VARIATION IN HERBICIDE DEPOSITION ACROSS A PLOT

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Summary. As part of a long-term trial into herbicide persistence at three Victorian sites, a study was undertaken into the variability of trifluralin and diclofop-methyl deposition across individual plots. The variability was assessed immediately after application by determining the herbicide concentration of 40 individual cores per plot. To assess if the processes of degradation and dispersal were adding to the initial variability, the herbicide concentration was measured again approximately one year later. This data was used to calculate the number of cores required to obtain confidence intervals of ± 10 and 20% of the plot mean. The plot mean was compared to the theoretical herbicide concentration to determine how much of the spray was actually reaching the soil.

INTRODUCTION

Valid conclusions regarding herbicide persistence, carryover into the subsequent cropping season, and accumulation in soil, can only be drawn if the actual concentration in the soil is determined over a number of cropping seasons. Samples for herbicide residue analysis must be precisely taken and be representative of the area under consideration.

It is widely accepted that less than the theoretical amount of herbicide reaches the target due to the inaccuracies involved in its actual application. Factors influencing the amount and pattern of herbicide deposition include: the nature of the formulation and slight variations in its strength; the spray apparatus, especially factors such as nozzle type and pump pressure which affect droplet size and spray pattern; operator technique; environmental conditions (particularly those affecting volatility and spray drift); and soil incorporation techniques. The interaction of these factors and their resultant effect on herbicide concentration in the soil must necessarily vary for each application. For residue samples taken sometime later in the cropping season additional factors may contribute to the variability of herbicide concentration in the soil. These may include: degradation processes; adsorption of the herbicide onto soil and plant matter; climatic conditions, especially soil temperature and moisture; plant uptake and management practices such as burning off and grazing of stubble and cultivation.

The factors listed above can influence the variability of herbicide concentration across a field. A knowledge of this variability, and hence the confidence interval of the results, is essential if reasonable conclusions are to be drawn from herbicide residue results.

METHODS

Field trial. Three experimental sites were located in Victoria at Walpeup, Rutherglen and Dooen. The herbicides were applied by back tank using precision boom sprayers with fan nozzles. The trifluralin formulation 'Treflan' was applied at a rate of 1.0 L/ha and double harrowed. Diclofop-methyl as 'Hoegrass' was applied at a rate of 1.5 L/ha. Forty cores, 2 cm in diameter and 10 cm in depth, were taken from each plot, ground and sieved and then frozen until laboratory analysis. The cores were either analysed individually to determine variability across the plot or bulked to form one sample from which a 10 or 20 g sample was taken for analysis

Pot trial. To minimize the initial variability, soil from each site was fortified with trifluralin to a level of 0.35 ppm. This soil was placed into 10 cm plastic pots with porous bottoms which were buried level to the surface and removed periodically throughout the cropping season. Those removed after one year were used to determine the variability due to the degradation processes.

Analytical methodology. The soil concentration of trifluralin was determined using a methanol/water extraction procedure followed by quantification on a gas liquid chromatograph with an electron capture detector (GLC/ECD). Diclofop-methyl undergoes hydrolysis to the herbicidally active metabolite diclofop. Therefore, we developed a procedure to quantify both compounds (1). The procedure uses a 1% phosphoric acid extracting solution and quantification by GLC/ECD after methylation.

RESULTS AND DISCUSSION

The analytical error was assessed by determining the recoveries at two concentrations. For trifluralin, mean recoveries of 95% (coefficient of variation (c.v.) 5.7%) and 97% (c.v. 4.3%) were obtained at 0.02 and 0.20 ppm respectively. For diclofop-methyl the mean recoveries were 101% (c.v. 10.4%) and 91% (c.v. 6.3%) and for diclofop 102% (c.v. 5.3%) and 97% (c.v. 3.7%) at 0.05 and 0.50 ppm respectively. The variability introduced by the sub-sampling and analytical techniques was determined by 10 replicate analyses giving c.v.'s of 6% for trifluralin and 8% for diclofop-methyl.

