



Know-how for Horticulture™

**Improved herbicide
management for
increased yield and
quality**

Phillip Frost et al
Serve-Ag Pty Ltd
& University of Tasmania

Project Number: VX99011

VX99011

This report is published by Horticulture Australia Ltd to pass on information concerning horticultural research and development undertaken for the vegetable industry.

The research contained in this report was funded by Horticulture Australia Ltd with the financial support of the Serve-Ag Pty Ltd and the vegetable industry.

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ISBN 0 7341 0597 5

Published and distributed by:

Horticultural Australia Ltd

Level 1

50 Carrington Street

Sydney NSW 2000

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E-Mail: horticulture@horticulture.com.au

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Improved herbicide management for increased yield and quality

Conducted on behalf of

*Horticulture Australia Ltd
(Project VX99011)*

Final Report

by

Phillip Frost et al.

Serve-Ag Research and University of Tasmania

November 22, 2002

Horticulture Australia Ltd Project VX99011

22 November 2002

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This report was funded by Horticulture Australia Ltd to improve the understanding of a number of residual herbicides on a range of soil types.

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Funding Sources:

- Horticulture Australia Ltd
- University of Tasmania
- Harvest Moon Pty Ltd
- Serve-Ag Pty Ltd
- Tasmanian Institute of Agricultural Research
- Elliot Chemicals New Zealand
- Botanical Resources Australia
- FMC International AG
- Tasmanian Alkaloids Pty Ltd

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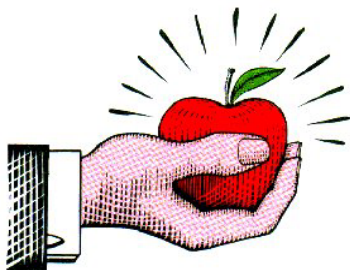
Harvest Moon Pty Ltd



*Serve-Ag Pty Ltd
Institute of*



*Tasmanian
Agricultural Research*



Elliot Chemicals New Zealand



**Botanical Resources
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FMC International AG

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Media Summary

Soil active pre emergent herbicides are widely used in horticultural and broadacre cropping systems throughout Australia. Such herbicides provide a number of benefits in these cropping systems; however, variations in crop safety and weed efficacy, and herbicide carry over to susceptible crops are issues associated with the use of pre emergent herbicides. This 3-year Horticulture Australia Ltd project examined some of the key factors influencing herbicide activity and persistence, and also looked at developing more rapid and cost effective analysis methods for quantifying herbicide levels in soils and relating these to crop growth responses.

The attraction of herbicides to soil particles (sorption) is important in controlling the activity and also the breakdown of pre emergent herbicides. The sorption of pendimethalin, clomazone and metribuzin varied according to soil type, in each case increasing in the order kurosol, sodosol, vertosol, ferrosol.

Herbicide breakdown studies showed half-life values of clomazone ranging from 79 to 124 days, while values for pendimethalin ranged from 64 to 117 days. Metribuzin dissipated more quickly with half-life values of between 30 and 64 days. Soil moisture was shown to be a critical factor for herbicide breakdown on all soils. Cultivation of the soil did not increase the rate of herbicide breakdown when compared to herbicide applied to the soil surface and not cultivated.

A series of replicated trials and sampling from commercial crops was conducted to determine critical herbicide concentrations affecting crop growth. Poppy crops were found to be particularly sensitive to pendimethalin, with concentrations above 300-400 ppb significantly reducing yield. Critical concentration for clomazone in onions was 400-500 ppb, oxyfluorfen in zucchini was 100-150 ppb, and metribuzin in swedes was 140 ppb. No negative effects on yield were observed with oxyfluorfen at 254 ppb in squash and sulfentrazone at 24 ppb in poppies and onions.

Herbicide concentrations have shown to provide a reliable indication of crop yield responses in this study and could potentially be used to plan crop rotations and diagnose herbicide carry over effects on susceptible crops. The use of soil herbicide analysis along with adjusting herbicide rates for different soil types and the strategic use of agronomic practices such as irrigation to increase herbicide breakdown can be effectively used to minimise the impact of residual herbicides on following crops.

An effective way of communicating information on herbicide soil type interactions to end users is via herbicide labels. Information generated as part of this project has been used in the development of rate recommendations based on soil type for both Command and Frontier Optima. This information will be documented on the product labels. Regular field days, conference presentations and seminars were also conducted throughout the project.

Technical Summary

Soil active pre emergent herbicides are widely used in horticultural and broadacre cropping systems throughout Australia. Such herbicides provide a number of benefits in these cropping systems; however, there are a number of issues with pre emergent herbicides, in particular variations in crop safety and weed efficacy, and herbicide carry over to susceptible crops. This 3-year Horticulture Australia Ltd project examined some of the key factors influencing herbicide activity and persistence, and also looked at developing analysis methods for quantifying herbicide levels in soils and relating these to crop growth responses. The effects of different agronomic factors on herbicide breakdown were also evaluated. Herbicide active ingredients included in the study were pendimethalin, clomazone, metribuzin, oxyfluorfen, sulfentrazone and dimethenamid. Soil types included in the study were ferrosol, vertosol, kurosol and sodosol.

Sorption of herbicides to soil particles is important in controlling the activity and also the dissipation of herbicides. The sorption of pendimethalin, clomazone and metribuzin varied according to soil type, in each case increasing in the order kurosol, sodosol, vertosol, ferrosol. This indicates that, at the same application rate, a greater amount of metribuzin would be found in the soil solution than clomazone or pendimethalin, and availability would be greater for each herbicide in the kurosol and sodosol soils than in the vertosol and ferrosol soils. Metribuzin also desorbed more readily than clomazone or pendimethalin. Due to the hydrophobic nature of the molecule, pendimethalin showed a strong affinity for organic surfaces with rapid sorption and a very low degree of desorption. Clomazone showed a strong affinity for organic matter and also smectite clays. Clomazone showed a moderate degree of both adsorption and desorption, and the organic coatings on soil particles can represent a significant source of available herbicide, particularly in the kurosol and vertosol soils.

Herbicide dissipation studies showed half-life values of clomazone ranging from 79 to 124 days, while values for pendimethalin ranged from 64 to 117 days. Metribuzin dissipated more quickly, with half-life values of between 30 and 64 days. Soil moisture was shown to be a critical factor for herbicide breakdown on all soils. There was a rapid drop in herbicide concentrations within three days of application, particularly for clomazone on the ferrosol soil. This could not be attributed to volatilisation, leaching or microbial degradation, so it was thought to be related to rapid sorption and partitioning of the herbicide.

A series of replicated trials and sampling from commercial crops was conducted to determine critical herbicide concentrations affecting crop growth. Poppy crops were found to be particularly sensitive to pendimethalin, with concentrations above 300-400 ppb significantly reducing yield. Critical concentration for clomazone in onions was 400-500 ppb, oxyfluorfen in zucchini was 100-150 ppb and metribuzin in Swedes was 140 ppb.

Herbicide concentrations measured using the 1:5 (soil:water) extraction for recovery of the plant available herbicide pool, and subsequent analysis using gas chromatography and mass spectrophotometry, have shown to provide a reliable indication of crop yield responses in this study. Super critical fluid extraction gave variable results, depending on soil moisture levels, and did not appear to be reliable enough for wide spread analysis of herbicide levels in soils.

Information generated as part of this project has been used in the development of rate recommendations based on soil type for both clomazone and dimethenamid. This information has been documented on the product labels. Regular field days, conference presentations and seminars were conducted throughout the project.

Recommendations

- Field and laboratory trials have shown that by adjusting herbicide application rates for different soil types, the use of soil herbicide analysis to quantify herbicide concentrations at planting and the strategic use of agronomic practices such as irrigation to increase herbicide breakdown during fallow periods, effects of residual herbicides on following crops can be reduced.
- Soil herbicide analysis has shown potential for estimating plant available herbicide levels in soils and predicting crop responses. For this to be adopted by industry it would need to be run as a commercial service, possibly by a laboratory which is already set up for analysis of pesticides in plants.
- Understanding the behaviour of different herbicides in different soil types and the effect of environmental and agronomic factors on this behaviour is a complex area. This study has helped this understanding however further work could be conducted particularly in the areas of soil moisture and its influence on herbicide behaviour and also key physical and chemical properties of soils influencing the behaviour of different herbicides in soils.

Background

Soil active pre emergent herbicides are widely used in a number of horticultural crops. With the introduction of pre emergent herbicides, significant improvements in weed management have been achieved. Pre emergent herbicides can control successive weed germinations and hence reduce the need for repeated post emergent herbicide applications. Due to their action, pre emergent herbicides can often achieve greater selectivity, for example between established crops and germinating weeds.

Poor crop vigour is often blamed on herbicide residues from a previous crop, and in some cases crop failure has occurred. More intensive and diverse rotations, along with less tolerant, higher yielding varieties, may have increased these problems, which become particularly pronounced when new herbicides are used or when herbicides are used in new production regions.

Variations in efficacy and crop safety on different soil types and under different environmental conditions are also issues with pre emergent herbicides. Generally, lower rates are required on lighter soils than heavier textured soils to provide equivalent weed efficacy.

This collaborative project between Serve-Ag and the University of Tasmania was funded by Horticulture Australia Ltd, with industry support from Tasmanian Alkaloids Pty Ltd, Botanical Resources Australia, Elliot Chemicals New Zealand, Harvest Moon Pty Ltd and FMC International AG.

Aims

- Examine the persistence of herbicides in cropping soils.
- Identify key soil factors influencing persistence.
- Determine critical concentrations of herbicides that reduce crop yield and quality.
- Develop management practices to reduce the risk of herbicide carry-over effects.

Materials and Methods - General

Product Formulations

Product	Active Ingredient	Concentration of Active	Formulation	Herbicide Group*
Command	clomazone	480 g/L	Emulsifiable Concentrate	F
Stomp	pendimethalin	330 g/L	Emulsifiable Concentrate	D
Authority	sulfentrazone	750 g/kg	Water Dispersible Granule	G
Goal WP	oxyfluorfen	400 g/L	Wettable Powder	G
Lexone	metribuzin	750 g/kg	Water Dispersible Granule	C
Frontier	dimethenamid	900 g/L	Emulsifiable Concentrate	K

* The herbicide group, used for resistance management, was developed by Avcare (Appendix iii).

Soil Analyses

SITE NO.		5 - 8
Location		Forthside
Soil Type		Ferrosol
pH (H₂O)		6.2
pH (CaCl₂)		5.6
Organic Carbon (%)		3.1
% Sand	Fine	56
	Coarse	6
% Silt		20
% Clay		18

Description of Soil Types

Ferrosol

Ferrosol soils are defined as permeable clay soils with high free iron oxide content (>5%Fe) within the B2 horizons, which lack strong texture contrast between A and B horizons. Common forms of ferrosol have very favourable physical properties suitable for agricultural purposes. In Tasmania, red ferrosol soils are common in the north of the State, and support a wide range of agricultural crops.

Sodosol

Sodosol soils are characterised by having a strong texture contrast between A horizons and sodic B horizons which are not strongly acid. The B horizons have an exchangeable sodium percentage (ESP) value is 6 or greater in the upper part and are generally clayey. The soils are usually low in organic matter and are poorly draining. In Tasmania, these soils are found in the south-east and in a belt through the Midlands to the north of the State.

Vertosol

Vertosol soils, or black cracking clays, are clay soils (>35% clay content) with shrink-swell properties which cause deep and wide cracking on drying. A lenticular structure and slickensides occur at some depth in the solum. Soils vary in colour and range from strongly acid to highly calcareous. Black vertosol soil is one of the most highly productive soils in Australian agriculture. In Tasmania, vertosol soils occur in the north-west and north-east of the State.

Kurosol

Kurosol soils are defined by a clear or abrupt texture contrast between the A and B horizons. The upper part of the B horizon is strongly acid. Many of these soils have unusual subsoil chemical features such as high exchangeable magnesium, sodium and aluminium and very low calcium. In Tasmania, kurosol soils occur in the south-east and far north-east of the State.

1. Adsorption and Desorption Reactions

Introduction

The efficacy of soil applied herbicides is strongly influenced by soil factors (Moomaw, 1992), with sorption of herbicides to soil colloids identified as the most important process controlling the activity and fate of herbicides in soil (Bailey and White, 1964; Hamaker and Thomson, 1972; Saltzman and Yaron, 1986). In principle, sorption occurs when the attractive forces between the solid surface and the herbicide are greater than the attractive forces between the herbicide and the solvent (soil water), and any repulsive forces between the surface and the herbicide. The sorption of herbicides in the soil may be likened to a form of fixation whereby either energy, or changes in the balance of the soil equilibrium, are needed to release the chemical into the aqueous soil environment. As a result, sorption has important implications for both the activity and fate of herbicides in soil. Sorption reactions influence volatility, plant availability, availability for microbial degradation, leaching and chemical degradation. The degree of sorption, the reversibility of the process, and the kinetics of the forward and reverse reactions are all regulated by the nature of the herbicide molecule, the nature of the soil particle surfaces, and the impact of attendant phenomena such as pH, soil moisture level, temperature, and solute composition and concentration in the soil water (Upchurch, 1972).

Objectives

- To assess the sorption properties of residual herbicides in a range of soil types using clomazone, metribuzin and pendimethalin as reference compounds;
- To identify the implications of the described sorption reactions for efficacy and dissipation;
- Identify soil properties critical to both sorption and desorption behaviour.

1. Adsorption and Desorption Reactions (Cont.)

Materials and Methods

Ferrosol, kurosol, sodosol and vertosol soils were collected from 4 sites used in the field dissipation study. Soil was collected from areas where the herbicides used in this study had not previously been applied. Technical grade analytical standards of clomazone, metribuzin and pendimethalin were obtained from the Australian Standards Laboratory.

Soil adsorption experiments

Herbicide standards were prepared by diluting appropriate volumes of analytical grade compound in 0.01 M calcium chloride to give the following concentrations: 0.1, 0.5, 1, 5, and 10 mg/L. Adsorption was determined in triplicate on a 1:5 sorbent/solvent ratio (5 grams of soil: 25 mL of herbicide solution). Samples were placed in sealed 50 mL centrifuge tubes for equilibrium by end over end shaking for 24 hours. Sorbent and solution phases were subsequently separated by centrifugation at 10,000 rpm for 10 minutes. The supernatant from this centrifugation was then poured off for solvent extraction of herbicide. In addition, to establish mass balance in a selected number of samples, the solid phase was also subjected to solvent extraction.

Soil desorption experiments

Herbicide standards were prepared by diluting the appropriate volume in 0.01 M calcium chloride to give a concentration of 10 mg/L. Desorption was determined in triplicate using a sorbent to solution ratio of 1:5. Samples were placed in sealed 50 mL centrifuge tubes for equilibrium by end over end shaking for 24 hours. Sorbent and solution phases were subsequently separated by centrifugation at 10,000 rpm for 10 minutes. The supernatant from this centrifugation was then poured off for solvent extraction of herbicide. After the supernatant was poured off, the same volume of 0.01 M calcium chloride was added and the tubes were shaken to disperse the soil pellet. The samples were then equilibrated for 24 hours as described above and re-centrifuged. The desorption equilibration process was repeated four times, resulting in five supernatant samples. Solvent extraction of herbicide was performed for each sample. Herbicide concentrations were determined using GCMS. The gas chromatograph was operated at 280°C. Samples (2µL) were injected into the column at 40°C using a carrier gas of helium at a flow rate of 2 mL min⁻¹. This temperature was maintained for 1 minute. The column temperature was increased to 190°C at 30°C min⁻¹, then increased at a rate of 10°C min⁻¹ to 280°C and held for 6 minutes. Under these conditions, the retention time for clomazone was 21 minutes and the lower detection limit was 10 ppb (Rowbottom, pers comm).

1. Adsorption and Desorption Reactions (Cont.)

Data analysis

Experimental data from the batch equilibrium method was first analysed to determine the concentration of herbicide sorbed to the solid phase. The amount of herbicide sorbed was taken as the difference between the initial concentration of herbicide in solution and the equilibrium (supernatant) concentration in solution. Adsorption and desorption data is described by the Freundlich equation, which is expressed as :

$$q = K_{fa}C^{1/n}$$

Where:

q = the amount sorbed

C = equilibrium concentration

K_{fa} = Freundlich coefficient

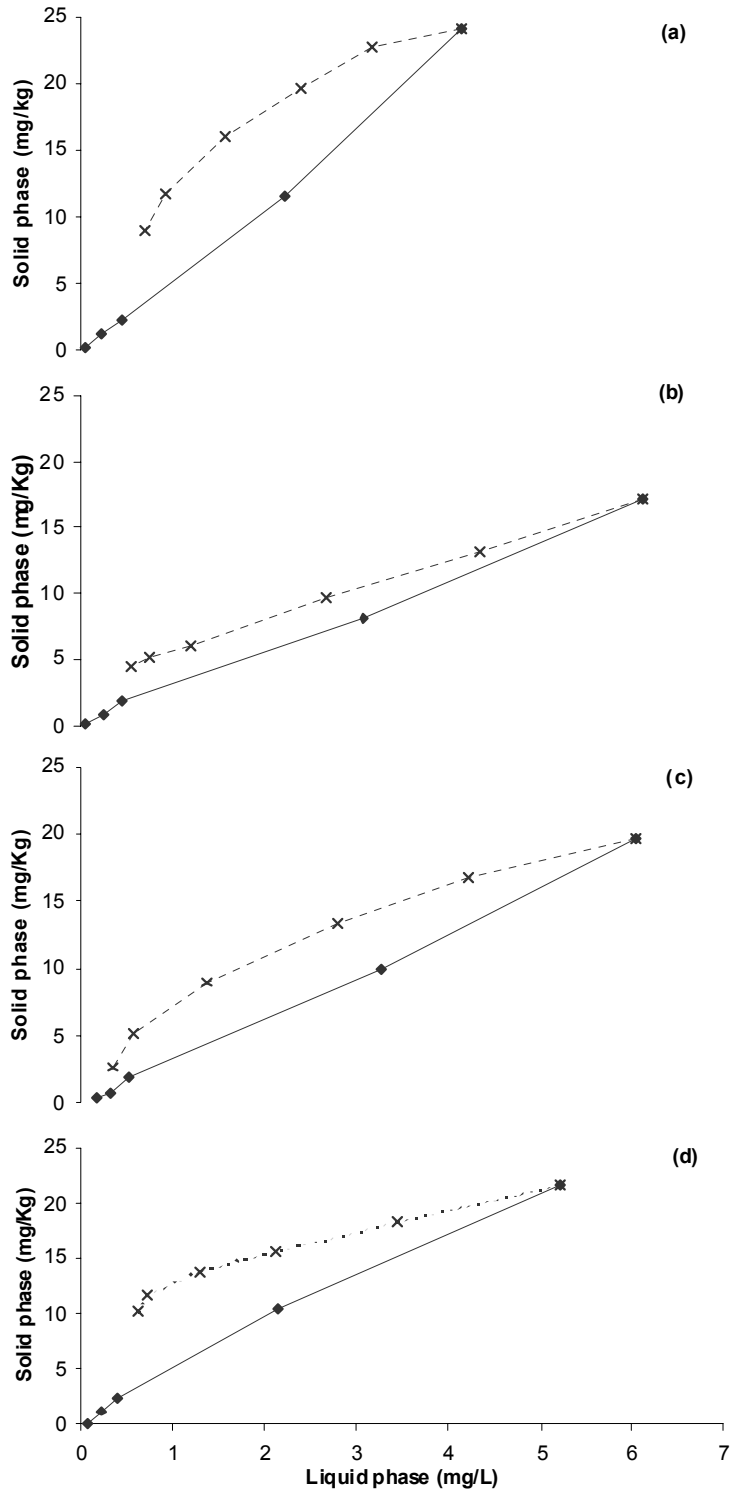
1/n = correction constant

By plotting the linear form of the equation $\log q$ vs. $1/n \log C + \log K_{fa}$, the slope is 1/n and the intercept is $\log K_{fa}$. The constant K_{fa} is a measure of the degree or strength of adsorption and the constant 1/n indicates the degree of non-linearity between the solution concentration and the amount sorbed. If 1/n is equal to 1 then the relationship is linear and the Freundlich equation may be reduced to the form $q = K_{fa}C$. In this relationship, adsorption is directly proportional to solution concentration with a constant partitioning between the solution phase and the sorbent. In this case, K_{fa} becomes known as the partition adsorption coefficient (K_d), describing the partitioning of herbicide between the sorbent and solution phases.

1. Adsorption and Desorption Reactions (Cont.)

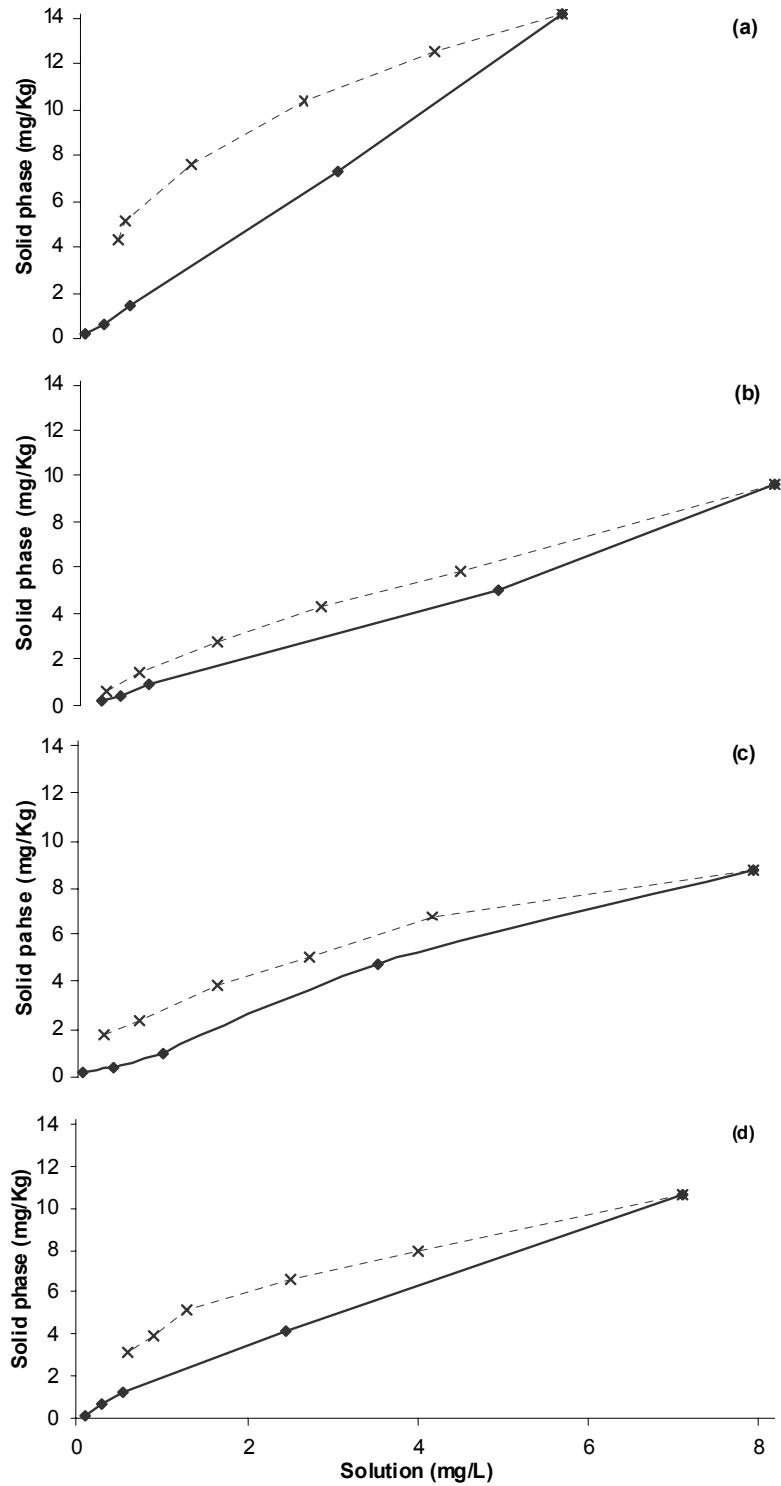
Results

Graph 1 - Adsorption (solid line) and desorption (dotted line) isotherms for clomazone in ferrosol (a), kurosol (b), sodosol (c) and vertosol (d) soils.



