AGRICULTURAL SPRAY DEPOSIT QUANTIFICATION METHODS

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ABSTRACT. *Spray deposit evaluations have been used in research as a tool to develop and improve pesticide application techniques. Lab tests were conducted to compare methods for deposit quantification using different tracers (Brilliant Blue food dye, copper and sodium ions, Rhodamine B, and tebuconazole) on different targets. The artificial targets, were more efficient in recovering the spray deposits, except when capturing Brilliant Blue dye. The copper tracer (Cobox®) and the fungicide gave us better results on artificial and natural targets. The results have also shown a good suitability for the use of Brilliant Blue, particularly on natural targets. The selection and reliability of quantitative analysis methods for spray deposits were dependent on the target nature (natural or artificial), tracer substance, and target-tracer interaction.*

Keywords. *Application technology, Tracer, Target.*

Many research trials have been conducted with application technologies for testing spray deposition and drift of pesticides.

Spray efficacy of application techniques and equipment used in pest, disease, and weed control have been evaluated through deposition studies, and it is important that minimum product be applied to obtain the intended biological effect, considering the environment. Spray deposit evaluations have been used in research as a tool to develop and improve pesticide application techniques.

Natural or artificial targets can be used in a droplet deposition study. Both types of targets have strengths and weaknesses. Cooke and Hislop (1993) indicated that the choice between targets (natural and artificial) depends on the circumstances of use and research priority. Natural targets should be preferred, but their complexity and natural variability affect spray retention and spreading. Artificial targets are more uniform and, can be positioned on pre-established locales and help establish the relative differences between treatments. However, the behavior of artificial targets differs from that of natural targets. As a function of the age natural targets behavior can be variable in relation to spraying retention and spreading.

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Tracer substances, such as mineral chelates (iron, cobalt, copper, manganese, molybdenum, and zinc), perform similarly to pesticides under the similar conditions. These mineral chelates are used as horticultural leaf fertilizers, and hence, their use in normal concentrations does not damage the crop (Nuyttens et al., 2004). Fluorescent pigments in food dyes and pesticides have also been quite practicable for evaluating spray deposits. Yates and Akesson (1963) reported that a product to be used as a tracer must include features such as high sensitivity to detection, the ability to be used quickly in quantitative analysis, solubility when added to a spray mix, have minimal physical effect on droplet spraying and evaporation, and have distinct properties to allow differentiation of the tracer from other substances; in addition, they must be stable, nontoxic, and of moderate cost. These characteristics have been supported by Palladini et al. (2005) in spray tracer selection.

Different methods can be used to quantify tracers on target surfaces. Palladini et al. (2005) used a spectrofluorometer to detect the Brilliant Blue food dye tracer. Christovam et al. (2010) used atomic absorption spectrophotometry to quantify copper ion, and Popp et al. (2010) used high-efficiency liquid chromatography coupled to mass spectrometry, which allows the determination and quantification of chemical compounds in solutions. Other analysis methods can also be used. For example, flame photometry can be used to measure sodium and potassium ions (Bauer and Raetano, 2000) and spectrofluorometry can be used, which allows for the detection of fluorescent substances such as Rhodamine B fluorescent tracer (Salyani and Whitney, 1988).

Due to the wide range of tracers available on the market for this type of research, a comparative study between tracers applied to natural and artificial targets was performed. This study aimed to compare the methods for quantification of spray deposits using different tracers on

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natural [*Phaseolus vulgaris* L. and *Brachiaria plantaginea* (Link) Hitchc] and artificial targets, with the goal of identifying the method that best represents the spray deposition for quantitative studies on crop canopies.

