[25]. Non-target species of fungicides include, and are not limited to, amphibians, algae, prokaryotes, and nitrifying bacteria[44,45].

The U.S. Environmental Protection Agency's Office of Pesticide Program (OPP) records acute and chronic toxicity for registered pesticides. Chronic toxicity occurs when an organism is exposed over a long period of time, while acute toxicity occurs from a single exposure over a short duration. The chronic threshold is generally lower than acute due to the effect of time (Table A1). However, these benchmarks are only for freshwater aquatic life such as fish, macroinvertebrates, vascular plants, and non-vascular plants [46]. As of May 2018, the European Union (EU) completely banned the use of several pesticide classes, including neonicotinoid pesticides. However, the prevalence of pesticides within U.S. waters elevates the importance of understanding the dynamics of their transport mechanisms into recreational waters and overall fate once entering reservoirs.

Pesticides have become pervasive in both agricultural and urban streams [47–51]. However, few studies have evaluated pesticide accumulation in waterbodies (i.e., reservoirs, lakes). Recent reports have found pesticides in urban and agricultural reservoirs, including northeastern Nebraska and Midwestern national park lakes [52–54]. However, to our knowledge, the occurrence and persistence of neonicotinoids and fungicides have not been evaluated in the lacustrine environment. Therefore, the goal of this study was to investigate the current state of recreational lakes in three distinct watersheds in Nebraska, U.S. and provide one of the first evaluations of potential exposure to pesticide contamination and persistence longitudinally in recreational lakes located in the Midwestern U.S. The primary objectives of the project were to (1) assess average neonicotinoid and strobilurin concentrations and loadings entering recreational lakes in three distinct watersheds and (2) evaluate pesticide persistence longitudinally throughout the lakes. It was hypothesized the agricultural watershed would have the highest loading of pesticides and higher concentrations would be observed near the inlet of each lake.

Materials and Methods

Site Description

Three recreational lakes were evaluated in the Lower Platte River Basin of Nebraska: (1) herbaceous (Pawnee), (2) urban (Holmes) and (3) agricultural (Wagon Train) (Figure 2.1). The lakes, each classified as reservoirs, will be referenced using herbaceous, urban, and agricultural for the remainder of this manuscript. The lacustrine ecosystems received runoff from diverse mixes of agricultural and urban land uses within each watershed. Specifically, herbaceous was comprised of 22.3% cultivated crop, 5.0% developed, and 66.2% herbaceous/forested, while urban was comprised of 2.8% cultivated crop, 83.4% developed, and 12.3% herbaceous/forested. Lastly, agricultural was comprised of 59.5% cultivated crop, 4.3% developed, and 31.4% herbaceous/forested.

Each of the subwatersheds resided in the Salt Creek watershed (10200203) [55]. The 0.45 km^2 urban lake had a drainage area of 7.4 km^2, predominantly from Antelope Creek. The Hickman Branch drained a 33.9 km^2 watershed flowing into the agricultural lake (1.3 km^2). The herbaceous lake was the largest of the three study sites with an area of 3.0 km^2. The main source of water was from Middle Creek with a drainage area of 70.3 km^2.

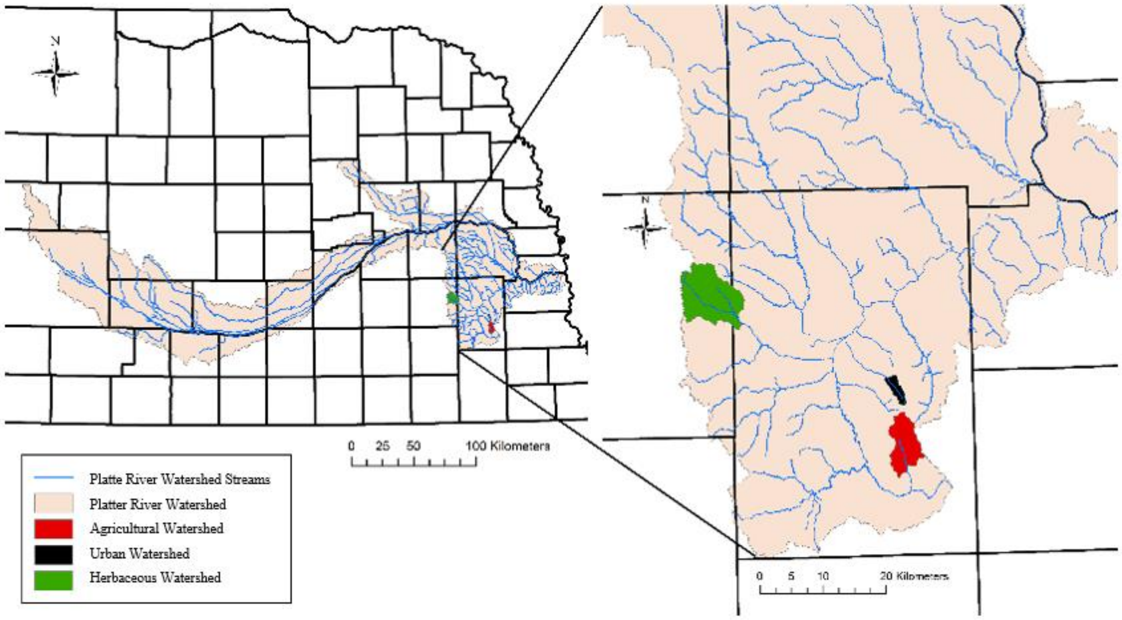


Figure 2.1 Location of our three study watersheds (urban, agricultural, herbaceous) within the Platte River Watershed.

POCIS Sampling

Often times grab samples miss peak flows and thus the large concentration of pesticides. Passive samplers were created for hazardous sampling at super fund sites in order to add a level of safety, or in this case for easy continual sampling[56]. Therefore, polar organic chemical integrative samplers (POCIS), passive samplers, were utilized for this project and placed at the inlet of each lake at the beginning of each sampling period in the center of the contributing stream (Figure 2.2). This particular sampling method used membranes, encased in a flow-through cage, to collect the pesticides. Unlike grab samples, POCIS samplers are deployed for long periods of time, which allows a larger accumulation of analytes and provides a more representative sample of the concentration of pesticides entering the lakes and reduced costs for both data collection and analysis[57].

POCIS were deployed at the beginning of six-monthly 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 average monthly concentrations of pesticides entering the waterbodies. POCIS enabled the average concentrations of each individual pesticide to be measured and then adjusted based on stream flow to estimate the load of pesticides entering the three lakes during each assessment period.

