



Widespread occurrence of neonicotinoid insecticides in streams in a high corn and soybean producing region, USA



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ABSTRACT

Neonicotinoid insecticides are of environmental concern, but little is known about their occurrence in surface water. An area of intense corn and soybean production in the Midwestern United States was chosen to study this issue because of the high agricultural use of neonicotinoids via both seed treatments and other forms of application. Water samples were collected from nine stream sites during the 2013 growing season. The results for the 79 water samples documented similar patterns among sites for both frequency of detection and concentration (maximum:median) with clothianidin (75%, 257 ng/L:8.2 ng/L) > thiamethoxam (47%, 185 ng/L:<2 ng/L) > imidacloprid (23%, 42.7 ng/L: <2 ng/L). Neonicotinoids were detected at all nine sites sampled even though the basin areas spanned four orders of magnitude. Temporal patterns in concentrations reveal pulses of neonicotinoids associated with rainfall events during crop planting, suggesting seed treatments as their likely source.

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1. Introduction

Insecticide use has long been an integral part of crop protection and management strategies in the United States (U.S.). Historically, insecticides in Midwestern U.S. streams have been less frequently detected and at lower concentrations (Gilliom et al., 2006; Schnoebelen et al., 2003) than the ubiquitous occurrence of herbicides and their associated degradation products (Battaglin et al., 2005). In recent years, however, insecticide use on crops has changed dramatically in terms of both active ingredients used and application techniques. The use of organophosphate (e.g., chlorpyrifos, methyl parathion, phorate, terbufos) and carbamate (e.g., carbaryl, carbofuran) insecticides on corn and soybeans has declined while use of neonicotinoid insecticides across the U.S., particularly in the Midwestern U.S., has dramatically increased over the last decade (USGS, 2014; Fig. SI-1). The most commonly-used neonicotinoids on corn and soybeans include clothianidin, imidacloprid, and thiamethoxam (Table 1). Imidacloprid also has a variety of other uses including lawn and garden and topical flea medicines (Jeschke et al., 2011).

In addition to changes in active ingredients, there has also been a corresponding change in insecticide management techniques. This is primarily reflected in a switch from broadcast applications for insect control to the use of pesticide-treated seeds, coinciding with a push in precision agriculture (Elbert et al., 2008). The use of treated seeds in the U.S. has tripled in the last decade (Haire, 2014) to the point where nearly all corn and soybeans planted in the U.S. have a seed treatment (i.e., coating), many of which include neonicotinoids. This rapidly growing neonicotinoid use is clearly shown for both Iowa (Fig. 1) and the Midwestern U.S. (Fig. SI-1).

Neonicotinoids are receiving increased scrutiny since they have been implicated in adversely affecting pollinators and linked to colony collapse disorder in bees (Spivak et al., 2011; vanEngelsdorp et al., 2009). Thiamethoxam has been linked to decreased survival in honeybees (Henry et al., 2012), while imidacloprid has been linked to reduced colony growth and queen performance in bumble bees (Whitehorn et al., 2012) and sublethal effects to flies (Charpentier et al., 2014). An important mechanism of neurotoxicity for neonicotinoids is the almost irreversible binding to nicotinic acetylcholine receptors in insects (Jeschke and Nauen, 2008). Therefore, continued exposures to neonicotinoids may lead to a cumulative effect in insects (Tennekes and Sanchez-Bayo, 2011). Birds are also susceptible to neonicotinoid exposure, including both the direct ingestion of treated seeds and through contamination of the aquatic

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Table 1
Properties of commonly used neonicotinoid insecticides and the amount applied in Iowa in 2013.

Neonicotinoid	Log K_{ow} ^a	Log K_{oc} ^{a,b}	Aqueous dissipation half-life (days) ^a	Soil degradation half-life (days) ^a	Amount applied to crops in Iowa in 2013 (kg) ^c
Acetamiprid	0.80	2.3	4.7	3	–
Clothianidin	0.91	2.1	40.3	545	215,000
Dinotefuran	–0.55	1.4	– ^d	82	–
Imidacloprid	0.57	2.1–2.5	30	191	70,700
Thiacloprid	1.26	NA	8.5	15.5	–
Thiamethoxam	–0.13	1.8	30.6	50	49,900

^a UOH (2013).

^b CDPR (2006).

^c Baker and Stone (2014).

^d – = not available.

food chain (Mineau and Palmer, 2013). There is evidence that neonicotinoids can cause immune suppression in insects (bees) and in fish (Di Prisco et al., 2013; Mason et al., 2013). In 2013, the European Commission adopted a proposal to restrict the use of 3 neonicotinoids (clothianidin, imidacloprid and thiamethoxam) for a period of 2 years, including their use for seed treatment (EU, 2013).

In the environment, neonicotinoids are highly soluble in water (log K_{ow} –0.55 to 1.26) and somewhat persistent (Table 1), with clothianidin having the longest soil degradation half-life (545 days). Thus, neonicotinoids are likely to be transported away from the initial application area to surface water and groundwater. The

transport to surface water can occur via overland runoff from rainfall or irrigation, or through tile drain lines. Monitoring data for neonicotinoids in the environment are limited, with most studies only analyzing for imidacloprid. Of the studies that measured multiple neonicotinoids, two were in wetlands (Anderson et al., 2013; Main et al., 2014) and two were in streams (Hladik and Calhoun, 2012; Sanchez-Bayo and Hyne, 2014). More detailed research on the geographic occurrence and concentrations of neonicotinoids in surface waters, especially from use on treated seeds, is essential in determining possible implications to biota, including pollinators and aquatic invertebrates.

