SESSION 6B

ADVANCES IN FORMULATION AND APPLICATION TECHNOLOGY

Chairman & Session Organiser:	Professor M G Ford *University of Portsmouth, UK*
Papers:	6B-1 to 6B-4

Development of a new deltamethrin formulation for Europe

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ABSTRACT

The market for crop protection in Europe is increasingly influenced by new trends such as environmental concerns, the consumers and applicators' safety added to the fundamental requirement of efficacy. To comply with market demands the product requires not only favourable profile for the active(s) but also minimal impact by its formulants. The project team for the new European formulation of deltamethrin considered all of these issues. The selection of an EW formulation (Decis Protech®) permitted a move away from petroleum distillates as solvents without losing activity. By matching deltamethrin concentration with selection of formulants from food industry and pharmaceutical uses it was also possible to produce a product with no EU classification regarding operator handling.

INTRODUCTION

Deltamethrin is highly successful in controlling a wide range of sucking and biting insects in foliar spray applications when formulated as an emulsifiable concentrate, (deltamethrin 25EC). The EC is still a reference in the market place, but several deltamethrin formulations have also been developed to match specific local market needs around the world. Bayer CropScience has sought to address regulatory and legislative pressures in terms of storage of agrochemicals and to minimise the impact of deltamethrin and its formulation on the environment.

Over the last decade, formulation work targeted the elimination of most of the organic solvent in the EC by designing new solid and liquid formulations to ultimately replace the EC. Field trials found that not all options for deltamethrin formulation were suitable for the European use pattern.

The first breakthrough in this project was an emulsifiable granule (EG) known as the "Micro" formulation. This uses a granule incorporating deltamethrin solubilised in an organic solvent whose content was adjusted to maximise the deltamethrin biological efficacy (Henriet M & Roâ L 1987). Upon preparing spray mixtures, the granules disintegrate and release the deltamethrin containing organic solvent, which is emulsified in the spray solution. Close contact with regulatory authorities, the food industry and marketing studies with growers identified developing needs in the foliar spray application segment in terms of toxicology and ecotoxicology profiles in Europe. To address those needs the next step was to substitute traditional petroleum distillates used as solvents : a new liquid deltamethrin formulation has been developed as an emulsion in water (EW).

MARKET REQUIREMENTS

Developing formulations to satisfy changing needs in regulatory and food industry areas is just one part of successful product evolution. Meeting the needs of product users is also critical and the decision to market the EW recognises that in choosing foliar insecticides, apart from the efficacy and cost per ha, other important expectations are emerging appear in the minds of European growers.

In March/April 2002, a panel of 2109 French farmers representing 279100 ha (average farm 139 ha) were surveyed. Taking a global assessment, 94% of these farmers were either very (15%) or rather satisfied (79%) with the foliar insecticides they were currently using.

However when the ranking of individual buying criteria was assessed, operator safety and respect of the environment emerged close behind efficacy and the cost per ha. Considering their present importance versus previous surveys these are new factors influencing the insecticide market at the grower level. Interestingly, 33% of the farmers were not satisfied regarding these two factors. When asked "Which improvements should new foliar insecticides provide?" the (unprompted) ranking was: -

1. Toxicity to the end-user : 19%
2. Residual activity: 17 %
3. Respect of the environment :14 %

PROFILE OF THE CHOSEN EW FORMULATION

The new deltamethrin EW formulation consists of a dispersion of fine droplets containing deltamethrin a.i. solubilised in an organic solvent in a continuous aqueous phase. The co-formulants in the new deltamethrin EW formulation have been selected among raw materials commonly used in the pharmaceutical and food industries. Like the EC, the new deltamethrin EW formulation requires a suitable organic solvent to solubilise the solid deltamethrin active ingredient. Although a major part of the organic solvent used in the EC also acts as a carrier to achieve the targeted a.i. loading in the formulated product, only water is used as the carrier in the concentrated emulsion (EW) formulation. This permits the option of minimising the solvent concentration to the quantity needed to solubilise the deltamethrin active ingredient.

As opposed to the EC which incorporates a mixture of aromatic hydrocarbons, the new deltamethrin EW formulation uses a different organic solvent system designed to:

- maintain the bioefficacy profile of the standard deltamethrin 25 EC formulation
- minimize toxicological concern (acute toxicology profile)
- minimize transport and storage hazards (high flash point)
- prevent deltamethrin a.i. crystallization in the formulated product as well as upon dilution in the spray solution.

The solvent system required much attention in order to meet these requirements and obtain the necessary a.i. concentration in the formulated product. Ultimately, the system satisfying the product parameters of deltamethrin EW15 is based upon a mixture of acid esters and a powerful polar solvent.

The optimum biological performance shown by the new EW formulation is further achieved by producing a very fine emulsion, i.e. a monomodal droplet size distribution with a mean diameter of 0.5 µm, after dispersion of the organic phase in the aqueous phase when manufacturing the formulated product. This is obtained by the combination of several factors:

- The selection of a specific emulsifier system incorporated in the organic phase which emulsifies the deltamethrin containing organic solution in the continuous aqueous phase. It comprises a mixture of anionic and nonionic surfactants.
- The use of a polyvinyl pyrrolidone derivative incorporated in the aqueous phase acting as a steric stabilizer which further synergizes the emulsifier action in obtaining and keeping the very fine droplet size pattern upon storage, thus maximising the long lasting activity of the emulsifier system.
- The manufacturing process which uses a powerful high shear mixer to disperse the organic phase into the aqueous phase.

The new formulation also incorporates a glycol derivative, which has a double function as antifreeze and humectant. As a humectant it slows water evaporation from the fine droplets, thus maintaining the droplet longer in a liquid state, extending further the activity of the emulsifier system and the bioefficacy of the a.i..

Choosing an EW was correct for the product profile required, but other additives became necessary. Defoamers had to be included, to suppress foam produced during the manufacture of the formulated product and during application, and as a water based formulation the new product contains preservatives to prevent the unwanted development of microorganisms. Finally the new deltamethrin EW formulation needed to survive storage tests under different conditions without any emulsion breakdown or a.i. chemical degradation.

PERFORMANCE OF DELTAMETHRIN EW FORMULATION

Market and regulatory trends are important but European development of an EW formulation would not have gained momentum without showing potential against aphids.

Table 1. Activity of deltamethrin EW 15 on *Aphis fabae* in bean (lab. test)

	Dosage ppm ai	% Efficacy at			
		1 DAA	3 DAA	5 DAA	7 DAA
Deltamethrin EW 15	1	99	99	100	100
	0.3	97	99	97	96
Deltamethrin EC 25	1	99	99	99	99
	0.3	90	92	93	88

Test PS 01 042

The basic formulation was selected after extensive laboratory testing of several candidate EW blends In table 1. efficacy against aphids was comparable to the standard EC. Quick knock-down was not limited to aphids and contact activity against *Plutella xylostella* (not shown) was more rapid with the EW compared to the EC

Field performance

Regardless of promising results in the laboratory, experience has shown that field trials remain essential in the development of new formulations. A range of insect pests was targeted in Europe in a programme designed to confirm that the spectrum of activity for the candidate was at least as good as EC references. Excellent efficacy of deltamethrin EW15 was recorded on a wide pest spectrum from the coleopteran, lepidopteran and aphididae pest species. Despite the move away from aromatic petroleum solvent, deltamethrin EW15 appears equivalent or better than the deltamethrin EC and other pyrethroid competitors.