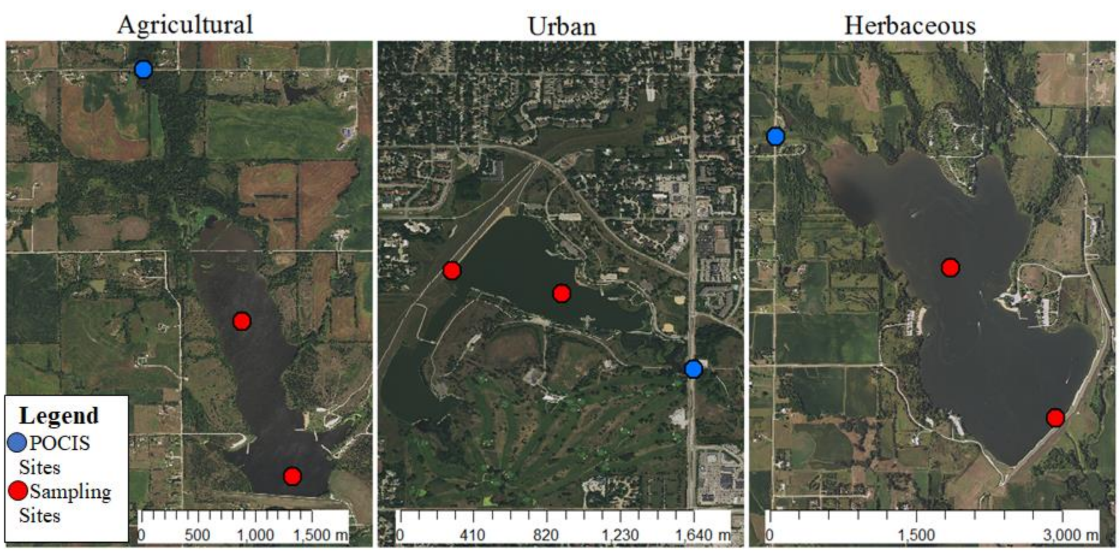


Figure 2.2: Sampling locations for agricultural, urban, and herbaceous lakes. Blue dots represent where both grab samples were taken and POCIS were located.

Grab Samples

At the beginning of each sampling period, grab samples were taken at the POCIS locations in addition to two locations within the reservoirs (Figure 2.2). Samples were collected in 500 mL amber glass bottles, at approximately 15 cm below the air/water interface in order to prevent photolytic degradation of the pesticides during sampling.

The samples were transported on ice to the Nebraska Water Sciences Laboratory (Lincoln, NE), where they were stored frozen (-20^{o}C) until processing and analysis.

Extraction

Water samples were divided into 100 milliliter (mL) portions, spiked with 50 nanograms 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 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 fortified with 50 ng stable isotope labelled internal standards (clothianidin-d3, imidacloprid-d4, metalaxyl-d6, thiamethoxam-d3, pyraclostrobin-d3). Residue was reconstituted with a mix of reagent water and 25% methanol, and transferred to an autosampler vial equipped with a salinized glass insert.

POCIS devices 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^{o} C to approximately five milliliters. 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 described below.

Instrumentation

Quantification of target pesticides in POCIS and grab samples were performed by isotope-dilution using liquid chromatography-tandem mass spectrometry (LC-MS) at the University of Nebraska-Lincoln 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®, Milford, MA). Ionization of neonicotinoid analytes was performed in the positive ion mode APCI and ESI. 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. LC-MS settings can be found in table 2.1.

Instrument detection limits (POCIS=0.2ng, Grab=0.01ug/L) were determined by repeated injection of the lowest standard (=3 x standard deviation) and method detection limit using 8-10 replicates of a fortified low-level blank[58]. Quality controls analyzed with the samples and POCIS extracts include 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).

Table 2.1: LC-MS settings for cone voltage, collision energy, and retention time pertaining to standards and analytes of specific pesticides and fungicides analyzed in this study.

Compound	Parent Ion (m/z)	Product Ion (m/z)	Cone Voltage (V)	Collision Energy (eV)	Retention Time (min)	R_S (L/d)[59]
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*

POCIS Ambient Water Concentrations

POCIS analysis produced a mass of analytes per POCIS, which were converted using experimentally determined uptake rates for each evaluated analyte to determine time-weighted average concentrations (Equation 1)

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

where C_w is the ambient chemical concentration in ng/L, N is the mass accumulation in ng, R_s is the experimentally determined uptake rates for POCIS in L/d and t is the exposure time (sampling period) in d. R_s values were determined at the UNL Water Sciences Lab and can vary between investigations [57] due to analysis types and POCIS membrane variations. Uptake rates of 0.38, 0.18, 0.22, 0.40, 0.16, 0.18, 0.45, 0.08, 0.03, 0.39, 0.25, 0.43 L/d for acetamiprid, azoxystrobin, clothianidin, dimethoate, dinotefuran, imidacloprid, metalaxyl, picoxystrobin, pyraclostrobin, thiacloprid, thiamethoxam, and trifloxystrobin, respectively [59,60].

Estimated Loads

To estimate the flux or mass loading of pesticides entering the 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 (SCS CN) method [61] was applied with the goal of calculating approximate runoff into each lake. Though there is uncertainty in assuming all of the 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 uncertainty as using a simple runoff method such as the curve number.

Runoff was computed using a combination of the Equations 2-5 to determine maximum retention estimates and runoff. Equations 2 and 3 use CN (II) in order to calculate the wet or dry antecedent curve number [62]

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

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

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

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

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

where, CN (I) was the curve number for dry antecedent conditions (unit-less), CN (III) was the curve number for wet antecedent conditions (unit-less), CN (II) was the average curve number (unit-less) determined from known tables and charts [63], S was the potential maximum retention (unit-less), P is the rainfall (mm), Q is the runoff (mm), and A is area (ha).

Data from the High Plains Regional Climate Center were utilized to estimate precipitation during each rainfall event during the study [64] (Table 2.2). 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 watershed (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).

Table 2.2: 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**

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 [61]. The CN (II), a function of the land use and hydrologic soil group, were obtained from the *"USDA Urban Hydrology for Small Watersheds"* [63]. Since each watershed consisted of multiple land uses and soil types, a weighted CN was calculated (Table 2.3). CN (II) was then modified based on the antecedent moisture conditions at the time of a precipitation event. CN (I) accounted for dry conditions and CN (III) considered 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 [62]. The limit of five days was chosen because it was assumed the vadose zone would drain during that period based on local geology.

Table 2.3: Weighted Curve numbers based on soil type, area, and CN(II) for each watershed.

Site	Soil Type	Area (ha)	CN (II) [63]	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	

Statistics

All pesticide data was normalized by log transformation and analyzed using one-way analysis of variance (ANOVA) with post-hoc 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 (State College, Pennsylvania, MA).

Results and Discussion

Mean Pesticide Concentrations

Both POCIS and grab samples were analyzed for twelve pesticide residues. Four of the target pesticides, picoxystrobin, pyraclostrobin, thiacloprid, and trifloxystrobin, were not detected (<0.2 ng/POCIS) in any of the POCIS extracts. 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 is summarized in Figure 3. Azoxystrobin, clothianidin, and imidacloprid were detected most frequently in both sampling methods.

