THE ENVIRONMENTAL BEHAVIOUR OF HERBICIDES IN AUSTRALIAN VITICULTURE

by

GUANG-GUO YING
B. Sc. (Zhejiang University)
M. Sc. (The Chinese Academy of Sciences)

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Department of Environmental Science and Management
The University of Adelaide

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TABLE OF CONTENTS

ABSTRACT

Herbicides have been used widely in the control of weeds in South Australia vineyards. Due to the persistence and movement of the herbicides after application, they can cause some environmental problems. They may contaminate water through leaching and run-off . They may also damage vines and contaminate grapes and, in some cases, the wine made from contaminated grapes will also be contaminated.

This thesis reports on the results of a study on the environmental behaviour of several herbicides *viz.* norflurazon, oxadiazon, oxyfluorfen, trifluralin and simazine used in South Australian viticulture. The mobility and degradation of these herbicides were assessed through a combination of laboratory and field experiments. The fate of the herbicides from vine to wine was also investigated. A proposal for good environmental management of herbicide use in vineyards in order to minimise the effects of herbicide residues in the environment has been developed.

Sorption of herbicides is an important process that occurs in soils following application. The sorption coefficients of norflurazon, oxadiazon and trifluralin in several key soils from the Barossa Valley ranged from 3.48 to 5.27 for norflurazon, from 16.07 to 23.38 for oxadiazon, and from 189.63 to 310.78 for trifluralin. Trifluralin had high sorption on the soils while norflurazon had low sorption on these soils. Sorption tests on suspended sediments in water showed that higher percentages of the herbicides were sorbed under stirred conditions than under non-stirred conditions. Sorption of the herbicides on soils or suspended sediments was in the following order: trifluralin > oxadiazon > norflurazon. This study also showed that the herbicides could be strongly adsorbed by charcoal.

Laboratory studies on packed soil columns indicated that the decreasing order of leaching potential of the herbicides in soils was: norflurazon > oxadiazon . trifluralin > oxyfluorfen. The timing of rainfall or watering following herbicide

application had an effect on the leaching of the herbicides. The shorter the time interval between herbicide application and watering (or rainfall), the further and more quickly the herbicides (eg. norflurazon) moved in soil.

Laboratory studies on intact soil columns from the Mountadam, Nuriootpa and Koonunga vineyards showed that simazine and norflurazon leached from the sandy soil columns after two weeks of 20 mm “daily rainfall”. Distribution of herbicides in soil profiles after leaching clearly showed that norflurazon and simazine moved to the bottom of the soil columns while trifluralin, oxadiazon and oxyfluorfen remained mainly in the top of soil profiles (0-10 cm).

Leaching studies on dry intact soil columns from Kalimna and Koonunga Hill vineyards showed that norflurazon and simazine could leach out by rainfall or irrigation in clayey soils without wetting the soil columns before herbicide application. Non-equilibrium and preferential flow were believed to be responsible for the leaching of norflurazon and simazine in clayey soils. It is confirmed in this study that a herbicide mixture (norflurazon with other herbicides) reduced the leaching of norflurazon in soil. More norflurazon was leached from the intact soil column to which only norflurazon was applied than from the intact soil column with the mixed herbicides under the same conditions.

The dissipation rates of the herbicides in the field varied from one year to another. The dissipation half lives ranged from 2 weeks for oxadiazon to 16 weeks for oxyfluorfen in the Mountadam vineyard soil. Oxyfluorfen was the most persistent herbicide, while oxadiazon, trifluralin and norflurazon dissipated relatively faster in the soil. The distribution of herbicides in soil profiles after application showed that the herbicides (norflurazon, oxadiazon and trifluralin) stayed in the top soil layers before the onset of rain, and that they were leached in the soil profiles to different extents due to their different physiochemical parameters.

Herbicides in shallow groundwater following application were monitored using installed lysimeter tubes in the Mountadam vineyard. The herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) were detected in the shallow groundwater in the first year following application, while only norflurazon was detected in the following year. The concentration of norflurazon in groundwater was high, but the concentrations of oxadiazon, trifluralin and oxyfluorfen were relatively very low, ranging from several ppb to tens of ppb in the groundwater. The concentrations of the herbicides were correlated positively with the weekly rainfall. Norflurazon was found to be the only herbicide which moved laterally from a plot 7 meters away from the lysimeters.

Laboratory and field studies showed that simazine and norflurazon were relatively more mobile, and oxadiazon, trifluralin and oxyfluorfen less mobile in soils. the leaching potential of the herbicides in soil was in the following order: simazine > norflurazon > oxadiazon > trifluralin > oxyfluorfen. Movement of the herbicides could result from mass flow or from preferential flow and non-equilibrium partitioning through soil matrices as well as macropores.

The half lives for photolysis of the herbicides in soil ranged from 3.53 days for trifluralin to 5.53 days for norflurazon. However, the herbicides degraded more rapidly in water under sunlight. Trifluralin and oxyfluorfen photodecomposed very rapidly in de-ionised water with half lives of 2 hours for trifluralin and 4.8 hours for oxyfluorfen. Norflurazon and oxadiazon photodecomposed more slowly than trifluralin and oxyfluorfen, with half lives of 1.53 days for norflurazon and 2.62 days for oxadiazon in water. The addition of H_2O_2 in water did not have obvious effects on the photolysis of norflurazon and oxadiazon studied in water. However the photolysis of norflurazon and oxadiazon was retarded in natural water due to sunlight attenuation by organic and inorganic matter in water. Several photoproducts were identified by GC-MS after photolysis of each herbicide (norflurazon, oxadiazon and oxyfluorfen) in water under sunlight. The photochemical pathways mainly involved the loss of small functional groups such as chlorine atoms, methyl and nitro groups.

The study on herbicide residues on red and white grapes from the Roseworthy Campus vineyard and the Nuriootpa Research Station showed that norflurazon and oxadiazon dissipated much more slowly than oxyfluorfen and trifluralin on grape

surfaces. Trifluralin and oxyfluorfen were not detected in grapes from Roseworthy Campus vineyard 4 days after treatment, but remained in red grapes from Nuriootpa Research Station vineyard as long as one week. Norflurazon and oxadiazon residues remained in grapes for as long as one month. White grapes were found to retain more herbicide residues on their surface than red grapes due to the different textures and surface waxes of red and white grape surfaces. About 14 % of norflurazon was found to have penetrated into grape flesh in the white grapes, while only 1.47 % of norflurazon penetrated into grape flesh in the red grapes.

Treated and untreated red grapes from Nuriootpa Research Station vineyard were used to make wine at the Roseworthy Campus winery. This facet of the study showed that the herbicides *viz.* norflurazon, oxadiazon, trifluralin and oxyfluorfen did not have obvious effects on fermentative microflora. Oxadiazon, oxyfluorfen and trifluralin degraded more rapidly in red wine than did norflurazon. The herbicides, except for norflurazon, were not detected after 24 days, but norflurazon was present in the finished wine. Herbicide contaminated wine could be cleaned up using charcoal with diatomaceous earth during wine making processes, or with a cellulose pad before bottling.

Finally, arising out of the results of this research, some suggestions on good environmental management in viticulture were proposed, these included: (1) choose appropriate herbicides and use the minimum dosage, (2) properly apply the herbicides, (3) avoid damage to vines and contamination of grapes, and (4) avoid damage to the environment. In order to reduce possible leaching of herbicides in soil, it is better to choose less mobile and rapidly degraded herbicides. Caution should be exercised in using mobile herbicides such as simazine and norflurazon in sandy soils. Herbicides should not be applied either on rainy days, or when there will be rain in the following several days after application. Herbicides should also not be applied too close to grape harvest in order to avoid contamination of grapes in vineyards. Before applying herbicides, such factors as herbicide properties, soil type, weed species and weather conditions need to be considered.

DECLARATION

This thesis contains no material that has been accepted for the award of any other degree in any university, and, to the best of my knowledge and belief, it contains no material previously published or written by another person, except when due reference is made in the text.

I consent to allow this thesis to be borrowed or copied, any information contained herein cited elsewhere provided the author is duly acknowledged.

GUANG-GUO YING

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LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Since World War II, the use of pesticides, especially herbicides has increased substantially in agriculture. Of the total pesticide use, roughly 70%, 20%, and 10% by weight are accounted for by herbicides, insecticides and fungicides respectively in the United States (Pimentel *et al.*, 1991). Similarly, in Australia, herbicides comprise more than half of the amount of pesticides used, with insecticides and fungicides next in importance. For example, of the South Australian total pesticide chemicals used in 1986-87, the largest groups are herbicides ($ 46 million), insecticides ($ 7.3 million) and fungicides ($ 6.3 million) (Environmental Protection Council of South Australia, 1988). These chemicals have contributed to increased crop yields and have decreased production costs in many cases. A large proportion of the herbicides in South Australia are applied to horticultural and viticultural crops to control weeds instead of mechanical tilling. However, the application of chemicals can affect the quality of soil and water and the natural environment. Moreover, residues of some chemicals can remain in the soil and water following application, or on produce after harvest. For instance, analyses of water samples from the Piccadilly Valley in South Australia have indicated comparatively high levels of certain pesticides, including insecticides, herbicides and fungicides (DDT, DDE, TDE, Lindane, Chloropyrifos, Parathion, Endosulfan, Chlorothalonil, Vinclozolin, Chlorthal-dimethyl, and Propyzamide), of which the herbicides were detected at the highest levels with chlorthal-dimethyl at 17 μg/l and propyzamide at 28 μg/l (Environmental Protection Council of South Australia, 1988). This is particularly of concern as the Piccadilly Valley is situated within the catchment of Mount Bold Reservoir, a storage for Happy Valley Reservoir which supplies unfiltered water to about 40% of metropolitan Adelaide.

South Australia is an important wine producing area in Australia. Many herbicides are registered for use in weed control in vineyards. Norflurazon, oxadiazon, trifluralin, and oxyfluorfen are some common soil-applied residual herbicides registered for use in vineyards. They belong to four different chemical classes: norflurazon - pyridazinone, oxadiazon - oxadiazolone, trifluralin - dinitroaniline and oxyfluorfen - diphenyl ether. The terms "soil-applied," "residual," and "preemergence" refer to herbicides that have to be applied on the soil's surface before germination and /or growth of weeds. Application of residual herbicides must be followed by rainfall, sprinkler irrigation, or mechanical tillage to incorporate the herbicides into the top 1 to 2 inches of soil where weed seeds germinate. Properly applied residual herbicides can persist from a few months to a year or more. The use of these herbicides may also create problems because of their persistence in the environment, and they pose a potential threat to the human health and natural environment. Therefore knowledge about the fate of these herbicides in the environment is highly desirable.

1.2 HERBICIDE PERSISTENCE

In order to assess the potential hazard posed by a herbicide and to determine optimum levels for use, we need to understand the chemistry and behaviour of that substance in the environment. One of the key factors determining the availability and potential movement of a herbicide is its persistence in soil. The time between the application and degradation of a chemical is known as persistence which in turn depends on its chemistry and the surrounding environment. Herbicide persistence may be beneficial where long-term weed control is desired. On the other hand, the persistence may be hazardous because it increases the possibility of poisoning non-target organisms and the chances for the herbicide to move into surface waters and groundwater.

Some studies have examined the persistence of some herbicides like norflurazon, oxadiazon, oxyfluorfen and trifluralin. Braunschweiler (1992) studied the persistence of several pesticides including trifluralin, methabenzthiazuron, metazachlor, iprodione, fenitrothion, fenvalerate and furathiocarb in cultivated clay, fine sand and organic soils at Jokioinen, Southern Finland in 1985-88; and found that trifluralin was the most persistent of the pesticides. Residues of trifluralin on the surface of peat soil were still high 1.5 years after treatment (Braunschweiler, 1992). Eleftherohorinos and Kotoula-Syka (1990) also reported the field persistence of herbicides (dinitramine,ethalfluralin, trifluralin and pendimethalin) in soils planted to cotton in Greece. Their three year study indicated that trifluralin and pendimethalin had longer persistence than dinitramine and ethalfluralin, and that all the herbicides persisted longer in soils with higher organic matter and clay content. Golab *et al.* (1979) investigated the degradation of trifluralin in soil under natural conditions over a three year period, and isolated 28 transformation products. None of the isolated transformation products exceeded 3% of the initially applied trifluralin. Jolley and Johnstone (1994) have studied trilfuralin degradation in three Victorian soils under field and laboratory conditions and found that trifluralin degradation increased with both increasing moisture and increasing temperature. All of these studies showed that trifluralin is a very persistent herbicide. Moreover, occurrence of trifluralin in water systems has often been reported (Willis *et al.*, 1983; Spalding *et al.*, 1994; and Donald and Syrgiannis, 1995).

There are a few reports on norflurazon, oxadiazon and oxyfluorfen (*eg*. Hubbs and Lavy, 1990; Ambrosi *et al.*, 1977 and Frank *et al.*, 1991). Schroeder and Banks (1986a and b) evaluated the persistence of norflurazon in five Georgia soils and found that cool and /or dry environmental conditions combined with higher soil organic matter content caused slower herbicide loss. This result is similar to that of Jolley and Johnstone's (1994) study. Oxadiazon also transformed slowly in soils and was postulated to adsorb strongly on soil organic matter (Ambrosi *et al.*, 1977 and Carringer *et al.*, 1975). Surface water contamination can be caused by runoff loss of herbicides. Shiraishi *et al.* (1988) examined pesticides such as oxadiazon, isoprothiolane, diazinon, IBP, simetryn and thiobencarb at ppb levels in Lake Kasumigaura, Japan, caused by surface runoff from rice paddy fields. Southwick *et al.* (1993b) reported the runoff losses of norflurazon from subsurface-drained land planted to soybeans in southern Louisiana and found a direct relationship between time after herbicide application of runoff-producing rainfall and the magnitude of pesticide loss in runoff.

Application of herbicides may contaminate not only the water system but also crops (food). Some researchers have reported oxyfluorfen and its amine residues in garbanzo beans (Zhou and Miles,1991); trifluralin residues in carrots (D'Amato *et al.,* 1993 and Mortimer *et al.,* 1994); residues of oxadiazon and its metabolites in peanuts (Bingham *et al.,* 1980), and in green and dry hops and hop foliage (George, 1982). All the above studies show that the persistence of herbicides has brought about some environmental problems. The persistence of many pesticides depends very much on the surrounding environment including climate, soil and crops. Parathion can be used as an example. This compound has a half-life of about 78 days on citrus crops, 3-6 days on apples, and 2 days on alfalfa (Gunther and Jeppson, 1960). It is also found that the persistence of herbicides depends on the extent of physical removal processes such as leaching, runoff and evaporation, as well as decomposition. Different herbicides differ greatly in their susceptibility to these processes and this is reflected in a wide variation in their persistence. Therefore, understanding the behaviour of herbicides in the environment could help solve the problems caused by their persistence.

1.3 THE PROBLEM

Herbicides such as norflurazon, oxadiazon, trifluralin, simazine and oxyfluorfen have been widely used in the vineyards of Barossa Valley and other areas in Australia. The Barossa Valley is Australia's largest and most famous viticultural and wine-producing area. It has a unique environment with a Mediterranean type climate and sandy soil features. Herbicides play an important role in grape production of Australia, but their residues may cause environmental problems. Their mobility through soil has allowed them to migrate into groundwater; runoff loss of herbicides may also contaminate surface waters. Water is seen as a priority issue in wine industry planning. Water must not contain any herbicides or other pesticides that might impact on vines and / or influence grape and wine quality.

On the other hand, herbicide residues in soils may also injure vines and / or reduce the yield of grapes. They might also persist during vinification and affect wine quality. Pesticide residues have been detected in the grapes and wines of many wine producing countries (Cabras *et al.,* 1995a and 1987; and Watterson, 1991), and most of them were widely used fungicides and insecticides. But some herbicides such as paraquat, diquat, oxadiazon, glyphosate and simazine were also listed by Watterson as known "nasty and possibly hazardous" pesticides used on grapes with some insecticides and fungicides (Watterson, 1991). Therefore, the use of herbicides requires sufficient understanding of their dissipation and movement in the environment. Unfortunately, little research has been undertaken on the behaviour of herbicides under Australian field conditions. The wine industry is so important to the Barossa Valley as well as to Australia that it is necessary to understand the factors affecting the fate of herbicides in Australian vineyards.

1.4 THE OBJECTIVES OF THE THESIS

The aim of this research is to investigate the fate of some persistent herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) used in Australian viticulture, which includes the following aspects:

(1) mobility of these herbicides in soil;
(2) photodegradation of these herbicides in soil and water;
(3) residues in grape and wine; and
(4) factors determining the dissipation of these herbicides in the environment.

An understanding of the mobility and retention of herbicides in soil is essential if we are to understand their hehaviour in the vineyards. There is a need to understand the leachability of herbicides in vineyard soils. The Barossa region was chosen as the study area due to its important position in the Australian wine industry. The mobility of herbicides will be obtained from the studies on the leaching of these chemicals in soil both in the laboratory and the field.

Because of the hot and dry climate in summer of South Australia, the sunlight-induced transformation of herbicides on soil and in water is important in determining the environmental fate of these widely distributed chemicals. For this reason photolysis of these herbicides on soil surfaces and in water under sunlight will be investigated. Degradation of a herbicide does not necessarily mean that its toxicity potential is eliminated since its degradation products can still be toxic. From an environmental point of view, we need to know how fast a herbicide will degrade. We also need to know the way in which it degrades so that we can evaluate the potential hazards from any of the degradation products.

In order to study the effect of possible grape and wine contamination caused by herbicide application, we will study the degradation of herbicides on grape surfaces and in wine made from contaminated grapes. Wine samples will be analysed at different intervals to see how rapidly these herbicides degraded during fermentation. Through the studies on mobility, degradation and fate of possible residues in wine, we can better understand the factors affecting the dissipation of these herbicides in Australian viticulture. As a corollary, it may be possible to find ways to clean or remediate the herbicide residues in soil, water and wine.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Once an agricultural chemical has been applied, physical, chemical and biological processes determine its fate and persistence in the environment. Some common processes are included in the following:

1. Sorption and desorption to soil and retention by crops and crop residues;
2. Volatilisation;
3. Leaching and runoff in either dissolved or sorbed state; and
4. Degradation, including biodegradation, chemical degradation (e.g. hydrolysis); and photolysis under sunlight.

The relative importance of each of the above processes depends on the physio-chemical nature and toxicological properties of the chemicals and prevailing environmental conditions (Weber and Miller, 1989). In order to reliably predict the environmental behaviour of chemicals, we need to understand the processes occurring in the environment and the factors influencing these processes. The chemicals whose environmental fate is the subject of this study are four herbicides: norflurazon, oxadiazon, trifluralin and oxyfluorfen, and, when used, simazine is mentioned in some sections. This chapter presents an overview of the physiochemical properties of the herbicides and sets out some of the processes such as sorption, transport and degradation of herbicides in the environment.

2.2 HERBICIDE PROFILES

2.2.1 *Norflurazon*

Norflurazon is a pre-emergent herbicide used to control many grasses and broadleaf weeds. Cotton, cranberries, and many fruit and nut tree crops have a practical crop tolerance for norflurazon. Its principal tradenames are, 'Evital' (Sandoz), 'Solicam' (Sandoz), 'Zorial' (Sandoz).

Norflurazon is categorized as a photosynthesis inhibitor due to its ability to inhibit the biosynthesis of carotenoids. Following root absorption, the compound is effectively translocated to growing portions of susceptible plants. Norflurazon causes light-grown seedlings to emerge with chlorotic leaves and to then die following exhaustion of food reserves (Tomlin, 1994; and Ashton and Crafts, 1981).

Norflurazon is of relatively low toxicity environmentally, both to humans and to other animals. It is not irritating to the eyes or skin. The acute oral lethal dose for 50% of the population, or LD_{50} for rats is > 9000 mg/kg. The LC_{50} (lethal concentration 50) for catfish and goldfish is > 200 mg/l (Tomlin, 1994).

Norflurazon is the common name of this herbicide and it belongs to pyridazinone family. Its IUPAC and C.A. names are 4-chloro-5-methylamino-2-(α,α,α-trifluoro-*m*-tolyl)pyridazin-3(2*H*)-one and 4-chloro-5-(methylamino)-2-[3-(trifluoromethyl)phenyl]-3(2*H*)-pyridazinone respectively, and it has a molecular formula of $C_{12}H_9ClF_3N_3O$. Purified norflurazon is an odourless white to brownish gray crystalline powder. It is stable in aqueous solution (< 8 % loss after 24 days at 50 °C) and under alkaline and acidic conditions (Tomlin, 1994). It is soluble in water and many organic solvents (Table 2.1), but it is sparingly soluble in hydrocarbons. Its octanol/water partition coefficient (K_{ow}) is relatively low.

2.2.2 Oxadiazon

Oxadiazon is a herbicide with both pre-emergent and post-emergent activity against grasses and broadleaf weeds in rice, turf, orchards, cotton, vines, soybeans, sunflower, sugarcane, onions and peanuts. Its tradename is 'Ronstar' (Rhone-Poulenc).

Oxadiazon may be translocated to the roots in very susceptible species when it is applied postemergence (Humburg *et al.,* 1989). The mechanism of exposure action is through contact by affecting the young shoot as it grows through the treated zone (preemergence) and by complete coverage (postemergence).

Table 2.1 Physio-chemical properties of the herbicides studied*

	Norflurazon	Oxadiazon	Trifluralin	Oxyfluorfen
Molecular weight	303.7	345.2	335.3	361.7
Melting point (°C)	174-180	87	48.5-49	85-90
Vapor pressure (mPa)	0.0028	<0.1	9.5	0.0267
K_{ow}	280	63100	187000	29400
Solubility (in water, mg/l)	28	1	0.221	0.116

* Data in this table are adapted from Tomlin (1994).

Oxadiazon has been shown to be mildly irritating to eyes and negligibly irritant to skin. The acute oral LD_{50} for rats is >5000 mg/kg and the acute LD_{50} for mallard ducks and bobwhite quail are >1000 mg/kg and 6000 mg/kg respectively. The LC_{50} for fresh water fish is >2 ppm for all species tested (Humburg *et al.,* 1989 and Tomlin, 1994).

The IUPAC and the C.A. names of oxadiazon are 5-*tert*-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3*H*)-one and 3-[2,4-dichloro-5-(1-methylethoxy)phenyl-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2(3*H*)-one respectively, with a molecular formula of $C_{15}H_{18}O_3N_2Cl_2$. In pure form it exists as colourless, odourless crystals. It has low solubility in water at 1.0 mg/l at 20 °C while it has high solubility in organic solvents such as in methanol and ethanol about 100 g/l (Tomlin, 1994). There is negligible loss of oxadiazon due to volatilization under normal field conditions because of its low vapor pressure (Table 2.1).

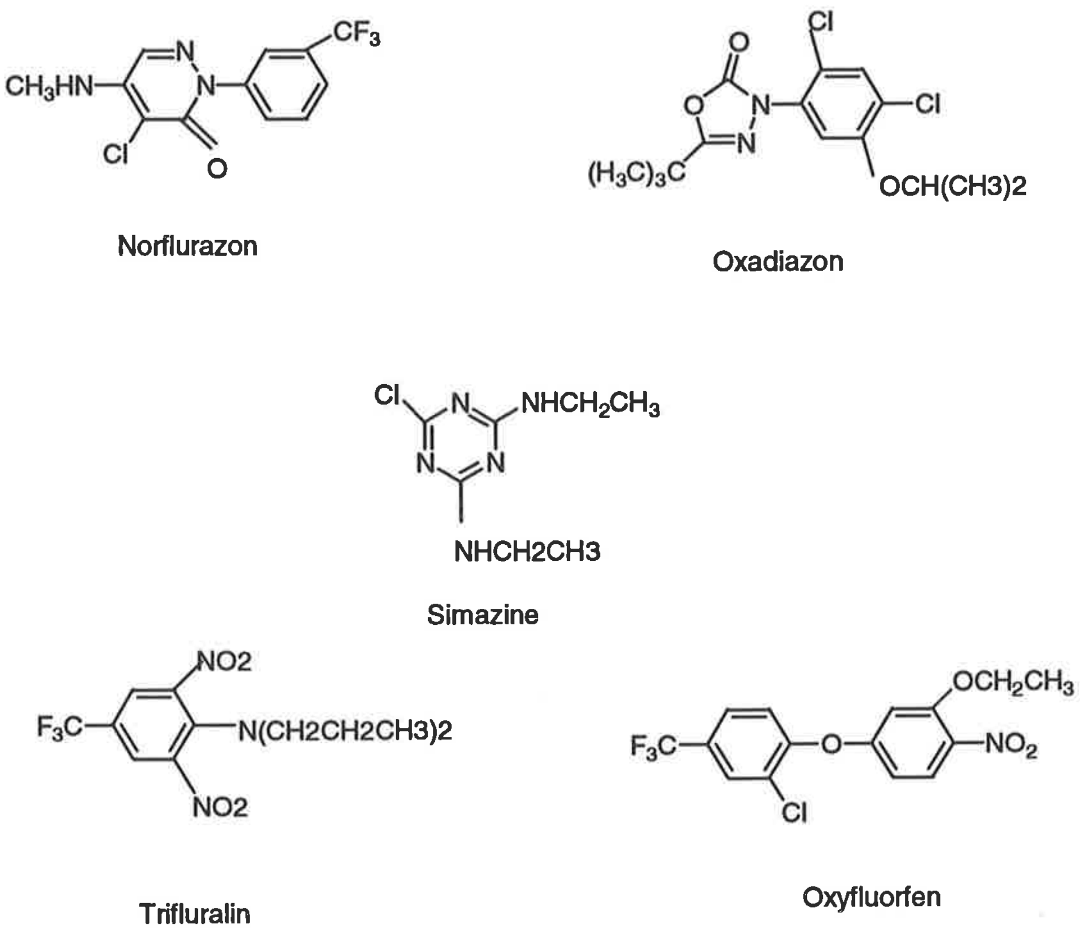


Figure 2.1 Chemical structures of herbicides

2.2.3 Oxyfluorfen

Oxyfluorfen is a selective pre-emergent and post-emergent herbicide for weed control in a variety of agronomic, viticultural, horticultural and tropical plantation crops. It is a contact herbicide and light is required for it to affect the target plant. There is very little movement within treated plants. It is not readily metabolized in plants, but since it is not readily absorbed through root systems, plant residues are exceedingly low (Humberg *et al.,* 1989). Its principal tradename is 'Goal' (Rohm & Hass).

Oxyfluorfen is highly toxic to aquatic invertebrates, freshwater clams, oysters, aquatic plants, wildlife and fish. The oral LD_{50} for technical oxyfluorfen in rats is 5000 mg/kg and >5000 mg/kg in dogs while the dermal LD_{50} on rabbits is >10000 mg/kg (Meister, 1992 and Tomlin, 1994).

Oxyfluorfen belongs to the diphenyl ether class. Its IUPAC name is 2-chloro-α,α,α-trifluoro-*p*-tolyl-3-ethoxy-4-nitrophenyl ether and its C.A. name is 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene with $C_{15}H_{11}ClF_3NO_4$ as its molecular formula. Oxyfluorfen is a white to orange or red brown semi-solid with a smoke-like odour. It may decompose by UV irradiation but it is stable under normal temperatures and pressures. Oxyfluorfen is nearly insoluble in water (0.1 ppm) (Table 2.1) but readily soluble in most organic solvents e.g. 72.5 % in acetone. Oxyfluorfen is strongly adsorbed on soil and shows negligible leaching with an organic carbon sorption coefficient (K_{oc}) from 2891 (sand) to 32,381 (silty clay loam) (Tomlin, 1994).

2.2.4 Trifluralin

Trifluralin is a selective preemergence dinitoaniline herbicide used to control many annual grasses and broadleaf weeds in tree fruits, vegetables and grain crops. There is no significant absorption or translocation of trifluralin in crops grown in soils treated with trifluralin. Trifluralin acts by entering the seedling in the hypocotyl region, and disrupting cell division and also inhibits root development. It has many tradenames such as 'Treflan', 'Tri-4', 'Trust' and 'Elancolan'.

Trifluralin is not acutely toxic to test animals by oral, dermal or inhalation routes of exposure. But it is toxic to fish and other aquatic organisms when directly added to water containing fish (Humburg *et al.,* 1989). The acute percutaneous LD_{50} in rabbits is >5000 mg/kg while LC_{50} (96 hour) is 0.01-0.04 mg/l for young rainbow trout and 0.02-0.09 mg/l for young bluegill sunfish (Tomlin, 1994). The USEPA considers trifluralin and oxyfluorfen to be possible human carcinogens (US Environmental Protection Agency, 1989 and 1992).

The IUPAC name of trifluralin is α,α,α-trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine while the C.A. name is 2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine with the molecular formula of $C_{13}H_{16}F_3N_3O_4$. Trifluralin is a yellow to orange crystalline material. It will decompose under sunlight but it is stable under normal temperature and pressure. Its octanol/water partition coefficient (K_{ow}) is 67900 at pH 6-7.5 and 20 °C (Table 2.1), so it is strongly adsorbed by the soil. Trifluralin has a very low solubility in water (0.221 ppm at pH 7) but a high solubility in organic solvents such as acetone and chloroform (>1000 g/l). It is volatile with a relatively high vapor pressure (Table 2.1).

2.2.5 Simazine

Simazine is a selective triazine herbicide widely used to control broadleaf weeds and annual grasses in the field, berry fruit, vegetable and ornamental crops, in turfgrass and in orchards and vineyards. Following root absorption it is translocated acropetally in the xylem, accumulating in the apical meristems and leaves of plants. The mechanism of action of this herbicide is by inhibition of photosynthesis (Humburg *et al.*, 1989).

Simazine is highly toxic if inhaled, moderately toxic if ingested and slightly toxic via dermal exposure. The oral LD_{50} for technical simazine in rats and mice is > 5,000 mg/kg while the dermal LD_{50} in rabbits is 3,000 to 10,000 mg/kg.

Simazine belongs to the 1,3,5-triazine class. Its IUPAC name is 6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine and its C.A. name is 6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine. Some of its physiochemical properties are: vapor pressure 2.94 μPa (25 °C), water solubility 6.2 mg/l (20°C) (Tomlin, 1994).

Simazine is persistent and it does not adsorb strongly to soil (K_{oc} = 138 ml/g). In combination with a lengthy soil half-life (36 to 234 days in sandy loam), these factors suggest that simazine is likely to contaminate groundwater (Alva and Singh, 1990). Under normal field conditions, loss of simazine on soil due to photodegradation and volatilization is insignificant (Humburg *et al.*, 1989). However, microbial degradation in soils probably accounts for the decomposition of a significant amount of simazine.

2.3 SORPTION

2.3.1 Sorption mechanisms

Sorption is considered to be one of the major processes affecting the interactions occurring between pesticides and the solid phase in the soil environment and it also influences the magnitude of the effect of other processes directly or indirectly (Khan, 1980). The main constituents representing the solid phase in soil are organic matter, clay minerals, oxides and hydroxides of aluminium and silicon. Clay and organic matter are the two major components of significance to sorption in soil. There are two types of clay minerals: the 1:1 type clay, such as kaolinite; and the 2:1 type clay, such as montmorillonite and vermiculite. The latter type minerals have a higher cation exchange capacity and higher surface area, thus having a higher sorption of chemicals on it. Soil organic matter plays an important role in the sorption process. It contains nonhumic and humic substances. Nonhumic materials include proteins, carbohydrates, waxes, pigments and other low molecular weight compounds which comprise a relatively small percent of the soil organic matter content. Humic substances are highly polymerized, high molecular weight materials which are commonly divided into three categories: fulvic acid, humic acid and humin.

Soil organic matter has an intimate association with inorganic components of soil, including layer silicate clay minerals and hydrous iron and aluminium oxides. Surface area studies (Burford *et al.*, 1964) indicated that organic matter associated with clay in the clay-organic matter complex is able to prevent access of nitrogen gas molecules to many of the clay surfaces. Dudas and Payluk (1969) found that while organic matter occupied the edges and surfaces of the clay minerals studied by them, no interlamellar adsorption was detected. Walker and Crawford (1968) have observed the importance of organic matter - clay complexes in the sorption process ,and also found that up to 6% organic matter content, both mineral and organic surfaces are involved in sorption. However, at higher organic matter contents, sorption will occur mostly on organic surfaces (Walker and Crawford, 1968). All these studies show that sorption of pesticides is closely related to the organic matter content in the soil.

Sorption occurs when the free energy of the sorption reaction is negative: $\Delta G = \Delta H - T\Delta S$. The free energy of a sorption reaction can be negative because of the enthalpy term or because of the entropy term or due to the contribution of both. The enthalpy term is primarily a function of the difference in bonding between the adsorbing surface and sorbate (solute) and bonding between the solvent (water) and the solute. Enthalpy related sorption forces include London van der Waals, Coulombic-electrostatic, charge transfer, π bonds, hydrogen bonding, ligand exchange, dipole-dipole or orientation energy, induction or dipole-induced dipole and chemisorption (Hassett and Banwart, 1989). The entropy term is related to the increase or decrease in the order of the system upon sorption. Hydrophobic sorption tends to be entropy driven process. *Hydrophobic sorption is the partitioning of nonpolar organics out of the polar aqueous phase onto hydrophobic surfaces in the soil* (Hassett and Banwart, 1989). The nature of the surface on the different particles in the soil varies widely. The hydrophobic surfaces are mainly due to the organic matter in the soil and may also be due to the Si-O-Si bonds at the mineral surfaces. The " like dissolves like" rule can be used to help explain the sorption of nonpolar compounds (Brusseau and Bohn, 1996). Organic matter in soil is generally less polar than water and provides a more favorable environment for nonpolar pesticides. Thus nonpolar pesticides prefer to associate with the soil organic matter. Sorption of nonionic (nonpolar) pesticides has a clear correlation with the soil organic matter content.

2.3.2 *Sorption isotherms*

Sorption is a process by which pesticide molecules transfer from mobile phase (liquid or vapor) to stationary phase (soil particles). Sorption can be described by using sorption isotherms. The most commonly used mathematical expression of a sorption isotherm is the Freundlich equation, which defines a nonlinear relationship between the amount sorbed and the equilibrium solution concentration:

$$S = K_f C^n \tag{2-1}$$

where S is the concentration of pesticide sorbed by the soil (mg/kg); K_f is the Freundlich sorption coefficient (l/kg or ml/g); C is the equilibrium solution concentration (mg/l) and n is a power function related to the sorption mechanism. When the value of n is unity, we have the simplest linear isotherm:

$$S = K_d C \tag{2-2}$$

where K_d is the sorption coefficient (ml/g). The parameter K_d is frequently used to characterize the sorption of pesticides in soils and is an important parameter governing the mobility of pesticides in the soil system.

Many studies show that the sorption of pesticides closely depends on the organic content in the soil. By normalizing sorption from a total soil basis to an organic carbon basis, we define a new coefficient , the organic carbon sorption coefficient (K_{oc}):

$$K_{oc} = K_d \,/\, \%\text{organic carbon} \tag{2-3}$$

The organic carbon sorption coefficient (K_{oc}) is generally regarded as independent of soil for nonpolar pesticides. On this basis, the K_{oc} value of a pesticide can be estimated from empirical relationships with its water solubility or octanol-water partition coefficient (K_{ow}). Some empirical equations are described in the literature (Rao *et al.*, 1983; Chiou. 1989; Hassett and Banwart, 1989; and Weber and Miller, 1989). Karickhoff et al. (1979) obtained the following equations from the measured data of 10 nonionizable hydrophobic organics:

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \tag{2-4}$$

$$\log K_{oc} = -0.54 \log S + 0.44 \tag{2-5}$$

where K_{ow} = octanol-water partition coefficient, and S = water solubility (mole fraction × 10^9).

The sorption coefficient is measured at equilibrium. But it cannot represent the partition mechanism at work in a real situation (Bilkert and Rao, 1985; and Pignatello and Huang, 1990). Considerable advances have been made in the study of the kinetics of sorption recently (Brusseau and Rao,1989; Hamaker *et al.*, 1996; and Li *et al.*, 1996). A two-stage model has been proposed to explain the sorption of pesticides in soils. This model assumes at least two kinetically different processes: a relatively fast labile sorption followed by slow diffusion into nonlabile sites (Li *et al*, 1996). The relationship between the phases is defined by:

$$C \leftrightarrow S_1 \leftrightarrow S_2$$

where C, S_1 and S_2 represent the solution phase, the labile sorbed and nonlabile phases respectively (Li *et al.*, 1996; Turco and Kladivko, 1994; and Gerstl, 1991). Labile uptake of pesticides has been treated as an instantaneous process, described by a sorption isotherm. An initially fast sorption of pesticides by soils is followed by a second stage that is much slower and apparently irreversible and it is suggested that the pesticides slowly diffuse into the interior of the soil particles (Brusseau and Rao, 1989; and Hamaker *et al.*, 1996). This nonlabile sorption phenomenon is readily observed by using a recently developed online microfiltration--high-performance liquid chromatography system (MF-HPLC). Li *et al.* (1996) used this technique to study the atrazine sorption by a mineral soil and found that the uptake of atrazine can be partitioned into labile and nonlabile contributions. The labile sorption capacity is 0.40×10^{-6} mol/g while that of nonlabile binding sites is $< 10^{-4}$ mol/g (Li *et al.*, 1996).

