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**FEASIBILITY OF USING
RAPESEED OIL AS A CARRIER
IN PESTICIDE APPLICATIONS**

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FEASIBILITY OF USING RAPESEED OIL AS A CARRIER IN PESTICIDE APPLICATIONS

by

E. C. HISLOP, A. MALARIN, N. M. WESTERN AND M. BIESWAL

IACR Long Ashton Research Station, Department of Agricultural Sciences,

University of Bristol, Long Ashton, Bristol BS18 9AF

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SUMMARY

A commercial twin-fluid nozzle coupled with an electric gear pump was used to apply rapeseed oil to several plant species at volume rates of less than 10 l/ha. An aqueous spray system delivering 220 l/ha was used for comparison. The droplet spectra of the oil sprays were extremely fine compared to the aqueous system and were only variable to a limited degree by alterations to oil flow rate and air pressure.

Oil sprays were particularly well retained on cereal plants, deposits being seven-fold greater than aqueous sprays. On fat hen seedlings, oil deposition efficiency was increased approximately three-fold compared with water. Rapeseed oil applied to young wheat, sugar beet and tomato plants produced no visible phytotoxic symptoms or significant changes to plant weights. Topik 240EC (clodinafop-propargyl), a species-specific graminicide, applied to oat seedlings in 6 l/ha of rapeseed oil had an ED50 value of 4.0 g a.i./ha compared with an aqueous spray value of 9.0g a.i./ha. In contrast, applications of Betanal E (phenmedipham) to fat hen seedlings were less effective in oil compared with water by a factor of almost four. Topik applied to oats at two sub-lethal doses was more effective in methylated rapeseed oil than un-methylated oil while a mineral oil had an intermediate efficacy.

These results are discussed with reference to relevant literature. The practical problems relating to the use of oils as carriers for pesticides are highlighted.

INTRODUCTION

Most pesticides used in agriculture and horticulture are applied as dilute aqueous solutions, suspensions or emulsions. These liquids are usually sprayed under pressure through simple and cheap hydraulic nozzles, the orifice dimensions of which serve to regulate liquid flow. It is a characteristic of all sprays produced from hydraulic pressure nozzles that they contain a wide range of droplet sizes. Small droplets ($< \text{approximately } 100 \mu\text{m}$) with low energy are not easily transported safely to biological targets but, if they do impact on them, they are usually well retained at many sites. Droplets larger than approximately $250 \mu\text{m}$ are targeted more precisely but often poorly retained by foliage. Interactions between aqueous spray droplet sizes, spray volumes and the efficacy of pesticides is complex and often controversial. For herbicide applications, this subject has been reviewed recently by Knoche (1994).

Water, being usually readily available, cheap and non-phytotoxic, is a very suitable medium in which to dilute pesticides, so that they can be evenly distributed in small quantities at many biological sites. However, the transport of large, heavy, volumes of water is costly, has logistic penalties and can damage the soil. Further, since many biological targets have hydrophobic surfaces, it is not the ideal medium to facilitate deposition or uptake (Hassall, 1990; Holloway, 1994). To counteract such problems, pesticides to be diluted in water have to be carefully formulated in an attempt to optimise performance.

Some fifty years ago, the fungicide lime sulphur, which was usually sprayed onto fruit trees in large volumes of water, was applied undiluted, heralding the process of ultra low volume (ULV) spraying. In the intervening years, pesticides have become more active, so neat applications are now rarely an option. However, ULV spraying was developed for specialised applications, particularly in developing countries where plot sizes were small and where capital for machinery and the availability of water was limited. Hand-held rotary atomisers were developed to produce large numbers of small droplets, which were wind-borne to targets. Importantly, the pesticides were formulated in oil, rather than in water, since the latter was too volatile for many uses. Application volumes were as low as one litre per hectare and biological efficacy was very satisfactory.

The possible use of oil as a carrier for ULV pesticide applications to broad acre crops in developed agriculture was boosted by the development of the Electrodyn spraying system (Coffee, 1979). Although not now used in mainstream agriculture, this highly efficient electrostatic sprayer clearly showed the potential for oil-based spraying (Hislop *et al.*, 1983).

Oil-based sprays cannot be atomised through conventional hydraulic nozzles or through the relatively high-throughput twin-fluid nozzles currently being used for aqueous spraying. But oils can be atomised by certain twin-fluid nozzle designs as demonstrated and studied for agricultural use by McWhorter *et al.* (1988) and Hanks and McWhorter (1993).

Oils are natural products separable as two main groups, the mineral and vegetable oils. Traditionally, mineral (or petroleum) oils were used most often in crop protection (Herron *et al.*, 1995; Northover and Schneider, 1996). They are a non-renewable resource composed of linear and branched chain alkanes and the so-called naphthenes (Gauvrit, 1994). Vegetable oils are biosynthesised and, as such, are derived by the "acetate" pathway and show a distinct preponderance of compounds with an even number of carbon atoms (Hamilton, 1993). In recent years, there has been considerable interest in the use of vegetable oils as adjuvants and carriers in crop protection (Hatchard *et al.* 1989).

SCOPE AND AIMS OF THE PROJECT

Compared with water, vegetable oils are costly, potentially phytotoxic and likely to persist in the environment. Thus, we set the maximum experimental application volume rate at 10 l/ha. We worked with two herbicides and two plant species to maximise the production of biological assay results. We avoided the use of rotary atomisers and placed no emphasis on the selection of the most suitable spray delivery system.

The aims of the project were :-

1. To select and evaluate a readily available atomiser capable of spraying rapeseed oil at less than 10 l/ha.
2. Measure the foliage-retention characteristics of rapeseed oil using a suitable tracer dye, compared with the deposition of a high-volume aqueous spray.
3. Assess the phytotoxicity of oil sprays to several crop plant species.
4. Compare the activity of two herbicides applied at low volume in rapeseed oil with the same products sprayed as high volume aqueous emulsions.
5. Compare the activity of one herbicide sprayed in low volumes of rapeseed oil, methylated rapeseed oil and a mineral oil.

EXPERIMENTAL METHODS

Spray application

An industrial twin-fluid nozzle from Spraying Systems Co. (Wheaton, IL, USA) was selected to atomise oil-based sprays. This comprised a standard nozzle body with opposed apertures to receive oil and air separately. A low-flow fluid cap (No. 1650) was fitted with an external mixing air cap (No. 67228) giving a nominal 45-degree flat-fan spray. Oil was fed to the nozzle from a measuring cylinder via an electrically driven gear pump and a speed control system. Air for atomisation was delivered to the nozzle via a pressure regulator and pressure gauge. This setup is shown diagrammatically in Fig. 1, and as used in a spray chamber, in Plate 1. During use, oil flow rates were between 3-20 ml/min and air pressures varied between 6-12 kPa. For most experiments, spray speed was 1 m/sec. The nozzle to target distance was 45 cm.

Aqueous spray applications were applied in a separate spray chamber using an E015-F80 fan nozzle (Lurmark, UK) operated at 200 kPa pressure and a flow rate of 0.48 l/min. Spray speed was 0.45 m/sec and the nozzle to target distance was 40 cm.

Spray calibration and deposit measurements

Oil sprays were measured with the fluorescent tracer Uvitex OB (Ciba Geigy, UK) dissolved in xylene (3% w/v) which was added to the oil to give a final concentration of 1.5 g tracer/l. Water-based sprays were supplemented with emulsifiable Uvitex as a tracer at 0.005% w/v.

Spray volume rates on the ground directly beneath both spray nozzles were measured using polyethylene discs as artificial targets (23.6 cm²). Spray deposits on plants under the nozzles were also measured for both spray systems. Spray deposits containing Uvitex were extracted in hexane and the concentration determined using a Perkin-Elmer spectrofluorimeter with an excitation wavelength of 360 nm and an emission wavelength of 426 nm. Samples of the spray liquids were also measured to determine the exact concentration of the tracer. The recovery efficiency of tracers from artificial and natural targets was shown to be better than 95%.

The aqueous spray volume rate was constant at 220 l/ha. Oil spray rates varied between approximately 1 and 10 l/ha. To facilitate comparisons of spray deposits on plants, they were normalised as ng tracer deposited per g dry weight per g tracer applied per hectare to give deposit per unit emission (DUE).