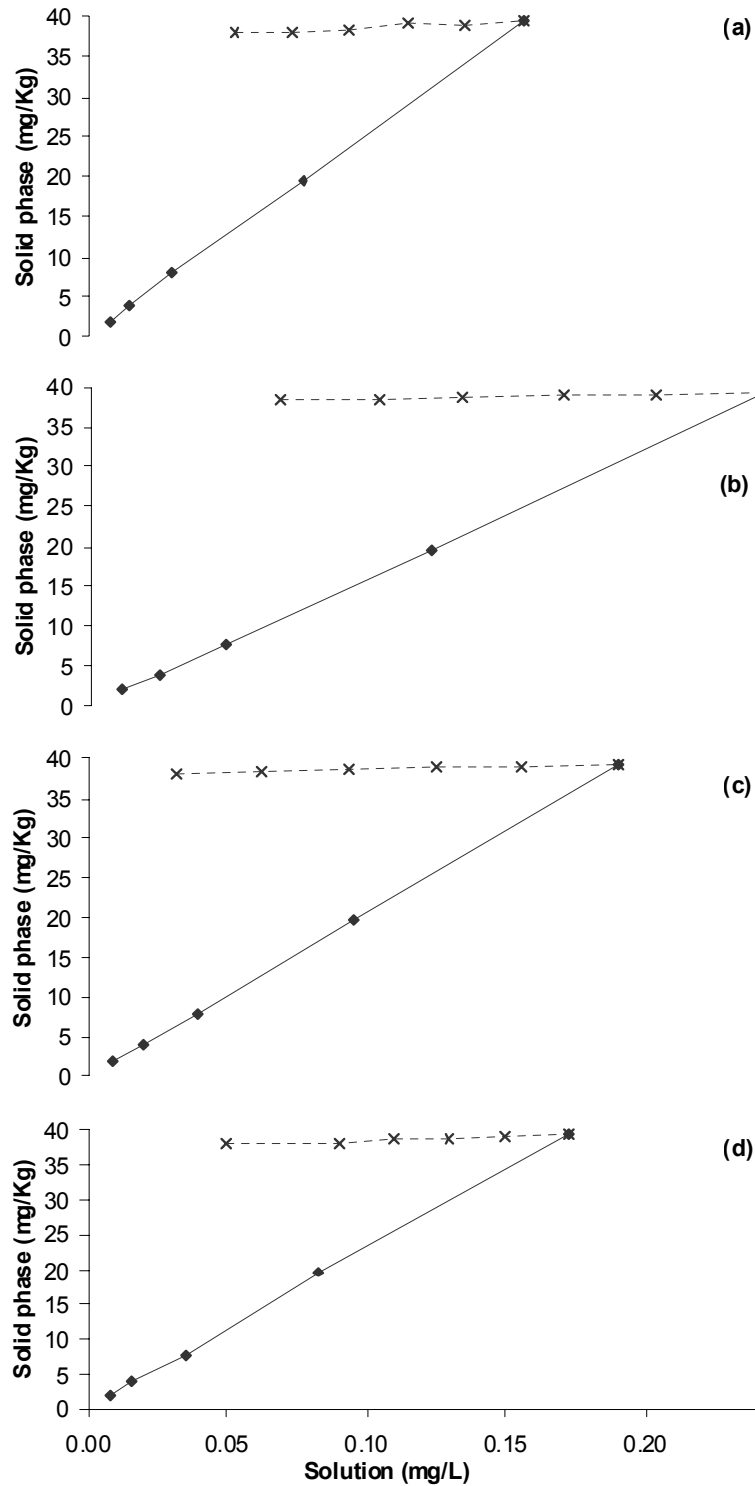
1. Adsorption and Desorption Reactions (Cont.)

Graph 2 - Adsorption (solid line) and desorption (dotted line) isotherms for metribuzin in ferrosol (a), kurosol (b), sodosol (c) and vertosol (d) soils.



1. Adsorption and Desorption Reactions (Cont.)

Graph 3 - Adsorption (solid line) and desorption (dotted line) isotherms for pendimethalin in ferrosol (a), kurosol (b), sodosol (c) and vertosol (d) soils.



1. Adsorption and Desorption Reactions (Cont.)

Discussion

Clomazone

The sorption of clomazone varied according to soil type, increasing in the order kurosol, sodosol, vertosol, ferrosol. In all cases, the sorption isotherms (Graph 1) exhibited close to linear behaviour ($1/n$ approximately 1), allowing K_{fa} to be represented by the distribution constant K_d . When normalised for organic carbon content, the distribution constant values for the four soils were 143 ± 57 (kurosol), 117 ± 47 (sodosol), 120 ± 36 (vertosol) and 85 ± 20 (ferrosol). Clomazone desorption varied according to soil type, with values for the Freundlich constant of 5.8 ± 1.1 (kurosol), 6.5 ± 1.2 (sodosol), 11.5 ± 1.1 (ferrosol) and 12.3 ± 1.1 (vertosol). Desorption showed considerable hysteresis (Graph 1) which was most pronounced in the ferrosol and vertosol soils.

Regression of Freundlich coefficient against soil properties yielded a significant positive correlation with soil organic carbon content ($r = 0.96$, $P < 0.05$). A significant positive correlation was also found between the Freundlich desorption coefficient and soil clay content.

Metribuzin

The sorption of metribuzin varied according to soil type, increasing in the order kurosol, sodosol, vertosol, ferrosol. In all cases, the sorption isotherms (Graph 2) exhibited close to linear behaviour ($1/n$ approximately 1) allowing K_{fa} to be represented by the distribution constant K_d . When normalised for organic carbon content, the distribution constant values for the four soils were 42.4 ± 19 (kurosol), 52.6 ± 28 (sodosol), 59.4 ± 39 (vertosol) and 72.1 ± 19 (ferrosol).

Metribuzin desorption varied according to soil type, with values for the Freundlich constant of 1.8 ± 1 (kurosol), 3.1 ± 1 (sodosol), 4.2 ± 1.2 (vertosol) and 6.5 ± 1.2 (ferrosol). Desorption showed considerable hysteresis (Graph 2) which was again most pronounced in the ferrosol and vertosol soils.

Regression of Freundlich coefficient against soil properties yielded a significant positive correlation with soil organic carbon content ($r = 0.95$, $P < 0.05$). Again, a significant positive correlation was also found between the Freundlich desorption coefficient and soil clay content.

Pendimethalin

The sorption of pendimethalin varied according to soil type, increasing in the order kurosol, sodosol, vertosol, ferrosol. In all cases, the sorption isotherms (Graph 3) exhibited close to linear behaviour ($1/n$ approximately 1) allowing K_{fa} to be represented by the distribution constant K_d . When normalised for organic carbon content, the distribution constant values for the four soils were 10503 ± 58 (kurosol), 9183 ± 47 (sodosol), 7876 ± 36 (vertosol) and 5216 ± 21 (ferrosol).

1. Adsorption and Desorption Reactions (Cont.)

Very little desorption of pendimethalin was noted in the experiment. The shape of the desorption curves (Graph 3) indicates that the fraction of pendimethalin desorbed was both very small and relatively constant with successive desorption steps. The low desorption values resulted in large residual amounts of pendimethalin in each soil after 4 desorption (washing) steps, with 92% (kurosol), 94% (sodosol), 93% (ferrosol) and 94% (vertosol) of initial amounts recovered after 4 washes.

Regression of Freundlich coefficient against soil properties yielded a significant positive correlation with soil organic carbon content ($r = 0.97$, $P < 0.05$). No significant correlations were found between the Freundlich desorption coefficient and soil properties.

2. Sorption Reactions of Soil Fractions

Introduction

Clomazone and pendimethalin sorption kinetics were examined on the separated fractions of four Tasmanian soils. In all soils, the K_d of clomazone and pendimethalin sorption increased in the order of sand < silt < clay < particulate organic matter. The kinetics of sorption increased in the order of, slowest to fastest, clay < silt < sand < particulate organic matter. The degree of sorption of both herbicides increased with increasing humification of organic matter associated with soil fractions. Pendimethalin exhibited greater sorption and faster kinetics on all soil fractions compared with clomazone, which may explain accumulation of pendimethalin soil residues.

Materials and Methods

Soils

The kinetics of clomazone and pendimethalin sorption were studied in soil fractions of four soils; clay loam ferrosol with > 5% free iron oxides (ferrosol), acidic silty loam (sodosol), smectitic black cracking clay (vertosol), and a hydrophobic loamy sand with large amounts of particulate organic matter (kurosol). All soils were classified according to the Australian soil classification system (Isbell, 1996).

Soils were fractionated into sand (>20 μm), silt (2-20 μm) and clay (2 μm) by sedimentation according to the method of Kunze and Dixon (1986). No chemical agents were used, disruption of aggregates being achieved by mechanical agitation and sonification. Particulate organic matter (POM) was separated using an aqueous solution of sodium polytungstate ($\text{Na}_6(\text{H}_2\text{W}_{12}\text{O}_{40})\cdot\text{H}_2\text{O}$) of density 1.6 Mg m^{-3} (Golchin *et al.*, 1994). Clay-fraction separation of whole clay (<2 μm) and fine clay (<0.02 μm) fractions was achieved by sedimentation and centrifugation (Laird *et al.*, 1991). A sample of the clay fractions extracted from the ferrosol and vertosol was also treated with 30% H_2O_2 for removal of organic matter (Kunze and Dixon, 1986). This oxidised ferrosol sample was also treated with sodium dithionite and sodium citrate in a system buffered with sodium bicarbonate (DCB treatment) for removal of free Fe compounds (Kunze and Dixon, 1986).

The chemistry of the clay fractions was investigated by X-ray diffraction (XRD), selected fractions also being examined by scanning electron microscopy (SEM). Total carbon was determined by dry combustion in a LECO furnace, and total N by Kjeldahl digestion.

Sorption kinetics of herbicides onto the soils

The kinetics of clomazone and pendimethalin adsorption by the soil fractions were determined using the batch equilibration method. Each soil fraction (1.0 g or 0.5 g for POM, in triplicate) was equilibrated with 0.01M CaCl_2 (5 mL) containing clomazone (1 mg/L) or pendimethalin (0.4 mg/L). Incubation times were 0.5, 1, 2, 4, 8 and 24 hours, after which samples were centrifuged for 5 min at 10,000 rpm, filtered to 0.45 μm and extracted with dichloromethane.

2. Sorption Reactions of Soil Fractions (Cont.)

Chemicals and analysis

Analytical grade (99.1%) clomazone and pendimethalin were obtained from the Australian Standards Laboratory. All quantification was performed using a Varian Saturn GC-MS/MS operated at 28°C. Samples (2 µL) were injected into the column at 40°C using a carrier gas of helium at a flow rate of 2 mL min⁻¹. This column temperature was maintained for 1 minute, increased to 190°C at 30°C min⁻¹, and finally increased at 10°C min⁻¹ to 280° C and held there for 6 minutes.

The key chemical components of each soil fraction are presented in Table 1. The organic matter associated with each soil fraction was qualitatively assessed according to palynological classification (Tyson,1995) to determine the most dominant type of organic matter present.

2. Sorption Reactions of Soil Fractions (Cont.)

Results

Table 1 - Characteristics of soil fractions and organic matter.

Soil fraction	Mass (%) ^a	Total carbon (%)	C:N ratio	Organic matter type ^b	Clay matrix ^c
Kurosol	100	2.1	21	PH/AOM/CH	SM/IL
POM	1.2	27	29	PH/CH	-
Sand	90	1.35	22	AOM	-
Silt & clay	9	9.29	13	CM	
Sand-OM	-	-	-	-	-
Sodosol	100	2.4	19	AOM/PH/CM	Kaolin
POM	1	28	25	PH	-
Sand	85		23	AOM	-
Silt & clay	12		15	CM/AOM	Kaolin
Silt & clay-OM ^d	-	-	-	-	
Ferrosol	100	5.3	12	CM/PH/OAM	Kaolin
POM	2.1	25	24	PH	-
Sand & silt	12	6.28	21	OAM	-
Clay	82	5.22	10	CM	Kaolin
Clay-OM&Fe ^e	-	-	-	-	-
Vertosol	100	3.4	14	CM/OAM/PH	Smectite
POM	0.8	26	29	PH/CH	-
Sand & silt	46	1.72	34	OAM	-
Clay	33	4.33	10	CM	Smectite
Fine clay	18	1.84	7	CM	SM/IL
Fine clay -OM	-	-	-	-	SM/IL

^a Percentage of the total soil mass.

^b Dominant organic matter present in order of content in each fraction; PH - phytoclast material, AOM - amorphous organic matter, CH - charcoal, CM - clay/humic association (Tyson, 1995).

^c Clay mineralogy as determined by XRD; a single entry represents greater than 90% of a dominant mineral present, SM/IL indicates mixed smectite/illmenite.

^d Treated with H₂O₂ to remove organic matter.

^e Treated with H₂O₂ to remove organic matter and DCB to remove free iron compounds.

2. Sorption Reactions of Soil Fractions (Cont.)

Table 2 - Sorption of clomazone and pendimethalin by the soil fractions.

Soil fraction	% soil mass ^a	Clomazone Kd (ml g ⁻¹)	% contribution to soil Kd ^b	Pendimethalin Kd (ml g ⁻¹)	% contribution to soil Kd ^c
Kurosol	100	1.8	-	157	-
POM	1.2	7.6	5	1806	14
Sand	90	1.5	85	111	79
Silt & clay	9	3.5	10	202	8
Sand-OM	-	0.1	-	26	-
Sodosol	100	1.7	-	170	-
POM	1	6.6	5	1962	13
Sand	85	1.2	68	115	63
Silt & clay	12	2.7	27	247	24
Silt & clay-OM ^d	-	0.8	-	88	-
Ferrosol	100	3.6	-	194	-
POM	2.1	7.2	5	1693	19
Sand & silt	12	3.7	55	108	28
Clay	82	2.5	46	176	53
Clay-OM&Fe ^e	-	1.2	-	112	-
Vertosol	100	2.4	-	191	-
POM	0.8	13	6	1994	11
Sand & silt	46	1.1	21	80	17
Clay	33	2.6	51	218	48
Fine clay	18	2.1	22	203	24
Fine clay -OM	-	1.8	-	164	-

^a Percentage of the total soil mass.

^b Percentage contribution of soil fraction to whole soil clomazone sorption.

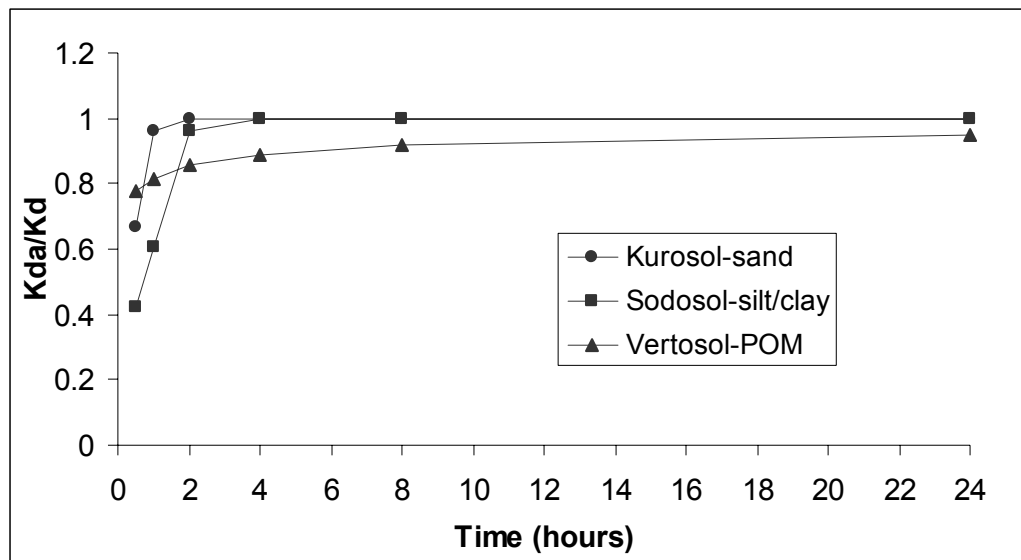
^c Percentage contribution of soil fraction to whole soil pendimethalin sorption.

^d Treated with H₂O₂ to remove organic matter.

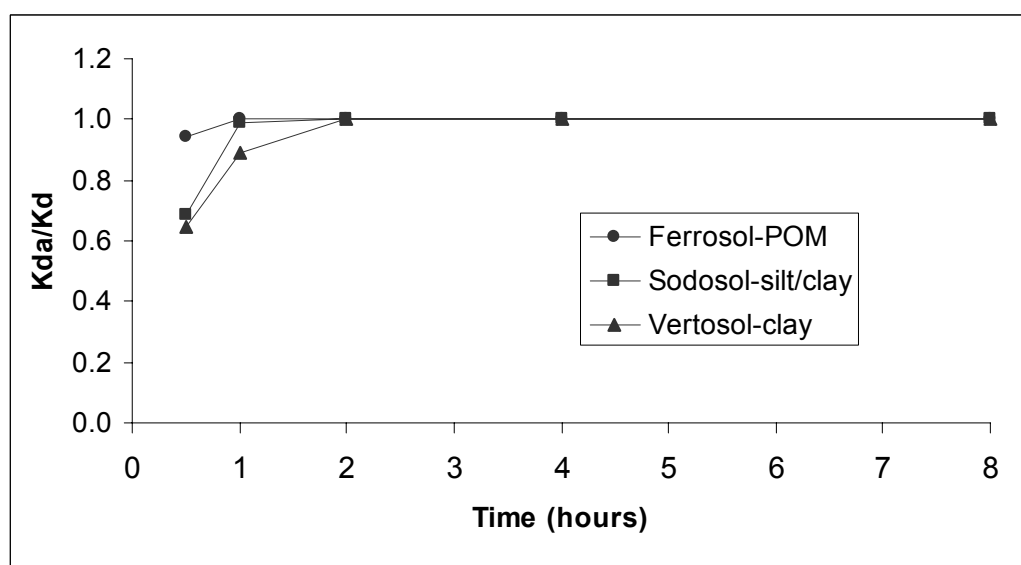
^e Treated with H₂O₂ to remove organic matter and DCB to remove free iron compounds.

2. Sorption Reactions of Soil Fractions (Cont.)

Graph 4 - The apparent sorption coefficient of clomazone normalized by equilibrium sorption coefficient (K_{da}/K_d) versus time.



Graph 5 - The apparent sorption coefficient of pendimethalin normalized by equilibrium sorption coefficient (K_{da}/K_d) versus time.



3. Dissipation of herbicides under field conditions

Introduction

The field dissipation of the three herbicides, clomazone, metribuzin and pendimethalin was studied over a period of one year in four soils under field conditions. The aim of this experiment was to describe the dissipation behaviour of the chemicals under local conditions and document the associated half-life values. To date, published information addressing the dissipation behaviour of residual herbicides in Australia is extremely limited, and does not include the products examined in this project. Thus, there remains a crucial deficit in the knowledge required to precisely manage the application of residual herbicides in local cropping systems.

Rationale

Herbicide field dissipation is often examined to gauge the behaviour of a herbicidal products in a given environmental and soil system. The description of behaviour is usually in terms of total extractable concentrations over time, and may also feature some measurement of bioavailable herbicide. The measurement of bioavailable herbicide may be made by utilising bioassays (Mills et al., 1989) or by measuring soil solution concentrations (Garcia-Valcarcel and Tadeo, 1999). In the current experiment, both total solvent extractable, and soil solution concentrations over time were measured, allowing an estimate of herbicide desorption and bioavailability.

Raw data describing dissipation is also commonly fitted to half-life models, which may describe dissipation in terms of zero order, first order, mixed order, and exponential functions (Hamaker et al. 1968; Hamaker 1972; Zhimdahl et al. 1994). The first order model is by far the most commonly used model in describing herbicide dissipation in soils (Alexander and Scow 1989), and as such allows wide comparison of generated half-lives with published data sets. The models commonly used to fit data are in essence empirical (Hamaker, 1972), and as such are open to wide interpretation. In particular, the widely used first order model describes the dissipation of herbicide residues adequately in some, but not all cases. As a result, alternative models for dissipation have shown better fit to data sets (Hance and McKone, 1971; LaFleur, 1980; Reyes and Zimdahl, 1988), including the hoerl equation (Zimdahl et al., 1994). The current data set is, therefore, described by the first order model for comparison with published data, and the hoerl equation, in an effort to produce more accurate determinations of field half-life.

Objectives

The objectives of field dissipation trials were to:

- Relate field dissipation behaviour to soil and environmental factors;
- Validate the apparent relationship between sorption reactions, bioavailability and dissipation in the soils examined;
- Generate practical half-life and apparent bioavailability information for cropping systems in the Tasmanian environment.

3. Dissipation of herbicides under field conditions (Cont.)

Materials and Methods

Treatments

No.	Product	Active Ingredient (g/ha)
1	Command	clomazone 960
2	Sencor	metribuzin 480
3	Stomp	pendimethalin 1300

Trial Details

SITE NO.	1	2	3	4
Year	1998/99			
Location	Forthside 41° 12'19" S 146° 15' 47" E 130 m asl	Cressy 41° 43'26" S 147° 04'48" E 150 m asl	Cambridge 42° 50' 20" S 147° 29' 57" E 4 m asl	Cambridge 42° 50' 20" S 147° 29' 57" E 4 m asl
Soil Type	Ferrosol	Sodosol	Vertosol	Kurosol
Crop	Nil			
Trial Design	Randomised Complete Block			
Replicates	3			
Plot Size	5 m x 2 m			

All locations were in a stubble fallow from the previous season, and six weeks prior to herbicide application were sprayed with a 2 L/ha⁻¹ application of glyphosate (Roundup® 450 g/L⁻¹) and cultivated to a depth of 12.5 cm using a conventional rotary hoe. All field experiments were conducted on areas with no prior clomazone, metribuzin or pendimethalin application.

3. Dissipation of herbicides under field conditions (Cont.)

Application Details

APPLICATION EQUIPMENT	
Equipment	CO ₂ pressurised plot sprayer fitted with a 2 m boom
Jets	Spraying Systems 8002 fan nozzles
Volume	250 L/ha
Pressure	275 kPa
TREATMENT APPLICATIONS	
Date	11/10/98
Treatments Applied	All

3. Dissipation of herbicides under field conditions (Cont.)

Soil Sampling and Sample Analysis

Prior to herbicide application, all plots were sampled for background residues by taking six random cores (5 cm inner diameter and 10 cm deep) from each plot. Six soil cores were taken from each plot at 0, 1, 3, 5, 7, 14, 28, 42, 56, 70, 84, 112, 140 and 365 days after treatment. All samples were stored for later analysis in sealed polythene bags, frozen at -18°C . Prior to extraction, all samples were thawed for 3 hours at 10°C , thoroughly mixed, passed through a 2 mm sieve and sub sampled. Soil moisture content of all samples was determined at each sampling date.

A 10 g soil sub-sample from each treatment was weighed and placed in a 50 mL teflon centrifuge tube with 10 mL of dichloromethane (DCM). The centrifuge tubes were then agitated on a rotary mixer for 6 hours at 20 rpm. Each sample was centrifuged for 15 minutes at 5000 rpm, the supernatant filtered and collected. A 2 mL aliquot was transferred to a 2 mL vial for quantification by gas chromatography, mass spectrometry/spectrometry (GC,MS/MS).

Statistical Analysis

Data were fitted to the first order dissipation model expressed as:

$$C = C_0 E^{-kt} \quad [1]$$

Where C is the concentration at time t , C_0 is initial concentration, and K is the rate constant.

The half-life (DT50) of degradation was calculated using the generated rate constants from the equation:

$$\text{DT50} = \ln 2/k = 0.693/k \quad [2]$$

Where DT50 is the herbicide half-life in days, \ln is the natural logarithm, and k is the first-order dissipation rate constant.

The Hoerl equation (Hoerl 1954) was also chosen as it has been used successfully to describe the dissipation of metribuzin and pendimethalin in soils (Zimdahl et al 1994). It is given as:

$$C = a e^{bt} t^c \quad [3]$$

Where C is concentration at time t , a , b and c are determined constants from plots of log transformed data. Deviation from exponential behaviour is measured by c , whereas a and b are interpreted as they are in any exponential equation. The Hoerl and first order equations were evaluated for goodness of fit by calculating the Root Mean Squared Error (RMSE) associated with the residuals of predicted versus observed values. A lower RMSE implies better fit. All statistical analyses were performed using SAS statistical software Version 8.

3. Dissipation of herbicides under field conditions (Cont.)

Table 3 - Summary of rainfall and temperatures occurring in October of 1998 through October of 1999 at Site 1 (ferrosol), Site 2 (sodosol) and Sites 3 & 4 (kurosol and vertosol)

Month	Mean monthly temperature			Monthly precipitation		
	Site 1	Site 2	Sites 3 & 4	Site 1	Site 2	Sites 3 & 4
	C			mm		
October ^a	11	11	12	107	49	51
November	13	13	14	105	48	72
December	14	15	16	62	19	14
January	16	16	17	33	107	69
February	16	17	17	112	47	91
March	15	15	16	55	48	45
April	13	11	13	32	58	21
May	10	9	11	112	54	15
June	8	6	9	51	35	27
July	8	6	8	49	78	10
August	8	8	9	137	47	15
September	9	9	11	56	30	24
October	11	11	12	74	54	38
Total				985.2 (987) ^b	674 (635)	491 (509)

^a Herbicide application to all sites on 11/10/98. ^b Values in parentheses represent 30 year average annual rainfall for each site.

Environmental monitoring

Rainfall and temperature data for the 12 month study period may be found in Table 3. The relatively large amounts of rainfall received at Site 1 (ferrosol) in the first two months following herbicide application should be noted. Recorded site temperature data shows that mean average temperature variation between all sites was never greater than 2°C.

3. Dissipation of herbicides under field conditions (Cont.)

Results

Graph 6 - Clomazone field dissipation curves for the ferrosol (●), kurosol (▲), sodosol (□) and vertosol (×) soils over the study period.

