Ecotoxicology (2017) 26:876–888
DOI 10.1007/s10646-017-1818-z

Fate and transport of furrow-applied granular tefluthrin and seed-coated clothianidin insecticides: Comparison of field-scale observations and model estimates

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Accepted: 17 May 2017 / Published online: 30 May 2017

Abstract The transport of agricultural insecticides to water bodies may create risk of exposure to non-target organisms. Similarly, widespread use of furrow-applied and seed-coated insecticides may increase risk of exposure, yet accessible exposure models are not easily adapted for furrow application, and only a few examples of model validation of furrow-applied insecticides exist using actual field data. The goal of the current project was to apply an exposure model, the Pesticide in Water Calculator (PWC), to estimate the concentrations of two in-furrow insecticides applied to maize: the granular pyrethroid, tefluthrin, and the seed-coated neonicotinoid, clothianidin. The concentrations of tefluthrin and clothianidin in surface runoff water, sampled from a field in central Illinois (USA), were compared to the PWC modeled pesticide concentrations in surface runoff. The tefluthrin concentrations were used to optimize the application method in the PWC, and the addition of particulate matter and guttation droplets improved the models prediction of clothianidin concentrations. Next, the tefluthrin and clothianidin concentrations were calculated for a standard farm pond using both the optimized application method and the application methods provided in PWC. Estimated concentrations in a standard farm pond varied by a factor of 100 for tefluthrin and 50 for clothianidin depending on the application method used. The addition of guttation droplets and particulate matter to the model increased the annual clothianidin concentration in a standard farm pond by a factor of 1.5, which suggested that these transport routes should also be considered when assessing neonicotinoid exposure.

Keywords Furrow-applied insecticides · Seed coating · Exposure model · Clothianidin · Tefluthrin

Introduction

Insecticides have widespread use in agriculture due to their ability to reduce insect pressure and improve crop yields. However, insecticides can be transported off-site to adjacent environments and have the potential to expose non-target species (Stehle and Schulz 2015). The risk of transport and exposure can be minimized by using insecticide formulations that reduce off-site transport and concentrate the insecticide where it is most effective, thereby decreasing the cost to the user (Schulz 2004). Granular insecticides, for example, are often applied to the base of the seed furrow. Tefluthrin is a soil-active synthetic pyrethroid that is commonly found in granular formulations. Tefluthrin targets corn rootworm and cutworm activity in maize (*Zea mays*). In the United States, approximately 90,000 kg of tefluthrin was applied to agricultural fields in 2010 (Baker and Stone 2015), and this accounted for 15% of the total insecticide applied to maize crops (NASS 2011). Tefluthrin is a sodium channel modulator (Nauen et al. 2012) and it is toxic to aquatic organisms (Pesticide Ecotoxicity Database 2000).

Electronic supplementary material The online version of this article (doi:10.1007/s10646-017-1818-z) contains supplementary material, which is available to authorized users.

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The exposure risk to non-target species can also be reduced by applying the pesticide directly to the seed. Seed coatings (also known as dressings or treatments) commonly consist of an insecticide, fungicide, or a mixture of active ingredients that improves seed emergence and provides protection from insects and pathogens (Munkvold et al. 2014). Seed coatings may contain neonicotinoids, which are neurotoxic compounds that selectively bind to the insect nicotinic acetylcholine receptor (Jeschke and Nauen 2008). Rapid increases in the use of neonicotinoid seed treatments have occurred since their introduction in the mid-1990s. In 2011, 79–100% of the maize grown in the U.S. was treated with a neonicotinoid seed coating (Douglas and Tooker 2015).

One advantage of the use of neonicotinoid insecticides in seed coatings is that they are systemic (Goulson 2013) and transport to the roots, stalks, and leaves, which reduces insect herbivory (Munkvold et al. 2014). However, non-target aquatic invertebrates (Morrissey et al. 2015) and pollinators, such as honey bees (*Apis* sp.) may be at risk of neonicotinoid exposure (Stewart et al. 2014). Fields sowed with a seed coating containing clothianidin reduced the nearby density of mason bee (*Osmia bicornis)* and bumblebees (*Bombus terrestris*), reduced the nesting of mason bees, and reduced the colony growth and reproduction in bumblebees (Rundlöf et al. 2015). Furthermore, neonicotinoids may be transported from the seed coating to fluid excreted by guttation (Tapparo et al. 2011), the process by which plants secrete excess water through hydrathodes when soil moisture levels are high and their stomata are closed (Singh 2013). Neonicotinoids in guttation fluid may pose a risk to honey bees during foraging (Reetz et al. 2016). Neonicotinoid insecticides can also be transported from the seed coating to the environment as dust or particulate matter during planting (Xue et al. 2015). Exposure to neonicotinoid-contaminated particulate matter during maize sowing may contribute to spring bee loss (Girolami et al. 2012). The surface soil also intercepts the emission of neonicotinoid-contaminated dust (Limay-Rios et al. 2016), which may impact neonicotinoid soil concentrations.

Surface waters frequently contain agricultural insecticides at concentrations that exceed regulatory threshold levels (Stehle and Schulz 2015). Thus, understanding granular pyrethroid and neonicotinoid transport from the furrow application site is crucial to estimating the impact of these insecticides to ecosystems near agricultural fields. Field measurements of insecticide transport to non-target environments are sparse due to the number of pesticides in current use world-wide, the cost of monitoring, and the variability in application methods. For these reasons, transport of pesticides to non-target environments and the exposure of pesticides to non-target species is often estimated using fate and exposure models. However, while modeling surface runoff from spray-and ground-applied pesticides has been evaluated (Zhang and Goh 2015) only a few direct comparisons between modeled and measured furrow-applied insecticides have been made using readily accessible fate or exposure models. For example, the USEPA's Pesticide Root-Zone Model (PRZM) has been adapted to the watershed scale, and the modeled toxic units in sediment for four pyrethroids, bifenthrin, λ-cyhalothrin, esfenvalerate, and permethrin, compared well with measured stream suspended solid concentrations in the California Central Valley (Luo and Zhang 2011). The European Union's exposure model, FOrum for the Co-ordination and their Use (FOCUS), was used to compare modeled insecticide concentrations, including 10 pyrethroids, to measured concentrations from 22 field studies (Knäbel et al. 2012). In this meta-analysis, even when more realistic input parameters were used, environmental concentrations tended to be underestimated in comparison to predicted concentrations, especially for hydrophobic pesticides (Knäbel et al. 2012), although these results have been disputed (Reichenberger 2013). A risk assessment of neonicotinoids using a fugacity model coupled to a risk classification ranking indicated high risk of clothianidin to surface water systems (Miranda et al. 2011); however, no comparison was made to field data. Recently, Agatz and Brown (2017) reported the first two-dimensional model that simulates a furrow-applied application of insecticides through the root zone, but this model is not currently incorporated in an accessible fate or exposure model.

