



AGRARIAN SCIENCES

Environmental risk for aquatic and terrestrial organisms associated with drift from pesticides used in soybean crops

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Abstract: Several countries included the assessment of environmental drift contamination risk for the registration of pesticides. This practice is not yet totality effective in Brazil; however, due to the large number of pesticides in use, it is important to identify the real contamination risk during pesticide spraying. Therefore, this study determined the indices of environmental risks for exposure to drift from terrestrial applications of fungicides, herbicides, and insecticides that are used in soybean crops under Brazilian climate conditions and established buffer zones for the application of these products. Based on the three prediction drift models for soybeans in Brazil, risk indices were computed for aquatic organisms and terrestrial organisms according to the modelling procedures proposed by the POCER (Pesticide Occupation and Environmental Risk) and HAIR (Harmonized Environmental Indicators for Pesticide Risk) methodologies. In general, aquatic organisms are the most sensitive to drift contamination, being chlorothalonil, trifluralin and chlorpyrifos the ones that presented the higher risk indexes. No risk was found for earthworms; in contrast, the insecticides chlorpyrifos, spinosad and thiamethoxam presented risks to bees regardless of the nozzle (droplet size) used for the determination of the drift curve, resulting in the demand for different buffer zones.

Key words: drift curves, *Glycine max*, pesticide application technology, risk assessment.

INTRODUCTION

Phytosanitary products play an important role in agriculture due to the growing need for high yields and the intensive production of food in a sustainable way. However, the consumption of chemicals used in treatments and the subsequent extensive use of compounds can be a threat to aquatic and terrestrial ecosystems (Kasiotis et al. 2014). In soybean, the main grain crop grown in Brazil, 20 to 25% of the total cost of production is spent in applying phytosanitary products to control diseases, weeds and pest insects (Conab 2017).

Drift from the application of plant protection products is one of the main sources

of environmental contamination in agriculture (Jong et al. 2008, Kruijne et al. 2011, Maski and Durairaj 2010, Tsai et al. 2005, Vercruysse and Steurbaut 2002). In Europe, guidelines (European Commission 2002) force applicators of phytosanitary products (farmers) to have greater control of their applications, especially in terms of drifting.

One of the ways to better address the drift problem is through the use of drift prediction models (Lebeau et al. 2011), or drift curves (functions). These models express the quantity of drift deposited in the soil (percentage of application per hectare) as a function of the distance between an application area and

another area of interest (neighbouring non-target area) (Rautmann et al. 2001).

From these curves, it is possible to calculate the risk index of contamination of other areas, animals and people caused by particles derived from the application of pesticide products.

POCER (Pesticide Occupation and Environmental Risk) is a methodology developed in Flanders (Belgium) with the purpose of quantifying the possible risks of using pesticides in agriculture to the environment and human health using a set of indicators including items for aquatic organisms, such as daphnia, algae and fish; items for terrestrial organisms, such as birds, mammals, earthworms and bees; and occupational risk items for operators, spectators and residents (Vercruyssen and Steurbaut 2002). This set of indicators was considered to be the best among 19 studied by Labite et al. (2011).

HAIR (Harmonised Environmental Indicators for Pesticide Risk) is a more recent methodology developed by the European Community and it is also used to calculate these risk indicators in which more modules and indices have been added, and different toxicological reference values have been used (Garreyn et al. 2007, Kruijne et al. 2011).

As these two methodologies were developed in Europe, it is important for each country to use specific information (toxicological and physical-chemical properties of phytosanitary products, drift curves and climatic data) from the own region in order to obtain greater accuracy in evaluations (Ramos et al. 2000).

Conventionally, the risk of the use of plant protection products is estimated by a risk indicator (RI) calculated as the ratio between the estimated human exposure or predicted environmental concentration (PEC) and a specific toxicological reference value characteristic of each active ingredient (Vercruyssen and Steurbaut 2002, Cunha et al. 2012).

By calculating these risk indices, it is possible to establish buffer zones to reduce exposure, especially that of water bodies to drifting from sprays (European Commission 2009a). These zones are adjacent bands of vegetation that cannot receive the application of pesticide products to protect a sensitive area. The width of these zones is based on distances at which acceptable risk indices are obtained (De Schampheleire et al. 2007). The acceptable index should be less than 1 ($RI < 1$); if this index is greater than or equal to 1, there is a potential environmental risk (CEC 1994, Kruijne et al. 2011, Vercruyssen and Steurbaut 2002).

The unavoidable presence of phytosanitary product molecules in the environment and the possibility of health risks associated with the presence of residues in various commodities have directed the research community to better evaluate the current environmental situation and propose mitigation measures (Kasiotis et al. 2014).

However, studies involving the environmental risk, mainly due to drift, are still sparse, although there are already some models of drift forecasting that have recently been developed for the cultivation of coffee (Alves and Cunha 2014), beans (Bueno et al. 2016a) and soybeans (Bueno et al. 2016b).

