4.
Adjuvant and Formulation Effectiveness

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EFFECT OF ADDITIVES ON FOLIAR WETTING AND UPTAKE OF GLYPHOSATE INTO GORSE (Ulex europaeus)

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ABSTRACT

Formulations of glyphosate (at 2.2. kg a.i./300 litres) were tested with various surfactants. Initial screening of formulations was by contact angle values of droplets on a film of gorse foliar wax: contact angle values below 50° were generally considered most suitable. ^{14}C-Glyphosate was added to selected formulations and these were applied to the foliage of gorse plants growing in a controlled environment. Higher incorporations were obtained from spray formulations with lower contact angles. Field testing of the best combination (with Silwet L-77) showed the expected improvement in herbicidal effectiveness but results depended on plant growth stage and environmental conditions.

INTRODUCTION

Control of mature gorse (Ulex europaeus) plants using herbicides based on 2,4,5-T is at best difficult and at worst virtually ineffective (Balneaves 1980, Ivens 1979). There is a need for a herbicide that can translocate into the root system, provide complete stem kill, and prevent subsequent resprouting.

One such herbicide is glyphosate. There is little field evidence to suggest its commercial formulation (Roundup) is effective on mature plants although it can be used with varying success on seedlings (Ivens 1977, Preest 1980). Other workers (Turner & Loader 1978) have found enhanced herbicidal effects with altered glyphosate formulations. These scant results suggest that the apparent ineffectiveness could be due to poor incorporation into mature plant foliage.

It was observed (Zabkiewicz & Gaskin unpublished) in trials with different 2,4,5-T formulations that improved performance was related to reduced contact angle (CA) values. These values were determined by applying small droplets of the formulation on to a glass surface coated with wax extracted from gorse foliage. In a similar approach (Wyrill & Burnside 1977), it was concluded that there was no relationship between formulation effectiveness and CA values for the plant species studied, if leaf surfaces were used.

Measurement of droplet CA values on an artificial wax surface is purely a measure of the potential wetting of the leaf in vivo; formulations have to be further evaluated by measurement of the actual incorporation into the leaf. This is most easily done by using ^{14}C-glyphosate. The most appropriate formulations were tested on gorse plants grown in controlled environment conditions using clonal plant material.

The best combinations were chosen for field trials and formulations were applied at different times of the year to mature gorse stands. Assessments were made 18 to 24 months later for mortality and growth inhibition.

METHODS AND MATERIALS

Contact angle determinations

Cuticular wax was extracted from mature gorse foliage. A portion of the wax was dissolved in chloroform (1% w/v) of which 10 ul was spread over the surface of a cleaned glass slide (3 x 80 mm) to give an even wax film after drying. Formulations (3 ul) were applied to the waxed glass surface and the CA calculated from the measurements of the radius and height of the projected image of the droplet by the equation and method given in the literature (Fogg 1947). Glyphosate concentration was 2.2 kg a.i./300 litres water/ha, i.e. equivalent to 6 litres Roundup per ha. The additives selected represented several different chemical classes and were: diesel oil (local supply); butyl acid phosphate (Dr Turner, WRO, Oxford); Triton X-45 and AG-98 (Rohm & Haas); X-77 (Colloidal Products Corp.); Bardac 22 (Lonza, USA); Nuodex (Tenneco, USA); Vantoc CL (ICI, NZ); Silwet L-77, 7001, 7002, 7600, 7607 (Union Carbide); Reversil 9 (Monsanto, NZ).

Incorporation experiments

Cuttings (10 cm long) were taken from selected gorse bushes, set in pots and allowed to root; plants of comparable size were selected from within three clones and further preconditioned in controlled environment cabinets (see Table 1 for conditions). There was inevitably a difference between the 1980 and 1981 plants in age and condition as well as origin.

TABLE 1

Operational dates, plant and growth cabinet conditions for ^{14}C-glyphosate incorporation experiments

	1980 Series	1981 Series
Time cuttings set	December 1979	December 1980
Plants into cabinet	2.10.80	22.4.81
Size	40-50 cm (10 mths)	40-50 cm (4 mths)
Stabilised	4 weeks	12 weeks
Labelled	4.11.80	14-15.7.81
Size (at labelling)	45-55 cm	60-70 cm
Needle condition	"hardened current" (Flush Aug/Sept) hardened - 2 mths	"current" (Flush May/June) hardened - 1 mth
Day/night temp	$20^{o}/15^{o}$	$20^{o}/15^{o}$ (6 weeks) $16^{o}/12^{o}$ (6 weeks)

Other conditions were: 16 h photoperiod with 12 h photosynthesis period of light intensity 100 watts m^{-2} and 85% R.H.

Standard solutions of glyphosate (as Roundup or Mon 0139) equivalent to 2.2 kg a.i./300 litres water had ^{14}C-glyphosate (95% pure) added at a concentration of 1.86 or 1.75 uCi/ml. Additives were added to the stock solutions immediately prior to use; solutions were thoroughly mixed and sonicated for several minutes prior to application.

Twenty consecutive, hardened off, current growth spines along the plant's main shoot were selected for treatment. Care was taken to leave 10-15 cm of shoot above the treated section and there was always at least 20 cm of shoot below the treated section. Solutions were applied to the spine surfaces with a fine paint brush, taking care to avoid surface run-off and splashes. Plants were left for 48 h, then removed, and each was cut into appropriate segments. The total plant sections including the treated spines plus stem section were washed individually in water (100 ml x 2), then chloroform (150 ml), in the 1980 series; water plus 0.05% Tween 80 only in 1981. Water washes were frozen then freeze dried; chloroform extracts were evaporated to dryness at room temperature. Wash residues were dissolved in 500 ul methanol plus 10 ml scintillant solution and counted in a Packard 3320 scintillation counter to $\pm$ 2% accuracy.

Individual plant sections were freeze dried, weighed and then ground in a Wiley Mill. Five to ten milligram amounts were used in duplicate in a Micro-Mat combustion apparatus. Radioactivity per combusted sample was converted to mean tissue radioactivity, then total plant tissue radioactivity, and these values were used together with the radioactivity found in the wash samples to calculate the amount incorporated into the plant.

Field trials

Spray formulations of glyphosate were made up at 2.2 and 3.6 kg a.i./300 litres/ha together with 0.5% L-77 per carrier volume for both Roundup and Mon 0139. The site was at Mt Thomas in Canterbury (elevation 300 m) with even 5-year-old gorse regrowth. Plots were 5 x 2 m, treatments replicated thrice in randomised complete blocks for each spray time. A CO_2 boom sprayer (077039 flat fan nozzles, 205 kPa) held 1 m above the canopy was used in a double pass to give the required applied volume. All spraying was between 6 a.m. and 8 a.m. with calm weather, temperature below 16°C, and about 80% RH. In each plot 60 individual gorse stems were evaluated at 5 cm intervals along a diagonal transect. Stems were categorised as "dead" if no live cambium at stem base; "sick" if obviously dead foliage but some regrowth with live cambium at stem base; and "healthy" if green foliage and apparently unaffected. Results were statistically evaluated using analysis of variance.

RESULTS AND DISCUSSION

Typical CA values obtained with various glyphosate spray formulations are listed in Table 2. Roundup alone has a CA well over 70°; from past experience, formulations with CA values of 50^{o} or less are considered as having good wetting capability, while complete wetting is possible if the value is 20° or less. Using these (somewhat arbitrary) criteria, only one additive, L-77, is capable of complete wetting, while Diesel, Triton X-45, L-7607, Triton AG-98 and Rev 9 can provide improved wetting.

The additives were also tested with Mon 0139 (unformulated glyphosate solution); the same four additives gave lowest CA values but their values were lower for equivalent concentrations. Amounts of 2.2 or 4.4 kg a.i. of Mon 0139 plus 0.01% L-77 gave CA values of 33^{o} and 39^{o} respectively. This indicates that there is an antagonistic effect with the Roundup formulation where 0.01% L-77 had little or no beneficial effect (Table 2B). There is a difference of around 6^{o} between the 1980 and 1981 series of results for the glyphosate stock solution. The reason is unknown but is considered to be of little practical significance since the same controls can be included in each batch and far larger differences are needed before one can expect real differences in wetting ability.