In addition to the lack of comparisons between modeled and measured concentrations of furrow-applied insecticides, alternate routes of transport from the furrow application site to the surface may need to be considered. In particular, the role of insecticide transport from the seed coating off-site via particulate matter and guttation droplet has not been examined. The goal of the current project was to evaluate a recently released exposure model, the Pesticide in Water Calculator (PWC) (Young 2016a), using two insecticides that were applied in the furrow: the granular pyrethroid tefluthrin and the seed-coated neonicotinoid clothianidin. The measured concentrations of tefluthrin and clothianidin in surface water runoff from a continuous maize no-till field were compared to concentrations estimated by PWC and the comparison was evaluated. Specific objectives of the project were: (1) to evaluate the role the furrow-applied application method (uniform below vs. linearly increasing with depth vs. at-depth) had on the model, using the tefluthrin granular furrow-applied treatment to calibrate the model; (2) to compare clothianidin seed coating concentrations estimated using PWC to surface water concentrations from the field; (3) to estimate the effect of particulate matter and guttation droplets on neonicotinoid concentrations; and, (4) to estimate tefluthrin and clothianidin concentrations in a

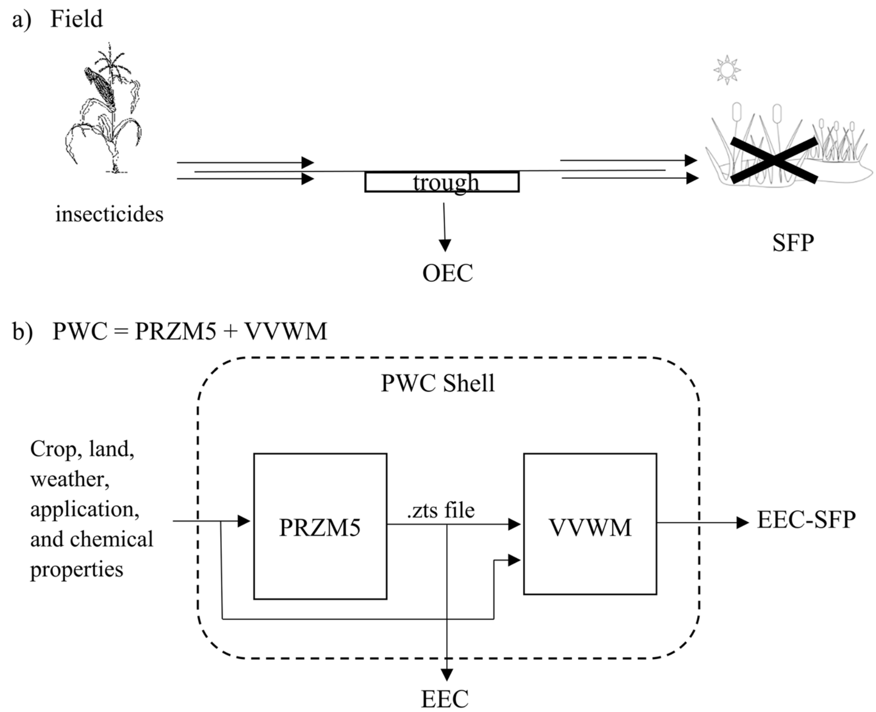

Fig. 1 Depiction of field and model setup and data outputs. **a** Insecticides were applied to the maize field followed by surface and below-surface transportation of insecticides to in-field troughs where runoff water samples were collected to measure observed environmental concentrations (OEC). A standard farm pond (SFP) was not located near the field site. **b** The Pesticide in Water Calculator (PWC) consisted of the Pesticide Root Zone Model (PRZM5) and the Variable Volume Water Model (VVWM). Crop, land, weather, application, and chemical properties were inputted to PWC, and PRZM5 calculated a.zts file. The.zts file was used to calculate the estimated environmental concentrations (EEC), which were compared to the OEC (i.e., the concentration of insecticides in runoff water) in the field (**a**). The.zts file and parameters were entered into VVWM, and the estimated environmental concentrations in the standard farm pond (EEC-SFP) were outputted

hypothetical standard farm pond and show the differences that may occur by using other application methods.

Methods

The overall design of the current project consisted of the comparison of field measurements (Whiting et al. 2014, and this work) to an exposure model (Fig. 1). For the field measurements, surface water was sampled using in-field troughs, which served as the observed environmental concentrations (OEC) for the insecticides (Fig. 1a). Three field seasons of surface runoff data were used in the current project, including the prior work of Whiting et al. (2014) for 2012 and 2013 field seasons and the current work for the 2014 field season (Table S1). The exposure model, PWC version 1.52 (Fig. 1b), which consisted of PRZM5 (version 5.02) and the Variable Volume Water Body Model (VVWM) version 1.02, calculated the estimated environmental concentrations (EEC) of insecticides in surface water runoff within the field. First, field measurements of the granular insecticide, tefluthrin, in surface water runoff were used to optimize the furrow-applied application parameters by comparing OEC values of tefluthrin in surface runoff water to the EECs values calculated by PWC. Next, the optimized application method was applied to the seed-coated insecticide clothianidin, and then was adjusted for two additional surface application routes due to particulate matter created at planting and the transport of clothianidin through the maize seeding to guttation droplets. The clothianidin EEC values were compared to clothianidin OEC values and role of application routes were assessed. By using the adjusted application scenarios, PWC estimated the concentrations of insecticides in a standard farm pond (EEC-SFP) by using the VVWM. The methods used in the current project are described in detail below.

Field site description and insecticide measurements

The OEC values for tefluthrin and clothianidin were measured during a three-year study conducted on a 36 ha farm in Christian County, IL. The farm was operated as a no-till system in continuous maize beginning in 2010 and through the 2014 growing season. The average physical characteristics of the top soil were 27.4% clay, 69.7% silt, and 2.9% sand and the organic matter content was 3.8% (Mueting et al. 2014). Standard farming practices were used and the details are described in Whiting et al. (2014). Clothianidin-coated maize seed was planted using a John Deere 1770NT 24 row planter (Moline, IL, USA) with a furrow depth ranging from 3.8 to 5.1 cm. The tefluthrin was applied in a granular form directly behind the seed in the furrow, and the furrow was immediately closed by a press wheel. Tefluthrin was applied at two different rates (full rate and no tefluthrin) in a 24-row repeating pattern, and clothianidin was applied at a single rate because uncoated seed could not be obtained.

