Risks of exposure to systemic insecticides in agricultural soil in Ontario, Canada for the hoary squash bee (*Peponapis pruinosa*) and other ground-nesting bee species

D. Susan Willis Chan[1], Ryan S. Prosser[1], Jose L. Rodríguez-Gil[2], Nigel E. Raine[1]

[1] School of Environmental Sciences, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

[2] Department of Biology, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

Email: dchan05@uoguelph.ca

Abstract

Insecticide exposure is an environmental factor of concern relating to pollinator health. Recent increases in use of systemic insecticides, particularly neonicotinoids, have led to considerable research into the potential impacts for bees of exposure to these insecticide residues via the nectar and pollen of treated crops or contaminated wild flowers. However, although the majority of bee species are ground-nesting, the risk of exposure to insecticides in soil has not yet been evaluated. Here we use the hoary squash bee (*Peponapis pruinosa*) as a model system to provide the first evaluation of the risk of exposure to insecticide residues in soil to ground-nesting solitary bee species. The evaluation assessed agrochemical residues from the nectar, pollen and soil from Cucurbita-crops (e.g. squash and pumpkin) grown in southern Ontario in 2016, and soil insecticide residue data collected from field crops by the Ontario government. Systemic insecticide residues were rarely detected in the nectar and pollen of Cucurbita-crops in 2016, and hazard assessment deemed these potential routes of exposure to be non-hazardous for honey bee lethal dose endpoints. In contrast, quantifiable pesticide residues were frequently detected in soil suggesting this route of exposure to be hazardous for honey bee lethal dose endpoints, leading to further assessment using probabilistic risk assessments. Concentrations of clothianidin, imidacloprid, thiamethoxam (neonicotinoid insecticides) and chlorantraniliprole (an anthranilic diamide insecticide) in soil samples were plotted to produce an environmental exposure distribution for each insecticide. A honey bee LC_{50} and a solitary bee LC_{50} endpoint were converted to exposure endpoints using the amount of soil excavated by hoary squash bees during nest construction, for both acute and chronic exposure scenarios. The probability of exceedance of each exposure endpoint was calculated and compared to an acceptable risk threshold (i.e. 5% exceedance). In the acute exposure scenario, risk to hoary squash bees was below acceptable

threshold levels for all residues evaluated using the honey bee LC_{50}, but exceeded the threshold for clothianidin and imidacloprid using the solitary bee LC_{50}. In the chronic exposure scenario, risk from exposure to clothianidin and imidacloprid exceeded the threshold for both the honey bee and solitary bee LC_{50}s, and for chlorantraniliprole risk only exceeded the threshold for the solitary bee LC_{50}. Using the hoary squash bee as a model, the wider implications for other ground-nesting bees that pollinate crops was explored using insecticide residues from soil samples taken from Ontario field crops. Probabilistic risk assessments suggest that risk to ground-nesting bees is high from clothianidin residues in soils, even when exposure is acute, and substantial for both thiamethoxam and imidacloprid under chronic exposure scenarios. These results demonstrate the urgent need to consider direct exposure to pesticides in soil for ground-nesting bees as part of risk assessments and provides a potential model for evaluating risk from this type of exposure.

Keywords: crop pollination; environmental exposure distribution; insect pollinators; neonicotinoid insecticide; probabilistic risk assessment; solitary bees; systemic pesticides

Introduction

Global insect pollinator declines are being driven by multiple interacting environmental stressors, including land-use intensification, pathogens, invasive species and climate change, and may threaten the production of crops that depend directly or indirectly on the pollination services that bees provide (Calderone 2012; Vanbergen *et al*. 2013). For bee populations living in proximity to agricultural production, exposure to pesticides is one of the major environmental stressors likely affecting population health (Krupke *et al*. 2012; Vanbergen *et al*. 2013).

Cucurbita crops (e.g., pumpkin, squash, summer squash, and gourds) are grown globally for their fruits. Because of their imperfect flowers and heavy, oily pollen, they are dependent upon bees to mediate pollination (Whitaker 1962). *Cucurbita* crops grown in Ontario have several economically important pests, the most serious of which is the cucumber beetle (*Acalymma vittatum*), a vector of bacterial wilt (*Erwinia tracheiphilaa*) (OMAFRA 2009). The insecticides used to control pests in *Cucurbita* crops can also harm beneficial insect pollinators, setting up a tension between the need to control pests while maintaining the health of bee populations for the essential pollination services they provide.

In Ontario, three neonicotinoids (imidacloprid, clothianidin, thiamethoxam) are commonly used in *Cucurbita*-crop production to control insect pests (OMAFRA 2014). Although they are highly effective against pests, neonicotinoid insecticides are of environmental concern because of their relatively high toxicity to insects, their systemic nature, their persistence, and their extensive use in agriculture (Jeschke *et al*. 2011; Goulson 2013). In agriculture globally, about 60% of neonicotinoids are applied as seed coatings or as in-furrow soil applications, with the remaining applied as foliar sprays (Jeschke *et al*. 2011). Neonicotinoid residues have been found in agricultural soil (Krupke *et al.* 2012; Goulson 2013) and in the nectar and pollen of *Cucurbita* flowers (Dively & Kamal 2012; Stoner & Eitzer 2012). Neonicotinoids have also been found to persist in soil resulting in their detection in agricultural soils in the season following their application (Goulson 2013, Jones *et al*. 2014 - Britain; MOECC 2016 - Canada).

Although little is known about their impacts on most wild bees, the impacts of exposure to neonicotinoids on managed bees are well documented and include sublethal effects at sub-cellular to population levels, among eusocial and solitary bees, and at both adult and larval stages (Godfray *et al.* 2014, 2015; Alkassab & Kirchner 2017).

Possible routes of insecticide exposure for bees including oral exposure via ingestion of nectar, pollen, aphid honeydew, guttation water, chemigation water from soil treatments and contact exposure from abraded dust, sprays, microencapsulated particles, guttation water, and chemigation water from soil treatments (Godfray *et al*. 2014, 2015; Boyle *et al*. 2018). For non-*Apis* bees, all developmental stages (adult and larvae) may be exposed to pesticide residues in nectar and pollen, though the extent of exposure is likely greatest for adult females because they consume pollen and nectar during sexual maturation and egg laying (Michener 2007; Cane 2016; Sgolastra *et al*. 2018), consume nectar to fuel their foraging flights and nest building activities throughout their lives, and handle both pollen and nectar to provide food for their offspring (Mathewson 1968; Cane 2016). Males consume nectar and pollen during sexual maturation and nectar thereafter to fuel flight (Michener 2007). Larval stages consume pollen and nectar in their larval provisions and contact those provisions topically within their nest cells because the they lie directly on their provisions as they consume them (Michener 2007). For non-*Apis* bees, exposure may also be via nesting sites and nesting materials (Fisher & Moriarty 2011; Sgolastra *et al*. 2018). For ground-nesting bees, exposure from nesting sites is via soil contacted during nest excavation and construction for adult females, and via contact with the soil that forms nest cells

during larval development. However, the nest cells of many ground-nesting bee species have a water-resistant coating that may preclude exposure to pesticide residues in soil for larvae (Michener 2007). As adult male ground-nesting bees do not participate in nest construction (Michener 2007), they are not expected to be substantially exposed to pesticide residues in soil.

The persistence of neonicotinoid residues in soil generates the potential for both acute and chronic contact exposure for ground-nesting bees. The hydrophilic properties of this class of insecticides mean that they do not easily penetrate the intact cuticle of insects, and therefore that lethal contact exposures to neonicotinoids are typically higher, and show much less variability among bee species, than lethal oral exposures (Decourtye & Devillers 2012). Although no published data quantifying the extent of neonicotinoid uptake from soil by ground-nesting bees exist, the translocation of neonicotinoids to bees from residues in dust during corn planting is well documented (Girolami *et al*. 2013), and may be somewhat representative of translocation of neonicotinoids from soil to bees that excavate ground nests.

In eastern North America, the hoary squash bee (*Peponapis pruinosa*) is among the most important pollinators of *Cucurbita* crops, along with honey bees (*Apis mellifera*), and bumble bees (*Bombus* spp.) (Willis & Kevan 1995; Artz *et al.* 2011). Hoary squash bees are solitary bees that excavate soil to build their nests in the ground (Figure 1) within and around agricultural fields where *Cucurbita* crops are grown (Willis 1991). They are oligolectic, consuming a diet consisting almost entirely of *Cucurbita* pollen and nectar (Hurd *et al*. 1974). Because they have no wild host plants in eastern North America, they are obligately associated with *Cucurbita* crops (Lopez-Uribe *et al*. 2016). In 2014, in recognition of the unique risk to hoary squash bees from exposure to neonicotinoids, the Pest Management Regulatory Agency (PMRA) of Health Canada initiated a special review of registered neonicotinoid insecticides used on cucurbit crops (PMRA 2014). Because the hoary squash bee is common, nests in large noticeable aggregations, and has a well-documented natural history (Mathewson 1968; Hurd *et al*.1974; Willis 1991; Willis & Kevan 1995), this species is a good candidate to be a model species for evaluating risk from exposure to pesticides in Ontario agricultural soils for other less-studied, more elusive ground-nesting solitary bee species.

Substantial knowledge gaps remain around the toxicity and effects of neonicotinoids encountered by arthropods in soil, including bees that excavate nests and undergo development in the ground. This study is the first to address the potential risk of soil as a route of direct exposure to

insecticides for ground-nesting bees. The aims of this study are (1) to evaluate which insecticides pose a potential hazard to hoary squash bees; (2) to evaluate which exposure matrices (soil, pollen, and nectar) pose the greatest potential hazard to hoary squash bees; (3) to determine which hoary squash bee developmental stage (adult female or larvae) is at greatest hazard; and (4) to evaluate risk for all ground-nesting solitary bees on farms using the exposure profile of hoary squash bees as a surrogate. We anticipate that data from this study will contribute to risk assessments for hoary squash bees and other solitary bees.

Methods

Sampling

In July and August 2016, the period during which adult female hoary squash bees are building nests and foraging on *Cucurbita* crops, 29 samples of soil, nectar and pollen were taken from 18 farms across southern Ontario (11 farms were sampled twice, and 7 farms were sampled once). Potential for cross contamination of samples was minimized by using disposable gloves, single-use containers and instruments, and thorough cleaning of the soil corer between farms. Soil samples were taken from fields where *Cucurbita* crops were growing as this is often where hoary squash bees construct their nests. Using a soil corer, ten soil samples were taken per field from the top 15 cm of soil. The ten core samples were combined and subsampled to produce a single 3 g sample for residue analysis.

To maximize the amount of pollen and nectar available for sampling, and to prevent contamination from flower visitors, nectar and pollen samples were collected directly from staminate (male) flowers from which insects had been excluded. Nectar was harvested from 25 staminate flowers into a single 2 mL micro-centrifuge tube using a 20 µL micro-pipette until the micro-centrifuge tube was full. To collect pollen, synandria from the same 25 staminate flowers were excised, and the pollen from all 25 synandria was dislodged into a single-use plastic container using a disposable knife and weighed.

To determine the maximum number of pollen grains per synandrium, forty synandria with full pollen were gathered individually into 2 mL microcentrifuge tubes to which 0.5 mL of 70% alcohol was added. In the lab, pollen was dislodged from synandria by centrifuging at 2500 rpm for 3 minutes. The stripped synandria were then removed and spot checked to confirm that the

method effectively removed all pollen. Subsequently, the microcentrifuge tubes were topped up with 50% glycerin solution to bring the total volume of liquid in the tubes to 2 mL. The number of pollen grains in a full synandrium was calculated by averaging the number of pollen grains counted in five 5-µL aliquots and relating this back to the full 2 mL volume. Before removing aliquots, the pollen was thoroughly distributed in the glycerin solution by mixing with a mini vortex mixer.

Residue Analysis

All soil, pollen, and nectar samples collected from farms were submitted for analysis to University of Guelph Agri-Food Laboratories (ISO/IEC 17025 accredited). Samples were analyzed using their TOPS-142 LC pesticide screen, modified from the Canadian Food Inspection Agency (CFIA) PMR-006-V1.0 method. Pesticides were extracted using the QuEChERS Method (Schenck and Hobbs 2004). Extracts were analyzed using high performance liquid chromatography paired with electrospray ionization and tandem mass spectrometry and gas chromatography paired with tandem mass spectrometry. Limits of detection and quantification for all residues detected in samples of soil, pollen, and nectar by the University of Guelph Agri-Food Laboratories are summarized in Table 3.

Extent of Exposure

Information from the literature and this study were used to determine the realistic amount of pollen, nectar, and soil that hoary squash bees would be exposed to via contact or ingestion. This study examined exposure amounts for adult female and larval squash bees only, as information is lacking about exposure in male hoary squash bees. However, it is reasonable to expect that males are less exposed to pollen and nectar than females because they do not provision nest cells. Males are not exposed to soil during this period of the lifecycle as they do not participate in nest construction (Mathewson 1968).

In this study, the mass of a single *Cucurbita* pollen grain was determined by dividing the mean mass of pollen grains per synandrium (mean = 0.0302 g; n = 25) by the mean number of pollen grains per synandrium (mean = 18,438, n = 40)(0.0302 g / 18,438 pollen grains = 1.64×10^{-6} g/pollen grain). For larvae, the amount of pollen consumed (0.0468 g pollen/nest cell) was calculated by multiplying by the mass of a single pollen grain (as calculated above = 1.64×10^{-6}

g/pollen grain) by the mean number of pollen grains in hoary squash bee larval provisions (i.e., 28,543 pollen grains: Willis 1991). Larval exposure to pesticide residues via cuticular contact with pollen in provisions was not evaluated because of lack of information on the proportion of pesticide transferred across the nest lining, and contact toxicity of pesticides to larvae.

Contact exposure for adult females was assessed to be five times that for each larva because each female provisions five cells within a nest (Mathewson 1968). The amount of pollen ingested by adult females could not be calculated because information on their nutritional demands is lacking. Currently no data exist regarding the nectar requirements of either adult female or larval hoary squash bees. However, pollen-collecting honey bee workers are most like adult female hoary squash bees in their foraging behaviour. For honey bees, pollen-collecting foraging workers have been estimated to consume 10.4 mg sugar/day to fly between their nest to forage patches and from flower-to-flower within those patches (Rortais *et al*. 2008). Based on this assumption, and that pumpkin (*Cucurbita pepo*) nectar contains 40% sugar (Willis 1991), female hoary squash bees that forage during a 30-day period, would need to consume approximately 312 mg sugar in 780 mg of *Cucurbita* nectar to meet their lifetime energy requirements. This is likely an overestimation of nectar consumption for female hoary squash bees as the foraging radius of squash bees from nest to flower patch is much smaller than that of honey bees (honey bee foraging radius: mean = 5.5, maximum = 15 km (Beekman & Ratnieks 2000); oligolectic solitary bee foraging radius is < 260 m (Gathmann & Tscharnke 2002)).

Using hoary squash bee nest dimensions from Mathewson (1968), the volume of soil excavated by a female squash bee to build a nest is 25.19 cm^3 (Table 1). This can be multiplied by the bulk density (BD) of loam soil, a type common in agricultural soils (BD_{loam} = 1.33 g/cm^3: USDA 2008), to calculate the soil mass to which a female hoary squash bee is exposed (25.19 cm^3 x 1.33 g/cm^3 = 33.51 g). This mass represents the total amount of soil to which a female hoary squash bee is exposed cumulatively during construction of a single nest over 30 days of activity. Acute (48 h) exposure was calculated by dividing cumulative exposure by 15 (33.5g / 15 = 2.23 g). A summary of exposure routes and extent of exposure for the hoary squash bee are provided in Table 2.

Effect Endpoints

Effect endpoints (e.g., the concentration causing a 50% reduction in survival, LC_{50}) are required in a risk assessment to characterize the effect of a chemical. Unfortunately, effect endpoints are not currently known for the hoary squash bee at any developmental stage for any pesticide, which represents a considerable knowledge gap for this agriculturally-relevant species. For this hazard assessment, the adult honey bee LD_{50} for oral exposure to nectar or pollen or the adult honey bee LC_{50} for contact exposure to pollen or soil was used. Honey bee values were used because current regulatory standards consider the honey bee to be an adequate proxy for all bee species (US-EPA 2014), and lethal doses for larval stages are rarely available (Godfray *et al.* 2014; Alkassab & Kirchner 2017). Honey bee LD_{50} and LC_{50} values were obtained from the US-EPA Pesticide Ecotoxicity Database of the Office of Pesticide Programs, Ecological Fate and Effects Division, of the U.S. Environmental Protection Agency (database: http://www.ipmcenters.org/Ecotox/) and published literature. Multiple LC_{50} values were available for clothianidin, imidacloprid, and thiamethoxam. Consequently, the geometric mean of these lethal doses, reported from seven sources (US-EPA database; Iwasa *et al*. 2004; European Commission EU pesticides database; Sanchez-Bayo & Goka 2014; Ruzhong *et al.* 1991; Stark *et al*. 1995; Goulson *et al*. 2008) were used in this study (Table 4). For adult female hoary squash bees, contact honey bee LC_{50} values were used for soil and pollen as exposure to these matrices would be via contact, rather than ingestion. Oral honey bee LD_{50} values were used for adult female hoary squash bee ingestion of nectar, and larval hoary squash bee ingestion of pollen.