Initial gorse foliage ^{14}C-glyphosate incorporation trials (Table 3) tested additives of various chemical types and wetting ability. Due to a lack of plants at that time, only two replicates were possible and not

TABLE 2

Contact angles of glyphosate formulations based on 2.2 kg a.i./300 litres/ha Roundup

% Additive	Contact angle	Standard deviation	Chemical type
A			
None	74.8	2.6	
16% Diesel (+ 2% X-45)	50.9	2.7	Hydrocarbon oil
50% Diesel (+ 2% X-45)	40.9	2.1	
1% Butyl acid phosphate	56.3	2.2	Acidic phosphate ester
2% Butyl acid phosphate	48.2	1.7	
.2% Triton X-45	48.6	3.2	Polyoxyethanol ester
.5% Triton X-45	40.8	2.0	
1% Triton X-45	42.2	1.6	
.1% X-77	70.3	2.4	Polyethoxyethanol ester
.1% Bardac	61.3	2.7	Alkylammonium salt
.1% Nuodex	61.4	3.1	Alkylammonium salt
.1% Vantoc CL	63.6	2.1	Alkylammonium salt
.1% Silwet L-77	45.4	1.6	Organosilicone
.5% Silwet L-77	8.4	1.6	
B			
None	80.8	2.2	
.5% Silwet L-7001	76.4	1.9	
.5% Silwet L-7002	75.5	2.1	Organosilicone
.5% Silwet L-7600	60.5	2.2	Organosilicone
.5% Silwet L-7607	51.9	3.3	Organosilicone
1% Silwet L-7607	43.2	2.3	
.5% Triton AG-98	52.3	2.8	Polyoxyethylene ester
1% Triton AG-98	41.2	3.2	
.5% Reversil 9	51.6	2.0	Non-ionic organic ester
1% Reversil 9	43.4	2.4	
.01% Silwet L-77	72.8	2.5	Organosilicone
.1% Silwet L-77	51.9	1.9	
.5% Silwet L-77	16.1	1.6	

A 1980 series: water was 103.0° (± 2.3 at 20° and 52% RH).
B 1981 series: water was 103.9-105.6° (± 2.2 to ± 1.9 at 19° and 61% RH)

all were of equivalent development stage. The spines selected for labelling were of a "hardened current" type except for the two cases indicated in Table 3 which were "current" foliage type, i.e. younger foliage. All treatments to equivalent foliage gave substantially increased incorporations except for Nuodex. Best results were obtained with L-77 and Diesel. Much reduced incorporations were recorded for formulations with L-77 and X-45 applied on to the younger foliage.

Subsequent experience with recovering glyphosate off gorse foliage leads to the belief that, due to the lack of additional surfactant in the water wash (see Methods section), the treatments with Roundup alone may show an exaggerated incorporation. In that event the results with the additives would be proportionately better.

TABLE 3

Incorporation after 48 h into gorse of ^{14}C-glyphosate from 2.2 kg a.i. Roundup alone and with additives (1980 Series).

Additive	%	Wash DPM	Extraction DPM	% incorp.	Av. % incorp. Hardened	Av. % incorp. current
Nil		5816	1745	23.1	30.2	
		16309	9684	37.3		
BAP	1.0	19129	14990	43.9	51.2	
		18729	26253	58.4		
L-77	0.5	27251	9990	26.8		26.8*
		18307	30467	62.5	62.5	
X-45	0.2	19526	18589	48.8	48.8	
		14996	6335	29.7		29.7*
Nuodex	0.1	16006	10552	39.7	36.2	
		12504	6086	32.7		
Diesel	16.0	15188	21157	58.2	59.8	
		12947	20541	61.3		

* Different leaf growth stages; used "current" spines while others were "hardened current".

A further series of additives were tested in relation to L-77. Work with diesel was deferred as there is a general requirement that its use be curtailed. All treatments involving additives gave increased incorporations (Table 4). Best results were with 0.5% L-77 (a mean 70.1% vs 7.1%) giving a ten-fold enhancement over the Roundup alone. The other three additive results were fairly similar at 15.2%, 15.3% and 25% incorporations, reflecting their similar formulation CA values. A further trio of plants kept outside the building at all times was labelled under quite different conditions during the winter (temperature 9^{o} at treatment; daily maximum/minimum temperature 20^{o}/6^{o}; RH 15%). There, the incorporation of glyphosate from Roundup plus 0.5% L-77 was down to 40.3%, but it still gave the second best result in this series. An equivalent series of treatments using Mon 0139 instead of the Roundup formulation gave very similar incorporation results and trends.

Although replication was restricted in these controlled environment trials, the consistently higher incorporations of ^{14}C-glyphosate with L-77 surfactant made this the obvious combination for further testing in the field.

TABLE 4

Incorporation after 48 h into gorse of ^{14}C-glyphosate from 2.2 kg a.i. Roundup alone with additives (1981 Series)

Additive	%	Wash DPM	Extraction DPM	% incorp.	Av. % incorp.
		90934	8128	8.2	
Nil		172045	16496	8.8	7.1
		148782	6863	4.4	
L-77	0.5	148447	246871	62.5	
		139603	435200	75.7	70.1
		96734	250753	72.2	
L-7607	1.0	243208	81959	25.2	
		294338	95327	24.5	25.0
		303509	103111	25.4	
AG-98	1.0	125448	32118	20.4	
		283313	41374	12.7	15.2
		231266	33053	12.5	
Rev 9	1.0	130862	16042	10.9	
		238390	47443	16.6	15.3
		323149	72121	18.3	
L-77*	0.5	47215	46960	49.9	
		114614	52799	31.5	40.3
		61760	40482	39.6	

* Outside treatment

The results from the field trials are given in Table 5 for the 3.6 kg a.i./ha concentration as the lower dose of 2.2 kg a.i./ha proved ineffective. Herbicide was applied in summer (25/11), late summer (3/2) and autumn (14/4) growth phases. Little or no gorse kill was obtained from any treatment. However, addition of L-77 caused an increase in the "sick" plant category, particularly for the late summer and autumn applications. There was also some indication that the Mon 0139 spray formulation without L-77 was better than the corresponding Roundup formulation but the addition of L-77 reduced this difference. Greater herbicidal effectiveness was obtained with late-season applications.

CONCLUSIONS

The value of initially screening glyphosate formulations using CA determinations on extracted wax films has been confirmed for gorse. In all cases, formulations which had lowest CA values, gave highest incorporations of glyphosate into gorse. However, despite low CA values, other surfactant/plant interactions affected final uptake. More work would be required to define this interaction or the factors controlling it.

TABLE 5

Field assessment (November 1983) of glyphosate ± L-77 on gorse using Roundup and Mon 0139 formulations.

Date sprayed	Plant condition (% mean)					
	- L77			+ L77		
	Dead	Sick	Healthy	Dead	Sick	Healthy
3.6 kg a.i./ha Roundup						
25.11.81	2	24	74[c]	6	35	59[ed]
3. 2.82	0	1	99[a]	2	39	59[ed]
14. 4.82	2	9	89[b]	2	43	55[e]
3.6 kg a.i./ha Mon 0139						
25.11.81	0	25	75[c]	0	25	75[c]
3. 2.82	5	17	78[c]	0	41	59[ed]
14. 4.82	2	35	63[d]	12	48	40[f]

Superscript letters indicate ranking and sig. diff. at $p = 0.01$ level

Although insufficient herbicide was used in the field trials to give substantial gorse mortality, the enhanced herbicidal effectiveness of sprays containing L-77 was demonstrated particularly for late-season applications. The improvement in herbicidal effectiveness in late-season treatments where L-77 is added to glyphosate has practical significance and potential. Indeed, current trials show that higher amounts of glyphosate applied late in the season with L-77 appear to give effective gorse control (Balneaves, unpublished).

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REFERENCES

Balneaves, J.M. (1980) A programme for gorse control in forestry using a double kill spray regime. Proceedings of the 33rd New Zealand Weed and Pest Control Conference, 170-173.

Fogg, G.E. (1947) Quantitative studies on the wetting of leaves by water. Proceedings of the Royal Society of London, Series B. 134, 503-522.

Ivens, G.W. (1977) Susceptibility of seedling gorse to herbicides. Proceedings of the 30th New Zealand Weed Pest Control Conference, 61-65.

Ivens, G.W. (1979) Effects of sprays on gorse re-growth at different growth stages. Proceedings of the 32nd New Zealand Weed & Pest Control Conference, 303-306.
Preest, D. (1980) Seasonal variation in seedling gorse susceptibility to four herbicides. Proceedings of the 23rd New Zealand Weed and Pest Control Conference, 165-169.
Turner, D.J.; Loader, M.P.C. (1978) Complexing agents as herbicide additives. Weed Research, 18, 199-207.
Wyrill, J.B.; Burnside O.C. (1977) Glyphosate toxicity to common milkweed and hemp dogbane as influenced by surfactants. Weed Science, 25, 275-287.

STUDIES WITH ALTERNATIVE GLYPHOSATE FORMULATIONS

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ABSTRACT

Salts of glyphosate can be made by warming glyphosate acid with ethoxylated surfactants derived from fatty amines. One such salt made with Ethomeen S12 surfactant is oil soluble and has properties not normally associated with glyphosate, including an ability to penetrate bark. It is about as active against herbaceous species as the commercial isopropylamine salt formulation, Roundup. As with Roundup, the addition of ammonium sulphate and/or surfactants may enhance phytotoxicity.

Glyphosate acid in water without surfactants is relatively non-phytotoxic. However when Ethomeen T25 surfactant or ammonium sulphate with Ethomeen C12 is added, phytotoxicity is greatly increased, perhaps as a result of ion exchange between the acid and the cationic surfactants.

Potential uses of these formulations are discussed briefly.

INTRODUCTION

Glyphosate, a foliage acting herbicide with little selectivity, is used in a variety of situations for controlling unwanted vegetation (Roberts, 1982). First used as the free acid (Baird et al., 1971), glyphosate was later formulated as sodium, dimethylamine or isopropylamine salts (Franz, 1979). These are much more water soluble than the free acid. The monoisopropylamine salt with a surfactant of undisclosed structure is sold as the commercial formulation, Roundup. This gives good results in most situations. When low doses are used, activity can be improved by addition of surfactant and/or ammonium sulphate (Turner & Loader, 1980).

Little information is available about other glyphosate derivatives. According to Franz (1979), many have been made, including esters, hydrazides and amides. None of these have come into general use. However, the trimethyl sulfonium salt of glyphosate has been sold recently under the names SC0224, or sulfosate.