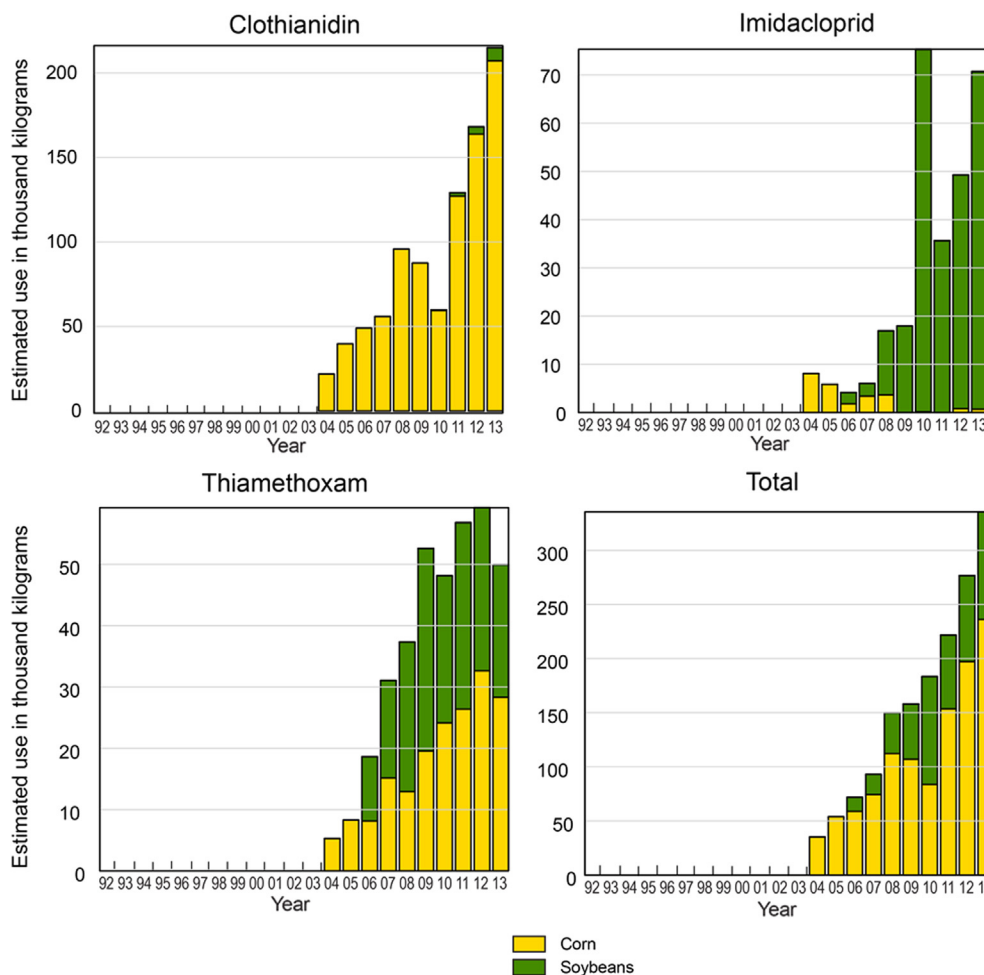


Fig. 1. Estimated annual pesticide (Epest-high) use for Iowa 1992–2013 for the three most commonly applied neonicotinoids and the total for all 3 compounds (data from Baker and Stone, 2014).

The purpose of this study is to describe the occurrence of six neonicotinoids in select streams in a high corn and soybean producing region during the 2013 growing season. The six neonicotinoids analyzed were acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid and thiamethoxam. Iowa is the top producer of corn and soybeans in the U.S. (USDA, 2014), with a correspondingly large amount of neonicotinoid use (Fig. SI-1; USGS, 2014). Thus, Iowa streams were ideal for determining the potential off-field transport of neonicotinoids. This study provides the first broad-scale investigation of multiple neonicotinoids in the Midwestern U.S. and one of the first conducted within the entire U.S.

2. Methods

2.1. Sampling

Seventy-nine water samples from a network of nine sites across Iowa (U.S.) were collected during the 2013 growing season. The sampling sites were selected to provide a range of basin size (521–836,000 km²), basin crop intensity, and geographic distribution across the state (Table 2, Fig. 2). The sites included seven stream basins within Iowa having substantial areas of corn and soybean production, ranging from 59 to 86% of the basin areas, and two sites on the Missouri and Mississippi Rivers with extensive basin areas outside of Iowa and more diverse landuse (Table 2, Fig. 2). Several of the sampling sites were nested within the basins of other sampled sites, but nested basins were generally not a dominant portion of the corresponding downstream basin (Fig. 2). Sample collection started in March or April in the smaller basins before the start of field preparations for the current planting season and later (May) in the Missouri and Mississippi Rivers. All sampling continued through October on roughly a monthly basis for eight of the nine sites (Table SI-1). One site (Old Mans Creek near Iowa City) was sampled more frequently, with timing based on hydrologic conditions (e.g., runoff events, Fig. SI-2 through Fig. SI-6) to provide more detailed information on the variability of stream neonicotinoid concentrations over time through the 2013 growing season (Table SI-1). This basin was selected for more frequent sampling because neonicotinoid concentrations were expected to be higher in smaller basins and logistics allowed for a rapid sampling response to rainfall events at this site.

Water samples were collected in the field via depth and width-integrated composites (USGS, 2006) into 1-L amber glass bottles where possible or as grab samples in the centroid of flow (i.e. smaller streams sites). Samples were chilled immediately, shipped to the U. S. Geological Survey (USGS) Sacramento, California Laboratory, and refrigerated at 4 °C until extraction (within 7 days of collection).

