

TOPIC 3B

INFLUENCE OF FORMULATION AND ENVIRONMENTAL
FACTORS ON PERFORMANCE

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PROCESSES IN SOIL WHICH CONTROL THE AVAILABILITY OF PESTICIDES

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ABSTRACT

Recent developments in the study of adsorption and mobility are reviewed particularly those concerned with minimum tillage practices and with the effect of formulations and application factors. There is also some consideration of the kinetics of pesticide decomposition and the factors which control pesticide persistence in the soil.

INTRODUCTION

It is neither possible nor appropriate to attempt a comprehensive summary of soil processes and their effect on pesticide availability here. The object of this paper will be to try to draw attention to some areas where recent work suggests a re-assessment might be useful, or where changes in conditions have exposed uncertainties in understanding or gaps in our factual knowledge.

The availability of a toxicant to its target is a function of concentration, time and distribution. In the context of soil-applied pesticides, concentration usually means concentration in soil solution or in soil air. Except when some sort of mechanical incorporation of the pesticide into the soil occurs, concentrations in soil water and air also control movement and hence distribution. They also affect the availability of a pesticide to the processes by which it is lost from the soil, whether they involve physical removal as vapour or in drainage water, or the various chemical, photochemical and microbiological decompositions that may occur.

PESTICIDE CONCENTRATION AND DISTRIBUTION IN SOIL SOLUTION

Effect of sorption processes

Many of our ideas concerning sorption are based on observations made in the laboratory under conditions where it is hoped that equilibria have time to establish. However, frequently equilibrium conditions do not occur. Davidson *et al.* (1980), for example, illustrated the contortions necessary to reconcile model calculations of solute movement in soil columns with experimental observations and concluded that our mathematical ability exceeded the experimental data base needed to evaluate models. In the field the difficulties are of course greater and Hance *et al.* (1981) concluded, on the basis of experiments involving studies of the mobility of chloride (as a tracer for water), fluometuron, simazine and $^{144}\text{Ce}^{3+}$ (as a tracer of soil particle movement), that soil structural effects may be more important than adsorption in controlling the movement of solutes. This idea assumes that soil water can be divided into mobile and immobile fractions and that at least a proportion of the mobile water does not come to equilibrium with solutes in the soil. At the moment there seems to be no way of measuring quantitatively the size of these water fractions although Nicholls *et al.* (1982) showed that an empirical model, which assumed a division between the two fractions at a water content corresponding with a retention pressure of -200 kPa, described water contents in various soil layers accurately, although it was not so good with respect to the solutes atrazine and metribuzin.

Part of this discrepancy presumably results from deviations from ideal sorption behaviour. The time needed to bring pesticides applied as sprays into soil solution may also be significant although Hance and Embling (1979) found that soil solution concentrations of simazine, metribuzin and linuron sprayed onto soil at a moisture content of about pF 2.5 (on the wetting cycle) approached those predicted from slurry adsorption measurements quite quickly. However, spray applications to air dry soil resulted in much lower soil solution concentrations, particularly if an appreciable time elapsed between spraying and wetting the soil.

The experiments reviewed so far were carried out either with carefully sieved soil or in fields which had been cultivated to produce a seed-bed. Many pesticides, however, are applied to fields that have received little or no tillage and may be covered with substantial quantities of crop residues. Study of the behaviour of pesticides applied in these conditions presents a severe experimental challenge which has been avoided by most workers. Bauman (1976) found that an 85% mulch cover prevented 30% of an atrazine application from reaching the soil measured over a 90 day period. Addy (1982) measured metolochlor residues in soil 3 weeks after application so his results also include the effect of the mulch on soil moisture and temperature and hence herbicide persistence (Table 1).

TABLE 1
Effect of maize stover levels on amount of metolochlor in the soil 3 weeks after treatment (Taken from Addy, 1982).

Application rate (kg/ha)	Metolochlor concentration (g/ha)			
	Stover level (t/ha)			
	0	5	10	15
0.9	117	63	86	40
1.2	171	23	140	63
1.5	315	99	50	95
1.8	400	122	95	27

The levels he found on average ranged from just over 30% of the control value under a 5 t ha⁻¹ mulch to about 23% under 15 t ha⁻¹ but the variability of these results clearly made such work unrewarding.

In the UK and some other countries straw residues are commonly burnt in the field but little attention has been paid to the possible effects of straw ash residues on pesticide performance. Occasional reports (see for example Hurle 1978, Nyfeller & Blair 1978) that it can reduce pesticide activity seem to have been received with indifference. Currently, however, the topic has become of interest in the UK as a result of investigations into the occasional failures of substituted urea herbicides to control *Alopecurus myosuroides* in winter cereals. Cussans *et al.* (1982) reported observations made in forty four fields scattered over central, eastern and north-eastern England which showed that poor herbicide performance was associated with direct drilling and a high adsorptive capacity of the soil in the top 2.5 cm layer. Adsorption was sometimes much greater than

expected from the soil organic matter content of direct drilled fields which pointed to the possibility that burnt straw residues were involved. Embling *et al.* (1983) therefore investigated the properties of straw burnt under a

TABLE 2

Freundlich constants, based on unheated weight, for chlortoluron with heat treated straw (Embling *et al.*, 1983)

Temperature ($^{\circ}$ C)	Heating time (minutes)					
	1		3		5	
	K	1/n	K	1/n	K	1/n
Untreated	35	1.05	-	-	-	-
500	67	0.57	160	0.45	211	0.42
600	229	0.40	267	0.35	258	0.42
700	258	0.33	285	0.32	452	0.32

range of conditions. They found that chlortoluron adsorption increased with increasing temperature and duration of heat treatment over the range examined (Table 2). They calculated that it would be possible for a burnt straw residue to increase adsorption in the top 1 cm layer of soil to a level equivalent to that of a soil containing 10% organic matter and so reach the top of the range for which the manufacturers recommend the product. However, these results were obtained with fresh ash but Hurle (1978) has shown that the activity of straw ash mixed with soil declines with time at a rate which varies with soil moisture content. Work in progress at the moment (E.G. Cotterill, pers. comm.) confirms that adsorptive activity declines fairly rapidly initially but reaches a steady state after 5-10 days and that inactivation is enhanced by wetting. The mechanism is obscure; since the adsorption measurements themselves are made by shaking slurries of ash in water it is surprising that an effect of wetting on the rate of inactivation can be observed.

At the moment it seems doubtful that increased adsorption is the sole reason for the tendency for poor herbicide performance in low tillage systems but we are now fairly confident that adsorption by the surface soil increases rapidly following the adoption of such a system and in the worst case may approach the level at which chlortoluron performance is uncertain after only 2-3 years (S.R. Moss & E.G. Cotterill, pers. comm.).

Thus the subject of adsorption and related phenomena is enjoying something of a resurgence but in relation to dynamic systems in contrast to the emphasis on equilibria that was characteristic of much of the work of 20 years ago.

Effect of application factors

Application factors which affect the concentration and distribution of pesticides in the soil can be divided into those concerned with application equipment and those concerned with the properties of the formulation.

Except in the case of granule and controlled release formulations, the

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application of soil applied compounds has received little attention. There is abundant evidence (see for example Hurle & Walker, 1980) that deposits of pesticides on the soil are very variable so there is reason to wonder how far this explains variability in performance when it occurs. Addala et al. (1983) have attempted to assess the degree of uniformity of horizontal distribution needed in order to achieve reasonable performance from several soil-applied herbicides. In greenhouse experiments, chlortoluron, propyzamide and terbutryne were as active whether applied with a rotary atomiser at 30 l/ha or with a conventional hydraulic nozzle at 400 l/ha (Table 3).

TABLE 3
Effect of application method on the performance of some pre-emergence herbicides (Addala et al., 1983a).

		% reduction in population		% reduction in fresh wt.	
		Rot.atomizer	Hydr.nozzle	Rot.atomizer	Hydr.nozzle
Chlortoluron	<u>A.myosuroides</u>	51	44	81	82
	<u>S.media</u>	55	58	65	76
	<u>C.album</u>	60	56	58	68
	<u>Per.ryegrass</u>	62	55	78	74
	<u>Radish</u>	71	51	81	73
	<u>A.fatua</u>	76	74	90	87
Nitrofen	<u>A.myosuroides</u>	68	78	78	78
	<u>C.album</u>	47	68	70	75
	<u>A.fatua</u>	1	29	19	50
Propyzamide	<u>S.media</u>	48	23	57	50
	<u>A.fatua</u>	55	50	65	58
Terbutryne	<u>A.myosuroides</u>	47	38	65	49
	<u>S.media</u>	46	43	60	57

Only nitrofen activity against Avena fatua varied, being less active following the rotary atomizer application. All except nitrofen also showed appreciable activity applied as discrete drops 2 cm apart at rates equivalent to 2 kg a.i./ha to plants growing equidistant from the drops. Field results were similar, the performance of chlortoluron, propyzamide and terbutryne being about the same from both hydraulic nozzle and rotary atomizer applications. A dribble bar with orifices spaced at 2 cm intervals was as effective as the sprayers for all but nitrofen and although the horizontal variability in herbicide concentrations in the soil was very large, plant response was uniform. Thus it appears that for herbicides at least, uniformity of lateral distribution is likely to be critical only for the least mobile of the currently available materials.

Most pesticides are formulated with adjuvants but apart from simple comparisons of performance, for example of granules and e.c.s, only sporadic studies have been reported of the effects of adjuvants on the behaviour of soil-applied compounds. Admittedly some results suggest that formulation adjuvants used at normal rates have little or no effect. However, surfactants may compete for adsorption sites, hence increase mobility, or increase retention by forming micelles round the pesticide molecule that are adsorbed more than the pesticide itself, or have no apparent interaction at

all (Bayer & Foy, 1982).

There seems to have been little work on the effect of surfactants on the phytotoxicity of soil acting herbicides other than that reported by Yapel (1972) and Van Valkenberg & Yapel (1972). They found that the pre-emergence phytotoxicity of a range of *m*- and *p*-substituted trifluoromethanesulphanilides was affected by the presence of 1 g/l Tween 80 and that the change (either positive or negative) could be related to the change in octanol/water partition coefficient (K_{ow}) although for the *p*-substituted series there was also a strong correlation with the Hammett sigma constant. This approach does not seem to have been pursued, at least in published work, but it raises intriguing questions and possibilities. For example Briggs (1981) showed that the relationship $\log K_1 = a \log K_2 + b$, where K_1 and K_2 are any partition coefficients, can be used to derive relationships between K_{ow} , adsorption by soil organic matter, solubility and bioconcentration factors and that a K_{ow} of 10^3 represented about the upper limit for systemic activity in plants. Later Briggs *et al.* (1982) suggested that translocation of *O*-methylcarbamoyloximes and substituted phenylureas in plants reached a maximum for compounds with a $\log K_{ow}$ of 1.5-2 as a result of a two-step process, the first being partitioning into lipophilic root solids (which increases with K_{ow}) and the second being uptake into the aqueous phase in the free space and in cells (which decreases with K_{ow}). Yapel (1972) showed that the presence of 1 g/l Tween 80 could change the K_{ow} by more than one order of magnitude in some cases so the biological changes he reported are consistent with the ideas of Briggs, assuming that the effect of surfactant on K_{ow} is also expressed in an effect on soil adsorption and in the partitioning processes in plants. It would be interesting to know if this is so and also how different types of surfactant would compare in this respect but unfortunately there is little information (Norris, 1982). The view that some s.c. formulations seem to be more active than the corresponding e.c. or w.p. formulations (D.V. Clay, pers. comm.) might be given a theoretical base if this sort of information was generated and it would also be possible to speculate more confidently on the likely behaviour of materials formulated for electrohydrodynamic application.

PERSISTENCE

In the laboratory, rates of degradation of pesticides in the soil are affected by soil moisture content, temperature and often pesticide concentration. Knowledge of the relationship between the kinetics of breakdown and these factors obtained in the laboratory can be used to give a good approximation of field dissipation rates of many compounds (Hurle & Walker, 1980; Laskowski *et al.*, 1983). The nature of the formulation may also have an effect but account can easily be taken of this in the design of the laboratory programme. This approach is useful for many purposes but there are a number of limitations which will require conceptual and experimental refinement before they are overcome.

A major problem is to classify the kinetics of decomposition adequately. Many reactions to a first approximation follow the first order rate equation $dC/dt = kC$, where C is pesticide concentration and k is the rate constant, but frequently breakdown curves are described better by equations of higher order (Kempson-Jones & Hance, 1979). Experimental artefacts may be involved as the apparent order of the reaction can vary depending on how the incubation is carried out (Hance & Haynes, 1981). The great disadvantage is the need for a range of laboratory incubation data obtained under different conditions in order to cope with the differences between soils which can be substantial. For example Walker *et al.* (1983) in

a collaborative study with 15 soils noted that the first order half life of simazine incubated in the laboratory with soil at 20°C and 60% FC varied from 24 days to 156 days and Laskowski *et al.* (1983), reviewing the literature, noted variations in degradation rates in different soils under reportedly identical conditions ranged from 2-fold with propyzamide to 80-fold for nitrilotriacetate. Given enough data it would be possible to characterise the degradative abilities of soils using regression methods but fundamental approaches might be more attractive.

Frehse & Anderson (1983) suggested a model which includes values for adsorption and biomass survival as well as laboratory measurements of dissipation rates and thus is able to take account of two of the major soil characteristics that affect persistence. They also suggested preliminary tests to assess the importance of abiotic processes. Soulas (1982) proposed a two compartment model consisting of a liquid phase containing soluble substrates and biomass and an adsorptive solid phase. He expresses mineralisable carbon as a function of total C and soil water assuming that carbon solubilization is a first order reaction. He then classifies soil organisms into those that can and cannot degrade the pesticide. The group that can degrade the compound is divided into those which do (metabolic) and do not (cometabolic) derive energy from the process, and the other into those which are and are not tolerant of the compound. The aim is to use laboratory studies of microbial growth in batch or continuous cultures to provide the basic data needed to use the model predictively. Unfortunately even this level of complication is likely to be inadequate, particularly in view of the suggestion of Senior *et al.* (1976) that communities of microorganisms will be more effective than single species at degrading xenobiotics, but at least it should provide a useful framework for future work.

Only the work of Frehse & Anderson takes account of photochemical or chemical processes which are known to occur in soil even though they are difficult to quantify (see Miller & Zepp (1983) for a recent review). Predictions based on laboratory observations tend to underestimate decomposition rates (Walker *et al.*, 1983) which might, in part, be the result of omitting these processes. Increasing pesticide use in Australia has stimulated several programmes to study pesticide persistence (R. Truscott, I.G. Ferris, pers. comm.). Since, during the hot, dry summer months microbial action is likely to be slow there will be particular interest in comparing the results of this work with those obtained elsewhere.

An important feature of both the Frehse & Anderson and Soulas approaches is that they can make provision for the effect of other chemicals (including nutrients) that may be present. This seems to be an increasingly important consideration particularly in relation to inductive phenomena. It has been known for a long time that some compounds, such as the phenoxyalkanoic acids, can induce adaptive changes in the soil microbial population so that after an initial "lag phase" they are decomposed rapidly. Until recently this phenomenon has been regarded as of more academic than practical interest but this attitude is now changing as evidence accumulates of microbial adaptations and cross-adaptations to other compounds (Kaufman & Edwards 1983). Controlling this process by the use of microbiological inhibitors (see Obrigawitch *et al.* 1983 for a recent example) and perhaps even exploiting it provides a fascinating challenge in soil microbiology.

CONCLUSION

These topics represent only a few examples of the difficulties facing those who seek to understand and quantify the processes to which a pesticide is subjected in the soil. All of them, however, support the feeling of mild surprise experienced by many of us that soil applied pesticides work at all. Graham-Bryce (1976) calculated that only 2.9% of soil-applied disulfoton actually reaches the target aphid and Addala *et al.* (1983) have shown that as little as 10 ng of chlortoluron can reduce the fresh weight of an *A. fatua* plant by up to 40%. Thus pest control with such materials is achieved at the moment only by the use of the overdoses that are possible with selective compounds. The theoretical opportunity of improving the efficiency of chemicals by devising better procedures to transfer them to the target site remains a tantalising technical possibility which justifies continuing research on the physical and biological processes that control the distribution, concentrations and persistence of pesticide in the soil.