The OEC values of tefluthrin and clothianidin were measured in the surface runoff water that was collected from polyvinyl chloride troughs measuring 1.8 m by 30 cm. The top of each trough was at ground level and oriented perpendicular to the slope in the field. The troughs were placed in the middle of each treatment (Whiting et al. 2014). Runoff water samples were collected from troughs within 24 h after precipitation events greater than 1.27 cm. Troughs were cleaned prior to runoff water collected and sampled within 24 h after each runoff event to reduce contamination. Eighteen troughs were sampled in 2012 and 2013 and 10 troughs were sampled in 2014. Half of the troughs were sampled in rows where no tefluthrin was applied. These troughs served as controls, and very little carryover was observed between the full-rate and no applied tefluthrin sites (Whiting et al. 2014), thus only data from the full rate tefluthrin sites sampled were used in the current project. In addition, it should be noted that a pilot study was conducted and acetone washes showed that the loss of the target pesticides to the PVC troughs were not significant. The number of replicates for each sample set is included in Table S1.

The sample preparation, tefluthrin and clothianidin analysis methods, and quality assurance/quality control have previously been described (Whiting et al. 2014), and a summary is provided here. Water samples were spiked with surrogate compounds (4,4′-dibromooctafluorobiphenyl and decachlorobiphenyl), liquid-liquid extracted, and cleaned using an ENVI-carb solid phase extraction (SPE) cartridge. Clothianidin and surrogates were separated from tefluthrin and its respective surrogates on the SPE cartridge using different elution solvent mixtures. Samples containing tefluthrin were analyzed using dual-column gas chromatography with electron capture detection, and samples containing clothianidin were analyzed using high performance liquid chromatography with diode array detection (see Whiting et al. (2014) for experimental details). The reporting limit (RL) for each compound were set as three times the method detection limit (MDL), where the MDL was calculated as the product of the standard deviation of seven replicate samples spiked near the detection limit and the Student's t value at 99% using six degrees of freedom. The RL for tefluthrin was 3.1 ng/L, and the RL for clothianidin was 24 ng/L (Whiting et al. 2014).

Table 1 Physical properties of insecticides and selected model inputs[a]

	Tefluthrin	Clothianidin
Molecular weight (g/mol)	418.7	249.7
Solubility (mg/L)	0.020[b]	340
K_{oc} (mL/g)	19850[c]	60
Vapor pressure (torr)	6×10^{-5}	2.1×10^{-13}
Soil half-life, aerobic (d)[e]	180	545[g]
Water column metabolism half-life (d)[e,h]	180	214
Benthic metabolism half-life (d)[e,i]	90[d]	27
Hydrolysis half-life (d)[f]	730	33
Aquatic direct photolysis half-life (d)[e]	64	0.1
Application rate (kg/ha)	0.15	0.0419
Application method	at-depth, 2 cm[j]	at-depth, 2 cm[j]
Efficiency	0.25	0.25
Drift	0	0
Henry's law constant (dimensionless)	0.0674[k]	0[k,l]
Air diffusion coefficient (cm^2/d)	790[k]	0[k,l]
Heat of Henry (kJ/mol)	45700[m]	0[k,l]

[a] Sources were HSDB (2005); HSDB (2011); Bonmatin et al. (2015) unless indicated

[b] Shiu et al. (1990)

[c] Reported values ranged from 11,200 to 28,500, median value used

[d] Half the soil aerobic half-life (Burns 2007)

[e] Reference temperature 20 °C

[f] Reference latitude 40°

[g] Reported values ranged from 148 to 5155 days, median value used

[h] Also known as aerobic aquatic half-life

[i] Also known as anaerobic aquatic half-life

[j] Applied at −10 days prior to emergence (at sowing) and once per year, every year

[k] Calculated following from Rothman et al. 2015

[l] Henry's Law constant for clothianidin (2.9×10^{-16} atm-m^3/mol, HSDB 2005), air diffusion coefficient, and Heat of Henry can be set to zero (Rothman et al. 2015)

[m] Calculated using Estimation Programs Interface Suite (USEPA 2012)

Modeled insecticide concentrations using PWC

The PWC (version 1.52, Young 2016a; Young and Fry 2016; Young 2016b) was used to calculate EECs for tefluthrin and clothianidin. To calculate the EEC, the chemical and physical properties of each pesticide along with standard chemical application scenarios, crop type, land descriptors, weather, and runoff and erosion parameters were input for PWC. PRZM5 calculated a.zts file, where the mass of pesticide transported over the soil surface for each simulation day was used to estimate the insecticide concentrations in the surface runoff water.

The physical and chemical properties used for tefluthrin and clothianidin are summarized in Table 1. The runoff depth was assumed to be 2 cm, with a 1.55 cm^{-1} exponential decline in the runoff interaction term as a function of depth, and 0.266 as the fraction of runoff flow that interacts with the soil (efficiency), while erosion depth and decline were 0.1 cm and 0 cm^{-1}, respectively. For weather, a daily weather file (.dvf) was generated consisting of the 24-h precipitation, evaporation rate, average temperature, average wind speed, and solar radiation. The daily meteorological data were obtained from a weather station installed at the field site, and a full description can be found in Supporting Information. The weather station at the field site collected data from 2010 to 2014, and this 5-year data set was repeated twice to create a 15-year.dvf.

The PWC calculated daily insecticide concentrations over the simulation time frame (15 to 30 years) in a standard farm pond that received runoff from a cropped field, and the model determined the EEC values in a standard farm pond (EEC-SFP) as the 90th percentile of the peak, 21-d average, 60-d average, and annual average concentrations of the insecticide. While these values were critical in assessing the risk of exposure to insecticides, the field site where the OEC values were measured lacked a farm pond; therefore, insecticide concentrations were measured instead from samples collected from surface water runoff troughs within the field. The calculated insecticide concentration in the pond was likely lower than runoff into the troughs, because it was diluted as it enters the pond, degraded during storage, and sequestered due to interaction with benthic sediment. Thus, the pond concentrations do not accurately reflect insecticide concentrations in the field runoff. For this reason, the standard farm pond concentrations cannot be directly compared to OEC values in the current study. Instead, the PRZM5 portion of PWC calculated a daily time-series vile (.zts) that included the pesticide masses that were exported off-field due to surface runoff as a flux. Thus, the EEC values in the surface runoff water were calculated as the quotient of the runoff flux (mass of insecticide exported in surface water per watershed area in g/cm^2) and the runoff depth (in cm). This quotient, converted to ng/L (assuming the density of water was approximately 1 g/cm^3) was the EEC in surface runoff water for each simulation day and compared to the OEC measured at the field site.

