Neonicotinoid insecticide removal by prairie strips in row-cropped watersheds with historical seed coating use

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Neonicotinoid insecticide removal by prairie strips in row-cropped watersheds with historical seed coating use

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Abstract

Neonicotinoids are a widely used class of insecticides that are commonly applied as seed coatings for agricultural crops. Such neonicotinoid use may pose a risk to non-target insects, including pollinators and natural enemies of crop pests, and ecosystems. This study assessed neonicotinoid residues in groundwater, surface runoff water, soil, and native plants adjacent to corn and soybean crop fields with a history of being planted with neonicotinoid-treated seeds from 2008 to 2013. Data from six sites with the same crop management history, three with and three without in-field prairie strips, were collected in 2015–2016, 2–3 years after neonicotinoid (clothianidin and imidacloprid) seed treatments were last used. Three of the six neonicotinoids analyzed were detected in at least one environmental matrix: the two applied as seed coatings on the fields (clothianidin and imidacloprid) and another widely used neonicotinoid (thiamethoxam). Sites with prairie strips generally had lower concentrations of neonicotinoids: groundwater and footslope soil neonicotinoid concentrations were significantly lower in the sites with prairie strips than in those without; mean concentrations for groundwater were 11 and 20 ng/L (p = 0.048) and <1 and 6 ng/g (p = 0.0004) for soil, respectively. Surface runoff water concentrations were not significantly (p = 0.38) different for control sites (44 ng/L) or sites with prairie strips (140 ng/L). Consistent with the decreased inputs of neonicotinoids, concentrations tended to decrease over the sampling timeframe. Two sites recorded concentration increases, however, potentially due to disturbance of previous applications or influence from nearby fields where use of seed treatments continued. There were no detections (limit of detection: 1 ng/g) of neonicotinoids in the foliage or roots of plants comprising prairie strips, indicating a low likelihood of exposure to pollinators and other insects visiting these plants following the cessation of seed coating use. Offsite transport of neonicotinoids to aquatic systems through the groundwater and surface water were furthermore reduced with prairie strips. This study demonstrates the potential for prairie strips comprising 10% of an agricultural catchment to mitigate the non-target impacts of neonicotinoids.

1. Introduction

Neonicotinoids are currently the most widely used class of insecticides in the world and are frequently applied as seed coatings for a variety of crops including corn and soybeans (Douglas and Tooker, 2015). Neonicotinoids may pose a risk to pollinators and non-target insects that use plants with neonicotinoid residues as food sources and to aquatic life due to water contamination through runoff (Bonmatin et al., 2015). Neonicotinoid insecticides are water-soluble; they can be transported offsite predominately via surface and groundwater, and less so with soil particulates (Bonmatin et al., 2015). The offsite transport of neonicotinoids has been documented by their frequent detections in streams across the Midwestern United States in areas of high corn and soybean production (Hladik et al., 2014) and also their detections in foliage and pollen adjacent to agricultural fields including corn (Krupke et al., 2012) and oilseed rape (Botías et al., 2016). Vegetated buffer and filter strips including prairie strips can limit offsite transport of water, sediment and pesticides from agricultural fields (Liu et al., 2008; Helmers et al., 2012;
Hernandez-Santana et al., 2013), and thus have the potential to also limit transport of neonicotinoids, protecting downstream water quality.

This study presents the rare opportunity to compare concentrations of neonicotinoids in shallow groundwater, surface water runoff, soil, and plant tissues from crop fields with and without prairie strips that were planted with clothianidin and imidacloprid treated corn and soybean seeds from 2008 to 2013. Because the use of treated seeds ended at the study site in 2013 and initial measurements were not started until 2015, the results can provide insights on both the off field dissipation of neonicotinoid concentrations from their use as seed coatings and the potential effectiveness of prairie strips in limiting their offsite transport.

