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**Herbicide Safeners,
Additives and Formulants**

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FORMULANTS AND ADDITIVES AND THEIR IMPACT ON PRODUCT PERFORMANCE

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ABSTRACT

The Formulation Chemist aims to provide a product to apply a relatively small amount of active ingredient evenly over a large area to achieve the maximum desired biological effect. In addition, the end user and others who make or handle the product, measure product quality by its safety, ease of use, environmental impact and cost effectiveness.

The selection of the formulation and the ingredients which make up the formulation, called formulators, must be made to meet to all these performance criteria whilst conforming to the increasing number of regulatory and legislative constraints and requirements.

In an ever changing and diverse marketplace, formulators and additives offer opportunities to optimise not only the active ingredient effect but all aspects of product performance.

INTRODUCTION

Although the intrinsic activity of a pesticide product originates from the active ingredient (AI) it is the formulation which determines the ease by which it can be made, stored, handled and applied to achieve the full potential from that AI. Product performance is measured by a number of factors including:

- 1) Biological efficacy
- 2) Safety during handling (human toxicity)
- 3) Environmental impact
- 4) Economics

The type of formulation and the choice of formula ingredients and process can greatly enhance product performance in these respects.

Before discussing how the formulation and its ingredients affect product performance, it is worth looking at what a formulation is and why we formulate.

WHY FORMULATE?

Pesticide molecules are relatively active requiring a small amount to be spread over a large area to have their effect. Even at dose rates of kilogram quantities per hectare, for instance, simple application of the raw pesticide would be practically impossible and unlikely to achieve its full potential. With recent advances leading to materials active at a few grammes per hectare, this homogeneous distribution could be even more difficult.

Formulation together with application techniques are a means to achieve this even distribution and delivery of the AI to the target. In the majority of cases, pesticides are applied as aqueous dilutions using hydraulic sprayers and the paper will focus on these. However, many other methods of application are also used (e.g. CDA, ULV, placement and broadcast of granules, seed treatment) and specific formulations are developed for these uses.

The technical AI is not normally suitable for dilution or dispersion in a farmers spray tank. There are occasional exceptions; difenzoquat herbicide was sold for some years as the technical simply ground to a fine particle size to aid dissolution. However, in the vast majority of cases the technical AI is not water-soluble and will not wet and disperse in the spray water to give an adequately stable dilution. Formulation, by the inclusion of other ingredients, called formulants, aims to manipulate the chemical and physical properties of the technical AI to achieve the desired requirements. Table 1 gives some simple examples of herbicide AI types and possible formulations.

TABLE 1: Classification of active ingredients and possible formulations types.

<u>Solubility</u>	<u>Example</u>	<u>Possible end Formulations</u>
Water-soluble	Amitrole Sulphuric acid TCA	{ Soluble liquid (SL) Soluble powder (SP) Soluble granule (SG)
Water-soluble salt	Bromoxynil-potassium Imazethapyr-ammonium Glyphosate-triethylammonium	{ Soluble liquid (SL) Soluble powder (SP) Soluble granule (SG)
Solvent soluble solid	Propanil Pendimethalin Bromoxynil-octanoate	{ Emulsifiable concentrate (EC) Emulsion in water (EW) Suspension concentrate (SC)* Capsule suspension (CS) Wettable powder (WP)*
Solvent miscible liquid	Clomazone Metolachlor Sethoxydim	{ Capsule suspension (CS) Wettable powder (WP) (difficult) Emulsifiable concentrate (EC) Emulsion in water (EW)
Insoluble solid	Isoproturon Isoxaben Chlorsulfuron	{ Wettable powder (WP) Water dispersible granule (WG) Suspension concentrate (SC)

* AI melting point <50°C has more constraints

Due to the increasing difficulty and costs of introducing new AIs, there has been an increase in coformulations containing a number of AIs to obtain the desired biological effect. A review of the UK Pesticide Guide 1993 reveals, for instance, that 38% of the 498 entries are for products which are coformulations. These are mainly of two actives but three actives are common and there are examples of coformulations which contain four active ingredients. The inclusion of safeners and adjuvants into the formulation can be treated as coformulations by the formulation chemist as the physico-chemical properties of the safener or adjuvant will impact on formulation type, concentration and choice of formulants.

These coformulations present challenges to the formulation chemist in that often the physico-chemical properties of the co-actives, built-in safener or adjuvant are different (e.g. water-soluble salt and insoluble solid) and can require innovative approaches.

FORMULATION TYPES

The GIFAP technical monograph No2 (3rd edition, February 1989) lists 71 formulation types, but an analysis of the UK and French crop protection markets reveals that four types; aqueous solutions (SL), emulsifiable concentrates (EC), wettable powders (WP) and suspension concentrates (SC) are used for the large majority of products (Table 2). Although water-dispersible granules (WG) represent a small part of the market currently, the trend is towards more of this type. WG, along with SC, can provide a means to safen a dusty WP but WG have the added advantage that they can also be packed in easier to dispose of cardboard-type packaging. In the USA, the pattern is similar although WG rather than SC have increased at the expense of WP. This is partially due to the formulation of most sulphonylurea herbicides as WG. However, other formulation types are important in their particular niche. For instance, microencapsulated suspensions (CS) of alachlor are essential for sale in some countries and, tablet formulations of highly active materials, e.g. tribenuron-methyl, have appeared on the market in recent years.

The requirement for coformulations, as outlined above, is one reason for the appearance of complex multi-phase formulations such as solubilised systems (eg based on mecoprop-potassium and bromoxynil and ioxynil as both potassium salts and octanoate esters), concentrated emulsions (EW) (e.g. pendimethalin and imazethapyr), suspo-emulsions (SE) (e.g. based on metolachlor and atrazine) and solvent based suspensions (e.g. based on pendimethalin, metolachlor and terbuthylazine). A patented technology, where the solid or liquid AI or oil adjuvant is suspended in a large ordered aqueous surfactant structure, has been used, in some cases, to improve product performance including biological activity (Newton *et al*, 1993).

TABLE 2: Major formulation types sold in the Crop Protection market

	UK 1993 %	France 1992 %	USA 1992 %
SL	17	13	16
EC	21	23	29
SC	23	21	9
WP	15	26	14
WG	4	6	11
Misc	20	11	22

Sources: Crop Protection Chemicals Reference (1992), 8th Edition, J Wiley
The UK Pesticide Guide (1993), G W Ivens, 6th Edition, CAB
 International and BCPC
Index Phytosanitaire (1991), R Robbe-Durand, 27th Edition, ACTA

CHOICE OF FORMULATIONS

The ability to achieve the full product performance begins with selecting the correct formulation type. As discussed, the physical and chemical properties of the AIs dictate which formulation types are possible. In some cases, only one type may be feasible or novel formulation approaches may be required to achieve even this.

In most cases, choice of formulation is determined by biological requirements, safety and regulatory conformance, market demands, cost and timelines.

Where a choice is possible, it may be made considering the mode of action. For instance, particulate types (e.g. SC, WP, WG) may be preferred for a residual AI while a solution (SL, EC, EW) may aid penetration of a contact pesticide. Note, particle size (e.g. WP, WG, SC) and droplet size (EW, SE) in products can be important for biological efficacy. For instance, there is an 64 fold increase in particle number and therefore active sites, in moving from a 20 μm particle to a 5 μm particle. Processing techniques allow a finer product to be produced for a SC than a WP. Encapsulated and coated formulations may reduce unwanted losses of pesticides due to volatilisation, photodegradation, microbial breakdown, soil adsorption and leaching or other extended control by slow release for instance. This can result in a reduction in the amount of active applied. Extensive testing are often needed to make the selection of formulation type on biological efficacy.

The OECD have made proposals to set targets to replace hazardous pesticide products by safer materials and so reformulation to achieve this is taking place. Formulations which can produce dust or solvent vapour (e.g. WP, EC) are often avoided due to the risk of the hazard in manufacture, storage, transport and use. Dust can be overcome by granulation of WP to WG which also gives free-flowing products with improved handling properties. These are important benefits as in Italy the classification system shows preference to WG as it treats powders and liquids as having higher inhalation toxicity. Actives with toxicity concerns can also be safened by microencapsulation as liquids (CS), or eye/skin irritancy reduced by moving from solvent-based liquids (EC) to partially water based systems (EW) or particulates (SC, WP).

Formulation type may also be influenced by the possible packaging options as pack disposal is becoming more of an environmental concern. Current regulations in Canada requiring return of pesticide packaging and similar proposals in USA and Europe may lead to the use of different pack types which in turn need different formulations. More concentrated formulations which can be packed in easily-disposed lighter weight packs or water-soluble bags (e.g. WP, WG, EC (as gel)) have distinct advantages. Water-soluble bags also offer improved operator safety. Simple solutions (EC, SL) lend themselves better to reusable packs such as mini-bulk and small-volume returnables (SVR) being used in USA and tested in Europe. However, examples of multi-phase formulations (e.g. EW of imazaquin and pendimethalin) are on the market in this form but a high degree of stability to prevent separation is required.

Restrictions on the transport, storage and packaging of flammable materials has led to a move away from solvent based formulations (e.g. pendimethalin, 33% EC to 40% aqueous SC) although EC based on high-flash solvents are still widely developed.

Economics and timelines also play a role. For example, traditional formulations (SL, EC, WP) tend to be straightforward to develop and make, but often a WG requires longer and more extensive development and can lead to significant capital investment to build a manufacturing plant.

The actual formulation type chosen may be the best compromise after considering all the factors above.

CHOICE OF FORMULANTS

As discussed earlier, the formulation turns the AI into a useable product meeting a number of quality criteria. A formulation may contain many ingredients other than the AIs to achieve these requirements. These materials function as surfactants, solvents, antifreezes, antifoams, fillers, flow-aids, disintegrants, rheological modifiers, emetics, preservatives, dyes and buffers, for instance. All play a role in product performance. There is a vast array of functional materials available, although there are restrictions; the EPA have a positive list of approved ingredients and there is an increasing demand for toxicological and environmental data in some countries (e.g. Austria). As this is a costly task for formulant suppliers it is likely to have the effect of reducing the number of materials and suppliers. Any material with toxicological or environmental concerns would be avoided by a diligent formulation chemist.

Nearly all formulations for spray dilution contain surfactants. The primary function of surfactants is to work at the solid-water and oil-water interfaces either in the product concentrate or in the spray dilution by:

- solubilising the AIs (e.g. EC, microemulsions).
- maintaining stable, fluid dispersions long term (years) in products (e.g. EW, SC).
- maintaining short term (hours) stable spray dilutions regardless of temperature, water hardness or presence of tank-mix additives.
- various roles in wetting, spreading and penetration of the spray droplet on the target.

As surfactants work at interfaces, certain types, depending on concentration, are able to dissolve skin greases and can lead to irritancy and possible enhanced AI toxic effects. Liaison with the toxicologist ensures correct selection. Biodegradability is also a concern. For instance, nonyl phenol ethoxylates, widely used in a wide variety of formulations and adjuvants, are under close scrutiny. However, alternatives are in place (e.g. based on alcohols) and new, low hazard, environmentally friendly surfactants (e.g. sucroglycerides) are becoming increasingly available which, in some cases, are highly active (e.g. polymeric, fluorinated and silicone-based chemicals). After the AI, surfactants can form the next biggest ingredient cost and so careful selection of type and concentration on economic grounds may also be necessary.

Solvent-based formulations are still important (see Table 2). However, the nature of solvents used has changed. For example, chlorinated solvents (e.g. monochlorobenzene) are being phased out on toxicological grounds and xylene from a flammability (flash point 21°C) point. New materials are being used to provide solvency power (pyrrolidone derivatives, fatty acid esters) and which are biodegradable. Higher aromatic solvents are less flammable and pose reduced environmental concerns. However, careful selection to avoid unwanted side effects such as phytotoxicity is required. Where possible, water is the preferred solvent (as in SL) or otherwise it is used as the dispersing medium for suspensions and emulsions (e.g. CS, SC, EW). Water-based products can provide benefits in terms of reduced flammability, decreased irritancy, increased AI concentration and lower cost.

Other formulation additives, although in small quantity in the formulation can have significant effects on product performance. Antifreezes (in SL, SC) and flow-aids (in WP) are used to ensure the product is useable after storage at extremes of temperature. Antifoams are used to prevent foam generation during the manufacturing process and in use in the spray tank. Amine stearates in WP can help increase rainfastness (Stickle, 1992). UV absorbents can reduce loss of AI after spraying due to photodegradation. Preservatives prevent microbial spoilage of aqueous products. Emetics and bitters can prevent poisoning by ingestion. Coating of the AI with polymers (e.g. poly-vinyl pyrrolidone) can reduce leaching to ground water and may reduce volatilisation and photodegradation of AIs. Rheological modifiers can alter the nature of suspensions and gels making them near solids on standing (e.g. during storage) but water-fluid when shaken and poured. This latter effect is of particular importance to maximise the removal of the product from the pack (this includes mini-bulk and SVR) and to give good dispersion in the spray tank and, in the future, direct into the spray room.

BIOLOGICAL ADJUVANTS

As discussed earlier, formulations are devised to achieve the maximum biological efficacy under all expected circumstances. Often this is achieved by optimising the formulation type, the formulants such as solvents and surfactants and perhaps, parameters like particle size of suspensions or droplet size of diluted emulsions. However, there are products where this optimisation is achieved by the use of specialist additives whose prime function is to maximise the biological efficacy and perhaps reduce chemical usage and therefore environmental impact. In the UK Pesticide Guide 1993, there are 70 registered adjuvants which include surfactants, mineral and vegetable oils and their derivatives, and silicic materials. This is an expanding area which is now taken seriously by users, the market and the agrochemical industry. In one USA report (Foy, 1992), from 485 products (19 companies) surveyed 49% recommended addition of adjuvants. Wherever possible, these additives or adjuvants are incorporated in the product in order to ensure the farmer obtains the right result every time. Also, by building in the additive it is registered as part of the formulation and allows greater flexibility in adjuvant selection. Where it is not feasible, specific tank mix recommendations are made.

The inclusion of adjuvants into formulation can present the formulation chemist with some specific challenges and dramatically effect the product type and its dose rate.

High dose AIs may require an equivalent or greater concentration of adjuvant in the product to achieve the correct spray concentration over a range of spray volumes. With a highly active, low dose AI the adjuvant may be at 10-20 times the concentration of the AI. In some cases, this makes a commercial product unfeasible as the volumes to be handled are not acceptable to the manufacturer, the distributor or the end user. However, there are examples of adjuvant inclusion in the market which show what the formulator can do. Imazamethabenz-methyl is sold as 300 g/L SC containing 150 g/L nonionic wetter; a patented novel suspension formulation (Bell, 1989). Glyphosate/tallow amine ethoxylate liquid formulations are well known but solid formulations (SG) containing new wetter types have been introduced by Monsanto over the past 12 months. Oily flowables of phenmedipham where vegetable adjuvant oils are incorporated into the formula are also being developed by Schering.

FUTURE

The types of ingredients available for use in pesticide formulations will be in flux as some commonly used materials become restricted or banned and new alternatives are developed or come to light from parallel industries.

The formulation chemist will need to become more skilled in the use of available ingredients to develop formulations which will meet the requirements presented by pack disposal issues (e.g. increased use of water-soluble bags, more concentrated products, new solid formulations) and reduced operator exposure (e.g. closed transfer systems, in-boom injection, returnables).

Continued optimisation of formulations and the inclusion of adjuvants and safeners to enhance and protect biological activity will continue to be of importance.

The future for formulation chemistry looks challenging and will require stronger links with other scientific disciplines, the market, the regulator and the end user to achieve the greater demands placed on the formulation chemist.

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EFFECT OF SPRAY ADDITIVES ON DROPLET SIZE AND DRIFT POTENTIAL OF AERIAL SPRAYS.

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ABSTRACT

Wind tunnel atomization tests and aerial spray trials were carried out to investigate the effects of drift control additives upon the droplet size distribution spectra and relative drift potential of the picloram herbicide, Grazon PCTM (4-Amino-3,5,6-trichloropicolinic acid). Droplet size spectra were evaluated using a Malvern laser particle size analyzer immediately upon mixing and again after recirculation in the aircraft spray system. The polymer based additive significantly changed the droplet size spectra but showed signs of breakdown with agitation. The emulsifying suspension additive did not change the droplet size spectra or show signs of breakdown after recirculation of the material through the pump. Aerial spray applications with the additives were made using a Cessna Ag Husky that could spray the test material and a reference standard simultaneously. Relative drift potential was determined from the recovery of fluorescent tracers on vertical strings placed downwind of the sprayed area. Both additives reduced spray drift. Results with the polymer additive were variable and may be due to breakdown of the additive with shear. The results hold several implications for future research on the impact of additives upon spray drift.

INTRODUCTION

Numerous studies have shown that pesticide drift and deposition are affected by application equipment, wind speed, air turbulence, temperature, humidity, and formulation characteristics. However, droplet size is probably recognized as the major factor and spray additives are commercially available that can alter the droplet size produced at atomisation by modifying the physical properties of the spray mixture. (Gratkowski and Stewart, 1973; Yates *et al.*, 1976; Bouse *et al.*, 1988). One type of additive commonly used is the spray thickener, these are usually polymer based products. Another type of additive, often based on emulsifying oils, claim to affect droplet size and reduce drift by decreasing evaporation. Most investigations with additives only look at either droplet size changes or at drift reduction. Recent droplet size studies have shown that some of these products may breakdown due to shear from the pumping system (Bouse *et al.*, 1988; Chapple *et al.*, 1992) and the changes in droplet size can depend on airstream velocity (Sanderson *et al.*, 1993). Additional information on the performance of additives is needed. The objective of this study was to investigate the effect of two different types of additives on both droplet size spectra and drift potential of aerial sprays.

MATERIALS AND METHODS

Atomization studies

The atomization tests were conducted in the wind tunnel facility at New Mexico State University, Las Cruces, New Mexico. The tunnel is a straight through blower type designed around a 122 cm (48 in) diameter FMC orchard sprayer fan driven by a 351 cu.in gasoline-powered Ford engine. The air passes through a 1.8 m by 1.8 m (6ft x 6ft) settling chamber and is then contracted through a 56 cm (22 in) wide working section. This is connected to an expansion region which slows the air down and collects the sprayed material to prevent release of chemicals into the environment.

The test nozzle was mounted on a computer-controlled traversing mechanism which moved the nozzle vertically through the working section of the wind tunnel. The amount of travel was set so as to sample the whole spray plume. The droplet size spectra of the spray cloud were measured downwind of the nozzle using a Malvern 2600c laser-diffraction particle size analyzer. All measurements were made with an 800mm focal length lens. The calibration of the Malvern was verified using a Gilson BS-90 Reticle (Gilson Company Inc., OH). Data and results were obtained using Malvern version b.0D software. The droplet size spectra were calculated using Model Independent Analysis. All droplet size spectra determinations were replicated three times for each test solution and the mean volumetric droplet size spectra parameters calculated.

