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Year-round presence of neonicotinoid insecticides in tributaries to the Great Lakes, USA☆

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ABSTRACT

To better characterize the transport of neonicotinoid insecticides to the world's largest freshwater ecosystem, monthly samples (October 2015–September 2016) were collected from 10 major tributaries to the Great Lakes, USA. For the monthly tributary samples, neonicotinoids were detected in every month sampled and five of the six target neonicotinoids were detected. At least one neonicotinoid was detected in 74% of the monthly samples with up to three neonicotinoids detected in an individual sample (10% of all samples). The most frequently detected neonicotinoid was imidacloprid (53%), followed by clothianidin (44%), thiamethoxam (22%), acetamiprid (2%), and dinotefuran (1%). Thiacloprid was not detected in any samples. The maximum concentration for an individual neonicotinoid was 230 ng L^{-1} and the maximum total neonicotinoids in an individual sample was 400 ng L^{-1}. The median detected individual neonicotinoid concentrations ranged from non-detect to 10 ng L^{-1}. The detections of clothianidin and thiamethoxam significantly increased as the percent of cultivated crops in the basins increased ($\rho = 0.73$, $P = .01$; $\rho = 0.66$, $P = .04$, respectively). In contrast, imidacloprid detections significantly increased as the percent of the urbanization in the basins increased ($\rho = 0.66$, $P = .03$). Neonicotinoid concentrations generally increased in spring through summer coinciding with the planting of neonicotinoid-treated seeds and broadcast applications of neonicotinoids. More spatially intensive samples were collected in an agriculturally dominated basin (8 sites along the Maumee River, Ohio) twice during the spring, 2016 planting season to provide further information on neonicotinoid inputs to the Great Lakes. Three neonicotinoids were ubiquitously detected (clothianidin, imidacloprid, thiamethoxam) in all water samples collected within this basin. Maximum individual neonicotinoid concentrations was 330 ng L^{-1} and maximum total neonicotinoid concentration was 670 ng L^{-1}; median detected individual neonicotinoid concentrations were 7.0 to 39 ng L^{-1}.

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1. Introduction

Neonicotinoid insecticides are the most heavily used insecticides in the world (Simon-Delso et al., 2015). In the United States, their use has continued to increase since 2004 (USGS, 2017; Douglas and Tooker, 2015). As the use of neonicotinoids increases, there is increasing concern about their effects in both aquatic and terrestrial environments (Gibbons et al., 2015; Pisa et al., 2015; Sánchez-Bayo et al., 2016). Neonicotinoids are applied to both agricultural (foliar sprays, in-furrow treatments and seed coatings) and urban (lawn and garden foliar sprays, granular, tree injections, companion animal flea treatment) settings (Simon-Delso et al., 2015).

Surface water exposures to neonicotinoids have been correlated

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with direct effects on invertebrates (Van Dijk et al., 2013; Prosser et al., 2016), and indirect effects on insectivorous birds (Hallmann et al., 2014) and some fish (Gibbons et al., 2015). More recent neonicotinoid research has focused on their chronic toxicity, especially aquatic invertebrates that may be exposed via surface water (Morrissey et al., 2015; Sánchez-Bayo et al., 2016; Miles et al., 2017).

While many studies on neonicotinoid exposure in surface water have focused on agricultural drains or "edge of field" samples, there have been few studies that have measured neonicotinoids in broader riverine systems in the U.S. (Hladik et al., 2014; Hladik and Kolpin, 2016). A lack of data on the concentrations of neonicotinoids in surface water are considered an important knowledge gap (Goulson, 2013) as this information is needed to accurately assess potential environmental effects from neonicotinoid via stream exposures.

One region of the U.S. that was lacking baseline data on neonicotinoid concentrations were tributaries to the Great Lakes. These lakes are important as the world's largest freshwater system supplying 84% of North America's surface fresh water, and thus sensitive to pollutants (USEPA, 2017b). Neonicotinoids are commonly used heavily in both cultivated crops (*e.g.*, corn (maize) and soybeans) and in urban settings, both of which are important land uses in the watersheds of the Great Lakes (USGS, 2017, Fig. 1); therefore, neonicotinoids are hypothesized to be transported into the Great Lakes via such stream tributaries. In fact, neonicotinoids have been measured in surface waters of southern Ontario, Canada, which flow into Lake Erie and Lake Ontario (Struger et al., 2017), but no corresponding data have been reported for tributaries flowing into the Great Lakes from the U.S. The current study documents the occurrence of six neonicotinoids in 10 tributaries to the Great Lakes over a 12-month period. In addition, more spatially intensive samples were collected within a large agriculturally (cultivated-crops) dominated tributary at two separate time points during the spring planting season to provide further information on neonicotinoid inputs. This information will help to document seasonality in neonicotinoid concentrations and assess the potential impact to aquatic life in this sensitive freshwater ecosystem.