Sorption hysteresis (*i.e.* nonreversible adsorption) has been widely reported. Turin and Bowman (1997) studied the sorption behaviour and competition of bromacil, napropamide and prometryn. Their results showed all three herbicides displayed apparent sorption hysteresis and also suggested that sorption nonlinearity and competition may increase field-scale transport velocities by 10% or more. Studies on the sorption-desorption of imazamethabenz on three Spanish soils (Carton *et al.*, 1997) showed a two-step profile, with a fast initial adsorption during the first few hours followed by a slow adsorption during the remainder of the concentration range studied, and also showed an important hysteresis phenomenon. Hence, hysteresis is demonstrable and it can be explained by the two-stage model. Hysteresis has an influence on the fate and transport of a pesticide.

Oxyfluorfen has a strong tendency to adsorb to soil particles and is nearly insoluble in water (Tomlin, 1994; Fadayomi and Warren, 1977). Once oxyfluorfen is adsorbed to soil particles, it is not readily removed.

There have been a few studies on the sorption of the three herbicides norflurazon, oxadiazon and trifluralin in soils. Wehtje *et al.* (1993) have evaluated the sorption of oxadiazon in three "soil-less" media and a mineral soil at concentrations between 0.1 and 100 mg/kg. Its sorption was not influenced by absorbent type or by oxadiazon concentration. Sorption of diuron and norflurazon in Florida citrus soils has been investigated and it was found that their sorption was influenced by soil properties (Reddy *et al.*, 1992; and Alva and Singh, 1990). Francioso *et al.*

(1992) studied the sorption of atrazine and trifluralin in selected soils and found their sorption was influenced by organic matter as well as inorganic components in the soil. The K_{oc} data of norflurazon, oxadiazon and trifluralin have been given in several papers (Alva and Singh, 1990; Reddy *et al.*, 1992; Hubbs and Lavy,1990; Francioso *et al.*, 1992; and Wauchope *et al.*, 1991); but there is considerable variation in the reported data. Many studies show that organic matter is the predominant component governing the behaviour of nonionic pesticides, but the significance of sorption on mineral surfaces should not be ignored, especially in soils with low organic contents. Different behaviour is observed when herbicides are applied to mineral soils with low organic matter content or to sandy soils with low sorbing surfaces (Grover, 1974). Since the hydrophobic sites associated with mineral surfaces are not covered by organic matter in low organic matter soils and hence can contribute to the sorption, the K_{oc} values might be in error. The soil samples used in the present study are low in organic matter. In order to better understand the mobility of these herbicides in the soils, it is necessary to first study the sorption of these herbicides on these low organic matter soils characteristic of Australian vineyards.

The herbicide contamination of water systems has been of major concern in recent years. An understanding of the sorption of herbicides onto some solid materials could be used to solve this problem. Activated carbon and clay minerals have been studied for their ability to remove pesticides such as DDT (Carollo,1945), 2,4-D (Aly and Faust,1965), parathion, endrin, dieldrin and lindane (Robeck *et al.*, 1965), diquat and paraquat (Faust and Zarins, 1969; Weber *et al.*, 1965) from water. Sorption of several chemicals on clay minerals (bentonite and sepiolite) and activated carbon has been investigated (Gonzalez-Pradas *et al.*, 1983; 1993 and 1997). Gonzalez-Pradas *et al.* (1997) have studied the adsorption of atrazine from aqueous solution on natural and activated bentonite. Their experiments indicate that acid-treated bentonite is effective in removing atrazine from water. Grover (1974) investigated the sorption of trifluralin, triallate and diallate on several sorptive surfaces. Sorption was very high on activated charcoal, and least on montmorillonite. These results are widely used in water treatment plants. However, if dams, lakes and rivers near vineyards for example are contaminated by pesticides, cleanup of the water by using activated carbon and clay minerals may not be practical or economical. However because of the strong sorption of nonpolar pesticides in soil, it may be possible to directly use nearby soil to remove pesticides from the water. Therefore, in this study the interaction between the herbicides and sediments (soils) and sorption of herbicides onto sediments under different water systems was examined.

2.4 MOVEMENT

As a result of increasing public concern regarding pesticide contamination of groundwater and surface water, movement of pesticides in the soil and vadose zone and in the groundwater has received significant attention. Movement of a pesticide in soil can occur by diffusion-dispersion, mass flow (convection) as well as runoff and volatilization or evaporation. Diffusion is the process by which matter is transported as a result of random molecular motions caused by thermal energy (Letey and Farmer, 1974). Thus, the molecules gradually become uniformly distributed in the system and there is a net movement from regions of higher concentrations to regions of lower concentrations. Diffusion in soil is slower than in free solution, because the pathway through the pores is restricted and tortuous, and the chemical interacts with the structural solids. The dispersion process (hydrodynamic dispersion) is a mechanical mixing caused by flow through porous media. Dispersion is attributed to the non-uniformity of velocity distributions that results from the characteristics of flow through narrow pores and from the complex geometry of the pore system (Triegel and Guo, 1994). Mass flow occurs as a result of external forces acting on the carriers (soil and water). Mass flow arises as the response of water to a variety of forces, such as gravitational and capillary forces. Leaching of pesticides in the field is mainly caused by mass flow. In addition to these two main processes of the movement of pesticides in soil: mass flow and diffusion-dispersion, pesticide losses in soil can also be from runoff by surface water flow and volatilization. The following sub-sections will briefly introduce volatilization and runoff , then discuss the theory of mass flow and diffusion-dispersion processes, followed by the mobility of herbicides in soils.

2.4.1 Volatilisation

The volatilisation process involves two stages: the upward movement to soil surface and the escape from the soil surface, so pesticides can be distributed throughout the soil profile by vapor phase movement and eventually lost via surface evaporation. Volatilization of pesticides is described by Henry's law:

$$C_g = H\,C_w \tag{2-6}$$

where C_g is concentration of pesticide in the gas phase (in mg/l), C_w is concentration of pesticide in the water (mg/l) and H is Henry's contant (dimensionless). Henry's constant (H) is a useful measure of volatilization tendency of dilute solutes from water. Henry's constant (coefficient) of a pesticide can be calculated by the equation (Loch, 1991):

$$H = 0.12\ PM/TS \tag{2-7}$$

where

H = Henry coefficient

P = saturated vapor pressure of the pure compound (Pa)

M = molecular weight

T = temperature (K)

S = solubility in water (mg/dm^3)

From the above equation, the volatilization of a pesticide is determined by its saturated vapor pressure and water solubility. About 80 % of the pesticides have low volatility with a Henry constant $<10^{-5}$ (Loch, 1991). Trifluralin is a relatively volatile herbicide with a high vapor pressure and low water solubility. However, the actual volatilization of a pesticide also depends on the environmental conditions. The factors controlling the volatilization of pesticides are: vapor pressure, pesticide concentration, soil water content, adsorptivity of soil, diffusion rate in soil, temperature and air movement (Cheng and Koskinen, 1986; Khan, 1980). Although volatilization losses are usually most rapid immediately following pesticide application, the continued slow loss over an extended period in an arid area can also be significant (Cheng and Koskinen, 1980).

Volatilization is strongly dependent on the moisture and temperature regimes of the soil involved. An increase in temperature results in an increase in the volatilization rate of a pesticide by a direct influence on the vapor pressure of a pesticide and soil properties and related diffusion process (Khan, 1980). Water plays an important role in the volatilization of pesticides in soils. Pesticides volatize more rapidly from wet than from dry soil (Khan, 1980). In very dry soils, evaporation can be expected to increase with increasing soil moisture content because many pesticides are very strongly sorbed by dry surfaces and would be partially displaced by water (Graham-Bryce, 1981). Under typical soil moisture conditions, the rate of evaporation of a pesticide is more likely to be limited by the rate at which it is transported to the soil surface. When the soil is wet enough, the " wick" action of water brings pesticides with it to the surface very effectively (Hartley, 1969). Hubbs and Lavy's (1990) studies showed upward movement of norflurazon and atrazine in the soil was facilitated by movement of capillary water (wick effect). Diffusion processes control the volatilization of soil-incorporated pesticides. As soon as loss occurs at the soil surface, a concentration gradient is established causing pesticide diffusion to the surface replacing that lost by volatilisation (Letey and Farmer, 1974).

2.4.2 Runoff

Runoff is pesticide loss from the original site by the force of surface water flow. It occurs when input exceeds infiltration. Pesticide runoff includes losses from the dissolved and sediment-adsorbed pesticides. Factors affecting losses of runoff include rainfall, pesticide properties, hydrological condition, soil, and application method (Cheng and Koskinen, 1986).

Pesticide presence in surface water has been widely reported (*e.g.* Thurman *et al.*, 1991 and 1992; Southwick *et al.*, 1993; Spalding *et al.*, 1994). Thurman *et al.* (1992) detected some preemergent herbicides and their metabolites, particularly simazine, atrazine, deethylatrazine and metolachlor caused by storm runoff from 1989 to 1990 in the majority of rivers and streams in the midwestern United States and found that their concentrations related to the stream discharge during the summer months. Spalding *et al.*(1994) detected some pesticides (including trifluralin and simazine) in two closely spaced lakes in northeastern Nebraska with maximum concentrations of 0.13 and 0.11 μg/l for simazine and trifluralin. They found that maximum pesticide impacts were associated with a flush of pesticides during periods of overland runoff in the months of May and June when runoff pesticide concentrations were quite elevated. Southwick *et al.* (1993b) reported runoff losses of norflurazon from subsurface-drained land planted to soybeans in southern Louisiana. Their runoff data showed a close relationship between time elapsed between application and runoff-producing rainfall with respect to pesticide losses in the runoff. Wauchope (1978) found that unless severe rainfall occurred shortly after pesticide application, total losses for the majority of pesticides due to runoff were less than 0.5% of the amount applied in most cases. But single-event losses from small plots or watersheds can be much greater. Worst case loss by single runoff events may reach up to 17 % for atrazine (Wauchope, 1978).

2.4.3 Mechanisms of chemical transport in soil

Mass flow and diffusion-dispersion are two important processes representing the movement of pesticides in soils. Knowledge of the mass flow and diffusion-dispersion processes can be useful to predict the rate of chemical movement in soils. Mathematical equations have been developed to describe the movement of a pesticide through soil (Campbell, 1985; Helling and Gish, 1986; Wierenga, 1996; Letey and Farmer, 1974).

Chemicals dissolved in water often move through soil with the water. This process is called mass transport or convection or mass flow. The rate of this passive movement is called flux density (J_m) which can be described by the equation:

$$J_m = qC \tag{2-8}$$

where J_m is the flux density (kg m^{-2} day^{-1}), q is the Darcian velocity (m/day) and C is the concentration of the chemical in the pore water (mg/l).

In addition to mass flow, chemicals redistribute slowly within the soil pore water by molecular diffusion. Diffusive transport (J_D) can be expressed by Fick's law of diffusion:

$$J_D = -\theta D_m \partial C / \partial z \tag{2-9}$$

where θ is the water content, D_m (m^2/day) is the porous medium diffusion coefficient and z is the distance (m).

Hydrodynamic dispersion is caused by the tendency of the soil solution to move more slowly in narrow pores than in large ones and at the edges of pores than in their centres. Dispersion is greater when soil is saturated and flow occurs mostly in large pores between aggregates than under unsaturated conditions when water moves more slowly and mainly in smaller pores within aggregates (Graham-Bryce, 1981). This process can be described by the following equation which is similar to equation (2-9):

$$J_h = -\theta D_h \partial C / \partial z \tag{2-10}$$

where J_h is dispersive transport and D_h is the dispersion coefficient. The value of the dispersion coefficient increases with increasing water velocity. So the dispersion coefficient has a relationship as follows:

$$D_h = \alpha v \tag{2-11}$$

where α is the dispersity and v ($= q / \theta$) is pore water velocity (m /day). Because D_m and D_h are macroscopically similar, they can be added:

$$D = D_m + D_h \tag{2-12}$$

where D is the longitudinal hydrodynamic dispersion coefficient. D is also called diffusion-dispersion coefficient.

Combining equations (2-8), (2-9), (2-10), and (2-12) yields the chemical flux Js:

$$Js = -\theta D \, \partial C / \partial z + q C \tag{2-13}$$

In order to fully describe chemical transport by water through soil, equation (2-13) needs to be combined with the equation of continuity:

$$\theta \, \partial C / \partial t = -\partial Js / \partial z \tag{2-14}$$

where t is time. Then combining equation (2-13) and (2-14) yields the general chemical transport equation in one dimension:

$$\partial C / \partial t = \partial / \partial z \, [(D \, \partial C / \partial z) - \nu C] \tag{2-15}$$

A chemical can be sorbed by soil and is thus prevented from moving with the water. It can also degrade by various actions in soil. In order to account for the effect of sorption and degradation on chemical transport, the above equation is modified to the following (Brusseau and Bohn, 1996; Helling and Gish, 1986):

$$R \, \partial C / \partial t = D \, \partial^2 C / \partial z^2 - \nu \, \partial C / \partial z - \mu C \tag{2-16}$$

where

$$R = 1 + \rho K_d / \theta = \nu_w / \nu_p = d_w / d_p \tag{2-17}$$

$$S = K_d C$$

and

$$\mu = 0.693 / t_{1/2} \tag{2-18}$$

Here, R is the retardation factor; ρ is the soil bulk density; θ is the moisture content of the soil, which is equal to porosity when the soil is saturated; ν_w is the velocity of water; ν_p is the velocity of the chemical; d_w is the distance travelled by water; d_p is the distance travelled by the chemical; S is the concentration of the chemical sorbed by soil; K_d is the sorption coefficient; C is the concentration of the chemical in water; μ is the first-order degradation coefficient; and $t_{1/2}$ is the half-life of the chemical. In the equation (2-16) $\mu\ C$ is a degradation sink term, other sinks could also be added (*e.g.* plant uptake and volatilization). The retardation factor (R) in equation (2-17) is one of the simplest approaches for classifying the potential of chemicals to contaminate groundwater.

Various mathematical models have been developed to simulate the transport of chemicals in soils based on the above chemical transport equations. Many factors are known to influence the chemical transport processes (diffusion-dispersion and convection) in soils and they need to be considered in modelling of pesticide transport in soil.

2.4.3.1 Diffusion-dispersion

Depending on the water velocity, either diffusion or dispersion would be the dominating mechanism (Helling and Gish, 1986; Gerstl, 1991). For relatively mobile chemicals, D is directly related to the pore water velocity. At high water fluxes hydrodynamic dispersion is dominant in soil and diffusion becomes unimportant. D can be expressed by the equation (2-4). Dispersion is mainly determined by soil properties and is practically independent of the compound's properties. Large pores in a soil caused by cracking, soil fauna, or old root channels make a large contribution to dispersion of a chemical (Loch, 1991). On the other hand, diffusion may be the dominant mechanism controlling the magnitude of D, especially if water flow is slow. Under this situation, the diffusion can be estimated by using the Millington and Quirk tortuosity model (Hellington and Gish, 1986):

$$D = (\theta^{10/3} / \phi^{2}) D_w \qquad (2\text{-}19)$$

where ϕ is the porosity of the bulk soil and D_w is the diffusion coefficient in water, which can be approximated as 4.3×10^{-5} m^2 /day.

Diffusion of pesticides in soils depends on a number of soil properties including water content, soil bulk density, air-filled porosity and temperature, and on the chemical properties of the pesticide (*e.g.* solubility, vapor pressure and diffusion coefficient). Diffusion can occur in solution or at the air-water or air-solid interfaces. Diffusion in each phase depends on the water content in soil. Shearer *et al.* (1973) studied the diffusion of lindane through silt loam soil. They measured the vapor and non-vapor diffusion components as a function of soil water content. They found that essentially no diffusion occurred in dry soil, but increased rapidly with increasing water content reaching a maximum at about 4% water content. Further an increase in water content caused a decline in total diffusion until at 30 % water content when an increase in diffusion occurred with increasing with water. Vapor diffusion decreased slightly as water content increased from 4 % to 20 % and then decreased rapidly at the water content above 20 %. Scott and Phillips (1972) measured the diffusion of several herbicides through a Lanto silty clay loam at different soil water contents and found that the diffusion coefficient for prometone, atrazine, simazine, prometryne, diphenamid and chloropropham all increased with the water content; but the *D* value of trifluralin was not significantly affected by the water content in soil. Trifluralin is considered to be the most volatile of the herbicides tested and the diffusion results are explained based on vapor phase diffusion. In addition to the influence of the soil water content on diffusion, sorption of a chemical on soil and the soil bulk density tend to decrease the diffusion of the chemical while temperature tends to increase the diffusion (Khan, 1980; Letey and Farmer, 1974).

2.4.3.2 Convection (mass flow)

Mass flow of a pesticide through soil depends on the direction and rate of water flow and sorption of the pesticide on soil. The sorption controls the distance of the movement and the concentration of the pesticide. There is a inverse relationship between sorption and movement of pesticides by water through soil. In the one-dimensional chemical transport model with first-order degradation (Equation 2-16), the hydraulic conductivity is the most important soil parameter, followed by organic matter and soil bulk density (ρ) (Helling and Gish, 1986). Pesticide movement in soil is very sensitive to the magnitude of the hydraulic conductivity. Soils with hydraulic conductivities within a factor of 4 can yield dramatically different concentration profiles.

Oddson et al. (1970) found that the depth of pesticide movement is dependent on a parameter K ($K = \rho K_d / \theta$). The position of maximum pesticide concentration in the soil profile is equal to the depth of water penetration divided by K. The depth of movement is regarded as independent of the amount applied (Letey and Farmer, 1974). But both maximum concentrations and the shape of the concentration distribution in soil can be significantly altered by the nonsingularity or nonequilibrium of the sorption and desorption because equation (2-16) assumes sorption equilibrium. The nonequilibrium of sorption causes pesticides to move through soil faster than expected, thus increasing the likelihood of groundwater pollution. It also causes desorption of pesticides to be longer than expected (Gerstl, 1991).

In addition to nonequilibrium effects, by-pass flow and complexation of a pesticide with either dissolved organic matter or with colloidal particulate matter can result in enhanced movement of the pesticide (Gerstl, 1991). By-pass is caused by large variations in the pore size distribution in the soil profile which may contain soil cracks and large pores. Flury *et al.* (1995) found that the three herbicides triasulfuron (K_{oc} = 9.33 ml/g), atrazine (K_{oc} = 100 ml/g) and terbuthylazine (K_{oc} = 357 ml/g) moved to the same maximum depth in a loamy soil. Similar results were reported from Kladivko *et al.* (1991) and Traub-Eberhard *et al.* (1995). This phenomenon was explained by preferential flow mechanisms, where solutes move only through a portion of the available pore space in soil (Flury, 1996).

2.4.4 Mobility of herbicides in soils

Herbicides have been found not only in surface water, but also in ground water. The US Environmental Protection Agency (USEPA) made a national pesticide survey of wells from 1985 to 1990, and found that 10.5 % of community and 4.2 % of rural water supplies contained at least one pesticide (Kearney, 1994). Groundwater contamination resulting from herbicide leaching has become a public concern in major agricultural regions of the world (Hallberg, 1988). As this concern is growing, it is neccessary therefore to understand the mobility of herbicides.

Some research has been undertaken on the mobility of the herbicides norflurazon, oxadiazon, trifluralin, oxyfluorfen, and simazine. Gomez de Barreda *et al.* (1991) found some herbicides at a depth of more than 60 cm in the soils in some Spanish orchards following long term herbicide use. Trifluralin along with other herbicides had been applied in the Benifayo orchard in 1988-89. No herbicides were detected in summer 1989 in the water samples from an irrigation well surrounded by untilled plots with the water level 15 m below ground, but in the following winter some residues were found in the well water with a trifluralin concentration of 4.1 µg/l (Gomez de Barreda *et al.*, 1991). The leaching potential of these herbicides on soil columns, in decreasing order was: bromacil > atrazine > simazine > terbumetone > terbuthylazine >terbutryne = diuron > trifluralin (Gomez de Barreda *et al.*, 1993). So even the least leachable trifluralin could reach the well water. Singh *et al.* (1985) investigated the movement of bromacil and norflurazon in a subtropical Florida citrus sandy soil. By the end of 8 weeks, the norflurazon detected was 5 ppm in the 0 to 7.5 cm deep soil as compared to 6.5 ppm in the 7.5 to 15 cm deep soil. Norflurazon remained in the top layers of soil considerably longer than did bromacil and had a higher loss from volatilization and photodecomposition (Singh *et al.*, 1985). Southwick *et al.* (1993a) reported leaching losses of norflurazon on subsurface drained plots on Mississippi River alluvial soil and noticed slightly retarded leaching of norflurazon with respect to atrazine. But the application of norflurazon was incorporated to 10-15 cm soil, which is different to surface spraying with no deep incorporation. Both results indicate that norflurazon has the potential to leach into groundwater.

Oxadiazon has been reported to be strongly adsorbed by soil colloids and humus, such that very little migration or leaching occurs in soil (Humburg, 1989; Ambrosi and Helling, 1977). Wehtje *et al.* (1993) found that oxadiazon hardly leached 4 cm below surface in a mineral soil and three container media. Ambrosi and Helling (1977) used soil thin-layer chromatographic plates to study the leaching of oxadiazon and phosalone in soils. Oxadiazon was nearly immobile in four soils, but moved to R_f ~0.3 in Lakeland sandy loam with a clay content of 16.4 %, a silt content of 12 % and organic matter content of 0.9 % (Ambrosi and Helling, 1977). Leaching of oxadiazon also occurred on a sandy loam soil and a sandy soil (Fourie, 1992 and 1993). Oxadiazon leached >15 cm below the soil surface. Niemczyk and Krause (1994) conducted a two-year project in 1988-89 evaluating the behaviour and mobility of the commonly used preemergent herbicides, benfluralin, trifluralin, pendimethalin, bensulide, oxadiazon and DCPA in field turfgrass situations with high organic matter contents(> 4.5 %). They did not detect any residues of trifluralin in the 22.5-25 cm zone but on two occasions, oxadiazon residues of 0.01 and 0.02 kg/ha were found in 1989. The above results may suggest that the movement of oxadiazon is influenced greatly by soil texture.

Oxyfluorfen is often characterized by low water solubility (0.1 ppm) and strong sorption to organic matter which limits movement in soil (Humburg, 1989). Fadayomi and Warren (1977) found essentially no movement of oxyfluorfen through 5 cm columns of a silt loam soil and a fine sand soil with < 2% leached. But Valliappan *et al.* (1990) studied the leaching of the herbicides oxadiazon, butachlor, benthiocar, oxyfluorfen and pyrazosulfuron-ethyl using PVC tubes (30 cm × 10 cm diameter) filled with sandy loam and found that oxadiazon was shown to be the least mobile herbicide, butachlor and benthiocar to be moderately mobile and oxyfluorfen and pyrazosulfuron-ethyl to have leached the furthest. Horowitz and Elmore (1991), using a bentgrass bioassay for herbicide detection, evaluated the sorption and leaching of oxyfluorfen in columns of soilless media and soils.

Depth of herbicide leaching increased in order in the following soils: peat and sand (1:1) mix, Stockton clay soil, Yolo fine sandy loam soil, and redwood bark and sand (3:1) mix. Riley *et al.* (1994) monitored oxfluorfen residues in a pond near a commercial nursery and found that the higher levels were observed in either the month of or in the month following significant applications with the highest concentration in water of 0.04 μg/ml.

The extent of herbicide leaching could be related to herbicide properties. Laskowski *et al.* (cited by Funari *et al.*, 1991) proposed a simple leaching index (LI):

$$LI = (S \ t_{1/2}) / (V_p K_{oc}) \tag{2-20}$$

where S is the water solubility, $t_{1/2}$ is the field dissipation half-life and V_p is the vapor pressure in mmHg at 25 °C. There is measure of leaching viz. Gustafson's groundwater ubiquity score (GUS) (Funari *et al.*, 1991):

$$GUS = \log_{10} t_{1/2} \times (4 - \log_{10} K_{oc}) \tag{2-21}$$

These equations have been used to approximately estimate the relative potential of herbicide leaching into groundwater (Funari *et al.*, 1991). But herbicide leaching is a complex process influenced by many factors including herbicide properties, soil type and structure, rainfall, irrigation, and crop. The vulnerability of groundwater to pesticide residues depends on the ratio of their persistence and residence time in the overlying soil. A compound with sufficient persistence will reach the groundwater in the long run, even if it has a long residence time in the soil. Chlorinated hydrocarbons are good examples. In the past, chemicals were thought to move slowly through soil pores and it was also thought that most of them would dissipate in the surface soil long before they could reach to the groundwater. However, recent studies (*e.g.* Flury, 1996) have shown that chemicals can quickly leach to subsurface soil and shallow groundwater by preferential flow through cracks, worm holes and other macropores in unsaturated, structured soil or through finger or funnel flow in sandy, unstructured soil (Weed *et al.*, 1995).

Although there have been some studies on the leaching of these herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen, and also simazine, knowledge of their leachability is limited, and moreover, little information is known about their mobility in vineyard soils in Australia. The results of the individual experimental studies are mostly highly specific to the experimental conditions used and cannot be transferred to other situations mainly due to different soil type and structure, climatic condition, and hydrological condition. Groundwater and dam water are normally used to water the vines in South Australia. Clean water is very important for South Australian viticultural areas if they are to have good quality grapes and wines. Therefore, in our study, the movement of these commonly used herbicides in the vineyards was investigated using a combination of laboratory soil column tests and field experiments.

2.5 TRANSFORMATION PROCESSES

Chemicals entering the soil and water are subjected to both abiotic and biotic transformations. They can be transformed by chemical, photochemical and biochemical means. The relative intensity of chemical degradation, biodegradation and photodecomposition depends on the properties of the chemical and of the medium and the environmental conditions. In the root zone, degradation proceeds mainly by microbial processes. However, below the root zone the degradation processes of the chemical are mainly abiotic (Gerstl, 1991). In water, the degradation processes active on the chemical may be predominantly hydrolysis and photolysis.

2.5.1 Chemical degradation

Chemical degradation of pesticides can occur as solutes in the aqueous phase or in the adsorbed forms on the soil surfaces. Degradation includes hydrolysis and redox reactions (oxidation and reduction). Hydrolysis is the significant abiotic reaction in the presence of water. The key factors in hydrolysis are the charge properties of the chemical molecules and the pH. Hydrolysis is essentially an interaction between nucleophiles and electrophiles. Thus, the charge properties of its molecules govern the chemical's reactivity with water. For many chemicals, hydrolysis may be catalyzed or enhanced under acidic or basic conditions. Hydrolysis can also be influenced by its sorption on soils. The presence of catalytic surfaces in the soil can help bring about hydrolysis reactions. Studies found that atrazine hydrolysis was faster in soils than in a soil free system at similar pH and, parathion sorbed on clays decomposed directly by hydrolysis or through an intermediary rearrangement step (as cited by Gerstl, 1991). The pH at the surface of many soils is lower than that of the water surrounding the soil particles; thus, an acid-catalyzed hydrolysis reaction is enhanced when the chemical is sorbed on the soil (Brusseau and Bohn, 1996). Kinetic studies for some selected organic compounds indicate that in the sorbed phase alkaline hydrolysis is retarded, neutral hydrolysis is unaffected, and acid hydrolysis is enhanced (Gerstl, 1991). But the real picture is not so clear-cut. Sorption of a chemical on soil organic matter or clay minerals can result in protection of the chemical from degradation (Farmer and Aochi, 1987). Noblet *et al.* (1996) studied the influence of natural dissolved organic matter, temperature and mixing on the abiotic hydrolysis of triazine and organophosphate pesticides, and found that for the triazines, dissolved humic substances alone are not sufficient to catalyze transformations and that a solid substrate (sediment or soil) may play an important role. The data for the organophosphates suggest that in addition to facilitating transport, dissolved organic matter (DOM) may also impede the abiotic hydrolytic degradation of these pesticides (Noblet *et al.*, 1996).

2.5.2 Biodegradation

Degradation through microbial activity is the primary transformation occurring in the soil and water. Biodegradation can lead to the complete breakdown of chemicals in the environment. During biodegradation, microorganisms can either utilize chemicals as substrates for energy and nutrients or cometabolize the chemicals by microbial metabolic reactions (Triegel and Guo, 1994). There are many chemical and environmental factors which affect biodegradation of a chemical in the field. The most important influencing factors are soil properties (pH, organic matter), temperature and water content (Schroeder and Banks, 1986; Jolley and Johnstone, 1994; Barrett and Lavy, 1984; Gerstl, 1991). Their influences on the degradation are very complex and hard to quantify. The persistence of a pesticide may vary from one environment to another. Under most circumstances, decreasing temperature and moisture in soil tends to decrease the degradation rate of a chemical.

2.5.3 Photodecomposition

Sunlight can bring about transformations of a chemical in the soil , water and plant surfaces. Chemicals generally absorb sunlight most readily in the ultraviolet region with a wavelength between 290 to 450 nm. The photodecomposition of a chemical depends on many factors such as the intensity of light, chemical properties of the chemical, the nature of the supporting medium and photosensitizers.

Photodecomposition can be divided into direct and indirect photolysis (Miller and Hebert, 1987). Direct photolysis involves absorption of light by the chemical, which then reacts with available environmental reactants. The number of molecules undergoing photochemical reaction divided by the number of photons absorbed is termed the quantum yield. In the laboratory, *p*-nitroanisole (PNA) and *p*-nitroacetophenone (PNAP) with pyridine are commonly used quantum yield actinometers. Indirect photolysis occurs when sunlight is absorbed by some substance which then initiates a series of reactions that result in the transformation of the chemical. In the environment, indirect photolysis can result from absorption of sunlight by sentitizers, which can be any organic (humic) or inorganic substance.

Since many chemicals are sprayed on the soil or plant surfaces, photolysis of the chemicals is likely to be a significant process. But photodegradation of chemicals in soil is limited by the low penetration of sunlight into soil, it only occurs on soil surfaces to less than 1 mm depth (Miller and Hebert, 1987; Khan, 1980).

2.5.4 Degradation kinetics

Although many models such as the power rate model and the hyperbolic rate model have been proposed to describe degradation of pesticides in the environment, most of the pesticide degradations can be simply expressed as a first order reaction with respect to pesticide concentration. The rate of degradation can be described with a first order equation:

$$dC/dt = k\,C \tag{2-22}$$

or

$$\ln C - \ln C_0 = -k\,t \tag{2-23}$$

where C is the concentration of a chemical, C_0 is the initial concentration of a chemical, t is time, and k is the degradation rate contant. For degradation reactions it is useful to define a half-life, which is the time required for half of the original pesticide to be transformed. The half-life$t_{1/2}$ is defined as

$$t_{1/2} = 0.693\,/\,k \tag{2-24}$$

The kinetics of pesticide degradation is affected by many factors such as the availability of the pesticide, activity of microorganisms, environmental conditions (*e.g.* temperature, soil moisture, pH, aeration), and various soil parameters. A two-site model similar to the two-stage sorption was proposed in which a fraction of the pesticide in soil is considered to be unavailable to degradation. This could explain quite successfully pesticide biodegradation in soil (Gerstl, 1991). Miller *et al.* (1989) suggested that photolysis of pesticides on soils did not generally follow first order reaction rates because rapid initial loss of pesticides occurs followed by slowing of the rate until no further loss is observed. Biodegradation follows a similar pattern (Helweg, 1991). In spite of the inadequacy of the first order reaction rate model, for practical purposes it is still widely used to express degradation occurring in the environment.

2.5.5 Degradation of herbicides

When a herbicide reaches soil, it is in an environment that can change its molecular structure. On the surface of the soils and plants, the chemical is exposed to sunlight which is active in photodecomposition. In the soil, chemical degradation may start after contact between the herbicide and the soil water, or after sorption to active surfaces in the soils. However, the most important process is biodegradation caused by enzymes produced by fungi or bacteria in soil environment. If the herbicide reaches water, all these degradation processes may also happen in the water.

Degradation of the herbicides trifluralin, norflurazon, oxadiazon and oxfluorfen has been investigated to different extents. The degradation of trifluralin has been extensively studied in soils (Golab *et al.*, 1979; Golab and Occolowitz, 1979) and in water (Crosby and Leitis, 1973). In the field and laboratory soils, 28 products derived from trifluralin have been detected (Golab *et al.*, 1979; Golab and Occolowitz, 1979). A study by Golab *et al.* (1979) shows that transformation reactions involved with the degradation of trifluralin in soil are oxidative dealkylation of the *N*-propyl groups, reduction of nitro groups and a combination of both reactions, cyclization in the form of benzimidazoles, dimeric condensation in the form of azoxy and azo derivatives, and as well as oxidation / hydroxylation and reduction reactions. The trifluoromethyl group of trifluralin remained intact through those reaction with a few exceptions (Golab *et al.*, 1979). Crosby and Leitis (1973) described a very rapid photodecomposition of trifluralin in aqueous methanol, and detected 6 products after less than two minutes and about 25 products after 3 hours. They also found that photodecomposition of trifluralin in aqueous suspensions, with or with soil was about one tenth as rapid, but the products were the same. Margulies *et al.* (1992) studied the photochemical behaviour of trifluralin adsorbed on montmorillonite with or without the organic cation thioflavin co-adsorbed and observed considerable photostabilization of trifluralin, as compared with the herbicide in its free form. They suggested that photostabilization is due to steric hindrance imposed by the clay surface on the cyclization step of the photochemical reaction. Sun and Pignatello (1993) investigated abiotic degradation of some pesticides in water using hydrogen peroxide and iron(III) chelates and found that hydrogen peroxide greatly increased the degradation of baygon, carbaryl, picloram, 2,4-D, 2,4,5,-T and atrazine, but had no obvious influence on trifluralin. Trifluralin is considered as a very persistent herbicide and degrades slowly in soil. Corbin *et al.* (1994) has monitored dissipation of fluometuron and trifluralin residues after 9 or 10 years continuous use in two Arkansas soils (Dundee silt loam soil and Sharkey silty clay soil) and found higher levels of trifluralin and fluometuron in the Sharkey soil than in the Dundee soil. The half life of fluometuron in the Dundee silt soil was 1.5 to 1.7 months while that in Sharkey silty clay soil was 7.3 to 11.1 months under field conditions. However, the half lives of trifluralin in the Dundee soil and Sharkey soil were 8.7 to 10.1 months and 11.2 to 14.9 months, respectively (Corbin *et al.*, 1994). Jolley and Johnstone (1994) investigated the degradation of trifluralin in three Victorian soils (medium clay, clay loam and sandy loam) with half lives ranging from 100 to 214 days under field conditions. Laboratory studies (Jolley and Johnstone, 1994) showed that trifluralin degradation increased with increasing moisture and increasing temperature.

There have been some investigations on the degradation of norflurazon, oxadiazon and oxyfluorfen in soil and organisms. Oxadiazon degrades very quickly in high water content soils (Ambrosi *et al.*, 1977; Barrett and Lavy, 1984). Ambrosi *et al.* (1977) found less than 25 % of oxadiazon was degraded after 175 days in soil under moist and flooded conditions. Barrett and Lavy (1984) studied the effects of soil water content on oxadiazon dissipation and found dissipation of incorporated oxadiazon varied little between continuous flood and alternate flood laboratory treatments at 25 °C, with an average of 59 % remaining after 20 weeks. But in the field, 50% of the surface applied oxadiazon dissipated from the soil within 6 to 11 days when the soil was flush irrigated and then flooded, compared to 15 to 17 days when the soil was irrigated but not flooded in two rice management systems. Ambrosi *et al.* (1977) found that oxadiazon was metabolized to a carboxylic acid, a phenol, a dealkylated derivative and several polar products in soils. Chakraborty *et al.* (1995) isolated from soil eleven metabolites degraded by soil fungus *Fusarium solani*. Oxadiazon and its metabolites have been detected from pond snails and mussels (Ambrosi *et al.*, 1978; Murakami *et al.*, 1993), and from terrapin and corb shell processed foods (Murakami et al, 1994). Most of the oxadiazon metabolites were regarded to be formed through dechlorination, *N*-decarboxymethylation, acetylation and ring cleavage (Adityachaudhury*et al.*, 1994).