MATERIALS AND METHODS

TRIALS

Experimental trials were performed at São Paulo State University in Botucatu City, SP, Brazil. *P. vulgaris* (dicotyledonous plant) and *B. plantaginea* (monocotyledonous plant) were used in the trials. At the moment of application, the average air temperature was 20°C, and the ambient relative humidity was 72%. The bean plants were chosen because the season's weather was ideal for their germination and also due their importance in Brazilian diet. Among all the *Brachiaria*-species, *B. plantaginea* was selected because it is a predominant weed species in agricultural crops and because of its less pronounced trichomes. The problem with trichomes is that they hold the spray droplets high above the leaf surface and do not allow direct contact with the leaf epidermis. This leads to relatively low droplet retention (Xu et al., 2010). These plants were grown in a greenhouse to serve as natural targets in this study. The test used bean plants 50 days after sowing (DAS) at the R5 reproductive stage, and Alexandergrass at 74 DAS. Spraying was performed using an indoor move boom track sprayer with speed and pressure control with a complement of six nozzles. The spray volume was equivalent to 100 L.ha^{-1} using a Teejet XR 110015 nozzle (Wheaton, Ill.) with pressure of 150 kPa and spraying velocity of 5 km h^{-1}. The spray boom was positioned at a height of 0.50 m from the targets. The beans and Alexandergrass were sprayed separately. The experimental array was a completely randomized design (CRD) with five treatments and four replications. Each replication was represented by 10 pots for a total of 40 pots per treatment. Each pot for the *Phaseolus* trial contained one bean plant, and each pot (or the *Brachiaria* trial) contained two plants of Alexandergrass. The quantity of plants per pot was determined by the fact that the bean plant is larger than the Alexandergrass. The treatments (tracers) and dosages are illustrated in table 1.

The tracers used in this experiment were ones commonly used for spray deposition studies in Brazil. The fungicide tebuconazole is registered for bean crops in the dosage used for this study, but its use is not registered for Alexandergrass and was thus used for this target as a tracer only. The tracer concentrations used for the quantitative spray deposit assessments were determined by methods reported in the literature for each tracer (table 1). The tebuconazole concentration was established by the record dose for a spray volume equivalent to 100 L ha^{-1} (Andrei, 2009). For all treatments, spray deposits were compared on natural targets (beans and Alexandergrass) and artificial targets: blotting paper for Rhodamine B, filter paper for the other treatments, and glass slides for all treatments, used as a hydrophilic standard surface.

Table 1. Treatments, methodology and dosages used for natural and artificial targets.

Treatments	Methodology Used	Dosages[a]
Brilliant blue FD&C blue n. 1	(Palladini et al., 2005)	1.5
Cobox®	(Christovam et al., 2010)	2.5
Sodium chloride	(Bauer & Raetano, 2000)	20.0
Rhodamine B	(Serra et al., 2008)	0.05
Tebuconazole	(Ferracini et al., 2004) (Andrei, 2009); (Antuniassi et al., 2007)	2.0

[a] g of product /L of water.

The artificial target of 3- × 4-cm filter paper (for the Brilliant Blue, sodium ion, copper ion, and tebuconazole tracers) or blotting paper (for the Rhodamine tracer) was fixed (stapled on one upper leaf) on each plant. Therefore, 40 bean pots plus 40 papers (3 × 4 cm) and 40 Alexandergrass pots plus 40 papers (3 × 4 cm) per treatment were set up. In addition, two more target types were placed at the same plant heights: 12 glass slides (2.5 × 7.5 cm) and 12 glass slides completely covered with a piece of filter paper (fig. 1). Glass slides on support rods were placed between the plant pots to represent an ideal smooth, horizontal target. Deposition on the glass slides was used for comparison with spray deposit extractions. Separate applications were made for each tracer treatment.

Previous Tests to Validate the Quantitative Methods

Two validation tests were conducted using the Rhodamine B tracer. The first was performed to detect the time glass slides would be immersed in water to extract this tracer. Thus, the treatments (immersion time) consisted of five replicates of glass slides. The spraying was performed in a Potter Precision Laboratory Spray Tower (Burkard Manufacturing Company Limited, Rickmansworth-Herts, England) with 2 mL of sprayed solution volume. After treatment, the slides were placed inside Petri dishes and immersed in 20 mL of deionized water for a period of 0, 24, 48, or 72 h to extract the marker. After these periods, the solutions containing the tracer were taken from the Petri dishes, placed in amber glass vials and stored until analysis. The second test was performed with filter paper and blotting paper to compare the tracer amount extracted from these two targets. The treatments (paper type) involved four repetitions. After spraying, the papers were placed inside amber glass vials with 20 mL of deionized water. Solutions from the washing step were subjected to tracer analysis using a fluorescence spectrometer.

Another laboratory validation test was performed to obtain tracer extraction coefficients for the different targets using five replicates for each target type used in this study. A solution containing a known amount of each tracer (40 µL) was distributed onto each target using an automatic pipette. After 10 min, the Brilliant Blue, sodium ion, Rhodamine B and tebuconazole tracers were extracted with 20 mL of deionized water, and the same amount of nitric acid 1.0 M was used to extract the copper ion tracer. The solutions obtained from the extractions were analyzed, and the tracer extraction coefficients for each target were determined from the tracer quantity extracted from the targets.