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INTERNAL AND EXTERNAL PLANT RESIDUES AND RELATIONSHIPS TO ACTIVITY OF PESTICIDES

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ABSTRACT

The activity of a pesticide depends on the numerous factors which limit a toxic amount of chemical reaching the site of action or contacting the pest. Three general limiting areas are the pesticide and application technique, the plant, and environmental conditions. Application of pesticides may not directly contact the pest and hence the pesticide must have persistency to act as a protectant, or the ability to partition into the plant for eradication action, or to be translocated within the plant to the organism or the site of action. Residue analysis can determine minute amounts of chemical, but if the sample does not represent the portion of the plant where the pest is present, then erroneous conclusions may be drawn regarding the concentration of the pesticide and its activity.

INTRODUCTION

Many processes are involved with the fate of a pesticide. Ebeling (1963) discussed the basic processes involved in the deposition, degradation, persistence, and effectiveness of pesticides on plants. Few of the principles have changed in the ensuing 20 years, yet we observe today many of the questions and problems present then.

Pesticide residues are determined for a variety of reasons including registration, regulation and compliance of terminal food residues and safe use patterns, environmental impact studies, and to support basic research on efficacy, uptake, penetration, translocation, metabolism, and mode of action. Despite the sophistication of present day techniques and instruments, the analytical data can only be as good as the sample analyzed. Hence, the plant protectionist must liaise with the analytical chemist to understand the goal of the analysis and to determine the experimental design and sampling techniques so that meaningful data is generated and correct interpretations can be reached. This paper discusses some aspects of the influence of the pesticide, formulation, and environmental conditions on pesticide residue behaviour and the relationship to activity on or in the plant.

INITIAL DEPOSIT OF PESTICIDE

Several factors influence the amount of initial deposit of pesticide on a crop after application. The rate of application ($\text{kg}\cdot\text{ha}^{-1}$) is perhaps the most obvious factor with increasing deposit occurring with increasing rate. A limit is reached, however, beyond which the pesticide can be placed on the plant surface. The actual spray operation can influence the deposit as loss can occur through runoff, volatility, or misdirected spray. Lougheed *et al.* (1983) observed that concentrated (5X) spray of apple trees resulted in higher terminal deposits of daminozide on apples compared to dilute (1X) sprays. Ritcey *et al.* (1981) sprayed alfalfa, rye, and oats with different pesticides but under identical conditions and at the same dosage and found that initial deposits were much higher

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with less volatile pesticides (Table 1). Residue deposit was slightly affected by the height of the boom above the plant canopy and slightly lower residues were determined in the middle portion of the plant canopy compared to the top. These results suggest application of highly volatile pesticides, such as dichlorvos, naled or mevinphos, as a aqueous spray may be inefficient.

TABLE 1

Residue deposit as a function of vapour pressure, height of sprayer, and plant portion sampled

Insecticide	V.P. (mm Hg)	Height (cm)	Crop	Residue (mg.kg ⁻¹)	
				Top	Middle
Naled	2X10 ⁻³	10	oats	0.87	0.62
Naled	2X10 ⁻³	40	oats	1.2	0.45
Naled	2X10 ⁻³	20	alfalfa	0.72	0.69
Methamidophos	3X10 ⁻⁴	10	oats	3.5	2.1
Methamidophos	3X10 ⁻⁴	40	oats	4.9	2.8
Methamidophos	3X10 ⁻⁴	20	alfalfa	25.	23.
Parathion	4X10 ⁻⁵	10	oats	7.9	5.3
Parathion	4X10 ⁻⁵	40	oats	9.0	3.2
Parathion	4X10 ⁻⁵	20	alfalfa	28.	25.
Acephate	2X10 ⁻⁶	10	oats	9.2	2.9
Acephate	2X10 ⁻⁶	40	oats	6.4	2.8

The nature of the plant surface, morphology, and the surface area/plant mass ratio of the crop intercepting the pesticide spray can produce a differential deposit over the crop. With celery, most of the residue is deposited on the top leaves compared to the marketable stalks. Trimming 12% (by wt) removed 57% of a diazinon residue and trimming 20% removed 86%; analysis of trimmings from a parathion treatment indicated over ten times as much residue on the leaves (Braun *et al.* 1982). Similarly, most of an EBDC residue deposit on head crops is found on the outer wrapper leaves (Ripley 1979). An order of magnitude difference was found in zineb residues on strawberry leaves, calyx, and berry, respectively (Ripley 1979). With captan there was 10 times the residue on strawberry leaves compared to the fruit and less dense foliage resulted in a greater deposit of captan and dicarboximide fungicides on berries (Ripley & Edgington 1983). Feathery carrot foliage had a much higher (10X) residue of parathion than onion tops but in each case about 90% of the initial deposit disappeared in the first 48 h (McEwen *et al.* 1980). Marginal accumulation occurs due to repeated weekly application of pesticides.

Formulation also affects residue deposit and in most instances a lower residue is found with wettable powders compared to emulsifiable concentrates (e.c.) or flowable formulations; e.c. formulations may increase penetration thus preventing early physical loss of pesticide and prolonging persistence, and indeed, these formulations or addition of oils or adjuvants are often found to be phytotoxic to plants.

Dislodgeable residues

With respect to worker safety and re-entry intervals, surface dislodgeable residues are very important. The dislodgeable surface residue may be

recovered from leaf surfaces using a soap-water solution (Iwata *et al.* 1977) or by organic solvent washes (Cahill *et al.* 1975). The soapy water will remove true surface residues (particulate deposit) whereas solvent washes can be used to preferentially remove residues on the surface, in embedded and epicuticular waxes, and those penetrated into cells. Buck *et al.* (1980) used solvent washes (based on pesticide solubility) and found these surface residues to be as appropriate as the detergent water extractions.

Residues on the surface generally decrease with time and comparison can be made between disappearance rates and the effects of environmental conditions. McEwen *et al.* (1980) found that the total and dislodgeable residues of parathion and phosalone declined similarly on apple leaves, although the per cent dislodged decreased with time. With parathion, considerably less residue was dislodged onto gloves that touched the foliage compared to that recovered with aqueous Triton X-100 shaking. There is less dislodgeable residue from e.c. formulations compared to w.p. (Nigg 1979).

DISSIPATION OF PESTICIDE AFTER APPLICATION

Persistence is defined (Greenhalgh 1980) as the residence time of a pesticide in a defined compartment of the environment expressed in units of time relative to a benchmark. Most studies of foliar residues on fruit or vegetables relate to total residues on the marketable commodity per pesticide residue tolerance or as dislodgeable portions. Such residues may not provide meaningful information to the crop protectionist since the residue may not be at the site of action or is not expressed as the toxophore *per se*. Many chemicals are extremely active at the site of action yet large amounts of pesticide often have to be applied to achieve the desired control.

Factors affecting the disappearance of a pesticide after application can be divided into those due to the crop (morphology, cuticle characteristics, stage of growth at treatment and rate of growth), those relating to the pesticide (formulation, volatility, water solubility, log P, susceptibility to chemical and biological degradation), and those due to environmental conditions (rain, wind, humidity, temperature, and light).

In studies of pesticide residues on lettuce (Braun *et al.* 1980, 1982), large differences in residue concentration of the various pesticides immediately after application were found consistently despite the fact that application rate and procedures were the same. Differences in the vapour pressure of the pesticides probably contributed to these variations in initial deposit. Subsequent dissipation of the chemicals can be attributed to the dissimilarity in the properties of the pesticide particularly as influenced by environmental conditions.

MODELLING OF PESTICIDE DISSIPATION ON PLANTS

There are several criteria that should be considered in developing a model for pesticide behaviour (McFarlane *et al.* 1977, NRCC 1981). In general models originate from phenomenological or theoretical concepts, and ultimately, through amalgamation of many principles and observations, become an integration of multiple components or compartments representing the sum of the many varied possibilities that affect the fate of the chemical. Each pesticide, with its individual characteristics, will behave differently yet hopefully predictably.

Examination of pesticides from the phenomenological approach, however, also provides useful information in understanding the behaviour of the

specific compound. Most "models" start with the empirical correlation of observed data with known physical, chemical, or biological phenomena. Hence, the behaviour of the compound can be attributed largely to one or two processes (volatilization, hydrolysis, photodecomposition), or to its physical properties (vapour pressure, water solubility, partition coefficient). Modelling of pesticide dissipation usually involves correlation of residue data with time, weather, or other environmental parameters.

Disappearance curves for most pesticides after foliar application show an exponential decline. In many cases, (pseudo) first-order reaction kinetics are used to explain the decline in pesticide residue. This approach is useful since the slope of the straight line of the logarithm of residue concentration versus time after treatment can be used to calculate the half-life of the pesticide; the time required to lose a certain percentage of the residue is independent of residue concentration. Often these studies only consider a portion of the disappearance curve ($t > 1d$) or 1-2 half-life periods. Discrepancies are usually accredited to sampling or analytical errors. In reality, several different or mixed-order rate equations may be operable over the life time of the pesticide depending on the processes involved with its fate, and indeed, bi-or trilinear curves are observed (Ebeling 1963). Many studies fail to account for the large initial residue loss in the early period after deposit (volatility, rub-off) or the apparent long persistence of low concentrations of the chemical in the plant. "Half-life" is usually not defined and often represents the time required to lose half the initial deposit (disappearance time, DT, for 50%) and is not the half-life in the kinetic sense of radioactive decay. In many cases, regression analysis using semilog first-order approaches does not yield good correlations particularly where two or more apparent first-order processes are involved in the dissipation.

Stamper *et al.* (1979) proposed an alternative to first-order approaches for organophosphorus insecticide residues on leaf surfaces by showing a high correlation between the log of concentration (C) and the log of time (t). This model appears valid for a wide range of OP compounds and environmental conditions. Rationale for the model is based on diffusion of the chemical from the leaf surface and it could be useful for prediction of worker re-entry intervals. The model only accounts for surface residues and their behaviour from day 1-3 after deposit, neglecting the initial early rapid decline of residue. Plumb *et al.* (1977) explained the decline of 2,4-D and 2,4,5-T residues in chamise (*Adenostoma fasciculatum*) and soil under arid California conditions using equations in terms of log C versus log (1+t). This model also could not account for the rapid early decline of residue and $t > 0$ day was used to model the disappearance.

Sirons *et al.* (1982) examined the persistence of hormone-type herbicides in susceptible crop plants under simulated drift conditions and found a relation in terms of $C = \text{rate} (a - b \cdot \log t)$. This equation explained the early rapid dissipation of residue and part of the long persistence of trace concentrations although the algorithm tends to create negative residue results at long time periods. Within limits, the data could also be explained by first-order equations. Real time values (1 min, 1 h, 3 h) were used for the initial t value whereas many other studies tend to ignore the $t = 0d$ and initial concentration (C_0) datum.

Nigg *et al.* (1977) proposed a model based on the assumed additive and linear contribution of weather and environmental factors on the dissipation of pesticides from citrus foliage in Florida so that $\ln C = \ln C_0 + \sum (a_i \int x_i dt)$

where a_i = coefficients for the environmental factors x_i over time. Using cumulative temperature and rainfall data, better correlations were obtained compared to first-order approaches.

In other studies, good correlations are obtained with both time alone and with weather variables alone, and since time often correlates with cumulative weather variables it may be impossible to ascertain the relative importance or contribution of a particular variable. Nevertheless, one particular influence (rain, light, temperature) can lead to dramatic changes in residue concentration (and activity) yet not be evident in the regression equation. Multiyear studies yield mean data amenable to modelling and breaks in curves from individual studies at certain time periods correlated with specific environmental conditions can explain a particular performance of the chemical. Anomalous data points should be considered in terms of a physical or environmental process such as volatilization and vapour phase redistribution, or washoff and redistribution by rain.

Under similar conditions, two chemicals can show different results demonstrating that the fate of each chemical should be considered separately. Table 2 shows data for metalaxyl and mancozeb as a formulation mixture on lettuce in two years with dissimilar rainfall. Mancozeb deposits appear to be removed by rainfall whereas metalaxyl shows similar dissipation in both years. Variations are observed between cos, leaf and endive lettuce and between the EBDC applied (Braun *et al.* 1982), however, over a 4-year period the EBDC data are very similar and recommendations can be made on days to harvest and terminal residues.

MOVEMENT INTO PLANTS

Following foliar application, the pesticide can remain on the surface or partition (absorb) into the leaf cuticle and enter cells and vascular tissue. Environmental and application variables determine the deposit of chemical available for uptake. Desirable physical characteristics of the pesticide, such as log P (Edgington 1981, Briggs *et al.* 1982), regulate the uptake and translocation of the chemical, while formulation and adjuvants can aid in the partition process (Price 1977, Hartley & Graham-Bryce 1980).

TABLE 2

Mean residue concentration in lettuce (cos, leaf, and endive) following foliar treatment with a metalaxyl/mancozeb formulation for two years with cumulative rainfall data.

Days after application	Σ rain mm	1981		Σ rain mm	1982	
		residue $\mu\text{g}\cdot\text{g}^{-1}$			residue $\mu\text{g}\cdot\text{g}^{-1}$	
		metalaxyl	mancozeb		metalaxyl	mancozeb
0	0	4.6	31	2.0	8.8	42
1	0	1.6	28	29.0	2.5	17
3	0	1.2	21	29.8	1.3	7.9
7	36.2	0.27	7.7	33.8	0.47	3.0
10	36.2	0.065	4.7	38.2	0.15	1.4
14	43.1	ND	0.88	44.0	0.065	0.66
$t_{1/2}$ (days)		1.5	2.8		2.1	2.5

Physical barriers, such as the cuticle, cell walls and the plasmalemma, must be overcome by the chemical to reach the plant protoplast.

Diffusion is the main process governing the movement of the pesticide through the cuticle whereas partitioning is involved with entry into the cuticle and across membranes. Most cuticular penetration occurs from the spray solution via liquid-liquid partitioning; surfactants facilitate the uptake but may cause phytotoxic effects. Uptake may also occur less rapidly from dried deposits; high humidity conditions promote penetration. Nigg *et al.* (1981) observed that the movement of parathion from citrus leaf surfaces to the wax and from the wax to cells resembled the process $A \rightarrow B \rightarrow C$ with each reaction following first-order kinetics. Apoplastic pesticides can also move from the transpiration stream to leaf surfaces.

The lipophilicity of the pesticide will determine the rate of penetration and diffusion in the cuticle. Lipophilic labile groups are often attached to the toxophore to aid in penetration and movement to cells; analysis should identify the exact nature of the residue. Many systemic fungicides are formulated as an e.c. to permit rapid partitioning. Other fungicides with some systemic nature (benomyl, dicarboximides) are formulated as a w.p. to take advantage of their protectant qualities.

Penetration studies of a pesticide can be examined by washing the leaf with methanol (or detergent solution) to remove surface residues, chloroform to recover residues in the wax, and cellular residues can be extracted with an appropriate organic solvent using homogenization. Hydrolysis can be used to recover bound or conjugated residues. The total amount of residue declines with time but the concentration in each of the compartments shows different behaviour. Surface residues decline with time while residues in the wax may increase for several days before declining; cellular residues also peak after several days and may remain fairly constant or decline rapidly due to enzymatic metabolism (Nigg *et al.* 1981). Metabolic stability is one prerequisite for a systemic pesticide (Edgington 1981). In expanding substrates, the absolute amount of chemical (μg) may remain constant for long periods although dilution due to growth results in declining residues on a $\mu\text{g.g}^{-1}$ basis (Sironi *et al.* 1982).

RESIDUES WITHIN THE PLANT

The plant pathologist is concerned with whether fungicides are protectants, eradicants, pseudoapoplastic systemics or symplastic systemics. In actual practice, chemicals such as thiabendazole or benomyl applied to potato tubers, bananas, or citrus fruit after harvest are essentially acting as both protectants and eradicants. They protect the surface and may penetrate a few cell layers to eradicate previous infections. However, when applied to growing transpiring plants, benomyl and many other fungicides are partitioned into the plant becoming pseudoapoplastic. Therefore the activity and residue picture is very dependent on water movement in plant tissue at the time of application.

