POSTER SESSION 5C
SPRAY APPLICATION TECHNIQUES

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Evaluating the potential of a weed wiper for *Molinia caerulea* (L.) Moench control in upland moorland

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ABSTRACT

British heather moorlands are ecosystems of great ecological importance and are an important source of income in rural areas. Despite protection under British and European legislation these habitats remain under threat. One newly perceived threat is an increase in *Molinia caerulea* to the detriment of *Calluna vulgaris* and other dwarf shrubs. Only glyphosate is currently cleared for the treatment of *Molinia* in upland moorlands yet previous research has shown that glyphosate can damage remnant moorland species in the sward. This study assessed the potential of a weed wiper to apply glyphosate selectively to *Molinia* whilst leaving other species unharmed. Our results suggest that greater herbicide concentrations would be needed to obtain control similar to those achieved by conventional spraying. The implications for moorland management are discussed.

INTRODUCTION

British upland moorlands are important cultural landscapes and have a high biodiversity interest. In spite of this the quality of existing moorlands are under threat. One perceived threat is an increase in *Molinia caerulea* (L.) Moench, a tough, perennial grass, at the expense of *Calluna vulgaris* (L.) Hull (Welch, 1986). In order to restore *Calluna*-dominated communities, there will have to be substantial reductions in current *Molinia* levels on many sites.

One solution to this problem would be to develop an herbicide-based strategy as these are relatively cheap and most land managers are equipped for such operations. At present, only the non-selective, glyphosate is cleared for *Molinia* control on moorlands, but this herbicide affects non-target species and its use may damage the conservation value of the moorland (Milligan, *et al*., 1999). This paper describes our efforts to develop more selective methods of applying glyphosate onto *Molinia*.

Weed wipers have been in development since the 1980's with a range of designs, usually using herbicide-laden wicks, rollers or cloths. They apply herbicides to the vegetation directly by topical application, and selectivity is achieved by application height. Tall plants are affected and low-growing, non-target species untreated and so unharmed. Other benefits include low application volumes (Hollowell, 1983); reduced water requirements for dilution, minimal spray drift and reduced operator exposure (Lane, 1984a,b).

Previous research has compared weed wipers with more conventional application techniques (Boerboom & Wyse 1988) but they have yet to be tested in moorland situations for *Molinia* control. Information is needed on their effectiveness both on ‘white’ moorland (*Molinia* dominant) and on ‘grey’ moorland (*Molinia* in mixture with dwarf shrub heath species). In order to assess the suitability of a weed wiper for use in *Molini*a control, we compared (1) the deposition patterns of a conventional spray boom and a weed wiper using an artificial tracer, and (2) the efficacy of glyphosate application using these two application techniques under both laboratory and field conditions.

MATERIALS AND METHODS

Herbicide depositions patterns from both a weed wiper and spray applications were made on both ‘white’ and ‘grey’ moorland at Tinkers Hill, Barnsley (SK 169034) in July 1995. Tartrazine, an artificial tracer, was used instead of glyphosate’s active ingredient. Tartrazine was applied (2 g litre^{-1}) in an aqueous solution containing glyphosate’s surfactant (ethoxylated tallowamine) at 15% w/w. Three herbicide treatments were compared to untreated controls: (a) single pass of weed wiper; (b) double pass of weed wiper and (c) spraying with conventional boom. The double wipe treatment aimed to test whether a reversal of the wiper roller over vegetation already treated could increase deposition whilst retaining selectivity. A randomised block split-plot design with three blocks each containing four main plots (5 m x 10 m) was used with the application method as the main treatment and the height layers as the sub treatment.

Wiping was carried out using a ‘Rotowiper’ (Cobhasa Limited) with a Flojet 2100 self priming pump, pulled behind an ATV. The wiper was set *ca.* 25 cm above ground level on ‘white’ sites and 20 cm above ground level at ‘grey’ sites. Application volumes were estimated in test runs over ‘white’ moorland to be *ca.* 87 litres ha^{-1}. Spraying was carried out with a knapsack sprayer with an application volume of 170 litres ha^{-1}.

One hour after application, when the applied mixture was dry, 10 ten 0.25 m^2 quadrats were selected randomly in each plot. Plant material was cut at 10 cm height depth intervals within the sward (0-10 cm, 10-20 cm, 20-30 cm and +30 cm). Each sample was placed into plastic bags and refrigerated unlit until analysis (< 2 days later). Afterwards, the vegetation samples were sorted: (1) Graminoids (*Molinia*, *Deschampsia flexuosa, Eriophorum vaginatum*) and (2) Ericoids (*Calluna*, *Erica tetralix*, *Empetrum nigrum*, *Vaccinium myrtillus*, *V. oxycoccus*). Each vegetation fraction was placed in a polythene bag with 15 ml of de-ionised water and the bags shaken to re-dissolve the deposited tracer. Test samples, where treated plant material was washed sequentially, showed one washing re-dissolved 99% of the tartrazine present. The absorbance of the tartrazine samples was measured at 426 nm, and deposition was calculated as concentration of tartrazine per unit dry weight of vegetation (mg g^{-1}).

Performance of weed wiper under laboratory and field conditions

In June 1996, *Molinia* tussocks were collected from Tinkers Hill and the constituent basal internodes individually planted into nutrient rich, acid compost. Two non-destructive measures were made pre-treatment (fresh weight (g); tiller number) to account for differences between individuals. Solutions of glyphosate (Roundup-Biactive, Monsanto PLC) were prepared immediately before use and applied at the following rates: 0, 0.03, 0.07, 1.44, 2.88 and 5.76 kg ai ha^{-1} to cover the manufacturer’s recommended range (0.72-2.16 kg ai ha^{-1}). Fifteen individual plants were tested per treatment. Plants were sprayed using a Mardrive

Precision Sprayer set at 2.0 bar pressure to spray 200 litres ha^{-1}. Alternatively herbicide was applied using a sheepskin paint roller to mimic the action of the weed wiper. After 8 weeks the final number of tillers, final fresh weight and dry weight of *Molinia* shoots and roots and were determined.

In July 1996 glyphosate (Roundup Biactive) was applied to an area of 'white' moorland at Ramsgill Bents, North Yorkshire (National grid reference SE 408470) using both the Rotowiper (as detailed previously) and a knapsack sprayer at application rates equivalent to 0.54 and 1.08 kg ai ha^{-1} (termed low and high respectively). A fully-factorial randomised block, model was used with two 5 m x 10 m blocks separated by a 3 m wide buffer zone to allow for manoeuvring of the machinery. Species cover was assessed in four 1 m x 1 m sub-quadrats in each plot after treatment in August 1996 and one year later in August 1997.

All datasets were normalised using where appropriate and analysed using PROC ANOVA (SAS 1985). Tukey's HSD's (T) were used to separate significantly different means.

RESULTS

Evaluation of weed wiper deposition using artificial tracers

At the 'white' site, where only graminoid samples were collected, there were no significant differences in the amounts of tartrazine deposited by the three herbicide application techniques ($P = 0.58$). However, there were significant differences between the amounts deposited throughout the vegetation sward (Figure 1a; $P<0.05$; T=0.50) as all application techniques deposited greater amounts of tartrazine in the uppermost layers (20-30 cm and +30 cm) compared to the lowest layer (0-10 cm). In contrast, at the 'grey' sites spraying and wiping twice applied significantly more tartrazine onto the graminoid fraction than a single wipe (Figure 1b, $P<0.05$, T=0.15). Spraying deposited more tartrazine in the upper most layers whilst wiping deposited greatest amounts in the 10-20 cm layer ($P < 0.01$, T = 0.01). Very little ericoid material was collected in the two uppermost levels at the 'grey' site, thus these data were removed from the analysis. Much less tartrazine was recovered from the ericoid fraction collected at the 'grey' sites than levels recorded from graminoids from both the 'white' and 'grey' sites. Similar amounts of tartrazine were deposited amongst the remaining plant layers (0-10 cm and 10-20 cm levels, $P=0.07$). However, significantly more tartrazine ($P < 0.01$, T = 0.02) was deposited onto the ericaceous species by spraying than either of the two wiping treatments (Figure 1c).

Efficiency of the weed wiper under controlled conditions

Spraying glyphosate onto *Molinia* plants significantly reduced the dry weight of roots and shoots and fresh weights more than wiping (Table 1). However, there were no main treatment differences between the two application techniques on tiller number, but was a significant interaction between the treatments and doses used - as the glyphosate concentration increases the reduction in control produced by wiping declines (Figure 2). The standard errors on these data were large, indicating the highly variable response of *Molinia* to glyphosate.