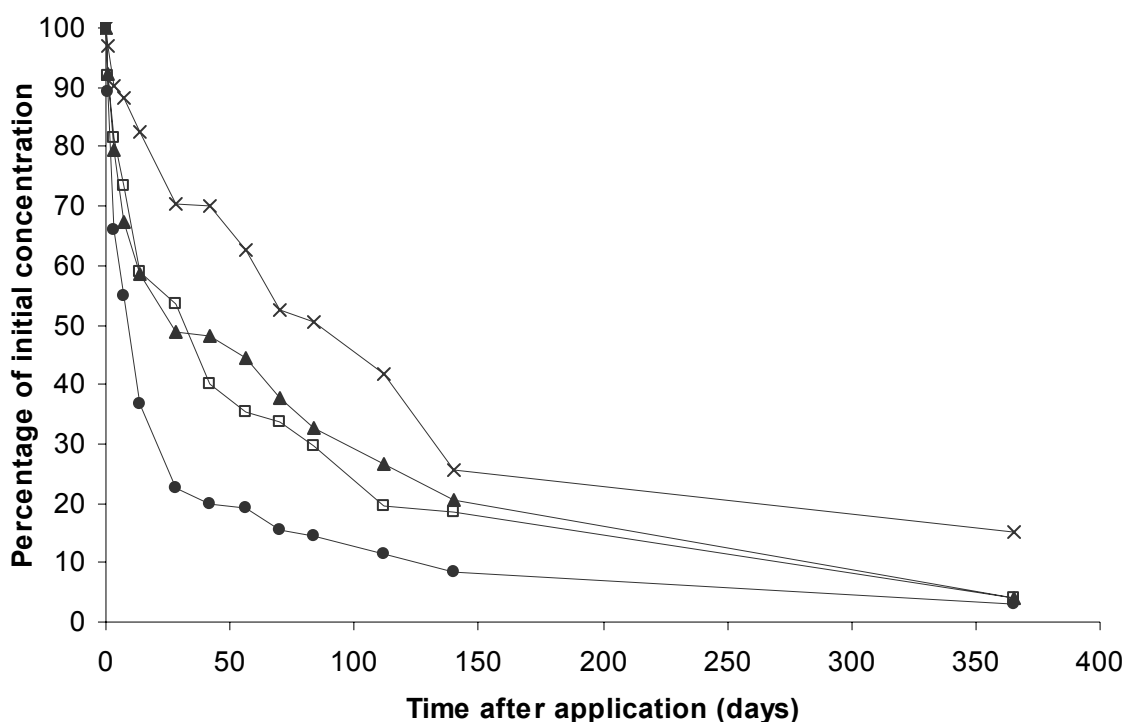


Table 4 - Soil physical and chemical properties, and clomazone half-life values for the four soils examined.

Soil Type ^a	pH	CEC	Organic Carbon	clay ^b	Rainfall	Half-life ^c
		meq/100 g	%	%	mm/yr	days
Ferrosol	6.3	17	4.3	53 K	985	79 (6)
Kurosol	5.6	4.1	3.4	5 S/I	491	82 (47)
Sodosol	4.9	6.1	2.5	15 K	674	83 (26)
Vertosol	7.2	43	2.1	61 S	491	124 (59)

^aSoil properties determined by standard methods (Rayment and Higginson,1992).

^bClay content, and dominant clay mineralogy; K - kaolin, S - smectite, S/I - mixed smectite/illmenite.

^c1st order half-lives, with Hoerl derived half-lives in parentheses.

3. Dissipation of herbicides under field conditions (Cont.)

Graph 7 - Metribuzin field dissipation curves for the ferrosol (●), kurosol (▲), sodosol (□) and vertosol (×) soils over the study period

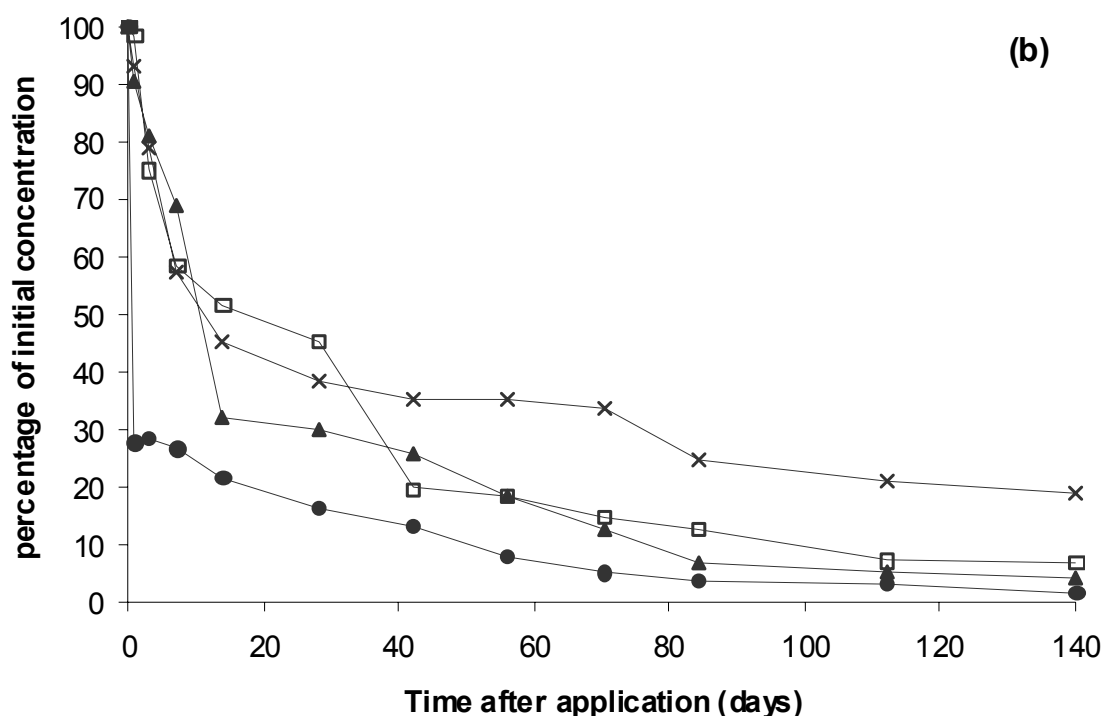


Table 5 - Soil physical and chemical properties, and metribuzin half-life values for the four soils examined.

Soil Type ^a	pH	CEC	Organic Carbon	clay ^b	Rainfall	Half-life ^c
		meq/100 g	%	%	mm/yr	days
Ferrosol	6.3	17	4.3	53 K	985	30 (11)
Kurosol	5.6	4.1	3.4	5 S/I	491	30 (6)
Sodosol	4.9	6.1	2.5	15 K	674	35 (8)
Vertosol	7.2	43	2.1	61 S	491	64 (11)

^aSoil properties determined by standard methods (Rayment and Higginson,1992).

^bClay content, and dominant clay mineralogy; K - kaolin, S - smectite, S/I - mixed smectite/illmenite.

^c 1st order half-lives, with Hoerl derived half-lives in parentheses.

3. Dissipation of herbicides under field conditions (Cont.)

Graph 8 - Pendimethalin field dissipation curves for the ferrosol (●), kurosol (▲), sodosol (□) and vertosol (×) soils over the study period.

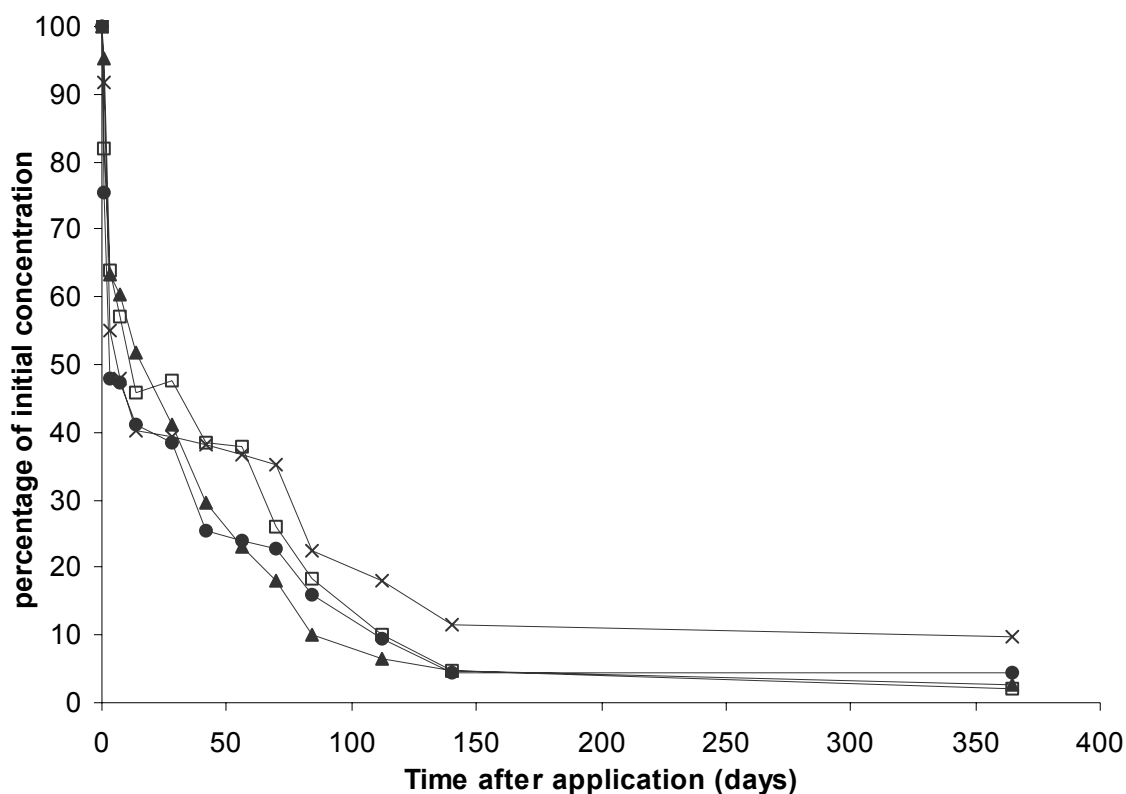


Table 6 - Soil physical and chemical properties, and pendimethalin half-life values for the four soils examined.

Soil Type ^a	pH	CEC	Organic Carbon	clay ^b	Rainfall	Half-life ^c
		meq/100 g	%	%	mm/yr	days
Ferrosol	6.3	17	4.3	53 K	985	83 (9)
Kurosol	5.6	4.1	3.4	5 S/I	491	76 (5)
Sodosol	4.9	6.1	2.5	15 K	674	64 (16)
Vertosol	7.2	43	2.1	61 S	491	117 (17)

^aSoil properties determined by standard methods (Rayment and Higginson,1992).

^bClay content, and dominant clay mineralogy; K - kaolin, S - smectite, S/I - mixed smectite/illmenite.

^c1st order half-lives, with Hoerl derived half-lives in parentheses.

3. Dissipation of herbicides under field conditions (Cont.)

Discussion

Herbicide dissipation

The observed dissipation behaviour showed significant variation according to chemical type, soil type and environmental conditions. Key differences in dissipation between soils and sites were exhibited for all three herbicides examined. To aid the identification of differences in dissipation kinetics, all data for dissipation is additionally expressed as a percentage of the concentration detected immediately after application.

Clomazone

Extractable clomazone concentrations in soils immediately following application were 0.77 ± 0.04 (ferrosol), 0.91 ± 0.03 (kurosol), 1.08 ± 0.03 (sodosol), and 0.92 ± 0.03 kg ai ha⁻¹ (vertosol). The observed variation in initial concentration may be a result of local differences in application across sites, or herbicide losses due to volatilisation or very rapid binding reactions with soil components. The concentration of clomazone in the ferrosol 14 days after application was only 0.28 ± 0.02 kg ai ha⁻¹ (37% \pm 2 % of that applied). In the kurosol and sodosol dissipation was slower, with 0.53 ± 0.03 kg ai ha⁻¹ (59% \pm 3% of applied) and 0.64 ± 0.01 kg ai ha⁻¹ (59% \pm 1% of applied) remaining after 14 days respectively. Dissipation was slowest in the vertosol, with 0.76 ± 0.03 kg ai ha⁻¹ (82% \pm 3% of that applied) remaining after 14 days.

The trend in dissipation continued with time, so that at the end of the 365 day study period, clomazone soil concentration was 0.04 ± 0.01 kg ai ha⁻¹ (4.1% \pm 1% of applied) in both the kurosol and sodosol, whilst after 365 days, clomazone concentration in the two clay soils were markedly different from each other, with 0.02 ± 0.01 kg ai ha⁻¹ (3.1% \pm 1% of applied) and 0.14 ± 0.01 kg ai ha⁻¹ (15% \pm 1% of applied) in the ferrosol and vertosol respectively (Graph 6).

Half-life values calculated from the dissipation curve data were lowest for the ferrosol and highest for the vertosol. No strong relationships between soil properties and half-life were evident (Table 4).

Metribuzin

Extractable metribuzin concentrations in soils immediately following application were 0.36 ± 0.02 (ferrosol), 0.15 ± 0.01 (kurosol), 0.11 ± 0.01 (sodosol), and 0.36 ± 0.01 kg ai ha⁻¹ (vertosol). The low initial concentration observed in the sodosol and kurosol is a result of error during the application procedure rather than analysis, as subsequent extractable soil and solution concentrations are consistent with a low effective application rate. The concentration of metribuzin in the ferrosol 7 days after application was only 0.10 ± 0.01 kg ai ha⁻¹ (27% \pm 3 % of that applied). In the kurosol and sodosol, dissipation was slower, with 0.10 ± 0.01 kg ai ha⁻¹ (69% \pm 6% of applied) and 0.06 ± 0.01 kg ai ha⁻¹ (58% \pm 5% of applied) remaining after 7 days respectively, whilst dissipation was also relatively slow in the vertosol, with 0.21 ± 0.02 kg ai ha⁻¹ (57% \pm 5% of that applied) remaining after 7 days. As was the case for clomazone dissipation, loss of metribuzin in the ferrosol was very rapid in the days following application. In particular, metribuzin dissipation in the first 7 days in the ferrosol is very rapid, and accounts for approximately 70% of applied metribuzin (Graph 7).

3. Dissipation of herbicides under field conditions (Cont.)

In all soils except the vertosol, residues were only detectable up to 140 days, at which time residual amounts were 0.013 ± 0.01 (ferrosol), 0.006 ± 0.002 (kurosol), 0.008 ± 0.003 (sodosol), and $0.07 \pm 0.01 \text{ kg ai ha}^{-1}$ (vertosol). Metribuzin was most preserved in the vertosol, with $0.06 \pm 0.01 \text{ kg ai ha}^{-1}$ ($17\% \pm 2\%$ of that applied) remaining after 365 days.

Metribuzin half-life values were much shorter than the clomazone values and again did not appear to be closely linked to any of the soil physical and chemical properties measured in the study (Table 5).

Pendimethalin

Extractable pendimethalin concentrations in soils immediately following application were 1.18 ± 0.06 (ferrosol), 1.76 ± 0.06 (kurosol), 0.93 ± 0.04 (sodosol), and $1.65 \pm 0.07 \text{ kg ai ha}^{-1}$ (vertosol). The observed variation in initial soil concentration is likely to be a result of error during the application procedure rather than analysis, as subsequent extractable soil and solution concentrations are consistent with a discrepancy in application rates. The most striking feature of the dissipation behaviour of pendimethalin is the apparent large loss of pendimethalin in the first 3 days after application in all soils (Graph 8). In particular, pendimethalin dissipation is most rapid in the ferrosol, with only $0.59 \pm 0.03 \text{ kg ai ha}^{-1}$ or $48 \pm 5 \%$ of applied pendimethalin remaining 3 days after application.

Within 7 days of application, less than 60 % of applied pendimethalin remained in all soils (Graph 8). Extractable pendimethalin concentrations, as a percentage of initial concentration 7 days after application, were $41 \pm 4 \%$ (ferrosol), $52 \pm 3 \%$ (kurosol), $46 \pm 3 \%$ (sodosol), and $40 \pm 3 \%$ (vertosol). The variation in soil type is such that after 84 days, pendimethalin soil concentrations, as a percentage of initial, were $16 \pm 2 \%$ (ferrosol), $10 \pm 1 \%$ (kurosol), $18 \pm 2 \%$ (sodosol), and $23 \pm 2 \%$ (vertosol).

A decline in the rate of pendimethalin loss with time resulted in detectable pendimethalin residues in all soils 365 days after application. Detectable residues of pendimethalin 365 days after application, expressed as a percentage of initial, were $4 \pm 1 \%$ (ferrosol), $3 \pm 1 \%$ (kurosol), $2 \pm 1 \%$ (sodosol), and $10 \pm 2 \%$ (vertosol).

Half-life values for pendimethalin in the four soils approached those of clomazone, with the longest half-life again recorded in the vertosol soil (Table 6).

Field half-lives were greatest for clomazone and least for metribuzin. The Hoerl equation provided a better fit to the measured field concentration at all four sites than a first order equation. The description of herbicide half-lives in soil has traditionally been dominated by the use of a first order equation due to the simplicity of the mathematics involved, and the assumption that, in a majority of cases, the model will correctly describe behaviour. In practice, the first order equation works adequately in describing residue loss in a number of situations, but not all.

Possible mechanisms influencing rates of dissipation of the herbicides include volatilisation, microbial degradation, leaching and irreversible binding/partitioning reactions. Soil water content also appears to be an important factor in the dissipation reactions. Further research examining leaching, volatilisation, microbial degradation, and soil/herbicide reactions at different moisture levels was identified as a priority from this study.

4. Herbicide movement and degradation processes

Introduction

Analysis of the rates of dissipation of clomazone, pendimethalin and metribuzin in field soils revealed that half-lives varied between soils and herbicides, and were higher in the lighter soils for all herbicides. It was observed during the field dissipation study that the initial loss of herbicide following application was greatest on the acid ferrosol soil (high clay content, high moisture content at application) and that the concentration of all herbicides in all soils generally decreased following rainfall events. The first observation was considered to be linked to either a rapid binding, biodegradation or partitioning of herbicide (making it unavailable for extraction) or loss through volatilisation. Vapour loss may be enhanced by higher temperatures and/or higher moisture content. The second observation suggested leaching of the herbicides following rainfall or increased biodegradation or binding/partitioning to non-extractable fractions with increased soil moisture. These two aspects were examined further in laboratory trials.

Objectives

The objectives of the herbicide movement and degradation trials were to:

- Examine the rate of leaching of clomazone in soils;
- Examine the rate of loss of clomazone from soils due to volatilisation, and determine if movement of clomazone in the vapour phase contributes to distribution in soils;
- Determine the effect of wetting and drying cycles on herbicide extractability from soils.

Background literature

Herbicide applied to soil is subject to a number of transport and phase transport reactions. An applied herbicide may be present in at least three phases in soil, depending upon its physical properties and on its sorption to soil surfaces. It may be dissolved in the aqueous phase, evolve as a vapour in soil pore space or adsorb to mineral and organic surfaces. It is common for herbicides to be found in more than one of these phases in a soil; therefore, it is necessary to describe the reactions of exchange between the phases to predict herbicide fate.

Herbicide present in the various soil phases may undergo transport reactions immediately following application including adsorption, plant absorption, volatilisation, leaching, microbial, and chemical degradation. The result of these processes in the 48 hours immediately following herbicide application can be the apparent loss of up to 50% of the applied herbicide. Rapid decreases in extractable pendimethalin and clomazone were recorded in the field dissipation study, highlighting the need for further understanding of these processes for improved management of herbicides in cropping soils.

Liquid phase transport: Liquid phase – unsaturated flow

Soil water flow is caused by a driving force resulting from an effective potential gradient, with water moving from areas of high potential to low potential through the processes of advection and dispersion. The rate of flow or flux is proportional to the potential gradient and is affected by the geometric properties of the pore channels through which flow takes place (Hillel, 1971). This general principle applies to soil water flow in both saturated and unsaturated conditions. Whilst the driving force of water flow in a saturated soil is a positive pressure and gravitational potential, water in an unsaturated soil is driven by matric suction potential. The matric suction potential is due to the physical affinity of the water to the soil-particle surfaces and capillary pores (Hillel, 1971).

4. Herbicide movement and degradation processes (Cont.)

It is this affinity of water for the surface of soil particles and fine pore walls that allows the movement of water despite greatly reduced hydraulic conductivity in an unsaturated soil. Water in an unsaturated soil often exists as discrete pockets in small pore spaces, with many larger pores filled with air and, therefore, unable to contribute to the hydraulic conductivity of the soil. Thus, water in an unsaturated soil is held in a more intimate contact with many of the surfaces in the fine pore space, and hence any solute present is also afforded greater access to pore wall surfaces. It is for this reason in particular that the behaviour of soil water under unsaturated conditions is critical for the phase transport reactions of herbicides.

Obviously, in such a heterogenous media as soil, variations in soil pore geometry, particle distribution, and particle surface dynamics will have important consequences for water flow. In simplistic terms, coarse textured soils (sandy and gravelly soils) have large available pore spaces for the conduction of water, whilst in fine textured soils (clays and silt) the pore space is dominated by small micropores. Therefore, it follows that under saturated conditions, a sandy soil will conduct water far more rapidly than a clay soil. However, this may not be the case under unsaturated conditions, as the large and more conductive pores are the first to empty, becoming non-conductive as suction develops, trapping water in small capillary wedges at the contact points of particles (Hillel, 1971). In a clay soil with many micropores, many of the pores may remain full and conductive even at high suction, so that the hydraulic conductivity of a clay soil may not decrease as rapidly as in a sandy soil. Thus, given that soil under field conditions is mostly in an unsaturated state, the actual dynamics of water flow are dependant upon the interaction of gravitational, dispersive, hydraulic and matric potentials.

Unsaturated flow is particularly relevant to herbicide movement in soils because the majority of processes involving soil water flow in a natural system occur whilst a soil is in an unsaturated state.

Liquid phase transport: Liquid phase - herbicide transport

Herbicides present as a solute in the soil solution are subject to the same forces as the soil solution and the additional forces of transfer to the solid and gas phases via adsorption and volatilisation. Herbicides present within the soil solution may move either by bulk flow (convection) of soil solution, or by diffusion within the solution phase (Jury and Ghodrati, 1989). In practical terms, given the totuosity of soil as a porus media, the variable flow velocities of water in such a complex system is represented as hydrodynamic dispersion (Day and Forsythe, 1957). Therefore, the sum of convection, diffusion, and dispersion is termed the convective-dispersive flux of a dissolved solute (Jury and Ghodrati, 1989).

In a simple homogenous porous media, dissolved solutes are assumed to flow through the entire wetted pore space (Biggar and Nielsen, 1967). However, given that soil is a heterogenous porous media, solute transport in soils has been described by models in which the water phase is regarded as partly mobile and partly stagnant (Van Genuchten and Wierenga, 1976). Therefore, in soil, solutes move by convection and dispersion in the mobile phase, and move into and out of the stagnant regions by a rate limited diffusion process (Jury and Ghodrati, 1989). Given the range of forces responsible for herbicide liquid phase transport, soil and chemical factors have a large influence upon the dynamics of herbicide transport in the liquid phase.

4. Herbicide movement and degradation processes (Cont.)

Critical to any herbicide transport in the liquid phase is the interaction between the dissolved and the adsorbed phases. Interaction with the solid phase has obvious consequences for the movement of herbicide in the liquid phase, due to possible reduction in liquid phase concentration. In turn, adsorption in many soils may be limited by the rate of diffusion from the solution to stationary adsorption sites, particularly at high water flow rates (Jury and Ghodrati, 1989). Thus, the exchange of herbicide between the dissolved phase and the adsorbed phase under conditions of water flux is a special case.

The behaviour of a given solute under conditions of water flux is also largely determined by the chemical properties of the compound. In particular, molecular polarity and water solubility are critical in determining the transport behaviour of a chemical in the liquid phase. Polar compounds with high solubility in water (eg. clomazone 1100 mg/L) have a greater potential for transport in the liquid phase than non-polar sparingly soluble compounds (eg. pendimethalin 360 ug/L). Further, given the greater affinity of non-polar compounds for organic adsorption sites (Hamaker, 1972; Weber et al, 1993), non-polar compounds are also more likely to partition to the solid phase and not be subject to solute transport processes in the liquid phase. This case holds true for pendimethalin, which shows a strong affinity for soil organic surfaces, and a low potential for leaching movement (Cooper et al, 1994; Zheng et al, 1993). Clomazone, however, is a polar compound with a moderate water solubility (100 mg/L), and therefore must be considered to have some potential for leaching movement in soils.

Vapour phase transport: Phase transfer and equilibrium

Herbicides can diffuse through soils in both the liquid and vapour phases. The actual diffusion of herbicide in a soil is a complex function of the different pathways available for diffusion through a soil: vapour phase, air/water interface, water phase, and water solid interphase (Spencer, 1970). Herbicide applied to a soil will reach equilibrium via any number of simultaneous equilibration reactions in each of the three main phases: solid, liquid and gaseous. Equilibrium is usually achieved at considerably different concentrations in each of the phases (Glotfelty and Schomburg, 1989), according to intrinsic herbicide and soil properties. The partitioning between phases is expressed by relating the chemical potential in each phase, according to the concept of fugacity (Mackay 1979). Fugacity is often called the escaping tendency of a pesticide from a phase, and it describes the potential of a chemical to move from one phase to another by mass diffusion.

Gas phase diffusion is approximately 10^4 times greater than liquid phase diffusion, but because of the small fugacity of the air phase in soil, only a small fraction of pesticide exists in the soil gas phase (Glotfelty and Schomburg, 1989). In addition, the intrinsic vapour pressure or fugacity of a herbicide in the soil gas phase is modified by interaction with the soil solid and liquid phases. The interaction of non-ionic herbicides with soils is primarily with soil organic matter (Hamaker, 1972, Chiou et al, 1989), and as soil organic matter content increases, the vapour pressure of the herbicide in the soil gas phase goes down (Glotfelty and Schomburg, 1989). In the pure liquid or solid state, increasing temperature causes an increase in herbicide vapour pressure and solubility; thus, when a herbicide is present in a moist soil, desorption of herbicide into solution and the vapour pressure increase. However, when soil moisture falls below a value that is at equilibrium with air at 90% relative humidity, mineral surfaces with high adsorptive capacities are exposed (Glotfelty and Schomburg; 1989). The adsorption capacity of dry soil for organic vapours is at least two orders of magnitude greater than moist soil (Chiou and Shoup, 1985), with values of up to 5000 times greater reported for some herbicides (Spencer and Cliath, 1974).