Airstream velocity adjacent to the nozzle was measured with a pitot static tube. Air speed, temperature and relative humidity were monitored with a data logger and recorded on the Malvern printouts immediately prior to each test sample run.

Aerial trials

Comparison of aerial spray drift between materials is extremely difficult due to changing meteorological conditions. Wind speed, wind direction, turbulence and atmospheric stability can easily change in the time required to empty, clean and re-load an aircraft between spray applications. To compare drift of different materials under similar conditions, a Cessna T188C Ag Husky fitted with a dual spray system (Sanderson, et al. 1991) permitting simultaneous application was used in this study. The primary spray system was the standard factory fitted liquid dispersal system. The secondary system was fed from a 133 litres fiberglass tank mounted in the aft portion of the existing hopper. A panel mounted vernier control diverts hydraulic fluid to two pump motors simultaneously. Each hydraulic motor drives a centrifugal pump which feed separate standard one-inch round booms. The booms are mounted in tandem on Cessna drop brackets. Each set of booms had 24 nozzles fitted with D8-46 tips and was calibrated to apply 23.4 l/ha (2.5 gal/a) for a swath width of 15.25 m (50 ft.) and a flight speed of 188 km/hr (117 mph). Nozzles were orientated 45° down and back.

Grazon PC was mixed with water at a rate of 0.28 kg a.i/ha (0.25 lb/ac). The polymer based additive (Staput™) was added at a rate of 1.5% v/v and the emulsifying oil (Bivert™) was added at a rate of 1.25% v/v. Grazon PC without an additive was used as a reference material in treatments 1 and 2. Treatment 3 compared Bivert and Staput. Brilliant Sulfo Flavine dye was added to the material in the secondary system at the rate of 950

mg/litre. Rhodamine WT was added to the material in the primary system at a rate of 0.1 % v/v. The additive mixture and the reference materials were sprayed simultaneously.

Spray applications were made 61 m upwind of a sampling mast. Each pass was approximately 320m or 160m on each side of the mast. Applications were made at a 2.5m (10ft) flying height. Treatments were always made perpendicular to the wind direction as observed by a wind vane 2 m above the ground near the mast. The 61m sampling distance was chosen to reduce the impact of swath displacement at higher wind speeds and to improve the probability of sampling a high percentage of the spray cloud. Temperatures ranged from 20 to 24°C (68-75°F), relative humidity 22-27%, and wind 1.1 to 4.5 m/sec (2.5-10mph). Treatments were replicated. All replications of a treatment were applied sequentially.

Airborne spray was sampled using one mm diameter cotton string (WRK Inc. Manhattan, KS) stretched from the ground to the top of the 10 m (33.3 ft.) mast and back to the ground. String collectors are efficient, inexpensive and are a easy way sample spray clouds (Sanderson, *et al.*, 1986). The string was collected after the spray cloud had passed and the sample placed in a 946 ml plastic bag and stored in a freezer until analysis. Tracer dyes were extracted from the string samples by washing for 10 minutes in 60 ml of methanol/water (50% v/v). The samples were analyzed using a Turner Model 111 Fluorometer. A primary and secondary combination of filters of 546 nm and 590 nm was used for Rhodamine WT and a primary/secondary combination of 405 nm and 495 nm was used for Brilliant Sulfo Flavine. This selection of filters excluded response to one dye while measuring the other (Goering and Butler, 1974). Tank samples were run as a reference.

RESULTS AND DISCUSSION

Volumetric droplet size distributions are often described by using $D_{v,0.X}$ and Relative Span values, where the $D_{v,0.X}$ values are defined as the droplet diameters in micrometers (μm) where 0.X fraction of the total liquid volume is contained in droplets of a smaller diameter. The $D_{v,0.5}$ is the droplet diameter at which 50 % of the total liquid volume is contained in droplets of a smaller diameter, and 50 % is in larger droplets. The $D_{v,0.5}$, also termed the Volume Median Diameter (VMD), is one of the most commonly used parameters to describe a droplet size spectrum. Relative Span indicates the range or spread of droplet sizes in a spray (the spectrum width relative to the $D_{v,0.5}$). It is calculated by: $\text{Span} = (D_{v,0.9} - D_{v,0.1})/D_{v,0.5}$. The percentage of the spray volume less than 105 μm is used to indicate the amount of small, driftable droplets.

Samples for atomization tests were taken immediately following mixing of the material in the aircraft hopper and again at the end of each aerial trial. The 'after' samples had been subjected to at least 15 minutes of agitation. The results of the atomization tests are shown in Table 1. The emulsifying oil additive (Bivert) had little effect upon the droplet size spectra. The polymer based additive (Staput) increased the volume median diameter of the spray from 237 μm to 603 μm and also increased the percent volume less than 105 μm from 8.8% to 10.6%. The volume median diameters decreased after recirculation of the polymer based additive suggesting some breakdown of the polymers due to shear, this has been previously observed with polymer based additives (Bouse *et al.*, 1988, Chapple *et al.*, 1991, Sanderson *et al.* 1993). An additional series of wind tunnel tests were conducted with the polymer based additive to further investigate the breakdown of the material. Three rates of

the additive (0.5, 1.0, and 1.5% v/v) were tested with and without the herbicide. Droplet size spectra were evaluated after different amounts of agitation. The mixtures were agitated in a test bench equipped with the same type of centrifugal pump as used on the aircraft. The pump was driven by an electric motor at 1741rpm and recirculated the material at 26 L/min. Figures 1 and 2 clearly shows the breakdown of the polymer based additive and shows that the change in droplet size depends on additive concentration.

In the aerial trials both additives reduced drift potential. On average the emulsifying oil reduced drift by 14% and the polymer reduced drift by 5%. The low mean value for the polymer additive was due to the high variability in the replicates (Table 2) and may have been due to the breakdown of the polymer. When the two additives were applied simultaneously the emulsifying oil gave 16% less drift compared to the polymer.

This study indicates that drift cannot be predicted on the basis of droplet size alone. Comprehensive droplet size data and drift potential measurement are required in the evaluation of spray additives.

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Table 1. Droplet size spectra parameters for formulations of Grazon and adjuvants sprayed through a D8-46 nozzle at 45° to a 188 km/hr (117mph) airstream before and after field trials. (New Mexico, 1993)

TRT	ADJUVANT	TESTED	Dv0.1	Dv0.5	Dv0.9	Span	% Vol < 105
1	None	Before	97	237	526	1.81	8.8
		After	99	238	564	1.95	8.4
	Bivert	Before	100	230	489	1.70	8.2
		After	100	227	495	1.74	8.4
2	None	Before	103	247	548	1.80	7.7
		After	102	241	621	2.15	8.0
	Staput	Before	87	603	1311	2.03	10.6
		After	83	528	1285	2.27	11.2
3	Bivert	Before	98	228	444	1.52	8.7
		After	102	226	461	1.59	8.1
	Staput	Before	83	516	1284	2.33	11.3
		After	59	321	996	2.92	17.0

Table 2. Drift Potential for formulations of Grazon and adjuvants. Drift Potential is relative to formulation with no adjuvant except where drift potential of Bivert is relative to Staput formulation.

REP	Relative Drift Potential									MEAN
	1	2	3	4	5	6	7	8	9	
Biv/Std	1.00	0.75	0.62	0.83	0.87	0.89	0.97	0.91		0.86
Staput/Std	0.77	0.87	0.81	1.06	1.25	0.69	0.87	1.31		0.95
Biv/Staput	1.29	0.88	0.81	1.01	1.15	0.92	0.46	0.39	0.69	0.84

Figure 1. Volume median diameter after different amount of agitation for water with and three rates of the polymer additive Staput. Wind tunnel tests with D8-46 nozzle, 45 degree orientation to 188 km/hr (117mph) airstream.

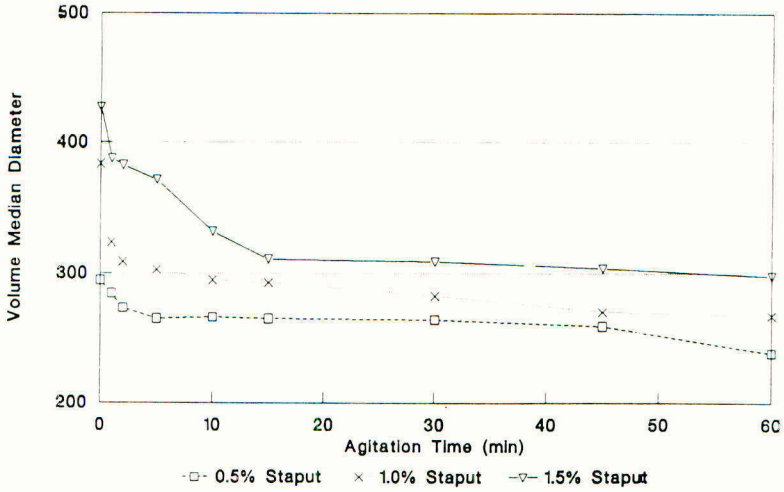
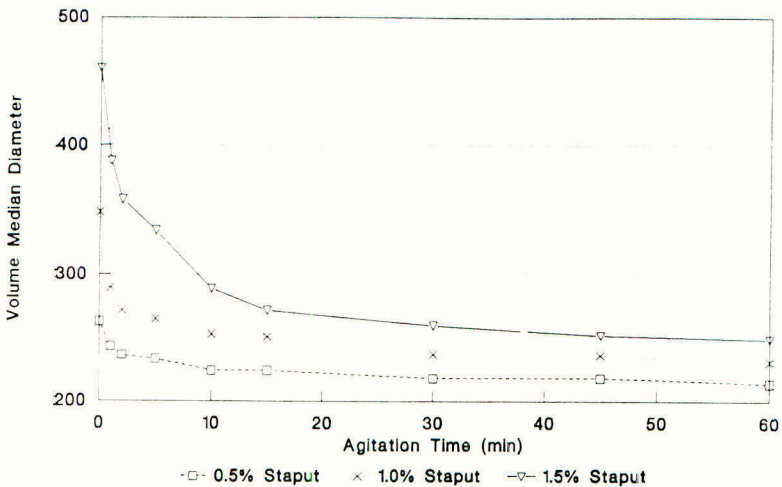


Figure 2. Volume median diameter after different amount of agitation for Grazon PC, water with and three rates of the polymer additive Staput. Wind tunnel tests with D8-46 nozzle, 45 degree orientation to 188 km/hr (117mph) airstream.



DYNAMIC SURFACE TENSION EFFECTS ON SPRAY DROPLET ADHESION OF ORGANOSILICONES

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ABSTRACT

The dynamic surface tension of spray solutions is the most important factor controlling the adhesion of droplets on leaf surfaces. Sprays containing organosilicone wetting agents have been shown to increase adhesion relative to conventional surfactants, such as alkylphenol ethoxylates. Mixtures of organosilicone SILWET L-77[®] Surfactant (TSE) and acetylenic diol ethoxylates (ADE) give a faster dynamic surface tension, improved droplet adhesion, and increased spreading relative to the individual components. The degree of interaction between these surfactants is inversely related to the polyethyleneoxide content (EO) of the ADE. Therefore, the degree of interaction increases with a decrease in the wt % EO of the ADE.

INTRODUCTION

The application of pesticide sprays to waxy, foliar surfaces often requires a wetting agent to promote effective adhesion of spray droplets. This adhesion to these water repellent surfaces plays an important role in the efficacy of the pesticide (Green & Green, 1991). Some of the key factors involved in droplet adhesion and spray coverage are the dynamic surface tension, and the spreadability of the spray solution. Organosilicone wetting agents have been shown to enhance the coverage of pesticidal sprays on difficult to wet leaf surfaces (Stevens *et al.*, 1992 a,b).

SURFACTANTS

Table 1 describes the surfactants used as examples in this paper. All of the surfactants are nonionic in nature:

TABLE 1. Description of Surfactants

SURFACTANT	DESCRIPTION
TSE	TRISILOXANE ETHOXYLATE (8 EO, METHYL CAPPED)
ADE-40	ACETYLENIC DIOL ETHOXYLATE (40 % EO)
ADE-65	ACETYLENIC DIOL ETHOXYLATE (65 % EO)
ADE-85	ACETYLENIC DIOL ETHOXYLATE (85 % EO)
OP-10	OCTYLPHENOL ETHOXYLATE (10 EO)

SURFACE TENSION

Table 2 compares the dynamic and equilibrium surface tension of the ADE's with the organosilicone, TSE. The equilibrium surface tension of the TSE is significantly lower than the ADE's. The dynamic surface tension, on the other hand, approaches equilibrium faster with the ADE's ($\Delta S.T. = 4$ to 8) than with the TSE ($\Delta S.T. = 26$).

TABLE 2. Comparison of Dynamic and Equilibrium Surface Tension

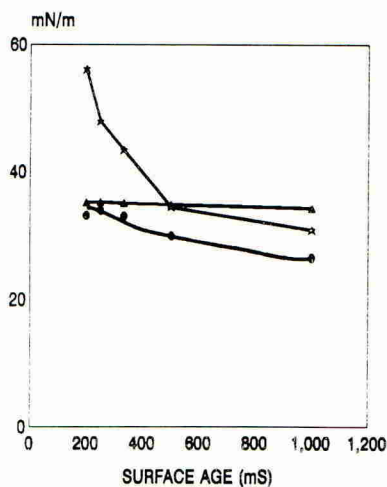
SURFACTANT	SURFACE TENSION		$\Delta S.T.$
	DYNAMIC ^(a)	EQUILIBRIUM ^(b)	
ADE-40	36	32	4
ADE-65	45	40	5
ADE-85	55	47	8
TSE	48	22	26

- a. Dynamic Surface Tension at 200 mS Interface Development Time, Using a Sensadyne 6000, Maximum Bubble Surface Tensiometer (25°C).
- b. Equilibrium Surface Tension was Measured by the Wilhelmy Plate Method, in $5 \times 10^{-3} M$ NaCl at 25°C.
- c. $\Delta S.T. =$ Change in Surface (Dynamic - Equilibrium)

Aqueous mixtures of ADE's with TSE show improved dynamic properties, and in some cases are synergistic. Figure 1 illustrates the type of interaction observed for a 3:1 mixture of ADE-40 and TSE. The dynamic surface tension of a 0.1 wt% solution of the mixture is significantly faster than the equivalent concentration of the individual components alone. The degree of interaction is influenced by the EO content of the ADE. The lower the EO, the greater the degree of interaction. This is further demonstrated by a 3:1 mixture of ADE-85 and TSE (Figure 2). The dynamic surface tension of the mixture is more of an average of the two components. Only within a very short time regime (≤ 200 mS) is a slight improvement in the dynamic surface tension observed for this mixture.

FIGURE 1

DYNAMIC SURFACE TENSION PROFILE
ADE-40/ TSE BLENDS

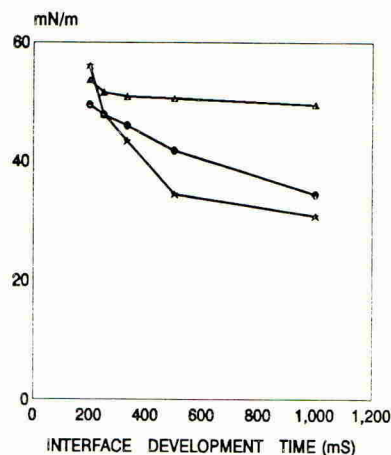


▲ ADE-40 ● 3:1 BLEND ★ TSE

0.1 wt% Actives

FIGURE 2

DYNAMIC SURFACE TENSION PROFILE
ADE-85/ TSE BLENDS



▲ ADE-85 ● 3:1 BLEND ★ TSE

0.1 wt% Actives

DROPLET ADHESION

The effect of this improvement in dynamic surface tension is further evidenced by an increase in the adhesion of spray droplets on pea leaf (*Pisum sativum*). Surfactant solutions were applied to pea leaf using a piezoelectric droplet generator, employing a method previously described (Stevens *et al.*, 1992, a). The droplet size, for this experiment, had an average diameter of 821 μm ($\pm 30 \mu\text{m}$), with an impact velocity of 1.19 to 1.25 m/s for a 50 mm free fall distance (FFD), and 1.46 to 1.51 m/s, for 100 mm FFD.

Table 3 demonstrates the influence of the various surfactants and mixtures on droplet adhesion, at a 22.5° angle of incidence, and a 50 mm FFD. The degree of adhesion increases with surfactant concentration. Also, within the group of ADE's, adhesion decreases with an increase in the EO content (85 < 65 < 40). There is a small improvement in adhesion observed for mixture of the TSE and ADE-65 and ADE-85. This becomes more obvious when the angle of incidence is increased to 45°, and the FFD to 100 mm (Figure 3). The mixture of ADE-40 and the TSE give a greater degree of adhesion than the individual components alone. This indicates that the observed improvement in dynamic surface tension for these mixtures relates to droplet adhesion.

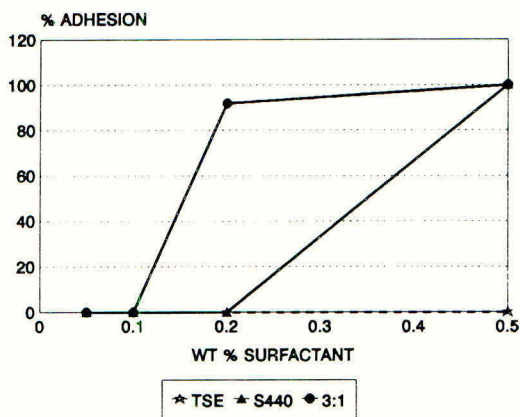
TABLE 3. INFLUENCE OF SURFACTANT ON DROPLET ADHESION^(a)

SURFACTANT	PERCENT OF DROPLETS ADHERING			
	0.05	WEIGHT % SURFACTANT		0.5
		0.1	0.2	
TSE	0	0	40	100
ADE-40	44	100	100	100
3:1 BLEND ^(b)	24	100	100	100
ADE-65	0	24	100	100
3:1 BLEND	0	52	100	100
ADE-85	0	0	0	0
3:1 BLEND	0	0	0	100

a. Adhesion at 50 mm Free Fall Distance; 22.5° Angle of Incidence.

b. 3:1 Blends ADE/TSE

FIGURE 3. Effect of Surfactants on Droplet Adhesion



FFD = 100 mm; ANGLE = 45 Deg.