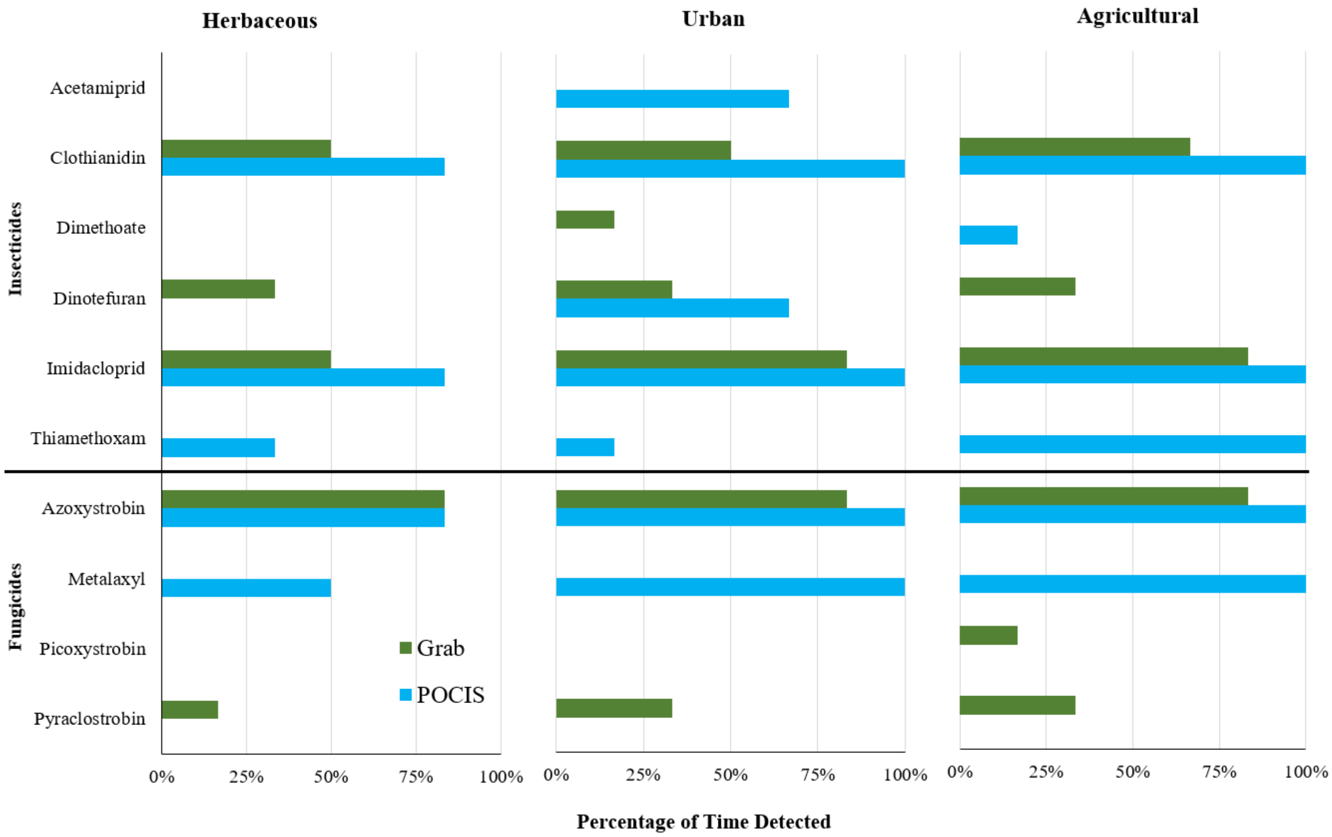
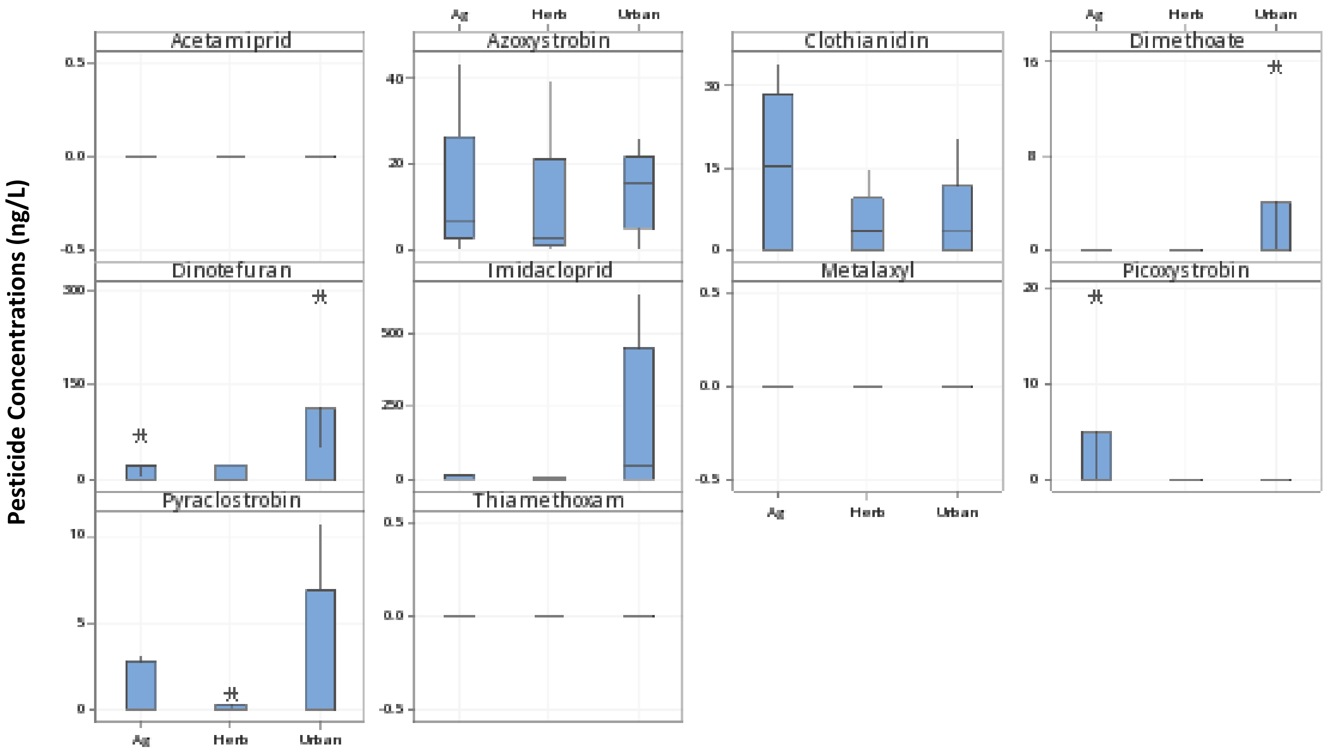


Figure 2.3: Percent of time pesticides were detected where both POCIS and grab data was available.

While azoxystrobin, clothianidin, and imidacloprid were detected most often at each of the lake inlets, concentrations were significantly different depending on land use and sampling location (Figure 4; α=0.05). For example, although thiamethoxam was detected in each lake, it was not detected in inlet grab samples (Figure 4A). Further, the urban watershed contributed the significantly higher pesticide concentrations compared to the other two watersheds (α=0.05).

Metalaxyl time-weighted average concentrations were consistently higher in the POCIS samples than the inlet grab samples in all of the watersheds. Azoxystrobin and dimethoate concentrations from the herbaceous site and dimethoate and pyraclostrobin from the agricultural site were higher than the corresponding POCIS time-weighted average concentrations. Lastly, in comparing the concentrations from grab samples to each other, metalaxyl concentrations were higher at the outlet and middle than compared to the inlet. All other comparisons between sampling locations and type did not show any kind of statistical significance (α=0.05).