The transformation of oxyfluorfen by microbial and photochemical means has been studied (Adityachaudhury *et al.*, 1994). Oxyfluorfen and its amine resides in crops have been reported (Zhou and Miles, 1991; Adler *et al.*, 1978). Brodsky *et al.* (1992) identified a number of photoproducts by using mass spectrometry and suggested that their generation pathways were mainly by Ar-O bond cleavage, dechlorination and photocyclisation. The photodegradation experiments were undertaken in a methanolic solution, not in water.

Few studies of norflurazon degradation have been done. Willian and Mueller (1994) reported a liquid chromatographic determination of norflurazon and its initial metabolite desmethylnorflurazon in soil. Schroeder and Banks (1986a and b) studied the persistence of norflurazon in five Georgia soils and found it was characerized by rapid initial degradation followed by slow loss of the herbicide. Field research (Schroeder and Banks, 1986a) indicates that the rate of norflurazon loss is inversely related to soil organic matter content, is slowed by cool or dry environmental conditions and not influenced by initial concentration.

Past studies have shown that the degradation of herbicides depends on many factors such as herbicide properties and environmental conditions. Degradation of trifluralin has been well studied and there have been also a few investigations on biodegradation of other herbicides oxadiazon, oxyfluorfen and norflurazon in soil, but their degradation pathways are not well understood. There have been no reports on their degradation in water to our knowledge, for example, the photolysis rates of the herbicides. Therefore, in this study, we studied photodecomposition of these herbicides in water with trifluralin as a reference and also monitored their dissipation under the Mediterranean climate found in a Australian vineyard.

2.6 SUMMARY

After having reviewed previous literature related to the behaviour of these herbicides viz. norflurazon, trifluralin, oxadiazon, oxyfluorfen and simazine in the environment, we believed that the following issues need to be addressed:

(1) Mobility and dissipation of the herbicides in South Australian vineyard soils;
(2) Sorption of herbicides on soils, which could help understand the mobility and dissipation of the herbicides in soils;
(3) Photodegradation of norflurazon, oxadiazon and oxyfluorfen in water and on soils;
(4) Degradation of herbicides on grape and during wine-making processes; and
(5) Minimizing the effect of herbicide residues in soil, water and wine.

CHAPTER 3

STUDY AREA

3.1 INTRODUCTION

The use of some chemicals in agriculture may create some environmental problems. It largely depends not only on the physio-chemical nature and toxicological properties of the chemicals used, but also the surrounding environment. Most of the field studies reported have been undertaken in the Barossa region. The climate, soil and water properties, groundwater and landscape can influence the behaviour of chemicals in the environment. Therefore, it is appropriate to review the study area, the Barossa region in this chapter.

The Barossa is Australia's best known viticultural and winemaking region comprising the historic Barossa Valley and Eden Valley. It is located north of the city of Adelaide in the state of South Australia (Figure 3.1). The Barossa wine industry commenced in the 1850's. Currently there are more than 50 wineries in this region. The Mountadam vineyard, where field leaching study was undertaken, is located at the summit of High Eden Ridge and is world famous for its Chardonnay, recently ranked sixth best in the world, and regarded by many as the finest in the land. The Barossa region has a Mediterranean type climate and some of the best soils suitable for growing vines.

3.2 SOILS

The soils in the Barossa region were mainly formed during earlier geologic times by alluvial materials, which were deposited by the erosion of the Mt. Lofty Ranges and the north Para River. Sand ridges on the western side of the Barossa were probably formed in more recent times during a very dry period (French *et al.*, 1989). Most of the soils in the region are very suitable for vines.

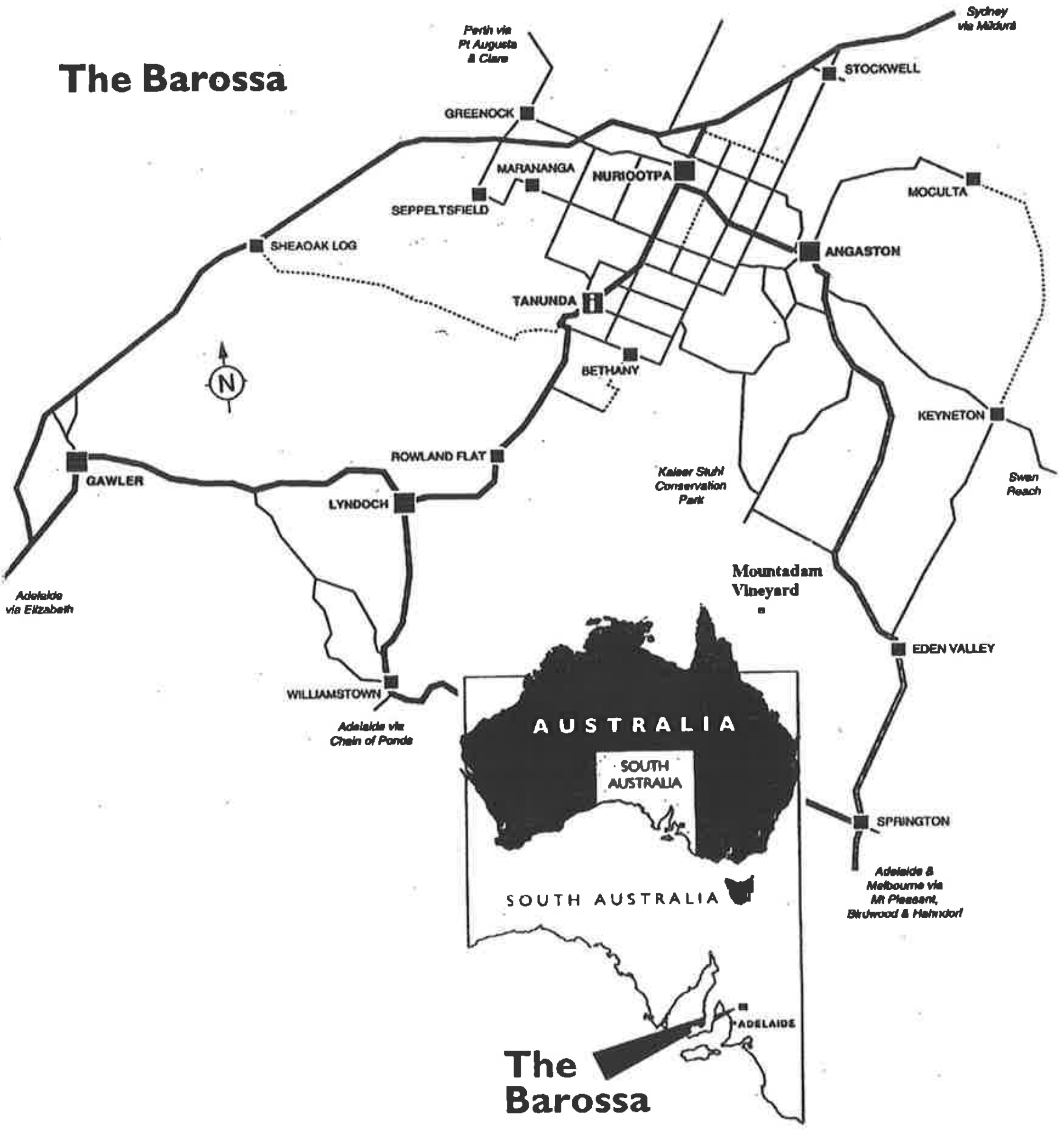


Figure 3.1 Map of Barossa region.

The soils in the Barossa region can be classified into six groups: alluvial soils, red-brown earths, dark brown cracking clays, sand over clay soils, podzolic and solodic soils, and skeletal soils, of which the best soils are red-brown earths, dark-brown cracking clays and alluvial soils because they can store more water. Table 3.1 lists the area of vines growing on each soil type. Most of the vines are grown on sandy topsoils in the region.

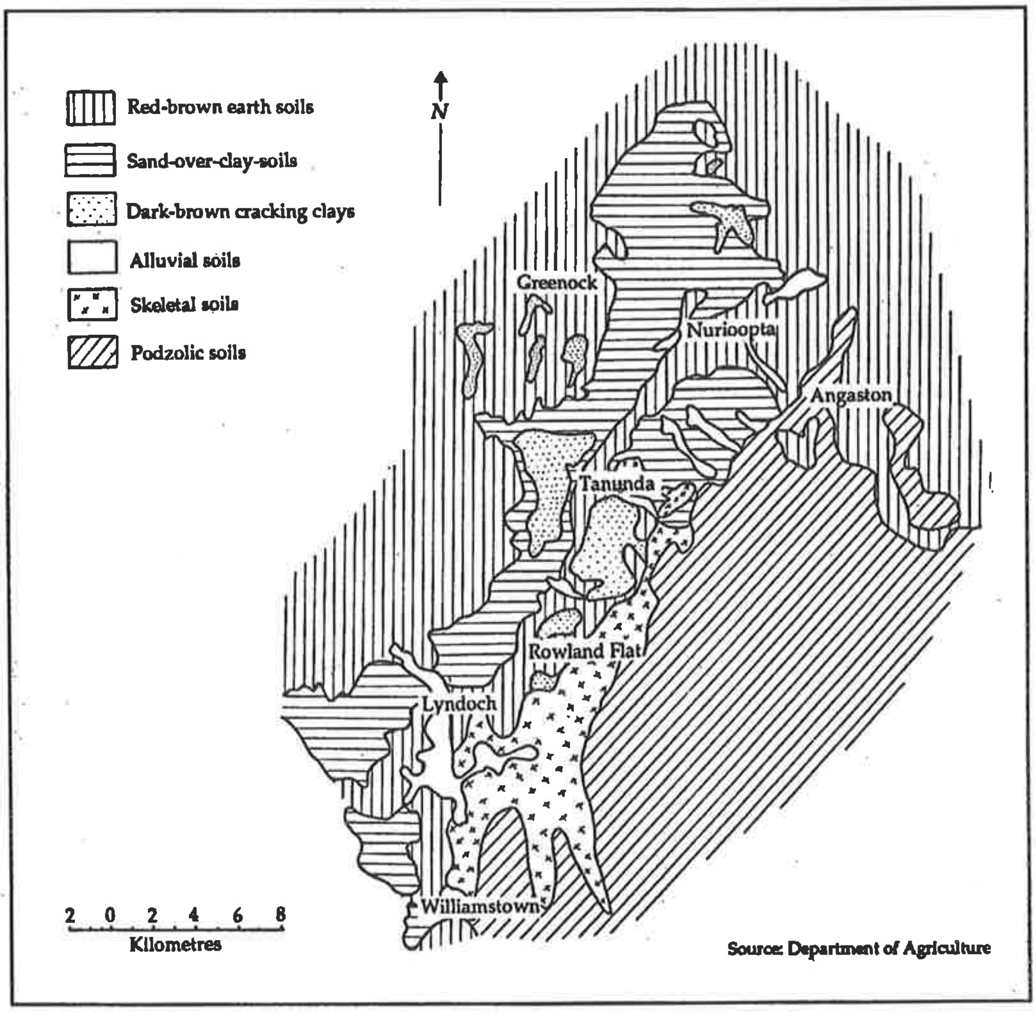
The red-brown earths, sand over clay soils, dark brown cracking clays (heavy textured soils) and alluvial soils are found in the valley floor and western side while the podzolic and solodic soils and skeletal soils are mainly in the Barossa ranges (Figure 3.2). The surface soils of red-brown earths vary in texture from fine sandy loam to clay. However, the majority of surface soils are sandy loams with only small areas of clay loam in the Lyndoch area. The podzolic and solodic soils are the dominant soils in the higher rainfall areas of the hills (French *et al.,* 1989). They have a grey-brown loamy sand to sandy surface soil of variable depth over a yellow-brown clay to sandy clay.

In the northern hills (*e. g.* Koonunga, Greenock), several dissimilar soils always occur together in the field, and often in a pattern resembling a mosaic. Often the same soils occur in several mosaics, but in different proportions. The red-brown earths of this area have coherent, somewhat brown-coloured surface horizons in contrast to the white, more bleached surface of the sandy Plain-edge soils.

Table 3.1 Soils and area of vine planting in the Barossa region*

Soil groups	*Area under vines (ha)*	*Percent of total vine area*
Alluvial soils	884	10.2
Red-brown earths		
(a) Sandy	2922	33.9
(b) Loamy	118	1.4
(c) Clayey	309	3.6
Dark-brown cracking clays	172	2.0
Sand over clay soils		
(a) Solodised solonetz	1812	21.0
(b) Deep sands	1020	11.7
Podzolic and solodic soils	1313	15.2
Skeletal soils	89	1.0
Total	8639	100.0

* Data from the Department of Agriculture and Fisheries (French et al., 1989)



Source: Department of Agriculture

Figure 3.2 Simplified soil association map of Barossa region.

3.3 CLIMATE

The Barossa region, as well as most other areas around Adelaide has a Mediterranean type climate with hot dry summers and a cool wet winter with an average annual rainfall of 585 mm. The annual rainfall in the region varies from about 500 mm in the east to 750 mm in the hills and most of the rain over the year falls during the winter (from April to October). Table 3.2 lists monthly rainfall data at Mountadam vineyard in 1996 and 1997. The rainfall was much lower in June and July of 1997 than of 1996. The annual rainfall in the Barossa region is well below the optimum of 900 mm for vines. So any factor used to increase the water supply could increase the grape yield. Many dams have been built to store water in vineyards. This practice can increase water supply to vines by irrigation.

Table 3.2 Rainfall recorded at Mountadam vineyard for years 1996 and 1997.

YEAR	JAN	FEB	MAR	APL	MAY	JNE	JUL	AUG	SEPT	OCT	NOV	DEC
1996	26.8	12.4	40.0	26.4	22.8	212.8	182.8	152.7	157.1	38.6	9.0	22.2
1997	30.3	42.2	2.0	3.0	82.7	22.0	40.8	126.4	102.0	58.2	38.1	31.7

The mean maximum temperatures in the Barossa region range from between 29.6 °C in January and 15.0 °C in July. The temperature for the region meets the requirements of grape production. For example, Nuriootpa has absolute maximum air temperatures from 19.0 to 42.8 °C and also meets the requirements for maturity by having four months with mean temperatures more than 18.7 °C (French *et al.*, 1989).

CHAPTER 4

MATERIALS AND METHODS

4.1 INTRODUCTION

In order to understand the environmental fate of herbicides in Australia viticulture, we need to study their behaviour in the environment, and the factors determining their availability and movement in the environment. In this study, we will investigate the leaching and adsorption of herbicides on different soils and investigate how fast they degrade in water and soil. The possible contamination of herbicides in grapes and wine will also be investigated. Therefore, some experiments were developed to examine these problems. In this chapter, the experimental design and analytical methods used in the research are described. Some detailed experiments such as leaching, sorption, photolysis and wine-making will be introduced in the following chapters where relevant.

4.2 EXPERIMENTAL DESIGN

Water contamination of pesticides has been recognised as a problem for some time. Pesticides have been commonly detected in surface water and ground water, especially in rural areas. Data on their leaching behaviour and adsorption are necessary to assess water contamination potential. In order to investigate the mobility of these herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen), predrilled plastic pipes were placed in a small plot in the Mountadam vineyard to collect subsurface water after the application of herbicides. Water samples were analysed every week during the rain season to evaluate the leachability of herbicides. Mountadam vineyard was chosen because it has a typical sandy soil and most vines in Australia are growing on sandy topsoil. A laboratory leaching study was also undertaken by using soil columns. Herbicides were spiked on the top of each soil column and defined amounts of water were applied at regular intervals. The relative leachability of herbicides was obtained by analysing water eluted from the column. Soil sorption coefficients (K_d) of herbicides were measured on four different soils from the Barossa region using a batch-equilibrium technique.

Sorption coefficient is an important parameter in studying the mobility of herbicides in soils. Leaching on intact soil columns was also conducted in order to better simulate the situation in the field. Data obtained from laboratory and field were compared and combined to better understand the movement in the environment.

The dissipation of herbicides on soil was monitored after the application of herbicides in the Mountadam vineyard. Surface soil samples and as well as soil cores were extracted and analysed at regular intervals. Moreover, photodegradation of herbicides was conducted on soil TLC plates and in water in summer because of hot climate in Australia. Degradation rates of herbicides were calculated and degradation products were analysed for each herbicide.

These herbicides are widely used in vineyards, so it is important to ensure that the wine on the table is clean. Therefore we studied the impact of possible grape contamination on wine quality. Some grapes in a vineyard were dipped in a herbicide solution and then these grapes were used to make wine. Residues of herbicides on grapes, in must and in wine were analysed and their impact on fermentation and wine quality was studied.

Data on leaching, sorption and degradation of these herbicides and their possible residues in wine can be used to develop best management practices for Australian vineyards and to develop and verify models for predicting pesticide transport in the environment.

4.3 MATERIALS

The solvents used in this research were hexane, methanol, ethanol, acetonitrile and ethyl acetate. Hexane (nanograde) was from Mallinckrodt Australia Pty Ltd., ethyl acetate of analytical grade from Ajax Chemicals-Sydney, methanol of HPLC grade from BDH Laboratory Supplies, acetonitrile of HPLC grade from BDH Laboratory Supplies, and ethanol of analytical grade from Merck Pty Ltd..

All chemical standards (norflurazon, trifluralin, oxadiazon, oxyfluorfen and simazine) were of >99.0 % purity from Chem Service (USA). Commercial herbicide 'Solicam DF' with active constituent (norflurazon) of 800 g/kg was from Sandoz Australia Pty Ltd. while 'Trifluralin 400' with active constituent trifluralin 400 g/l from Farmoz Pty Ltd.. 'Goal' (active constituent oxyfluorfen 240 g/l) was provided by Mountadam vineyard and 'Ronstar' granules (active constituent oxadiazon 20 g/kg) were from Rhone-Poulenc Rural Australia Pty Ltd..

The extraction cartridges, Waters Sep-Pak C_{18} cartridges were from Millipore Corporation. Waters Sep-Pak cartridges are convenient, reproducible, disposable solid-phase extraction devices for chromatographic sample preparation. We used 3 cc 500 mg and 6 cc 1 gram C_{18} and tC_{18} Sep-Pak Vac cartridges which were used under a vacuum manifold. C_{18} cartridges contain a reverse phase sorbent, which can be used for the isolation of hydrophobic species from aqueous solutions and trace organics in environmental water samples.

ENVI^{TM}-18 DSK 47 mm solid phase extraction disks were also used to extract large samples. Samples up to 1 litre or more can be processed through a 47mm ENVI-18 DSK disk. ENVI-18 DSK solid phase extraction disks consist of a glass fibre disk embedded with surface-modified silica. The octadecyl (C_{18}) bonded phase is acid resistant. The total capacity of the disk, approximately 20 mg, includes all analytes and interferences which are well-retained.

Soil samples used for the laboratory study were taken from the Barossa region as follows: Nuriootpa viticulture research station, Mountadam vineyard, Lyndoch and Tanunda. Lyndoch soil was taken from a site near the Barossa Valley highway and Lyndoch oval, and Tanunda soil taken from a vineyard near the intersection of Rifle Range road and Nicolai road. These four soils represent the major soil types in the Barossa region. Soil samples were also taken from the northern hills of Barossa region, viz: at Koonunga, Kalimna and Koonunga Hill. These soil samples were used in the leaching study.

4.4 SOIL PHYSIO-CHEMICAL ANALYSES

4.4.1 Particle size analysis

Particle size analysis involves dispersing the soil in water and measuring the amounts of silt and clay by sedimentation techniques. The hydrometer method was used in this study to measure soil particle size distribution. The procedure described below is adapted from a routine method used in the Department of Soil Science, the University of Adelaide.

About 50 ml Calgon solution and 5 ml 0.6 M NaOH were added to a sedimentation cylinder. Distilled water was added to the volume to 1000 ml and mixed. The temperature of the solution was measured. Then the hydrometer was carefully lowered into the solution and the scale reading R_L was recorded as a blank reading. The blank reading R_L was used to calibrate the following measured reading R. So the actual reading was R minus R_L which was used to calculate the particle size distribution in a soil.

About 40 g air-dry soil was weighed and transferred to a 600 ml squat beaker. And 150 ml distilled water, 50 ml Calgon solution and 5 ml 0.6 M NaOH were also added. Then the sample was dispersed using the ultrasonic probe on maximum power for 3 minutes, or over a shaker for 24 hours. The contents of the beaker were washed into a one litre sedimentation cylinder and diluted to the mark with distilled water. Any remaining froth on the liquid can be damped by adding several drops of amyl alcohol. The cylinder was shaken end over end for about one minute.

The cylinder was then placed on the bench and the time of commencement of sedimentation was recorded. The hydrometer was carefully inserted so that it was in a position for reading. Under our conditions, the first reading was taken after 5 minutes, and this gave % silt and clay by using the formula: $(R - R_L) \times 100 / 40 =$ % silt and clay. The second reading was taken after 5 hours and gave % clay using the same formula: $(R - R_L) \times 100 / 40 =$ % clay. The remainder was % sand.

4.4.2 *Soil bulk density and porosity*

Soil bulk density and porosity were determined by measuring its dry weight and volume. Core samplers (made from stainless steel tubes with internal diameter i.d. = 70 mm, and height h = 50 mm) sharpened at one end were driven into soil with as few blows as possible. Cores were dug out, cut smooth at both ends, cleaned from outside. Then soil samples were dried at 105 ℃ in an oven and weighed. The bulk density (ρ) and porosity (ϕ) were calculated using the following formula:

$$\rho = \text{dry mass (m)} / \text{volume (v)}$$

$$\phi = 1 - \rho / 2.65$$

4.4.3 *Soil pH and organic matter*

Soil pH is a measure of soil acidity. It is conventionally measured in a 1 to 2.5 w/v soil to water or soil to 0.01 M $CaCl_2$ solution using a pH meter (McRae, 1988).

A PHM61 Laboratory pH meter was calibrated using buffer solutions with pH 4 and 7. Ten grams of dry soil was weighed in a small beaker and 25 ml of distilled water was added and stirred. The solution was allowed to stand for 10 minutes. The pH value was recorded when stable.

Two methods were used in this study to determine organic carbon in soil. One used combustion procedures. Soil organic matter was determined by the LECO® CN-2000 Carbon and Nitrogen Analyser. Analysis begins by weighing around 2 g dry soil and placing it into the sample holder. When the sample was pushed into the combustion chamber, the furnace and flow of oxygen gas caused the sample to combust. The combustion process then converted any elemental carbon into carbon dioxide (CO_2) which was detected as a level of energy at the detector.

The other method was Walkley and Black's rapid titration procedure. In this method, the soil was digested with chromic and sulphuric acids. Making use of the heat of dilution of sulphuric acid. A known quantity of dichromate was the source of the chromic acid and the excess chromic acid not reduced by the organic matter of the soil was determined by subsequent titration with standard ferrous sulphate using o-phenanthroline as indicator. One gram soil sample was weighed into 500 ml conical flask. 10 ml of the 1 N potassium dichromate solution was added and then 20 ml of concentrated sulphuric acid was added carefully. After half an hour, about 200 ml of water, 10 ml of concentrated orthophosphoric acid and 0.5 ml of indicator were added into the flask. After a while, the excess chromic acid was titrated by adding ferrous sulphate solution from a burette until the solution turned from green to red. A blank determination needed to be carried out. Ferrous sulphate must be standardised by titration with potassium dichromate. The organic carbon content in soil was calculated, given that each ml of 1 N potassium dichromate used was equal to 3 mg of carbon.

4.5 EXTRACTION

In order to study the dissipation of these herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) in the environment, an efficient method of extracting and analysing these herbicides in soil, water, and food was required. Traditionally, liquid-liquid extraction for water samples and Soxhlet extraction for soil and plant samples were used, then the extracts were cleaned up with a column or thin layer chromatography (TLC). This method has been widely applied in the isolation of pesticides, but it uses a large amount of sample, requires lots of solvents and time, and sometimes has low recoveries.

Recently, solid-phase extraction (SPE) has been developed to extract pesticides from water and wine (Kobyashi *et al.*, 1993; de la Colina *et al.*, 1995; and Holland *et al.*, 1994), and to clean up the extracts from soils and plants using various solvents (Krause and Miemczyk, 1990 and 1992). It is a simple and effective method which uses solid sorbents in a cartridge or disk to retain trace organic compounds through adsorption and/or partitioning. The technique has been reviewed in relation to its use in water (Calverley, 1988 and Font *et al.*, 1993), and foods and soils (Hsu et al., 1991 and Pico *et al.*, 1994). There are various sorbents, of which a C_{18} phase is most widely used in any environmental chemistry study. A C_{18} cartridge is a reversed phase cartridge which can be used to extract and clean up pesticides in environmental samples. Before use, a reversed phase cartridge needs to be conditioned with 6 to 10 cartridge hold-up volumes of methanol or acetonitrile, and flushed with 6 to 10 hold-up volumes of water or buffer. Then the sample in a high-polarity solvent is loaded on the cartridge. The bound components are eluted using an appropriate solvent (Figure 4.1). In our study, this technique was used to develop rapid and efficient methods for the recovery of the herbicides. The herbicides in soils and grapes were extracted with supersonication, then cleaned up by using SPE C_{18} cartridges (Waters). For water and wine samples, SPE C_{18} cartridges were used to extract and clean up the herbicides

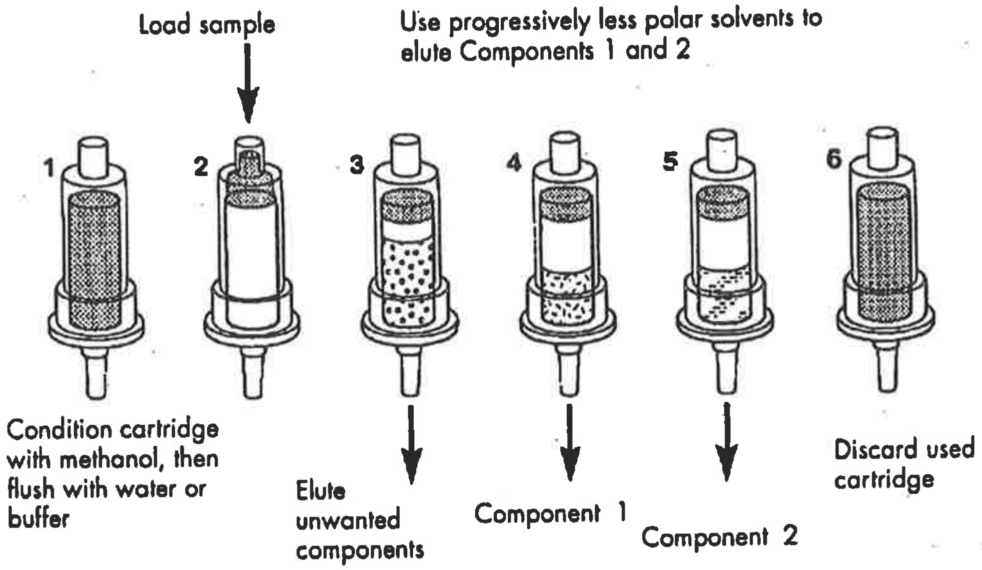


Figure 4.1 General elution protocol for reversed-phase chromatography on Sep-Pak cartridges.

4.5.1 Soil and water

Water samples taken in the field were filtered through Millipore filter (0.45 µm) before they were loaded onto a Sep-Pak cartridge. The C_{18} cartridge was conditioned with about 20 ml methanol and 20 ml Milli-Q water at a flow rate of 5 to 10 ml/min, and was kept wet before loading the water sample. The water sample was drawn through the cartridge under a vacuum system at the flow rate of 2 to 5 ml/min. Then the cartridge was dried by passing air through it for about 30 minutes. The dried cartridge was stored in the refrigerator or eluted with about 4 ml of methanol or ethyl acetate. The eluate was transferred to a small vial and blown down under a gentle nitrogen stream. A measured amount of solvent (methanol) was added to the vial and the solution subjected to GC and GC-MS analyses. The recovery study of the four herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) in water was performed by spiking the herbicides in Milli-Q water at 100 µg/l. As shown in Table 4.1, the recoveries were better than 80 %.

Table 4.1 Recoveries (%) of herbicides in water, soil, wine and grape*

Herbicide	Water	Soil	Wine	Grape
Norflurazon	97.7±2.1	97.5±4.5	93.3±3.7	96.1±2.8
Oxadiazon	98.5±3.4	92.8±3.4	89.1±2.6	90.7±3.2
Trifluralin	96.4±2.5	83.7±5.2	80.6±3.8	82.5±4.7
Oxyfluorfen	85.2±2.7	78.5±2.8	81.5±5.1	81.8±3.9

* Values are the mean of four experiments.

Soil samples (about 10 g) were first extracted with methanol under supersonication for more than 15 minutes. The mixture was shaken and stirred, and the extract was filtered by vacuum on Buchner funnel. This process was repeated twice. The filtrates were combined and concentrated using a vacuum rotatory evaporator. Then the filtrates were diluted with deionised water making the resultant solution about 20% methanol. The solution was then transferred onto a pre-conditioned C_{18} cartridge. The solution was passed through the cartridge and eluted as described above in water extraction. The recovery of the herbicides was tested at 2.5 ppm concentration in four different soils (Mountadam, Nuriootpa, Lyndoch and Tanunda soils). The recoveries were between 78 and 97 % (Table 4.1).

Calverley (1988) and Mills and Thurman (1992) have studied the effect of the addition of methanol to the sample. Their results suggest that the step of involving methanol evaporation from soil extracts could be eliminated. Hence, in this study, the methanol extracts were sometimes diluted with water and applied directly onto the C_{18} cartridges. In this way, the sample preparation time can be decreased.

4.5.2 Grape and wine

Wine samples were directly passed through C_{18} cartridges which were conditioned with methanol and a 20% ethanol solution. Then the cartridges were rinsed with Milli-Q water and 20% ethanol solution, and dried by passing air through them for more than 30 minutes. The herbicides were eluted with ethyl acetate from the cartridges and transferred to small vials. The eluates were blown down under a gentle nitrogen stream. The recovery study of herbicides was performed by spiking at a 5 ppm level in wine. The recoveries were more than 80 %.

For grape and must samples, pre-treatment was needed. Grapes were first mixed and extracted with acetonitrile in a container using Ronson Maxi-Mix mixer. The mixture was filtered through a bed of celite or through a Buchner funnel without any filter paper, then through a glass fibre (GF/A) and a Millipore filter until it was clear. Water was added to the flitrate making the resultant solution 20% acetonitrile and the solution was then transferred onto the cartridge which had been conditioned with methanol and ethanol/water (20:80). Other procedures used are the same as for the wine samples.

4.6 ANALYTICAL METHODS

Various analytical methods have been developed to analyse pesticides in soil, water and food. The most common methods are high-performance liquid chromatography (HPLC) with UV detector and gas chromatography (GC) with various detectors such as electron-capture detector (ECD) and nitrogen-phosphorus detector (NPD), but each has certain inherent limitations. Recently, the gas chromatography-atomic emission detection system (GC-AED) has been developed to detect almost any element and is very sensitive to pesticides (Wylie and Oguchi, 1990). However, gas chromatography-mass spectrometry (GC-MS) is the most powerful technique in the analysis of pesticides (Liao *et al.*, 1991).

Applications of these analytical methods for the herbicides used in this study have been reported. Krause and Niemczyk (1990 and 1992) used megabore column gas chromatography with ECD and NPD to quantify oxadiazon, trifluralin and benfluralin residues in turfgrass thatch and soil. Willian and Mueller (1994) and Essington *et al.* (1995) have described methanol extraction and HPLC methods for the determination of norflurazon and its metabolite in soils with recoveries more than 90 %. Their study shows that the recovery of norflurazon from fortified soils was significantly influenced by equilibration time, loading rate and soil type, and that the recovery decreased as herbicide contact time with soil increased (Essington *et al.*, 1995). Spalding et al. (1994) detected twelve pesticides including trifluralin, simazine and atrazine in the lake waters in Northeastern Nebraska by gas chromatography with a mass selective detector. Oxadiazon and its metabolites in shellfishes and some processed foods were detected by GC-ECD, GC-NP-FID (nitrogen-phosphorus and flame ionisation detector) and GC-MS (Murakami *et al.*, 1993 and 1994). Determination of norflurazon and desmethyl norflurazon in fruit crops by HPLC (Draper and Street, 1981) and mixed crop matrices by GC-ECD (Winkler *et al.*, 1981) has been reported. Oxyfluorfen residues in water, sediment, soil and crops have been determined by high pressure liquid chromatography (HPLC) with UV detection (Riley *et al.*, 1994) and photodiode array detector (Bushway and Perkins, 1993) and gas chromatography with a 63Ni electron capture detector (Adler *et al.*, 1978). Zhou and Miles (1991) have described the determination of oxyfluorfen and its amine residues in garbanzo beans by LC with UV and photoconductivity detection (PCD). Trifluralin residues in carrots have been analysed by GC-ECD, LC-UV or NMR (D'Amato *et al.*, 1993 and Mortimer *et al.*, 1994). Because norflurazon, oxadiazon, trifluralin and oxyfluorfen all contain nitrogen and halogen elements, GC-NPD, as well as GC-ECD and GC-MS is used in the analyses of herbicides in our research. NPD is very selective to nitrogen and phosphorus containing compounds, while ECD is very sensitive to halogen containing compounds. The mass spectrometer is a universal detector widely used in the confirmation and identification of unknown compounds.

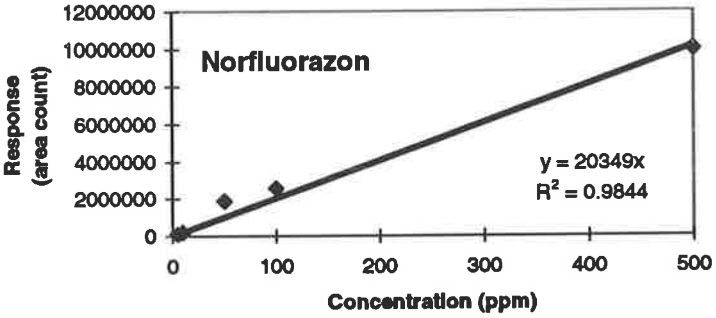
4.6.1 Gas chromatography with nitrogen-phosphorus detection

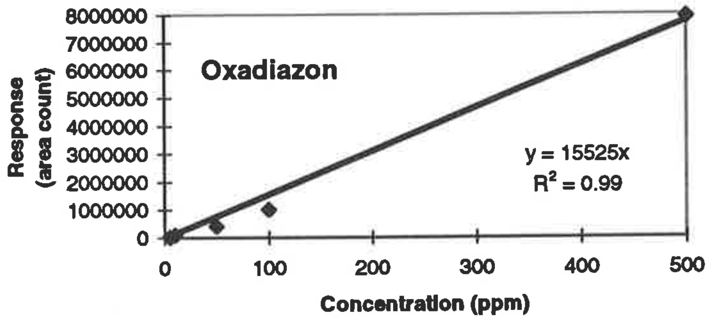
The nitrogen-phosphorus detector (NPD) is widely used in the analysis of pesticides because of its selectivity and sensitivity. A Hewlett-Packard 5890A gas chromatograph equipped with a nitrogen-phosphorus detector (NPD) or electron capture detector (ECD) and a split/splitless injector was used to analyse the herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) in this study. Chromatography data acquisition and processing were accomplished with an integrator. Detector responses were measured uniformly by peak area. The column used for the analyses was fused silica capillary column HP-1, 25 m × 0.25 mm, stationary phase methyl silicone.

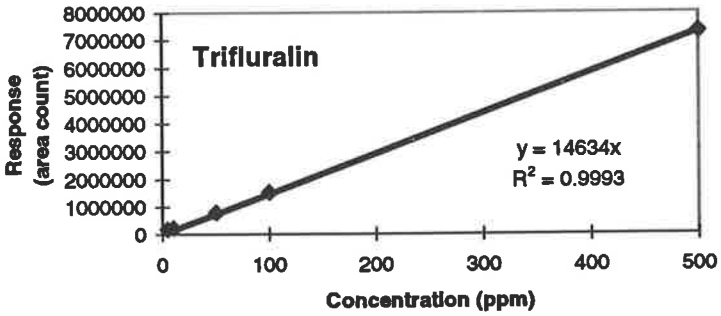
The GC injection port and detector temperatures were 200 ℃ and 300 ℃, respectively. The oven temperature program used was as follows: 200 ℃ (held for 1 min), increased at 10 ℃ /min to 300 ℃ (held at 5 min). Nitrogen (N_2) was used as the carrier gas and make-up gas at the flow rate of 30 ml/min for NPD and 80 ml/min for ECD. Hydrogen was used at the flow rate of 3.5 ml/min and air 110 ml/min.

Quantitation of the herbicides was made by comparison with standards. Standards were run every time before samples were run. Calibration curves for norflurazon, oxadiazon, trifluralin and oxyfluorfen illustrate linearity in detector response (peak area) over two orders of magnitude in concentration (Figure 4.2).