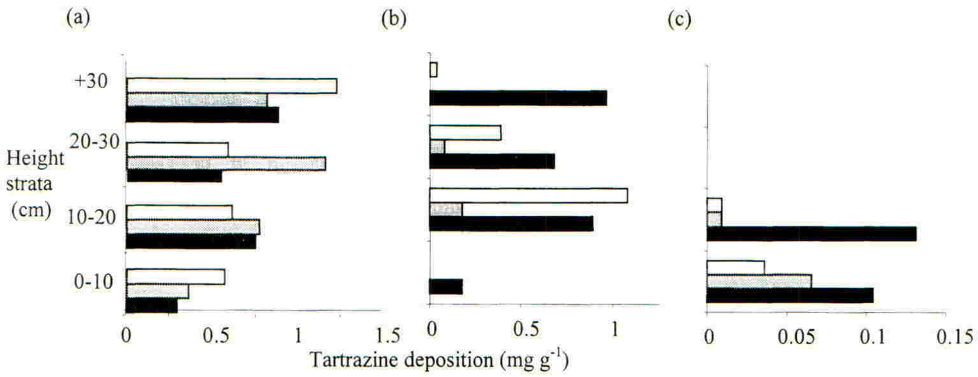

Figure 1. Tartrazine deposited (mgg^{-1}) by spraying (clear), and by single wipe (grey) and double wipe (black) application from a weed wiper in (a) graminoids on'white' moorland, (T=0.50), (b) graminoids on 'grey' moorland (T=0.35), and (c) ericoids on 'grey' moorland (T=0.03).

Significant differences ($P < 0.01$) were found with respect to dose (all parameters), application treatment (all parameters except Final–Initial tiller number), and dose x treatment interaction (Final–Initial tiller number only).

Table 1. Relative efficacy of spraying and weed wiper herbicide application techniques as indicated by differences in various parameters of *Molinia* growth. S=sprayed, W=wiped; mean values ± SE (n = 15) are presented

Plant parameter		Dose					
		0	0.30	0.07	1.44	2.88	5.76
Shoot dry wt	S	0.44±0.04	0.15±0.03	0.17±0.01	0.15±0.03	0.14±0.02	0.17±0.02
(g)	W	0.50±0.05	0.30±0.03	0.39±0.07	0.30±0.04	0.23±0.02	0.23±0.03
Root dry wt	S	0.26±0.03	0.16±0.03	0.19±0.02	0.17±0.02	0.13±0.02	0.11±0.01
(g)	W	0.29±0.04	0.28±0.03	0.30±0.03	0.29±0.03	0.19±0.02	0.22±0.03
Final –	S	1.45±0.21	0.140.05	0.23±0.08	0.27±0.14	0.19±0.14	0.10±0.03
initial fresh wt (g)	W	1.32±0.04	0.93±0.03	0.92±0.17	0.53±0.11	0.36±0.06	0.29±0.09
Final –	S	1.87±0.50	0.67±0.67	0.13±0.09	0	0.13±0.13	0.07±0.07
initial tiller number	W	1.73±0.31	1.06±0.55	1.34±0.48	0.34±0.16	0.07±0.07	0.27±0.15

Efficacy of weed wiper in field conditions

Four weeks after treatment in 1996 the percentage of live *Molinia* cover was assessed in wiped and control plots. No significant differences were found between the wiped plots and the untreated plots (mean percentage *Molinia* cover for control plots (±SE) = 73.22±2.75, glyphosate wiped plots at high dose = 54.50±1.30, low dose = 60.50±2.30, P=0.18) and no significant difference was found between the high and low doses used (P=0.28). On return in 1997, no significant differences were recorded (mean live cover on control plots 58.21±1.12, plots treated with low doses of glyphosate = 52.51±1.63, high doses = 53.65±2.96). The second most abundant species at these sites was *Deschampsia flexuosa*. Cover of this species also remained unaffected by the weed wiper herbicide application treatments during both years (P=0.54 for 1996 and P=0.92 for 1997).

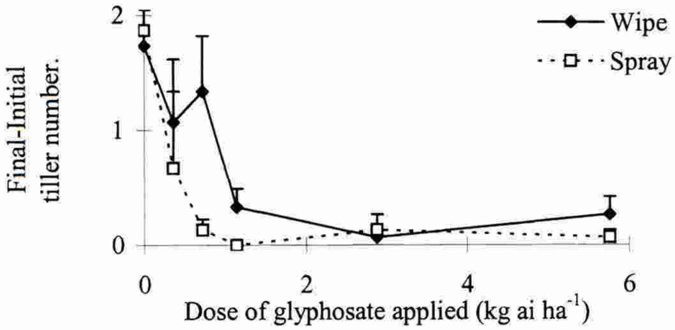

Figure 2. Effect of increasing dose of glyphosate applied by spraying or weed wiping on the difference in tiller number in *Molinia*. Mean numbers (±SE, n=15) are presented.

DISCUSSION

As little was known about weed wiper use on upland moors we first assessed the herbicide deposition patterns of the weed wiper on 'white' and 'grey' moorland. To do this safely we used an artificial tracer in the first instance, with obvious limitations: (1) tartrazine may not mimic the action of the herbicide active ingredient, (2) the results may not hold in field situations as herbicide activity is influenced by many external influences, e.g. drought (Boydston, 1992), temperature (McMullan, 1996) and soil type. Thus conclusions gained from this trial must be tentative. Moreover, estimation of the volume applied by weed wipers is notoriously difficult (Lane, 1984a), as this depends on application speed, terrain and the vegetation. Here, the weed wiper application volume was calculated at 87 litres ha^{-1}, half that of the sprayer (170 litres ha^{-1}), illustrating the potential for reducing volumes and costs.

Our results show there was no benefit in using a weed wiper on 'white' sites, which is effectively mono-dominant *Molinia*. A double wipe of the tartrazine mixture did not lead to increased depositions. This may be due to the ATV and wiper crushing the vegetation in the first pass so that there was poor contact with the *Molinia* in the reverse pass. At the 'grey' site, the spray and double wipe treatments applied significantly more tartrazine than the single wipe treatment. The double wipe placed up to 5 times more tartrazine on to the graminoids than a single wipe. This suggests that where *Molinia* and other grasses are present in relatively low densities with *Calluna* the action of the weed wiper and ATV does not flatten the vegetation to the extent seen in the 'white' site, and increases the deposition. A double wipe at 'grey' sites may be beneficial as it appears to increase deposition but does not reduce selectivity.

All treatments exhibited similar deposition patterns on the graminoids - in general the maximum deposition occurred in the 10-20 cm zone. As there was a clear height difference between the graminoids and the ericoids at the 'grey' site, the two wiper treatments successfully deposited significantly less herbicide onto the ericoid species than the spray boom. The vegetation at the 'grey' site often has much more open nature and this may have allowed spray droplets to penetrate to the lower levels, increasing deposition onto the ericoids. The laboratory studies indicated at least 20% less damage occurred after wiping than spraying. As the concentration of herbicide applied increased the difference between the two application techniques decreased. It is possible therefore, that increasing the herbicide concentration applied by weed wiper would produce better control in the field.

Using these results we devised field trials for the weed wiper using glyphosate on field populations of *Molinia*. However, we found even high doses of glyphosate applied with the weed wiper did not affect the cover of live *Molinia* adversely. Higher doses may have been more effective but with increased costs and increased risks to potential users. Previous work has shown that increasing doses of herbicide can affect the amounts of translocation and therefore do not necessarily lead to increased control levels (Boerboom & Wyse, 1988). Poor translocation of herbicides within *Molinia* could make control measures inadequate or temporary. Weed wiper design and technology is rapidly developing so it is possible that a wiper, meeting the specific requirements of the moorland terrain will be developed to facilitate greater deposition rates. The addition of more effective surfactants may also help.

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Effect of adjuvants on fruit and leaf calcium concentrations in Golden Delicious apple following calcium nitrate applications for the control of bitter pit

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ABSTRACT

In a field trial, A nonylphenol ethoxylate (0.006% v/v) and four alternative liquid-formulation adjuvants, plus an adjuvant-free control treatment, were evaluated in terms of their respective abilities to promote calcium (Ca) uptake by the leaves and fruit of 'Golden Delicious' apple. Leaf and fruit sampling was carried out after the application of 6, 9 and 12 sprays, each containing granular calcium nitrate at 0.45% m/v, and an adjuvant. No bitter pit was found after 12 sprays (at harvest), or after cold storage. A non-ionic organo-modified siloxane (0.025% v/v), and an alkyl poly glycoside surfactant AG6210 (0.05% v/v), were associated with significantly ($P = 0.05$) increased fruit Ca concentrations, relative to the control, after nine sprays. None of the adjuvant treatments affected fruit Ca concentrations after 12 sprays. Increased leaf Ca concentrations, also relative to the control, were observed after 9 sprays where siloxane (0.025% v/v), sugar ester (0.05% v/v), a second alkyl poly glycoside AL2575 (at 0.05% v/v and 0.10% v/v) and AG6210 (0.10% v/v) were added. Only the sugar ester, at 0.05%, increased leaf Ca levels after six sprays. At harvest, the fruit and leaf Ca concentrations in none of the treatments were greater than in the control. At none of the sampling dates did the 0.06% nonylphenol ethoxylate treatment have any effect on fruit or leaf Ca concentrations. No bitter pit was observed.

INTRODUCTION

South African export apple producers are required to apply calcium (Ca) sprays for the control of bitter pit, a Ca deficiency-related physiological disorder of the fruit which is promoted by a variety of orchard environmental factors (Wooldridge, 2000). Although a range of Ca carriers are currently available, calcium nitrate ($Ca(NO_3)_2$) remains in widespread use. Following, and probably preceding trials by Terblanche, *et al.* (1968) it became common practice to add a wetting agent, such as Agral, a nonylphenol ethoxylate, to each $Ca(NO_3)_2$ spray mix. Subsequently, Hanekom & de Villiers (1977) showed that Ca uptake by Golden Delicious fruit from $Ca(NO_3)_2$ sprays was promoted by 0.006% Agral-90, in contrast to seven other simultaneously-tested adjuvants that significantly inhibited uptake.