4. Herbicide movement and degradation processes (Cont.)

Therefore, it is often concluded that the effect of soil moisture upon pesticide volatilisation far outweighs the influence of soil organic matter content and temperature (Glottfelty et al, 1984, Harper et al, 1976).

Vapour phase transport: Herbicide volatilisation

Loss of herbicide on the soil surface via volatilisation is driven by either diffusion or convective flow in a soil, depending upon complex interactions between the chemical and the soil matrix. Intrinsic soil properties such as organic matter content and bulk density have a large bearing upon mass transfer processes in the gas phase. It has been established that soil organic matter reduces herbicide vapour pressure in the soil gas phase (Glottfelty and Schomburg, 1989), thereby reducing the contribution of convective flow to volatilisation (Jury et al, 1980). Soil bulk density is inversely related to diffusive flux in a soil (Jury et al, 1980), so that as soil bulk density increases (and porosity decreases) the contribution of diffusive flow to volatilisation decreases. In addition, chemical properties such as high water solubility can enhance volatilisation loss by increasing co-distillation during water evaporation from the soil surface.

Experimental rationale

Herbicide transport under unsaturated conditions

The leaching behaviour of herbicides in an unsaturated soil system was measured using the Bodman-Colman apparatus. The key features of the apparatus are that the soil is never allowed to reach saturation point, such that downward moving soil water is effectively in constant contact with the soil. This allows for a range of soil – herbicide – water reactions to take place whilst the herbicide solution moves through the system.

Herbicide vapour movement in soil columns

The aim of this experiment was to give a brief assessment of the potential movement of clomazone as a vapour within a soil system. Clomazone has a vapour pressure of 1.44×10^{-4} mm Hg at 25°C and, as such, has shown potential for volatilisation in the field (Curran et al, 1992) and laboratory (Mervosh et al, 1995) studies. Soil columns were set up with the dual purpose of assessing the amount of clomazone movement as vapour and to estimate distances of vapour movement within a soil.

Assessment of short-term volatilisation and microbial loss

The aim of this experiment was to assess individually the possible contribution of volatilisation and microbial degradation to the loss of applied clomazone over a 48-hour period. It was a key finding of field dissipation studies that clomazone dissipation appeared to proceed at an accelerated rate in the days immediately after application. There are a number of possible causes of the observed phenomenon. As mentioned previously, leaching and vapour movement have been singled out and examined. In particular, dissipation in the ferrosol soil proceeded at a rapid rate in the days immediately after clomazone application. Given the high organic matter levels in the ferrosol, high porosity and elevated moisture status, microbial loss is a distinct possibility. In addition, the mediation of sorption reactions, and in turn, volatilisation by soil moisture has the potential to be a key fate controlling parameter.

4. Herbicide movement and degradation processes (Cont.)

Microbial degradation of clomazone and pendimethalin

The presence of microbial populations with the metabolic capability to degrade an applied herbicide is a critical factor in determining dissipation rate. Whilst overall degradation rates in a soil system are closely related to environmental factors such as temperature, soil moisture and carbon sources, the ability of microbes to degrade a product as a sole C source in pure culture is an intrinsic metabolic trait. Thus the identification of isolates in a soil capable of degrading a herbicide as a sole C source is confirmation of apparent observed whole soil scale microbial degradation.

4. Herbicide movement and degradation processes (Cont.)

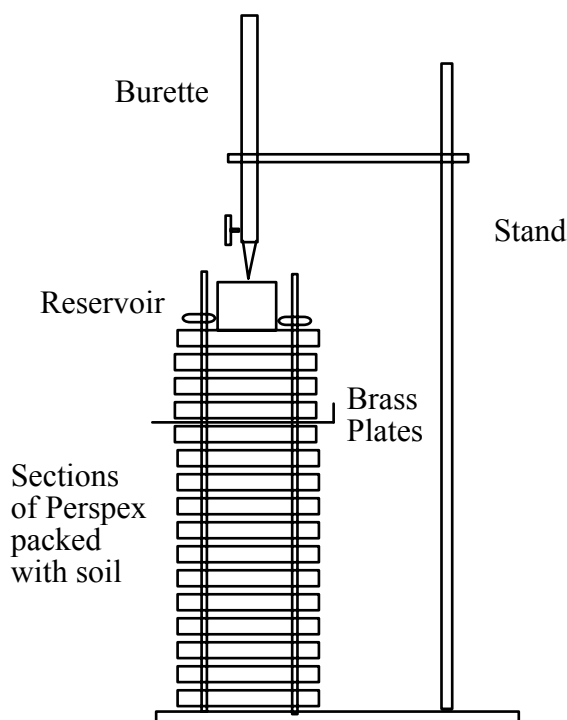
Materials and Methods

Herbicide transport under unsaturated conditions

The leaching behaviour of herbicides in an unsaturated soil system was measured using the Bodman-Colman (Bodman and Colman, 1943) apparatus (Figure 1). The column was assembled by packing with air-dry soil. One half of the columns were then brought to field capacity with the addition of distilled water prior to herbicide application. Herbicide was added by dropping 1 mL of 100 mg/L solution of clomazone in methanol to give an effective concentration on an area basis of 1 L/ha of active ingredient (100 µg per column). Following application, the methanol was allowed to evaporate to dryness and a control sample was taken from selected columns for analysis. All columns were then allowed to equilibrate for 24 hours, with field capacity columns wrapped in plastic film to maintain constant moisture. Following the equilibration period, all columns had 50 mL of distilled water added to encourage downward water flow through the columns. The addition of water was carefully monitored to ensure that no saturated flow occurred. At the completion of water addition, the columns were destructively sampled at the three depths of 0-2 cm, 5-6 cm, and 10-11 cm. Herbicide extraction was achieved from a 10 gram soil sample shaken in 10 mL of DCM for 4 hours. Appropriate soil moisture corrections were made prior to reporting of results.

Figure 1 - Bodman and Colman Apparatus

BODMAN AND COLMAN APPARATUS



4. Herbicide movement and degradation processes (Cont.)

Herbicide vapour movement in soil columns

A Bodman-Colman apparatus was utilised to assess clomazone vapour movement within a soil column. The column was constructed to half of its complete height. At this height, a steel divider was placed below a 2 cm soil slice to be spiked with clomazone. The marked soil slice was spiked with 1 mL of 100 mg/L (100 µg) clomazone in a methanol solution. Following application, a steel divider was placed above the spiked slice and sections and soil were added until the column was complete. The steel dividers were then removed from the column and the soil was allowed to equilibrate for 24 hrs. At the completion of the equilibration period, soil sections at distances of 1-2 cm and 5-6 cm were sampled to determine herbicide concentration. The experiment was completed in triplicate.

Assessment of short term volatilisation and microbial loss

Two soil materials were used for this experiment, the ferrosol, as previously studied, and a bleached quartz sand (63-250 µm). The quartz sand was used to provide a relatively unreactive matrix for the herbicide so as to assess the role of adsorption upon volatilisation and recovery of applied herbicide. For all determinations, 15 grams of soil was placed in an autoclaved stainless steel dish. The autoclaved treatments were autoclaved for 2 hours and allowed to rest prior to herbicide application. The autoclave treatment was applied to eliminate microorganisms from the soil samples and hence allow determination of rates of microbial degradation through comparisons with non-autoclaved samples. Selected replicates were moistened to field capacity by the addition of a pre-determined volume of distilled water. Each replication was spiked with 1 mL of 100 mg/L (100 µg) clomazone in a methanol solution. One set of replicates was extracted immediately as a control to determine the starting concentration, whilst all other treatments were allowed to equilibrate for 48 hours and were then sampled for solvent extraction. Herbicide extraction was achieved from a 10 g soil sample shaken in 10 mL of DCM for 4 hours. Appropriate soil moisture corrections were made prior to reporting of results.

Microbial degradation of clomazone and pendimethalin

The enrichment culture technique adapted from Kulshrestha et al, 2000 was used to isolate microorganisms capable of degrading clomazone and pendimethalin. 1 g of air dried < 0.5 mm sieved soil (ferrosol, vertosol, kurosol and sodosol) with no previous herbicide exposure was placed in a 125 mL Erlenmyer flask. To each of these was added 50 mL Basal Mineral Salts medium [KNO₃, K₂HPO₄ 75 g/L, MgSO₄·7H₂O 15 g/L, CaCl₂ 2 g/L, FeCl₃ 1.5 g/L, pH 7.0 ± 0.2 at 25°C] (Mullings and Parish, 1984) containing 50 mg/L clomazone or 6 mg/L pendimethalin. A replicate containing 0.5% urea as a nitrogen source was also prepared, and all enrichments were incubated at 25 (±1) °C for 10 days. Following incubation, a 0.5 mL aliquot of liquid broth from each enrichment was taken and transferred to a second enrichment containing the same medium without soil and incubated at 25 (±1) °C for an additional 10 days.

At this second enrichment step, 0.1 mL aliquots of serial dilutions in sterile distilled water were spread onto Basal Mineral Salts (BMS) plates (15 g Davis agar in 1 L of Basal Mineral Salts medium) containing 50 mg/L clomazone or 6 mg/L pendimethalin respectively. Following incubation for 14 days at 25 (±1) °C representative colonies were isolated and purified by streaking onto BMS + agar + 50 mg/L clomazone or 6 mg/L pendimethalin. Isolates were identified based on gram stain and morphological characteristics.

4. Herbicide movement and degradation processes (Cont.)

Each isolate was tested for its ability to degrade the respective herbicide from which it was enriched in pure culture. Cells grown on BMS + agar + 6 mg/L pendimethalin or 50 mg/L clomazone were then incubated at 25(±1) °C for 14 days suspended in 1 mL sterile distilled water. The suspension was then used to inoculate 20 mL BMS + 50 ppm clomazone or 6 ppm pendimethalin in 125 mL conical flasks and incubated at 25 (±1) °C. After 0, 48 hours and 7 days, 5 mL of medium was removed, and clomazone and pendimethalin were extracted with DCM and analysed by GCMS.

Effects of wetting and drying cycles

A preliminary study into the effects of wetting and drying cycles on clomazone availability in vertosol and kurosol soil was undertaken under laboratory conditions. Soil samples were spiked with 1 mL of 100 mg/L (100 µg) clomazone in a methanol solution. Three soil moisture treatments (air dry soil, field capacity soil, and repeated wetting and drying cycles) were used and clomazone concentration was measured six times over 75 hours.

4. Herbicide movement and degradation processes (Cont.)

Results and Discussion

Herbicide transport under unsaturated conditions

Leaching of clomazone was recorded in each of the soil columns, with greater movement occurring in the kurosol than the ferrosol soil. As presented in Table 7, all results represent clomazone concentration with depth in response to applied leaching water.

Table 7 - Clomazone (μg per given sample depth)

Initial addition of 100 μg of clomazone to the surface of each column.

Depth	Ferrosol AD ^a	Ferrosol FC ^b	Kurosol FC ^b
0-2 cm	74.97	71.68	56.11
2.1-5 cm	11.93	10.61	17.68
5.1-10 cm	7.85	3.6	10.14
10.1-15.5 cm	0.58	0.51	5.86

^aAD indicates air dry soil and ^bFC indicates soil at field capacity.

Key points

AD and FC ferrosol

Around 95% of the applied herbicide was recovered from destructive sampling of the AD column, and 90% from the FC column. This indicates that there is very little loss due to volatilisation or sorption reactions interfering with the extraction procedure. It is interesting to note that there is more movement of clomazone below 5 cm than in the FC column than in the AD column. This result appears counter to most of our current theories of leaching. The result may be explained by sorptive processes, as discussed below.

FC kurosol

Around 90% of the applied herbicide was recovered from this column. The key result appears to be the larger amount of clomazone leached below 5cm in the column. Over 30% of applied herbicide can be found below 2 cm, with around 15% below 5 cm. It is possible that some of the product was leached below the sampling depth and lost in the leachate, with vapour loss, microbial degradation and irreversible binding or partitioning being other possible pathways to explain the less than 100% recovery.

4. Herbicide movement and degradation processes (Cont.)

Herbicide vapour movement in soil columns

Clomazone movement in the vapour phase was observed in the air dry soil columns. The data is presented below, with the arrows indicating the direction of movement in the column, either upwards or downwards, from the application point.

Soil Distance	Clomazone (μg)
5-6 cm ↑	<1
1-2 cm ↑	9
0 cm	85
1-2 cm ↓	5
5-6 cm ↓	<1

As is indicated from the results, clomazone movement as vapour is a feasible transport mechanism within soils. The high porosity of the ferrosol soil used in the study provides an important physical dimension for vapour diffusion. It is worth noting that there appears to be some movement in both directions in the column. The higher concentration detected in the section 1-2 cm above the application point is likely to be due to slightly closer proximity to the applied herbicide (herbicide applied to the top of the 1 cm thick soil slice). Whilst the concentrations found in the soil at distance are small, their significance to the overall transport of clomazone within a soil should not be discounted.

Assessment of short-term volatilisation and microbial loss

Table 8 - Clomazone values for various soil treatments after 48hrs incubation at 25 °C and control (at application) from an application of approx. 100 μg of clomazone.

Soil and treatment	Clomazone (μg)
Sand AD ^a AC ^b control	109 ± 4
Sand AD AC	108 ± 8
Sand AD NT ^c	112 ± 4
Ferrosol AD AC control	112 ± 3
Ferrosol AD AC	88 ± 2
Ferrosol AD NT	91 ± 3
Ferrosol FC ^d AC control	108 ± 8
Ferrosol FC AC	92 ± 5
Ferrosol FC NT	93 ± 6

^aAD indicates air dry soil and ^dFC indicates soil at field capacity. AC^b Indicates soil autoclaved to restrict microbial activity, and ^cNT indicates no treatment.

4. Herbicide movement and degradation processes (Cont.)

Key points

Sand

There was no significant change in concentration over the 48-hour equilibration period, with complete recovery of applied herbicide from samples. This indicated no loss due to volatilisation, microbial activity or irreversible binding/partitioning reactions.

Air dry ferrosol

The air dry ferrosol exhibited a loss of approximately 10% of the clomazone applied regardless of sterilisation treatment. This indicates that microbial decay was not exerting a controlling influence upon short clomazone dissipation under conditions of low soil moisture. As volatile loss was unlikely to have occurred (no loss observed from sand), the reduced amounts of clomazone extracted from the soil after 48 hours suggest binding or partitioning of the herbicide to soil fractions from which it could not be extracted.

Field capacity ferrosol

The field capacity ferrosol exhibited a loss of approximately 10% of the clomazone applied regardless of sterilisation treatment. Again this indicates that microbial activity over the 48-hour period was not significant, but that binding or partitioning reactions could play a significant role in determining herbicide availability.

Microbial degradation of clomazone and pendimethalin

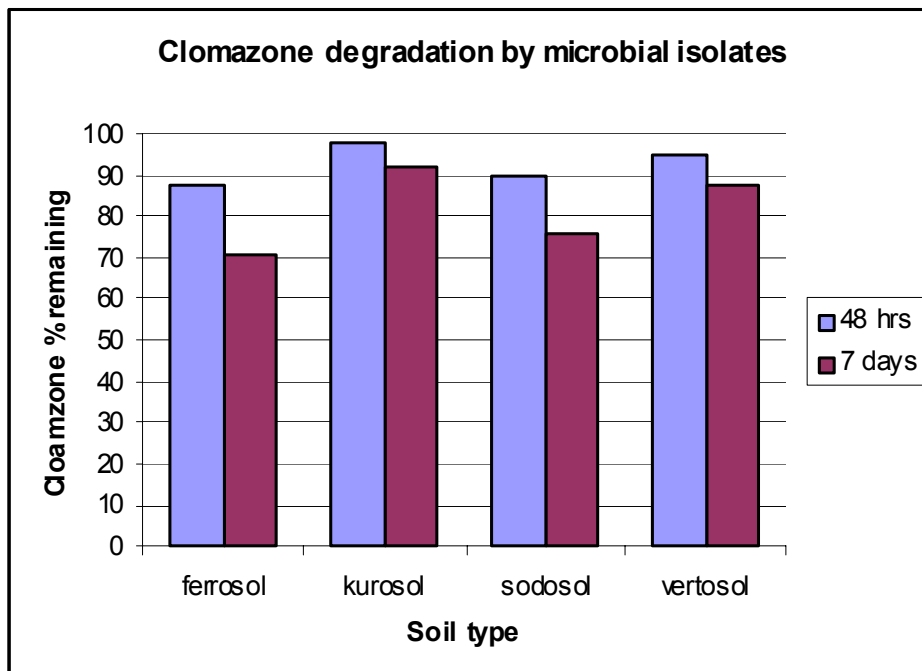
Microbial degradation of clomazone and pendimethalin was demonstrated for each of the soils used in the study (Graphs 9 & 10). While the rate of degradation in the field cannot be estimated from this work, the potential for microbial degradation has been proven.

Microbial isolates

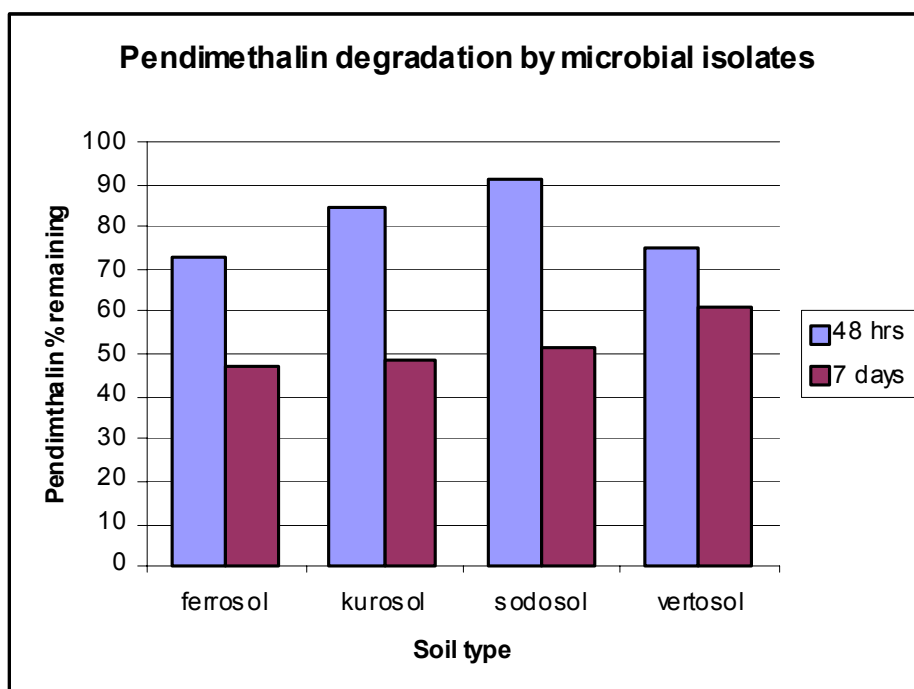
The dominant microorganism capable of degrading pendimethalin in pure culture was isolated and identified as *Pseudomonas* spp. for all soils examined. *Pseudomonas* spp. was also the dominant isolate identified as capable of degrading clomazone in the ferrosol and the sodosol, whilst in the kurosol and the vertosol *Coryniform* spp. was isolated and identified. In addition, the fungus of the *Fusarium* spp. was isolated separately from all samples.

4. Herbicide movement and degradation processes (Cont.)

Graph 9 - Clomazone degradation by microbial isolates



Graph 10 - Pendimethalin degradation by microbial isolates

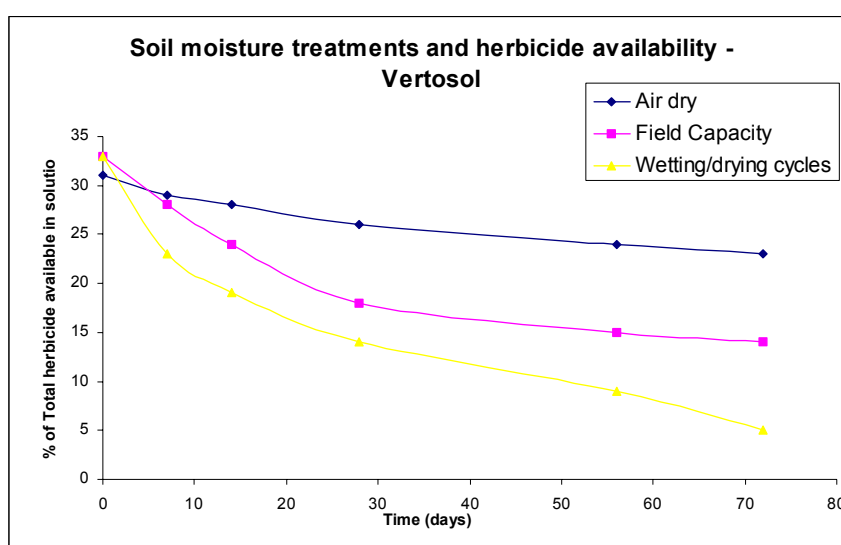


4. Herbicide movement and degradation processes (Cont.)

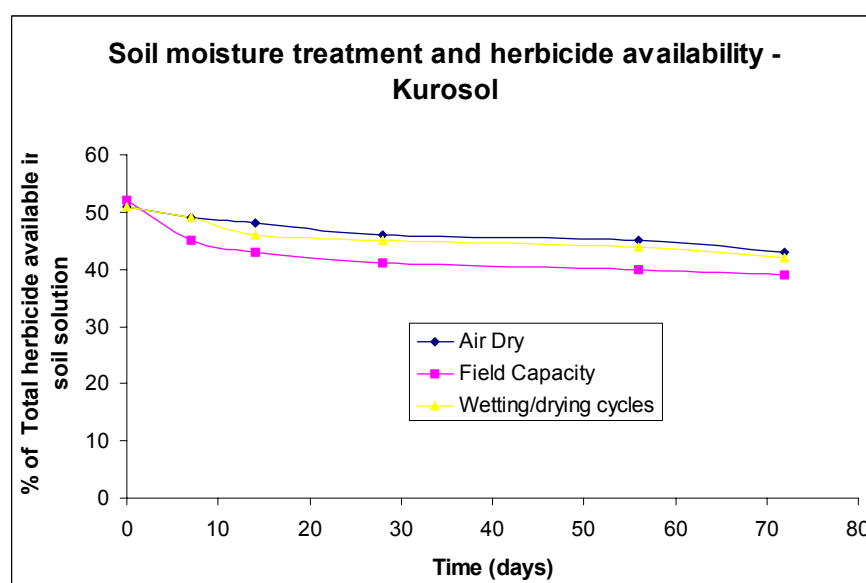
Effects of wetting and drying cycles

Repeated wetting and drying of the vertosol (black clay) soil following herbicide application reduced herbicide availability when compared to either air dry or field capacity soil samples (Graph 11). The shrinking/swelling nature of the clay may have led to increased partitioning of herbicide to clay lattices during the wetting and drying cycles. Herbicide concentration decreased more rapidly in wet than dry soil through increased microbial activity and/or increased partitioning into clay lattices. There was little difference between treatments in the kurosol (sandy loam) soil, possibly due to very low clay content in the soil (Graph 12).