Figure 4.3 shows the chromatogram of these herbicides (norflurazon, oxadiazon, oxyfluorfen, and trifluralin). The chromatographic tailing of norflurazon, oxadiazon and simazine has been observed when using GC-NPD. It can be reduced by rinsing the column using hexane before the samples were injected. Response to the herbicides will decrease as the source ages and can be improved by recoating the NPD source with rubidium and alumina powder as necessary.







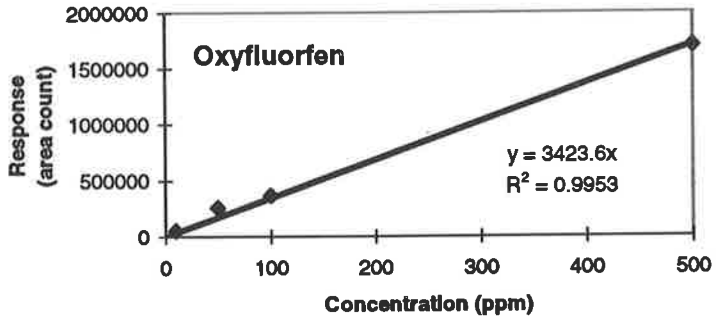


Figure 4.2 Calibration curves for the herbicides.

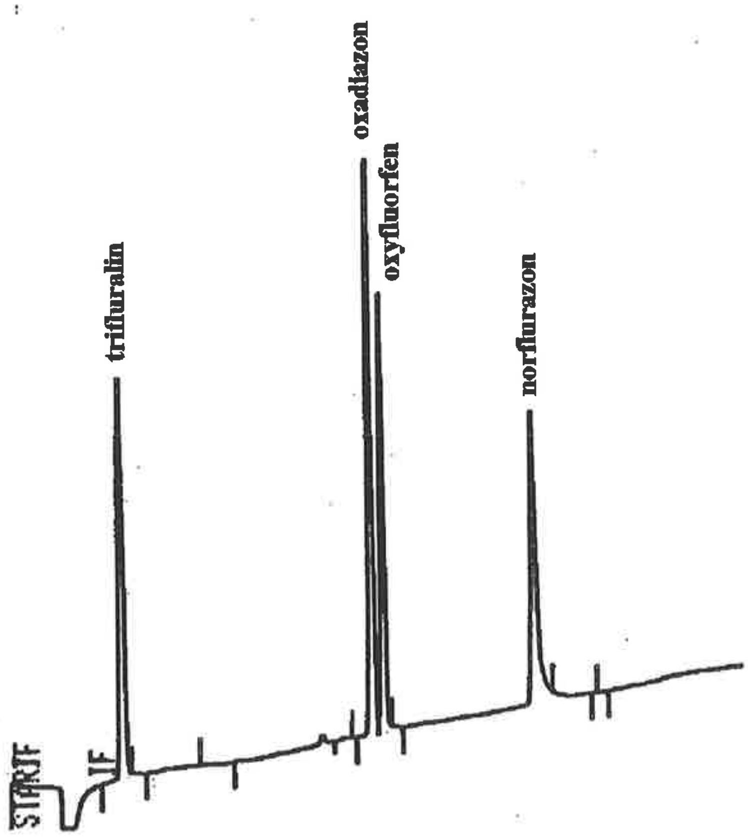


Figure 4.3 GC-NPD chromatogram for the herbicides.

4.6.2 Gas chromatography-mass spectrometry

GC-MS analyses were performed using Hewlett Packard 5890 Series 2 gas chromatograph, equipped with a 30 m × 0.25 µm film thickness × 0.25mm diameter J & W DB5-ms capillary column and HP 5971 mass selective detector. Interface temperature was 230 °C and mass detection at 1scan/sec from 50 amu to 550 amu. Injections were done in splitless mode using the following two temperature programs:

(a) Injector temperature at 200 °C; oven temperature programmed at 10 °C from initial 60 °C (1 min) to 300 °C (15 minutes hold); (b) Injector temperature at 200 °C; oven temperature programmed from initial temperature 50 °C (1 min) at 10 °C /min to 150 °C, and at 30 °C /min to 280 °C (5 minutes hold). Compound identification was made using a combination of the standard, mass spectra analysis, and library references.

CHAPTER 5

SORPTION OF NORFLURAZON, OXADIAZON AND TRIFLURALIN

5.1 INTRODUCTION

Sorption is an important process which influences the behaviour and fate of herbicides in the environment. Sorption of herbicides is determined by the complex interrelationship between the physiochemical properties of the adsorbate, the nature of soil constituents, and the experimental and environmental conditions under which sorption occurs (Gerstl, 1991).

There have been many investigations into the mechanisms by which chemicals are adsorbed by fractions of soil, particularly the clay minerals and humic acid fractions. There has been less work on the mechanisms of adsorption by whole soils, largely because the heterogeneity of surfaces makes the results hard to interpret (Graham-Bryce, 1981). Soil organic matter has been shown to be highly correlated with herbicide sorption (Hassett and Banwart, 1989; Francioso *et al.*, 1992 and Chiang *et al.*, 1997). The soil sorption coefficient (K_d) and the soil sorption constant (K_{oc}) could be used for assessing the strength of soil sorption. Chiou *et al.* (1983) suggested that the sorption of nonionic organic compounds by organic matter is essentially a partitioning process. For nonionic herbicides K_{oc} can be considered a compound property. The K_{oc} can be predicted from other compound properties such as water solubility or octanol-water partition coefficient (K_{ow}) and from the molecular structure of the compound (Hassett and Banwart, 1989). Other soil properties such as the type and amount of clay, soil pH, and hydrous oxide content may have an effect on the sorption, especially in low organic matter soils. Walker and Crawford (1968) observed that up to an organic matter content of about 6%, both mineral and organic surfaces are involved in the adsorption.

There have been a few studies on the sorption of the nonionic herbicides norflurazon, oxadiazon and trifluralin. Wehtje *et al.* (1993) evaluated the adsorption of ^{14}C-labelled oxadiazon in three soil-less media and a mineral soil at concentrations between 0.1 and 100 mg/kg. They found that adsorption, which was at least 96%, was not influenced by absorbent type or by oxadiazon concentration. However no K_d data was given. Sorption of several herbicides, including norflurazon, in Florida citrus soils, was studied and it was found that the K_d of norflurazon was significantly related to organic carbon content as well as soil pH and cation exchange capacity (Reddy *et al.*, 1992 and Alva and Singh, 1990). The sorption of atrazine and trifluralin was decreased considerably when soil with high organic matter content was treated with sodium hypochlorite; moreover, the sorption of trifluralin also seems to be influenced by the inorganic components of the soil (Francioso *et al.*, 1992).

The pollution of water environments with herbicides is effected through their use in the control of aquatic weeds, leaching and runoff from agricultural fields. Adsorption of some pesticides (atrazine and thiram) onto solid substances, such as clay minerals or activated carbon has been studied to control the level of residues in the water (Gonzalez-Pradas *et al.*,1987; 1993; and 1997).

Although there have been a few studies on the sorption of norflurazon, oxadiazon and trifluralin, there is even less information on the sorption of these herbicides on the low organic matter soils in the South Australian vineyards and their effect on the nearby aquatic systems. The purpose of this chapter is to study the sorption of the above three herbicides in four soils representative of the Barossa Valley and examine their interaction with sediments (soils) in aquatic systems.

5.2 MATERIALS AND METHODS

5.2.1 *Soils*

Surface soils were taken from four places *viz.* Mountadam, Nuriootpa, Lyndoch and Tanunda in the Barossa Valley. These four soil types abbreviated as M, N, L, and T in the thesis are typical of the vine growing area and were used to measure sorption coefficients of the three herbicides. Soil samples were air-dried, ground and sieved to pass through 2-mm sieve. Selected soil properties were measured using the methods given in chapter 4 and shown in table 5.1. These soils are sand soil, sandy loam, sandy clay loam and clay loam. The pH value of Mountadam soil is lower than those of the other soils. The soils in the Barossa Valley are relatively low in organic carbon contents.

Table 5.1 Properties of soils in the Barossa region.

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

5.2.2 Sorption test

A batch-equilibrium technique was employed to determine sorption of norflurazon, trifluralin and oxadiazon on four different soils. Two grams of air dried soil was put into 10 ml test tubes and 5 ml 0.01 M $CaCl_2$ added. Then the tubes were spiked with stock solutions of the chemicals (0.5 mg/ml for norflurazon, 1 mg/ml for other herbicides) to make their concentrations in soil (in μg/g) as follows: 1.25, 2.5, 5, 10, 20 for norflurazon and 12.5, 25, 50, 100, 200 (μg/g) for oxadiazon and trifluralin. Then the tubes were stirred by supersonication for 5 minutes and allowed to equilibrate for 24 hours.

After the 24 hour equilibration period, the mixtures were centrifuged at 5000 rpm for 15 min and the amount of herbicide sorbed was determined by analysing 2.5 ml of the supernatant obtained. The 2.5 ml of supernatant was transferred to a 10 ml tube. The herbicides in the supernatants were extracted using SPE C_{18} cartridges. The water samples were passed through the SPE C_{18} cartridges which were conditioned by 20 ml methanol and 20 ml water. Herbicides were eluted from the dried cartridges by adding 3-5 ml ethyl acetate or methanol and analysed by GC-NPD or GC-ECD.

The sorption coefficient (K_d) was calculated as the ratio between the amount of herbicide sorbed to the soil and the amount of herbicide in the water at equilibrium. The sorption characteristics of a herbicide can be normalised to obtain a general soil sorption constant (K_{oc}) based on the organic carbon content by the equation $K_{oc} = (K_d \times 100)/$ (% of the organic carbon).

Effects of pH on the sorption of the three herbicides were examined using the Mountadam soil at concentrations of 10, 50 and 75 µg/g in soils. The pH values of the solutions were adjusted with diluted HCl and NaOH to 3, 5, 7, 10. After a 24 hour equilibration period and centrifugation, 2.5 ml supernatant from each tube was taken and saturated with NaCl. The herbicides were extracted twice with ethyl acetate and analysed by GC.

5.2.3 Experiments on the interaction between herbicides and sediments

The interaction between herbicides and sediments was investigated by adding dry soils into 500 ml of water in glass beakers with a dry-sediment-water ratio of 0, 1 and 5%, respectively under stirred and non-stirred conditions. Stirred and non-stirred conditions are used to simulate situations of moving water (*e.g.* rivers) and stagnant water (*e.g.* lakes and dams). Mountadam and Tanunda soils were used in the experiments. The 0 % sediment treatment served as a control. The experiments were performed in the laboratory at room temperature (20 °C). Two ppm of norflurazon, oxadiazon and trifluralin were added to the glass beakers. After 24 hours, the stirrers were turned off. Two days after treatment, 100 ml of the supernatant was taken from each beaker and extracted using C_{18} SPE cartridges. The beakers containing Tanunda soil under non-stirred conditions, as well as the control were monitored further at 6 and 13 days after treatment. This is used to study the effects of sediments on the degradation of the herbicides in water.

Sorption of herbicides on charcoal, activated decolorizing powder from BDH, was also studied in the laboratory by adding 0, 10 and 20 mg of charcoal into 500 ml of water which was spiked with 2 ppm each of norflurazon, oxadiazon and trifluralin. Two ppm of each herbicide in pure water was used as a control allowing the concentrations of herbicides in water to be calculated. The solutions in the beakers were stirred on the first day. The herbicides in the beakers were monitored after 1, 3 and 24 hours and 5 days by removing 100ml of water at the appropriate time interval. At the same time, the degradation of norflurazon, oxadiazon and trifluralin in pure water, each with a concentration of about 1 ppm for each herbicide was also investigated under the same conditions. All the herbicides were extracted with C_{18} cartridges and analysed by GC-NPD.

5.3 SORPTION

5.3.1 *Sorption coefficient*

The sorption isotherms for norflurazon, oxadiazon and trifluralin (Figures 5.1, 5.2 and 5.3) show that trifluralin has the highest sorption on soils, and norflurazon has the lowest sorption. Their sorption in decreasing order is: trifluralin > oxadiazon > norflurazon. The experimental data were subjected to regression analysis using a linear model ($Y = a + bX$, where Y = uptake of a herbicide by soil and X = equilibrium concentration). The different b values reflect the sorption process of herbicides in the soils. The higher the b value is, the stronger the sorption of a herbicide on a soil is. The b values for trifluralin vary from 525.9 of Nuriootpa soil to 1217.2 of Tanunda soil, the b values for oxadiazon range from 21.1 of Nuriootpa soil to 29.8 of Lyndoch soil, and the b values for norflurazon range from 2.9 of Nuriootpa soil to 5.4 of Mountadam soil. Nuriootpa soil with a relatively lower organic matter content was found to have the lowest sorption for all the herbicides in this study. The results suggest that sorption of a herbicide is mainly dependent on its physiochemical nature and that herbicide sorption varies from soil to soil due to different soil properties. The b values of the herbicides on soils are somewhat similar to the measured K_d values which are shown in Table 5.2.

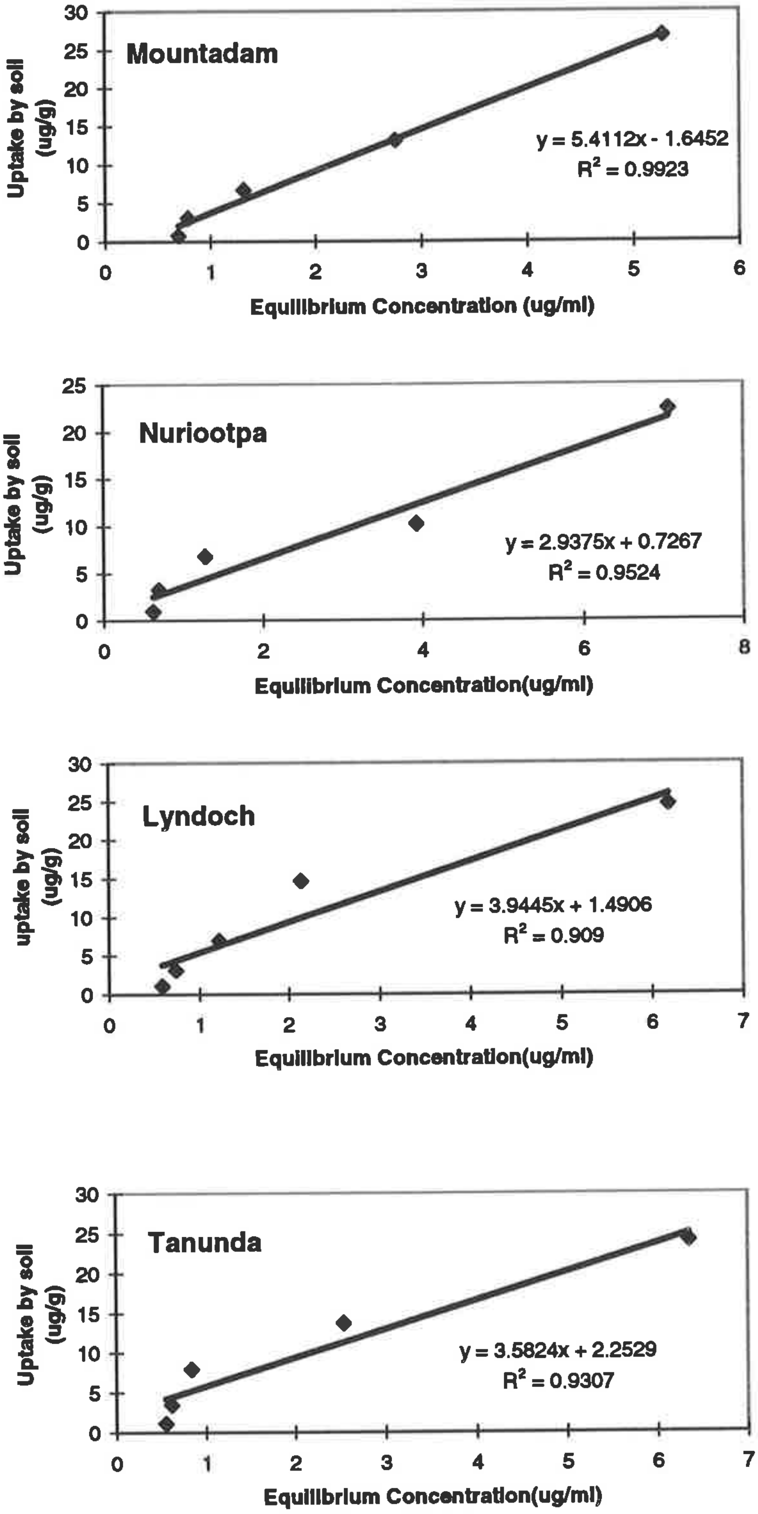


Figure 5.1 Sorption isotherms of norflurazon on soils.

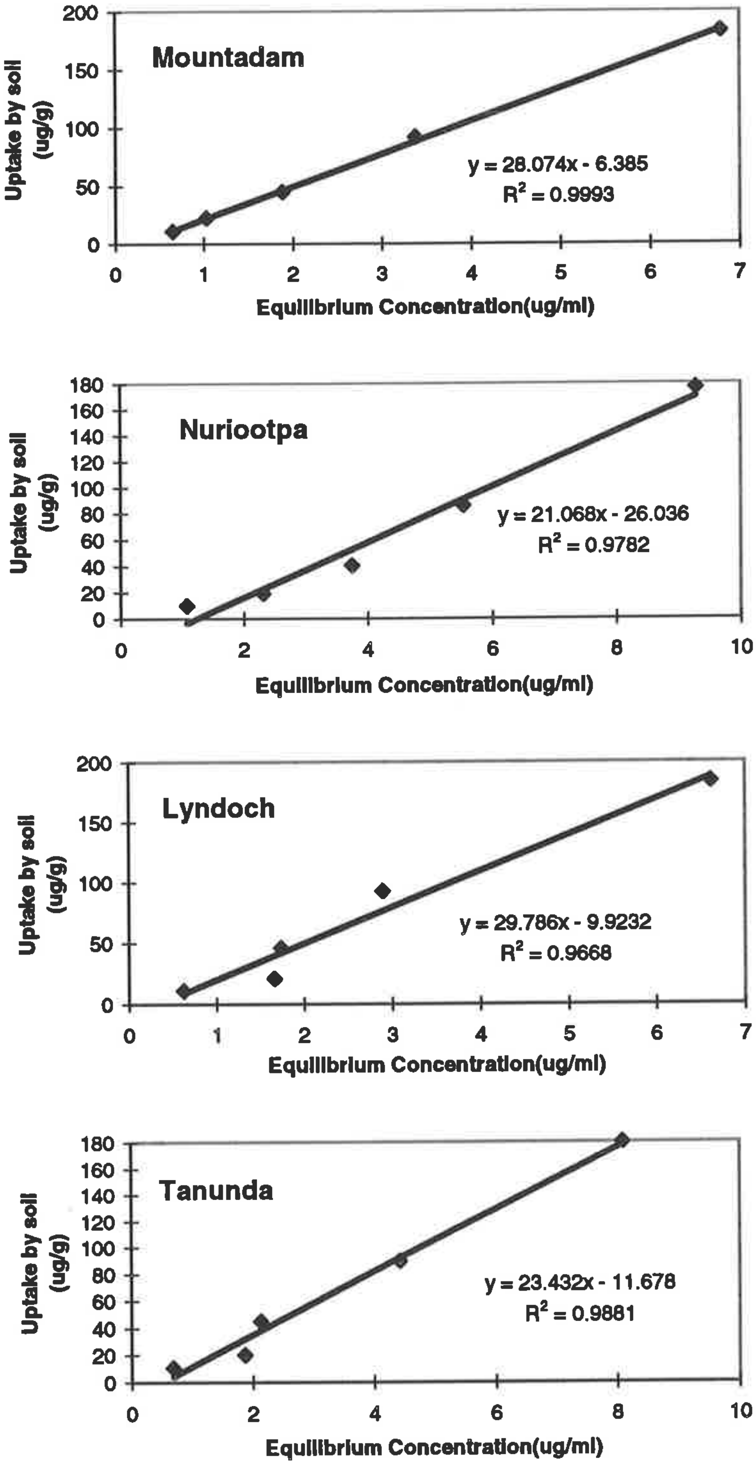


Figure 5.2 Sorption isotherms of oxadiazon on soils.

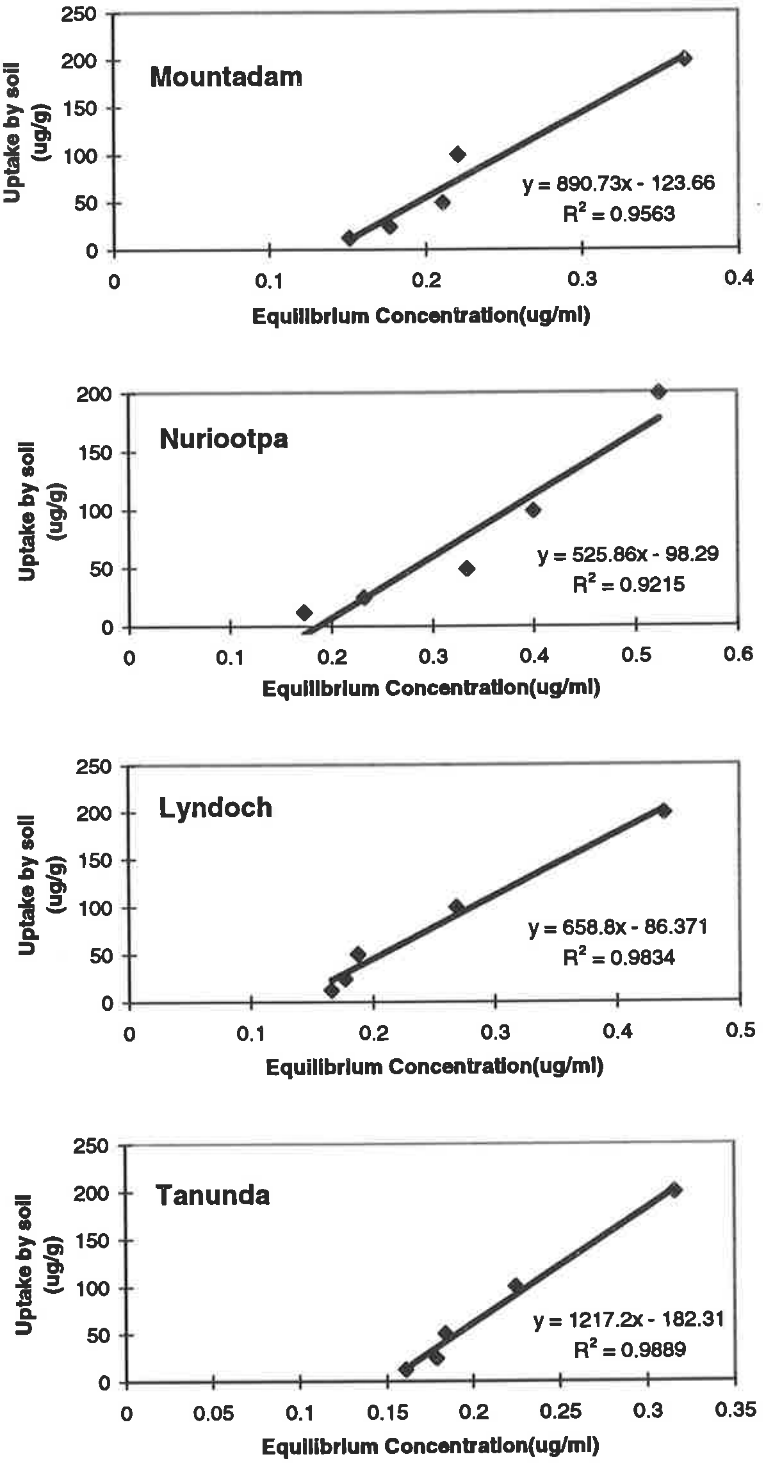


Figure 5.3 Sorption isotherms of trifluralin on soils.

Table 5.2 Sorption coefficients of herbicides on the Barossa soils

Soil	Norflurazon		Oxadiazon		Trifluralin	
	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
Mountadam	3.97	467	23.38	2751	289.48	34059
Nuriootpa	3.48	669	16.07	3090	189.63	36467
Lyndoch	4.51	447	23.21	2298	259.46	25689
Tanunda	5.27	527	17.95	1795	310.78	31078

The K_d values for the four soils and the herbicides studied are reported in Table 5.2 together with the K_{oc} values. From the table, the sorption of herbicides is related to the organic carbon contents in the soils. For the Nuriootpa soil with a lowest organic carbon content (0.52 %), the sorption of the three herbicides is always lowest. For norflurazon, the sorption coefficients (K_d) on the four soils increases in the following order: Nuriootpa < Mountadam < Lyndoch < Tanunda. This suggests that the sorption of norflurazon depends not only on soil organic matter but also on clay minerals. Lyndoch and Tanunda soils have high clay contents which may contribute to the sorption of norflurazon. However, for oxadiazon and trifluralin, the contribution of clay minerals in soil is not so obvious. Mountadam soil has a similar organic carbon content to the Lyndoch and Tanunda soils but has a very low clay content. The K_d values of herbicides of oxadiazon and trifluralin for Lyndoch and Tanunda soils were similar to those for Mountadam soil. That means there is less contribution to sorption from clay minerals in these cases.

Sorption of the herbicides norflurazon, oxadiazon and trifluralin on the Mountadam soil were investigated under different pH conditions (Figure 5.4). No significant pH effects on the sorption of oxadiazon and trifluralin were observed at pH ranging from 3 to 10. But there is a slight increase in sorption of norflurazon at pH 3 to pH 10. The sorbed norflurazon on the Mountadam soil increased from 88 % at pH 3 to 95 % at pH 10.

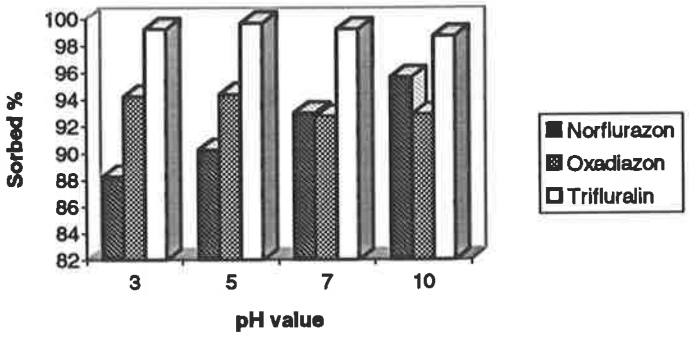


Figure 5.4 Effect of pH values on sorption of herbicides on soil.

5.3.2 Discussion

The experiments in this study show that sorption of a herbicide depends on the properties of the chemical and of the soil. Sorption coefficients of herbicides norflurazon, oxadiazon and trifluralin differ from soil to soil, trifluralin has highest sorption on all soils tested while norflurazon has lowest sorption on all soils. Soil organic matter is the predominant component affecting the sorption of herbicides. Furthermore, sorption of norflurazon increases with the soil pH value. But soil pH has no effect on the sorption of the other two herbicides (oxadiazon and trifluralin).

Many studies have shown that sorption of pesticides can be correlated to the soil organic matter contents, but not with clay mineral contents, thus sorption of a chemical has often been expressed in terms of organic carbon contents (K_{oc}). Alva and Singh (1990) studied sorption of bromacil,diuron, norflurazon and simazine and found that organic matter content was highly correlated with sorption of all four herbicides. Reddy *et al.* (1992) studied the sorption and desorption of diuron and norflurazon and found similar results. Sorption coefficients (K_d) ranged from 0.63 to 2.20 for norflurazon and were significantly related to organic carbon content, soil pH, and cation exchange capacity. But there is no significant relationship between K_d and selected soil properties. Francioso *et al.* (1992) found considerably decreased sorption of atrazine and trifluralin when the soil with high organic matter content was treated with sodium hypochlorite. The present study indicates that sorption of norflurazon, oxadiazon and trifluralin increases with organic matter and clay content, although the sorption of oxadiazon and trifluralin seems to have no obvious correlation with clay content. Of course, lack of correlation may not mean no contribution to sorption of oxadiazon and trifluralin from clay minerals. It has been observed that for organic matter contents up to 6%, both mineral and organic surfaces are involved in sorption (Walker and Crawford, 1968). Therefore, the significance of sorption on mineral surfaces should not be ignored in the soils with low organic carbon contents from the Barossa region.

The experimental results for this study and those of Reddy *et al.* (1992) all show that sorption of norflurazon is related to the soil pH values. Normally, sorption of weak acidic and basic pesticides is influenced by soil pH values (Graham-Bryce, 1981; Loch, 1991). The effects of pH on sorption of weak acids and bases are complicated because of the interactions between soil mineral surfaces and ions in the soil solution. However, all the herbicides in the present study are non-ionic compounds. Soil pH value normally has no effect on sorption of non-ionic herbicides. The reason behind the effect of pH values on sorption of norflurazon needs to be further investigated.

For nonpolar pesticides, K_{oc} is found to be highly correlated with water solubility (S) or octanol-water partition coefficient (K_{ow}) (Chiou, 1989; Hassett and

Banwart, 1989; Karickhoff *et al.*, 1979). So K_{oc} values can be derived from these properties. The correlation equations given by Hassett and Banwart (1989) were as follows:

$$\text{Log } K_{oc} = -0.62 \log S \text{ (mg/l)} + 3.95 \qquad (5\text{-}1)$$

and

$$\text{Log } K_{oc} = 0.08 + 0.909 \log K_{ow} \qquad (5\text{-}2)$$

The above two equations are similar to those (equations 2-4 and 2-5) mentioned in chapter 2. The K_{oc} values calculated from equations 5-1 and 5-2 are included in Table 5.3. The solubility and octanol-water partition coefficient data used are from Table 2.1. From Table 5.3 and 5.2, comparison of measured and estimated K_{oc} values could be made. The estimated K_{oc} values are much higher than the measured ones except K_{oc} 205 for norflurazon estimated by its octanol-water partition coefficient and K_{oc} 22723 for trifluralin estimated by its solubility. Because these indirect correlation based methods do not take into consideration the role of soil and the environmental variables in the sorption process, the estimated K_{oc} data should be used only as a first approximation for nonpolar pesticides.

Table 5.3 The estimated soil sorption constants (K_{oc})

Sorption constant	Norflurazon	Oxadiazon	Trifluralin
K_{oc}^{*}	1129	8912	22723
K_{oc}^{ϕ}	205	28263	75875

* The data calculated using equation (5-1).

ϕ The data calculated using equation (5-2).

5.4 BEHAVIOUR OF HERBICIDES IN WATER

5.4.1 Sorption of herbicides on sediments

The environmental behaviour of herbicides in lakes, rivers and dams is in part affected by the interactions between herbicides and sediments. Sorption of herbicides on suspended particulates and bottom sediments has some effect on the fate of these herbicides in water systems. Our experimental results indicate greater sorption of norflurazon, oxadiazon and trifluralin on stirred sediments than on unstirred sediments 2 days after treatment (DAT) and no obvious differences between the Mountadam soil and Tanunda soil (Figure 5.5). Under stirred conditions, herbicides have more contact with adsorbing surfaces in sediments. Mountadam and Tanunda soils have similar organic matter contents, but Tanunda soil has a much higher clay content. Our sorption results suggest that organic matter is the predominant component in the sorption of chemicals in water systems and clay minerals contribute little to the sorption of these chemicals.

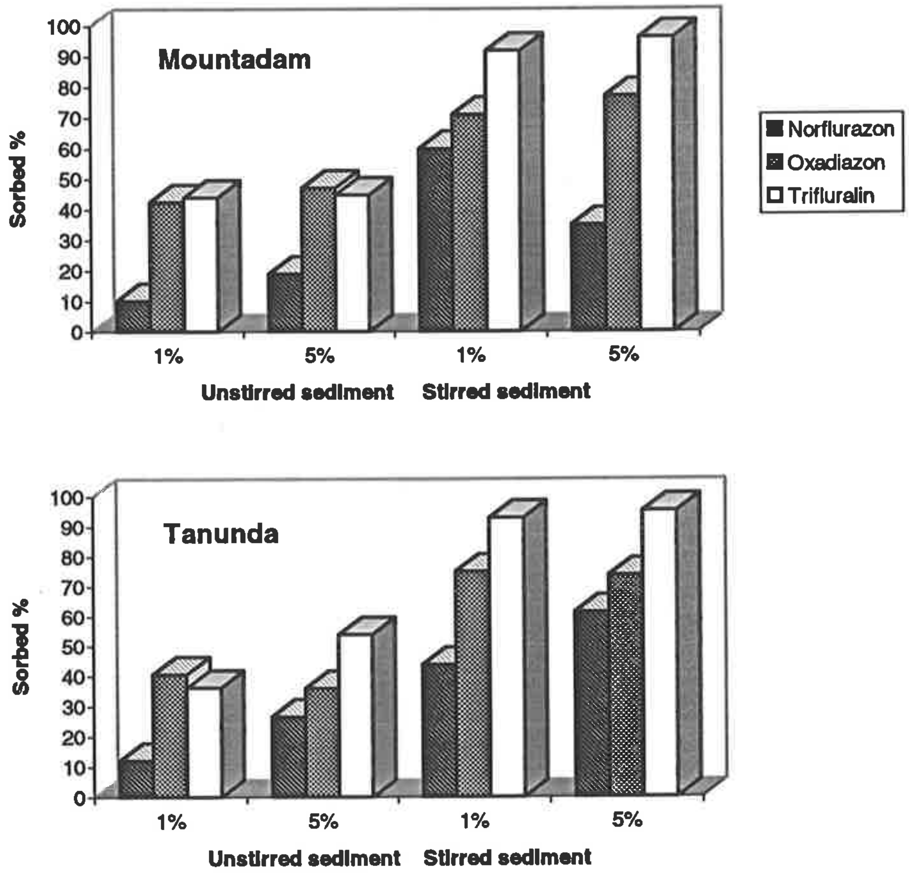


Figure 5.5 Sorption of herbicides on stirred and unstirred sediments. 1 % and 5 % refer to the sediment-water ratios, which are the same in Figure 5.7.

There is little difference in sorption between 1 % and 5 % of sediment in water under both stirred and non-stirred conditions (Figure 5.5). This suggests that there are high enough sediment levels in waters for herbicides to sorb on. The sorption of herbicides are in the same order as that in above sorption test: trifluralin > oxadiazon > norflurazon. But they have slightly smaller differences on sorption. Under non-stirred conditions, 10.1 to 26.6 % of norflurazon, 36 to 47.2 % of oxadiazon and 36.3 to 53.9 % of trifluralin were sorbed onto sediments, while under stirred conditions 35 to 61.4 % of norflurazon, 71 to 77 % of oxadiazon and 92 to 96.4 % of trifluralin were sorbed onto sediments. Trifluralin has the largest sorption and norflurazon has the lowest sorption under both stirred and non-stirred conditions. The extent of sorption of these herbicides on sediments was very high under stirred conditions.

5.4.2 Sorption of herbicides on charcoal

The experimental results show charcoal (activated carbon) can strongly absorb herbicides such as norflurazon, oxadiazon and trifluralin. In 40 ppm (w/v) charcoal solution, the herbicides were almost completely sorbed by the charcoal. In 20 ppm (w/v) charcoal solution, the herbicides were detected at concentrations of 16.9 ppb for norflurazon, 23.6 ppb for oxadiazon and 2.3 ppb for trifluralin after one hour and were not detected after 5 days. This is clearly shown in the GC traces after different sorption time intervals (Figure 5.6). Thus, charcoal is very effective in cleaning up herbicide contaminated water.