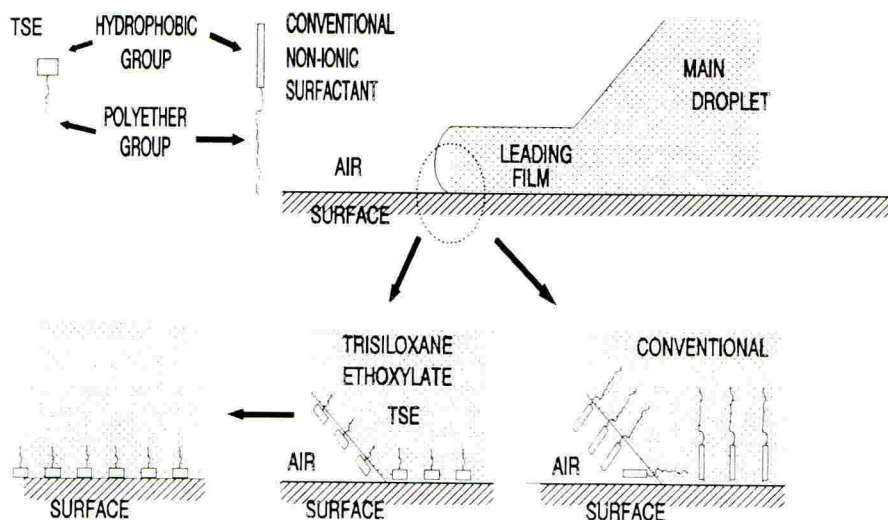
SPREADING

Spreading ability was determined by applying 10 μL of surfactant solution to a polyester film and measuring the spread area ratio (SAR), relative to water.

The spreading ability of the TSE is related to its potential to reduce the surface tension of aqueous solutions (≈ 21 mN/m), and to its compact structure (Goddard *et al.*, 1992). A convenient way of visualizing the spreading mechanism is illustrated in Figure 4. Here it is suggested (Goddard *et al.*, 1992) that the compact hydrophobic portion of the TSE allows it to readily transfer from the air liquid interface of the advancing solution to a low energy surface, such as a waxy leaf cuticle. This phenomenon is likened to a "Molecular Zippering" of the liquid/solid interface. Similarly, the conventional surfactant is depicted with a large bulky hydrophobe (i.e., octylphenol group) that tends to act like a prop for the advancing droplet. This propping effect causes interference with the spreading of the solution. In short, the "zipper" jams.

Judicious selection of cosurfactants for the TSE is critical when formulating pesticide sprays. Many conventional/ organosilicone surfactant combinations will afford adequate adhesion properties. However, the inclusion of a secondary surfactant, with the TSE, will often interfere with the spreading properties associated with organosilicones (Murphy *et al.*, 1992). For example, a 0.25 % solution of a conventional spreader, OP-10, has an SAR of 7, compared to TSE at 0.062% with an SAR of 86. A 3:1 mixture of the two components has an SAR of 5, demonstrating the antagonistic nature some conventional surfactants have on the spreadability of the TSE.

FIGURE 4. Molecular Zipper Action



Unlike many conventional surfactants, which interfere with the aqueous spreading of the organosilicones, the ADE's are favorable cosurfactants. These materials in fact increase the spreading ability of the TSE (Table 4). The greatest increase in spreading is observed with ADE/TSE mixtures (3:1), where the ADE contains 40% EO.

TABLE 4. Influence of Cosurfactants on TSE Spreading

<u>SURFACTANT</u>	<u>WT%</u>	<u>SPREAD AREA RATIO^(a)</u>	
		<u>ALONE</u>	<u>3:1 WITH TSE</u>
TSE	0.062	86	N/A
X-100	0.250	5	7
ADE-40	0.250	4	136
ADE-65	0.250	2	107
ADE-85	0.250	2	96

a. Spread Area Ratio Relative to Water.

The combination of the ADE's with trisiloxane based surfactants offer the advantage of quick dynamic surface tension properties and improved spreading performance of spray formulations, relative to the individual components alone.

ACKNOWLEDGEMENTS

The authors would like to thank Mary Ann Paccione for providing the dynamic surface tension evaluations.

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VARYING RESPONSES AMONG WEED SPECIES TO GLYPHOSATE-TRIMESIUM IN THE PRESENCE OF AN ORGANOSILICONE SURFACTANT.

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ABSTRACT

Glyphosate-trimesium is a highly water soluble herbicide used for total vegetation control. Slow absorption of glyphosate salts into leaves can present a rainfastness problem. Silwet L-77 is an organosilicone surfactant capable of inducing sufficiently low surface tensions in aqueous solutions to produce excellent spreading on leaf surfaces and stomatal infiltration. Enabling entry *via* stomata has been reported as increasing the rainfastness of glyphosate salts. However, it is also known that in the absence of rain, reductions in activity can occur.

This paper examines the contrasting responses of different species to the addition of Silwet L-77 to glyphosate-trimesium. Species showing increased susceptibility or tolerance to glyphosate-trimesium in the presence of Silwet L-77 were identified in glasshouse experiments. The type of response to Silwet L-77 is discussed in terms of the nature of the leaf surface of each species and overall plant morphology, and theories of mechanisms of organosilicone surfactant activity on leaf surfaces.

INTRODUCTION

Organosilicone surfactants such as Silwet-L-77 (Union Carbide) have the ability to lower the surface tension of aqueous solutions to approaching 20 mNm^{-1} which permits spray solutions to infiltrate stomata (Schonherr & Bukovac, 1972; Stevens *et al.*, 1992). This allows extremely rapid absorption of active ingredients (Stevens *et al.*, 1991). Under conditions where rainfall soon after spray application may restrict the efficacy of herbicides, the addition of such an adjuvant can impart rainfastness (Field & Bishop, 1988; Thonke *et al.*, 1989).

Glyphosate-trimesium is a broad-spectrum translocated herbicide. Glyphosate salts have been found to be particularly responsive to Silwet L-77 in the control of several species even in the absence of post-application rainfall, *eg.* gorse (*Ulex europaeus*) (Balneaves & Frederic, 1988) and perennial ryegrass (*Lolium perenne*) (Bishop & Field, 1983). However, the addition of Silwet L-77 has antagonised the control other weed species by glyphosate (Field *et al.*, 1992). In general, such antagonism seems more likely to occur on grasses than on broad-leaved species.

The species-dependent variability in the influence of Silwet L-77 on the efficacy of control by glyphosate salts obviously restricts the application of this adjuvant. Benefits will occur when rainfall sufficient to otherwise remove herbicide deposits from the leaf surface follows application. In the absence of such rainfall, reductions in weed control may ensue.

The objective of the present studies was to determine the effects of Silwet L-77 on the control of several weed species by glyphosate-trimesium in the absence of rainfall, and to attempt to explain these in terms of the characteristics of the morphology of the leaf surface and entire shoots of each species.

MATERIALS AND METHODS

Glasshouse Experiments

Three experiments were conducted under warm or temperate glasshouse conditions appropriate to each of the selection of broad-leaved, grass and sedge species investigated. Plants were grown three to a 10 cm pot and sprayed in a tracksprayer using 200 l/ha water. A commercially available formulation of glyphosate-trimesium containing a surfactant system was applied at rates of 62.5-2000 g/ha. In Experiment 1, Silwet L-77 was added to the spray solution at 0.0625-5% (v/v). In Experiments 2 and 3, only the 0.5% concentration was tested. Grasses and sedge had 3-6 leaves, and broad-leaved species 4-6 leaves at time of treatment. Data are reported here as rates of glyphosate-trimesium required for 90% control of each species calculated by least squares regression of visual assessments of gross herbicidal activity made 25-27 days after treatment.

Microscopy

Samples of fresh leaf tissue from each species were observed with a Jeol JSM 6300 scanning electron microscope at an accelerating potential of 3 kV.

RESULTS

Glasshouse Experiments

The addition of Silwet L-77 at any concentration did not significantly affect the rate of glyphosate-trimesium resulting in 90% control of *Amaranthus retroflexus*, *Chenopodium album*, and *Digitaria sanguinalis* (Table 1). On *Elymus repens* and *Setaria viridis*, the trend was towards greater antagonism with increasing Silwet L-77 concentration; with *Matricaria perforata* the trend was for greater efficacy with increasing adjuvant concentration.

On broad-leaved weeds (Table 1a), all concentrations of Silwet L-77 significantly ($p = 0.05$) increased the efficacy of glyphosate-trimesium on *Conyza canadensis*, but antagonised control of *Euphorbia heterophylla*. Antagonism increased with Silwet L-77 concentration on *Polygonum aviculare*. On grasses (Table 1b), all concentrations of Silwet L-77 increased the efficacy of glyphosate-trimesium on *Lolium perenne*, but antagonised control of *Sorghum halepense*. Antagonism increased with Silwet L-77 concentration on *Eleusine indica*. On the sedge, *Cyperus rotundus*, Silwet L-77 at all concentrations increased efficacy, but all cases were non-significant.

The effects of 0.5% Silwet L-77 on six species in three experiments are compared in Table 2. On broad-leaved weeds, Silwet L-77 consistently increased the efficacy of glyphosate-trimesium on *Matricaria perforata* and antagonised control of *Polygonum aviculare*. Effects on *Euphorbia heterophylla* varied. On grasses, control of *Sorghum halepense* was markedly antagonised in two experiments, effects on *Lolium perenne* varied. On *Cyperus rotundus* effects were always clearly beneficial, but reductions in the rate of glyphosate-trimesium required for 90% control always just failed to attain statistical significance. However, closer examination of the data (not shown) indicated large benefits at sub-optimal rates, improving control from less than 20% up to 80%.

Table 1. Rates of glyphosate-trimesium required for 90% control of several weed species at various concentrations of Silwet L-77.

* = significantly different from no Silwet treatment at $p = 0.05$.
= 60% control

a) Broad-leaved Weeds

Species	Silwet L-77 concentration (% v/v)				
	0	0.0625	0.125	0.25	0.5
<i>Amaranthus retroflexus</i>	186	192	228	229	141
<i>Chenopodium album</i>	712	744	625	970	722
<i>Conyza canadensis</i> #	709	361*	298*	337*	169*
<i>Euphorbia heterophylla</i> #	418	706*	802*	759*	696*
<i>Matricaria perforata</i>	450	503	505	282	232
<i>Polygonum aviculare</i>	711	697	802	1079	2080*

b) Grass and Sedge Weeds

Species	Silwet L-77 concentration (% v/v)				
	0	0.0625	0.125	0.25	0.5
<i>Eleusine indica</i>	725	644	923	863	1338*
<i>Elymus repens</i>	399	422	428	480	503
<i>Digitaria sanguinalis</i>	361	346	375	400	406
<i>Lolium perenne</i>	692	522*	577	549	494*
<i>Setaria viridis</i>	181	160	238	265	321
<i>Sorghum halepense</i>	283	405*	490*	546*	547*
<i>Cyperus rotundus</i>	1037	657	791	898	748

Table 2. Rates of glyphosate-trimesium required for 90% control of several weed species with Silwet L-77 added at 0.5% (v/v) in three experiments.

* = significantly different from 0 Silwet treatment at $p = 0.05$.

= 60% control

Species	Experiment 1		Experiment 2		Experiment 3	
	No Silwet	0.5% Silwet	No Silwet	0.5% Silwet	No Silwet	0.5% Silwet
<i>Euphorbia heterophylla</i>	418#	696#*	1804	2001	1871	1391
<i>Matricaria perforata</i>	450	233	358	184*	345	81*
<i>Polygonum aviculare</i>	711	2080*	840	2515*	540	650
<i>Lolium perenne</i>	692	494*	433	715*	610	637
<i>Sorghum halepense</i>	283	547*	298	780*	372	358
<i>Cyperus rotundus</i>	1037	748	2084	1469	1810	942

Microscopy

Cyperus rotundus was the only species without stomata on the adaxial (upper) leaf surface (Table 3). All grasses had crystalline epicuticular wax on adaxial leaf surfaces which were not wettable by water. Some grasses had reduced amounts or amorphous wax on the abaxial (lower) leaf surface. The abaxial surfaces of *Lolium perenne* and *Setaria viridis* were, as such, readily wettable. Broad-leaved species varied in the nature of surface wax deposits. Those with crystalline wax were not wettable, those with amorphous wax were readily wetted by water.

Species differed widely in gross shoot morphology. Of the broad-leaved weeds, *Matricaria perforata* and *Conyza canadensis* contrasted with other species in that they had a rosette-type habit. Other species had leaves borne on 10-15 cm of stem at the time of treatment. All grasses were erect and the youngest fully-emerged lamina on main stems had sheaths 10-15 cm in length. The sedge, *Cyperus rotundus*, in contrast to the grasses, had no pseudo-stem of leaf sheaths.

DISCUSSION

The effects of Silwet L-77 on the efficacy of glyphosate-trimesium clearly varied with target species. The response to Silwet L-77 was independent of whether weeds were broad-leaved or grasses. The effective concentration of Silwet L-77 also varied with species. Furthermore there were some inconsistencies in the response of individual species to the presence of Silwet L-77.

Table 3. Leaf surface characteristics of weed species and wettability.
c = crystalline wax, a = amorphous wax.

a) Broad-leaved Weeds

Species	Adaxial leaf surface			Abaxial leaf surface
	Stomata	Wax	Wettable	
<i>Amaranthus retroflexus</i>	yes	a	yes	similar
<i>Chenopodium album</i>	yes	c	no	similar
<i>Conyza canadensis</i>	yes	a	yes	similar
<i>Euphorbia heterophylla</i>	yes	c	no	similar
<i>Matricaria perforata</i>	yes	a	yes	similar
<i>Polygonum aviculare</i>	yes	c	no	similar

b) Grass and Sedge Weeds

Species	Adaxial leaf surface			Abaxial leaf surface
	Stomata	Wax	Wettable	
<i>Eleusine indica</i>	yes	c	no	similar
<i>Elymus repens</i>	yes	c	no	fewer stomata, less crystalline wax
<i>Digitaria sanguinalis</i>	yes	c	no	similar
<i>Lolium perenne</i>	yes	c	no	astomatous, amorphous wax, readily wettable
<i>Setaria viridis</i>	yes	c	no	amorphous wax, readily wettable
<i>Sorghum halepense</i>	yes	c	no	similar
<i>Cyperus rotundus</i>	no	a	yes	stomata present

The literature on the adjuvant properties of Silwet L-77 overwhelmingly concentrates on its ability to facilitate stomatal infiltration and consequent rapid uptake of herbicide. Concentrations of at least 0.2% have been suggested as being necessary for this to occur (Stevens *et al.*, 1991, 1992). The present studies have yielded equivocal results, but a new perspective to the adjuvant effects of Silwet L-77 is suggested.

In *Cyperus rotundus*, there are no stomata on the adaxial leaf surface, yet there were consistent increases in the activity of glyphosate-trimesium. These occurred at concentrations of Silwet L-77 down to 0.0625%. There were also similar benefits on *Coryza canadensis* and, at higher concentrations, on *Matricaria perforata*. Although, obviously very different in detailed morphology, these all have leaf arrangements and angles which suggest that much of the spread of spray solutions promoted by the presence of Silwet L-77 would be directed towards growing points, expediting the effective placement of the herbicide. In contrast, antagonism on species such as *Sorghum halepense* and *Polygonum aviculare* may be explained by spray droplets containing Silwet L-77 readily running-off leaf lamina to no useful end. The characteristics of leaf surfaces with respect to their epicuticular wax crystallinity and the accessibility of abaxial surfaces in some species merit further research.

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NEW GLYPHOSATE FORMULATIONS SET NEW STANDARDS OF OPERATOR AND ENVIRONMENTAL SAFETY

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ABSTRACT

Recent developments in adjuvant technology were employed to develop new formulations of glyphosate which, by comparison with the already high standards set the current 360 g a.e./l formulation, have improved operator and environmental safety characteristics. This was achieved by primary selection of candidate adjuvants on toxicological criteria, and secondary selection on efficacy criteria. Further development resulted in soluble liquid (MON 52276) and soluble granule (MON 44068) formulations which, as well as exhibiting large reductions in mammalian and aquatic toxicity, possess superior efficacy and tank-mixture compatibility to the standard glyphosate formulation. In addition, volumetric measurement and mixing of the MON 44068 formulation is facilitated by its predictable bulk density and its rapid dissolution in water, while the dry product form will enable a move from rigid plastic packaging to a more readily disposable alternative.

INTRODUCTION

Roundup® herbicide (glyphosate 360 g a.e./l) has, for many years, been widely recognised for its particularly low hazard profile among pesticides. This reputation results from the broad generality of the operator, consumer and environmental safety characteristics of the formulation, but especially from the low toxicity of glyphosate to man and wildlife (Atkinson, 1985), its rapid inactivation and breakdown in soils (Torstensson, 1985) and its rapid dissipation and breakdown in aquatic environments (Goldsborough & Beck, 1989; Chen et al, 1989).

In anticipation of a continuation in the rising regulatory and public expectations of standards in pesticide safety, and of further increases in use of glyphosate, Monsanto have looked to recent developments in adjuvant technology to enhance the characteristics of its 360 g a.e./l glyphosate product. This project, initiated in 1989, was aimed at further reducing the aquatic toxicity of the product (which is already registered for the control of emerged aquatic weeds) and at eliminating any classification of operator hazard. Concurrently, a project to develop a second formulation was initiated, retaining the above objectives but incorporating a requirement for a water soluble granular product with additional, potential benefits, such as the ability to meet future requirements for reductions in the packaging waste stream.

MATERIALS AND METHODS

Initially, available data on the toxicology of a large number of potential

replacements for the ethoxylated tallow-amine (ETA) surfactant, used in the majority of 360 g a.e./l products, was examined with the cooperation a number of adjuvant manufacturers. This process identified a small number of surfactants, representing several structurally similar groups of compounds. These were individually assessed for oral and dermal toxicity, and eye and skin irritancy (ODES values), and fish and daphnia toxicity, using rapid screening techniques.

The surfactant candidates which exhibited low levels of the above attributes were then progressed to efficacy screening where, in tank mixture with technical isopropylamine (IPA) salt of glyphosate in aqueous solution, their adjuvant activity against indicator species (*Elymus repens*, *Lolium rigidum*, *Geranium molle* and *Brassica napus*) sown in pots in greenhouse trials (Split Plot design, 4 replicates) was compared with the standard 360 g a.e./l formulation of glyphosate at low (360-540 g a.e./ha), intermediate (720-900 g a.e./ha) and a high (1080-1440 g a.e./ha) rates of application. Assessment was of visual foliar effect for all species. Further assessments of regrowth of *E. repens* was carried out six weeks after treatment.

Those candidates which imparted good efficacy to glyphosate were then used to prepare speculative formulations for field efficacy testing, against the major annual and perennial weeds prevalent in each agricultural zone throughout Europe. Experience gained from these trials was used to identify the final choice of replacement surfactants, and to prepare final formulations. The desired enhancements in operator and environmental safety were confirmed in these by European Community guideline study testing (Anon., 1984).

The result of this selection process was a soluble liquid formulation (MON 52276), containing 360 g a.e./l glyphosate, and a water soluble granule formulation (MON 44068), containing 420 g a.e./kg glyphosate.

In the UK since 1991, further Small Plot Replicated (x4) field trials have evaluated the efficacy of the MON 52276 and MON 44068 formulations, applied by conventional hydraulic plot sprayer, against a wide range of weeds and in all major usage situations, at rates and application volumes equivalent to those currently recommended on the standard 360 g a.e./l product label (Anon., 1991).