For the probabilistic risk assessment in this study, which focused on soil exposure, the effect endpoints relevant to solitary bees include: (1) the geometric mean honey bee contact LC_{50} endpoint, (2) the lowest reported honey bee contact LC_{50} endpoint in the literature (Iwasa *et al.* 2004; US-EPA database), (3) surrogate solitary bee contact lethal endpoints (honeybee $LC_{50}/10$; Arena & Sgolastra 2014; EFSA 2018), and (4) the concentration causing no observable adverse effect (NOAEC) endpoint from contact with clothianidin for honey bees (1.25 ng/bee; Lambin *et al*. 2001). No NOAEC was available for the active ingredients (a.i.) imidacloprid, thiamethoxam, or chlorantraniliprole. For clothianidin, imidacloprid, thiamethoxam, and chlorantraniliprole, contact effect endpoints were converted to soil-exposure endpoints as follows:

$$Exposure\ Endpoint(ng\ a.i./g\ matrix) = \frac{Effect\ Endpoint\ (ng\ a.i./bee)}{Amount\ of\ soil\ exposure\ (g\ matrix/bee)}$$

Hazard Quotients

The hazard quotient (HQ) was calculated for each residue detected in each exposure matrix as follows:

$$Hazard\ Quotient\ = \frac{(Concentration\ of\ residue\ in\ matrix)(Amount\ of\ exposure\ to\ matrix)}{Honey\ bee\ LD50\ or\ LC50}$$

considerable hazard to hoary squash bee populations because exposure exceeds the honey bee lethal dose. In this hazard assessment, the concentration of residues was calculated by taking the geometric mean of all quantifiable concentrations in samples in the study for each matrix, ignoring all samples that were below the limit of detection (LOD). Concentrations of residue in each matrix were reported in ng a.i./g matrix, amount of exposure to the given matrix was reported in g matrix/bee, and LD_{50}s or LC_{50}s are reported in ng a.i./bee.

Hazard quotients were summed for each type of pesticide (fungicide or insecticide) and exposure matrix (soil, pollen, nectar) to determine which pesticide type and matrix were potentially most hazardous to hoary squash bees. Hazard quotients were also summed for adult females and larvae to determine which developmental stage faced the greatest hazard.

Environmental Exposure Distributions

Distributions

To evaluate the risk to ground-nesting bees from exposure to soil during nest excavation and construction, empirical environmental exposure distributions (EEDs) were generated from the concentration of insecticides measured in soil by fitting the data to a log-normal or gamma distribution via maximum likelihood estimation (MLE), using the fitdistrcens function in the R package fitdistrplus (Delignette-Muller *et al*. 2010; R Development Core Team 2008). This function allows for the fit of censored (right-, left-, or interval-censored) data enabling the use of the available “non-detect”, and interval (LOD-LOQ) data. The fitdistrplus function calculates the probability plotting position using Hazen’s rule, with probability points of the empirical distribution calculated as (1:n - 0.5)/n, where n is the total number of data points (Delignette-Muller *et al*. 2010). Interval data (non-detects, LOD-LOQ) were ranked according to the midpoint of the interval. Confidence intervals (95%) for the distribution parameters and distribution estimates were calculated via nonparametric bootstrapping (1000 iterations) with the bootdiscens function in the fitdistrplus package. The fit to other distributions (Weibull and

Exponential) were also tested, and the best fit was chosen via comparison of the Akaike information criterion (AIC supported by visual inspection of the fit to the actual data). The gamma distribution provided the best fit to construct EEDs for clothianidin and chlorantraniliprole measured in soil, and the log-normal distribution provided the best fit for imidacloprid and thiamethoxam. The percent rank was subtracted from 100 to determine the percent exceedance. For clothianidin, imidacloprid, thiamethoxam, and chlorantraniliprole EEDs, exposure endpoints (Table S1), exceedances (Table S2), and model parameters (Table S3) are listed in supplementary information.

The exposure endpoints described (geomean LC_{50}, least LC_{50}, solitary bee surrogate LC_{50}, NOAEC) were used to calculate the percent exceedance of the EEDs. In this study, percent exceedance is the probability that hoary squash bee adult females will be exposed to insecticide residues at concentrations higher than the pre-determined exposure endpoints. For the purposes of this assessment, an exceedance value lower than 5% was assigned as an acceptable risk for this species because it assures protection 95% of the time.

Exposure Scenarios

Chronic and Acute

Exposure endpoints for the soil matrix were calculated for both acute and chronic exposure scenarios. In the chronic exposure scenario, exposure was to the total amount of soil that an adult female excavates during the construction of a single nest, typically containing 5 nest cells and constructed during a 30-day period (Mathewson 1968; Table 1). For the acute exposure scenario, exposure was the total amount of soil that adult females excavate in a 48-hour period, calculated by dividing the chronic exposure amount of soil by 15. The chronic exposure level was 33.5 g of soil, and the acute soil exposure amount was 2.23 g.

Environmental exposure distributions (EEDs) were constructed for each neonicotinoid for chronic exposure to soil (30 days, 33.5 g soil) because the effects of neonicotinoids on the nicotinic acetylcholine receptors (nAChRs) of insects are cumulative and irreversible (Tennekes & Sanchez-Bayo 2011) and neonicotinoids have been shown to be relatively persistent in soil (Jones *et al*. 2014 – Britain; MOECC 2016 – Canada). EEDs for an acute exposure scenario (48 h, 2.23 g soil) for neonicotinoid residues in soil were also constructed. EEDs for chlorantraniliprole were only estimated for acute exposure as existing evidence from honey bees

suggests their effects may be transient (Dinter *et al*. 2009). Honey bees dosed with chlorantraniliprole, orally or topically under artificial test conditions, became lethargic but recovered within 48-72 hours after exposure (Dinter *et al*. 2009).

Cucurbita and Field Crop Soils

To compare exposure of hoary squash bees on *Cucurbita*-crop farms, and to expand the scope of this assessment to all solitary ground-nesting bees that nest in agricultural soil, EEDs were created using data from both the *Cucurbita*-crop farms sampled in this study and from a publicly-available dataset provided by the Ontario Ministry of the Environment and Climate Change (MOECC 2016). These MOECC data reported neonicotinoid residues in soil from 38 agricultural sites in southern Ontario in 2016. Only data from soil samples taken at a depth of 15 cm prior to seeding or pesticide application in the spring were used from this MOECC data set. The limit of detection reported for the MOECC data set was 0.05 ng/g for clothianidin, imidacloprid, and thiamethoxam.

Insecticide residues in the samples taken as part of this study represent biologically-relevant exposure specifically for the hoary squash bee on *Curcurbita* farms. Neonicotinoid residues in the MOECC samples represent the "background" levels of neonicotinoids in Ontario agricultural soils that persist from a previous cropping cycle, rather than concentrations that are detected after neonicotinoids are applied within the current cropping cycle. Therefore, MOECC data levels represent the minimum exposure to neonicotinoids for ground-nesting bees in soil within an Ontario agricultural context. In reality these bees could experience greater exposure if they are nesting in soil after neonicotinoids are applied in the current cropping cycle.

Hoary squash bee exposure to soil during nest excavation was used as a surrogate for exposure in all ground-nesting solitary bee species. Although using squash bee exposure as a surrogate for other ground-nesting bee species is not a perfect model, it is a starting point to understand risk from insecticide residues in soil for ground-nesting solitary bees. For ground-nesting solitary bees, tunnel diameter is related to bee size (because bees excavate tunnels and nest cells large enough for themselves: Michener 2007). However, bee body size does not necessarily appear to be correlated to the depth that vertical tunnels in nests are excavated in soil (Cane 1991). Solitary bees are physiologically limited in their reproductive capacity and generally build 1-8 brood cells per nest (Michener 2007). Although other solitary ground-nesting bee species may be appreciably larger or smaller than squash bees, the ratio of their body size to the volume of soil

they excavate when building a nest may be similar, providing a basis upon which to compare exposure for different solitary bee species in the future. Although smaller bees are generally more sensitive to insecticide residues (Devillers *et al*. 2003), they will handle less soil (and be less exposed) than larger bees because the diameter of their nest tunnels and cells are smaller.

Results

Pesticides in *Curcurbita*-farm Samples

Residues of 7 insecticides, 6 fungicides, and 2 herbicides were detected in samples taken from farms growing *Cucurbita* crops. The list of pesticides detected, including information about limits of detection and quantification (LOD/LOQ), frequency of detection, and mean and maximum concentrations in each exposure matrix are presented in Table 3. Herbicide residues were not assessed further in this study as resulting hazard quotients were extremely low, which is not surprising considering that herbicides are targeted to remove plants rather than insects.

The three exposure matrices (pollen, nectar, soil) show different frequencies of detection and pesticide residue profiles (Figure 2; Table 3). Soil was the most contaminated with 5/7 insecticides and 5/6 fungicides detected. Pollen contained residues of 4/7 insecticides and residues of all 6 fungicides, but maximum residue concentrations were lower, and residues were detected much less frequently, than in soil - despite generally lower LODs for nectar and pollen than soil. Nectar was the least contaminated exposure matrix with only 3/7 insecticides and 3/6 fungicides detected, with the lowest residue concentrations and lowest frequency of detection. However, imidacloprid was found with the same frequency in both nectar and pollen, and was the only insecticide detected in all three matrices. Imidacloprid was detected in 21% of soil samples, 3% of pollen samples and 3% of nectar samples. Thiamethoxam was present only in a single soil sample. Clothianidin was detected in 34% of soil samples, but was not detected in either nectar or pollen. The insecticides chlorantraniliprole and carbaryl were detected in soil samples (24% and 10% respectively) and pollen samples (3% and 7% respectively), but were not detected in nectar. The insecticides methomyl and dimethoate were not detected in soil, but dimethoate was detected infrequently in pollen and nectar (both 3%), and methomyl was detected 7% of nectar samples. The fungicide picoxystrobin was also detected infrequently in nectar (3%) and pollen (10%). The fungicides pyraclostrobin, and propamocarb were detected in

all three matrices, while boscalid, quinoxyfen and difenoconazole were detected in soil and pollen, but not in nectar.

Hazard Assessment

Pesticides

Hazard quotients for fungicide and insecticide residues are presented for each exposure matrix (soil, pollen, nectar) for either adult females or larvae as appropriate in Table 4. As expected, insecticides exhibited a considerably higher combined hazard quotient ($HQ_{insecticide}$ = 15.11) across all exposure matrices than fungicides ($HQ_{fungicide}$ = 0.03: Table 4).

Among the insecticides detected, only the neonicotinoids clothianidin, imidacloprid, and thiamethoxam, had HQs ≥ 1 in soil, while the combined HQ of all non-neonicotinoid insecticides was less than 1 in the same matrix ($HQ_{non\text{-}neonicotinoid}$ = 0.15: Table 4). However, although chlorantraniliprole had an HQ < 1, it was included in further probabilistic risk assessment for comparative purposes because it was found in 24% of samples and is also systemic insecticide. The physical, chemical and environmental fate properties of imidacloprid, clothianidin, thiamethoxam and chlorantraniliprole are summarized in Table 5.

Exposure Matrices

HQ values for pollen, including both adult and larval exposure (HQ = 0.36), and nectar were low (HQ = 0.18) relative to values for soil (Table 4). However, only adult female exposure was assessed for nectar as no information exists in the literature about the amount of nectar consumed by larvae or adult males. Chlorantraniliprole, a newer systemic insecticide that is being used within *Cucurbita* crop systems in Ontario, was detected in only one pollen sample and not found in nectar samples. Imidacloprid was also detected in one pollen sample and 6.9% of nectar samples; other neonicotinoids were not detected in these matrices. Low hazard quotients for pollen and nectar in this study reflect the low concentrations of all the insecticides detected in these exposure matrices. Imidacloprid was the largest contributor to the combined HQs for these matrices, with a contribution of 89% and 99% of hazard in pollen and nectar, respectively (Table 4). As HQs for pollen and nectar were < 1, no further assessment of risk was deemed necessary for these exposure matrices.

The combined HQ for insecticides in soil was very high (HQ_{soil} = 14.56) relative to nectar and pollen (Table 4). The soil HQ was mostly attributable to the neonicotinoid residues ($HQ_{Imidacloprid}$ = 2.65, $HQ_{Clothianidin}$ = 1.93, $HQ_{thiamethoxam}$ = 9.41: Table 4). However, the HQ calculation for thiamethoxam is less reliable as it is based on a single sample containing detectable residues. This underlines the need to assess risk using probabilistic methods.

Developmental Stage

There appears to be a much greater hazard to adult females ($HQ_{adult\ female}$ = 15.05 including thiamethoxam; $HQ_{adult\ female}$ = 5.03 excluding thiamethoxam) relative to larval hoary squash bees (HQ_{larvae} = 0.06), mostly because of their exposure to neonicotinoid residues in soil during nest construction (HQ_{soil} = 13.99 including thiamethoxam; HQ_{soil} = 4.58 excluding thiamethoxam: Table 4).

Probabilistic Risk Assessment

Hoary Squash Bees in *Cucurbita* Crop System

Environmental exposure distributions (EEDs) for the acute exposure scenario (exposure to 2.23 g soil in 48 hours), indicate that clothianidin soil residues showed exceedance below 5% based on the geometric mean honey bee LC_{50} and the lowest honey bee LC_{50} endpoints. However, the exceedance for the solitary bee surrogate lethal dose endpoint was high (28.3%), as was exceedance for the honey bee NOAEC endpoint (11.4%: Figure 3A, Table S2). Imidacloprid showed exceedance below 5% for the geometric mean honey bee LC_{50} (3.5%) and exceedances greater than 5% for both the lowest honey bee LC_{50} (8.9%) and the solitary bee surrogate LC_{50} (31.2%: Figure 3B, Table S2). In the acute exposure scenario, Chlorantraniliprole did not exceed 5% for any of the effect endpoints (Table S2) and so appears to pose no risk.

For the chronic exposure scenario (exposure to 33.5 g soil over 30 days), exceedance for clothianidin was relatively high for all soil exposure endpoints in *Cucurbita* growing systems (Figure 4A, Table S2). The geometric mean honey bee LC_{50}s resulted in a 35.8% exceedance, with increasing exceedances for the lowest honey bee LC_{50} (44.3%), the honey bee NOAEC (57.1%) and the solitary bee surrogate lethal dose (68.7%: Figure 4A, Table S2). For imidacloprid, the exceedance for all exposure endpoints was also high under the chronic exposure scenario, at 39.8% for the geometric mean honey bee LC_{50}s, 57.8% for the lowest

honey bee LC_{50}, and 85.4% for the solitary bee surrogate LC_{50} (Figure 4B, Table S2). Exceedance under the chronic exposure scenario for chlorantraniliprole was below the acceptable range of 5% for the geometric mean honey bee LC_{50} and lowest honey bee LC_{50} (Figure 4C, Table S2). However, for the solitary bee surrogate LC_{50}, exceedance was 11.9%, more than double the acceptable exposure probability (Figure 4C, Table S2). Because of high limits of detection and quantification (LOD/LOQ) for thiamethoxam rendered only a single quantifiable residue sample, EEDs could not be reliably fitted to data for this active insecticide for either exposure scenario.

All Ground-Nesting Bees in Field Crop System

Based on publicly-available data (MOECC 2016) for Ontario's agricultural soils, 96.34% of soil samples (n = 82) had detectable clothianidin residues, 10.97% of soil samples had detectable imidacloprid residues, and 81.48% had detectable thiamethoxam residues. For both the acute and chronic exposure scenarios for all ground-nesting solitary bees in Ontario's agricultural soils, EEDs were constructed using hoary squash bee exposure amounts (2.23 g soil-acute; 33.5 g soil-chronic) as a surrogate.