A)



B)

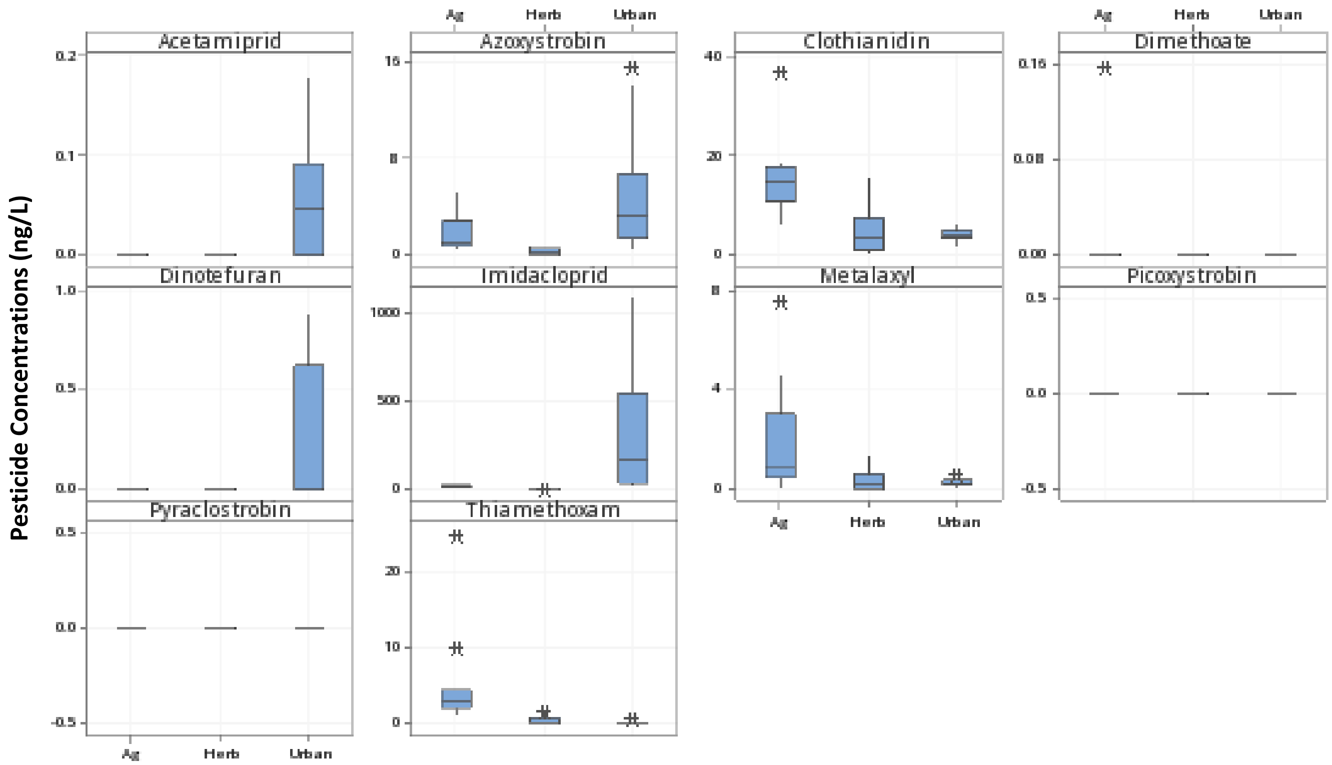


Figure 4: Box plots for all pesticide concentrations throughout the study period for the agricultural (Ag), herbaceous (Herb) and urban watersheds at the inlet dependent on: A) Grab sampling and B) POCIS sampling.

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 in China, Canada, and the U.S. [65–67]. 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 agricultural and residential land uses. POCIS samples measured 53 ng/L of thiamethoxam in the agricultural areas (vegetable field areas) compared to average concentrations of 5.2 ng/L observed in our study. Further imidacloprid concentrations were 249 ng/L in the Chinese residential (urban) system, compared to average concentrations of 324 ng/L in our study. The differences in imidacloprid concentrations between Xiong et al. (2019) and our study is likely attributed to the increased application in the United States to prevent the spread of the emerald ash borer, an invasive species in the U.S. that attacks ash trees.

In comparison, Metcalf et. al. (2016) investigated 6 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. POCIS were deployed in streams and lakes for approximately 30 days and tested for 22 pesticides. Of the 22 pesticides analyzed, only azoxystrobin was assessed in our study as well. Azoxystrobin was not detected in any of their samples [66]. Similarly, Metcalf et. al. (2019) in the Great Lakes region in Michigan did not observe detectable azoxystrobin concentrations [67]. They did however find more pyraclostrobin, a sister product to azoxystrobin, than we did. Concentrations of pesticides vary across state lines as well as country borders due to preferred use of different regions.

Metcalf et al. (2019) assessed the occurrence of 29 pesticides in Michigan watersheds during May and June, including eight of the same pesticides that were evaluated in our study. Similar to our study, Metcalf et al. (2019) evaluated results from both POCIS and grab samples from the same locations. The project evaluated runoff inputs using data from 18 monitoring sites with land uses ranging from urban, wetland, pasture, orchards, etc. and watershed areas varying from 1,900 to 671,200 hectares. In comparison to our study, Metcalf et al (2019) reported higher grab sample concentrations compared to

POCIS time-weighted averages. Table 4 summarizes comparisons between studies of maximum concentrations using the two sampling methods (POCIS and grab sampling).

Table 2.4: Comparison of pesticide concentrations and sampling method between Metcalf et al. (2019) and this study.
*** Indicates values exceeding acute toxicity. ** Indicates values exceeding chronic toxicity.**

Pesticide	Max POCIS	Max Grab	Max POCIS	Max Grab
	Michigan (ng/L)		Nebraska (ng/L)	
Imidacloprid	972*	1333*	1033*	640*
Thiamethoxam	914**	1607**	17	79
Clothianidin	740**	778**	25	40
Thiacloprid	4	7	0	0
Acetamiprid	249	109	0.15	0
Pyraclostrobin	43	14	0	11

Ecotoxicity Concerns

For non-target species such as honey bees, neonicotinoid insecticides are considered “highly toxic”. LD_{50} oral values of 17.9, 21.8, and 29.9 ng/bee for imidacloprid, clothianidin, and thiamethoxam respectively [68]. Consequently, high concentrations as observed in our study have the potential to result in adverse effects on non-target species. POCIS concentrations within each watershed compared to chronic and acute invertebrate toxicity limits for this study found in “*Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides*” were assessed (Figure 2.5) [46].

Average imidacloprid concentrations were observed above the chronic toxicity level (10 ng/L) at the urban site for each sampling period. For clothianidin and thiamethoxam, the agricultural site displayed the highest concentrations, but was well below the chronic and acute toxicity limits for both pesticides. In comparison, Metcalf et al (2019) observed toxicity limit exceedances for imidacloprid, thiamethoxam, and clothianidin.