Table 2. Efficacy of deltamethrin EW15 on *Meligethes aeneus* in Winter Oilseed Rape

	Dose gai/ha	% Efficacy at	
		4 DAA	7 DAA
Untreated (adults/100 shoots)		(126)	(70)
Deltamethrin EW15	7.5	100	86
Alpha-cypermethrin WG 15%	10	100	86
Cypermethrin EC 100	25	100	64

(Beverley, UK 2001) Trial ID01GBRA05DH01

Table 3. Efficacy of Deltamethrin EW 15 on *Laspeyreysia nigricana* in Peas

	Dose gai/ha	% Damaged Pods at 28 DAA
Untreated		19.2
Deltamethrin EW 15	6.25	5.2
Lambda-cyhalothrin EC 50	6.25	8.0

(Perrieres, France 1999) Trial IR99FRAP11YRD1

Table 4. Efficacy of deltamethrin EW15 on *Rhopalosiphum padi* in Winter Barley

	Dose gai/ha	% Efficacy at		
		7 DAA	15 DAA	30 DAA
Untreated (% infested plants)		(15.3)	(21)	(43)
deltamethrin EW15	7.5	91	79	76
Lambda-cyhalothrin CS 100	7.5	76	79	72
Alpha-cypermethrin WG 15%	10.5	75	53	70

(Epernay-sous-Gevrey, France 2001) Trial ID02FRAC01BOU1

TOXICOLOGY PROFILE

Addressing the concerns of growers regarding operator safety was a key aim during development of the deltamethrin EW15 formulation. Three elements have been associated in one formulation in order to reach the best toxicological profile: a low concentration of deltamethrin in the formulation, an EW type and a low content of petroleum solvents. The benefit of the attention paid (in Table 5) is no EU classification.

Table 5. Toxicological properties of deltamethrin EW15 g/L compared to EC25 g/L

	Deltamethrin EW15	EU*	Deltamethrin EC25	EU*
Oral LD50 (rat)	> 2000 mg/kg bw	-	431 mg/kg bw	R 22
Dermal LD50 (rat)	> 2000 mg/kg bw	-	> 2000 mg/kg bw	-
Eye irritation (rabbit)	No irritation	-	Very irritant	R 41
Skin irritation (rabbit)	No irritation	-	Slightly irritant	-
Skin sensitisation (?)	No sensitisation	-	No sensitising	-

EU* : EU classification according to current EU classification criteria
: unclassified

ECOTOXICOLOGY PROFILE

The environmental impact of the deltamethrin EW15 formulation is similar to deltamethrin EC25 and other deltamethrin containing formulations, as long as GAPs are followed and labels recommendations are respected :

- a low risk to terrestrial and aquatic ecosystems
- a low risk with regard to deltamethrin groundwater contamination

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The potential for safe use of deltamethrin with honeybees is well recognised. Less is known of the field interactions between synthetic pyrethroids and bumblebees. Deltamethrin EW15 was evaluated against *Bombus terrestis* using an experimental protocol adapted from the C.E.B. method n°129.

Table 6. Impact of deltamethrin EW on foraging bumblebees in flowering *Phacelia*

	Dose gai/ha	Bumblebee mortality (number of dead bees)		Foraging activity in treated area (bumblebees/m2)		
		on treatment day (1)	after treatment (2)	Just before treatment	Just after treatment	mid afternoon of treatment day
water treatment		0	1	3.7	4.8	5.9
deltamethrin EW 15	12.5	2	1	6.9	3.5	6.9
phosalone SC 500	600	0	0	2.9	2.3	3.5

Trial carried out by Testapi, 2000

(1) cumulative mortality from treatment day evening to next day morning

(2) average daily mortality on day 2 and day 3 after treatment

The deltamethrin EW 15 treatment caused a temporary decrease in foraging activity with no impact on daily mortality when compared to the non-toxic reference and the water only spray treatment.

CONCLUSION

Development of successful product formulations has never been solely the preserve of the formulation chemist. In this case study of deltamethrin EW15 it is our view that the final unclassified formulation has benefited from growing the project team to include the views of colleagues in close contact with regulatory authorities and the food industry. Of course, although the formulation is very capable it joins a crowded European market including deltamethrin EC, how will it succeed? We believe that success is not just about the right product, it is also about the right time. Based upon the opinions expressed in recent market research the correct timing is now.

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Acylated lignin: a matrix for controlled release formulations of pesticides

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ABSTRACT

Controlled release pesticide formulations address the need to reduce pesticide toxicity, environmental impact, and to improve efficiency and efficacy. Matrix formulations based on biodegradable polymers offer advantages especially for granules and seed treatments. To improve compatibility with pesticides a polar lignin was modified by forming biodegradable derivatives. A lignin (organosolv) was modified to form the acetate, octanoate and laurate esters and formulated (with bromacil as representative pesticide) to prepare matrix glasses which were then granulated. The release kinetics from the granules determined by release into water were fitted to the generalised model and showed a delayed release followed by an increasing rate and have potential for applications, amongst others, in protecting pesticide sensitive plant stages

INTRODUCTION

Controlled release pesticide formulations address the need to reduce the risk of pesticide toxicity, the impact on the environment, and to improve efficiency and efficacy (Wilkins, 1990). Matrix formulations based on biodegradable polymers offer advantages especially for granules and seed treatments. By controlling the release rate such formulations can reduce leaching, extend the period of protection without increasing the dosage and improve the safety to the germinating seed or seedling crop. Lignin, a biodegradable polyphenylpropane, is the second-most abundant naturally occurring macromolecule in the world, and a byproduct of the pulp and paper industry.

Matrix formulations release the pesticide according to internal diffusion which is dependant upon the degree of compatibility of the active ingredient with the matrix material. Many of the biodegradable materials used in matrix formulations are often polar polymers (e.g. starches, lignins) and thus have limited compatibility with some pesticides (Wilkins, 1999). To improve compatibility with a range of pesticides a polar lignin was modified by forming less polar biodegradable derivatives (Glasser & Jain, 1993). The hydroxyl groups of a water-insoluble lignin were modified to form the acetate, octanoate and laurate esters and their solubility parameters were calculated. The resulting acylated lignins were formulated (with bromacil as a representative pesticide) to prepare matrix glasses which were then granulated. The release kinetics from the granules were determined by release into water.