Recently, concerns have arisen concerning possible hormonal side effects associated with the use of nonylphenol ethoxylates (Stock, 1997). These concerns led to a resurgence of interest in the use of adjuvants with Ca carriers, and have prompted a search for safe, environmentally-friendly alternatives. The trial reported in this article was carried out to evaluate four adjuvants, plus a nonylphenol ethoxylate, in terms of their effectiveness in facilitating the entry of spray-applied Ca into apple fruit and leaves from $Ca(NO_3)_2$ sprays.

MATERIALS AND METHODS

Treatments

Mature apple trees of the cultivar 'Golden Delicious' were sprayed with commercial granular $Ca(NO_3)_2$, (Nutrifert, Omnia Specialities, Gauteng, South Africa), containing 155 g N and 19.0 g Ca / kg) at the rate of 0.45% m/v, once every week for 12 weeks, commencing in mid November 2002, about four weeks after full bloom. The control treatment consisted of $Ca(NO_3)_2$ sprays applied without adjuvant. A conventional treatment (0.45% m/v $Ca(NO_3)_2$, tank mixed with nonylphenol ethoxylate at 0.006%, was also applied. The remaining treatments consisted of 0.45% $Ca(NO_3)_2$ mixed with: a non-ionic organo-modified siloxane (Break-Thru S 240 Degussa Goldschmidt:, at 0.025% v/v and 0.010% v/v; a sugar ester wetter (SEW, Plaaskem (Pty) Ltd, Houghton, South Africa), at 0.05% v/v and 0.10% v/v; two bio-degradable, non-ionic alkyl poly glycoside surfactants with good wetting properties, AL2575 (Uniqema), at 0.05% v/v and 1.10% v/v; and AG 6210 (AKZO Nobel), also at 0.05% v/v and 1.10% v/v. The spray treatments were applied, using a motorised knapsack blower, until run-off was observed from the leaves and fruit.

Location and design

The trial was carried out in an orchard of mature uniformly-performing trees at Elgin Experiment Farm (S34°08', E019°02') in the Elgin fruit-producing area of the Western Cape, South Africa. A fully randomised block design was used in which each treatment was applied to a single 3-tree plot in each of three blocks. Treatments were well separated to prevent contamination through spray drift. In all respects except the Ca sprays the orchard was managed in accordance with standard industry practice.

Sampling

Samples of leaves and fruit were obtained on 13 November 2002, before the first spray treatment was applied, and on 03 and 21 January 2003, one week after the 6^{th} and 9^{th} sprays, respectively. Sampling of both leaves and fruit was also carried out at harvest, on 13 February 2003, when a total of 90 fruit were removed from similar tree positions in each 3-tree plot. Each such sample was divided by random selection into two 45-fruit sub samples. The fruit from one of each pair of sub samples were inspected to determine whether bitter pit was present or absent, then subjected to routine analysis. The remaining sub samples were stored for 28-days at -0.5°C then examined for bitter pit. Each leaf and fruit sample was subjected to routine analysis to determine tissue Ca concentration using a Varian inductively-coupled plasma-emission spectroscope.

Statistical analysis

Results were subjected to an analysis of variance using SAS (SAS, 1999). Student's-t least significant difference values were calculated at the 5% probability level to facilitate differences between treatment means. Values which differed at P = 0.05 were considered to be significant.

RESULTS

Bitter pit

No bitter pit was observed, either at harvest, after 28-days storage at -0.5°C, or after a further period of ripening in the presence of ethylene.

Fruit Ca concentration

Effect of sampling date

Averaged across all adjuvant treatments, Ca concentrations decreased sharply, by 64.9%, between 13 November and 03 January, then decreased gradually until harvest, at which point fruit Ca concentration had decreased by 75.7% relative to the 13 November value (Table 1).

Table 1. Effect of sampling date on calcium (Ca) concentrations in the fruit (mg 100 g fresh mass and % of value on 13 Nov. 2002), and leaves (% of dry mass, and % of value on 13 Nov.) of Golden Delicious apple. Values for each sampling date are averages for 10 calcium nitrate / adjuvant spray treatments.

Parameter	Sampling date and number of Ca sprays			
	13 Nov. 2002 0 sprays	03 Jan. 2003 6 sprays	21 Jan. 2003 9 sprays	13 Feb. 2003 (Harvest)12 sprays
	Fruit calcium concentration (fresh mass)			
mg/100g	19.7a	6.92b	5.81c	4.78d
% of 13 Nov.	100.0	35.1	29.5	24.3
	Leaf calcium concentration (dry mass)			
% of dry mass	0.69c	1.21b	1.16b	1.58a
% of 13 Nov.	100.0	175.4	168.1	229.0

Values in the same row, which are followed by the same letter, do not differ at $P = 0.05$.

Effect of adjuvant

After six sprays, and at harvest, none of the adjuvant treatments significantly affected fruit Ca levels, relative to the control (Table 2). However, siloxane (at 0.025%) and AG6210 (at 0.05%) were associated with relatively increased fruit Ca levels on 21 January, after nine sprays. The nonylphenol ethoxylate did not affect fruit Ca concentration after 9 sprays.

Leaf Ca concentration

Effect of sampling date

Leaf Ca concentrations showed a general increase as the season progressed, in the sampling date sequence: 13 November < January (both sampling dates) < 13 February.

Table 2. Effect of adjuvants on the calcium concentrations in the fruit (mg 100 g fresh mass) and leaves (% of dry mass) of calcium nitrate sprayed Golden Delicious apple on 13 November, 03 January, 21 January and 13 February (harvest).

Adjuvant and concentration (% v/v)	Fruit calcium (mg 100 g fresh mass)			Leaf calcium (% dry mass)		
	03 Jan. 6 sprays	21 Jan. 9 sprays	13 Feb. 12 sprays	03 Jan. 6 sprays	21 Jan. 9 sprays	13 Feb. 12 sprays
Control 0.00%	6.76 ab	5.06 c	4.4 a	1.15 b	0.95 b	1.52 ab
Nonylphenol ethoxylate 0.06%	6.4 ab	5.9 abc	4.93 a	1.16 ab	1.11 ab	1.46 b
Siloxane 0.01%	7.96 a	5.86 abc	4.43 a	1.27 ab	1.12 ab	1.47 b
Siloxane 0.025%	7.5 a	6.8 a	5.43 a	1.22 ab	1.19 a	1.61 ab
Sugar ester 0.05%	5.3 b	5.06 c	4.86 a	1.31 a	1.24 a	1.57 ab
Sugar ester 0.10%	7.56 a	5.63 abc	5.0 a	1.20 ab	1.16 ab	1.64 ab
AL2575 0.05%	6.43 ab	5.7 abc	4.73 a	1.16 ab	1.26 a	1.65 ab
AL2575 0.10%	7.86a	6.10a bc	4.23 a	1.23 ab	1.18 a	1.62 ab
AG6210 0.05%	7.26a	6.7ab	4.96 a	1.16 ab	1.15 ab	1.70 a
AG6210 0.10%	6.13a b	5.26b c	4.83 a	1.21 ab	1.27 a	1.60 ab

Values in the same row, which are followed by the same letter, do not differ at P = 0.05.

Effect of adjuvant

Relative to the control, increased leaf Ca concentrations were observed in the 0.05% sugar ester treatment on 13 January. On 21 January five treatments (sugar ester and AL2575 at the low, and siloxane, AL2575 and AG6210 at the higher rates of application) were effective in significantly increasing leaf Ca levels. None of the adjuvants significantly affected leaf Ca levels, relative to the control, at harvest. The nonylphenol ethoxylate had no effect on leaf Ca levels at any sampling date.

DISCUSSION

Leaf Ca concentrations on 03 January were within or above the adequate range of 1.1-2.0% specified by Robinson, *et al* (1997), implying that the Ca nutritional status of the leaves, after six sprays, was normal. No bitter pit was observed, even though the fruit Ca concentrations were below those calculated for freedom from bitter pit in unsprayed and sprayed apple fruit (respectively, >5.4 and > 6.6 mg 100 g fresh mass) by (Terblanche, *et al*., 1980). This was not unexpected given the seasonal variability that is a characteristic of bitter pit, and the wide variety of contributory factors (Wooldridge, 2000).

The observation that few instances occurred where the adjuvant treatments significantly increased fruit Ca concentrations, relative to the control, agrees with the early trial results of Terblanche, *et al.* (1968) who found that the presence or absence of Agral and Triton B1956 had no effect on the effectiveness of Ca sprays, and also accords with the finding that most of the adjuvants tested by Hanekom & de Villiers (1977) were not effective. That nonylphenol ethoxylate at 0.006%, had no significant effect on fruit and leaf Ca concentrations in the present trial suggests that the continued use of this product as a Ca spray adjuvant should be the subject of further critical appraisal. Nevertheless, fruit Ca concentration in the 0.06% nonylphenol ethoxylate treatment did not differ significantly from those in the 0.025% siloxane or the 0.05% AG6210 treatments; yet in both of these latter treatments, the fruit Ca concentration differed significantly (by 34.4% and 32.4, respectively) from the zero-adjuvant control.