Polar derivatives such as the isopropylamine and trimethyl sulfonium salts control most herbaceous weeds well but have shortcomings when there is a need for glyphosate to pass through bark or thick leaf cuticle. In these circumstances, an oil soluble formulation may be more effective; oil-soluble esters of 2,4-D and 2,4,5-T are for example recommended for controlling woody weeds and heather (Sale, Tabbush & Lane, 1983). Unfortunately most glyphosate derivatives including esters are relatively insoluble in oils (personal communication, E.G. Cotterill). A special kind of oil based formulation can be made by solubilizing the isopropylamine salt with surfactants (Turner & Loader, 1974) but this appears to be immobile within plants (D.J. Turner, unpublished results) and is relatively expensive.

Esters are used most often but other oil soluble derivatives of herbicides can be made. For example acid herbicides can react with a long chain fatty amine to make an oil soluble salt. This method has been used to make oil soluble, non volatile derivatives of 2,4-D and 2,4,5-T. Some of these formulations are as active as esters (Sterrett, 1965). Jansen (1965) examined a range of salts of 2,4-D with long chain ethoxylated amines used as surfactants. These had both herbicidal and surfactant properties.

Mr Malcolm Lulham, of the Armour Hess Division of Akzo Chemie (U.K.) Ltd., suggested that surfactant salts of glyphosate might be soluble in oil. Work on the toxicity of this type of formulation is described in this paper. Additionally, some experiments have been carried out with free glyphosate acid mixed with adjuvants which enhance the effects of the commercial formulation, Roundup (Turner & Loader, 1980).

MATERIALS AND METHODS

Glyphosate acid was precipitated from Roundup by adding excess of 10M hydrochloric acid. The precipitate was washed first with water and then repeatedly with acetone. It was dried under vacuum in a desiccator.

In preliminary trials several surfactant salts of glyphosate were made by warming glyphosate acid with a little water and an excess of the surfactant. However, at an early stage attention was concentrated on the Ethomeen S-12 salt, which appeared to be unusually soluble in oils. Glyphosate acid was heated with about eight times its weight of Ethomeen S12 and a little water, at 100^{o}C for 1 h. This treatment converted the acid to a brown treacly solid. Excess surfactant and water was removed by washing with acetone. The material was then dissolved in xylene and the purified salt recovered by adding an excess of acetone. After further washing with acetone, the salt was dried under vacuum. Its glyphosate content, 166 g/kg a.e., was determined by the method used by the U.S. Food and Drugs Administration (Anon, 1980). In the initial experiments the Ethomeen S-12 salt was suspended in water or dissolved in domestic paraffin. Later, it was formulated as a solution in xylene with 30 g/l of a nonionic surfactant, Ethylan A2. This formulation, containing 56 g/l a.e., formed a much finer and more stable emulsion than the salt in water or paraffin.

Details of surfactants are given in Table 1. Laboratory reagent grades of other formulation materials were used. Formulated glyphosate isopropylamine salt "Roundup" and technical isopropylamine salt were obtained from Monsanto Ltd., Leicester.

(1) Experiments with Populus x euramericana, cv Robusta

Bark applications, injection and cut end treatments were made by methods described previously (Ivens, 1972; Turner, 1973; Turner & Loader, 1974). Briefly, treatments were applied to 1-year old cuttings, 0.3 m long and 15-25 mm in diameter. Each experiment had 6-10 replications.

Bark applications (Table 2) were made to an 0.1 m segment at the centre of the cuttings by placing them horizontally in racks and spraying them through a slit in a hardboard shield. This was aligned at right angles to the cuttings. The spray volume was 386 l/ha applied with a Spraying Systems "Teejet" 8004 nozzle operated at 210 kPa. Roundup was

TABLE 1

Details of surfactants used

Trade name	Structure	Source
Ethomeen S12 (cationic)	Tertiary amine derived from soya containing 2 mols ethylene oxide (EO) per mol of amine	Akzo Chemie
Ethomeen C12 (cationic)	Tertiary amine from coconut containing 2 mols EO per mol of amine	" "
Ethomeen C15 (cationic)	Tertiary amine from coconut containing 5 mols EO per mol of amine	" "
Ethomeen T25 (cationic)	Tertiary amine from tallow containing 15 mols EO per mol of amine	" "
Ethylan A2	Polyethylene glycol monooleate, M.W. about 200	Diamond Shamrock
Agral	Alkyl phenol ethylene oxide condensate	ICI Plant Protection Divn.
–	Glycerol monooleate	Croda Chemicals

TABLE 2

Effects of sprays applied to bark of Populus x euroamericana. Number of cuttings sprouted out of 10 and (in brackets) mean fresh wt. of shoots per cutting (g)

	Formulation		
Glyphosate concentration g a.i./l	Aqueous Roundup	Roundup solubilized in paraffin	Ethomeen S-12 salt in paraffin
Nil	10 (1.56)	10 (1.63)	8 (1.37)
5	10 (1.45)	9 (0.92)	8 (1.25)
10	9 (1.23)	10 (0.88)	10 (1.02)
20	9 (1.27)	10 (0.19)	10 (0.50)
Untreated control		10 (1.90)	
Standard error shoot wt. (144 df)		(0.28)	

solubilized into paraffin using a mixture of Agral and glycerol monooleate (Turner & Loader, 1974). After treatment the cuttings were left undisturbed for 24 h and then placed vertically in large pots of Levington compost. These were watered and kept in a glasshouse at 20^{o}-25^{o}C. The phytotoxicity of treatments was assessed by weighing shoots after 45 days.

Injection treatments (Table 3) were made by introducing 40 µl of solution into a 5 mm diameter hole cut with a corkborer to the depth of the outer wood at 50 mm from the upper end of cuttings. After treatment, the holes were sealed with PVC tape and the cuttings placed upright with the lower ends in 25 mm of water. After 24 h, each cutting was divided into three 0.1 m pieces. The upper treated piece was discarded and the central and lower segments placed in 25 mm x 50 mm glass specimen tubes containing water. These were kept in the glasshouse at 20-25^{o}C for 40 days when shoot growth was weighed.

Cut end applications (Table 4) were made by placing 500 µl of solution in a collar of PVC tape projecting 10 mm above the upper end of cuttings. The cuttings were stood upright in 25 mm of water and divided into three 0.1 cm pieces after 24 h or 96 h. The middle and lower segments were grown on as described above. Shoots were weighed after 60 days.

(2) Experiments with herbaceous plants

Wheat (cv Timmo) was grown in a glasshouse at 10-20^{o}C, in 10 cm pots containing Levington compost. Ten seeds were planted per pot and seedlings thinned to five soon after emergence. Spray treatments (Table 5) were applied at growth stage 31 (Tottman & Makepeace, 1979) in 198 l/ha spray volume, using a laboratory bench type sprayer incorporating a single nozzle (Spraying Systems "Teejet" 8001) operated at 210 kPa, 0.5 m above the plants. There were seven replicates. The foliage was dry at spraying. Thereafter plants were kept dry for 24 h, then watered copiously with a hand-held rose to wash off unabsorbed residues and returned to the glasshouse. After 25 days the fresh weight of live foliage was determined (Table 5).

Elymus repens (couch grass). All plants were of the "Begbroke" clone, grown in 15 cm "Long Tom" pots containing John Innes No. 3 compost. The plants used for preliminary experiments (Tables 6-7) were grown in the glasshouse, carrying 2-5 g fresh wt of rhizome and 2-4 stems each with 5-6 leaves. Treatments were applied in 198 l/ha spray volume, as described previously. In the first trial (Table 6) plants were kept dry for 24 h before watering. In the second experiment (Table 7) the time to watering was 10 min or 2 h. Randomised block layouts with 5 replicates were used. After treatment, pots were returned to the glasshouse. Treatment effects were assessed by cutting foliage at ground level 10 days after spraying and weighing regrowth after 7-9 weeks. In two other experiments (Tables 8-9), plants grown outdoors were used. At treatment these had 10-20 g fresh wt of rhizome and 3-6 shoots with 4-6 leaves. Sprays were again applied in 198 l/ha. In both these trials, Ethomeen S12 salt in xylene with Ethylan A2 was used. In the first experiment (Table 8) plants were kept dry for 24 h. In the second trial (Table 9) the time to watering was varied. After 14 days, rhizomes were washed, cut into single node pieces and replanted in seed trays of compost to assess bud variability, using methods published previously (Turner & Cussans, 1981).

(3) Experiment with trees and Calluna vulgaris grown in pots

Glyphosate treatments including emulsifiable Ethomeen S12 salt in xylene with 30 g/l Ethylan A2 were applied by sprayer to 2-year old beech,

TABLE 3

Effect of introducing glyphosate formulation into holes in the bark of *Populus* x *euroamericana* cuttings. No. of sprouted lower segments out of 9 and (brackets) mean fresh wt. of shoots per lower segment (g).

	Formulation			
Glyphosate dose, mg a.i. per cutting	Aqueous Roundup	Roundup solubilized in paraffin	Ethomeen S12 salt dispersed in water	Ethomeen S12 salt in paraffin
0.25	6 (0.30)	9 (0.28)	9 (0.41)	9 (0.38)
0.5	6 (0.23)	9 (0.43)	9 (0.43)	9 (0.40)
1	3 (0.11)	8 (0.36)	9 (0.48)	9 (0.50)
Untreated control	9 (0.47)			
Standard error, shoot wt. (216 df)	(0.06)			

TABLE 4

Effect of applying glyphosate formulations to the upper cut ends of *Populus* x *euro-americana* cuttings. Number of sprouted segments out of 24 and (in brackets) mean fresh wt. of shoots (g).

