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Factors influencing the occurrence and distribution of neonicotinoid insecticides in surface waters of southern Ontario, Canada

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HIGHLIGHTS

- Conducted a survey of neonicotinoids used in full range of agricultural activities in surface waters of Ontario.
- Statistical correlation of individual compounds with land use was investigated.
- Relationship between neonicotinoid occurrence and hydrology of water courses was assessed.
- Imidacloprid, clothianidin, and thiamethoxam detection frequency over 90% at over half the sites sampled.
- At 2 sites, the Canadian freshwater guideline value for imidacloprid (230 ng/L) was exceeded in 75% of samples.

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ABSTRACT

The widespread use of neonicotinoid insecticides and recent increased regulatory scrutiny requires the generation of monitoring data with sufficient scope and resolution to provide decision makers with a better understanding of occurrence and distribution in the environment. This study presents a wide-scale investigation of neonicotinoid insecticides used across the range of agricultural activities from fifteen surface water sites in southern Ontario. Using statistical analysis, the correlation of individual compounds with land use was investigated, and the relationship between neonicotinoid occurrence and hydrologic parameters in calibrated water courses was also assessed. Of the five neonicotinoids studied, imidacloprid, clothianidin and thiamethoxam exhibited detection rates above 90% at over half the sites sampled over a three year period (2012–2014). At two sites in southwestern Ontario, the Canadian Federal freshwater guideline value for imidacloprid (230 ng/L) was exceeded in roughly 75% of the samples collected. For some watersheds, there were correlations between the occurrence of neonicotinoids and precipitation and/or stream discharge. Some watersheds exhibited seasonal maxima in concentrations of neonicotinoids in spring and fall, particularly for those areas where row crop agriculture is predominant; these seasonal patterns were absent in some areas characterized by a broad range of agricultural activities.

1. Introduction

In the past decade, the use of organophosphorous insecticides has been superseded by neonicotinoid insecticides (Hladik et al., 2014; Hladik and Kolpin, 2015; Morrissey et al., 2015; Anderson et al., 2015). Neonicotinoids are active against a wide range of insects, are effective at low concentrations, are systemic, and can be applied using a variety of methods (Anderson et al., 2015). Registered uses of neonicotinoids in Canada include control of insects on field and greenhouse crops, orchards and nurseries, woodlots, flea control on household pets, and control of turf pests in urban areas, sod farms and golf courses. Neonicotinoids are regulated nationally by Health Canada's Pest Management Regulatory Agency (PMRA) with additional provincial restriction under the Province of Ontario's 2009 ban on cosmetic use of pesticides on lawns and gardens under the Ontario Pesticides Act (Ontario, 2016). Neonicotinoid formulations are also used for seed treatment of row crops such as corn, soybeans and canola, which has led to widespread use in Ontario (McGee et al., 2010; Farm and Food Care

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Ontario, 2016).

There has been growing concern about use of neonicotinoid pesticides and possible ecological and ecotoxicological effects on pollinators and invertebrates, and possible indirect effects on songbirds and waterfowl (Anderson et al., 2015). Anderson et al. (2015) recently reviewed fate, exposure and biological effects of neonicotinoids in the Canadian aquatic environment, while Morrissey et al. (2015) reviewed neonicotinoid contamination in surface waters globally and potential risk to aquatic invertebrates. The United States Geological Survey (USGS) has conducted both national- (Hladik and Kolpin, 2015) and regional-scale (Midwestern United States, Hladik et al., 2014) reconnaissance studies of neonicotinoids in streams in the United States. Imidacloprid, clothianidin and thiamethoxam were the most frequently detected; in the U.S. national study, clothianidin and thiamethoxam were positively correlated with percentage of land use in cultivated crop production, while imidacloprid was positively correlated with percentage of urban area (Hladik and Kolpin, 2015).

To make informed decisions with respect to use, registration, and effects guidelines, there is a requirement for knowledge of occurrence and distribution of neonicotinoid insecticides across jurisdictions. The purpose of this study was to assess occurrence and distribution of neonicotinoids in surface waters in different agricultural and urban areas of southern Ontario as part of a comprehensive pesticide monitoring program. The neonicotinoids analyzed were thiamethoxam, clothianidin, imidacloprid, thiacloprid and acetamiprid; registration for the first three compounds is currently being re-evaluated by the PMRA. Morrissey et al. (2015) identified a scarcity of neonicotinoid insecticide data globally that enables inferences regarding the fate of these compounds in relation to water body features and land use. Using statistical analysis, the correlation of individual compounds with land use was investigated and the relationship between neonicotinoid occurrence and hydrologic parameters in calibrated water courses. This study presents the first wide-scale investigation of neonicotinoid insecticides in surface waters across the range of agricultural activities in southern Ontario.