2.2. Analytical method

The six neonicotinoids were measured in the water samples using a previously published method (Hladik and Calhoun, 2012). Samples were filtered using a baked 0.7- μ m nominal pore size GF/F-grade glass-fiber filters (Whatman, Piscataway, New Jersey). Each sample was spiked in the laboratory with imidacloprid-*d*₄ (Cambridge Isotope, Andover, Massachusetts) as the surrogate to achieve an in-bottle concentration of 100 ng/L. An Oasis HLB solid-phase extraction (SPE) cartridge (6 cc, 500 mg; Waters Corporation, Milford, Massachusetts) was used for sample

concentration. The HLB cartridge was eluted with 10 mL of 50:50 DCM:acetone, the eluent was reduced to less than 0.2 mL and the internal standard, ¹³C₃-caffeine, was then added. 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) with a Zorbax Eclipse XDB-C18 column (2.1 mm × 150 mm × 3.5 mm; Agilent). The column flow rate was 0.6 mL/min and a gradient of 5 mM formic acid in water and acetonitrile were used (Hladik and Calhoun, 2012). The MS/MS was operated under electrospray (ESI) ionization in positive mode, data were collected in the multiple-reaction-monitoring (MRM) mode. The theoretical level of detection (LOD) was 2 ng/L and the method detection limits (MDLs; USEPA, 1997) ranged from 3.6 to 6.2 ng/L (Table SI-1).

Neonicotinoids concentrations were validated against a set of quality control parameters including: field blanks, replicate samples, matrix spikes, and surrogate recovery. Field blanks (3 samples), made from laboratory grade organic free water, had no detections of neonicotinoids measured. Field replicates (5 samples) had relative percent differences (RPD) between the regular and replicate sample of 6–22% (median RPD = 13%). Field matrix spike (4 samples) recoveries ranged from 71–89%. Recovery of the surrogate (imidacloprid-*d*₄) was 71–120% for all samples with a median of 83%; data was not recovery corrected.

3. Results and discussion

3.1. Detection frequency and concentrations

Neonicotinoid occurrence and concentrations were consistent with the amounts applied. The three neonicotinoids that account for the vast majority of use in Iowa (clothianidin, imidacloprid, thiamethoxam) were frequently detected in multiple samples (Table SI-1). In contrast, the much less used acetamiprid and dinotefuran were detected only once, and thiacloprid was never detected in the 79 stream water samples collected during the 2013 growing season (Table SI-1). Clothianidin was detected most frequently (75%), followed by thiamethoxam (47%) and imidacloprid (23%) (Table 2). These results are consistent with clothianidin being the most heavily used in Iowa (about 215,000 kg in 2013; Table 1). Use of both imidacloprid (70,700 kg) and thiamethoxam (49,900 kg) was substantially lower, but their frequency of occurrence was the reverse of the amount used in Iowa. This inconsistency could be the result of use in individual basins being different from the statewide use, different application methods (seed treatment versus aerial applications), or other factors. For water samples that had a detection of one or more neonicotinoids (60 samples), clothianidin was detected in all but one of those samples. The frequent detection of clothianidin was likely due to a combination of factors: 1) it is the most heavily used neonicotinoid in Iowa (Fig. 1), 2) it has a long soil degradation half-life (Table 1), and 3) is

Table 2
Sampling sites and summary of results for clothianidin, imidacloprid, and thiamethoxam.

Site name	USGS site ID	Drainage area (km ²)	% Cultivated crops ^a	Samples (N)	Clothianidin			Imidacloprid			Thiamethoxam		
					Det. freq. (%)	Max (ng/L)	Median (ng/L)	Det. freq. (%)	Max (ng/L)	Median (ng/L)	Det. freq. (%)	Max (ng/L)	Median (ng/L)
Old Mans Creek near Iowa City, IA	05455100	521	62	21	95	257	17.1	38	42.7	<2	52	185	2.4
South Fork Iowa River near New Providence, IA	05451210	580	86	7	57	38.0	9.2	14	9.2	<2	57	31.9	5.2
North Fork Maquoketa River near Fulton, IA	05418400	1310	59	7	57	73.8	4.6	14	4.8	<2	57	40.3	<2
Little Sioux River at 300 St near Spencer, IA	06604440	1360	74	8	50	6.3	<2	13	24.9	<2	13	2.4	<2
Maquoketa River near Spragueville, IA	05418600	4230	62	7	71	13.2	3.8	0	ND	<2	29	2.8	<2
Nishnabotna River at Hamburg, IA	06810000	7270	79	8	63	59.9	2.7	25	27.9	<2	38	57	<2
Iowa River at Wapello, IA	05465500	32400	73	9	100	78.8	12.6	33	43.0	<2	67	14.8	7.2
Mississippi River at Clinton, IA	05420500	222000	36	6	83	12.7	3.8	0	ND	<2	50	5.6	<2
Missouri River at Omaha, NE	06610000	836000	21	6	50	25.9	3.9	33	17.1	<2	50	7.2	2.6
Overall				79	75	257	8.2	23	42.7	<2	47	185	<2

^a Data from 2011 NLCD data.