MATERIALS AND METHODS

The hardwood organosolv lignin (Alcell® lignin) (Lora et al., 1989) was provided by Repap Technologies Inc (Valley Forge, PA, USA). Technical bromacil [5-bromo-6-methyl-3-(1-

methylpropyl)-2,4- (1H,3H)-pyrimidinedione] (purity 97%) was supplied by Griffin Corporation (Valdosta, Georgia, USA).

Acylation of lignin

The lignin (20 g) was dissolved in pyridine (40.0ml) and acetic anhydride (or an acyl chloride) was added dropwise under a current of nitrogen at a molar ratio of acylating agent to total hydroxyl groups of the lignin given in Table 1. The mixture was stirred in the sealed flask at ambient temperature in the dark for 48 hours and precipitated in 2M ice-cold dilute HCl (400ml). The product was filtered on a Buchner funnel, and thoroughly washed with deionised water until the pH of the filtrate was neutral. The product was then dried under vacuum for 24 hours and kept in a desiccator.

Table 1. Reagents used in the acylation of Alcell® Lignin

Code	Acylating agent	Molar ratio (acylating agent/-OH)	Solvent-Catalyst
L_p	None	-----	Pyridine: 40 ml
$L_{p\text{-}C2}$	Acetic anhydride	2.0:1	Pyridine: 40 ml
$L_{p\text{-}C8}$	Octanoyl chloride	0.25:1	Pyridine: 40 ml
$L_{p\text{-}C12}$	Lauryl chloride	0.25:1	Pyridine: 40 ml
L_{Ac}	None	-----	HOAc-NaOAc (40 ml, 3.5g)
$L_{Ac\text{-}C2\text{-}1}$	Acetic anhydride	2.0:1	HOAc-NaOAc (40 ml, 3.5g)
$L_{Ac\text{-}C2\text{-}2}$	Acetic anhydride	2.0:1	HOAc-NaOAc (40 ml, 3.5g)

For lignin octanoate and laurate, the precipitates were stirred with petroleum ether (50 ml, 60-80°C) for 30 mins at 0°C to remove the corresponding fatty acids produced (octanoic acid & lauric acid). The suspension was filtered immediately on a Buchner funnel and rewashed until the filtrate contained no free acid. A 'blank' acylation was also carried out omitting the acylating agent.

A corresponding pyridine-free acetic anhydride/acetic acid mixture (1:1) was also used for the lignin acetate. The lignin was acetylated using sodium acetate (0.1) as a catalyst (Glasser & Jain, 1993) using the quantities of table 1. After standing at ambient temperature in the dark for 48 hours, and refluxing for 1 hour, the mixture was precipitated in ice-cold water (800ml) and purified as above.

Characterization of lignin esters

The degrees of esterification of the washed and dried lignin esters were determined by NMR spectroscopy (based on the methoxyl content of the lignin) and by saponification with KOH. The solubilities of each of the lignins and esters were measured for a range of organic solvents using the colour or UV absorption at 277nm of the solution.

Preparation of lignin-based matrix granules

The lignin (Alcell® lignin and its acylated products) as a fine powder (1 g) and bromacil (1g) were weighed, thoroughly mixed and then heated on a hot plate at 140-160°C for 10 min (Ferraz et al., 1997). After cooling, the solid glass was granulated and sieved to the particle size of 0.7-1.0mm. The granules were analysed for pesticide content by extracting with acetone (sonicated) in triplicate, filtered through a nylon membrane and then by GC-FID.

In Vitro Release study

Bromacil release from the lignin-based granules (3 replicates, 50mg) was studied at 30°C in reagent bottles using a controlled environment incubator orbital shaker at 150 rpm. Immersion water was sampled at intervals and completely replaced with fresh deionised water (300ml) in order to maintain 'sink' conditions, filtered and analysed in duplicate by HPLC at 280nm.

RESULTS AND DISCUSSION

The degree of conversion is defined as the ratio of the hydroxyl group (-OH) converted to acyloxyl groups (-OCOR) to the total hydroxyl group per phenylpropane (C_9) unit. The conversion of hydroxyl groups (-OH) to acyloxyl groups (-OCOR) per C_9 unit was calculated by saponification and summarised in Table 2 (NMR analysis agreed with this). The degree of conversion was 0.74, 0.11 and 0.073 for lignin acetate, octanoate and laurate acylated in pyridine, and 0.70 and 0.68 for lignin acetates acetylated in acetic acid/sodium acetate.

Table 2. Phenylpropane (C_9) molecular formulae for lignin alkanoates based on saponification.

Lignin code	C_9 formula	% methoxyl	% hydroxyl	% Oacyl
L_o	$C_9H_{6.0}O_{1.0}(OMe)_{1.1}(OH)_{1.1}$	18.65	10.23	0
$L_{p\text{-}C2}$	$C_9H_{6.0}O_{1.0}(OMe)_{1.1}(OH)_{0.29}(OCOCH_3)_{0.81}$	15.73	2.27	22.04
$L_{p\text{-}C8}$	$C_9H_{6.0}O_{1.0}(OMe)_{1.1}(OH)_{0.98}(OCO(CH_2)_6CH_3)_{0.12}$	17.23	8.42	8.67
$L_{p\text{-}C12}$	$C_9H_{6.0}O_{1.0}(OMe)_{1.1}(OH)_{1.02}(OCO(CH_2)_{10}CH_3)_{0.08}$	17.28	8.78	8.07
$L_{Ac\text{-}C2\text{-}1}$	$C_9H_{6.0}O_{1.0}(OMe)_{1.1}(OH)_{0.33}(OCOCH_3)_{0.77}$	15.85	2.61	21.12
$L_{Ac\text{-}C2\text{-}2}$	$C_9H_{6.0}O_{1.0}(OMe)_{1.1}(OH)_{0.35}(OCOCH_3)_{0.75}$	15.91	2.78	20.65

All the lignin alkanoates completely dissolved in acetone, dioxane, dimethyl formamide, dimethyl sulfoxide, which possess solubility parameters ranging from 20.0 ~ 26.5 $MPa^{1/2}$ and moderate hydrogen bonding capacity. However, the solubilities of lignin alkanoates (Table 3) increased in the solvents with weak hydrogen-bonding capacity (i.e. carbon tetrachloride, acetonitrile) compared to the untreated and 'blank' acylated lignins. The solubilities of lignin alkanoates decreased in the solvents with strong hydrogen-bonding capacity, such as propanol, ethanol, and methanol. The change of solubility in those two groups of solvents was less for the low substituted lignin alkanoates ($L_{p\text{-}C8}$ & $L_{p\text{-}C12}$) than for the high substituted ones ($L_{p\text{-}C2}$, $L_{Ac\text{-}C2\text{-}1}$, $L_{Ac\text{-}C2\text{-}2}$) compared to the untreated and 'blank' acylated lignins. The changes in solubility of lignin alkanoates in the solvents with two extreme hydrogen-bonding capacities possibly indicate that the hydrophobicity of the resulting lignins might be increased by the acylation.