In the acute exposure scenario, exceedance was only greater than the 5% threshold for the solitary bee surrogate LC_{50} endpoint when considering EEDs for either imidacloprid (Figure S1) or thiamethoxam (Figure 5B). In contrast, the probability of exceedance was greater than 5% for all exposure endpoints for clothianidin (honey bee geometric mean LC_{50}: 11.72%; honey bee least LC_{50}: 27.25%; NOAEC: 57.88%; solitary bee surrogate LC_{50}: 81.85%), suggesting that risk to ground-nesting bees is high from clothianidin in soils, even when exposure is acute (Figure 5A).

The probability of exceedance for clothianidin in the chronic scenario was very high for all exposure endpoints (honey bee geometric mean LC_{50}: 87.68%; least honey bee LC_{50}: 92.4%; NOAEC: 96.76%; solitary bee surrogate LC_{50} t: 98.82%; Figure 6A). For thiamethoxam, probability of exceedance was lower (honey bee geometric mean LC_{50}: 35.7%; honey bee least LC_{50}: 37.36%; solitary bee surrogate LC_{50}: 78.42%) but still greatly exceeded the 5% acceptable exceedance threshold (Figure 6B). Probabilities of exceedance for imidacloprid under the chronic exposure scenario was below 5% for the honey bee geometric mean LC_{50} endpoint

(4.16%) and slightly exceeded this threshold for the honey bee least LC_{50} endpoint (5.89%) and the solitary bee surrogate LC_{50} endpoint (9.24%) (Figure S2; Table S2).

Discussion

The differences in the residue profiles of the exposure matrices (soil, pollen, nectar) in *Cucurbita* growing systems in Ontario (Figure 2) are related to the chemical and physical properties of the pesticides (Table 5), the application method (seed coating, direct soil application, or foliar spray) and timing of application. Comparing the three matrices, soil had the greatest number of neonicotinoids detected (clothianidin, imidacloprid and thiamethoxam present in a single sample), while imidacloprid was the only neonicotinoid detected in pollen and nectar. The maximum concentration of imidacloprid detected in soil (41.6 ng/g) was substantially greater than in pollen (4.3 ng/g) or nectar (1.1 ng/g). Analyses of the nectar and pollen of *Cucurbita* crops in the United States have reported higher mean imidacloprid residues concentrations (60.9 ng/g for pollen, 7.4 ng/g for nectar) and greater frequencies of detection (92% of pollen samples; 88% of nectar samples: Dively & Kamel 2012). These differences could be because samples in this study were taken 8 weeks after pesticide application corresponding to the period of *Cucurbita* flowering and hoary squash bee activity in Ontario compared to samples taken 5 weeks after application by Dively and Kamel (2012). Stoner and Eitzer (2012) reported higher concentrations of imidacloprid and thiamethoxam in *Cucurbita* crops after application to soil than found in this study, which may be because they included anther and nectary tissue in their analysis of residues in pollen and nectar.

Hazard Assessment

It is important to highlight that calculations in the analysis of the hazard of pesticides to the hoary squash bee within *Cucurbita* crops in Ontario are based on lethal doses for adult honey bees, as this species is presently the regulatory standard for testing toxicity in bees (US-EPA 2014). However not all bee species (Arena & Sgolastra 2014; Rundlöf *et al.* 2015; Woodcock *et al*. 2017), nor all developmental stages of bees (Atkins & Kellum 1986), are equally sensitive to all pesticides. Neonicotinoids are often more toxic to bees when exposure is via ingestion (Suchail *et al*. 2001; Iwasa *et al*. 2004; Godfray *et al*. 2014, 2015), and solitary bees are more sensitive than either honey bees or bumble bees to oral exposure (Devillers *et al*. 2003; Rundlöf

et al. 2015; Woodcock *et al*. 2017), therefore the use of oral honey bee LD_{50} values in this study may under-represent oral toxicity to hoary squash bees. However, toxicity via contact exposure varies much less among species (Decourtye & Devillers 2012; Arena & Sgolastra 2014), thus honey bee contact LC_{50} values may adequately represent contact toxicity for adult female hoary squash bees, especially because the two species have similar body size. The evaluation of hazard to larval squash bees using adult honey bee LD_{50} or LC_{50} values in this study may be an underestimation of hazard because of species and developmental stage differences in sensitivity to neonicotinoids (Godfray *et al*. 2014, 2015; Bonmatin *et al*. 2015).

Pesticides

Although the hazard from thiamethoxam appears to be relatively high (HQ = 9.41), this is strongly influenced by a single detection in soil in which relatively high residues (6.8 ng a.i./g soil) were found. Although only one sample had detectable concentrations of thiamethoxam, clothianidin residues detected in soil samples could in fact be the breakdown products of applied thiamethoxam, rather than of applied clothianidin itself (Bonmatin *et al*, 2015; Hilton *et al*, 2016).

Our results suggest that both clothianidin (HQ = 1.93) and imidacloprid (HQ = 3.15) pose a hazard in *Cucurbita* growing systems in Ontario because they are both detected frequently, and their respective HQs exceed 1 when summed across all exposure matrices. Imidacloprid appears to be substantially more hazardous in this cropping system than clothianidin based on this deterministic approach. The combined hazard of all neonicotinoids in the system was also high ($HQ_{combined}$ = 14.49 including thiamethoxam; $HQ_{combined}$ = 5.08 without thiamethoxam), meaning that hoary squash bee populations may be at hazard of exposure to lethal concentrations of neonicotinoids in a worst-case scenario. As such, further risk analysis using a probabilistic approach of the neonicotinoids thiamethoxam, clothianidin, and imidacloprid was warranted.

Although combined hazard from chlorantraniliprole in all matrices was low (HQ = 0.11) it was included in further probabilistic risk analysis for comparative purposes because it is a persistent, systemic insecticide that was detected frequently (24% soil samples) in *Cucurbita* growing systems in Ontario.

Exposure Matrices

There is common agreement that bees can be exposed to neonicotinoids from nectar and pollen in the flowers upon which they forage (EFSA 2012; Godfray *et al*. 2014, 2015). However, there are currently no studies that evaluate the risks to ground-nesting bees from direct exposure to neonicotinoids in soil, although some studies evaluating direct effects on other soil fauna exist (de Lima e Silva *et al*. 2017). This study demonstrates that there is low hazard to adult hoary squash bees from pesticide exposure via nectar (HQ = 0.18), or to adult and larval hoary squash bees from pollen ($HQ_{adult + larva} = 0.36$), during their period of foraging and nesting activity in Ontario despite their specialized diet. In comparison, hazard quotients associated with pesticide residues from the pollen loads collected by honey bees, an example of a diet generalist, ranged from 0.01 to 75,000 (Stoner & Eitzer 2013). Such wide differences in HQs likely reflect the significant variability in the pesticide residues found in nectar and pollen of different crops, and even among varieties of the same crop (Bonmatin *et al*. 2015).

Because both imidacloprid and thiamethoxam (and the resulting breakdown metabolite, clothianidin) can be applied directly to the soil in *Cucurbita* cropping systems, and may persist in the soil for longer than a single growing season in Canada (MOECC 2016), it is unsurprising that the hazard to the ground-nesting hoary squash bee from neonicotinoids in soil ($HQ_{soil} = 12.99$) is much higher than even the combined hazard from both pollen and nectar ($HQ_{pollen+nectar} = 0.54$) in this cropping system. Even if we remove the contribution of thiamethoxam, whose hazard may be over-inflated in this study, the hazard from soil remains high (HQ_{soil}, thiamethoxam removed = 3.58) and appears to be the most important route of exposure for hoary squash bees in Ontario.

Developmental Stage

Our analysis of hazard by developmental stage in this study excluded the hazard to adult male hoary squash bees from pollen and nectar consumption and hazard to larval stages from consumption of nectar and contact with their pollen provisions. Both adult male hoary squash bees and larvae can be expected to consume much less nectar than adult females because they are not involved in energy-expensive foraging activities to provision nest cells, nor are they involved in nest excavation and construction. For honey bees, larvae are reported to consume 150% less nectar than adult pollen foragers (Rortais *et al*. 2005). Furthermore, male hoary squash bees spend about 18 hours per day sleeping in wilted *Cucurbita* blossoms (Willis and Kevan 1995),

whereas females are active throughout the daylight hours, engaged in foraging activities in the morning and nest excavation in the afternoon (Hurd & Linsley 1974).

Hazard to larval hoary squash bees was not particularly high from their main exposure matrix, consumption of pollen ($HQ_{larvae,pollen}$ = 0.06), and would not likely be high from nectar because relative consumption by adult females is much higher than it would be for larvae (Rortais *et al.* 2005) and $HQ_{nectar,adult\ female}$ was less than 1. This study assumes that larval hoary squash bees are protected from direct exposure to neonicotinoids in soil (both adhering to soil particles and in soil water) because of the waterproof nature of the lining of hoary squash bee nest cells (Mathewson 1968), an assumption that requires further investigation.

The combined hazard for adult female hoary squash bees from all exposure matrices (soil, pollen, nectar) is high ($HQ_{adult\ female}$= 5.03 excluding thiamethoxam), of which 91% is attributable to exposure to neonicotinoids in soil ($HQ_{adult\ female,\ soil}$ = 4.58; 4.58/5.03 = 91%). Thus, adult female hoary squash bees are at hazard of being exposed to lethal doses of clothianidin and/or imidacloprid as they complete construction of a single nest. Mathewson (1968) suggests that hoary squash bees can construct more than one nest per season when environmental conditions (e.g. nectar and pollen resources, weather) permit. However, in this study, female hoary squash bees were already exposed to doses above lethal levels of both imidacloprid and clothianidin (HQs >1) as they constructed a single nest, rendering it unlikely they would be able to construct a second. Indeed, under present soil neonicotinoid residue conditions in Ontario *Cucurbita* cropping systems, pesticide exposure conditions may preclude the construction of more than one nest in a season even if all other conditions are favourable.

In summary, hazard appears to be low for larval hoary squash bees in *Cucurbita* cropping systems in Ontario, though this conclusion depends upon the assumed protection provided to them by their waterproof nest cell lining during development. For adult female hoary squash bees, the hazard was relatively high and mostly attributable to neonicotinoid residues in soil.

Probabilistic Risk Analysis

Hoary Squash Bee in *Cucurbita* System

For the hoary squash bee, it is clear from the EEDs for acute exposure (48 h, 2.23 g soil; Figure 3, Table S2), that probability of exceedance of the mean honey bee LC_{50} is below the acceptable

5% threshold for imidacloprid, clothianidin and chlorantraniliprole. If the solitary bee surrogate LC_{50} endpoint is used, both imidacloprid (31.2%) and clothianidin (28.3%) residues in soil pose an unacceptable risk to the hoary squash bee (Figure 3, Table S2).

The chronic exposure scenario presented a more troubling risk picture because the amount of exposure to soil was much greater (30 days, 33.5 g soil) than in the acute exposure scenario (Figure 4). In the chronic exposure scenario, imidacloprid and clothianidin pose an unacceptably high risk of exceedance for all exposure endpoints (mean honey bee LC_{50}, least honey bee LC_{50}, and solitary bee surrogate LC_{50}: Figure 4A,B), whereas risk from chlorantraniliprole exceeds the 5% threshold for only the solitary bee surrogate LC_{50} (Figure 4C). It is very probable that at least some of the clothianidin found in *Cucurbita* crops systems may in fact be metabolites from the application of thiamethoxam to soil (Bonmatin *et al*. 2015). For example, ~3-46 % of the residues recovered from soil sampled more than 60 days after thiamethoxam application have been found to be the metabolite, clothianidin (Hilton *et al*. 2016). Further work on the fate of thiamethoxam in *Cucurbita* crop fields is required to determine whether seed-applied or soil-applied thiamethoxam poses a risk to hoary squash bees via its metabolite, clothianidin.

There were at least three issues generating uncertainty when attempting to assess the potential risk posed by neonicotinoid residues in soil to hoary squash bees. Firstly, the lack of information about insecticide toxicity for this species, or indeed any other solitary ground-nesting surrogate species. As the hoary squash bee is similar in size to the honey bee it may be well represented by the available toxicity data for honey bees, especially for contact exposure which tends to vary less among species than measures of oral exposure (Decourtye & Devillers 2012). However, this has not yet been empirically established for the hoary squash bee. Secondly, although soil-applied neonicotinoids are known to elicit negative effects on Lepidoptera that pupate in soil (Dilling *et al*. 2009), Carabid beetles that live in soil at all life stages (Kenkel *et al*. 2001) and Hexapoda, Collembola, Thysanoptera, and Coleoptera adults (Peck 2009), we could find no information on the extent to which insecticide residues in soil can pass through the cuticle or into spiracles of insects that burrow in soil. In this study we assumed a worst-case scenario in which all the soil residues are translocated during exposure, but this is unlikely, even though neonicotinoids have relatively low organic carbon-water partition coefficients (Koc; Table 5; Wettstein *et al*. 2016). Nevertheless, if even if 50% of the neonicotinoids from the chronic exposure scenario were bioavailable, exceedance of the solitary bee surrogate LC_{50} would still be

substantially higher than the 5% threshold for both clothianidin (38.8%) and imidacloprid (33.2%). Lastly, the probabilistic risk assessment has certain limitations. Despite low detection limits for soil reported by the Guelph University Agri-Food Labs, there is a need for even lower detection limits in soil to bring them in line with exposure concentrations corresponding to the lowest honey bee LC_{50}, the NOAEC, or the solitary bee surrogate LC_{50} (Table S1) for some compounds. Confidence intervals for the environmental exposure distributions in this study are comparatively wide due to limited sample size (n = 29) and high limits of detection, and results must be understood within this context. However, this study is valuable and significant because it represents the first attempt to evaluate risk from insecticide residues in soil for any ground-nesting bee. Interestingly, even at the extreme high values for confidence intervals (where exceedance would be lowest), exceedance remains above the acceptable limit (5%) for the solitary bee surrogate lethal dose endpoint for clothianidin and imidacloprid in both the acute and chronic scenarios (Figures 3, 4).

All Ground-Nesting Bees in Field Crop System

About 70% of solitary bees in eastern Canada nest in the ground (Packer *et al*. 2007), many of which (including species in the genera *Agapostemon*, *Andrena*, *Anthophora*, *Colletes*, *Eucera*, *Halictus*, *Lasioglossum*, *Megachile* and *Melissodes*) are associated with agriculture (Pindar *et al.* 2017; USDA 2017). Because there is little information about exposure to soil for most ground-nesting bees, this study used exposure of the hoary squash bee to the soil matrix during nest construction as a surrogate for exposure in all ground-nesting bees as a first step. It is interesting to compare our estimates of soil exposure of 33.5g for a hoary squash bee female excavating a single nest (using nest architecture data from Mathewson 1968) with other ground-nesting bee species for which nest data exist. For example, total exposure to soil for *Andrena prunorum* females is estimated to be 30.23 g using nest dimensions described by Milczky (2008), and the amount of soil excavated by the female alkali bee (*Nomia melanderi*) when building nests is estimated to be 26.3 ± 5.7 g (Cane 2003). The difference between the low-end estimate of soil excavated by *N. melanderi* (20.6 g) and hoary squash bees (33.5 g) could represent as much as 38.5% of the latter species exposure, and highlights that there is potential for appreciable variability in exposure via soil across species. Using the amount of soil exposure for the hoary squash bee as a surrogate for all ground-nesting bee species may therefore have its limitations.

Ground-nesting bees vary greatly in size (Michener 2007), and many are much smaller than hoary squash bees or honey bees. These smaller bees may have lower exposure to neonicotinoids in soil because they construct narrower tunnels and nest cells to fit their smaller bodies (Michener 2007), therefore contact smaller soil volumes overall. This could be counteracted by interspecific differences in sensitivity to residues to which they are exposed based on body size and other factors (Devillers *et al*. 2003; Arena & Sgolastra 2014; Sgolastra *et al.* 2018). However, until more information emerges, using the hoary squash bee as a surrogate for all ground-nesting bees is the best model available to evaluate risk from exposure to neonicotinoid residues in agricultural soil.