Figure 1. Trial details – (A) natural target – plants; (B) artificial target – filter paper fixed on the plants; (C) artificial target – filter paper fixed on the glass slides; (D) artificial target – glass slides.

Quantification of Spray Deposition on Targets

The tracers and dosages used for quantitative assessment of the spray deposits are shown in table 1. The methodologies used for the extraction and analysis described by the authors are also shown in table 1. After the tracers were sprayed on the plants and artificial targets, tweezers were used to detach the filter papers and the blotting paper from the plants and from the glass slides. These papers were then placed in 30-mL amber glass vials. Twenty milliliters of deionized water, used as an extracting solution, was added to the amber glass vials, except for the copper ion tracer, for which 1.0-Mol/L nitric acid was used as the extracting solution. The glass slides without filter paper were washed for 30 s inside Petri dishes containing 20 mL of deionized water (or nitric acid for the copper ion tracer), and these solutions were also placed in 30-mL amber glass vials. The bottles containing filter papers were agitated for 15 min at a speed of 220 rpm on a shaker table for better tracer extraction from the filter paper. After removing the filter papers, blotting papers, and glass slides, the plants (beans and Alexandergrass) were cut near the soil surface, collected, and placed individually in plastic bags, labeled, and stored in a refrigerator (8 ± 3°C) until the end of the applications. Each plastic bag with a bean plant was filled with 200 mL of deionized water, and each bag with Alexandergrass was filled with 50 mL of deionized water, except for the copper ion tracer, for which a nitric acid extracting solution at 1.0-Mol/L concentration was used. The washing volume of the extracting solution was different for both natural targets due to their area; the area for the beans was greater than the area for the Alexandergrass. The tracers were extracted from the natural targets by shaking the bags for 30 s and keeping a portion of the washing solution in 30-mL amber glass vials.

After tracer extraction, each plant area measurement was performed using a leaf area meter benchmark (LI-COR 3100, Lincoln, Neb.). All of the tracer solutions were stored in a refrigerator (8 ± 3°C) until analysis.

Analysis of the tracer deposits was performed using the appropriate instruments for the detection of each tracer. A UV/Visible, double-beam spectrophotometer (Shimadzu UV-1601 PC, Kyoto, Japan) equipped with a 630-nanometer wavelength filter was used to quantify the Brilliant Blue tracer; a flame photometer (Digimed DM-61, São Paulo, Brazil) was used to quantify the sodium ions; a fluorescence spectrometer (PerkinElmer LS-55, Waltham, Mass.) equipped with an exciter filter wavelength of 540 nm and a 585-nm emitter filter was used to quantify the Rhodamine B; and an atomic absorption spectrophotometer (PerkinElmer 2380, Waltham, Mass.) was used to quantify the copper ions (Cu). For the quantification of tebuconazole, an analytical method was developed using a liquid chromatography, equipped with Shimadzu LCMS solution software, and a mass detector LCMS-2010 EV. This method produces uniform results for groups of compounds with similar characteristics, while maintaining a constant ratio between the signal intensity (chromatographic peak area) and the concentration of different compounds expressed in molar units.

From the original tracer solutions applied to the plants and artificial targets, linear standard curves were created for each tracer. The tracer concentrations (mg L^{-1}) obtained using the different measuring techniques for the washing solutions from the natural and artificial targets and initial concentration used in the tracer solution (table 1) permitted determination of the volume retained on the target, according to equation 1. The values of the spray deposits per unit area (mL cm^{-2}) were obtained by the relationship between the volume captured on the target and the target's respective area.

$$Ci.\ Vi = Cf.\ Vf \quad (1)$$

where

Ci = spray mix initial concentration (mg L^{-1})
Vi = volume extracted from the target (mL)
Cf = concentration detected in optical density (mg L^{-1})
Vf = dilution volume of each target sample (mL)

STATISTICAL ANALYSIS

The values of the spray deposits were analyzed by Sisvar (Ferreira, 2000) followed by means comparison using Tukey's Pairwise Comparison Test ($P<0.05$). The percentage of spray deposits retained on the targets was used to determine the tracer recovery coefficients.