The percentage of total residue applied which is inside the cuticle is usually minimal. Thus a half-life for the total residue does not reveal much in terms of the toxophore within the plant. Of that residue within the plant cuticle some interesting observations may be made. To our knowledge, any systemic pesticide can pass through the cell plasmalemma membrane and is thus subject to attack by plant enzymes. Many herbicides are toxic to plants at this point and therefore are not good subjects for study of the normal translocation of xenobiotics within the plant. Those herbicides which are translocated to meristems, such as the root apex, before affecting the plant growth are often present in only trace amounts.

Export of herbicide residues out of leaves seems to fall into three groups. 1) Some of the weak acids which enter the phloem (sieve tube-companion cell complex) as molecules and then ionize within the phloem and are translocated in the direction of photosynthates may have from 5-50% movement out of leaves. The amount remaining in the leaves to move acropetally with the transpiration stream is essentially that portion not loaded, or retained, within the phloem. 2) The weak acids, such as diclofop-methyl, with isopropyl groups appear unable to "load" and only about 1 to 5% is translocated in the phloem (Boldt & Putnam 1980, Hall *et al.* 1982). Also, a large group of nonionic herbicides (bentazon, chlorsulfuron) have recently been developed that appear to load very little. They are translocated in very low amounts (about 0.1 to 2%) but they exhibit sufficient chemical stability to reach the roots intact; they must be highly active at concentrations of 10^{-7} to 10^{-9} M. Obviously, residue analyses in these cases may lead to the erroneous conclusion that residues in roots are insignificant. 3) Another group of herbicides which exhibit excellent basipetal translocation within the phloem are some of the organic phosphates exemplified by glyphosate and fosamine. While glyphosate has been considered as ionic in the apoplast, and thus not rapidly "loading", it probably forms a divalent ion within the phloem and is therefore quite effectively retained. Autoradiographs of veins suggest varying degrees of accumulation depending on the experimental plant. Bean (*Phaseolus vulgaris*) displays distinct vein accumulation for us while Gougler and Geiger (1981) found no accumulation in sugar beet. Similarly, glyphosate is a much less effective herbicide against field bindweed (*Convolvulus arvensis*) displaying minimal accumulation in veins.

Amongst fungicides, almost all residues within plants, reported from foliar or seed application, are in the transpiring organs indicating minimal phloem transport. However, a critical analysis will show trace amounts of residue, even as the toxophore, in meristems of roots and shoots, especially soon after application, indicating some phloem transport. Why is this? Among the chemical groupings discussed for herbicides, there are no weak acids (Group 1). There are almost no nonionic, chemically stable but highly active toxophores which act at 10^{-7} to 10^{-9} M. The one exception may be metalaxyl. Several researchers have reported some therapy of root diseases, but only with development of very sensitive capillary gas chromatographic techniques have Bruin *et al.* (1982) been able to relate residues in harvest potato tubers (0.02 to 0.04 $\mu\text{g}\cdot\text{g}^{-1}$) as a result of foliar sprays during the growing season, to protection against potato late blight (*Phytophthora infestans*). Metalaxyl also induces an accompanying physiological effect on tubers to give control of several tuber decay fungi not attributable to metalaxyl itself.

As for Group 3, there are no organic phosphate toxophores, which are translocated with phloem assimilates, clearly proven. Fosetyl Al {aluminium tris (ethyl phosphate)}, while reported to have some effects on Oomycete fungi *in vitro*, is not translocated as such. Labelled P^{32} studies with fosetyl Al show movement basipetally in veins (Bertrand *et al.* 1977), but this may only be the phosphoric moiety. Phosphoric acid is known to be phloem mobile.

The residues entering into phloem may also be affected by other factors not completely understood. For example, GAF 141 {(2-chloroethyl) phosphonic acid plus N-methylpyrrolidine} applied with three herbicides altered the root-sink balance and enhanced the movement to roots (Chykaliuk *et al.* 1982). Herbicides are quite different in their mode of action, and therefore, it would seem that GAF 141 might enhance transport of fungicides to roots.

This assumes that the toxophore is metabolically stable in the phloem. If toxophores are deficient in metabolic stability within plants, then the timing of fungicide application, to achieve maximum transport along with photosynthates, needs to be considered. The toxophore needs to act before it is degraded.

In summary, residue analysis and half-life calculations may be important from a regulatory viewpoint, but the interpretation physiologically is an entirely different matter. There is a profound need to develop highly active systemic fungicides which are metabolically stable.

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CONTROLLED RELEASE - PRESENT AND FUTURE

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ABSTRACT

The scope and objectives of controlled release formulations in plant protection and related areas are outlined. The types of controlled release formulations presently used are described according to release mechanisms and the environment into which the agent is released. The most promising developments and trends in future applications are reviewed and the stimulation of and obstacles to these developments are considered.

INTRODUCTION

There are probably as many definitions of controlled release and its function and potential role in plant protection as there are people who know of its application. Some have considered controlled release as a panacea that will correct pesticide application and usage problems, while, at the other extreme, are those who consider such developments as a 'last stand' effort to prolong the use of chemicals for pest control. It may also not be realized that the increase in persistence of short-lived pesticides that controlled release formulations can provide is important in making the use of pheromones for plant protection a viable proposition.

Controlled release finds applications in a host of different areas, of which plant protection is possibly one of the least exploited. The definition of controlled release is not synonymous with, but includes a number of other terms, such as slow release, sustained release, timed release etc. Each of these terms has its own description but controlled release has been defined as a method in which bioactive materials are made available to a specified target at a rate and duration designed to accomplish an intended effect (Kydonieus, 1980). In most cases it is the permeation-moderated transfer of an active material from a reservoir to a surface for specified period although other mechanisms (surface erosion or degradation and evaporation) may be involved, diffusion is usually the rate-controlling step. In this way controlled release simulates natural processes to a certain extent, reducing the concentrations of available active agents and exploiting optimum delivery pathways. Both aspects tend to reduce losses and side-effects on non-target organisms.

Through the use of controlled release the potential savings in wasted material could be considerable. This greater efficiency in use could be revealed as either a lower application rate providing the same duration of effect as a conventional treatment or greater persistency for equivalent amounts and fewer applications. It is fair to say that for most of the successful formulations this has been generally substantiated in field studies. For example, the success of controlled release formulations of volatile, short-lived insect sex pheromones as persistent treatments for crop protection attests to this (Plimmer, J. R., 10th International Congress of Plant Protection, 1983). Likewise, application of systemic insecticides in controlled release formulations to soil both extends the period of activity (Gauthier, 1978) and reduces the amount of insecticide needed (Wilkins et al., 1983).

Many other benefits can ensue from the utilization of controlled release systems in plant protection and these may be critical to the success of the application (Allan et al., 1973). However, improvements in efficiency can be provided by small changes in the formulation which can not strictly be considered as controlled release, e.g. the use of stickers, spreaders, humectants, clay granules, UV filters, anti-oxidants and extenders such as microbial inhibitors. This difficulty in precisely defining controlled release is theoretical as in practice a range of control of release is evident and no formulation can claim to be truly controlled release (Hartley & Graham-Bryce, 1981). Frequently, claims for controlled release in product literature exceed the capabilities of the formulation concerned.

COMMERCIAL APPLICATIONS

In selecting systems for the controlled release of agents for plant protection the cost and availability of the polymeric ingredients are often more important than biological efficiency. Especially under environmentally-exposed conditions, the simpler monolithic systems with time dependant release kinetics are as useful as the more expensive formulations with constant release rates. The formulations commercially available will be considered on the basis of type of release mechanism. However, release rates have not been adequately categorised under actual use conditions (Wilkins, 1983) and thus these formulation types are usually based on 'in-vitro' assessments.

In general, physically-based systems are dominant and no chemically-based formulation has reached the agricultural market place.

Reservoir systems with rate-controlling membranes

These include encapsulation methods where release may be controlled by diffusion or leakage through the capsule wall, rupture or osmotic breakage or erosion of the wall. Although constant or pseudo-constant (timed release) release can be achieved with this membrane system more often under field conditions a square root of time (\sqrt{t}) relationship is observed.

The use of microcapsules is probably the most successful of the controlled release technologies to date used in plant protection. Some commercial products are listed in Table 1.

Table 1. Commercial plant protection applications of microencapsulation

Product*	active agent	application	company
Penncap-M	methyl parathion	insect control	Pennwalt Corp.
Penncap-E	ethyl parathion	insect control	Pennwalt Corp.
Knox Out 2FM	diazinon	insect control	Pennwalt Corp.
Altosid 10SR	methoprene	insect growth regulator	Zoecon Corp.
Micro-Sect	synergised pyrethrins	insect control	3M
Cap-Cyc.	chlormequat	plant growth regulator	3M
Dyfonate MS	fonofos	soil insecticide	Stauffer.
Tox-Hyd	warfarin	rodent control	WARF Inst.

* registered trade names.

Microencapsulated methyl parathion has reduced the toxicity hazard to field workers as well as improving persistence. Another advantage is that

microcapsules can be applied by conventional spraying. Greater efficiency through better targetting is exemplified by diazinon microcapsules. These can be picked up on cockroach hairs and then ingested following cleaning behaviour, leading to massive dosing which is very effective even against diazinon-resistant individuals. Rain-fastness on plants is a problem, particularly to the application to pheromone release and although success has been achieved in the field (Campion, 1982) no products have yet been marketed for insect mating disruption.

Reservoir systems without rate-controlling membranes

These include hollow fibres, porous and fibrous structures and possibly hydrogels. Hollow fibres have been mainly used for delivering volatile agents, particularly insect sex pheromones and inhibitors. The liquid active ingredient is held in a capillary, closed at one end. Release occurs by evaporation and diffusion through the column of air above the liquid. As the pheromone evaporates the column of stagnant air lengthens and the rate slows according to the \sqrt{t} . An advantage is the lack of a manufactured membrane, thus avoiding production variation typical of encapsulated systems. This system, developed by Albany International, has been used with the pheromone for the cotton pink bollworm, *Gossypium*, for mating disruption. In the U.S.A. up to 125,000 ac have been treated. It is claimed that the addition of a small amount of a synthetic pyrethroid to the sticker can reduce the amount of pheromone needed for high levels of control. This system, apparently, has not been used to deliver other volatile agents, such as fumigants.

Monolithic systems

Generally, these are the simplest to formulate and the least expensive way to moderate the release of bioactive agents. The agent is dissolved or dispersed in a polymeric matrix and this can be achieved by the normal processes of the plastics or rubber industries. Release occurs by diffusion, sometimes aided by dissolution or by erosion. Release rates are normally dependant on \sqrt{t} .

Applications for this system have been surprisingly limited partly as a result of the cost of the polymer matrix and the type of application for

Table 2. Monolithic systems for pest control agents

Product*	Active agent	matrix	application	company
Dursban 10CR	chlorpyrifos	chlorinated polyethylene	mosquito larvicide	Dow Chemical Co.
Ecopro 1700	temephos	polyethylene blend plus calcium carbonate	larvicide	Environmental Chemicals Inc.
Ecopro 1330	tributyltin fluoride	polyethylene & ethylene vinylacetate copolymer	aquatic molluscicide	Environmental Chemicals Inc.
Ecopro 1000	copper sulphate	ethylene propylene copolymer	molluscicide	Environmental Chemicals Inc.
BioMet-SRM	tributyltin oxide	natural rubber	molluscicide	M&T Chemicals Inc.
CBL-9B	tributyltin fluoride	natural rubber	molluscicide	Creative Biology Laboratory

Incracide E-51	copper sulphate	ethylene elastomer	molluscicide	International Copper Research Assoc.
14 ACE-B	2,4-D	rubber	herbicide	Creative Biology Laboratory
Reforest-Aid	2,4-D	kraft lignin	herbicide & tree stimulant	Greenshield of Washington

* registered trade names.

which this system is suited. One of the earliest controlled release pesticides available was the No-Pest Strip^R (Shell), a plasticised PVC matrix containing a volatile insecticide, dichlorvos. A pseudo-linear release rate is obtained by only using part of the release profile; much of the active ingredient remains after the release rate has fallen to inadequate levels. Many variations are now available for control of flying insects indoors as well as flea and tick collars for domestic animals and cattle ear-tags. Other monolithic systems used for pest control are listed in Table 2. Few of these approaches will have much relevance to the vast bulk of plant protection requirements where the need to maximise activity and minimise adverse effect is greatest.

One promising area is the use of biodegradable polymers derived as natural waste or by-products. Such a material is kraft lignin, a by-product of paper-making, with few commercial uses (except as a low-calorific fuel). This material can form a matrix and has shown uses in crops (Dellicolli, 1977; Wilkins et al, 1983) and in forestry, particularly with 2,4-D (Reforest-Aid^R). Controlled delivery, in these examples, has revealed the beneficial side effects referred to previously. These include long-term conifer growth stimulation by 2,4-D and possible improvement of antifeedant properties of carbofuran in the rice crop. This could have considerable value in control of certain plant virus diseases by a systemic approach rather than a residual foliar application which is limited in duration.

Purely surface-erodible monolithic systems (as opposed to most polymers which undergo bulk erosion or degradation in the environment) and swellable hydrogels are few and generally too expensive for agriculture. One exception may be the water-soluble inorganic glasses which are mainly suitable for the incorporation of inorganic nutrients and pesticides.

Laminated structures

These consisted of several layers of plastic films adhered or laminated together. The centre layers of a 3-layer laminate is the reservoir and contains a large amount of the active ingredient. The outer layers are rate-controlling membranes and may be the same or different to the reservoir layer. Within limitations, a steady concentration gradient may be set up across the barrier membrane and thus the system can achieve 'zero order' kinetics. This type of formulation can be produced in large sheets, strips, small pieces (or confetti), granules or ground to give a sprayable wetttable powder. Commercial pesticide products based on this technology (Hercon) include insecticide strips and fly traps (Insectape^R and Roach-Tape^R) and pheromone releasers (Lure TapeTM). Traps for the control of the gypsy moth (*Lymantria dispar*) are available under the trade-name Lure N KillTM as are flakes for mating disruption (DisruptTM). Traps for the cotton boll weevil (*Anthonomus grandis*), releasing grandlure, based on a laminated emitter are also available (Boll Weevil ScoutTM) as are baits for stored

product pests. The number of applications is increasing; especially useful are formulations of unstable materials such as pheromone aldehydes.

Successful field studies for the release of conventional agrochemicals have been carried out (Collins et al., 1981) but no commercial products have yet appeared, probably due to the unattractive economics of this formulation in this, more realistic market.

DEVELOPMENTS

Interest in plant protection applications of controlled release is still intense with new patents appearing weekly. Numerous systems have been developed, some have been field tested and some are being groomed for commercial release. For example, considerable field trials and economic studies have been carried out on a xanthate cross-linked starch matrix developed by the U.S. Department of Agriculture. One obstacle to commercialization of this may be the use of carbon disulphide in its preparation but other complexing materials such as borate (Sasha, et al., 1983) may avoid this. Another system is based upon a matrix of thermoplastic polymer blends with a water-soluble agent (porosigen) to promote leaching. A product (Ecopro™ 1700; Table 2) is available for aquatic larvae control and formulations for soil application may be produced but this may be limited by the problems of delivery to the soil environment. Other systems under development include sprayable latex for pesticides and pheromones and "in-flight" encapsulation. Perennial favourites are coated granules using waxes, vinyl or urea-form polymers. Such systems often merely extend activity rather than altering the delivery rate. An example is a plastic-coated granule containing 5% carbofuran (Yaltox^R). Speciality products for the garden centre market should also be mentioned.

Technical obstacles to development always exist. A thorough understanding of the chosen controlled release system, both in theory and in the field and how it fits in with farming practice is vital. Often a new attitude is essential to identifying appropriate applications. Consumer acceptance can be another problem unless the advantages are clear, as in the case of some pheromone delivery systems. Other obstacles lie in the special need for clearance and registration, problems of potential residues and resistance and the difficulties of clear patent protection. One particular problem for soil applications, especially for pesticides of short persistence is the possible adaptation of microflora to metabolise these chemicals.

THE FUTURE

The need for controlled release will increase in the foreseeable future. It is likely that the trend to chemical agents with shorter persistence will continue. Also their costs and also efficacy will rise. Fewer new pesticides will encourage manufacturers to develop new and better products from existing ones. However, the increase in controlled release products will be cautious as it has in the past, in spite of a prediction made in 1975 that "hundreds of new pest control products based on controlled release will reach the market place over the next decade". It is possible that new chemical agents will be introduced on the assumption that these will be used in controlled release formulations, as has occurred with pheromones and methoprene. As delivery systems more closely resemble natural processes then additional benefits may be realized. Areas where this could happen are plant growth regulators and other semiochemicals (e.g. alarm pheromones, oviposition inhibitors). Undoubtedly, variations

in the basic formulation types will occur spurred on by patent loopholes, economics and politics as well as superior performance. As the development of more accurate delivery systems proceeds so will our understanding of pest and crop relationships leading to better and more efficient pest control methods.