The objectives of this study were to estimate the risk of environmental contamination for aquatic and terrestrial organisms due to exposure to particle drift of terrestrial applications of fungicides, herbicides and insecticides used and recommended for soybean cultivation in Brazil by means of the POCER and HAIR methodologies and to establish buffer zones for the application of these products.

MATERIALS AND METHODS

The risk estimates derived from the drift of the application of phytosanitary products in

soybean crops were calculated according to the models proposed by the POCER (Vercruyssen and Steurbaut 2002) and HAIR methodologies (Kruijne et al. 2011).

The risk indices were based on the drift deposits (\hat{Y}) as a function of the distance from the applied area in metres (x), and these values were obtained by means of the drift prediction models generated for the crop of soybeans cultivated in Brazil proposed by Bueno et al. (2016a) (Table I). For the drift calculation, three spectra of droplet sizes were considered, which were fine, medium and coarse.

It is important to highlight that the drift models were generated in Tropical climatic conditions, so the risk assessment in the present work is more intended to these climatic conditions, in special to the *Cerrado* (Brazilian savanna) ecosystem, which are the most important soybean producing region in Brazil (Rezende et al. 2012).

These drift curves are analogous to the “Dutch Model” or “IMAG” proposed by Holterman and van de Zande (2003) (decreasing exponential regressions with four parameters). The main factors that affect drift are the droplet size and the wind speed. The drift curves, used in the risk assessment, were estimated from three droplet spectra and ten replicates under different weather conditions (wind speed around $9.3 \pm 2.7 \text{ km h}^{-1}$) (Bueno et al. 2016a), representing the average drift for each droplet size. The worst cases for spray drift were when fine droplets are used, and the best results with less drift were found. The maximum wind speed recommended to pesticide application is 10 km h^{-1} (Costa et al. 2007).

The focus of this study was to calculate the risk index for targets susceptible to intoxication by droplets derived from sprays. Thus, the risk indices for aquatic organisms (daphnia, algae

Table I. Exponential drift curve models for four parameters estimated in percentile 90 (P90) for soybean crops cultivated in Brazil.

Nozzle Type	Droplet Size ¹	Prediction Drift Model ²	R ² (%) ³
XR 11002	Fine	$\hat{Y} = 19.2760e^{-0.7277x} + 0.2732e^{-0.0353x}$	99.89
TT 11002	Medium	$\hat{Y} = 12.5031e^{-0.6532x} + 0.2362e^{-0.0353x}$	99.91
AIXR 11002	Coarse	$\hat{Y} = 4.2753e^{-0.6477x} + 0.2092e^{-0.0305x}$	99.53

The droplet sizes produced by each tip are in accordance with ASABE standards (S572.1) and the Teejet® manufacturer’s catalogue. ² \hat{Y} : drift deposits (% drift) and x : distance from the applied area (m). ³Significant models according to the F test at the 0.05 significance level. Source: Bueno et al. (2016a).

and fish) and terrestrial organisms (bees and earthworms) were calculated.

The studied pesticides (fungicides, herbicides and insecticides) were selected based on a survey carried out with technical consultants and producers in the region (*Triângulo Mineiro* region) regarding the most-used products in soybean crops. Ten growers and ten agronomists were chosen randomly. After selecting the products, consultations were made to the Agrofit website (Agrofit 2018) to verify whether they were all registered for application in Brazil.

Finally, consultations were carried out with the European Commission database (Dg Sanco 2017) and with the records of the European Food Safety Authority (EFSA 2014) to obtain the ecotoxicological data for each product, since most of the safety data sheet of the products sold in Brazil do not have all the necessary information for risk calculations. The names and characteristics of the chosen products are shown in Tables II, III and IV, and the ecotoxicological data can be found in Table V.

The risk assessment was calculated considering the dose of one application for each pesticide. It is difficult to quantify the number of applications during the soybean season since it

Table II. Fungicides recommended for the chemical control of diseases in soybean crops.

Active Ingredient	Commercial Name - Formulation	Chemical Group	Company	Some Controlled Diseases	Concentration (g L ⁻¹ / g kg ⁻¹)	Dose (kg ha ⁻¹ / L ha ⁻¹)	Toxicological Class ¹	Environmental Class ^{2*}
azoxystrobin + cyproconazole	Priori Xtra CS ¹	Strobirulin + Triazole	Syngenta	<i>Colletotrichum truncatum</i> <i>Corynespora cassiicola</i> <i>Phakopsora pachyrhizi</i>	200 + 80	0.3	III	II
carbendazim	Derosal 500 CS	Benzimidazole	Bayer	<i>Cercospora kikuchii</i> <i>Septoria glycines</i> <i>Microsphaera diffusa</i>	500	0.5	II	III
chlorothalonil	Bravonil CS	Nitriles	Syngenta	<i>Peronospora manshurica</i> <i>Phakopsora pachyrhizi</i> <i>Microsphaera diffusa</i>	500	2.0 a 3.0	II	II
pyraclostrobin + metconazole	Opera Ultra EC ²	Strobirulin + Triazole	Basf	<i>Cercospora kikuchii</i> <i>Corynespora cassiicola</i> <i>Microsphaera diffusa</i>	130 + 80	0.5 a 0.6	I	II
procymidone	Sumilex 500 WP ³	Dicarboximide	Sumitomo	<i>Sclerotinia sclerotiorum</i>	500	1.0	II	II
thiophanate-methyl	Cercobin 700 WP	Benzimidazole	Iharabras	<i>Septoria glycines</i> <i>Cercospora kikuchii</i> <i>Erysiphe diffusa</i>	700	0.43 a 0.6	I	II
trifloxystrobin + prothioconazole	Fox CS	Strobirulin + Triazole	Bayer	<i>Microsphaera diffusa</i> <i>Corynespora cassiicola</i> <i>Phakopsora pachyrhizi</i>	150 + 175	0.3 a 0.4	I	II

