



Application of QuEChERS Method in Spray Deposition Studies

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Pesticides are widely used in agriculture for the management of pests (weeds, insects or pathogens). They are generally applied as a spray to cover the target (e.g. an insect, leaf surfaces or part of a plant) with pesticide-laden droplets. Spray may, however, be lost to non-target areas within a crop through deposition on to the soil or on non-target plant surfaces. The plant architecture of the crop and weed species can influence the distribution of the spray droplets. The action of wind may also result in spray moving away from the spray area. By selecting and using spray equipment and techniques that maximise deposition of pesticides onto the target, it is possible to both maximise the effectiveness of the pesticide application and reduce the amount of off-target deposition and damage. Hence, it is necessary to measure the distribution of spray deposits in the leaves of different crop canopies in relation to droplet size, droplet trajectory, spray application volume and canopy structure. A study on the deposition of spray chemicals on cotton crop was conducted using three methods namely i) Gravimetry method ii) Leaf Area Index and iii) QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method and the efficiency of the methods on the requirement of effective volume of spray chemicals for unit cropped area was determined.

Key words: Spray Deposition, Leaf Area Index, QuEChERS Method

Traditional pesticide application deliver chemicals for the complete crop area, but increasing concern about environmental safety, in recent decades, has resulted in developing new methods to regulate pesticide application to target area or create new types of bio-pesticide, in order to promote crop yield and minimize damage to the environment. By selecting and using spray equipment and techniques that maximize deposition of pesticides onto the target it is possible to both maximize the effectiveness of the pesticide application and reduce the amount of off-target deposition and damage. The purpose of this study was to measure the distribution of spray deposits in the leaves of different crop canopies in relation to droplet size, droplet trajectory, spray application volume and canopy structure. As well as providing useful information on the proportion of spray reaching the intended target, this will provide data that subsequently can be used to improve models of spray interception by plant canopies.

Stermer *et al.* (1988) compared several artificial targets to collect spray droplets, and concluded that depositions on collectors that most nearly modeled the live plants in physical size, orientation and shape had the highest correlation with deposits on the plant leaves. They found that water-sensitive cards could provide useful information on uniformity of swath and coverage and relative droplet size. Monofilament

has also been used to collect spray deposit and a dual-side leaf washer was developed to elute spray deposit separately from either surface of cotton leaves (Carlton, 1992a, b). Richardson and Newton (2000) measured spray deposition within plant canopies of bracken fern (*Pteridium aquilinum*) and greenleaf manzanita (*Arctostaphylos patula*) following ground application of a spray mixture containing water, a fluorescent tracer and surfactant. A high proportion of spray (35-38 %) reached the ground through manzanita canopies whereas only 1-13 % reached the ground through a bracken canopy. Fritz *et al.*, (2009) evaluated deposition and droplet sizing characterization of a laboratory spray table small-scale laboratory studies to assess the various materials on the various crops and pests at varying rates and spray spectra can identify promising combinations for field evaluation. Sonnentag *et al.*, (2007) carried out a study on direct and indirect measurements of leaf area index to characterize the shrub canopy in an ombrotrophic peatland, Leaf Area Index (LAI) is an important ecological parameter that characterizes the interface between a vegetation canopy and the atmosphere. Indirect measurements of LAI using optical techniques such as the LAI-2000 plant canopy analyzer have been routinely conducted for different vegetation canopies including forest and agricultural crops.

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Materials and Methods

Determination of size of spray droplets

The deposition of spray chemical on the plant canopy depends on the size of spray droplets and distribution of spray droplets. Droplet size ranging between 100 and 200 μ provides appreciable deposition on plants. Droplets below 100 μ size are susceptible to wind resulting in loss of chemicals through drift. Droplets above 200 μ size are large enough to be subjected to free flow under the action of gravitational force without being deposited on the plant canopy (Matthew, 1976). The droplet size depends mainly on the pressure of application. Hence, the pressure of application needs to be optimized to atomize the spray liquid to a droplet size of 100 to 200 μ , for conducting the spray deposition studies.

The droplet size was determined by measuring the diameter of circles formed by droplet deposition on white photographic paper. Methylene blue solution was used as the dye solution, at a concentration of 10 g l⁻¹. The photographic paper was cut into 70 X 70 mm size. The photographic paper was kept on a horizontal surface directly below the nozzle. The target was enclosed in a ring and covered by a top sheet. The nozzle was made to spray at different nozzle pressure, and top cover was momentarily opened and closed, so that the samples obtained were allowed to dry without disturbance. The samples were analyzed by using image analysis software. The images were captured using digital photo micrographic equipment. The droplet images were digitalized and transferred for analysis to personnel computer. The image analysis software developed using MATLAB was used to study the samples collected with respect to Volume Mean Diameter (VMD), Numeric Mean Diameter (NMD), VMD /NMD ratio, applied volume and percent area covered and the results were recorded.

Volume Mean Diameter (VMD)

Volume Mean Diameter (VMD) is the diameter of spray droplet which divides the volume of the spray into two equal halves.

