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Grape and Wine
Research and
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Fate, dissipation and mobility of some persistent herbicides used in Australian viticulture

FINAL REPORT to
GRAPE AND WINE RESEARCH & DEVELOPMENT CORPORATION

Project Number: **UA 97/1**

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Summary

The environmental behaviour of a number of important herbicides registered for use in viticulture have been studied as a function of the properties of key viticultural soils.

In order to follow the fate of these herbicides in a variety of matrices including soil and soil-water a robust and efficient procedure for extracting and concentrating the low levels of herbicide involved was developed.

Photochemical degradation has been studied on soil and in water both with and without radical promoters. Each of the herbicides studied underwent photochemical transformation giving rise to photo-products. The toxicological and environmental properties of these photo-products were not further investigated.

The photochemical dissipation from water followed first-order kinetics. Enhancement of the rate of degradation was attempted using hydrogen peroxide in the presence of natural sunlight. No significant enhancement in rate was observed. Further work is necessary with cofactors such as organic acids in order to improve degradation of the herbicides under these conditions.

Dissipation of the herbicides from soil is an important factor governing the environmental persistence of agricultural chemicals. Dissipation followed first-order kinetics in all soils studied. Half-lives were generally longer than has been found in studies overseas for the same chemical. This finding underscores the importance of knowing the behaviour of herbicides under Australian/South Australian field conditions prior to their use. The half-lives for dissipation ranged from 300 days to 150 days indicating the potential for contamination of ground-water of grapes and wine.

Mobility of the herbicides in soil was studied initially in the Mountadam soil and as expected mobility in this light sandy soil correlated with the physico-chemical properties of the herbicides. Norflurazon was the most mobile herbicide under the conditions of this study.

A laboratory study was then carried out using monoliths of the six key viticultural soils identified by Cass's group. In this study mobility correlated well with soil organic matter. Once again norflurazon was the most mobile herbicide and demonstr4ated the greatest potential to contaminate ground-water.

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Background

The Wine Industry's Strategy 2025 and associated Five Year Plan identify, as one of the advantages enjoyed by the industry, a "clean, green physical environment". The Five Year Plan goes on to point out that "new vineyard investment will have to meet best practice parameters on, *inter alia*, cost efficiency, quality specification , environmental sustainability…". Indeed environmental management is mentioned as an important factor in the projected increase in grape production. The Strategy document subsequently identifies spray drift and the qualified use of agricultural chemicals as among some of the issues that have to be addressed.

Water is also seen as a priority issue in wine industry planning. Projected vineyard expansion will clearly create an additional demand for water, and that water must not contain any agricultural chemical residues that could impact on vines or potentially influence grape quality.

Weed control in broad-acre cropping enterprises using current herbicides has seen an increase in the occurrence of residue problems both in soil and water and adverse impacts on subsequent crops (depending on the rotation used). Control of weeds using herbicides is an important aspect of vineyard management. The use of herbicides, especially persistent herbicides, requires care and sufficient understanding of the factors affecting the fate and dissipation of herbicides if subsequent environmental problems are to be avoided and more particularly herbicide damage to vines eliminated.

Thoma and Hartley first drew attention to the lack of information on the environmental fate and behaviour of herbicides used in South Australia in their 1983 review. They clearly identified the need for studies related to the fate, dissipation and transport of agricultural chemicals used in viticulture in Australia, or in related fields such as horticulture and vegetable production. Almost every chemical they reviewed in their view required further study to determine its fate. Generally, Australian studies related to agricultural chemicals are concerned with the presence and/or level of residues in the commodity. Or, alternatively, the studies reported are concerned with the efficacy of the active ingredient in viticultural situations, as for example, the control of weeds in vines. Little work has been conducted on the persistence and fate of the pesticides in Australian vineyards in the period subsequent to pesticide application.

It is worth noting that the United States Environment Protection Authority (USEPA) has been critical of many U.S. studies on fate and mobility presented in support of registration of agricultural chemicals, because there was no definition of relevant soil parameters given, making transport of data to other sites impossible.

In studies where photochemical degradation was believed to be important, the USEPA was also critical of the failure to identify any photo-products produced and the failure to make an assessment of their environmental behaviour.

Objectives

(1) To determine the dissipation rates of several classes of persistent herbicides used for weed control in Australian viticulture as a function of soil parameters such as organic carbon content, clay content and pH in 5 key soil types. The herbicides being studied are: norflurazon, oxadiazon, oxyfluorfen and trifluralin and dichlofop.

(2) To assess the mobility of these herbicides through soil and into ground-water and hence their potential to contaminate farm dams.

(3) To develop rapid, robust and cost- effective analyses for these herbicides in soil and water matrices.

(4) To assess the importance of photodegradation (both direct and indirect photolysis) in the dissipation of these herbicides in water and on soil, and to discover whether photodegradation rates can be enhanced so that the possibility of reusing water contaminated with herbicide residues is minimised.

Introduction to the problem

The overall aim of this research work is to assess the fate, specifically mobility and dissipation, of several key persistent herbicides registered for use in Australian viticulture. The mobility into ground-water is being studied as a function of selected soil parameters such as pH and organic carbon content. Dissipation of each herbicide from soil and from dam-water is being followed in separate experiments.