RESULTS AND DISCUSSION

EXTRACTION COEFFICIENTS ON DIFFERENT TARGETS

In Brazil, the National Agency for Sanitary Surveillance – ANVISA - recommends extraction percentages for validation of at least 80% to 120% for analytical methods (Anvisa, 2002). For the Brilliant Blue tracer, only the glass slides collected 100% of the tracer, while the filter paper target retained the tracer best. However filter paper was not a suitable target for Brilliant Blue tracer due its low extraction coefficient; the use of this tracer on natural targets seems to be effective for spray deposit assessments because its extraction coefficient was 93% (table 2).

The copper ion tracer was effective on all the targets used, with a more than 80% level of extraction (table 3). These results demonstrate the possibility of using copper-based products as tracers in spray deposition studies with their detection by spectrophotometry.

The methodology using the sodium ion and Rhodamine B as tracers on natural targets cannot be validated by ANVISA because these methods produced extraction coefficients below 80%. However, these tracers presented an average extraction coefficient of 91% on artificial targets. The methodology used for extraction as well as the limitations of the tracer and target combination may have been responsible for the low coefficient (tables 4 and 5).

The bean plants appear to have retained or absorbed more fungicide than the Alexandergrass plants and exhibited an extraction coefficient lower than that for Alexandergrass (table 6). Differences in the architecture and morphology of the leaf surface may have affected extraction. Leaf waxiness, pubescence (hairiness), and orientation are among the characteristics that affect spray retention. The wetting difficulty with spray solution (organosilicone at 0.01%) on the hairy vegetal surface of *Abutilon theophrasti* was reported by Lo and Hopkinson (1995). Sparse leaf pubescence or hairs may help retain spray droplets, but dense pubescence can hold spray droplets above the leaf surface and reduce spray contact with the leaf (Peterson et al., 2001). A plant maceration procedure may be necessary for total extraction of the fungicide.

Table 2. Brilliant blue food dye extraction coefficients for different targets.

Target	Amount Deposited on the Target[a]	Extraction Coefficient[b]
Glass slides	40	100
Filter paper	40	72
Phaseolus vulgaris plants	40	93
Brachiaria plantaginea plants	40	93

[a] µL.
[b] %, average values (n = 5).

Table 3. Copper ion tracer extraction coefficients (%) for different targets.

Target	Amount Deposited on the Target[a]	Extraction Coefficient[b]
Glass slides	40	95
Filter paper	40	95
Phaseolus vulgaris plants	40	88
Brachiaria plantaginea plants	40	83

[a] µL.
[b] %, Average values (n = 5).

Table 4. Sodium ion tracer extraction coefficients for different targets.

Target	Amount Deposited on the Target[a]	Extraction Coefficient[b]
Glass slides	40	88
Filter paper	40	90
Phaseolus vulgaris plants	40	75
Brachiaria plantaginea plants	40	75

[a] µL.
[b] %, Average values (n = 5).

Table 5. Rhodamine B tracer extraction coefficients for different targets.

Targets	Amount Deposited on the Target[a]	Extraction Coefficient[b]
Glass slides	40	93
Blotting paper	40	93
Phaseolus vulgaris plants	40	58
Brachiaria plantaginea plants	40	48

[a] µL.
[b] %, Average values (n = 5).

Table 6. Tebuconazole extraction coefficients for different targets.

Targets	Amount Deposited on the Target [a]	Extraction Coefficient [b]
Glass slides	40	95
Filter paper	40	85
Phaseolus vulgaris plants	40	73
Brachiaria plantaginea plants	40	105

[a] µL.
[b] %, Average values (n = 5).

PREVIOUS TESTS WITH RHODAMINE B TRACER

Lower spray deposit values were obtained when the glass slides were washed instantly in the previous tests that we performed. After immersion in water for 24 h, the spray deposits values were similar, so Rhodamine B, when used on glass as a standard hydrophilic target for spray deposits, must be immersed in water solution for at least 24 h before proceeding with the removal of the tracer solution (table 7).

Another preliminary test indicated the differences between filter paper and blotting paper in capturing the

Table 7. Spray deposit average values (± standard deviation) using Rhodamine B tracer on glass slides, after being immersed for 0, 24, 48, or 72 h in aqueous solution.