2. Materials and methods

2.1. Study area

The study site was located at the Neal Smith National Wildlife Refuge (NSNWR; 41°33’ N; 93°16’ W), a 3000-ha area managed by the U.S. National Fish and Wildlife Service, located in the Walnut Creek watershed in Jasper County, Iowa (Fig. 1). Created by an Act of Congress in 1990, the refuge’s mission is to reconstruct Iowa’s pre-settlement vegetation, particularly native tallgrass prairie. Portions of the refuge awaiting restoration are either leased to area farmers for crop production or maintained in perennial pasture (Zhou et al., 2010; Helmers et al., 2012). For this site, daily precipitation was obtained from the National Ocean and Atmospheric Administration station at the NSNWR.

Study sites spanned six of the 12 catchments comprising the Science-based Trials of Row crops Integrated with Prairie Strips (STRIPS) experiment at the refuge (Table 1; Zhou et al., 2010). The two treatments considered here—a 100% row crop (control) and a 90% row crop: 10% prairie strips treatment—were randomly allocated to study sites located across three blocks when the experiment was established. In September 2006, the row cropland was converted from cool-season perennial grasses, primarily Bromus inermis, and thereafter farmed on a soybean-corn rotation using no-till soil management techniques. In July 2007, reconstructed prairie vegetation was established within approximately 10% of the catchment area in the foote slope position on three of sites. The prairie was established by broadcast seeding 32 native species; one additional species was hand sown the following spring (Hirsh et al., 2013). All sites had treated seeds planted through 2013; clothianidin-treated corn seeds planted starting in 2008 and imidacloprid-treated soybeans starting in 2011. One
growing season without the use of treated seeds (2014) occurred at all sites before sampling for neonicotinoids began in April 2015; sampling continued through May 2016.

2.2. Sample collection

2.2.1. Groundwater

Groundwater samples were collected in May 2015, November 2015 and April 2016, at all six sites (Table 2). Shallow groundwater wells were previously installed at the footslope positions in November 2004. Wells were constructed of 50 mm i.d. polyvinyl chloride with 0.6-m well screens. Well depths varied between 2.9 and 5.4 m (Zhou et al., 2010). Groundwater wells were purged before groundwater samples were taken; samples were collected by inserting a new nylon tube into the groundwater well, which was connected to a new 2 L HDPE filter flask. Suction was applied to the flask via a hand-operated air pump. The sample (~100 mL) was transferred from the filter flask to a HDPE bottle and stored at 4 °C until analysis.

2.2.2. Surface runoff water

Surface water samples were collected in June 2015 from all six sites and in April 2016 for only three sites; not all sites were able to be sampled in April 2016 due to a lack of runoff (Table 2). Each study site was instrumented in 2005 with an H-flume and ISCO 6712 automated water sampler located at the base of the catchment. Surface water runoff was guided passively via drainage channels to a single sampling point at the H-flume where samples

Table 1
Site names and characteristics; the reconstructed prairie vegetation is all located at the footslope of hydrological catchments for sites with 10% prairie.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Abbreviation</th>
<th>Land cover</th>
<th>Size (ha)*</th>
<th>Mean slope (%)b</th>
<th>Soil typeb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basswood-1</td>
<td>B1</td>
<td>90% row crop 10% prairie</td>
<td>0.53</td>
<td>7.5</td>
<td>Ladoga silt loam, Lamoni silty clay loam</td>
</tr>
<tr>
<td>Basswood-6</td>
<td>B6</td>
<td>100% row crop</td>
<td>0.84</td>
<td>10.5</td>
<td>Ladoga silt loam, Gara-Armstrong loam</td>
</tr>
<tr>
<td>Interim-2</td>
<td>I2</td>
<td>90% row crop</td>
<td>1.18</td>
<td>6.1</td>
<td>Clarinda silt loam, Ladoga silt loam, Otley silty clay loam, Ackmore-Colo complex</td>
</tr>
<tr>
<td>Interim-3</td>
<td>I3</td>
<td>100% row crop</td>
<td>0.73</td>
<td>9.3</td>
<td>Shelby-Aadair complex, Lagoda silt loam, Gara loam</td>
</tr>
<tr>
<td>Orbweaver-1</td>
<td>W1</td>
<td>90% row crop 10% prairie</td>
<td>1.24</td>
<td>6.6</td>
<td>Ladoga silt loam, Gara loam, Otley silty clay</td>
</tr>
<tr>
<td>Orbweaver-3</td>
<td>W3</td>
<td>100% row crop</td>
<td>1.24</td>
<td>6.6</td>
<td>Ladoga silt loam, Otley silty clay loam</td>
</tr>
</tbody>
</table>