Pesticide tank-mix compatibility was assessed for both new formulations (Anon, 1986) and, for the MON 44068 formulation, bulk density and solubility were measured, the latter by measuring the number of inversions required to dissolve concentrations of up to 35% w/v, made up to 100 ml with demineralised and 342 ppm Ca/Mg water (WHO) at 5° and 20° C.

RESULTS

Adjuvant screening resulted in the selection of two surfactants, which form the basis of the surfactant system in the MON 52276 and MON 44068 formulations. Aquatic toxicity and skin/eye irritancy values show significant improvement over the standard 360 g/l glyphosate formulation, while the very low oral and dermal acute toxicity of the standard is maintained in the new formulations (Table 1).

TABLE 1. ODES, fish and daphnia toxicity values - a comparison of the MON 52276 and MON 44068 formulations with the standard 360 g a.e./l glyphosate formulation.

	MON 52276	MON 44068	Standard
Acute Oral LD_{50} Rat	> 5000 mg/kg	4999 mg/kg	> 5000 mg/kg
Acute Dermal LD_{50} Rat	> 5000 mg/kg	> 5000 mg/kg	> 5000 mg/kg
Skin/Eye Irritancy	Non Irritant - EC Classification	Non Irritant - EC Classification	Irritant - EC Classification
LC_{50} Trout (96 h)	> 989 mg/l	> 1020 mg/l	8.2 mg/l
LC_{50} Daphnia (48 h)	676 mg/l	> 970 mg/l	5.3 mg/l

Long-term *E. repens* control from MON 52276 or MON 44068 application in U.K. field trials demonstrate the consistency of control in the absence of the additional surfactant necessary to limit the variability in efficacy of the standard formulation (Fig. 1).

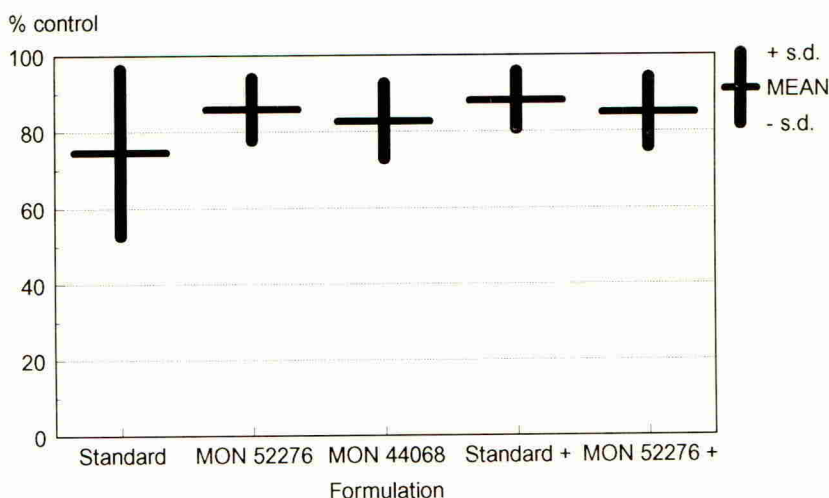


Figure 1. *Elymus repens* control, calculated from shoot counts, assessed one year after treatment with 720 g a.e./ha glyphosate as MON 52276, MON 44068 and standard 360 g a.e./l formulations (+ - additional surfactant at a rate of 0.5% of spray volume) - 9 trials.

Both formulations were capable of tank-mixture with a wide range of herbicides for use before emergence of cereal and other crops, in fruit crops and in non-crop situations, a feature which is absent in current 360 g a.e./l glyphosate formulations. In addition, foam production was markedly reduced by comparison with the standard.

The MON 44068 formulation is a dust-free extruded granule. Measurement of the bulk density of freshly poured MON 44068 product from 93 manufactured batches gave a range of 1.41 to 1.51 l/kg, with a mean of 1.45 l/kg. The MON 44068 formulation dissolved readily at widely disparate concentrations and temperatures, and in contrasting water types (Table 2).

TABLE 2. Number of inversions required to dissolve specified concentrations of the MON 44068 formulation in two water types at two temperatures.

MON 44068 Concentration (% w/v)	Demineralised water		342 ppm Ca/Mg	
	5°C	20°C	5°C	20° C
1	13	7	11	7
13	14	9	14	9
25	17	11	17	11

DISCUSSION

At the completion of this project, formulation innovation has enabled the realisation of a challenging objective, namely, that of creating two new products which meet the requirement for enhanced operator and environmental safety, while retaining the considerable efficacy potential of standard 360 g a.e./l glyphosate. In fact, the surfactant systems which underpin the MON 52276 and MON 44068 glyphosate products have exceeded their original specification, precluding the need for added surfactant at low rates and giving highly compatible, low foaming products.

The dust-free nature and predictable bulk density of the MON 44068 formulation are such that it will be possible for the user to measure part-packs, without respiratory hazard, by volumetric means. Because the formulation also dissolves rapidly, it retains the convenience of a liquid formulation and offers the additional potential for a move away from rigid plastic containers to a more environmentally acceptable alternative.

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SEED OIL AND SEED OIL DERIVATIVES AS ADJUVANTS FOR METAMITRON

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ABSTRACT

The influence of two rapeseed oils, one rapeseed oil methyl ester and one mineral oil on foliar penetration of different metamilron formulations was investigated. Foliar penetration was determined by two methods. Firstly, by monitoring quench parameters of chlorophyll fluorescence to obtain information about the effect on initial uptake kinetics. These experiments were carried out with Goltix WG70, a combination of Goltix WG70/Betanal Progress and a new Goltix Triple formulation containing metamilron, phenmedipham and ethofumesate. Secondly, foliar penetration was measured by determining uptake of ^{14}C -labelled metamilron (WP70) over a period of 48-72 h. Tested species were *Beta vulgaris*, *Matricaria chamomilla*, *Galium aparine* and *Amaranthus retroflexus*.

The results of the fluorescence technique and the ^{14}C -method correspond basically but not in every detail. Considering all species, the most effective adjuvant is rapeseed oil methyl ester followed by the two rapeseed oils Telmion and Rako/Binol and the mineral oil.

INTRODUCTION

Mineral oils have been commonly used as adjuvants for post-emergence weed control with the herbicide metamilron. In future, rapeseed oils will increasingly substitute mineral oils. We were interested in the magnitude of foliar uptake enhancement of metamilron by different oil adjuvants under laboratory conditions. Chlorophyll fluorescence and uptake of ^{14}C -labelled metamilron were used to measure the influence of two rapeseed oils, one rapeseed oil methyl ester and one mineral oil. The chlorophyll fluorescence technique was especially used as a quick and non-invasive method for an evaluation of different adjuvants.

MATERIAL AND METHODS

Formulations and adjuvants

For chlorophyll fluorescence measurements metamilron was applied as Goltix WG70 (3 kg/ha), as a tank mix of Goltix WG70 (1 kg/ha)/ Betanal Progress[®] EC (1 l/ha) and as a recently developed Goltix Triple WG (2 kg/ha), comprising of 28 % metamilron, 6.5 % phenmedipham, 6.5 % ethofumesate and surfactant. The water volume was always 300 l. Experiments with ^{14}C -labelled metamilron were conducted with a WP70 (1.2 kg/ha/250L) which corresponded to the WG70. The specific activity was 4.33 kBq/mg Al.

¹Betanal Progress[®] = phenmedipham, ethofumesate and desmedipham (registered trademark of Schering AG)

Adjuvants were a mineral oil (95 % mineral oil, 5 % surfactant, = Min Oil), the rapeseed oil Telmion from Hoechst AG (85 % rapeseed oil, 15 % surfactant, = RSO1), the rapeseed oil Rako/Binol from Karlshamns (95 % rapeseed oil, 5 % surfactant, = RSO2) and the formulated rapeseed oil methyl ester Edenor Me-SU from Henkel AG (90 % Edenor Me-SU, 10 % surfactant, = R-ME). The concentration of all adjuvants was 0.33 %.

Plant material

All plants were grown in a glasshouse in 10 x 10 cm pots. Two days before starting experiments plants were transferred to a growth chamber (12 h light, 1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$, 20 °C/18 °C, 60 % RH). The growth stage was 12 (BBCH scale, Bleiholder et al., 1990).

Chlorophyll-fluorescence measurements

Chlorophyll-fluorescence was measured from a leaf surface of about 2-3 cm^2 with a pulse-amplitude-modulation (PAM) fluorometer from Walz (Effeltrich, Germany). The fluorescence signal is monitored through a fibre optic with a weak modulated measuring beam of 655 nm (for details see Schreiber et al. 1986). The minimal (F_0) and maximal (F_m) fluorescence signals of dark adapted leaves were measured, with all PSII reaction centres fully open or closed. The light intensity of the saturation pulse (0.7 s) for F_m determination was 700 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (white light). After F_m determination the actinic light was switched on (14 $\mu\text{mol m}^{-2} \text{s}^{-1}$, 659 nm LED). Additional, saturation pulses were given every 20 s to give an F_m' signal, which is defined as the maximal fluorescence yield of an illuminated leaf. From these parameters fluorescence quench coefficients were calculated on-line (DA-100 software, Walz). For our purpose the photochemical quench coefficient QP ($\text{QP} = \frac{F_m' - F_t}{F_m' - F_0}$) was the most suitable and this may vary between 0 and 1 and reflects the changes in fluorescence intensity linked to the oxidation/reduction of Q_A . The QP value of an untreated leaf stabilised at about 0.8-0.9 within 5 min of illumination. While fluorescence was measured continuously 5 μl of diluted formulation was delivered to the upper leaf surface. To overcome the problem of different droplet spreading the droplet was covered by a cover-slide.

The results are expressed as per cent inhibition of QP related to the QP value during the steady state before application of the herbicide. From these graphs (Fig. 1) the time to cause 30 % inhibition of the QP (I_{30} in min) was taken to compare the different treatments.

^{14}C -uptake studies

On the upper leaf surface 4 x 2 μl droplets of the radiolabelled metamiltron WP70 were applied. At indicated time intervals the portion of radioactivity which was not taken up by the leaf was removed from the site of application by cellulose-acetate stripping (Silcox and Holloway, 1986). The penetration of radioactivity was subsequently confirmed by combustion-LSC analysis of the treated leaf. Uptake is defined as the percentage of radioactivity recovered within the leaf related to the sum of recovered ^{14}C . The total recovery of ^{14}C varied between 80-90 % of the applied activity.

Statistics

All experiments were conducted with five replicates. Results are shown as mean values \pm standard error. In appropriate cases data were subjected to analysis of variance. Significance of mean values were tested with Duncan's Multiple Range Test ($\alpha=0.05$). Mean values followed by the same letter were not significantly different.

RESULTS AND DISCUSSION

Chlorophyll fluorescence

As metamiltron directly blocks the electron transport chain of PSII, an instant response of the fluorescence signal, depending on the uptake velocity of the herbicide into the mesophyll, is expected. In Fig. 1 a typical inhibition kinetic of the QP-value of a WG70 formulation of metamiltron to which different adjuvants were added is shown. Since all tested adjuvants, when applied alone, had no effect on the fluorescence signal during the test period, it appears plausible to interpret the data as an enhancement of the foliar penetration of metamiltron by the adjuvants. This has been shown before with diuron and phenmedipham (Percival et al. 1990, Voss et al. 1984).

Figure 1: Influence of adjuvants on the inhibition of the QP by metamiltron WG70 (*G. aparine*)

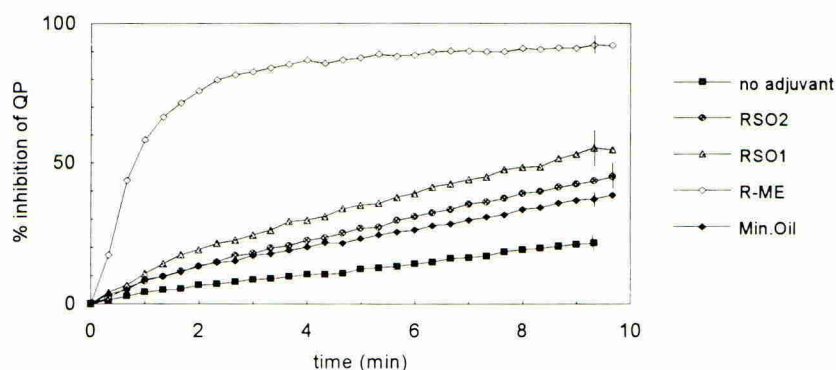
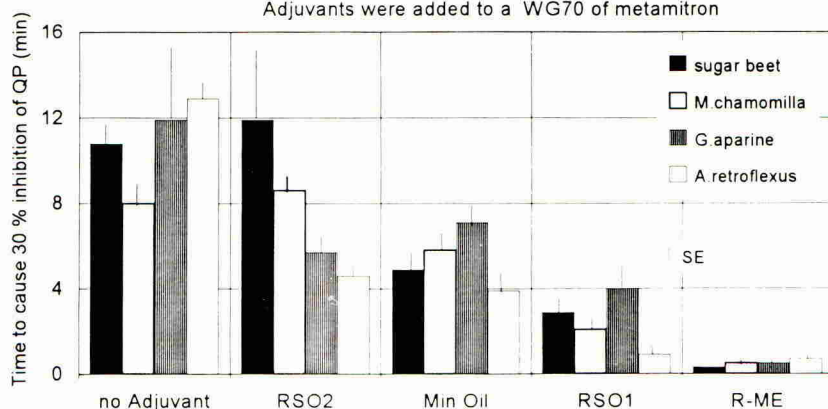


Figure 2: Influence of adjuvants on the inhibition of the QP
Adjuvants were added to a WG70 of metamiltron



The l_{30} values (time to cause 30 % inhibition of QP) of all species treated with the WG70 formulation are shown in Fig. 2. A high l_{30} corresponds to a slow inhibition and vice versa. It can be seen that the WG70 without any adjuvant exhibited the slowest inhibition of QP (l_{30} 7-13 min), certainly due to the low surfactant content. Considering all species, the

most effective adjuvant in enhancing metamitron uptake was the rapeseed oil methyl ester. It exhibited a 13 to 20 fold increase of the inhibition velocity (t_{30} 0.3-0.7 min). The effect of the rapeseed oil RSO2 was species dependent but usually RSO2 showed the lowest effect. The second tested rapeseed oil RSO1 was a more powerful adjuvant compared to RSO2 and the mineral oil. This may be attributed to the higher surfactant concentration of this product.

Figure 3: Influence of adjuvants on the inhibition of the QP

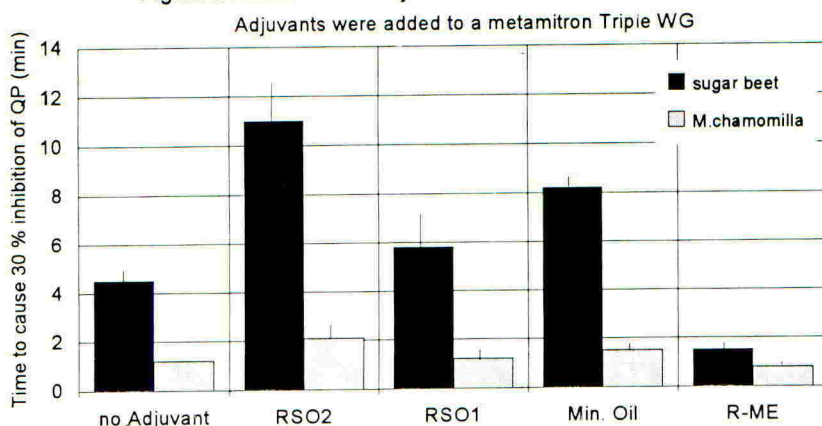
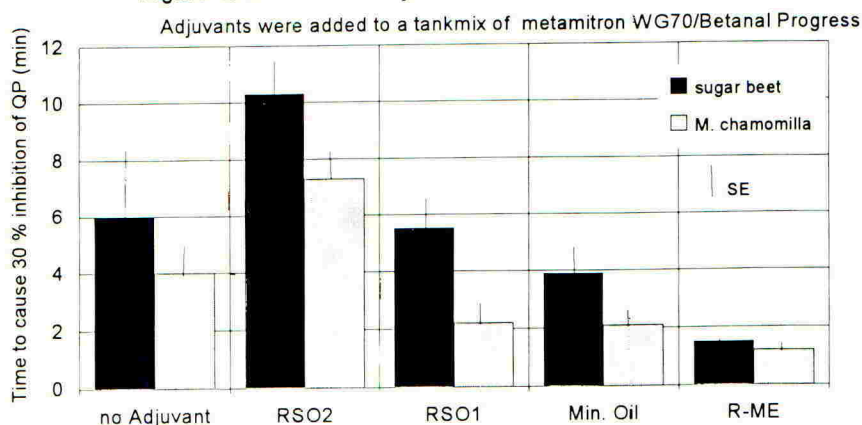


Figure 4: Influence of adjuvants on the inhibition of the QP



We then tested the adjuvants with the new Triple formulation and the tank mix of metamitron WG70/ Betanal Progress (Figs. 3 and 4). Again, R-ME and RSO1 promoted the quickest inhibition of QP. However, since the Triple formulation and the tank mix with Betanal Progress themselves contained higher amounts of surfactants or solvents, which increased the uptake of the herbicide, the effect of additional added adjuvants was far lower as with the WG70. An uptake enhancement of metamitron by phenmedipham EC formulation after spray application has been observed earlier (Wirth et al. 1991). They also showed the rather weak effect of a mineral oil. The observed antagonistic effect of RSO2 with both formulations is presumably attributed only to the beginning of the uptake kinetics (see below).

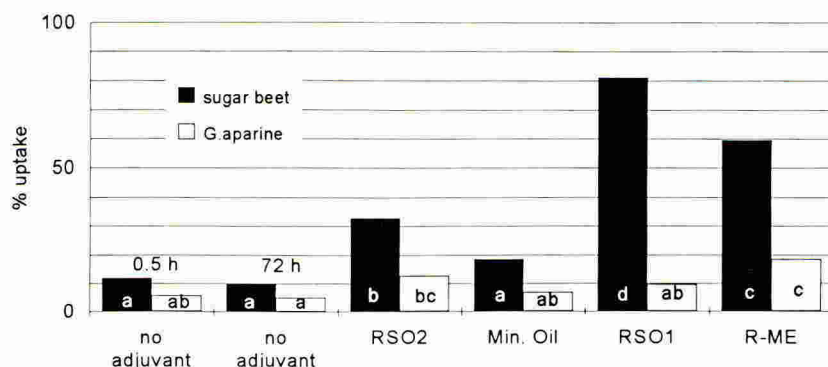
In Fig. 3 and 4 a selectivity effect was also visible throughout the treatments. The inhibition of QP was much faster in *Matricaria chamomilla* than in sugar beet. This was due to the fact that in sugar beet phenmedipham had virtually no effect on the fluorescence signal during the observed time period which was not the case in *M. chamomilla* (data not shown).