Time Glass Slides Remained after Spraying (h)	µL cm^{-2}[a]
0	0.24 ± 0.04 a
24	0.38 ± 0.06 b
48	0.39 ± 0.01 b
72	0.42 ± 0 02 b
CV[b]	10.92

[a] Means followed by the same lowercase letter in the column do not differ by Tukey test ($P<0.05$).
[b] CV = coefficient of variation (%).

Table 8. Spray deposit average values (± standard deviation) using Rhodamine B tracer on filter paper and blotting paper.

Paper Type	µL.cm^{-2}[a]
Blotting paper	0.57 b
Filter paper	0.40 a
CV [b]	8.81

[a] Means followed by the same lowercase letter in the column do not differ by Tukey test (P<0.05).
[b] CV = coefficient of variation (%).

Rhodamine B tracer. The blotting paper, used by Ferracini et al. (2004), was able to capture a higher quantity of tracer (table 8), most likely due to its higher gram weight (250 g/m²) compared to filter paper (80 g/m²). When a paper has a higher gram weight, like the blotting paper, technically the paper can retain more spray volume, while on the filter paper, the spray volume would just drain off the paper.

SPRAY DEPOSITS ON DIFFERENT TARGETS

The glass slides have shown good performance in evaluating the amount of solution reaching the area above the canopy with Brilliant Blue tracer in both experiments, as indicated by collecting a significantly higher volume than if using filter paper on glass slides (tables 9 and 10). The fact that a higher volume of deposits was obtained on the glass slides compared to those obtained on filter paper on glass slides, which implies greater extraction of the amount applied, justifies the adoption of this target as a standard hydrophilic surface in experiments involving spray solution studies (Iost and Raetano, 2010). An ideal tracer for quantitative droplet deposition studies is one that can be extracted or recovered completely from the target even when the deposits are found in the dry state (Cooke and Hislop, 1993). The glass slides and Petri dishes are made of inert material and allow for the full extraction of dyes, retrieving the majority of spray deposits. Most studies in the Brazilian literature have used the Brilliant Blue tracer to assess the spray deposition on natural targets or on Petri dishes to evaluate spraying losses. However, when the deposits obtained on the glass slides were compared to those obtained on natural targets, there was a relative reduction in deposits, according to the values shown for beans and Alexandergrass (tables 9 and 10). Marchi et al. (2005) concluded that the Brilliant Blue tracer is ideal when used on inert materials in the field and for a period of up to 10.0 h of sun exposure without significant losses. However, the authors reported that the Brilliant Blue tracer has had contact restriction with natural targets up to 6.0 h, when losses by tissue retention begins on *Eichhornia crassipes* (Mart.) Solms. Palladini et al. (2005) showed that the Brilliant Blue tracer remains stable when deposited on individual citrus leaves for a period up to 8.0 h. Thus, as in this work, when the plants were not allowed to be exposed to the sun, the lower level of deposition found on Alexandergrass plants compared to glass slides is suggested to be due to the morphological characteristics of the plants (table 10). Viganò and Raetano (2007) evaluated the spray deposition on red rice (*Oryza sativa* L.) under fodder radish (*Raphanus sativus* L.*)* cultivation, comparing different technologies and application volumes. The authors used the same concentration (1,5 g L^{-1}) and volume of 100 L ha^{-1} and found an average spray deposition of 0.30 µL cm^2 on red rice plants, similar to the deposit value observed for Alexandergrass (table 10). Cunha et al. (2005) evaluated the spray volume retained on bean leaves at the top and bottom of the canopy in the field using flat fan nozzles and a spray volume of 125 L ha^{-1}, resulting in an average deposition of 0.361 µL cm^{-2} for the entire bean plant, which agrees with the data in this study (table 9) that were obtained in the lab without wind and under controlled temperature and humidity. Usually, the highest spray volume also results in a greater spray deposit amount on the target, but in the field, variables such as the wind support drift, resulting in greater product losses before reaching the target.

When using copper ions as a tracer, the glass slides and the glass slides + paper were the best targets, with an average deposition of 1.09 µL cm^2 (tables 9 and 10). The methodology used in Brazilian trials, involving attaching papers to the crop to obtain the spray deposits with this tracer, represents an efficient method because the deposit values have been shown to be close to those obtained on

Table 9. Average values of tracer deposits (µL cm^{-2}) (± standard deviation) on different targets using *Phaseolus vulgaris* as a natural target.