Neonicotinoid residues detected in Ontario's agricultural soils reflect variation in usage for different crops. For *Cucurbita* crops, imidacloprid and clothianidin are the most commonly detected neonicotinoids with very little detection of thiamethoxam. For agricultural soils where field crops such as corn and soybeans are grown, residues of clothianidin and thiamethoxam are more commonly detected, with fewer imidacloprid residues. Clothianidin was found in 96.34% of agricultural soil samples taken from field cropping areas in the spring following the year of application, suggesting that exposure to clothianidin residues for bees nesting in agricultural soils is likely to be both ubiquitous and chronic. This is not surprising as clothianidin-treated seeds are commonly used in the production of field corn in Ontario with about 1.5 million acres planted with clothianidin-treated seed in the 2015-2016 season (MOECC 2017). The resulting EED for clothianidin in Ontario's agricultural soils in the spring, before a new cropping cycle, shows unacceptable likelihoods of exceedance of all the exposure endpoints for both the acute (Figure 5) and chronic (Figure 6) exposure scenarios for ground-nesting bees. For the acute scenario, the lowest exceedance (honey bee LC_{50} exposure endpoint) is 11.72%, more than twice the acceptable threshold level, and the exceedance for the solitary bee surrogate LC_{50} endpoint is extremely high (81.85 %: Figure 5). Exceedances for the chronic exposure scenario are greater than those for the acute scenario. As clothianidin-treated seeds are planted in a new cropping cycle, these exceedances can be expected to increase as neonicotinoids are released into the soil. Ground-nesting solitary bees from 13 genera have been collected in corn and soybean fields in Iowa (Wheelock & O'Neal 2016; Wheelock *et al*. 2016). Although this does not conclusively prove that these species were nesting within fields, the small foraging ranges of solitary bees (Gathmann & Tscharntke 2002) would suggest that many likely were. Different bees are active

at different times during the season (Packer *et al.* 2007; Richards *et al*. 2011). Those species active in the early spring may only be exposed to the minimum residue concentrations described here, but those that are active in the summer, or throughout the season, may be exposed to much higher neonicotinoid concentrations in soil.

Risk to ground-nesting bees from exposure to clothianidin residues in the field crop soil is high, and action should be taken to mitigate that risk to preserve the pollination services of these bees. When evaluating risk to ground-nesting bees from soil-applied neonicotinoids, it is important to differentiate between clothianidin residues which originate from direct applications of clothianidin and those that originate from the breakdown of thiamethoxam applications. As thiamethoxam is broken down into clothianidin relatively quickly in soil (Bonmatin *et al.* 2015), one mitigation strategy would be to reduce use of thiamethoxam-treated seed.

Risk to ground-nesting bees from acute exposure to thiamethoxam residues in field crop soil in Ontario is below the acceptable level of exceedance (i.e. 5%) for all exposure endpoints, except the solitary bee surrogate LC_{50} (25.56 %: Figure 5). However, for the chronic exposure scenario, risk to ground-nesting bees from thiamethoxam residues in field crop soil is high for all endpoints (Figure 6). Thiamethoxam is used as a seed treatment on both field corn and soybean crops in Ontario and was applied to 1.98 million acres in the 2015-2016 season (MOECC 2017). The apparently lower risk to ground-nesting bees associated with thiamethoxam may be the product of its shorter environmental half-life (Table 5) or, as stated earlier, its tendency to break down quickly into clothianidin in soil (Bonmatin *et al.* 2015).

Risk to ground-nesting bees from acute exposure to imidacloprid residues in field crop soil in Ontario is below the acceptable level of exceedance (i.e. 5%) for all exposure endpoints (Figure S1). For the chronic exposure scenario, exceedance is greater than 5% for only the solitary bee surrogate LC_{50} (9.24 %: Figure S2). The lower risk to ground-nesting bees associated with imidacloprid in soil may be because use of this insecticide as a seed treatment for these field crops is much lower (317,253 acres, 7% of total seed-treated field crop acreage). This differs substantially from the situation in *Cucurbita*-crops, which rely heavily on soil-applied imidacloprid and show greatest risk to hoary squash bees from imidacloprid residues. This indicates that one of the main concerns around neonicotinoid insecticide exposure for ground-nesting bees is their use in soil applications as either treated seed or in-furrow soil drenches. This

use has been partially mitigated in Ontario by increased regulation of the sale of neonicotinoid-treated corn and soybean seed (OMAFRA 2015) but has not been addressed for other crops.

Conclusions

Neonicotinoid residues in soil may pose a considerable risk to female hoary squash bees as they construct their nests in *Cucurbita*-crop growing systems. Furthermore, if squash bees are used as a surrogate for all ground-nesting species that are found in association with agriculture, then all these species should be considered at risk of harm from exposure to neonicotinoids in soils of neonicotinoid-treated field crops (e.g. corn and soy) in Ontario, based on pesticide residue levels detected in the MOECC data set. There are still areas of uncertainty, and further work is needed to determine the sensitivity of the hoary squash bee to neonicotinoids relative to the honey bee and to explicitly determine larval hoary squash bee exposure in soil. Advances in analytical techniques are also needed to allow for detection of lower residue concentrations in soil and to bring detection more in line with exposure endpoints for ground-nesting solitary bees. Recognition and mitigation of risks to ground-nesting bees from exposure to neonicotinoid residues in agricultural soil are needed to protect these important crop pollinators and inform pesticide use guidelines.

Acknowledgements

We would like to thank all 18 Ontario farmers who allowed us access to their land and crops, Beatrice Chan and Katie Fisher for their assistance with field sampling, Linda Lissemore for advice on residue analyses, Elaine Roddy for providing input into production practices and pesticide use patterns on farms, providing farm contacts, and sampling on all the farms in southwestern Ontario, and Jim Chaput for technical advice on pesticide registration and use in *Cucurbita* crops. This work was supported by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) grant UofG2015-2466 (awarded to N.E.R and D.S.W.C.), the Ontario Ministry of Environment and Climate Change (MOECC) Best in Science grant BIS201617-06 (awarded to N.E.R.), Natural Sciences and Engineering Research Council (NSERC) Discovery grants 2015-06783, 2018- 04641 (awarded to N.E.R. and R.S.P. respectively), the Fresh Vegetable Growers of Ontario (FVGO: awarded to N.E.R and D.S.W.C.), and the Food from Thought: Agricultural Systems for a Healthy Planet Initiative, by the Canada First Research Excellent Fund (grant 000054). D.S.W.C. was supported by the George and Lois Whetham

Scholarship in Food Systems, an Ontario Graduate Fellowship, the Keith and June Laver Scholarship in Horticulture, the Fred W. Presant Scholarship, and a Latournelle Travel Scholarship. N.E.R. is supported as the Rebanks Family Chair in Pollinator Conservation by The W. Garfield Weston Foundation.

Author Contributions

D.S.W.C., R.S.P. and N.E.R. conceived and designed the project. D.S.W.C. carried out the experimental work and collated MOECC datasets. D.S.W.C., R.S.P. and J.L.R-G. carried out the probabilistic risk assessments and statistical analyses. All authors contributed to writing the paper.

References

Alkassab AT, Kirchner WH (2017) Sublethal exposure to neonicotinoids and related side effects on insect pollinators: honeybees, bumblebees, and solitary bees. Journal of Plant Diseases and Protection 124:1–30. doi:10.1007/s41348-016-0041-0

Arena M, Sgolastra F (2014) Meta-analysis comparing the sensitivity of bees to pesticides. Ecotoxicology 23:324–334. doi:10.1007/s10646-014-1190-1

Artz DR, Nault BA (2011) Performance of *Apis mellifera*, *Bombus impatiens*, and *Peponapis pruinosa* (Hymenoptera: Apidae) as pollinators of pumpkin. Journal of Economic Entomology 104:1153–1161. doi:10.1603/EC10431

Atkins ELD, Kellum D (1986) Comparative morphogenic and toxicity studies on the effect of pesticides on honeybee brood. Journal of Apicultural Research 25:242–255. doi:10.1080/00218839.1986.11100725

Beekman M, Ratnieks FLW (2000) Long-range foraging by the honey-bee, *Apis mellifera* L. Functional Ecology 14:490-496.

Bonmatin JM, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke C, *et al*. (2015) Environmental fate and exposure: neonicotinoids and fipronil. Environmental Science and Pollution Research 22: 35. doi:10.1007/s11356-014-3332-7

Boyle NK, Pitts-Singer TL, Abbott J, Alix A, Cox-Foster DL, Hinarejos S *et al*. (2018) Workshop on pesticide exposure assessment paradigm for non-*Apis* bees: foundation and summaries. Environmental Entomology: doi:10.1093/ee/nvy103

Calderone NW (2012) Insect pollinated crops, insect pollinators and US agriculture: trend analysis of aggregate data for the period 1992–2009. PLoS ONE 7:e37235. doi:10.1371/journal.pone.0037235

Cane JH (1991) Soils of ground-nesting bees (Hymenoptera: Apoidea): texture, moisture, cell depth and climate. Journal of the Kansas Entomological Society 64:406-413.

Cane JH (2003) Annual displacement of soil in nest tumuli of alkali bees (*Nomia melanderi*) (Hymenoptera: Apiformes: Halictidae) across an agricultural landscape. Journal of the Kansas Entomological Society 76:172-176.

Cane JH (2016) Adult pollen diet essential for egg maturation by a solitary *Osmia* bee. Journal of Insect Physiology 95:105-109. doi:10.1016/j.jinsphys.2016.09.011

Casida JE, Durkin KA (2013) Neuroactive insecticides: targets, selectivity, resistance, and secondary effects. Annual Review of Entomology 58:99–117. doi:10.1146/annurev-ento-120811-153645

Cordova D, Benner EA, Sacher MD, Rauh JJ, Sopa JS, Lahm GP, *et al*. (2006) Anthranilic diamides: a new cass of insecticides with a novel mode of action, ryanodine receptor activation. Pesticide Biochemistry and Physiology 84:196–214. doi:10.1016/j.pestbp.2005.07.005

Decourtye A, Devillers J (2012) Ecotoxicity of neonicotinoid insecticides to bees. In: Insect Nicotinic Acetylcholine Receptors. Thany SE (ed.). Landes Bioscience / Springer Science & Business Media, LLC dual imprint/ Springer series: Advances in Experimental Medicine and Biology 683:96-106.

Delignette-Muller ML, Pouillot R, Denis J-B, Dutang C (2010) Fitdistrplus: help to fit of a parametric distribution to non-censored or censored data. R package version 0.1-3, https://CRAN.R-project.org/package=fitdistrplus

de Lima e Silva C, Brennan N, Brouwer JM, Commandeur D, Verweij RA, van Gestel CAM (2017) Comparative toxicity of imidacloprid and thiacloprid to different species of soil invertebrates. Ecotoxicology 2:555-564. doi:10.1007/s10646-017-1790-7

Devillers J, Decourtye A, Budzinski H, Pham-Delègue MH, Cluzeau S, Maurin G (2003) Comparative toxicity and hazards of pesticides to *Apis* and non-*Apis* bees. A chemometrical study. SAR and QSAR in Environmental Research 14:389-403. doi:10.1080/10629360310001623980

Dilling C, Lambdin P, Grant J, Rhea R (2009) Community response of insects associated with eastern hemlock to imidacloprid and horticultural oil treatments. Environmental Entomology 38:53–66. doi:10.1603/022.038.0108

Dinter A, Brugger KE, Frost N-M, Woodward MD (2009) Chlorantraniliprole (Rynaxypyr): a novel DuPont insecticide with low toxicity and low risk for honey bees (*Apis mellifera*) and bumble bees (*Bombus terrestris*) providing excellent tools for uses in integrated pest management. Julius-Kühn-Archives 423:84-96.

Dively GP, Kamel A (2012) Insecticide residues in pollen and nectar of a cucurbit crop and their potential exposure to pollinators. Journal of Agriculture and Food Chemistry 60: 4449-56. doi:10.1021/jf205393x.

EFSA Panel on Plant Protection Products and their Residues (2012) Scientific opinion on the science behind the development of a risk assessment of plant protection products on bees (*Apis mellifera*, *Bombus* spp. and solitary bees). EFSA Journal 10:2668.

EFSA (2018) Conclusion on the peer review of the pesticide risk assessment for bees for the active substance imidacloprid considering the uses as seed treatments and granules. EFSA Journal 16:5178. doi:10.2903/j.efsa.2018.5178

European Commission. EU pesticides database. Accessed April 24, 2018 from http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/.

Fungicide Resistance Action Committee (2018) FRAC Code List ©*2018: Fungicides sorted by mode of action (including FRAC Code numbering). Accessed April 5, 2018 from http://www.frac.info/docs/default-source/publications/frac-code-list/frac_code_list_2018-final.pdf?sfvrsn=6144b9a_2.

Gathmann A, Tscharntke T (2002) Foraging ranges of solitary bees. Journal of Animal Ecology 71:757-764. doi:10.1046/j.1365-2656.2002.00641.x

Girolami V, Marzaro M, Vivan L, Mazzon L, Giorio C, Marton D, *et al*. (2013) Aerial powdering of bees inside mobile cages and the extent of neonicotinoid cloud surrounding corn drillers. Journal of Applied Entomology 137:35–44. doi:10.1111/j.1439-0418.2012.01718.x

Godfray HCJ, Blacquière T, Field LM, Hails RS, Petrokofsky G, Potts SG, *et al*. (2014) A restatement of the natural science evidence base concerning neonicotinoid insecticides and insect pollinators. Proceedings of the Royal Society B-Biological Sciences 281:20140558. doi:10.1098/rspb.2014.0558

Godfray HCJ, Blacquière T, Field LM, Hails RS, Potts SG, Raine NE, *et al*. (2015) A restatement of recent advances in the natural science evidence base concerning neonicotinoid insecticides and insect pollinators.. Proceedings of the Royal Society B-Biological Sciences 282: 20151821. doi:10.1098/rspb.2015.1821

Goulson D (2013) An overview of the environmental risks posed by neonicotinoid insecticides. *Journal of Applied* Ecology 50: 977-987. doi:10.1111/1365-2664.12111

Goulson D, Lye GC, Darvill B (2008) Decline and conservation of bumble bees. Annual Review of Entomology 53:191–208. doi:10.1146/annurev.ento.53.103106.093454

Gupta S, Gajbhiye V, Gupta R (2008) Soil dissipation and leaching behavior of a neonicotinoid insecticide thiamethoxam. Bulletin of Environmental Contamination and Toxicology 80:431-437. doi:10.1007/s00128-008-9420-y

Helsel DR (2012) Statistics for censored environmental data using minitab® and R, 2nd ed. John Wiley & Sons, Inc. Hoboken, New Jersey, pp. 343.

Hilton MJ, Jarvis TD, Ricketts DC (2016) The degradation rate of thiamethoxam in European field studies. Pesticide Management Science 72:388–397. doi:10.1002/ps.4024

Hurd PD Jr, Linsley EG, Michelbacher AE (1974) Ecology of the squash and gourd bee, *Peponapis pruinosa*, on cultivated cucurbits in California (Hymenoptera: Apoidea). Smithsonian Contributions to Zoology 168. Smithsonian Institution Press, Washington, D.C.

Ishaque M, Jung MR, Tuerk H, Schroeder-Grimonpont T, Reinhard K, Schnabel G, *et al*. (2012) Polymers for increasing the soil mobility of low-solubility insecticides. http://www.google.com/patents/US20120053221.

Iwasa T, Motoyama N, Ambrose JT, Roe RM (2004) Mechanism for the differential toxicity of neonicotinoid insecticides in the honey bee, *Apis mellifera*. Crop Protection 23:371–378. doi:10.1016/j.cropro.2003.08.018

Jeschke P, Nauen R, Schindler M, Elbert A (2011) Overview of the status and global strategy for neonicotinoids. Journal of Agricultural and Food Chemistry 59:2897–2908. doi:10.1021/jf101303g

Jones A, Harrington P, Turnbull G (2014). Neonicotinoid concentrations in arable soils after seed treatment applications in preceding years. Pest Management Science 70:1780-1784. doi:10.1002/ps.3836

Krupke CH, Hunt GJ, Eitzer BD, Andino G, Given K (2012) Multiple routes of pesticide exposure for honey bees living near agricultural fields. PLoS One 7:e29268. doi:10.1371/journal.pone.0029268

Kunkel BA, Held DW, Potter DA (2001) Lethal and sub-lethal effects of bendiocarb, halofenozide, and imidacloprid on *Harpalus pennysylvanicus* (Coleoptera: Carabidae) following different modes of exposure in turfgrass. Journal Economic Entomology 94:60–67. doi:10.1603/0022-0493-94.1.60

Lambin M, Armengaud C, Raymond S, Gauthier M (2001) Imidacloprid-induced facilitation of the proboscis extension reflex habituation in the honeybee. Archives of Insect Biochemistry and Physiology 48:129–134.

Lopez-Uribe MM, Cane JH, Minckley RL, Danforth BN (2016) Crop domestication facilitated rapid geographical expansion of a specialist pollinator, the squash bee *Peponapis pruinosa*. Proceedings of the Royal Society B 283:20160443. doi:10.1098/rspb.2016.0443

Mathewson JA (1968) Nest construction and life history of the eastern cucurbit bee, *Peponapis pruinosa* (Hymenoptera: Apoidea). Jounal of the Kansas Entomological Society 41:255-261.