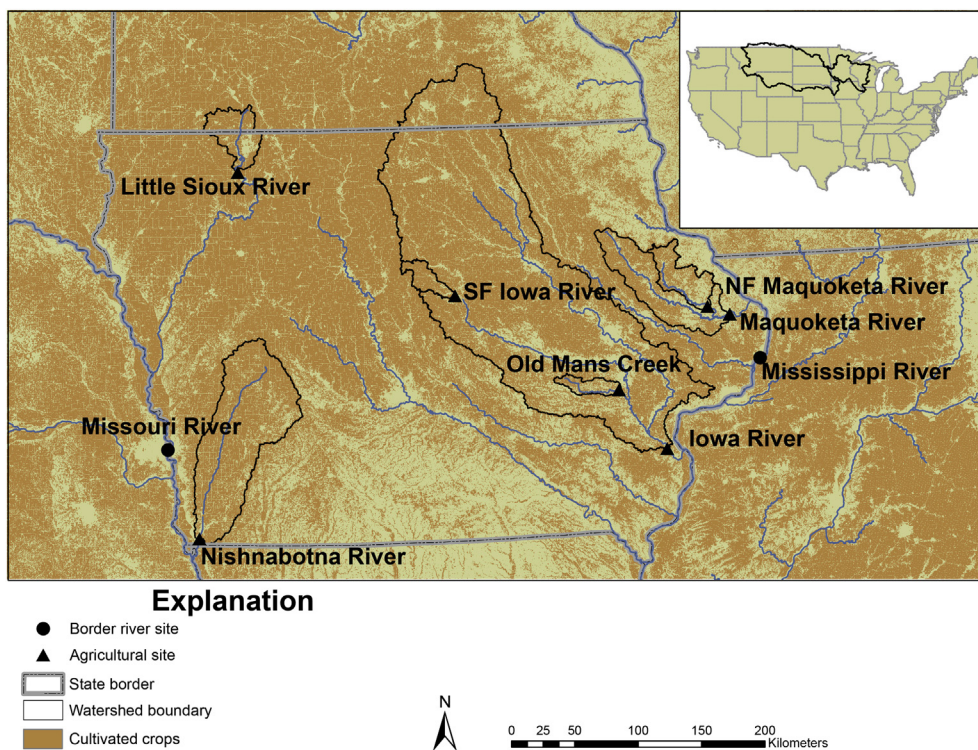


Fig. 2. Locations of sites in Iowa sampled for neonicotinoids in 2013. Watersheds for the Mississippi River and Missouri River sites are shown in the inset.

also a transformation product of thiamethoxam (Nauen et al., 2003).

Neonicotinoids were detected at all of the sites sampled, including the Mississippi and Missouri Rivers, even though the percentage of cultivated crops ranged from 21–86% and the basin areas spanned four orders of magnitude (Table 2). Maximum and median concentrations (maximum:median) across all sites and samples followed the same pattern as detection frequencies with clothianidin (257 ng/L; 8.2 ng/L) > thiamethoxam (185 ng/L; < 2 ng/L) > imidacloprid (42.7 ng/L; < 2 ng/L) (Table 2). Multiple neonicotinoids were common, with three neonicotinoids detected in 23% of the samples. The concentrations of the three most frequently detected neonicotinoids had significant correlations with each other (Fig. 3), suggesting that they are coming from a similar source (*i.e.*, use in corn and soybean production). Thiamethoxam concentrations were significantly correlated with clothianidin concentrations ($\rho = 0.79$, $p < 0.0001$), their co-occurrence can be explained by their use in the same watershed and because clothianidin is a transformation product of thiamethoxam. Imidacloprid, although detected less frequently than clothianidin or thiamethoxam (samples with imidacloprid detections are noted in Fig. 2 with blue circles), was also correlated with clothianidin and thiamethoxam concentrations ($\rho = 0.64$, $p < 0.0001$; $\rho = 0.66$, $p < 0.0001$, respectively).

There are limited published data on neonicotinoid concentrations in surface waters. Studies have been done in both wetlands and streams. Samples collected from wetlands near areas of intense cultivation contained multiple neonicotinoids. In the Prairie Pothole Region of Canada, four neonicotinoids (acetamiprid, clothianidin, imidacloprid and thiamethoxam) were detected, with at least one in over half the samples at concentrations up to 3100 ng/L for clothianidin, although mean concentrations were lower, <100 ng/L for total neonicotinoids (Main et al., 2014). In playa lakes in cropland basins of the Southern High Plains of the U.S., two neonicotinoids (acetamiprid and thiamethoxam) were detected at

concentrations up to 44,000 ng/L, with mean concentrations ranging from 2000 to 4000 ng/L (Anderson et al., 2013). Samples collected from rivers after storm events in Sydney, Australia (Sanchez-Bayo and Hyne, 2014) contained detectable concentrations of five neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid and thiamethoxam) in basins with a variety of landuses (*e.g.*, residential, farms) with most samples containing more than two neonicotinoids. The maximum concentrations observed for imidacloprid and thiacloprid were 4600 and 1400 ng/L, respectively. In agricultural streams in Ontario, Canada in the fall

