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Methods to Estimate Losses in Preemergence Herbicide Sprays

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Contamination of the environment by agrochemicals, especially in non-target areas, has brought up severe criticism against the use of these products, and great concerns with regard to their harmful effects. The most commonly employed process to study the fate of agrochemical sprays has been the analysis of deposits of these substances on the surface of plants, on artificial targets, or by means of specific sampling equipment. The addition of easily detectable tracers to the spraying mixes has become a largely employed practice. The cost of the analyses, the availability of analytical equipment and the desired precision for the results represent important factors in the selection of the tracer to be used in the assays (Chaim et al., 1999). Some researchers have utilized as tracers the agrochemical itself (Cavenaghi et al., 2002), fluorescent particles, such as ZnCaS (Murray and Vaugham, 1970), marked agrochemicals (Maybank et al., 1974), radioisotopes (Dobson et al.,1983), salts, such as NaCl (Velini et al., 1995), fluorescent pigments, and food dyes (Palladini, 2000). The following collector types can be used to quantify losses: air sample volumetric collectors, rotary collectors, passive surfaces, laser-based systems, and indicator plants (Miller, 1993). The objective of this work was to develop and compare methods to estimate losses in preemergence herbicide applications, using the herbicide Tebuthiuron and Brilliant Blue dye as tracers. Tracer losses by settling and by air transport were measured by means of passive collecting surfaces.

MATERIALS AND METHODS

The experiment was installed and conducted in a one hectare area without plant cover, of Faculdade de Ciências Agronômicas of Universidade Estadual Paulista, in the Botucatu Campus, where the soil was a medium-textured Dark Red Dystrophic Latosol, allowing preemergence applications.

The tracers used to estimate spray losses were the herbicide Tebuthiuron, in the suspension concentrate formulation (commercial product Combine 500 SC), and the Brilliant Blue food dye (FD&C no.1). Losses originated from tracer deposition out of the treated area (settling) were determined on styrofoam trays measuring 0.173 × 0.256 m (0.044288 m^2) and 1.5 cm in height. The exposure area of each

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tray was filled with 100g of soil, collected superficially at the assay location and dried prior to use in a greenhouse. The collectors, 100 in number, were randomly distributed through the experiment area. Nylon strands with a diameter of 2 mm, stretched and fixed in a parallel fashion along iron tubes measuring 6 m in length and 1.59 cm in diameter were used to estimate air-transport losses (drift). Each tube had two strands with a usable length of 5 m each, fixed at 1m intervals.

A 0.34 ha area from the central section of the total area of the experiment, which was equivalent to 1 ha, was selected to perform the application, resulting in one area surrounded by 4 areas adjacent to it (sides). In order to estimate air-transport loss, the collectors were fixed and aligned at distances of 1, 2, 4, 8, and 16 m from the application swaths, with 4 replicates for each distance, on each side.

Two Condor M-12 boom sprayers, with 12 m spray booms, 600 L capacity tanks and 24 SF 11002 spray nozzles, spaced at 0.50 m intervals, were used for the applications. The herbicide Tebuthiuron (0.73% and 167.75 $L.ha^{-1}$) was used in one of the sprayers, while the other received the Brilliant Blue dye (0.60% and 163.75 $L.ha^{-1}$); both applications were performed simultaneously in the same area. The work pressure and the travel speed were, respectively, 45 psi and 6 $km.h^{-1}$, in both sprays. The boom height in relation to the ground was 0.50 m. During the applications, wind speed and direction at a 2.0 m height from the ground, relative humidity, and air temperature, were recorded at 3-minute intervals. A digital anemometer and a digital thermohygrometer, a windsleeve and a compass were used to that effect. Upon finishing the application, samples were taken from the mixes by collecting the liquid sprayed at the spraying tips, for later determination of the precise concentrations of the applied solutions and, 30 minutes after applying, the collection and packaging of samples was initiated. The Nylon strands were sectioned so as to produce five collection height intervals in relation to the ground: 0 to 1, 1 to 2, 2 to 3, 3 to 4 and 4 to 5 m. The strand sections and soil samples of the deposition collectors were packaged in polyethylene bags; the bags were later stored in a dark room maintained at a temperature of 20 ± 2 °C, until the moment of tracer extraction in the laboratory.

For fortification of the samples, portions of 10 g soil and 1 m Nylon strand were contaminated using 100 e 3 μL, respectively, of standard solutions with 1,000, 2,000, 3,000, 4,000, 5,000 and 6,000 $mg.L^{-1}$ of herbicide and 1,250, 2,500, 3750, 5,000, 6,250 e 7,500 $mg.L^{-1}$ of Brilliant Blue, with 6 replications for each tracer. For simulate the deposit of spraying drops on collectors, chromatography microserying of 250 μL for soil and 5 μL for strand were used, being the volume distributed at different sites on matrixes for each drop made at exit of needle, with minor size possible. The source of Tebuthiuron was provided by Lilly Elanco with 99.5% purity and the Brilliant Blue was bought at Duas Rodas Ltda Company, with 100% purity.