The importance of photodegradation on soil surfaces and in dam-water as pathways for the dissipation of each herbicide is also being studied. The five herbicides chosen for this study represent different chemical classes so that information on the relative mobility as a function of chemical structure can be derived. A reference herbicide, trifluralin, has been included in the study on the because its fate in terms of dissipation and mobility are well recognised and it can therefore function as a convenient marker in our field work.

Consultation with staff at the National Registration Authority, and the Commonwealth Environment Protection Group, highlighted the fact that for the majority of pesticides used in Australia, the data on which registration is granted is obtained from overseas studies. An acknowledged problem with overseas studies is that the soils used and the climatic conditions involved are usually significantly different from those found in Australia. Hence the need for Australian studies to establish whether the mobility and dissipation follows pathways similar to those seen in the overseas studies.

The herbicides being studied, along with trifluralin as a reference chemical, are from different chemical classes and are listed in the "Agrochemicals Grid", published by The Australian Wine Research Institute, for use in all states. The chemicals selected for study were the pyridazinone – norflurazon, the oxadiazolone – oxadiazon, the diphenyl ether – oxyfluorfen, the phenoxyether – haloxyfop-R methyl ester and the dinitroaniline – trifluralin. Information from IAMA indicates that although the chemicals are used in each State, the patterns of use of each chemical are different for

each State. Nevertheless the results of this study will provide data on the environmental behaviour of each of the chemical classes which can be used in all States. The use of test chemicals from different chemical classes will allow general conclusions to be drawn regarding likely soil/water behaviour of any newer products belonging to that class that are released in the future.

Although the initial research work centered on the use of a typical sandy soil from the Barossa wine region, consultations with soils research staff from PISA (D. Maschnedt, pers. comm.) and staff from the CRC in Soils & Land Management (A. Cass, pers. comm.) identified 5 soil types with a range of pH's and levels of organic carbon and clay contents that are associated with viticultural production, which will be used in this study.

Research methodology

To investigate the mobility of the herbicides, pre-drilled plastic pipes, with the in-ground end sealed and the top capped with a removable cover, have been placed into the soil on the downslope side of the vine rows, in the intervine row area, in a rectangular pattern at Mountadam. Following application of the herbicides onto the soil at the appropriate field rates, the water flowing into the pipes from the soil profile, following rainfall, is removed at regular intervals for analysis by GLC - NPD. Sampling is continued until rainfall ceases and no further leachate is found in the pipes.

During this year it is planned to place additional pipes down the slope at Mountadam, along a more accurate grid, so that a better assessment of rate of movement can be obtained. Extending the study to include the mobility and dissipation in the key viticultural soils identified by Dr. A. Cass' group was a later addition to the present study. For these soils, the use of soil monoliths of the selected key soil types was adopted as the most appropriate methodology. The study was carried out by using square metal sections which were driven into the soil and subsequently removed by digging underneath the frame. Application of the herbicide being studied to each soil followed by application of simulated rainfall allows mobility through the soil column to be assessed. Profiles of the residual herbicide down the soil monolith was determined by sectioning the soil at the end of the "rainfall" and extracting the herbicide. Residue analysis was then carried out as described below.

The dissipation rate from each soil is assessed by coating each of the chemicals onto a TLC plate made from each soil and exposing the plates to sunlight for known periods of time. A chemical actinometer is used to measure quantum yields so that degradation rates can be related to sunlight intensity. Measurement of residual herbicide is determined by extracting the soil with water, solid phase extraction (SPE) of the aqueous solution, followed by analysis by GLC – NPD.

Dissipation of each of the herbicides from farm- dam water is followed by spiking a sample of water (Mountadam) in a borosilicate flask with the herbicide, exposing the flask to sunlight and analysing the solution for residual herbicide, again using solid phase extraction techniques for sample concentration. Analysis is carried out by GLC - NPD. Dissipation rate constants (and/or half-lives) will be calculated for each herbicide.

Photochemical degradation is studied by exposing each herbicide dissolved in dam-water to sunlight and using SPE techniques to extract and concentrate the photo-products produced. Identification of the photo-products will be done using the GLC - MS system available in the Faculty/University.

Results

Development of Rapid Analytical Methods

A robust, simple and efficient method of extracting herbicide residues and their metabolites from aqueous solutions such as dam water or leachate was developed using solid phase extraction with Sep-Pak® C_{18} solid phase extraction cartridges (adsorbent 500 mg, hold-up volume 3 cc). Essentially the solution containing herbicide residues was drawn through a conditioned cartridge at a flow rate of 2-5 mL/min. Following drying of the cartridge by passage of air for around 30 min., the adsorbed herbicide residues were eluted with 2 one mL volumes of methanol or ethyl acetate. The methanol (or ethyl acetate) eluates were combined and made up to 2 mL as required with the appropriate solvent for subsequent analysis by GLC, HPLC or GC-MS.