Generally, this kind of chlorophyll fluorescence experiment gave information on the uptake velocity of metamitron during the first minutes after application. During this time no drying of the applied droplet occurred and no information was obtained about absolute amounts of metamitron taken up over a longer period.

¹⁴C-uptake

In order to establish, to what extent the fluorescence data can be extrapolated to a longer penetration period we conducted uptake experiments with ¹⁴C-labelled metamitron (WP70) up to 72 h.

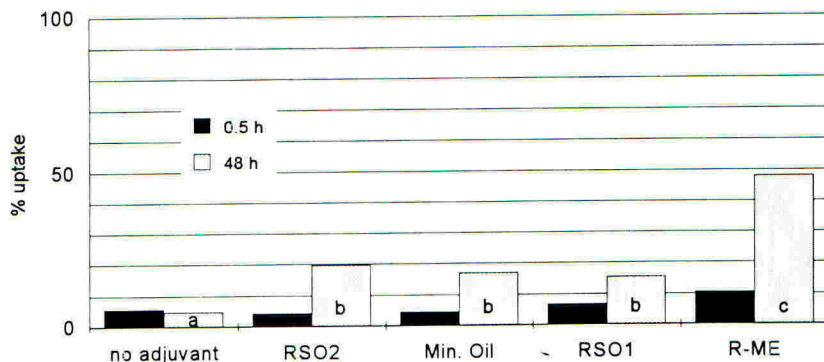
Figure 5: Influence of adjuvants on the uptake of radio labelled metamitron WP70 (after 72 h)



In the first two experiments we measured the influence of adjuvants on the foliar penetration in *Galium aparine* and sugar beet after 72 h (Fig. 5). In comparison to the control with no added adjuvant, a significant uptake enhancement in *G. aparine* was observed with R-ME (4 fold) and RSO2 (2 fold). In sugar beet, uptake was increased considerably by RSO1 (8 fold), R-ME (6 fold) and RSO2 (3 fold). In both species the mineral oil showed no significant enhancement. The good performance of RSO2 was not expected from the fluorescence data. Presumably, the antagonistic effect during the first minutes after application does not necessarily result in an uptake reduction after a longer period. From the control sample we also measured the uptake of metamitron after 30 min, just after desiccation of the droplet. It can be seen that the uptake was apparently completed after 30 min and that no further uptake occurred during the remaining 71.5 h.

To prove this also for the uptake kinetics of the adjuvant treated samples we conducted an experiment with *A. retroflexus* (Fig. 6). Again, the WP70 without adjuvant exhibited no further uptake of metamitron after 30 min. In all treatments with adjuvant, however, the uptake of metamitron is prolonged beyond that time. This was probably due to a humectifying or solubilizing effect of the adjuvants on the drying droplet residue but this remains to be confirmed. The most powerful adjuvant in *A. retroflexus* was R-ME (10 fold increase after 48 h). Both rapeseed oils and the mineral oil increased uptake 3-4 fold.

Figure 6: Influence of adjuvants on the foliar uptake of radio labelled met amitron WP70 in *A. retroflexus*



CONCLUSION

The uptake of met amitron was measured by chlorophyll fluorescence over a period of several minutes and by ^{14}C -tracer technique over a period of several days. With both methods basically similar results were obtained in estimating the uptake enhancing properties of different oil adjuvants. The most effective adjuvant tested was the rapeseed oil methyl ester followed by the rapeseed oils and the mineral oil.

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TESTING OF ADDITIVES WITH SUGAR BEET HERBICIDES - A SIMPLE OR COMPLEX UNDERTAKING?

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ABSTRACT

Over the period 1990 to 1993 various spray additives were used with half doses of phenmedipham (200 g AI/ha) or phenmedipham plus metamitron (97 g + 438 g AI/ha respectively) and the activity of these mixes compared against that of full doses of these herbicides without additives. A range of additives including a mineral oil, a vegetable oil, tallow amines, a silicone additive and a novel type have been tested. There was much variability between years and, to a lesser extent, between sites. Assessment method, such as the use of weed counts or weed vigour scores, could lead to different interpretation of results.

INTRODUCTION

Mineral adjuvant oils are used with certain post-emergence herbicides and herbicide mixtures in sugar beet, partly to increase weed control activity, but particularly to ensure reliability of weed control. Many additives are available and are considered by some to offer the possibility of reducing weed control costs through reductions of the doses of the active ingredient applied. This report summarises the results of a series of experiments carried out over four years to determine the effectiveness and reliability of spray additives with sugar beet herbicides.

METHOD

Experiments were carried out at each of two sites in the years 1990 to 1993 inclusive. These were a loamy sand (LS) at Colney or Attlebridge (1993 only) and a sandy loam (SL) at Morley, each in Norfolk. Programmes compared normal recommended doses of phenmedipham alone (399 g AI/ha) or with metamitron (194 + 875 g AI/ha respectively) with half doses of these two treatments applied alone or with an additive. A description of the additives used is in Table 1 with doses of additives in Table 2 and spray dates in Table 3. Except in 1991, the treatments were repeated where subsequent sprays were used (Table 3). In 1991, the third applications in the programme used metamitron + ethofumesate + chloridazon (1050 + 275 + 170 g AI/ha = full dose) instead of phenmedipham, and metamitron + phenmedipham + ethofumesate (700 + 160 + 200 g AI/ha = full dose) instead of phenmedipham + metamitron. Half these doses were used with additive treatments. The experiments were of randomised block design with four replicates. Plots were 24 m long by 2 m (4 rows) wide. No pre-emergence herbicides were used at either experiment site.

The first treatments were applied when weeds were at the cotyledon stage (LS sites) or two true leaf stage (SL). Where used, subsequent treatments were applied when the next flush of weeds were at the cotyledon stage. The main weeds at the SL site were *Polygonum aviculare*, *Fallopia convolvulus* and *Chenopodium album* whilst at the LS site they were *P. aviculare*, *F. convolvulus*, *Stellaria media* and *Viola arvensis*. Treatments were applied with a Van der Weij (Azo) knapsack sprayer using 80° or 110° 01 size flat fan nozzles at 2 bar

pressure to apply 80 l/ha water volume. Assessments were by scores or counts. Weed and beet vigour scores used a 0 to 10 linear scale where 0 = dead and 10 = normal healthy growth.

TABLE 1. Type of additive used in the experiments

Additive	Type
Actipron	97% mineral adjuvant oil*
Ethokem	870 g/l polyoxyethylene tallow amine ethoxylate*
Ethokem C/12	cationic surfactant*
Galion	60% polyoxyalkylene glycol*
NAS 329	96% vegetable oil
NAS 353	silicone based adjuvant

* as described by Ivens (1993)

TABLE 2. Dose of additives and years tested

Additive	Dose of additive (l/ha)		Years tested	Abbreviation used throughout paper
	used with phenmedipham:- alone	+ metamiltron		
Actipron	1.7	1.0	1990	mineral
Actipron	1.0	1.0	1991, 1992, 1993	mineral
Ethokem	0.5	0.5	1990, 1991, 1992	cationic
Ethokem C/12	0.5	0.5	1993	cationic
Galion 0.5	0.5	1990, 1991, 1992		NAS 306
NAS 329	1.7	1.0	1990	NAS 329L
NAS 329	1.0, 3.5	1.0, 2.95	1991, 1992, 1993	NAS 329H
NAS 353	0.5	0.5	1991, 1992, 1993	NAS 353

TABLE 3. Date of post-emergence spray applications

Site	Year	Applications
1990	LS	27/4 & 3/5
1991	LS	7/5, 22/5 & 11/6
1992	LS	29/4 & 15/5
1993	LS	1/5
	SL	1/5 & 18/5
	SL	17/5
	SL	13/5 & 28/5
	SL	4/5 & 22/5

RESULTS

In most years, all treatments reduced weed numbers compared to the untreated (Table 4) but differences between treatments were generally small. However in 1991 at the SL site, NAS 306 worked well with phenmedipham either alone or with metamiltron and NAS 353 worked well with phenmedipham + metamiltron. At the LS site in that year, NAS 306 worked well with phenmedipham + metamiltron. In 1993, the cationic surfactant with phenmedipham + metamiltron, at the SL site, resulted in poorer control than most other treatments, including reduced dose phenmedipham + metamiltron alone.

TABLE 4. Total number of weeds/m² following treatment by herbicide with and without additives

Herbicide (dose in g AI/ha) and additive	11/6/90		15/6/90		11/6/91		1/7/91		3/7/92		3/6/92		8/6/93		25/5/93	
	SL	LS	SL	LS	SL	LS	SL	LS	SL	LS	SL	LS	SL	LS	SL	LS
Untreated	32.2	92.6	16.4	54.1	21.6	28.6	49.6	25.7								
phenmedipham																
399	16.4	28.3	12.0	16.5	12.8	17.1	26.1	16.9								
200	-	-	11.6	37.3	18.7	23.1	31.7	25.1								
200	21.2	40.8	12.4	25.2	16.8	22.0	28.2	13.6								
200	15.3	40.4	12.2	24.1	14.4	13.9	25.3	11.7								
200	17.3	44.7	9.7	16.0	14.5	21.2	-	-								
200	19.1	40.2	13.3	22.9	15.3	19.1	32.9	10.9								
200	-	-	14.5	15.2	12.1	14.3	-	16.1								
200	-	-	13.7	13.7	14.1	21.7	29.3	13.1								
phenmedipham + metatriton																
194+875	5.5	32.8	10.3	16.0	10.2	15.0	27.1	10.6								
97+438	-	-	14.9	36.1	16.0	16.3	28.9	12.6								
97+438	9.1	42.2	13.2	23.0	17.2	14.6	52.3	17.3								
97+438	6.1	41.9	11.4	27.0	11.3	15.2	28.3	11.1								
97+438	7.1	36.2	10.6	7.9	13.2	13.5	-	-								
97+438	8.5	30.2	14.4	17.0	12.2	12.1	19.1	23.9								
97+438	-	-	13.2	13.8	13.1	11.0	-	12.3								
97+438	-	-	9.6	18.8	12.9	12.7	17.0	16.9								
SED	3.42	9.69	1.86	9.46	2.57	2.75	5.53	7.17								

TABLE 5. Effect of herbicides with and without spray additives on weed (all sites) and beet (SL 1993 only) vigour scores (0 to 10 linear scale where 0 = dead and 10 = normal healthy growth)

Herbicide (dose in g AI/ha) and additive		Weed vigour								Beet vigour
		SL 25/6/90	LS 15/6/90	SL 9/7/91	LS 5/7/91	SL 18/6/92	LS 16/6/92	SL 8/6/93	LS 24/5/93	SL 8/6/93
Untreated		9.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
phenmedipham										
399	nil	2.8	2.3	7.3	7.0	5.8	2.8	1.8	1.5	8.3
200	nil	-	-	8.3	7.5	9.5	6.3	2.0	3.3	9.5
200	+ cationic	4.5	3.8	7.8	8.0	4.0	4.0	1.0	1.8	5.5
200	+ mineral	3.8	2.8	8.3	7.8	6.3	1.8	1.8	1.5	7.0
200	+ NAS 306	4.5	3.3	8.8	6.5	6.5	3.3	-	-	-
200	+ NAS 329L	3.8	2.5	9.5	8.0	7.0	3.5	2.0	2.3	7.0
200	+ NAS 329H	-	-	8.3	8.0	6.0	1.5	-	2.0	-
200	+ NAS 353	-	-	8.3	7.5	5.0	3.0	1.3	2.3	6.3
phenmedipham + metamitron										
194+875	nil	2.5	2.0	7.5	6.5	4.8	2.0	1.5	1.3	8.8
97+438	nil	-	-	8.8	8.8	7.0	3.0	2.5	2.0	9.5
97+438	+ cationic	2.5	2.0	8.3	8.0	4.8	2.8	3.0	2.8	8.3
97+438	+ mineral	4.0	3.0	8.0	8.3	5.0	3.8	1.5	1.5	9.5
97+438	+ NAS 306	3.8	2.5	6.3	5.3	4.8	3.0	-	-	-
97+438	+ NAS 329L	4.0	1.5	8.0	6.3	6.3	2.3	1.8	1.8	8.5
97+438	+ NAS 329H	-	-	8.5	5.3	4.0	1.6	-	1.8	-
97+438	+ NAS 353	-	-	7.0	7.0	7.0	2.8	1.0	1.5	6.3
SED		1.08	0.89	0.80	0.94	1.12	0.87	0.36	0.39	0.58

In 1991 the addition of mineral oil to either herbicide treatment gave poorer control at the LS compared to the SL site. There was no evidence to suggest that control of individual weed species was affected by additive choice (data not presented).

The effect on weed vigour (Table 5) tended to be greater than that on weed numbers, although vigour reductions in 1991 were generally low. These scores indicated other differences between treatments (compared to that measured on weed numbers as given in Table 4), with good effects from NAS 329 mixed with phenmedipham + metamiltron at the LS site in 1991 and from the higher dose of NAS 329 with phenmedipham alone or + metamiltron at that site in 1992.

Table 6 shows the data (meaned over the years) for % control of weed numbers and % reduction of weed vigour, minimum and maximum values are also shown. These data indicate that the additives, in general, improved the control achieved by half doses of herbicides but some were more consistent in their activity than others. On both weed vigour and weed numbers, the full dose gave the highest and least variable control whilst the half doses gave poorest control and most variation.

TABLE 6. Overall % control of weed numbers and reduction of weed vigour (mean of all years), and range of control as minimum and maximum values

Herbicide (dose in g AI/ha) and additive		% control of numbers			% reduction of vigour		
		mean	min	max	mean	min	max
phenmedipham							
399	nil	47.2	26.8	69.5	60.5	27.0	85.0
200	nil	21.9	2.3	36.1	38.5	5.0	80.0
200	+ cationic	37.9	22.2	55.9	55.8	20.0	90.0
200	+ mineral	47.3	25.6	56.4	56.8	17.0	85.0
200	+ NAS 306	44.7	25.9	70.4	44.3	12.0	67.0
200	+ NAS 329L	40.9	18.9	57.7	51.2	5.0	80.0
200	+ NAS 329H	43.0	11.6	71.9	48.4	17.0	85.0
200	+ NAS 353	40.0	16.5	74.7	54.3	17.0	87.0
phenmedipham + metamiltron							
194+875	nil	57.4	37.2	82.9	64.5	25.0	87.0
97+438	nil	34.0	9.1	51.0	46.5	12.0	80.0
97+438	+ cationic	37.5	0.0	71.7	56.9	17.0	80.0
97+438	+ mineral	51.3	30.5	81.1	55.6	17.0	85.0
97+438	+ NAS 306	58.6	35.4	85.4	56.5	37.0	75.0
97+438	+ NAS 329L	48.9	7.0	73.6	59.4	20.0	85.0
97+438	+ NAS 329H	49.4	19.5	74.5	57.6	15.0	84.0
97+438	+ NAS 353	50.4	34.2	65.7	56.2	30.0	90.0

Data on beet populations, vigour and yield are not presented but, in most years, effects on the crop from the herbicide + additive treatments were either not statistically significant or of no commercial consequence. At the SL site in 1993 most of the additive treatments used with phenmedipham (especially cationic surfactant and NAS 353) and NAS 353 with phenmedipham + metamiltron reduced crop vigour severely and this was significant ($P=0.001$) compared to the full dose treatments (without additive), Table 5. Effects on yield were recorded in some years but appeared to be related to weed competition rather than herbicide activity.

DISCUSSION

The experiments were designed to highlight differences between treatments and therefore weed control was poorer than would be expected in commercial practice. These results appear to show smaller differences between additives than in earlier experiments (May & Hilton, 1990). The generally good effect of adjuvants compared to half dose herbicide treatments applied without additives may be a reflection of the reduced amounts of wetters in such low dose sprays and the additives were able to improve activity by restoring some of this reduction.

Growers often use mineral oil with phenmedipham + metamitron (Anon, 1992), especially under dry growing conditions. These experiments were carried out under generally dry conditions and therefore it might be expected that use of mineral oil with half doses might give relatively high consistent levels of weed control compared to the treatments without additive. The variability of mineral oil treatments did not appear to reflect prevailing weather conditions and it was dry in 1992 at the LS site where mineral oil had relatively poor effect. A study of weather records failed to suggest that weed control activity could be related to conditions at, before or after application. It is possible that effects were related more to subtle differences in growth habit and wax layers on plants which might not be predicted by simple meteorological records.

The differences observed did not appear to be related to the rates of adjuvants tested and it is unlikely that manufacturers quality control would allow variations between the batches of herbicide or adjuvant which were fresh each year. The change of cationic surfactant for 1993 might explain the relatively poor control by this additive in that year. However, prior to 1987 some poor results were recorded with this adjuvant (Hilton, *pers. comm.*).

The differences suggested by the results for vigour reduction and control of weed numbers may be a reflection of the herbicide distribution and retention on weeds. Similar unexplained effects have been observed following the use of twin fluid or sleeve boom sprayers for applications of sugar beet herbicides (May & Hilton, 1992).

The results confirm that herbicide dose remains the primary source of potential activity, but that some additives have the potential to improve this activity in some seasons. However, the relative cost of additive and herbicide will also determine whether reduced dose mixtures of herbicide and additive are cost effective. The conclusion from this work must be that additives require testing over a range of conditions and seasons for each use for which they are considered. More than one parameter should be assessed and all results require relating to the effects desired by the user rather than a simple reduction of weed numbers.

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Session 10B

**Fate and Significance of
Herbicide Residues in Soil
and Water - Modelling**

Chairman	Dr A WALKER
Session Organiser	Dr A D CARTER
Papers	10B-1 to 10B-3

THE DEVELOPMENT AND APPLICATION OF AN INTEGRATED DATABASE FOR MODELLING THE ENVIRONMENTAL FATE OF HERBICIDES

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ABSTRACT

Increasingly, mathematical models are being used as tools to predict the possible environmental fate and behaviour of herbicides. The models range in complexity from simple screening techniques to the detailed mechanistic simulation of biological and physico-chemical processes. But however detailed the model used, the relevance of its predictions depend on the relevance of the environmental scenario used to select its input data. An integrated database system for England and Wales is being developed to enable the user to define a specific combination of soil, crop and climate characteristics, to map its distribution throughout the two countries and then to access the detailed soil and weather data relevant to the mapped scenario. The principles, and techniques used to develop and interact these databases are described, together with their use in extrapolating model results to produce spatial vulnerability assessments. The potential for developing similar database systems for European and global use is also discussed.