Three different furrow-applied application methods (uniform below, linearly increasing with depth, and at-depth) were tested to optimize PWC for an insecticide applied at the bottom of the furrow in granular form and as a seed coating. The uniform below option distributed the insecticide uniformly from the surface to the specified depth, while the linearly increasing method distributed the insecticide to greater amount at depth. The at-depth option placed the insecticide in a single compartment at the specified depth, and the fraction of the total insecticide applied that interacts with the soil was adjusted using the efficiency. The uniform below and linearly increasing options overestimated the EEC in comparison to the OEC for both tefluthrin and clothianidin, even after reducing the application efficiency to 0.25. The at-depth application method and the tefluthrin OEC were used to optimize the application method, because the clothianidin may have additional surface application routes.

In addition to furrow-applied application methods, two scenarios for secondary surface application of clothianidin were tested. The first was particulate matter deposition on the soil surface due to planting operations. Between 0.5 and 2% of the neonicotinoid active ingredient in the seed coating can be released as particulate matter from the wastepipe of a Monosem drilling machine (Tapparo et al. 2012). An application amount was derived from particulate matter emission factors for Poncho seed coating formulations for 2008, 2009, and 2010, which averaged 0.81×10^{-3} kg clothianidin/ha for 1.25 mg active ingredient (a.i.)/seed (Tapparo et al. 2012). The active ingredient level in the current study was lower (0.5 mg a.i./seed), thus the emission factor was rationed according to the amount of active ingredient, so that an additional 0.323×10^{-3} kg clothianidin/ha was added to the model, and it was assumed that 99% of particulate matter lands on the soil surface within 24 h of planting.

The second scenario considered the role of clothianidin translocation from the seed coating to guttation droplets, which have the potential to land on the soil surface or rinse off of the maize leaves due to precipitation. The clothianidin concentration and guttation volume per day measured by Tapparo et al. (2011) was normalized for the active ingredient seed coating and the number of seeds planted per acre at the IL field site and was converted into a daily below crop application rate (Table 2). These rates assume that 95% of the seeds germinated, that guttation occurred in the first 20 days after emergence, and that 50% of the clothianidin mass from the guttation droplets was deposited on the soil surface and available for runoff.

The selected model parameters were evaluated on the basis of the agreement between the estimated concentrations

Table 2 Application rates for clothianidin due to surface interception of guttation droplets[a]

Days post-planting[b]	Estimated clothianidin in guttation droplet, mg/L[c]	Application rate, kg/ha per day[d]
11	14.4	1.03×10^{-4}
12–13	10	7.19×10^{-5}
14–15	8.8	6.32×10^{-5}
16–17	5.6	4.02×10^{-5}
18–20	3.53	2.53×10^{-5}
21–29	12.7	9.09×10^{-5}

[a] Surface interception efficiency assumed to be 0.5

[b] Assumes emergence occurred 10 days after planting, and guttation droplets occurred 1 to 19 days after emergence

[c] Rationed for 0.5 mg a.i./seed relative to 1.25 mg a.i./seed (Tapparo et al. 2011)

[d] Assumes 90 μL/day for each plant (median of the 30–150 μL/day per plant reported by Tapparo et al. (2011), planted at 34,000 seeds/acre and assumed 95% germination

and observed concentrations. The normal root mean square error (NRMSE, Eq. 1) assessed the accuracy of the predicted values in comparison

$$\mathrm{NRMSE} = \frac{1}{\overline{\mathrm{OEC}}}\sqrt{\frac{1}{n}\sum_{n}\left(\mathrm{OEC}_i - \mathrm{EEC}_i\right)^2} \quad (1)$$

to the observations, where $\overline{\mathrm{OEC}}$ was the average of the OEC values, and n was the number of observed values. The OEC values for each day post-application, i, were compared to the running five-day average of the daily EEC values. Smaller NRMSE values indicated better agreement between modeled and measured concentrations. The coefficient of residual mass (CRM, Eq. 2) was used to estimate the systematic error of the predicted values in comparison to the observed values, where values greater than zero indicated bias toward observed concentrations, and values less than zero indicated a bias towards estimated concentrations (Noshadi et al. 2011).

$$\mathrm{CRM} = \frac{\sum_n \mathrm{OEC}_i - \sum_n \mathrm{EEC}_i}{\sum_n \mathrm{OEC}_i} \quad (2)$$

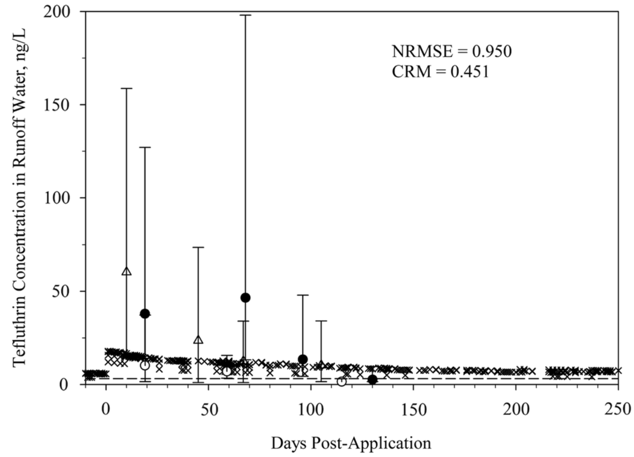

Fig. 2 Tefluthrin concentration in surface runoff water as a function of days after planting maize seed with tefluthrin granular insecticide in the furrow. Observed environmental concentrations (OEC) corresponded to average measured concentrations for 2012 (*black dot*), 2013 (*triangle*), and 2014 (*dot*) field seasons, and error bars represented the range of OEC. The reporting limit for the OEC values for tefluthrin was 3.1 ng/L (*dashed lines*, Table S1). The normalized root mean square error (NRMSE) and coefficient of residual mass (CRM) were calculated according to Eqs. 1 and 2. The sample sizes were variable due to sampling design and the numbers of samples per treatment were provided in SI. The estimated environmental concentrations (×) are shown only for non-zero runoff values for all simulation years and for post-application through the end of the calendar year

Results and discussion

Tefluthrin observed and estimated concentrations and application method optimization

An examination of the tefluthrin OEC values in surface runoff water showed that the concentrations tended to be highest immediately after application of tefluthrin at planting, up to 78 ng/L, and decreased through the field season to below the reporting limit (3.1 ng/L) (Fig. 2 and Table S1). Tefluthrin is a non-polar insecticide (log $K_{\mathrm{ow}} = 6.5$ (Shamim et al. 2008)) with low water solubility (0.020 mg/L, Table 1), and tends to bind to organic particles in soils and sediments ($K_{\mathrm{OC}} = 19{,}850$ mL/g, Table 1) rather than dissolve in water.