The observed decrease in fruit Ca concentration with advancing season was similar to that reported by North & Wooldridge (2003), and was attributed to dilution. If, as postulated by North & Wooldridge (2003), bitter pit incidence is more closely related to pre-harvest Ca treatments and fruit Ca concentrations than to fruit Ca at harvest, then siloxane (at 0.025%) and AG6210 (at 0.05%) may have potential beneficial effects on bitter pit, relative to the control, in seasons when the incidence of bitter pit is high. Nevertheless, the only treatment which significantly increased Ca concentrations in both the fruit and leaves on 21 January was siloxane at 0.025%.

Apple leaf Ca concentrations naturally tend to change as the season progresses (Kotzé, 2001). The extent to which this increase was facilitated by the Ca sprays could not be determined in this trial and, indeed, the observation that the leaf Ca concentrations did not show an upward trend between the 03 January and 21 January sampling dates was at variance with the fact that three Ca sprays were applied during the interim period.

The observation that more treatments significantly affected Ca concentrations in the leaves than in the fruit was attributed to the considerable differences in surface area to volume ratio, and to differences in the composition and anatomy of the epidermal structures and internal tissues between fruit and leaves. None of the treatments suppressed fruit Ca concentrations below the levels observed in the controls.

Although the results of a single trial cannot be considered to be definitive, the outcome of this trial nevertheless implies that adjuvants differ in terms of their ability to facilitate the movement of Ca into Golden Delicious apple fruit and leaves from $Ca(NO_3)_2$ sprays. These differences probably reflect differences in the chemical formulation, and mode of operation, of the products concerned. A consistent tendency for fruit and leaf Ca concentrations to increase, or decrease, with increasing adjuvant concentration was not observed. Siloxane and AG6210, at 0.025% and 0.05%, respectively, would appear to be particularly worthy of further investigation.

ACKNOWLEDGEMENTS

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Assessment of environmental concentrations of pesticide from spray drift

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ABSTRACT

An assessment was made of the validity of the ESCORT 2 approach for estimating the exposure of non-target terrestrial organisms to plant protection products via spray drift. This involved field and wind tunnel measurements, and a review and re-analysis of published data. It is concluded that the proposed approach may significantly underestimate the potential exposure, but that more investigation of the interaction between airborne spray clouds and non-target vegetation is essential.

INTRODUCTION

Assessment of the toxicity of plant protection products to off-field non-target organisms is an important part of product registration. For the off-field aquatic environment this involves a well developed tiered approach. The spray drift data, from which the exposure of aquatic non-target organisms is derived is based on tables developed by BBA (2000). For the off-field terrestrial environment (non-target plants and arthropods) a methodology for risk assessment has been proposed (ESCORT 2, 2000). This defines the proportion of the applied dose that the off-field environment is exposed to, from a single application, as a Drift factor divided by a Vegetation Distribution Factor.

There is, however, a lack of data on which to base both the drift and the vegetation distribution factors. The drift factor is currently based on the same BBA tables as for aquatic organisms, and the vegetation distribution factor fixed at 10. It is likely that drift deposition on three-dimensional structures, such as hedgerows, cannot adequately be assumed from such two-dimensional drift deposition data, since no account can be taken of the structure and density of vegetation and its ability to intercept sprays. Although a method has been proposed for converting two-dimensional spray drift exposure to three-dimensional off-crop plant surface exposure using a "vegetation distribution factor" of 10 (Gonzalez-Valero, 2000), the basic assumptions of this model could be challenged and there has been no validation of this technique.

This paper reports on work undertaken to assess the validity of the ESCORT 2 approach to estimate terrestrial exposure from spray drift from boom sprayers in the UK, based on published data and a limited set of new experimental data.

The ESCORT 2 approach requires assessment of exposure at a distance of 1 m from the edge of the crop. There is no agreement of the distance from the spray boom that this represents, and so clearly the worst case is of 1 m from the centre of the last nozzle. There is insufficient spray drift data in the literature at this distance since most studies begin at around 2 m or greater. There will be difficulties in extrapolating from these data sets to 1 m from the nozzle because this is the steepest part of the curve and may be the most sensitive to application variables. Existing data has been used, but there was also a need to obtain data sets that includes 1 m downwind data, for a limited range of application conditions.

Much spray drift measurement uses collection of spray on horizontal ground collectors, measuring sedimentation rather than airborne spray. While this is relevant to assessment of deposition on water courses, it is likely that the quantities deposited on vertical targets with a range of geometries are different, and that the highest concentrations may not be on the ground.

MATERIALS AND METHODS

A baseline condition was chosen to represent typical spraying speeds and volumes for the UK, but with a boom height of 0.7 m. The experiment was conducted over cut grass (approximately 0.1 m tall), with wind speeds measured at 2 m above the ground using a sonic anemometer. Two experiments were conducted, one with a full 24 m boom and one with the final two downwind nozzles, to assess how to scale up from two nozzles (as in a wind tunnel) to a full boom. Mean wind speeds of 3.9 m/s (full boom) and 4.8 m/s (two nozzles) were recorded.

Three different types of collectors were used: polypropylene collecting lines of 0.5 m length and 1.98 mm diameter, arranged horizontally in a vertical plane from 0.1 m above the ground to 2 m; collecting strips of chromatography paper, 1 m long and 40 mm wide placed on wooden laths; petri dishes with 60 mm diameter filter paper discs placed inside. Measurements were made at three distances 1, 3 and 5 m from the centre of the last nozzle. Four passes were made with the sprayer at a forward speed of 10 kph from the same direction for each measurement, and three replicate measurements were made.

A wind tunnel experiment was set up to simulate the field experiment with a two-nozzle boom. The wind tunnel floor was covered with artificial grass matting – significantly shorter than the cut grass in the field trial. The settings were: wind speed of 4 m/s at boom height; 0.7 m boom height; FF110-04 nozzle at 3.0 bar pressure, 10 kph forward speed. Ground and line collectors were used.

RESULTS AND DISCUSSION

Figure 1 shows the vertical profiles from the full boom experiment. It can be seen that the height of the peak concentration increases with downwind distance. This would be expected, because of the filtering effect of cut grass and the air turbulence. The peak value at 0.2 m above the ground, at almost 25% of the applied rate, is significantly higher than the ESCORT 2 data suggest. However, wind speeds for this trial (mean of 3.9 m/s) were higher than recommended for spray application.

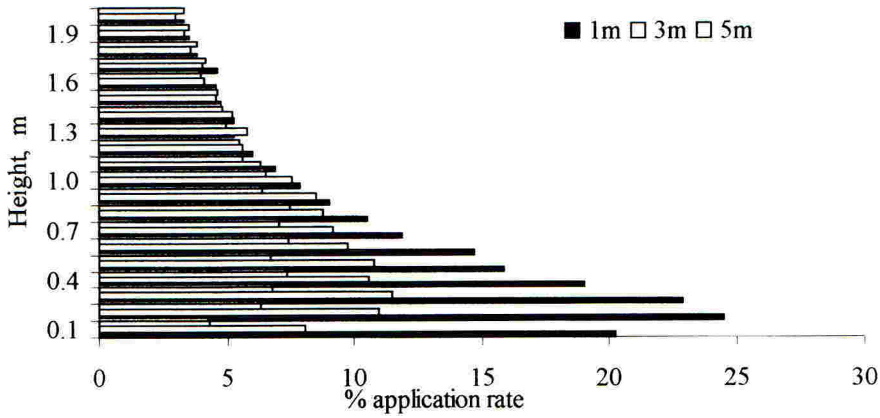

Figure 1. Vertical profiles, full boom – field data.

The data obtained from the two-nozzle experiment were summed over 24 m to allow a comparison between two nozzles and a full boom. Unfortunately, the wind increased slightly between the full boom experiment and the two-nozzle experiment, so the data from the latter were scaled according to previous measurements of the effect of wind speed upon total airborne spray (Rutherford & Miller, 1993). Figure 2 shows that, although at 1 m from the nozzle the estimate is reasonable, further away from the boom the deposit is consistently over-estimated by the summation technique. Scaling from a boom section to a full boom needs to take account of the structure of the spray and interactions between adjacent nozzles, which requires further investigations.

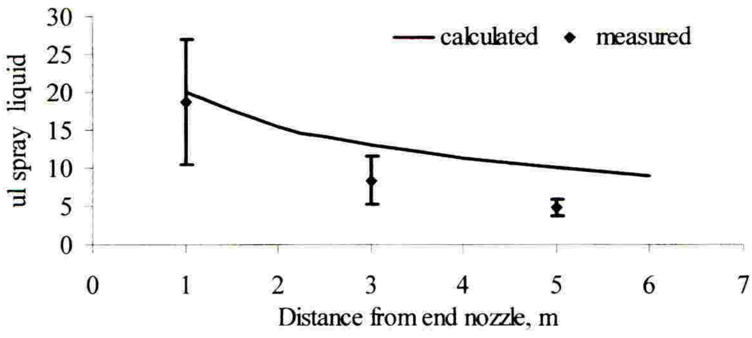

Figure 2. Comparisons between deposits calculated from two-nozzle boom and measured on collecting lines for 24 m boom, at 0.2 m above the ground, with standard deviation error bars.