*Toxicological classification: I- Extremely Toxic, II- Highly Toxic, III- Moderately Toxic, IV- Somewhat Toxic; **Environmental Hazard Classification: I- Highly Dangerous, II- Very Dangerous, III- Dangerous, IV- Not Very Dangerous (Yamashita and Santos 2009); ¹CS: Concentrated Suspension; ²EC: Emulsifiable Concentrate; ³WP: Wettable Powder.

Table III. Herbicides recommended for the chemical control of weeds in soybean crops.

Active Ingredient	Commercial Name - Formulation	TA ^{**}	Chemical Group	Company	Some Controlled Weeds	Concentration (g L ⁻¹ / g kg ⁻¹)	Dose (kg ha ⁻¹ / L ha ⁻¹)	Toxicological Class ^{**}	Environmental Class ^{**}
2,4 D amine	2,4-D Amine 72 SC ¹	D ⁶	Auxin mimic	Atanor	<i>Euphorbia heterophylla</i> <i>Bidens pilosa</i> <i>Amaranthus viridis</i>	720	1.0 a 1.5	I	III
bentazone	Basagram 600 SC	Pos ⁷	FS II Inhibitor	Basf	<i>Ipomoea grandifolia</i> <i>Bidens pilosa</i> <i>Commelina benghalensis</i>	600	1.2	I	III
fluazifop-P-butyl + fomesafen [#]	Robust ME ²	Pos	ACCase Inhibitor + PROTOX Inhibitor	Syngenta	<i>Euphorbia heterophylla</i> <i>Digitaria horizontalis</i> <i>Amaranthus hybridus</i>	200 + 250	0.8 a 1.0	III	I
flumioxazin	Flumizim 500 WP ³	Pre ⁸ / Pos	PROTOX Inhibitor	Sumitomo	<i>Euphorbia heterophylla</i> <i>Ipomoea grandifolia</i>	500	0.04 a 0.1	II	III
glyphosate	Round up WG ⁴	D / Pos	EPSPs Inhibitor	Monsanto	<i>Digitaria insularis</i> <i>Amaranthus hybridus</i> <i>Ipomoea grandifolia</i>	720	0.5 a 3.5	IV	III
haloxyfop-R methyl ester	Verdict EC ⁵	Pos	ACCCase Inhibitor	Dow Agrosience	<i>Digitaria insularis</i> <i>Eleusine indica</i> <i>Brachiaria plantaginea</i>	124.7	0.4 a 0.5	I	III
paraquat	Gramoxone 200 SC	D	FS I Inhibitor	Syngenta	<i>Amaranthus retroflexus</i> <i>Bidens pilosa</i> <i>Commelina benghalensis</i>	200	1.5 a 2.0	I	II
S-metolachlor	Dual Gold EC	Pre	Tubulin Polymerization Inhibitor	Syngenta	<i>Commelina benghalensis</i> <i>Digitaria horizontalis</i> <i>Amaranthus hybridus</i>	960	1.5 a 2.0	I	II
trifluralin	Premerlin 600 EC	Pre / PIP ⁹	Cell Division Inhibitor	Adama	<i>Alternanthera tenella</i> <i>Amaranthus retroflexus</i>	600	4.0	I	II

^{**}TA: Time of Application; *Toxicological Classification: I- Extremely Toxic, II- Highly Toxic, III- Moderately Toxic, IV- Somewhat Toxic; **Environmental Hazard Classification: I- Highly Dangerous, II- Very Dangerous, III- Dangerous, IV- Not Very Dangerous (Yamashita and Santos 2009); ¹SC: Soluble Concentrate; ²ME: Microemulsion; ³WP: Wettable Powder; ⁴WG: Dispersible Granules; ⁵CE or EC: Emulsifiable Concentrate; ⁶D: Desiccation; ⁷Pos: Post-Emergence; ⁸Pré: Pre-Emergence; ⁹PIP: Pre-incorporated Planting; #There is no information on ecotoxicological data for this active ingredient in the European Union Agrochemicals Database (Dg Sanco 2017) or in the European Food Safety Authority (EFSA 2014) records.