Table 3. Solubility (g / 100 ml) of lignins and acylated lignins in solvents with weak or strong hydrogen bonding capacity

Solvent	L_0	L_p	L_{Ac}	$L_{p\text{-}C2}$	$L_{Ac\text{-}C2\text{-}1}$	$L_{Ac\text{-}C2\text{-}2}$	$L_{p\text{-}C8}$	$L_{p\text{-}C12}$
CCl_4	0.055	0.056	0.100	0.703	0.794	0.774	0.185	0.267
acetonitrile	1.205	1.205	1.177	1.398	1.675	1.777	1.280	1.348
propanol	0.760	0.694	0.704	0.220	0.248	0.228	0.476	0.394
ethanol	0.827	1.047	0.828	0.421	0.256	0.361	0.677	0.715
methanol	1.172	1.204	1.038	0.554	0.530	0.511	1.001	0.524

Compatibility of acylated lignins with bromacil

The compatibility for blending lignins with pesticides is normally considered from the solubility parameter (δ) of each of the components in the matrix (Chanse & Wilkins 1987). Polymers have a maximum solubility in solvents with δ-values closest to their own. The solubility parameter of good solvents for lignin falls in the range of 20 ~ 23 $MPa^{1/2}$ (Schuerch, 1952). All the lignins examined completely dissolved in solvents of solubility parameters 20.5 ~ 26.5 $MPa^{1/2}$ and moderate hydrogen bonding capacity. The lignin alkanoates have the solubility parameters similar to the Alcell® lignin, with the values ranging between 20.5 and 26.5 $MPa^{1/2}$.

When the lignin alkanoates were used as formulating materials the processing temperature was reduced (140~150°C) compared to the untreated Alcell® lignin (150~160°C). Bromacil has a melting point of 157°C. The time taken for completely melting the mixture was also reduced from ca. 10 to ca. 3 minutes. The change in the requirement (time & temperature) in matrix processing was due to a drop in the glass transition temperature (T_g) of the lignin esters (Glasser and Jain, 1993).

Release kinetics from lignin alkanoates used as formulating material

The release kinetics of bromacil for the lignins and ester granules into water are shown in Figures 1 and 2, separated on the basis of the acylation method; those formulations prepared with esters made in pyridine having a faster release rate than those in sodium acetate. Uniquely amongst controlled release formulations, there is a slow initial release followed by an increasing rate (delayed release), which may be appropriate for pesticide delivery to germinating seeds. The data (Table 4) is fitted to the generalized model: $\frac{M_t}{M_\infty} = k \bullet t^n$, where M_t/M_∞ is the fraction of the active ingredient released at time t, k is a constant incorporating characteristics of the matrix, and diffusion exponent n.(Ritger & Peppas (1987). Values of n over 0.85 indicate a role of swelling and matrix relaxation, rather than diffusion in controlling release and is classified as anomalous. The presence of small amounts of water-soluble lignin also affected the release kinetics (Zhao and Wilkins, 2000).

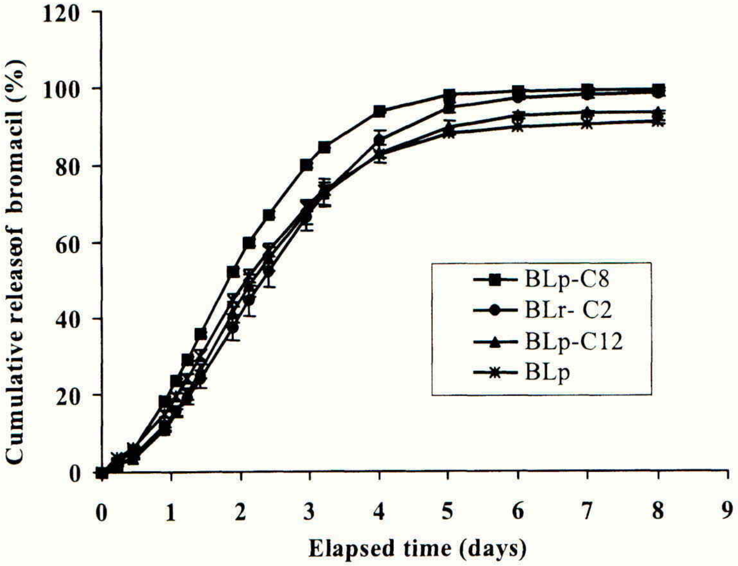

Fig. 1 Release of bromacil from the matrix granules based on various lignin alkanoates acylated in pyridine-acylating agent mixture (The error bars represent the standard deviation (n=3). The bars are smaller than the symbols where not shown).

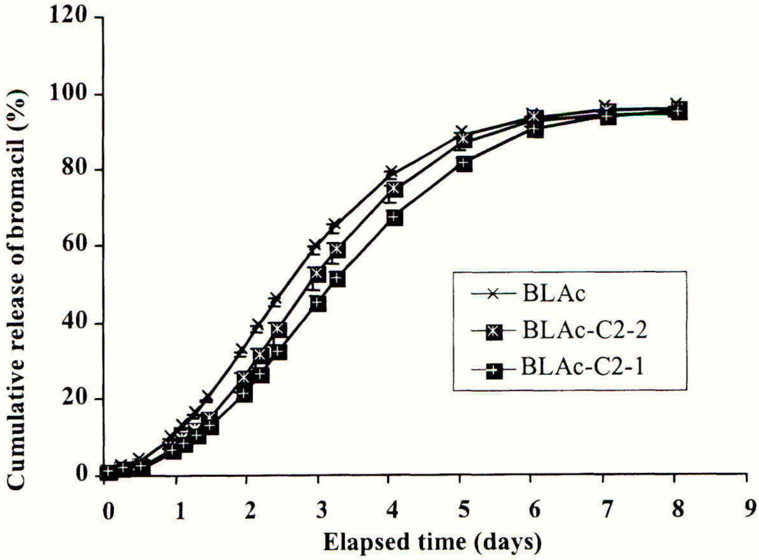

Fig. 2 Release of bromacil from the matrix granules based on lignin acetates acylated in pyridine-free acetic acid-acetic anhydride mixture (The error bars represent the standard deviation (n=3). The bars are smaller than the symbols where not shown).

This anomalous release kinetic shown by all the formulations, has a delay followed by increasing release and thus, may be useful for protecting sensitive seeds and seedlings.