2. Methods

2.1. Sampling

Sample collection began in October 2015 and continued through September 2016 from 10 strategically selected watersheds to the Great Lakes (U.S.) (Fig. 1; Table SI-1). The sampling sites were selected to provide a geographic distribution across Great Lake tributaries along with a range of urbanization (up to 92%), percentage of cultivated crop agriculture (*e.g.*, maize, soybeans; up to 73%) and basin size (101–16,400 km^2) (Table 1). Samples were collected on a fixed monthly schedule and were not collected in response to a hydrologic event or flow condition. Additionally, eight sites (530–17,000 km^2) nested within one of the monthly watersheds (Maumee River) that had a high degree of cultivated crops (Table 1) and high potential for neonicotinoid use were sampled twice during the spring planting season (May and June 2016; Fig. 1; Table SI-2).

Water samples were collected at each of the 10 major tributaries via equal-width-integrated composites (USGS, 2006). Subsamples were composited in a 14 L Teflon churn, homogenized, and poured into a 1 L baked amber-glass bottle. Samples from the sites nested in the Maumee River watershed were collected as 3–4 d composites using autosamplers and Teflon bags as previously described (Kahl et al., 2014) or as grab samples where the composite sample did not provide sufficient volume (Table SI-2). A subsample from each composite was poured into a 1 L baked amber-glass bottle for neonicotinoid analysis. Samples were chilled during shipment to U. S. Geological Survey (USGS) Sacramento, California Laboratory, and refrigerated at 4 °C until extraction (within 7 days of collection).

2.2. Analytical method

Six neonicotinoids: acetamiprid (ACE), clothianidin (CLO), dinotefuran (DIN), imidacloprid (IMD), thiacloprid and thiamethoxam (THX), were measured in the water samples using a previously published method (Hladik and Calhoun, 2012). Briefly, 1 L samples were filtered (0.7 μm GF/F-grade glass-fiber; Whatman, Piscataway, New Jersey), spiked with imidacloprid-d_4 (Cambridge Isotope, Andover, Massachusetts), and extracted onto an Oasis HLB solid-phase extraction (SPE) cartridge (6 cc, 500 mg; Waters Corporation, Milford, Massachusetts). Extracts were analyzed on an Agilent 1260 bio-inert liquid chromatograph (LC) coupled to an Agilent 6430 tandem mass spectrometer (MS/MS) (Santa Clara, California) The theoretical level of detection (LOD) was 2 ng L^{-1} and the method detection limits (MDL) ranged from 3.3 to 4.5 ng L^{-1} (Table SI-1).

Quality assurance/quality control samples included: field blanks, replicate samples, and surrogate recovery. There were no detections of any of the neonicotinoids in the field blanks (7 samples, Tables SI-1 and SI-2). Field replicates (4 samples; Table SI-1) had relative percent differences (RPD) between the regular and replicate sample of 0–14% (median RPD = 3%). Recovery of the surrogate (imidacloprid-d_4) was 71–119% for all samples with a mean of 87% (±12%); data were not recovery corrected.

Data analyses were performed with SigmaPlot® 13.0. Concentrations (maximum) and detection frequency for each site were analyzed against land cover data using paired Spearman's rank correlations. Tributary and nested sites from May and June were compared using a Mann-Whitney rank-sum Test; non-detects were set at 1 ng L^{-1}. Concentrations of individual neonicotinoids for each sample are shown in Table SI-1 and Table SI-2; data can also be found online at USGS National Water Information System (https://waterdata.usgs.gov/nwis).

3. Results and discussion

3.1. Detection frequency and concentrations

For the 120 monthly water samples collected from the 10 Great Lakes tributaries, five neonicotinoids were detected (detection frequency in parentheses): IMD (53%), CLO (44%), THX (22%), ACE (2%), and DIN (1%). Thiacloprid was not detected during this study. At least one neonicotinoid was detected in 74% of the samples; 38% of the samples had two or more neonicotinoids present, and 10% of the samples had three neonicotinoids present (the maximum number of neonicotinoids detected in any individual sample). The three most frequently detected neonicotinoids (IMD, CLO, THX; Table 2) were also the three most frequently detected in previous studies (Hladik et al., 2014; Hladik and Kolpin, 2016; Struger et al., 2017); the less frequent detections of ACE and DIN were also similar to previous research in the U.S (Hladik and Kolpin, 2016) and Canada (Struger et al., 2017). These detection frequencies reflect the usage patterns of these neonicotinoids (USGS, 2017). Concentrations of individual neonicotinoids ranged from ND to 230 ng L^{-1} and the maximum total neonicotinoids in an individual sample was 400 ng L^{-1} (Fig. 2). Median detected individual neonicotinoid concentrations for all sites were <10 ng L^{-1}; total neonicotinoid median concentration was 10 ng L^{-1} (Fig. 2).