As seen in Table 1, the variability in concentration for 40 individual cores immediately after application was large and varied for the sites and herbicides. The inherent variability of herbicide application coupled with factors that vary between locations contribute to the variability of the results. The soil incorporated volatile herbicide trifluralin, had a high variability across the plots with c.v.'s of 56%, 105% and 129% for Dooen, Walpeup and Rutherglen respectively. To some extent the high variability for trifluralin concentrations at Walpeup and Rutherglen may be due to soil type. Walpeup and Rutherglen soils are lighter and sandier than the medium clay at Dooen. This may influence the volatility of trifluralin and may contribute to the high variation at Walpeup and Rutherglen. Diclofop-methyl exhibited less variability with c.v.'s ranging from 32-52% for the three sites. When comparing these results to the analytical errors it becomes obvious that the variation introduced by the initial application is much larger than that resulting from the analytical procedures.

Table 1. Mean herbicide concentration (ppm) of forty individual cores taken immediately after 1983 herbicide application

	Trifluralin			Diclofop-methyl		
	Mean[a]	c.v.	Range	Mean	c.v.	Range
Dooen	0.41 ± 0.07	56%	0.01 - 0.99	0.98 ± 0.16	50%	0.43 - 2.77
Walpeup	0.20 ± 0.07	105%	0.01 - 1.09	0.56 ± 0.09	52%	0.19 - 1.37
Rutherglen	0.07 ± 0.03	129%	0.0 - 0.44	0.19 ± 0.02	32%	0.07 - 0.36

[a]mean (ppm) ± 2 s.d's

The statistical data obtained from the analysis of the 40 individual cores for the 3 sites and 2 herbicides was used to determine the number of cores required to estimate the mean to within ± 10 and 20% for each particular plot with 95% confidence.

The following formula was used: $n = \frac{(t\ /2 \text{ x } s)^2}{(\text{ C.I. })}$

where: n is the size of the samples (i.e. number of cores), t /2 is the value of the t distribution leaving an area of /2 to the right, s is the standard deviation, and C.I. is the confidence interval, the amount within the addition and subtraction of which the mean lies for the chosen probability 1 - .

The number of cores required to obtain a confidence interval of ± 10% of the mean is impractically high for trifluralin at all three sites. The number of cores required is 120, 404, and 683 at Dooen, Walpeup and Rutherglen respectively. A confidence interval of ± 20% would be achievable only at Dooen (31 cores) since 106 would be required at Walpeup and 170 at Rutherglen. Diclofop-methyl has a much lower variability with ± 10% being practical at Rutherglen (38 cores). The number of cores, however, increases to 96 for Dooen and 107 for Walpeup. For ± 20% the number of cores required is 24, 27 and 10 at Dooen, Walpeup and Rutherglen respectively.

The relationship between the number of cores and the confidence interval (Fig. 1) can be seen for trifluralin and diclofop-methyl on Walpeup soil. An increase in the number of cores from 10 to 20 gives a dramatic improvement in the confidence interval of the mean. As the number of cores increases, the change in the confidence interval becomes progressively less and the slope approaches unity. The number of cores to be taken should be around the number where increasing the number of cores improves the confidence interval by only about one percent of the mean. For trifluralin in Walpeup soil, ideally, the number of cores taken should be between 70 to 90 and for diclofop-methyl between 40 to 60.