Table 4. Constants from fitting the generalised model $M_t/M_\infty = kt^n$ to the release data of bromacil from lignin-based matrix granules

matrix	k (day^{-n})±SE	n±SE	r^{2} [a]	T_{50} (days) [b]	$T_{50\text{-}BLx} / T_{50\text{-}BL0}$ [c]
BL_0	46.16±0.52	1.21±0.04	0.9992	1.07	1
BL_{HCl}	39.18±0.50	1.48±0.05	0.9982	1.18	1.18
BL_p	19.30±0.24	1.22±0.02	0.9982	2.18	2.18
$BL_{p\text{-}C2}$	14.52±0.43	1.44±0.04	0.9995	2.36	2.20
$BL_{p\text{-}C8}$	20.76±0.24	1.44±0.02	0.9988	1.84	1.72
$BL_{p\text{-}C12}$	12.96±0.23	1.58±0.02	0.9982	2.35	2.20
BL_{Ac}	11.38±0.14	1.55±0.02	0.9989	2.60	2.60
$BL_{Ac\text{-}C2\text{-}1}$	6.85±0.19	1.67±0.03	0.9984	3.29	3.07
$BL_{Ac\text{-}C2\text{-}2}$	7.75±0.42	1.74±0.06	0.9993	2.92	2.73

a: Correlation coefficient, significant at P=0.001. b: The time for 50% release of bromacil.
c: The ratio of T_{50} value to that of the parent Alcell® lignin-based granules.

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Current status of application technology for greenhouses across Europe and associated occupational exposure to pesticides

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ABSTRACT

The area of land covered by greenhouses continues to grow in many regions of Europe and neighbouring Mediterranean countries, as they allow cultivation of a wider range of crops in cold climates as in Nordic countries such as Finland, or to increase the production in Mediterranean countries such as Spain. The warm and humid conditions often encountered inside greenhouses cause high pest and disease pressure. The high value of the crops being cultivated combined with high quality demands by retailers and consumers has tended to require high levels of pest and disease control. This has lead to intensive pesticide use in certain areas of Europe, which has had consequences for the health of the local environment and greenhouse workers. The application methods employed vary depending on local conditions, but are generally high volume hand held application techniques. Rigorous monitoring of residues by exporting and importing countries is required to ensure that MRL's are not exceeded. In northern Europe a reduction in pesticide use through the introduction of Integrated Crop Management (ICM) has occurred. This has lead to a safer working environment for workers, and a reduced reliance on pesticides for pest and disease control. As part of a 4th Framework SMT (Standards Measurement and Testing) project, the most commonly used application techniques in greenhouses were identified, and field studies were done to provide corroborative evidence of the deposition efficiency of pesticide on the crop. More importantly, the potential exposure of the operators of the application equipment was evaluated, as well as workers who have to enter the greenhouse following the application. The re-entry exposure can in some cases be higher than the exposure of the sprayer operators in southern Europe. Various predictive operator exposure models have been used (Kangas & Silhoven, 1996). In Europe a common model is being developed, but lacked robust exposure data for the hand held application technique in Southern Europe (Glass & Gilbert, 1996). The SMT project generated potential dermal exposure data to begin to rectify this.

MATERIALS AND METHODS

Information was collected on the range of application methods used in greenhouses in Southern Europe to identify the most common techniques used to apply pesticides. The information was obtained from local agronomists involved with pesticide application in each of the regions under study (Almería and Seville in Spain; Algarve and Oeste regions of Portugal; Albenga region of Italy and the Greek island of Crete. Once the application techniques had been identified potential operator exposure studies were carried out together with an assessment of bystander and re-entry potential exposure.

Potential dermal exposure data were generated following a common protocol for whole body dosimetry, i.e. wearing a coverall which could be used to extract tracer or pesticide contamination. Sontara garments were identified as being suitable whole body dosimeters, as the critical factor in measuring potential dermal exposure is to ensure that all of the liquid that comes into contact with the body is retained by the sampling media, as specified by the OECD Guideline Protocol (OECD 1997). Any losses due to run off or penetration of the dosimeters would lead to an underestimation of the potential dermal exposure. The outer absorbent coverall was used in conjunction with an inner Tyvek coverall to collect liquid penetrating the outer garment. The sample media used for collecting potential exposure to the hands were cotton gloves with rubber gloves beneath.

The studies were done in a range of typical greenhouse crops in each region, e.g. tomato, courgette, pepper and French bean. Most studies were done with the mature crops, often at least 2 metres in height. Initial studies were done with visible tracers (Machera, *et al.*, 2001), with the bulk of the studies done with a range of commonly applied pesticides e.g. procymidone.

RESULTS

The majority of pesticides in southern Europe were found to be applied with a high volume hand held application technique. High volume techniques often involve application rates of >800 litres/ha, with pressures of usually between 15 and 25 bar. There were a number of specific techniques used, but all involved a hand held lance or single nozzle "gun" fed by hoses of various lengths. In the larger greenhouses (>2 ha), such as found in the Almería region, the pesticide was mixed in large static 1000 litre tanks at the pumping station. The pesticide mixture is fed via fixed pipework (usually underground), to the greenhouse where there are a number of outlets. The operator can connect the hose to the outlets positioned at intervals along the central alley of the greenhouse.

Another common technique involves a tractor drawn sprayer which supplies pesticide mixture to the lance via a hose. The pesticide is loaded into the sprayer at the filling point, usually next to the pesticide store, and the tractor (mini tractor) and sprayer is then driven to the greenhouse. The tractor can be driven into the greenhouse alley or left outside, depending on the size of the greenhouse, and the length of the hose.

Semi stationary (wheelbarrow) sprayers were common for small to medium sized greenhouses (up to around 0.25 ha size). This technique is similar to that employing the tractor drawn sprayer, allowing the operator to position the sprayer inside the greenhouse, with a hose fed lance.

In addition to the traditional high volume application techniques, some reduced volume application techniques were seen. In Portugal motorised knapsack mistblowers are used occasionally, and in Spain some of the more modern greenhouses were experimenting with automated space treatments, using applicators such as the Enbar. This technique is often termed LVM (low volume misting) in the UK, but is more akin to cold fogging.

Once the predominance of the high volume hand held application technique had been established, field sites were selected to perform potential operator exposure studies with this technique. Some studies were also done in Portugal with the motorised knapsack mistblowers.

There are a number of ways in which "operator exposure" data can be both generated and expressed, which may lead to some difficulties when evaluating what exactly the data mean in terms of operator safety. Formats for operator exposure data range from potential dermal operator exposure (the contamination of the operator's clothing) to actual systemic exposure (absorbed dose). Systemic exposure studies typically involve the quantification of the parent compound or its metabolites in the urine of the operator (Tuomainen, *et al.*, 2001).

Over 100 data sets have been generated in Portugal, Spain, Italy and Greece, with potential dermal exposure values for the applicator ranging from 20 to 600 ml/h, with a coefficient of variation over 150%. Even for similar conditions within a single region the coefficient of variation is over 100%. The potential dermal exposure data have been collated in two formats, as either volume (ml) of contamination per hour of application, or as a proportion of the amount of active substance applied during the tasks involved with the field study. Each type of data has its particular advantage in expressing potential dermal exposure. However, in cases where a range of application techniques are used it is important to know the rate of liquid contamination, as this often has a bearing on the protective factor of PPE being worn by the applicator.