Recovery studies using all the herbicides separately and as mixtures showed that the technique gave recoveries of the herbicides from the leachates and from dam water at the part per billion level with efficiencies ranging from 90% to quantitative. The solvents used to elute the adsorbed herbicides from the cartridge could be changed to suit the analytical technique to be used.
No specialised apparatus was necessary to effect the extraction using the cartridges. The procedure was used in all facets of the research involving soil and soil-water (leachate) studies.

Photodegradation

Photodegradation was conducted using natural sunlight in order to mimic as closely as possible the behaviour of the chemicals in real viticultural systems. Photodegradation of the herbicides norflurazon, oxadiazon, oxyfluorfen and trifluralin was examined on soil plates and in pure water, natural water and water to which hydrogen peroxide had been added.

Photo-dissipation of herbicides from soil plates and from the water was conducted during the summer period. Residual herbicide levels were determined by extraction and analysis using GLC and defined time intervals. Kinetic analysis was used to determine the half-lives of each herbicide. The half-lives of the herbicides studied in both soil and the various water types are shown in Table 1.

Time	Media	Norflurazon	Oxadiazon	Trifluralin	Oxyfluorfen
February	Soil	5.53	4.65	3.53	5.19
February	Natural water	2.34	8.09	–	–
February	Milli-Q water	1.53	2.62	0.17	0.40
April		3.45	4.84	–	–
February	Milli-Q water with H_2O_2	1.59	2.44	–	–
April		1.94	5.30	–	–

Table 1. The half-lives (days) and kinetic parameters of the herbicides in water and on soil.

Photo-product isolation and identification experiments were also conducted in summer. Following exposure of each herbicide in water to sunlight, the photo-products were extracted using the SPE technique and subsequently analysed by GC-MS. Identification of the photo-products was by computer library-matching where this was possible or by examination of the ions produced on electron impact.

Photolysis of norflurazon produced three novel products which were identified as, de-chlorinated norflurazon, desmethyl-norflurazon and an isomer of norflurazon. Residual norflurazon was also detected. The structures are shown in Figure 2.

Oaxdiazon similarly produced three compounds on photolysis which were identified as, a de-chlorinated oxadiazon and two isomeric hydroxy derivatives of oxadiazon following de-chlorination. Again there was residual oxadiazon present. The structures of the products are shown in Figure 3.

Oxyfluorfen also underwent photodegradation giving rise to a compound which showed loss of the nitro group from the parent molecule, a second compound which showed loss of a chlorine from the parent herbicide and a third compound which was identified as a photocyclic dibenzfuran derivative. Figure 4 sets out the structures of the photo-products for oxyfluorfen.

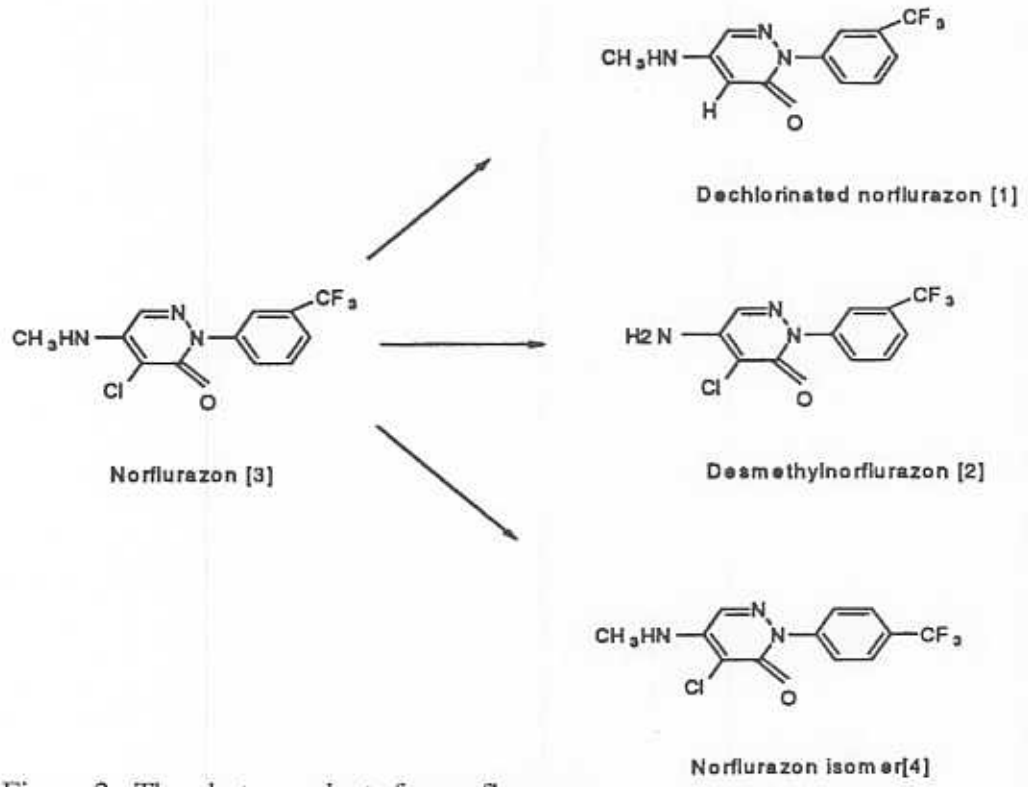


Figure 2. The photo-products for norflurazon.