Michener C (2007). The Bees of the World, 2nd ed. The John Hopkins University Press, Baltimore, MD. Pp. 733.

Miliczky E (2008) Observations on the nesting biology of *Andrena* (*Plastandrena*) *prunorum* Cockerell in Washington State (Hymenoptera: Andrenidae). Journal of the Kansas Entomological Society 81:110-121

MOECC (2016) Soil neonicotinoid monitoring study. Accessed Feb 3, 2018 from https://www.ontario.ca/data/soil-neonicotinoid-monitoring-study

MOECC (2017) Corn and soybean neonicotinoid-treated seed data. Accessed June 13, 2018 from https://www.ontario.ca/data/corn-and-soybean-neonicotinoid-treated-seed-data

OMAFRA (2009) Ontario Crop IPM: Cucumber Beetles. Accessed March 20, 2018 from www.omafra.gov.on.ca/IPM/english/cucurbits/insects/cucumber-beetles.html

OMAFRA (2014) Vegetable Crop Protection Guide 2014-2015. Publication 838 Ontario Ministry of Agriculture, Food and Rural Affairs. pp. 82-83.

OMAFRA (2015) Neonicotinoid regulations. Accessed June 13, 2018 from https://www.ontario.ca/page/neonicotinoid-regulations

Packer L, Genaro JA, Sheffield CS (2007) The Bee Genera of Eastern Canada. Canadian Journal of Arthropod Identification No. 3, 25 September 2007, available online at doi:10.3752/cjai.2007.03.

Peck DC, Olmstead D (2010) Neonicotinoid insecticides disrupt predation on the eggs of turf-infesting scarab beetles. Bulletin Entomological Research 100:689–700. doi:10.1017/S0007485310000040

Pilling ED, Jepson PC (1993) Synergism between EBI fungicides and a pyrethroid insecticide in the honeybee (*Apis mellifera*). Pesticide Science 39:293–297. doi:10.1002/ps.2780390407

Pindar A, Mullen EK, Tonge MB, Guzman-Novoa E, Raine NE (2017) Status and Trends of Pollinator Health in Ontario. University of Guelph report prepared for Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA). 238 pages. Accessed August 16, 2018 from https://rainelab.files.wordpress.com/2015/12/status-and-trends-of-pollinator-health-in-ontario-march-8-2017-tagged.pdf

Pisanty G, Mandelik Y (2015) Profiling crop pollinators: life history traits predict habitat use and crop visitation by Mediterranean wild bees. Ecological Applications 25:742-52. doi:10.1890/14-0910.1

PMRA (2014) Re-evaluation Note REV2014-06, Special Reviews: potential environmental risk related to *Peponapis pruinosa* exposure to Clothianidin, Imidacloprid and Thiamethoxam used on cucurbits. Available from: https://www.canada.ca/en/health-canada/services/consumer-product-safety/reports-publications/pesticides-pest-management/decisions-updates/reevaluation-note/2014/peponapis-pruinosa-exposure-clothianidin-imidacloprid-thiamethoxam-rev2014-06.html.

R Development Core Team. (2008). R: A Language and Environment for Statistical Computing. Vienna, Austria: R Foundation for Statistical Computing, http://www.r-project.org/.

Richards MH, Rutgers-Kelly A, Gibbs J, Vickruck JL (2011) Bee diversity in naturalizing patches of Carolinian grasslands in southern Ontario, Canada. Canadian Entomologist 143:279-299. doi:10.4039/n11-010

Rortais A, Arnold G, Halm MP, Touffet-Briens F (2005) Modes of honeybee's exposure to systemic insecticides: estimated amounts of contaminated pollen and nectar consumed by different categories of bees. Apidologie 36:71-83. doi:10.1051/apido:2004071

Rundlöf M, Andersson GKS, Bommarco R, Fries I, Hederström V, Herbertsson L, *et al.* (2015) Seed coating with a neonicotinoid insecticide negatively affects wild bees. Nature 521:77–80. doi:10.1038/nature14420

Ruzhong G, Rui C, Liangyan C (1999) Evaluation on toxicity and safety of imidacloprid to environmental organisms. Pesticide Science and Administration 20(3).

Sanchez-Bayo F, Goka K (2014) Pesticide residues and bees – a risk assessment. PLoS One 9:e94482 doi:10.1371/journal.pone.0094482

Schenck FJ, Hobbs JE (2004) Evaluation of the quick, easy, cheap, effective, rugged, and safe (QuEChERS) approach to pesticide residue analysis. Bulletin of Environmental Contamination and Toxicology 73:24-30. doi:10.1007/s00128-004-0388-y

Shuler RE, Roulston TH, Farris GE (2005) Foraging behavior, pollinator effectiveness, and management potential of the new world squash bees *Peponapis pruinosa* and *Xenoglossa strentia* (Apidae: Eucerini). HortScience 42:459.

Sgolastra F, Hinarejos S, Pitts-Singer TL, Boyle NK, Joseph T, Lückmann J *et al*. (2018) Pesticide exposure assessment paradigm for solitary bees. Environmental Entomology: doi:10.1093/ee/nvy105

Stark JD, Jepson PC, Mayer DF (1995) Limitation to use of topical toxicity data for prediction of pesticide side effect in the field. Journal of Economic Entomology 88:1081-1088. doi:10.1093/jee/88.5.1081

Stoner KA, Eitzer BD (2012) Movement of soil-applied imidacloprid and thiamethoxam into nectar and pollen of squash (*Cucurbita pepo*). PLoS One 7: e39114. doi:10.1371/journal.pone.0039114

Stoner KA, Eitzer BD (2013) Using a hazard quotient to evaluate pesticide residues detected in pollen trapped from honey bees (*Apis mellifera*) in Connecticut. PLoS One 8:e77550. doi:10.1371/journal.pone.0077550

Suchail S, Guez, D, Belzunces LP (2001) Discrepancy between acute and chronic toxicity induced by imidacloprid and its metabolites in *Apis mellifera*. Environmental Toxicology and Chemistry 20:2482–2486. doi:10.1002/etc.5620201113

Tennekes HA, Sanchez-Bayo F (2011) Time-dependent toxicity of neonicotinoids and other toxicants: implications for a new approach to risk assessment. Journal of Environmental and Analytical Toxicology S4:1-8. doi:10.4172/2161-0525.S4-001

Tomlin CDS (2003) e-Pesticide Manual 2002-2003 (Twelfth edition) Version 2.2. British Crop Protection Council.

TOXNET. Hazardous Substances Data Bank (HSDB). US National Library of Medicine. Accessed June 12, 2018 from https://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm.

USDA Natural Resources Conservation Service (2008) Soil quality indicators. Accessed November 17, 2017 from https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_053256.pdf.

USDA (2017) Attractiveness of agricultural crops to pollinating bees for the collection of nectar and/or pollen. Accessed June 15, 2018 from https://www.ars.usda.gov/ARSUserFiles/OPMP/Attractiveness%20of%20Agriculture%20Crops%20to%20Pollinating%20Bees%20Report-FINAL_Web%20Version_Jan%203_2018.pdf.

US-EPA (2014) Guidance for assessing pesticide risks to bees. Office of Chemical Safety and Pollution Prevention Office of Pesticide Programs Environmental Fate and Effects Division, Environmental Protection Agency, Washington DC; Environmental Assessment Directorate, Pest Management Regulatory Agency, Health Canada, Ottawa, CN; California Department of Pesticide Regulation.

US-EPA Pesticide Ecotoxicity Database of the Office of Pesticide Programs, Ecological Fate and Effects Division. Accessed November 22, 2017 http://www.ipmcenters.org/Ecotox/.

Vanbergen AJ, *et al*. (2013) Threats to an ecosystem service: pressures on pollinators. Frontiers in Ecology and the Environment 11: 251-259. doi:10.1890/120126

Wheelock MJ (2014) Insect pollinators in corn and soybean agricultural fields. MSc. dissertation, Iowa State University. Accessed June 15, 2018 from https://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=5201&context=etd

Wheelock MJ, O'Neal ME (2016) Insect pollinators in Iowa cornfields: community identification and trapping method analysis. PLoS One 11:e0143479. doi:10.1371/journal.pone.0143479

Wheelock MJ, ReyKP, O'Neal ME (2016) Defining the insect pollinator community found in Iowa corn and soybean fields: implications for pollinator conservation. Environmental Entomology 4:1099-1106. doi:10.1093/ee/nvw1087

Whitaker TW, Davis GN (1962) Cucurbits: botany, cultivation and utilization. New York: Interscience, 250 pp.

Willis DS (1991). The pollination system of *Cucurbita pepo* and *Peponapis pruinosa* in southern Ontario. MSc. dissertation, University of Guelph, Ontario, Canada. 110 pp.

Willis DS, Kevan PG. (1995). Foraging dynamics of *Peponapis pruinosa* (Hymenoptera: Anthophoridae) on pumpkin (*Cucurbita pepo*) in southern Ontario. The Canadian Entomologist 27:167-175. doi:10.4039/Ent127167-2

Winfree R, Williams NM, Gaines H, Ascher JS, Kremen C (2008) Wild bee pollinators provide the majority of crop visitation across land-use gradients in New Jersey and Pennsylvania, USA. Journal of Applied Ecology 45:793–802. doi:10.1111/j.1365-2664.2007.01418.x

Woodcock BA, Bullock JM, Shore RF, Heard MS, Pereira MG, Redhead J, *et al.* (2017) Country-specific effects of neonicotinoid pesticides on honey bees and wild bees. Science 356:1393-1395. doi:10.1126/science.aaa1190

Figure 1. Nest of a hoary squash bee (*Peponapis pruinosa*) showing an adult female excavating a lateral tunnel and 4 immature stages (larvae) in sealed nest cells. Each nest cell is coated with a water-resistant lining. Soil from the main tunnel is moved to the soil surface and soil from lateral tunnels is backfilled into the vertical tunnel. The length of lateral tunnels varies. Graphic produced

by Ann Sanderson and reproduced with permission.

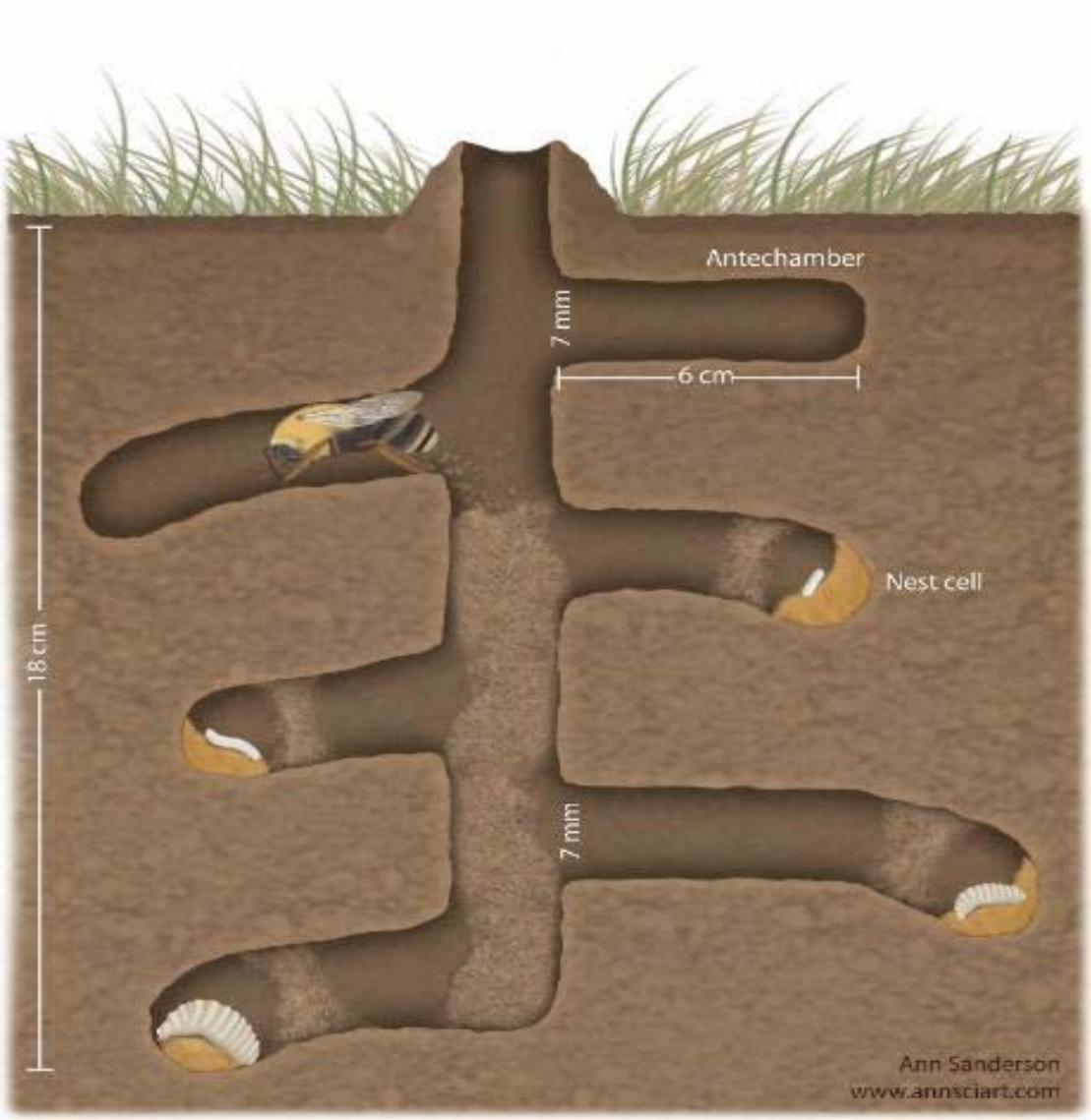


Figure 2. Percentage of samples with detectable insecticides and fungicides in three exposure matrices (pollen, nectar and soil) from 18 farms growing *Cucurbita* crops in Ontario, Canada in 2016 (n = 29 samples). Limits of detection and quantification (LOD/LOQ) for each compound are listed in Table 3.

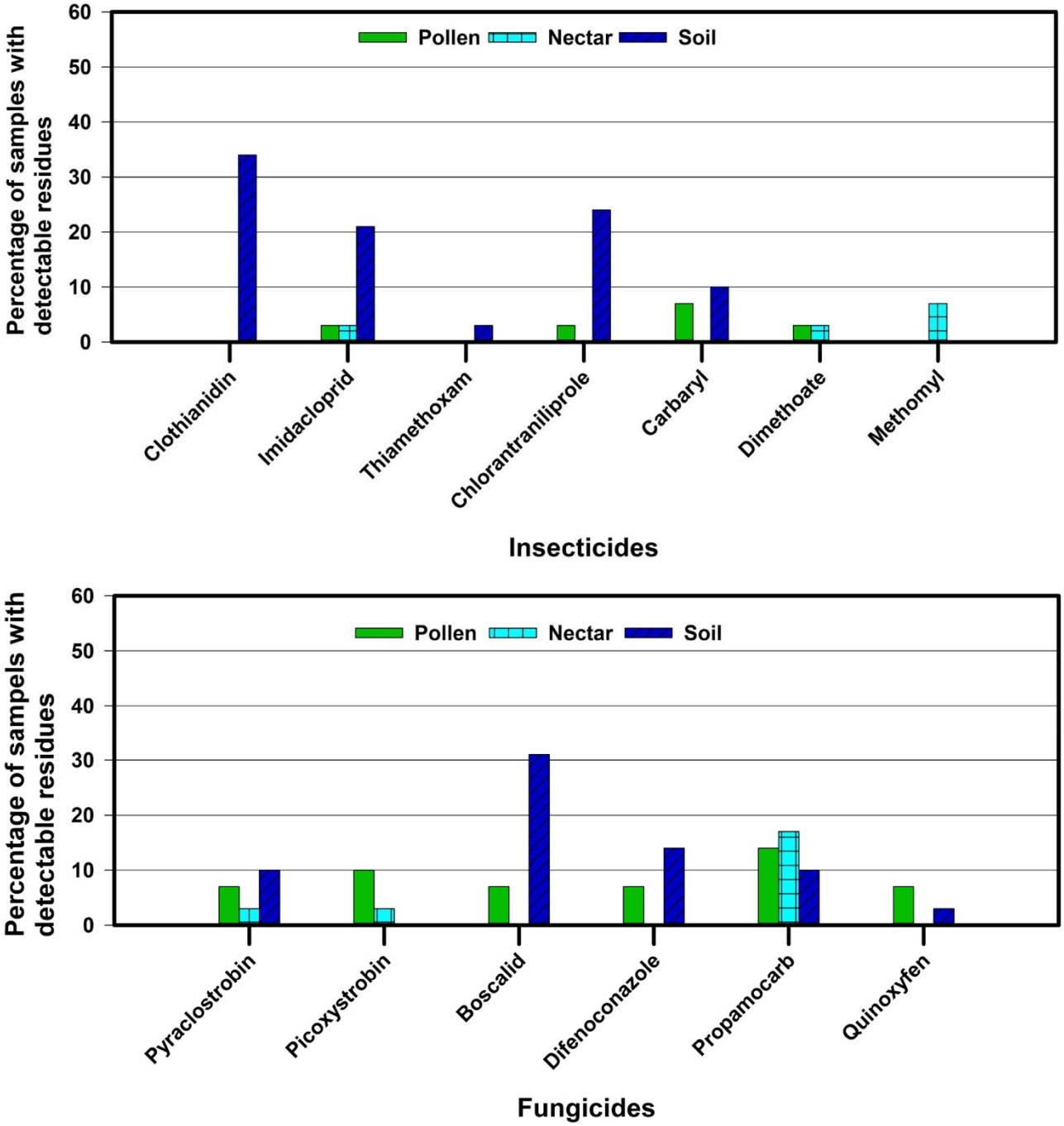


Figure 3. Environmental Exposure Distribution (EED) for (A) clothianidin and (B) imidacloprid concentrations measured in soil samples taken from 0-15 cm depth in *Cucurbita*-crop fields in Ontario, 2016. Effects benchmark concentrations for acute exposure (48 h, 2.23 g soil) for the hoary squash bee, *Peponapis pruinosa* (i.e. honey bee geometric mean LC_{50}, honey bee lowest LC_{50}, honey bee NOAEC, solitary bee surrogate LC_{50}), are represented by vertical lines on the EED. Exceedance of these endpoints is calculated by subtracting the cumulative probability from 1.0. Grey horizontal lines represent individual samples below the limit of detection.