In Figure 1 the data are expressed as a proportion of the active substance applied, by determining the mass of pesticide on the clothing of the operator (mg of active substance) and calculating the mass of active substance applied to the crop (kg of active substance) for the duration of the field study. This removes possible distortion of the data due to the application volume rate (the amount of water applied to the crop with the pesticide). For example, an application volume rate of 800 l/ha is more likely to contaminate the applicator with spray liquid than one carried out with 200 l/ha, for similar crop and application conditions. However the pesticide would be applied in a more concentrated form with the lower application volume.

These data illustrate the variability encountered, and also indicate that the contamination of the hands is generally less than the body. In cases where hand contamination is high, it is likely to be as a result of faulty equipment or unusual events, such the hand coming into contact with nozzle, either accidentally or intentionally (e.g. to remove blockage from nozzle).

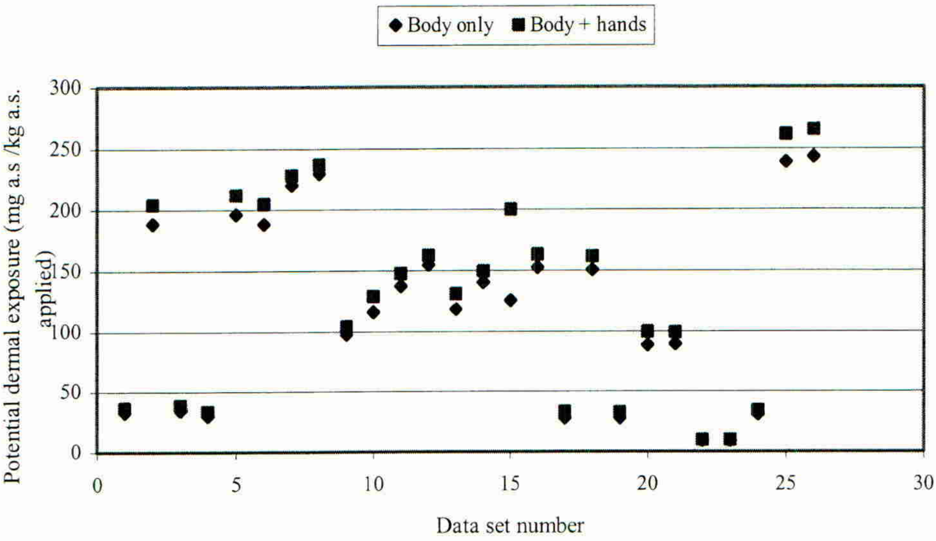

Figure 1. Example of data for potential dermal exposure expressed as a proportion of the active substance (a.s.) applied (mg a.s. per kg a.s. applied)

DISCUSSION

Traditional high volume applications involving >800 litres/ha of water are still the most common way of treating greenhouse crops with pesticides in southern Europe. In some cases the application rates exceed 2000 litres/ha. Such techniques are labour intensive, usually requiring two people to do the spraying. One person deals with the long hose, ensuring that it does not snag on the crop and other obstacles as the applicator walks up and down each of the individual rows. It is not uncommon for the hoseman to have a higher potential dermal exposure to the pesticide than the applicator holding the spray gun or lance.

Studies in the UK with vertical pipe-rail booms (Lee *et al*, 2000) indicated that deposits from conventional pipe-rail booms are not further increased when operating at volume application rates above 2800 litres ha-1 and that application rates above this level lead to run-off. Optimum application rates were found to be 400 to 500 litres/ha.

Studies in Portugal (Moreira, *et al.*, 2000) have shown similar potential dermal exposure values with hand held lances (2143 litres/ha) and motorised knapsack (565 litres/ha) application techniques. Deposition of pesticide on the crop was found to be poorer at the top of the tomato plants (2 m high) with the motorised knapsack.

Traditional greenhouses in areas such as Almería are not completely closed, as in northern Europe, making space treatments (fogging and misting) more difficult or ineffective. Studies done by the Central Science Laboratory with automated space treatments in the UK indicated that deposition of pesticide on the crop accounted for only 50% of the pesticide applied to the greenhouse. The pesticide is applied as a cold fog over the top of the crop, carried in the airflow form fans on the applicator itself and also fans situated within the greenhouse. As the pesticide droplets begin to sediment they are deposited on upper leaf surfaces and other surfaces within the greenhouse.

In terms of occupational exposure to pesticides, there are key differences between the high volume and reduced volume application techniques. When the pesticides are applied with hand held lances at high volumes (500 to 2000 litres/ha) the pesticide is often at low concentrations, often < 1g/litre of active substance. Therefore if the pesticide mix comes into contact with the operator the hazard is lower than for more concentrated pesticide mixes encountered with reduced volume applications, where the concentration of active substance is normally 10 to 20 g/litre. However the protective factor of personal protective equipment is affected by the rate of liquid contamination. Therefore the higher rate of contamination with high volume applications results in greater penetration of PPE such as cotton coveralls.

In the warm conditions encountered in greenhouses the liquid contamination of coveralls can dry during the application task, if the rate of liquid contamination is low (e.g. 50 ml/hour). For the automated space treatments or automated gantry sprayers the operator is usually not in the greenhouse during the application, so avoiding exposure. Exposure would only occur during the mixing and loading, or if the operator had to enter the greenhouse during the application if a fault occurred.

Post application (re-entry) exposure to pesticide in greenhouses can occur when workers are involved with tasks such as harvesting or crop maintenance usually the day following the application. Pesticide applied as fogs can remain airborne for 12 hours, requiring the greenhouse to be vented before workers can enter. However, pesticides applied as high volume sprays can also result in pesticide being airborne several days after the application (Capri, *et al.*, 1999). The hot daytime conditions are thought to cause volatilisation of the pesticide deposited on the crop, resulting in an increase in the airborne pesticide concentration during the day.

Pesticide application systems are being used increasingly for the application of biological control agents such as insect parasitic nematodes. However there appears to be need for greater control over the fate of the applied liquid in this case, as the nematodes remain viable for only a few hours on the plant surface, so must be deposited close to, or even on, the pest host if adequate control is to be achieved..

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Measurements of spray deposits on and off target surfaces within and beyond the treatment zone: the need for an embracing International Standard to measure and account all potential losses from container to target surfaces

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ABSTRACT

Discreet International Standards are being produced that will permit many aspects of sprayer performance to be meaningfully judged. Whilst all these Standards are critically needed, the commercial incentive to fulfil one set of needs may, in so doing, pose a threat to a further core purpose that seeks improvements in application delivery. It is proposed to integrate some aspects of existing Standards within one that embraces all aspects of spray accounting; a need that may be easily recognised but not readily gained. Some difficulties to spray accounting include variability of applied dose as well as interpretation of data. Nonetheless, the need to be able to identify where real improvements are being made and where most research activity should be focussed in the future implies that Test Methods and Performance Limits for spray accounting should be considered by the appropriate experts in the near future.