The best application method and parameters were determined by minimizing the difference between the tefluthrin surface water runoff OEC and the modeled EEC as determined by the NRMSE (Eq. 1) and CRM (Eq. 2) values. The use of the uniform below method overpredicted the EEC values by a factor greater than 50 in comparison to the OEC values, and therefore the at-depth option for application method was applied. The at-depth option for the application method represents the chemical (in this case, tefluthrin) being deposited in a single compartment at a depth specified by the user. However, the actual furrow depth was 4–5 cm, and because the modeled runoff only interacts with the top 2 cm of the soil surface, using a 4 cm depth resulted in no tefluthrin in the runoff. Because our observed concentrations showed that tefluthrin enters the surface-sampled soil, sediment, and runoff water (Whiting et al. 2014), this implied that a portion of the granular tefluthrin must migrate from the bottom of the furrow to the soil surface. Explanations for this include near-surface water flow within the soil, also known as interflow (Beven 1989) and gas exchange through soil pores. The PWC model does not take these factors into account, thus we simulated this effect by selecting the maximum at-depth value (2 cm) that would interact with the surface runoff, and then adjusted the efficiency value to best fit the EEC values to the OEC values. The best fit of the data occurred with the efficiency value set to 0.25, and this optimized the NRMSE and CRM, while it allowed the late-field season EEC values to decrease to near the reporting limit.

The EEC predicted by PWC was compared to OEC measured in the 2012, 2013, and 2014 field seasons (Fig. 2). Runoff is triggered by precipitation, and precipitation is not a daily occurrence for this field site; therefore, the EEC values were grouped according to days post-application relative to planting for each year in the 15-year simulation. Only non-zero values were plotted to show the EEC when precipitation and runoff occurred. The EEC for tefluthrin in surface runoff decreased through the field season to a

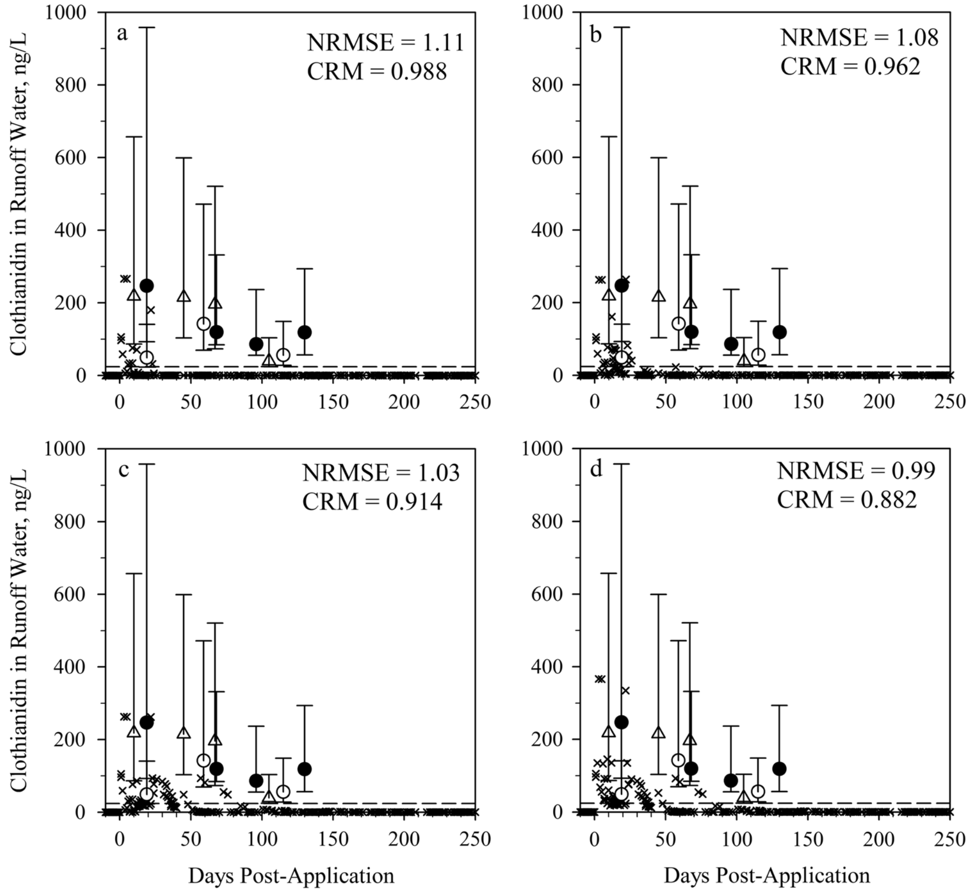

Fig. 3 Clothianidin concentration in surface runoff water as a function of days after planting maize with clothianidin seed coating. Observed environmental concentrations (OEC) correspond to average measured concentrations for 2012 (*black dot*), 2013 (*triangle*), and 2014 (*dot*) field seasons, and error bars show the range of OEC, and the 24 ng/L clothianidin reporting limit (*dashed lines* Table S1). The normalized root mean square error (NRMSE) and coefficient of residual mass (CRM) were calculated according to Eqs. 1 and 2. The sample sizes were variable due to sampling design and the numbers of samples per treatment are provided in SI. The environmental estimated concentrations (EEC) (×) are shown only for non-zero runoff values for all simulation years and for post-application through the end of the calendar year. The EEC were calculated using different application scenarios: **a** applied at-depth of 2 cm and 0.25 efficiency; **b** applied at-depth of 2 cm and 0.25 efficiency and surface application that simulates particulate matter from the planter; **c** applied at-depth of 2 cm and 0.25 efficiency and surface application that simulates guttation droplets; and, **d** applied at-depth of 2 cm and 0.25 efficiency and surface application that simulates particulate matter from the planter and guttation droplets

minimum (approximately 3.7 ng/L) by approximately 100 days post-application. The OEC after application in 2012 and 2013 were higher than the EEC by a factor ranging from two to six, while the 2014 OEC were similar to the EEC. The timing of the decrease in tefluthrin concentration in surface runoff water was similar; however, and the EEC reached the tefluthrin reporting limit (3.1 ng/L, Table S1) approximately 180 days after application, and OEC values reached the reporting limit about 120 days after application. The NRMSE was 0.950 and the CRM was 0.451, showing that the PWC under-predicted EEC values in comparison to the field values.