These maximum concentrations were generally lower than previous research where IMD concentrations of up to 10,400 ng L^{-1}

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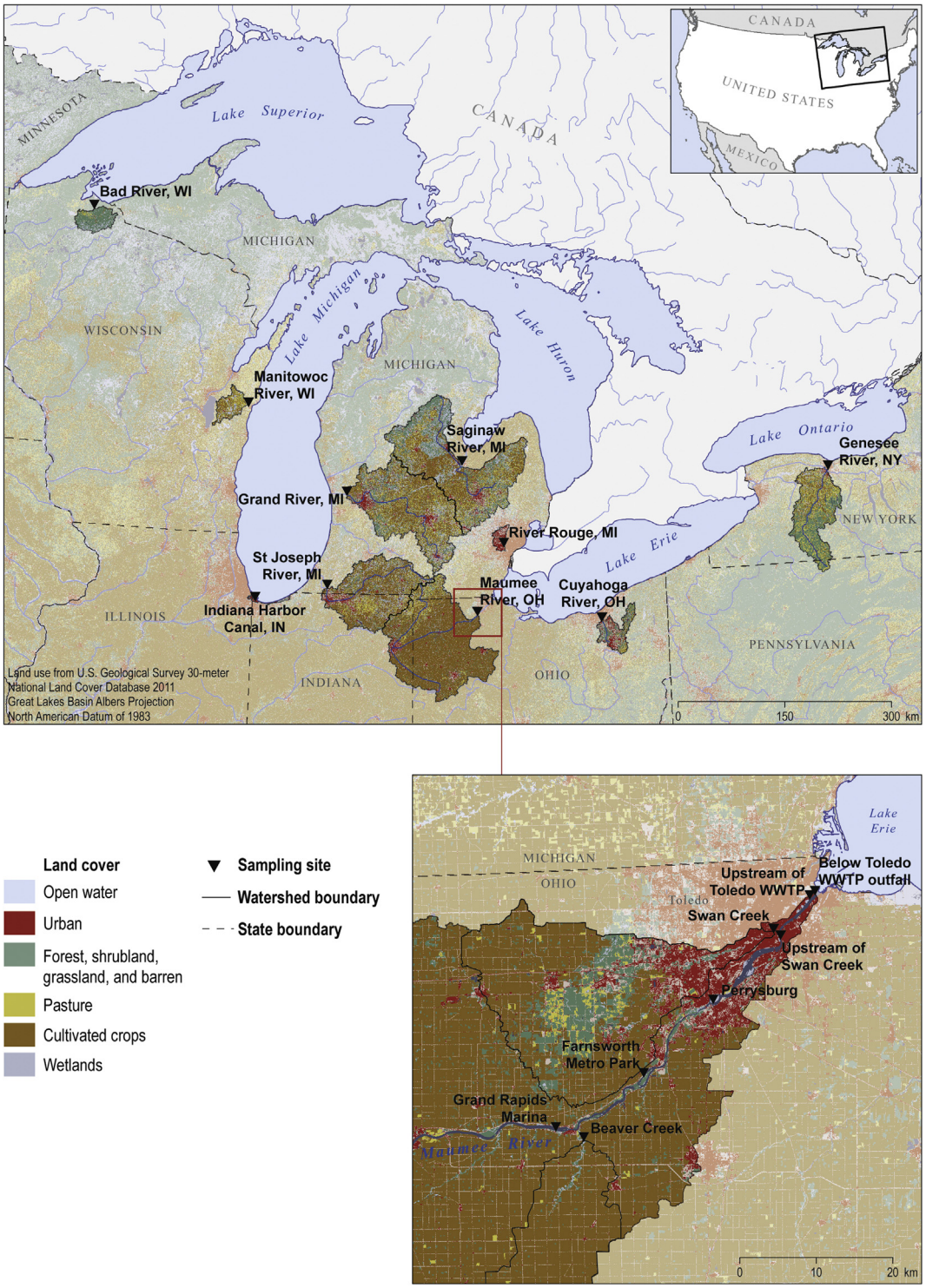

Fig. 1. Locations of sampling sites in the Great Lakes Region, USA. The top map includes the tributaries; the bottom map is the Maumee River nested sites. NLCD 2011 from Homer et al. (2015).