Table IV. Insecticides recommended for the chemical control of insect pests in soybean crops.

Active Ingredient	Commercial Name - Formulation	Chemical Group	Company	Some Controlled Pests	Concentration (g L ⁻¹ / g kg ⁻¹)	Dose (kg ha ⁻¹ / L ha ⁻¹)	Toxicological Class ³	Environmental Class ^{2*}
chlorpyrifos	Nufos 480 EC ¹	Organophosphorus	Cheminova	<i>Epinotia aporema</i>	480	0.8	I	II
spinosad	Tracer CS ²	Spinosinas	Dow AgroScience	<i>Anticarsia gemmatalis</i> <i>Helicoverpa armigera</i>	480	0.012 a 0.05	III	III
flubendiamide	Belt CS	Phthalic acid diamide	Bayer	<i>Chrysodeixis</i> includes <i>Spodoptera frugiperda</i> <i>Helicoverpa armigera</i>	480	0.02 a 0.07	III	III
lambda-cyhalothrin + chlorantraniliprole	Ampligo CS	Pyrethroid + Antranilamide	Syngenta	<i>Hedylepta indicata</i> <i>Pseudoplusia includens</i>	50 + 100	0.05 a 0.075	II	I
lufenuron	Match EC	Physiological (Benzoylurea)	Syngenta	<i>Anticarsia gemmatalis</i>	50	0.225 ⁴	IV	II
methomyl	Lannate BR SC ³	Carbamate	Du Pont	<i>Anticarsia gemmatalis</i> <i>Epinotia aporema</i>	215	0.3 a 2.0	I	II
thiamethoxam + lambda-cyhalothrin	Engego Pleno CS	Neonicotinoid + Pyrethroid	Syngenta	<i>Anticarsia gemmatalis</i> <i>Euschistus heros</i> <i>Nezara viridula</i>	141 + 106	0.15 a 0.2	III	I

*Toxicological classification: I- Extremely Toxic, II- Highly Toxic, III- Moderately Toxic, IV- Somewhat Toxic; **Environmental Hazard Classification: I- Highly Dangerous, II- Very Dangerous, III- Dangerous, IV- Not Very Dangerous (Yamashita and Santos 2009); ¹EC: Emulsifiable Concentrate; ²CS: Concentrated Suspension; ³SC: Soluble Concentrate; ⁴Dose adjusted for the application rate of 150 L ha⁻¹ according to the recommendation of 150 mL of commercial product for each 100 L of water.

Table V. Ecotoxicological data on phytosanitary products recommended in soybean crops in Brazil used to calculate the risk indices of environmental contamination by drift.

Fungicides					
Active ingredient	Dose* (kg or L a.i. ha ⁻¹)	min(NORM _{AO}) ¹ (mg L ⁻¹)	LD ₅₀ bees (µg a.i. bee ⁻¹)	LC ₅₀ earthworms (mg kg soil ⁻¹)	Application Number /Year*
azoxystrobin	0.06	0.13 ^D	25	283	1-2
carbendazim	0.25	0.15 ^D	50	5.4	1-2
chlorothalonil	1.50	0.038 ^F	40	268.5	1-2
cyproconazole	0.024	0.021 ^A	100	167.5	1-2
metconazole	0.048	2.1 ^F	85	500	1-4
procymidone	0.5	1.8 ^D	100	1000	1-2
prothioconazole	0.07	1.3 ^D	71	1000	1-2
pyraclostrobin	0.078	0.006 ^F	73.1	567	1-4
thiophanate-methyl	0.42	5.4 ^D	100	13.2	1-2
trifloxystrobin	0.06	0.011 ^D	200	1000	1-2
Herbicides					
2,4 D amine	1.08	100 ^{D,F}	94	350	1
bentazone	0.72	64 ^D	200	870	1
fluazifop-P-butyl	0.20	0.62 ^D	200	500	1
flumioxazin	0.05	2.6 ^F	200	982	1
glyphosate	2.52	930 ^D	100	480	1-3
haloxyfop-R methyl ester	0.062	0.0884 ^F	100	672	1
paraquat	0.60	4.4 ^D	9.06	1000	1-2
s-metolachlor	1.92	1.23 ^F	85	570	1
trifluralin	2.40	0.088 ^F	100	500	1
Insecticides					
chlorantraniliprole	0.008	0.0116 ^D	4	1000	1-2
chlorpyrifos	0.384	0.001 ^A	0.059	129	1-2
spinosad	0.024	1.0 ^D	0.0036	458	1-2
flubendiamide	0.034	0.06 ^D	200	500	1-2
lambda-cyhalothrin	0.021	0.00021 ^F	0.038	1000	1-2
lufenuron	0.011	0.0013 ^D	197	500	1-2
methomyl	0.43	0.017 ^D	0.16	19	1-3
thiamethoxam	0.028	100 ^D	0.005	1000	1-2

¹Toxicological reference value used for aquatic organisms; ^ANOEC_{Algae}; ^DEC50_{Daphnia}; ^FLC50_{Fish}. *Information from the product safety data sheet. Further information on ecotoxicological data taken from the European Union Agrochemicals Database (Dg Sanco 2017) and European Food Safety Authority (EFSA 2014) records.

depends on the occurrence of pests. Moreover, normally the growers try to use different active ingredients to minimize the problems regarding pesticide resistance, thus, it is not common to apply the same product many times in the same area.