The decay of deposit with distance for both wind tunnel and field data follows similar trends (Figure 3) suggesting that a simple scaling factor would be a useful way of extrapolating from wind tunnel to field, at least between 1 and 5 m. At one metre from the last nozzle, the wind tunnel produces deposits that are an order of magnitude (around 8 – 10 times) higher than those in the field, when measured on or near the ground. At greater heights, e.g. boom height, The total airborne spray collected (up to 2 m height in the field, and up to 0.7 m in the wind tunnel) were also greater in the wind tunnel, by a factor of 4 at 1 m from the nozzle, and a factor of 2 at 5 m from the nozzle. While the difference between wind tunnel and field measurements outlined above indicates a route for using wind tunnel measurements to estimate field values, there is insufficient information to know whether the factor of 8 – 10 at 1 m from the nozzle can be extrapolated to conditions other than those used here.

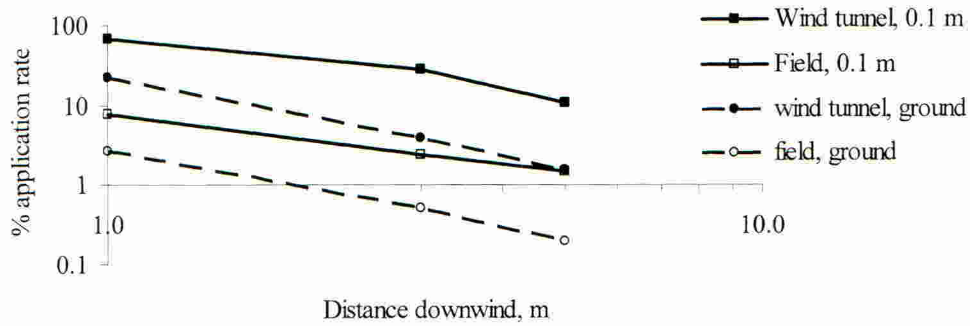

Figure 3. Deposits measured at 1, 3, and 5 m downwind of the nozzle, on the ground and at 0.1 m height, in wind tunnel and field studies under similar application conditions.

Comparison with BBA data and other literature values

The dataset used in ESCORT 2 for field crops is the 90th percentile of ground sediment, and at 1 m is 2.77% of the application rate. Ganzelmeier & Rautmann (2000) added further trials to the database on which the ESCORT 2 tables are based and republished the 95th percentiles which were to be used in the authorisation procedure. This proposes 3.4% drift at 1 m. UK data used to define a field-based drift profile for LERAP low-drift status claims suggests a mean value of around 4% at 1 m (Gilbert, 2000). There are, however, a number of sources that demonstrate drift significantly higher than these values. Van der Zande, *et al.* (2002) shows typical Dutch drift values that are of the order of 10-fold higher than BBA data.

Measurements made at Silsoe Research Institute (Webb, *et al.*, 2002), when re-analysed, showed deposits of around 16% of the application rate on ground-based horizontal targets 1 m from the last nozzle. Miller, *et al.* (2000) evaluated the effect of vegetation in the field margin on drift. Measurements were made on line collectors at heights up to 2 m above the ground, and from 2.25 from the centre of the end nozzle, with different levels of vegetation. Data obtained by Longley and Sotherton (1997a & b) who measured drift in hedgerows on straws under a range of conditions, is taken for windspeeds 3 – 4 m/s at an estimated 1.25 m from the last nozzle. All of these, together with ESCORT 2 data and the field trial were re-calculated to be compatible and plotted in Figure 4.

Clearly, there are discrepancies between different datasets that can be accounted for by the range of application conditions as well as the different measurement techniques. Despite a wide range of conditions, including wind speed, nozzle type and ground conditions, in the data presented in Figure 4, the drift tables used in ESCORT 2 are consistently lower than all other measurements, at least up to 3 m from the nozzle. All ground collectors gave lower values than lines or straws, which would be expected as the latter collect both sedimenting and airborne spray drift. Where data was collected at a range of heights, the peak value is shown.

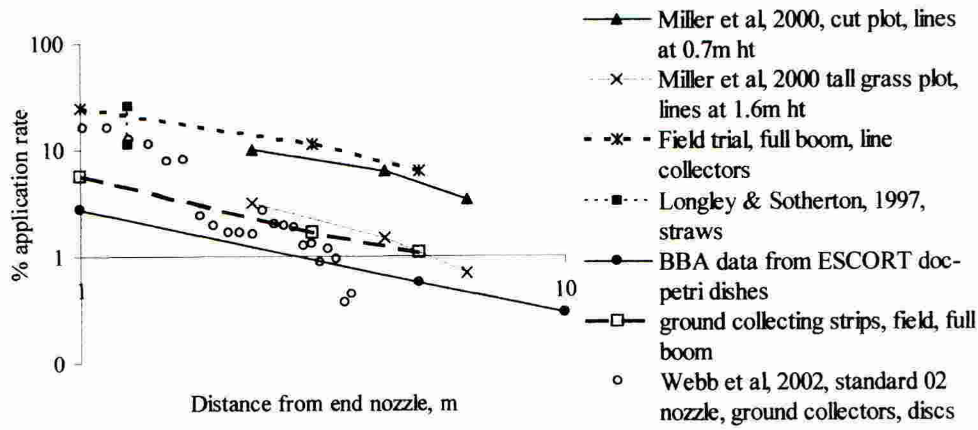

Figure 4. Drift levels, % application rate for field trials from published data.

Many of the above sets of data will have one or more "worst case" conditions – for example, the BBA data is the 95th percentile, was measured over bare ground and included some high wind speeds. However, it also used relatively low drift application techniques when compared with standard UK practice. Our own field trial was over cut grass and at a high wind speed. Webb *et al.* (2002) used low (but not atypical) volumes from smaller output nozzle or increased forward speed, again over cut grass. Miller *et al.* (2000) used probably the most realistic "standard" conditions, with wind speeds between 2 and 3 m/s, 240 litres/ha application volume, a conventional flat fan nozzle, a modest forward speed (8 kph) and some (minimal) field margin vegetation to act as a filter. The data in Figure 4 suggests that the drift dataset proposed in ESCORT 2 may significantly underestimate the potential exposure of non-target species.

The ability of vegetation to filter spray drift was demonstrated by Miller *et al.* (2000). The two examples shown in Figure 4 represent extremes of vegetation, and reduce drift by a factor no more than three. Longley and Sotherton (1997a) showed the height of vegetation influenced the deposition, with an increase in peak deposition with the vegetation in some circumstances. This evidence suggests it is not reasonable to propose a universal "Vegetation Distribution Factor" as proposed in ESCORT 2.

The deposits on non-target plants that would result from drift will depend upon the interaction between the spray cloud, the structure and position within the sward of the plant. Some data on deposits on real plants is becoming available (e.g. Weisser *et al.*, 2002), but significantly more information is needed to be able to make realistic predictions of exposure of non-target species.

CONCLUSIONS

The data used in ESCORT 2 is consistently lower than other data sets, strongly suggesting it is not an appropriate baseline for estimating doses applied to off-crop vegetation. A more robust baseline dataset should be obtained for airborne spray drift, together with data to allow mitigating circumstances to be assessed. The vegetation distribution factor of 10 cannot be justified and the use of such a factor is unlikely to be universally applicable. Where there is significant vegetation that is as tall as the crop, a factor of 3 may be appropriate.

There is a shortage of data relating to how an airborne spray cloud interacts with vegetation in order to quantify both the filter effect and the deposit. Further work must be undertaken to enable a robust prediction of the exposure to individual indicator species.

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Comparison of operator exposure for five different greenhouse spraying applications

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ABSTRACT

The European Crop Protection Association (ECPA) and CLO-DVL joined forces in a project to stimulate a safe use of pesticides in Southern European countries. A quantitative method to evaluate spray deposits, using mineral chelates, is used to compare operator exposure from several spraying techniques. The operator exposure measurements were of a comparative nature. Five application methods were investigated, i.e. a standard spray gun with an operator walking forwards, a spray lance with an operator walking forwards and backwards, a trolley and a vehicle both with vertical spray booms. The exposure was measured at 15 different places of the body on a coverall with patches and on gloves. Walking backwards reduced the exposure by a factor of 7. The exposures on the collectors with the trolley and the vehicle, were factors of 25 and 100 lower respectively than with the standard spray gun. Besides a very large difference in exposure between the five techniques, there was also a large difference in exposure between the various parts of the body. This data is important in consideration of operator safety and for the parts of the body that need to be protected most.

INTRODUCTION

The general objective of the 'ECPA Safe Use Initiative' is to stimulate a safe use of pesticides in Southern European countries through the introduction of novel, innovative spraying equipment and techniques and by teaching users how to handle, clean and maintain their equipment. This subproject deals with novel and traditional spray equipment for the application of crop protection products in greenhouses in Southern Europe. The objective was to compare the operator exposure for five different application methods. Mineral chelates were used as tracers for quantitative operator exposure measurements under field conditions.