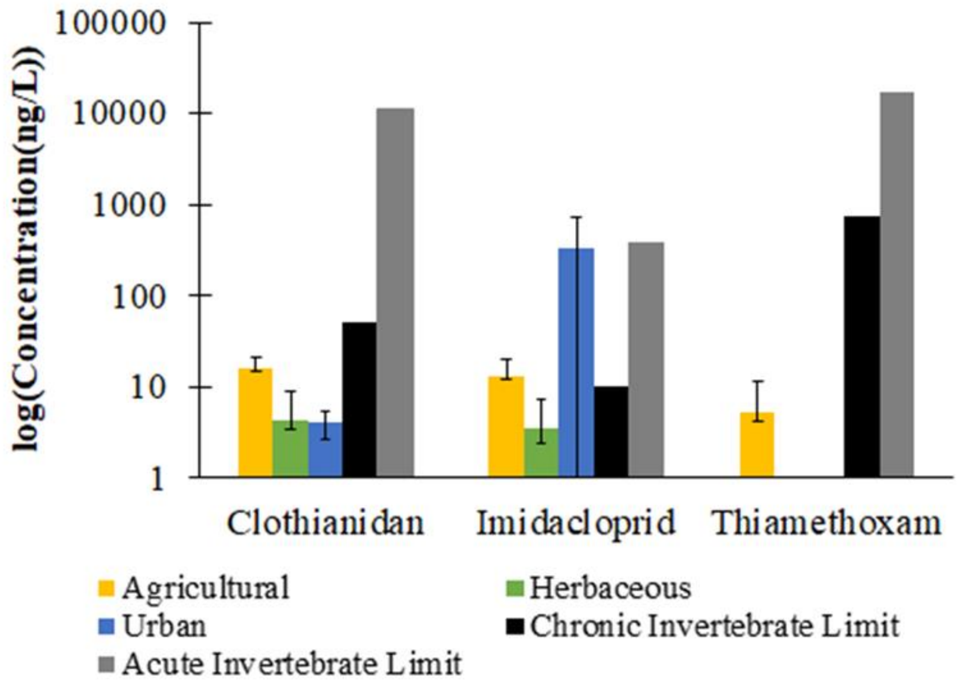


Figure 2.5: POCIS concentrations averaged over the whole study at each of the lakes. Chronic and acute invertebrate limits were added for comparison. Error bars represent the standard deviation of the means for each pesticide within each watershed. * Note imidacloprid is the only pesticide to exceed toxicity limits for this study.

Similar pesticide concentration trends were observed in the grab samples (Figure 2.6). Since thiamethoxam was not found at any of the inlets with the grab samples, the figure below only compares clothianidin and imidacloprid. As mentioned previously, imidacloprid is seen to exceed chronic toxicity limits at the agricultural and urban sites.

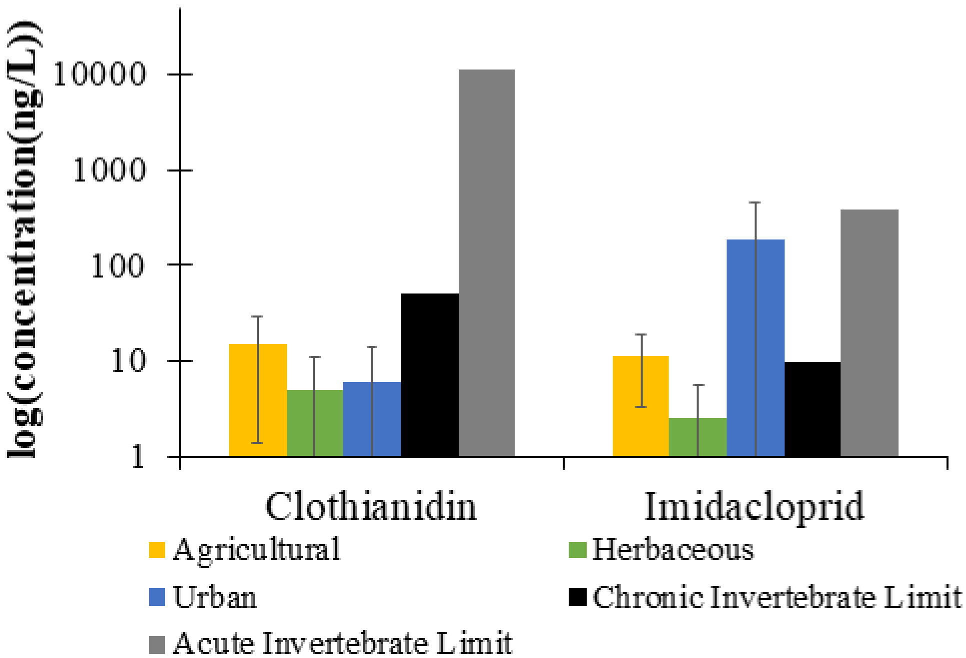


Figure 2.6: Average inlet grab concentrations for the whole study at each of the lakes. Chronic and acute invertebrate limits were added for comparison. Error bars represent the standard deviation of the means for each pesticide within each watershed.

Williams and Sweetman (2018) evaluated pesticide concentrations in wetlands of west central Minnesota near agricultural landscapes, reported similar findings to our observations. Grab samples were collected in April, May, and June in Minnesota. Williams and Sweetmans' (2019) study sites ranged from 1 – 10 hectares while we evaluated 530 – 6880 hectare watersheds. Clothianidin, imidacloprid, and thiamethoxam were found to be similar to concentrations in our study with observed concentrations being 8.6, 13.1, and 10.6 ng/L respectively [69], while we observed concentrations of 25.7, 16.4, and 8.9 ng/L, respectively, at the agricultural site

Comparison of POCIS and Grab Samples

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. It is hypothesized that they were not picked up in the POCIS samples due to how low the uptake rates were (0.08 and 0.03 L/d respectively). 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 reservoirs. Grab sampling can miss important pulses that may be measured using POCIS sampling. For example, thiamethoxam at the inlet vs. the POCIS samples (Figures 4) varies between each site. The POCIS samples detect some thiamethoxam while the inlet grab samples do not. POCIS observations indicate relatively uniform thiamethoxam concentrations throughout the sampling periods. Further, while POCIS sampling was more costly, samples were overall more representative of the pesticide concentration entering a waterbody through time [70,71].

Occurrence and Persistence of Pesticides Entering Recreational Lakes

Pesticide concentrations entering the lakes were assessed between sampling periods and specific locations throughout the lakes to gain an improved understanding of pesticide transport and persistence within these systems. Imidacloprid exceeded acute and chronic invertebrate levels 11% and 61% of the POCIS sampling periods, respectively (Figure 2.7). Imidacloprid is often used to protect trees and shrubs from the insect species such as emerald ash borer [72], grasshoppers, weevils, etc [73]. Therefore, the peak observed during monitoring period three in the urban watershed was likely due to limited regulations on pesticide application rates resulting in over application of pesticides to lawns and gardens during a period of higher insect damage.