Graph 11 - Soil moisture treatments and herbicide availability - Vertosol



Graph 12 - Soil moisture treatments and herbicide availability – Kurosol



5. Agronomic practices influencing herbicide breakdown

Materials and Methods

Treatments - Rates/ha

Site 5 - 2000/01

No.	Treatment	Rate of a.i. (g/ha)	Tillage	Irrigation
1	Command 1 L	clomazone 480	Not Incorporated	Irrigated
2	Stomp 3 L	pendimethalin 990		
3	Command 1 L	clomazone 480	Incorporated	
4	Stomp 3 L	pendimethalin 990		
5	Authority 500 g	sulfentrazone 375	Not Incorporated	
6	Goal WP 1 kg	oxyfluorfen 400		
7	Untreated Control			
8	Command 1 L	clomazone 480	Not Incorporated	Not Irrigated
9	Stomp 3 L	pendimethalin 990		
10	Command 1 L	clomazone 480	Incorporated	
11	Stomp 3 L	pendimethalin 990		
12	Authority 500 g	sulfentrazone 375	Not Incorporated	
13	Goal WP 1 kg	oxyfluorfen 400		
14	Untreated Control			

5. Agronomic practices influencing herbicide breakdown (Cont.)

Site 6 - 2001/02

No.	Treatment	Rate of a.i. (g/ha)	Tillage	Irrigation
1	Goal WP 1 kg	oxyfluorfen 400	Incorporated	Irrigated
2	Stomp 3 L	pendimethalin 990		
3	Command 1 L	clomazone 480		
4	Authority 500 g	sulfentrazone 375		
5	Goal WP 1 kg	oxyfluorfen 400	Not Incorporated	
6	Stomp 3 L	pendimethalin 990		
7	Command 1 L	clomazone 480		
8	Authority 500 g	sulfentrazone 375		
9	Goal WP 1 kg	oxyfluorfen 400	Not Incorporated	Not Irrigated
10	Stomp 3 L	pendimethalin 990		
11	Command 1 L	clomazone 480		
12	Authority 500 g	sulfentrazone 375		
13	Untreated Control			

5. Agronomic practices influencing herbicide breakdown (Cont.)

Trial Details

SITE NO.	5	6
Year	2000/01	2001/02
Location	Forthside	
Soil Type	Ferrosol	
Crop	Nil	
Trial Design	Randomised Complete Block	
Replicates	3	
Plot Size	2 m x 11 m	2 m x 12 m

Trial Plan - Site 5, 2000/01

Irrigated Un-irrigated

4	5	2	7	1	3	6	Replicate 1	11	12	9	14	8	10	13	Replicate 1
3	6	1	5	4	7	2	Replicate 2	10	13	8	12	11	14	9	Replicate 2
1	7	4	3	2	6	5	Replicate 3	8	14	11	10	9	13	12	Replicate 3

N ↗

Trial Plan - Site 6, 2001/02

Irrigated

Not irrigated

13	7	1	4	2	8	5	6	3	7 m Buffer	12	9	11	10	Replicate 3
3	5	4	6	7	1	8	13	2		11	10	9	12	Replicate 2
1	2	8	5	7	6	13	4	3		9	12	10	11	Replicate 1

N ↙

5. Agronomic practices influencing herbicide breakdown (Cont.)

Application Details

Site	5	6
APPLICATION EQUIPMENT		
Equipment	Knapsack CO ₂ precision sprayer fitted with a 2-metre boom.	
Jets	Spraying Systems 11002 Fan Jets	Spraying Systems DG8002 Fan Jets
Volume	220 L/ha	300 L/ha
Pressure	280 kPa	
TREATMENT APPLICATIONS		
Dates	21/11/00	23/01/02
Temperature (°C)	21.4	22.4
Relative Humidity (%)	41.2	43
Cloud Cover (%)	1	0
Wind Direction & Speed (m/sec)	SW 1.8 - 2.4 (gusting)	SW 0 – 1.8
Soil Moisture*	Dry	Not recorded

* Appendix vi

5. Agronomic practices influencing herbicide breakdown (Cont.)

IRRIGATION DETAILS (SITES 5 & 6)	
Equipment	Solid set sprinklers
Volume	15 mm
Dates	Irrigation timings based on 25% of pan evaporation
Treatments Irrigated	Water to irrigation plots only

CULTIVATION DETAILS (SITES 5 & 6)	
Equipment	Rotary hoe
Date	21/11/00 (Site 5), 23/01/02 (Site 6)
Treatments Cultivated	Cultivation treatments only
Method	Soil cultivated to 15 cm following application of herbicide treatments

5. Agronomic practices influencing herbicide breakdown (Cont.)

Assessments

1. HERBICIDE CONCENTRATIONS

Site 5

Site 6

SAMPLING DATES - 21/11/00, 21/12/00, 21/01/01, 23/02/01, 22/03/01
25/01/02, 28/02/02, 28/03/03, 26/04/02

SAMPLE SIZE - ~ 200 g soil

METHOD - Core sampled 0 - 10 cm. 6 random cores / plot

EXTRACTION METHOD - Herbicides were desorbed from soil samples using a 1:5 soil:water ratio. Samples were placed in sealed 50 mL centrifuge tubes for equilibrium by end over end shaking for 24 hours. Sorbent and solution phases were subsequently separated by centrifugation at 10,000 rpm for 10 minutes. The supernatant from this centrifugation was then poured off for solvent extraction of herbicide. Herbicide concentrations were determined using GCMS. The gas chromatograph was operated at 280°C. Samples (2 µL) were injected into the column at 40°C using a carrier gas of helium at a flow rate of 2 mL min⁻¹. This temperature was maintained for 1 minute. The column temperature was increased to 190°C at 30°C min⁻¹, then increased at a rate of 10°C min⁻¹ to 280°C and held for 6 minutes. Under these conditions the retention time for clomazone was 21 minutes and the lower detection limit was 10 ppb (Rowbottom, pers comm).

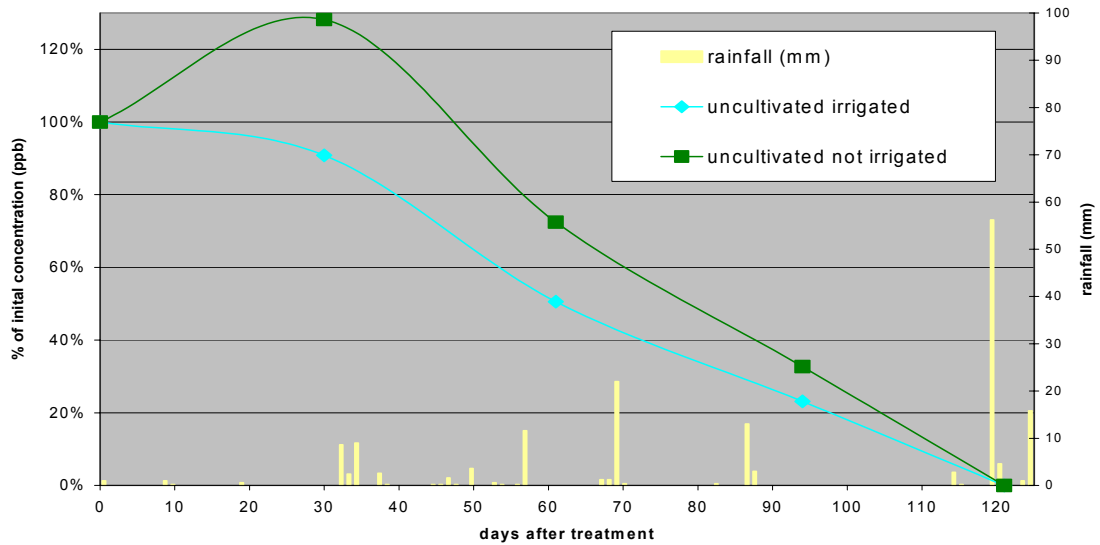
RATING SCALE - Parts per billion (ppb)

SUMMARISED RESULTS - Graphs 13 - 20

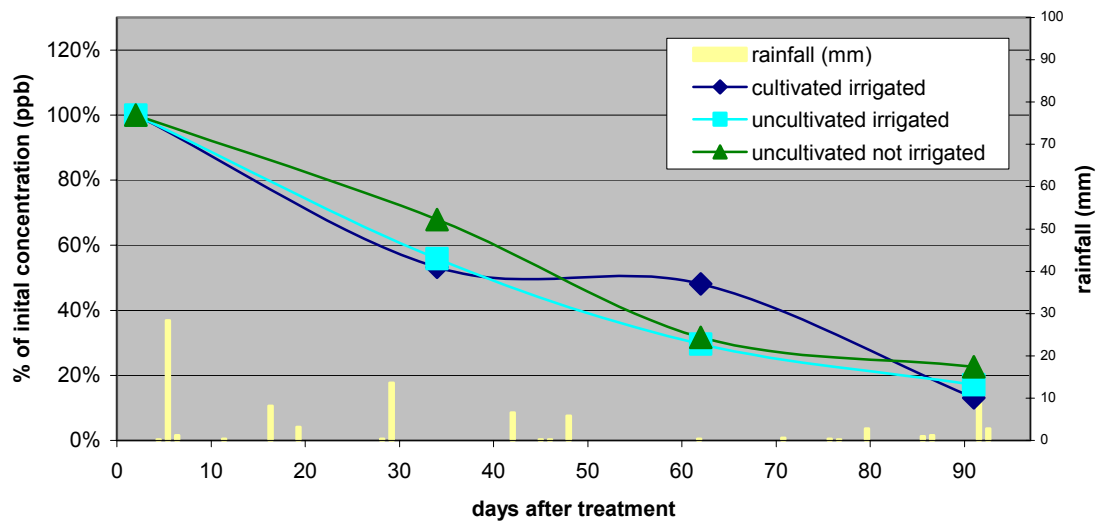
5. Agronomic practices influencing herbicide breakdown (Cont.)

Results

Graph 13 - Effects of irrigation on residues of Authority (sulfentrazone), Site 5

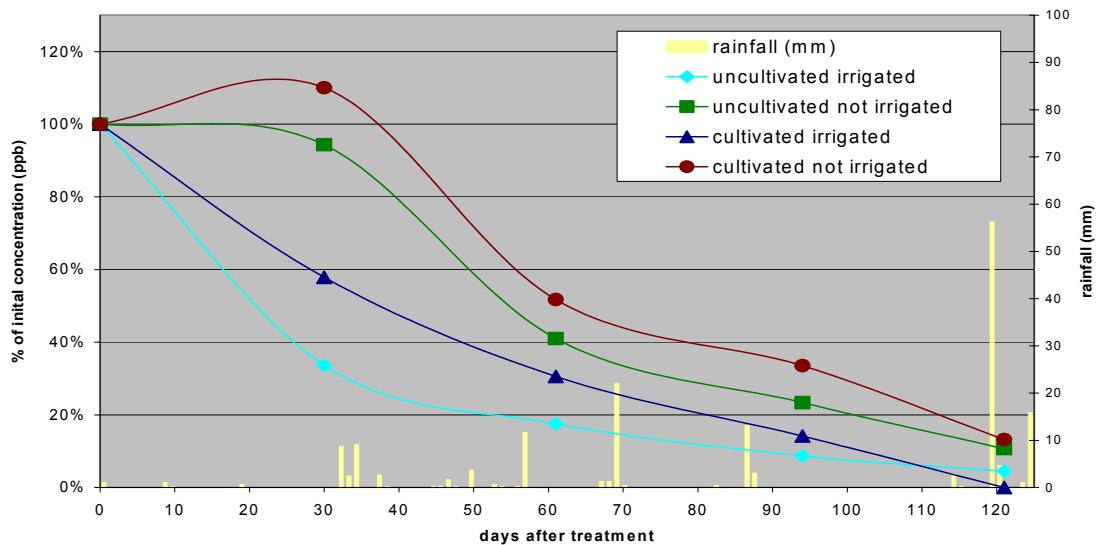


Graph 14 - Effects of irrigation and cultivation on residues of Authority (sulfentrazone), Site 6

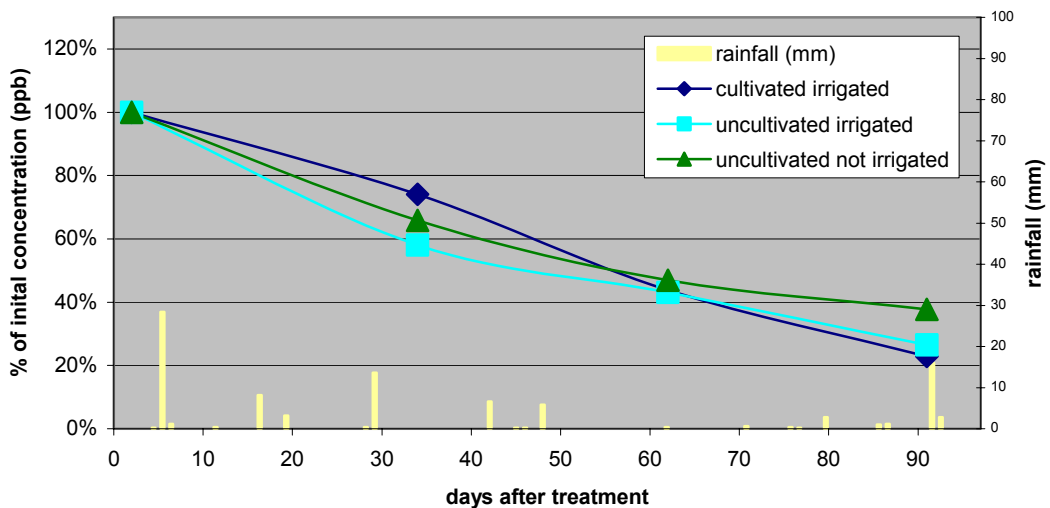


5. Agronomic practices influencing herbicide breakdown (Cont.)

Graph 15 - Effects of irrigation and cultivation on residues of Command (clomazone), Site 5

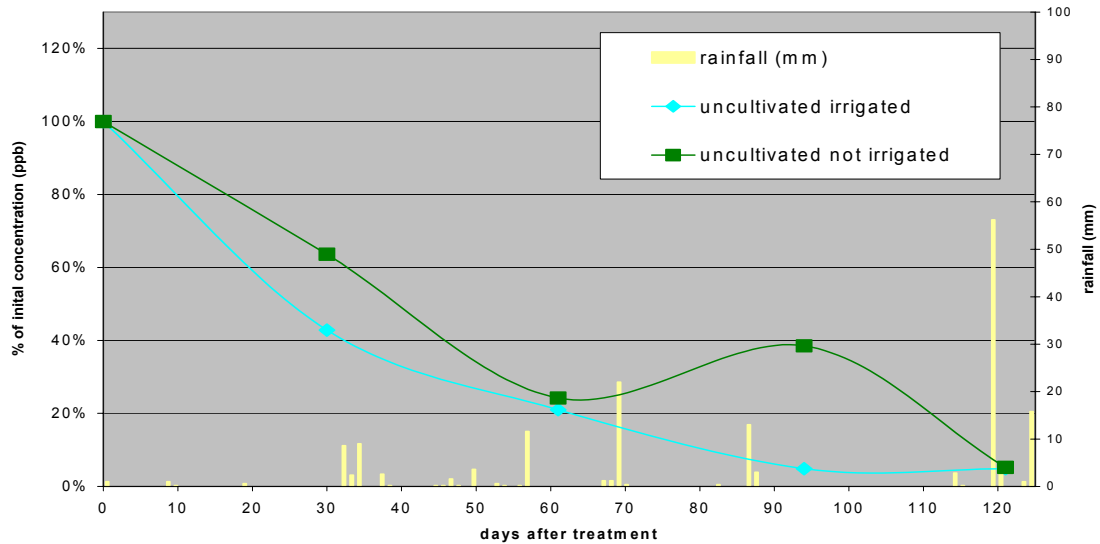


Graph 16 - Effects of irrigation and cultivation on residues of Command (clomazone), Site 6

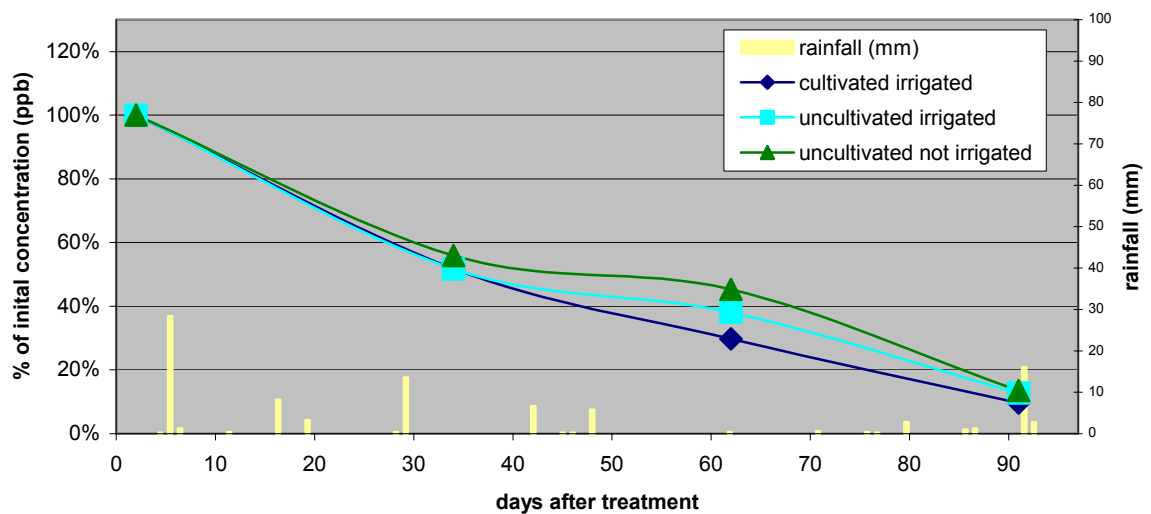


5. Agronomic practices influencing herbicide breakdown (Cont.)

Graph 17 - Effects of irrigation on residues of Goal WP (oxyfluorfen), Site 5

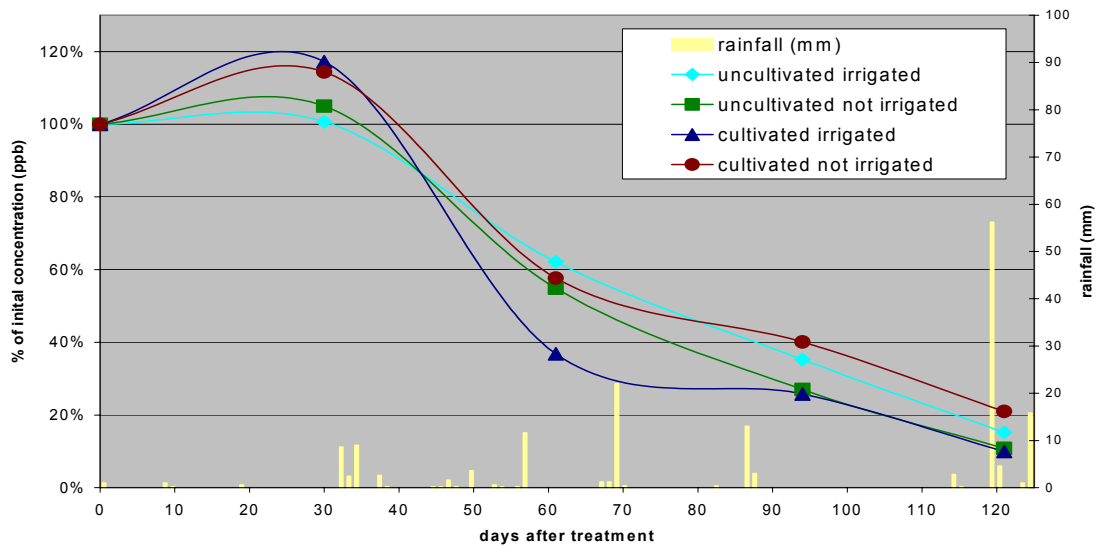


Graph 18 - Effects of irrigation and cultivation on residues of Goal WP (oxyfluorfen), Site 6

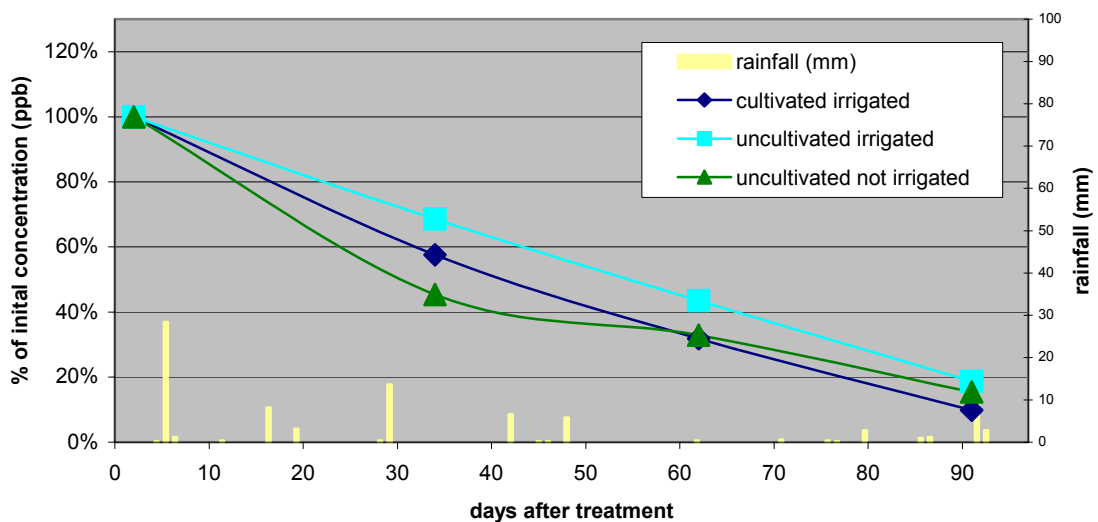


5. Agronomic practices influencing herbicide breakdown (Cont.)

Graph 19 - Effects of irrigation and cultivation on residues of Stomp (pendimethalin), Site 5



Graph 20 - Effects of irrigation and cultivation on residues of Stomp (pendimethalin), Site 6



5. Agronomic practices influencing herbicide breakdown (Cont.)

Discussion

Description of Trial

This trial was conducted over two seasons to investigate the effects of cultivation and irrigation on the breakdown of herbicide residues in the soil. The trial was conducted on a ferrosol soil at the Forthside Vegetable Research Station, Forth, North West Tasmania. Herbicide treatments applied were Authority 500 g/ha, Command 1 L/ha, Goal WP 1 kg/ha and Stomp 3 L/ha. Cultivation of the appropriate treatment plots occurred on the day of treatment application and was achieved by rotary hoeing the soil to a depth of 15 cm. Irrigation volumes of 15 mm were applied to irrigation plots and timed based on 25% of pan evaporation. Rainfall data was collected over the period of the trial at the weather station on site. Sampling of herbicide residues began on the day of application (Site 5) and 2 days after application (Site 6) and continued every month for 4 months (Site 5) and 3 months (Site 6). Six randomly placed core samples were taken from each plot and herbicide residues were extracted using a 1:5 soil:water ratio, and residues were detected using gas chromatography / mass spectrophotometry.

Authority (sulfentrazone)

Site 5

Authority 500 g/ha was applied to uncultivated plots with and without irrigation. Irrigation appeared to increase the rate of residue breakdown; however, both the irrigated and un-irrigated plots did not appear to show a decreasing trend until significant rainfall was experienced 32 days after treatment applications. At 121 days after treatment application, no levels of Authority were detected in either treatment (Graph 13).

Site 6

Authority 500 g/ha was applied to uncultivated plots with and without irrigation and to plots with both cultivation and irrigation. The results showed a decreasing rate of Authority residue in the soil over time, however no differences were observed across the 3 treatments (Graph 14). It is thought that this was due to significant rainfall being recorded in the early stages of the trial (62.6 mm rainfall recorded in first 48 days of trial). At the third assessment (62 days after application), where rainfall had reduced and soil had begun to dry out, levels of Authority had reduced to 30 – 48% of initial concentration. At 91 days after application, residues were between 8 to 22 ppb.

Command (clomazone)

Site 5

Command 1 L/ha was applied to cultivated and uncultivated plots, both with and without irrigation. Irrigation increased the rate of Command breakdown over the period of the trial. Residue levels for both of the irrigated treatments were substantially less than the un-irrigated treatments within the first 30 days of the trial when minimal rainfall had been recorded. This suggests that irrigation had an effect on the breakdown of Command. Uncultivated plots showed slightly lower levels of residue for both the treatments with and without irrigation. At 121 days after application, levels of Command in all plots were below 23 ppb (Graph 15).

5. Agronomic practices influencing herbicide breakdown (Cont.)

Site 6

Command 1 L/ha was applied to uncultivated plots with and without irrigation and to plots with both cultivation and irrigation. The results showed a decreasing rate of Command residue in the soil over time; however, no differences were observed across the 3 treatments (Graph 16). It is thought that this was due to significant rainfall being recorded in the early stages of the trial. At the third assessment, where rainfall had reduced and soil had begun to dry out, levels of Command had reduced to 43 – 47% of initial concentration. At 91 days after application, residues were between 56 to 119 ppb.

Goal WP (oxyfluorfen)

Site 5

Goal WP 1kg was applied to uncultivated plots with and without irrigation. Residue levels decreased substantially within the first 30 days for both treatments, suggesting irrigation or rainfall is not critical in the reduction of oxyfluorfen residue. At 121 days after treatment application, levels of Goal WP in both the irrigated and un-irrigated plots were below 7 ppb (Graph 17).

Site 6

Goal WP 1 kg/ha was applied to uncultivated plots with and without irrigation and to plots with both cultivation and irrigation. The results showed a decreasing rate of Goal WP residue in the soil over time; however, no differences were observed across the 3 treatments (Graph 18). Based on data collected from Site 2, rainfall was probably not a significant influence on the reduction of oxyfluorfen levels in the soil. At 91 days after application, residues were between 12 to 22 ppb.

Stomp (pendimethalin)

Site 5

Stomp 3 L was applied to cultivated and uncultivated plots, both with and without irrigation. No substantial differences were observed between cultivated and uncultivated plots or between irrigated and un-irrigated plots. Residue levels began to decrease after 30 days from treatment application, suggesting rainfall is a critical factor in the reduction of soil residues. At 121 days after treatment, levels of Stomp in all plots were below 23 ppb (Graph 19).

Site 6

Stomp 3 L/ha was applied to uncultivated plots with and without irrigation and to plots with both cultivation and irrigation. The results showed a decreasing rate of Stomp residue in the soil over time; however, no differences were observed across the 3 treatments (Graph 20). It is thought that this was due to significant rainfall being recorded in the early stages of the trial. At the third assessment, where rainfall had reduced and soil had begun to dry out, levels of Stomp had reduced to 10 - 19% of initial concentration. At 91 days after application, residues were between 36 to 114 ppb.