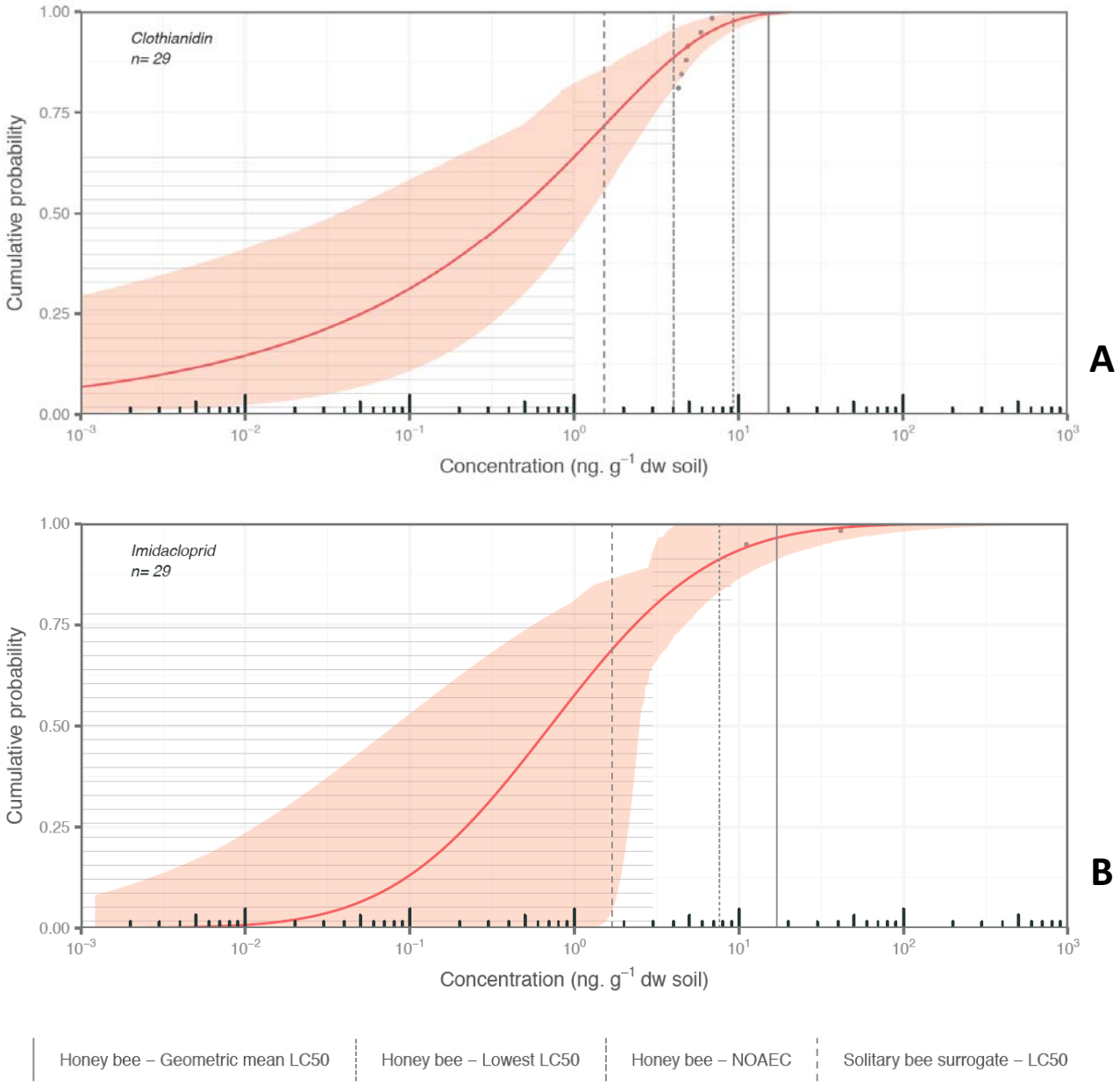


Figure 4. Environmental Exposure Distribution (EED) for (A) clothianidin, (B) imidacloprid, and (C) chlorantraniliprole concentrations in soil samples taken from 0-15 cm depth in *Cucurbita*-crop fields in Ontario, 2016. Effects benchmark concentrations for chronic exposure (30 days, 33.5 g soil) for the hoary squash bee, *Peponapis pruinosa* (i.e. honey bee geometric mean LC_{50}, honey bee NOAEC, solitary bee surrogate LC_{50}), are represented by vertical lines on the EED. Exceedance of these endpoints is calculated by subtracting the cumulative probability from 1.0. Grey horizontal lines represent individual samples below the limit of detection.

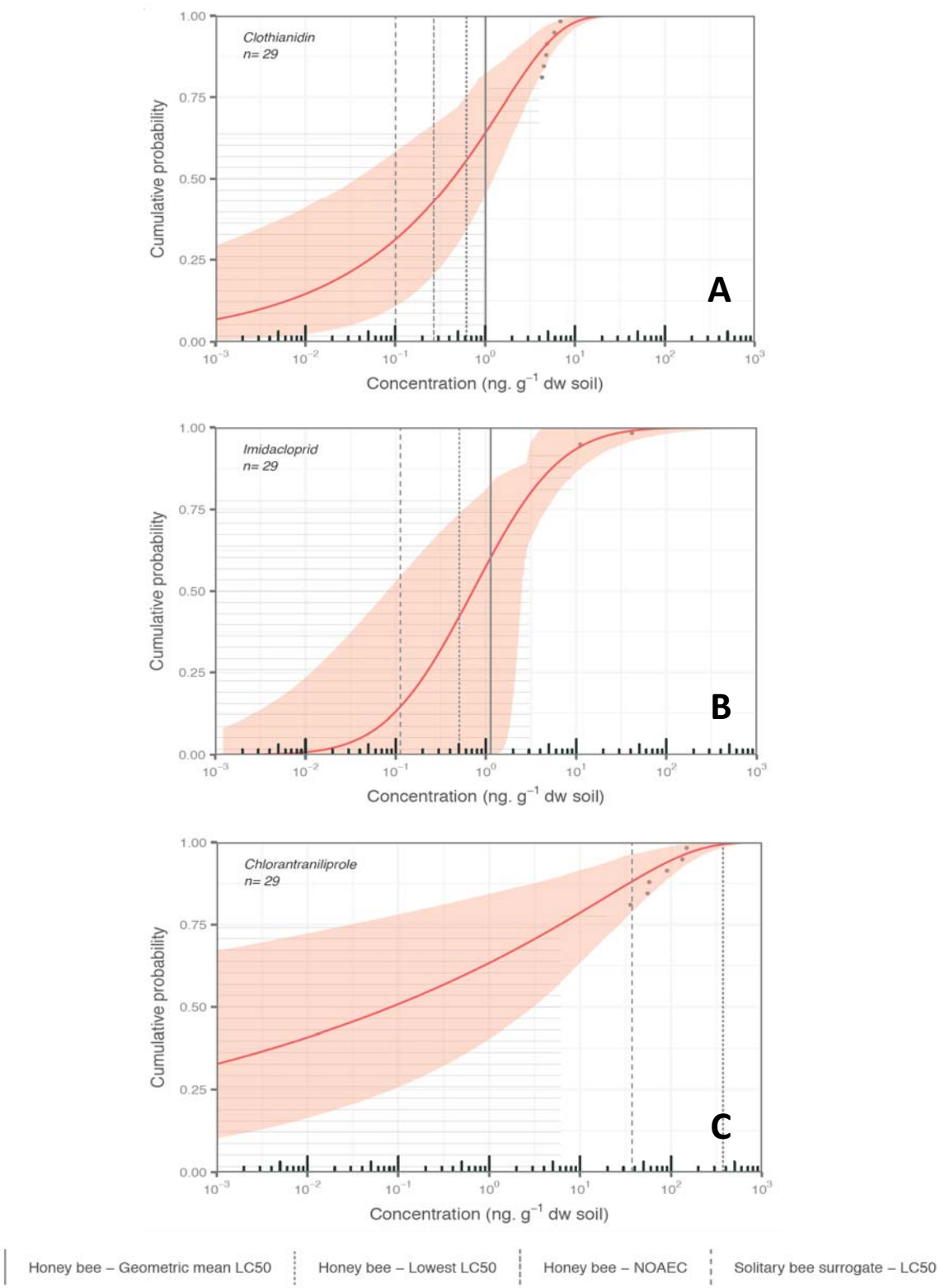
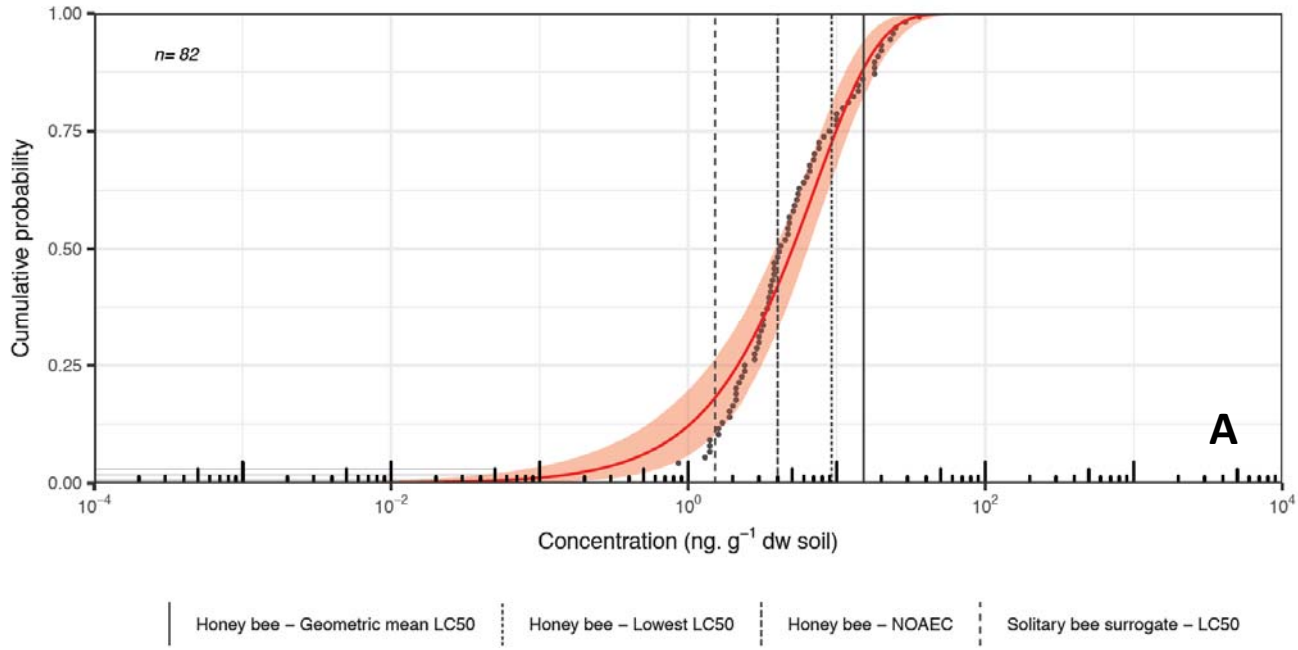


Figure 5. Environmental Exposure Distribution (EED) for (A) clothianidin and (B) thiamethoxam in soil from field crops (corn, soybeans, wheat) based on MOECC data. Soil samples taken from 0-15 cm depth from agricultural soil in southern Ontario, 2016. Effects benchmark concentrations for acute exposure (48 h, 2.23 g soil) for solitary ground-nesting bees are based on hoary squash bee surrogate exposure amounts. Effects measures (i.e. honey bee geometric mean LC_{50}, honey bee NOAEC, solitary bee surrogate LC_{50}) are represented by vertical lines on the EED. Exceedance of these endpoints is calculated by subtracting the cumulative probability from 1.0. Grey horizontal lines represent individual samples below the limit of detection.



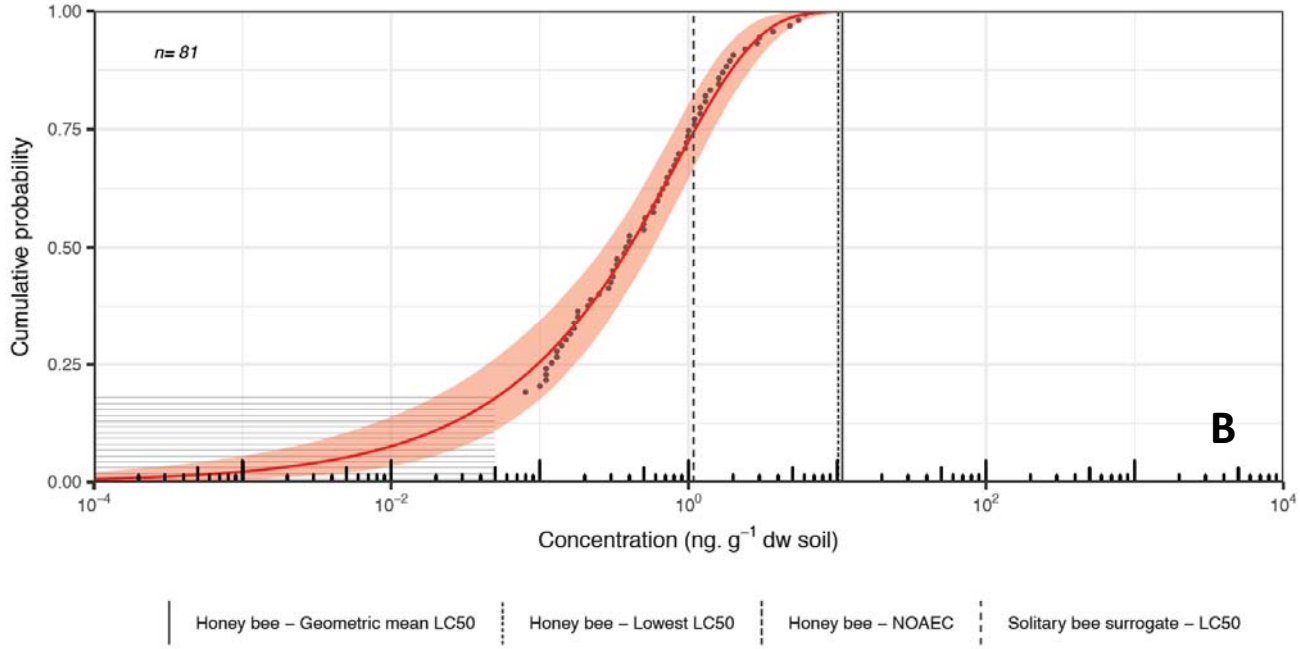


Figure 6. Environmental Exposure Distribution (EED) for (A) clothianidin and (B) thiamethoxam in soil from field crops (corn, soybeans, wheat) based on MOECC data. Soil samples taken from 0-15 cm depth from agricultural soil in southern Ontario, 2016. Effects benchmark concentrations for chronic exposure (30 days, 33.5 g soil) for solitary ground-nesting bees are based on hoary squash bee surrogate exposure amounts. Effects measures (i.e. honey bee geometric mean LC_{50}, honey bee NOAEC, solitary bee surrogate LC_{50}) are represented by vertical lines on the EED. Exceedance of these endpoints is calculated by subtracting the cumulative probability from 1.0. Grey horizontal lines represent individual samples below the limit of detection.