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EFFECTS OF TEMPERATURE AND SOIL MOISTURE ON LOSS OF SOIL-APPLIED HERBICIDES

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Background and objectives

Environmental conditions affect the loss of soil-applied herbicides. In most cases, temperature and soil moisture have a decisive influence on the loss process.

The objectives of this study were to evaluate the effect of soil moisture and temperature on the loss of pendimethalin, ethofumesate and metolachlor.

Materials and Methods

A series of laboratory experiments was carried out on sandy loam soil (o.m. content 2.97%, pH 6.43). The soil-applied herbicides were used at a rate of: pendimethalin 1.98 kg ai/ha, ethofumesate 1.40 kg ai/ha, metolachlor 2.0 kg ai/ha. The trials were conducted using plastic pots containing 300 g soil. In two of the trials the pots were covered with polyethylene and in a third trial they were not covered. Soil moisture was maintained at 20, 40 and 60% FC; five replications of each treatment were incubated at constant temperature of 0-4, 10-13 and 28-30°C for 30 days. Bioassay experiments using oat plants were carried out in controlled environmental chambers. The test plants were harvested 14 days after planting. As an index of phytotoxicity, average shoot height and shoot fresh weight were measured for the five most uniform plants in each pot; data are reported as percent of the untreated control.

Results and conclusions

The temperature and the soil moisture affect the loss of pendimethalin, ethofumesate and metolachlor in soil. At the temperature 0-4°C and soil moisture of 20, 40 or 60% FC, the difference in weight of the test plants between the various treatments was insignificant. At this low temperature, the loss of the herbicides tested was slow, irrespective of the soil moisture content.

At the temperature of 10-13°C, the soil moisture has a decisive influence on the loss of pendimethalin, ethofumesate and metolachlor. At a soil moisture of 20% FC the fresh weight of test plants treated with pendimethalin was 10% of that of the untreated control (100%) and the fresh weights were 16 and 20% respectively at soil moistures of 40 and 60% FC. At the same temperature and soil moisture, the weights of the test plants were 22, 28 and 30% after ethofumesate treatment and 40, 50 and 53% after metolachlor treatment.

At the temperature of 28-30°C, the rate of degradation of the three herbicides is greatly influenced by soil moisture. After 30 days at 28-30°C and a soil moisture of 40% FC, pendimethalin, ethofumesate and metolachlor were degraded 26, 35 and 50% respectively.

The overall results from the trials show the loss of the herbicides in soil increased in the order: pendimethalin < ethofumesate < metolachlor.

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3B-R2

ENVIRONMENTAL FATE OF [¹⁴C] TRIADIMENOL IN RELATION TO THE PRESENCE OF OTHER FUNGICIDES COMPONENTS

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Background and objectives

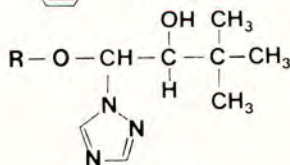
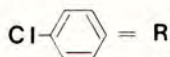
Soil borne and/or seed borne phytopathogenic diseases to plants are generally controlled either by application of fungicides into the soil or by localised seed treatment. The deliberate combination of pesticides for seed treatment to improve diseases and pest control has gained increasing importance in recent years because of the ban on mercury containing pesticides in the Federal Republic of Germany. In this investigation we studied the combined effect of the fungicides triadimenol, imazalil and fuberidazol formulation applied as seed treatment on the persistence, residue behaviour and metabolism of [¹⁴C] triadimenol in soil and wheat plants under field conditions.

Materials and Methods

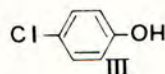
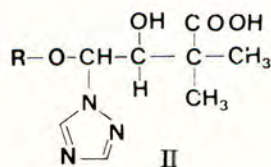
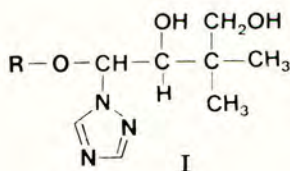
The experiments were conducted with Spring wheat (cv. Kolibri) in lysimeters (0.28 m² surface area, filled with 60 cm para brown soil) under the field conditions in the vegetation period of 1982. [¹⁴C] Triadimenol was investigated in its diastereoisomeric form (three 82:18 erythro) as used in the practice in combination with imazalil and fuberidazol (three component product Baytan-Universal) and compared to its application as a single component. [¹⁴C] triadimenol together with imazalil and fuberidazol (22+3.3+3 %) was mixed with the Baytan-Universal formulation material as dry powder and used for seed treatment. Seed treatment was performed in the laboratory and gave a uniform seed coating as determined by radiocarbon measurements. The average radioactivity was 0.46 uCi/seed, and the seed coating was equivalent to the recommended dose of 150 g/100 kg seeds. The uptake and distribution of [¹⁴C] triadimenol residues in the wheat plants and the soil were followed by radiocarbon analysis. The determination of metabolites in grains, ear-chaff, straw, stubbel-roots, soil and leached water was carried out after cold extraction of the samples with methanol and chromatographic analysis.

Results and Conclusions

The results of analysis of the wheat plants at the dead ripe stage showed that the total uptake of radiocarbon in the one component system was 9.6 % and in the three component system 14.8 % of the applied radioactivity by seed treatment. The differences in uptake in the two experiments were mainly due to the presence of greater amount of radiocarbon in the aerial plant parts than in the roots. The transport in the grains was 0.05 % radiocarbon (0.02 mg/kg) in the one component system whereas 0.06 % (0.02 mg/kg) in the three component system. The ear-chaff contained 0.3 % (0.25 mg/kg) and 0.7 % (0.48 mg/kg) of the radiocarbon. It appears that the presence of imazalil and fuberidazol of the three component system inhibit the soil microorganisms so that a larger quantity of triadimenol was available for translocation to the upper plant parts without being metabolised in the root region. This is suggested from the quantity of [¹⁴C] triadimenol found in the upper 5 cm soil which was 84.1 % and 89.3 % in the one and the three component system respectively. However, it seems that there was a shift in the diastereoisomeric ratio of triadimenol which was more in the three component system (76:24) than that in the one component system (80:20). The metabolites identified in the plants were similar in the two experiments and there was little difference in their quantities. The identity of the metabolites was determined by comparison with authentic standards. The following metabolites were identified in different plant parts: 4-(4-chlorophenoxy)-2,2-dimethyl 4-(1H-1,2,4-triazol-1-yl)-1,3-butandiol(I); 4-(4-chlorophenoxy)-3-hydroxy-2,2-dimethyl-4-(1H-1,2,4-triazol-1-yl)-butane acid (II); and 4-chlorophenol (III).



Triadimenol



FACTORS INFLUENCING EFFICACY OF INSECTICIDES AGAINST SOIL-INHABITING LARVAE

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Introduction

Three general factors which influence the efficacy and reliability of soil insecticides are intrinsic toxicity, persistence and the efficiency of dosage transfer from soil to insect (Nicholls, Farnham and Buxton 1981). The object of the present work is to identify those physico-chemical properties of insecticides which give efficient uptake of lethal doses from soils in a range of soil types and conditions.

Models (Nicholls, Walker & Baker, 1982) which simulate the movement and persistence of pesticides may, in the future, be extended to include uptake of lethal doses by insects once the important processes are identified.

Materials and Methods

Samples of aldrin, bendiocarb, carbofuran, carbophenothion, chlorfenvinphos, DDT, deltamethrin, demeton-S-methyl, 2,3,4,5,6-pentafluorobenzyl(1RS)-trans 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate (PFDCP), dimethoate, permethrin, phorate, tetrachlorvinphos and thionazin (purity >90%) were used for tests. Eight soils (organic carbon contents in the range 0.5-3.3%) were taken from the top 15cm at the different sites, air dried and sieved (2mm). Moist soil was prepared by wetting air-dried soil to a water content corresponding to -10^3 Pa (-0.1 bar) water pressure.

Larvae of the corn root worm *Diabrotica balteata* 10-12 days old were used for insecticide bioassays by topical application, after uptake from soil, and by fumigant action from soil or filter paper. The efficiency of dosage transfer from soil was calculated from: (LD50 topical)/(LD50 after uptake from soil).

Results and conclusions

Intrinsic toxicity is represented by topical application results in which pyrethroids were most and aldrin least potent.

The most potent insecticides after uptake from moist sandy-loam soil were the pyrethroids, bendiocarb, phorate and thionazin. However, greatest efficiency of dosage transfer was achieved by those compounds which exhibited fumigant action, observed in tests on insects held above moist sandy-loam soil, and these included additionally aldrin. These chemicals have favourable air/wet-soil partition coefficients due to their physico-chemical properties, a combination of high vapour pressure and low water solubility.

Acknowledgement

We thank Dr. G.G. Briggs for gift of (PFDCP).

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3B-R4

SOIL MOISTURE AND TEMPERATURE AFFECT THE ACTIVITY OF DICLOFOP-METHYL

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BACKGROUND AND OBJECTIVES

Field, glasshouse and controlled environment studies show that dry soil conditions reduce the activity of diclofop-methyl, but the influence of soil water contents above field capacity have not been reported. Wet soil and cool weather conditions have been suggested as factors contributing to diclofop-methyl damage to winter wheat. The aim of this controlled environment study was to determine the effect of soil moisture and temperature regimes on diclofop-methyl activity on *Avena fatua* and winter wheat cv. Score.

MATERIALS AND METHODS

Winter wheat, vernalised for six weeks at 4/2°C and unvernalsed *A. fatua* were planted in sandy loam soil of known weight and moisture content contained in 9.5 cm diameter pots with sealed drainage holes. The pots were weighed every two days and water added to maintain the soil water content close to 21 g water/100 g dry soil (approximately field capacity) and adjustments were made for plant weight as the experiment progressed. The plants were grown in a controlled environment room where the light intensity was 95 Wm⁻² for 14 h, the temperature 16/11°C and humidity 75/86% rh for day/night respectively. In both temperature and soil moisture experiments the plants were divided into three groups and different temperature (11/6, 16/11 and 26/16°C) or soil moisture regimes (6, 21 and 43% wt/wt) were initiated 4-6 h before spraying. Diclofop-methyl, formulated as 'Hoegrass' was applied to the foliage by laboratory sprayer fitted with an 8001 'Teejet' nozzle delivering 200 l/ha at growth stage 1.4, 2.1-3. The fresh foliage was weighed when the control plants had six to seven leaves. Entry and movement of ¹⁴C labelled diclofop-methyl was followed after application to the last two fully expanded leaves (growth stage 1.5, 2.3-4) of 10 x 0.5 µl drops containing 5 µg a.i./µl of formulated herbicide (2.5 x 10⁴ dpm). After 1, 3, 7 and 14 days ¹⁴C activity was determined on the surface and within the treated leaves, the rest of the foliage, the meristematic region and the roots.

RESULTS AND DISCUSSION

At the median soil moisture, 1 kg ai of diclofop-methyl reduced *A. fatua* foliage fresh weight to 40% of untreated controls. This level of herbicide activity was approximately halved under the dry regime and doubled on plants in the wet soil. Herbicide tolerance of the winter wheat was significantly reduced in the wet regime, compared with the drier soils. Shoot entry and movement studies with ¹⁴C-labelled diclofop-methyl revealed no differences in these processes in contrasting soil water regimes. Wheat tolerance to diclofop-methyl was unaffected by temperature, but *A. fatua* was controlled better at 16/10°C than at 26/16 and 11/6°C. These results suggest that water content of the soil has greater influence on diclofop-methyl performance than temperature. Since the herbicide was applied only to the foliage, the soil water status effects on herbicide activity must result from physiological and biochemical changes in the plant and the ¹⁴C tracer studies show these are not directly related to entry and movement. The results show that wet soil increases the risk of diclofop-methyl damage to wheat and use of this herbicide should be avoided on sites prone to waterlogging. Alternatively since activity against *A. fatua* is increased in these situations lower doses could be used.

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BENZOFURANYLCARBAMATES. EFFECT OF N-SULFENYLATION ON ENVIRONMENTAL BEHAVIOUR.

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Background and objectives

The benzofuranylcarbamate carbofuran, a well-known insecticide used for foliar and soil application, has high acute mammalian toxicity and can cause environmental contamination problems mainly due to its mobility in soil. N-sulfenylation can change the toxicological properties of the molecule (Black *et al.* 1973) and will also alter the physico-chemical characteristics and thus environmental behaviour. To demonstrate the latter, comparative laboratory studies on hydrolysis, adsorption, mobility and degradation in soil were carried out with ^{14}C -labelled CGA 73102 [O-n-butyl-O'-(2,2-dimethyl-2,3-dihydrobenzofuran-7-yl)-N,N'-dimethyl-N,N'-thiodicarbamate], carbosulfan [2,3-dihydro-2,2-dimethyl-7-benzofuranyl-(di-n-butylamino-sulfonyl)-methylcarbamate] and carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-methylcarbamate).

Materials and methods

Hydrolysis studies at pH 5,7 and 9 were performed with all 3 substances in aqueous buffer solutions as described by Burkhard *et al.* (1975). In case of carbosulfan, acetone had to be added as a cosolvent. Instead of screw-capped Erlenmeyer flasks, ampules were used to avoid volatilization losses.

Adsorption constants were determined by the slurry procedure and mobility was studied in dismantled metal columns with several soil types as described by Guth *et al.* (1976).

Studies on rates and pathways of transformation in soil were carried out either in Erlenmeyer flasks according to the German BBA-guideline Nr. 36 or in a flow-through system described elsewhere (Guth 1980).

Aqueous buffer solutions were directly analysed by HPLC using spectrophotometric detection and/or measuring radioactivity in flow-through cells. Soil samples, after extraction with appropriate solvents, were also analysed by HPLC or by TLC using a thin-layer scanner.

Non-extractable material in soil was determined by combustion.

Results and conclusions

The sulfenylated compounds CGA 73102 and carbosulfan were found to be more strongly adsorbed on soil than carbofuran. Consequently, mobility of the sulfenylated products is drastically reduced in comparison to carbofuran. The order of decreasing mobility was carbofuran >> CGA 73102 > carbosulfan clearly demonstrated by the relative mobility factors (RMF) of 3.0, 0.14 and 0.08, respectively. Although both sulfenylated compounds were converted to carbofuran during the mobility studies the rates of conversion were sufficiently low so that even under the drastic conditions of the model studies only low amounts of the pesticide moieties were eluted from the soil columns compared to carbofuran.

Hydrolysis of the sulfenylated compounds leads to carbofuran and/or the corresponding phenol. The hydrolytic stability of CGA 73102 is generally higher than that of carbofuran and carbosulfan. Only at pH 9 the hydrolysis half-lives of the sulfenylated substances are of approx. the same order of magnitude (5 days at 20°C). The hydrolysis half-lives of CGA 73102 and carbofuran decrease with increasing pH, whereas carbosulfan shows the inverse relationship.

In soils of low microbial activity the three substances showed a pH dependency similar to that observed in aqueous buffer systems. Generally, carbofuran ($T_{0.5} = 11$ to 70 days) and carbosulfan ($T_{0.5} = 6.1$ to 26 days) were found more stable in soil than CGA 73102 ($T_{0.5} = 0.5$ to 4.4 days). Transformation of CGA 73102 and carbosulfan proceeds via carbofuran and traces of polar products to non-extractable radioactivity and finally to ^{14}C -carbon dioxide.

In conclusion, N-sulfenylation of the carbofuran molecule drastically reduces the mobility in soil of this insecticide moiety. However, conversion into the active principle carbofuran is reasonably fast for CGA 73102 but significantly slower for carbosulfan.

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Background and objectives

Naproanilide [1-(2-naphthoxy)propionanilide] has a selective herbicidal activity on cyperaceous and broad-leaved weeds in rice fields. In recent years, control of perennial weeds such as *C. serotinus* has been a serious problem in paddy fields in Japan. Since perennial weeds regenerate or propagate through their vegetative parts such as rhizome, tuber or bulb, inhibition of tuberization by herbicides is an important step in the control of *C. serotinus*. Our previous study demonstrated that naproanilide inhibited the tuber initiation from rhizome of *C. serotinus* with slight inhibition on shoot and root growth.