Numeric Mean Diameter (NMD)

Numeric Mean Diameter (NMD) is the average diameter of the droplet, which divides the number of droplets into two equal halves.

VMD/NMD ratio

VMD/NMD ratio is a factor used for indicating breadth of the spectra. The VMD/NMD ratio was calculated for the results obtained in the droplet size measurements.

Determination of quantity of spray deposition

There are two methods for the determination of quantity of spray deposition namely. i. Destructive method and ii. Non destructive method.

In destructive method (crude method), the plants are totally uprooted from the field and taken to the laboratory for further study. Gravimetry method was used for the quantification of the spray deposits. In non destructive method, the observations are recorded either in the field itself or by collecting representative samples of plant parts, preferably leaves and analyzing in the laboratory.

Destructive method (Gravimetry method)

In this method, five plants were selected randomly in the field and uprooted and roots were washed to remove soil particles. The weight of the plant was measured using electronic balance. Then the plant was clamped vertically in a stand to simulate the field condition and prophenophos at a concentration of 3.5ml/lit was sprayed on the plant in the laboratory condition. The plant was shaken lightly to remove any free chemical on the plant and the weight of the plant with spray deposition was determined. The weight of chemical deposited on the plant was calculated as detailed below.

$$W=W_2-W_1$$

where,

W = Weight of spray deposition, g

W₁ = Weight of plant before spraying, g

W₂ = Weight of plant after spraying, g

Leaf Area Index

Leaf Area Index (LAI) is an important structural property of crop canopy. LAI is defined as the ratio of total upper leaf surface of vegetation divided by the surface area of the land on which the vegetation grows. LAI is used to predict the photosynthesis capacity of a crop and as a reference tool for crop growth. Leaf Area Index can be measured by two methods they are direct measurement method and indirect measurement method.

Direct Measurement

Direct measurements of LAI are considered to be the most accurate but all direct measurements have the disadvantage of being very time consuming; there are two-step processes consisting of leaf collection by either harvesting (e.g., destructive sampling) or non-harvesting (e.g., litter traps) methods, and subsequent leaf area calculation based on either planimetric (e.g., scanning planimeter LI-3000, LICOR, Lincoln, NE, USA) or gravimetric (e.g., predetermined green leaf area-to-dry weight-ratios) methods (Jonckheere *et al.*, 2004).

Five plants were selected randomly in the field and twenty leaves in each plant at different heights were plucked. The maximum length and width of the leaves were measured. The areas of the corresponding leaves were measured using a Leaf Area Meter and tabulated. A linear relation between

the length, width and area of leaves was established by regression analysis.

QuEChERS method

Sample leaves of 50 to 100 g were collected from the same plant used in the gravimetry method at random after 5 min of spray at different heights of plant and taken for analysis by quencher's method. The sample leaves of 50 to 100 g were also taken from the unsprayed plants in the field for comparison. The sample leaves were blended separately. 10 g of sample leaves was taken in 50 ml centrifuge tube. The sample was mixed with 20 ml ethyl acetate, 4 g magnesium sulphate and 1 g sodium chloride. After the addition, the mixture was stirred well at 10000 rpm for 10 min in centrifuge. Four ml of supernatants was taken from the extract of the sample in 30 ml centrifuge tube with screw type cap. The supernatant was mixed with 100 mg primary and secondary amine, 600 mg magnesium sulphate. The mixture was shaken well for 2 min and centrifuge at 500 rpm for 5 min. One ml of hexane was added to that tube, rinsed well and transferred to the injection vial for analysis in Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GCMS). The spray deposition on leaves was calculated by using QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) formula given below.

$$\text{Residue in ppm} = \frac{\text{Sample area}}{\text{Standard area}} \times \frac{\text{Nanagramo standard}}{\text{Weight of sample}} \times \frac{\text{Final volume of extract}}{\text{Inject volume of extract}}$$

Results and Discussion

Determination of spray droplet size

Volume Mean Diameter (VMD)

The results on Volume Mean Diameter (VMD), Numeric Mean Diameter (NMD), VMD /NMD ratio, applied volume and percent area covered were analysed and graphically represented in Fig. 1, 2 and Fig. 3.

It was observed from Fig.1 that, at the increased pressure the VMD was decreased from 270 μ to 120 μ . At a pressure of 0.1 MPa, the VMD was 270 μ

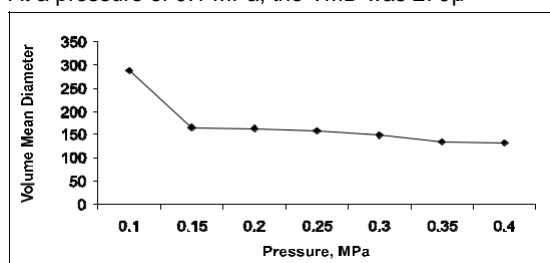


Fig. 1. Effect of pressure on VMD

and observed as medium spray (201 to 400 μ). At pressure 0.15 to 0.4 MPa, the VMD was 150 μ to 120 μ and classified as fine spray (101 to 200 μ), (Matthew, 1976).