Risk indicators for aquatic organisms

The aquatic indicators express the risk to the aquatic organisms (including algae, daphnia and fish) present in lakes, rivers, ponds and other bodies of water close to agricultural areas and subject to contamination due to the deposition of particles from the drift of the applications of pesticide products.

The descriptions and parameter values of the equations used to calculate the risk indices for aquatic and terrestrial organisms are described in Table VI.

According to the POCER indicator, the predictable environmental concentration (PEC) for aquatic organisms is expressed by Equation 1 (Vercruyse and Steurbaut 2002):

$$PEC_{AO} = \frac{(AR \times \%drift) \times n}{d_{ditch} \times 1000} \quad (1)$$

In which, PEC_{AO} = expected environmental concentration in aquatic organisms ($mg L^{-1}$), AR = active ingredient dose applied ($kg a.i. ha^{-1}$), $\%drift$ = percentage of drift deposited (%), n = number of times the dose was applied and d_{ditch} = depth of water course (m).

The risk index for aquatic organisms ($RI_{Aquaticorganisms}$) was calculated as the ratio between PEC_{AO} and the reference value for aquatic organisms ($\min(NORM_{AO})$) (Equation 5), which is based on the acute toxicity to three groups of aquatic organisms (fish, daphnia and algae). The lowest of the three quotients is used as the toxicological reference for aquatic organisms (Equations 2 to 4) (Bozdogan 2014, Cunha et al. 2012, Vercruyse and Steurbaut 2002).

$$Fish = \frac{LC_{50\ Fish}}{100} \quad (2)$$

In which, $Fish$ = acute toxicity to fish ($mg L^{-1}$) and $LC_{50\ Fish}$ = lethal concentration of the product capable of causing the death of 50% of the test fish population ($mg L^{-1}$).

$$Daphnia = \frac{EC_{50\ Daphnia}}{100} \quad (3)$$

In which, $Daphnia$ = acute toxicity to *Daphnia* ($mg L^{-1}$) and $EC_{50\ Daphnia}$ = lethal effect of the product capable of killing 50% of the population of *Daphnia* (*Daphnia* spp. Leydig) ($mg L^{-1}$).

$$Algae = \frac{NOEC_{Algae}}{10} \quad (4)$$

In which, $Algae$ = acute toxicity to *Algae* ($mg L^{-1}$) and $NOEC_{Algae}$ = No observed effect concentration (highest a.i. concentration that causes no observable adverse effects on an algae test population) ($mg L^{-1}$).

$$RI_{AquaticOrganisms} = \frac{PEC_{AO}}{\min(NORM_{AO})} \quad (5)$$

In which, $RI_{AquaticOrganisms}$ = risk index for aquatic organisms, PEC_{AO} = expected environmental concentration in aquatic organisms ($mg L^{-1}$) and $\min(NORM_{AO})$ = reference for aquatic organisms ($mg L^{-1}$).

In the calculation of the risk indices for aquatic organisms, the distance of 2.5 m in favour of the wind from the edge of the sprayed area was adopted since, in addition to representing the worst case of drift due to proximity to the sprayed area, this is generally the distance between the carriers and the plots within a Brazilian agricultural property. De Schampheleire et al. (2007) established even shorter distances to calculate the risk indices for aquatic and terrestrial organisms associated

Table VI. Descriptions and values used to calculate the risk indices for aquatic (fish, daphnia and algae) and terrestrial (bees and earthworms) organisms.

Parameter	Description	Units	Value used in the study
n	number of times the dose was applied	-	1
d_{ditch}	depth of water course	m	0.5 ¹
f	fraction of deposited a.i. intercepted by the culture	-	0 ¹
d_{Soil}	depth of soil where the drift is deposited	m	0.05 ¹
ρ_{Soil}	soil density	kg m ⁻³	1300 ²

¹The coefficients used in the equations are defined according to the guidelines of European Standard 1107/2009 (European Commission 2009b). ²Average soil density value for the area where drift curve studies were carried out for soybean crops (Resende et al. 2012).

with target crops such as barley, potato, sugarcane and pasture.

It is important to note that Brazilian environmental legislation establishes a minimum distance between agricultural areas and watercourses (rivers, streams and lakes), which varies according to the type and size of each body of water (Brasil 2012). Thus, it is important to adapt this approach to each region.