(Struger et al., 2017) in tributaries to Lake Erie and Lake Ontario were observed. The differences in maximum concentrations between this study and previous research could be due to the targeting of agricultural areas for the smaller basins and the precipitation-driven sampling captured during the previous research (Struger et al., 2017). Both of these factors have been shown to have an effect on stream pesticide concentrations where a general inverse relation has been documented between pesticide concentration and basin size (Larson et al., 1995) and neonicotinoid transport to streams has been shown to be driven by use and precipitation (Hladik et al., 2014).

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Table 1
Site names, drainage area, and land cover for the 10 sampled Great Lakes tributaries and eight sites nested within the Maumee River.

Site name	USGS station number	Drainage area (km^2)[a]	Land cover (percent)[b]			
			Urban	Agri-culture	Cultivated crops	Forest
Great Lakes Tributaries - Monthly Sites						
Bad River, WI	04027000	1550	3.4	5.8	2.1	71.1
Cuyahoga River, OH	04208000	1830	40.0	17.5	8.9	33.1
Genesee River, NY	04231600	6410	6.6	45.3	19.0	37.9
Grand River, MI	04119400	13700	14.8	54.0	36.8	16.2
Indiana Harbor Canal, IN	04092750	101	84.1	1.0	0.1	3.3
Manitowoc River, WI	04085427	1360	7.0	69.9	38.1	6.2
Maumee River, OH	04193500	16400	10.7	78.7	73.3	6.4
River Rouge, MI	04166500	484	92.0	0.1	0.0	4.5
Saginaw River, MI	04157005	15700	12.2	44.5	30.5	23.4
St. Joseph River, MI	04101500	9500	13.8	60.4	47.5	9.8
Maumee River Nested Sites						
Maumee R. - Grand Rapids Marina	412447083531201	15600	10.8	78.4	72.7	6.6
Beaver Creek	412403083503601	480	7.0	90.6	89.9	1.7
Maumee R. - Farnsworth Metro Park	412835083445600	16300	10.6	78.8	73.3	6.4
Maumee R. - Perrysburg	413342083382100	16400	10.8	78.6	73.2	6.4
Maumee R. - Upstream of Swan Creek	413812083315700	16500	11.1	78.3	72.9	6.4
Swan Creek	413840083323501	530	23.9	54.1	49.6	18.3
Maumee R. - Upstream of Toledo WWTP	414101083290800	17000	11.5	77.5	72.1	6.8
Maumee R. - Below Toledo WWTP Outfall	414120083283800	17000	11.5	77.5	72.1	6.8

[a] Drainage area from USGS National Water Information System (NWIS) unless unavailable, then GIS computed.
[b] Data from National Land Cover Database (NLCD) 2011 (Homer et al., 2015).

Table 2
Detection frequency, median concentrations, and maximum concentrations of the three most frequently detected neonicotinoids for the monthly samples. CLO = clothianidin; IMD = imidacloprid; THX = thiamethoxam; ND = not detected.

Site name	Dominant Land Cover	Detection Frequency (%)			Median Concentration (ng L^{-1})			Maximum Concentration (ng L^{-1})		
		CLO	IMD	THX	CLO	IMD	THX	CLO	IMD	THX
Bad River, WI	Forest	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cuyahoga River, OH	Urban	8	100	17	ND	10.3	ND	4.3	49.3	5.6
Genesee River, NY	Crops/Forest	8	ND	17	ND	ND	ND	3.2	ND	3.3
Grand River, MI	Crops	50	92	ND	2.0	5.3	ND	7.9	17.4	ND
Indiana Harbor Canal, IN	Urban	8	75	ND	ND	4.0	ND	2.2	10.1	ND
Manitowoc, WI	Crops	100	8	75	6.7	ND	3.7	8.6	2.4	7.6
Maumee River, OH	Crops	100	100	75	27.0	9.7	4.2	225.6	102.8	74.8
River Rouge, MI	Urban	17	92	ND	ND	8.3	ND	3.8	152.7	ND
Saginaw River, MI	Crops	100	58	25	6.4	2.2	ND	11.7	13.8	9.6
St. Joseph River, MI	Crops	50	8	8	2.0	ND	ND	20.6	3.4	3.0