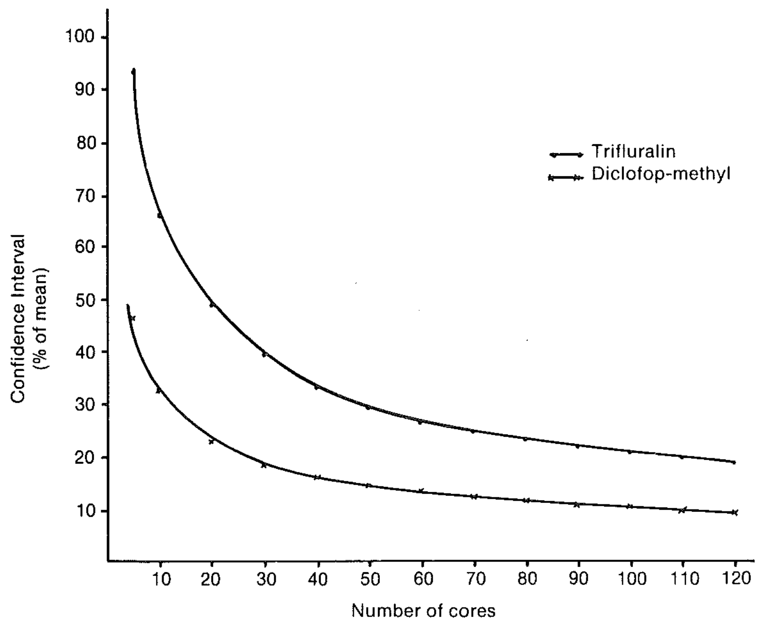

Figure 1. Relationship between the calculated confidence interval (%) and the number of cores of soil at Walpeup for trifluralin and diclofop-methyl

Similar results have been reported overseas, to those we have obtained when assessing variation in herbicide concentrations in soil. In an experiment by Taylor *et al.* (3) a c.v. of 80% was obtained on 108 cores after normal application of dieldrin. Taylor suggested that the c.v. cannot be reduced below 20% for this type of work. Wauchope *et al.* (5) investigated soil sample variation using a copper sulphate tracer and obtained c.v.'s of between 40-50% on 360 cores for four treatments. As the variability of herbicide across the soil is high, sampling strategies must be developed which take this into account.

It has been suggested that while the principal cause of variability in soil residues is the unevenness of the initial application, the mechanisms of degradation and dispersal can add to this variability. A field study conducted by Walker & Brown (4) indicates that the variability in soil herbicide residues increases with time after application. The variability in trifluralin concentrations one year after application was, therefore, investigated. The c.v.'s for these residue samples were similar or less than those found immediately after application. At Dooen the c.v. increased from 56% immediately after application to 61% for residue samples one year later; at Walpeup it decreased from 105% to 67%; and at Rutherglen from 129% to 81%. Hence, at our 3 sites the degradation processes do not add greatly to the existing variability of trifluralin concentrations across a plot. This is supported by the results of a pot trial. For several pots containing well mixed soil fortified with trifluralin the c.v.'s one year after burial ranged from 4-10% compared to 4-6% for pots removed on the day of burial. Hence it would be reasonable to use the variability immediately after application as a basis for determining the sampling strategy one year later.

To determine how much of the herbicide spray was actually reaching the soil, the amount detected was compared with the theoretical concentration calculated on the basis of the application rate. The actual concentration found immediately after application is quite different at the 3 sites; 0.32, 0.14 and 0.11 ppm at Dooen, Walpeup and Rutherglen respectively. This corresponds to a percentage of the theoretical concentration of 84%, 51% and 32% for Dooen, Walpeup and Rutherglen respectively when the bulk density at these sites is taken into account. This shows that considerable losses occur during application and incorporation. Morrison (2) reports that for trifluralin only 25-40% of the expected amount was detected in an experiment conducted at the University of Manitoba. For valid conclusions to be made regarding herbicide persistence at different sites, the initial concentration must be determined in addition to the residue concentration. This is also essential if half lives for different sites are to be compared.

Variability in herbicide concentration across a plot is high. As pre-sampling is often impractical the variability should be estimated and calculations done to determine the approximate number of cores required to obtain results with the desired confidence intervals. For example, our studies and those overseas Taylor *et al.* (3), Wauchope *et al.* (5) indicate that c.v's of 30-130% can be associated with the concentration of herbicide across a field. If the worst case is assumed then a proposed sampling strategy of one bulked sample of 30 cores gives an estimated confidence interval of $\pm$ 47%. For 15 cores the confidence interval increases to $\pm$ 66%. Interpretation of results with such large confidence intervals is difficult especially if they are being compared to other mean concentrations. The sampling plan must be chosen and assessed with respect to the accuracy required in the final result. This means that before sampling to measure herbicide soil residues, a study of the sampling variability should be undertaken.

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