MATERIALS AND METHODS

The spraying equipment

Five different application methods were investigated (Figure 1). The standard short spray gun is the most common spray equipment in Southern Europe and was used as a reference. A second traditional equipment is the spray lance. Experiments with this spray lance were done walking forwards and backwards. Besides the traditional techniques, two kinds of novel spraying equipment with vertical spray booms were investigated: a manually pulled trolley and a self propelled vehicle, the Fumimatic. As recommended in the report 'Optimisation of a vertical spray boom' (Nuyttens, *et al.*, 2003), the nozzle spacing of the twelve flat fan Teejet nozzles (spray angle: 80°) on the vertical booms was 35 cm.

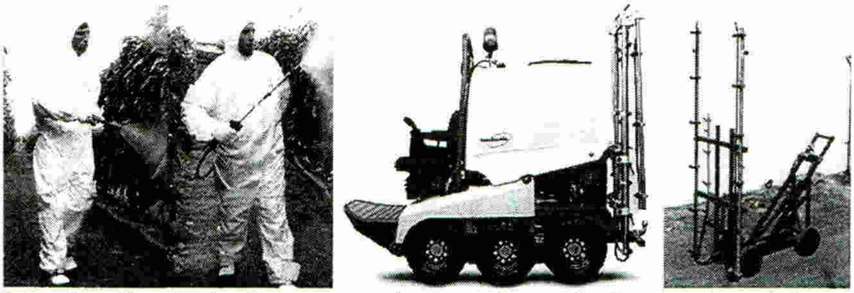

Figure 1. The standard spray gun, the spray lance, the Fumimatic and the manually pulled trolley.

Chelates method with patches on the operator

Mineral chelates were used as tracers on collectors to evaluate spray deposits quantitatively in order to measure operator exposure. Manganese, cobalt, molybdenum, zinc and boron chelates were used. These products are normally used as horticultural leaf fertilisers, hence their use in normal concentrations does not damage the crop and is no risk to the operator. For each application method, another chelate was used. The concentration of each mineral in the tank mixture was about 1500 mg/l. Before each spraying, a tank sample was taken to know the exact concentration and to adjust the exposure results. Inductively Coupled Plasma analysis was used throughout to determine the amount of tracers on the collectors after extraction with 14N nitric acid (HNO_3). Earlier experiments proved that there is no interference between these minerals which is important for the ICP analysis (De Moor, 2002).

A total of 13 patches (head, back, breast, upper arms, under arms, upper legs, lower legs and feet), each measuring 10 x 10 cm², were attached to each operator's Tyvek coverall. Each patch was composed of different layers, i.e. one layer of strong paper, one layer of plastic foil, two layers of Schleicher & Schuell filter paper and one thin layer of gauze (Vercruysse, 2000). These patches were made at CLO-DVL. The plastic foil had to avoid the penetration of spray liquid through the patches to the coverall. Each operator was also wearing a pair of cotton gloves and a pair of latex gloves under the cotton gloves to avoid penetration to the skin.

The exposure of the different patches was determined by measuring the amount of chelates on a surface of 10 x 10 cm². Because of the larger surface of the gloves, the amount of chelates on the gloves was corrected by multiplying the latter with a correction factor of 0.244 because the average surface of one hand is about 410 cm² (Chester, 1995).

Experimental set up

The operator exposure experiments were performed under field conditions in two pepper greenhouses, a very popular crop in the South of Spain. The number of running metres of plants for each greenhouse was about 5000 metres/ha. The driving and walking speeds for the different techniques (Fumimatic: ± 2 m/s, trolley: ± 1 m/s, spray gun and spray lance: ± 0.6 m/s) were measured to determine which nozzle type and which pressure had to be used to spray about 1000 litres/ha. Five different techniques were tested, each by four different operators. This makes a total of 20 sprayings. For each spraying, a distance of 130 metres of crop was treated. Because of the specific problems associated with operator exposure studies, it was important to have a good placement of the operators and the techniques in both greenhouses and a good timing of the different sprayings. The timing and the locations of the measurements were organised in such a way that the different sprayings did not interfere with each other. Because another chelate was used for each application technique, the operators could use the same collectors for the five techniques.

RESULTS

In Figure 2, the total exposure on the 15 collectors for the different techniques is compared with the standard technique, namely the spray gun (set as 100%).

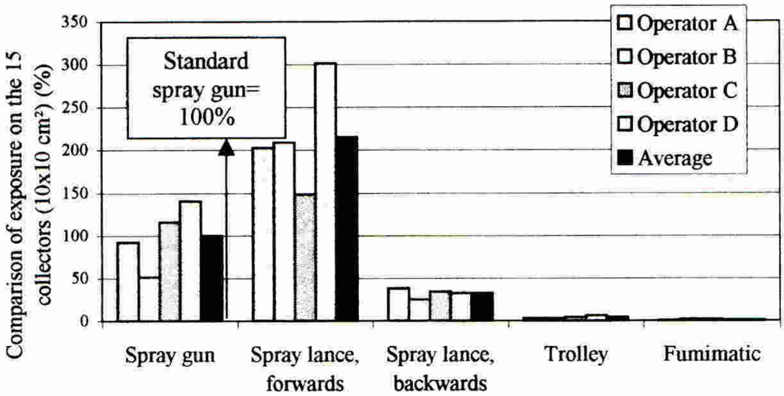

Figure 2. Comparison of the total exposure on the 15 collectors with the standard spray gun set as 100%.

It is clear that the difference in exposure between the different techniques is very high. The repeatability between the operators for the same spraying technique was good, a factor two was the maximum difference. The highest exposure occurred with the spray lance walking forwards. With a comparable technique, the spray gun and walking forwards, the average total exposure was less than half of that with the spray lance walking forward (100% vs. 216%). The most important reasons for this difference are:

(1) The difference in length between the spray gun and the spray lance (40 cm) whereby the spray cloud with the spray lance extends ± 25 cm higher and ± 25 cm lower than with the spray gun (higher exposure at the upper and lower parts of the operator). For example, the exposure on the head was 10 times higher for the spray lance compared to the spray gun (Figure 3).
(2) The ease with which the spray gun is handled compared to the spray lance. In the South of Spain, operators are not used to spraying with a lance.
(3) The spray lance had three nozzles spraying in different directions, forming a bigger spray cloud and resulting in a larger exposure over the entire body.

Walking backwards with the spray lance, the exposure of the collectors was only about 32% compared with the standard spray gun while the exposure with the spray lance walking forwards was about 216%. This means that walking backwards reduces the exposure by a factor of about seven, mainly because the operator doesn't walk into the spray cloud. In addition, it is an easy technique which doesn't require any investments. The exposure on the collectors with the techniques with the vertical spray booms was very low compared with the spray gun, about 4% for the trolley and 1% for the Fumimatic. Compared to the 'worst' technique, i.e. the spray lance and walking forwards, the reduction factors are about 50 and 200. The difference between the Fumimatic and the trolley is mainly caused by the difference in speed (± 2 m/s vs. ± 1 m/s) which halves the exposure time for the trolley compared to the Fumimatic. Besides the total body exposure, it was interesting investigating the exposure on different parts of the body when using different spraying techniques. These results, combined with information about the pesticides used, can be helpful in advising growers what protective clothing they should wear. For the different techniques, the amount of spray liquid found on an area of 10 x 10 cm² when 1000 litres at a dose of 1000 litres/ha are applied is presented based on 4 repetitions (4 operators) in Figures 2, 3 and 4. Each operator was right-handed. For the upper parts of the body (Figure 3), the exposure with the spray lance walking forwards was clearly the highest and the exposure with the Fumimatic the lowest.

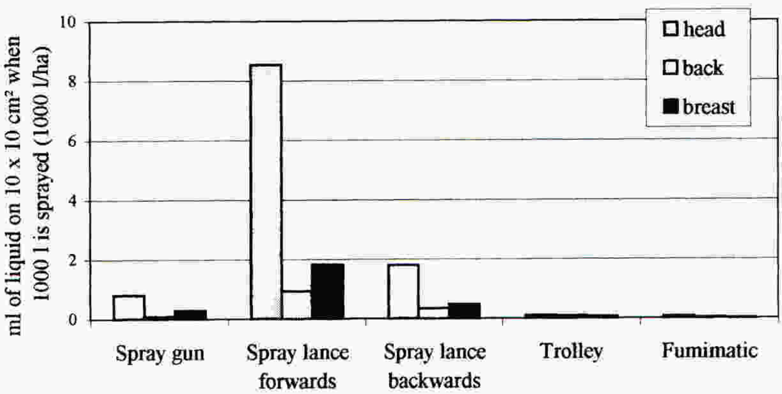

Figure 3. Exposure on head, back and breast on an area of 10 x 10 cm² for the different techniques when 1000 litres at a dose of 1000 litres/ha are applied.

The highest exposure on the hands was measured with the spray lance for the left as well as the right hand (Figure 4). Nevertheless there is a considerable difference between the left and the right hand using the spray lance because of the formation of a big spray cloud close to the right hand. With the spray gun, the exposure of the hands is low compared both with the rest of the arms and with the spray lance and no larger than with the trolley or the Fumimatic. With these innovative techniques, the exposure of the hands is higher than other parts of the arms and the body. The main reason for this is probably that most of the spray deposits on the hands don't come from the spray cloud or the drift but from touching the equipment.