INTRODUCTION

Increasingly, mathematical models are being used as a tool for predicting the environmental fate of herbicides and to extrapolate the results of local field monitoring and lysimeter studies. A large number of models are now available and a number of detailed reviews of the different modelling approaches employed have been published (*e.g.* Wagenet & Rao, 1991). These models simulate the various environmental processes affecting pesticide fate at different levels of detail but however detailed and mechanistic the approach used, model results and predictions can only relate to the range of the chosen input parameters. The agricultural ecosystem is heterogeneous in nature and most of the factors which influence environmental fate vary spatially and/or temporally. Thus a single set of model input parameters usually represents only one of many possible environmental scenarios. In recognition of this, evaluations of environmental fate based on model simulations usually adopt one of three basic approaches: a single model simulation using 'realistic worst-case' input parameters; a limited number of simulations using specific environmental scenarios representative of a range of conditions within the area of interest; stochastic techniques to produce a statistical analysis of the distribution of results from repeated model simulations based on the likely numerical ranges of important model parameters within the area of interest. Whichever of these approaches is adopted, the results are relevant only if there is sufficient environmental data available to identify the desired scenarios or to make realistic estimates of the required parameter ranges (Hutson, 1992). Where the area of interest is a single field or small catchment, such data requirements may be small and relatively easily obtained by on-site measurement. At the larger catchment, regional or national scale, however, comprehensive environmental databases are necessary. The difficulties in obtaining, managing and manipulating such databases pose a major problem for the realistic interpretation of environmental fate models (IUPAC, 1987). In recognition of this, a Database and Model Parameter Analysis System (DBAPE) was developed to facilitate the use of spatial and parameter data relating to agricultural soils in the USA (Carsel *et al.*, 1991). The DBAPE system has facilitated the

realistic use of environmental fate models within the USA but, as yet, no similar system exists for other countries. This paper describes the development of a comprehensive relational environmental database management system for England and Wales and illustrates how this system can be used to extrapolate model results to the national level.

CORE DATABASES

The environmental database management system, named SEISMIC (Spatial Environmental Information System for Modelling the Impact of Chemicals), is built around six core databases which can be manipulated, interacted and interrogated by means of on-screen menus which initiate software functions. The databases comprise four spatial 'raster' datasets holding cropping, climate and soil data for each of the 6,456 5 x 5 km grid blocks that cover the whole of England and Wales and two parameter datasets holding individual soil series and daily weather data representing the range of conditions within the two countries.

Spatial cropping data

Spatial data relating to actual and potential cropping are held within the system. Actual crop distribution is based on the 1988 Parish Agricultural Census data gathered by the Ministry of Agriculture, Fisheries and Food. This data has been aggregated by staff of the Edinburgh University Data Library to derive a 5 x 5 km resolution digital dataset for the UK and part of this dataset has been incorporated into the SEISMIC system. Each georeferenced 5 x 5 km pixel in the cropping dataset comprises a list of component crops and their percentage cover. The full list of included crops is given in Table 1.

Potential cropping data is based on simple crop suitability models developed by the Soil Survey and Land Research Centre (SSLRC), incorporating land qualities based on soil, land and climate interactions. The models classify land into one of four suitability categories ranging from 'Well Suited' to 'Unsuited'. Each 5 x 5 km area of England and Wales has been categorised in this way based on its agroclimatic characteristics and the properties of its most common soil series (Jones & Thomasson, 1987). This data has been further simplified so that for a specific crop, all 5 x 5 km blocks that are at least marginally suited are categorised as being *potentially suitable*. Each georeferenced pixel in the resulting database contains a list of seven crops (winter cereals, spring cereals, oilseed rape, sugar beet, maincrop potatoes, forage maize and grassland) with their potential suitability specified as 'Yes' or 'No'.

Spatial climatic data

Spatial climatic datasets incorporated into the system are derived directly from the SSLRC's Agroclimatic database (Jones & Thomasson, 1985). This comprises long term mean values of agriculturally important climatic parameters calculated for each 5 x 5 km block in England and Wales using empirical regression algorithms which relate each climatic parameter to altitude, latitude and longitude. Each algorithm is derived from statistical analysis of measured data from a number of sites throughout the two countries. Data for average annual rainfall, maximum accumulated potential soil moisture deficit, duration of the field capacity period and excess winter rain are held for each georeferenced 5 x 5 km pixel.

Spatial soil data

The spatial soil data within SEISMIC relates to the 1:250,000 scale regional soil maps of England and Wales. These show the spatial distribution of 296 *soil associations* each of which comprises between one and eight main *soil series* which are found

associated together within the landscape. Soil series are characterised by a precisely defined set of soil and substrate properties. They form the basic unit of soil characterisation and mapping in England and Wales (Avery, 1980). Based on the field data collected and recorded during the making of the 1:250,000 scale soil maps, an estimate of the average proportion of each soil series within each soil association has been made, with a total of 412 main soil series being recognised on the complete national map. All six regional soil vector maps of England and Wales have been digitised and resampled to create a raster database of 100 x 100 metre pixel resolution. Using this dataset a national soil series dataset at 5km resolution has been created by integrating the proportion of every soil association in each 5 x 5 km block with the proportion of each soil series within each soil association. Each georeferenced 5 x 5km pixel in the dataset thus comprises a list of component series along with their percentage cover.

TABLE 1. Categories of crop included in the SEISMIC system

Grassland	Brussel Sprouts	Other Top Fruit
Grassland - short term	Cabbage (summer &	All Small Fruit
Grassland - long term	autumn)	Strawberries
Rough Grazing	Other Cabbage	Rasberries
Cereals	Cauliflower	Blackcurrants
Wheat	Calabrese	Gooseberries
Winter Barley	Carrots	Other Small Fruit
Spring Barley	Parsnips	All Hardy Nursery
Oats	Beetroot	Stock
Mixed Corn	Onions	Fruit trees, bushes and
Rye	Broad Beans	other fruit stock
Maize	Runner Beans	Roses
Potatoes	French Beans	Shrubs, Conifers etc.
Sugar Beet	Field Celery	Ornamental Trees
Hops	Lettuce	Herbaceous Plants
Horticultural Crops	Sweet Corn	Other hardy nursery
Field Beans	Other Vegetables	stock
Oilseed Rape	All Top Fruit	All Bulbs & Flowers
Turnips & Swedes	Apples (dessert &	grown in Open
Fodder Beet & Mangolds	cooking)	Bulbs, Corms, Tubers &
Kale, Cabbage etc.	Cider Apples & Perry	Rhizomes
Peas (for harvesting dry)	Pears	Dahlias
All vegetables grown in	Pears	Chrysanthemums
the open	Plums	All other flowers
Peas	Cherries	

Soil parameter data

Soil parameter data are held in SEISMIC for each of the 412 soil series included on the 5km resolution soil series spatial database. For each series, parameter data is available for each characteristic soil layer present under each of four different land uses; Arable, short term rotational (Ley) grassland, long term (Permanent) managed grassland and 'Other' land under semi-natural vegetation or recreational use. An example of the data available for a single soil series / land use combination is given in Table 2.

TABLE 2. Example of soil parameter data for the Cuckney soil series under arable.

Parameter	Soil layer			
	A	Bw1	Bw2	C
Upper depth (cm)	0	35	50	100
Lower depth (cm)	35	50	100	150
Total sand %	83 (3.5)	86 (3.1)	89 (4.3)	93 (2.6)
Total silt %	10 (2.9)	10 (3.2)	7 (4.3)	4 (1.7)
Total clay %	7 (2.8)	4 (0.5)	4 (0.5)	3 (1.0)
Fine sand %	23 (5.7)	12 (n.d.)	12 (n.d.)	15 (n.d.)
Organic carbon %	1.1 (0.5)	0.3 (0.1)	0.2 (0.1)	0.1 (0)
pH (1 :2.5 H ₂ O)	6.9 (0.7)	7.0 (0.3)	7.1 (0.2)	6.6 (0.7)
Bulk density (g/cm ³)	1.46 (0.08)	1.50 (0.06)	1.48 (0.05)	1.51 (0.01)
%vol. water at 5kPa	19 (3.2)	17 (2.8)	16 (3.2)	12 (1.5)
%vol. water at 10kPa	17 (2.7)	14 (2.7)	14 (2.7)	10 (0.6)
%vol. water at 40kPa	14 (2.7)	12 (1.9)	11 (1.7)	8 (0.1)
%vol. water at 200kPa	9 (3.2)	8 (1.3)	7 (1.6)	5 (2.0)
%vol. water at 1500kPa	6 (1.3)	5 (0.7)	4 (0.8)	4 (1.5)
%vol. Total porosity	45 (3.9)	43 (2.1)	44 (1.9)	43 (0.4)
Saturated conductivity (cm/day)	232	232	300	440
Conductivity at 5kPa (cm/day)	0.161	0.175	0.156	0.094

Note: Figures in parentheses indicate standard deviations

The parameter data is derived from the SSLRC's analytical databases. Mineral particle size data is calculated directly from individual analyses of samples from soil horizons taken from over 1,500 profiles sampled to characterise soil series during detailed field survey. For some series there was only one set of analytical data per soil horizon, but for the majority, multiple datasets were available to characterise the particle size fractions in terms of mean values and standard deviations. Mineral particle-size distribution is not affected by land use so the dataset was not stratified according to this category. Topsoil organic carbon content and pH were derived from the National Soil Inventory database which comprises analysed values of a wide range of topsoil characteristics for each of 5,692 samples taken at 5 km grid intersect points across England and Wales (McGrath & Loveland, 1992). Because both parameters are very dependent on land use, even within soil series, the data was stratified into each of the four land use categories defined above. Statistical analysis of this dataset gave mean values and standard deviations of organic carbon content and pH for all land use / soil series combinations. Data for subsoil organic carbon content and pH were derived from the soil profile analytical data collected to characterise soil series. However, this dataset was not comprehensive enough to characterise all combinations of soil series and land use and so expert judgement was used to estimate values where data was missing.

For many soil series, bulk density data was derived directly from the soil physical property database. This comprises water retention, porosity and density measurements from over 5,000 soil horizons sampled from the 1,500 profiles of the soil series analytical database (Thomasson & Carter, 1992). However, bulk density is also a property that depends, at least partly, on land use and the data was insufficient to directly characterise all combinations of series and land use. The soil physical property database was therefore stratified into 15 groups according to soil and/or horizon type and analysed statistically to derive empirical regression equations relating bulk density to organic carbon, clay and silt content. These equations, which explained between 42 and 91% of the variation in

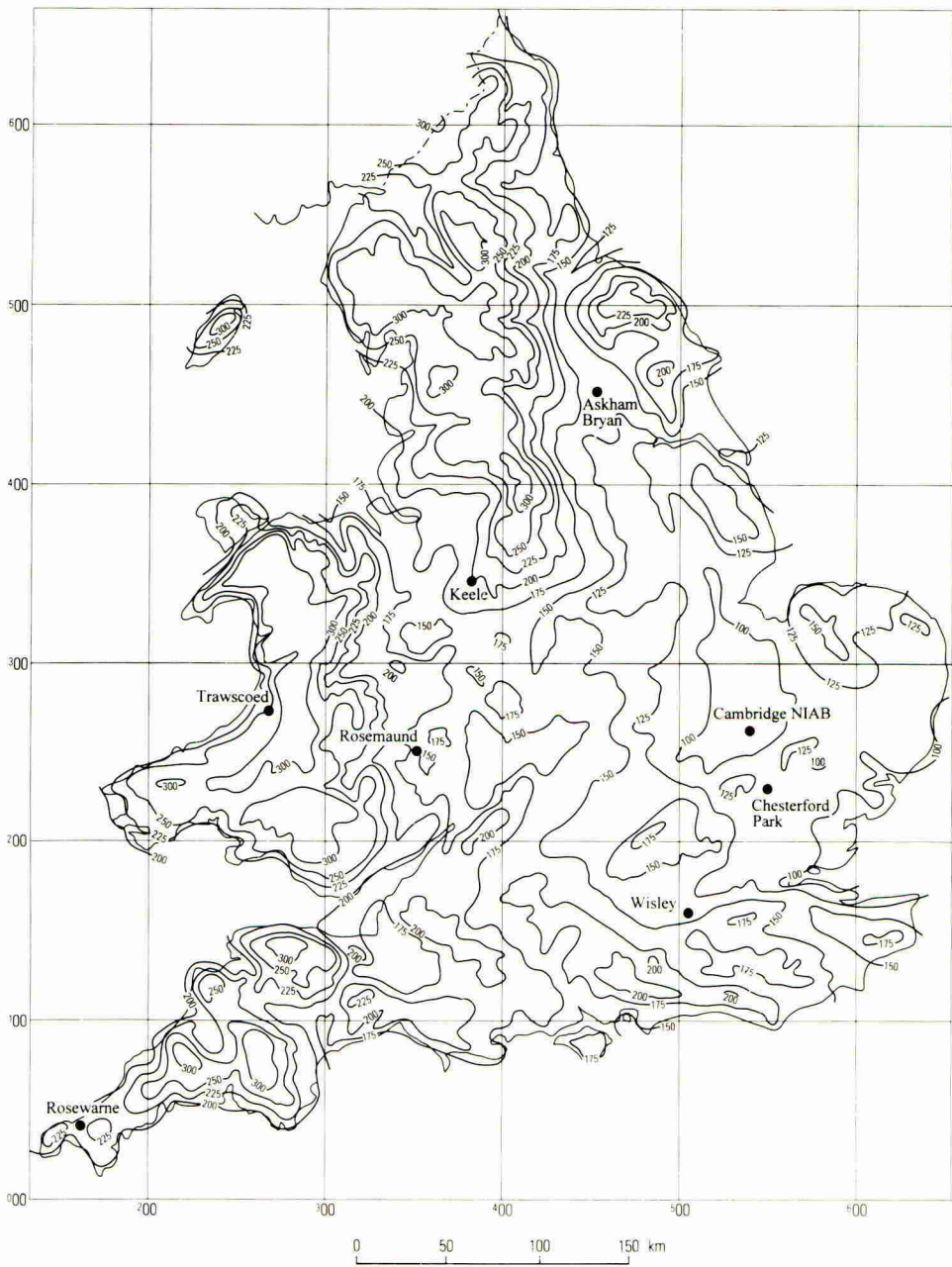


FIGURE 1. Location of representative weather datasets in relation to duration of the field capacity period

measured bulk density depending on the soil grouping, were then used to predict bulk density values where data was missing.

Water retention and unsaturated hydraulic conductivity values were predicted from the closed form equation of Van Genuchten (1980), using non-linear regression equations incorporating bulk density, organic carbon, clay, silt and sand content to estimate the parameters B and n . These regressions were based on statistical analysis of the soil physical dataset and the combined technique gives very accurate prediction of the soil water retention curves (Simota & Loveland *in preparation*). Finally, saturated conductivity values were predicted from empirical regression equations relating conductivity to air filled porosity at 5 kPa soil water pressure. These relationships were derived from a limited dataset of saturated conductivity measurements and explained between 56 and 84% of the measured variation in saturated conductivity depending on the soil texture (Hollis & Woods, 1989). Hydraulic conductivity at 5 kPa was then estimated from the relationship between saturated conductivity, unsaturated conductivity and soil water content using the closed form equations of Van Genuchten (1980).

Weather data

Weather patterns show considerable temporal and spatial variation and so, if such data is to be used in a realistic way, it is necessary to ensure that it encompasses the likely variation within the area of interest. Thus, for modelling purposes within England and Wales, it is necessary to have a number of datasets that cover long periods of time and also represent the different climatic regimes present. The SEISMIC system holds daily weather datasets covering a period of at least 10 years, for eight representative sites across the two countries. Because of the difficulties in obtaining such comprehensive measured data, each dataset has been simulated using a weather generator model. The model used is that of Richardson & Wright (1984) which generates daily weather data from a set of probability distribution parameters derived from statistical analysis of measured weather data. Comparisons of long term monthly averages have shown that weather datasets generated in such a way are closely representative of measured weather patterns, especially if they are calibrated using monthly averages based on measured rainfall and temperature. The eight weather datasets in SEISMIC were generated using the appropriate probability distribution parameters derived from statistical analysis of measured weather data for each site. Each data set comprises daily values of rainfall, maximum temperature, minimum temperature and solar radiation. The climatic range represented by the eight datasets is illustrated in Fig. 1.

BASIC STRUCTURE AND FUNCTIONS OF THE SYSTEM

A basic overview of the SEISMIC system is illustrated in Fig. 2 and its functions shown in Table 3. The system has been developed using the 'Clipper' database language (CA Associates, 1992) and is designed to run on a stand-alone desktop or portable notebook IBM/PC compatible micro-computer - ensuring the widest usage for the system. SEISMIC requires a powerful i80386/i80486 with approximately 80Mb of free hard disk space and 4Mb of 'EMS' RAM. Maps and reports generated by SEISMIC may be directed to screen, disk file or printer.

Upon initiating a SEISMIC session, the user is transferred to the 'Select Soil' function. Soil types can be selected according to predetermined scenarios which group them into a limited number of relatively homogeneous hydrological classes (Boorman & Hollis, 1990), pesticide leaching potential classes, pesticide run-off potential classes, overall soil leaching potential classes (NRA, 1992) or pedological subgroups (Avery, 1980). Alternatively, users can select their own soil scenarios according to topsoil and/or subsoil textures or specified ranges of topsoil pH and organic carbon, clay and silt content.

FIGURE 2. Overview of the SEISMIC System

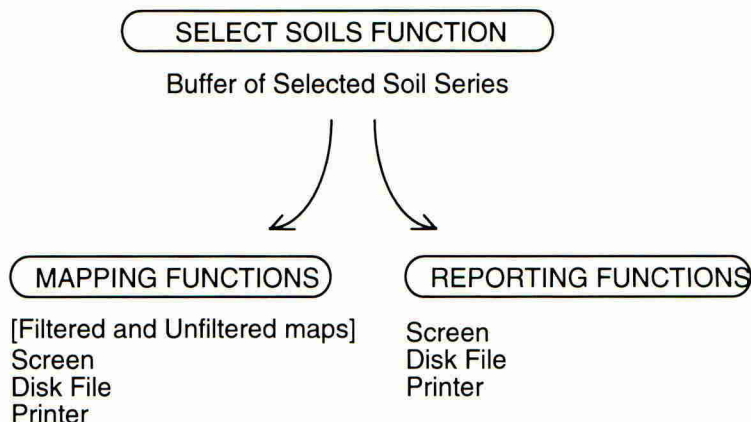


TABLE 3. Menus and functions of the SEISMIC System

Toplevel Menu	Menu 3: Analysis and Presentation
Run a SEISMIC session	Textual Report
Utility options	Mapped display
About SEISMIC	Change selected soils
Quit SEISMIC to DOS	Return to Toplevel menu
Menu 2: Select Soils	Menu 4: Map presentation
By soil series	Map soil series
By hydrological class	Filter by crop suitability
By pesticide leaching potential	Filter by actual cropping
By pesticide run-off potential	Filter by climate
By overall soil leaching potential	Reset filters
By soil subgroup	Return to Toplevel menu
By topsoil and/or subsoil texture	Menu 5: Utility options
By topsoil characteristics	List session images
Unselect all selected soils	Configure environment
Display all selected soils	Return to Toplevel menu
Analysis and Presentation	
Return to Toplevel menu	

All the soil series that conform to the selected scenario are added to a buffer and further menu options allow users to add, delete or modify the contents of this buffer.