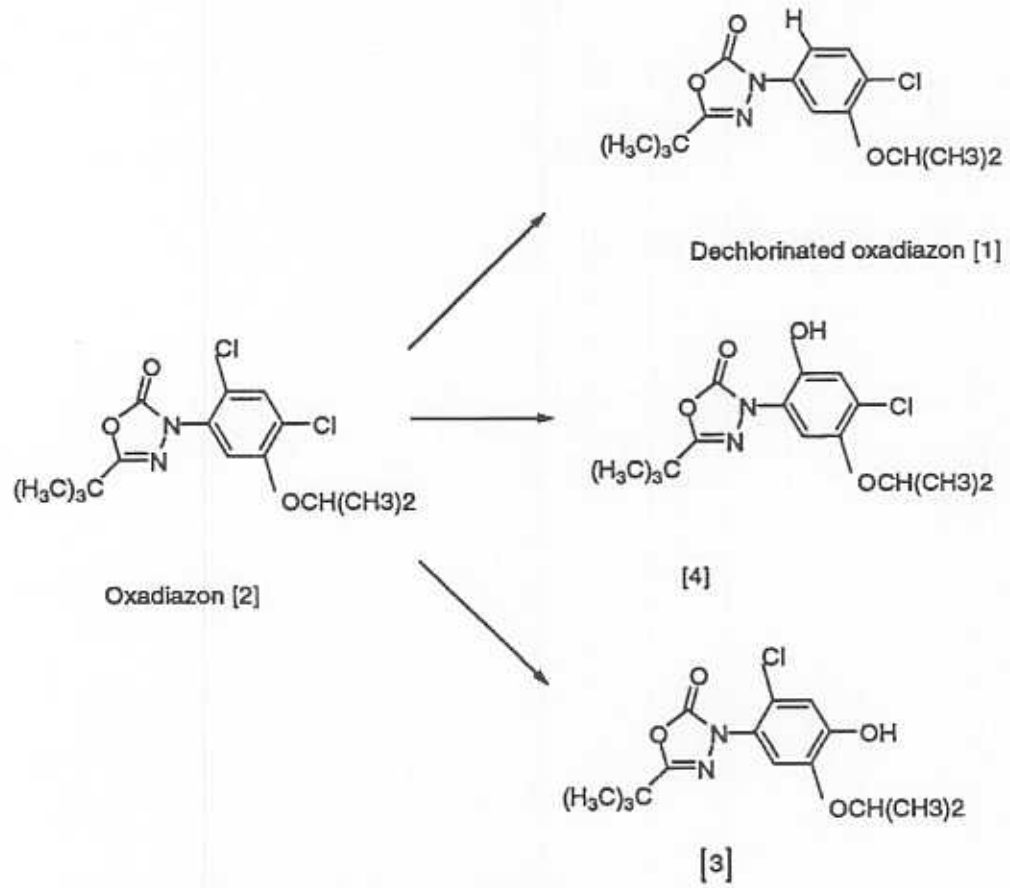


Figure 3. The photo-products for oxadiazon.