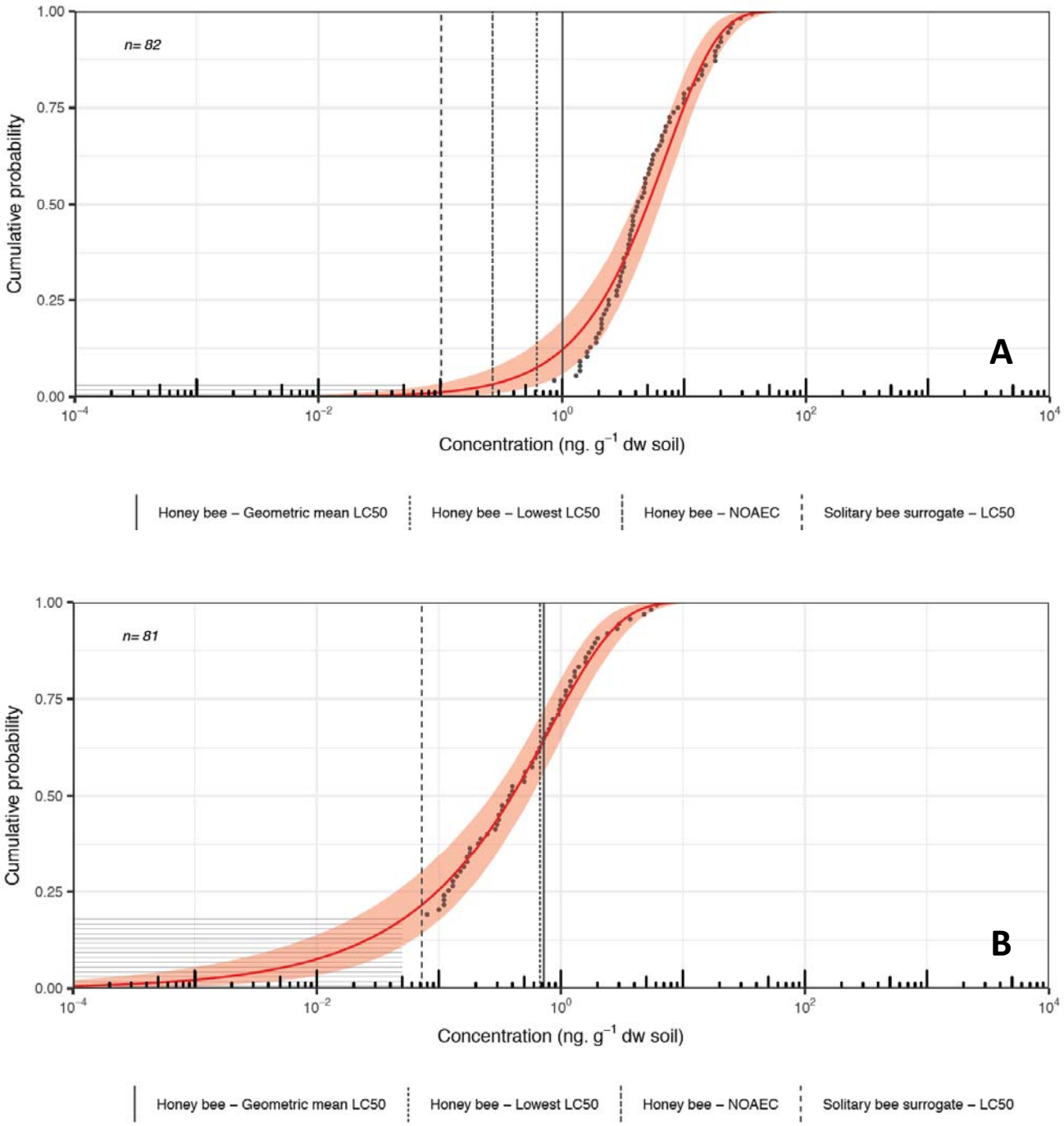


Figure S1. Environmental Exposure Distribution (EED) for acute exposure (48h, 2.23 g soil) to imidacloprid in soil for solitary ground-nesting bees. Based on MOECC data and hoary squash bee surrogate exposure amounts. Soil samples taken from 0-15 cm depth from agricultural soil in southern Ontario, 2016. Effects benchmark concentrations for acute exposure (48 h, 2.23 g soil) for the hoary squash bee, *Peponapis pruinosa* (i.e. honey bee geometric mean LC_{50}, honey bee NOAEC, solitary bee surrogate LC_{50}) are represented by vertical lines on the EED. Exceedance of these endpoints is calculated by subtracting the cumulative probability from 1.0. Grey horizontal lines represent individual samples below the limit of detection.

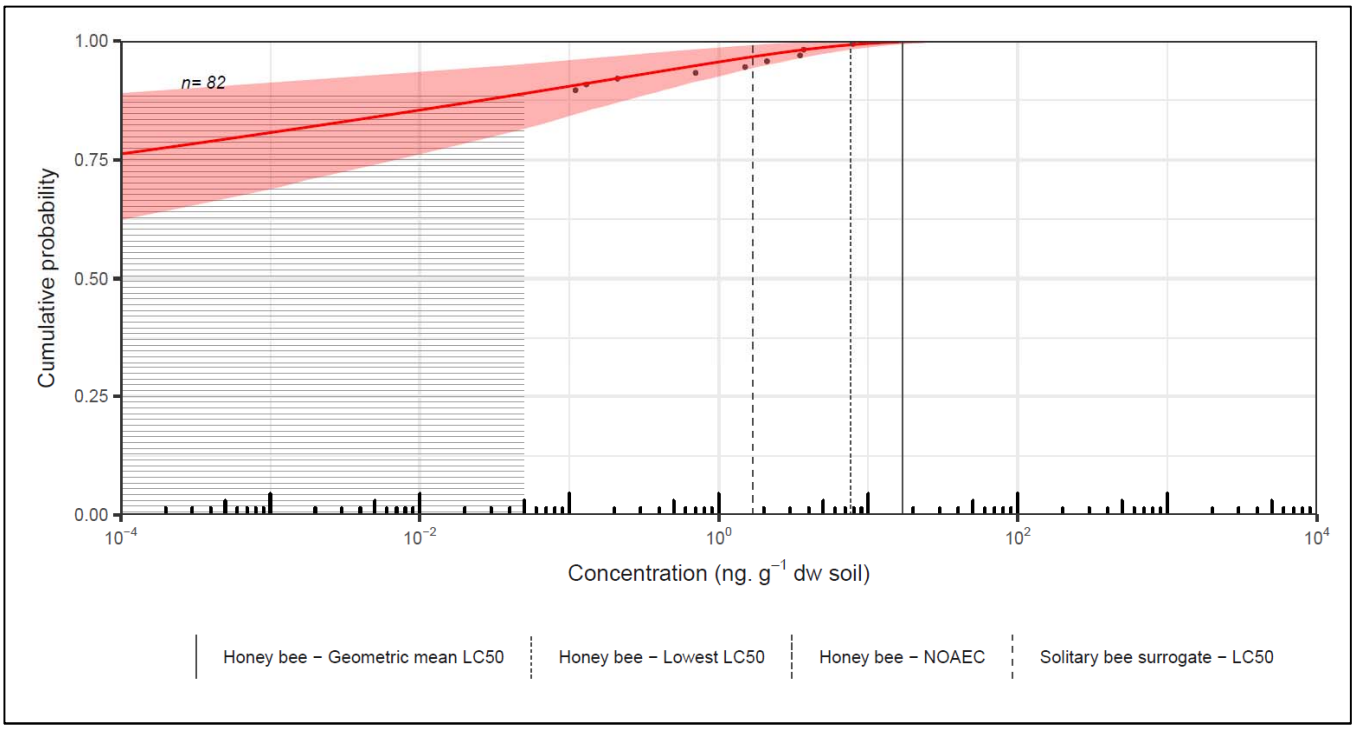


Figure S2. Environmental Exposure Distribution (EED) for chronic exposure (30 days, 33.5 g soil) to imidacloprid in soil for solitary ground-nesting bees. Based on MOECC data and hoary squash bee surrogate exposure amounts. Soil samples taken from 0-15 cm depth from agricultural soil in southern Ontario, 2016. Effects benchmark concentrations for chronic exposure (30 days, 33.5 g soil) for the hoary squash bee, *Peponapis pruinosa* (i.e. honey bee geometric mean LC_{50}, honey bee NOAEC, solitary bee surrogate LC_{50}) are represented by vertical lines on the EED. Exceedance of these endpoints is calculated by subtracting the cumulative probability from 1.0. Grey horizontal lines represent individual samples below the limit of detection.

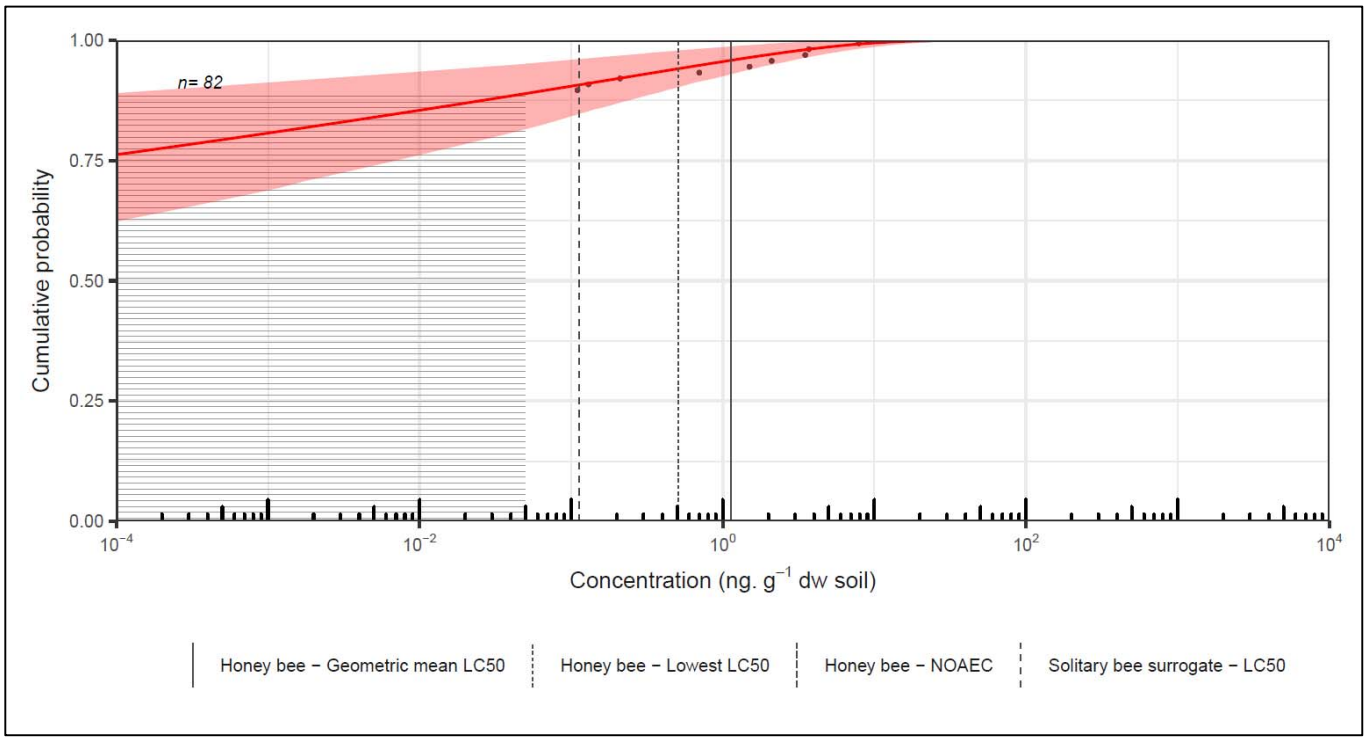


Table 1. Calculations of the volume, and therefore, mass of soil excavated by a female hoary squash bee (*Peponapis pruinosa*) to construct an underground nest, from which to determine potential insecticide exposure via soil. Nest dimensions follow data from Mathewson (1968).

Part of Nest	**Soil volume/ mass**
a. Main vertical shaft (7 mm diameter x 18 cm long)	6.92 cm^3
b. Antechamber (7 mm diameter x 6 cm long)	2.31 cm^3
c. 5 brood cells (7 mm diameter x 7.3 cm long = 2.81 cm^3 each)	14.04 cm^3
d. 5 brood caps (7 mm diameter x 1 cm thick = 0.3847 cm^3 each) Estimated from our own observations	1.92 cm^3
Total volume of soil excavated (a + b + c + d)	25.19 cm^3
Total mass of soil excavated (Total volume x Bulk density (BD) of loam; BD = 1.33 g/cm^3)	**33.51 g**

Table 2. Summary of pesticide exposure routes, exposure types, exposure amount, and exposure period for the hoary squash bee (*Peponapis pruinosa*).

Exposure Route	Developmental Stage	Exposure type	Exposure amount	Period of Exposure
Soil	Adult Female	Contact	33.51 g [a]	Construction of 1 nest ~30 days
Soil	Larva	Contact	Putatively not exposed [a]	10 months
Nectar	Adult Female	Oral	<<780 mg; based on pollen-foraging honey bee [b]	30+ days
Nectar	Adult Male	Oral	Unknown, <adult female	30+ days
Nectar	Larva	Oral	Unknown, < adult females	15 days
Pollen	Larva	Oral	49.2 mg [c]	15 days
Pollen	Larva	Contact	Unknown	15 days
Pollen	Adult Female	Contact	246 mg (5x larval exposure)	30 days
Pollen	Adult Female	Oral	Unknown	During oocyte maturation[d]

[a] Mathewson 1968
[b] Rortais *et al*. 2008
[c] Willis 1991 & present study
[d] Michener 2007

Table 3. All residues detected in soil, pollen, and nectar of *Cucurbita*-crop growing systems in Ontario, Canada, 2016, showing limits of detection and quantification (LOD/LOQ), maximum concentrations, geometric mean concentrations, and frequency of detection for each residue (n = 29 samples, nd = not detected). Frequency of detection is based on samples in which residues were detectable but not necessarily quantifiable (>LOD).

		Soil				**Pollen**				**Nectar**			
		LOD/ LOQ	**Max Conc.**	**Mean Conc.**	**Freq. Detection**	**LOD/ LOQ**	**Max Conc.**	**Mean Conc.**	**Freq. Detection**	**LOD/ LOQ**	**Max Conc.**	**Mean Conc.**	**Freq. Detection**
Type of pesticide	**Active ingredient**	ppb	ng a.i./g matrix	ng a.i./g matrix	%	ppb	ng a.i./g matrix	ng a.i./g matrix	%	ppb	ng a.i./g matrix	ng a.i./g matrix	%
Insecticide	Clothianidin	1/4	5.9	2.0	34	2/8	nd	nd	0	1/4	nd	nd	0
	Imidacloprid	3/9	41.6	3.0	21	2/8	4.3	4.3	3	1/4	1.1	0.9	3
	Thiamethoxam	5/20	6.8	6.8	3	2/8	nd	nd	0	0.6/2	nd	nd	0
	Chlorantraniliprole	6/20	148.5	36.8	24	3/10	68	68	3	2/6	nd	nd	0
	Carbaryl	1/4	352.8	14.2	10	2/7	31.1	16.5	7	0.6/2	nd	nd	0
	Methomyl	7/20	nd	nd	0	2/6	nd	nd	0	0.3/0.9	0.5	0.4	7
	Dimethoate	2/6	nd	nd	0	0.5/2	6.2	6.2	3	0.4/1	0.5	0.5	3
Fungicide	Pyraclostrobin	4/10	16.7	3.8	10	1/4	399.6	29.6	7	0.4/1	2	2	3
	Picoxystrobin	0.4/1	nd	nd	0	0.7/2	110.2	4.6	10	0.2/0.7	0.3	0.3	3
	Boscalid	3/9	374.9	46.2	31	2/6	25	17.8	7	2/8	nd	nd	0
	Propamocarb	20/50	64.4	23.0	10	0.9/3	402.6	222.1	14	0.2/0.5	74.5	11.2	17
	Quinoxyfen	5/10	14.7	7.9	3	3/8	94.9	79.1	7	1/3	nd	nd	0
	Difenoconazole	4/10	40.7	18.9	14	2/5	22.4	16.5	7	0.7/2	nd	nd	0
Herbicide	Napropamide	1/4	59.4	2.8	7	0.4/1	5.0	5.0	3	0.1/0.4	nd	nd	0
	Linuron	5/10	0.8	0.8	0	1/4	nd	nd	0	0.8/2	nd	nd	0

Table 4. Hazard quotients (HQ) for each active ingredient, and pesticide type (insecticide, fungicide) in three exposure matrices (soil, pollen, nectar) and both developmental stages (adult female or larvae) based on honey bee LD_{50} values (taken from US-EPA database, unless otherwise noted), and mean residue concentration in the exposure matrices for all pesticide residues found detected on 18 *Cucurbita*-crop farms in Ontario in 2016. Numbers shown in bold face are combined hazard quotients for a pesticide type, an exposure matrix, or a developmental stage. Where "nd" is indicated, residues were not detected in samples. a.i. = active ingredient.