* Data from Zhou et al. (2010).
* Data from USDA NRCS (2016).

Table 2
Concentrations of neonicotinoids detected in water (ng/L), soil (ng/g dry weight) and plants (ng/g dry weight) at paired sites with and without prairie strips. Surface water runoff values (mm) during each sampling are standardized for drainage area. ND = not detected; NS = not sampled.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Date</th>
<th>Neonicotinoid</th>
<th>B6</th>
<th>I3</th>
<th>W3</th>
<th>B1</th>
<th>I2</th>
<th>W1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>May-15</td>
<td>Clothianidin</td>
<td>44.6</td>
<td>88.1</td>
<td>90.1</td>
<td>ND</td>
<td>12.2</td>
<td>36.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Nov-15</td>
<td>Clothianidin</td>
<td>35.9</td>
<td>13.7</td>
<td>72.0</td>
<td>ND</td>
<td>ND</td>
<td>30.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Mar-16</td>
<td>Clothianidin</td>
<td>26.0</td>
<td>10.5</td>
<td>53.2</td>
<td>8.9</td>
<td>24.9</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>18.1</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thiamethoxam</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>26.1</td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Runoff</td>
<td>&lt;0.05</td>
<td>1.42</td>
<td>0.07</td>
<td>0.95</td>
<td>0.14</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>Surface Water</td>
<td>Clothianidin</td>
<td>40.1</td>
<td>143.0</td>
<td>51.9</td>
<td>ND</td>
<td>ND</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>Jun-15</td>
<td>Imidacloprid</td>
<td>ND</td>
<td>95.6</td>
<td>37.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thiamethoxam</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Apr-16</td>
<td>Runoff</td>
<td>0.66</td>
<td>2.19</td>
<td>ND</td>
<td>ND</td>
<td>0.11</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Clothianidin</td>
<td>91.7</td>
<td>62.1</td>
<td>NS</td>
<td>NS</td>
<td>1222.3</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>8.5</td>
<td>35.5</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thiamethoxam</td>
<td>94.3</td>
<td>44.3</td>
<td>NS</td>
<td>NS</td>
<td>376.0</td>
<td>NS</td>
</tr>
<tr>
<td>Soil</td>
<td>Apr-15</td>
<td>Clothianidin</td>
<td>9.3</td>
<td>4.5</td>
<td>10.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>8.2</td>
<td>1.5</td>
<td>5.5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Nov-15</td>
<td>Clothianidin</td>
<td>7.3</td>
<td>4.7</td>
<td>7.5</td>
<td>2.8</td>
<td>1.2</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>3.1</td>
<td>0.9</td>
<td>7.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>May-16</td>
<td>Clothianidin</td>
<td>18.0</td>
<td>4.1</td>
<td>22.7</td>
<td>1.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>10.5</td>
<td>3.3</td>
<td>25.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plants: Schizachyrium scoparium roots</td>
<td>Apr-15</td>
<td>Clothianidin</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plants: Solidago spp. flowers</td>
<td>Sep-15</td>
<td>Clothianidin</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plants: Zizia aurea flowers</td>
<td>May-16</td>
<td>Clothianidin</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Imidacloprid</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thiamethoxam</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
were collected. Homogenized subsamples (~100 mL) were taken from field-collected composite samples, and placed into a new HDPE bottle, and stored at 4 °C until analysis. The surface water runoff data were standardized for drainage area so that the values could compared across sites.