The present study was aimed at investigation of absorption, translocation and metabolism of naproanilide in relation to its effects on tuberization and on RNA synthesis of organs of *C. serotinus*.

Materials and methods

C. serotinus was grown to the 4-leaf stage in a round pot filled with sand under a short-day condition in an environment-controlled room. ¹⁴C-Naproanilide was absorbed through the underground parts. Rates of absorption and translocation were determined by a sample combustion method and autoradiography, and metabolism of ¹⁴C-naproanilide was investigated by thin-layer chromatography.

By the application of naproanilide and its related compounds to the surface water in the pot, effects of them on tuberization and RNA synthesis were measured. RNA fractionation and estimation were done according to the modified method of Ogur and Rosen. Rate of RNA synthesis in each organ was expressed by ¹⁴C-uracil incorporation into RNA.

Results and conclusions

During the absorption-period, ¹⁴C-naproanilide was absorbed linearly with time through the underground parts, and translocated considerably to the shoot. But the amount of ¹⁴C-radioactivity not only in the underground parts but also in the shoot was remarkably decreased after the underground parts were transferred to the naproanilide-free solution. However, the amount of ¹⁴C-radioactivity was found the highest in rhizome among the organs at any time. The ¹⁴C-radioactivities in the metabolic products, 1-(2-naphthoxy)propionic acid (M-1), methyl-1-(2-naphthoxy)propionate (M-2) and their conjugates, were increased with time in any organ with a compensating decrease in naproanilide after the treatment. But the rates of M-1 and M-2 formation were kept especially higher in rhizome than in the others at any given time.

Both M-1 and M-2 as well as naproanilide directly inhibited the tuber initiation and stimulated RNA synthesis in rhizome more remarkably than in the other organs. It was suggested that naproanilide, M-1 and M-2 stimulated RNA synthesis of rhizome and that the resulting disturbance of RNA metabolism in rhizome might induce the inhibition of tuber initiation.

There was a good correlation between concentrations of M-1 and M-2 in rhizome and promotion of RNA synthesis in rhizome induced by naproanilide application, although the concentration of naproanilide was not correlated with the effect on RNA synthesis. As it has been known that naproanilide *per se* has no herbicidal activity, it can be postulated that naproanilide converts to either M-1 or M-2 which inhibits tuber initiation through their action on the RNA synthetic process related to the development of rhizome.

SOIL MOVEMENT OF ETHOPROPHOS

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Background and objectives

The diffusion of the nematicide ethoprophos (O-ethyl S,S-dipropyl phosphorodithioate) in soil is said to be influenced by the presence of clay minerals and more precisely layered silicate minerals which are highly susceptible to adsorb insecticides molecules via the formation of a complex "protonated insecticide molecule-negatively charged clay minerals" (Udy). However others tests demonstrate a very limited penetration of the insecticide even in soils having a low clay content (no more than 2%) but a high organic matter content (7%). (Smelt, Leistra, Voerman, 1977). So the following experiment was designed to precise if only these two factors could explain the soil diffusion of ethoprophos.

Materials and Methods

Soil samples with a low organic matter ($< 1.5\%$) and a low clay content ($< 10\%$) (sandy loam soil) were used. Technical ethoprophos in acetone was sprayed on 3 m x 3 m areas. Application rate was 20 kg active/ha. After treatment 5 cm (diameter) steel cylinders, 45 cm long were driven into the ground to a depth of 30 cm; 100 ml of water were added and the opening was closed. At intervals through the test period water was added. Soil samples were obtained at 40 hours, 7, 21, 42 and 90 days after application; soils cores were forced out of cylinders and 2.5 cm thick sections obtained for analysis.

Results and conclusions

40 hours after application, ethoprophos has already moved down-according to a uniform distribution - to a depth of 15 cm; twenty one days later there is a slight accumulation between 7.5 and 18 cm. So in a light soil with a little organic matter content, ethoprophos moves well and rapidly. All these data allow us to conclude that both organic matter and clay are able to adsorb ethoprophos even in wet conditions; the incorporation of the product is the most appropriate method to improve its effectiveness in heavy or organic soils.

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METHODS TO INCREASE THE PERFORMANCE OF METHYL BROMIDE SOIL DISINFESTATION

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Background and objectives

For reasons of environmental aspects, safety during application and performance, it was presumed that methyl bromide (MB) should be applied at a low dose and consequentially aided by better sealing techniques and/or effectivity improving admixed compounds. The submitted research report deals with biological tests and chemical analysis on soil depth penetration and diffusion patterns of MB in admixture with methyl chloride (MC), bromide uptake by tomato resulting from analogous treatments and uptake by lettuce plants grown on soil disinfested under gas tight sealing material.

Materials and methods

Rhizoctonia solani, Fusarium oxysporum f.sp. lycopersici and Trichoderma longibrachiatum cultures, and Lepidium sativum seeds inserted at 10, 20, 30 and 40 cm depth in sandy loam soil were used for fungicidal and phytotoxic action studies. A modified polyethylene ('Waloplast Combi XX' from Wolff Walsrode, W-Germany), thickness 40 μ m, for soil sealing purposes was compared with the classic low density polyethylene (LDPE), thickness 30 μ m, in another column diffusion experiment and for disinfestation before a lettuce culture. Tomato (cv. 'Marmande') and lettuce (cv. 'Amon') were grown on the same soil type as for column experiments after disinfestation with MB or MB + MC. MB doses varied between 25 and 90 g/m². MC was added in amounts equivalent to MB on chemical or weight base. Soil analysis for MB and bromide residues was done by glc and ion selective measurements respectively. Crop analysis for bromide content was done by glc.

Results and conclusions

Admixture of MC enhanced the performance of MB when compared to the same dose of MB used alone, even at 30 g MB + 16 g MC/m² after a 5 days sealing period. A dose of 45 g MB + 24 g MC/m² was more effective in the R. solani control than a dose of 90 g MB whereas a control of F. oxysporum was observed at a depth of 20 cm by using the same mixture. The antagonistic fungus T. longibrachiatum was much less affected by soil disinfestation with or without mixture as was already often observed before in the latter case. The phytotoxicity for the same mixture also reached further than the lowest point of biological detection as well for a 2 days as for a 5 days sealing period. MB diffusion measurements in soil columns however showed indeed more free MB in the soil gas phase when applied together with MC. During the first two days after fumigation a concentration of free MB in the range of 30-10 mg/l gas could be observed at 20, 30 and 40 cm depth. Bromide residues in soil both in column and crop growing experiments were less when a mixture of MB + MC was used. Residues in soil columns in the 20-30 cm layer (28 days after fumigation) were 40 mg/l dry soil in the case of the combined application and 52 mg/l when MB was applied alone. The use of the more gas tight 'Waloplast' increased MB concentrations at 30 and 40 cm depth in disturbed soil to a tenfold of the concentrations found with LDPE within 4 days after fumigation. That means in figures for the 40 cm depth : about 100 mg MB/l soil gas phase under Waloplast seal and about 10 mg MB/l under LDPE at an application rate of 35 g MB/m². Bromide concentrations in soil and plant material were more than twofold. Admixture of MC decreased bromide residues in tomato fruits and lettuce but this effect was nearly lost when applied under gas tight seal. Bromide residues in tomato fruits of the 1st truss were 16.5, 13.5 and 10.5 mg/kg for application doses of 50 g MB, 50 g MB + 50 g MC and 25 g MB/m² respectively. The effect was maintained in the 5th truss, namely : 6.2, 4.3 and 3.8 mg/kg respectively. Residues in lettuce were 215 and 955 mg/kg when grown on unleached soil fumigated under LDPE and Waloplast respectively, at a dose of 50 g MB + 50 g MC/m². Residue analysis showed that the normal 80 % dissipation when compared to equivalent KBr application occurred already during the sealed period in the case of LDPE. Gas tight seals allow decreasing dosages of MB but mineralization is more intense, thus causing no direct advantages in residues reduction. The use of the mixture described, or the potential use of other admixed compounds is most promising. The use of better sealing material and consequentially lower doses of MB needs more severe control during the application with regard to effectiveness but offers less environmental problems and danger at the time of application. A lot of other plastic types are still under consideration and offer a varied choice in sealing capacities and from an economical point of view, in price.

MOVEMENT OF METHYL BROMIDE VAPOUR THROUGH A CONCRETE PLATE

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Background and objectives

Methyl bromide is a widely used non-flammable chemical for fumigation of stored grain, soil and buildings, but it is toxic to mammals. It is of great concern that fumigant applied in a grain storehouse may leak through one of the walls since the concrete plate or wall is often slightly porous and, if significant, this could present an environmental hazard. However, there are few studies on the diffusion of a fumigant through concrete used in construction. Diffusion of this vapour through a concrete plate has therefore been investigated by measuring concentration of the fumigant through a bioassay over a period of time.

Materials and methods

Concentration of methyl bromide in a glass jar (11.7 litre) with a hole bored in the top and a concrete plate as a base (30 x 30 x 6 cm), was determined at various intervals up to 50 hours using a photoelastic gas detector. "Knock down" of adults of the adzuki bean weevil, *Callosobruchus chinensis* L., being kept within a glass cell at 20°C (165 or 475 ml) fitted to the underside of the concrete plate was carefully observed, and the percentage of the weevils knocked down was calculated.

Results and conclusions

A gradual decrease in concentration of the fumigant took place over time. This fact appeared to be caused by diffusion through the concrete plate, as the weevils in the cell were gradually knocked down. Using the data obtained, diffusion coefficient (D) of the fumigant in the concrete was calculated by the following equation: $D = H(C - C_t)V / ACt$, where H is the thickness of the concrete plate; C is the initial concentration of methyl bromide in the bell jar; C_t is the concentration of methyl bromide after diffusion period, t; V is the volume of the jar; and A is the cross sectional area of the jar. The calculated D value was about $0.003 \text{ cm}^2 \cdot \text{sec}^{-1}$ at 20°C, this value is 1 : 30 in round numbers for the gas to air, $0.097 \text{ cm}^2 \cdot \text{sec}^{-1}$.

Thus it appears that methyl bromide vapour is slightly permeable through a concrete plate or wall used in the construction of a structure such as a grain storehouse.

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EFFECTS OF MICROENCAPSULATED METHYL PARATHION ON BENEFICIAL INSECTS

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Introduction

In 1976 reports of substantial honey bee losses, allegedly arising from the use of 'PENNCAP-M®' microencapsulated methyl parathion (MMP) in the Lewiston, Idaho area, were published in the news media. This incident resulted in a number of retrospective studies in which researchers attempted, after bee loss incidents occurred, to determine the cause of bee mortality and to find evidence of a special hazard to bees from MMP. Lacking comparative reports on other insecticides (except carbaryl), it is not surprising that finding a hazard produced conclusions that microencapsulation represented a special hazard to bees. Recent controlled studies comparing MMP with other common insecticides have shown that MMP is generally not more, and is sometimes less, hazardous to bees than competitive insecticides including methyl parathion emulsifiable concentrate (MPEC).

Results

In tests conducted at Pennwalt's Warminster, PA Research Station a blooming rape field was sprayed 4 times with a mixture of MMP, parathion 15W, azinphos-methyl 50W, and carbaryl 50W. Analysis of pollen collected by bees placed near the treated field showed residues of all four insecticides, with the ratio of concentrations in the pollen approximating the ratio in the spray mixture. This result suggested that the insecticides were adsorbed on the pollen grains regardless of formulation, and that the likelihood of being carried to the hive was similar for all four products.

Recently U.S. Department of Agriculture (USDA) researchers have conducted a number of carefully controlled studies of bee-toxic insecticides applied to blooming crops. In the Texas High Plains MMP was less hazardous to bees than MPEC when applied to blooming sunflowers. In Wyoming, bees fed pollen cake or dry pollen containing 0.01 to 1.0 ppm of methyl parathion in the form of MMP were unaffected, while 10 ppm resulted in mortality in adults and production of less brood. MPEC was more toxic than MMP. An Arizona study found light to moderate bee mortality in hives near cotton fields treated 4 times with MMP (except for higher mortality in an apiary located only 6 meters from a sprayed field). Studies in Oklahoma also showed fewer bees killed and less pesticide carried back to the hive with MMP when compared with MPEC.

Studies comparing MMP to insecticides other than MPEC have also shown a lesser hazard for MMP. In Wisconsin carbaryl plus parathion (early), carbaryl plus parathion (standard timing), and carbofuran all produced greater bee mortality on pollen-shedding sweet corn than did MMP. A retrospective study of bee losses in Wisconsin following applications of methomyl to sweet corn has shown methomyl residues in comb samples which persisted for at least 8 months in the hive.

While the foregoing studies have indicated little difference in bee hazard between MMP and competitive insecticides, recent results with adjuvants have shown promise in reducing the hazard of MMP to bees. In Pennwalt tests the addition of a "sticker" formulation at 1% solids reduced bee mortality by from 65 to over 90% in the absence of heavy dews. Increasing the sticker concentration to 2% provided a modest additional reduction over the 1% level. Large-scale field trials in Texas and California produced similar results.

During field testing of MMP numerous observations were made of its effects on entomophagous insects. In the majority of these tests, populations of these beneficial insects were reduced by less than 50%. In several tests the populations of beneficial insects were even observed to increase after treatment with MMP.

Conclusion

In summary, recent studies have shown that microencapsulated methyl parathion does not represent a special hazard to bees. To the contrary, it has shown less hazard than methyl parathion emulsifiable concentrate in some studies, and less hazard than other competitive products in others. The hazard can be further reduced by addition of certain adjuvants of the "sticker" type. The moderate effects on entomophagous insects suggest considering the use of encapsulated methyl parathion in Integrated Pest Management programs.

CONTROLLED RELEASE PESTICIDES IN POLYMER BASED GRANULES AND MICROCAPSULES

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Introduction

Consolidated Fertilizers Limited (CFL) is developing two formulation techniques which enable the sustained and controlled release of biologically active substances. The granular formulation is produced by incorporating the active constituent and porosity modifiers in a thermoplastic matrix, which is extruded as a strand and pelletised. Release of the active constituent involves a leaching process. Products can be designed to suit specific crop and pest situations by varying formulation parameters affecting the release rate.

'In-flight' encapsulation involves the incorporation of the active constituent with a polymer and various modifiers in a liquid phase which is applied to the target area as a spray. During spray droplet formation, transport and impingement, microcapsules are formed. Release of the active constituent will vary with the type of polymer, the active constituent, capsule wall thickness and the use of modifying agents.

Research Facilities

During 1982, CFL installed an extrusion pilot plant to produce commercial grade polymer granules for experimental use. It is designed for processing heat sensitive and toxic substances. Release rates of formulations in potted soils are measured under varying climatic and moisture regimes. Storage and shelf-life studies are undertaken.

'In-flight' formulation design effects on encapsulation properties and release rates are being studied using chemical and bioassay procedures in a research project commenced in 1983 by CFL with the Victorian Department of Agriculture and the Agricultural Chemicals Application Research Unit.

CFL's research agronomists undertake field evaluation of both types of formulations that perform satisfactorily in the release rate and bioassay testing programs. Several research organisations in Australia and South East Asia are also involved in further evaluation of the formulations under development.

Results

The soil insecticides chlorpyrifos, terbufos, fonofos, phorate and 2, 3-dihydro-2, 2-dimethyl-7 benzofuranyl [(dibutylamino) thio] methyl carbamate (proposed common name; carbosulfan) have been successfully incorporated in polymer granules. Fenitrothion, methomyl, permethrin, phoxim and pheromones have been produced as 'In-flight' formulations.

Bioassay and chemical residue studies to determine the residual life of controlled release chlorpyrifos formulations in soil were commenced by the Bureau of Sugar Experiment Stations (BSES) in 1979 (BSES 1982). These studies showed that several formulations applied at a concentration of 64 mg/kg a.i. were effective in controlling canegrub larvae 3 years after application (Hitchcock, B.E. unpublished data). Field trials using CFL produced chlorpyrifos formulations were established by BSES in 1981 in tests against several major species of canegrub (*Dermolepida albohirtum*, *Lepidiota consobrina* and *L. frenchi*). Canegrub control was achieved in the plant cane harvested in 1982 with significant yield increases over control plots in all trials (Hitchcock, B.E. unpublished data).