Two portions of 10 g soil from each replicate were used to extract the tracers contained in the soil from the deposition collectors; one portion was washed with 50 mL distilled water, to extract the Brilliant Blue dye, and the other was washed with 50 mL methanol to extract the Tebuthiuron. Those samples were stirred on a stirring table for soil analysis, with the tubes in the vertical position, for 2 hours at 230 rpm, and were later submitted to ultrasound treatment for 15 minutes. The soil washing process was concluded by leaving the samples to rest for 24 hours, in order to allow the soil particles to settle. The Nylon strand sections from each replicate were rinsed with 40 mL distilled water to extract both tracers, within their own polyethylene plastic bags. The washing solutions thus obtained were filtered with 3.0 ml polyethylene syringes, equipped with a model HV Millex polyethylene Millipore brand filter with a durapore membrane 0.45 micrometer (μm) in thickness and a diameter of 13.0 mm.

For quantify the Tebuthiuron, the washing solutions of the soil and strand samples were beforehand prepared in movable phase (v.v^{-1}): methanol:water (50:50) for injection and analyze in a high resolution liquid chromatograph, model LC-10 AC, with UV-visible spectrophotometric detector (absorbance at 254 nm), model LC-10 AD, both of them brand Shimadzu, equipped with column silica-octadecyl-polymer (C_{18}). For quantify the Brilliant Blue, it was determined the optic density (absorbance) at 630 nm, directly from soil and strand washing solutions, using UV-visible spectrophotometer, brand GBC and model Cintra 40.

For the field samples, the original concentration of the soil washing solution, in mg L^{-1}, was transformed into percentage of tracer deposit, in relation to the total applied, by dividing the concentration of the original solution of the samples by the expected (theoretical) concentration in the washing solution (50 ml water), considering that all the applied mix containing the tracers reached the soil (100%). For the strand washing solutions, the concentrations found in the samples were transformed into application volume deposited per strand surface area (nL.cm^{-2}).

The data for tracer mix deposits (Tebuthiuron and Brilliant Blue) on the drift collectors, in nL.cm^{-2}, were analyzed as a completely randomized design in a 4 × 5 × 5 factorial scheme, with 4 collector sides, 5 distances and 5 heights in relation to the applied area, and the means were compared by t test ($p<0.05$). The tracer deposit percentage values for the deposition collector data were adjusted to Gompertz model to represent accumulated frequency, expressed as percentages, with the SAS statistical software program. The model was simplified and the values for mode, median and coefficient of variation were calculated according to Velini (1995). The level of precision of Gompertz's model was evaluated by the coefficients of determination and by the residual sums of squares for the equations.

RESULTS AND DISCUSSION

The mean values for temperature, wind speed and relative humidity recorded during tracer application were: 25.8 °C, 7.1 km.h^{-1} and 43.5%. The predominant wind directions, at a 2 m height, were NE and SE. The tracer concentrations in the application mix samples, after spectrophotometry and chromatography analyses, were 4,315.27 mg.L^{-1} for Brilliant Blue and 5,453.10 mg.L^{-1} for Tebuthiuron.

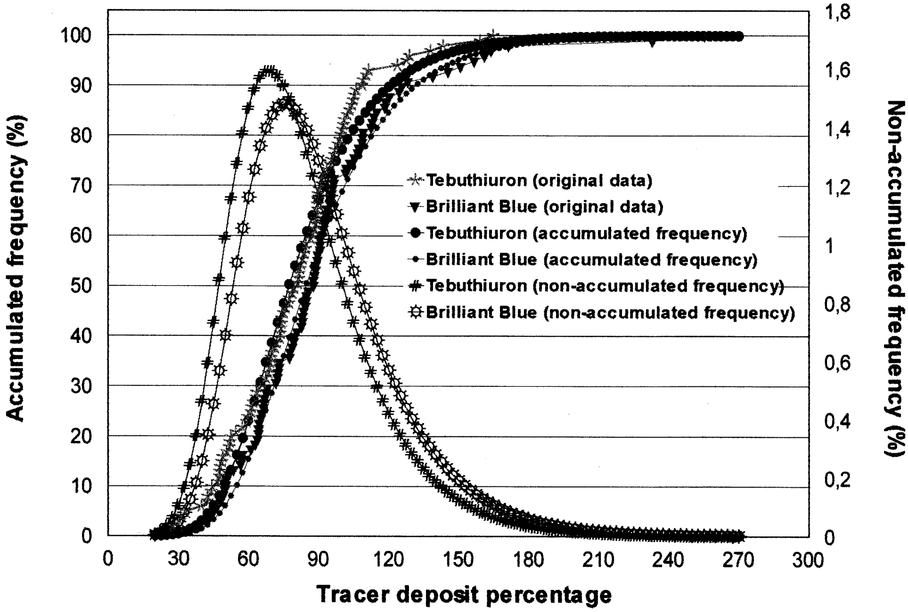

Figure 1. Accumulated and non-accumulated frequencies as a function of deposit percentages for the Brilliant Blue tracer, in relation to the total amount applied (adjusted data).