2.2.3. Soil and plants

Soil samples were collected in April 2015, November 2015, and May 2016 at all six sites (Table 2). Ten subsamples (100 g each) of soil were collected to a depth of 5 cm using a standard soil core and in a zigzag pattern across the foostripe of each site. Plant material (intact roots, stems, leaves, and flowers, if present) from *Schizachyrium scoparium*, *Solidago* spp., and *Zizia aurea* were collected in April 2015, September 2015 and May 2016, respectively. Soil or plant samples from each site and period were composited and stored in Ziploc® bags at −20 °C until analysis.

2.3. Neonicotinoid analysis

2.3.1. Water

Extraction followed a previously published method (Hladik and Calhoun, 2012). Samples were filtered in the laboratory through a baked 0.7-mm glass-fiber filter (Whatman), spiked with a surrogate (imidacloprid-d₄; Cambridge Isotope), and passed through an Oasis® HLB solid-phase extraction (SPE) cartridge (6 cc, 500 mg; Waters Corporation). The cartridge was eluted with 10 mL of 50:50 acetone:dichloromethane, reduced, exchanged into acetonitrile, and reduced to 200 μL.

2.3.2. Soil and plants

Approximately 2–3 g of soil or plants (roots for *Schizachyrium scoparium*; composite of leaves and flowers for *Solidago* spp. and *Zizia aurea*) were dried and homogenized with sodium sulfate, spiked with a surrogate, (imidacloprid-d₄) and extracted on an ASE® 200 (Dionex) using a 50:50 mixture of acetone:dichloromethane (1500 psi; 100 °C). The extracts were solvent exchanged into acetonitrile and added to centrifuge tubes containing 900 mg of magnesium sulfate, 300 mg of ZSep+ (Sigma-Aldrich) and 500 mg graphitized carbon (Restek). After being vortexed, the samples were centrifuged and decanted into clean glass concentrator tubes, and evaporated to 200 μL.

2.3.3. LC–MS/MS analysis

Prior to analysis, an internal standard, ¹³C₃-caffeine, was added. Extracts were analyzed on an Agilent 1260 bio-inert liquid chromatograph (LC) coupled to an Agilent 6430 tandem mass spectrometer (MS–MS). Instrument details are given elsewhere (Hladik and Calhoun, 2012). Six neonicotinoids: acetamiprid, clothianidin, dinofeturan, imidacloprid, thiacloprid, and thiamethoxam were measured. The theoretical level of detection (LOD) for each neonicotinoid was 10 ng/L for 100 mL water samples; 1 ng/g dry weight for soil and plant samples.

2.3.4. QA/QC

Neonicotinoid concentrations were validated against quality control samples including: field blanks (1 water), replicate samples (2 each of soil and plant), matrix spikes (1 each soil and plant) and surrogate recovery. No compounds were detected in any of the blanks, field replicates had relative percentage differences (RPD) between the regular and replicate sample of <25%. Matrix spike recoveries ranged from 76 to 92%. Recovery of the surrogate (imidacloprid-d₄) ranged from 70 to 110% for all samples; data presented here were not recovery-corrected.

2.3.5. Data analysis

Data were analyzed with SigmaPlot® 13.0 using paired t-tests, two-tailed, comparing data collected from 100% row-crop controls and 10% foostripe prairie strip treatments located within the same block. Non-detects were set at one-half of the LOD. Data were evaluated by pairing individual neonicotinoid concentrations at control and prairie sites, rather than summing the total neonicotinoid concentrations as the different neonicotinoids may have

![Fig. 2. Concentrations of neonicotinoids detected in groundwater at paired sites with and without prairie strips. ND = not detected.](image-url)
different sources. One surface water sample (with three individual results) was excluded from the analysis because it lacked a paired sample. All data used in these analyses are publicly available online at: https://github.com/ISU-STRIPS/STRIPS_Hladik.