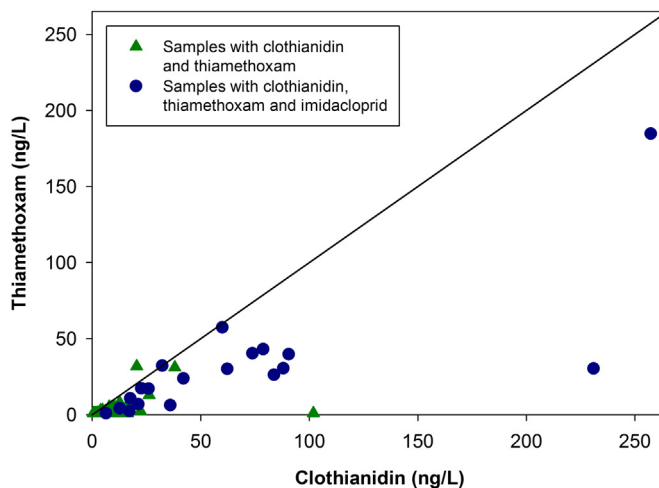


Fig. 3. Thiamethoxam versus clothianidin concentrations, different symbols indicate samples with and without imidacloprid detection. Straight line represents 1:1 concentrations. Spearman's rank correlation: thiamethoxam versus clothianidin, $\rho = 0.79$, $p < 0.0001$; imidacloprid versus clothianidin, $\rho = 0.64$, $p < 0.0001$; imidacloprid versus thiamethoxam, $\rho = 0.66$, $p < 0.0001$.

of 2011 (5–6 months after their use in seed treatment), nine samples had frequent detections of clothianidin, imidacloprid and thiamethoxam with concentrations up to 174 ng/L (thiamethoxam) (Environment Canada as shown in Mineau and Palmer, 2013). In Georgia streams, samples from basins with mixed landuse (forest/urban/agriculture) had multiple detections of acetamiprid and dinotefuran (concentrations up to 46 ng/L) and frequent detections of imidacloprid (85%; up to 66 ng/L) (Hladik and Calhoun, 2012; unpublished data). Only imidacloprid was measured in California rivers, creeks, and drains in an intensive agricultural area during the dry weather irrigation season and was frequently detected (89%) with concentrations > 1000 ng/L in 19% of the samples (Starner and Goh, 2012).

Historical studies in the U.S. (1992–2001) detected insecticides in <20% of samples from corn and soybean areas with chlorpyrifos detected most frequently (Gilliom et al., 2006). In stream samples collected in Iowa from 1996 to 1998, carbofuran (16%) and chlorpyrifos (7%) were the most frequently detected insecticides (Schnoebelen et al., 2003). The substantially greater neonicotinoid detection frequency observed for this study compared to historical detections of other insecticides despite lower annual use (USGS, 2014) could be influenced by their high mobility (e.g., higher water solubility) and greater persistence.

3.2. Patterns and variability among sites

Given the relatively sparse sampling at each site, neonicotinoid detections are remarkably consistent (Fig. 4) in relation to relative use intensity (based on percentage of basin in row crops; Table 2). The Mississippi and Missouri River basins were far larger than the other sites and have much lower basin percentages of row crop cultivation (Table 2); as a result, they generally had low and less variable concentrations (Fig. 4). The six small to medium-sized Iowa streams were also sampled monthly (also indicated with blue circles in Fig. 4) but have a higher percentage of row crops (59–86%). The concentrations at these sites were generally higher

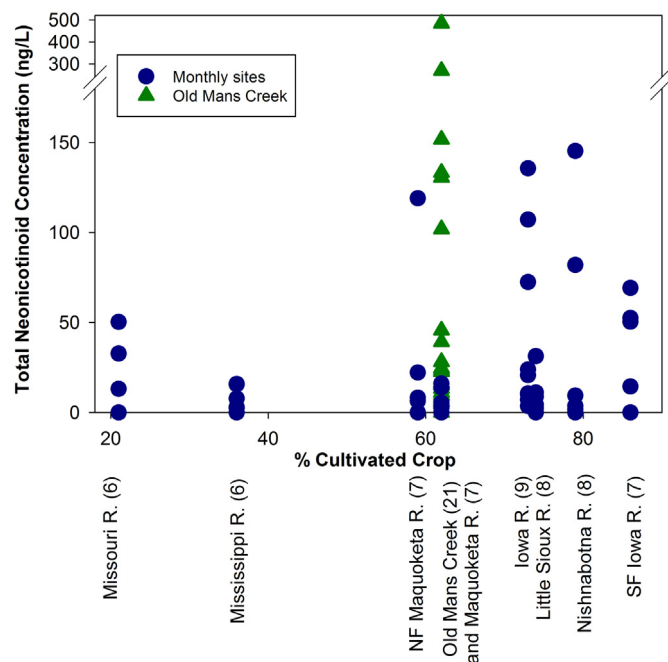


Fig. 4. Distribution of total neonicotinoids concentrations at each site in relation to the amount of cultivated crops in the watershed. The number of samples collected at each site are shown in parentheses.

than in the Mississippi and Missouri Rivers. On the other extreme, Old Mans Creek has the smallest watershed, was extensively cultivated (62%), and was sampled by a much different design that involved almost three times the number of samples being collected during specific flow conditions. This site, probably due to the more intensive and hydrologic-based sampling design, had the highest measured concentrations of all studied sites.

3.3. Seasonal patterns

To better understand the seasonal patterns of neonicotinoids in Iowa streams, the results were divided into five groups based on the timing of sample collection and crop production activities (USDA, 2013): pre-planting (March–April), planting (May–June), mid-growing season (July), late growing season (August–September), and harvest (October) (Fig. 5). This approach reveals a clear seasonal pattern in neonicotinoid results in both frequency of detection and concentration. In general, the three neonicotinoids follow the classic “spring flush” phenomenon documented for herbicides in streams across the Midwestern U.S. (Thurman et al., 1992), in which concentrations substantially increase in May through June following applications associated with crop planting.