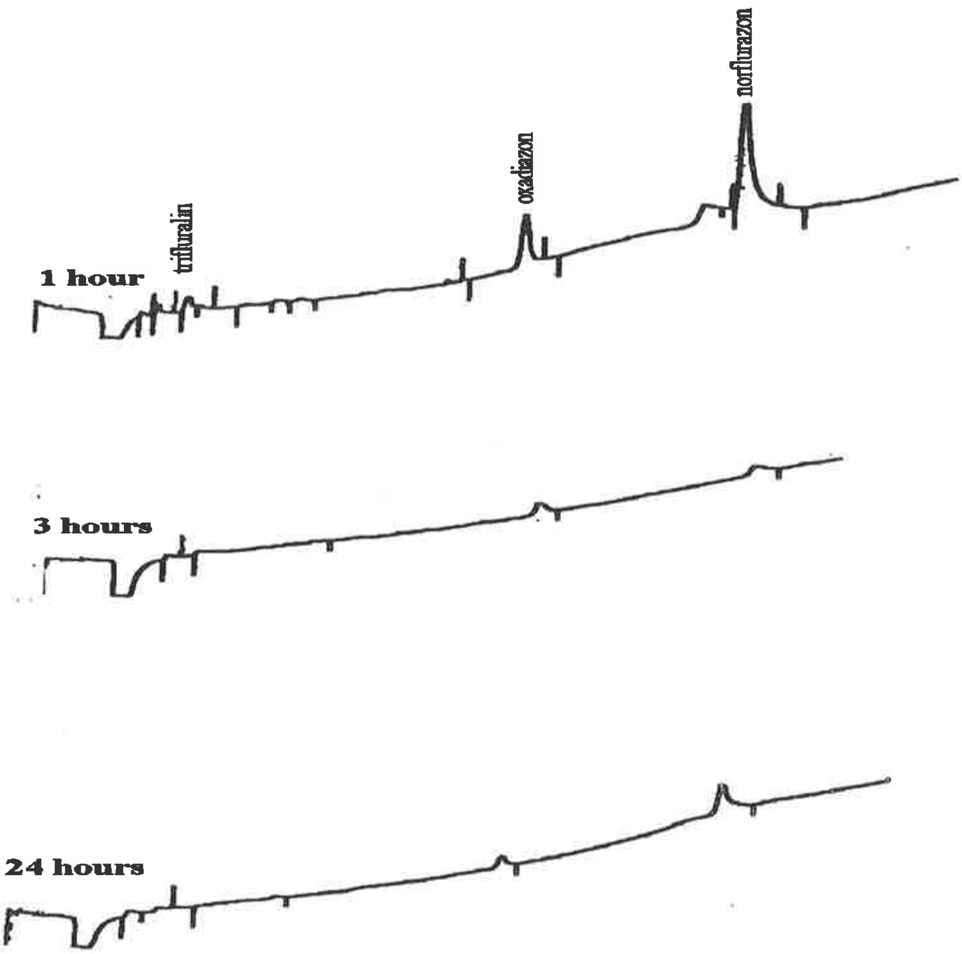


Figure 5.6 GC traces of the herbicides in water after sorption on charcoal.

5.4.3 Degradation of herbicides in water

Sorption of herbicides on sediments has some impact on the degradation of these chemicals in water. Our studies show that the relative concentrations of norflurazon, oxadiazon and trifluralin in water containing sediments (Tanunda soil) 6 and 13 days after treatment (DAT) were higher than those in pure water (Figure 5.7). The degradation rates of norflurazon, oxadiazon and trifluralin in pure water were faster than in waters containing 1 and 5 % Tanunda soil. But at the 13th day after treatment, the relative concentrations of trifluralin in sediment waters are lower than in pure water, which may be due to its strong sorption. In fact, the concentrations of these herbicides in pure water were: 0.27 ppm for norflurazon, 0.28 ppm for oxadiazon and 0.09 ppm for trifluralin while the concentrations in water containing sediments were: 0.36–0.37 ppm for norflurazon, 0.27–0.24 ppm for oxadiazon and 0.04–0.01 ppm for trifluralin at 13 DAT. Significant percentages of these herbicides in water-sediment systems have been sorbed onto sediments. Together with those sorbed on sediments, the total concentrations of the herbicides in waters containing sediments would be much higher than those in pure water. Therefore, sediments in water systems can enable the chemicals persist in water longer.

The degradation of herbicides in pure water is characterised by initial rapid loss followed by very slow degradation (Figure 5.8). Trifluralin degraded faster than the other two herbicides norflurazon and oxadiazon. Their half lives in water under laboratory conditions are 8.96 days for norflurazon, 7.38 days for oxadiazon and 1.84 days for trifluralin calculated using first order equations. The degradation of these herbicides in water was believed to be brought about by biotic and abiotic hydrolyses.

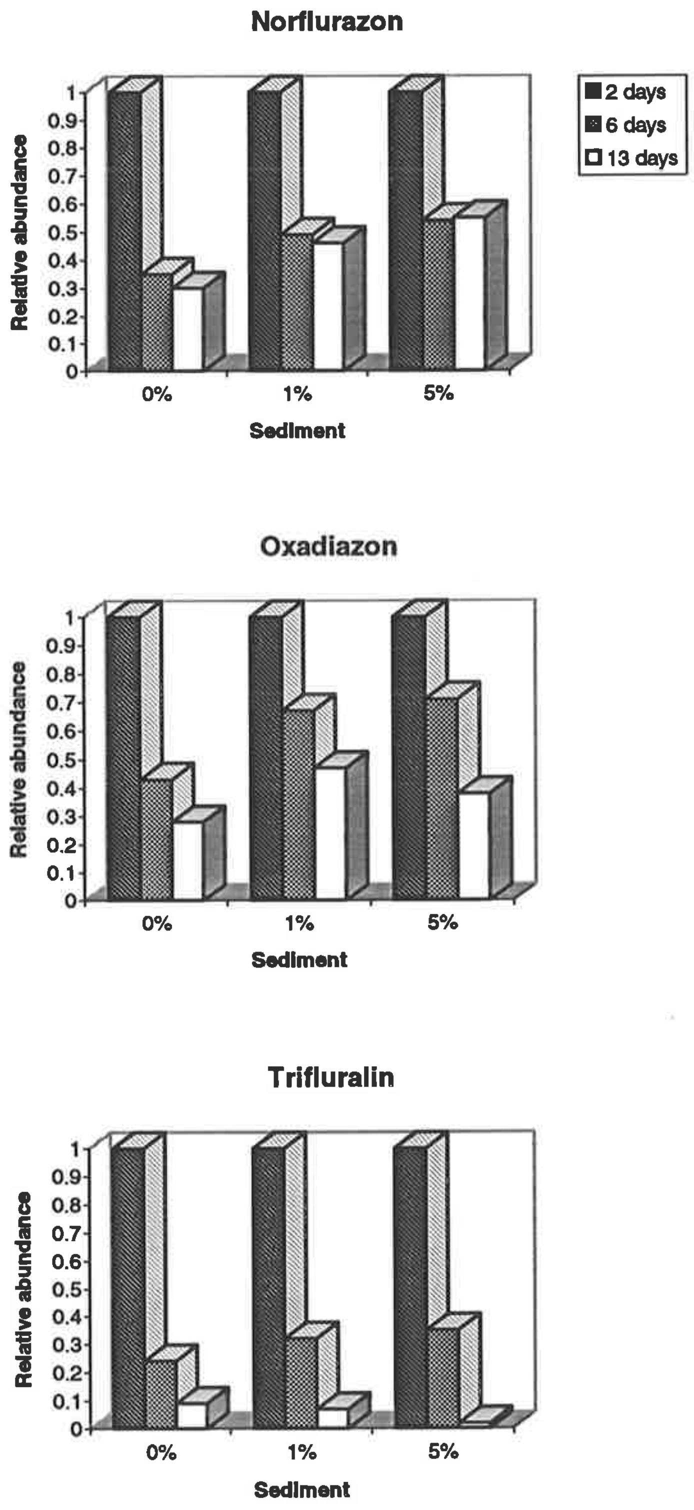


Figure 5.7 Sorption effect on degradation of herbicides.

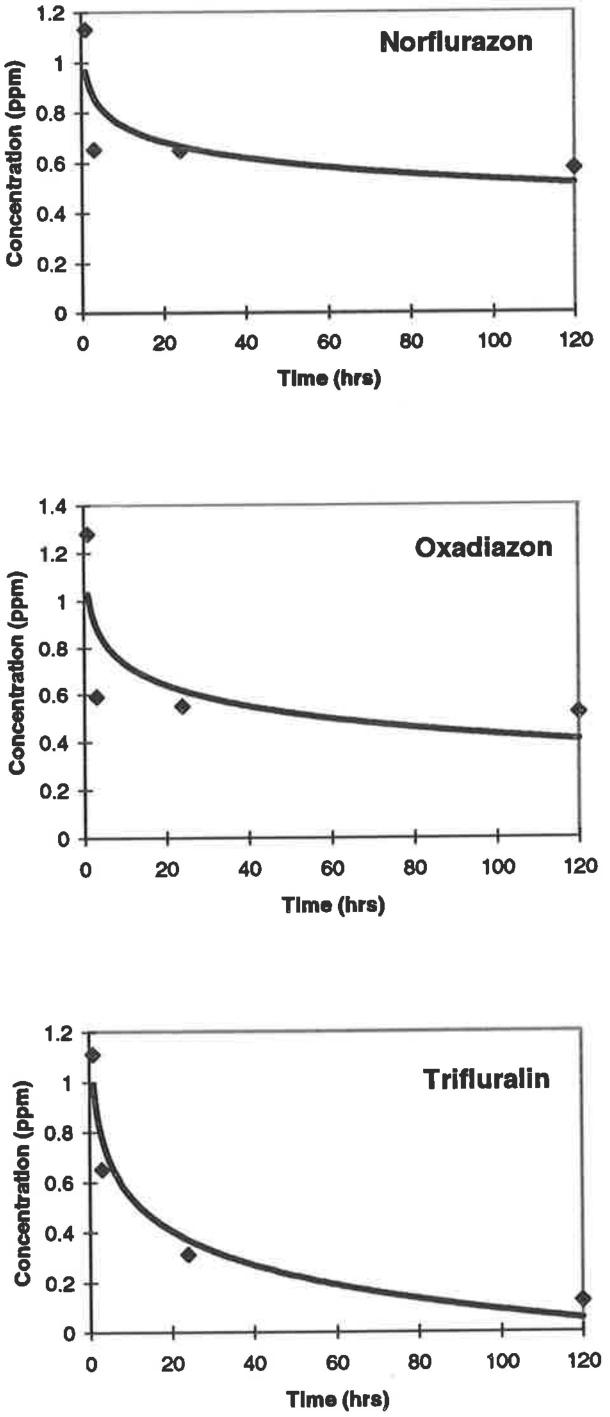


Figure 5.8 Degradation of herbicides in water under laboratory conditions.

5.4.4 Discussion

The experiments in this part of the study indicate that the herbicides norflurazon, oxadiazon and trifluralin degraded rapidly in water. But when these herbicides were sorbed on sediments, their persistence in water increased. Sorption of norflurazon, oxadiazon and trifluralin on soil could retard their degradation in water. These three herbicides had strong adsorption on charcoal, as well as on sediments (soils) in water systems. Sorption of these herbicides on sediments was much higher under stirred conditions than under non-stirred conditions. Sorption of these herbicides on sediments in water is determined by the soil organic matter.

Suspended sediments and bottom sediments in water can have great influence on water physiochemical conditions, thus affecting the degradation of chemicals in water. Hydrolysis, whether biotic or abiotic, is the main process occurring in water systems. For many chemicals, hydrolysis may be catalysed or enhanced under acidic or basic conditions. Hydrolysis can also be influenced by the sorption of a chemical on soil. The presence of catalytic surfaces in the soil can help bring about hydrolysis reactions. For example, studies have found that atrazine hydrolysis was faster in soils than in a soil free system at similar pH, and parathion sorbed on clays decomposed directly by hydrolysis or through an intermediary rearrangement step (as cited by Gerstl, 1991). The pH at the surface of many soils is lower than that of the water surrounding the soil particles; thus, an acid-catalysed hydrolysis reaction is enhanced when the chemical is sorbed on the soil (Brusseau and Bohn, 1996). Kinetic studies for some selected organic compounds indicate that in the sorbed phase alkaline hydrolysis is retarded, neutral hydrolysis is unaffected, and acid hydrolysis is enhanced (Gerstl, 1991). But the real picture is not so clear-cut, sorption of a chemical on soil organic matter or clay minerals can result in protection of the chemical from degradation (Farmer and Aochi, 1987). Noblet *et al.* (1996) studied the influence of natural dissolved organic matter, temperature and mixing on the abiotic hydrolysis of triazine and organophosphate pesticides, and found that for the triazines, dissolved humic substances alone are not sufficient to catalyse transformations and that a solid substrate (sediment or soil) may play an important role. The data for the organophosphates suggests that in addition to facilitating transport, dissolved organic matter (DOM) may also impede the abiotic hydrolytic degradation of these pesticides (Noblet *et al.*, 1996). Our experiments show that the degradation rates of norflurazon, oxadiazon and trifluralin in water containing sediments were lower than those in pure water due to the effects of sediments on physiochemical conditions in water or due to protection by suspended sediments. Sorption on suspended or bottom sediments can reduce the availability of herbicides to degradation in water systems. According to the two-site sorption model (Brusseau and Rao, 1989; Li *et al.*, 1996; Carton *et al.*, 1997), an initially fast sorption of pesticides by soils is followed by a second stage that is much slower and apparently irreversible, and the chemicals slowly diffuse into the interior of the soil particles. This nonlabile sorption makes the chemicals difficult to desorb and to be subjected to various degradation processes.

Sorption on clay minerals and activated carbon (charcoal) has been investigated for its potential for the removal of pesticides from water (Aly and Faust, 1965; Gomaa and Faust, 1974; Gonzalez-Pradas *et al.*, 1997). Hu *et al.* (1997) studied adsorbability of pesticides in water on powdered activated carbon. The amount of activated carbon needed for lowering pesticide concentration from 500 μg/l to 50 μg/l was 688.5 mg/l for hymexazol, and 5.1 mg/l for thiobencarb, which suggests that pesticides with a high polarity are difficult to remove by powered activated carbon. Faust and Zarins (1969) studied the removal of diquat and paraquat from water by activated carbon and clay minerals. A 1.0 mg/l diquat concentration was reported to be reduced to 0.01 mg/l with 143 mg/l carbon at pH 7.2. Our results show that 2 ppm of norflurazon, oxadiazon and trifluralin can be reduced to 16.9 ppb, 23.6 ppb and 2.3 ppb after 1 hour and removed almost completely after 1 day by 20 mg/l charcoal, and completely removed after 1 hour by 40 mg/l charcoal. Therefore, charcoal can very effectively remove these herbicides from water.

The possible use of clay minerals in the removal of pesticides from water has been evaluated by many investigators. Gonzalez-Pradas *et al.* (1997) studied the potential use of bentonite in removing atrazine from water and found that the removal efficiency ranged from 2.71% for natural bentonite to 83.5% for activated bentonite. Weber *et al.* (1965) found that the dipyridylium herbicides, diquat and paraquat, are strongly sorbed on montmorillonite clay. But Schwartz (1967) found that clay minerals suspended in dilute solutions adsorbed a small amount of 2,4-D and CIPC. This study on the interaction between herbicides and sediments in water systems showed that about 35–62% of norflurazon, 71–77% of oxadiazon and 92–97% of trifluralin were adsorbed on sediments (soils) in water in well stirred experiments. But the percentages of sorbed herbicides in unstirred experiments were much lower. This suggests that suspended sediments in water systems take greater amounts of pesticides than bottom sediments due to their more significant contact with pesticides in water. Organic pesticides in a water system can be distributed into several compartments, depending on their water solubility. These compartments include water, aquatic organisms, suspended sediment and bottom sediment. The more hydrophilic organic pesticides are primarily transported in the aqueous phase, while hydrophobic pesticides are associated with the organic carbon of the suspended and bottom sediments (Rostad, 1997). Movement of suspended sediment can transport pesticides from one place to another. They may end in the tissues of organisms, or settle down in the bottom sediments. For example, suspended sediments of the Mississippi River transport substantial amounts of lipophilic organochlorine pesticides (Rostad, 1997). Rostad (1997) identified some halogenated pesticides associated with suspended sediments in the Mississippi River, including PCBs, trifluralin, DCPA, aldrin, dieldrin, etc. This suggests that spraying soil into a contaminated water could reduce its pesticide level through mixing with water. Soil can sorb more chemicals from water than clay minerals because soil contains varying amounts of organic matter. Unlike charcoal, soil is natural substance and more acceptable ecologically to water environments. So it may be easier and cheaper to use soil in cleaning up the chemical contaminated waters.

In conclusion, sorption of the herbicides on soil increased in the following order: norflurazon > oxadiazon > trifluralin. The sorption of all these herbicides increased with an increasing organic content in soil, and increased with pH values for norflurazon. This study also indicates that moving suspended sediments in water systems can absorb more of the herbicides in water than bottom sediments, and that charcoal can strongly absorb these herbicides from water. This suggests that charcoal and sediment (soil) can be used to clean up water contaminated by herbicides. In addition, sorption of herbicides on suspended sediments could reduce the degradation rates of the herbicides in water.

CHAPTER 6

LABORATORY STUDY ON LEACHABILITY OF HERBICIDES

6.1 INTRODUCTION

Pesticides have been frequently detected in various water systems. The USEPA national survey of pesticides in drinking water in 1990 showed that some 446,000 of the nation's rural domestic wells may contain at least one pesticide (Turco and Kladivko, 1994). Since 1979, at least 74 pesticides have been detected in ground water in 38 states in the United States. It is estimated that between 1988 and 1989, 11.1 to 16.2% of all private, rural wells used for drinking water in Iowa were contaminated with at least one pesticide, and 1.2 % had pesticide concentrations above US EPA health advisory levels (cited by Weed *et al.*, 1995). Contamination of ground water by pesticides has been of increasing concern in recent years. Therefore, a clear understanding of the transport and dissipation of these pesticides in soil is essential for this issue to be dealt with satisfactorily.

Pesticide mobility will be studied in the laboratory in this chapter and in the field in the next chapter. Laboratory experiments can provide useful information on the behaviour of pesticides in soil. Leaching behaviour can be predicted by laboratory soil column studies, performed under a variety of water flow conditions (Weber *et al.*, 1993; Lopez-Avila *et al.*, 1986; and Gomez de Barreda *et al.*, 1993). Until recently, most laboratory studies used columns of sieved, repacked soil to study movement of pesticides under steady-state flow conditions. Leaching of bromacil, diuron, norflurazon and simazine in a Candler fine sand of Florida was studied by Tan and Singh (1995) and Reddy and Singh (1993). Leaching was evaluated using soil columns 8 cm long and 7 cm inner diameter. Bromacil completely leached followed by simazine (82 %), norflurazon (67%) and diuron (62%) in a total of five pore volumes. The relative leaching of herbicides in decreasing order was: bromacil > simazine > norflurazon > diuron. Tan and Singh (1995) also studied the effect of the mixture on leaching of bromacil and norflurazon in soils and found that metolachlor, terbacil, oxadiazon, simazine and trifluralin could decrease the leaching of norflurazon by different degrees. Gomez de Barreda *et al.*(1993) studied residual herbicide movement using Spanish orchard loam soil columns (40 cm in length, 9 cm interior diameter). The leaching potential in decreasing order was: bromacil > atrazine > simazine > terbumetone > terbuthylazine > terbutryne = diuron > trifluralin. Packed soil columns are very useful to understand the relative leaching potential of pesticides. But the occurrence of pesticides much deeper in soil profiles than expected, or their arrival at a water table much faster than predicted, suggests that laboratory packed soil columns are not sufficiently realistic to describe transport of pesticides in the field (Turco and Kladivko, 1994). So intact soil columns, sampled from the field, were seen as being able to more realistically simulate the movement of pesticides that might occur in the field.

The objective of this chapter is to investigate the leachability of the herbicides norflurazon, oxadiazon, oxyfluorfen, trifluralin, as well as simazine for comparison in Australian vineyard soils in the laboratory. This includes the relative leaching potential of these herbicides and the effect of the time of rainfall events on their leaching using packed soil columns, and mobility of these herbicides using intact soil columns.

6.2 MATERIALS AND METHODS

6.2.1 Packed soil columns

Glass columns (30 cm long, 2 cm inner diameter) were employed to investigate the relative mobility of norflurazon, oxadiazon, oxyfluorfen and trifluralin. Each column was packed with 40g of soils from Mountadam, Nuriootpa, Lyndoch and Tanunda in the Barossa region of South Australia, respectively to a depth of 15 cm. Water was added to each column to saturate soil overnight. Herbicides (0.5 mg of norflurazon standard and 1 mg each of oxadiazon and trifluralin) were applied on the top of each column. Herbicides were leached from the soil columns by applying 40 ml of distilled water per application, repeated 4 times. Leachates were collected after each addition of 40 ml of water on the column.

In order to test the effect of different treatments (including different column dimensions) on the leaching order of the herbicides, two additional columns were packed with 30 g each of Mountadam and Nuriootpa soils to the depth of only about 11 cm.The soil columns were saturated with deionised water overnight. The Mountadam soil column was spiked with 1.5 mg of norflurazon and 3 mg each of oxadiazon and trifluralin, while the Nuriootpa soil column was spiked with 1.5 mg of norflurazon and 3 mg each of oxyfluorfen and trifluralin. The two soil columns were each leached with a 30 ml volume of deionised water repeated 4 times. Leachates were collected after each addition of 30 ml of water. Each volume of leachate will be denoted by numbers(1, 2, 3, and 4).

The effect of watering time (or rainfall event) on leaching of herbicides was studied using three soil columns. Each column was packed tightly with about 70 g of Nuriootpa soil to 20 cm in length. The columns were saturated with distilled water overnight, then 0.5 mg each of norflurazon, oxadiazon, oxyfluorfen and trifluralin was applied to the top of each column. The soil columns were left one day for the first column, two weeks for second column and four weeks for third column before the addition of 40 ml of water to each column. Each addition of 40 ml of water was repeated for 4 times and the leachates were collected. Then each soil column was sectioned into 4 segments (5 cm long each).

6.2.2 Intact soil columns

6.2.2.1 Leaching tests

Leaching of simazine, norflurazon, oxadiazon, oxyfluorfen and trifluralin was studied in intact soil columns. Soil cores were taken using steel tubes sharpened at one end. Samples were taken from the appropriate vineyards in the Barossa region *viz*: Mountadam, Nuriootpa, Lyndoch, Tanunda, as well as Koonunga, Kalimna and Koonunga Hill. The soil properties of Mountadam, Nuriootpa, Lyndoch and Tanunda soils were given in the previous chapter (Table 5.1). Here, the compositional properties of the other three soils are presented in Table 6.1. The physical properties of all soils are given in Table 6.2. The columns were 30 cm long with an inner diameter of 7 cm and had a bottom lined with a thin nylon mesh.

The soil columns were placed on Buchner funnels fitted with a quartz fibre pad and No.4 filter paper. The soil columns were saturated with distilled water overnight. However, water did not leach out from the soil columns from Lyndoch, Tanunda and Koonunga Hill. The water only infiltrated to a depth of about 15 to 20 cm. Water did flow out of the soil column from Kalimna, but at an extremely low rate. So the Lyndoch and Tanunda soil columns were not proceeded with and only soil columns from Mountadam, Nuriootpa and Koonunga were used in the intact column leaching tests. Leaching of herbicides on dry intact soil columns from Kalimna and Koonunga Hill were also studied but without wetting soil before herbicide application.

It is a common practice to use herbicide mixtures in South Australian vineyards, so herbicide mixtures were applied in this experiment. Each soil column was spiked with 1 mg of each herbicide and following application, left for one night. Each day, 80 ml of water (equivalent to 20 mm rainfall per day) was applied to each column for a period of two weeks. The columns were covered between each application of "rainfall". For the soil columns from Kalimna and Koonunga Hill, water was applied until the sixth day in each case because water did not leach down effectively. The leachates were collected in flasks. After leaching was completed, the soil cores were sectioned into 10 segments of approximately 3 cm.

Table 6.1 Properties of three soils from Koonunga, Kalimna and Koonunga Hill.

Soil type	Depth (cm)	pH	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)
Koonunga	0-10	6.2	60.0	22.5	17.5	0.45
	20-30	--	55.0	20.0	25.0	0.38
Kalimna	0-10	6.1	75.0	7.5	17.5	0.79
	20-30	--	62.5	5.0	32.5	0.82
Koonunga Hill	0-10	5.8	43.7	6.3	50.0	1.13
	20-30	--	21.2	13.8	66.0	0.68

Table 6.2 The physical properties for the seven soils from the Barossa Valley.

Soil type	Depth	Bulk density	Porosity	Saturated conductivity (g s/m^3)	
	(cm)	ρ (g/cm^3)	ϕ	k_s^*	$k_s^\dagger$
Mountadam	0-10	1.505	0.431	1.453	2.753
Nuriootpa	0-10	1.435	0.458	1.174	1.981
Lyndoch	0-10	1.593	0.399	0.327	0.250
Tanunda	0-10	1.600	0.389	0.214	0.135
Koonunga	0-10	1.658	0.374	0.364	0.520
	20-30	--	--	0.294	0.340
Kalimna	0-10	1.549	0.415	0.689	0.906
	20-30	--	--	0.405	0.353
Koonunga Hill	0-10	1.300	0.509	0.182	0.106
	20-30	--	--	0.067	0.025

* calculated using the equation: $k_s = 2 \times 10^{-3} \exp[-4.26(m_s + m_c)]$

† calculated using the equation: $k_s = 4 \times 10^{-3} \exp(-6.9 m_c - 3.7 m_s)$

where m_s and m_c are silt and clay mass fractions (Campbell, 1985).

6.2.2.2 Effect of herbicide mixture on leaching of norflurazon

Two intact soil columns were taken from the same location in the Mountadam vineyard. They were labelled column A and column B and these used to study the effect of herbicide mixtures on the leaching of norflurazon in soil. A herbicide mixture of norflurazon, oxadiazon, trifluralin, oxyfluorfen and simazine (5 mg each) was applied to pre-saturated soil column A. Only norflurazon (5 mg) was applied to column B. Then pore volumes of water were applied continuously to each soil column and each pore volume of leachate was collected. After leaching, the soil cores were cut into 10 sections and extracted.

6.2.3 Extraction and analysis

Herbicide residues in the leachates were directly extracted by passing through C_{18} cartridges which were conditioned using methanol and water. Soil samples were soaked in methanol overnight and then mixed in a sonicator. The samples were then filtered into flasks. The filtrates were diluted with deionised water and passed through pre-conditioned C_{18} cartridges. All cartridges were dried by passing air for some time and then the extracted herbicides were eluted into small vials from these cartridges with several millilitres of methanol. The methanol extracts in vials was blown down using a gentle nitrogen gas stream. Finally the herbicide residues were analysed by GC-NPD.

6.3 LEACHING OF HERBICIDES ON PACKED SOIL COLUMNS

6.3.1 Relative mobility of herbicides

Figures 6.1 and 6.2 show clearly that the order of leaching potential of the herbicides in these soils was: norflurazon > oxadiazon > trifluralin > oxyfluorfen. More norflurazon was found in the leachates from every soil column. Norflurazon was the most leachable chemical among the four herbicides. The experiments on two different column dimensions gave the same order of leaching potential of the herbicides in soils.

This study shows that the leaching potential of the herbicides was different in the four soils: Mountadam, Nuriootpa, Lyndoch and Tanunda. Figure 6.1 shows that the herbicides leached more easily on the columns packed with Mountadam and Nuriootpa soils than on the columns packed with Lyndoch and Tanunda soils. The patterns in Figures 6.1 and 6.2 indicated that the herbicides had different leaching potential in different soils. Large percentages of the herbicides on the columns packed with Mountadam and Nuriootpa soils leached out after the first water application, while most of the herbicides on the columns packed with Lyndoch and Tanunda soils leached out after second or third water application. More of the herbicides remained in the clayey soil columns than in the sandy soil columns.

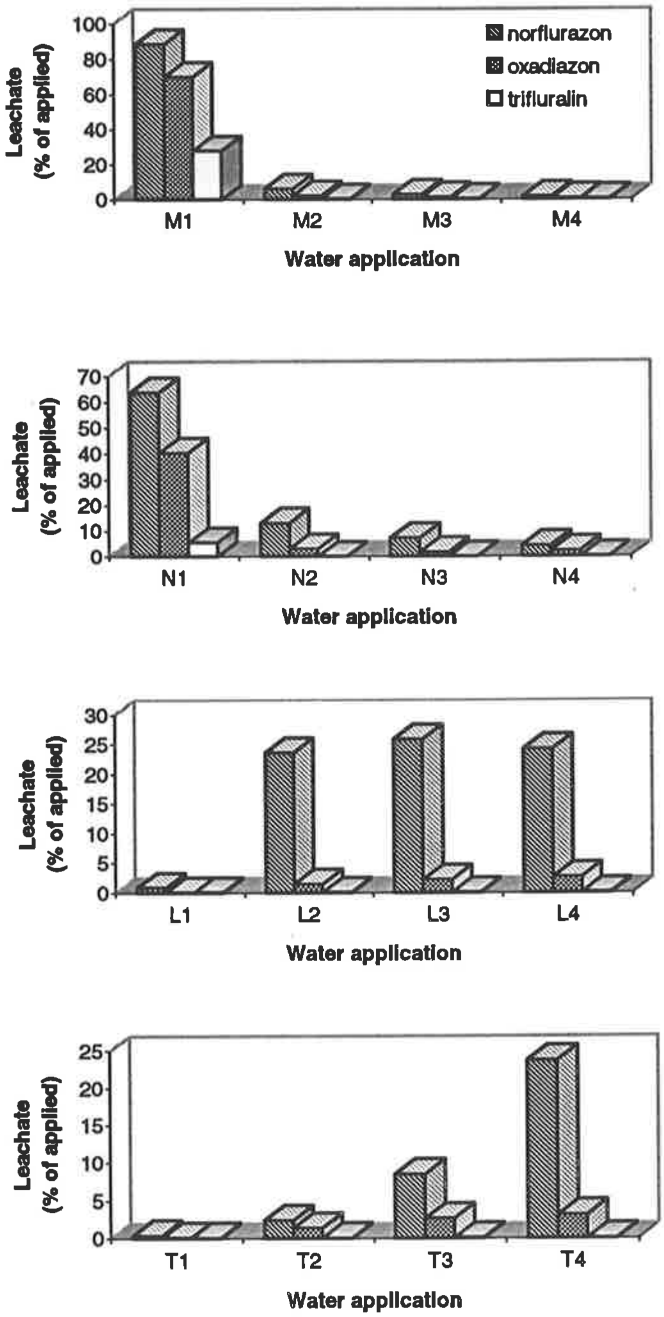
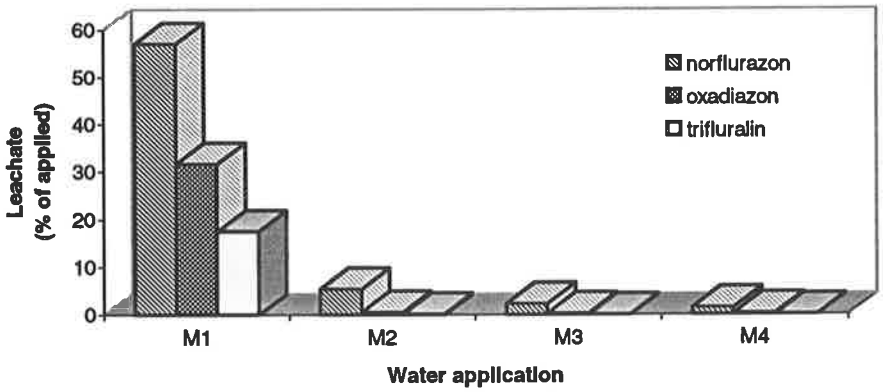


Figure 6.1 Leaching of herbicides on 15 cm soil columns. 40 ml of water was added onto each column at each application. M, N, L and T represent the soil types of Mountadam, Nuriootpa, Lyndoch and Tanunda soils. Numbers 1, 2, 3 and 4 indicate the water application. These are the same in the following.



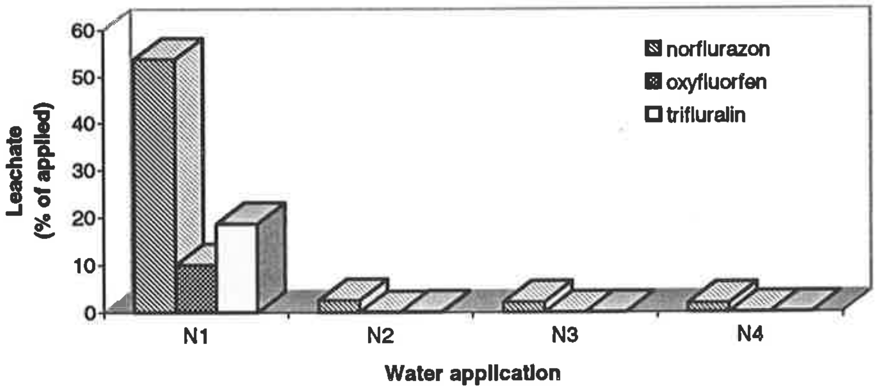


Figure 6.2 Leaching of herbicides on 11 cm soil columns. 30 ml of water was added to each column each application.

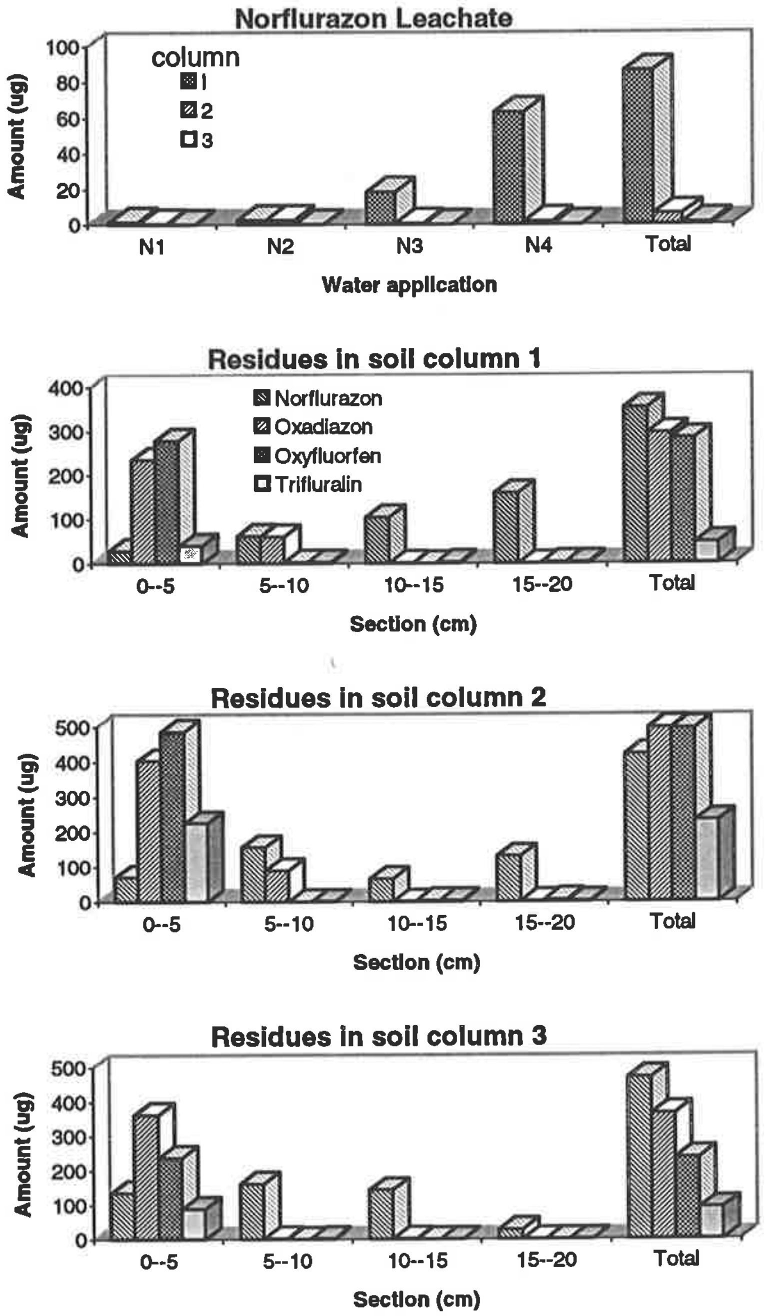


Figure 6.3 Norflurazon in leachates and herbicide distribution in soil columns after leaching. Water was applied on columns 1, 2 and 3 respectively one day, two and four weeks after herbicide application.

6.3.2 Time effect of watering on herbicide leaching

The leaching of the herbicides in soil was studied by applying water at different times: 1 day, 2 weeks and 4 weeks after treatment. In this experiment, only norflurazon was detected in the leachates from the three soil columns. The amounts of norflurazon in the leachates were 86.3 µg from the first soil column, 6.12 µg from the second soil column and trace from the third soil column (Figure 6.3). This indicates that norflurazon leached faster through the first soil column where water was applied 1 day later after herbicide application than where the application of water was delayed.

Distribution of the herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen after leaching shows the different extents of herbicide movement in the soils (Figure 6.3). Most of the trifluralin, oxadiazon and oxyfluorfen remained on the top soil section. Trifluralin had very low recoveries in the experiment, which might be related to its rapid degradation in water. The shorter the time was between herbicide application and watering, the further and more quickly the norflurazon moved.