Treatments	Plant[a]	Paper + Plant	Glass Slides	Glass Slides + Paper
Brilliant blue FD&C blue n. 1	0.36 ± 0.10 b A	0.25 ± 0.10 a A	0.69 ± 0.21 b B	0.40 ± 0.20 a A
Cobox ®	0.39 ± 0.07 b A	1.02 ± 0.05 c B	1.25 ± 0.15 d C	1.08 ± 0.10 b BC
Sodium chloride	0.16 ± 0.04 a A	0.61 ± 0.07 b B	0.59 ± 0.05 b B	0.52 ± 0.07 a B
Rhodamine B	0.16 ± 0.02 a A	0.42 ± 0.08 a B	0.23 ± 0.04 a A	0.51 ± 0.08 a B
Tebuconazole	0.26 ± 0.06 abA	1.00 ± 0.34 c B	1.02 ± 0.29 c B	1.27 ± 0.29 c C
CV[b]	26.74			

[a] Means followed by the same letter, lowercase letters in the column and uppercase letters on the line, do not differ by Tukey test (P<0.05)
[b] CV = coefficient of variation (%).

Table 10. Average values of tracer deposits (µL cm^{-2}) (± standard deviation) on different targets using *Brachiaria plantaginea* as a natural target.

Treatments	Plant[a]	Paper + Plant	Glass Slides	Glass Slides + Paper
Brilliant blue FD&C blue n. 1	0.29 ± 0.10 b A	0.25 ± 0.10 a A	0.64 ± 0.21 b B	0.45 ± 0.20 a A
Cobox ®	0.38 ± 0.07 b A	0.86 ± 0.05 c B	1.09 ± 0.15 d C	0.95 ± 0.10 b BC
Sodium chloride	0.15 ± 0.04 a A	0.57 ± 0.07 b B	0.68 ± 0.05 b B	0.67 ± 0.07 a B
Rhodamine B	0.13 ± 0.02 a A	0.47 ± 0.08 a B	0.30 ± 0.04 a A	0.49 ± 0.08 a B
Tebuconazole	0.26 ± 0.06 abA	0.95 ± 0.34 c B	1.03 ± 0.29 c B	1.22 ± 0.29 c C
CV[b]	25.67			

[a] Means followed by the same letter, lowercase letters in the column and uppercase letters on the line, do not differ by Tukey test (P<0.05).
[b] CV = coefficient of variation (%).

the glass slides + paper. This is a good target for evaluation of spray deposition. According to Prado et al. (2010), the use of atomic absorption spectrometry enabled values of copper recovery of more than 99% to be obtained for the targets used in that study.

The sodium ion tracer showed the same behavior when sprayed on beans and Alexandergrass. The amount of deposits captured between the artificial targets was similar, ranging between 0.52 and 0.68 μL cm^2 (tables 9 and 10). Good results were obtained by Bauer and Raetano (2000) using sodium chloride as a tracer on soybean crops. With calibrated equipment to spray 100 L ha^{-1}, they obtained deposits of 0.028 μL cm² in the whole plant. We found spray deposit values with this tracer for both beans and Alexandergrass, which were 0.16 and 0.15 μL cm², respectively (tables 9 and 10). However, the sodium ion concentration used by Bauer and Raetano (2000) was four times lower than the concentration used in this study, and those authors also held the soybean plants for 12 h under refrigeration until washing the leaves, while in this study the plants were washed 4 h after spraying. Maciel et al. (2001) evaluated the spray deposition distribution performance on post-emergence bean plants and *Brachiaria* spp. using electric conductivity and with an application volume of 100 L ha^{-1} and obtained average deposits of 1.22 μL cm^{-2} in the bean plants and 0.085 μL cm^{-2} in the *Brachiaria* plants, which were placed under the bean crop. This technique to measure spray deposits is very interesting because it is a less costly and time-consuming method.

When Rhodamine B was used as a tracer, the best targets were those with blotting paper. The papers were stored in 20 mL of deionized water and shaken at 200 rpm for 15 min. This treatment may have favored the extraction of the tracer from the blotting paper because the plant and the glass slides were washed instantly. Salyani and Whitney (1988) compared spray deposit methods with Rhodamine B and copper ion tracers. They obtained lower spray deposition values for Rhodamine B on citrus leaves and on artificial targets (Mylar targets) than for the copper ion tracer. This difference, according to those authors, is due to the degradation of Rhodamine B. These authors concluded that fluorometry is simple, fast, and reliable, but because most fluorescent dyes are photosensitive, this method requires more care and careful equipment calibration. Although not as sensitive as fluorometry, colorimetry (spectrophotometry) is also simple and quick, as well as cheaper and more reliable than fluorometry because there is no tracer degradation and it does not require a limited time for analysis.