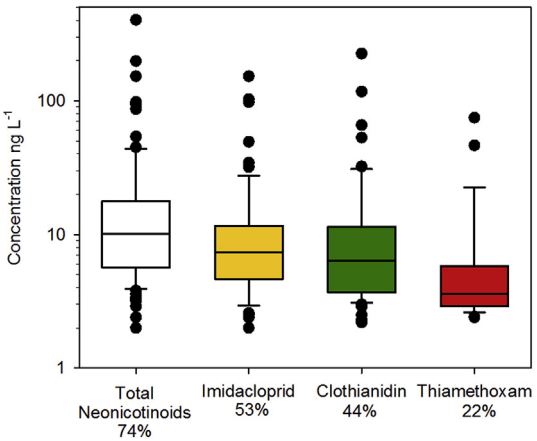

Fig. 2. Box plots of detected concentrations of the total neonicotinoids (sum of all neonicotinoids detected in an individual sample) and the three most frequently detected neonicotinoids (imidacloprid, clothianidin and thiamethoxam) in 10 sampled tributaries to the Great Lakes. Overall detection frequency is provided below each x-axis label.

3.2. Neonicotinoid correlations with land cover

No neonicotinoids were detected at the only tributary sampled that was dominated by forest (Bad River, WI; Table 2) and that had correspondingly low urban land cover and cultivated crop agriculture (Table 1). At those sites that were dominated by cultivated crops (*e.g.*, maize, soybeans) (Table 1), CLO and THX were more frequently detected and had higher median concentrations than other neonicotinoids (Table 2). The detections of CLO and THX increased as the percent of cultivated crops increased (Figure SI-1); the site on the Maumee River with over 70% of the land cover containing cultivated crops, had the highest detection frequency and median concentrations of CLO and THX (Table 2). For CLO and THX, there were positive correlations (Table SI-3) between the percentage of cultivated crops and both the detection frequency ($\rho = 0.73$, $P = .01$; $\rho = 0.66$, $P = .04$, respectively) and maximum concentrations ($\rho = 0.86$, $P < .01$; $\rho = 0.64$, $P = .04$, respectively); these relationships were similar to those found previously for CLO and THX in a nationwide study (Hladik and Kolpin, 2016). In addition, there was a positive correlation between the co-occurrence of CLO and THX ($\rho = 0.66$, $P = .03$); this relation could

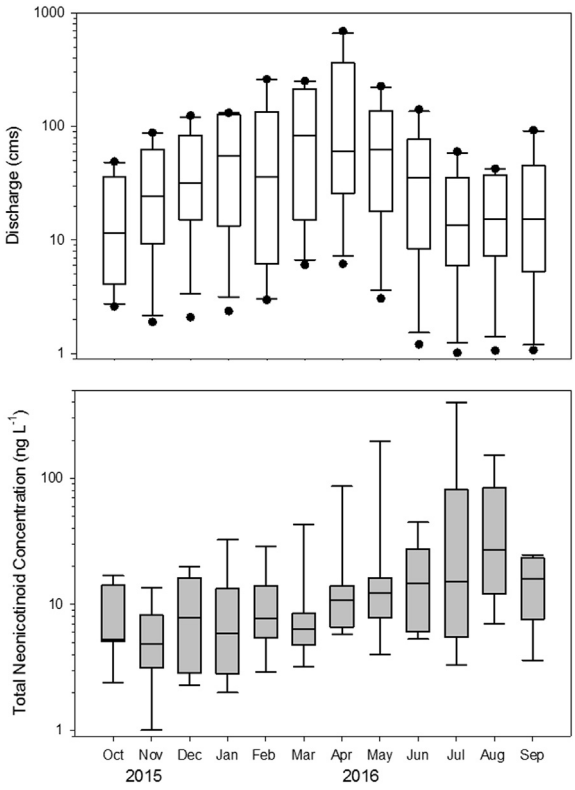

Fig. 3. Mean daily discharge (top) and total neonicotinoid concentrations measured (bottom) during each month at 10 sites.

be attributed to the application of both compounds in the same area (USGS, 2017) and that CLO is also a biological transformation product of THX (Nauen et al., 2003).