6.4 LEACHING OF HERBICIDES ON INTACT SOIL COLUMNS

6.4.1 Leaching on intact soil columns

Studies on the leaching of herbicides on intact soil columns in the laboratory can provide realistic information on the leaching potential of herbicides in soil. The leachates collected from the intact soil columns from Mountadam, Nuriootpa and Koonunga showed that norflurazon and simazine leached down from the soil columns after the equivalent of two weeks of 20 mm daily rainfalls (Figure 6.4). The total amounts of herbicides in the leachates were 11.96 µg of norflurazon and 28.09 µg of simazine from the Mountadam intact soil column, 6.15 µg and 26 µg from the Nuriootpa soil column, and 9.21 µg and 122.89 µg from the Koonunga soil column. The total amount of simazine leached from the Koonunga soil column was much higher than from the other two soil columns. Each leachate, collected daily from the Mountadam, Nuriootpa and Koonunga intact soil columns, was also analysed (Figure 6.5). Simazine was the first component to leach out from the soil columns. Norflurazon was first detected in the leachates on the seventh or eighth day and its amounts increased from day 6 to day 14. Simazine was detected from the second day for the Koonunga soil column and from the fifth day for the Mountadam and Nuriootpa intact soil columns (Figure 6.5).

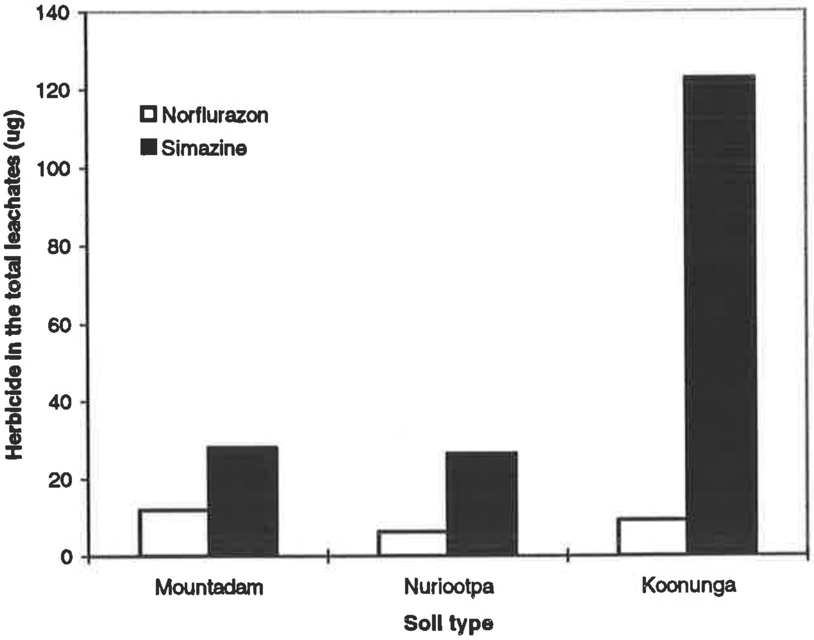


Figure 6.4 Norflurazon and simazine in the total leachates from the intact soil columns from Mountadam, Nuriootpa and Koonunga.

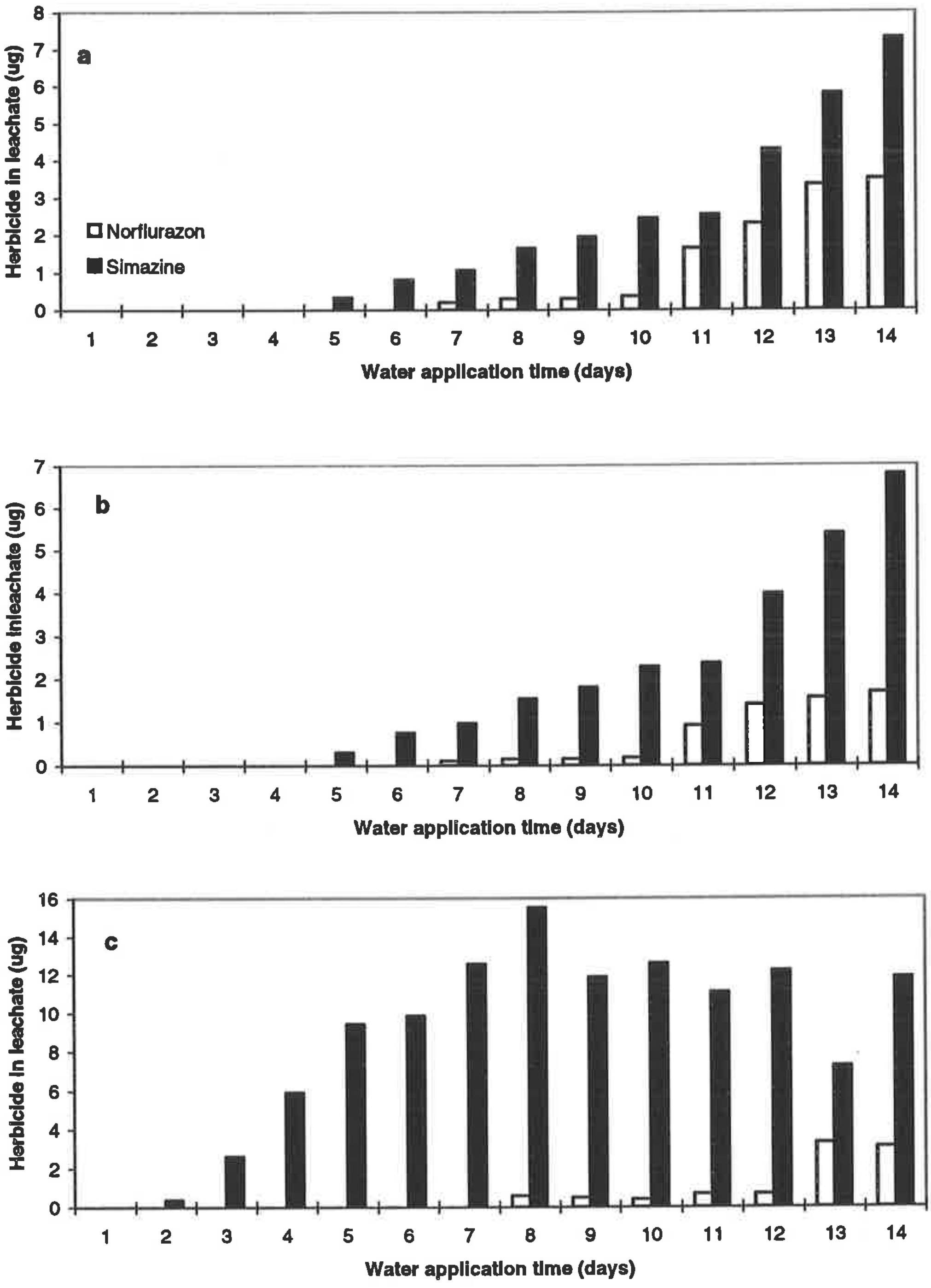
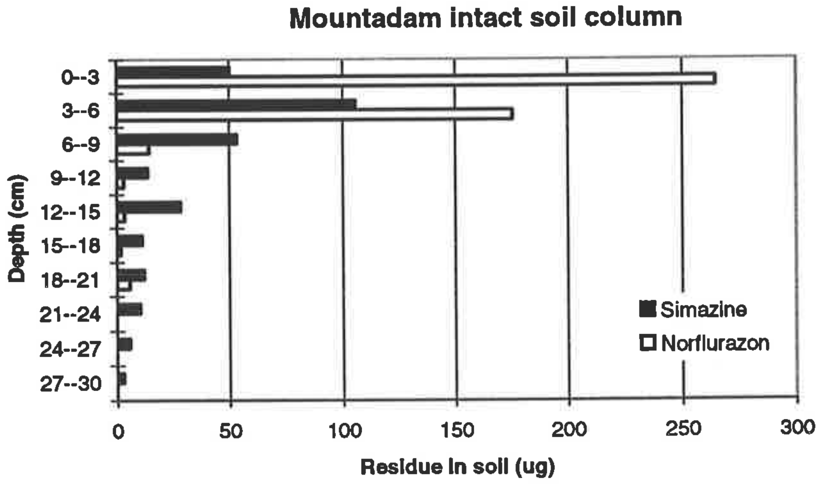


Figure 6.5 Norflurazon and simazine in the daily leachates collected from (a) Mountadam, (b) Nuriootpa and (c) Koonunga intact soil columns.

Distribution of the herbicides in the soil profiles after leaching was investigated (Figures 6.6, 6.7 and 6.8). The distribution of the herbicides in the three intact soil columns clearly shows that norflurazon and simazine leached to the bottom of the soil columns while trifluralin, oxadiazon and oxyfluorfen remained in the top of soil profiles (0—10 cm). The amounts of simazine remaining in the soil columns were lower than those of norflurazon.

A leaching study on dry intact soil columns from Kalimna and Koonunga Hill vineyards demonstrated that norflurazon and simazine could leach in clayey soils. After only six days' leaching with the equivalent of a daily rainfall of 20 mm, norflurazon and simazine moved to the bottom of the soil columns, while the other herbicides remained in the top of the soil columns (Figures 6.9 and 6.10). Leachates were collected from day 3 to day 6 from the Kalimna intact soil column, however little leachate was collected from the Koonunga Hill intact soil column. The total amounts of norflurazon and simazine in the leachates from the Kalimna soil column were 4.74 µg and 29.13 µg, respectively. The amounts of each herbicide leached from the Kalimna soil column were very high after only six days' leaching compared to the leaching of the herbicides on the Mountadam and Nuriootpa intact soil columns.



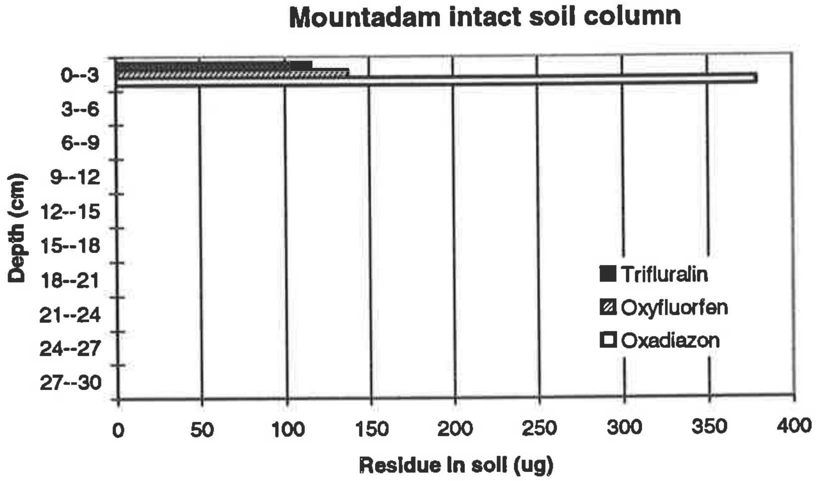
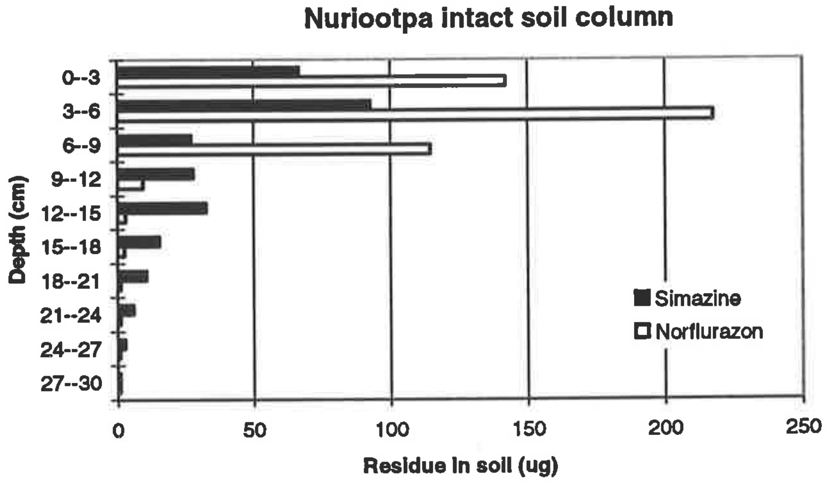


Figure 6.6 Distribution of herbicides in the Mountadam intact soil column after leaching.



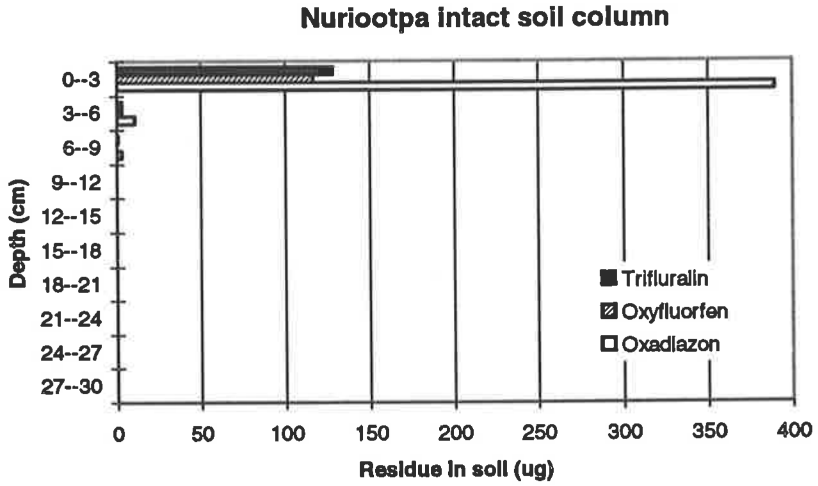
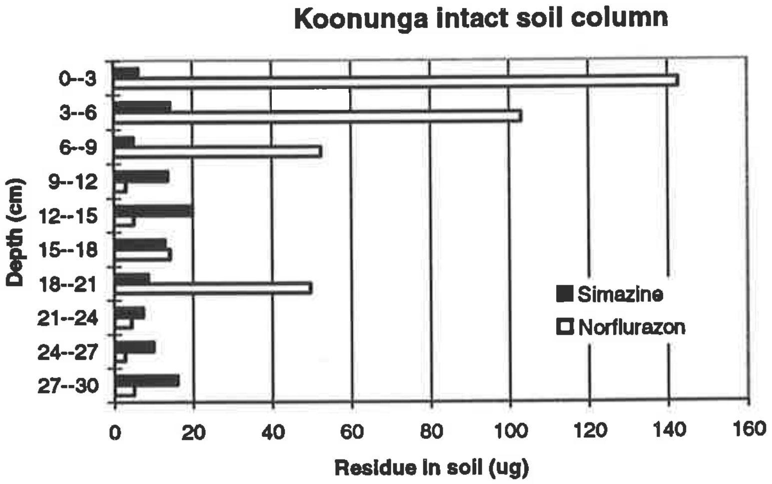


Figure 6.7 Distribution of herbicides in the Nuriootpa intact soil column after leaching.



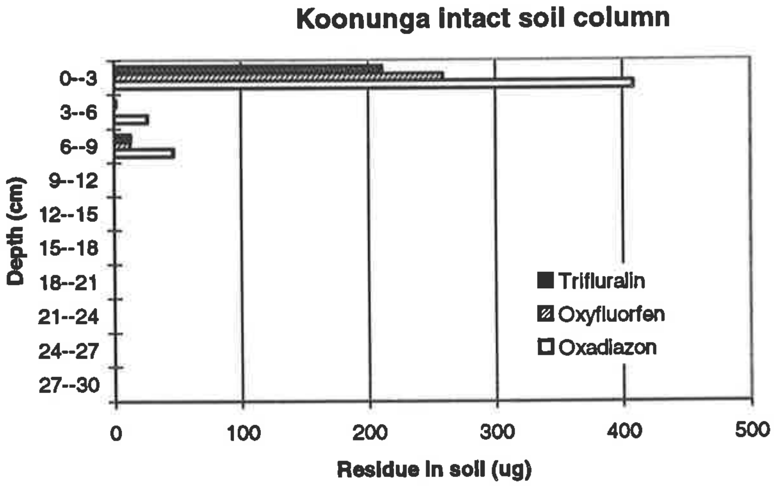
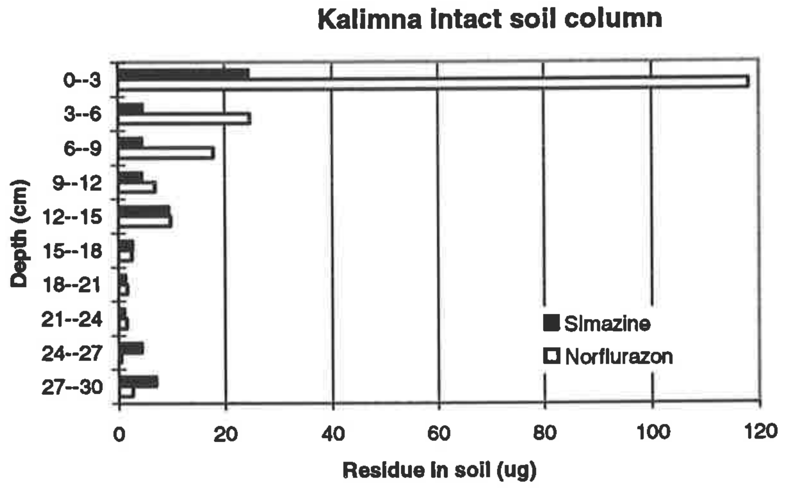


Figure 6.8 Distribution of herbicides in the Koonunga intact soil column after leaching.



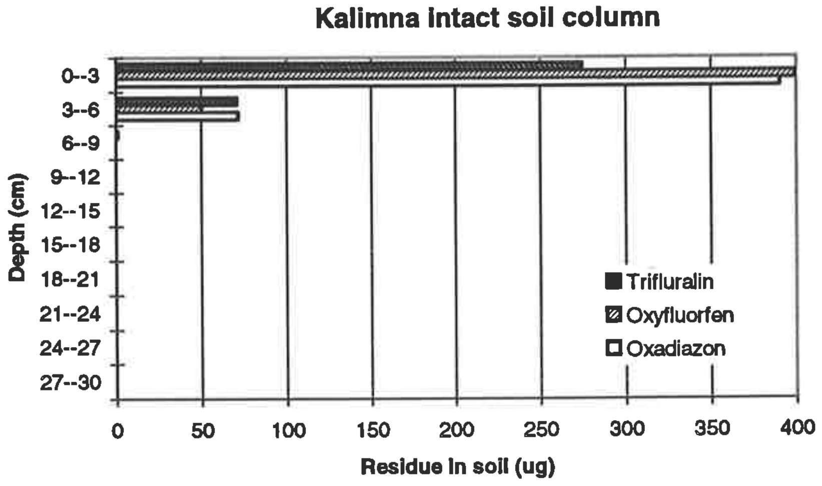
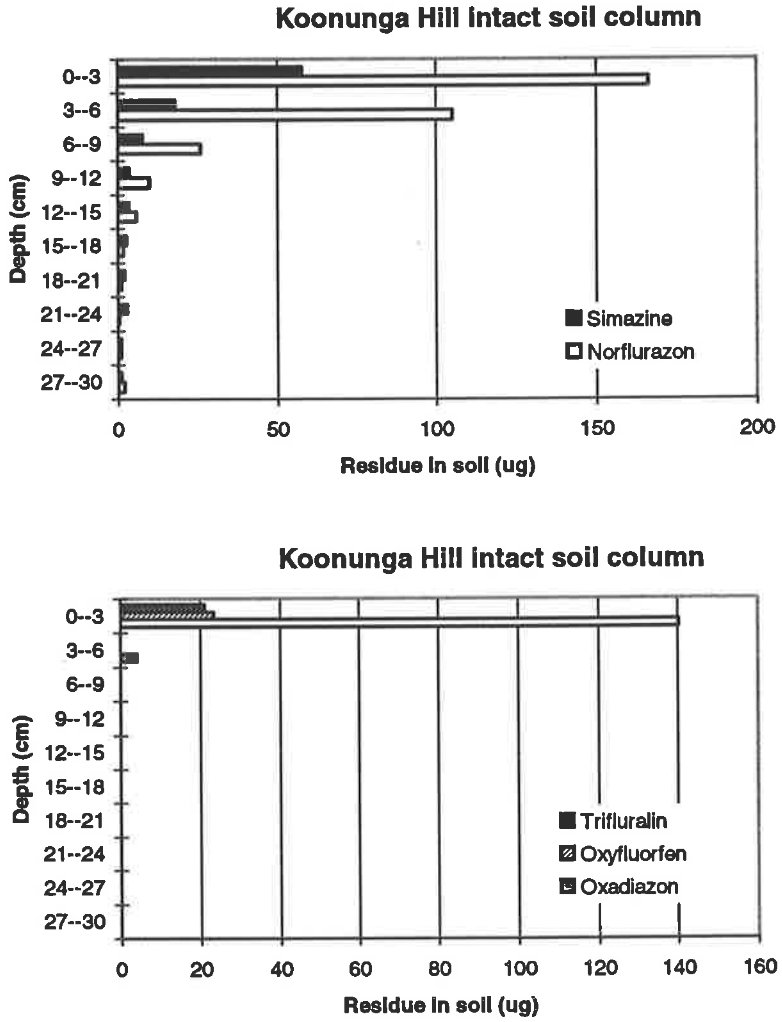


Figure 6.9 Distribution of herbicides in the Kalimna intact soil column after leaching.



Koonunga Hill intact soil column

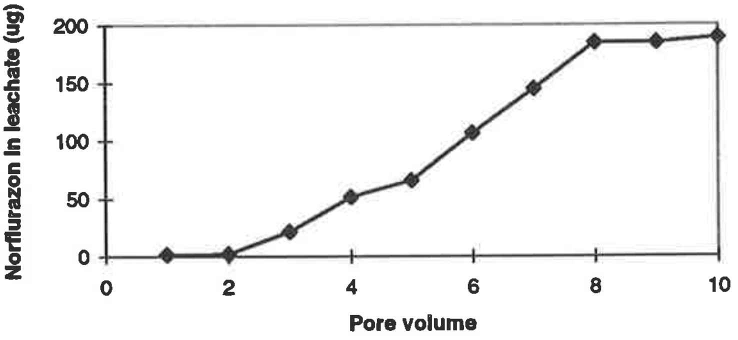
Koonunga Hill intact soil column

Figure 6.10 Distribution of herbicides in the Koonunga Hill intact soil column after leaching.

6.4.2 *Effect of herbicide mixture on leaching of norflurazon*

The effect of a herbicide mixture on the leaching of norflurazon was investigated on the two Mountadam intact soil columns, (i) applied with herbicide mixture (norflurazon, oxadiazon, oxyfluorfen, trifluralin, and simazine) and (ii) with only norflurazon. The breakthrough data from the intact soil column to which only norflurazon was applied are presented in Figure 6.11. Norflurazon leached out in the first pore volume of water. The amount of norflurazon in the leachate increased from the second water application. The total amount of norflurazon leached from the soil column was about 901 µg in a total of 10 pore volumes of water. The distribution of norflurazon in the soil column was shown also in Figure 6.11. The maximum peak of the norflurazon residue in the soil profile was to the depth of 18 to 21 cm.

The breakthrough data from the Mountadam intact soil column following application of the herbicide mixture are shown in Figure 6.12. Both norflurazon and simazine were detected in the leachates. It indicates that the amount of norflurazon in leachates increased from pore volume 6. The total amount of norflurazon leached from the soil column was 166.53 µg, which was much lower than that from the soil column to which only norflurazon was applied. The amount of simazine leached from the same soil column was 1407.18 µg, which was much higher than that of norflurazon. Simazine in the leachates increased from pore volume 1 to pore volume 3 rapidly and then was stable afterwards (Figure 6.12). The distribution of herbicides in the soil column also reflects the fact that norflurazon and simazine can leach down the soil profile (Figure 6.13). The maximum peak of the norflurazon residue in the soil column after the leaching test was located at the section of 9 to 12 cm. The other three herbicides (trifluralin, oxadiazon and oxyfluorfen) remained in the top soil layer (0 to 10 cm).



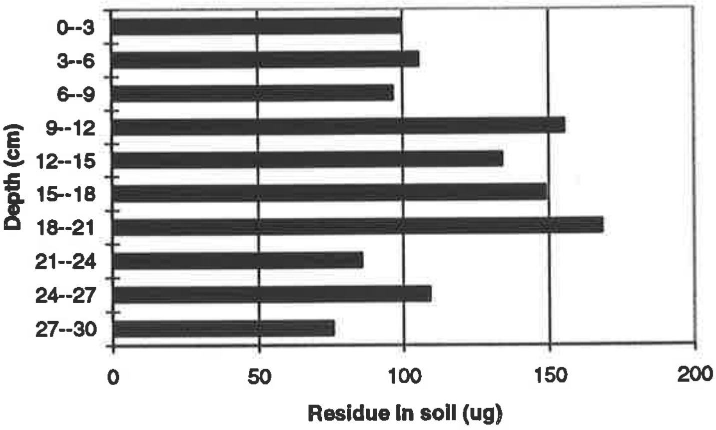


Figure 6.11 Norflurazon in leachates and its distribution in the Mountadam intact soil column applied only with norflurazon after application of 10 pore volumes of water.

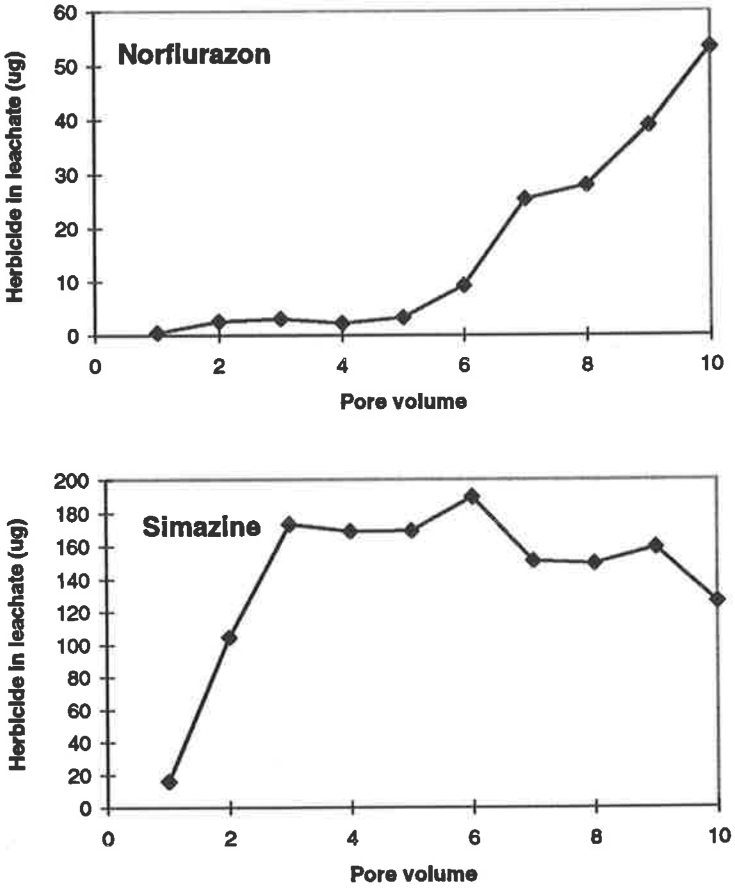


Figure 6.12 Breakthrough curves for norflurazon and simazine from the Mountadam intact soil column applied with herbicide mixture.

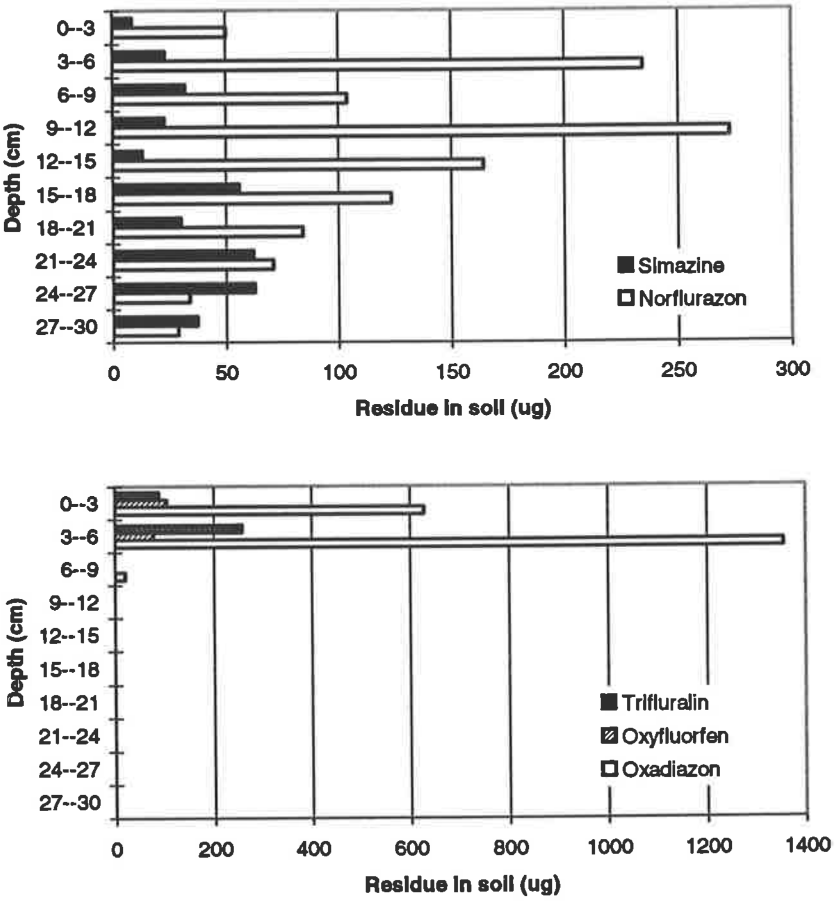


Figure 6.13 Distribution of herbicides in the Mountadam intact soil column after application of 10 pore volume of water.

6.5 DISCUSSION

Movement of chemicals in soil is an important process occurring in the field after chemical application. The mobility of herbicides in soils needs to be investigated in order to understand their environmental behaviour in the field. The relative mobility of the herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen in soils were studied using packed soil columns in the laboratory. The results of herbicide leaching experiments on packed soil columns showed that norflurazon was the most mobile chemical of the four herbicides studied, viz: norflurazon, oxadiazon, oxyfluorfen and trifluralin. Reddy and Singh (1993) and Gomez de Barreda *et al.* (1993) have also used packed soil columns to investigate the mobility of herbicides in soils. They found that the leaching potential of simazine was higher than those of norflurazon and trifluralin in soils. Leaching studies of herbicides on intact soil columns examined in this study found that more simazine leached from intact soil columns than norflurazon and the other investigated herbicides. This indicates the more mobile nature of simazine in soils. In fact, simazine and norflurazon were the only two chemicals leached out from the intact soil columns by water.

This study shows that soil type and soil structure are important factors in the leaching of herbicides in soils. The movement of herbicides varies in different soils. Leaching tests of herbicides on packed soil columns showed that more of the herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) were detected in leachates from sandy soils (Mountadam and Nuriootpa soils) than from clayey soils (Lyndoch and Tanunda soils). Organic matter is an important component in sorption of herbicides in soil, and it therefore influences leaching in soil. But due to the low organic matter contents in soils from the Barossa region (Tables 5.1 and 6.1), its influence on leaching of the herbicides is relatively smaller in those soils studied. Different soil types possess different soil physical properties (Table 6.2). These physical properties such as porosity and saturated conductivity are crucial factors in determining the movement of herbicides in soil. Mountadam and

Nuriootpa sandy soils have higher saturated conductivities, so water and herbicides move faster in these soils.

The other three soils (Koonunga, Kalimna and Koonunga Hill) from Greenock area of Northern Hills in the Barossa region contain relatively high clay contents (Table 6.1), and water flowed slowly in those intact soil columns. As expected, those soils had higher measured bulk densities and lower calculated saturated conductivities than did the two sandier soils. However, the soil samples collected from Koonunga Hill are an exception. Koonunga Hill Soil had a low bulk density and high porosity, possibly because the Koonunga Hill vineyard may have just been cultivated before sampling took place. But the calculated saturated conductivities of this soil from soil silt and clay contents were very low due to its high clay content. So water leached out extremely slowly, and no leachates from Koonunga Hill intact soil column were analysed. Leaching tests conducted on Koonunga Hill and Kalimna dry intact soil columns show that herbicides move to the bottom of the soil columns although leaching was very slow. Simazine and norflurazon were present in several of the leachates collected from the Kalimna intact soil column. The distribution of herbicides in these two soil columns also indicates that simazine and norflurazon can leach even in clayey soil like Koonunga Hill and Kalimna soils. Simazine and norflurazon are believed to move through soil macropores, not through the soil matrix. Macropores in soils are formed in most cases due to the wedging action of plant roots, or contractive forces that cause the soil (especially clayey soil) to shrink and crack on drying. So macropores such as cracks and holes may be the important pathways in the movement of herbicides in soil. This is also confirmed by the leaching of herbicides on Koonunga intact soil column. Although water flowed much more slowly in the Koonunga soil column, with a lower porosity and saturated conductivity, simazine and norflurazon were high in the leachates from this column. A low organic carbon content (0.38 to 0.45 %) is a contributing factor for the leaching of herbicides in the Koonunga soil.

This study also shows that the equilibrium time between herbicide application and incidence of rainfall had some influence on leaching of herbicides in soil. The longer the interval between herbicide application and rain (or water application), the less the herbicide (norflurazon in this case) leached. This might be interpreted as the herbicides needing a longer time to reach sorption equilibrium between water and soil, or that herbicides enter the soil mineral sorption sites slowly and once they are trapped inside, are able to resist leaching.

This study on the effect of herbicide mixture on leaching of norflurazon confirmed the previous findings by Tan and Singh (1995) on Florida citrus soil. More norflurazon was leached from the intact soil column treated only with norfurazon than from the intact soil column treated with herbicide mixture. Tan and Singh (1995) found that effect of herbicide mixture on norflurazon leaching depended on the amount of water applied. Oxadiazon and simazine significantly reduced norflurazon leaching when three or four pore volumes of water were applied. Trifluralin decreased norflurazon leaching when two or three pore volumes of water were applied. Oxyfluorfen had no impact on norflurazon leaching (Tan and Singh, 1995). The reason why these herbicides can influence norflurazon leaching is still unclear.

In summary, it can be concluded that the relative leaching of herbicides in soil in decreasing order was simazine > norflurazon > oxadiazon > trifluralin > oxyfluorfen. A packed soil column is an effective way to study the relative mobility of herbicides in soil. Many factors such as herbicide properties, soil type, rainfall and soil structure affect herbicide leaching. Among these factors, physical properties, especially saturated conductivity, are believed to be important in the leaching of a herbicide in soil. Soil structure of clayey soil also need be considered. This study also indicate that herbicide mixture could have some impact on norflurazon leaching. Finally, the longer the interval between herbicide application and the incidence of rainfall the less was the herbicide leached from the soil.

CHAPTER 7

DISSIPATION AND MOBILITY OF HERBICIDES IN A VINEYARD

7.1 INTRODUCTION

Herbicides are widely applied to control weeds in vineyards. The application of herbicides may result in the accumulation of their residues or degradates in soils, groundwater or surface water, with the potential to cause vine injuries. Their persistence and mobility are a major concern to the wine industry.

The fate and behaviour of herbicides in the soil are influenced by many factors, including soil properties, soil management, chemical application methods, landscape, crops and climate conditions. Applying a pesticide to the soil surface without incorporation, which is typical practice for conservation tillage can increase the amount of pesticide leaching and dissipation shortly after application (Fermanich and Daniel, 1991; Locke and Harper, 1991). Barrett and Lavy (1984) found great differences in the dissipation of oxadiazon between the air-dry treatment and the moist treatments (field capacity, alternate flood and continuous flood), but no significant differences between the moist treatments. This indicates that changes in soil water content above some minimum level will not affect the sum of the processes responsible for oxadiazon dissipation. There was a greater dissipation in the field initially because oxadiazon was concentrated on the surface and not incorporated as in the laboratory study (Barrett and Lavy, 1984). Other studies on norflurazon (Schroeder and Banks, 1986) and trifluralin (Jolley and Johnstone, 1994) also confirmed that cool and/or dry environmental conditions caused long persistence of herbicides.

In order to minimise the risk of herbicide contamination in vineyards, studies on their dissipation and mobility need to be carried out. Laboratory studies on sorption and leaching of herbicides in soils have provided much useful information. However, laboratory experiments can not simulate many field conditions. For example, one of the limitations in laboratory leaching studies is the boundary effect on the movement of chemicals because the lower part of a soil column is not under the same soil water conditions as it is in the field. Hence field experiments provide the most reliable method for determining the fate of chemicals in soils and groundwater. Many case studies show that results from laboratory studies can differ greatly from what happened in the field due to many variables (Turco and Kladivko, 1994; Flury, 1996; Redondo et al., 1997). In recent years, herbicides were sometimes found to occur deeper in soil profiles than was expected, or move faster than predicted on the basis of laboratory studies (Flury, 1996; Jury et al., 1986; Kladivko et al., 1991). Kladivko et al. (1991) found all applied chemicals (both bromide and pesticides) appeared at the same time in the drains used in their studies and the detected pesticides appeared in the drains much sooner than predicted by models that assume convective-dispersive transport. Strongly adsorbing chemicals can move as fast through soil as mobile chemicals (Flury, 1996). In a field study, Jury et al. (1986) reported that 20% of the applied mass of napropamide migrated far below the maximum depth predicted to be reached if it had undergone equilibrium adsorption. A preferential flow mechanism was considered to be responsible for this phenomena. Macropores such as earthworm burrows, root channels or cracks provide potential pathways for preferential flow. Graham et al. (1992) reported in a field study that herbicide residues (atrazine, at levels of 2 to 3750 ppb) in a cultivated California Vertisol were detected not only at the surface, but in crack walls and directly below open cracks to a depth of 125 cm, but no resides were detected within the soil matrix between open cracks. This suggested that the herbicides have moved preferentially via the cracks.