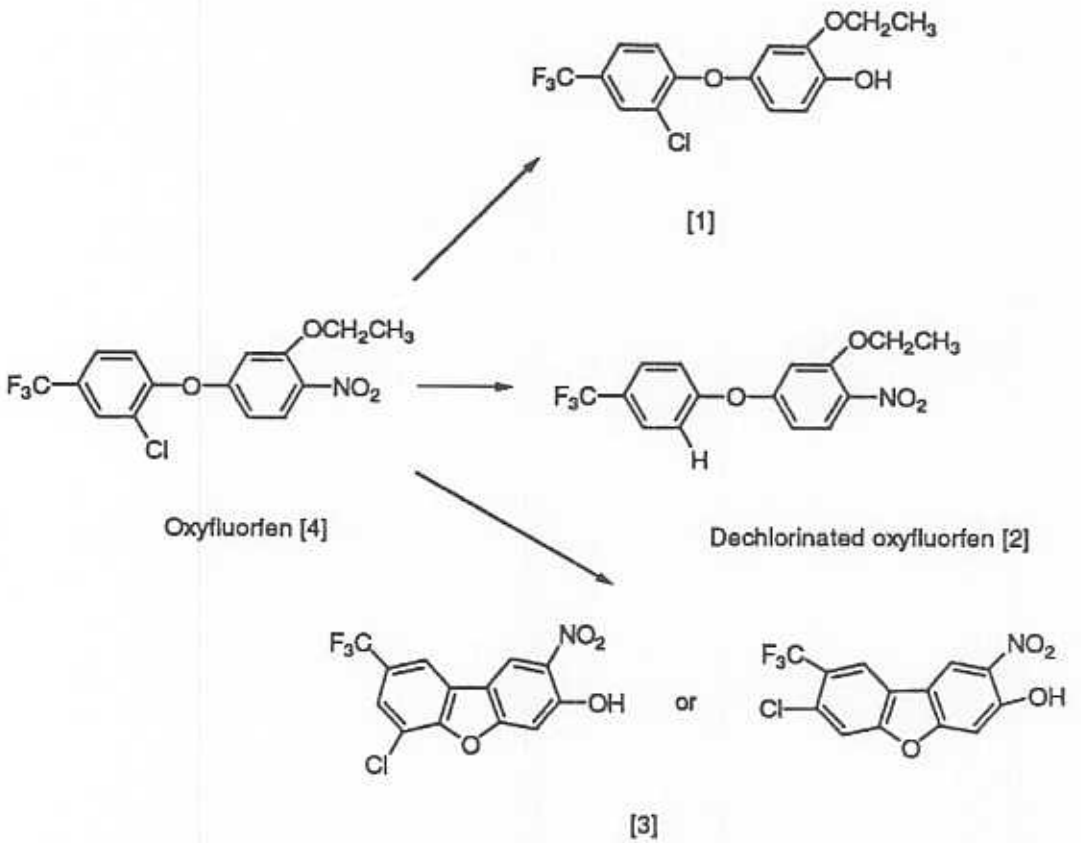


Figure 4. The photo-products for oxyfluorfen.

Dissipation of the herbicides from the key soil types

In the initial phase to validate the methodology, four herbicides were applied to sloping plots in the Mountadam vineyard at field application rates. The dissipation from the soil was then followed over a two-year period by sampling and residue analysis. The properties of the Mountadam soil are given in Table 2.

Soil type	Sand (%)	Silt (%)	Clay (%)	pH	Organic carbon (%)
Mountadam	92.5	4.5	3.0	4.7	0.86
Nuriootpa	87.5	5.0	7.5	6.5	0.52
Lyndoch	57.5	5.0	37.5	7.7	1.01
Tanunda	47.5	7.0	45.5	7.2	1.00

Table 2. The properties of some soils in the Barossa Region.

The measured rate constants for the disappearance of the herbicides from the Mountadam soil and the half-lives are shown in Table 3. The dissipation rates for the herbicides fitted first-order reaction kinetics.

Herbicide	Rate constant (k, week^{-1})		Half-life (weeks)	
	1996	1997	1996	1997
Norflurazon	0.0969	0.221	7.2	3.1
Oxadiazon	–	0.347	–	2
Oxyfluorfen	0.0422	–	16.4	–
Trifluralin	0.1778	0.1623	3.9	4.3

Table 3. The rate constants and half-lives for the dissipation of the herbicides from the Mountadam soil type.

Dissipation in the six key soil types was then studied using just two of the herbicides from quite different chemical classes. In these experiments, norflurazon and haloxyfop-R methyl ester were separately applied at field rates to each of the soils set out in large trays in a glasshouse. Soils were maintained under moist field conditions. Samples of the treated soil were taken at randomly selected sites over a period of 56 days and the residual herbicide determined by GLC or HPLC as appropriate following extraction of residues from the soil.

The relevant characteristics of the six key viticultural soils used in these experiments are set out in Table 4.

Soil type	pH	Organic matter (%)	Sand	Silt	Clay
			(%)		
Terra rossa	7.8	1.43	1	9	90
Terra nigro	7.0	0.72	91	8	1
Saprolite	5.7	2.07	40	55	5
Red-brown earth	6.7	1.25	9	10	81
Low organic matter sandy loam	6.5	0.81	71	19	10
Low clay sand	6.7	0.86	84	12	4

Table 4. The characteristics of the six viticultural soils.

The results expressed as time for dissipation (DT_{50}) of half the applied herbicide are shown in Table 5.

Soil type	DT_{50} (days)	
	norflurazon	haloxyfop-R ME and acid
Saprolite	300	135
Terra rossa	270	98
Red-brown earth	230	89
Low organic matter sandy loam	190	16
Low clay sand	160	7
Terra nigro	150	7

Table 5. The dissipation half-lives (DT_{50}) of norflurazon and haloxyfop-R methyl ester in six soils under laboratory conditions.

In order to account for possible losses due to microbial degradation, samples of each of the soils were autoclaved and the dissipation procedure repeated. The dissipation of each of the herbicides in the autoclaved soils is shown in Table 6.

Soil type	DT_{50} (day)	
	norflurazon	haloxyfop-R ME and acid
Terra rossa	280	143
Terra nigro	155	10
Saprolite	319	178
Red-brown earth	238	153
Low organic matter sandy loam	196	24
Low clay sand	167	11

Table 6. The dissipation half-lives (DT_{50}) of norflurazon and haloxyfop-R methyl ester in six autoclaved soils under laboratory conditions.

Mobility of the herbicides in the key soil types

The study as originally planned made use of lysimeters arranged on sloping plots in the Mountadam vineyard. The herbicides norflurazon, oxyfluorfen and trifluralin were applied to the plots at field rates on the up-slope above the lysimeters during two successive seasons. Leachate was sampled from the tubes every week throughout the rainy season or until no further leachate appeared in the lysimeter tubes. Leachates were again sampled in the next year following the fresh application of norflurazon and trifluralin and the first application of oxadiazon.