Formulation	Middle segment	Lower segment	Mean
Roundup	6 (0.03)	7 (0.12)	6 (0.08)
" + 5 g/l Ethomeen T25	9 (0.07)	6 (0.03)	7 (0.05)
" + 50 g/l $(NH_4)_2SO_4$+5 g/l Eth.C12	8 (0.03)	7 (0.01)	7 (0.02)
Tech. isopropylamine salt	4 (0.01)	12 (0.09)	8 (0.05)
" " + 5 g/l Ethomeen T25	5 (0.03)	11 (0.06)	8 (0.04)
" " + 50 g/l $(NH_4)_2SO_4$ + 5 g/l Eth. C12	7 (0.05)	6 (0.03)	7 (0.04)
Free acid	1 (Trace)	8 (0.06)	5 (0.03)
" + 5 g/l Ethomeen T25	4 (0.01)	8 (0.12)	6 (0.06)
" + 50 g/l $(NH_4)_2SO_4$ + 5 g/l Eth. C12	5 (0.03)	8 (0.06)	7 (0.05)
Solubilized Roundup in paraffin	23 (0.45)	24 (0.62)	24 (0.54)
Solubilized Roundup in paraffin, dispersed in water	11 (0.08)	18 (0.42)	15 (0.25)
Ethomeen S-12 salt dispersed in water	8 (0.08)	15 (0.13)	12 (0.11)
" " dissolved in paraffin	17 (0.11)	15 (0.11)	16 (0.11)
" " paraffin solution dispersed in water	9 (0.04)	5 (0.01)	7 (0.03)
Untreated control	24 (0.55)	24 (0.59)	24 (0.57)

Standard error, fresh wt of shoots. (275 df)	Body of Table	(0.035)
	Formulation means	(0.025)

C. vulgaris, Douglas fir and Lodgepole pine grown outdoors in large (20-25 cm) pots of soil. There were 4 replicates of each species. At treatment on March 20, beeches were leafless and conifer buds dormant. The treatments were applied in 200 l/ha spray volume, using a spray boom carrying two nozzles (Spraying Systems "Teejet" 8004) 0.5 m apart, operated at 210 kPa 1.5 m above the plants. After 24 h the plants were returned outdoors and watered from above. Phytotoxicity was assessed by weighing live above-ground growth (C. vulgaris), live leaves (beech) or the current season's growth (conifers) in July.

(4) Field observation on Sitka spruce and Calluna vulgaris
Ethomeen S-12 glyphosate salt formulated in xylene with Ethylan A2 was applied on August 9th, 1983, in 200 l/ha of water to observation plots in Glentress Forest, Border Region. The glyphosate dose was 1 kg a.i./ha. Adjacent plots were treated with 2.5 kg a.i./ha glyphosate, as Roundup. The herbicides were applied in dry sunny weather by means of a 'Polyclair' knapsack sprayer fitted with a Cooper Pegler VLV 200 nozzle. No significant rain fell until August 22nd. The vegetation was an almost pure stand of C. vulgaris beneath 10-year old Sitka spruce trees which were making poor growth and showed needle discolouration characteristic of nitrogen deficiency.

RESULTS

(1) Experiments with Populus x euramericana. The effects of bark application are shown in Table 2. Aqueous Roundup had no effect, even at 20 g a.i./l concentration. None of the formulations killed the buds outright but treatment with solubilized Roundup or the Ethomeen S-12 glyphosate salt greatly reduced shoot growth. Solubilized Roundup had most effect. As well as reducing shoot size, the treatments caused severe leaf deformity in developing shoots.

The effects of injections are shown in Table 3. Only data for the lower parts of cuttings are given but effects on the middle segments were similar. Of the formulations tested, only Roundup showed any sign of movement along the cuttings.

Table 4 shows the effects of applying formulations to the upper cut surfaces. Glyphosate doses of 0.25 μg and 1 μg were tested. The higher dose was more phytotoxic and most movement occurred when the cuttings were sub-divided after 4 days. However, formulation effects were more important and, for simplicity, only the mean effects of the treatments are shown. Roundup, technical glyphosate-isopropylamine and free glyphosate acid all moved down the cuttings. Additions of Ethomeen T25 or Ethomeen C12 with ammonium sulphate had little effect. Solubilized Roundup was relatively immobile, particularly when applied in paraffin. However some Ethomeen S12 salt moved down the cuttings, its effects being intermediate between those of water soluble formulations and solubilized Roundup.

(2) Experiments with herbaceous species The results of the wheat experiment are shown in Table 5. Free glyphosate acid without adjuvants was almost inactive. However both adjuvant treatments greatly increased phytotoxicity to about the level of Roundup with the same additives. The Ethomeen S-12 salt in paraffin or water was about as active as Roundup without adjuvants. Early experiments with E. repens are summarised in Tables 6-7. In both experiments the Ethomeen S12 salt was significantly less phytotoxic than Roundup or glyphosate acid with adjuvants. Further

TABLE 5 Effects of glyphosate formulations on wheat. Wt. of live above-ground foliage after 25 days (g). In brackets, Log x + 1 transformed data.

Formulation	Glyphosate, kg a.i./ha			
	0.05	0.1	0.2	Mean
Roundup	6.9 (0.89)	1.6 (0.39)	0 (0.00)	2.8 (0.43)
Roundup + 5 g/l Ethomeen T25	0.2 (0.05)	0 (0.0)	0 (0.0)	0.1 (0.02)
Roundup + 50 g/l (NH4(2SO4 + 5 g/l Ethomeen C12	0.8 (0.23)	0 (0.0)	0 (0.0)	0.3 (0.08)
Free acid	10.3 (1.05)	10.2 (1.05)	9.5 (1.02)	10.0 (1.04)
Acid + 5 g/l Ethomeen T25	0.6 (0.18)	0.1 (0.03)	0 (0.0)	0.2 (0.07)
Acid + 50 g/l (NH4)2SO4 + 5 g/l Ethomeen C12	1.4 (0.34)	0.1 (0.02)	0 (0.0)	0.5 (0.12)
Ethomeen S-12 salt in paraffin	2.3 (0.50)	0.1 (0.02)	0 (0.0)	0.8 (0.18)
Ethomeen S-12 salt dispersed in water	4.0 (0.68)	1.5 (0.39)	0.3 (0.07)	1.9 (0.38)
Ethomeen S-12 salt in paraffin, dispersed in water	3.6 (0.65)	2.0 (0.44)	1.4 (0.73)	3.3 (0.61)
Untreated control		11.2 (1.08)		

Standard error Body of Table (0.039)
(156 df) Formulation means (0.013)

TABLE 6 Effects of glyphosate formulations on E. repens. Fresh wt. of regrowth after 34 days (g)

Formulation	Glyphosate, kg a.i./ha		
	0.05	0.2	Mean
Roundup	0.62	0.79	0.71
Roundup + 5 g/l Ethomeen T25	0.73	0.09	0.41
Roundup + 50 g/l $(NH_4)_2SO_4$ + 5 g/l Ethomeen C12	0.58	0.05	0.32
Free acid	0.68	0.82	0.75
Free acid + 5 g/l Ethomeen T25	0.69	0.25	0.47
Free acid + 50 g/l $(NH_4)_2(SO_4)$ + 5 g/l Ethomeen C12	0.82	0.00	0.41
Ethomeen S-12 salt dispersed in water	0.71	0.75	0.73
Ethomeen S-12 salt in paraffin, dispersed in water	0.75	0.88	0.81
Untreated control	0.82		

Standard error Body of Table 0.082
(68 df) Formulation means 0.058

experiments with E. repens (Tables 8-9) used Ethomeen S12 salt in xylene with Ethylan A2 emulsifier. Adjuvants greatly increased the phytotoxicity of this formulation and Roundup but there were large differences between the responses of the formulations. Highly significant formulation x adjuvant interactions occurred, in particular addition of Ethomeen C12 with ammonium sulphate which enhanced Roundup phytoxicity reduced the effects of the Ethomeen S12 salt (Table 8). In the second experiment investigating the effects of watering, the Ethomeen S12 salt was significantly more phytotoxic (Table 9). When residues were washed off after 4 h, Ethomeen S12 salt with ammonium sulphate and Ethomeen T25 had significantly more effect than other treatments. However, when watering was deferred there were no significant differences.

(3) Experiments with pot-grown trees and C. vulgaris

Roundup in water, with or without adjuvants, had no effect on any of the test species. The Ethomeen S12 salt in paraffin caused malformation in beech but did not significantly reduce leaf weights. There were no visible effects on conifers but Ethomeen S12 salt treatments and solubilized Roundup severely injured heather. Plants sprayed with 3 kg a.i./ha glyphosate as Roundup were unaffected but those treated with solublized Roundup or the Ethomeen S12 salt in paraffin weighed 64% and 47% of the control, respectively.

(4) Field observation on Sitka spruce and C. vulgaris

This trial is still in progress but after 2 months it is clear that treatment with 1 kg a.i./ha glyphosate as the Ethomeen S12 salt has almost completely killed the heather. Where contact was made with the lower branches of the Sitka spruce, damage was caused but needle analysis of upper undamaged foliage indicates marked improvement in nitrogen content. Similar effects have been obtained with 2.5 kg a.i./ha Roundup. Unfortunately, no dose-for-dose comparison is possible but the results suggest that glyphosate formulated as the Ethomeen S12 salt is considerably more phytotoxic than Roundup.