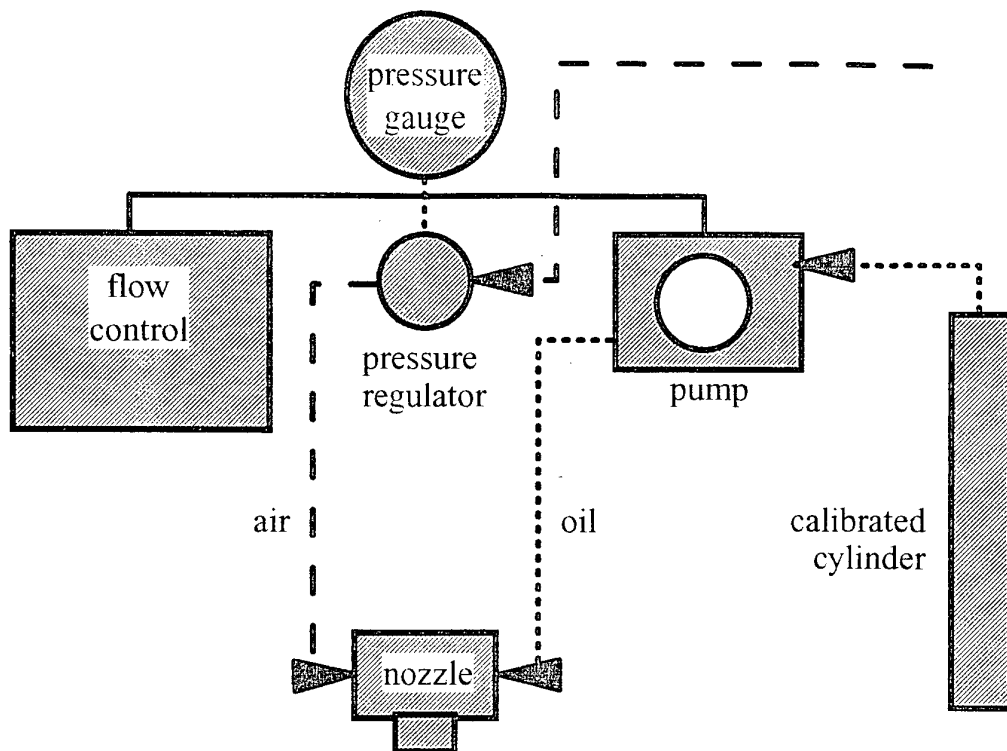


Fig. 1 Diagram of nozzle and control system

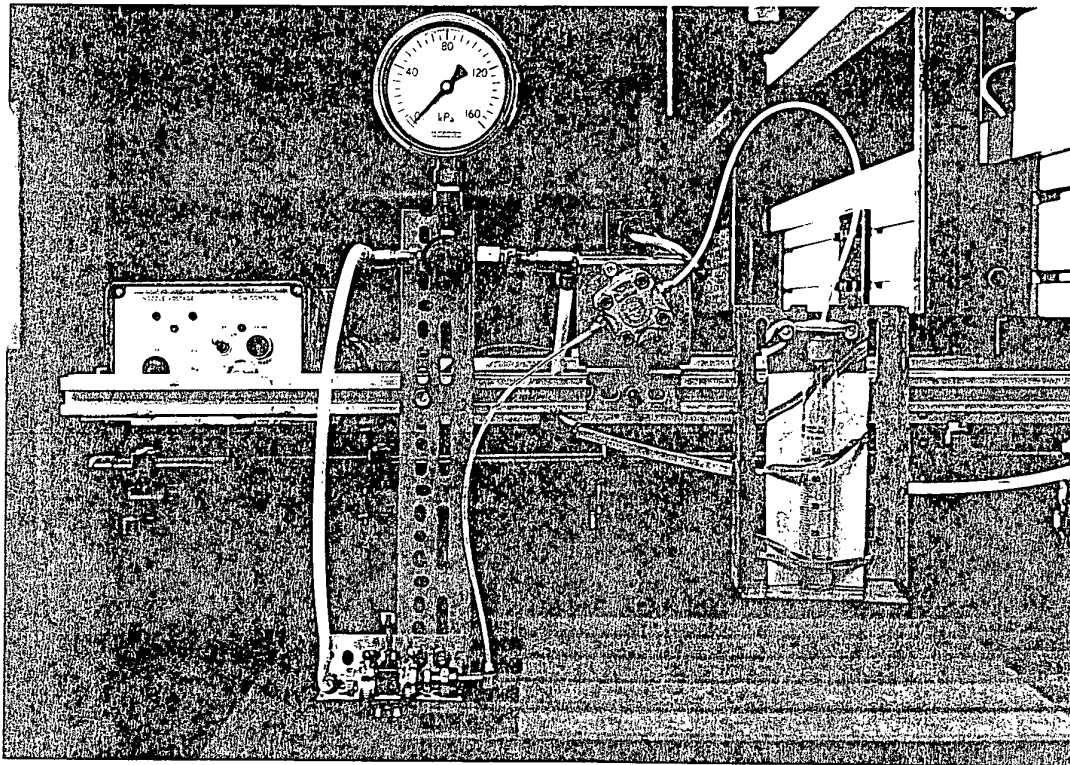


Plate 1 Nozzle and control system

Plant species

Phytotoxicity of rapeseed oil was assessed on young glasshouse-grown sugar beet (cv. Regina), wheat (cv. Longbow) and tomato (cv. Ailsa Craig) plants. All plants were grown in 9 cm square pots containing John Innes compost supplemented with Osmocote 3-4 month fertiliser at 3.3 g/l. Sugar beet and tomato plants were grown singly, while 9 oat seeds were sown per pot. Eight replicate pots of each species were sprayed with approximately 3, 6 or 9 l oil/ha and then returned to cool glasshouse benches in a fully randomised design. Plants were examined regularly for visible symptoms of phytotoxicity and then harvested for dry weight measurements after approximately two weeks of growth. No variance-stabilising transformations were necessary in data analysis.

Assessments of the toxicity of two herbicides applied in oil or water were made with oat seedlings with 2 - 3 true leaves (GS 11-12, Zadoks *et al.*, 1974), to mimic activity against wild oats, or with four fat hen (*Chenopodium album*) seedlings having 2 - 4 true leaves per pot. The plants were grown as described above. Seven replicate pots of oats and six of fat hen were used for each herbicide dose applied. Sprayed plants were kept in the glasshouse for approximately 14 days, when mortality was recorded, and the plants harvested for fresh weight measurements. Weights were transformed to log_e and ED50 values calculated from non-linear regression analysis.

Spray mixtures

Most experiments were done with low erucic rapeseed oil (Seatons, Hull, UK) with the composition shown in Table 1. The samples of methylated rapeseed oil and solvent neutral 150 mineral oil used in one experiment were also supplied by Seatons.

The herbicides examined were commercial formulations of Topik 240EC, containing 240 g/l clodinafop-propargyl plus 60 g/l clonquitocet-methyl (Ciba Geigy), and Betanal E containing 114 g/l of phenmedipham (AgrEvo). Topik was used as a mixture in rapeseed oil and applied to oat seedlings in 6 l/ha., giving doses ranging from $\times 2$ to $\times \frac{1}{32}$ of the recommended field rate of 60 g a.i./ha. Fat hen seedlings were sprayed with 10 l/ha. oil containing doses of $\times \frac{1}{2}$ to $\times \frac{1}{64}$ of the recommended maximum dose of 1140 g a.i./ha. A similar range of doses of both herbicides was also sprayed as aqueous emulsions with the addition of 0.1% v/v Agral non-ionic wetting agent (Zeneca) at the application volume rate of 220 l/ha.

Topik was also applied to oat seedlings at sub-lethal doses of 15.63 and 7.81 g a.i./ha as mixtures with rapeseed oil, methylated rapeseed oil and mineral oil at

approximately 6 l/ha.