The average concentration of the herbicides norflurazon, trifluralin and oxyfluorfen in the water flowing into the lysimeters tubes over the sampling period is shown in Figure 5. Concentrations of norflurazon in the leachate ranged from 66 ppb to 1130 ppb. For trifluralin concentrations ranged from 1 ppb to 22 ppb and for oxyfluorfen concentrations ranged from 3 – 8 ppb. Norflurazon always had the highest concentration in the leachate while oxyfluorfen had the lowest concentration.

The average concentration of norflurazon, trifluralin and oxyfluorfen found in the lysimeter tubes correlated with the weekly rainfall as is shown in Figure 5.

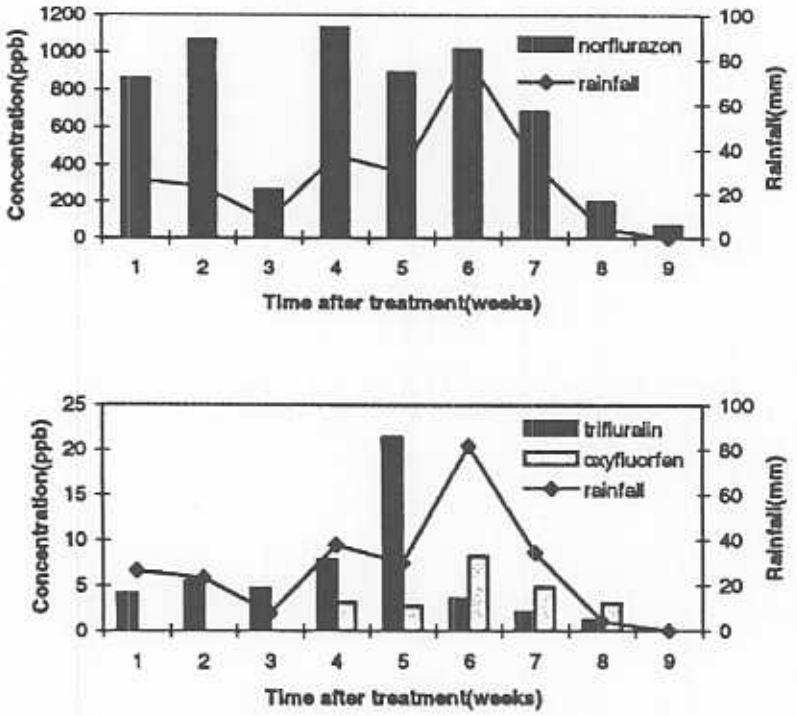


Figure 5. The concentration of herbicides in the lysimeter tubes at the Mountadam site superimposed on rainfall for the period.

The study of the mobility of norflurazon and haloxyfop-R methyl ester on the six key soil types was conducted using soil monoliths. The monoliths were sprayed with

herbicide at equivalent field-rates and irrigated to simulate "annual rainfall" for one week.
The concentration of norflurazon in the leachates from each of the six key soil types is shown in Figure 6.
The concentration of haloxyfop-R methyl ester in the leachates from each of the six key soil types is shown in Figure 7.

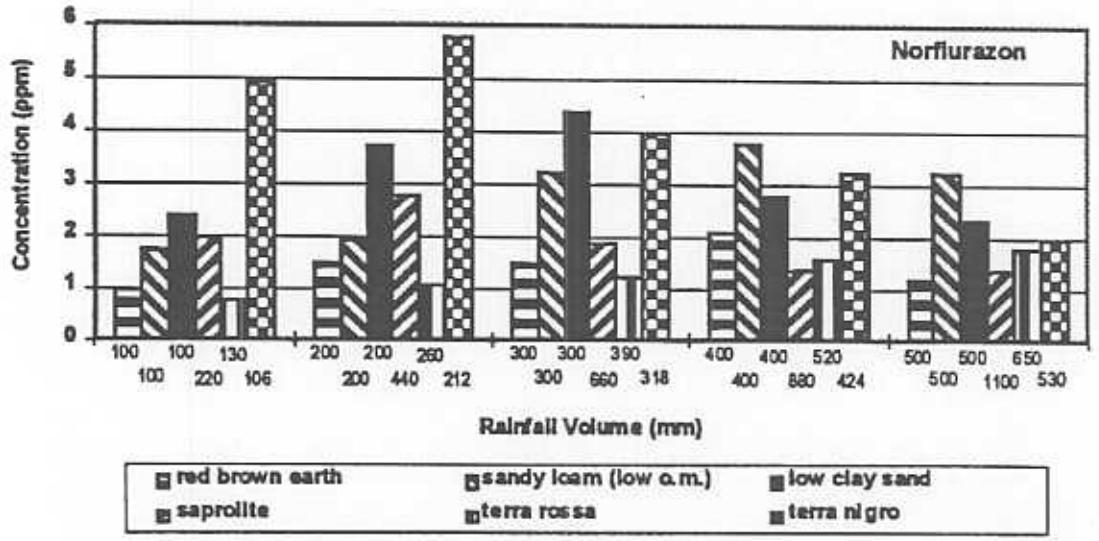


Figure 6. The concentration of norflurazon in the leachates from the six key soils.