TABLE 7

Effect of glyphosate formulations on E. repens. Fresh wt. of regrowth after 29 days (g). Treatment with 0.25 kg a.i./ha glyphosate

Formulation	Time to foliage wash		Mean
	10 min	2 h	
Roundup	2.8	2.1	2.4
Roundup + 5 g/l Ethomeen T25	0.8	1.0	0.9
Ethomeen S12 salt in paraffin, dispersed in water	5.0	4.1	4.5

Untreated control 5.4
Standard error Body of Table 0.55
(52 df) Formulation means 0.39

TABLE 8

Effect of glyphosate formulations on E. repens. No. of emerged shoots 14 days after rhizomes were fragmented and replanted. Mean effects of 0.25 kg a.i./ha and 0.5 kg a.i./ha glyphosate

	Formulation			
Surfactant	Roundup		Ethomeen S.12 salt (as emulsifiable concentrate)	
	Ammonium sulphate			
	Nil	50 g/l	Nil	50 g/l
None	4.4	2.6	3.9	0.8
5 g/l Ethomeen C12	1.6	0.6	3.6	6.9
5 g/l Ethomeen C15	3.3	0.3	1.2	0.0
5 g/l Ethomeen T25	0.6	0.7	1.8	1.2

Untreated control 28.9
Standard error, Body of Table 0.98
(124 df)

TABLE 9

Effect of glyphosate formulations on E. repens. No. of emerged shoots 30 days after rhizomes were fragmented and replanted. Mean effects of 0.5 kg a.i./ha and 1 kg a.i./ha glyphosate

	Roundup		Ethomeen S-12 salt (as emulsifiable concentrate)	
	Adjuvants*			
Time to foliage washing	-	+	-	+
4 h	89	53	60	26
24 h	27	6	13	4

Untreated control 160
Standard error, Body of Table 7.8

* 50 g/l ammonium sulphate with 5 g/l Ethomeen T25

DISCUSSION

In an interim report, lengthy discussion is probably not appropriate. However it is clear that salts made by reacting glyphosate with amine surfactants can have unusual and potentially useful properties. At present only the Ethomeen S12 salt has received much attention, but others may repay investigation. The use of these derivatives provides a method of formulating glyphosate in oil, which has apparently not been available previously. As has been shown, the Ethomeen S12 salt apparently passes readily through bark (Table 2). It may however sometimes be less mobile within plants than water soluble formulations (Tables 3, 4).

Formulating the salt in xylene with an emulsifier appeared to improve its phytotoxicity, but no direct comparison has been made between this formulation and the water- or paraffin-based dispersion used in earlier experiments. The phytotoxicity of the emulsifiable formulation to herbaceous plants was similar to that of the commercial formulation, Roundup. As with Roundup, adjuvants often improved phytotoxicity (Tables 8, 9). However, a mixture with ammonium sulphate and Ethomeen C12 surfactant, which increased Roundup activity, was strongly antagonistic with the Ethomeen S12 salt (Table 8). This result is difficult to explain and may repay investigation. Interactions between ammonium sulphate and an oil soluble herbicide are not known to have been demonstrated previously, activation normally being associated only with water soluble formulations (Turner & Loader, 1984).

The data shown in Table 9 suggest that Ethomeen S12 salt with appropriate adjuvants may have more effect than Roundup when rain occurs within a few hours of spraying. This result may be worth exploring further; a formulation technique which improves rainfastness is likely to be of practical interest.

Interesting results were also obtained with free glyphosate acid. When applied to the ends of cuttings this treatment was as phytotoxic as Roundup. However, glyphosate acid was much less active as a foliage spray, unless surfactants and/or ammonium sulphate were added. When this was done, its phytotoxicity was equivalent to that of Roundup. The responses of the free acid to adjuvants appear to be identical with those of isopropylamine salt or Roundup (Turner & Loader, 1980). It is possible that an ion exchange reaction takes place when the acid and the amine surfactant are mixed in solution. It has been noticed that glyphosate acid is much more soluble in Ethomeen T25 solution than in pure water.

It is premature to discuss the practical implications of this work; in particular, the cost of making surfactant salts is unknown. However the formulations may find special uses where Roundup is inactive, for example for bark applications or for treating dormant heather. The results of the field observation trial suggest that the Ethomeen S12 salt may be more phytotoxic than Roundup to conifer crops. This activity may be of interest for the control of dense natural regeneration of conifers, and also indicates that trials on other waxy-leaved woody plants such as Rhododendron ponticum L. might prove fruitful.

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REFERENCES

Anon (1980) Pesticide Analytical Manual. Food and Drug Administration Washington, D.C., Pesticide Regional Section, 180.364.

Baird, D.D.; Upchurch, R.P.; Homesley, W.P.; Franz, J.E.; (1971) Introduction of a new broad spectrum post emergence herbicide class with utility for herbaceous perennial weed control. Proceedings, 26th North Central Weed Conference, 64-68.

Franz, J.E. (1979) Glyphosate and related chemistry. In Advances in Pesticide Science. Symposium papers presented at the 4th International Congress of Pesicide Chemistry, Zurich, July 1978. (Ed. H. Geissbuhler), 139-147.

Ivens, G.W. (1972) Movement of herbicide applied to cut ends of Populus x gelrica stems. Weed Research 12, 272-283.

Jansen, L.L. (1965) Herbicidal and surfactant properties of long-chain alkylamine salts of 2,4-D in water and oil sprays. Weeds 13, 123-130.

Roberts, H.A. (ed) (1982) Weed control handbook: principles. 7th edn. Blackwell Scientific Publications, Oxford.

Sale, J.S.P.; Tabbush, P.M.; Lane, P.B. (1983) The use of herbicides in the forest - 1983. Forestry Commission Booklet 51.

Sterrett, J.P. (1965) Brush control with oil soluble amines and wettable powder acid formulations of 2,4-D and 2,4,5-T. Proceedings 18th Southern Weed Control Conference, 396-405.

Tottman, D.R.; Makepeace, R.J. (1979) An explanation of the decimal code for growth stages of cereals with illustrations. Annals of Applied Biology 93, 221-234.

Turner, D.J. (1973) Laboratory experiments on "cut bark" treatments with herbicides, using cuttings of Populus x euroamericana 1-78. Weed Research 13, 91-100.

Turner, D.J.; Cussans, G.W. (1981) Techniques for the assessment of perennial grass weeds. Proceedings Association of Applied Biologists Conference, Grass Weeds in Cereals in the United Kingdom, Reading University, 6-7 Jan. 1981, 109-114.

Turner, D.J.; Loader, M.P.C. (1974) Studies with solubilized herbicide formulations. Proceedings 12th British Weed Control Conference, 177-184.

Turner, D.J.; Loader, M.P.C. (1980) Effect of ammonium sulphate and other additives on the phytotoxicity of glyphosate to Agropyron repens (L.) Beauv. Weed Research 20, 139-146.

Turner, D.J.; Loader, M.P.C. (1984) Effect of ammonium sulphate and related salts on the phytotoxicity of dichlorprop and other herbicides used for broadleaved weed control in cereals. Weed Resarch 24, 67-77.

THE EFFECT OF A SURFACTANT ON ALLOXYDIM-SODIUM AND SETHOXYDIM POTENCY

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ABSTRACT

The purpose of this study was to assess the bioactivity of alloxydim-sodium in winter wheat and sethoxydim in winter barley when increasing amount of a surfactant was added to the spray solution.

In a factorial experiment, winter wheat grown in greenhouse, was sprayed with 5 doses of alloxydim-sodium at six levels of a 82% mineral oil surfactant 'Fevinol Plus'. The sethoxydim experiment was designed almost similar to the above-mentioned but used winter barley as a test plant and was run out-doors.

The results indicated that in neither experiments did 'Fevinol Plus' affect plant growth when applied alone. Hence, the six herbicide dose response curves, each representing a surfactant level, were assumed parallel when the plant response was plotted against the logarithm of the herbicide dose, and thus the relative potencies between the herbicide applied alone and with different levels of surfactant were independent of response-level considered.

In both experiments the surfactant promoted the action of the herbicide increasingly with increasing amount of surfactant added to the spray solution. The relationship between alloxydim-sodium and sethoxydim potency and amount of surfactant in the spray solution was linear on a logarithmic scale, but the straight line fit for alloxydim-sodium and sethoxydim had different location probably caused by different herbicide and test plant.

INTRODUCTION

The purpose of adding surfactants to a spray solution is, among other things to increase the adherence of droplets to leaves and to facilitate rapid penetration into living plant tissue (Bayer & Lumb 1973; Chow & Mac Gregor 1983). Another aspect is the economic consideration of reducing the dose of a relatively expensive herbicide by adding a relatively inexpensive surfactant to the spray solution without loss of efficacy.

An approach to measuring the effect of surfactants on herbicidal activity is to rank the herbicide according to the dose required to yield similar biological response. For example, if we assume that the surfactant in itself is a biologically inert substance when applied alone, then the dose response curves of the same herbicide in a spraying solution with various concentrations of the surfactant all ought to be parallel, their horizontal displacements being a measure of the potency of the herbicide relative to some standard preparation (Streibig 1984). A first approach to analysing such data is to formulate a hypothesis for whether or not surfactants affect the plant growth when acting alone. An extensive outline of how to design and test this kind of assays is given by Finney (1978, 1979).

The purpose of this study was to assess how increasing amount of a surfactant affected the potency of alloxydim-sodium and sethoxydim in winter wheat and winter barley.