Droplet spectrum measurements

Droplet size distributions from the twin-fluid nozzle were measured at selected oil flow rates and air pressures using a phase/doppler particle analyser (Aerometrics Inc., USA). Sprays were sampled 25 cm below the nozzle as two long-axis scans, each replicated three times.

The droplet spectrum for the hydraulic nozzle was measured in the centre of the spray fan 40cm below the nozzle, emitting 0.48 l/min of 0.1% aqueous Agral.

RESULTS

Measured oil flow rates showed a reliable correlation ($r=0.97$) with volume rates calculated from data recorded on sample discs placed under the nozzle (Fig. 2). These results were only obtained in the line parallel to the nozzle movement. Tracer recovery from discs placed 12.5 cm at each side of the centre line showed variable deposition due to turbulence affecting the fine spray cloud (Table 2).

Most of the rapeseed oil droplets produced at flow rates between 6 - 20 ml/min and air pressures between 6 - 12 kPa were very small compared with the water spray droplets (Table 3). Increasing flow rates increased the volume median diameter (VMD) and reduced their mean velocities. At a constant air pressure of 9 kPa, the maximum VMD was 62.3 μm and the minimum 49.7 μm was obtained with volumes of 20 ml/min and 6 ml/min, respectively. For a constant oil flow rate of 9 ml/min, an increase in air pressure reduced the VMD values. Maximum values were obtained at 6 kPa (VMD=58.9 μm) and the minimum at 12 kPa (VMD=49.8). The highest (3 m/s) and the lowest mean velocity (2.19 m/s) in the experiment, were obtained at 20 kPa and 6 kPa, respectively. Data are shown in Tables 3 and 4. The spray mist is shown under static conditions in Plate 2 and, in full operation, in Plate 3, where the spreading of the cloud due to movement is evident. There were no significant differences ($P<0.05$) between the DUE values recorded for the oil spray volumes examined in various experiments (Appendices 1 & 2). The mean DUE value for oats sprayed with oil was 1648, an increase of more than 6-fold compared with water-based spray deposition, where the DUE value was 252. For fat hen, the back-transformed mean DUE value of 6726 for oil, was nearly 3-fold the value for water (DUE= 2414).

No obvious phytotoxic symptoms were visible on wheat, sugar beet or tomato plants treated with volumes up to approximately 10 l/ha rapeseed oil, after 14 days. Oil

Table 1 Percentage fatty acid composition of triacylglycerols of refined rapeseed oil (low erucic)

Myristic (C14)	trace
Palmitic (C16)	4 - 6
Palmitoleic (C16:1)	trace
Stearic (C18)	1 - 2
Oleic (C18:1)	55 - 65
Linoleic (C18:2)	20 - 25
Linolenic (C18:3)	8 - 12
Arachidic (C20)	trace
Behenic (C22)	trace
Erucic (C22:1)	trace

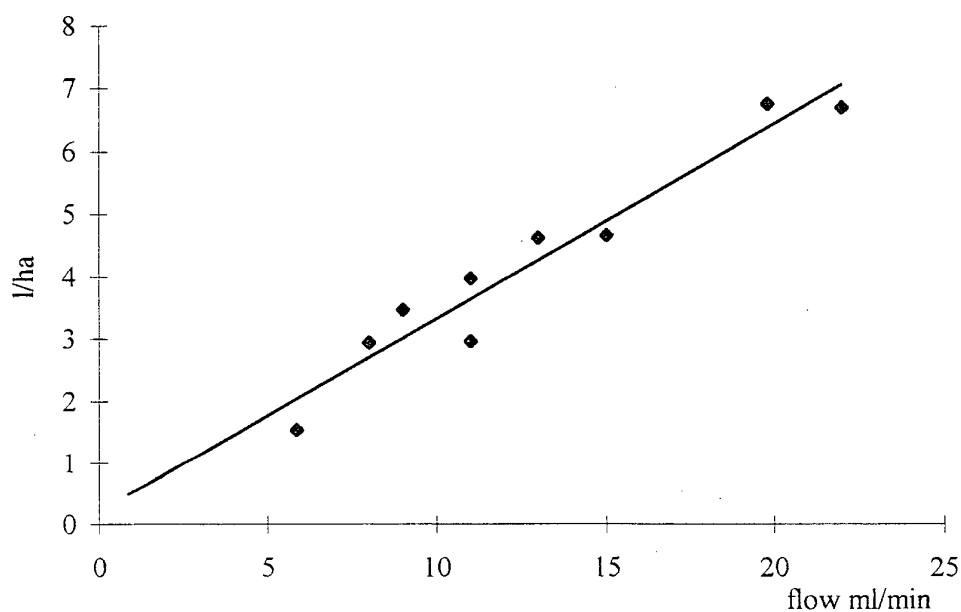


Fig. 2 Correlation between oil flow rates and application volume (l/ha) calculated from the deposit measurements on sample discs placed 0.45 m under the nozzle.

Plate 2. Characteristics of the
spray mist under static conditions

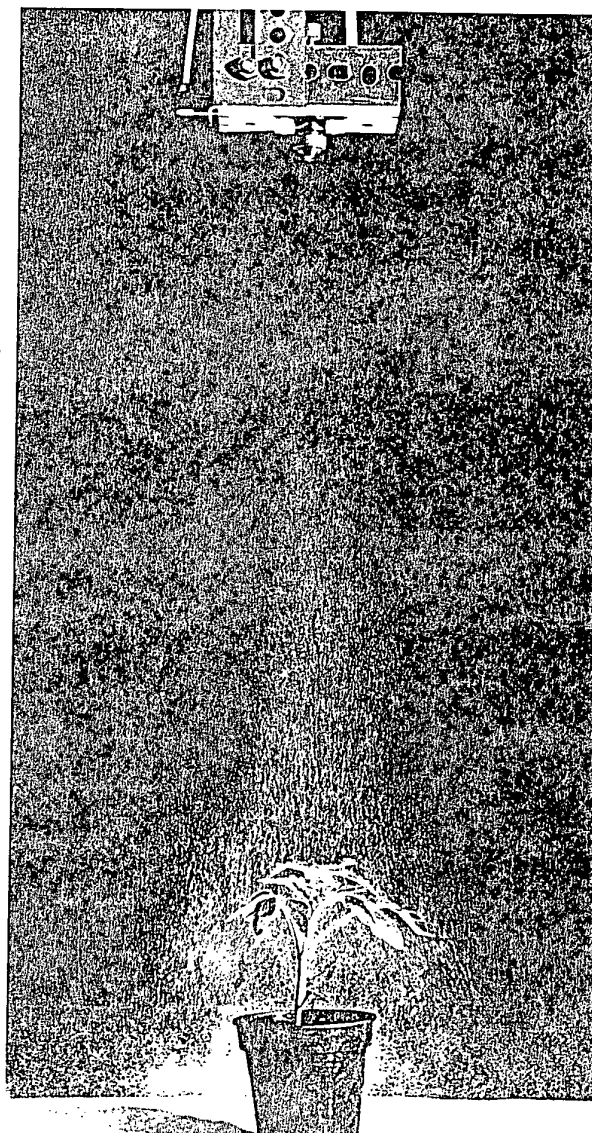
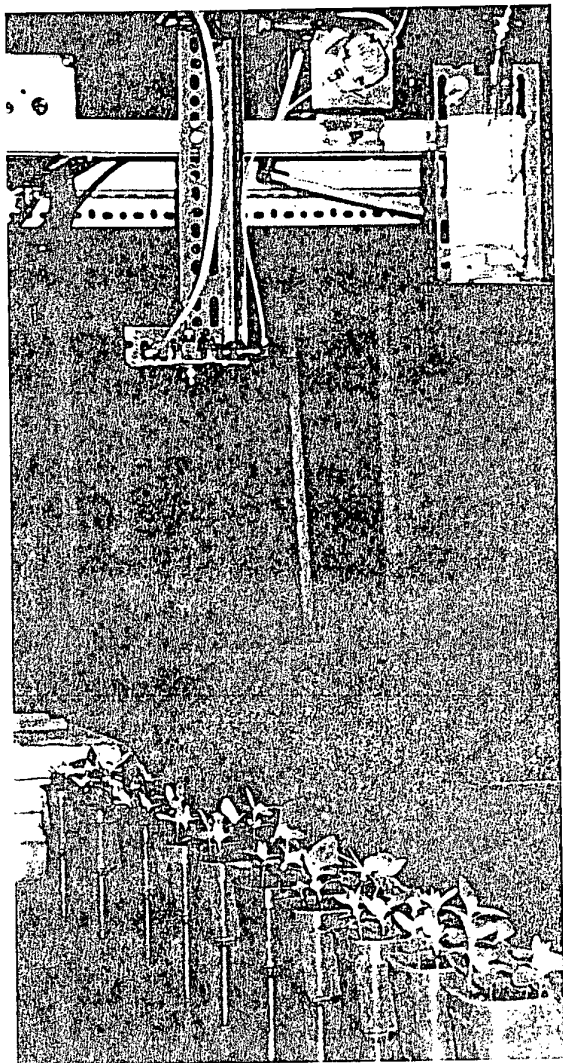