The '**Analysis and Presentation**' function allows the user either to generate a textual report giving the soil parameter data for each soil series within the buffer or to transfer to the '**Map Presentation**' function. Map presentation allows the user either to map the distribution of the selected soil scenario or to refine that scenario by adding filters for crop

suitability, actual cropping patterns and/or climate characteristics. Crop suitability filters are activated by specifying one or more crops of interest, whereas actual cropping and climate filters require selection using defined % cover thresholds and parameter ranges respectively. Any combination of crop suitabilities and climate characteristics or actual crops and climate characteristics can be selected. The resultant map will reflect the filter selected. Thus, for example, the filtered map presentation may show the percentage distribution of the selected soil scenario, but only in areas where winter wheat occupies more than 10% of the land, sugar beet occupies more than 5% and the long term average annual excess winter rain is more than 500 mm. Both the textual reports and the maps generated by SEISMIC may be saved to disk file in ASCII and PCX formats respectively. These can be directly accessed for use in mathematical modelling and environmental extrapolation.

USING SEISMIC FOR MODELLING ENVIRONMENTAL FATE

Using the SEISMIC system in conjunction with mathematical models, it is possible to predict the likely fate of a pesticide in soil under a range of specific scenarios and to show the relevance of those predictions within England and Wales. This is illustrated in the following examples for a broad range cereal herbicide.

In SEISMIC, from the 'select soil' function, the option **All soil series** is selected. All 412 soil series will be placed in the selection buffer. Proceeding to the map presentation option via the menus, the cropping filter is selected for the broad crop type 'Cereals', at a threshold of 5%. This produces a map showing the distribution of all areas in England and Wales with more than 5% cereal cropping and illustrates the realistic 'target area' for the herbicide. Returning to the 'select soil' menu, one or more soil scenarios may be selected depending on the desired modelling approach. For example, if a 'worst case' scenario for surface water vulnerability is required, it may be best to select soils according to the predetermined pesticide run-off potential classes. Classes with the highest potential can be selected and their distribution mapped in relation to cereal crops and climate characteristics, until the most extensive 'worst case' soil/crop/climate scenario is achieved. When selecting worst case climate characteristics it is probably best to use a combination of excess winter rain and field capacity days. In each case, the largest values indicate the worst conditions. Having selected the worst case soil/crop/climate scenario, the most appropriate weather datasets for this scenario is selected by comparing the sites shown on Fig.1 with the selected field capacity day climate ranges. Using the text report function, these weather datasets, along with the appropriate arable soil parameter data for each soil series conforming to the selected worst case scenario, are then stored in disk-files ready for modelling use.

Alternatively, the user may wish to use models to extrapolate the results of field or laboratory mobility and persistence studies. SEISMIC can be used to select a matching soil and climate scenario which may be mapped in relation to cereal crops. From the resulting map the most appropriate weather station dataset can be identified. The appropriate soil and weather data may then be exported for modelling use. The results of the modelling exercise are then valid for all areas covered by the original mapped scenario.

If stochastic modelling is desired then a range of soil scenarios can be selected and their distribution within areas of cereal cropping examined using the map and filter functions. For example, in order to examine the range of soils appropriate to groundwater vulnerability, the select soil function can be used to select all soils with a moderate, moderately high or high pesticide leaching potential. The distribution of these soils can then be mapped in relation to cereal crops and one or more weather datasets identified as representing the mapped scenario. Stochastic modelling based on the identified range of

weather and soil parameters will then give an estimate of the probability of soil leachate concentrations exceeding a specific threshold within the area mapped.

THE POTENTIAL FOR SIMILAR DATABASE SYSTEMS IN EUROPE

In 1985 a 1:1,000,000 scale soil map covering all 12 EC countries was published (CEC, 1985). This map was digitised in vector form as part of the CORINE-project (Platou *et al.*, 1989) and an enhanced version of this database has now been developed (King & Daroussin, *in press*). Because of its vector format, the database is very large and requires a powerful UNIX based computer workstation and GIS facility to handle it. Currently, efforts are being made to establish an associated soil parameter database linked to the soil map (Madsen & Jones, *in press*). Collection of soil data is being co-ordinated by the Soil and GIS Support Group of the Monitoring Agriculture by Remote Sensing (MARS) project, at the Joint Research Centre, Ispra, Italy, but the database is at an early stage of development and there are problems in ensuring a consistent level of data for each EC country. Climate and weather data representing the EC is also held as part of the MARS project along with remotely sensed land use data.

Within Europe therefore, whilst databases relating to soil, climate, weather and land use are either available or in preparation, none are held in such an easily accessible format as those of SEISMIC and there is no management system for their manipulation, correlation and interrogation. However, the techniques and principles used in the development of SEISMIC could be applied at a European level to provide an easily accessible data management system for predicting pesticide environmental fate.

CONCLUSIONS

It is in the interests of industry, regulators and consumers alike that the benefits of pesticide usage are maintained whilst their environmental impact is minimised. If this goal is to be realised, it is imperative that accurate techniques be developed for assessing the likely environmental impact arising from usage of plant protection products. The SEISMIC system is an important tool for making such a process possible. As well as giving easy access to the comprehensive soil and weather data necessary to run predictive models in England and Wales, it enables realistic environmental scenarios to be identified and their national distribution mapped. The EC 'Authorisation' directive 91/414/EEC on the harmonisation of national procedures for the regulation of plant protection products, aims to facilitate registration and review throughout the EC. If this is to succeed it is imperative that databases and management systems similar to those of SEISMIC and DBAPE be developed for use on a community wide basis. Only through such systems can environmental fate data packages and model predictions be placed in their correct European context.

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DEVELOPMENT OF EXPERT SYSTEMS TO AID HERBICIDE USE WITH REGARD TO THEIR BEHAVIOUR IN SOIL

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Abstract

A review of the development of decision support systems from simple equations to calculate herbicide persistence to expert systems to aid herbicide selection is given. However, most available systems failed to consider herbicide behaviour in soil. Recently simulation models for predicting herbicide persistence and leaching have been implemented into geographical information systems to assess herbicide impact on a larger scale. The system PEMOSYS (Pesticide Monitoring System) considers spatial variability in soil properties and transfers results to a larger scale for a regional analysis. The concept and structure of this system are outlined.

INTRODUCTION

Increasing public concern about side-effects of pesticide use has created a need for more effective investigation of pesticides in the environment. Of special interest is behaviour in soil, namely degradation and leaching. Field experiments are expensive and time-consuming, therefore strategy shifts more and more to the use of models to simulate pesticide behaviour. However, modelling cannot be a substitute for field data, but should be used for evaluating existing information e.g. from field or lysimeter studies (Jones, 1992). Models are, depending on their structure, a valuable tool for the assessment of the environmental impact of pesticide use, for regulatory purposes and also to aid herbicide use by farmers (Wauchope & Duffy, 1992).

Most mathematical models for the evaluation of pesticide behaviour are research models, requiring a complex structure and a wide range of input data. Using them e.g. for large scale monitoring or to aid herbicide selection often causes problems in establishing full input data sets. Large-scale monitoring of groundwater pollution risk by pesticides was carried out in the United States (Kellogg et al., 1992). Many of the input parameters for the model had to be estimated from similar or standard soils, which can cause great inaccuracy (Dibbern & Pestemer 1992). Since models which include a great number of physical processes often tend to have a higher degree of predictive uncertainty, models for monitoring should be as simple as possible for a given situation (DeCoursey, 1992). Reliable results should be possible with an easily obtained basic data set, e.g. soil type, K_{oc} -value, half life in soil and

weather data. The system should be user-friendly to enable the assessment of a large number of scenarios within a short time and to visualize results for a quick overview, which implies the combination of simulation models with geographical information systems (GIS). Expert systems, designed to use data and model outputs as a base for conclusions and to explain the results and their inherent uncertainties can make these facilities available to a wider group of users.

Most expert systems developed so far aid the selection of herbicides according to their efficacy against weed species or based on seedling population and weed seedbank in soil. Herbicide behaviour in soil is taken into account only by the systems developed by Ferris et al. (1988, 1992) and Gottesbüren et al. (1990). In this paper, the route from simple degradation equations via complicated research leaching/degradation models to easy-to-handle expert systems will be described. The concept of a new Pesticide Monitoring System (PEMOSYS) to assess degradation and leaching behaviour of pesticides on a large scale which takes into account spatial variability is outlined.

USE OF MODELS TO SIMULATE HERBICIDE BEHAVIOUR IN SOIL

For long-term prediction of herbicide residues in soil after repeated applications, first-order kinetics type equations have been used and led to acceptable results for predicted residues after several years (e.g. Hamaker, 1966). The main disadvantage of these calculations was the lack of allowance for the influence of climate on degradation and therefore they were not suitable for specific situations. An equation based on regressions which included different weather and soil conditions was presented by Hamaker et al. (1967), but this was specific for picloram.

A major advance was the development of a simulation model suitable for various pesticides under different climatic and edaphic conditions by Walker (1974). This model was based on the Arrhenius equation for temperature dependence and an empirical equation for moisture dependence of degradation. Herbicide constants for the degradation model were established in time-consuming laboratory experiments under different moisture and temperature conditions in different soils. Field soil conditions were calculated from daily weather data which made this programme suitable for specific situations. However, for advisory purposes in the UK, this model was simplified with average values for temperature and moisture influence and with six herbicide persistence classes (Walker & Eagle, 1983). To predict damage to succeeding crops, the simulated residue level was compared with average crop sensitivity levels derived from field trials.

Though this model gave results of satisfying accuracy, herbicide adsorption was not considered. Crop sensitivity levels were estimated from field trials, where soil properties, especially organic carbon content, greatly influence adsorption and availability to plants of the herbicides and thus their efficacy. Stalder & Pestemer (1980) developed a water extraction method for herbicide residues to estimate the amount of herbicide in soil available to plants. This was combined with a bioassay method in hydroponic culture to assess available residues regarding their potential damage to following crops (Pestemer, 1983). Using herbicide dose-response curves for several plants and herbicides, potential crop damage could be predicted.

Further progress was made when the revised model of Walker & Barnes (1981) was combined with the bioassay method of Stalder & Pestemer (1980) by Pestemer & Auspurg (1987). The available portion of the simulated herbicide residues was calculated using laboratory derived K_d -values for the herbicide-soil combination in question established in the laboratory. This amount was compared with the sensitivity levels of the plant species to the herbicide in hydroponic culture.

Still the simulation model was not easy to handle, and searching for the appropriate bioassay data and K_d -values was time-consuming. The first approaches to include a simulation model for herbicide degradation (Walker & Barnes, 1981) into an expert system for advice on carryover and recropping were made by Ferris et al. (1988, 1992) and Gottesbüren et al. (1990). These systems allowed not only the selection of appropriate herbicides but also the prediction of potential damage to following crops by herbicide applications. Thus agricultural extension services and farmers were able to use a scientific model.

The detection of herbicides in groundwater raised other issues such as herbicide leaching to groundwater (Jones, 1992) and the influence of spatial variability (Boesten, 1991). Several models of varying complexity for the simulation of pesticide movement in soil have been developed (e.g. Jury et al., 1983; Carsel et al., 1984, Boesten, 1986; Leonard et al., 1987; Walker, 1987; Wagenet & Rao, 1990, Richter et al. 1991). Their use for risk assessment in agriculture however, was limited because of the high requirements for input data sets and user skills.

During the pesticide registration procedure in Germany, however, modelling is used to assess the risk of groundwater pollution (Kloskowski et al., 1992). If results of model runs under realistic worst case scenarios suggest leaching to the groundwater, lysimeter studies are required. Also in the USA, modelling of pesticide leaching behaviour is used as a comparative tool in the registration procedure (Behl, 1992).

The implementation of the model FLOWCONC (Walker, 1987) for simulating herbicide persistence and leaching into the herbicide advisory system HERBASYS facilitated easier handling and the use of databases (Gottesbüren et al., 1992). Still a system like this cannot be released as an advisory tool because the requirements of background knowledge for the interpretation of results are too high. On the other hand it would be a valuable tool for pesticide monitoring by trained personnel.

A qualitative approach was used in a cooperative programme in the USA where the soil/pesticide interaction screening program (SPISP) was designed to assist field personnel in the selection of appropriate pesticides (Goss, 1992). Soils and pesticides were ranked according to leaching and runoff potential and the overall scoring for leaching potential was determined to identify critical situations. A similar rule-based concept for the qualitative assessment of groundwater pollution risk by pesticides was presented by Blume & Brümmer (1987) and implemented into the expert system HERBASYS by Gottesbüren et al. (1990). This allowed non-scientific users to check many pesticides with regard to their potential for groundwater pollution.

In the UK, the system SEISMIC (Spatial Environmental Information System for Modelling the Impact of Chemicals) to predict herbicide contamination of water sources is under development (Carter et al., 1991). Physical and chemical soil data

(Carter, 1989) are combined with pesticide properties and mathematical equations (Hollis, 1990) in a GIS to map the vulnerability of aquifers on a national scale (Hollis, 1991).

For the monitoring of pesticide behaviour on a large scale, the spatial variability of soil properties is very important. Even within distances of only 10 m between sample points it can be considerable (Bunte et al., 1992). To account for this, many simulations can be necessary for a relatively small area, which will take a lot of time. The automatic input of parameters for every site and the visualization of results in maps of the area would allow easier handling. GISs combined with simulation models can serve as an excellent tool for this purpose. First steps in this direction have been made e.g. by Hollis (1991), Kellogg et al. (1992) using GLEAMS (Leonard et al., 1987), Dendrou (1993, personal communication) with PRZM (Carsel et al., 1984) and Lücke et al. (1994) with FLOWCONC.

THE CONCEPT OF PEMOSYS

According to a proposal of the FAO, post-registration activities to investigate long-term effects should be included in this process. PEMOSYS was designed to facilitate this large-scale monitoring, e.g. evaluating the relative extent of movement, determining the significance of factors affecting the behaviour, aid in planning field studies, extending the usefulness of field data through interpolation or extrapolation or substituting field studies where results clearly indicate environmental safety.

PEMOSYS is based on the earlier site-specific expert system HERBASYS (herbicide advisory system, Gottesbüren et al., 1990). To enable use on a wide range of soils (0.8 to 15% org. C) and climatic conditions (annual rainfall ranging from 500 to 1000 mm), the field trial sites of the Federal Biological Research Centre were included as reference sites. The following facilities are available:

- simulation of degradation in the top 10 cm of soil, including the prediction of potential crop damage by herbicide residues
- simulation of degradation and leaching
- rule based qualitative assessment of potential risk of groundwater contamination according to the concept of Blume & Brümmer (1987).

The integrated simulation models are VARLEACH for the simulation of pesticide leaching and degradation, and ANPROG to simulate herbicide persistence in soil and to assess potential damage to rotational crops. VARLEACH is a modification of the FLOWCONC model developed by Nicholls et al. (1982) and modified by Walker (1987). It has been validated e.g. by Walker (1987), Bunte et al. (1992) and Dibbern & Pestemer (1992). The second model is ANPROG, a modification of PERSIST, developed by Walker (1974) and Walker & Barnes (1981). It has been validated in many studies, e.g. Walker & Barnes (1981), Walker & Eagle (1983), Walker et al. (1983) and Pestemer & Auspurg (1987).

The graphic representation of input data, in combination with the results obtained from these, is a very effective tool for getting impressions on possible correlations. Therefore, maps of the sites were established, which allow the

presentation of stored data and results, as well as the selection of field data (e.g. soil properties, cropping dates). The design under MS-Windows allows easy handling by mouse and popup menus. For example, input data files are generated automatically by simply selecting the field sites on the map.

THE SYSTEM STRUCTURE OF PEMOSYS

PEMOSYS is functionally divided into three levels as shown in figure 1. The top level is the user interface level which is responsible for handling user requests, sending commands to the operation level and presenting the results. For this task, several windows may be simultaneously displayed on the screen to show e.g. a map of the region in question, the input mask and a degradation curve. The user interface was established in window-layer-technique using object-orientated programming (TOOLBOOK, Anon. 1989). Several layers may be defined within one window where each layer shows different features, e.g. soil properties or modelling outputs as distributed for the region, with the underlying electronic map to allow an easy selection of input values and better understanding of the results.

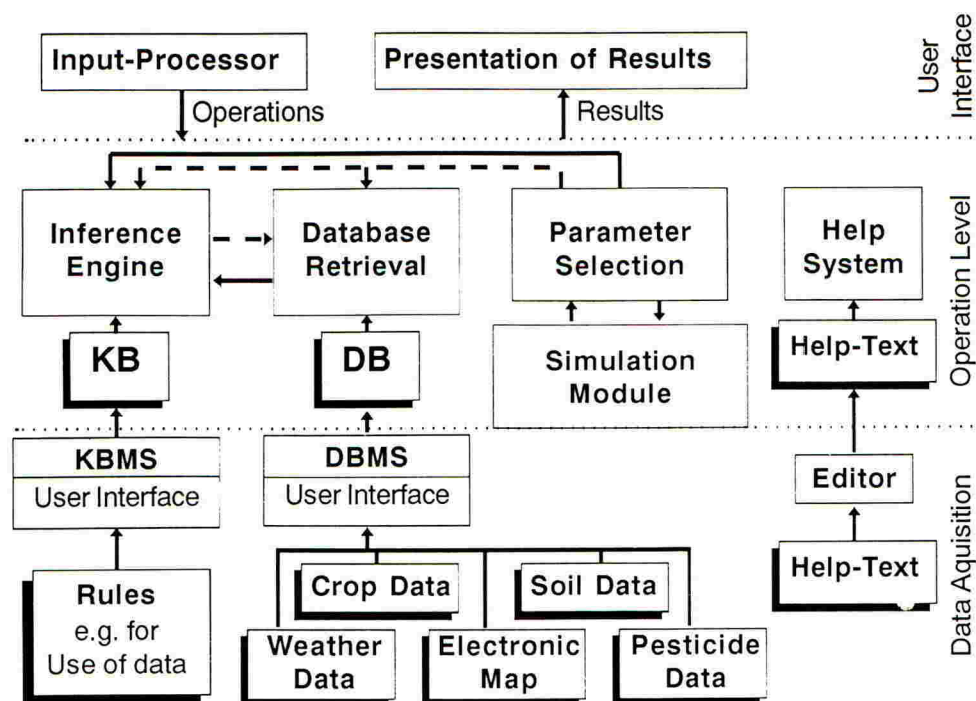


Fig. 1: System Structure of PEMOSYS: KB = Knowledge Base, KBMS = Knowledge Base Management System, DB = Data Base, DBMS = Data Base Management System, dotted lines: control flow, straight lines: data flow

The operation level contains all the logical functionalities of PEMOSYS. These are further divided into five groups. The inference engine is connected with a know-

ledge base containing all rules necessary to control the run of the programme. The rule-based strategy of CHEMPROG is also controlled by this component. This module was written in PDC Prolog, a language especially designed for artificial intelligence programmes. The database retrieval module is responsible for handling the databases where all informations about pesticides, crops, weeds, weather and soil are stored in the form of text, graphics or pictures. The database management module is based on the SQL language. In the parameter selection module, the rules for determining the best fit sorption and degradation parameters for the simulation modules according to the user input are implemented. This module is also written in Prolog. In the simulation module, currently the two simulation models described above are included. Both are written in the procedural language Borland C++. The last module is a context sensitive help system based on hyper-text technology which provides information e.g. about the use of the system and the meanings of terminologies.