The means recuperations on soil fortified samples were 90.49 for Brilliant Blue and 90.60 and for Tebuthiuron. However, these values may vary with soil type. Cavenaghi et al. (2002) obtained a mean recovery of 67.75% in the extraction of the same herbicide in the soil, using a similar deposition collector (trays containing 240 g soil) and high resolution liquid chromatography in the analysis of samples. With regard to tracers in the drift collectors (strand fortified samples), mean recoveries of 95.64 and 74.55% were verified for Brilliant Blue and Tebuthiuron, respectively. The limit of detection of analytical methods for both tracers was 0.05 mg.L^{-1}.

Figure 1 presents rows corresponding to the accumulated and non-accumulated frequencies as a function of deposition, represented as percentages of tracer deposits (Tebuthiuron and Brilliant Blue), in relation to the total applied (original and estimated data). The regression analysis results, coefficients of determination, F values for the regression at the 1% probability level, as well as the parameters used by the model for the tracer deposit percentages in relation to the total applied, can be found in Table 1.

It can be seen that the slopes of the accumulated frequency curves for the original and adjusted data were very similar for both tracers, indicating very close data dispersion; the same is true of the probability density curves (Figure 1); this is confirmed by the proximity of the parameter “c” values, shown in Table 1. In addition, the coefficients of determination suggest a high level of precision since the Gompertz model was used to fit the data. However, there is little difference between the concavities of the non-accumulated frequency curves, with the Brilliant Blue dye curve being flatter than the curve for the herbicide Tebuthiuron. According to Velini (1995), the greater the kurtosis (i.e., the flatter the curve) the greater the frequency of extreme values. In this sense, this difference can be explained based on the original data, where the highest percentage of deposits obtained for Brilliant Blue and Tebuthiuron, respectively, was eight- and six-fold greater than the smallest percentage found for each of those tracers. According to Tofoli (2002), this irregularity in deposition could lead to the need for increasing the rate of applied herbicides to compensate for drift losses.

Table 1. Regression analysis results between the tracer deposit percentages (Brilliant Blue and Tebuthiuron), in relation to the total applied, using Gompertz model.

Gompertz Model	Tracer	
Y = e**(A-e**(-B-C*X))	Brilliant Blue	Tebuthiuron
Estimate for parameters	A = 4.605170 B = -3.040705 C = 0.040241	A = 4.605170 B = -2.983045 C = 0.043329
Total SS	327,678.32616	341,683.16831
Regression SS	328,350.50515	340,284.14052
Residual SS	672.17900	1,399.02779
Regression F	23,155.61332**	12,039.83912**
R^2	0.991684	0.983376

Y = accumulated frequency percentage; X = tracer deposit percentage in relation to total applied; A, B and C are model parameter estimates for the respective tracers; ** significant at 1% probability.

The mean, median, mode and coefficient of variation values for the deposit percentages of their corresponding tracers in relation to the total applied were very close: 87.6%, 81.5%, 75.6%, 40.3%, and 79.8%, 77.3%, 68.8%, 34%, for Brilliant Blue and Tebuthiuron, respectively. Tofoli (2001) questions the use of mean values to indicate deposition of agricultural sprays, because when a certain rate of a given herbicide is applied, the most frequent point dose (mode) in the area can be quite lower than the mean dose. Considering the mode as a parameter for comparison of losses occurred between preemergence tracer applications, it can be inferred that the resulting losses showed very close values: 24.4% for Brilliant Blue and 31.2% for Tebuthiuron, in relation to the applied totals for each tracer.

The method used for deposition loss evaluation proved to be a viable alternative to estimate preemergence spray losses, since it presents deposit data with a high degree of reliability and precision. In addition, deposition collectors are inexpensive, and are easy to assemble and to handle. According to observations by Palladini (2000) and Maciel (2001), the dye demonstrated to be advantageous in this type of study because it is atoxic, inexpensive, non volatile, is not photodegradable until 8 hours after applying, does not change the water's surface tension, allows for complex and costly chromatographic procedures involved in the detection and quantification of herbicides to be replaced with simple and low-cost spectrophotometric procedures.