	LC_{50} Endpoint (Honey bee)		**SOIL**		**POLLEN**		**NECTAR**			**COMBINED HAZARD QUOTIENT**		
	Contact	**Oral**	**Mean Conc. in Matrix**	**HQ Adult female**	**Mean Conc. in Matrix**	**HQ Larvae**	**HQ Adult Female**	**Mean Conc. in Matrix**	**HQ Adult Female**	**Across Exposure Matrix**	**Adult Female**	**Larvae**
	ng a.i./bee	ng a.i./bee	ng a.i./g	=33.5 g/bee *Matrix Conc. /LD_{50}	ng a.i./g	=0.0492 g/bee * Matrix Conc. /LD_{50}	=5*0.0492 g/bee* Matrix Conc. /LD_{50}	ng a.i./g	=0.78 g/bee* Matrix Conc. /LD_{50}	∑HQ	∑HQ	∑HQ
INSECTICIDE ∑HQ				**14.56**		**0.06**	**0.30**		**0.18**	**15.11**	**15.05**	**0.06**
Clothianidin (geomean) [1]	35.88	-	1.95	1.93	nd	0	0	nd	0	**1.93**		
Imidacloprid (geomean) [2]	40.03	3.90	2.99	2.65	4.3	0.05	0.27	0.88	0.18	**3.15**		
Thiamethoxam (geomean) [3]	25.64	-	6.8	9.41	nd	0	0	nd	0	**9.41**		
Chlorantraniliprole [4]	12500	-	36.82	0.10	68	2.68E-4	1.34E-3	nd	0	**0.11**		
Carbaryl [5]	1100	-	14.2	0.46	16.47	7.37E-4	3.68E-3	nd	0	**0.46**		
Dimethoate [5]	-	56.00	nd	0.00	6.20	5.45E-3	2.72E-2	0.50	0.01	**0.04**		
Methomyl [5]	-	290.00	nd	0.00	nd	0	0	0.39	1.04E-3	**0.00**		
FUNGICIDE ∑HQ				**0.03**		**1.24E-4**	**6.19E-4**		**9.19E-5**	**0.03**	**3.07E-2**	**1.24E-4**
Pyraclostrobin [5]	100000	-	3.8	0.00	29.65	1.46E-5	7.29E-5	2	1.56E-5	**0.00**		
Picoxystrobin [5]	200000	-	nd	0.00	4.55	1.12E-6	5.60E-6	0.3	1.17E-06	**0.00**		
Boscalid [5]	200000	166000	46.22	0.01	17.82	5.28E-6	2.64E-5	nd	0	**0.01**		
Propamocarb [5]	100000	116000	23.03	0.01	222.06	9.42E-5	4.71E-4	11.18	7.52E-05	**0.01**		
Quinoxyfen [5]	100000	1000000	7.86	0.00	79.14	3.89E-6	1.95E-5	nd	0	**0.00**		
Difenoconazole [5]	100000	177000	18.87	0.01	16.46	4.58E-6	2.29E-5	nd	0	**0.01**		
Napropamide [6]	-	113500	3.6	0.00	0.3	1.30E-7	6.30E-7	nd	0	**0.00**		

[1]US-EPA database; Iwasa *et al.* 2004; EC database; Sanchez-Bayo & Goka 2014
[2]US-EPA database; Iwasa *et al.* 2004; Sanchez-Bayo & Goka 2014; Rhuzhong *et al.* 1991; Stark *et al.* 1995
[3]US-EPA database; EC database; Sanchez-Bayo & Goka 2014; Goulson *et al.* 2008
[4]Dinter *et al.* 2009
[5]US-EPA database
[6]Stoner & Eitzer 2013

Table 5. Physical, chemical, and environmental fate properties of imidacloprid, clothianidin, thiamethoxam and chlorantraniliprole

Active Ingredient	Imidacloprid	Clothianidin	Thiamethoxam	Chlorantraniliprole
Chemical Name[a]	1-[(6-Chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine	(E)-1-(2-chloro-1, 3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine	3-[(2-chloro-5-thiazolyl) methyl]tetrahydro-5-methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine	3-bromo-N-(4-chloro-2-methyl-6-((methylamino) carbonyl)phenyl)-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxamide
Insecticide class	Neonicotinoid	Neonicotinoid	Neonicotinoid	Anthranilic diamide
Formula[a]	$C_9H_{10}ClN_5O_2$	$C_6N_5H_8SO_2Cl$	$C_8H_{10}ClN_5O_3S$	C18-H14-Br-Cl2-N5-O2
CAS No.[a]	138261-41-3	210880-92-5	153719-23-4	500008-45-7
Molecular Weight[1] (g/mol) [a]	255.69	327	297.1	483.2
Solubility in water at 20° C, pH 7 (mg/L) [a]	610 [a]	327[b]	4100 [a]	0.9-1.0 [a]
Adsorption to Particles (soil) Koc at pH 7 [a]	156-800	60	68.4	244-468
Volatility (air) Vapour pressure [a] (mm Hg at 25°C)	$7.0x10^{-12}$	$9.8x10^{-10}$	$4.95x10^{-11}$	$1.2x10^{-14}$
Log Kow [a]	0.57	0.7	-0.13	2.76
Bio-degradation DT50 (days)	48-190 [a]	148-1155 [a]	46.3-301[c]	60-365

[a] TOXNET Toxicology Data Network. https://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm. Accessed June 12, 2018.
[b] USEPA/Office of Pesticide Programs; New Pesticide Fact Sheet-Clothianidin (May 2003). http://www.epa.gov/opprd001/factsheets/ Accessed July 24, 2018
[c] Gupta et al., 2008

Table S1. Exposure endpoints for amounts of soil handled by the hoary squash bee in acute (48h, 2.23 g soil) and chronic (30 days, 33.5 g soil) exposure scenarios based on various effect endpoints in the scientific literature (a. US-EPA database; b. Iwasa *et al*. 2004; c. EC database; d. Sanchez-Bayo & Goka 2014; e. Arena & Sgolastra 2014; f. Rhuzhong *et al.* 1991; g. Stark *et al*. 1995; h. Goulson *et al*. 2008; i. Dinter *et al*. 2009). HB = honey bee, SB = solitary bee.

Insecticide	Exposure type	Effect endpoint	Effect endpoint concentration (ng a.i./bee) A	Exposure amount (g soil/bee) B	Exposure endpoint (A/B) (ng a.i./g soil)	Source for effect endpoint
Clothianidin	Acute	Geomean HB LD_{50}	35.88	2.23	15.16	a-d
		Lowest HB LD_{50}	22	2.23	9.29	b
		SB Surrogate LD_{50}	3.588	2.23	1.52	e
		NOAEC	9.5	2.23	4.01	
	Chronic	Geomean HB LD_{50}	35.88	33.5	1.01	a-d
		Lowest HB LD_{50}	22	33.5	0.62	b
		SB Surrogate LD_{50}	3.588	33.5	0.10	e
		NOAEC	9.5	33.5	0.27	a
Imidacloprid	Acute	Geomean HB LD_{50}	40.03	2.23	16.91	a,b,d,f,g
		Lowest HB LD_{50}	18	2.23	7.61	b
		SB Surrogate LD_{50}	4.003	2.23	1.69	e
	Chronic	Geomean HB LD_{50}	40.03	33.5	1.13	a,b,d,f,g
		Lowest HB LD_{50}	18	33.5	0.51	b
		SB Surrogate LD_{50}	4.003	33.5	0.113	e
Thiamethoxam	Acute	Geomean HB LD_{50}	25.64	2.23	10.83	a,c,d,h
		Lowest HB LD_{50}	24	2.23	10.14	a
		SB Surrogate LD_{50}	2.564	2.23	1.08	e
	Chronic	Geomean HB LD_{50}	25.64	33.5	0.722	a,c,d,h
		Lowest HB LD_{50}	24	33.5	0.676	a
		SB Surrogate LD_{50}	2.564	33.5	0.072	e
Chlorantraniliprole	Acute	Lowest HB LD_{50}	12,500	2.23	5595.35	i
		SB Surrogate LD_{50}	1250	2.23	559.5	e
	Chronic	Lowest HB LD_{50}	12,500	33.5	373.02	i
		SB Surrogate LD_{50}	1250	33.5	37.3	e

Table S2. Exceedance probabilities (i.e. the frequency that effect endpoints were exceeded), with upper and lower limits of the 95% confidence interval and the exposure concentrations associated with each effect endpoint, for all neonicotinoids detected in soil of *Cucurbita* and other agricultural field crops in Ontario for both chronic (30 days, 33.5 g soil) and acute (48h, 2.23 g soil) exposure scenarios. HB = honey bee, SB = solitary bee. Data from field crop soils taken from MOECC (2016).

Insecticide	Exposure type	Crop system	Effect endpoint	% Exceedance	Lower limit of 95% CI	Upper limit of 95% CI	Effect concentration ng ai/g soil
Clothianidin	Chronic	Cucurbita	Lowest HB LC_{50}	44.3	65.9	24.5	0.6
Clothianidin	Chronic	Cucurbita	Geomean LC_{50}	35.8	54.9	17.7	1.0
Clothianidin	Chronic	Cucurbita	SB Surrogate LD_{50}	68.7	89.1	41.5	0.1
Clothianidin	Chronic	Cucurbita	HB NOAEC	57.1	79.5	33.2	0.3
Clothianidin	Acute	Cucurbita	Lowest HB LC_{50}	2.4	4.6	0.4	9.3
Clothianidin	Acute	Cucurbita	Geomean LC_{50}	0.5	1.4	0.04	15.2
Clothianidin	Acute	Cucurbita	SB Surrogate LD_{50}	28.3	44.5	14.2	1.5
Clothianidin	Acute	Cucurbita	HB NOAEC	11.4	19.0	4.5	4.0
Imidacloprid	Chronic	Cucurbita	Lowest HB LC_{50}	57.8	100	26.2	0.5
Imidacloprid	Chronic	Cucurbita	Geomean LC_{50}	39.8	99.9	17.2	1.1
Imidacloprid	Chronic	Cucurbita	SB Surrogate LD_{50}	85.4	100	45.4	0.1
Imidacloprid	Acute	Cucurbita	Lowest HB LC_{50}	8.9	17.0	0.0	7.6
Imidacloprid	Acute	Cucurbita	Geomean LC_{50}	3.5	9.0	0.0	16.9
Imidacloprid	Acute	Cucurbita	SB Surrogate LD_{50}	31.2	95.6	13.7	1.7
Thiamethoxam	Chronic	Cucurbita	Lowest HB LC_{50}	0.6	1.6	0.0	373.0
Thiamethoxam	Chronic	Cucurbita	Geomean LC_{50}	0.0	0.0	0.0	NA
Thiamethoxam	Chronic	Cucurbita	SB Surrogate LD_{50}	11.9	21.1	3.69	37.3
Thiamethoxam	Acute	Cucurbita	Lowest HB LC_{50}	0.0	0.0	0.0	5595.3
Thiamethoxam	Acute	Cucurbita	Geomean LC_{50}	0.0	0.0	0.0	NA
Thiamethoxam	Acute	Cucurbita	SB Surrogate LD_{50}	0.2	0.7	0.0	559.5

Table S2 continued.

Insecticide	Exposure type	Crop system	Effect endpoint	% Exceedance	Lower limit of 95% CI	Upper limit of 95% CI	Effect concentration ng ai/g soil
Chlorantraniliprole	Chronic	Cucurbita	Lowest HB LC_{50}	0.6	1.6	0.02	373.0
Chlorantraniliprole	Chronic	Cucurbita	SB Surrogate LD_{50}	11.9	21.1	3.7	37.3
Chlorantraniliprole	Acute	Cucurbita	Lowest HB LC_{50}	0	0	0	5595.3
Chlorantraniliprole	Acute	Cucurbita	SB Surrogate LD_{50}	0.2	0.7	0	559.5
Clothianidin	Chronic	Field crops	Lowest HB LC_{50}	92.4	97.0	86.0	0.6
Clothianidin	Chronic	Field crops	Geomean LC_{50}	87.7	94.0	80.1	1.0
Clothianidin	Chronic	Field crops	SB Surrogate LD_{50}	98.8	99.8	96.5	0.1
Clothianidin	Chronic	Field crops	HB NOAEC	96.8	99.1	92.5	0.3
Clothianidin	Acute	Field crops	Lowest HB LC_{50}	27.3	35.3	19.1	9.3
Clothianidin	Acute	Field crops	Geomean LC_{50}	11.7	17.6	5.8	15.2
Clothianidin	Acute	Field crops	SB Surrogate LD_{50}	81.9	89.7	73.6	1.5
Clothianidin	Acute	Field crops	HB NOAEC	57.8	67.3	48.7	4.0
Imidacloprid	Chronic	Field crops	Lowest HB LC_{50}	5.9	9.7	2.1	0.5
Imidacloprid	Chronic	Field crops	Geomean LC_{50}	4.2	7.1	1.3	1.1
Imidacloprid	Chronic	Field crops	SB Surrogate LD_{50}	9.2	15.3	3.9	0.1
Imidacloprid	Acute	Field crops	Lowest HB LC_{50}	0.8	1.8	0.0	7.6
Imidacloprid	Acute	Field crops	Geomean LC_{50}	0.2	0.7	0.0	16.9
Imidacloprid	Acute	Field crops	SB Surrogate LD_{50}	3.3	5.6	0.9	1.7
Thiamethoxam	Chronic	Field crops	Lowest HB LC_{50}	37.4	45.8	29.4	0.7
Thiamethoxam	Chronic	Field crops	Geomean LC_{50}	35.7	43.95	27.85	0.7
Thiamethoxam	Chronic	Field crops	SB Surrogate LD_{50}	78.4	85.8	69.7	0.1
Thiamethoxam	Acute	Field crops	Lowest HB LC_{50}	0.0	0.3	0.0	10.1
Thiamethoxam	Acute	Field crops	Geomean LC_{50}	0.0	0.2	0.0	10.8
Thiamethoxam	Acute	Field crops	SB Surrogate LD_{50}	25.6	33.1	17.8	1.1

Table S3. Parameters (shape and rate) and associated 95% confidence interval for the gamma model that was fit to the distribution of measured concentrations of each insecticide and the Akaike Information Criterion (AIC) for each model.

Insecticide	Sample depth/ cm	Crop type	shape	shape_2.5	shape_97.5	rate	rate_2.5	rate_97.5	AIC
Clothianidin	0-15	Cucurbita	0.343044	0.14723308	0.667891188	0.228469	0.1387103	0.39616228	76.90513
Imidacloprid	0-15	Cucurbita	-0.050371212	-2.517200493	0.910929857	1.589229598	0.216341429	3.155708277	56.83654323
Thiamethoxam	0-15	Cucurbita	1.0504021	1.033572828	1.222289678	0.316636	0.01405871	0.33334101	12.69971
Chlorantraniliprole	0-15	Cucurbita	0.09636	0.03413813	0.200792325	0.005212	0.0028537	0.01328973	107.6332
Clothianidin	0-15	Field crops	1.067537	0.75563551	1.533034186	0.15031	0.0997477	0.23856296	508.4322
Imidacloprid	0-15	Field crops	0.025425	0.01082193	0.044708698	0.109763	0.0471882	0.39990766	91.718
Thiamethoxam	0-15	Field crops	0.535504	0.39735558	0.737929321	0.647974	0.4363275	1.09491352	205.267