Risk indicators for terrestrial organisms

The terrestrial risk indicators were calculated for bees, as they are beneficial insects subject to contamination by pesticide products, mainly when the applications are carried out during the flowering period, the time during which these insects are present in large quantities in cultivated areas. The calculation of the acute risk index consists of evaluating the impact of spray droplets from a single application on bee survival (Flari et al. 2007). This index takes into account only cultivation in an open field during the pre-flowering, flowering or other period of attraction for bees but does not take into consideration the presence or absence of flowering weeds in the area of application.

The risk index for bees (RI_{Bees}) was calculated using Equation 6 (Cunha et al. 2012, De Schampheleire et al. 2007, Vercruysse & Steurbaut 2002).

$$RI_{Bees} = \frac{AR \times \%drift}{(LD_{50Bees} \times 50)} \times 1000 \quad (6)$$

In which, RI_{Bees} = risk index for bees, AR = active ingredient dose applied (kg a.i. ha⁻¹), $\%drift$ = percentage of drift deposited (%) and $LD_{50 bees}$ = lowest value between oral LD_{50} and contact LD_{50} ($\mu\text{g a.i. bee}^{-1}$).

The risk index for earthworms ($RI_{Earthworms}$) was also calculated because the droplets can be deposited in the soil due to drift, thereby contaminating the organisms which live within it (Equation 8). In this way, the PEC_{Soil} used for the calculation refers to the soil (Equation 7). The depth to which the drift was assumed to be deposited in the soil was 5 cm (Bozdogan 2014, De Schampheleire et al. 2007, Vercruysse and Steurbaut 2002).

$$PEC_{Soil} = \frac{(AR \times \%drift \times n \times (1 - f))}{(d_{Soil} \times \rho_{Soil})} \quad (7)$$

In which, PEC_{Soil} = predicted soil environmental concentration (mg kg⁻¹ soil), AR = active ingredient dose applied (kg a.i. ha⁻¹), $\%drift$ = percentage of drift deposited (%), n = number of times the dose was applied, f = fraction of deposited a.i. intercepted by the culture, d_{Soil} = depth of soil where the drift is deposited (m) and ρ_{Soil} = soil density (kg m⁻³).

$$RI_{Earthworms} = \frac{PEC_{Soil} \times 10}{LC_{50 Earthworms}} \quad (8)$$

In which, $RI_{Earthworms}$ = risk index for earthworms, PEC_{Soil} = predicted soil environmental concentration ($mg\ kg^{-1}$ soil) and $LC_{50 Earthworms}$ = the acute median lethal concentration for earthworms ($mg\ kg\ soil^{-1}$).

For the calculation of risk indices and buffer zones for terrestrial organisms (earthworms and bees), a distance of 2.5 m in favour of the wind was also adopted from the edge of the sprayed area.

RESULTS AND DISCUSSION

Risk index for aquatic organisms

The fungicide carbendazim and the herbicide S-metolachlor presented a risk to aquatic organisms only if sprayed using fine droplets (XR tip) and therefore require a buffer zone at least 3 m away from the application area (Table VII).

The fungicides chlorothalonil, pyraclostrobin and trifloxystrobin, the herbicide trifluralin and the insecticides lambda-cyhalothrin, lufenuron and methomyl presented environmental risk when applied at any of the three droplet sizes studied: fine, medium and coarse (XR 11002, TT 11002 and AIXR 11002, respectively); however, increasing the drop pattern size reduced the risk index and consequently decreased the distance from the buffer zone required for all these active ingredients (Table VII) with the exception of lambda-cyhalothrin because of the inclination of the curves at distances close to 50 m.

An increase in droplet size (from fine to coarse) failed to reduce the risk index of only the insecticide chlorpyrifos, which therefore required a buffer zone greater than 50 m.

Chlorpyrifos is an insecticide in the group of organophosphates widely used in Brazil and is the only product registered for application in three different ways: aerial, terrestrial and through chemigation. However, this product has a high risk to aquatic organisms, mainly due to the low concentrations at which species of *Daphnia* are affected (EPA 2002). Thus, the high risk values and the need to establish large buffer zones were already expected for this active ingredient.

The creation of buffer zones, in addition to being a barrier when there is spray drift (some of the droplets can move away from the sprayed area and be deposited elsewhere), also help to limit the flow of product waste to the water surface and groundwater losses due to soil losses (Carluer et al. 2011).

Thus, it is essential to comply with environmental laws, respecting the distance between arable areas and legal reserves, permanent preservation areas and water bodies, in order to minimize the contamination of the organisms living in aquatic environments. Furthermore, this study considered the worst situation, in which the watercourse occurs 2.5 m from the target area.

Risk index for terrestrial organisms

No environmental risk due to the drift caused by the application of the fungicides and herbicides evaluated in soybean cultivation to bees located 2.5 m away from the target area was shown (Table VIII).

The insecticides chlorpyrifos, spinosad and thiamethoxam presented contamination potential for all droplet sizes ($RI > 1$). An increase in the droplet size reduced the risk indices for these products, but these values were only less than one when buffer zones of between 3 and 5 m were established. Methomyl also presented a risk with the use of fine and medium droplets (SZ

Table VII. Risk indices and buffer zones for aquatic organisms due to drift 2.5 m from the target area resulting from the application of recommended phytosanitary products to control diseases, weeds and pests in soybean.