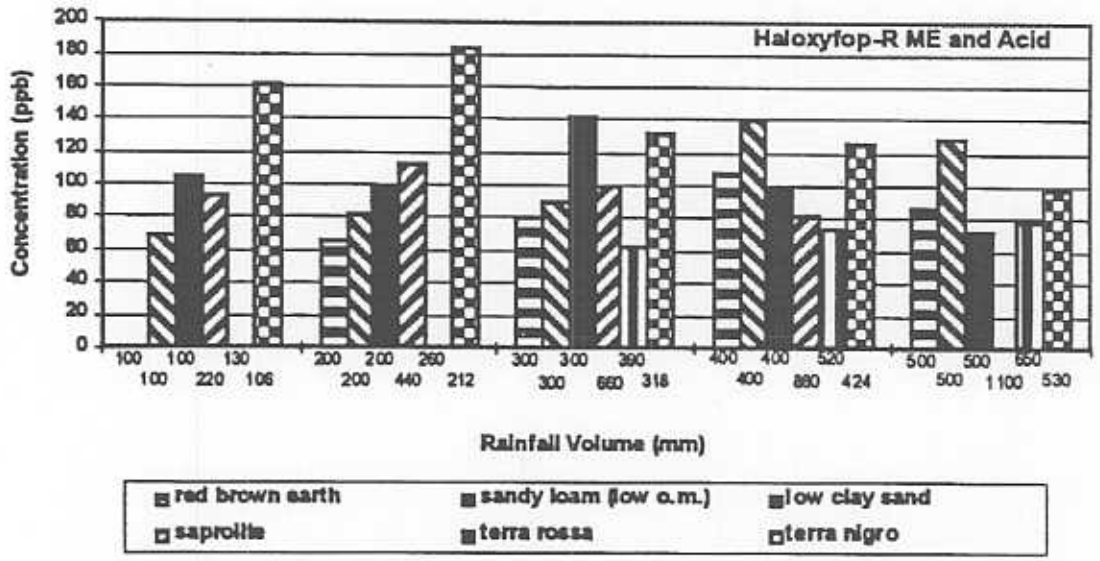


Figure 7. The concentration of haloxyfop-R methyl ester in the leachates from the six key soil types.

Discussion

Development of Rapid Analytical Methods

The analysis of herbicide residues in large numbers of water and soil-water samples requires access to rapid and efficient methods of residue extraction and concentration if necessary. The use of solid phase extraction cartridges provides a convenient and efficacious procedure for herbicide residue analysis. The procedures developed to underpin this study were robust, rapid, efficient and cost effective. Recoveries from water samples spiked at the part per billion level ranged from 90% to quantitative. The procedure was used in all leachate and mobility studies reported herein.

Photodegradation

There are two main aspects of the effect of natural sunlight on agricultural chemicals such as herbicides in water and on soil. The first aspect is that the photodegradation of the herbicide can lead to new chemicals which may have different behaviours in the environment compared with the parent. In addition, the toxicity and persistence may be quite different leading to unexpected and unplanned consequences.

The photodegradation studies reported on here have shown that each herbicide in water can be transformed into other chemicals which can be rationally related to the parent. The new chemicals produced on photo-irradiation are not necessarily predictable and actual studies are necessary to determine whether each chemical will photo-degrade under the environmental conditions found in South Australia.

Mass spectrometry allows identification of the compounds produced although resolution of ambiguity between possible isomers is not possible. Synthesis of the possible products would be required and this is beyond the scope of the present study.

The structures shown in Figures 2-4 are based on accurate masses and, where possible, on computer-based library matching of fragmentation patterns.

Photo-dissipation from soil is an important pathway leading to loss of the herbicide and which ultimately affects environmental persistence. The half-lives on soil for each herbicide were longer than in water. This is not unexpected as attenuation of sunlight by soil allows some herbicide trapped in the interior of soil particles to be protected from degradation by the sunlight. Half-lives on soil ranged from 3.5 days for trifluralin to 5.5 days for norflurazon. Losses from soil did not follow first order kinetics particularly well, and this observation has also been reported by other workers. The reduction in photolysis rates observed on soil compared with water reflects the greater attenuation of light in soil. In this study, the use of a relatively sandy soil low in organic matter, which is more transparent, will increase the rate of photolysis.

In water the rate of photolysis is much more rapid. In this study the rate of degradation of trifluralin and oxyfluorfen in pure water were 2 and 4.8 hours respectively. Norflurazon and oxadiazon were relatively slower with half-lives of 1.5 and 2.6 days respectively.

One of the issues associated with the use of herbicides is persistence, especially in situations where for example the herbicide has entered a waterbody. The use of environmentally benign agents that act to accelerate the photolytic degradation of is reasonably well established. In this project, the efficacy of hydrogen peroxide on the breakdown of the herbicides was examined. Previous studies on the enhancement of photolysis in the presence of hydrogen peroxide have shown increases in degradation rate of an order of magnitude. Our results show that the photolysis of norflurazon was not affected by the addition of hydrogen peroxide and that there was a minor increase in the rate of degradation for oxadiazon. Hydrogen peroxide photo-decomposes to give hydroxyl radicals and these in turn will degrade organic molecules. Further work is required to determine the conditions for effective use of hydrogen peroxide in remediation of water contaminated with herbicide.