3. Results and discussion

Consistent with the planting of treated seeds from 2008–2013, clothianidin (CLO), and imidacloprid (IMD) were commonly detected; an additional neonicotinoid, thiamethoxam (THX), that is also widely used in corn and soybeans seed coatings (Douglas and Tooker, 2015) was also detected. In groundwater samples, detection frequencies were 94%, 11% and 22% for CLO, IMD and THX, respectively; surface water detection frequencies were 78%, 44% and 33%. Detection frequencies of CLO, IMD and THX in footslope soil were 67%, 50% and 0%, respectively. Neonicotinoids are highly water soluble and not expected to appreciably sorb to soils; their high water solubility makes them available for plant uptake (Bonnatin et al., 2015), though no neonicotinoids were detected in the plant material for this study. Note the occurrence of THX is likely due to transport from neighboring farms, since THX-treated seeds were not planted in the study seeds.

3.1. Groundwater

In groundwater samples, CLO was the most frequently detected neonicotinoid. It was detected in 100% of control sites and in 89% of the samples from sites with prairie strips. THX was detected in 11% of control sites and 33% of sites with prairie strips, while IMD was only detected in sites with prairie strips (22%). IMD was not detected in the groundwater at any of the control sites.

The mean concentrations of CLO in the groundwater samples for the control sites were 72, 41, and 30 ng/L for spring 2015, fall 2015 and spring 2016, respectively while those for the sites with a prairie strip were 16, 10 and 20 ng/L, respectively. Concentrations detected in this study are similar to those published in previous research. In fields planted with CLO-treated corn seed, De Perre et al. (2015) reported CLO mean groundwater concentrations that ranged from ND to >120 ng/L. For paired control and prairie strip sites (n = 27; see Table 2) mean groundwater neonicotinoid concentrations from prairie strips sites (11 ng/L) were significantly lower than mean concentrations collected at control sites (20 ng/L; p = 0.048). These results suggest less offsite transport of neonicotinoid through the groundwater at sites with prairie strips.

Neonicotinoid concentrations were higher in spring than fall 2015 groundwater samples (Fig. 2), perhaps due to more time elapsing since the last neonicotinoid application or due to seasonal patterns (e.g., frequency and intensity of precipitation). Concentrations at five of the groundwater sample sites had approximately 1.2- to 6.4-fold lower concentrations in the fall (the sixth site had non-detectable levels in the spring and fall). For the three control sites, spring 2015 concentrations were also 1.7–8.4-fold higher than spring 2016 samples (Fig. 2). Spring 2016 concentrations at two of the three sites with prairie strips were greater than those detected in the spring of 2015, including a site that had non-detectable levels in 2015. Spring 2016 samples at sites with prairie strips also had the only detections of IMD in groundwater; the two sites (B1 and I2) that had IMD also had THX, which was not detected in the spring or fall of 2015. The 2016 increase in neonicotinoid groundwater concentrations in the sites with prairie strips may reflect subsurface temporal and spatial variability in historical neonicotinoid soil concentrations (especially for IMD, last applied in 2013), transport of neonicotinoids from upslope fields, or influences from other sites/locations (especially for THX which was not applied as a seed coating in these fields).

3.2. Surface runoff water

Surface water runoff samples were collected after rainfall events of 17–80 mm; corresponding runoff amounts varied by site and ranged from 0 to 3.44 mm (Table 2). There were no significant (p = 0.829) differences in the runoff from the paired control sites

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**Fig. 3.** Concentrations of neonicotinoids detected in surface water runoff at paired sites with and without prairie strips. ND = not detected; NS = not sampled due to lack of runoff.
and those sites with prairie strips. Similar to the groundwater samples, CLO was detected in 100% of the surface water runoff samples collected from control sites and in 50% of the samples collected from sites with prairie strips. Detections of THX and IMD also occurred at the controls sites (40% and 80% of the samples, respectively). For sites with prairie strips, THX was detected in 25% of the samples, with no IMD detections.