The herbicides norflurazon, oxadiazon, oxyfluorfen and trifluralin are widely used in Australian viticulture. There have been some studies on leaching of the herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen. Southwick *et al.* (1993a) studied leaching loss of norflurazon on subsurface drained plots on Mississippi River alluvial soil with incorporation of the herbicide into soil of 10-15 cm deep and found that norflurazon loss in drains was greater in 1989-1990 than in 1988-1989, which was related to the rainfall for the two seasons. Schroeder and Banks (1986a) found movement of norflurazon through the soil profile (0 to 30 cm) 110 days after application to five Georgia soils. There was essentially no movement of oxyfluorfen through 5 cm columns of a silt loam soil and a fine sand soil due to strong adsorption of this herbicide onto soil (Fadayomi and Warren, 1977). However, previous studies have shown that this herbicide may be carried in runoff water (Keese *et al.*, 1994) or leached from the containers (Horowitz and Elmore, 1991). Riley *et al.* (1994) determined the level of oxyfluorfen in pond water and sediment from container plant nurseries with the highest concentrations to be 0.04 µg/ml in water and 4 µg/g in sediment. In general the higher levels were observed in the month following significant applications (Riley*et al.*, 1994).

Wehtje *et al.*'s (1993) study shows that oxadiazon was sufficiently adsorbed to resist leaching-based displacement. Niemczyk and Krause (1994) studied mobility of trifluralin and oxadiazon and two other herbicides in turfgrass in 1988-89. They reported that trifluralin remained in the 0–5 cm zone while residues of oxadiazon were detected on occasions in the 22.5-25 cm zone in 1989. Leaching of oxadiazon also occurred on a sandy loam soil and a sandy soil (Fourie, 1992 and 1993). The presence of oxadiazon in the 5-10 cm and 15-30 cm soil layers 15 days after application is a clear indication that leaching occurred during the preceding period (Fourie, 1993).

The objective of this part of the study is to investigate the dissipation of norflurazon, oxadiazon, trifluralin and oxyfluorfen in a vineyard of South Australia, and in particular, their distribution and movement in the vineyard soil.

7.2 MATERIALS AND METHODS

7.2.1 Experimental site and herbicide application

The field study was conducted on 3 plots (each 30m × 10m) in the Mountadam Vineyard, Eden Valley, South Australia. The experimental site is on the down slope of a vineyard adjacent to a dam. The slope is of the order of 5% (Figure 7.1). The groundwater below the study area flows to the dam. The soil within the study area is classified as sandy soil with an increasing clay content with depth.

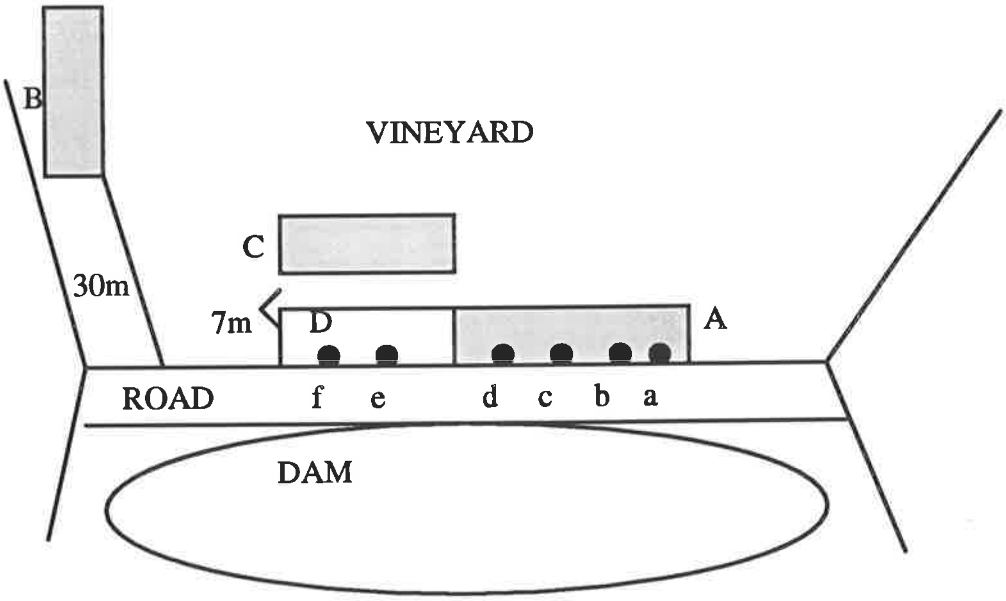


Figure 7.1 Field site with locations of plots and sampling tubes. Shaded plots (A, B and C) were sprayed with the herbicides and black dots in plots A and D were lysimeter tubes (a, b, c, d, e and f) used to collect water samples.

In 1996 and 1997, herbicides were applied at recommended rates without incorporation into soil on plots A, B and C to investigate their dissipation and movement in soil (Table 7.1). The application rates were 3.3 kg/ha for norflurazon (Solicam), 4 kg/ha for oxadiazon (Ronstar), 1.7 litres/ha for trifluralin and 10 litres/ha for oxyfluorfen (Goal). Norflurazon and trifluralin were sprayed on plot A on August 19, 1996 while oxyfluorfen was sprayed on the plot on September 2, 1996. Oxadiazon was sprayed on plot A on May 27,1997 and on plot B on July 7, 1997. Norflurazon and trifluralin were applied on plot B on May 27, 1997. Norflurazon, oxadiazon and trifluralin were also applied on plot C on August 19.1997. The tubes used to collect soil water, and their surrounding areas were covered by plastic films before herbicide application, which prevented water to flow preferentially into the tubes and their boundaries.

Table 7.1 Herbicide application timetable.

Plot	Norflurazon	Oxadiazon	Oxyfluorfen	Trifluralin
A	Aug. 19, 1996	May 27, 1997	Aug. 19, 1996	Aug. 19, 1996
B	May 27, 1997	July 7, 1997	–	May 27, 1997
C	Aug. 19, 1997	Aug. 19, 1997	–	Aug. 19, 1997

7.2.2 Sampling and residue analysis

Following herbicide application, soil and groundwater in the study area were monitored carefully during 1996-97. Surface soil and/or soil cores were taken by a hand auger (3.5 cm in diameter) at specified or predetermined intervals in plots A, B and C, which had been sprayed with the herbicides norflurazon, oxadiazon, oxyfluorfen and trifluralin. More than 10 surface soil samples (0-5 cm) were randomly taken on each occasion from each plot, mixed and analysed as a composite sample. The soil cores were cut into 5 cm sections, *i. e.* 0–5 cm, 5–10 cm, 10–15 cm and 15–20 cm depths. In 1996, surface soil was taken in a plastic bag immediately after application and put in the laboratory under dark conditions in order to compare the dissipation of herbicides under field and laboratory conditions.

Miniature lysimeters in the form of predrilled plastic tubes, with the in-ground end sealed and the top capped with a removable cover, were placed into the soil in plots A and D on the downslope side of the vineyard before herbicide application. The tubes were 1 m long and 10 cm diameter and had about 20 small holes (2mm in diameter) in the wall in the middle section, except for the top 10cm and bottom 20 cm. Water in the tubes (a, b, c, and d) of plot A were sampled in 1996 and again in 1997. In 1997, water samples were taken 2 weeks after oxadiazon application in plot A. The tubes in plot D were 7 m away from plot C and were used during 1997 to monitor the lateral herbicide movement. Sampling of groundwater was continued until the bulk of the season's rainfall had ceased and no further leachate was found in the tubes.

Soil samples were mixed with methanol under sonication and filtered through Millipore 0.45 µm filter papers. The filtrates were diluted with distilled water and the mixtures were extracted by C_{18} cartridges pre-conditioned with methanol and water. Groundwater samples (200 ml) were directly extracted with C_{18} cartridges after filtration through Millipore filter papers. The cartridges were dried by drawing air through them for half an hour. Then the adsorbed herbicides were eluted with 5 ml of methanol and analysed by GC-NPD.

7.3 DISSIPATION AND DISTRIBUTION OF HERBICIDES

7.3.1 Dissipation of herbicides in soil

The measurement of herbicides in plot A in 1996 and in plot B in 1997 shows that the dissipation of norflurazon, oxadiazon, trifluralin and oxyfluorfen in surface sandy soil was characterised by fast initial loss followed by slow subsequent degradation (Figure 7.2). Norflurazon, oxadiazon and trifluralin degraded relatively quickly while oxyfluorfen degraded very slowly. In May 1997, herbicides that were applied in 1996 to plot A were detected about 9 months after treatment at concentrations of 2.29 ppm for norflurazon, 0.56 ppm for trifluralin and 13.04 ppm for oxyfluorfen in the surface soil (0-5 cm). The dissipation rates of these herbicides in the surface soils were calculated according to first order reaction kinetics using equations 2.22/23/24 in Chapter 2 and the results are shown in Table 7.2. Oxyfluorfen had a longest dissipation half-life of 16.5 weeks while that for oxadiazon was only 2 weeks in surface soil. The dissipation half-life for trifluralin in surface soil was about 4 weeks, but that of norflurazon varied from about 7 weeks in 1996 to 3 weeks in 1997.

Table 7.2 The dissipation half lives and rate constants of herbicides in soil

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

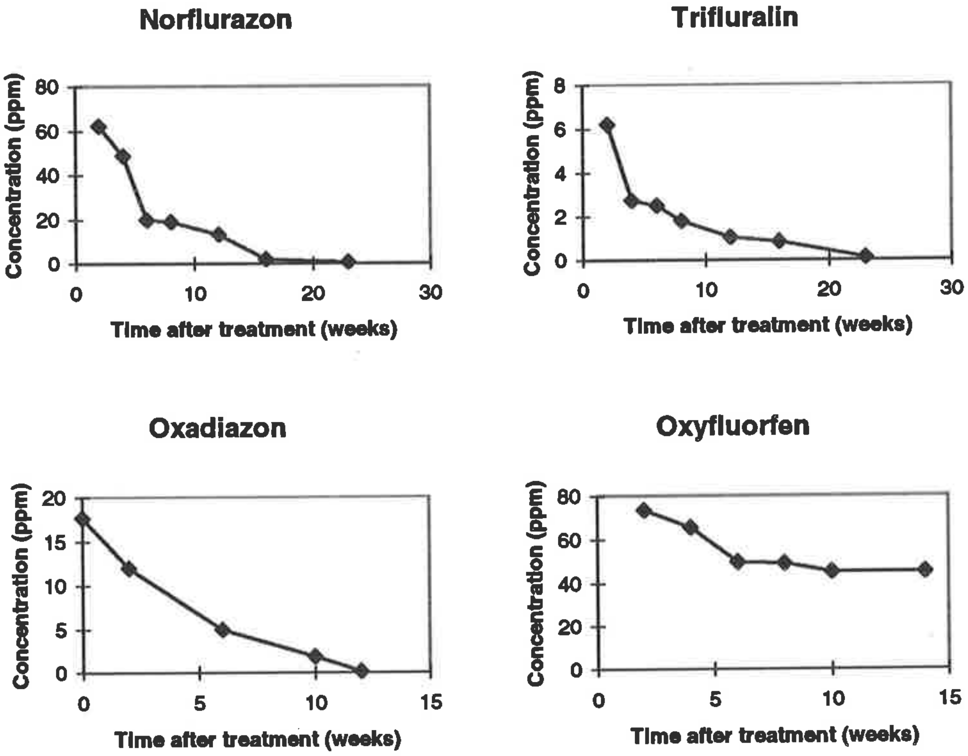


Figure 7.2 Dissipation of herbicides in soils. All data were measured in plot B in 1997 except oxyfluorfen which was measured in plot A in 1996.

Dissipation of norflurazon and trifluralin in soil in the field and laboratory is compared in Figure 7.3. It shows that norflurazon and trifluralin degraded very slowly under laboratory conditions. After 6 weeks in the laboratory, the levels varied little from the initial concentrations. However, these two herbicides dissipated much more quickly in the field. So the results of herbicide dissipation from laboratory studies, as mentioned earlier, could be very different from the situation found in the field.

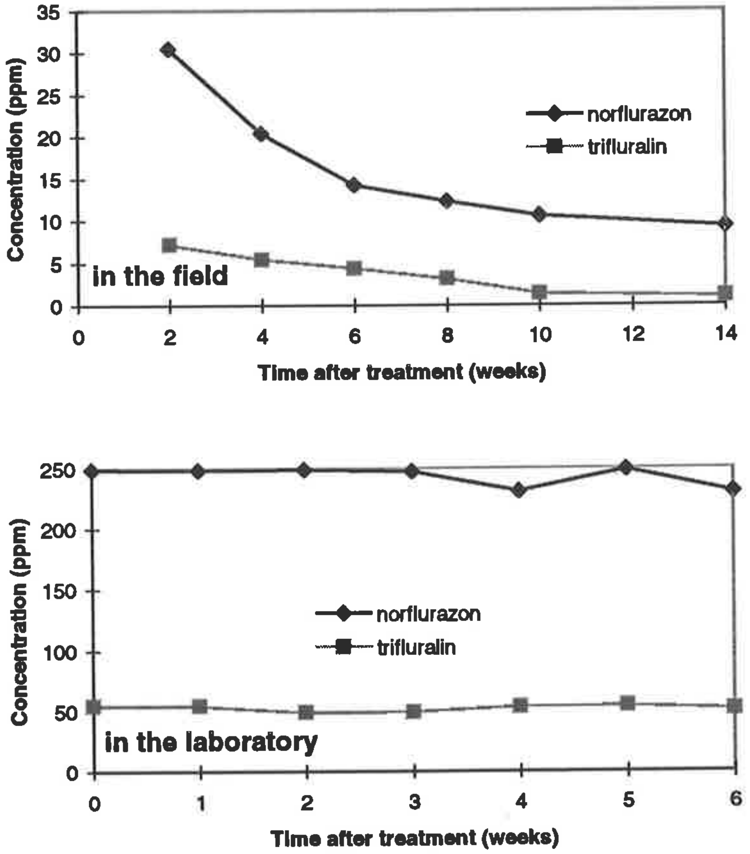


Figure 7.3 Comparison of dissipation of norflurazon and trifluralin in the soil of plot A in field and laboratory.

7.3.2 Distribution of herbicides in soil profiles

Distribution of the herbicides norflurazon, oxadiazon and trifluralin in soil profiles of plots B and C was monitored in 1997 to investigate their movement in the soil. The results from soil cores from plot B show that norflurazon, oxadiazon and trifluralin could leach down to a depth of 20 cm in soil profiles (Figure 7.4). It should also be pointed out that the time intervals between application and sampling were different for soil cores taken from plots B and C due to different application dates, although the soil cores might be taken at the same date. In the first 8 weeks, most of norflurazon and trifluralin stayed in the top soil layers (0-5 cm) although trace amounts of norflurazon and trifluralin were found below 5 cm. But from week twelve, more norflurazon and trifluralin were detected in the lower part of soil layers and their concentrations in the top layer decreased rapidly. However, the distribution of oxadiazon in the soil profiles was a little different from those of norflurazon and trifluralin. In the soil core taken in the sixth week for oxadiazon, which was taken at the same date as that for norfluralin and trifluralin (the twelfth week for plot B), only trace amounts of oxadiazon were detected below 5 cm and oxadiazon in the top layers also degraded rapidly. As an example, oxadiazon was detected at a concentration of 25 ppb in the 15-20 cm zone (Figure 7.4).

Studies on the two soil cores from plot C show similar results to plot B (Figure 7.5). Soil cores were taken from plot C 6 and 11 weeks after treatment, which were equivalent to the soil cores of eighteenth and twenty third weeks for norflurazon and trifluralin in plot B. Norflurazon could leach down to a depth > 20 cm while most trifluralin and oxadiazon remained at the top soil layers (0-5 cm). About 10 ppb of trifluralin was detected at the zone of 15-20 cm, but only trace of oxadiazon was detected in this layer.

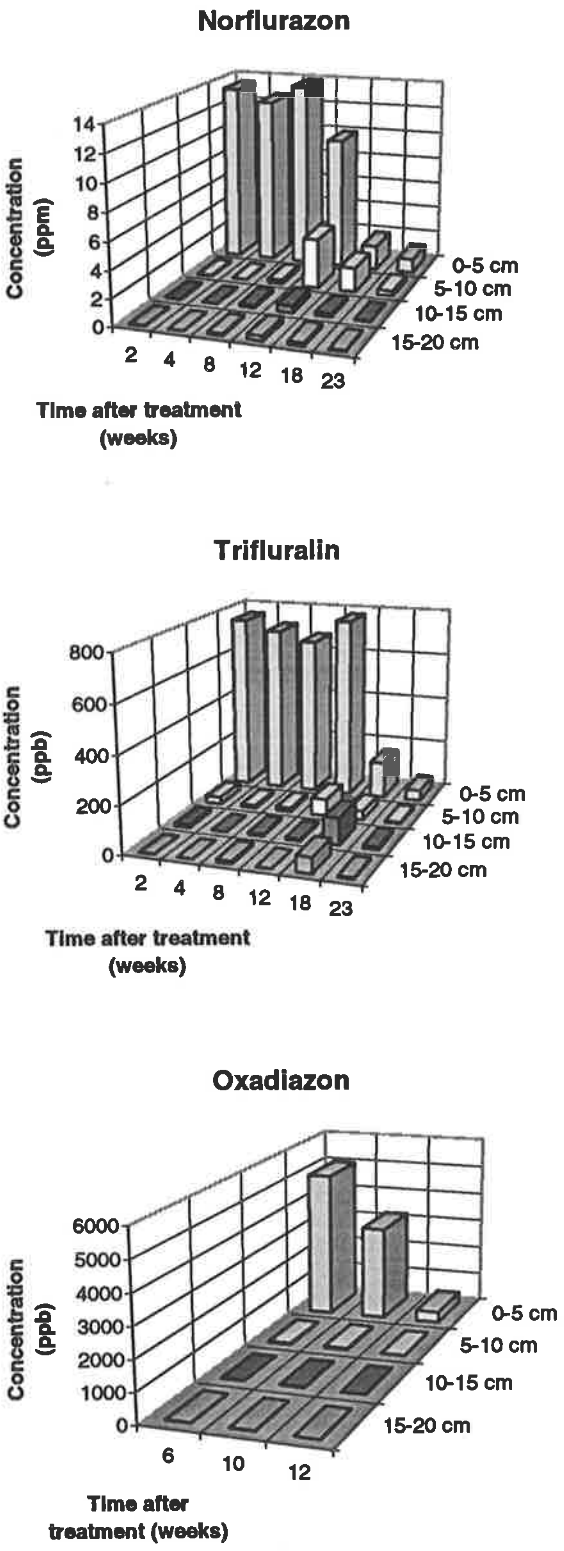


Figure 7.4 Distribution of herbicides in soil profiles of plot B.

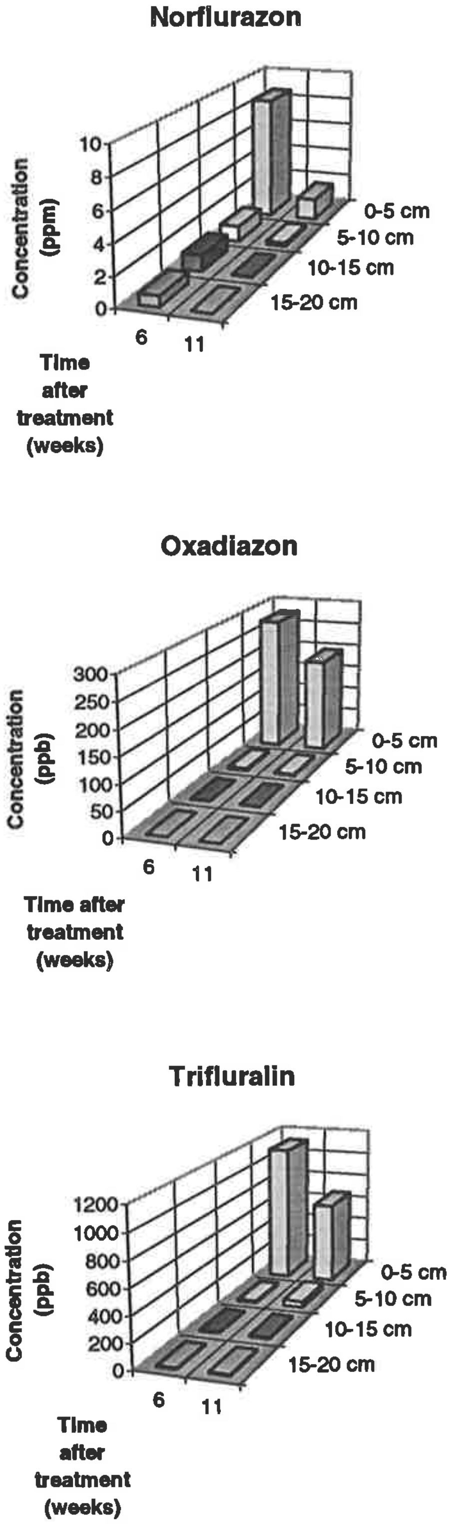


Figure 7.5 Distribution of herbicides in soil profiles of plot C.

7.4 HERBICIDE LEVELS IN GROUNDWATER

After application of the herbicides norflurazon, trifluralin and oxyfluorfen in 1996 and oxadiazon in 1997 in plot A, herbicides in groundwater were monitored by sampling from installed lysimeter tubes in the plot. The average herbicide concentrations in groundwater samples of 1996 are shown in Figure 7.6. It is seen from Figure 7.6 that norflurazon was detected at concentrations ranging from 66 ppb to 1130 ppb in groundwater and trifluralin from 1 ppb to 22 ppb and oxyfluorfen from 3 ppb to 8 ppb in groundwater. Oxyfluorfen had the lowest concentration in the groundwater while norflurazon had the highest concentration in the groundwater. The concentrations of norflurazon, trifluralin and oxyfluorfen in groundwater were correlated with the weekly rainfall (Figure 7.6).

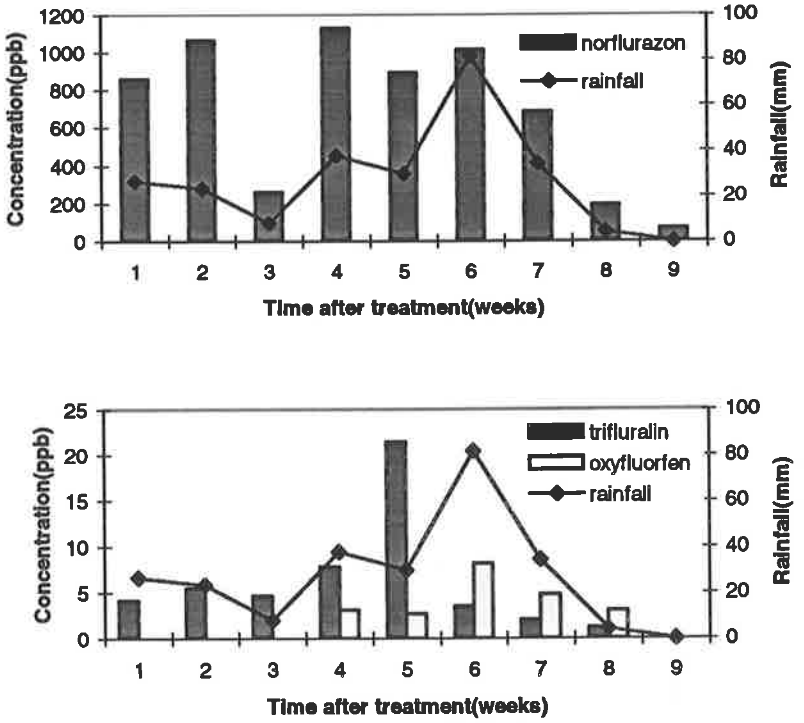


Figure 7.6 Average concentrations of herbicides in groundwater vs rainfall in 1996.

The data shown above were average concentrations of herbicides from four tubes in 1996. In fact, the concentrations of herbicides in different tubes varied greatly due to variable soil structures in the field (Figure 7.7). Herbicide concentrations in tube d were higher than other tubes (a, b, and c). Oxyfluorfen was detected only once in tube c, suggesting its strong adsorption on soil and less mobile nature. In seventh, eighth, and ninth weeks, no trifluralin was detected in tubes a and b (Figure 7.7), indicating a low mobility for this chemical. Norflurazon was the most mobile chemical, which was detected in the groundwater samples from every tube.

In 1997, monitoring of the groundwater in plot A continued. Norflurazon and newly applied oxadiazon were detected in groundwater for the first time in the second week after oxadiazon application (Figure 7.8). Norflurazon concentration varied from 831 ppb in week 17 to 46 ppb in the twenty third week following oxadiazon application to plot A. The concentration of oxadiazon in groundwater was relatively low varying from 1.5 ppb to 24 ppb. The concentrations of norflurazon were related to the rainfall with a small delay in its maximum values. From week 3 to week 10 following oxadiazon application, no water samples were collected because of insufficient rainfall. Trifluralin and oxyfluorfen were detected in soils from plot A in 1997, but they were not detected in groundwater. This suggests that norflurazon was more mobile and that trifluralin and oxyfluorfen were less mobile in soil.

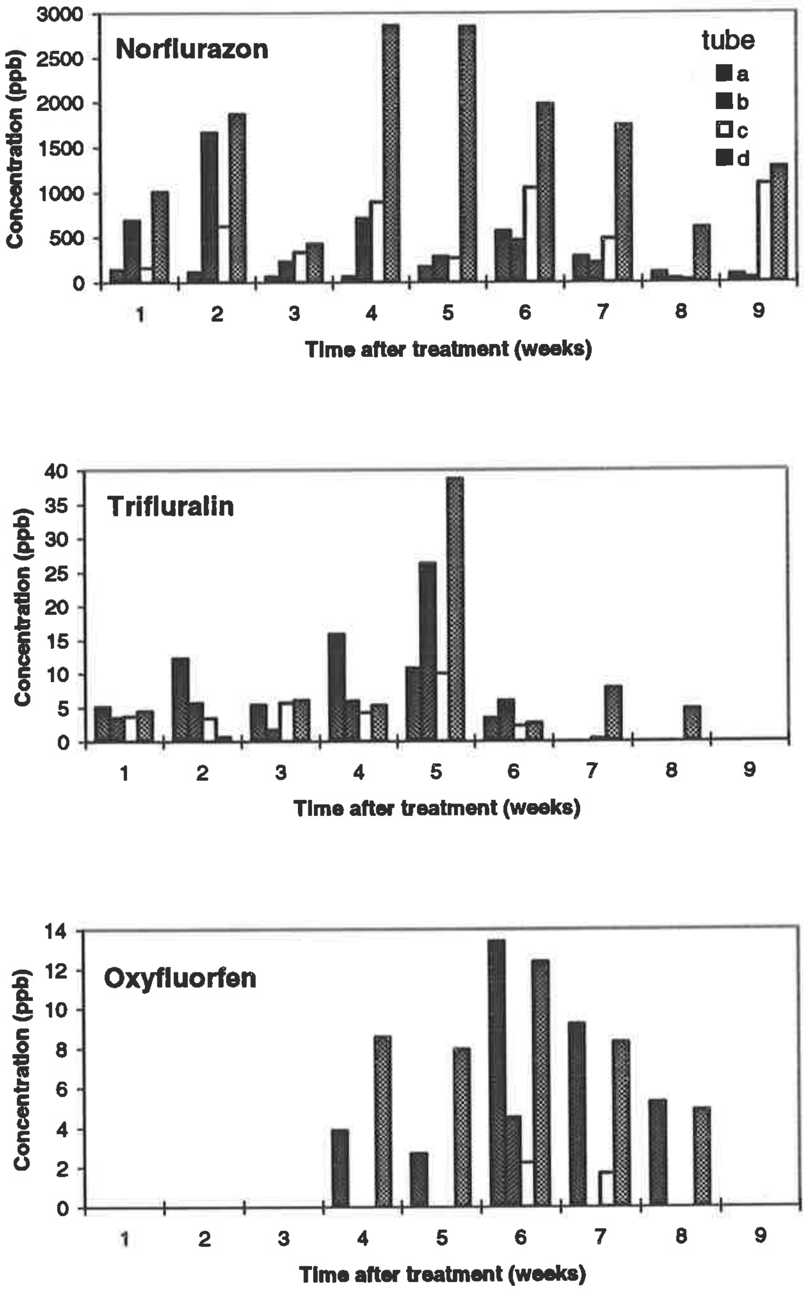


Figure 7.7 Variability of herbicide concentrations in groundwater from different tubes.

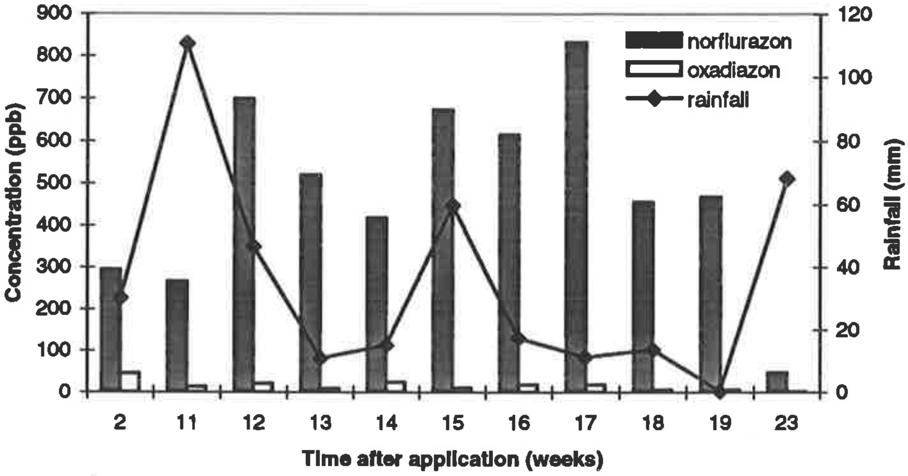


Figure 7.8 Norflurazon and oxadiazon in groundwater in plot A in 1997.

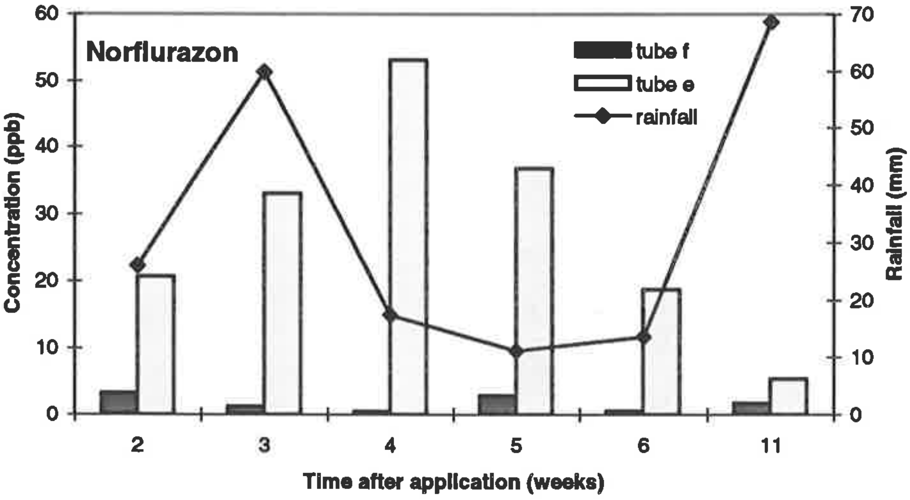


Figure 7.9 Norflurazon in groundwater of plot D.

Movement of the herbicides norflurazon, oxadiazon and trifluralin in soil was investigated during the winter of 1997 by installing lysimeter tubes in plot D, 7 m away from application plot C. After application of the herbicides to plot C, groundwater in two tubes in plot D was monitored every week until no further water could be collected from the tubes. Only norflurazon was detected in groundwater from two tubes of plot D (Figure 7.9). This indicates that the norflurazon in the ground water in plot C flowed to the tubes in plot D but oxadiazon and trifluralin did not. Norflurazon was much higher in tube e than in tube f. The concentrations of norflurazon in tube e ranged from 5 ppb to 53 ppb while those in tube f were very low ranging from 0.48 ppb to 3.22 ppb. The concentrations of norflurazon in tube e was also correlated to the rainfall except for the rainfall in the eleventh week which followed several weeks without rain.

7.5 DISCUSSION

The important results from this field investigation were that the dissipation half-lives for the four herbicides varied from 2 weeks to 16.42 weeks, and that norflurazon was leached to the greatest depth among them.

7.5.1 Dissipation

The persistence or dissipation of a chemical is mainly controlled by its physiochemical properties, management practices and environmental conditions including climate, soil physiochemistry and microbial activity in soil. Studies on norflurazon (Schroeder and Banks, 1986) and trifluralin (Jolley and Johnstone, 1994) suggested that cool and/or dry environmental conditions made them persist longer in soil. However, Barrett and Lavy (1984) found that changes in soil water content above some minimum level will not affect the sum of the processes responsible for oxadiazon dissipation. Jolley and Johnstone (1994) studied the effect of moisture content on the half life for trifluralin in three soils at 20 °C in the laboratory and the data obtained showed a similar result to Barrett and Lavy (1984)'s. The climate in the Barossa Valley is characterised by hot and dry summers and cool and wet winters. Our field studies were undertaken during winter, so the dissipation rates were expected to be affected by the cool and wet climate. Herbicides are normally applied at this time.

The reported half life values for norflurazon, oxadaizon, trifluralin and oxyfluorfen differ from those reported in this study. Schroeder and Banks (1986b) showed half lives of about 20-35 days for norflurazon in the five Georgia soils at 20-30 °C in a greenhouse. Rahn and Zimdahl (1973) in a laboratory study observed a half life of 70 days for norflurazon in a Colorado sandy loam at 35 °C. Southwick *et al.* (1993) found that DT_{50} (time to 50 % disappearance) for norflurazon in the top 15 cm of Mississippi River alluvial soil was about 40 days in the 1988-1989 season, and about 120 days in the 1989-1990 season. The authors did not explain why there was such a large difference between the two seasons. In fact, the rainfall was higher in 1989-1990 than in 1988-1989. Our field study also found quite different half lives for norflurazon: about 50 days in 1996 and about 22 days in 1997. In 1996, a slight rain after herbicide application helped the herbicide incorporate into soil due to its high mobility and therefore caused less loss from soil surface by volatilisation. On the other hand, leaching processes contributed partly to the dissipation of norflurazon in soil. But because of their low mobility, most of the trifluralin, oxadiazon and oxyfluorfen remained on the top of the soil and any dissipation was mainly controlled by microbial and chemical degradation and volatilisation losses.

Jolley and Johnstone (1994) found that half lives for trifluralin in three Victorian soils during 1985 to 1987 varied from 100 days to 214 days under field conditions. The half lives of trifluralin after 9 or 10 years of continued use were 8.7 to 10.1 months on Dundee silt loam and 15 to 11 months on Sharkey soil. So trifluralin dissipated very slowly in soil after long-term use. The field half lives determined by Wauchope *et al.* (1991) ranged from 60 to 132 days in various soils. The half life from our field study was about 4 weeks, which is lower than the above data. The reason for this short dissipation half life is believed to be due to microbial degradation and volatilisation loss. Trifluralin is subject to biodegradation in soil (Golab *et al.*, 1979). Trifluralin was not incorporated into soil after application and stayed mainly on the soil surface because of its low mobility in soil. Hence it was easily volatilised as expected due to its high vapour pressure.

The half lives for oxadiazon in the literature varied greatly ranging from 15 days to 180 days (Wauchope *et al.*, 1991). Its dissipation is largely influenced by the climate or soil moisture (Barrett and Lavy, 1984). Ambrosi *et al.* (1977) found less than 25% of oxadiazon was degraded after 175 days under both moist (75 % field capacity) and flooded conditions. Barrett and Lavy (1984) found that in the field, 50 % of the surface-applied oxadiazon dissipated from the soil within 6 to 11 days when soil was flush irrigated and then flooded, compared to 15 to 17 days when the soil was irrigated but not flooded in the two rice management systems. Similarly, in this study, in 1997 a half life of 2 weeks for oxadiazon was found. The short field half life in the vineyard was attributed to no incorporation of the herbicide into soil and its rapid degradation in moist soil.