Active Ingredient	Fungicides					
	Fine Droplets (XR 11002)		Medium Droplets (TT 11002)		Coarse Droplets (AIXR 11002)	
	RI _{AO}	SZ _{RI=1}	RI _{AO}	SZ _{RI=1}	RI _{AO}	SZ _{RI=1}
azoxystrobin	0.3116	-	0.2454	-	0.0961	-
cyproconazole	0.0772	-	0.6608	-	0.0238	-
carbendazim	1.1252	3.0 m	0.8862	-	0.3469	-
chlorothalonil	26.6501	22 m	20.9892	18 m	8.2149	16.5 m
metconazole	0.0154	-	0.0122	-	0.0048	-
procymidone	0.1875	-	0.1477	-	0.0578	-
prothioconazole	0.0364	-	0.0286	-	0.0112	-
pyraclostrobin	8.7768	7 m	6.9125	6.5 m	2.7054	5 m
thiophanate-methyl	0.0525	-	0.0414	-	0.0162	-
trifloxystrobin	3.6826	5 m	2.9003	4.5 m	1.1351	3 m
Herbicides						
2,4 D amine	0.0073	-	0.0057	-	0.0022	-
bentazone	0.0076	-	0.0060	-	0.0023	-
fluazifop-P-butyl	0.2178	-	0.1715	-	0.0671	-
flumioxazin	0.0130	-	0.0102	-	0.0040	-
glyphosate	0.0018	-	0.0014	-	0.0006	-
haloxyfop-R methyl ester	0.4762	-	0.3750	-	0.1468	-
paraquat	0.0921	-	0.0725	-	0.0284	-
s-metolachlor	1.0539	3 m	0.8300	-	0.3249	-
trifluralin	18.4128	12 m	14.5017	10.5 m	5.6757	8.5 m
Insecticides						
chlorantraniliprole	0.4365	-	0.3438	-	0.1346	-
chlorpyrifos	2.592.5184	> 50 m	2.041.8336	> 50 m	799.1444	> 50 m
spinosad	0.0162	-	0.0128	-	0.0050	-
flubendiamide	0.3781	-	0.2978	-	0.1165	-
lambda-cyhalothrin	68.1565	48.5 m	53.6792	44.5 m	21.0093	47.5 m
lufenuron	5.8425	5.5 m	4.6015	5.5 m	1.8010	4 m
methomyl	17.0769	11 m	13.4496	9.5 m	5.2640	8 m
thiamethoxam	0.0002	-	0.0001	-	0.0001	-

RI_{AO}: Indicator of risk to aquatic organisms 2.5 m from the target area of application; SZ_{RI=1} = 1: Buffer zone for aquatic organisms considering a risk of less than or equal to one.

= 3.5 m), while the use of coarse droplets did not present a potential risk (Table VIII). Methomyl is a carbamate insecticide toxic to bees both by direct contact and through ingestion (Mayer et al 1989). Therefore, applications should be coordinated with periods of minimum bee activity.

Chlorpyrifos is highly toxic to bees, and, as also occurred with aquatic organisms, some type of risk was already expected (EPA 2002). Regarding thiamethoxam, Antunes-Kenyon & Kennedy (2001) found that, independent of the form of contamination (spray, intake, or residue on the surface of the culture), it was extremely toxic to bees, causing the death of more than 80% of the specimens after 3 days. Although the action occurs in the nervous system, secondary targets may also be affected by this compound.

Spinosad is an insecticide of biological origin. Its mechanism of action causes hyperexcitation of the insect nervous system. Because of the mode of action of this product, it can affect not only insect pests but also beneficial organisms, such as pollinating bees. Thus, as studies on the real risk of spinosad to bees are still necessary, one of the ways to prevent this risk is to reduce the dose of the product when possible and using products with lower ecotoxicological effects (De Schampheleire et al. 2007).

All active ingredients showed zero or low contamination risk for earthworms at a distance of 2.5 m or more from the target area of application (Table IX). Even when these ingredients are applied using fine (XR 11002) or medium (TT 11002) droplet production tips, there is no risk. However, the choice of the spray tip involves several other factors (environmental, technical, type of crop, target application) and therefore cannot be based solely on risk analysis.

The herbicide glyphosate is one of the most widely used products in the world, including

Brazil, mainly after the switch from conventional crops to herbicide-resistant genetically modified crops. This change caused a generalized change in the patterns of herbicide use and cultivation practices (Cerdeira et al. 2007, Graef et al. 2007, Kleter et al. 2008). The main change was the use of this herbicide not only for desiccation but also for post-emergence application, consequently increasing the presence of residues of this active ingredient in the soil and in the environment.

The present study did not detect any environmental risk related to the drift of glyphosate applications in soybean crops for any of the tips (XR 11002, TT 11002 and AIXR 11002) or droplet sizes (fine, medium and coarse). A study of herbicide risk assessment in transgenic maize crops also found no risk of glyphosate contamination for aquatic organisms, bees, earthworms or bystanders (Devos et al. 2008).