Sites with a greater percentage of urbanization generally had higher IMD detection frequencies and mean concentrations (Table 2, Figure SI-2). Imidacloprid is the oldest neonicotinoid and is registered for a variety of uses including those used in urban areas such as lawn care, tree drenches, etc (Simon-Delso et al., 2015) and thus likely to be detected more frequently in areas of greater urbanization (Sáchez-Bayo and Hyne, 2014). The detection frequency and maximum concentration of IMD increased as the percent of urbanization increased ($\rho = 0.66$, $P = .03$; $\rho = 0.72$, $P = .02$; Table SI-3; Figure SI-2), again similar to what was seen in a nationwide study (Hladik and Kolpin, 2016). While still significant, the relation between land cover and IMD was not as strong as for CLO and THX as IMD can also be used in agricultural seed coatings and broadcast applications (Simon-Delso et al., 2015) making its detection common in areas with both land covers.

3.3. Temporal variation

On a monthly basis, IMD and CLO were detected in at least one tributary in each month of the year. Concentrations were greatest during spring and summer (Fig. 3) coinciding with the application of neonicotinoids as seed coatings (spring) and broadcast applications. The timing of the maximum total neonicotinoid concentration, however, varied for each site (Table SI-1). The Maumee River (73% agriculture) had an increase in neonicotinoid concentrations beginning in May, but the maximum concentrations for all three of the frequently detected neonicotinoids (CLO, IMD, THX) were in July (Fig. 3). The increase in neonicotinoid concentrations in May are likely due to planting of treated seeds while the maximum concentration observed in July maximum could be due to broadcast applications or runoff from previous applications.

While some samples from the current study represent increased flow conditions, this study was not designed to focus on hydrologic events; prior studies have indicated that neonicotinoid concentrations were greater during periods of increased flow than during low-flow periods (Hladik et al., 2014; Struger et al., 2017). Due to this study design, peak late spring concentrations, coinciding with the planting of row crops with seed coatings, may be underestimated in this study. The May 3, 2016, Maumee sample was collected near the maximum discharge (725 cms) of a recent rain event (Fig. 4); however, at the time of the May sampling only 27% of corn was planted in Ohio; by the time the June sample was collected, 96% of the corn was planted (USDA, 2016). The July 5, 2016 sample was collected 11 days after a rain event (maximum discharge of 498 cms on June 24, 2016), so the maximum concentration was likely not captured for the summer sample. The River Rouge (92% urban) had lower fluctuations in flow and IMD concentrations; the peak measured concentrations were in August (Fig. 4). Additionally, Struger et al. (2017) did not observe a seasonal trend in neonicotinoid concentrations in areas with non-row-crop agricultural activities.

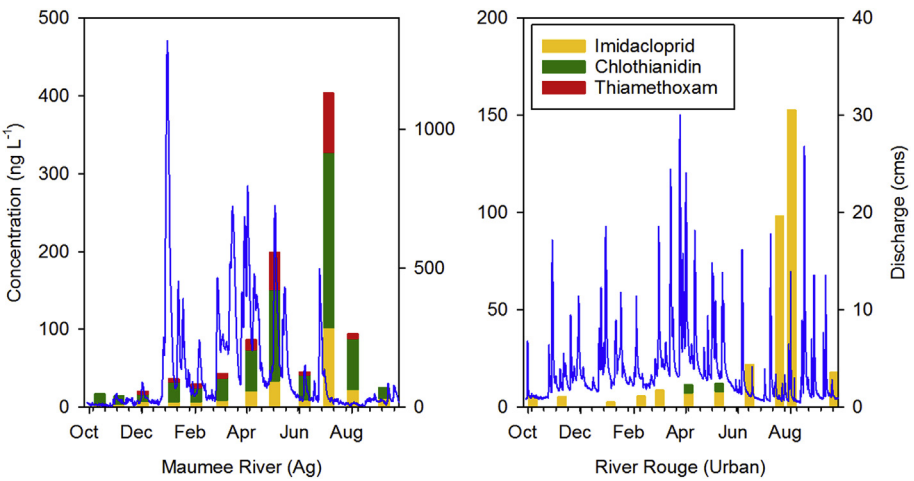

Fig. 4. Concentrations (left axes) of the three most frequently detected neonicotinoids over one year along with the hydrograph (right axes) for two sites (one with a high percent of cultivated crops and the other a high percent urban).