Surface water concentrations of CLO and THX ranged from 40 to 140 ng/L and 44 to 94 ng/L in the control sites’ samples, respectively (Fig. 3). For sites with prairie strips, concentrations of CLO ranged 18 to 1200 ng/L. One prairie strip sample had a THX concentration of 380 ng/L. Mean concentrations in this study were generally lower than those previously measured in surface water runoff from crop fields. Schaafsma et al. (2015) reported means of 1000 to 2000 ng/L for CLO and THX in Ontario, while De Perre et al. (2015) reported means of ND to 850 ng/L for CLO. These previous studies were conducted in fields with on-going use of coated seeds and would be expected to have higher concentrations than all sites described in this report. When sites were paired and compared (n=9; Table 2), mean neonicotinoid concentrations were lower at the control sites (44 ng/L) versus the sites with prairie strips (140 ng/L); the difference was not significant (p=0.38) and may be due to a low number of samples (lack of runoff), especially in 2016.

There was no correlation between the amount of runoff at each site and the individual neonicotinoid concentrations measured (Spearman’s rank correlation; \( r = 0.08 \), \( p = 0.70 \)) indicating that runoff amount was not the major factor in neonicotinoid movement from the fields. In general, surface water neonicotinoid concentrations were lower for sites with prairie strips than the control except for one site in spring 2016, which had a much higher concentration than all other water samples in the study (Table 2, Fig. 3). This site also had increased concentrations of neonicotinoids in groundwater in spring 2016 than in previous samples (additional comparison of the spring 2016 data are limited by lack of surface water runoff to comprise samples for the other two sites with prairie strips). This inconsistency may potentially be due to disturbance of soil with planting or influence from nearby fields where use of seed treatments continued; the influence from nearby fields is indicated by THX which was not applied as a seed coating to the fields in this study.

3.3. Soil

Consistent with the water samples, CLO was detected in 100% of control site footslope soil samples and in 33% of the footslope soil samples with prairie strips. IMD was detected in 100% of the control footslope soils and 0% of the footslope soils with prairie strips. THX was not detected in any of the footslope soil samples. In contrast to the groundwater and surface water samples the only neonicotinoids detected in the footslope soil, CLO and IMD, were ones that had been previously applied as seed coatings.

The mean concentrations of CLO+IMD in the footslope soil samples for the control sites were 13, 10, and 28 ng/g for spring 2015, fall 2015 and spring 2016, respectively while those for the prairie strip sites were ND, 2, and ND ng/g, respectively. The footslope soil concentrations in the control sites are similar to those reported previously (De Perre et al., 2015; Schaafsma et al., 2015; Xu et al., 2016); concentrations of neonicotinoids ranged from 4 to 18 ng/g within fields with multiple years of planting with treated seeds.

When samples for each paired control and prairie strip sites (n=27) were compared (Table 2), mean neonicotinoid concentrations at the prairie strip sites (<1 ng/g) were significantly lower than the mean concentrations at the control sites (6 ng/g; \( p = 0.0004 \)). Neonicotinoids were generally non-detectable in the footslope soils at the sites with prairie strips, potentially due to enhanced microbial degradation or plant uptake; however, as noted below neonicotinoids were not detected in sampled plants. Vegetated filter strips have been shown to effectively reduce off-field movement of soil-associated pesticides (Liu et al., 2008); however, neonicotinoid insecticides, due to their high water
solubility and low affinity for organic carbon, are expected to move with subsurface and surface water rather than soil particles (Bonmatin et al., 2015).