VMD/NMD ratio

The value of VMD/NMD recorded almost nearer

to 1.0 as presented in Fig. 2. At pressure 0.1 MPa VMD/NMD ratio was 1.92. For the pressure range of 0.15 MPa to 0.4 MPa the droplet spectrum was uniform. The VMD/NMD ratio arrived at pressure range of 0.15 to 0.4 MPa were nearly 1.0 which is classified as ideal (Senthil Kumar, 1995).

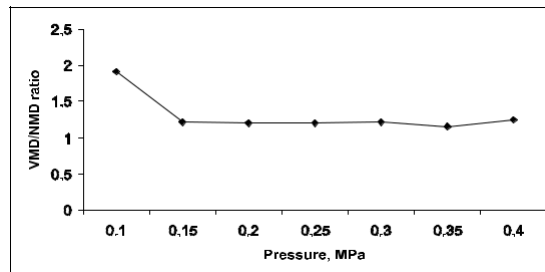


Fig. 2. Effect of pressure on VMD/NMD ratio
Applied volume

It is observed that applied volume was less in lower pressures and uniformity was maintained, except at 0.1 MPa, 0.15 MPa and 0.4 MPa was 0.2, 0.16 and 0.19 litre/cm². Uniform applied volume was observed in pressure range 0.2 to 0.3 MPa was 0.18 liter/cm² as presented in Fig. 3.

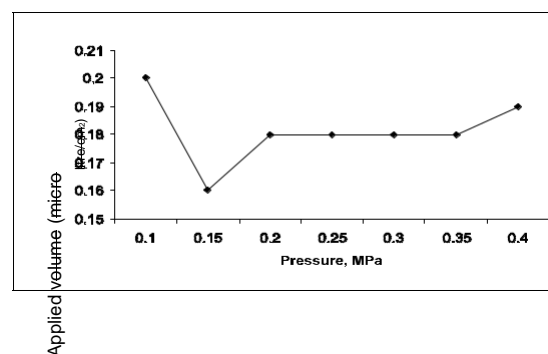


Fig.3. Effect of pressure on applied volume

Determination of quantity of spray deposition

The three methods namely i) Gravimetry method ii) Leaf Area Index and iii) QuEChERS method were used for the quantification of spray deposition and the results were compared.

Gravimetry method (Crude method)

Number of leaves and plant weight before and after spraying and the calculated amount of spray deposition were presented in Table1.

Table 1. Plant parameters and spray deposition

Plant No	Total number of leaves	Weight of the sample before spraying (g)	Weight of the sample after spraying (g)	Amount of spray deposited (g)
P1	30	338	78	42000
P2	54	734	116	91000
P3	28	283	66	35000
P4	30	283	68	35000
P5	21	340	46	42000

Leaf Area Index

The length, width and area of leaves were recorded and a mathematical model was developed

by regression analysis correlating the area, length and width of the plant.

CORRELATION MATRIX

	AREA	LENGTH	WIDTH
AREA	1.000	0.976**	0.969**
LENGTH	0.976	1.000	0.991**
WIDTH	0.969	0.991	1.000

Regression Equation : $Y = -36.93 + 10 (\text{Length}) + 1 (\text{Width})$

	Coefficient	Standard Error	T-Test
LENGTH	10.4028506	3.18517294	3.27**
WIDTH	1.21133769	2.70791116	0.45ns

Applying the above relation the total canopy area of the crop can be determined by multiplying with the number of leaves per plant and the plant population per unit area and accordingly the amount of chemical actually deposited on the plants can be determined.

QuEChERS method

The deposition of chemical on plant is calculated using the QuEChERS formula using standard constants and the results were tabulated in Table 2.

Table 2. Amount of spray deposition

Plant No	Weight of the sample plant (g)	Amount of spray deposited(g)
P1	338	41912
P2	734	91016
P3	283	35092
P4	283	35092
P5	340	42160

The amount of spray deposited increased with increase in plant weight, since it is a destructive method, it cannot be practically applied. Hence, the values were compared with other non destructive methods.

Comparison of different methods of determination of spray deposition

The amounts of spray chemical deposited as concluded by gravimetry method and QuEChERS method were presented in Table 3.

Table 3. Comparison of different methods of determination of spray chemical deposition

Plant No	Amount of spray chemical deposited (g)	
	Gravimetry method	QuEChERS
P1	42000	41912
P2	91000	91016
P3	35000	35092
P4	35000	35092
P5	42000	42160

It is observed that the amount of chemical deposited as calculated by QuEChERS method (Non destructive method) was almost closer to that by gravimetry method (Destructive method). Hence, QuEChERS method can be adopted for estimation of spray chemical deposition, without uprooting or destroying the field crops.

Conclusion

The quantity of chemical deposited was calculated by QuEChERS method and gravimetry method were almost same. Hence the QuEChERS method can be adopted to find the amount of chemical deposited without destroying the plant as in the case of gravimetry method. Leaf area can be calculated using the mathematical model $Y = -36.93 + 10 (\text{LENGTH}) + 1 (\text{WIDTH})$ for cotton crop from which the vegetative area per unit land area can be determined and the amount of chemical to be sprayed on the target can be determined based on the recommended dose.

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