INTRODUCTION

A group of International Standards are being developed for arable crop sprayers that will describe how key measurements are to be made and the required attainment level with which they will need to comply for conformity. Many aspects of their performance are being considered but, understandably, have been introduced as and when they are needed to meet current interests. For example, concerns about downwind drift damage, contamination of environmentally sensitive and water catchments areas, very quickly triggered a developing Standard for measuring these losses from the treatment zone; a drift protocol being now at the Committee Draft stage for full international response.

Protocols are prepared by experts from many interested parties and include independent workers and representatives of regulatory interests as well as commercial companies. Working Groups for drift classification, sprayer cleaning, knapsacks, boom steadiness are just some that specifically deal with the issues that need to be addressed. Agreed WG protocols are internationally circulated by ISO for comment and when these have been considered, performance limits are proposed. Interested Bodies from independent and commercial sectors can then follow – if they wish – a recognised protocol and produce values that may be utilised by workers wherever they are based in the world. Sometimes, subject to independent verification, values generated may be transferred between Regulatory Bodies from different countries to afford locally recognised levels of achievement.

INTERNATIONAL STANDARDS

International Standards encourage the adoption of the highest level of performance that is identified within Guidance Notes or Codes of Conduct or as Good Agricultural Practice and reflects, too, that which is commercially attainable. The individual success's of these discreet Standards for arable sprayers are considerable but at some time in the near future, facets of them may benefit from being harmonised within one overall 'spray accountability' framework.

A single purpose, discreet Standard approach, may introduce the risk of encouraging better practices within one application parameter but at the cost of another. For example, the use of nozzles that are independently listed as Low Drift Equipment pose one such dilemma; they may atomise spray liquid into a Very Coarse spray that will certainly be well confined within the treatment zone but may not effectively reach, impact, be retained or prompt the level of biological efficacy that is associated with more conventional delivery systems.

These possible conflicts of purpose may be avoided if they were formally set within a structure that directly respects a more common aim of these Standard activities; to encourage techniques that will maximise on-target deposits and minimise those that are off-target - the latter being a loose definition that includes operators, equipment, those areas out of the treatment zone and, depending on product, even surfaces within it too.

A higher tiered Standard that encompasses all existing Standards and can quantify efficiency of delivery and all losses may be needed. This full spray account should help to ensure efforts and resources in application technique are effectively directed towards a measurable improvement in pesticide delivery and give, for example the agrochemical industry, an indication of likely impact of their product performance from application related changes.

PRESENT STATUS

Developing Standards for crop spraying have been recently well described by Herbst & Ganzelmeier (2002). Some, such as ISO 12057 and 22368, will be directly capable of contributing a value for use within a general 'spray account' whilst the sampling methods (Table 1) proposed by WG8 for air-assisted sprayer evaluation, could be particularly relevant to field crop sprayers too. Standards that are not involved with spray accounting on target surfaces such as cleaning, would still contribute to the overall assessment and so too would 'Sprayer Testing' that helps to ensure expected performances are maintained. These protocols and limits are self-contained and are not focussed on in this paper whose purpose is to debate more whether spray accounting within the treatment zone is needed and is possible.

Table 1. Status of crop spraying Standards in 2002 (Herbst & Ganzelmeier, 2002)

Standard	WG	Body	Title	Project stage
EN 13790-1	3	AFNOR	Inspection of sprayers in use-Low crop sprayers	pr
EN13790-2	3	AFNOR	Air assisted sprayers for bushes and tree crops	pr
ISO	3	AFNOR	Boom steadiness	NP
ISO 12057	4	BSI	Methods for field measurements of spray drfit	CD
ISO 19932-1	5	BSI	Manually operated sprayers – test Methods	CD
ISO 19932-2	5	BSI	Manually operated sprayers- performance limits	CD
ISO 22368-1	6	DIN	Internal cleaning of complete sprayer	CD
ISO 22368-2	6	DIN	External cleaning of complete sprayer	WD
ISO 22368-3	6	DIN	Internal cleaning of tank	CD
ISO	7	DIN	Drift classification procedures for sprayers and nozzles	WD
ISO/TC 22763	7	DIN	Demonstration track for field crop sprayers	CD
ISO	8	AFNOR	In situ test for air assisted sprayers	NP

Proposed experimental details noted by the air assisted Working Group have considered the measuring of spray deposits and losses from air assisted spraying practice (Planas, *pers com*) concepts and approaches that may be adaptable to a 'spray account' Standard for crop sprayers too. This developing Standard considers the target structure, growth stage, sampling methods and potential losses for the pesticide when measuring application efficiency. Details required by the emerging protocol include:

- Description of the tree or bush; Phenologic stage; Morphological parameters.
- Mass measurements; Leaf Area Index; Leaf Density in every sample zone; height; depth; geometry, shape; tree row (bush) volume; tree or bush distance, row width.
- Sampling of spray deposit on the targets; at least one tree within every replication will be chosen to carry out the measurements of spray deposit on the defined appropriate targets.
- Number and location of samples; must be relatable to the total crop volume to ensure the accuracy of, for example, comparable mean deposit values. Total crop volume must be equal to the integer multiple of sample volume (See a suggested typical tree sampling position for targets, their numbers and calculations).
- Use of artificial targets for mass or volume measurements; when not possible to use natural targets (such as leaves) then the description of number, position, material, attaching system and other relevant details - must be provided.
- Soil deposition; Horizontal, flat collectors of a collecting area ≥ 150 cm^2 may be used to measure spray deposit on the ground, at six locations across the treated row. Two samples will be taken from each position.

It is envisaged that this approach could be modified and used to quantify those effects attributable to applications for crop spraying purposes and be simply expressed for general communication within a schematic representation (Figure 1)

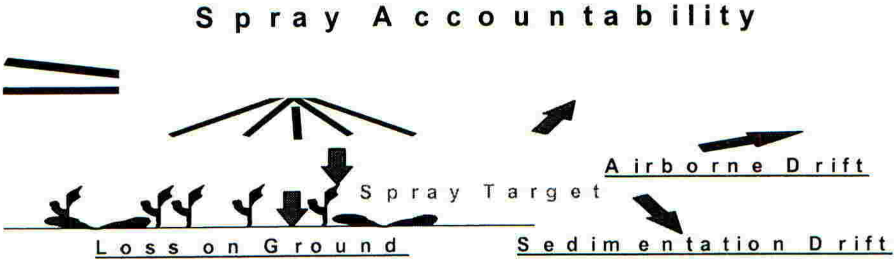

Figure 1: The overall performance of spray delivery systems needs to be recognised within a new Spray Accountability Standard. The example shown may be relevant to disease and pest control of a *Gramminacae* crop from the point of spray emission (the nozzles) to target surface retention.