Clothianidin observed and estimated concentrations

Similar to tefluthrin, the clothianidin concentration in surface runoff water tended to be highest in the first sample collected after sowing, up to 247 ng/L in 2013 (Fig. 3a, Table S1). The clothianidin OEC values decreased through the growing season, but remained above the reporting limit (24 ng/L, Table S1) up to 130 days post-application. Clothianidin is a slightly polar insecticide (log $K_{ow} = 0.7$ (HSDB 2005)) with moderate water solubility (340 mg/L, Table 1), thus clothianidin is transported with water over the surface as well as through the vadose zone. Most seed coating active ingredients either enter the soil (approximately 90% (Goulson 2013)), are bound to soil components (e.g., clay or organic matter) thereby increasing their persistence or they may move away from the seed through the soil (Paranjape et al. 2015). Furthermore, field measurements at the same site have confirmed the presence of clothianidin in soil pore water at 1 m depth and in water from 4 m wells (Whiting et al. 2014) demonstrating the mobility of clothianidin.

The same pesticide application scenario as tefluthrin was used to calculate clothianidin EEC, using an at-depth application method (2 cm) and a 0.25 efficiency value, because seed was sowed at the base of the furrow. However, the agreement between the clothianidin OEC values and EEC were generally poorer than the agreement between tefluthrin OEC and EEC (Fig. 3a). Clothianidin EEC in surface runoff water was highest immediately after application of clothianidin insecticide at planting, with concentrations as high as 260 ng/L. The EEC for clothianidin in surface runoff under this scenario decreased more rapidly than tefluthrin and was below the reporting limit (24 ng/L) within 30 days after application. The clothianidin EEC early in the field season were in reasonable agreement with the clothianidin surface water OEC. For example, the average clothianidin OEC was 247 ng/L at 19 days post-application in 2012, 218 ng/L at 10 days post-application in 2013, and 49 ng/L at 19 days post-application in 2014, while the clothianidin EEC reached 260 ng/L. However, the OEC showed a slower decline in surface runoff concentrations in comparison to the EEC. The OEC persisted above the 24 ng/L reporting limit for 130 days after application, whereas the EEC decreased to below the reporting limit only 30 days after application. Despite the relatively good agreement immediately after planting, the overall fit of the EEC to the OEC was poorer for clothianidin (NRMSE = 1.11). The CRM (0.988) indicated that the EEC underestimated the OEC values due to the higher residual clothianidin measures in the surface water through the growing season.

The range of OEC values was generally consistent with previous work (de Perre et al. 2015; Samson-Robert et al. 2014; Schaafsma et al. 2015). For example, the average clothianidin concentration in surface runoff water at a similar IL field site were 200 ng/L in 2011 and 800 ng/L in 2013, both collected within 1 month after planting (de Perre et al. 2015). Also, the average clothianidin concentration measured in puddles in fields sowed with clothianidin-coated seed maize 1 month after planting in Quebec, Canada was 523 ng/L with a range from 17 to 2300 ng/L indicating large variability, possibly due to variable sowing methods and seed coating amounts (Samson-Robert et al. 2014). The average total thiamethoxam + clothianidin concentration for in-field surface water in Ontario, Canada was 11,070 ng/L (Schaafsma et al. 2015). Furthermore, quantifiable concentrations of seed-coated thiamethoxam and clothianidin (as a degradation product) in the edge-of-field surface runoff water persisted for 2 years post-application (Chrétien et al. 2017). Thus, it is unlikely the OEC have been overestimated, and instead this suggested that the EEC were under-predicted by the PWC.

Contribution of particulate matter and guttation droplets to surface water concentrations

The PWC tended to under-predict clothianidin EEC in comparison to the OEC through the growing season. One explanation for this under-prediction was an additional route(s) of transport for clothianidin from the seed coating to the surface for runoff; e.g., clothianidin contamination of the particulate matter associated with planting. Using application amounts derived from particulate matter emission factors from Tapparo et al. (2012), EEC was calculated, and the results are shown in Fig. 3b. The addition to particulate matter at application increased the number of runoff events with concentrations greater than the reporting limit, especially within the first 30 days after planting, and improved the overall agreement between EEC and OEC (NRMSE = 1.08, CRM = 0.962). Although the maize in this current work was sowed using a different planter than Tapparo et al. (2012), if the planter caused a similar fraction of the seed coating to be transported and deposited on the surface, particulate matter from planting may have been a potentially important source of clothianidin in surface runoff within the first month after planting. However, the OEC was greater than the RL throughout the growing season (meaning that clothianidin showed higher sustained concentrations in the surface runoff through the growing season), while PWC predicted EEC below the RL through the growing season, which suggested additional furrow-to-surface transport mechanisms existed.

Due to translocation of clothianidin in the maize plant, clothianidin can be emitted as an aqueous secretion known as guttation droplets (Girolami et al. 2009). A surface application method (Table 2) for clothianidin due to guttation droplets in maize seedlings was derived from Tapparo et al. (2011). The clothianidin concentration in guttation droplets was rationed for the seed coating application amount per seed, and daily guttation was assumed for the first 19 days after maize seedling emergence. The fraction of clothianidin in guttation droplets that reached the surface was not known. Therefore, the efficiency of the interception of clothianidin in droplets by the surface was estimated to be 0.5 as a median value between complete transfer and no transfer. The addition of guttation droplets improved the agreement between the OEC and the EEC and increased the number of EEC values above the RL for the first 75 days post-planting (Fig. 3c, NRMSE = 1.03, CRM = 0.914).

It was also possible that a fraction of the clothianidin in the seed coating was transported from the furrow to runoff by both routes: particulate matter emission from planting and guttation droplets. Figure 3d shows this combination, and in comparison to the base case (Fig. 3a), the number of runoff events in the first 75 days after planting with EEC greater than the RL increased by a factor of four, which was more consistent with the OEC (NRMSE = 0.99, CRM = 0.882). The combination of exposure routes provided better agreement between EEC and OEC values. This agreement suggested that particulate matter at sowing and guttation droplets were both important contributors to clothianidin concentrations in surface runoff water.