It is important to highlight that the risk assessment was calculated considering the dose of one application, as explained in the methodology. However, sometimes glyphosate may be used more than one time during the season, so, in this case, more studies are necessary to understand this effect on the environmental risk.

Although the application of glyphosate did not present a potential risk, the continuous and exclusive use of the molecule in resistant plants is not always the best management practice. The ideal approach would be the rotation of herbicides with different mechanisms of action, since the repeated use of the same active ingredient may induce weed tolerance or resistance (Christoffoleti and López-Ovejero 2003).

The herbicide 2,4-D amine is also widely used in Brazilian agriculture for weed control during post-emergence and desiccation, but it is one of the main products whose use has been questioned regarding environmental risk (Souza

Table VIII. Risk indices and buffer zones for bees due to drift 2.5 m from the target area due to the application of recommended phytosanitary products for the control of diseases, weeds and pests in the soybean crop.

Active Ingredient	Fungicides					
	Fine Droplets (XR 11002)		Medium Droplets (TT 11002)		Coarse Droplets (AIXR 11002)	
	RI _B	SZ _{RI=1}	RI _B	SZ _{RI=1}	RI _B	SZ _{RI=1}
azoxystrobin	0.0016	-	0.0013	-	0.0005	-
cyproconazole	0.0002	-	0.0001	-	0.0000	-
carbendazim	0.0034	-	0.0027	-	0.0010	-
chlorothalonil	0.0253	-	0.0199	-	0.0078	-
metconazole	0.0004	-	0.0003	-	0.0001	-
procymidone	0.0034	-	0.0027	-	0.0010	-
prothioconazole	0.0007	-	0.0005	-	0.0002	-
pyraclostrobin	0.0007	-	0.0006	-	0.0002	-
thiophanate-methyl	0.0028	-	0.0022	-	0.0009	-
trifloxystrobin	0.0002	-	0.0002	-	0.0001	-
Herbicides						
2,4 D amine	0.0078	-	0.0061	-	0.0024	-
bentazone	0.0024	-	0.0019	-	0.0007	-
fluazifop-P-butyl	0.0007	-	0.0005	-	0.0002	-
flumioxazin	0.0002	-	0.0001	-	0.0001	-
glyphosate	0.0170	-	0.0134	-	0.0052	-
haloxyfop-R methyl ester	0.0004	-	0.0003	-	0.0001	-
paraquat	0.0437	-	0.0345	-	0.0135	-
s-metolachlor	0.0153	-	0.0120	-	0.0047	-
trifluralin	0.0162	-	0.0128	-	0.0050	-
Insecticides						
chlorantraniliprole	0.0013	-	0.0010	-	0.0004	-
chlorpyrifos	4.3941	5 m	3.4607	5 m	1.3545	3.5 m
spinosad	4.5009	5 m	3.5449	5 m	1.3874	3.5 m
flubendiamide	0.0001	-	0.0001	-	0.0000	-
lambda-cyhalothrin	0.3767	-	0.2966	-	0.1161	-
lufenuron	0.0000	-	0.0000	-	0.0000	-
methomyl	1.8144	3.5 m	1.4229	3.5 m	0.5593	-
thiamethoxam	3.8078	5 m	2.9989	4.5 m	1.1737	3 m

RI_B: Risk indicator for bees 2.5 m from target area of application; SZ_{RI=1}: Buffer zone for bees considering a risk equal to one.

et al. 2011). With extensive and often inadequate use, it has become a problem, mainly due to soil and groundwater contamination (Fu et al. 2009), and it causes problems in neighbouring areas, with damage to susceptible crops (Oliveira Júnior et al. 2007).

However, in this study, this active ingredient presented no risk potential for the groups of indicators studied (aquatic and terrestrial organisms) regardless of the droplet size used in the application. The 2,4-D ingredient also showed no environmental risk for any of these groups of indicators in the wheat crop in Turkey (Yarpuz-Bozdogan 2009).

CONCLUSIONS

Aquatic organisms, which have practical utility in current hazard assessment as an indicator, were the most sensitive to drifting contamination by the products considered in this study. The fungicide chlorothalonil, the herbicide trifluralin and the insecticides chlorpyrifos and lambda-cyhalothrin presented the highest risk levels, requiring, in some cases, buffer zones greater than 50 m in relation to the target area.

No environmental risk was observed for earthworms. For bees, the insecticides chlorpyrifos, spinosad and thiamethoxam presented risk regardless of the nozzle type (droplet size) used to produce the drift curve.

The use of nozzles that produce coarse droplets is generally able to considerably reduce the risks of drift contamination.

This study may be a useful tool for the selection of active ingredients of relatively low environmental impact for the chemical control of diseases, weeds and pests in soybean crops. In addition, it denotes the importance of investigating alternative cultural practices that allow the reduction of pesticide use.

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