THE ULTIMATE GOAL

Effectiveness of spray delivery to post emergent plants within the treatment zone has, surprisingly, not demanded much attention despite the enormous potential losses that may be occurring (Table 2). Target structures such as mono and dicotyledonous weeds are commonly sprayed in low population densities and at very small growth stages with herbicides; it is a practice that is vital to successful crop culture if crop competitive effects are to be minimised and viable weed seed numbers reduced. However, this spraying practice is very wasteful of the available active since target numbers, sizes and levels of concealment project such a small impact surface for drop impaction in proportion to that area actually sprayed. Losses within the treatment zone to intercepting surfaces such as a crop and to the ground may readily dominate over all other losses within the complete delivery process. Certainly, justifiable effort is directed to those situations which may tolerate on/off or variable dose applications to clustered weeds, diseases or pests but – even with these systems – once the application is committed then the transfer efficiency of the product to the target surface only – may be poor.

Table 2. Theoretical dose applied to horizontally projected leaf surfaces of a plant from a 1Kg/ha application

Target plant populations; m^2	1	10	100
Surface area projected; cm^2	1	2	3
Exposed dose; µg	10	200	3000
Product "loss"	99.9	99.8	97.0

Further evidence from topical applications of glyphosate to *Lanium purpureum* and *Sinapis arvensis* that has established their LD50 threshold dose can, with knowledge of a known population, say, 200 plants/square metre suggest, a dose of 1.4 and 3.2 g/ha would be adequate for control (Table 3, Kapple *pers com,* 2001). It could be argued that this dose is generous for topical applications of actives in large (relative to that which is normally retained) volumes of non-dispersed liquids are not normally the optimal form for activity and may not be applied to the most active site either; two factors that may suggest even lower doses are theoretically possible. Nonetheless, the spray machinery manufacturer has - and continues - to do much to improve delivery systems but a protocol that quantifies the impact of their design or use on how performance should be measured, would be welcomed - despite difficulties.

Table 3. Calculated LD50 values for *Lanium purpureum* and *Sinapis arvensis* to topically applied glyphosate

	Lanium purpureum	*Sinapis arvensis*
LD5	0.7μg / plant	1.6 μg / plant

CHALLENGES FOR SPRAY ACCOUNTING

Reducing losses from the treatment zone through drift and fallout are unlikely to have a measurable positive effect on the doses that are then available to such targets. Sprayed drops need to impact on the target surface, be retained and if retained, be in its most active form and most effective location. For example, *Gramminacae* herbicides are usually more active when they are deposited or become located in areas close to the meristematic zone rather than at more distal points of the leaf. In addition, retention of sprayed drops by these species are usually enhanced when applied as small drops that have low momentum and having a more pronounced lateral movement.

The level of uniformity of sprays distributed over all target surfaces within the treatment zone will further influence the maximum dose that may need to be applied to ensure adequate effects. Thus, if the delivered dose of glyphosate to *Lanium* varies ten fold from the lowest retained to the highest then the lowest dose may be inadequate to ensure the required effect and will have to be raised at the point of sprayer emission to mitigate that deficiency.

Retained doses will also be influenced by intercepting surfaces such as crop canopies that will reduce availability of product and increase variability. Spray patterns may be also be distorted through effects such as wind or boom movements. Biologically interpreting values just based on variability and/or mean retained doses, may not be as helpful as that which expresses frequencies a defined threshold dose is exceeded.

Spray accounting is not an easy challenge for Standardisation. As target structure decreases in size and drop spacing (Figure 2) becomes more discrete so further variations, in dose to which a plant may be exposed, still further confuse the complexity of this need to understand and define efficient, reliable application techniques.

In contradiction, to this apparently poor effectiveness of delivering spray solutions to target surfaces, sometimes losses may be minimal and some application techniques could be very effective and non-wasteful. Applications to exposed bare soil and those used to treat foliar targets presenting a complex, mature canopy that covers the treatment zone, may be very effectively transferred with minimal losses that can be attributed to the application process itself. Cereal 'ear' spraying may present a further opportunity for such an efficient spraying process.

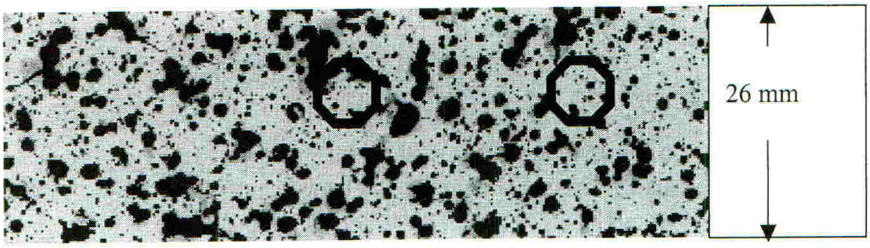

Figure 2: Targets [the areas shown are < 2 cm square] can be exposed to contrasting doses when air induction nozzles apply very coarse sprays at 150 l/ha

Directly applying pesticide solutions by contact to plant surfaces such as weeds – sometime exploiting height differences with a crop – may, in part, solve this dilemma. Advantages of transfer by contact are still further enhanced for spray losses beyond the treatment zone and within it are minimal too; but some important agronomic issues are very restrictive. For example, controlling weeds at these advanced growth stages demand higher doses, may not ensure that viable seeds are not returned to the soil and may be timed too late to avoid crop competition. Commercial uptake and use remains unattractive.

Some spraying methods can deposit more than that dose which has been predicted from simple area-based calculations. Lettuce may be grown as discreet raised structures within beds whose width matches that of the sprayer's boom (Figure 3). A Fine/Medium spray quality when conventionally applied assumes much lateral movement through wind or in the turbulent wake of the passing machine to reduce losses to the ground and enhance that on the raised structures (Table 4). This induced movement reduces soil contact and enhances that deposited on the outer leaves. Commercially, these characteristics are often too random to be effectively used and, for some products, the required optimal site may be, for example, aphid concealed within the young developing crowns.

Figure 3. Lettuce plants that are conventionally treated with a Fine quality spray may retain deposits greater than that predicted from their projected ones. Commercially, such characteristics are often too random to be effectively used where, for some actives, the required optimal site may be, for example, aphid concealed within the young, inner, developing crowns.

Table 4. Sprays with pronounced lateral movements may deposit more active product than that predicted from their projected areas; % increase beyond projected prediction

Projected area (cm^2)	Spray retained;	-µl/ 100l/ha applied	-% increase
314		488	55

CONCLUSIONS

Many difficulties can be recognised when writing protocols and developing databases for spray accounting. In particular, dealing with all the uncontrolled sources of variability that are associated with biological targets and introducing other factors such as weather that modifies an already quite complex system, are sound reasons to avoid this activity. In contrast, it is relatively easy and inexpensive to just choose components of the sprayer which involve equipment performance that allow direct physical measurements to be made, doing so with excellent reproducibility. But to ignore the spray accounting challenge, will invoke risks to the advancement of application technology and may even offset one core benefit against another.

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