Evaluation of the application method

The agreement between in-field surface water runoff concentrations from furrow-applied tefluthrin and seed-coated clothianidin and modeled concentrations was better if we used an at-depth application method with 2 cm and 0.25 efficiency, compared with other PWC-supplied application methods (such as uniform below or using at-depth with the actual furrow depth). This application method mimics the coated seed and granular insecticide placed at a bottom of the furrow, but a portion (0.25) of the insecticide was available for interaction with runoff water. The chosen application method provided the best available fit (NRMSE and CRM). The other more obvious application choices (uniform below and at-depth using 2 cm and an efficiency of 1) over-predicted insecticide runoff concentrations, and an at-depth method using 4 cm greatly underestimated insecticide runoff concentrations. Thus, this application method was limited, because the 2 cm at-depth and 0.25 efficiency choice was site-specific and cannot be extended to other fields (without further verification). The model could be improved; however, if near-surface pesticide transport mechanisms were included, because this could lead to systematic underestimation of surface water concentrations of furrow-applied insecticides. At least one other regulatory model (FOCUS) has been shown to underestimate insecticide exposure for pyrethroids, organophosphates, organochlorines (Knäbel et al. 2012) and fungicides (Knäbel et al. 2014), even with field-realistic inputs. Therefore, it is possible that exposure models could be improved by optimizing the application method and/or by considering interflow in pesticide near-surface transport.

Although the agreement between clothianidin EEC and OEC improved when both exposure routes were added to the model, these routes of clothianidin transport need better quantification in order to extend this work to other sites. The estimation of a particulate matter emission factor was based on the use of clothianidin at a different seed coating rate (0.5 mg a.i./seed vs. 1.25 mg a.i./seed in Tapparo et al. (2012)) and different sowing equipment. Although the assumptions of a direct relationship between seed coating active ingredient and particulate matter emission factor and that different sowing equipment provided similar particulate matter emission factors are reasonable, this has not yet been confirmed. In addition, the volume of guttation fluid exuded from plants depends on soil moisture and humidity levels (Singh 2013), indicating the field conditions could impact the amount of clothianidin transferred from the plant to the soil surface due the suppression or enhancement of guttation. While the efficiency of the clothianidin transport from guttation droplets to the soil surface is unknown, the agreement between measured and modeled values improved when guttation was included in the model.

Furthermore, the EEC calculated by PWC suggested that the clothianidin concentration in surface runoff water should drop below the RL after 75 days, while what was found was that OECs were greater than the RL even after 75 days. Thus, there may have been additional processes that enabled clothianidin transport from the seed coating to the surface. Also, in the no-till system, the degradation of clothianidin-contaminated plant material could lead to the release of clothianidin from the previous season (carryover). The translocation of neonicotinoid insecticides from seed coating through maize and other plants is a key data gap (Krupke and Long 2015), and none of these factors were accounted for in the current application scenario. Additional research is needed to determine the mass of clothianidin that could be transported from the seed coating to the surface to determine the full extent of the transfer of the seed coating from the seed to surface runoff water.

Estimation of tefluthrin and clothianidin concentrations in a standard farm pond

As previously discussed, a direct comparison of standard farm pond EEC to OEC in the current study were not appropriate, because the OEC represented surface water concentrations within the field, and the field in the current study did not outflow to a pond that could have been sampled. The PWC is a tool to estimate the environmental concentrations of pesticides in a body of water that receives runoff from a watershed with applied pesticides. The goal of this section was to assess the role of the optimized application method on the EEC-SFP in the watershed. Daily concentrations over the simulation time frame were calculated, and PWC reported the 90th percentile of the peak, 21-d average, 60-d average, and annual average concentrations of the tefluthrin and clothianidin in standard farm pond that receives runoff from a cropped field (Tables 3 and 4).

The role of the application method in the tefluthrin EEC-SFP is demonstrated in Table 3. The use of an application

Table 3 Tefluthrin estimated environmental concentrations (EECs) in standard farm pond (ng/L)[a]

Application method	At-depth 2 cm, efficiency = 0.25	At-depth 2 cm, efficiency = 1	Linearly increasing 2 cm, efficiency = 0.25	Uniform below 4 cm, efficiency = 1
Peak	3.54	14.2	20.0	352
21-d	0.573	2.29	3.95	61.8
60-d	0.432	1.73	3.14	42.6
Annual	0.196	0.783	1.39	13.8

[a] Water column (limnetic) 1 in 10-year concentrations

Table 4 Clothianidin estimated environmental concentrations (EECs) in standard farm pond (ng/L)[a]

Application method	At-depth 2 cm, efficiency = 0.25	At-depth 2 cm, efficiency = 0.25 + guttation	At-depth 2 cm, efficiency = 0.25 + particulate matter	At-depth 2 cm, efficiency = 0.25 + guttation + particulate matter	At-depth 2 cm, efficiency = 1	Linearly increasing 2 cm, efficiency = 0.25	Uniform below 4 cm, efficiency = 1
Peak	17.6	17.6	18.9	18.9	70.4	210	786
21-d	7.86	7.99	9.37	9.49	31.4	101	384
60-d	3.21	4.18	3.90	4.97	12.8	41.6	159
Annual	0.530	0.704	0.645	0.838	2.12	6.88	26.3