6. Critical Concentration for crop growth

Materials and Methods

Treatments - Rates/ha

TREATMENT		Crop					
Product (g/ha)	Active Ingredient (g/ha)	Brassicas	Onions	Poppies	Pyrethrum	Squash	Zucchini
Authority 62.5 g	sulfentrazone 46.87 g		✓	✓			
Authority 125 g	sulfentrazone 93.75 g		✓	✓			
Authority 250 g	sulfentrazone 187.5 g		✓	✓			
Command 187.5 mL	clomazone 90 g		✓		✓		
Command 375 mL	clomazone 180 g		✓		✓		
Command 750 mL	clomazone 360 g		✓		✓		
Goal WP 125 g	oxyfluorfen 50 g				✓		
Goal WP 250 g	oxyfluorfen 100 g				✓	✓	✓
Goal WP 500 g	oxyfluorfen 200 g				✓	✓	✓
Goal WP 1 kg	oxyfluorfen 400 g					✓	✓
Goal WP 2 kg	oxyfluorfen 800 g					✓	✓
Lexone 175 g	metribuzin 131.25 g	✓					
Lexone 350 g	metribuzin 262.5 g	✓					
Lexone 700 g	metribuzin 525 g	✓					
Stomp 250 mL	pendimethalin 82.5 g			✓			
Stomp 375 mL	pendimethalin 123.75 g	✓		✓			
Stomp 500 mL	pendimethalin 165 g			✓			
Stomp 750 mL	pendimethalin 247.5 g	✓		✓			
Stomp 1 L	pendimethalin 330 g			✓			
Stomp 1.5 L	pendimethalin 495 g	✓		✓			
Stomp 2 L	pendimethalin 660 g			✓			
Untreated Control		✓	✓	✓	✓	✓	✓

6. Critical Concentration for crop growth (Cont.)

Trial Details

SITE NO.	7	8	9	10	11
Year	2000/01	2001/02	2000		
Grower	Forthside Vegetable Research Station		Peter Beswick	Warren Parker	Warren Parker
Location	Forthside		Kindred	Don	Don
Soil Type	Ferrosol		Ferrosol		
Crop	Poppies Pyrethrum Onions Swedes	Poppies Squash Zucchini	Onions	Poppies	Swedes
Trial Design	Randomised Complete Block		Commercial crop		
Replicates	3	3	-	-	-
Plot Size	2 m x 11 m	2 m x 12 m	-	-	-

6. Critical Concentration for crop growth (Cont.)

Application Details

Site	7	8	
APPLICATION EQUIPMENT			
Equipment	Knapsack CO ₂ precision sprayer fitted with a 2-metre boom.		
Jets	Spraying Systems 11002 Fan Jets	Spraying Systems AI02VS Fan Jets	Spraying Systems DG8002 Fan Jets
Volume	220 L/ha	270 L/ha	
Pressure	280 kPa		
TREATMENT APPLICATIONS			
Dates	23/10/00	21/09/01	7/12/01
Treatments Applied	All	Poppy plots	Squash and zucchini plots
Temperature (°C)	Not recorded	8	21.4
Relative Humidity (%)	Not recorded	70	45
Cloud Cover (%)	40-70	0	20
Wind Direction & Speed (m/sec)	NW 0 - 2	SW 1 - 2	calm
Soil Moisture*	Moist below 3 cm	Surface dry	Surface dry
Crop Stage	Pre-plant	Pre-plant	Pre-plant

* Appendix iv

6. Critical Concentration for crop growth (Cont.)

Assessments

1. CROP TOLERANCE

SITE 7

SITE 8

DATES - Poppies: 8/12/00, 5/01/01
 Brassicas: 23/11/00, 8/12/00
 Onions: 13/12/00

Poppies: 1/11/01, 19/11/01
 Squash: 8/01/01, 18/01/01,
 12/02/01
 Zucchini: 8/01/01, 18/01/01

SAMPLE SIZE - Whole plot

Whole plot

METHOD - Subjective Rating

Subjective Rating

RATING SCALE - EWRS crop tolerance
 (Appendix i)

EWRS crop tolerance
 (Appendix i)

PHOTOGRAPHS -

Photograph 2

2. CROP YIELD ASSESSMENT

DATE - Poppies: 9/11/00
 Onions: 18/03/01

Poppies: 18/02/02
 Squash: 12/04/02
 Zucchini: 12/02/02,
 15/02/02, 22/02/02,
 26/02/02, 4/03/02, 12/03/02

SAMPLE SIZE - Poppies: Whole plot
 Onions: 1 bed x 2 m

Squash: Whole plot
 Zucchini: 5 plants

METHOD - Poppies: Capsules hand
 picked
 Onions: Harvested, foliage
 removed and weighed green

Squash: Collected all fruit
 from vines.
 Zucchini: Picked marketable
 fruit (>200 g, minimum 40
 mm diameter and 200 mm
 length).

RATING SCALE - Poppies: grams per plot
 converted to tonnes per
 hectare
 Onions: kg per plot
 converted to tonnes per
 hectare

SUMMARISED RESULTS - Graphs 21 & 22, 26 & 27

Graphs 23, 28 & 29

6. Critical Concentration for crop growth (Cont.)

2. CROP DENSITY

SITE 7

SITE 8

DATE - Brassicas: 23/11/00	-
SAMPLE SIZE - 1 m of row (Average of 4 counts per plot)	-
METHOD - Individual plants counted	-
SUMMARISED RESULTS - Graphs 24 & 25	-

4. HERBICIDE CONCENTRATIONS

SAMPLING DATES - 09/11/00	Poppies: 10/10/01 Squash, Zucchini: 13/12/01
SAMPLE SIZE - ~ 200 g soil	
METHOD - Core sampled 0 - 10 cm. 6 random cores / plot (trial) or paddock (commercial crop)	
RATING SCALE - Parts per billion (ppb)	
EXTRACTION METHOD - Herbicides were desorbed from soil samples using a 1:5 soil:water ratio. Samples were placed in sealed 50 mL centrifuge tubes for equilibrium by end over end shaking for 24 hours. Sorbent and solution phases were subsequently separated by centrifugation at 10,000 rpm for 10 minutes. The supernatant from this centrifugation was then poured off for solvent extraction of herbicide. Herbicide concentrations were determined using GCMS. The gas chromatograph was operated at 280°C. Samples (2µL) were injected into the column at 40°C using a carrier gas of helium at a flow rate of 2 mL min ⁻¹ . This temperature was maintained for 1 minute. The column temperature was increased to 190°C at 30°C min ⁻¹ , then increased at a rate of 10°C min ⁻¹ to 280°C and held for 6 minutes. Under these conditions the retention time for clomazone was 21 minutes and the lower detection limit was 10 ppb (Rowbottom, pers comm).	
SUMMARISED RESULTS - Graphs 21 & 22, 24- 27	Graphs 23, 28 & 29

6. Critical Concentration for crop growth (Cont.)

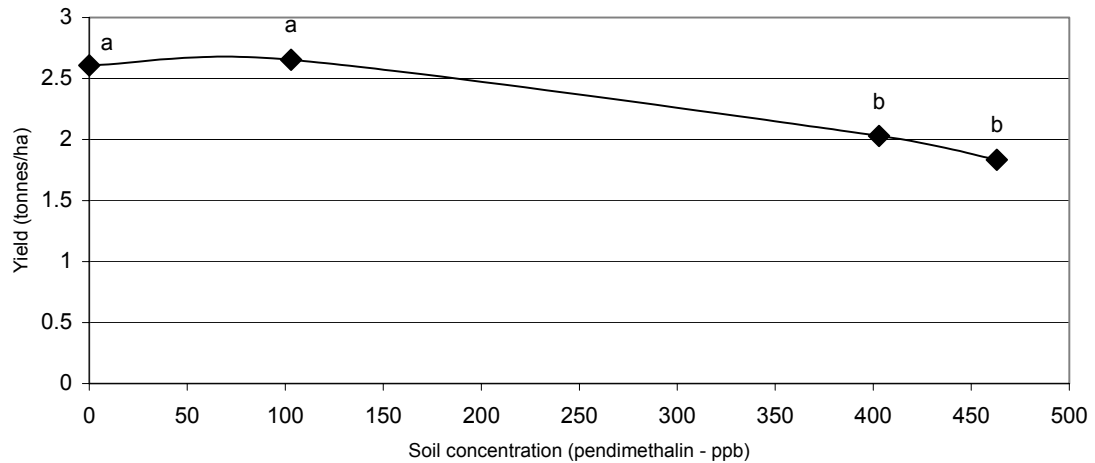
5. HERBICIDE CONCENTRATIONS

	SITE 9	SITE 10	SITE 11
SAMPLING DATES -	19/10/00	17/10/00	17/10/00
SAMPLE SIZE -	~ 200 g soil		
METHOD -	Core sampled 0 - 10 cm. 6 random cores / plot (trial) or paddock (commercial crop)		
RATING SCALE -	Parts per billion (ppb)		
EXTRACTION METHOD -	Herbicides were desorbed from soil samples using a 1:5 soil:water ratio. Samples were placed in sealed 50 mL centrifuge tubes for equilibrium by end over end shaking for 24 hours. Sorbent and solution phases were subsequently separated by centrifugation at 10,000 rpm for 10 minutes. The supernatant from this centrifugation was then poured off for solvent extraction of herbicide. Herbicide concentrations were determined using GCMS. The gas chromatograph was operated at 280°C. Samples (2µL) were injected into the column at 40°C using a carrier gas of helium at a flow rate of 2 mL min ⁻¹ . This temperature was maintained for 1 minute. The column temperature was increased to 190°C at 30°C min ⁻¹ , then increased at a rate of 10°C min ⁻¹ to 280°C and held for 6 minutes. Under these conditions the retention time for clomazone was 21 minutes and the lower detection limit was 10 ppb (Rowbottom, pers comm).		
SUMMARISED RESULTS -	Table 10, Graph 30	Table 11, Graph 31	Table 12 Graph 32

6. Critical Concentration for crop growth (Cont.)

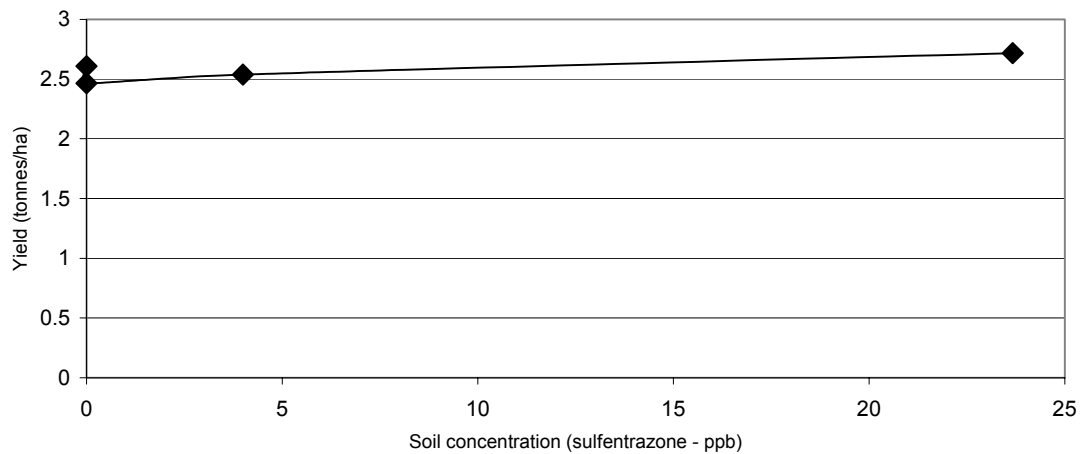
Results

Graph 21 - Capsule yield of poppies with pendimethalin residues, Site 7



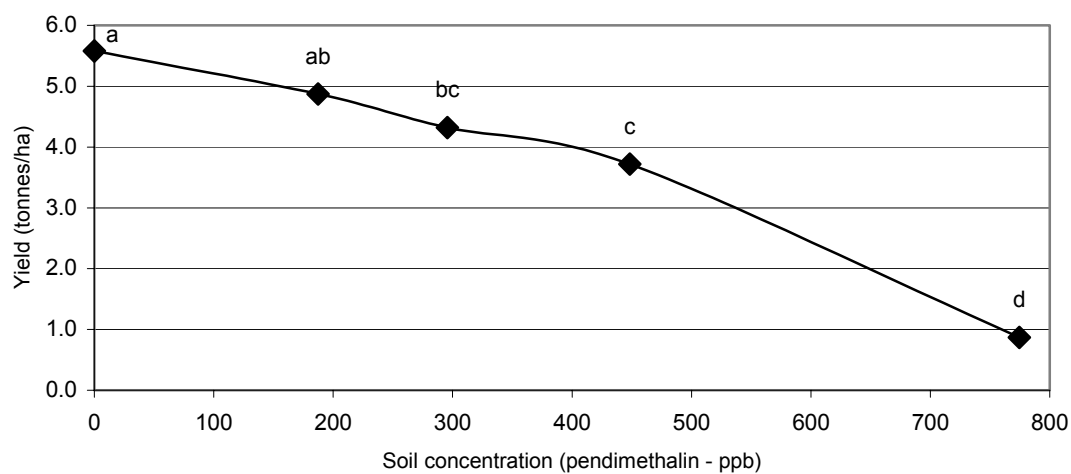
Means followed by the same letter are not significantly different at the 5% level using Duncan's New Multiple Range Test.

Graph 22 - Capsule yield of poppies with sulfentrazone residues, Site 7*



6. Critical Concentration for crop growth (Cont.)

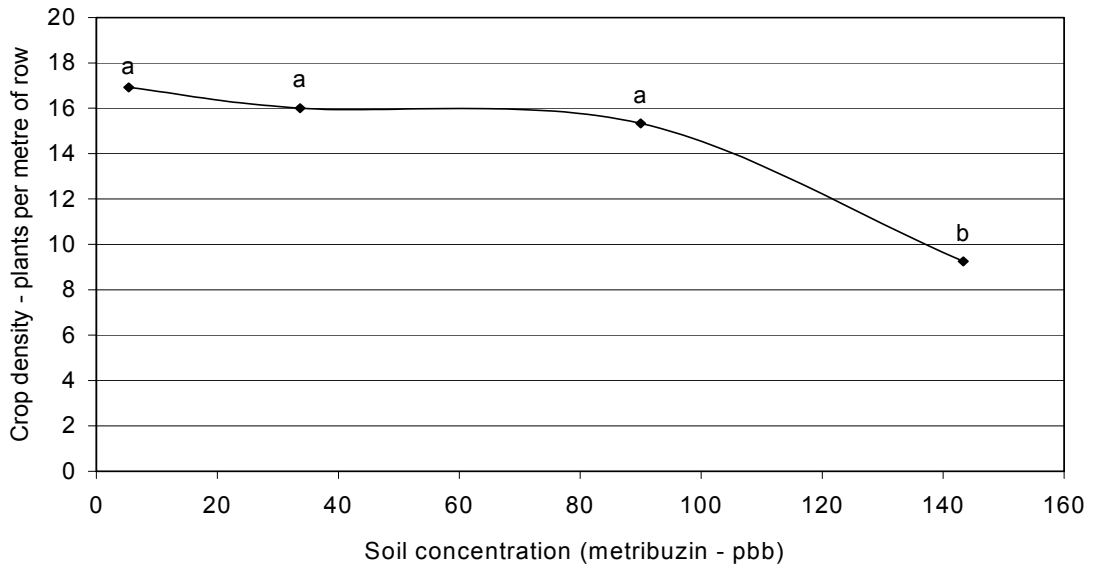
Graph 23 - Capsule yield of poppies with pendimethalin residues, Site 8



Means followed by the same letter are not significantly different at the 5% level using Duncan's New Multiple Range Test.

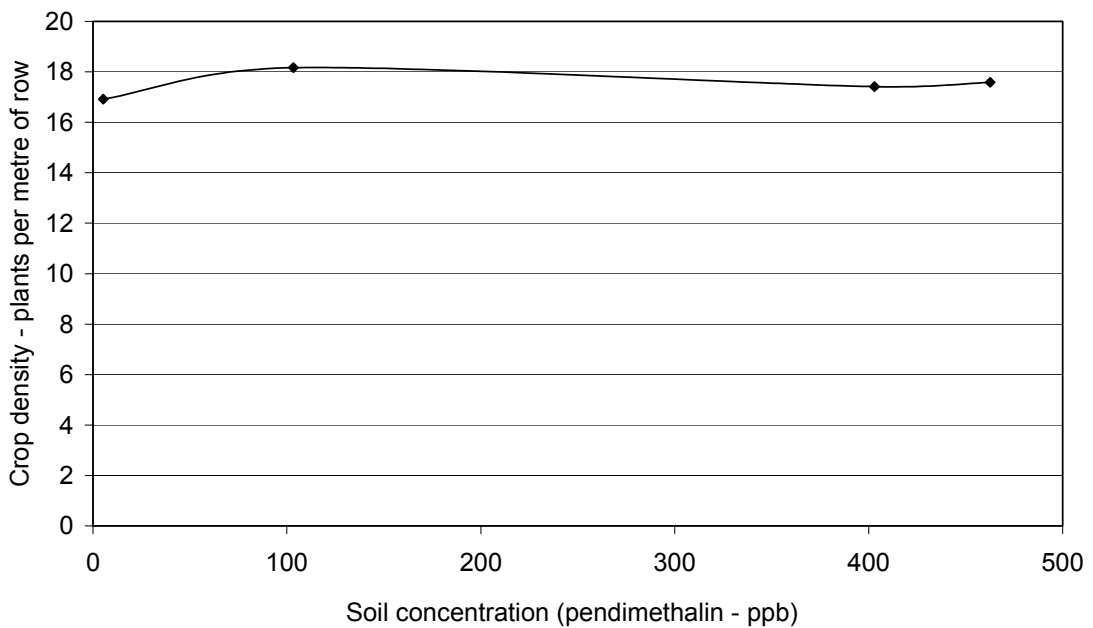
6. Critical Concentration for crop growth (Cont.)

Graph 24 - Crop density of swedes with metribuzin residues, Site 7



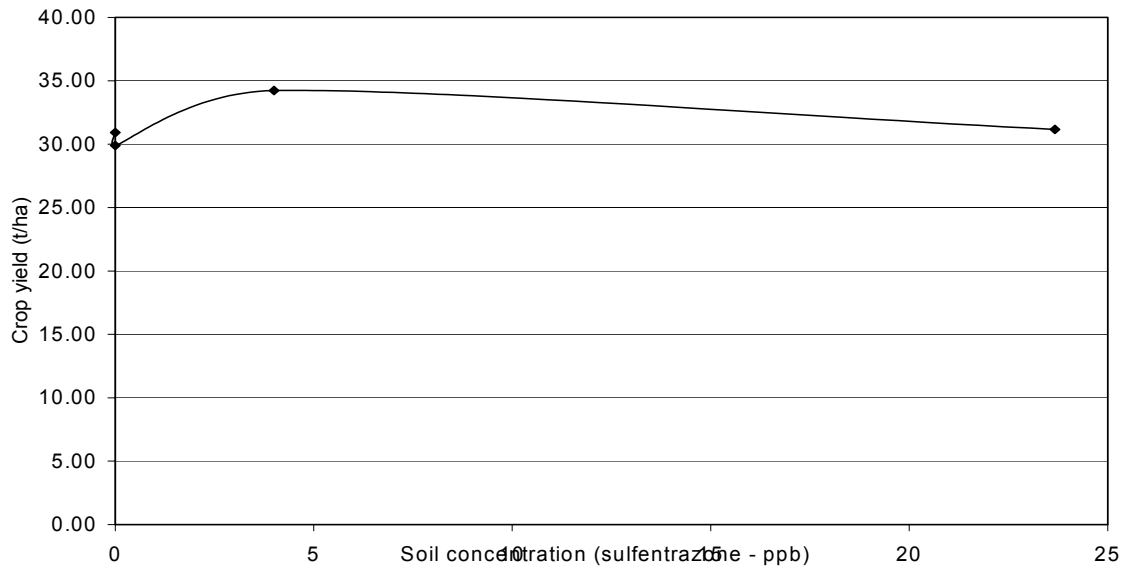
Means followed by the same letter are not significantly different at the 5% level using Duncan's New Multiple Range Test.

Graph 25 - Crop density of swedes with pendimethalin residues, Site 7*

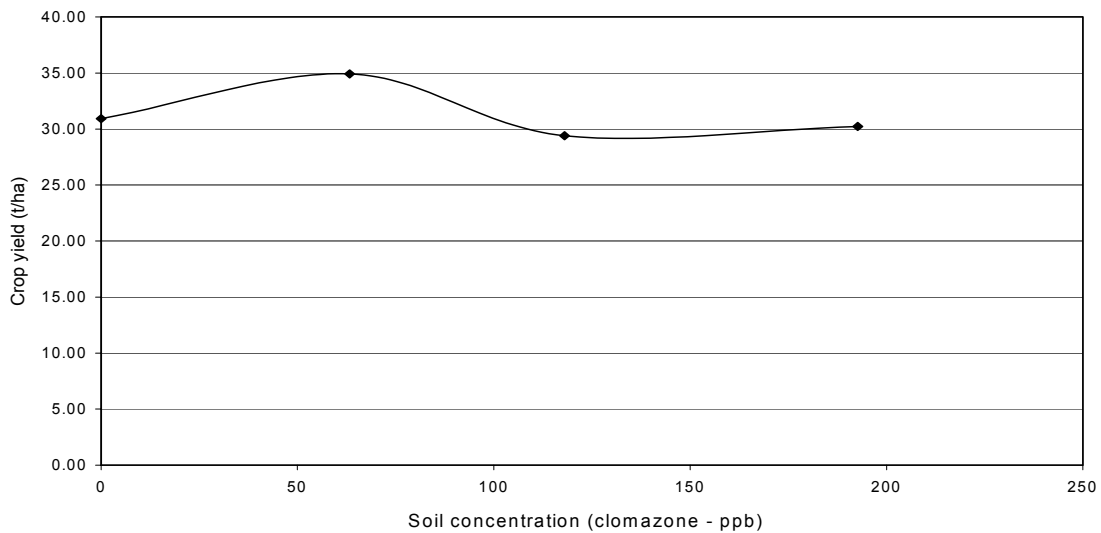


6. Critical Concentration for crop growth (Cont.)

Graph 26 - Crop yield of onions with sulfentrazone residues, Site 7*



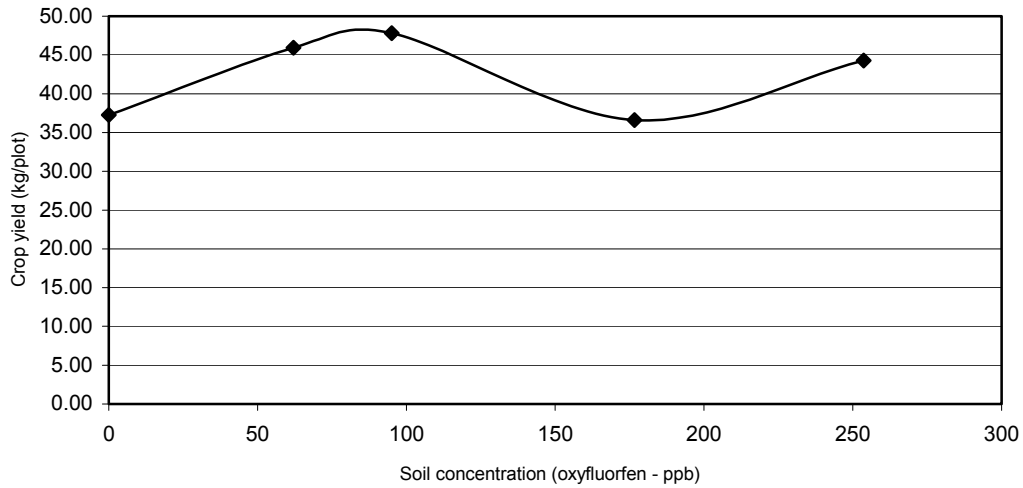
Graph 27 - Crop yield of onions with clomazone residues, Site 7*



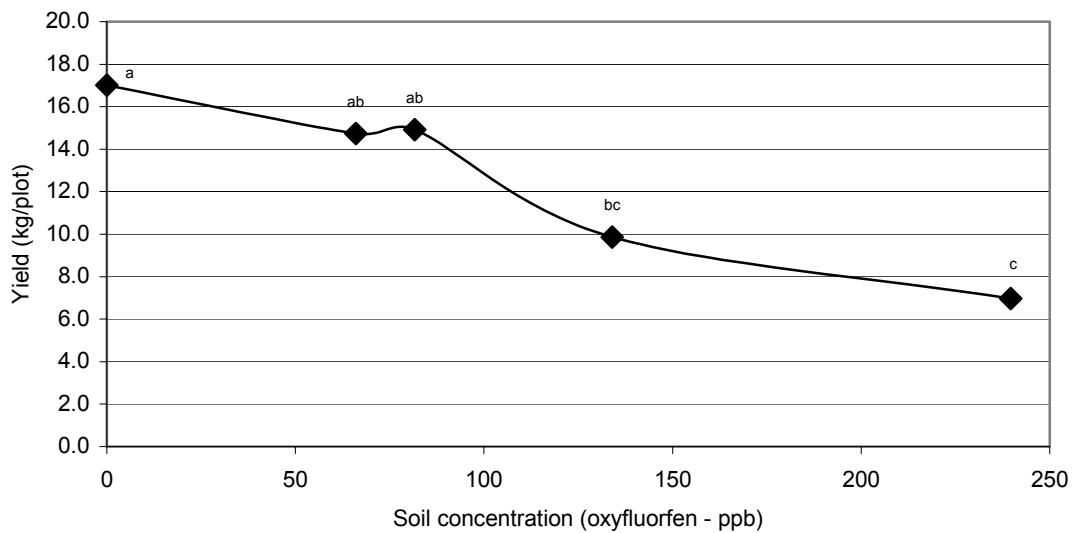
* no significant differences between treatments