Plate 3. Spraying system in operation

Table 2. Application volume (l/ha) calculated from the recovery of the fluorescent tracer Uvitex OB from sample discs placed directly under the nozzle and 12.5cm either side of the centre line

Flow ml/min	Application volume (l/ha)		
	Left	Centre	Right
9	3.35	3.46	2.27
11	4.36	3.97	3.73
22	9.39	7.80	8.07

Table 3. Mean droplet diameter and velocity for atomised rapeseed oil at three flow rates and a constant air pressure (9kPa)

Flow rate (ml/min)	Air pressure (kPa)	Droplet diameters (μm)				% volum <100 μm	Mean velocity (m/s)
		V(10)	VMD	V(90)	NMD		
6	9	16.23	49.71	92.42	10.70	93.82	2.65
9	9	19.09	54.08	93.06	9.36	93.05	2.59
20	9	24.29	62.34	101.40	9.50	89.40	2.43

Aqueous spray (E015-F80 spraying 0.1% Agral)

480	200 *	129.00	295.00	361.00	33.00	5.07	2.10
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* Hydraulic pressure

Table 4. Mean droplet diameter and velocity for atomised rapeseed oil at three air pressures and a constant flow rate (9 ml/min)

Flow rate (ml/min)	Air pressure (kPa)	Droplet diameters (μm)				% volum <100 μm	Mean velocity (m/s)
		V(10)	VMD	V(90)	NMD		
9	6	21.94	58.89	105.83	10.11	90.42	2.19
9	9	19.09	54.08	93.06	9.36	93.05	2.59
9	12	16.63	49.76	91.05	8.50	94.51	3.00

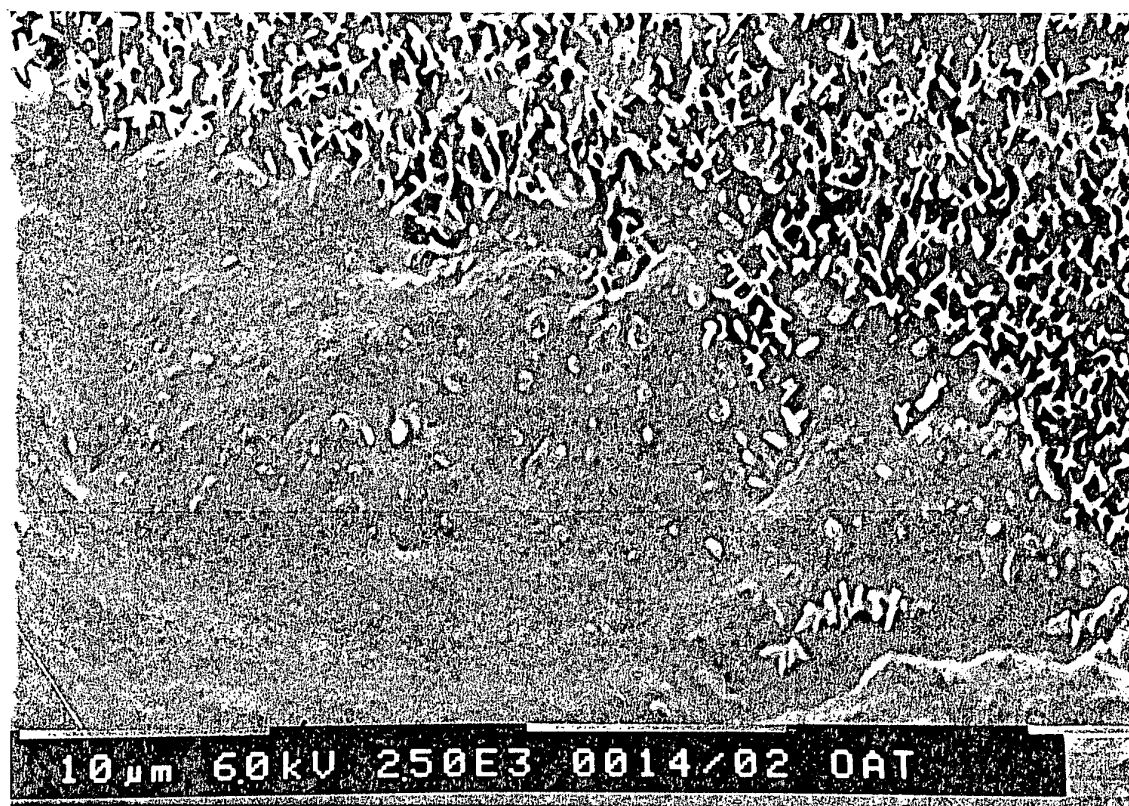
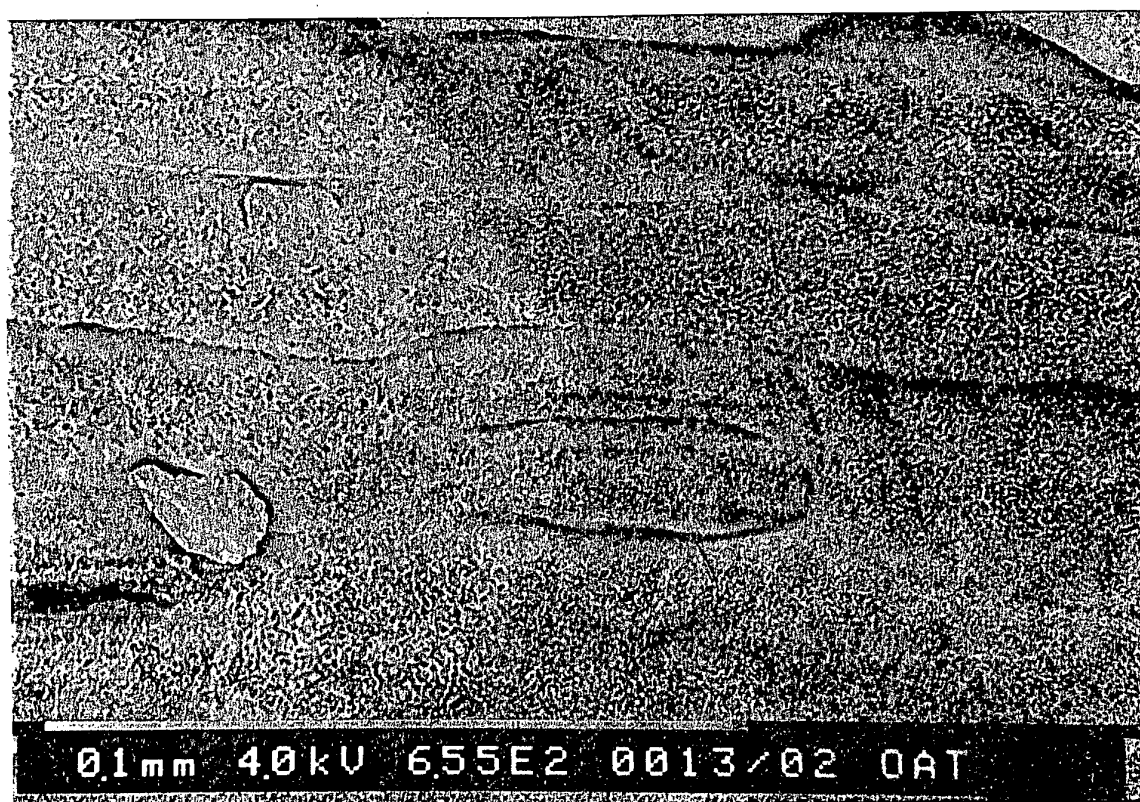


Plate 4. Scanning electron microscope photographs of oil deposits on the surface of oat leaves. Wax crystals can be seen through the oil but there is no visible evidence of damage to epidermal cells.