[a] Water column (limnetic) 1 in 10-year concentrations

method developed for furrow-applied insecticides (at a 2 cm depth and efficiency of 0.25) resulted in a peak tefluthrin EEC-SFP of 3.54 ng/L, and the annual EEC-SFP was 0.196 ng/L. The value of the application efficiency had a direct effect on EEC-SFP; when the efficiency was increased from 0.25 to 1, the EEC-SFP increased by a factor of four. Also, the type of application method affected the estimated concentrations. When linearly increasing to a depth of 2 cm using 0.25 efficiency were selected, the peak and annual EEC-SFP increased by a factor of five compared to the 2 cm at-depth/0.25 efficiency application method. When the uniform below application method and the field site's median furrow depth (4 cm) were selected, peak EEC-SFP increased by a factor of 100 in comparison to using the 2 cm at-depth/0.25 efficiency application method. The annual EEC-SFP was impacted as well; the use of the uniform below application method increased the EEC-SFP by a factor of 70. While the uniform below or linearly increasing method might have seemed to be a priori better simulation of the in-furrow granular tefluthrin application, these methods overestimated the tefluthrin concentration in the surface runoff water, and, therefore, may have overestimated the tefluthrin concentrations in a standard farm pond. The overestimation occurred because the uniform below application method treats the insecticide as if it were uniformly mixed from the surface to the bottom of the furrow (Young and Fry 2016). Thus, more insecticide was available for surface water runoff to a standard farm pond. In contrast, when the at-depth application method was selected, and the bottom of the furrow (4 cm) was used for depth, the tefluthrin EEC-SFP value was zero (data not shown). A zero value occurred because the runoff interaction in PWC extended to a depth of 2 cm, and by placing the insecticide in a single compartment below the runoff depth, the insecticide did not interact with the surface. However, these results conflicted with our observations of tefluthrin in the surface water and at the soil surface (Whiting et al. 2014). Thus, the application method was shown to have a direct impact on EEC-SFPs values, and using an optimized application method was likely to improve the estimate of exposure to non-target organisms.

The EEC-SFP for clothianidin was calculated using the same application method as tefluthrin (at-depth 2 cm/ 0.25 efficiency). The peak EEC-SFP was 17.6 ng/L and the annual EEC-SFP was 0.530 ng/L (Table 4). The effect of the application method (i.e., the use of uniform below and linearly increasing methods instead of the at-depth approach) on the clothianidin EEC-SFP was similar to the tefluthrin EEC-SFP. An increase an efficiency lead to higher EEC-SFP, selecting the uniform below method further increased EEC-SFP, and placing the clothianidin seed coating at a depth of 4 cm decreased the EEC-SFP to zero (data not shown). However, the clothianidin EEC in a standard farm pond (Table 4) were higher than the tefluthrin EEC for each application method (Table 3). This result contrasted with the application rates; the tefluthrin application rate (0.15 kg/ha) was higher than clothianidin (0.04 kg/ha). However, the higher clothianidin EEC were consistent with the OEC and the clothianidin concentrations were consistently higher than the tefluthrin concentrations in surface runoff. These observations can be explained by the physicochemical properties of each insecticide. Clothianidin has higher water solubility and a lower K_{oc} in comparison to tefluthrin (Table 1), and clothianidin tended to partition into the aqueous phase, and as a result, clothianidin was calculated to be at a higher concentration in bodies of water than tefluthrin.

The effect of secondary application methods on the EEC in a standard farm pond, including guttation and particulate matter dispersion, were tested for clothianidin (Table 4). The addition of guttation droplets increased the farm pond EEC, and to a greater extent on an annual basis than as peak concentration. The increase occurred because the transfer of clothianidin to the surface via guttation droplets was simulated by small, daily applications (Table 2), and while daily additions of a small amount of clothianidin did not impact the peak concentration, they did increase the overall clothianidin in surface runoff water that enters a standard farm pond. On the other hand, the addition of particulate matter to the application method caused an increase of the peak, 21-d, 60-d, and annual EEC-SFP, which suggested that particulate matter could cause a spike in clothianidin concentration, but also caused a long-term increase in EEC-SFP as well. Finally, when guttation and particulate matter were included in the application model, the farm pond EEC increased additively, and both the peak (18.9 ng/L) and the annual (0.838 ng/L) EEC-SFP increased. The effect on the annual EEC-SFP was greater; the addition of guttation droplets and particulate matter increased the annual EEC-SFP by a factor of 1.5. If particulate matter and guttation droplets were a significant source of clothianidin to surface runoff water, then omitting these processes would have caused an underestimation of clothianidin exposure in a standard farm pond. Therefore, understanding how clothianidin can be transported from the seeding coating to the surface and bypass the furrow is important to predicting the fate of clothianidin in agricultural watersheds.

Conclusions

The agreement between the observed concentrations of the furrow-applied tefluthrin and seed-coated applied clothianidin in surface runoff water and the concentrations estimated by PWC was improved when the application method was adjusted to fit the observed concentrations by using the at-depth application and adjusting the application efficiency. The selection of the application method has a direct effect on the estimation of the tefluthrin and clothianidin concentrations in surface water. The selection of uniform below and linearly increasing methods in the PWC may overestimate the edge-of-field concentrations of the furrow-applied insecticides, and as a result, the risk to non-target organisms. In addition, the application method developed for granular tefluthrin and seed-coated clothianidin compared favorably to field data. However, this method is empirical and it does not allow the user to adjust the exposure model to other field conditions, such as different furrow depths. The characterization of exposure to furrow-applied insecticides could be improved if the physical processes that govern insecticide transport from the furrow to the surface were incorporated into the model. While neonicotinoids are known to have variable photodegradation rates at the soil surface (Bonmatin et al. 2015), the loss of insecticide due to soil photolysis is not specifically included in the PRZM model. In addition, the exposure of insecticides depends on bioavailability of each insecticide, and bioavailability is not predicted by the existing model. Our findings underscore the need for both improved exposure models (Knäbel et al. 2012, 2014) and better geographic coverage of monitoring data for insecticides (Stehle and Schulz 2015).

One potential uncertainty of the current project was the assumption that the same application method may not be applied for both granular tefluthrin and seed-coated clothianidin. The desorption rates and amounts for granular and seed-coated insecticides may be different, due to either (and perhaps both) the physical differences in granules and coating or the chemical differences in tefluthrin and clothianidin. However, recent theoretical work has shown similar modeled water content and insecticide concentration in the soil profile for furrow-applied and seed-coated thiamethoxam (Agatz and Brown 2017).

In addition to furrow-applied insecticide transport through soil, the current project showed that unintentional and secondary surface application routes, such as particulate matter and guttation droplets, may contribute to clothianidin concentration in runoff water. The impact of clothianidin in guttation droplets on the surface runoff was only estimated in the current project. Future work should include further characterization, including determining the surface interception efficiency of guttation droplets, measuring the amount of clothianidin in guttation droplets through the growing season, using soil moisture to estimate the amount of guttation, and assessing the impact of rainfall intensity on pesticide flux in runoff. Finally, other surface application routes should be characterized, such as crop debris. These results highlight the need for more rigorous and comprehensive measures of neonicotinoid seed coating fate.

Acknowledgements The authors would like to thank K. Strain, S. Whiting, J. Thorngren, M. Lydy, S. Stoneski, A. Taylor, and J. Williams for sample collection and processing. Use of a company or product name does not imply approval or recommendation of the product by Southern Illinois University.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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