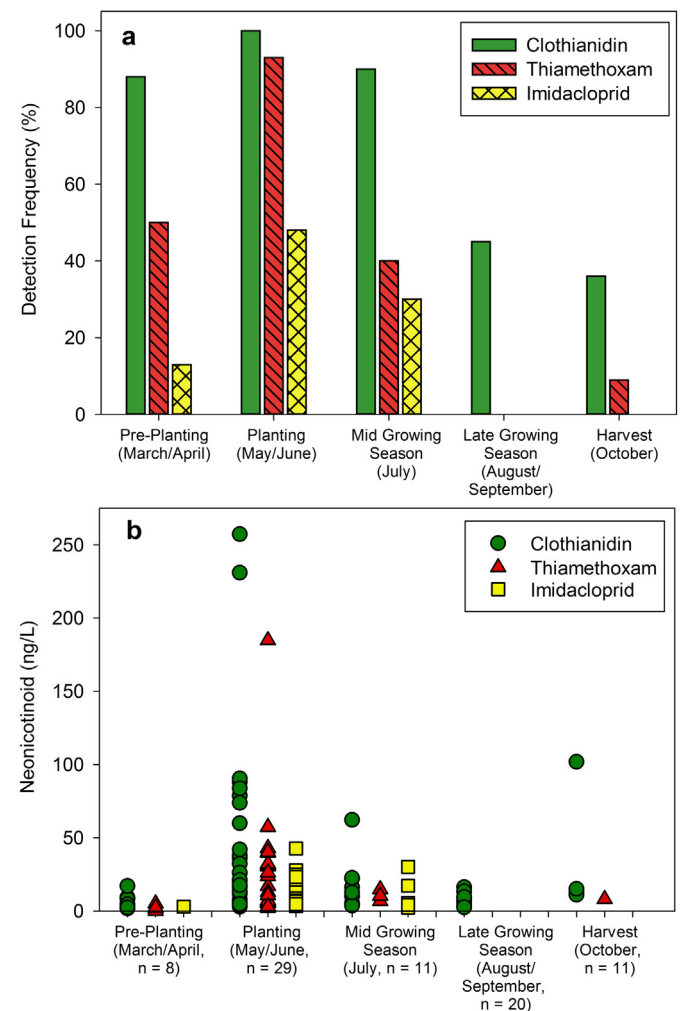


Fig. 5. Summary of (a) detection frequencies and (b) detected concentrations of the three most common neonicotinoids in 79 water samples collected from nine Iowa streams over the 2013 growing season. The number of samples (n) during each time period is listed with the detected concentrations (b).

A similar “spring flush” has been documented with previously used insecticides in the Midwest (Schnoebelen et al., 2003), although at lower detection frequencies (<50%). In addition, insecticide pulses have been documented in other areas, such as California; most notably, a winter pulse of water-soluble organophosphate insecticides (chlorpyrifos, diazinon, methidathion) was routinely observed following dormant-spray application and subsequent rainfall events (Kuivila and Foe, 1995).

Examining the statewide temporal patterns in more detail shows the frequent detections of neonicotinoids (particularly clothianidin and thiamethoxam) in streams during the pre-planting sampling period (Fig. 5) prior to their application during the 2013 growing season, but at low concentrations (generally <10 ng/L). Detections in the streams prior to new applications in 2013 are likely from uses during the previous growing season. This year-long persistence may have been accentuated by climatic conditions during the 2012 growing season when much of Iowa was in severe to exceptional drought conditions (Hillaker, 2013a). The lack of rainfall may have limited the transport of these neonicotinoids to streams. Subsequently, snowmelt and wet conditions in March and April 2013 may have provided the first opportunity for widespread chemical transport from agricultural fields to streams.

Comparing stream concentrations of neonicotinoids with the amount of corn and soybeans planted throughout the 2013 season documents an increase in neonicotinoid concentrations that follows the portion of fields planted (Fig. 6). As planting began, the three neonicotinoids were frequently detected at all sites, including the large border rivers (Table S11). Correspondingly, the concentrations increased with values as high as 257 ng/L for clothianidin and 485 ng/L for total neonicotinoids being measured (Figs. 5 and 6). Climatic conditions may have accentuated this pattern in 2013 as persistent wet conditions delayed the start of crop planting and compressed the planting season into a shorter than normal time window. For example, during one week in mid-May, 55% of the corn was planted for the entire state, making this the second highest amount of corn planted in a single week for Iowa over the last 5 years (USDA, 2013).

As the sampling progressed through the mid and late growing season, neonicotinoid detections and concentrations progressively decreased in streams (Figs. 5 and 6). This likely reflects the increasing amount of time since the planting of treated seeds and the transition from wet to dry climatic conditions (see Fig. 7 for flow conditions) thereby limiting transport to surface waters. Additionally, the increasing amount of time could lead to other environmental processes acting on the neonicotinoids (e.g., uptake into plants, sorption to sediment, transformation processes). During the late growing season, aerial pesticide applications were noted by field personnel although it is unknown if neonicotinoids were being applied. Regardless, the lack of rainfall (Hillaker, 2013b) that persisted across Iowa minimized transport via runoff to the corresponding streams.

During the final sampling period (harvest), there was a slight increase in the concentrations (clothianidin and thiamethoxam) and frequency of detections (thiamethoxam) (Fig. 5). The first significant rains since July 1 took place during this time period (Fig. 7). Thus, these slightly higher concentrations may have been due to pulses of neonicotinoids from any remaining residues from seed treatments during planting or from more recent aerial applications.

3.4. Temporal variation – Old Mans Creek

Overall, the more frequent sampling at Old Mans Creek (Fig. 7) confirmed the temporal trends found at the statewide level (Figs. 5 and 6), but also provides more details than available through the monthly sampling conducted at the other eight stream sites.