Controlled release carbofuran formulations produced on makeshift equipment were tested as soil applications in greenhouse studies at The International Rice Research Institute (IRRI) in 1981. Bioassay results for controlled release formulations were no different to equivalent rates of conventional formulation (IRRI 1982). Subsequently formulations which release at approximately twice the rate of those tested have been produced on the pilot extrusion plant but not yet re-tested in bioassay studies.

In bioassay studies conducted by CFL using *Heliothis punctiger* larvae on cotton, 'In-flight' formulations of methomyl and permethrin were compared with conventional formulations. The 'In-flight' formulations significantly increased the effective residual life of both chemicals and provided the same level of initial control. 'In-flight' methomyl sustained a larval mortality rate of over 90% 7 days after application compared to 20% for the conventional formulation.

Field and laboratory studies of 'In-flight' formulations of (E,E)-8,10-dodecadienol, the sex pheromone of the codling moth are being carried out in conjunction with the Commonwealth Scientific and Industrial Research Organisation (CSIRO).

The successful commercialisation of these two formulation techniques is expected to make a significant contribution to future crop protection programs.

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FORMULATIONS FOR TREATMENT OF TREE WOUNDS AND CANKERS

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Background and objectives

In fruit growing, wounds result from wind damage, excess crop, pruning or removal of dead or decaying wood from cankers. Normal practice is to paint wounds with a sealant in order to prevent entry of fungal pathogens. Such sealants, many of which incorporate a fungicide, effectively protect the wound as long as the layer remains intact: they rarely allow sufficient penetration of fungitoxicant into the wood to eradicate existing infections. They do, however, usually encourage the formation of callus tissue.

We show results of experiments designed to evaluate the alternative approach of establishing and maintaining protection beneath the wound, using systemic fungicides to protect against or eradicate ascomycete- and basidiomycete pathogens, in particular Nectria galligena Bres and Chondrostereum purpureum Pers. ex Fr.

Materials and Methods

Treatments were applied either as solutions in an inert organic solvent containing N-methyl-2-pyrrolidone to promote dissolution of the fungitoxicants, or as aqueous gels incorporating them in suspension. Solutions were prepared from technical active ingredients supplied by the manufacturer; gels incorporated the same materials or appropriate w.p. or e.c. formulations. Each component was present at 2.5% w/v except with Bayleton B.M. which contains twice as much carbendazim as triadimefon. Gels were prepared from sodium alginate, propylated alginate or a xanthan gum. The solution or gel was applied liberally to the surface of circular wounds formed by sawing off 2 - 3 cm diameter branches at or near their junction with larger branches. Samples of wood were taken at several times after treatment at 1 cm intervals below the wound surface and at 2 cm intervals from the wound centre both towards the tip and the base of the main branch. These were bio-assayed on agar against an appropriate fungus and the areas of inhibition of fungal growth used as a measure of the amount of fungitoxicant present in the sample.

Results and conclusions

Use of solutions resulted in extensive movement of fungitoxicant into and through the wood, although predominantly towards the trunk. This applied to carbendazim, triadimenol and also to triadimefon, which is converted enzymically, within the wood, to triadimenol. Movement towards the tip occurred only when materials were applied during the dormant season. Mass transfer in xylem was minimal and movement through wood was largely by diffusion. Fungitoxicant persisted beneath stub wounds for at least one year and beneath flush wounds for at least 100 days.

Less fungitoxicant moved into the wood when gels were used and lateral movement was more restricted. Nevertheless, a deposit of fungitoxicant was maintained beneath the wound surface for at least 100 days. Dissolving carbendazim and triadimefon or triadimenol in hypophosphorous acid before adding them to the gel gave a preparation which enabled more fungitoxicant to move into and through the wood. Following treatment with solutions, die-back of bark and cambium sometimes occurred but gels were non-phytotoxic and those containing carbendazim or thiophanate-methyl promoted callus tissue formation, particularly when applied during the growing season. Formulations prepared from propylated alginate or xanthan gum were more rain-fast than those from sodium alginate.

Gel formulations containing thiophanate-methyl or carbendazim and triadimenol, applied to un-scraped cankers, usually eradicated the infection and promoted wound healing and thus could be very cost effective.

These results suggest that the easily applied gel formulations could be an effective alternative to conventional wound sealants for protection of pruning wounds and treatment of cankers.

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THE USE OF POLYBUTENES IN CROP PROTECTION

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Background and objectives

The continuing rise in fuel costs has seen the introduction of new growing techniques in glasshouses i.e. Growbags, Rockwool, and nutrient film, which have eliminated the need to steam-sterilise the soil. Insects which pupate in or on the soil may be controlled by chemical drenches or granular applications, but these all need to be repeated every 3-4 weeks. Some are systemic and can accumulate in the fruit posing harvesting restrictions while others adversely affect beneficial insects through fumigant action early in the season when the ventilators are shut. A novel system compatible with beneficial insects was, therefore, devised for thrips control.

Materials

Polybutenes are synthetic hydrocarbon polymers manufactured in various grades ranging from Hyvis 03, a mobile liquid with little tackiness to Hyvis 600, a very viscous liquid with a high degree of tackiness. All remain permanently fluid on ageing.

Methods

Trials with various grades of polybutene applied as a medium volume spray direct to the floor covering under the crop showed that, although many thrips larvae from cucumbers were trapped, control was partial, and some of the materials were unsuitable for commercial use due to their high viscosities. Rather than physically trapping thrips it was decided to mix a suitable pesticide with lower viscosity polybutenes in order to ensure prolonged contact of pest with pesticide. From these trials a commercial product consisting of polybutene, an emulsifying agent, deltamethrin and water, was developed. This mixture is called Thripstick and has the advantage that it leaves the beneficial insects unaffected on the aerial parts of plants as the mixture is not volatile.

Results and conclusions

Tests showed that this material remains lethal for 24 weeks in the laboratory and for at least 12 weeks in the glasshouse.

Thrips on onions have also been controlled successfully by sprays of Thripstick applied to the soil and by foliar sprays, although slight phytotoxic damage was noticed on some varieties. Tests with the tomato leaf miner *Liriomyza bryoniae*, a soil pupating insect, have shown very promising results when Thripstick was applied either to polyethylene sheets below the crop or to the soil itself (Table 1).

Current research involves the use of various grades of Hyvis (polybutene) and emulsifying agents in an attempt to produce a non-phytotoxic material for foliar application. Work is also in progress at the G.C.R.I. and in Israel to evaluate polybutenes for prevention of virus transmission by aphid and whitefly vectors.

TABLE 1

Numbers of *Liriomyza bryoniae* trapped after use of Thripstick in July

Catch period (days after treatment)	Total catch	Number/plant/day
1-3	9500	61
4	3020	58
5	648	12
6	540	10

Hyvis is a registered Trade Mark of B.P. Chemicals, Belgrave House, 76 Buckingham Palace Road, London SW1 OSU.

Thripstick is a registered Trade Mark of Aquaspersions Ltd., Charlestown Works, Charlestown, Hebden Bridge, W. Yorkshire HX7 6PL.

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PHYSICO-CHEMICAL ASPECTS OF FOLIAR UPTAKE

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Background and objectives

The aerial surfaces of plants are covered by a thin, continuous lipophilic layer - the cuticle, consisting of cutin polymer matrix impregnated with wax, with epicuticular wax deposited on its outer surface. Foliar applied systemic crop protection chemicals must traverse the cuticle prior to movement and activity. Since the cuticle is non-cellular, penetration must be a physico-chemical process primarily governed by the properties of the a.i. and leaf surface and modified by formulation adjuvants.

In our experiments 15 chemicals (fungicides, herbicides, growth regulators and an insecticide) with widely differing molecular properties have been applied to the leaves of crop spp., selected for their surface and cuticular properties, in an attempt to determine the factors which control foliar uptake. As surfactants are major formulation additives all measurements have been made in the presence and absence of a non-ionic wetter.

Materials and Methods

Solutions of radiolabelled chemicals (1 g/l) have been applied as monosize droplets (c. 200 μm) to the adaxial surface of leaves in aqueous methanol, ethanol or acetone \pm surfactant (1 g/l Ethylan TU (NP8):- nonylphenol with average 8 moles ethylene oxide). Plants were grown and maintained during the treatment period in C.E. cabinets (20°C; 70% R.H.; 16h 470 $\mu\text{E m}^{-2} \text{s}^{-1}$; 40 - 60% pot capacity soil water). Uptake was measured after droplet drying (3 min) and at 24h. After treatment, surface residues were removed by aqueous solvent (2 x 1 ml), and chemical held in the epicuticular wax recovered successively in a cellulose acetate film and a chloroform/ether wash (500 μl). The treated region and remaining leaf tissue were combusted separately to recover ^{14}C . Radiotracer in all fractions was quantified by scintillation counting and examined for correlations with molecular size, partition coefficient, water solubility and volatility. Autoradiography and scanning electron microscopy have been used to study the droplet/leaf surface interaction and distribution of chemical within the deposit.

Results and conclusions

Preliminary studies in which glyphosate (free acid), 2,4-D and prochloraz were applied to 11 spp. enabled selection of maize, rape, strawberry and sugar-beet for investigation of the full range of chemicals.

Uptake (chemical not recovered in the initial aqueous solvent wash) over the 24h period varied markedly between chemicals and spp. being greatest into rape and strawberry and in all cases increased with addition of surfactant. In the presence of NP8 the amount of chemical in the epicuticular wax generally increased, being proportional to the thickness of the wax layer and inversely related to the log (water solubility) of the chemical. During droplet drying uptake was 50 - 100x faster than the mean rate for the remainder of the 24h period and appeared to correlate with partition coefficient, but with evidence of a molecular size limitation. Translocation as a % of uptake was almost invariably reduced by NP8, least so for maize, the spp. exhibiting highest levels of translocation. However, since overall uptake was increased by NP8, the total quantities of chemicals translocated were increased.

These results indicate that initial uptake is primarily a rapid partition process enhanced by surfactant whereas subsequent phases are slower and determined by complex interactions. Studies with chlormequat, 2,4-D and prochloraz show that while overall uptake increases with concentration of a.i., relative uptake varies with chemical, surfactant and spp. Chemicals frequently deposited in an annulus at the edge of the droplet area particularly on glaucous surfaces in the presence of NP8. However, there is no clear correlation between surface distribution and molecular properties of the applied chemical.

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HERBICIDE UPTAKE AND TRANSLOCATION IN GRASSES: EFFECT OF SITE OF APPLICATION

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Background and Objectives

Grass plants provide a unique target for applied herbicides and it is important that the pattern of uptake and distribution is understood if formulations are to be designed to make the most efficient use of applied herbicide. Earlier observations that application of herbicides to the lamina base of grass leaves resulted in improved herbicide performance have been confirmed by Coupland, Taylor and Caseley (1978) who suggested this resulted from reduced wax deposition and perhaps higher humidity at the ligule area allowing increased uptake of herbicide.

The importance of this site of application has been demonstrated in only a few species. In this study a wide range of species are investigated and the possible effects on selectivity between crop and weed species examined.

Materials and Methods

The growth conditions, species used and methods for herbicide application and radiotracer assay are described in detail in Speight (1982). ^{14}C asulam was a gift from May and Baker Ltd, and ^{14}C isoproturon a gift from Ciba-Geigy. In addition to radiotracer studies, contact angle measurements were made and plant surfaces examined by SEM using a Phillips 5000 instrument. Herbicide activity was assessed by visual examination and dry weight measurements.

Results and Conclusions

A range of species susceptible and resistant to both asulam and isoproturon were selected for study, including both crops and weeds. Regardless of these factors application of herbicide just above the ligule resulted in greatly increased uptake and in most cases increased movement of the herbicide when compared to application mid way along the length of the lamina. Uptake and translocation of herbicide from the lamina could be increased by continually rewetting the application zone but never approached the levels achieved by ligule application. Preliminary activity studies indicate that herbicide activity increases with ligule application without a loss of selectivity. SEM and contact angle results show that the increased absorption may be partly attributed to less organised and less dense wax deposits in the ligule area.

Increased uptake at the base of the lamina would appear to be a common feature of grass species irrespective of whether the herbicide is xylem or phloem mobile although probably only a minor factor in determining selectivity between crop and weed species.

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Background

Surfactants, dissolved in water, lower surface tension by adsorption at an interface, e.g. air/water, but if the interface is disturbed it takes some time (10-500 ms) for equilibrium to be restored. A newly formed surface will have a surface tension close to that of water ($\gamma = 73 \text{ mN m}^{-1}$) and the change in surface tension with time is referred to as dynamic surface tension. In contrast a solution of aqueous methanol or ethanol achieves virtually instantaneous surface equilibrium.

Surfactants in foliar sprays may aid retention in two ways. First, the droplet size produced by a hydraulic nozzle may be decreased and smaller droplets are better retained than large ones. Secondly a low surface tension may enhance retention of droplets following impaction on the leaf.

Effects of surfactants on droplet formation by a hydraulic nozzle

A hydraulic nozzle forms droplets within a few milliseconds and hence only spray adjuvants which can decrease surface tension within this time will reduce droplet size. We have determined volume median diameter (vmd) from a hydraulic nozzle (Spraying Systems 11003) operating at 300 kPa, using a Malvern Particle Size Analyser. Comparing an aqueous solution of methanol with low surface tension ($\gamma = 35 \text{ mN m}^{-1}$) with water we found a decrease of vmd of $\approx 20\%$ in accord with expectation. In an aqueous solution (3 g l^{-1}) of the surfactant Triton N150 (nonylphenol with average 15 moles ethylene oxide) it takes more than 30 ms for the surface tension of a newly-formed surface to reach 40 mN m^{-1} . Using the same nozzle and pressure as before and several solutions of Triton N150 ($0.1 - 3 \text{ g l}^{-1}$) we found that the vmd was always the same as for water, as predicted.

Effects of dynamic surface tension on droplet retention

Monosize droplets ($200 \mu\text{m}$ diameter) of aqueous methanol solutions were sprayed onto pea leaves (4-week-old greenhouse-grown plants) held at 55° to horizontal using a micro-sprayer. Retention ranged from 19% of applied dose at $\gamma = 40 \text{ mN m}^{-1}$ to 97% at 37 mN m^{-1} (cf Hartley & Brunskill). With aqueous solutions of Triton N150 ($\gamma = 35 \text{ mN m}^{-1}$) retention varied from 13% at 1 g l^{-1} to 74% at 5 g l^{-1} . A track-sprayer fitted with a Spraying Systems nozzle 110015 operating at 300 kPa was used to apply solutions of Synperonic NP15 (chemical composition very similar to Triton N150) to upright pea plants. Retention ranged from 48% at 1 g l^{-1} to 89% at 5 g l^{-1} . The greater retention observed using the track-sprayer compared with the micro-sprayer is probably related to the different (near-horizontal) disposition of the leaves under the track-sprayer and differences in droplet size and impact velocity. Retention figures on barley plants (4 leaf stage, grown in controlled environment) under the track-sprayer were much lower (6% at 1 g l^{-1} ; 14% at 5 g l^{-1} Synperonic NP15). This is probably because most of the barley leaves were close to vertical and the corrugations of the leaf surface made it more reflective than the pea leaf.

On impaction the droplet of surfactant solution flattens rapidly ($\approx 10 \text{ ms}$) and its surface tension is then much higher than that at equilibrium. The subsequent retraction is slower but is still complete within $\approx 40 \text{ ms}$. Thus unless the surfactant can reduce surface tension rapidly, it will not affect the retention process. Increasing the surfactant concentration accelerates adsorption at the interface and thus improves retention.

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THE USE OF ADJUVANTS TO ENHANCE ACTIVITY OF FLUAZIFOP-BUTYL ON JOHNSONGRASS

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Background and Objectives

Johnsongrass (Sorghum halepense) was introduced into the United States around 1800 for use as a forage crop. Through its extensive rhizome production and numerous seeds, it has spread through many of the states and is now one of the world's ten worst weeds. Fluzifop-butyl is a new systemic herbicide with selectivity in broadleaved crops that gives excellent control of S. halepense as well as a wide range of annual and perennial grasses. Since 1980, several greenhouse trials and more than 30 field trials were conducted in the United States to examine the influence of adjuvants on the activity of fluzifop-butyl on S. halepense. Objectives of these trials were to: 1) determine whether there was an advantage to using any adjuvant, 2) compare various rates of nonionic surfactants and oil concentrates, and 3) examine other factors which might influence the effects of adjuvants.