Table 2. Influence of side, distance and height of collectors on drift after tracer spraying in preemergence.

		Brilliant Blue	Tebuthiuron
Variation Factors	DF	F Values (α) and drift means (nL.cm^{-2})	F Values (α) and drift means (nL.cm^{-2})
Side (L)	3	8.32 (0.01)*	4.53 (0.40)*
Distance (D)	4	3.08 (1.66)*	2.08 (8.27)*
Height (H)	4	5.99 (0.01) *	2.42 (4.83)*
L × D	12	0.84 (60.60) n.s.	0.82 (62.71) n.s.
L × H	12	4.17 (0.01)*	1.09 (37.14) n.s.
D × H	16	0.98 (47.35) n.s.	0.84 (64.45) n.s.
L × D × H	48	0.56 (99.18) n.s.	0.66 (96.05) n.s.
CV (%)		359.44	560.86
Drift means (nL.cm^{-2})			
Side 1 (NE)		2.368 B	0.085 B
Side 2 (NO)		1.701 B	1.222 A
Side 3 (SO)		11.260 A	0.553 B
Side 4 (SE)		2.321 B	0.008 B
MSD 5%		3.701	0.612
1 m distance		9.034 A	1.090 A
2 m distance		5.575 AB	0.573 AB
4 m distance		4.238 BC	0.525 AB
8 m distance		1.932 BC	0.123 B
16 m distance		1.284 C	0.025 B
MSD 5%		4.138	0.684
0 to 1 m height		12.098 A	0.930 A
1 to 2 m height		3.414 B	0.957 A
2 to 3 m height		2.628 B	0.373 AB
3 to 4 m height		2.186 B	0.045 B
4 to 5 m height		1.736 B	0.030 B
MSD 5%		4.138	0.684

* significant at a probability level equal to the α value

n.s. = non significant, depending on α value

Means on the same column and within the same factor do not differ statistically among themselves by T test ($p<0.05$).

From Table 2, it can be verified that significant factor effects occurred, related to the positioning of the drift collectors, such as side, distance, and height, on tracer deposit levels. In general, these factors act upon drift independently. However, there were significant interactions between factors side and height for the Brilliant Blue tracer drift captured by the collectors. With regard to the Tebuthiuron tracer, it can be verified that side 2, at NO, showed the greatest drift values, on average 5.7 times higher than on the other positions. For this tracer, deposits detected from 0 to 1 and from 1 to 2 m in height differed significantly from those obtained at heights from 3 to 4 and from 4 to 5 m. It can be seen as well that the greatest deposits, for both tracers, occurred at a distance of 1.0 m from the applied area and, in general, the deposited drift decreased as the distance relative to the application area increased.

Table 3. Mean drift values ($nL.cm^{-2}$), after spraying the Brilliant Blue tracer in preemergence for the Side × Height (L × H) interaction.

Side	Height (meters)				
	0 to 1	1 to 2	2 to 3	3 to 4	4 to 5
Side 1 (NE)	3.604 a[1]A[2]	2.572 aA	1.892 aA	2.279 aA	1.494 aA
Side 2 (NO)	2.413 aA	1.465 aA	1.225 aA	1.178 aA	2.223 aA
Side 3 (SO)	38.062 bA	8.078 aB	5.246 aB	2.405 aB	2.511 aB
Side 4 (SE)	4.313 aA	1.541 aA	2.150 aA	2.881 aA	0.717 aA

[1,2] Means on the column and on the row, followed by the same lower and upper case letters, respectively, do not differ among themselves by T test ($p<0.05$).

Side 3 (SO) showed deposits significantly higher in relation to the other sides, only within the 0 to 1 m height (11.1 times higher, on average). Similarly, within factor height, only side 3 showed significant differences; at the height from 0 to 1 m tracer deposits were significantly higher (8.3 times, on average) than those found at the other heights (Table 3).

Based on the deposit means calculations, considering all levels of factors side, distance or height, it can be verified that the overall mean for the Brilliant Blue tracer deposits, of 4.413 $nL.cm^{-2}$, was almost nine-fold higher than that obtained for Tebuthiuron, with a value of 0.467 $nL.cm^{-2}$ (Table 2). In addition, the sum of tracer mix volumes detected in all drift collector replicates represents only 0.16 and 0.02% of the total mix volume applied in the experiment area (3,400 m^2), for the Brilliant Blue dye and the herbicide Tebuthiuron, respectively. Therefore, the estimates of losses by tracer settling during application, which showed very close percentage values (24.4 and 31.2%), did not indicate a relationship with deposits detected in the drift collectors, since the drift verified on the Nylon strands was much higher for Brilliant Blue. This suggests that tracers with similar drift potentials may generate different deposits on targets for the quantification of the process.

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