Table 5. Mean dry weight (g/pot) of three crop plants examined for phytotoxicity to rapeseed oil, 14DAT

	Control	3 l/ha	Oil	
			6 l/ha	9 l/ha
Wheat	2.20	2.28	2.29	2.35
Sugar be	2.67	2.61	2.81	3.00
Tomato	1.80	1.92		2.02

Table 6. Effect of clodinafop (g a.i./ha) on fresh weight (g) of wild oats when sprayed in rapeseed oil and water, 14DAT.

Ln dose	<u>Ln fresh weight</u>		Dose (g a.i./ha)	<u>Fresh weight (g)</u>	
	oil	water		oil	water
0.60	1.902	1.967	1.88	6.70	7.15
1.30	1.420	1.990	3.75	4.14	7.32
2.00	-0.359	1.709	7.50	0.70	5.52
2.70	-0.443	-0.248	15.00	0.64	0.78
3.40	-0.787	-0.560	30.00	0.46	0.57
4.10	-0.880	-0.923	60.00	0.41	0.40
4.70	-1.026	-0.938	120.00	0.36	0.39
control:	2.03		control:	7.60	

Table 7. Effect of phenmedipham (g a.i./ha) on fresh weight (g) of fat hen when sprayed in rapeseed oil and water, 14DAT.

Ln dose	<u>Ln fresh weight</u>		Dose (g a.i./ha)	<u>Fresh weight (g)</u>	
	oil	water		oil	water
2.9	2.132	2.456	17.8	8.43	11.66
3.6	2.126	1.913	35.6	8.38	6.77
4.3	1.664	1.288	71.2	5.28	3.63
5.0	1.367	0.440	142.5	3.92	1.55
5.6	1.198	0.012	285.0	3.31	1.01
6.3	0.461	-0.257	570.0	1.59	0.77
control:	2.570		control:	13.06	

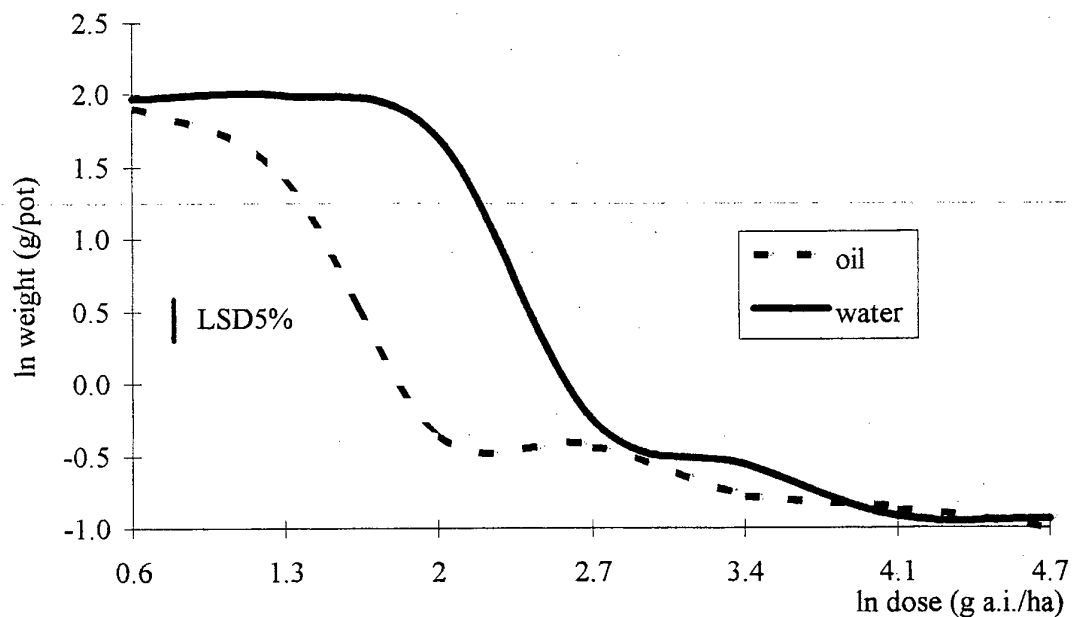


Fig. 3 Response (ln fresh weight g/pot) of oats to foliar-applied clodinafop using rape seed oil and water as carriers, 14 DAT. (LSD 5%=0.22)

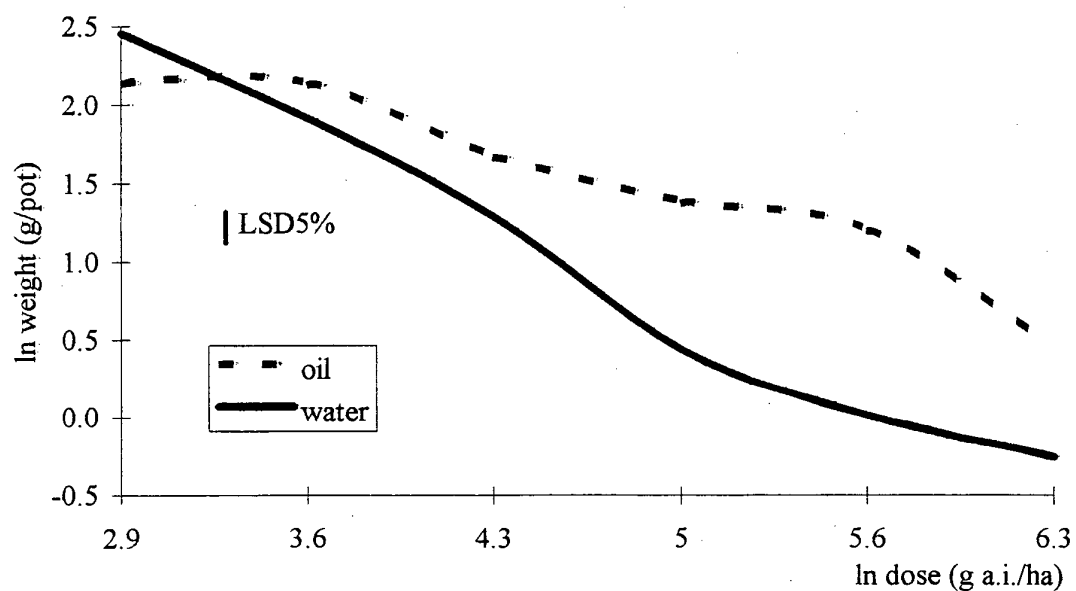


Fig. 4 Response (ln fresh weight) of fat hen to foliar-applied phenmedipham using rape seed oil and water as carriers, 14 DAT. (LSD 5%=0.295)

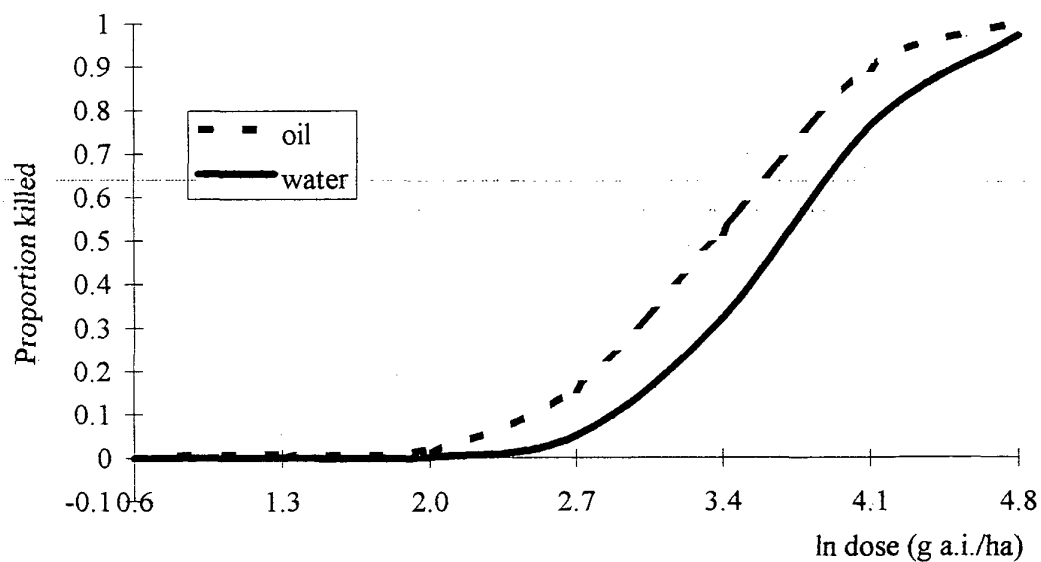


Fig. 5 Response (proportion killed) of oats to foliar-applied clodinafop using oil and water as carriers, 14 DAT.