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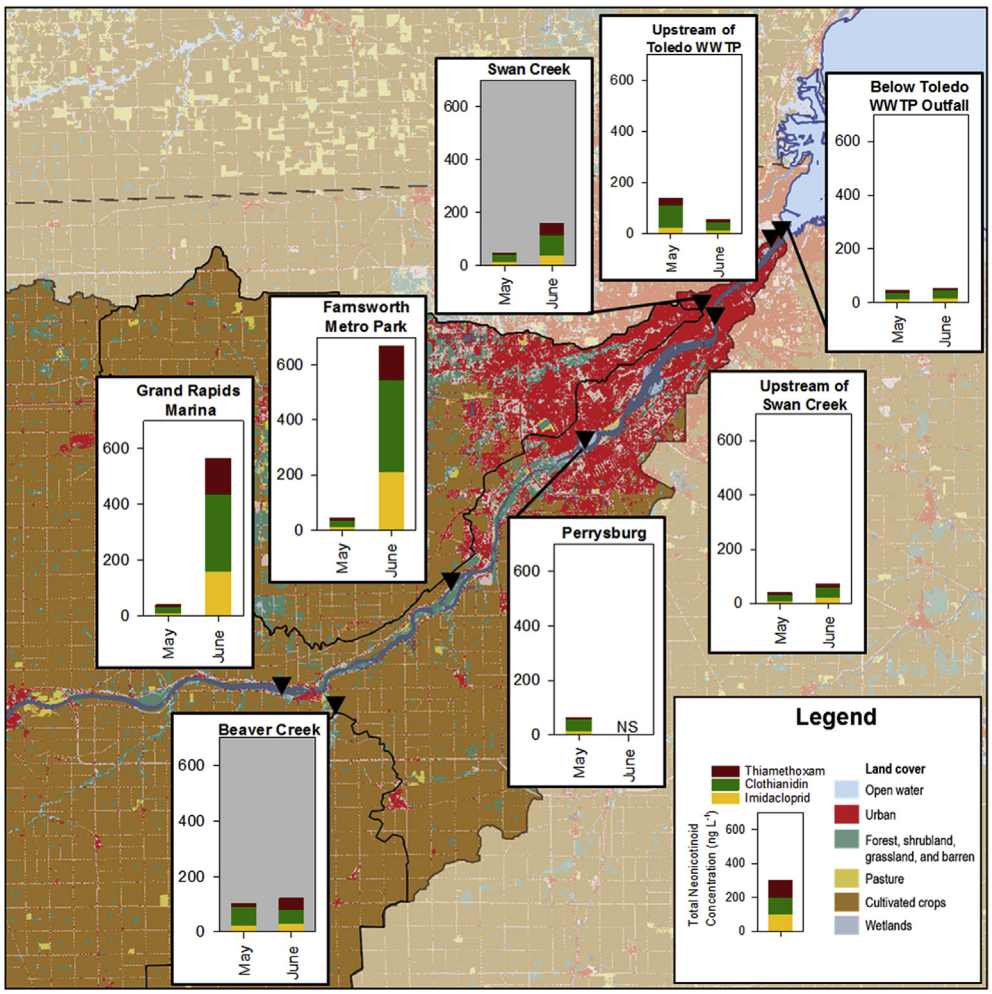

Fig. 5. Neonicotinoid concentrations collected in May and June 2016 at sites nested within the Maumee River watershed. Bar charts shaded in gray are tributaries to the Maumee River, those in white are from locations along the Maumee River. Land cover data from NLCD 2011 (Homer et al., 2015).

3.4. Maumee River nested sites

At the eight nested watersheds in the Maumee River basin (Fig. 1), three neonicotinoids (CLO, IMD, and THX) were ubiquitously detected in 100% of the samples collected (n = 15; one site measured only once). Concentrations of individual neonicotinoids ranged from 4.9 to 330 ng L^{-1} and the maximum total neonicotinoids in individual samples was 670 ng L^{-1} (Fig. 5; Table SI-2). Median neonicotinoid concentrations were 7.0 to 39 ng L^{-1} and total neonicotinoid concentrations were 65 ng L^{-1} (Fig. 6).

In general, concentrations observed in May were similar for all sites; total neonicotinoids ranged from 39 to 140 ng L^{-1} (Fig. 5). In the June samples, two sites had elevated concentrations (Grand Rapids Marina and Farnsworth Metro Park) with total neonicotinoids of 560 to 670 ng L^{-1} versus 53 to 160 ng L^{-1} at the other sites (Fig. 5). These increased upstream concentrations are potentially due to runoff from crops with increased dilution downstream. Even though the nested sites were multiple-day composites, the sampling did not follow a single parcel of water which may be reflected in the varying concentrations.