These objectives are illustrated with data taken from four representative field trials and two greenhouse trials.

Materials and Methods

S. halepense control results are from trials replicated three to four times comparing the performance of post-emergence applications of fluzifop-butyl mixed with various rates of either a nonionic surfactant or an oil concentrate or with no adjuvant. The fluzifop-butyl was applied at rates ranging from 0.14-1.12 kg ai/ha and the adjuvants were applied at rates from 0.1 to 2.5% v/v. All applications were made through flat fan nozzles and with pressures of 152-207 k Pa. Field trial treatments were applied in 200-300 l/ha and greenhouse treatments in 90 and 370 l/ha. The average height of S. halepense plants ranged from 30-75 cm at application. The percent control was estimated by visual assessment on at least three dates. In the greenhouse, a late-season field assessment was simulated by removing the top growth from the pots at two to three weeks after treatment, waiting for regrowth and counting the newly emerged shoots.

Results and Conclusions

Results from a North Carolina and a Mississippi field trial show a distinct enhancement of season-long S. halepense control by the addition of a nonionic surfactant at 0.1, 0.25 or 0.5% or an oil concentrate at 0.79-0.83% compared to fluzifop-butyl alone. Both trials were conducted in wide-row soybeans. Differences in control levels varied with the concentration and type of adjuvant.

In a North Carolina and a California field trial conducted in a noncrop situation, the addition of 0.25% nonionic surfactant was compared to the addition of 0.83-1.0% oil concentrate. The oil concentrate produced better control than the nonionic surfactant.

The initial visual assessments of the two greenhouse tests showed little differences. Shoot counts of regrowth were lower in treatments containing adjuvant than in treatments of fluzifop-butyl alone, indicating greater control. A nonionic surfactant at 0.25% generally gave slightly better regrowth control than at 0.1% or than an oil concentrate at 0.62 or 2.5%. In both tests, most treatments applied in 90 l/ha gave better control of regrowth than those applied in 370 l/ha. The level of activity, both for initial control and for the control of regrowth, was lower in the first test where intentional moisture stress was imposed.

Results of three years testing show that consistent control of S. halepense in the United States requires the addition of adjuvant to fluzifop-butyl treatments. The specific rate and type of adjuvant for optimum activity varies. Studies indicate that either a nonionic surfactant at 0.25% or an oil concentrate at about 1.0% may be used with excellent results. Factors such as spray volume and moisture stress can affect the activity of fluzifop-butyl and may influence the effects of adjuvants.

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3B-R18

THE RELATIVE TOXICITY OF SUSPENSION CONCENTRATE AND WETTABLE POWDER FORMULATIONS OF HERBICIDES TO STRAWBERRIES

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Background and Objectives

Since the introduction of suspension concentrate formulations of simazine and propachlor for strawberries in the UK there have been reports of crop damage from their use and the safety of the new formulations has been queried. Since there were no published results on the relative toxicity of s.c. and w.p. formulations to strawberries, their relative toxicity was investigated in a series of pot experiments.

Materials and methods

Experiments were conducted outdoors with young plants of cv. Cambridge Favourite using methods described by Clay (1980). The toxicity of foliar applications was tested on plants grown in sandy loam soil in 18 cm diam. pots. Herbicides were applied with a laboratory sprayer through an 8002 Teejet at a volume rate of 475 l/ha and pressure of 210 kPa.

The toxicity of applications to the roots was tested on plants growing in silica sand in 25 cm diam pots. Four doses of each herbicide were applied on 1 September to the sand surface in 500 ml nutrient solution.

Herbicide effects were assessed by visual scoring of plant condition, measuring number of damaged leaves, the area of leaf necrosis and leaf fresh weight.

Results and discussion

Simazine. When the s.c. and w.p. formulations were sprayed at 1 and 3 kg/ha on 27 August and the foliage subsequently kept dry no adverse effects were recorded. Where the plants received rain or overhead watering from 24 hours after spraying the s.c. at 3 kg/ha caused more damage (67% leaf weight reduction) than the w.p. (40% reduction). The 1 kg/ha rate had no adverse effect. The results suggest that differences in toxicity were due to root rather than foliar uptake.

When the two formulations were applied to the roots in sand the ED20 value (dose causing 20% reduction in leaf fresh weight compared with control) for the s.c. was 0.7 mg/pot and for the w.p. 1.5 mg/pot confirming the greater toxicity of the s.c. through root uptake.

Propachlor. When the s.c. and w.p. were sprayed at 4.5 and 18 kg/ha on 10 October the higher rate of s.c. caused greater leaf necrosis (93 cm²/plant) than the w.p. (17 cm²/plant). At the 4.5 kg/ha rate the s.c. gave slightly greater short term damage. These results confirm those of an earlier experiment where the s.c. was appreciably more toxic at a reduced volume rate of 240 l/ha (Clay, 1982).

When the two formulations were applied to roots in sand the ED20 value for the s.c. was 32 mg/pot and for the w.p. 72 mg/pot indicating greater toxicity of the s.c. from root uptake.

General conclusions. The experiments showed that the s.c. formulations of simazine and propachlor can be more damaging than the w.p., the simazine probably through root uptake only. However, significant differences occurred only at high doses. This suggests that the difference in formulation should not cause problems when the tolerance margin is large but if the margin is small, the s.c. formulations have a greater potential for damage. Further work is needed to establish the conditions that will lead to damage and reasons for the differences in toxicity.

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AN ULTRA LOW VOLUME FORMULATION OF DIMETHIPIN FOR COTTON DEFOLIATION

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Background and objectives

Dimethipin, 2,3-Dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetraoxide, was registered in the USA in 1982 by Uniroyal Inc. as a cotton defoliant and is sold as a water based flowable formulation (Harvade 5F®) containing 48% active ingredient. This formulation is miscible with water in all proportions, but is normally used at 540 milliliters in 47 liters water per hectare. Leaf coverage by aerial application of this formulation may not be optimum in hot dry climates, such as Arizona and the San Joaquin Valley in the USA, due to evaporation of water from spray droplets after they leave the spray nozzle and before they reach the plant (Maas 1971). Evaporation results in reduction in droplet size and if this goes below 50µm (Yates and Akesson 1973), spray drift is substantially increased. When the droplet lands on the leaf, evaporation to dryness retards the penetration of dimethipin through the leaf cuticle which inhibits defoliation activity. The application of agricultural chemicals in crop oils at ultra low volumes (ULV) to cotton by air has become accepted practice in certain parts of the USA to reduce evaporation and improve coverage. The standard water based flowable formulation is not compatible with these oils. A project was initiated to develop a formulation more suited to ULV aerial application, which would enhance penetration of active material into cotton leaves.

Materials and Methods

Formulation development: Key parameters in developing the formulation were solubility of dimethipin in candidate solvents, solvent vapor pressure, and leaf wetting properties. Dimethipin was found to be soluble in polyethylene glycols, the degree of solubility increasing with molecular weight. However, viscosity of these glycols increases with molecular weight. Polyethylene glycol-400 was chosen because it gave the best solubility to viscosity ratio. Dimethipin is also soluble in cyclohexanone, this was used as a co-solvent to further reduce viscosity and depress the freezing point. The leaf wetting property of the formulation was evaluated by measuring the contact angle of a droplet on a cotton leaf using a Rame' Hart goniometer. Pluronic 17P1, a block co-polymer, was incorporated into the formulation to reduce contact angle and maximize leaf wetting. A surfactant was also included in the formulation to improve dimethipin penetration.

Penetration studies: The optimal ratio of solvents and the identification of the most efficient surfactant was defined by conducting penetration studies with ^{14}C labelled dimethipin formulations applied as 1 µl droplets on cotton leaves. The treated leaves were washed after 48 hours with water, incinerated, and analyzed in a scintillation counter. Aerial field trials were conducted on cotton in Australia to verify laboratory conclusions regarding efficacy of the ULV formulation containing the identified surfactant.

Results and conclusions

Because of the low volatility and humectant properties of polyethylene glycol-400, droplets of this formulation remained in the liquid state ten times longer on cotton leaves than the standard aqueous based formulation. From penetration studies results indicated that 5 times as much dimethipin penetrated cotton leaves treated with ULV formulations compared to the standard aqueous flowable. In addition, penetration continued over a longer period of time. The final formulation is a ULV product designed to be used without dilution. Preliminary results from Australian field trials indicated defoliation activity using 0.16 kg a.i./ha of the ULV formulation was as effective as 0.32 kg a.i./ha of the standard water based flowable.

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Abstract

The use of ultra-low-volume (ULV) applications (i.e. applications at less than 0.5 gallon (US) per acre (4.67l/ha)) to cotton have been in existence since the early 1960s, but very limited use occurred on cotton prior to the pyrethroids in the late 1970s. The use of the pyrethroids (permethrin, cypermethrin and fenvalerate), has combined low rates of chemical (67 to 224 g ai/ha) in reduced volume (2.3 to 4.6 l/ha) of refined cotton or soybean oil.

In Texas and Mississippi, the two cotton growing states where ULV oil applications have taken a foothold, several application methods have been developed or refined. Early field work with ULV oil applications employed rotating atomizers to apply accurately a uniform particle in low volume. Recently, through expanded testing, the use of hydraulic systems with flat fan conventional nozzles has been adapted to oil applications.

Several large scale cotton trials were initiated in 1982 to compare permethrin ('AMBUSH' 4) fenvalerate ('PYDRIN'), flucythrinate ('PAY-OFF') with two formulations of cypermethrin ('CYMBUSH' 3E and 3OL). Two rates of cypermethrin were evaluated in ULV oil and conventional water applications. In-season insect monitoring counts and yield were collected for the bollworm/budworm complex (*Heliothis* spp.) and/or the boll weevil (*Anthonomus grandis*). These trials were conducted using a variety of nozzle types, placements and angles, also pressure, airspeed and swath width. However, in all cases, droplet sizes delivered were in the range 180-200 μ VMD.

For *Heliothis* control, applications in ULV oil were equivalent to conventional water applications when evaluated at comparable field rates (either 44 or 67 g ai/ha). The lower rate of cypermethrin (44 g ai/ha) either applied in oil or water was not as effective as the recommended field use rate (67 g ai/ha). Permethrin (112 g ai/ha), fenvalerate (112 g ai/ha) and flucythrinate (44 g ai/ha) when applied in oil gave equal *Heliothis* control.

For *Anthonomus* control, similar effects were recorded from equivalent rates of cypermethrin applied either in water or oil. Flucythrinate (44 g ai/ha) did not control *Anthonomus* as well as permethrin (112 g ai/ha) or fenvalerate (112 g ai/ha).

Although all chemicals tested gave excellent full-season control, the yields indicated that the high rate of cypermethrin (67 g ai/ha) in either diluent was the most effective treatment.

The benefits of ULV oil applications include: improved placement of chemical in the crop canopy; less evaporation; greater control of particle size distribution and more effective use of aircraft and greater maneuverability with smaller planes and light payloads.

PERSISTENCE OF INSECTICIDE RESIDUES ON COTTON FOLIAGE

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Background and objectives

Published information on residual activity of insecticides was found to be unsatisfactory for estimating their field persistence against Heliothis spp., and further research into this topic was undertaken.

To determine the most realistic index of persistence both chemical concentration on the leaf surface, and biological activity were measured simultaneously at intervals after application. Sprays are usually timed to kill hatching larvae which feed on young foliage near the plant terminal, persistence of insecticides on unfolding and fully developed foliage was therefore compared.

Materials and Methods

Insecticides were applied to cotton at normal rates by a pressure regulated knapsac sprayer. Leaf disc samples were collected at intervals from both fully expanded cotton leaves and unfolding terminal foliage. The samples were subjected separately to bioassay with neonate larvae and to chemical analysis of surface deposits. Other observations monitored the rate of leaf expansion during the growing season.

Results and conclusions

Taking as an index of persistence the number of days for larval mortality on successive samples to decline to 50% the intervals on old foliage were: fenvalerate 18; DDT-chlorcam, 12; profenofos, 9; and endosulfan 4.5. On new foliage values were 7, 5.5, 4 and 3 respectively for the above materials.

In comparison to the bioassay results, shorter residue life may be inferred from chemical data if absorption into the leaf and low lethal dose are not taken into account. Thus the chemical half life on old foliage expressed in days was: fenvalerate and DDT 12, profenofos, 1.3 and endosulfan 1. These results were similar to those obtained by Estesen et al. who concluded that the latter two materials were very short lived. Bioassay therefore appears to be the preferable procedure for prediction of the level of mortality at a given interval after pesticide application.

The comparison of kill on new and old foliage indicates that the full potential of persistent insecticides will not be achieved while rapid expansion of leaf area is taking place. This was found to occur during a 6 week period commencing 2 months after planting.

Because of the above growth dilution of insecticides spray timing has been proposed at intervals determined by rate of leaf expansion, in order to keep the plant permanently toxic to larvae. However under Australian conditions infestation are sporadic and prophylactic sprays have been found wasteful and conducive to development of insecticide resistance.

Normal practice is to search plants for eggs and larvae at three day intervals. Sprays are only applied when it is predicted that infestations will rise above predetermined action levels. Knowledge of the duration of activity of insecticides after application has allowed refinement of the predictions of larval survival. By these and other procedures spray number has been reduced by up to 50% compared with sprayings on fixed time schedules.

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3B-R22

THE BEHAVIOR OF SODIUM BICARBONATE ON PLANTS AND PATHOGENS

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Background and objectives

Sodium bicarbonate, which is the active ingredient of Noslan, occurs naturally in crops, soil, sea water, river water and many other substances in the natural environment in the form of H_2CO_3 , Na^+ , and HCO_3^- . It is used as one of medicaments, an acid adjusting agent, baking powder, etc. It consists entirely of edible components, and, therefore, is a very safe compound.

Sodium bicarbonate formulation shows activity in controlling citrus penicillium decays and various vegetable powdery mildews. For the purpose of clarifying the characteristics of the preparation, a study was made of its behavior on the cucumber powdery mildew fungus, *Sphaerotheca fuliginea*, and on the cucumber leaf surface, leaf hairs.

Materials and Methods

Conidia of *S. fuliginea* was inoculated on to healthy cucumber leaves and the inoculated in a green house for 3-4 days. Since conidial formation was confirmed by observation under an optical microscope, the preparation was applied by spraying at the time of observation and the material was incubated in the green house. The fine structures of conidia, conidiophores, leaf hairs and leaf surfaces were observed with a MINI SEM scanning electron microscope.

The solution of sodium bicarbonate (5000 ppm) was sprayed (50 ml/ 0.5 m²) on to rice plants. 1,2 and 3 days after spraying, rice plants that were cut 1 cm and all were added with 200 ml distilled water, and extracted with stirring up 30 minutes. After then the materials added with 200 ml distilled water again, and triturated by mixer for 15 minutes, centrifugalized at 3000 rpm for 20 minutes and supernate was gathered from the triturated materials. The pNas of the extract and the supernate were measured with an Orion Model 901 ionalyzer.

Results and conclusions

The top of the conidia on the conidiophore started to shrink 2 hours after treatment, and kept on shrinking for 4 hours after treatment. The shrinkage of the conidia gradually extended to the conidiophores and hyphae 24 hours after treatment, and the conidia, conidiophores and hyphae were completely destroyed 48 hours after treatment.

Sodium bicarbonate is clarified to translocate in plant tissues such as leaf hairs and leaf veins, and it appears to translocate in fungus also. Thus, disease lesions were disappeared, indicating a curative effect of Noslan on various powdery mildews.

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FIELD PERFORMANCE OF AC 222293 IN EUROPE DURING 1982

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Background and objectives

AC 222293, a member of the new class of imidazolinone type herbicides was announced in 1982 by Los, M. et al. Physical details, greenhouse results, translocation, plant metabolism and initial field studies have been published (Shaner et al 1982a and b, Kirkland et al 1982). The objective of this paper is to report on the results obtained during the 1982 European field programme.