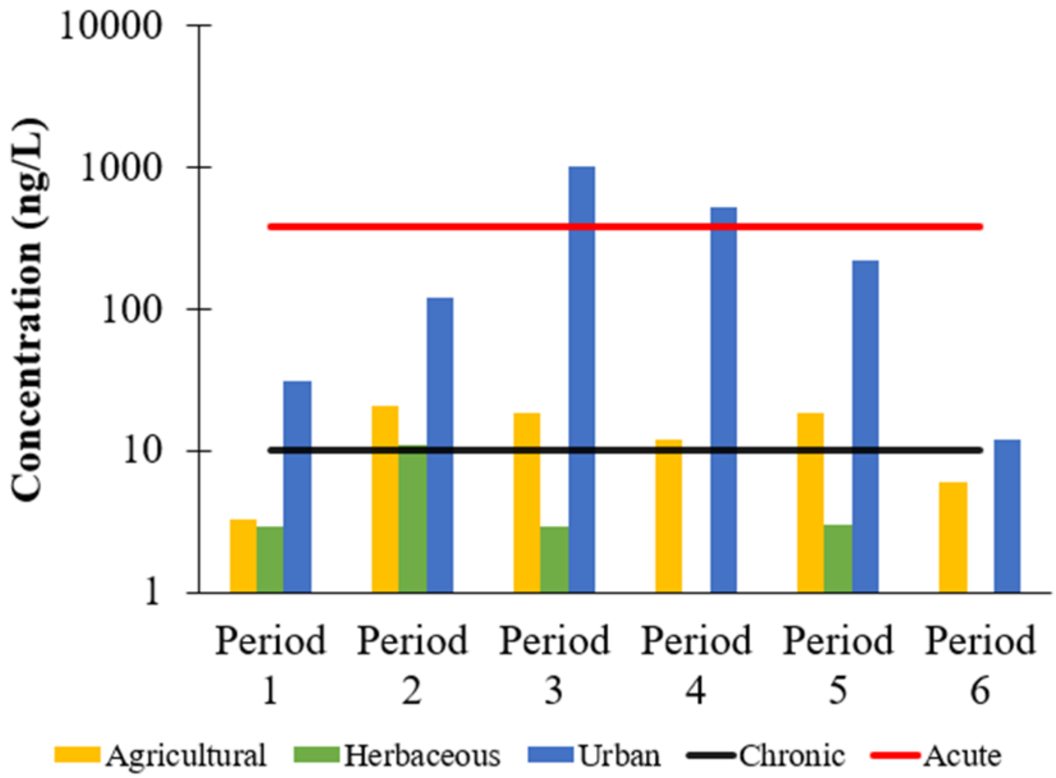


Figure 2.7: Imidacloprid POCIS concentrations at each lake throughout the length of the experiment. * POCIS membranes for the Herbaceous lake were not viable due to storage complications during Period 4. The red and black lines represent chronic and acute toxicity respectively.

There are very few comparative studies of application timing to these exact pesticides due to similar studies focusing on older pesticides like atrazine [12,53,66,67]. Atrazine is very commonly studied and has been found at concerning levels throughout the Midwest [12,53]. However, our observations validate the need for further field-scale studies on the occurance, persistence, and ecological impact of these pesticides on recreational waters [54,74].

The movement of pesticides from the inlet to the outlet of the reservoirs were also evaluted to assesse transport and persistance of each pesticide. Figure 2.2 illustrates sampling locations, while Figure 2.8 exhibits pesticide concentrations at each of the nine sampling locations. Slight trends were observed for clothianidin and imidacloprid at the agricultural site; the pesticides appeared to slowly move to the middle and outlet of the lake towards September and October (end of the growing season) 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 pesticides in Figure 8, clothiandin and imidacloprid show variations in concentrations. Clothiandan at the agricultural watershed had its highest concentrations in September and October and its lowest in May and June, each grouping significantly different than the other while July and August were similar to all of the sampling periods. On the other hand, imidacloprid at the urban watershed had higher values in July and then similar values in June, August, and October. The lowest values were measured in May and then June at the urban location which varied from each other and the other four months. However, thiamethoxam exhibited no trends at any of the sites or locations and was not deteced at the inlet during any of the monitoring periods. It is hypothesized that for the urban site, the golf course was the primary source of the thiamethoxam, which would bypass the inlet and go directly into the lake as runoff. Another potential explanation is the very nature of thiamethoxam is known to photolysize into clothianidin, which could then lead have led to observed the higher levels of clothiandin observed in the urban lake [16]. Lastly, lake management tends to spray pesticides around the edges of lakes introducing them to the water directly. While few trends were observed in our stuyd, further research is needed to provide more definitive findings using more replications and monitoring locations.

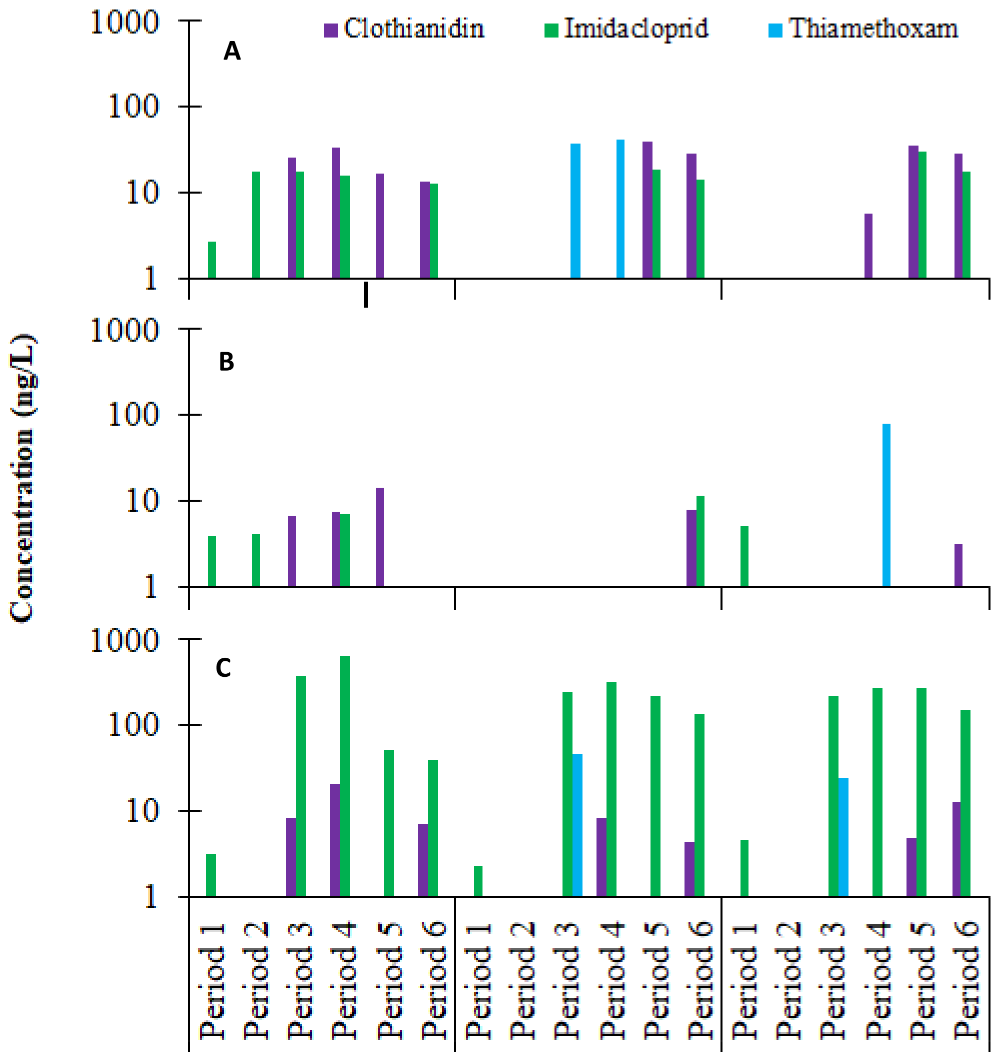


Figure 2.8: Grab pesticide concentrations of clothianidin, imidacloprid, and thiamethoxam at each sampling location in the agricultural (A), herbaceous (B), and urban (C).