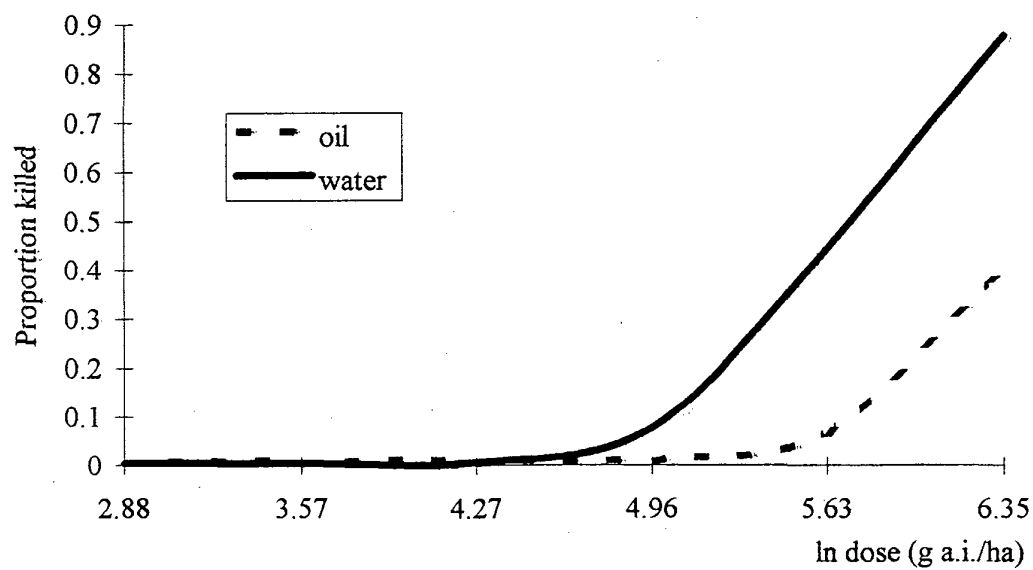


Fig. 6 Response (proportion killed) of fat hen sprayed with phenmedipham using water and oil as carriers, 14 DAT

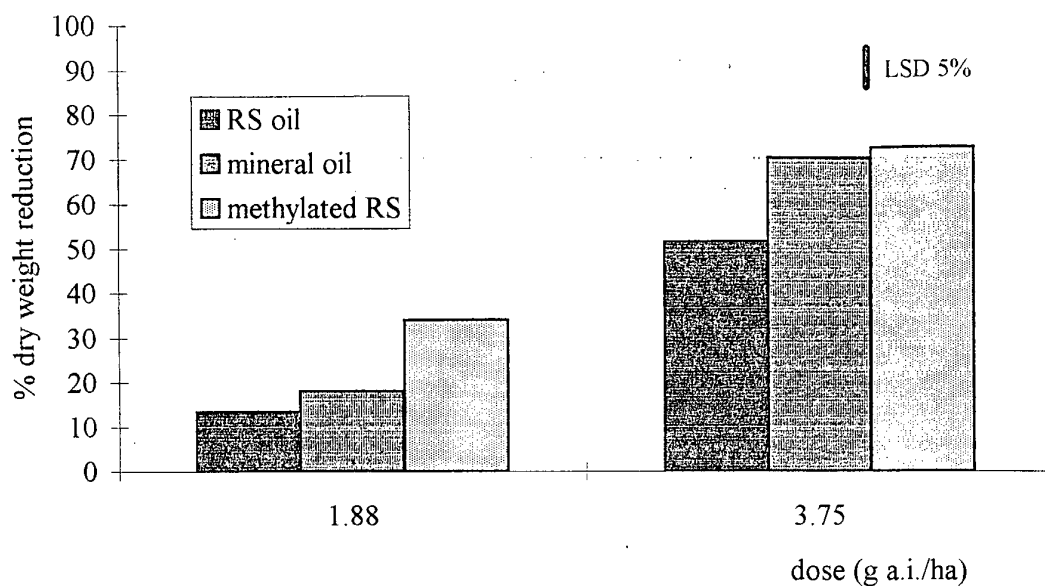


Fig. 7 Dose response (% dry weight reduction) in oats for two doses of clodinafop-propargyl when sprayed in rapeseed (RS), methylated RS, and mineral oil, 14 DAT. (LSD 5%=11.6)

deposits were visible and a scanning electron microscope examination (Plate 4) showed some modification to cuticular waxes by the oil droplets. Dry weights of sprayed plants were greater than corresponding control plants, but none of these increases were statistically significant (Table 5 and Appendices 3 & 4).

Characteristic visual symptoms were produced in oats and fat-hen, by Topik and Betanal E, respectively, when sprayed in rapeseed oil and as aqueous emulsions. The effect of Topik on the fresh weight of oats was increased when sprayed with rapeseed oil (ED50= 3.99 g a.i./ha, Appendix 5) compared with aqueous sprays (ED50=9.0 g a.i./ha, Appendix 6). Highly significant differences were found at rates between $x^{1/8}$ and $x^{1/16}$ of the recommended field dose ($P<0.01$). The percentage of plants killed (Appendix 8) was also higher in oil than in water (Appendix 9). For the experiment carried out using Betanal E, aqueous sprays (ED50=20.0 g a.i./ha, Appendix 10) were more active than rapeseed oil-based ones (ED50=79.3 g a.i./ha, Appendix 11). Highly-significant differences were found for doses between $x^{1/2}$ and $x^{1/16}$ ($P<0.01$). Compared with aqueous sprays, low % mortality was recorded for treatments in rapeseed oil. The mean fresh weights of plants treated with Topik and Betanal are recorded in Tables 6 (Appendix 7) and 7 (Appendix 12), respectively. Dose-response curves are shown for fresh weights in Figs 3 and 4 and for the proportion killed in Figs. 5 and 6.

Similar visual symptoms were observed in oat plants treated with two sub-lethal doses of Topik sprayed in rapeseed, methylated rapeseed and mineral oil. Weight reductions of >50%, compared with the control, were achieved by the higher dose of clodinafop-propargyl when sprayed in the three types of oil. A significant increase in effectiveness was observed in methylated oil compared with rapeseed oil for both doses and for the lowest dose, only with mineral oil (Fig. 7, Appendix 13).

DISCUSSION

The results obtained in this project confirm that it is possible to use rapeseed oil as a carrier for ULV pesticide applications.

The external-mix twin-fluid nozzle used permits only limited changes to droplet size by adjusting oil flow rates and air pressure, as reported by Hanks and McWhorter (1993). However, unlike the specially constructed nozzle they used, our work was done with a very fine spray quality, quite unsuitable for practical use because it would create a massive drift problem (Bode, 1987; Matthews, 1992). Nevertheless, the fact that oil is less volatile than water should mean that long-distance drift and loss of pesticide to the

upper atmosphere will be lower from small oil droplets compared with similarly sized water droplets.