THE PARALLEL LINE ASSAY

To succintly express the results of an experiment with different spray solutions containing the same active ingredients, but with various amounts of a surfactant, the principles of parallel line assay could be a first approach. The parallel line assay implicitly presupposes that if a dose ($\underline{z}_s$) of a standard (S) and a dose ($\underline{z}_t$) of a test preparation (T) contain the same active constituents, all other constituents are considered biologically inert, then the relative potency

$$\underline{p} = \underline{z}_s/\underline{z}_t$$

must be independent of the response level considered. If the response curve of the standard is

$$\underline{U}_s = \underline{a} + \underline{b}\cdot\log(\underline{z})$$

then the response curve for the test preparation must be

$$\underline{U}_t = \underline{a} + \underline{b}\cdot\log(\underline{pz}).$$

As shown elsewhere (Finney 1978) this can be generalized to also include non-linear response-curves.

In the terminology of Finney (1978) the present kind of assay is a comparative assay and need not have any validity under condition other than those of its estimations. This is because a surfactant, although almost inert when applied alone, may have a certain effect on for example the adherence of droplets to leaves and/or on the cuticule itself and hence the absorption of the herbicides. The potency of a test relative to a standard therefore would inevitably vary among species having different leaf surface characteristics. An extensive outline of how to distinguish between a so-called comparative assay with limited validity and an analytical assay with general validity, in which the relative potency being independent of the test plant used, is given by Jerne & Wood (1949) and Finney (1978).

MATERIALS AND METHODS

The experiment with winter wheat (cv. Kraka), conducted in a greenhouse, had a factorial lay-out with three complete randomised blocks (Table 1). Twenty test plants grew in 8 l pots containing a mixture of soil and peat (7:3) and were sprayed (Teejet 11002 nozzle; 2.8 bar; 120 l ha^{-1}) with alloxydim-sodium (75% w/w) and a 82% mineral oil surfactant 'Fevinol Plus' (Manufacturer ROL-Vendite Prodotti Chemic, Milano) at the 4-5 leaf stage. The seedlings were harvested 28 days following spraying. This experiment has previously been analysed by polynomial regressions and contour plots (Streibig & Thonke 1983).

Twenty winter barley seedlings (cv. Igri) were grown out-door in 8 l pots, containing soil/peat mixture, and were sprayed (Teejet 11003 nozzle; 200 l ha^{-1}) at the 4-5 leaf stage with sethoxydim (20% w/w) and 'Fevinol Plus'. The experimental lay-out with three complete randomised blocks (Table 2) aimed at dose ranges of sethoxydim that described the whole response curve from almost no effect at small doses to complete kill at large doses within each level of surfactant. The seedlings were harvested 21 days following spraying.

TABLE 1

Experimental lay-out of the alloxydim-sodium assay

Surfactant l/ha	Alloxydim-Sodium kg a.i./ha 0.00	0.05	0.15	0.45	1.35
0.00	x	x	x	x	x
0.11	x	x	x	x	x
0.33	x	x	x	x	x
1.00	x	x	x	x	x
3.00	x	x	x	x	x
9.00	x	x	x	x	x

TABLE 2

Experimental lay-out of the sethoxydim assay

Surfactant l/ha	Sethoxydim kg a.i./ha 0.000	0.002	0.006	0.020	0.060	0.120	0.540
0.00	x			x	x	x	x
0.11	x			x	x	x	x
0.33	x			x	x	x	x
1.00	x		x	x	x	x	
3.00	x		x	x	x	x	
9.00	x	x	x	x	x		

A sigmoid model

$$E(U) = (D-C)/\{1 + \exp[-2(a + b \cdot \log(z))]\} + C \; ; \; b < 0$$

was fitted simultaneously to each of the six response curves, one for each level of the surfactant. Each response curve within an experiment was supposed to have similar D, C, a, and b parameters. The different horizontal locations of the response curves of the test preparations with surfactant relative to the response curve of the pure herbicide were defined by $\log(pz)$ where p is the relative potency. The upper limit D denotes the expected plant response, $E(U)$, at zero dose whilst the lower limit, C denotes the value of $E(U)$ at large doses. The linear term $\{a + b \cdot \log(z)\}$ shows that the responses on a logit-scale can be represented as straight lines (Finney 1978).

In neither experiments was there any significant block effect. The method of fitting the response curve simultaneously, stabilizing the variance within doses as well as analysing the goodness of fit have been described previously (Streibig 1983; 1984).

RESULTS AND DISCUSSION

Alloxydim-sodium

The surfactant applied separately had only a slight effect on winter wheat growth. The untreated control yielded 230 g fresh weight per pot whilst

9 l/ha surfactant only reduced the yield to 220 g/pot. The result can therefore warrant the conclusion that the surfactant doses used did not affect the plant growth *per se*.

Previous analyses of these data showed a significant interaction between the effect of alloxydim-sodium and surfactant, and a contourplot clearly showed enhanced efficacy of the herbicide when mixed with surfactant (Streibig & Thonke 1983). The interaction was brought about by the dose-range for alloxydim-sodium, covering the whole range from virtually no effect to complete kill (Fig. 1).

Another way of analysing this kind of experiments is to measure the potency of alloxydim-sodium + surfactant relative to the potency of alloxydim-sodium applied alone. In contrast to an analysis of variance that concerns itself with differences in effect at particular dose-levels, the objective of applying the method of parallel line assay is to measure the horizontal displacement of the alloxydim-sodium + surfactant curves, i.e. to estimate biologically equivalent doses.

The assumption of parallel lines was not rejected (Table 3; Fig. 1) neither by a F-test for lack of fit ($F_{23,57} = 1.23$), nor by graphical analyses of the residuals. The relative potencies were thus independent of response level and increased with increasing amount of surfactant in the spray solution (Table 4).

TABLE 3

Summary of regression analyses. Standard deviation in parenthesis. The potency estimates are given in Tables 4 and 5.

Parameter estimates			
Upper limit D g/pot	Lower limit C g/pot	logit= $-(\underline{a} + \underline{b}\cdot\log(\underline{z}))$	ED_{50}* kg a.i./ha
	Alloxydim-sodium		
	Winter wheat		
229.84 (7.32)	14.18 (0.41)	1.632 + 2.121 log(z) (0.061) (0.099)	0.170 (0.011)
	Sethoxydim		
	Winter barley fresh weight		
272.34 (6.79)	7.31 (0.42)	3.308 + 3.830 log(z) (0.152) (0.209)	0.137 (0.005)
	Winter barley dry matter		
34.32 (0.59)	3.65 (0.13)	2.761 + 3.217 log(z) (0.140) (0.183)	0.139 (0.005)

*ED_{50}= antilog ($-\underline{a}/\underline{b}$)

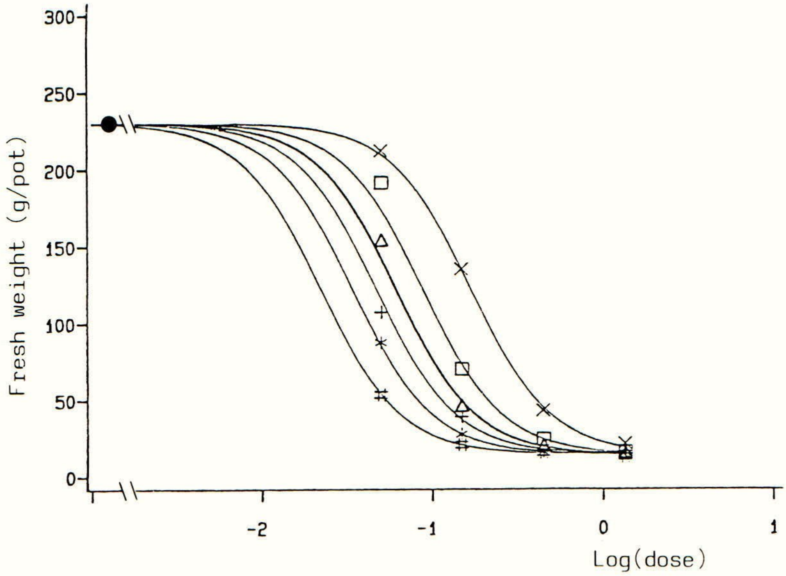

Fig. 1. Dose response curves of alloxydim-sodium on winter wheat applied alone (×) and with 0.11 (□), 0.33 (Δ), 1.00 (+), 3.00 (∗), 9 l surfactant/ha (#) and untreated control (●).

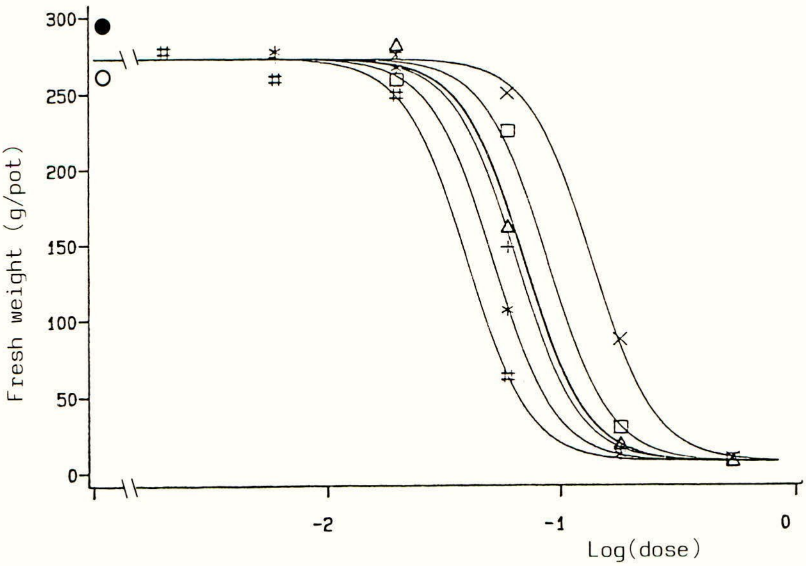

Fig. 2. Dose response curves of sethoxydim on winter barley. Symbols as in Fig. 1. 9 l surfactant without sethoxydim (○).