Watershed Contribution into Reservoirs

Lastly the pesticide load entering each lake was determined for six pesticides for the three studies watersheds (Figure 2.9). Strictly assessing pesticide load, the agricultural watershed contributed the most azoxystrobin, clothianidin, and thiamethoxam. However, if watershed areas are considered in order to normalize the dataset, the urban watershed delivered the largest pesticide load per unit area. This is due to the herbaceous watershed being 13 times the size of the urban watershed and 2 times larger than the agricultural watershed. Overall the urban watershed was the primary pesticide contributor per unit area likely due to lack of education and regulation for homeowners on the ideal timing and quantity of pesticide applications.

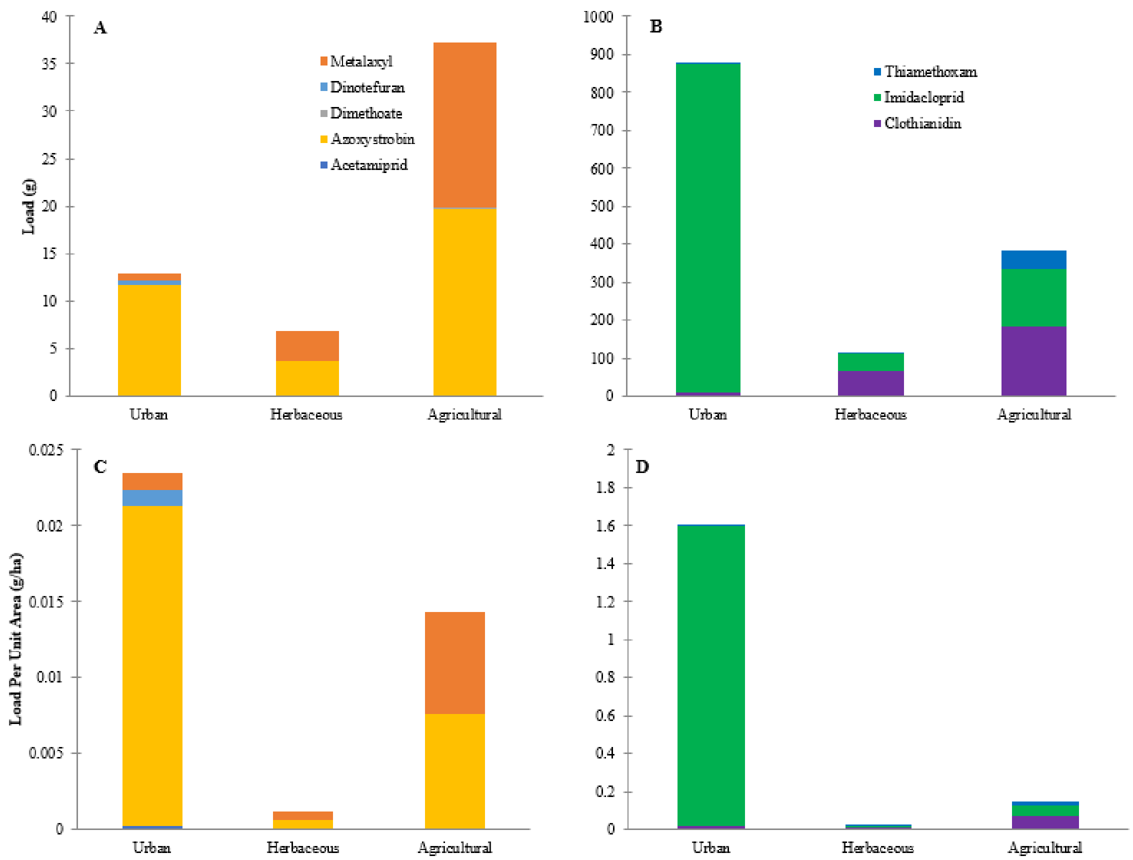


Figure 2.9: Comparison of pesticide load and watershed size for each lake. A and B) Total load of pesticides entering each lake. C and D) Total load entering each lake divided by the respective watershed size. *Note scales and units.

Conclusion

Overall pesticide concentrations were observed, specifically in the case of neonicotinoids (clothianidin, imidacloprid, and thiamethoxam), at exceedingly high levels and require further exploration for mitigation efforts in recreation waters. Pesticides observed at lower concentrations (dimethoate and metalaxyl) were older pesticides that are currently being phased out by the increasing use of newer ones [14].

Pesticides were both persistent entering and remaining within recreational waters throughout the year. Data collected from this project provides citizens and water resource managers' guidance strategies for monitoring pesticide exposure and ecotoxicity levels. Future research should focus on pesticide concentrations latitudinally throughout recreational lakes to provide more insight as to where the higher concentrations are located and move throughout the systems.

Further, development of POCIS innovative deployment methods requires exploration to ensure POCIS cages are able to adjust to representative flowpaths over long periods of time (~30 days). Overall this work provides a first look into possibilities for assessing pesticides entering and residing in recreational lakes and increased knowledge of their transport nature in these systems.

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CHAPTER 3: OVERALL CONCLUSIONS OF FINDINGS, RECCOMENDATIONS, AND FUTURE WORK

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Conclusions

Pesticides area a common way of protecting plants from unwanted pests and application levels are not going to decrease anytime soon, especially if there is no public education or continued research in these areas. Due to adverse effects caused by pesticides entering the environment after application, (air, water, etc.) further investigations are needed in order to identify fate and transport pathways and methods to reduce these pesticides entering recreational waterbodies. The following primary objectives were assessed in this Master's thesis along coupled major conclusions and findings below:

Objective: (1) Assess average neonicotinoid concentrations and loadings entering recreational lakes in three distinct watersheds; agricultural, urban, and herbaceous.

Conclusions: Both POCIS and grab samples exhibited the urban watershed had the highest pesticide concentrations. This was consistent after converting concentrations to pesticide load per unit area of the three watersheds, where the urban values were considerably higher for the 5 pesticides with the highest concentrations (Acetamiprid, azoxystrobin, dimethoate, dinotefuran, and imidacloprid). Further, pesticide concentrations for imidacloprid exceeded both chronic and acute toxicity levels for invertebrates as well as non-target species. The urban watershed was the largest contributor for imidacloprid and the agricultural watershed contributed the highest load of clothianidin and thiamethoxam. While the herbaceous watershed supplied the least amount of pesticides, it too has concentrations that exceeded toxicity limits.

Recommendations: Education for homeowners on proper pesticide application procedures is needed. For agriculture, shallow ponds with pumps to promote pesticide degradation mentioned in chapter 1.

Objective: (2) Evaluate pesticide persistence longitudinally throughout the lakes.

Conclusions: Pesticides persisted longitudinally through monitored recreational lakes regardless of pesticide or inlet concentration. Pesticides were even detected in regions of the lake, while not detected at inlets, likely due to applications to grass and beaches around the recreational lakes.

Recommendations: Regulation/education for park employees and golf course managers on correct pesticide application is recommended. Further, larger/improved placement of signs and warnings for toxic algal blooms and high pesticide concentrations at the lakes is also recommended.