The great number of small oil droplets sprayed, together with their physico-chemical characteristics, provided good deposition compared with aqueous sprays. This is especially true for vertical oat targets, because small droplets have a less vertical trajectory, as illustrated in Plate 3 (Spillman, 1984; Knoche, 1994). Generally, reflective plant surfaces govern the amount of active ingredient retained (Wirth *et al.*, 1991), but most oils have a low surface tension and a contact angle $<90^\circ$ with leaf surfaces (Gauvrit and Cabanne, 1993), allowing their droplets to spread better (McWhorter *et al.*, 1993) and to adhere without rebounding. In addition, finer drops and air assistance interact to increase the total spray deposition on plants (Hislop *et al.*, 1995).

Phytotoxicity tests were carried out on crops because most pesticide applications imply spraying pest and crop irrespectively. Phytotoxicity of oils is known to vary (Gauvrit and Cabanne, 1993), but most vegetable oils are considered to be suitable as vehicles to carry pesticides onto the surface of plants (Hamilton, 1993). In the experiments carried out for this project, low erucic rapeseed oil was harmless when sprayed on crop plants. Scanning electron microscope examinations suggest a partial dissolution of crystalline waxes, but according to Mc Whorter *et al.* (1993) these recrystallize after several weeks.

The results from spraying oats with Topik in oil and water, suggest that the activity of this herbicide is increased when carried in low volumes of rapeseed oil. The difference between the fresh weights of oats at lower and higher doses were relatively small compared with the significantly different results at the mid-doses. A comparison between dose-response curves, normally used to assess the potency of herbicide-adjuvant mixtures (Kudsk and Streibig, 1993), reveal a better performance of the ULV oil-herbicide combination compared with a conventional water spray. An experiment carried out on black-grass (*Alopecurus myosuroides*), using water as a carrier and the same herbicide, sprayed at different volume rates and spray quality, showed that the increase in the activity of clodinafop-propargyl is due to higher retention of the spray on the leaf surfaces (Cawood *et al.*, 1995), as also measured by us. Indeed, if the response to herbicides is proportional to doses deposited, we could have expected even greater activity of Topik in oil. However, several reports suggest that other factors may also affect the oil-herbicide interaction (Gauvrit and Cabanne, 1993; Knoche, 1994; Bohannan and Jordan, 1995). Advantages of oil carriers include the reduction in evaporation of the spray solutions, an increase in penetration of the waxy cuticles, improved rainfastness and an increase in the spread of the solution on the leaf

surface (Bohannon and Jordan, 1995). In spite of these advantages, oil carriers do not always provide the best control when compared with aqueous sprays, even when the herbicides belong to the same group (Gauvrit and Cabanne, 1993). We would also hypothesise that the distribution of herbicide on the plants sprayed with water and oil are likely to differ considerably. For example, water droplets are likely to have run into the axils of oat leaves, where uptake can be facilitated. The differential retention of oil-based sprays on oats and fat hen, compared with aqueous sprays, as measured here, is due to their contrasting morphology (vertical vs horizontal) and the fact that oats are difficult to wet with aqueous sprays compared with fat hen (see also Grayson et al., 1996).

Rapeseed oil did not enhance phenmedipham (Betanal E) activity on fat hen (*Chenopodium album*). A typical dose-response curve was impossible to obtain because the recommended field rates for phenmedipham were higher than the volume rate used in the ULV applications of this experiment. Nevertheless, from the results obtained, it was possible to demonstrate a significantly lower effect in most doses of phenmedipham in oil, compared with a conventional aqueous spray. However, the activity of phenmedipham on fat hen has been reported to be increased when oils were used as emulsifiable adjuvants; weed control using phenmedipham was influenced by type of oil, volume of oil additive and weed species (Miller and Nalewaja, 1973). One limitation of the commercial formulation used in the present report, is the crystallization of the herbicide solution in water, when the application is delayed. Rapeseed oil in the formulation inhibited the recrystallisation of phenmedipham (Darchy et al., 1990) and, therefore, should increase its penetration; however, if the oil interacts with this herbicide, the molar ratio oil:herbicide would certainly have an influence (Gauvrit, 1994). Because good retention was obtained on fat-hen when sprayed with rapeseed oil, it is possible that the commercial formulation of phenmedipham used in this experiment produced a negative interaction with the rapeseed oil at ULV. Unsuccessful weed control has also been reported with other herbicides using ULV application systems (Merritt and Taylor, 1977; Hatchard et al., 1989; Bohannon and Jordan, 1995). Comparisons between oil and water as the diluent at a very low rate suggest there may be situations when oil is preferable and others where water is the better choice (Merritt and Taylor, 1977). Droplet size and carrier volume effects result from the interaction of spray liquid and plant characteristics, including foliar uptake and biological response (Knoche, 1994). The herbicides chosen for the present report were both systemic having water-octanol partition coefficients which were lipophilic; therefore, their uptake should not be reduced much by the cuticle or cell membrane (Wade et al., 1993).

The effect of two sub-lethal doses of clodinafop-propargyl on oats differed when sprayed in three different oils in ULV applications. Methylated rapeseed oil proved to be a better carrier than rapeseed oil, while mineral oil was of intermediate efficacy. Similar comparisons were reviewed by Gauvrit (1994), who concluded that vegetable oils are generally less effective than petroleum oils at enhancing herbicide penetration, although their methylated derivatives perform as well. Experiments using maize demonstrated that methyl oleate penetrates leaves better than glyceryl trioleate; this might explain why diclofop-methyl has a greater activity when applied in methylated oil compared with the parental oil (Urvoy *et al.*, 1992). Conversely, when using isolated leaf cuticles from rubber and the fruits of pepper and tomato, Santier and Chamel (1996) concluded that the transfer efficiency of quizalofop-ethyl and fenoxaprop-ethyl through the cuticles, was related to the ability of the fatty acid methyl ester to partition into the cuticle; thus, the use of oil could result in an increase of fluidity of cuticular components depending on the plant species. Coincidentally, a positive relationship between an increase in pesticide diffusion and the ability of an oil to melt or solubilise waxes was reported by Gauvrit (1994). In addition, oils refined from petroleum usually spread much better than once-refined cotton seed or soybean oil, although methylated soybean oil and methylated sunflower oil spread well (McWhorter *et al.*, 1993).

CONCLUSIONS

ULV spraying in oil is certainly feasible, although whether or not it increases pesticide activity compared with higher volume aqueous sprays depends on complex formulation-plant interactions. Much additional work would be required to determine the precise benefits and disadvantages of oil-based applications. Even with a more suitable atomiser than that used here, the practical problems of metering very low volume flow rates are considerable. Further and, most importantly, pesticides registered for aqueous spraying would almost certainly need to be reformulated for use in oil, followed by very expensive field-testing and re-registration. It is highly unlikely that the manufacturers of agrochemicals would contemplate such work.

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APPENDICES

1.

Analysis of spray retention on foliage of oat seedlings

Analysis of Variance

variate: **D.U.E.**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
block stratum	9	806570	89619	1.15	
block.*Units*stratum					
volumes	2	162076	81083	1.04	0.374
Residual	18	1403249	77958		
Total	29	2371896			

Table of means

Grand mean	1648		
volumes	2.86 l/ha	6.05 l/ha	10.54 l/ha
	1569	1746	1628

Standard errors of differences of means

Table	vol.
rep.	10
d.f.	18
s.e.d.	124.9

2.

Analysis of spray retention on foliage of fat hen

Analysis of Variance

variate: **Ln D.U.E.**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
block stratum	9	0.42670	0.04741	1.59	
block.*Units*stratum					
volumes	2	0.09122	0.04561	1.53	0.243
Residual	18	0.53589	0.02977		
Total	29	1.05381			

Table of means

Grand mean	8.819		
volumes	3.02 l/ha	5.77 l/ha	9.59 l/ha
	8.842	8.872	8.743

Standard errors of differences of means

Table	vol.
rep.	10
d.f.	18
s.e.d.	0.0772

3.