Materials and Methods

A 50 WP formulation of AC 222293 was used in over 100 small plot field trials in Italy, Spain, France, the U.K. and Germany. Post-emergence applications included 0.6 l. Agral 90/ha. Trials were conducted in winter- and spring-wheat or barley with *Avena* spp. (AVESS), *Alopecurus myosuroides* (ALOMY), and *Apera spica-venti* (APESV) as main weeds.

Results and conclusions

The dose required for effective grass weed control reduces from north to southern Europe. Increased rates may be required to control grass weeds in the late tillering stage (Table 1).

TABLE 1. Effect of AC 222293 timing of application upon % grass weed control

Country	Dose kg a.i./ha	% Grass weed control and (number of trials)								
		A L O M Y			A V E S S			A P E S V		
		Z11-13	Z13-25	Z25-30	Z11-13	Z13-25	Z25-30	Z11-13	Z13-25	Z25-30
Italy	0.3	97 (9)	96 (2)	75 (2)	93 (14)	96 (1)	89 (1)	-	-	-
Spain	0.5	-	-	-	94 (11)	78 (2)	77 (2)	-	-	-
France	0.625	83 (8)	62 (4)	79 (4)	89 (12)	87 (6)	64 (6)	98(2)	90(2)	79(2)
U.K.	0.75	77 (5)	73 (5)	86 (5)	83 (8)	79 (8)	55 (8)	-	-	-
Germany	0.75	90 (5)	92 (5)	81 (5)	91 (6)	71 (6)	74 (6)	100(1)	100(1)	100(1)
Average	0.3→0.75	88 (27)	79 (16)	81 (16)	90 (51)	80 (23)	66 (23)	99(3)	93(3)	86(3)

The data show that the order of weed susceptibility is: APESV>AVESS>ALOMY. Better control is obtained if application of AC 222293 takes place at the early growth stages of weed.

AC 222293 has proved to be an exceptionally safe herbicide in 1982. All major varieties of winter- and spring-wheat or barley have, without exception, tolerated normal and double rates of AC 222293 in varietal trials. In regular field trials, no early crop phytotoxicity exceeded 15% in all of the 104 cereal trials at normal rate. At double rate and higher, only 5% of the trials (out of 99) showed between 15 and maximally 27% crop phytotoxicity. This crop phytotoxicity is observed as a delay in plant development but never as a reduction in plant numbers. A total of 35 yield trials were conducted at normal and higher rates. On average the yield was 111% of the controls.

AC 222293 has shown to exhibit some soil persistence. This may explain the control of late germinating grass weeds which has been observed. Residues do not pose so far a threat to following crops. Sensitive crops, e.g. sugarbeet and oilseed rape, sown as follow crops on previous trial sites (where up to 1.6 kg a.i./ha was applied) have never shown any phytotoxicity.

AC 222293 has been demonstrated to be an effective cereal grass weed herbicide, suited for application at the early growth stages of grass weeds so that competition with the crop is eliminated at a very early stage.

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THE MODE OF ACTION OF M & B 30775 AND M & B 34790 ON COTTON AND VELVET LEAF (Abutilon theophrasti)

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Background and objectives

M & B 30755 and M & B 34790 are two benzylimidazoles which show herbicidal activity when applied to the foliage of certain crop and weed species. They are closely related chemically but M & B 30755 is most active, being effective over a wider range of weed species.

The mode of action and basis of selectivity of both herbicides has been investigated on cotton and velvet leaf (Abutilon theophrasti)

Materials and methods

The test plants were grown in a greenhouse at 25°C (\pm 5°C) with supplementary lighting (14 h in 24 h). Herbicide activity on plants at the 1 - 2 leaf stage was assessed visually and by fresh weight measurement. The uptake and translocation of ^{14}C -M & B 30755 and ^{14}C -M & B 34790 was investigated using the method of Veerasekaran & Catchpole (1982). Herbicide effects on root tissue respiration were determined using a Gilson Differential Respirometer, while effects on photosynthesis and respiration of leaf discs was measured using an oxygen electrode (Rank Brothers). Effects of M & B 30755 and M & B 34790 on $^{14}\text{CO}_2$ fixation and ^{14}C -assimilate movement from leaves was measured (Lovell, Ho and Sagar, 1965) together with effects on leaf membrane permeability (Fletcher and Drexler, 1980). Metabolism of ^{14}C -M & B 30755 and ^{14}C -34790 within the plant was determined by extracting the treated leaf tissue in acetone with subsequent gel chromatography and thin layer chromatography (t.l.c.). ^{14}C -labelled metabolites were detected by autoradiography of the tlc plates. Binding of herbicides to isolated chloroplasts was investigated using the method of McIntosh (1981); effects of herbicide treatments on chlorophyll content and carotenoid analysis were also determined (Anderson and Boardman, 1964; Davies, 1976, respectively).

Results and conclusions

Both M & B 30755 and M & B 34790 caused leaf chlorosis, scorching and eventual death of the susceptible species. Selectivity did not appear to be due to differential retention, uptake, or translocation of the ^{14}C -herbicides, nor by inhibition of ^{14}C -assimilate flow within the plant. Neither herbicide was metabolised by susceptible or tolerant species within a 7 day treatment period. Root and leaf respiration was unaffected by both herbicides.

The photosynthetic mechanism appeared to be an important site of action of both herbicides. In vivo treatment with M & B 30755 and M & B 34790 inhibited $^{14}\text{CO}_2$ fixation by Abutilon. Using the oxygen electrode to measure photosynthetic rate, it was found that photosynthesis of Abutilon was inhibited by both herbicides; in vitro treatment with both herbicides inhibited photosynthesis in both species.

The permeability of leaf tissue membranes was increased by both herbicides in vivo in susceptible but not resistant species while in vitro treatment resulted in increased membrane permeability even in resistant plants.

The binding of both herbicides to isolated chloroplasts was examined. M & B 30755 bound to chloroplasts of both species while M & B 34790 showed little or no evidence of binding to either species. Chlorophyll and carotenoid contents of susceptible species were reduced by both herbicides; reduction in the pigment content increased in proportion to the herbicidal symptoms. Differences in the effect of in vivo and in vitro treatments on photosynthesis and leaf tissue membrane permeability suggests the possibility of selective inactivation or binding before reaching the site of action.

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REDISTRIBUTION OF A COPPER FUNGICIDE ON TOMATO LEAVES BY SIMULATED RAINFALL

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Previous research results indicate that it may be possible to improve the efficacy of agricultural chemicals when they are applied to crops using low-volume and ultra-low-volume techniques. There have been a number of field experiments which demonstrate the efficiency of these techniques; however, there is little data in the literature to elucidate the ability of the resultant chemicals on the leaves to withstand weathering. The research reported in this paper only deals with the rainfall aspect of weathering, and investigates the effect of rainfall on redistribution and tenacity of the small sized droplets produced by low-volume application. Tomato plants were sprayed with cupric hydroxide (Kocide 101) using high volume (HV) and ultra-low-volume (ULV) techniques; redistribution and tenacity of the fungicide were assessed after exposure of the plants to simulated rainfall.

Materials and methods

A track sprayer was used to apply cupric hydroxide at various HV and ULV rates to 5 weeks old tomato plants (cv. Kl0c) possessing 6 fully expanded leaves. The cupric hydroxide used in the HV treatment was an aqueous suspension of $2,000 \text{ mg l}^{-1}$ and was applied using a hydraulic nozzle (hollow cone-D4; Spraying Systems Ltd.) at a rate equivalent to 100 l ha^{-1} . The droplets which reached the target coalesced to form a continuous film on the surface of the leaf. Whereas the concentration of cupric hydroxide used in the ULV treatment was $80,000 \text{ mg l}^{-1}$ and was applied at a rate equivalent to 25 l ha^{-1} using a spinning disc which can deposit droplets of 140μ diameter on the tomato leaves. After an interval of 12 hours, some of the plants were exposed to simulated rain equivalent to 0, 0.5, 3.0 and 5.0 mm rainfall to determine the local redistribution of cupric hydroxide on the tomato plant; the remaining plants were exposed to 0, 0.5, 1, 2, 3, 4, 5, 10, 20, 30 and 40 mm rainfall to determine the amount of cupric hydroxide washed from the tomato plants. The amounts of copper on the leaves after the treatments were measured using standard atomic absorption spectrometric techniques.

Results and conclusions

A. Local redistribution of cupric hydroxide

The results show that cupric hydroxide applied to tomato plants by ULV techniques was washed uniformly from all areas of the plant. However, redistribution of the cupric hydroxide applied to plants by the HV techniques was non-uniform: a) more fungicide was found on the lower leaves than on the upper leaves after 0.5 mm of rainfall, a difference which was not evident after increased amounts of rainfall were applied; b) more cupric hydroxide was on the edge of the leaf than on the centre of the leaf after 1 mm of rainfall; c) more was on the apex of the leaf than on the base of the leaf after 5 mm of rainfall.

B. Washing of cupric hydroxide from the plant

The results show that after 4 mm of rainfall there was 51% of the cupric hydroxide remaining on the plants which had been treated by the HV technique, but only 31% of the fungicide remaining on the plants treated by the ULV technique. After 40 mm of rainfall the cupric hydroxide remaining on the plants in the HV treatment was 38% and in the ULV treatment 12%.

It can be deduced from these results that when cupric hydroxide is applied by the HV technique, the fungicide is redistributed on the plant surface before being washed from the leaf. Whereas, when the cupric hydroxide is applied by the ULV technique, the fungicide is not redistributed to the same extent but is washed from the plant surface. Furthermore, the cupric hydroxide applied by the ULV technique is less tenacious than that applied by the HV technique.

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COMPARISON OF ACTIVITIES OF DICAMBA AND ITS ALUMINUM SALTS

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Background and Objectives

The formulation and individual characteristics of 3,6-dichloro-o-anisic acid (dicamba) and the bis-dicambate aluminum hydroxide salt (Al salt) may alter efficacy of the compound. Environmental factors may also alter the activity. Laboratory, greenhouse and field studies were conducted to discern the parameters important in dicamba soil dissipation.

Results and Conclusions

Depending upon the characteristics of the Al salt, the percent of dicamba released from the Al salt with respect to time varies considerably. The Al salt formulation T 2 O.F. (oil flowable) releases only 7% dicamba after 48 hours. The formulation Al salt T (3) 50 W.P. (wetttable powder) releases 34% after 48 hours. Utilizing the Al salt of dicamba, we have been able to identify and select the potential formulation characteristics which appropriately modify the herbicidal properties of dicamba.

In at least 50% of the test locations, the 50 W.D.G. (water dispersible granules) and 2 O.F. formulations provided higher average yields than Banvel® Herbicide applied at two rates (0.5 and 1.0 lb a.e./A). When average yields were determined for all treatments within a test, the seven formulations of interest may be ranked high (1) to low (7) within each rate. These rankings are due to a composite response of variables such as formulation, rate, edaphic factors, weed population, and environmental stress. An example of the effectiveness of two of the seven formulations can be seen by the following yield rankings.

Formulation	Yield Rank (lb a.e./A)				Composite Ranking
	0.25	0.5	1.0	1.5	
Al salt T 50 W.D.G.	3	1	4	5	2
Al salt T 2 O.F.	1	2	1	1	1
Banvel® Herbicide	5	5	7	7	7

Growth chamber assays utilized a simple custom-designed polypropylene bioassay chamber with the native weed *Cassia obtusifolia* L. as the test species. A probit analysis of bioassay data proved the bioassay to be an effective research tool ($EC_{50} = 0.058 \pm 0.014$ mg/kg). The apparent first order kinetics of the bioassay simulate field conditions; most of the bioassay half-times vary from 16 to 36 days. This agrees well with field residue data.

Results of bioassay studies indicate that the two major processes in dicamba soil dissipation are volatilization, enhanced by soil water evaporation, and microbial degradation. At a dicamba acid concentration of 1.0 mg/kg (soil applied), the dicamba volatilization is 0.7 ug dicamba per g of water lost from the soil. Concerning microbial degradation, the metabolites of dicamba acid and its Al salt (after hydrolysis) were 2-hydroxy dicamba, 5-hydroxy dicamba, and 2,5-dihydroxy dicamba. Consequently, evaporative effects can be very important initially, and microbial effects can be important in the long-term dissipation and/or soil persistence of the compound.

These laboratory data provide an important basis for developing formulations. By retarding the rate of hydrolysis of the Al salt, the dissipation of dicamba through soil volatilization and microbial degradation are also retarded. Consequently, there is more dicamba acid in the soil for an extended period of time. The net effect is a new compound kinetically attuned to the edaphic environment.

MICRONUTRIENTS MODIFY ACTIVITY OF FUNGICIDES AGAINST RHIZOCTONIA SOLANI

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Background and objectives

Efficacy of fungicides against Rhizoctonia solani is influenced by soil conditions (soil pH, texture, moisture and temperature), organic manures, NPK fertilizers and herbicides. The present communication reports the influence of micronutrients on the activity of 9 fungicides used as seed treatment against seedling rot of cowpea (Vigna unguiculata) in a nutrient-deficient sandy soil (pH 8.05) infested with R. solani.

Materials and Methods

Soil (1kg/pot) was amended with boron (0.5 µg/g soil) as borax, manganese (10 µg/g) as manganese sulphate, copper (2.5 µg/g) as copper sulphate, iron (20 µg/g) as ferrous sulphate, zinc (5 µg/g) as zinc sulphate, or molybdenum (0.25 µg/g) as sodium molybdate and their mixture. Various amended soils were infested and sown with cowpea seeds treated with fungicides 1 g a.i./kg.

Results and conclusions

Six micronutrients and their mixture had variable effects on the efficacy of 6 systemic and 3 non-systemic fungicides. Fe reduced the efficacy of MEMC, quinterozone, captafol, thiophanate-methyl, chloroneb and carboxin. Cu and Zn annulled the activity of captafol, quinterozone, thiabendazole and thiophanate-methyl, and Mn decreased disease control by captafol and thiophanate-methyl. Boron reacted synergistically with quinterozone, MEMC, chloroneb and carboxin and improved disease control with these fungicides. Efficacy of quinterozone, thiabendazole, thiophanatemethyl and MEMC was poor in soil applied with mixture of micronutrients whereas carboxin and chloroneb gave better disease control in such soil.

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PERSISTENCE OF SOME ORGANOPHOSPHOROUS AND PYRETHROID INSECTICIDES ON GREEN PLANTS AFTER SPRAYING

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Comprehensive study of pesticides recommended for integrated control includes toxicological experiments and residue determination on treated plants and soil.

Wide commercial use of such organophosphorous insecticides as cyanox, metathion, metaphos, phosalone, carbophos, actellic, basudin, geterophos, and pyrethroid insecticides as decis, ambush, sumicidin etc. promoted us to study their dynamics on treated plants: apples, potatoes, cucumber, beagoons.

Correlation was established to exist between the structure of applied insecticides, meteorological conditions and preparation persistence on apples, cucumbers and beagoons.

The residues of some used in combination with microbiological formulations of standard and reduced rates has been determined. For example, cyanox residues were shown to be reduced to less than 0.1 mg/kg in 3 days after treatment by reduced insecticide rates, standard insecticide rates being used, insecticide residues (less than 0.1 mg/kg) were found in 14-20 days after the treatment. Metaphos residues constituted 0.01 mg/kg on apple varieties Wagner prisovoi, R. Simirenko and Starcrimson under the same conditions. Fosalone residues considerably exceeded those of metaphos being preserved during 6 days after treatment at one level and reduced in 22 days to 29.7% from the initial amount. The low persistence of actellic on cucumbers was found and constituted 0.06 mg/kg on the 8th day after treatment.

No insecticidal residues were found in potatoes harvested from the plots treated with 5-10% granulated basudin, volaton and geterophos.

Pyrethroids (decis, ambush, sumicidin) were as highly effective as organophosphorous insecticides against a number of orchard and vegetable crop pests (apples, potatoes, beagoons, cucumbers). We studied their persistence on the above mentioned crops. The results have shown that ambush residues on apple leaves immediately after treatment were higher than decis ones - 0.68-0.15 and 10.08-1.14 mg/100 g of leaves, respectively. Then residue quantity of both insecticides was gradually reduced and in 9 days after application constituted 0.26-0.03 and 6.27-1.14 mg/100 g of leaves, respectively. Sumicidin demonstrated rather high persistence on beagoon plants.

Thus, the data obtained have shown the proper application rates and time provided purity of the harvest.