6. Critical Concentration for crop growth (Cont.)

Graph 28 - Crop yield of squash with oxyfluorfen residues, Site 8*



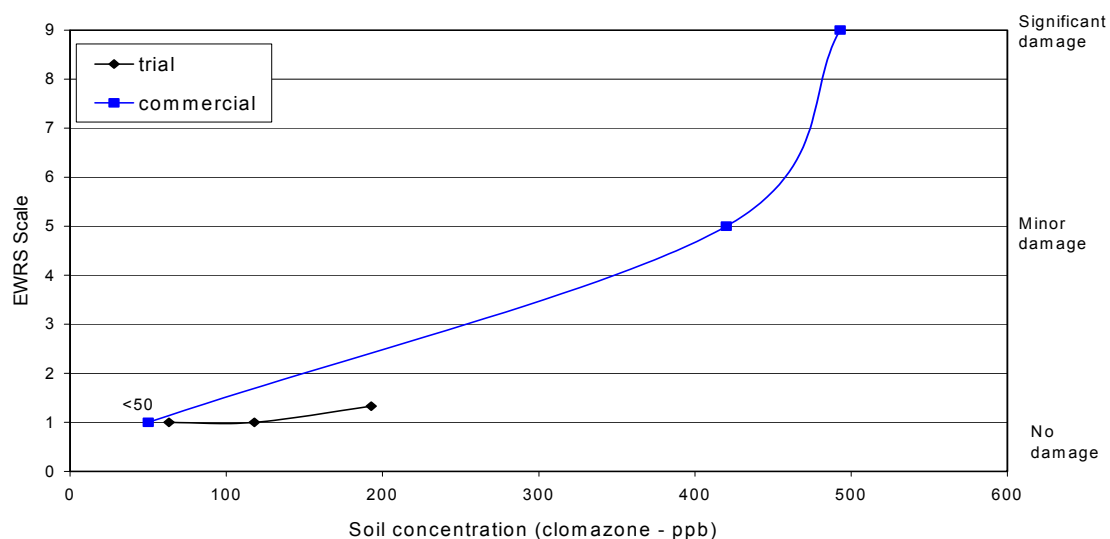
Graph 29 - Crop yield of zucchini with oxyfluorfen residues, Site 8



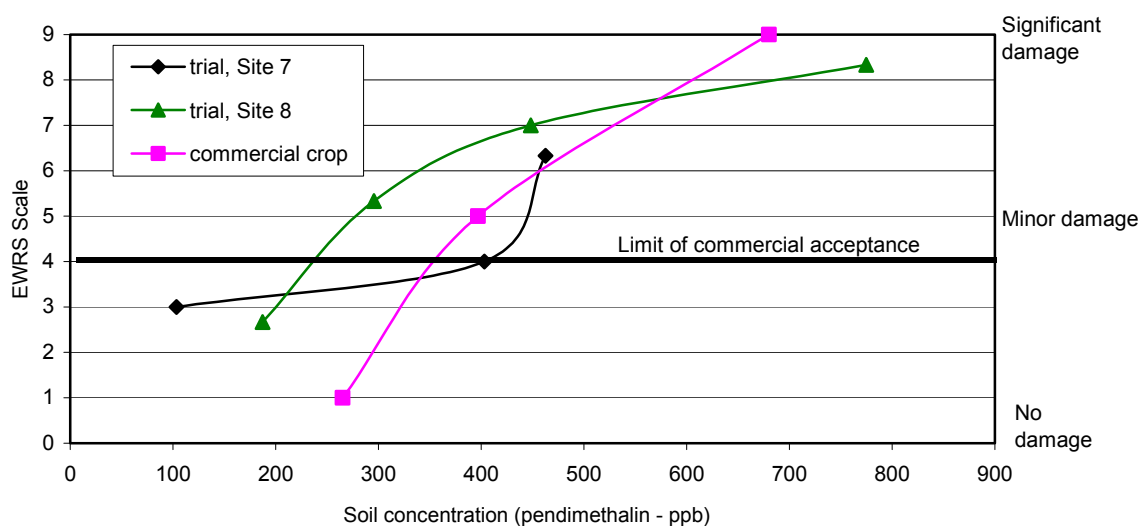
Means followed by the same letter are not significantly different at the 5% level using Duncan's New Multiple Range Test.

6. Critical Concentration for crop growth (Cont.)

Graph 30 - Analysis of clomazone residues on a commercial onion crop (Site 9) vs trial result.



Graph 31 - Analysis of pendimethalin residues on a commercial poppy crop (Site 10) vs trial result.



6. Critical Concentration for crop growth (Cont.)

Graph 32 - Analysis of pendimethalin residues on a commercial swede crop (Site 11) vs trial result.

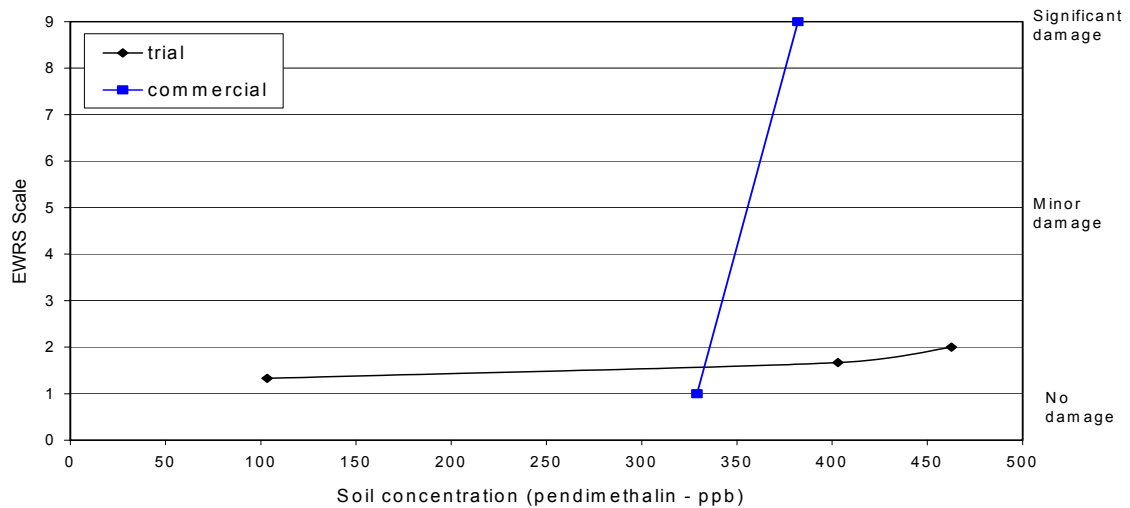


Table 9 - Critical Concentration for crop growth

Crop	Herbicide				
	clomazone	sulfentrazone	pendimethalin	oxyfluorfen	metribuzin
Onions	>193	>24	-	-	-
Poppies	-	>24	296	-	-
Swedes	-	-	>463	-	143
Zucchini	-	-	-	134	-
Squash	-	-	-	>254	-

6. Critical Concentration for crop growth (Cont.)

Table 10 - Suspected Command damage on a commercial crop of onions, Site 9

Herbicide Residue Analysis			
Grower	Peter Beswick		
Crop	Onions		
Crop Stage	4 - 6 leaf		
Location	Kindred, Tasmania		
Date	19/10/00		
Soil Type	Ferrosol		
Sample no.	1	2	3
Sample depth	0 - 10 cm		
Damage severity	No damage	Minor damage	Significant damage
Residual herbicide	Command (clomazone)		
Concentration (ppb)	<50	420	493
Photographs	Photograph 4		
Soil Analysis			
pH (H ₂ O)	5.8	5.4	5.1
pH (CaCl ₂)	5.3	4.8	4.7
Organic Carbon (%)	3.1	3.0	2.3
% Sand	Fine	29	20
	Coarse	4	3
% Silt	25	33	26
% Clay	42	44	64

6. Critical Concentration for crop growth (Cont.)

Table 11 - Suspected Stomp damage on a commercial crop of poppies, Site 10

Herbicide Residue Analysis			
Grower	Warren Parker		
Crop	Poppies		
Crop stage	6 - 8 leaf		
Location	Don, Tasmania		
Date	17/10/00		
Soil Type	Ferrosol		
Sample no.	6	7	8
Sample depth	0 - 10 cm		
Damage severity	No damage	Minor damage	Significant damage
Residual herbicide	Stomp (pendimethalin)		
Concentration (ppb)	265	397	680
Photographs	Photograph 3		
Soil Analysis			
pH (H₂O)	6.0	5.9	5.9
pH (CaCl₂)	5.4	5.4	5.4
Organic Carbon (%)	3.3	2.9	3.0
% Sand	Fine	30	33
	Coarse	6	2
% Silt	26	25	25
% Clay	38	40	17

6. Critical Concentration for crop growth (Cont.)

Table 12 - Suspected Stomp damage on a commercial crop of swedes, Site 11

Herbicide Residue Analysis			
Grower	Warren Parker		
Crop	Swedes		
Crop stage	Not recorded		
Location	Don, Tasmania		
Date	17/10/00		
Soil Type	Ferrosol		
Sample no.	4	5	
Sample depth	0 - 10 cm		
Damage severity	No damage	Significant damage	
Residual herbicide	Stomp (pendimethalin)		
Concentration (ppb)	329	382	
Soil Analysis			
pH (H₂O)	6.2	6.3	
pH (CaCl₂)	5.6	5.7	
Organic Carbon (%)	2.9	3.1	
% Sand	Fine	28	17
	Coarse	7	9
% Silt	25	19	
% Clay	40	55	

6. Critical Concentration for crop growth (Cont.)

Discussion

Description of Trials

Trials were conducted over two years to investigate crop effects of herbicide residues in soils for six crops, poppies, swedes, onions, pyrethrum, squash and zucchini. Poppies were the only crop to be trialed in both years. All trials were conducted on a ferrosol soil at the Forthside Vegetable Research Station, Forth, North West Tasmania. Herbicides applied for residue analysis were Stomp, Authority, Command, Goal WP and Lexone. Herbicides were applied 15 days before planting of swedes, onions and pyrethrum, 5 days before planting of squash and zucchini and 16 days before sowing of poppies (0 days for Site 8). The soil was then cultivated to an approximate depth of 15 cm. Herbicides were applied at various rates to achieve varying residues in the soil. Samples were taken for residue analysis within two days of crop planting. Six randomly placed core samples were taken from each plot and herbicide residues were extracted using a 1:5 soil:water ratio and detected using gas chromatography / mass spectrophotometry. Crop density after germination, crop tolerance and yield assessments were conducted.

In addition to the field trials, three commercial crops (onions, poppies and swedes) showing obvious effects of suspected herbicide residue damage were sampled. Samples were taken for soil analysis for all crops in damaged and undamaged areas of the crop. A crop tolerance value of 5 (EWRS scale) was given for minor crop damage and a value of 9 for significant crop damage. A value of 1 was given for no crop damage.

Poppies

Stomp (pendimethalin) was applied at three different rates, from 375 mL/ha to 1.5 L/ha, on poppies in the first year of trials and four different rates from 250 mL/ha to 2 L/ha in the second year. In the first year of trials, an increase in concentration of Stomp resulted in an increase in crop damage. At 403 ppb, crop tolerance was marginal, and at the highest concentration 463 ppb, crop tolerance was unacceptable. At the lowest concentration, 103 ppb, some reduction in crop vigour was evident but crop tolerance was acceptable. With an increase in concentration of Stomp, capsule yield decreased. The two highest rates of Stomp (750 mL and 1.5 L/ha) gave a significantly lower capsule yield than the lowest rate (375 mL) and the untreated control plots (Graph 21). In the second year of trials, it was found that, at 295 ppb, crop tolerance was marginal, and higher concentrations were unacceptable. At 295 ppb and higher concentrations, capsule yield was significantly reduced compared to the untreated control (Graph 23). In the commercial crop sampled, crop damage had occurred on poppies where Stomp residue had moved into a low-lying area of a paddock. Analysis of residue showed a strong correlation with trial results (Graph 31). Minor damage occurred on the crop between approximately 200 and 400 ppb of Stomp. Below these values, crop tolerance was acceptable and above these values, crop tolerance was unacceptable.

Authority (sulfentrazone) was applied in the first year of trials at 3 different rates. Residues of Authority up to 24 ppb showed no effect on crop tolerance, and there were no significant differences in capsule yield (Graph 22).

6. Critical Concentration for crop growth (Cont.)

Swedes

Lexone (metribuzin) and Stomp (pendimethalin) were applied at 3 different rates, from 112.5 to 450 g/ha (Lexone) and 375 to 1.5 L/ha (Stomp), on swedes in the first year of trials. With an increase in concentration of Lexone, crop damage increased. At the highest level of 143 ppb, crop tolerance was unacceptable at both assessments. At 90 ppb and lower, Lexone was safe to the crop. Crop density was lower with increasing levels of Lexone. At 143 ppb, crop density was significantly lower than the other 2 rates and the untreated control (Graph 24). Stomp did not appear to affect establishment or vigour for swedes. There were no significant differences for crop density or vigour for Stomp concentrations up to 463 ppb (Graph 25). In the commercial crop sampled, no difference in Stomp concentration was found between the damaged and undamaged section of the crop and the significant damage in the crop didn't correlate with the trial result (Graph 32, Table 12). This suggests that Stomp was not directly attributable to the commercial crop damage. Other factors, such as plant stress and a possible interaction with Stomp could have been an influence on the crop damage. Yield data was not collected for swedes.

Onions

Authority (sulfentrazone) and Command (clomazone) were applied at 3 different rates, from 62.5 to 250 g/ha (Authority) and from 187.5 to 750 mL/ha (Command), on onions in the first year of trials. No effect was observed on crop density, vigour or yield with Authority up to the highest concentration of 24 ppb or Command at 193 ppb (Graphs 26 & 27). In the sampled commercial crop, an increase in Command concentration resulted in an increase in crop damage. Command concentrations in the trial only occurred up to 193 ppb and showed little or no crop damage. In the commercial crop, the concentration of Command was recorded up to 493 ppb where significant crop damage had occurred, and 420 ppb where minor crop damage had occurred (Graph 30, Table 10).

Pyrethrum

Poor germination was achieved with the pyrethrum plot, so the trial was abandoned.

Squash

Goal WP (oxyfluorfen) was applied at 4 different rates, from 250 g/ha to 2 kg/ha, on squash in the second year of trials. At concentrations between 0 and 254 ppb, no significant differences were observed for plant density after germination, or crop yield (Graph 28). Crop tolerance was acceptable for all rates applied except Goal WP 2 kg/ha at the third assessment, where the crop tolerance was marginal.

6. Critical Concentration for crop growth (Cont.)

Zucchini

Goal WP (oxyfluorfen) was applied at 4 different rates, from 250 g/ha to 2 kg/ha, on zucchini in the second year of trials. With an increase in Goal WP concentration, crop damage increased. At 82 ppb, crop tolerance was marginal, and at higher rates, crop tolerance was unacceptable. At 66 ppb, crop tolerance was acceptable. No significant differences were observed between treatments for crop density after germination; however, Goal WP had an obvious effect on crop vigour. Fruit yield data was collected over 6 harvests in a 1-month period. With an increase in Goal WP concentration, crop yield decreased (Graph 29). At 134 ppb and higher rates, crop yield was significantly different to the untreated control. The number of fruit set decreased with an increase in Goal WP concentration. At the two highest rates, the number of fruit set was significantly reduced compared to the untreated control. No delayed effect on fruit development was observed over the 6 harvest dates.

7. Extraction and Analysis methods

Introduction

In recent years supercritical fluids have emerged as a powerful extraction tool for analytical chemists. In particular, the use of supercritical fluids in the area of environmental science and residue analysis has received considerable interest. The appeal of supercritical fluid extraction (SFE) lies in the potential to reduce sample preparation time, organic solvent usage, and human exposure to solvents. In SFE the extracting solvent is a supercritical fluid, that is a substance that is above its critical phase change pressure and temperature. Supercritical fluids exhibit combined gas-like mass transfer and liquid-like solvating characteristics. Mass transfer is faster in supercritical fluids than in a liquid solvent due to lower viscosity and higher analyte diffusivity. Commonly, carbon dioxide is preferred as the supercritical fluid as it has a relatively low critical temperature and pressure, low toxicity and reactivity, and high purity at low cost.

In brief, SFE involves the following extraction and recovery steps. Firstly, critical temperature and pressure conditions transform liquid carbon dioxide to a supercritical fluid before it reaches the sample extraction chamber. Supercritical fluid then dissolves and removes analytes (eg. herbicides) as it flows through the extraction thimble. The fluid is decompressed and discharged to the atmosphere, while the analyte is deposited onto a solid trap material. The analyte is then eluted with a suitable organic solvent, and the solubilized extract collected in glass vials ready for analysis. The extraction efficiency of a specific analyte by a supercritical fluid is influenced by a range of parameters such as addition of modifiers, extraction temperature, static and dynamic extraction time, trap temperature, fluid density and flow rate, and sample mass. In turn, these parameters must be optimised for each analyte of interest to achieve maximum recoveries. Under optimum conditions, reported extraction efficiencies for herbicides from soils have ranged from 55 to 100%.

Development of SFE methods

The cost of testing soil samples for pesticide residues is high due to the nature of the extraction and pesticide detection methodology. Existing methods are labour intensive and use large volumes of expensive and dangerous solvents. An alternative to these methods is supercritical fluid extraction and detection using GCMS. In addition to labour and cost savings, the methods may also permit extraction of different pools of herbicide from the soil (for example, the plant available fraction of the total amount present) by changing the extraction conditions. Extraction conditions using supercritical fluid were developed and tested on six soils. Percentage recovery of herbicide from spiked soil samples was similar in all soil types indicating the validity of the method for assessing total herbicide concentrations in soils. The extraction conditions were as follows:

7. Extraction and Analysis methods (Cont.)

1 g air dry soil mixed with 1 g hydromatrix and packed into extraction tubes with glass wool plugs at either end. Samples are extracted at 40°C and 150 Atmospheres with 20 g CO₂/50% MeOH. Static extraction undertaken for one minute prior to continuous extraction at a rate of 1 g/min with the restrictor at 65°C and the Florisil trap at -5°C. The extract is then desorbed with 1.5 mL MeOH (trap at 50°C) at 0.7 mL/min and the trap washed with 5 mL MeOH at 2 mL/min. The extracts are collected in GC autosampler vials, ready for analysis using GC/MS. Prior to each duplicate set of samples a blank extraction (no sample) is undertaken to prime the extractor. A standard (sample spiked with known concentration of herbicide) is run every sixth sample (ie one blank, 2 samples each in duplicate, standard).

The method was tested against all herbicides used in the project and with four soil types of very different characteristics. The SFE extraction conditions were selected to maximise recovery of fortified herbicide residues from soil samples. Recoveries in excess of 80% (Goal, Authority) and 90% (Stomp, Command) were achieved. The method is robust (apart from mechanical problems with the equipment) and rapid, so offers considerable potential for screening soil samples for herbicide residues.

Testing of extraction efficiency from soils at different moisture contents revealed variability of recovery between samples. This variability prevented the use of soil samples that had not been air dried for the SFE procedure. Examination of sample recovery results suggested that the method (using the extraction conditions established for air dry soil) could not be used to estimate plant available herbicide pools within the soil.

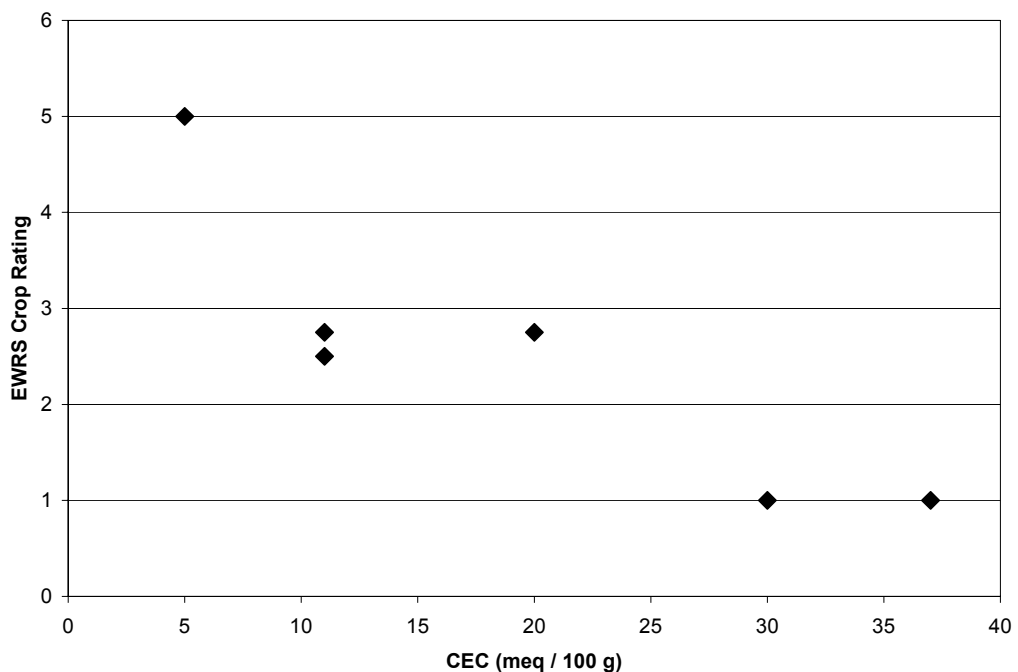
It was concluded that, while SFE works well for extraction of total herbicide residues from air-dry soil samples, the equipment available in the research laboratory was not sufficiently reliable to permit the method to be used routinely. In addition, the variability in extraction efficiency with differing soil moisture levels and inability to refine extraction conditions to select the plant available herbicide pool from soil samples, restricted the application of the method. Use of solvent extraction for total herbicide residue recovery, and 1:5 water extraction for recovery of the soil moisture herbicide pool, proved more reliable in this study.

8. Herbicide rate recommendations based on soil properties

Dimethenamid

Trials conducted with dimethenamid applied pre crop emergence in navy beans, green beans, processing peas, pumpkins, kabocha and sweet corn have shown that dimethenamid caused crop damage at the proposed label rates (675 - 1350 g ai/ha), at 4 out of 38 trial sites. All of these sites had low levels of both organic carbon and clay. Graphs 33 and 34 show the crop tolerance rating plotted against cation exchange capacity (CEC) for sweet corn, and green beans respectively. These graphs show the decreasing crop safety with decreasing CEC.

Graph 33 - Sweet Corn Crop Tolerance vs CEC (Dimethenamid 900 g ai/ha)



8. Herbicide rate recommendations based on soil properties

Graph 34 - Green Bean crop tolerance vs CEC (Dimethenamid 1350 g ai/ha)

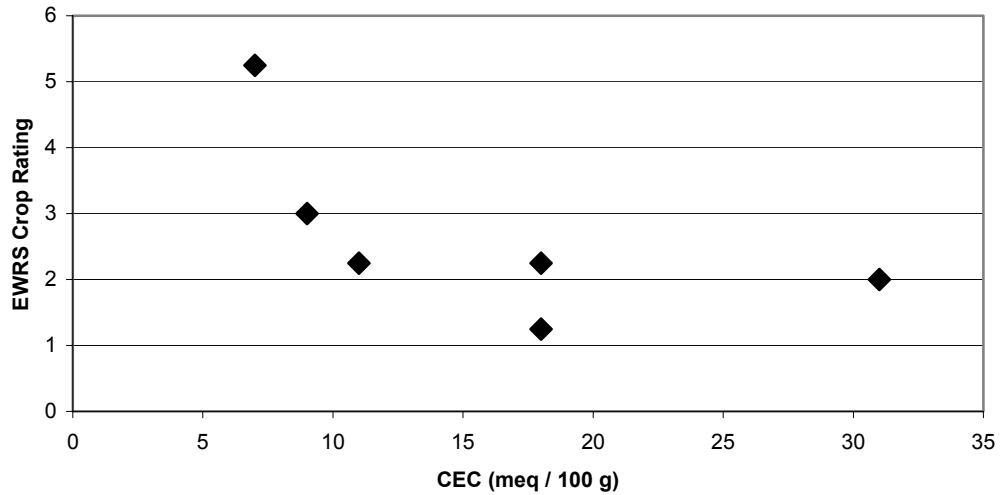


Table 13 - Dimethenamid application rates based on cation exchange capacity (CEC) of the soil

CEC (meq/100)	Dimethenamid Rate (g ai/ha)
<5	Do not use dimethenamid
5-9	675 g - 900 g
9-14	900 g - 1350 g
>14	1350 g

8. Herbicide rate recommendations based on soil properties

Table 14 - Dimethenamid application rates based on clay content and organic carbon content of the soil

Soil Texture	Clay Content	Organic Carbon Content	
		<2%	>2%
Sand, Loamy Sand, Silt	<10%	Do not use dimethenamid	750 mL - 1 L
Loam, Sandy Loam, Silt Loam	10-15%	750 mL - 1 L	1 L - 1.5 L
Sandy Clay Loam, Clay Loam, Silt Clay Loam, Silty Clay, Sandy Clay, Clay	>15%	1.5 L	1.5 L

1. Adsorption and Desorption Reactions

Laboratory studies were undertaken to quantify the adsorption and desorption reactions for clomazone, metribuzin and pendimethalin in four soil types. Differences in adsorption were recorded between herbicides and between soil types. The degree of adsorption was highest for pendimethalin and lowest for metribuzin. The sorption of each herbicide varied according to soil type, in each case increasing in the order kurosol, sodosol, vertosol, ferrosol. These results indicate that, at the same application rate, a greater amount of metribuzin would be found in the soil solution (plant available herbicide) than clomazone or pendimethalin, and availability would be greater for each herbicide in the kurosol and sodosol soils than the vertosol and ferrosol soils.