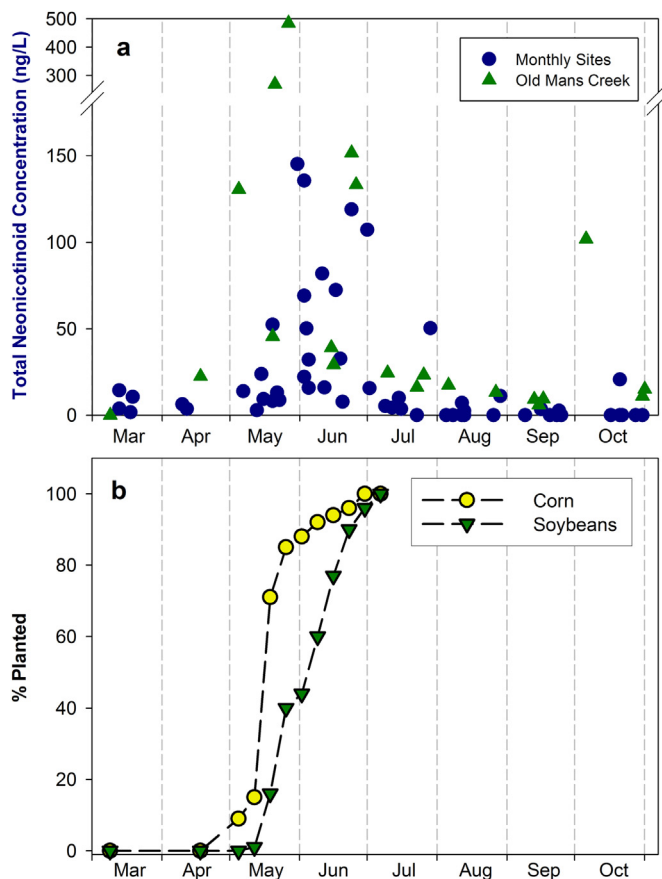


Fig. 6. Comparison of (a) total neonicotinoid concentrations (clothianidin + thiamethoxam + imidacloprid; ng/L) versus date sampled (Old Mans Creek had storm directed sampling so it is separated from the other eight sites that were sampled monthly) and (b) percent of corn and soybeans planted in Iowa (USDA, 2013).

Neonicotinoids were not detected in the first pre-planting sample from Old Mans Creek on March 9, 2013 but were detected in a subsequent pre-planting sample on April 18, 2013 (Table SI-1, Fig. SI-2). The primary difference in these two pre-plant samples was that the first was during rain and snowmelt with frozen soil conditions and the second was during rain with unfrozen soil conditions (Fig. SI-2). Therefore, the frozen soil during the March 9

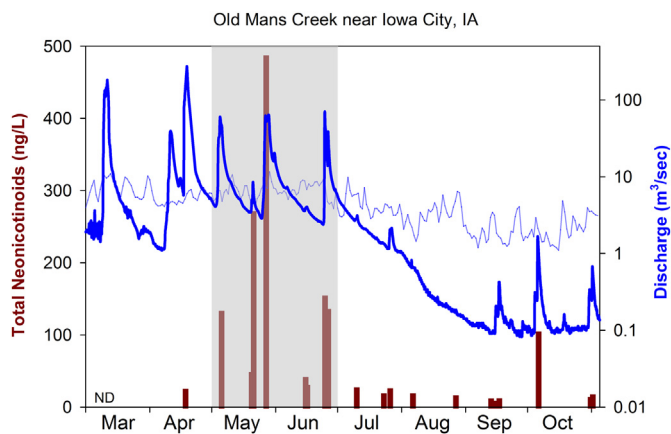


Fig. 7. Comparison of total neonicotinoid concentrations detected (bars) and discharge (dark line) at Old Mans Creek near Iowa City, IA during 2013. Average discharge (lighter line) is shown to highlight the wet spring and dry summer compared to average. The timing of corn and soybean planting is shown in the shaded box.

sample may have either limited neonicotinoid transport and/or the snowmelt may have diluted any neonicotinoid concentrations in the stream to below measurable levels.

The maximum neonicotinoid concentrations for this site were measured in the sample collected on May 27, 2013 (Table SI-1) in response to a recent intense rainfall event (Fig. 7). In fact, this sample had the highest concentrations of clothianidin (257 ng/L), thiamethoxam (185 ng/L), and imidacloprid (42.7 ng/L) measured during the entire study. This sample was collected following a time of rapid, extensive planting in the area, with roughly 95% of the corn and 55% of the soybeans in the basin planted at the time of this sample collection (USDA, 2013).

The pattern of precipitation in the Old Mans Creek basin (and for the entire state in general) switched from frequent, intense storms to sporadic, isolated events following the planting sampling period (see progressive drop in the hydrograph around July in Fig. 7). Correspondingly, the water samples collected during the mid and late growing season contained decreasing concentrations for all three neonicotinoids. Although clothianidin was still detected in the remaining samples collected throughout the growing season, the concentrations were low (roughly 10–20 ng/L, Table SI-1) with one exception (102 ng/L on 10/6/2013). Thiamethoxam and imidacloprid were generally not detected as the growing season progressed. The clothianidin concentrations detected could have been from the late-season applications of clothianidin or the degradation of thiamethoxam (Nauen et al., 2003).