There is also a substantial difference between the left and the right arm with the spray gun. The main reason for this is that the operators sprayed the left side of the row and consequently the spray cloud mainly 'touched' the left side of the body. Because of the short length of the spray gun, it is even possible that some liquid was sprayed directly on the operator. For the left upper arm, the exposure is even higher than with the spray lance. This is the only case where a higher exposure was found than with the spray lance. For the right arm, the exposure is much lower than with the spray lance and walking forwards, again an indication of a small spray cloud and only a little drift. The exposure on the right side of the entire body with the spray gun is about a factor of four smaller than on the left side of the body. With the spray lance and walking backwards, the exposure of the arms is significantly reduced compared with the spray gun. Using the trolley strongly reduces the exposure of the arms but some spray liquid is still found because the arms of the operator are relatively close to the spray cloud and there is no real separation between the spray cloud and the operator. With the Fumimatic, the exposure of the arms is almost nil because the spray cloud and the operator are separated by the tank and the arms are situated in front of the operator while driving.

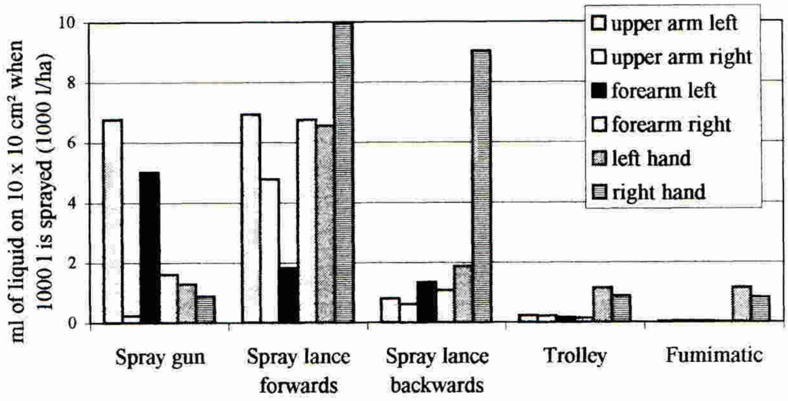

Figure 4. Exposure on the arms and hands on an area of 10 x 10 cm² for the different techniques when 1000 litres at a dose of 1000 litres/ha are applied.

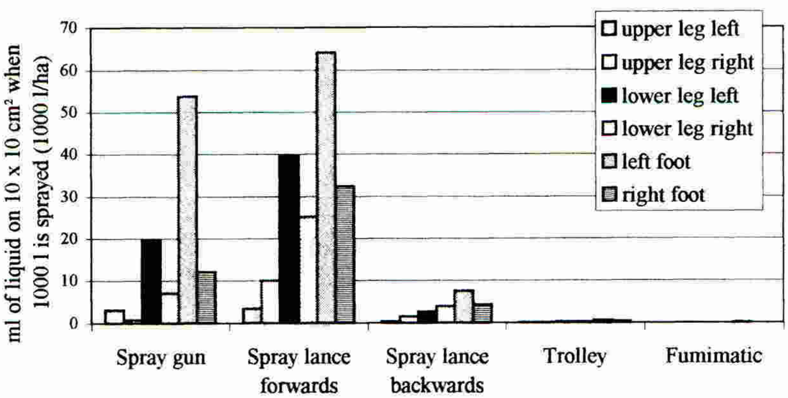

Figure 5. Exposure on the legs and feet on an area of 10 x 10 cm² for the different techniques when 1000 litres at a dose of 1000 litres/ha are applied.

Overall, the measured exposures on the feet were the highest of the entire body (Figure 5). These zones come easily into contact with the falling droplets and spray cloud. This explains the general trend that the lower the position on the legs, the higher the exposure. The exposure on the left foot is higher than on the right foot. With the spray lance and the spray gun, this can be explained by the fact that the operator sprays on the left side. With the trolley, it is because the operator pulls the trolley with his right hand, in that way the left foot is mostly closer to the spray cloud behind him. Again, the exposure with the spray gun is lower than with the spray lance and walking forwards. With the spray lance, walking backwards strongly reduces the exposure on the legs. In this case, the difference between the left and the right side of the body is less clear because some operators sprayed the right side of the crop while walking backwards. With the trolley, very small amounts of spray liquid are found on the legs and feet. The exposure on the legs with the Fumimatic is almost nil.

DISCUSSION

Chelates in combination with the patches and gloves are a very useful, safe, quantitative and relatively cheap way to perform operator exposure experiments. These experiments demonstrated that the difference in total body exposure between the different techniques was very high. The spray lance walking forwards resulted in the highest exposure, 216% compared with the standard spray gun (set at 100%). For the other techniques the following values were found: spray lance walking backward: 32%, trolley: 4% and Fumimatic: 1%. Hence, by walking backwards, an easy technique requiring no investments, operator exposure can be reduced with a factor 7 compared to walking forwards. Compared to the worst technique the exposure was a factor 50 lower when spraying with the trolley and 200 when spraying with the Fumimatic. In addition, these techniques may increase productivity, reduce labour costs and give a better spray distribution. Besides a very large difference in exposure between the five techniques, there was also a large difference in exposure between the various parts of the body. With the spray lance and the spray gun, the highest exposures were measured on the legs and feet. The lower the position the higher the exposure. There is also a high exposure on the hands, the forearms and the head. Depending on the side of the row that is sprayed with the lance or gun, there is a difference in exposure between the left and the right side of the body. With the manually pulled trolley and the Fumimatic, the exposure is the highest for the hands. With the Fumimatic, there was no significant exposure on the other parts of the body.

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Influence of adjuvants on the emission of pesticides to the atmosphere. Review, methodology and perspectives

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ABSTRACT

During application, emission can occur via drifted drops, aerosols and volatilization. After application, emission caused by volatilization from the soil and leaf surface may occur. In addition to the well-established controlled release formulations, adjuvants (surfactants, polymers and oils) are mentioned as tools to reduce emission during and after application. Developments in methodology to understand and to quantify the influence of adjuvants on the volatilization of pesticides are discussed and illustrated with the fungicide fluazinam. The experiments demonstrated that appropriate nozzle types and adjuvants with rather lipophilic ingredients can reduce the emission of the fungicide fluazinam. Although the influence of adjuvants on emission is a complex issue, reduction of emission and a more efficient use of pesticides warrant more attention for adjuvants and application technology as tools.

INTRODUCTION

It has been recognized that presence of pesticides in the atmosphere will contribute at least partly to the contamination of surface water and groundwater. Pesticides may come into the atmosphere during and after their application. During application emission can occur via drifted drops, aerosols and volatilization. So far, quantitative information on the importance of these different routes is not readily available. Drift of spray drops as an obvious loss of the pesticide has received much more attention than loss due to aerosol formation or volatilization during and after application. Drift depends on weather conditions, the application technology and the method of measurement. The literature indicates that drift from ground sprayers generally ranges from 0.1 to 10% of the applied amount (Combellack, 1982; Grover, *et al.*, 1985). After application of the pesticide, the pesticide may be emitted from the leaf and soil surface. Volatilization and formation of liquid or solid particle based aerosols may contribute to this emission. Experiments under field conditions revealed that this emission, expressed as percentage of the applied dose, can amount to 29% for tri-allate (Bor, *et al.*, 1995), 75% for EPTC (Cliath, *et al.*, 1980) and 21% for 2,4-D iso-octyl ester (Grover, *et al.*, 1985).

Formulations and adjuvants have been used as tools to minimise emission of pesticides during and after application. Design of controlled-release formulations using polymers and substitution of volatile esters by much less volatile amine salts are established strategies but fall beyond the scope of this report. Attention is paid to the direct influence of adjuvants on volatilization of pesticides during and after the flight of drops and the indirect influence by changing drop size and subsequently drift. Different experimental procedures can be followed to understand influence of adjuvants on pesticide emission. Here we illustrate these approaches with experiments on the fungicide fluazinam.

REPORTED INFLUENCE OF ADJUVANTS ON PESTICIDE EMISSION

Emission during application

Polymers (Zhu, *et al.*, 1997) and emulsifiable oils (Dexter, *et al.*, 2001) can be used as drift retardant by increasing drop size and some adjuvants are used as an anti-evaporant (Hall, *et al.*, 1993). An anti-evaporant may lower the water evaporation of the drop in flight and thus lowers the fraction of small drops susceptible to drift. Adjuvant can reduce drift potential or drift up to 80% (Hewitt, *et al.*, 2001). Published data does not indicate a direct influence of adjuvants on the release (volatilization) of active ingredients by the drops-in-flight. A simplified approach demonstrated that lipophilic adjuvants could reduce tenfold the concentration of the fungicide fluazinam in the headspace (air) above fluazinam-adjuvant solutions (Mol, *et al.*, 2001).

Emission after application

After application, adjuvants may influence the volatilization of active ingredients from both the leaf surface and from the soil. A more extensive recent review (de Ruiter, *et al.*, 2003) mentioned that post-application volatilization of pesticides may amount to a substantial percentage (25-100%) of the amount applied. The authors also concluded that it is doubtful whether surfactants can reduce volatilization of soil applied active ingredients, particularly in those situations where abundant water dilutes the applied chemicals. Once deposited on the leaf surface and after visible drying of the drop, it seems very reasonable to assume that adjuvants, present at relatively high concentrations, can influence the partitioning of active ingredients between deposit and air and between deposit and the leaf tissue.