When the nested sites in the Maumee River were compared to the tributary sites sampled in May and June, concentrations in the nested sites were generally higher than those for the 10 tributary sites (Fig. 6). Differences in median concentrations between the nested and tributary sites were significant (rank-sum test; $P = .002$, <.001, and .005 for CLO, THX, and IMD, respectively). The nested sites were cultivated crop (maize and soybean) and urban dominated and located in the tributary watershed (Maumee River) that

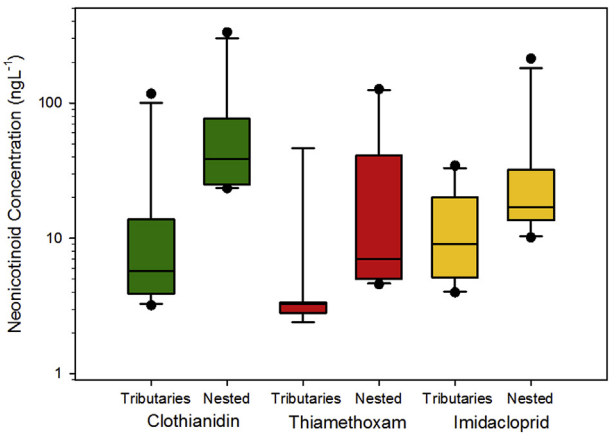

Fig. 6. Box plots of detected concentrations of the three most frequently detected neonicotinoids in tributaries (10 sites sampled monthly) and eight Maumee nested sites sampled during two time points in May and June 2016. Rank-sum test were significant for each pair; $P = .002$, <.001, and .005 for CLO, THX, and IMD, respectively.

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Table 3
Toxicity value comparsion for three neonicotinoids. CLO = clothianidin; IMD = imidacloprid; THX = thiamethoxam; NA = not available.

Source		Value (ng L^{-1})			# of Exceedances		
		CLO	IMD	THX	CLO	IMD	THX
USEPA Aquatic Life Benchmark – Invertebrates (USEPA, 2017a)	acute	11,000	385	17,500	0	0	0
	chronic	1100	10	NA	0	33	NA
Morrissey et al. (2015)	acute	200	200	200	3	1	0
	chronic	35	35	35	12	8	6

had some of the highest concentrations in the entire study; the increased neonicotinoid concentrations in the nested sites reflect this observation.

3.5. Potential toxicity

The U.S. Environmental Protection Agency has set acute and chronic invertebrate aquatic life benchmarks for CLO, IMD and THX that are in the range of tens to tens of thousands of ng L^{-1} (Table 3; USEPA, 2017a), with the more recently updated IMD values being substantially lower than those for CLO and THX. Other studies also suggest lower values (similar to the USEPA values for IMD) for acute (200 ng L^{-1}) and chronic (10 to 35 ng L^{-1}) individual neonicotinoid exposures (Mineau and Palmer, 2013; Morrissey et al., 2015).

No values detected in this study exceed the current acute USEPA aquatic life benchmarks; the chronic benchmarks were exceeded for IMD 33 times (24% of samples; Table 3). Because there are differences among neonicotinoid benchmarks from different sources and there is less information available on the aquatic toxicity of CLO and THX than for IMD, the values based on a meta-analysis of available literature on aquatic toxicity were used to put the current results into context (Morrissey et al., 2015). Two neonicotinoids, CLO and IMD, exceeded the more conservative acute value (200 ng L^{-1}): once in a monthly sample (July Maumee River), and three times (twice for CLO and once for IMD) in the June nested Maumee samples. If the chronic value from Morrissey et al. (2015) of 35 ng L^{-1} was used, however, then there were 26 individual neonicotinoid exceedances (11 exceedances in the monthly samples and 15 in the nested watershed samples). Of these individual exceedances CLO was higher than 35 ng L^{-1} 12 times (9% of all samples), IMD eight times (6% of all samples), and THX six times (4% of all samples). Samples collected in the Maumee River basin (monthly and small watersheds) accounted for 15 (58%) of the individual neonicotinoid concentrations over 35 ng L^{-1}; this was also the basin that had the highest percentage of cultivated crops (73%).

4. Conclusions

Three major neonicotinoids (CLO, IMD and THX) were found to be prevalent throughout the year in sampled tributaries to the Great Lakes, the largest freshwater ecosystem in the world; this included watersheds with both urban and agricultural (*i.e.*, cultivated crops) land cover. This represents a direct year-round exposure of neonicotinoids to aquatic organisms. Samples were not hydrologic based and therefore maximum peak concentrations were likely underestimated. While the concentrations were typically below acute toxicity levels, this study provides evidence of potential chronic toxicity impacts through the near constant neonicotinoid exposure to individual taxa as well as on ecosystem functions. Additionally, higher neonicotinoid concentrations occurred in spring and summer which may align with sensitive stages for aquatic organisms. More research is needed on the potential effects of year-round neonicotinoid exposures.

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Appendix B. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.01.013.

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