Similar to the observations with groundwater, CLO and IMD footslope soil concentrations at two of the three control sites where higher in spring 2015 as compared to fall 2015 (Fig. 4), which would be expected as more time elapsed since last neonicotinoid field applications but could also be from variability in the samples. Concentrations of CLO were detected at two sites with prairie strips and at levels just above the LOD in the fall of 2015; CLO was not detected in the spring of 2015, which likely reflects the overall variation of footslope soil concentrations at these low levels. Of note, in spring 2016, an increase in neonicotinoid concentrations was detected in two of the three control sites that were higher than those observed in 2015 concentrations. Similar year-to-year variability has been previously reported in pre-plant neonicotinoid soil concentrations in Ontario crop fields with an on-going use of treated seeds (Schaafsma et al., 2016). The increase in the spring 2016 soil concentrations could reflect enhanced, localized transport of neonicotinoid contaminated soil from upslope portions of the field to the footslope soil.

3.4 Plants

No neonicotinoids were detected in plant root material collected in spring 2015 or in blooming forbs or plants collected in fall 2015 and spring 2016 from the prairie strips (Table 2). Between May and June 2016, additional plant samples (Anemone canadensis and/or Zizia aurea) were collected and analyzed from the leading edge of prairie strips at three additional sites with active neonicotinoid seed treatment use, but neonicotinoids were not detected within leaf and flower tissues (preliminary data not shown). These results suggest that systemic uptake of the neonicotinoids by plants in prairie strips was not occurring at detectable levels. Of the 27 soil samples collected from these sites, only three had detectable levels of neonicotinoids (1–3 ng/g; LOD of 1 ng/g); hence, the lack of plant uptake may be due to a low soil concentration of neonicotinoids within the root zones of the sampled plants.

In spring 2015, plant roots were sampled in April, which was after spring snowmelt and 1–2 months before the first significant rain events. During this sampling event, neonicotinoids were detected in groundwater and surface water in two of the three sites with prairie strips. While the April plant sample suggests there was no prior year carryover of CLO, THX or IMD in the roots, these plant samples do not provide insights of potential exposure through surface or groundwater due to lateral flow caused by spring 2015 precipitation.

In March 2016, groundwater CLO was detected in all three sites (concentrations from 9 to 27 ng/L), and THX and IMD were detected in two of the three sites with prairie strips with concentrations of 12 to 26 ng/L; one site had April surface water concentrations of CLO and THX concentrations of 1200 and 380 ng/L, respectively. Yet, prairie plants sampled in May 2016 in these sites had non-detectable concentrations of the neonicotinoids, suggesting that even if plant uptake did occur in March (from groundwater) or April (from surface water), there was sufficient growth dilution and/or metabolism of the insecticides to result in non-detectable plant tissue concentrations over the course of 1–2 months. For these sites and with the noted limitations in sampling frequency/timing, results suggest that 2–3 years after the cessation of using neonicotinoid seed coatings, systemic uptake of neonicotinoids is not likely to result in exposure to pollinators or herbivorous insects.

4. Conclusions

Neonicotinoid concentrations in groundwater, surface water runoff, and footslope soil sampled from the 100% row-crop treatments 2–3 years after discontinuation of seed treatments were similar to those reported in other studies with on-going use of seed coating applications. By comparison, sites with prairie strips had lower concentrations of neonicotinoids in groundwater; had less frequent detects of neonicotinoids in surface water runoff; and rarely had detectable neonicotinoids in soils located at the footslope. Neonicotinoids were not detected from root, leaf, or flower tissues associated with prairie strips. Together these results indicate the potential of prairie strips to reduce neonicotinoid transport from the agricultural environment and provide safe habitat for pollinators and other insects within several years of discontinuing seed treatment. Neonicotinoids are highly water soluble; the majority of their transport is expected to happen through groundwater and surface water. The variability of surface water runoff concentrations at the study sites may be influenced by transport from nearby, upslope fields planted with treated seeds. The high water solubility of the neonicotinoids makes them available for plant uptake, which could be a mechanism responsible for the decreased neonicotinoid concentrations in the groundwater and footslope soils of fields with prairie strips. The degree to which the findings reported here extend to fields with on-going use of seed treatments is unknown. Future work should include gathering data from prairie strips in fields with a diversity of seed treatment use history and mechanistic studies to better understand the pathways by which prairie strips can mitigate off-field transport of neonicotinoids.

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