The methodology for determining the fungicide tebuconazole on targets was efficient and showed good sensitivity, making it a great choice for a spray deposit tracer in both plant target experiments (beans and Alexandergrass). The glass slides + paper were the best target, followed by the glass slides and filter paper on the plants (tables 9 and 10). The glass slides were used in the experiment for comparison and were positioned in a favorable location for spraying, and the filter paper attached to the plant was observed to represent an excellent target for capturing the spray (tables 9 and 10). The use of pesticides in spray deposit evaluation produces satisfactory results, but the high cost of analysis can be considered as a limiting factor because pesticides require appropriate reagents, sophisticated equipment and trained personnel to perform these tests.

With regard to using plants as targets in deposition trials, the tebuconazole, Brilliant Blue and copper ion tracers can be considered the most efficient tracers because they exhibited higher spray deposit averages on the plants than the other tracers studied (tables 9 and 10).

When using filter paper on the plant for spray deposition studies and subsequent extraction, the fungicide tebuconazole and copper ion were the best tracers, followed by the sodium ion, Rhodamine B and Brilliant Blue traces, exactly in that order (tables 9 and 10). When using the Brilliant Blue tracer, even after extraction attempts, filter paper retained the dye, proving the low feasibility of this method. This result is confirmed by the lower extraction coefficient obtained with the Brilliant Blue dye (table 2). The analysis costs for extracting chemicals by chromatography are known to be high, and the method demands more time; thus, the alternative would be to use copper, sodium chloride and Rhodamine B tracers with this type of target.

Pergher (2001) notes that solutions distributed on paper targets are rapidly absorbed and tend to spread over the entire paper surface. Preliminary work showed that a paper target of 0.48 × 0.08 m in size can hold up to 2.8 mL of solution, so larger volumes would spread outside of this area and cannot be fully sampled. Thus, we concluded that this method is reliable only when used to achieve deposit volumes smaller than 2.8 mL per collector or 7.29 μL cm^{-2} (729 L ha^{-1}).

The methodology using filter paper to capture the tracer used by Bauer and Raetano (2003), Christovam et al. (2010) and Prado et al. (2010) is supported by the test results presented in tables 9 and 10 because, although the applied volume was 100 L ha^{-1} and the expected residue volume for a flat area of 10.000 m^2 would be 1.00 μL cm^{-2}, the method achieved average deposits of 0.95 μL cm^{-2}, approaching the expected results.

A higher amount of copper ion deposits was captured on glass slides + filter paper than on the filter paper stapled to the plants (tables 9 and 10). This finding is most likely due to the positioning of the papers. When clipped onto the plants, the papers conform to the shape of the leaf and are not always completely perpendicular to the spray boom. Thus, fewer droplets may be captured on the papers than on the glass slides, which were perpendicular to the spray boom as discussed earlier.

The glass slide can be considered to be an excellent target for spray deposit studies because the tracers are easily removed due to the physical characteristics of the glass slide. However, the amount of Rhodamine B deposit captured was very low, 0.23 and 0.30 μL cm^2 for beans and Alexandergrass, respectively, suggesting that the slides must remain in the same extraction solution for a minimum of 24 h for optimal tracer extraction (table 7).

CONCLUSIONS

The selection and reliability of quantitative analysis methods for spray deposits depend on the target nature, tracer substance, and target-tracer interaction.

The extraction coefficient was generally higher for artificial targets, except for the Brilliant Blue tracer, for which the tracer extraction from filter paper was lower than the limit (80%) established by ANVISA for analytical method validation. The Rhodamine B and sodium ion tracers on natural targets also produced extraction coefficients below this limit.

For natural targets, copper ion, tebuconazole and Brilliant Blue tracers are more appropriate for quantitative spray assessment studies compared to sodium ion and Rhodamine B tracers. However, the costs associated with detecting and quantifying the copper ion and fungicide tracers will be higher than for the other tracers.

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