The data acquisition level contains functions for the management of the data bases and rule bases. Data bases may be edited by the user to adapt the system to local conditions, and facilities to check data input are available. Rule bases are accessible only to the experts.

CONCLUSIONS

The design of this model should allow an easier estimation of the risk of pesticide use on a large scale through the combination of rule based and simulation models with a GIS-type interface. Assessments like the one presented by Pestemer & Günther (1993) for a trial site of 42 ha with about 180 single model runs, are facilitated. Correlations between e.g. soil parameters and leaching depth can be visualized easily. Sensitive areas or soil properties which indicate a risk of groundwater pollution can be identified quickly. This system will be also a valuable tool for the assessment of relative pesticide behaviour in the post registration monitoring requested by the FAO for all participating countries.

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ADVANTAGES AND POTENTIAL PITFALLS IN THE USE OF MODELS FOR REGULATORY CONTROL OF PESTICIDE USAGE

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ABSTRACT

Screening and simulation models have found increasing use in the regulatory control of pesticide usage to prevent drinking water contamination. Models have several advantages over the other methods of managing pesticides. These advantages include cost, the ability to extrapolate from a small set of field data, and the potential for establishing standardized criteria for the registration of all such chemicals. However, there is still considerable scientific debate about the proper use of such techniques, and there have been instances where the models have been used inaccurately or the wrong model was selected for the question being addressed. Specific modelling examples involving alachlor, aldicarb, and several other chemicals will be examined in the paper. Despite the many potential pitfalls in this methodology, it will be shown that none of the other methods for regulatory control of pesticide usage are as cost-effective and accurate.

INTRODUCTION

The production of agricultural crops to supply food, fibre, and biologically-derived industrial feed-stocks will continue to be a cornerstone of the world's economy for the foreseeable future. Although it is in the process of being revolutionized through the introduction of new methods such as genetic engineering and other technological advances, crop production is certain to maintain a significant reliance upon chemical methods of pest, disease, and weed control. The demands of an exponentially-increasing world population will squeeze the ability of our current crop production systems to supply all consumers with the products they require while still maintaining a pristine and safe environment within and downstream of the agricultural regions. The impact of crop protection chemicals on water quality has quite naturally received an increasing amount of attention as society looks toward the future impact of more intensive and extensive crop production across the planet.

With the increasing regulatory scrutiny on pesticide usage, a number of control strategies have been employed to help manage their continued application. Among these are laboratory and field experiments carried out under conditions of varying levels of control, monitoring studies to measure concentrations in water bodies to assess the distribution and intensity of pesticide occurrence under current control strategies, and -- to an increasing extent -- mathematical and computer modelling methods for predicting and interpreting measured parameters. It is this third technique for regulatory control that will be the topic of this paper. After a brief overview of the available models, some of the advantages of these methods will be described. An equal amount of attention will then be given to some of their distinct disadvantages. An objective determination will then be made to balance the advantages and potential pitfalls of computer models as tools for the regulatory control of pesticide use.

AVAILABLE MODELS

Mathematical and computer models for describing pesticide fate and transport into drinking water supplies may be broadly classified as either screening or simulation models. Screening models typically require no computer, or only a simple spread-sheet type of calculation. They are often empirical or based on a number of severe simplifying assumptions in order to reduce to a bare minimum the amount of computation required. By contrast, simulation models can involve the need for considerable computational resources and generally attempt to describe the behaviour of the pesticide as a full function of time and at least one dimension (usually depth in the soil profile). These two classes of models are each widely used and have their own unique place in a comprehensive regulatory control management strategy. Some examples of the currently available models are described below.

Screening Models

Numerous screening models for classifying the drinking water contamination potential of pesticides have been proposed. A few of the more widely used examples are listed here:

Cohen Criteria

In the early 1980's, Stuart Cohen and others in the United States Environmental Protection Agency published (Cohen *et al.*, 1984) a list of physical properties which they had determined to be associated with pesticides likely to be found in ground water. Seven properties were given, including water solubility (> 30 mg/L), soil/water partition coefficients ($K_d < 10$ L/kg, $K_{oc} < 500$ L/kg), and soil degradation half-life ($> 2-3$ weeks). Other parameters such as volatility and acid dissociation constant were listed, as were some of the hydrogeologic conditions associated with contamination incidents: shallow water tables, sandy soils, and acidic sub-surface conditions.

Jury Screening Models

Also beginning in the early 1980's, William Jury of the University of California at Riverside published (Jury *et al.*, 1987) a number of papers describing analytical solutions to the convective dispersion equation (CDE) for describing one-dimensional fate and transport of pesticides through soil. The analytical solutions were made possible through the assumption of steady water flows, linear and completely reversible sorption isotherms, first-order and linear pesticide dissipation kinetics, and a number of other simplifying effects. However, a number of relatively sophisticated processes were included in some of these models, in particular volatilization and depth-dependent soil degradation rates for the pesticide.

Hornsby Screening Models

At the University of Florida (Gainesville), Art Hornsby and several co-workers have produced several screening models for describing pesticide leaching behaviour (Nofzinger and Hornsby, 1988). These models have the unique feature that they have been linked with a soils database for Florida and with a pesticide physical properties database. Most of the methods (such as CMLS and CHEMRANK) make a rather severe simplifying assumption regarding dispersion of the pesticide through the soil profile -- the pesticide moves as a pulse without spreading.

GUS

While at Monsanto in the late 1980's, the author proposed a single numerical index for predicting the water contamination potential of

pesticides based only on its soil/water partition coefficient (Koc) and the soil half-life (Gustafson, 1989). The index, named Ground water Ubiquity Score or GUS, has been used by the United States Soil Conservation Service as part of its screening technique and by regulatory agencies in Canada and elsewhere to help classify and prioritize pesticides.

Simulation Models

Simulation models are appropriate for those instances in which a considerable amount of computer power and data are available for a specific pesticide use scenario, and when there is a need to have more specific information about the concentrations of the pesticide in adjacent water bodies. Some of the important models are listed here:

PRZM

First released in 1984 by Bob Carsel and others at the US EPA's Environmental Research Laboratory in Athens, Georgia, the Pesticide Root Zone Model continues to be the most widely-used model when a full-fledged simulation of pesticide behaviour is required (Carsel *et al.*, 1984). Although a number of technical objections have been raised concerning the assumptions and solution methods utilized by the program, particularly in its handling of hydrology, there is not another model with the breadth of documentation and history of varied uses by a broad range of investigators. The most recent versions of PRZM include an excellent volatilization model and the possibility of modelling up to two degradate products during a single simulation. This last feature is particularly powerful and can be used to simulate non-linear dissipation kinetics for the parent pesticide if so desired.

PELMO

An important variant of the PRZM model has been developed for use in Germany (Klein, 1991). Called PELMO, it utilizes the Freundlich equation for describing pesticide sorption to soil, optional non-linear dissipation kinetics, a different method for estimating evapotranspiration, and an explicit treatment of the temperature-driven depth-dependence of pesticide degradation rate. Another feature of PELMO that makes it well-suited for certain regulatory applications is that virtually all of the scenario parameters have been hard-coded into the system, reducing the user's input choices to only a handful of very specific properties and dates. To a large extent, this "levels the playing field," and makes it possible to apply the model as a standardized regulatory tool.

CALF

The product of several researchers in the UK, primarily Peter Nicholls and Allan Walker, CALF is the only widely-used simulation model to directly account for the commonly observed slow increase of soil sorption with time (Addiscott and Wagenet, 1985; Walker and Barnes, 1982). A problem in the regulatory use of the CALF model is that there has been no careful version control, and therefore it is difficult to know which version one has when making comparison of runs performed by different parties. CALF is currently being modified to account for macropore or preferential flow processes, which will be a valuable and unique enhancement among available simulation models.

GLEAMS

This program and its predecessor, CREAMS, were both produced by the USDA Agricultural Research Service (Knisel, 1980; Leonard *et al.*, 1987). Among available models, it possesses the most widely-accepted representation of pesticide runoff processes. A considerable amount of field validation work has been reported for the model. It does not have

all of the flexibility of PRZM regarding numbers of soil layers or provisions for the use of more sophisticated solution techniques, but these limitations may not necessarily be important for many users or applications of the model.

ADVANTAGES OF MODELS

The advantages of models relative to other techniques for regulatory management of pesticide use have become evident over the past 10 years. Experience with the techniques have demonstrated that they are relatively inexpensive when compared with experimental work and monitoring studies, that they allow the full information value of available data to be extracted, and that they make possible the establishment of critically-required standardized registration criteria. Each of these features is explored further in the sections that follow.

Relatively Low-Cost

Experimental and monitoring studies to measure the drinking water contamination potential of pesticides are extremely expensive. Typical costs for field dissipation studies in the United States are several \$100K per location, and a monolith lysimeter study conducted according to the BBA-guidelines has a similar cost. Large-scale monitoring studies to measure the ambient concentrations of pesticides in drinking water supplies can often cost 10 times as much to perform. By contrast, even highly sophisticated simulation modelling involving hundreds of years worth of weather data and thousands of soil and crop scenarios can be completed within a few weeks utilizing widely-available computer resources at a small fraction of the cost associated with the experimental work.

The Power to Extrapolate

Not only are experimental studies very expensive, they are very limited -- either spatially or temporally -- in the information they provide. An intensive laboratory or field study in which the pesticide is applied and its fate and transport are studied in great detail provides a wealth of data: but only about the fate and transport of the pesticide in that soil under those conditions. Even a nationwide monitoring study to measure the concentrations of a pesticide in thousands of drinking water sources is very limited temporally, since it provides only a single "freeze-frame" snapshot of the state of water quality at that particular instant in time when each sample was collected. In each case, models can be used in an attempt to construct a spatially- and temporally-complete description of the behaviour of the pesticide at all drinking water extraction sites throughout the period during which pesticide use is to continue. When viewed in this manner, it can be seen that a very powerful synergy exists between experimentally-derived data and the models, in which the experiments provide useful validation and calibration data for the models, and the models in turn provide a mechanism for extrapolating beyond the restricted data set to a complete exposure assessment across all use conditions and scenarios.

Standardized Registration Criteria

Regulatory agencies are constantly presented with difficult choices regarding the safety of continued pesticide use. In most instances, the available field, laboratory, and monitoring information does not paint an entirely consistent picture regarding the drinking water contamination potential of the pesticide. Faced with similarly incomplete data sets for

a host of competing compounds, the task of the regulator becomes particularly difficult. Models, especially those such as PELMO with its many hard-coded assumptions, provide a mechanism for comparing differing compounds under identical (albeit hypothetical) use conditions. It then becomes possible to establish standardized registration criteria, such as no predicted drinking water concentrations above a certain fraction of a pre-set toxicity threshold level. Alternatively, the focus could be the avoidance of any concentrations above a completely arbitrary level -- such as the 0.1 µg/l level established by the EEC directive. The critical factor is that models make it possible to take experimentally determined parameters, such as soil/water partition coefficients and degradation rate constants, and apply them under standardized modelling conditions to compare the predicted behaviour against standard criteria. Regulatory decisions based on such methodologies will still not be error-free, but at least they would conform to known rules with predictable outcomes and have less bias when comparisons are made.

LIMITATIONS OF MODELS

Having described the many and varied advantages of models, it might seem that there is no reason to pause before adopting them throughout all aspects of regulatory management of pesticides as the final and ultimate control tool. Unfortunately, this is not the situation today due to a number of significant limitations to the available models. Among these is the question of model validity, the widespread use of inappropriate models for the specific question being asked, the unavailability of sufficient quantities and quality of input data, and the lack of any widely-accepted standards for the conduct of computer modelling assessments.

Model Validity

The effortless ability of computers to output a disturbingly large number of significant figures for any concentration value often masks the fact that the accuracy of the first digit -- and even the number of digits to the left of the decimal point -- may be completely incorrect. Many of the standard assumptions within simulation models are now known to be false. These include the common assumptions of: linear first-order dissipation kinetics, constant dispersion coefficient, linear and reversible soil-sorption isotherms, and overly simplified hydrology models for generating soil pore water velocities. Even PRZM, the most widely-accepted leaching model, does not allow for any capillary rise of water through soil during dry periods -- a simple hydrologic process widely known to be important for many pesticides. Model validity, or the lack of it, is a major source of uncertainty when considering the certainty of modelling results. Yet it is often ignored by those using Monte Carlo simulations and other probabilistic modelling approaches when describing results. For the regulator, the question of absolute model accuracy may not always be important if the tool is being used to make comparisons between alternative management strategies and if the various alternatives are biased in a similar direction and by a similar amount. However, the lack of knowledge about model complexity often breeds misunderstanding about the absolute accuracy of the models, and an undue faith in their ability to predict reality. Efforts should be made to incorporate model uncertainty and "fuzzy logic" into the decision-making process whenever modelled results are involved.

Inappropriate Choice of Model

The model developers usually have a very clear idea of what particular question their model is intended to answer. Knowing this, several simplifying assumptions are made in order to focus only on as accurate a representation as possible of the processes they believe are most important in order to address that issue. For instance, relatively simple runoff and erosion models are employed by PRZM because the program was originally intended to answer the question of whether a pesticide would leach. To the extent that runoff of pesticide affects the mass balance, the model developers felt that some effort should be made to correctly account for these losses. Other users of the simulation model, including the author, have been tempted to use the program to model runoff processes -- and it often appears to do a reasonable job. However, the accuracy and technical validity of the runoff curve number approach is probably questionable if absolute numbers are desired and an alternative such as CREAMS may be a more appropriate choice, since the developers of this models were focused only on answering the specific question of how much pesticide runoff occurs.

Unavailability of Input Data

Most environmental fate models are extremely "data-hungry." While the screening models can often be used with only a few inputs, simulation models generally require daily (or even hourly) meteorological data, extensive soil information (often as a function of depth), specific details concerning crop management and crop characteristics, and a wide range of physical property descriptors for the pesticide being modelled. The lack of sufficient data often means that the intrinsic accuracy of the model becomes meaningless due to the inability of the model to be run for the desired scenario. The utility of such simulation models can therefore be very limited for agricultural regions in which critical data are unavailable or prohibitively expensive to obtain. These models are also generally not appropriate for newly synthesized active ingredients which have not yet been fully characterized.

Lack of Good Modelling Practices

A major issue in the regulatory use of models, especially simulation models having a large number of inputs and adjustable parameters, is the lack of any universal standards for running the computer programs and then documenting the results. This situation is currently being addressed by certain regulatory bodies. BBA have recently issued (Gorlitz, 1993) a document entitled, "Rules for the Correct Performance and Evaluation of Model Calculations for Simulation of the Environmental Behavior of Pesticides." In the United States, the EPA has established an environmental modelling work-group with the National Agricultural Chemicals Association (NACA) which has been charged with the task of developing a document covering such issues. Until such standards are developed and become part of the regulatory framework, there will continue to be unresolvable discrepancies between the modelling results produced by different parties. There will also be modelling reports produced which are not reproducible due to the lack of appropriate documentation concerning input parameters, model version numbers, computer platform chosen, and undocumented manipulation of the modelling output.

CONCLUSIONS

Computers are dangerously powerful machines, and are becoming more powerful with an ever quickening pace. To a certain extent, the sophistication of computer modelling approaches for describing the drinking water contamination potential of pesticides has increased over the past several years in a similar manner. In most instances, however, the theoretical advances have significantly lagged behind the technological strides placing rapid computational power in the hands of regulatory personnel managing and hoping to control pesticide use. As discussed in this paper, the models have many limitations, and the net result today is that we are able to get the wrong answer much faster and with much flashier graphics than we could just a few years ago.

But this cynical conclusion is not entirely sound. There are significant efforts underway to improve the accuracy, appropriateness, and regulatory utility of environmental fate models. Over the past several years there have been a number of examples of the successful use of computer models as part of the regulatory control strategy. The most significant of these is undoubtedly the regulatory activity surrounding the issue of ground water contamination by aldicarb in certain sandy regions of the United States. In this case, PRZM was used by the registrant of the compound to systematically assess the leaching behaviour of the compound in each of the thousands of soil series throughout the potential use region. The results of these calculations were used to establish logical and effective well set-back distances for those areas in which leaching was shown to be possible. The effectiveness of this regulatory modelling strategy has been vindicated over time through an ever-decreasing number of new incidents of contamination.

Another modelling success story involved alachlor in the mid-1980's, which was found to occur in the surface water of certain agricultural regions of the United States. Monitoring information was used to calibrate and then validate a simulation model and a regression model for predicting the full time series of surface water concentrations and the annualized mean concentration, respectively. The monitoring and modelling work combined to convince regulatory bodies that the annualized mean concentration of the compound in even the most vulnerable watersheds would remain below the maximum contaminant level of 2 µg/l.

These two examples serve to re-demonstrate one of the important points raised in this paper, which is the critical interdependence of modelling and experimental work. As pointed out in this paper, it would require a prohibitively expensive amount of experimental work to completely characterize the spatial and temporal behaviour of a pesticide in the environment. However, an appropriate model can be selected, calibrated to experimental data, and used to extrapolate from the data set to a rich and full description of the compound across the range of soil and climatic conditions that the compound would encounter during its lifetime of use in the agricultural production system for which it is intended.

Thus, despite the many potential pitfalls in the use computer models, it seems clear that none of the other methods for regulatory control of pesticide usage have the same power, cost-effectiveness, and accuracy. Monitoring studies are limited in time, and controlled laboratory and field experiments are limited to the soils and environmental conditions in which they are conducted. Expanding either to a truly representative sub-set of the universe of agricultural units in which the compound is to be used is not feasible.

No other method for managing pesticide use has the potential to develop sound, standardized registration criteria. All experimental work is biased by the particular conditions existing during the study. Models can be used to combine results for the pesticide and compare them against standard pesticides, alternative pesticides, or absolute criteria such as a key concentration threshold in order to reach a regulatory decision. Before using the models in this way, however, it will be necessary to reach agreed-upon standards for good modelling practices.

Care must be taken in interpreting modelling results. This is especially true today because of the limited amount of true validation work that has been performed on the existing models, and due to the absence of good modelling practices for performing and documenting results. There is reason to be optimistic that the future will bring with it not only faster simulation models, but more accurate ones too. This circumstance will make it easier and more appropriate for regulatory agencies to more widely embrace computer models as the final, discriminating technique for establishing sound regulatory policies on pesticide use.

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