TABLE 4

The potencies of alloxydim-sodium + surfactant relative to alloxydim-sodium applied separately in winter wheat. Approximate 95% confidence interval in parenthesis.

Surfactant l/ha	Relative potency
0.11	1.937 (0.240)
0.33	2.779 (0.427)
1.00	3.638 (0.560)
3.00	4.205 (0.775)
9.00	7.651 (1.205)

Sethoxydim

In this assay winter barley yielded 292 g fresh weight per pot in the untreated control whereas 9 l surfactant in spray solution without sethoxydim yielded 262 g/pot. This 10% decrease in plant growth is significant and therefore assuming parallel lines is only an approximation. The analysis, however, following the same line as for the alloxydim-sodium assay was neither rejected for fresh weight (test for lack of fit $F_{23,58}$ = 0.41) nor for dry matter (test for lack of fit $F_{23,58}$ = 1.59) (Table 3; Fig. 2). The potency estimates were almost identical for fresh weight and dry weight (Table 5).

TABLE 5

The potency of sethoxydim + surfactant relative to sethoxydim applied separately in winter barley. Approximate 95% confidence interval in parenthesis.

Surfactant	Relative potency	
l/ha	Fresh weight	Dry matter
0.11	1.544 (0.130)	1.551 (0.137)
0.33	1.931 (0.198)	1.911 (0.227)
1.00	2.085 (0.223)	2.133 (0.264)
3.00	2.622 (0.289)	2.505 (0.313)
9.00	3.404 (0.352)	3.460 (0.388)

Another out-door experiment with alloxydim-sodium and winter barley, the objective of which was somewhat different from the above mentioned also included 'Fevinol Plus' at 3 l/ha (Data not shown). In this assay the ED_{50} for alloxydim-sodium was 0.226 (s=$\pm$ 0.023) and gave a relative potency of 2.606 (95% confidence interval $\pm$ 0.235) and thus is very similar to that of sethoxydim in Table 5.

Comparison of experiments

In both experiments the surfactant promoted the action of the herbicides increasingly with increasing doses of surfactant. This corresponds with the findings of Foy & Smith (1965) who showed that surfactants, although differing considerably in their influence on surface tension and wetting ability, all markedly enhanced the bioactivity of herbicides, increasingly with rate.

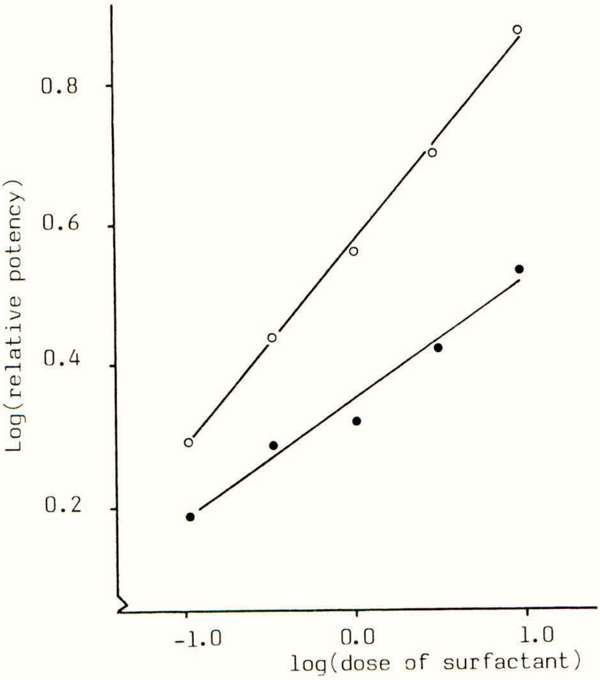

Fig. 3. Plots of the relative potency of alloxydim-sodium (O) in winter wheat and sethoxydim (●) in winter barley against the dose of surfactant in the spray solution.

Plotting the logarithm of the relative potency against the logarithm of surfactant dose (Fig. 3) clearly showed linear relationships but different locations, probably caused by different herbicide, test plant and environment. The results in Fig. 3 are general as they apply to all response levels considered.

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REFERENCES

Bayer, D.E.; Lumb, J.M. (1973) Penetration and translocation of herbicides. In: Pesticide Formulations. W. Van Valkenberg (Ed), Marcel Dekker, Inc. New York, pp 387-439.

Chow, P.N.P; MacGregor, A.W. (1983) Effect of ammonium sulfate and surfactants on activity of the herbicide Sethoxydim. Journal of Pesticide Science 8, 519-527.

Finney, D.J. (1978) Statistical Method in Biological Assay. C. Griffin & Co. London.

Finney, D.J. (1979) Bioassay and the practice of statistical inference. International statistical review 47, 1-12.

Foy, C.L.; Smith, L.W. (1965) Surface tension lowering wettability of paraffin and corn leaf surfaces, and herbicidal enhancement of dalapon by seven surfactants. Weeds 13, 15-18.

Jerne, N.K.; Wood, E.C. (1949) The validity and meaning of the results of biological assays. Biometrics 5, 273-299.

Streibig, J.C; Thonke, K.E. (1983) Fitting equations to herbicide bioassays: Using response surfaces in factorial design. Symposium Bioassay in Weed Science. Berichte aus dem Fachgebiet Herbologie der Universität Hohenheim 24, 183-193.

Streibig, J.C. (1983) Fitting equations to herbicide bioassays: Using the methods of parallel line assay for measuring joint action of herbicide mixtures. Symposium Bioassay in Weed Science. Berichte aus dem Fachgebiet Herbologie der Universität Hohenheim 24, 183-193.

Streibig, J.C. (1984) Measurement of phytotoxicity of commercial and unformulated soil-applied herbicides. Weed Research 24, 237-331.

THE EFFECT OF A SURFACTANT/OIL MIXTURE AND APPLICATION METHOD ON THE ACTIVITY OF DICHLORPROP FOR THE CONTROL OF BROAD-LEAVED WEEDS IN SPRING BARLEY

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ABSTRACT

In a single field experiment the influence of volume rate, application method and the addition of a surfactant/oil mixture on the activity of dichlorprop for the control of broad-leaved weeds in spring barley was investigated. The herbicide was applied at three doses, 0.5, 1.0 and 2.0 kg a.i./ha, and at three spray volume rates; 15 l/ha, using rotary atomizers and 60 and 240 l/ha using hydraulic nozzles. Treatments were applied with and without a surfactant/oil mixture, added at 5.0% v/v. All applications were made when the crop was fully tillered. Initial scores suggested some increase in herbicide activity where the surfactant/oil mixture was added to the spray solution. Final assessments, however, indicated that apart from the main effect of dose, differences between treatments were largely confined to volume rate. There were no differences between hydraulic nozzle treatments at either 240 or 60 l/ha but both were better than rotary atomizer treatments at 15 l/ha particularly at the highest dose rate. The overall effect of the surfactant/oil mixture was not significant, however at the intermediate dose applied at 240 l/ha its addition improved the level of weed control.

INTRODUCTION

The application of herbicides to cereals using spray volume rates of less than 100 l/ha offers considerable logistic advantages and improvements in spray timeliness. However some herbicides, notably those that are either contact or partially contact in effect, can lose biological activity, regardless of application method, when applied at these lower spray volumes. Whilst the performance of translocated herbicides applied at spray volumes of 40-45 l/ha are substantially unchanged poorer weed control can result when volume rates are further reduced (Ayres 1976, Ayres & Merritt 1978) There is, therefore, considerable scope for improving both the reliability and consistency of herbicides at lower spray volumes. At present most application studies are made using agrochemicals formulated to be applied through hydraulic nozzles at spray volume rates in excess of 100 l/ha. Whilst the costs of reformulating existing products may not be commercially attractive the addition of surfactants to low volume sprays has both biological and economic potential.

Previous field work (Taylor *et al.* 1982) suggested that a surfactant /oil mixture (designated as Mixture PF) could improve control of *Avena fatua* by difenzoquat with both hydraulic nozzle and rotary atomizer treatments.

In addition, pot experiments have indicated that the activity of dichlorprop salt might also be enhanced with this mixture. Further field testing was required and this paper describes a single field experiment to investigate the influence of volume rate, application method and the surfactant/oil mixture (hereafter refered to as Mixture B) on the activity of dichlorprop for the control of broad-leaved weeds in spring barley.

MATERIALS AND METHOD

The experiment was set up in spring barley at Lockinge Estate near Wantage, Oxon in 1982. A split plot randomised block design was used containing four replicates. Each replicate measured 70 x 12 m and comprised ten main plots measuring 7 x 12 m. Within each main plot were two sub-plots, measuring 2.5 x 12 m, separated by a 2 m pathway. Replicates were separated by a 2.5 m pathway and the entire experiment measured 70 x 55.5 m.