2. Methods

Fifteen sites in southern Ontario consisting of nine streams near agricultural areas (drainage area <100 km^2), and six larger streams/rivers (drainage area >100 km^2) were sampled (Fig. S1). These stream sites reflected a range of agricultural activities including row crops, fruits and vegetables, orchards and grapes, greenhouses, ornamental nurseries, and turf. The sites also included an urban stream (Indian Creek) and a reference stream (Spring Creek) located adjacent to a national park removed from agricultural activities. All neonicotinoid insecticide concentrations in samples from Spring Creek were below the method detection limits (Table S1). Precipitation was sampled at one additional site (Bear Creek).

2.1. Sampling methods

Whole water samples were collected by submersing sample bottles (1L amber glass with Teflon® lids) at mid-stream to a depth of 10–20 cm, and stored in coolers with ice packs for transport. Samples were collected bi-weekly through the growing season (May–September) with monthly sampling in April, October, November and December. Duplicate field samples and field blanks were collected for QA/QC purposes. General water quality characteristics including temperature, pH, conductivity and dissolved oxygen were also measured during each sampling event using a YSI® sonde.

2.2. Sample preparation

Surface water and precipitation samples (800 mL stored at 4 °C) were extracted at 5 mL/min using a Waters OASIS HLB (0.5 g) solid phase extraction (SPE) cartridge. The cartridge was rinsed with 5 mL of 5% methanol in water (v/v) and then dried on-line with nitrogen for 1 min. The cartridge was eluted with 10 mL of methanol at a flow rate of 2 mL/min. The final extract was concentrated to ~0.9 mL and 50 μL of internal standard (acetamiprid-d$_3$ at 0.97 μg/mL, imidacloprid-d$_4$ at 1.3 μg/mL and thiamethoxam-d$_3$ at 1.0 μg/mL) was added and the extract volume-adjusted with water to a 1.5 mL final volume.

2.3. Analysis

The five neonicotinoids analyzed were acetamiprid, clothianidin, imidacloprid, thiacloprid and thiamethoxam. An Agilent 1100 series HPLC system equipped with a Phenomenex Synergi Hydro-RP analytical column (3 × 100 mm i.d., 2.5 μm particle size) was used at a column temperature of 40° C and mobile phase flow rate of 250 μL/min. The mobile phase solvents were water (A) and 90% methanol (v/v) in water (B), each containing 5 mM ammonium formate used in a gradient elution program; initial composition 90% A:10% B; 90% A:10% B at 0.1 min; 5% A:95% B at 5.0 min and then held for duration of the 12 min run. The column was equilibrated for 5 min between 5 μL sample injections.

Neonicotinoid compounds were analyzed using an Applied Biosystems/Sciex API 2000 tandem mass spectrometer (MS) using an electrospray ionization (ESI) source in positive ion mode. The optimized positive ESI-MS conditions were; curtain gas (CUR) 35 psi, collision gas (CAD) 4 psi, TurboIon Spray source voltage (IS) 3000 v, heated nebulizer temperature 500° C, nebulizing gas (GS1) at 80 psi and auxiliary/heater gas (GS2) at 80 psi. The dwell time for each ion-pair was 50 ms. Resolution was set to achieve unit mass resolution for quadrupoles 1 and 3.

2.4. Statistical analysis

Summary statistics were estimated using the Kaplan-Meier method to account for values below detection limits using the NADA package in R (Helsel, 2012; R Core Team, 2016). Principal components analysis (PCA) was used to identify relationships between land-use, crop type, and neonicotinoid concentrations (Helsel and Hirsch, 2002). Prior to analysis by PCA all data were transformed to standard scores (z-score) as variables included have different units of measure. Association of individual neonicotinoids and association with precipitation and stream discharge were assessed using the Kendal rank correlation coefficient (Kendall's tau, τ). The PCA and correlation analyses were performed using JMP® Version 10 (SAS Institute Inc., Cary, NC).

3. Results and discussion

3.1. Occurrence and distribution of neonicotinoid insecticides in southern Ontario surface waters

As observed in other North American studies of neonicotinoids, imidacloprid, thiamethoxam and clothianidin were the most ubiquitous; occurrence and distribution data including surface water concentrations and frequency of detection for southern Ontario surface waters are shown in Table S1 and Fig. S2. Table S1 also includes the number of samples that exceeded the Canadian Council of Ministers of the Environment (CCME) interim freshwater guideline for protection of aquatic life value for imidacloprid (230 ng/L, CCME, 2007); this guideline is currently the only