Dissipation of the herbicides from the key soil types

The most important result from the research using the Mountadam vineyard soil type was the finding that the dissipation half-lives of the herbicides studied varied from 2 weeks to 16.4 weeks. Previous studies on typical soils in the USA had shown that the half-life for the dissipation of norflurazon was of the order of 20-35 days. Our study found that the dissipation half-life for norflurazon was of the order of 22–50 days. The dissipation half-life for oxadiazon in our study was comparable with the reported values at around 14 days. For oxyfluorfen however, our work showed that the dissipation half-life was of the order of 112 days compared with literature reports of 30-40 days. This represents a significant increase in persistence for this herbicide.

Dissipation and/or persistence are controlled by the chemical's physico-chemical properties and environmental factors including soil properties and climatic conditions. In order to assess the influence of soil type on the dissipation rates of the herbicides samples of the six key viticultural soil types, identified to us by Dr. A. Cass, were studied as outlined earlier. The herbicide in common with the preceding study was norflurazon with haloxyfop-R methyl ester being used as an example of a quite different chemical class. In the design of this latter study, the principal processes governing loss (dissipation) were degradation and volatilisation
The results show that the persistence of norflurazon for example was greatest on the saprolite soil (300 days) and least on the Terra nigro soil (150 days). The results show that dissipation was related to the soil's organic matter and not substantially affected by other soil parameters. Haloxyfop-R methyl ester showed similar behaviour with the range in persistence being from 135 days on the saprolite soil to 7 days on the Terra nigro.

In order to account for the contribution of micro-organisms to the dissipation of the herbicides, samples of each of the soils were autoclaved to destroy biological activity and the experiments repeated. The results showed considerable variation in DT_{50} (the time for half of the applied chemical to be dissipated). In each of the soils the persistence of the herbicides increased, as expected, suggesting that microbiological activity was significant and implicated in the dissipation of the herbicide. However the increases were generally modest and suggest that microbiological played a less important role in each herbicide's persistence than chemical processes.

The order of dissipation of both norflurazon and haloxyfop-R methyl ester in the six soils was
Saprolite < terra rose < red-brown earth < low organic matter sandy loam < low clay sand < terra nigro.

Mobility of the herbicides in the key soil types

The most important finding from this aspect of the research was the great mobility of norflurazon. In the studies conducted at the Mountadam site, each of the herbicides leached into the sub-surface water and reached the lysimeter tubes in the first year after application. Separate studies showed that each of the herbicides could be detected in the soil in the plots in the second year. However, only norflurazon was detected in the sub-surface water in the year following application. Furthermore, norflurazon was detected in lysimeter tubes some 7 metres from the plot on which it was sprayed, clearly demonstrating its very great mobility. Oxyfluorfen had the lowest concentration in the sub-surface water.

Generally the concentrations of each of the herbicides varied between the lysimeter tubes suggesting that preferential flow may be significant factor affecting the mobility of the herbicides in this sandy soil. Recent studies have shown that herbicides can quickly enter sub-surface water by infiltrating cracks, worm and root-holes and other macropores in sandy, unstructured soils.

The concentration of oxadiazon in the sub-surface soil was quite low which probably reflects its stronger absorption to soil compared with the other herbicides.
The concentrations of herbicides in the lysimeter tubes correlated with the rainfall from the preceding week.

When the mobility experiments were conducted on the six key viticultural soil monoliths, the concentration of norflurazon was relatively high in all soil leachates. The highest concentrations were found for the terra nigro soil and the low-clay sand than were found for the terra rose and red-brown earth. This result is in agreement with an earlier observation that norflurazon's mobility decreased as soil organic matter and clay content increased.

Compared with haloxyfop-R methyl ester, more norflurazon was found in the soil leachates and the lower sections of the soil monoliths after the leaching/mobility experiments which confirm the observation that norflurazon is the more mobile and leachable herbicide.

Since it is known that the potential of herbicides to contaminate ground-water (including sub-surface water) increases with increasing mobility and half-life, norflurazon has a greater potential than the other herbicides to contaminate ground-water.

Recommendations

More extensive field-based studies are required using all of these herbicides on the six key viticultural soils to provide a more extensive data set on leaching behaviour and mobility and hence persistence.

The photochemical studies involving the use of chemicals such as hydrogen peroxide to enhance photochemical degradation should be extended. Finding ways to enhance the production and action of naturally occurring chemicals such as hydrogen peroxide would be extremely useful should *in situ* remediation be required.

A major recommendation is that since the mobility and persistence is affected so significantly by soil organic matter it is important that viticulturalists be aware of or have data on the organic matter of their soil.

Intellectual Property

The research reported herein has been published in scientific journals but no intellectual property requiring protection in the form of patents and/or commercial in-confidence material was developed.

A presentation of this work was made to the Eden Valley wine grape growers meeting in December 1998.

Technical Summary

Apart from the residue extraction methodology developed in support of the chemical analysis reported herein, there are no other technical outcomes that require reporting.