Dichlorprop salt was applied at three doses, 0.5, 1.0 and 2.0 kg a.i./ha, and at three volume rates, 15, 60 and 240 l/ha using either hydraulic nozzle or rotary atomizer equipment. Treatments were split to include Mixture B which was added to the spray solutions at 5.0% v/v. Details of its chemical composition are given in Table 1.

TABLE 1

Chemical composition and ratio of constituents contained in Mixture B

Product	Ratio (% v/v)	Chemical composition	Supplier
Agral	16.5	Non-ionic wetting agent containing 90% alkyl phenol ethylene oxide condensate	I.C.I Plant Protection
Ethylan D252	16.5	Non-ionic synthetic primary alcohol - ethylene oxide condensate containing 28% ethylene oxide	Lankro Chemicals Ltd
Esso Blue	67.0	Premium grade domestic paraffin	Esso

Hydraulic nozzle treatments were applied at 60 and 240 l/ha using equipment mounted on a light weight vehicle described by Ayres (1984). The boom was fitted with Spraying Systems 8003 'TeeJet' nozzles placed at 0.5 m spacing and the herbicide solution was delivered at a pressure 210 kPa. The desired spray volume rate was achieved by increasing forward speed from 5 km/h (240 l/ha) to 20 km/h (60 l/ha).

Rotary atomizer treatments were applied at 15 l/ha using the Richmond Gibson CDA Sprayer (Hind, 1978) with two units of stacked discs. The herbicide solution was delivered from an independent CO_2 pressurized container and feed to the discs was controlled by fitting a Spraying Systems Orifice Plate, Number 4916-18 into the spray line immediately before the spray head. At a pressure of 105 kPa a constant flow of 120 mls/min to the head was achieved. A single drop size of 250 µm in diameter was used by rotating the discs at a speed of 1700 rev/min. The desired spray volume rate was achieved by calibrating the flow of herbicide to the discs, measuring the swath width and then adjusting the forward walking speed to 3.7 km/h.

Treatments were applied on 28 May 1982 when the crop had 5-6 leaves unfolded (GS 15-16 Zadoks *et al* 1974). The predominant weed was *Fumaria officinalis* with some *Stellaria media* and *Bilderdykia convolvulus*. Initial treatment effects on *F. officinalis* were assessed by visual scores eleven days after application. Final treatment effects were assessed six weeks after application by removing all surviving weeds from within five 1 x 1 m quadrats selected at random on each plot. Samples were dried for 24 hrs at 100^oC and then weighed.

RESULTS

TABLE 2

Scores for the initial effects of volume rate, dose rate and Mixture B on the activity of dichlorprop on *F. officinalis*. (0 = complete kill, 10 = as control)

	Dose (kg a.i./ha)					
	0.5		1.0		2.0	
Mixture B (5.0% v/v)	-	+	-	+	-	+
Volume rate (l/ha)						
15	5.3	4.3	5.3	3.5	3.5	2.5
60	4.8	4.5	3.8	2.3	2.8	1.5
240	4.5	3.3	3.8	3.0	3.0	2.0
S.E. of treatment means			± 0.59			
Unsprayed control			10.0			

Initial treatment scores (Table 2) indicated there was an overall effect of surfactant on the activity of dichlorprop against the predominant species present, *F. officinalis*. Dose respose was only evident at 15 and 60 l/ha whilst the effect of volume rate at this first assessment was not apparent.

TABLE 3

Influence of application method, volume rate and Mixture B on the activity of dichlorprop for the control of broad-leaved weeds (g dry weight/5 m^2).

	Dose (kg a.i./ha)					
	0.5		1.0		2.0	
Mixture B (5.0% v/v)	-	+	-	+	-	+
Volume rate (l/ha)						
15	5.72(1.74)	4.72(1.67)	6.01(1.75)	5.07(1.63)	4.73(1.64)	4.54(1.65)
60	3.58(1.54)	3.65(1.51)	2.68(1.36)	4.32(1.60)	1.87(1.19)	1.25(1.07)
240	5.42(1.73)	3.21(1.50)	4.35(1.55)	1.57(1.04)	0.91(0.94)	1.25(1.01)
S.E. of treatment means			± (0.120)			
Unsprayed control			29.72 (2.39)			
S.E. of control mean			± (0.102)			

Transformed data in brackets - Log_{10} (n x 10)

TABLE 4

Influence of volume rate and Mixture B (mean of three doses) on the activity of dichlorprop for the control of broad-leaved weeds (g dry weight/5 m^2).

	Mixture B (5.0% v/v) -	+	Mean	S.E. of volume rate means
Volume rate (l/ha)				
15	5.59(1.71)	4.78(1.65)	5.13(1.68)	
60	2.71(1.36)	3.07(1.39)	2.89(1.38)	± (0.059)
240	3.56(1.41)	2.01(1.18)	2.79(1.30)	
S.E. of treatment means	± (0.069)			
Mean	3.92(1.49)	3.29(1.41)		
S.E. of Mixture B means	± (0.030)			

Transformed data in brackets - Log_{10} (n x 10)

Dry weight assessments of the total broad-leaved weed population (Tables 3 and 4) show the main effect of both dose rate and spray volume to be significant. Differences in weed control due to volume rate rate were most marked at the highest dose where applications at 60 l/ha and 240 l/ha with hydraulic nozzles were better than the rotary atomizer treatment at 15 l/ha. Overall, the addition of surfactant did not improve weed control, however there was a significant response at 240 l/ha particularly at the intermediate dose rate.

DISCUSSION

Although the initial object of the experiment reported in this paper concerned the improvement in performance of dichlorprop, other aspects of the data also serve to confirm previous findings relating to low volume spraying. Neither the low volume rotary atomizer nor hydraulic nozzle treatments allowed a reduction of herbicide dose rate without corresponding loss of weed control. A reduction of 85% in dry weight of weed from the rotary atomizer treatment without Mixture B was not unexpected. Previous work (Ayres & Merritt 1978) has shown a similar reduction in broad-leaved weed control of some species from a mixture of dicamba, mecoprop and MCPA applied at the same spray volume rate. Further evidence of the effectiveness of high speed low volume spraying using hydraulic nozzles was also demonstrated. This technique allows the reduction of spray volume rate without increasing the risk of drift and has considerable practical advantages when allied with a light weight low ground pressure vehicle.

The lack of activity from the addition of Mixture B to the rotary atomizer treatments was disappointing. The initial treatment scores suggested some increase in herbicide activity but this was not evident in the final assessment on total weed dry weight. Although previous pot tests with this mixture had indicated the possibility of enhancing the performance of dichlorprop, the results from this field experiment do not confirm these findings. In earlier field work with difenzoquat (Taylor et al 1982) Mixture B improved control of A. fatua with both hydraulic nozzle and rotary atomizer treatments. The surfactant mixture markedly increasing the area of A.fatua leaves wetted by the rotary atomizer treatments and greatly reduced the difference between the two types of application. In the experiment reported here the only enhancement of activity occured at 240 l/ha. Other work (Clipsham, 1984) demonstrated increased activity of glyphosate and hexazinone against forest crop and weed species following the addition of Mixture B at spray volume rates of between 200 and 250 l/ha. The study also indicated that while the mixture had little effect on spray retention uptake was greatly increased. However the rate at which the mixture was added to the spray solution was twice that used in the experiment reported in this paper. Increasing the rate for use in cereals may lead to greater weed control but also may cause unacceptable crop scorch.

While results from a single experiment should be treated with caution they remain of interest as indicating a varying response in herbicide activity from the possible use of surfactants and spray additives. These treatments may serve to either increase or decrease activity depending on the herbicide or even weed species. In addition they may interact with spray volume rate and application method as indicated by Midgley (1982). Thus, selecting the appropiate surfactant or spray additives to match the herbicide, method of application or weed species, may present too many difficulties for all combinations to be fully examined. Nevertheless this approach for low volume rotary atomizer applications may have more potential than the present method of opting for greater drop cover by using smaller drops. The use of smaller drops is a short term answer and immediately increases the risk of drift.

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REFERENCES

Ayres, P (1976) Control of annual broad-leaved weeds in spring barley by controlled drop application: comparisons of the activity of two herbicide mixtures at three doses and four volume rates. Proceedings British Crop Protection Conference - Weeds, 895-904

Ayres, P. (1984) A vehicle mounted multiple treatment experimental plot sprayer Proceedings Sixth International Conference on Mechanisation of Field Experiments, 153-159

Ayres, P.; Merritt, C.R. (1978) Field experiments with controlled drop applications of herbicides for the control of dicotyledonous weeds. Weed Research, 1978, 18, (4), 209-214

Clipsham, I.D. (1984) The effect of an oil-surfactant additive on activity and leaf entry of hexazinone and glyphosate. Aspects of Applied Biology, 4, Weed Control and Vegetation Management in Forests and Amenity Areas, 143-150

Hind, N.J. (1978) The Richmond Gibson controlled drop application trials sprayer. British Crop Protection Council Monograph, 22, 117-119

Midgley S.J. (1982) Effects of surfactants on phenoxyalkanoic herbicides: a preliminary report. Aspects of Applied Biology, 1, Broadleaved Weeds and their Control in Cereals, 193-200

Taylor, M.J.; Ayres, P.; Turner, D.J. (1982) Effect of surfactants and oils on the phytotoxicity of difenzoquat to Avena fatua, barley and wheat. Annals of Applied Biology, 100, (2), 353-363

Zadoks, J.C.; Chang, T.T.; Konzak, C.F. (1974) A decimal code for the growth stage of cereals. Weed Research, 14, 415-421