Analysis of the phytotoxicity of rapeseed oil to wheat seedlings

Analysis of Variance

variate: **dry weight**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
column stratum	3	0.67948	0.22649	2.60	
row stratum	7	0.49045	0.07006	0.80	
column.row stratum					
oils	3	0.07488	0.02496	0.29	0.834 n.s.
Residual	18	1.56780	0.08710		
Total	31	2.81260			

Table of means

Grand mean 2.278

oils	Control	3 l/ha	6 l/ha	9 l/ha
	2.201	2.281	2.293	2.335

Standard errors of differences of means

Table

rep.	8
d.f.	18
s.e.d.	0.1476

4.

Analysis of the phytotoxicity of rapeseed oil to sugar beet seedlings

Analysis of Variance

variate: **dry weight**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
column stratum	3	0.4220	0.1407	0.78	
row stratum	7	1.0269	0.1467	0.81	
column.row stratum					
oils	3	0.7422	0.2474	1.36	0.286 n.s.
Residual	18	3.2667	0.1815		
Total	31	5.4579			

Table of means

Grand mean 2.770

oils	Control	3 l/ha	6 l/ha	9 l/ha
	2.666	2.605	2.806	3.001

Standard errors of differences of means

Table	oils
rep.	8
d.f.	18
s.e.d.	0.2130

5.

Estimation of the ED₅₀ of Topik applied to wheat in rapeseed oil

Nonlinear regression analysis

Response variate: **oil**

Explanatory: Lndose

Fitted curve: $A + C/(1 + \text{EXP}(-B*(X-M)))$

Summary analysis

	d.f.	s.s.	m.s.	v.r.
Regression	3	37.69293	12.56431	878.23
Residual	3	0.04292	0.01431	
Total	6	37.73585	6.28931	

Estimate of parameters

	estimate	s.e.
B	-5.0830	0.844
M	1.3826	0.0189
C	6.3710	0.181
A	0.4629	0.0608

Estimate of functions of parameters

	estimate	s.e.
ED ₅₀	3.9851	0.0755

6.

Estimation of the ED₅₀ of Topik applied to wheat as an aqueous spray

Nonlinear regression analysis

Response variate: **water**

Explanatory: Lndose

Fitted curve: $A + C/(1 + \text{EXP}(-B*(X-M)))$

Summary analysis

	d.f.	s.s.	m.s.	v.r.
Regression	3	66.56345	22.18782	1507.81
Residual	3	0.04415	0.01472	
Total	6	66.60759	11.10127	

Estimate of parameters

	estimate	s.e.
B	-5.912	0.678
M	2.1970	0.0250
C	6.806	0.116
A	0.4539	0.0708

Estimate of functions of parameters

	estimate	s.e.
ED ₅₀	8.998	0.225

7.

**Statistics for the dose-response curves describing the action of Topik
applied to wheat in oil and water**

Analysis of variance

variate: **Ln fresh weight**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
block stratum	6	0.32285	0.05381	1.03	
block*Units* stratum					
convstrt	1	21.79587	21.79587	417.27	<.001
convstrt.carrier	1	5.03443	5.03443	96.38	<.001
convstrt.conc	6	128.43485	21.40581	409.80	<.001
convstrt.carrier.conc	6	11.44972	1.90829	36.53	<.001
Residual	83(1)	4.33546	0.05223		
Total	103(1)	170.89619			

Table of means

Variate: Ln fresh weight

Grand mean 0.324

convstrt	control	treated	
	2.028	0.202	
	control	oil	water
	2.028	-0.025	0.429
	dose (g a.i./ha)		
	1.875	1.902	1.967
	3.75	1.420	1.992
	7.5	-0.359	1.709
	15	-0.444	-0.248
	30	-0.787	-0.560
	60	-0.880	-0.923
	120	-1.026	-0.938

8.

Estimation of the LD₅₀ of Topik applied in oil and water to wheat

Nonlinear regression analysis

Response variate: **killed**

Binomial totals: total

Distribution: Binomial

Summary of analysis

	d.f.	deviance	mean deviance
Regression	4	*	*
Residual	11	11.30	1.027
Total	15	*	*

Estimate of parameters

LD ₅₀ ['oil']	3.391
LD ₅₀ ['water']	3.676
Slope	1.691
PrMortal	0.000E +00

Source	d.f.	deviance	mean deviance	F ratio
Single line	1			
Parallel line	1	5.79	5.79	4.83 *
Residual	11	13.17	1.197	

9.

Estimation of the LD₅₀ of Betanal applied to fan hen in oil and water

Nonlinear regression analysis

Response variate: **killed**

Binomial totals: total

Distribution: Binomial

Summary of analysis

	d.f.	deviance	mean deviance
Regression	4	*	*
Residual	10	10.70	1.070
Total	14	*	*

Estimate of parameters

	estimate	s.e.
LD ₅₀ ['oil']	5.730	0.100
LD ₅₀ ['water']	7.195	0.134
Slope	1.879	0.334
PrMortal	0.0039	0.00597

Source	d.f.	deviance	mean deviance	F ratio
Single line	1			
Parallel line	1	80.54	80.54	75.27*
Residual	10	10.70	1.07	

10.

Estimation of the ED₅₀ for Betanal applied to fat hen as an aqueous spray

Nonlinear regression analysis

Response variate: **water**
 Explanatory: Lndose
 Fitted curve: $A + C/(1 + \text{EXP}(-B*(X-M)))$

Summary analysis

	d.f.	s.s.	m.s.	v.r.
Regression	3	91.52142	30.50714	887.15
Residual	2	0.06878	0.03439	
Total	5	91.59019	18.31804	

Estimate of parameters

	estimate	s.e.
B	-1.409	0.226
M	2.994	0.340
C	20.61	5.18
A	0.522	0.232

Estimate of functions of parameters

	estimate	s.e.
ED ₅₀	19.96	6.83

11.

Estimation of the ED₅₀ for Betanal applied to fan hen in oil

Nonlinear regression analysis

Response variate: oil

Explanatory: Lndose

Fitted curve: $A + C/(1 + \text{EXP}(-B*(X-M)))$

Summary analysis

	d.f.	s.s.	m.s.	v.r.
Regression	3	37.243	12.4144	15.63
Residual	2	1.589	0.7945	
Total	5	38.832	7.7664	

Estimate of parameters

	estimate	s.e.
B	-1.370	1.26
M	4.373	0.548
C	8.26	4.61
A	1.45	2.02

Estimate of functions of parameters

	estimate	s.e.
ED ₅₀	79.3	43.4

12.

**Statistics for the dose-response curves describing the action of Betanal
applied to fat hen in oil and water**

Analysis of variance

variate: **Ln fresh weight**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
block stratum	5	0.78990	0.15798	2.31	
block*Units* stratum					
convstrt	1	9.91902	9.91902	145.31	<.001
convstrt.carrier	1	4.84921	4.84921	71.04	<.001
convstrt.conc	5	43.28446	8.65689	126.82	<.001
convstrt.carrier.conc	5	4.44897	0.88979	13.04	<.001
Residual	59(1)	4.02744	0.06826		
Total	76(1)	66.39218			

Table of means

Variate: ln fresh weight

Grand mean 1.335

convstrt	control	treated	
	2.570	1.232	
	control	oil	water
	2.570	1.491	0.927
	Indose		
	2.90	2.132	2.456
	3.60	2.126	1.913
	4.30	1.664	1.288
	5.00	1.367	0.440
	5.60	1.198	0.012
	6.30	0.461	-0.275

Analysis of the effects of Topik applied to wheat in three oils

Analysis of variance

variate: **dry weight**

Source of Variation	d.f.	s.s.	m.s.	v.r.	F pr.
block stratum	5	0.22633	0.04527	1.50	
block*Units* stratum					
convstrt	1	2.24967	2.24967	74.41	<.001
convstrt.carrier	2	0.61177	0.30589	10.12	<.001
convstrt.conc	1	3.88747	8.65689	128.58	<.001
convstrt.carrier.conc	2	0.04484	0.88979	1.48	0.243
Residual	30	0.90699	0.06826		
Total	41	7.97190			

Table of means

Variate: dry weight

Grand mean 0.960

convstrt	control	treated		
	1.527	0.865		
	control	RSO	methyated	mineral
	1.527	1.032	0.713	0.851
	dose(g a.i./ha)			
	3.75	0.740	0.418	0.452
	1.88	1.323	1.008	1.250