After application of the herbicide, adjuvants reduced the volatility of 2,4-D iso-octyl ester under controlled conditions (Schubert, *et al.*, 1993). The authors indicated that this reduction could result from an adjuvant-accelerated penetration of the herbicide into the leaves. Volatilization of DDT from an inert surface (unformulated, chamber temperature 20-25°C and period 24 h) was reduced by 45 to 70%, when surfactants were added (Stevens & Bukovac, 1987). The authors suggested that DDT may be partly trapped within the surfactant deposit. A laboratory approach provided evidence that wax-based dispersions reduce the volatilization of fenpropimorph (fungicide) and methamidophos (insecticide) (Zeisberger, 2001).

METHODOLOGY

A multi-disciplinary approach with a focus on the different stages, seem most appropriate to understand the influence of adjuvants or formulations on pesticide emission. During spray application of the fungicide fluazinam, the influence of a few adjuvants on both drop size and presence of fluazinam in trapped air was measured under controlled conditions. The adjuvants used in the spray-application experiment were also used in the headspace experiments in which we measured the presence of fluazinam in the air above mildly shaken pesticide-adjuvant solutions. This approach allows us to verify the idea that adjuvants can change the partitioning between treatment solutions and the air.

SPRAY APPLICATION EXPERIMENTS

Materials and methods

A room (4.5 x 4.5 x 2.4 m) under controlled conditions (20°C and 70% RH) was used for the spray experiments. The air-change in the room was 24 times/hour. During the experiment, the nozzle moved in a 3D-traverse system. Spray quality and drop speed were measured 0.3 m below the nozzle using a Phase Doppler Particle Analyser (Aerometrics). Fluazinam in the air was trapped in a XAD-filter by creating an air flow of 30 litres/minute through the filter during the spraying (duration 10 minutes). This filter was placed in the corner of the room close to one of the four room-outlets. Fluazinam was quantified by GC-ECD. The product Shirlan Flow (SC formulation; 500 g a.i./litre; Syngenta) was used to apply fluazinam. The adjuvants included were: an emulsifier-free Montan wax (30%) (Agrocer 10, Clariant), an emulsifiable rapeseed oil (containing 10% (w/v) polyoxyethylene (5) C_{13}/C_{15} oxo alcohol; BASF) developed by de Ruiter, *et al.* (1997) and HM-2052, a proprietary blend of nonionic colloidal water dispersible polymers and paraffinic oil (Helena Chemical Company). Three replications (separate experiments) were conducted.

Three nozzles were used: an extended range flat fan F110/0.8/3.0, a pre-orifice FRD110/0.8/3.0 (Teejet XR11002VS and DG11002VS, respectively; Spraying Systems Ltd) and an air induction AI/120/0.8/3.0 (ID12002, Lechler Ltd).

Results and discussion

The results demonstrate that coarsening of the spray by nozzle selection reduced the percentage volume in droplets less than 100 µm diameter (V_{100}) from 18% to 1.5% (Table 2). The emulsifiable rape seed oil and HM 2052 coarsened the spray with all three nozzles. With the flat fan, the rapeseed oil and HM-2052 reduced the V_{100} from 18.2 to 13.3 and 15.5%, respectively. The Montan wax tended to increase the V_{100} with all nozzle types tested.

The flat fan gave a much higher fluazinam emission than the other nozzles (Table 2). The adjuvants reduced the emission of fluazinam with all nozzles tested, except the Montan wax with the pre-orifice nozzle (Table 2). HM-2052 was the most effective emission reducing adjuvant, followed by the rapeseed oil and then the Montan wax. This outcome, the Montan wax result with the pre-orifice nozzle included, correlates somewhat better with the influence of these adjuvants on the VMD (Table 2) than on the V_{100}. This result indicates that an increase of VMD reduced the emission of fluazinam. It should be emphasized that the physical form of the trapped fluazinam (either a vapour or aerosol or both) could not be established so far. The appearance of both forms will be reduced by a reduced liquid-air interface caused by a higher VMD.

Table 2. Influence of nozzle type and adjuvants on drop size and emission of fluazinam.

Nozzle[1]	Spray quality	Solution[2]	VMD[3] (µm)	V_{100}[3] (%)	Fluazinam in air (ng/litre)	Fluazinam in air (% per nozzle)
Extended range	Fine	water	195	18	-	-
Flat fan		Fluazinam	194	18.2	62	100
F110/0.8/3.0		Fluazinam + Montan wax	189	20.3	44	71
		Fluazinam + Rapeseed oil[4]	222	13.3	27	44
		Fluazinam + HM-2052[4]	215	15.5	24	39
Pre-orifice	Medium	water	288	6.8	-	-
FRD110/0.8/3.0		Fluazinam	304	5.8	11	100
		Fluazinam + Montan wax	288	7.5	17	153
		Fluazinam + Rapeseed oil[4]	311	6.2	5	44
		Fluazinam + HM-2052[4]	320	5.9	2.7	24
Air induction	Very	water	536	1.3	-	-
AI/120/0.8/3.0	coarse	Fluazinam	518	1.5	17.5	100
		Fluazinam + Montan wax	510	2.6	8.7	50
		Fluazinam + Rapeseed oil[4]	778	1.8	9.4	54
		Fluazinam + HM-2052[4]	797	0.9	3.5	20

[1]Pressure 300 kPa.
[2]Concentration of fluazinam was 1.25 g ai/litre; the Montan wax, HM-2052 and the emulsifiable rapeseed oil were included at 0.5% (v/v).
[3]VMD = Volume Median Diameter; V_{100} = volume fraction of spray drops with a diameter < 100 µm.
[4]Values are the best estimations of drop diameters. Oil particles interfered with laser light scattering caused by the drops.

HEADSPACE EXPERIMENTS

Materials and methods

Headspace vials of 22 ml were filled with 5 ml of fluazinam solution. The vials were closed with a septum cap, thoroughly mixed using a vortex, and placed in the auto-sampler tray of the HS-GC-ECD instrument. One by one the vials were automatically transferred into a thermostated compartment [50°C according to Mol, *et al.* (2001)] of the sampler where the mixture was homogenized again by vibrating the vial during 30 min. After equilibration, a needle was inserted in the vial to pressurize (with helium) the headspace, after which a sample of headspace was introduced into the GC system, via a transfer line, by time-controlled switching of valves. In the GC system, the compounds present in the gas mixture were separated and detected by an electron capture detector. For the determination of fluazinam in the headspace of formulations and standard solutions a Turbomatrix 40 headspace sampler (Perkin Elmer, Oosterhout, Netherlands) coupled to a GC (HP6890, Agilent Technologies, Wilmington, DE, USA) equipped with a µECD detector was used. The procedure was conducted in duplicate. The fluazinam solutions in the headspace vials contained commercially formulated fluazinam (Shirlan Flow; SC formulation; 500 g a.i./litre) at a concentration of 1 g a.i./litre, the Montan wax adjuvant and HM-2052 at 0.5% (w/v) and the emulsifiable rapeseed oil at 0.5% (v/v).

Results and discussion

All adjuvants tested reduced the volatilization of fluazinam: the emulsifiable rapeseed oil by 91%, HM-2052 by 84% and the Montan wax by 33% (Figure 1). This reductive approach demonstrates the potential of adjuvants to suppress volatilization by increasing the solubility of fluazinam in the solution. It is remarkable that the adjuvant effects of this approach shows a similarity with the outcome of the spray application experiments. The adjuvants HM-2052 and the emulsifiable rapeseed oil are more effective than the Montan wax. This similarity indicates that direct suppression of fluazinam volatilization from the spray drops may have contributed at least partly to the adjuvant effect. The same approach was also followed for the herbicide tri-allate and the same trends were recorded regarding the three adjuvants (data not shown).

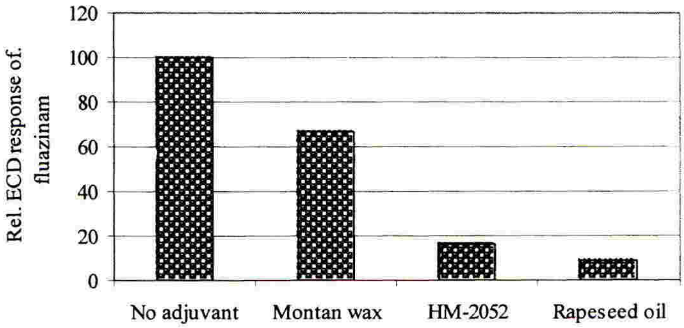

Figure 1.The influence of adjuvants on the volatilization of fluazinam (Shirlan Flow) using the headspace approach.

CONCLUDING REMARKS

The literature search demonstrates that adjuvants and formulation constituents can exert a substantial influence on volatilization of pesticides at different stages of the process. The spray application experiments and the headspace experiments demonstrate that adjuvants with rather lipophilic ingredients can reduce the emission of the fungicide fluazinam during spraying and from a solution. The data also demonstrate the very large influence of nozzle type on emission. We are currently developing technology to monitor the volatilization of pesticides from thin films on inert surfaces and under different conditions. This approach will give insight in the volatization from leaves and from the soil.

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