Future Work

Future projects should include the following:

(1) Latitudinal assessment of lakes in order to determine potential hot spots near the edges of lakes and transport of pesticides throughout lakes

(2) Increased grab samples throughout the lakes to better characterize water quality spatially

(3) Fish and/or sediment evaluations to assess accumulation of pesticides in waterbodies

(4) Increased toxicity and persistence evaluations of neonicotinoids

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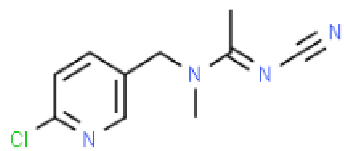
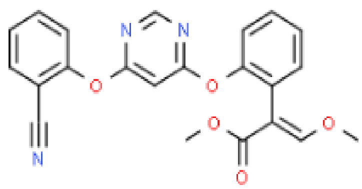
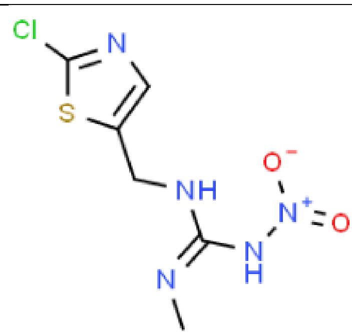
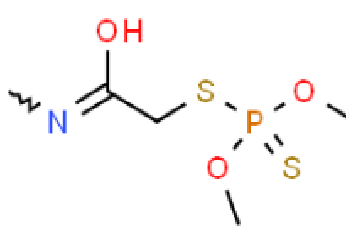
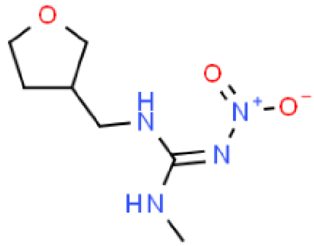
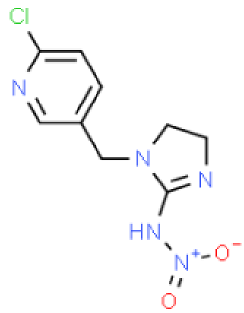
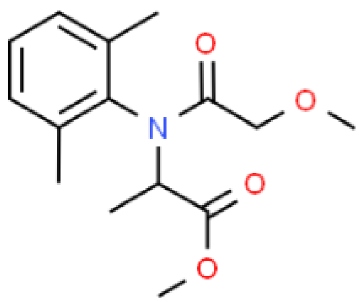
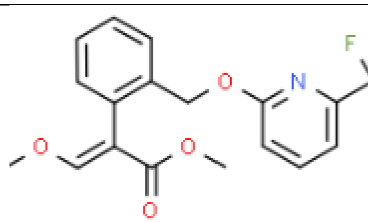
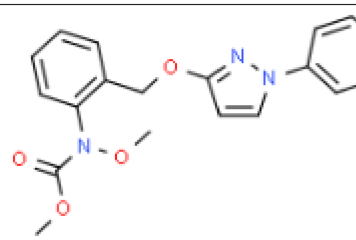
Appendix A

Table A1: Physical Properties of Pesticides

Pesticide (Trade Name)	Atomic Structure	Molar Mass (g/mol)	Class [4]	Usage	Toxicity (ng/L) [46]
Acetamiprid[75] (Assail™, Pristine™, and Chipco™)		223	Pyridylmethylamine neonicotinoid insecticide	Controls sucking insects for cotton, leafy vegetables, citrus	A:10,500 C:2,100
Azoxystrobin[76] (Heritage™ Fungicide)		403	Methoxyacrylate strobilurin fungicide	Golf courses and commercial turf farms	A:130,000 C:44,000
Clothianidin[77] (Poncho 600)		250	Nitroguanidine neonicotinoid and thiazole insecticide	Emerald Ash Borer Commercially for corn and canola	A:11,000 C: 50
Dimethoate [78] (Dimethoate 400)		229	Aliphatic amide organothiophosphate insecticide	Aphids, thrips, mites, grasshoppers	A: 21,500 C: 500

Dinotefuran [79] (Dinotefuran, MTI-446)		202	Nitroguanidine neonicotinoid insecticide	Emerald Ash Borer Golf courses, lawns, 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 [80]		279	Acylamino acid and anilide fungicide	Controls plant diseases caused by oomycetes	A: 14,000,000 C: 1,200,000
Picoxystrobin[81]		367	Carbanilate, phenylpyrazole, and methoxycarbanilate strobilurin fungicide	Barley, oats, wheat, soy beans, rye	A: 12,000 C: 1,000
Pyraclostrobin [82]		388	Phenylpyrazole and methoxyacrylate strobilurin fungicide	Citrus, dry beans, wheat, barley, tomatoes, bulb vegetables	A:7,850 C: 4,000

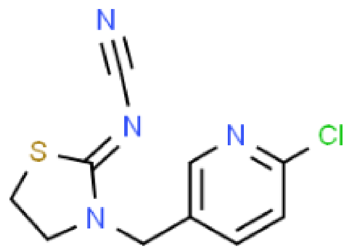
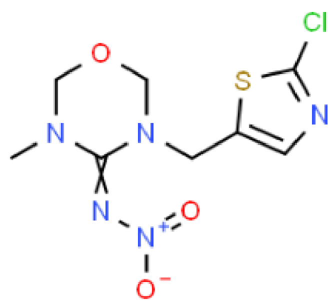
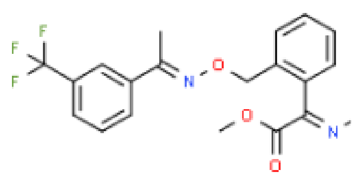
Thiacloprid		253	Pyridylmethylamine neonicotinoid and thiazolidine insecticide	A: 18,900 C: 970
Thiamethoxam		292	Nitroguanidine neonicotinoid and thiazole insecticide	A: 17,500 C: 740
Trifloxystrobin		408	Methoxyimino acetate strobilurin fungicide	A: 12.650 C: 2,760

Table A2: Statistical Differences

Table A2.1: Significance grouping for Urban POCIS samples by date

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

Table A2.2: Significance grouping for Agricultural POCIS samples by date

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

Table A2.2: Significance grouping for Urban samples by sample location

Urban P vs. Inlet	
Sample Site	Metalaxyl
1	A
11	B

*1 refers to POCIS. 11 refers to inlet grab sample.

Table SA.3: Significance grouping for Herbaceous samples by sample location

	Herbaceous P vs. Inlet		
Sample Site	Azoxystrobin	Dimethoate	Metalaxyl
2	B	B	A
21	A	A	B

*2 refers to POCIS. 21 refers to inlet grab sample.

Table A2.4: Significance grouping for agricultural samples by sample location

Agricultural P vs. Inlet				
Sample Site	Dimethoate	Metalaxyl	Pyraclostrobin	Thiamethoxam
3	B	A	B	A
31	A	B	A	B

*3 refers to POCIS. 31 refers to inlet grab sample.

Table A2.5: Significance grouping for all urban grab samples by date and by sampling location

Urban Grab	
Sample Site	Metalaxyl
11	B
12	A
13	A

*11 refers to inlet
12 refers to middle
13 refers to outlet

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

Table A2.6: Significance grouping for all herbaceous grab samples by date

Herbaceous Grab		
Date	Dimethoate	Pyraclostrobin
5/23/18	A	A
6/26/18	A	B
7/27/18	B	B
8/24/18	B	B
9/27/18	B	B

10/26/18	B	B

Table A2.7: Significance grouping for all agricultural grab samples by date

Agricultural Grab			
Date	Clothianidin	Picoxystrobin	Pyraclostrobin
5/23/18	B	B	A
6/26/18	B	A	A
7/27/18	AB	B	B
8/24/18	AB	B	B
9/27/18	A	B	B
10/26/18	A	B	B