Metribuzin also tended to desorb more readily than the other herbicides, resulting in it being more likely to dissipate rapidly in the soil environment through leaching, microbial degradation or chemical breakdown reactions. Pendimethalin, which has a very low solubility in water, displayed a very low degree of desorption, indicating that the herbicide can persist in the soil for a long period but that only small amounts would be found in the soil solution where it can be accessed by plants. Major changes in soil moisture levels are likely to influence the amount of herbicide in the soil solution. Clomazone displayed a moderate degree of both adsorption and desorption in the kurosol and sodosol soils, suggesting that it may be retained in those soils following application but has the capacity to desorb and become available in the soil solution over time. The degree of desorption was lower in the ferrosol, indicating that persistence of clomazone in that soil was unlikely to pose a significant risk through carryover to following crops.

2. Sorption Reactions of Soil Fractions

The particulate organic matter (POM) fractions in all soils contained large amounts of relatively undegraded plant debris or phytoclast (PH) material. In addition, the POM fraction of the vertosol, and to a lesser extent of the kurosol, contained appreciable amounts of charcoal. As has been reported previously (Karapanagioti *et al.*, 2000), the presence of charcoal may explain the comparatively high K_d value (Table 2) and slow sorption kinetics (Graph 4) for clomazone on the vertosol POM fraction. In contrast, the presence of amorphous organic coatings (AOM) in the sand fraction of the kurosol provides an important sorptive site for rapid uptake of clomazone (Graph 4). The silt/clay fraction of the sodosol shown in Graph 4 exhibits an intermediate reaction rate for the uptake of clomazone, which is indicative of a clay/humic association (CM).

Clomazone sorption kinetics increased in the order of, slowest to fastest, clay < sand < POM. The relative contribution of each soil fraction to the sorption of clomazone by the whole soil is affected by the type and distribution of organic matter. Soil clay fractions with a lower C:N ratio (Table 1), and hence more humified organic matter, exhibit a greater affinity for clomazone (Table 2), whilst the readily accessible POM, which constitutes less than 2% of soil mass in all soils, contributes over 5% to clomazone sorption by each soil (Table 2). Clomazone also exhibits an apparent affinity for pure clay fractions, in particular the smectite clay fraction of the vertosol (Table 2).

General Discussion (Cont.)

The hydrophobic pendimethalin molecule has a very strong affinity for organic surfaces, with very rapid sorption kinetics in each soil fraction (Graph 5), and in particular POM. In all soil fractions, pendimethalin sorption had reached equilibrium before 4 hours, if not 2 hours. In addition, POM fractions exhibit large K_d values for pendimethalin, and contribute significantly to whole soil sorption (Table 2). Pendimethalin also shows greater adsorption to clay than sand fractions, which is most likely linked to the degree of humification of OM in the clay fractions.

Importantly, clay fractions treated to remove organic matter also exhibit a strong affinity for, and relatively slow sorption kinetics for, pendimethalin (Table 2 & Graph 5).

Clomazone and pendimethalin exhibit a strong affinity for clay/humic associations (CM), which may result in accumulation of residues in the clay rich ferrosol and vertosol. In addition, exposed organic surfaces such as POM provide a site for rapid strong binding of herbicide. It is likely that exposed POM surfaces and AOM coatings in sand fractions represent a labile pool of bound herbicide in each soil. Such of a pool of herbicide would be readily subject to desorption given mechanical disruption and/or increased soil moisture.

3. Dissipation of Herbicides under Field Conditions

Clomazone Dissipation

Clomazone was most preserved in the vertosol soil, which may be a consequence of the dry field conditions, and the documented sorption affinity of clomazone for smectite (Loux et al, 1989). Low soil moisture at time of application (7% and 9% moisture respectively) in the kurosol and sodosol, together with low pH, is likely to have limited microbial activity and may have contributed to herbicide persistence. The organic rich, porous ferrosol (55% porosity) with high levels of soil water (22%) is likely to have high levels of biological activity. The short half-life of clomazone is likely to have been due to irreversible binding or partitioning reactions in the soil.

Variations in half-life (Table 4) and dissipation curves (Graph 6) between the kurosol and vertosol, both of which were located at the same site, indicates that dissipation is linked to soil factors. Furthermore, similar dissipation rates in the two light textured soils (kurosol and sodosol), despite slight climatic variation, suggested that clomazone dissipation was strongly linked to soil properties. Given that clomazone degradation has been shown to proceed faster as pH increases (Anonymous, 1987), dissipation in the kurosol (pH 5.6) compared with the sodosol (pH 4.9) appears to be limited by soil moisture. Whilst soil moisture appears critical, the small variation in mean temperatures between all sites appears to have no significant influence upon dissipation.

The influence of soil moisture upon clomazone dissipation is also evident in the large drop in soil concentration between day 114 and 140 in the vertosol (Graph 6), in which time over 130 mm or 25% of the annual rainfall was received. Increased soil moisture has been shown to increase clomazone dissipation by promoting desorption from soil colloids and increasing rates of biological mineralization (Mervosh et al. 1995). In addition, it is possible that some movement of clomazone below the sampling zone occurred as a result of intense rainfall events.

General Discussion (Cont.)

Clomazone desorption showed hysteresis, as evidenced by the increasing values of the equilibrium ratio (C_s/C_w , where C_s is solid phase concentration and C_w is liquid phase concentration) with successive desorption steps. Desorption hysteresis indicates that the sorption process is not entirely reversible, and that bound residues may be present within a soil. The presence of bound residues has important implications for the assessment of chemical bioavailability, due to the theory that strongly bound residues are unavailable for plant uptake or degradation (Simms et al, 1991). In the experiment, those amounts of clomazone remaining after five desorption steps were considered to be bound residues. Importantly, the values of the equilibrium ratio for the partitioning of clomazone between solid and solution phases (C_s/C_w) vary between each soil. This is consistent with variations in clomazone sorption capacities according to soil type (Mervosh et al, 1995).

The availability of clomazone in the soil solution varies considerably over time between soils (Graph 6), which indicates that estimation of phytotoxicity cannot be based purely upon total soil concentration. Importantly, in the kurosol and sodosol, even small amounts of clomazone residue may cause phytotoxic effects long after application, whilst in the ferrosol and vertosol, aged clomazone residues appear to be unavailable in the soil solution.

Metribuzin Dissipation

Soil moisture conditions in the ferrosol at the time of application were high (22% water w/w) and rainfall figures show that considerable amounts of precipitation were received in the first weeks after application (Table 3). Soil moisture has been positively correlated with metribuzin dissipation in the past (Ladlie et al, 1976; Sharom and Stephenson, 1976; Savage, 1977; Gallaher and Mueller, 1996; Zimdahl et al, 1994), therefore a large portion of the rapid dissipation in the ferrosol could be attributed to soil moisture conditions. Given the comparatively weak sorption of metribuzin in soils (Harper, 1988; Peter and Weber, 1985) dissipation of metribuzin from the sampling zone (0-10 cm) would also have been accentuated by leaching. Likewise, the comparatively slow initial dissipation rate in the vertosol and kurosol could be attributed to conditions of low soil moisture.

Dissipation in the two light textured soils (kurosol & sodosol) again appears to be similar, as evidenced by the close proximity of dissipation curves. It is possible that an interaction of soil moisture conditions and soil pH have combined to produce similar dissipation rates in the kurosol and sodosol. Low soil pH has been shown to increase metribuzin sorption and decrease dissipation rates (Ladlie et al, 1976), which may be a factor in the sodosol (pH 4.9). The P_{ka} value for metribuzin is 1 to 1.1 (Ladlie et al, 1976; Weber, 1980), and below pH 3 the molecule begins to assume some positive charge (Harper, 1988). Given that the pH at soil colloid surfaces may be 2 to 3 pH units lower than in bulk solution, a proportion of metribuzin may be bound by cation exchange in soils with a pH less than 5.

Metribuzin sorption has also been strongly correlated with soil clay content (Harper, 1988), which, together with dry soil conditions, may explain the slow dissipation rate in the vertosol (Graph 7). The vertosol was the only soil studied to have detectable levels of metribuzin after 365 days ($0.06 \text{ kg ai ha}^{-1}$ or 16% of that applied). Metribuzin residue in the vertosol at this date was irreversibly bound with no detectable amounts in a soil solution extract. This would suggest that sorption is exerting a controlling influence upon dissipation in the vertosol, such that only labile metribuzin is subject to biodegradation.

General Discussion (Cont.)

Metribuzin is not considered to be strongly bound in soils, with reported K values of between 0.56 and 1.84 (Sharom and Stephenson, 1976; Harper, 1988). The calculated equilibrium ratios for each soil, of 2.6 (ferrosol), 1.4 (kurosol), 1.8 (sodosol), and 2.4 (vertosol), are therefore high in comparison with published values of partitioning between solid and liquid phases. Accordingly, the varied equilibrium ratio values reflect the different sorptive capacities, and desorption kinetics for metribuzin in each of the soils. The vertosol was the only soil examined to have detectable levels of metribuzin remaining after 365 days, at which date greater than 95% of the remaining metribuzin was present as bound residue.

Desorption into the soil solution can be related to both phytotoxicity and leaching. Metribuzin phytotoxicity has been shown to vary with soil type (Ladlie et al, 1976; Sharom and Stephenson, 1976; Savage, 1977), which may also differ from the actual dissipation rate. Savage (1977) found that metribuzin phytotoxicity disappeared more rapidly in a clay loam than sandy loam soil, whilst actual dissipation rate was faster in the sandy loam.

Laboratory trials indicated that the rapid drop off in clomazone concentration within a few days of application could not be explained by microbial degradation, leaching or volatilisation, so was thought to be due to binding and partitioning in the soil.

Pendimethalin Dissipation

The loss of pendimethalin from the soil surface following application may be factor in the rapid dissipation, as up to 17% of surface-applied pendimethalin has been reportedly lost by photodecomposition in 7 days (Parochetti and Dec, 1978). Whilst photodecomposition can be significant in the days following application, rates usually decrease rapidly after the first 7 days of exposure on the soil surface (Parochetti and Dec, 1978; Savage and Jordan, 1980). It is likely, therefore, that photodecomposition could have made a significant contribution to pendimethalin dissipation in the days following application in all soils examined.

Given the shape of dissipation curves (Graph 8) and the hydrophobicity of pendimethalin (Anonymous, 1987), it is likely that moisture has a large influence upon dissipation in all soils. In particular, the irregular dissipation rate observed in the vertosol and ferrosol (Graph 8) corresponds with periods of fluctuating rainfall (Table 3). The observed dissipation rate in the vertosol appears to be checked by the lack of soil moisture between days 42 and 70, when only 14 mm of rainfall was received at the vertosol site. Likewise, the corresponding dissipation rate in the ferrosol for the same time period appears to slow when only 19 mm of rainfall was received. The sodosol exhibits some variation in apparent dissipation rate, but not to the extent exhibited by the two clay rich soils.

Interestingly, pendimethalin exhibits a relatively constant dissipation rate over the study period in the kurosol, which is somewhat surprising, given the dry soil conditions at the site (Graph 8). It does, however, lead to the conclusion that variation in dissipation as mediated by soil moisture may be related to the sorption properties of each soil. Pendimethalin rate of loss from soils has been shown to decrease with increasing soil organic matter content (Walker and Bond, 1977), which is a likely result of high soil Koc values. Given the hydrophobicity of pendimethalin, fluctuations in soil moisture levels are likely to have a greater effect upon dissipation in soils with high levels of organic matter. Thus, in the current context, the mediation of dissipation rates by soil moisture may be largely a consequence of variation in desorption from soil colloids.

The role of soil moisture in pendimethalin desorption and bioavailability should not detract from the direct influence of soil moisture upon biological mineralisation rates. Biological degradation has been identified as the primary loss mechanism for pendimethalin in soils (Anonymous, 1987; Savage, 1978; Kulshrestha et al, 2000), with degradation rates increasing with soil moisture content.

4. Herbicide Movement and Degradation Processes

This laboratory study was undertaken to investigate herbicide loss or degradation reactions, concentrating on clomazone due to its persistence in soils.

The results indicated that clomazone leaching was not a significant cause of concentration loss in the soil, with less than 5% of the applied clomazone leaching more than 5 cm under saturated soil conditions. Differences in leaching capacity exist between different soil types, with greater potential for leaching of clomazone in sandy soils. Movement of clomazone as a volatile in the soil profile was also shown to be very minor, with very low concentrations migrating from a treated soil section in a soil core. Microbial degradation of both clomazone and pendimethalin were demonstrated, but the results of the trial comparing autoclaved and non-autoclaved soils suggest that this mechanism is unlikely to contribute to the short-term decline in herbicide concentration in soils following application. Wetting and drying cycles in clay soils may result in decreased herbicide availability, with the possible mechanism for this decline in availability being partitioning of herbicide to positions within the clay lattice from which it is unavailable for extraction.

The results indicate that availability of the herbicides in the soil is influenced significantly by moisture content and that the mechanism of this effect may be altered sorption reactions (binding and partitioning).

5. Agronomic Practices Influencing Herbicide Breakdown

Field trials and laboratory studies have shown that soil moisture is a critical factor in the breakdown of clomazone and pendimethalin.

Breakdown of oxyfluorfen did not appear to be influenced by soil moisture. Prior research on oxyfluorfen suggests that sunlight is a significant factor contributing to the breakdown of the herbicide.

Trials conducted over two seasons showed that cultivation did not increase the rate of herbicide breakdown. Cultivation does, however, reduce the herbicide concentration due to dilution of the herbicide within the soil profile.

6. Critical Concentration for Crop Growth

Trials were conducted over two years to investigate crop effects of herbicide residues in soils for six crops, poppies, swedes, onions, pyrethrum, squash and zucchini. Crop effects varied, depending on the crop and herbicide. In addition to the trials, three commercial crops (onions, poppies and swedes), showing obvious effects of suspected herbicide damage, were sampled and tested. Soil herbicide concentrations were measured using a 1:5 soil:water extraction, with analysis using GCMS.

In poppy trials, the critical concentration of pendimethalin correlated with the damage observed on a commercial crop. Results from the trial and commercial crop sampling have shown that pendimethalin levels above 300 ppb are likely to impact on crop vigour and yield.

No crop damage was observed in poppies or onions with levels of sulfentrazone up to 24 ppb.

In swedes, trial results showed the crop to be not affected by pendimethalin levels up to 463 ppb, and metribuzin levels up to 143 ppb. Results from a commercial crop tested for suspected pendimethalin damage did not correlate with trial results, and suggest that the crop damage was not caused by pendimethalin.

In onions, while trial results showed that the crop was tolerant to clomazone up to 193 ppb, a commercial crop exhibited minor damage symptoms at 420 ppb and significant damage at 493 ppb, suggesting that the critical concentration is around 420 ppb.

Squash vigour and yield was acceptable with oxyfluorfen up to 254 ppb, the highest rate tested. Zucchini exhibited significant crop yield differences at 134 ppb of oxyfluorfen. No delayed effect on fruit development was observed for zucchini over the six harvest dates.

Herbicide concentrations measured using the 1:5 (soil:water) extraction for recovery of the plant available herbicide pool, and subsequent analysis using gas chromatography and mass spectrophotometry, have shown to provide a reliable indication of crop yield responses in a number of crops in this study. It must also be considered that, for any given herbicide concentration, the crop response may vary due to other factors including plant stress, type and level of herbicide incorporation, soil type, and interaction with other herbicides.

7. Extraction and Analysis methods

Testing of extraction efficiency from soils at different moisture contents revealed variability of recovery between samples. This variability prevented the use of soil samples that had not been air dried for the SFE procedure. Examination of sample recovery results suggested that the method (using the extraction conditions established for air dry soil) could not be used to estimate plant available herbicide pools within the soil.

General Discussion (Cont.)

It was concluded that, while SFE works well for extraction of total herbicide residues from air-dry soil samples, the equipment available in the research laboratory was not sufficiently reliable to permit the method to be used routinely. In addition, the variability in extraction efficiency with differing soil moisture levels, and inability to refine extraction conditions to select the plant available herbicide pool from soil samples, restricted the application of the method. Use of solvent extraction for total herbicide residue recovery, and 1:5 soil:water extraction for recovery of the soil moisture herbicide pool, proved more reliable in this study.

8. Herbicide rate recommendations based on soil properties

A number of experimental and commercially used pre emergent herbicides in various crops throughout Australia show variations in crop safety and weed efficacy with soil type. Generally, tolerance to these herbicides is reduced and weed efficacy is greater on light textured soils compared to heavier textured soils.

As an example, replicated field trials conducted across Australia over a number of seasons with dimethenamid have shown that crop tolerance and weed efficacy is influenced by soil type. Soil colloids (organic matter and clay particles) are the key soil components that influence the availability of dimethenamid in the soil.

Cation exchange capacity (CEC) is the most accurate indicator of the degree to which dimethenamid will bind to the colloidal component of any soil, and hence the likelihood of crop damage on any given soil. Table 13 will be included on the label for users to determine the most appropriate use rate for different soil types based on their CEC. The most important issue will be restricting the use of the product on soils with a CEC of less than 5 meq/100 g, as trial results have shown that crop safety on soils with a CEC of less than 5 meq/100 g is often marginal to unacceptable.

A similar table has been prepared for clay content and organic carbon content. Unfortunately, rate recommendations based on these parameters are not as accurate as with CEC because different clay types have different CEC values. For example, clays such as smectite, which are common in the black clay soils in regions such as the Lockyer Valley, have a greater CEC than kaolinite clays, which are found in more weathered soils. Despite this, Table 14 has been developed as an alternative if CEC information is not available.

Information generated as part of this project was also used to develop guidelines for the use of the herbicide Command on different soil types in Australia.

Grower and Industry Information Sessions

Regular field days, conference presentations and industry seminars were held throughout the project (Table 15). These sessions were well attended by growers, agronomic staff and other researchers.

Product Development

Data generated as part of this project was used in the development of label recommendations for two new horticultural herbicides. The first of these herbicides is Frontier Optima (dimethenamid), which has been submitted to the National Registration Authority for registration in a number of horticultural crops in Australia, including green beans, cucurbits, processing peas and sweet corn. The second product is Command (clomazone), which is currently registered in a number of crops including poppies, potatoes, green beans, cucurbits and navy beans. The use of this product had to be reviewed in some of these crops due to interactions between soil type, crop safety and weed efficacy.

This information will be extended to end users via directions on the product label.

Publications

A range of written material was produced throughout the project, such as milestone reports, project updates and conference proceedings (Table 15).

Technology Transfer (Cont.)

Table 15 - Technology transfer activities

Date	Technology Transfer Activity
Field Days	
November 2001	Field day at trial site as part of the Forthside Vegetable Research Station open day.
February 2002	Representatives from BASF Australia Ltd viewed trial sites.
Conference Presentations	
December 2000	Two Papers presented at the New Zealand soil science society annual conference: (1) Clomazone dissipation in four Tasmanian top soils; (2) Clomazone desorption and estimated bioavailability in four Tasmanian top soils.
September 2002	Two papers presented at the 13th Australian Weeds Conference held in Perth: (1) Improved management of residual herbicides; (2) Distribution of the herbicides clomazone and pendimethalin in soils, and implications for activity and persistence.
	Paper published in the journal Weed Science, titled "Clomazone dissipation in four Tasmanian top soils".
Industry Seminars	
July 1999	Presentation at the Agricultural Research and Advisory Committee presentations – Devonport, Tasmania.
December 1999	Industry Forum – Devonport, Tasmania.
May 2001	Overview of the project presented at the Botanical Resources Australia Research and Development Committee meeting.
August 2001	Presentation at the Agricultural Research and Advisory Committee presentations – Devonport, Tasmania.
March 2002	Industry Forum – Devonport, Tasmania,
March 2002	Filed visit and presentation to Vegetable R&D committee members, Industry Development Officers and representatives from Horticulture Australia Limited.
July 2002	Presentation at Tasmanian Alkaloids Research Day.
August 2002	Presentation at the Agricultural Research and Advisory Committee presentations – Devonport, Tasmania.
Media Events	

April 2001	Radio interview conducted on the "Country Hour".
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Acknowledgments

Philip Brown, John Paul-Cumming, Richard Doyle, Ian Macleod and Phillip Frost conducted this project.

The assistance of Lyndon Butler and Vaughan Trebilco from the Forthside Vegetable Research Station, who provided the trial sites and assistance, is gratefully acknowledged.

Other Serve-Ag staff who contributed to this project included Matthew Sheriff, Brendan Finch, Rebecca de Courcy, Pam Cox, Peter Aird, Doug Green, Rodney Burn and Mary Trebilco.

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Appendix i - EWRS Scale (for crop tolerance)

RATING	% EFFECT	
1	0	Healthy plant
2	0.1 - 2	Very mild symptoms
3	2.1 - 5	Mild but clearly recognisable symptoms
4	5.1 - 10	More severe symptoms without necessarily an effect on yield
	-----	Limit of commercial acceptability
5	10.1 - 18	Reduction in yield expected
6	18.1 - 30	
7	30.1 - 45	Heavy damage to total kill
8	45.1 - 70	
9	70.1 - 100	

Appendix ii - EWRS Scale (for weed control)

RATING	%	EFFECT
1	100	Complete weed kill
2	99.9 - 98	
3	97.9 - 95	
4	94.9 - 90	
	-----	Limit of commercial acceptability
5	89.9 - 82	
6	81.9 - 70	
7	69.9 - 55	
8	54.9 - 30	
9	29.9 - 0	Little to no effect on weeds

The EWRS (European Weed Research System) scale is based on comparison of the treated plots with the untreated control plot. The aim is to assess as accurately as possible the decrease in the natural number of plants per weed species (still visible in the untreated plot). This decrease in the weed population corresponds to the action of the product. The EWRS scale is logarithmic, the intervals decreasing as the action increases. This enables detailed assessment in the range of effective herbicide action.

Reference: Puntener W. 1981. Manual for Field Trials in Plant Protection. Second Edition. Ciba-Geigy Limited, Basle, Switzerland.

Appendix iii - Herbicide Grouping

Herbicide grouping based on mode of action (Developed by Avcare)

Group	Mode of Action	Chemical Group
A	Inhibitors of acetyl CoA carboxylase	Aryloxyphenoxypropionate ("fops") Cyclohexanedione ("dime")
B	Inhibitors of acetolactate synthase	Sulfonyl urea Imidazolinone Sulfonamid
C	Inhibitors of photosynthesis at photosystem II	Triazine Triazinone Urea Nitrile Benzothiadiazole Acetamide Pyridazinone Phenyl-pyridazinone Uracil
D	Inhibitors of tubulin formation	Dinitroaniline Benzoic acid
E	Inhibitors of mitosis	Thiocarbamate Carbamate Organophosphorus
F	Inhibitors of carotenoid biosynthesis	Nicotinamide Triazole Pyridazinone
G	Inhibitors of protoporphyrinogen oxidase	Diphenyl ether Oxidiazole
H	Inhibitors of protein synthesis	Thiocarbamate
I	Disrupters of cell growth	Phenoxy Benzoic acid Pyridine
J	Inhibitors of fat synthesis	Alkanoic acid
K	Herbicides with diverse sites of action	Amide Organoarsenic Carbamate Aminopropionate Benzofuran Phthalamate Nitrile
L	Inhibitors of photosynthesis at photosystem I	Bipyridyl
M	Inhibitors of EPSP synthase	Glycine (glyphosate; glyphosate-trimesium)
N	Inhibitors of glutamine synthetase	Glycine

Appendix iv - Soil Water Status

Soil Water Status	BEHAVIOUR OF SOILS SUBJECT TO FIELD TEST		
	Sands, Sandy loams	Loams	Clay Loams, Clays
D - Dry	Will flow through fingers or fragments will powder.	Will not ball when squeezed in hand. Fragments will powder.	Will not ball when squeezed in hand. Fragments will break to smaller fragments or peds.
T - Moderately Moist	Appears dry. Ball will not hold together.	Forms crumby ball on squeezing in hand.	Will ball. Will not ribbon.
M - Moist	Forms weak ball but will break easily.	Will ball. Will not ribbon.	Will ball. Will ribbon easily.
W - Wet	Ball leaves wet outline on hand when squeezed, or is wetter.	Ball leaves wet outline on hand when squeezed, or is wetter. Sticky.	Ball leaves wet outline on hand when squeezed, or is wetter. Sticky.

Dry is below wilting point. Material becomes darker or a lower colour value when moistened.
 Moderately Moist is the drier half of the available moisture range.
 Moist is the wetter half of the available moisture range.
 Wet is at, or exceeding, field capacity.

These guidelines may not apply with sodic 2:1 clays, as, for example, they may be moderately moist but below field capacity.

Reference - McDonald, R.C. Isbel, R.F. Speight, J.G. Walker, J. and Hopkins, M.S. (1990) Australian Soil and Land Survey – Field Handbook 2nd edn. CSIRO Australia

Photographs



Photograph 1 (Site 6, 23/01/01) - Herbicide breakdown trial showing irrigated plots, buffer and unirrigated plots to left of photograph



Photograph 2 (Site 8) - Untreated (left), Stomp 1 L (middle) and Stomp 2 L (right) on poppies



Photograph 3 (Site 10, 17/10/00) - Stomp damage in a commercial poppy crop



***Photograph 4 (Site 9, 19/10/00) - Command damage in a commercial onion crop
No damage (left), minor damage (middle) and significant damage (right)***