The two samples collected within roughly a 24-h period on May 20 and 21, 2013 (Table SI-1, Fig. 8) provide an even closer look at the relations between hydrologic conditions and concentrations. The initial sample was collected in response to recent rainfall that caused a rise in the stream hydrograph. Even though no additional rain took place following the May 20 sample, the stream experienced a higher second peak in the hydrograph the following day (Fig. 8). Because it was anticipated that neonicotinoid concentrations may be highest in runoff events during the planting time period, an additional water sample was collected. Thus, while the streamflow only increased by roughly 25% between these two sampling times, the total neonicotinoid concentrations increased by roughly 85% (Fig. 8). These results document that concentrations can vary dramatically during the planting season, depending on when the sample was collected during the storm hydrograph. Field personnel noted that the water was more turbid for the May 21 sample than observed during the previous day's sample collection. A possible explanation for this

substantial increase in concentration may be related to the trends in the stream hydrograph (Fig. 8). The first lower peak that was measured may have been driven by a local response to the recent rain event. The second higher peak may have been driven by a more widespread response in the basin to this rain event. This trend between samples collected on subsequent days may have been accentuated by its timing during the heart of the planting season. Subsequent closely spaced water samples collected at this site (Fig. 7, Table SI-1) were found to have similar neonicotinoid concentrations in contrast to the substantially different concentrations detected between the May 20 and May 21 samples.

3.5. Potential toxicity

The U.S. Environmental Protection Agency has set acute and chronic invertebrate aquatic life benchmarks for clothianidin (11,000 ng/L; 1100 ng/L) imidacloprid (34,500 ng/L; 1050 ng/L) and thiamethoxam (17,500 ng/L, only acute value listed) (USEPA, 2013). Other studies, however, suggest much lower values for acute (200 ng/L) and chronic (20 ng/L) exposures (Mineau and Palmer, 2013) to imidacloprid. Similarly, macrofauna abundance drops sharply in the range of 13 and 67 ng/L of imidacloprid (Van Dijk et al., 2013). While there is less information on the aquatic toxicity for clothianidin and thiamethoxam, their effects levels are expected to be in the general range of those for imidacloprid since they have a common mode of action (Yamamoto et al., 1995; Mineau and Palmer, 2013). As clothianidin and thiamethoxam were both detected at much higher concentrations than imidacloprid during this study (Table SI1), it is anticipated that a number of measured concentrations would also exceed chronic exposure levels, potentially even exceeding acute exposure levels for these two neonicotinoids. Moreover, the more frequent, hydrologic-based sampling at Old Mans Creek (which had a mid-range crop intensity) documented that much higher concentrations occur than were reliably characterized by sparse monthly sampling.

In addition to a lack of chronic toxicity levels for most neonicotinoids, even less is known about the additive or synergistic toxicity of neonicotinoid mixtures. In addition to the present study, other studies (Anderson et al., 2013; Hladik and Calhoun, 2012; Main et al., 2014; Mineau and Palmer, 2013; Sanchez-Bayo and Hyne, 2014) have found neonicotinoid mixtures to be common. There is also little known about potential toxicity of environmental degradates that may also be present in streams, previous studies have shown neonicotinoid metabolites to be as toxic as the parent compound (Suchail et al., 2004; Casida, 2011).

4. Conclusions

The use of neonicotinoid insecticides has dramatically increased in recent years, as a replacement for organophosphate and carbamate insecticides and with the increased use of seed treatments (nearly all corn and a majority of soybeans in the United States are now planted using treated seeds; CropLife Foundation, 2013). This study found that neonicotinoids are both mobile and persistent in the environment, with chemical use and precipitation being important driving factors for their off-field transport to streams. Neonicotinoids were found more frequently and in higher concentrations than historically-used organophosphates and carbamates in previous investigations of similar landuse areas. Temporal patterns in stream occurrence and concentration reveal a strong pulse of neonicotinoids associated with crop planting that follows the same trend as has been documented to occur annually with the spring application of herbicides in the Midwestern U.S. While this insecticide pulse is likely related to the increased use of neonicotinoids via seed treatments, the lack of use information on a

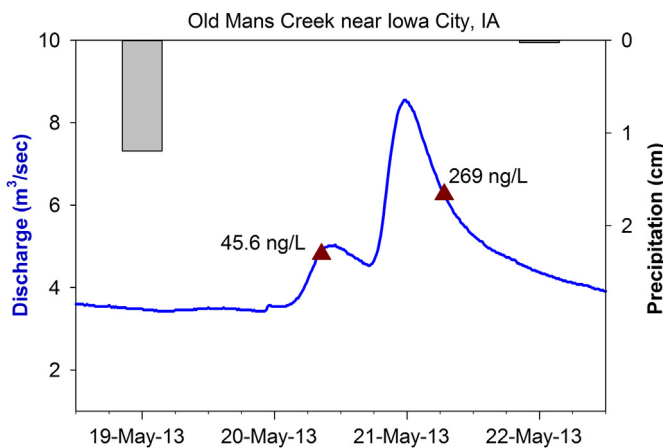


Fig. 8. Hydrograph (line) and precipitation (bar) from Old Mans Creek near Iowa City, IA and corresponding sample collection points (▲) during a 2-day period from May 20 to May 22, 2013. Concentrations listed above the collection points are the total neonicotinoid concentrations for each sample.

watershed scale inhibits clearly attributing seed treatments as the primary source of these neonicotinoid stream concentrations. Nevertheless, the use of neonicotinoids via seed treatments as a near universal pest management practice in the U.S. needs to be closely examined in relation to environmental impacts of these insecticides and its importance in the transport of neonicotinoids to streams.

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Appendix A. Supplementary data

Supplementary data related to this chapter can be found at <http://dx.doi.org/10.1016/j.envpol.2014.06.033>.

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