According to the Herbicide Handbook (Humburg *et al.*, 1989), the half life for oxyfluorfen is about 30 to 40 days. Our field study in 1996 showed a half life of about 16 weeks for oxyfluorfen in the Mountadam vineyard soil. In soils, oxyfluorfen is not subject to microbial degradation and is not subject to hydrolysis at pH 5-9 (Tomlin, 1994). It is therefore highly resistant to degradation in soil. The sorption coefficient of oxyfluorfen indicates that oxyfluorfen can strongly adsorb to soil particles. So the dissipation of oxyfluorfen was most likely due to volatilisation from the soil surface.

In summary, the different half lives for the herbicides are controlled by many factors including their own physiochemical properties and environmental conditions such as soil moisture, temperature and organic matter. As Aylmore *et al.* (1995) have pointed out, the order of ranking in dissipation may also change given a different set of environmental conditions, as each chemical may respond differently to dissipation in the new environment.

7.5.2 Leaching

The extent of herbicide leaching depends on a combination of factors that include the physicochemical characteristics of the herbicide, soil properties, climate, application method, the influence of crop cover and the depth to groundwater. The field studies in this project showed that the herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen could leach down to subsurface and shallow groundwater. But the mobility of the four herbicides varied greatly.

The distribution of the herbicides norflurazon, oxadiazon and trifluralin in the soil profiles in plot B indicated that most of the herbicides stayed in the top soil layers before rain season (Figure 7.4). From week 12 for norflurazon and trifluralin and week 6 for oxadiazon in plot B, more of each herbicide was leached by rainfall, because rain season started from the previous week. The concentrations of oxadiazon in the subsurface soils were very low, this might be due to its high degradation rate in soil in addition to its strong adsorption on soil.

Monitoring of groundwater from the tubes in plot A also showed that these four herbicides leached to groundwater in the first year after herbicide application. Although the herbicides persisted in the soil until the second year, only norflurazon was detected in the groundwater in the following year. In addition, norflurazon was detected in groundwater from the tubes in plot D, which is 7 meters away from the plot C which was sprayed with trifluralin, norflurazon and oxadiazon. This clearly demonstrated that norflurazon was the most mobile chemical among the four herbicides. The concentrations of norflurazon in groundwater were related to the rainfall. Strong rainfall events leached large amounts of the chemical through the soil.

The results reported are comparable to those of previous studies. Schroeder and Banks (1986) found that > 60 % of the norflurazon was within 8 cm of the surface with < 12 % detected deeper than 15 cm in five Georgia soils. Southwick *et al.* (1993) studied leaching losses of norflurazon through Mississippi River alluvial soil and detected norflurazon in subsurface drains. The concentration of norflurazon in drain was related to the rainfall. Oxadiazon, trifluralin and oxyfluorfen are less mobile in soil.

Although oxadiazon, trifluralin and oxyfluorfen were less mobile than norflurazon, they were found in groundwater from the tubes in plot A in the first year after application, but not found in groundwater from the tubes of plot D. This suggests that the mobility and leaching potential of oxadiazon, trifluralin and oxyfluorfen were limited in soils. Moreover, the herbicides might not be strongly adsorbed onto soil, as experiments by LaFleur (1979) indicated that sometimes several weeks were required for pesticide adsorption to reach dynamic equilibrium with soil organic matter. The detection of trifluralin, oxadiazon and oxyfluorfen in groundwater may be caused by preferential flow or movement in association with humic substances and small soil particles. This is reflected by the large variability in the data from different tubes of plot A (Figure 7.7). So the most important transport pathway for these herbicides may be preferential transport and not the soil matrix. Recent studies have shown that pesticides can quickly enter subsurface soil and shallow groundwater by infiltrating water through cracks, worm and root holes, and other macropores in unsaturated, structured soil or through finger or funnel flow in sandy, unstructured soils (Flury, 1996; Jury and Fluhler, 1992). Jury *et al.* (1986) found deeper penetration of napropamide in unsaturated soils than expected. Kladivko *et al.* (1991) found that all applied chemicals with different adsorption characteristics appeared at the same time in drain outflow. Flury *et al.* (1995) demonstrated that the three herbicides triasufuron, atrazine and terbuthylazine moved to the same maximum depth in a loamy soil. These examples show that chemicals can move along preferential pathways in soil.

Finally, it is known that the potential of herbicides to contaminate groundwater increases with increasing mobility and half life. From this study, norflurazon therefore has greater potential than the other three herbicides. But oxadiazon, trifluralin and oxyfluorfen may contaminate groundwater by preferential flow or other mechanisms during the first year after application.

CHAPTER 8

PHOTODEGRADATION OF HERBICIDES

8.1 INTRODUCTION

Degradation of herbicides is one of the important processes occurring after application, which has great effect on the fate of herbicides in the environment. Once the herbicides enter the soil, they are subject to various degradation processes including biodegradation, chemical degradation and photodegradation. The relative importance of various degradation processes of a chemical depends on the environmental compartments in which it resides. In the root zone, degradation proceeds mainly by microbial processes. Photodecomposition can happen in water and on soil and plant surfaces. In some systems, photodecomposition may be the primary degradative pathway of a chemical, but in another it may not be significant. Assessing the photodegradation of a chemical in various environmental compartments could help us better understand its fate in the environment.

Some studies have been undertaken on the degradation of norflurazon (Willian and Mueller, 1994), oxadiazon (Ambrosi *et al.*, 1977 and 1978; Chakraborty *et al.*, 1995), oxyfluorfen (Adler *et al.*, 1978; Adityachaudhury *et al.*, 1994; Brodsky *et al.*, 1992) and trifluralin (Crosby and Leitis, 1973; Golab and Occolowitz, 1979; Golab *et al.*, 1979) in soil and water. The degradation of trifluralin has been extensively studied in soils (Golab *et al.*, 1979; Golab and Occolowitz, 1979) and in water (Crosby and Leitis, 1973). In the field and laboratory soils, 28 products derived from trifluralin have been detected (Golab *et al.*, 1979; Golab and Occolowitz, 1979). A study by Golab *et al.* (1979) shows that transformation reactions involved with the degradation of trifluralin in soil are oxidative dealkylation of the *N*-propyl groups, reduction of nitro groups and a combination of both reactions, cyclization in the form of benzimidazoles, dimeric condensation in the form of azoxy and azo derivatives, as well as oxidation / hydroxylation and reduction reactions. The trifluoromethyl group of trifluralin remained intact through these reactions with a few exceptions (Golab *et al.*, 1979). Crosby and

Leitis (1973) described a very rapid photodecomposition of trifluralin in aqueous methanol, and detected 6 products after less than two minutes and about 25 products after 3 hours. They also found that photodecomposition of trifluralin in aqueous suspensions, with or without soil was about one tenth as rapid, but the products were the same. Margulies *et al.* (1992) studied the photochemical behaviour of trifluralin adsorbed on montmorillonite with and without the organic cation thioflavin coadsorbed and observed considerable photostabilization of trifluralin, as compared with the herbicide in its free form. He suggested that photostabilization is due to steric hindrance imposed by the clay surface on the cyclization step of the photochemical reaction. Sun and Pignatello (1993) investigated abiotic degradation of some pesticides in water using hydrogen peroxide and iron(III) chelates and found that hydrogen peroxide greatly increased the degradation of baygon, carbaryl, picloram, 2,4-D, 2,4,5,-T and atrazine, but had no obvious influence on trifluralin.

Ambrosi *et al.* (1977) found that oxadiazon was metabolised to a carboxylic acid, a phenol, a dealkylated derivative and several polar products in soils. Chakraborty *et al.* (1995) isolated eleven metabolites produced by the fungus *Fusarium solani* in soil. Oxadiazon and its metabolites have been detected from pond snails and mussels (Ambrosi *et al.*, 1978; Murakami *et al.*, 1993), and from terrapin and corb shell processed foods (Murakami *et al*, 1994). Most of the oxadiazon metabolites were regarded as being formed through dechlorination, *N*-decarboxymethylation, acetylation and ring cleavage (Adityachaudhury*et al.*, 1994).

Adityachaudhury *et al.*(1994) has studied the transformation of oxyfluorfen by microbial and photochemical means. Oxyfluorfen and its amine residues have been detected in crops (Zhou and Miles, 1991; Adler *et al.*, 1978). Brodsky *et al.* (1992) identified a number of photoproducts by using mass spectrometry and suggested that their generation pathways were mainly Ar-O bond cleavage, dechlorination and photocyclisation. The photodegradation experiments were undertaken in a methanolic solution, not in water. However, little information about norflurazon degradation has been reported. Willian and Mueller (1994) reported liquid chromatographic determination of norflurazon and its initial metabolite desmethylnorflurazon in soil.

Previous studies have examined the degradation of herbicides by microbial processes but, unfortunately, little work has been done on photodegradation of the herbicides except trifluralin. Although photolysis of oxyfluorfen in methanol has been studied using xenon and mercury lamps (Brodsky *et al.*, 1992), it may be different to the situation occurring in water under sunlight. Photolysis is an important process in the degradation of herbicides in the environment because of the long hot sunny weather in South Australia. The aim of this chapter is to study the photodegradation rate of norflurazon, oxadiazon and oxyfluorfen in soil and water with trifluralin as a reference, and to identify the photodegradation products produced in water.

8.2 MATERIALS AND METHODS

8.2.1 Soil plates

Four soil plates with a size of 20 cm × 20 cm were prepared using sandy soil from the Nuriootpa Research Station Vineyard. The plates were dried at room temperature. Every plate had a soil layer one mm thick. Each plate was divided into 6 equal zones. One each of the herbicide standards norflurazon, oxadiazon, trifluralin and oxyfluorfen was applied to each zone on one of the soil plates. Every part of a soil plate was spiked with 50 μg of a herbicide in methanol. After evaporation of methanol from the soil surface, all soil plates were placed outdoors under sunlight for 12 days in February 1997. During this period, photolyses of the herbicides were monitored by scraping off one zone of every soil plate every two days. Soil samples were extracted with 25 ml of methanol under sonication for 15 min. The extracts were filtered and diluted with water to 250 ml. The diluted extracts were passed through C_{18} cartridges which were preconditioned by methanol and water. The herbicides were eluted from C_{18} cartridges using methanol and the eluates were analysed by GC-NPD.

8.2.2 Water

Photodegradation of the herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen were investigated at the Roseworthy campus of the University of Adelaide during Feb-April 1997 in three aqueous media: milli-Q water, milli-Q water with added hydrogen peroxide, and natural water from the Murray River at Swan Reach, South Australia. A concentration of 1 ppm of each herbicide in water solution was prepared using 1000 ml round bottom borosilicate glass flasks. A 20 ppm aqueous solution of hydrogen peroxide (H_2O_2) was added to milli-Q water to study its effect on the photolysis of norflurazon and oxadiazon. A *p*-nitroacetophenone (PNAP)/ pyridine (pyr) solution was used as the actinometer to monitor the outdoor solar irradiance. The concentration of pyridine was adjusted to yield a quantum yield of 3.7×10^{-4} according to the equation of $\phi = 0.0169$ [*pyr*] (Dulin and Mill, 1982). The system consisted of a 22 mM pyridine solution with a 20 μM PNAP concentration.

The first group of photolysis tests were undertaken from February 11, 1997. A 1 ppm solution of norflurazon, oxadiazon, trifluralin and oxyfluorfen each in Milli-Q water was photolysed under outdoor sunlight. At regular intervals, 100 ml of water was taken from each flask and extracted by passing through C_{18} cartridges. The extracts of the herbicides and PNAP were analysed by GC-NPD. At the same time, a 1 ppm solution of norflurazon and oxadiazon each in Murray River water and Milli-Q water containing 20 ppm hydrogen peroxide was photolysed under sunlight. Water samples were monitored at regular intervals by taking 100 ml of water from each flask.

The second group of photolysis tests were undertaken from April 2, 1997. A 1 ppm solution of norflurazon and oxadiazon each in Milli-Q water and in Milli-Q water with hydrogen peroxide was photolysed under sunlight. The water was also monitored at regular intervals by taking 100 ml of water from each flask. The average temperatures outdoors in April were much lower at 10° to 21°C compared to 17° to 32°C in February.

8.2.3 Photoproducts

Photoproduct isolation and identification were conducted in the summer of 1998. 1 ppm of norflurazon, oxadiazon and oxyfluorfen in Milli-Q water in 1000 ml flasks were placed outdoor for several days. 1000 ml of each herbicide solution was passed through C_{18} disks which were preconditioned using methanol and water. The herbicides were eluted from the disks using several ml of methanol and analysed by GC-NPD and HPLC. Photoproducts of norflurazon, oxadiazon and oxyfluorfen were identified using GC-MS.

8.2.4 Analysis

Herbicide samples in this study were analysed by GC, HPLC and GC-MS. The operating conditions for each instrument were as follows:

GC analyses were performed using Hewlett Packard 5890 gas chromatograph, equipped with a nitrogen-phosphorus detector. The column used in this study was an HP fused silica capillary column coated with crosslinked methyl silicone (column length 25 m, column ID 0.31 mm, film thickness 0.52 micron). Nitrogen (N_2) was used as the carrier gas and make-up gas at the flow rate of 30 ml/min for NPD. Hydrogen was used at the flow rate of 3.5 ml/min and air 110 ml/min. Oven temperature was programmed from 200 °C (1 min) to 300 °C (5 min) at a rate of 10 °C/min, with injector temperature at 250 °C and detector temperature at 300 °C.

The photoproducts of norflurazon and oxyfluorfen were also analysed using Waters model 510 HPLC with Waters 490 programmable multiwavelength UV detector and Waters 745 integrator. The column used was a Nova-Pak® C_{18} reverse phase column (3.9 × 150 mm). The wavelength was 240 nm for norflurazon and 206 nm for oxyfluorfen. Acetonitrile: water (50:50) was used as solvent at a flow rate of 1 ml/min.

GC-MS was used to identify the photoproducts of norflurazon, oxadiazon and oxyfluorfen. The analysis was performed using HP 5890B gas chromatograph equipped with HP 597 mass selective detector. Injections were done in splitless mode on a J&W DB5-ms capillary column (30 m × 0.25 mm ID × 0.25 μm film thickness), with injector temperature at 200 °C and interface temperature at 230 °C. Two oven temperature programs were used: 60 °C (1 min) to 300 °C (15 min) at 10 °C/min; and 50 °C (1 min) to 150 °C at 10 °C/min and to 280 °C (5 min) at 30 °C/min. The compound identification was made using combination of standards, mass spectra and references.

8.3 PHOTODEGRADATION

8.3.1 Photolysis on soil

The photolysis of norflurazon, oxadiazon, trifluralin and oxyfluorfen on soil plates was undertaken in February, 1997. The half- lives for the herbicides, calculated using first order reaction kinetics, were 5.53 days for norflurazon, 4.65 days for oxadiazon, 3.53 days for trifluralin and 5.19 days for oxyfluorfen (Table8.1). Norflurazon and oxyfluorfen had relatively lower degradation rates than trifluralin and oxadiazon. However, Figure 8.1 illustrates that the photodegradation of the herbicides did not follow the first order reaction kinetics very well (Figure 8.1). The correlation coefficients (R^2) in the diagrams were relatively low ranging from 0.6712 for norflurazon to 0.9499 for oxadiazon.

Table 8.1 Half lives of the herbicides on soil and in water under sunlight (days).

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	–	–

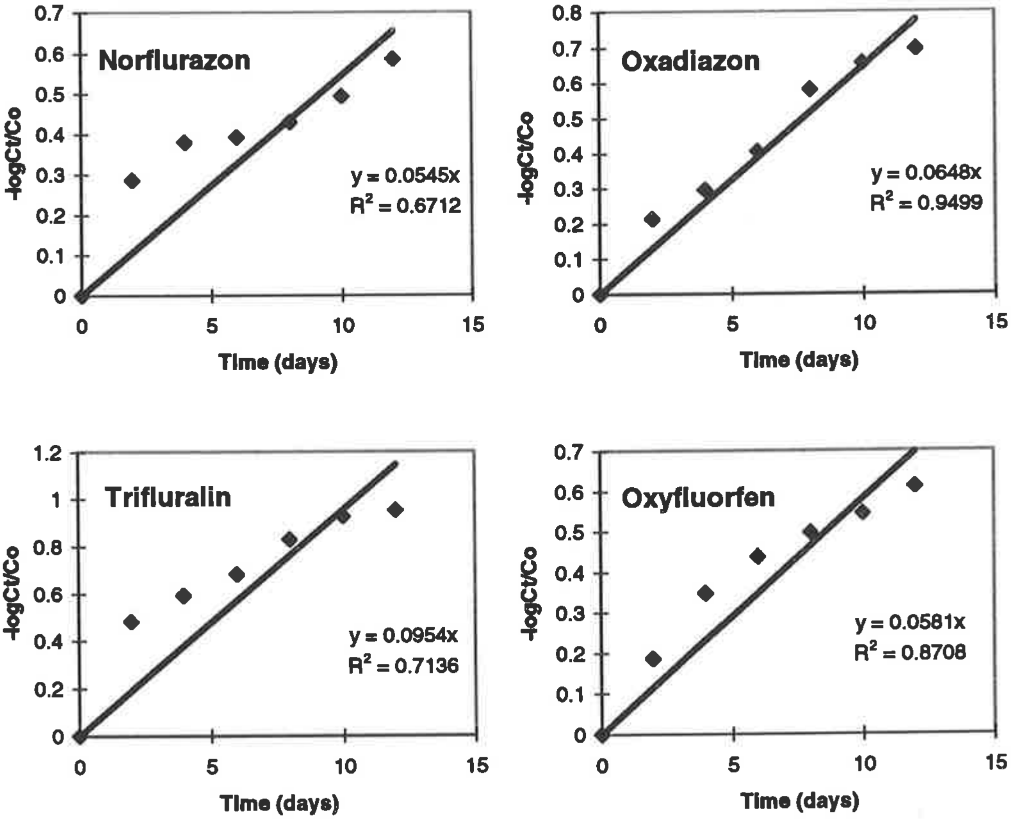


Figure 8.1 Photodegradation of norflurazon, oxadiazon, trifluralin and oxyfluorfen on soil.

8.3.2 Photolysis in water

Photolysis of norflurazon, oxadiazon, trifluralin and oxyfluorfen in water was carried out in February and April, 1997. Photolysis of the four herbicides in Milli-Q water in February shows that trifluralin and oxyfluorfen photodecomposed much faster than norflurazon and oxadiazon (Figure 8.2). The half lives for trifluralin and oxyfluorfen calculated using first order reaction kinetics were about 2 hours and 4.8 hours, respectively while those of norflurazon and oxadiazon were 1.53 days and 2.62 days, respectively (Table 8.1). Figure 8.2 illustrates no obvious effect of hydrogen peroxide on the photodegradation of norflurazon and oxadiazon in water. The half lives for norflurazon and oxadiazon in Milli-Q water with hydrogen peroxide were 1.59 and 2.44 days, respectively.

The photolyses of norflurazon and oxadiazon in Milli-Q water with or without hydrogen peroxide were repeated in April. The photodegradation rates of norflurazon and oxadiazon in water were lower due to lower intensity of UV light in April. The half lives for norflurazon in Milli-Q water were 3.45 and 4.84 days, respectively while those in Milli-Q water with hydrogen peroxide were 1.94 and 5.30 days, respectively (Table 8.1). The addition of hydrogen peroxide seems to have a little effect on the photolysis of norflurazon and oxadiazon in water. Norflurazon and oxadiazon in water with hydrogen peroxide appeared to degrade a little faster during the first several days (Figure 8.3)

Figure 8.4 shows the degradation of norflurazon and oxadiazon in the Murray River water under sun light. Their photodegradation rates in natural water were relatively low with a half life of 2.34 days for norflurazon and 8.09 days for oxadiazon.

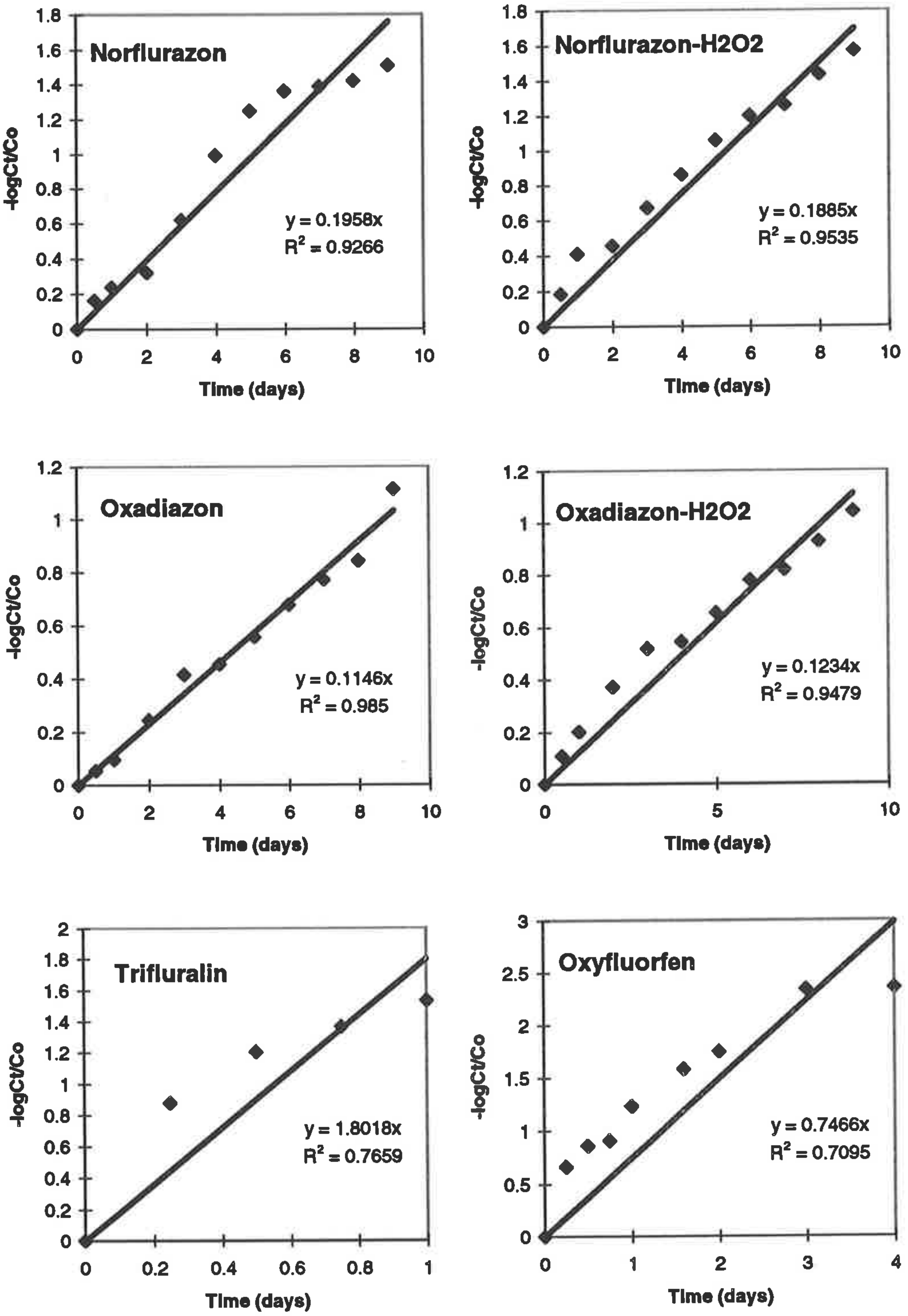


Figure 8.2 Photolysis of the herbicides in water in February.

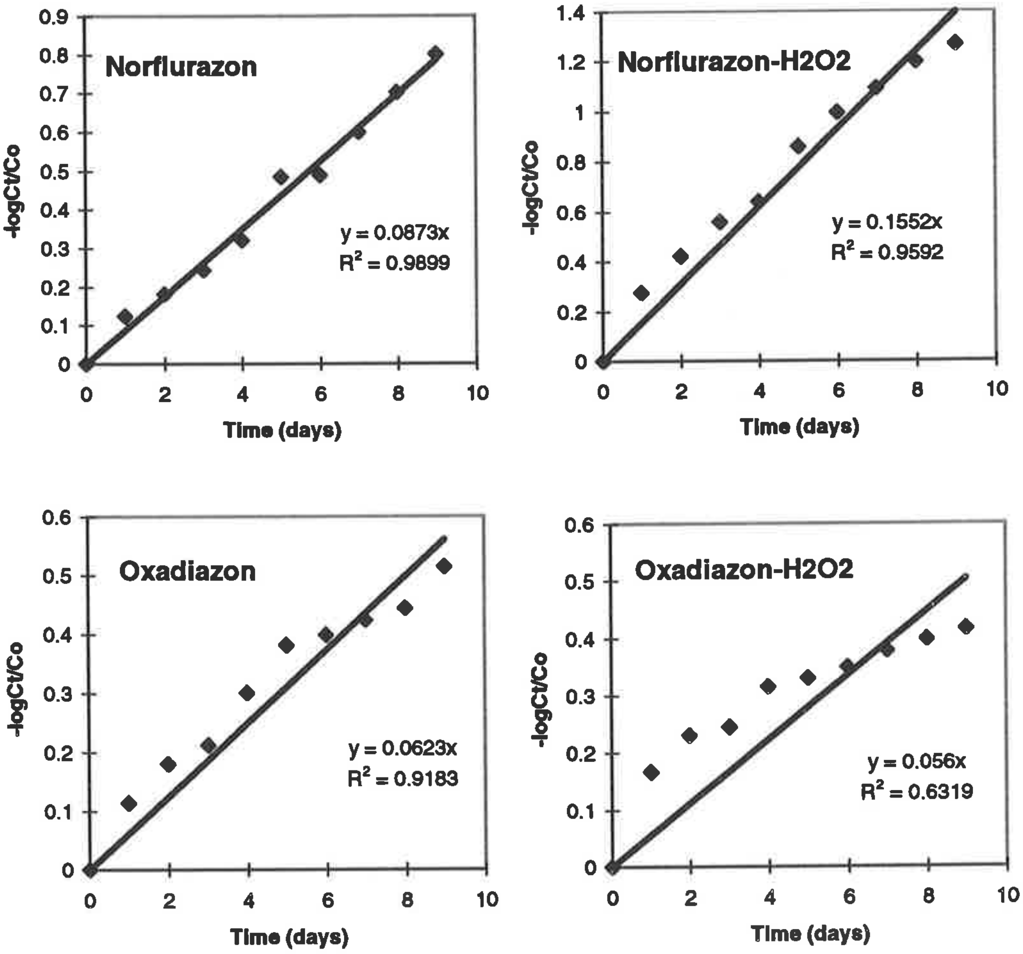
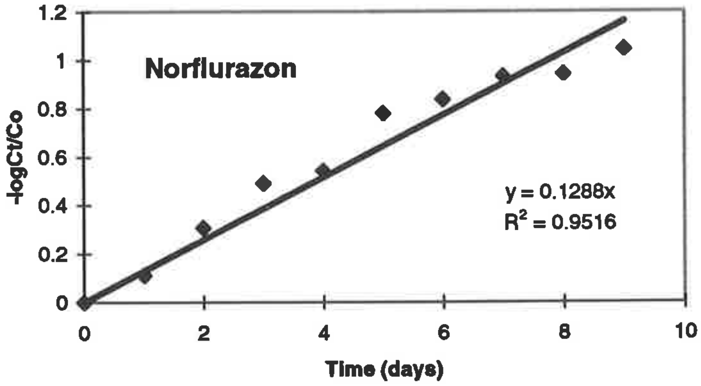


Figure 8.3 Photolysis of norflurazon and oxadiazon in Milli-Q water with or without H_2O_2 in April.



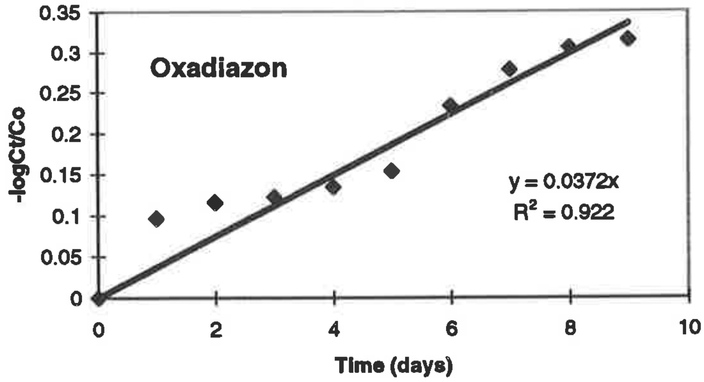


Figure 8.4 Photodegradation of norflurazon and oxadiazon in natural water.

8.3.3 Discussion

The results of the photolysis of the herbicides in water and on soil show that the rates of photolysis on soil surfaces were lower than in water. The photolysis of the herbicides on soil was conducted at the same time as the photolysis in water in February. The half lives for norflurazon, oxadiazon, trifluralin and oxyfluorfen on soil were longer than in Milli-Q water, especially for trifluralin and oxyfluorfen with half lives of 3.53 and 5.19 days, respectively (Table 8.1). This is primarily due to light attenuation by soils. Both the organic and inorganic fractions can attenuate light and limit the direct photolysis to less than 1 mm in depth (Miller *et al.*, 1989). The soil used in this study was sandy soil from Nuriootpa and is low in soil organic matter, so it is more transparent. Another factor influencing photolysis is the inner filter effect arising when a chemical becomes trapped within interior of the soil particles and is protected from photolysis in the interior (Yokley*et al.*, 1986).

A reduction in photolysis rate of compounds on soils was also observed by Nilles and Zabik (1975), and Miller and Zepp (1983). Nilles and Zabik (1975) found that rates of direct photolysis of pesticides on soil surfaces were much slower than in distilled water. They reported a loss of over 80 % of bentazone when irradiated in distilled water for 24 hours, while more than 50 % of bentazone remained after 120 hours of irradiation on soil surfaces. Miller and Zepp (1983) also found a substantial lower photolysis rate for flumetralin with a half life of 1 day, while in solution the half life was less than 30 min. under sunlight.

The results from this study also show that the photolysis on soil did not follow first order kinetics very well. Rapid initial loss of the herbicides occurred followed by slower degradation rates. After 2 days under sunlight, 48.2 % of norflurazon, 39.1 % of oxadiazon, 77.3 % of trifluralin and 34.9 % of oxyfluorfen were lost on soil surfaces. So the half life for photolysis on soil surfaces sometimes is misleading. This phenomena was also observed by Miller *et al.*(1989) for the photochemical loss on soils of flumetralin and disulfoton, and Miller and Zepp (1979) in experiments with DDE in suspended sediment. Because of the heterogeneity of soils, the photolysis of the herbicides on soils was different from that in water.

This study, on the photolysis of norflurazon, oxadiazon, trifluralin and oxyfluorfen in Milli-Q water in February, shows that trifluralin and oxyfluorfen degraded much faster with half lives of 2 and 4.8 hours than norflurazon and oxadiazon. Miller and Herbert (1987) reported a half life from 0.45 to 0.92 hours for trifluralin during midday photolysis. Crosby and Leitis (1973) found that the photolysis of trifluralin was very rapid in aqueous methanol, but the photolysis in aqueous suspensions, with or without soil, was about one tenth as rapid. Margulies et al. (1992) reported the photochemical behaviour of trifluralin adsorbed on montmorillonite, with and without the organic cation thioflavin co-adsorbed, and found the photodegradation was slowed, as compared with the herbicide in its free form. The low correlation coefficients for trifluralin and oxyfluorfen in the current experiments (Figure 8.2) might be due to their low solubility although they were dissolved first in small amounts of methanol before being added into water. Some of them might suspend in water, and those dissolved in water maybe degraded faster than suspended ones.

Figure 8.5 shows the photolysis of norflurazon and oxadiazon in different water media with PNAP/pyr as an actinometer. It clearly illustrates that the photodegradation of norflurazon and oxadiazon in natural water was much slower than in Milli-Q water with or without hydrogen peroxide. This could be explained by the attenuation of sunlight by naturally occurring organic and inorganic species in water. In natural waters humic substances, suspended sediments, algae and natural inorganic materials can have a great influence on the rate of direct photolysis because they will generally attenuate sunlight through the water column and therefore reduce direct photolysis rates (Miller and Zepp, 1979; Miller and Herbert, 1987).

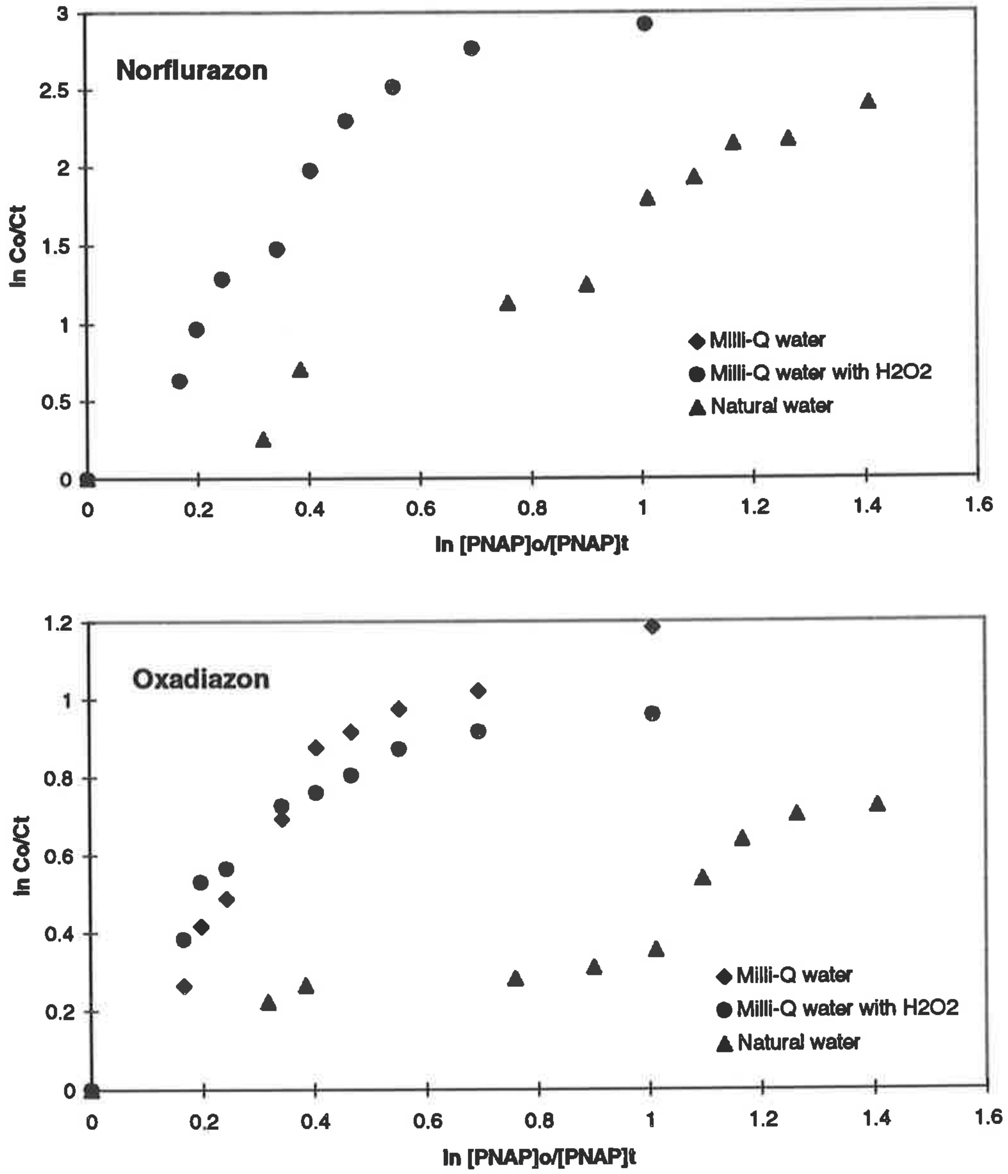


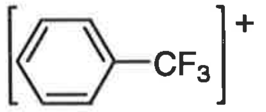
Figure 8.5 Comparison of the photolysis rates of norflurazon and oxadiazon in different waters.

In addition, the results of this study show that hydrogen peroxide added into Milli-Q water appeared to have no obvious effect on the photolysis rates of norflurazon and oxadiazon. Strong UV light in February might minimise the role of H_2O_2 in photolysis. However, in April's experiments, the addition of H_2O_2 into Milli-Q water caused an initial fast photodecomposation of oxadiazon followed by a subsequent slow degradation. It also caused faster photodecomposation of norflurazon in April. Hydrogen peroxide can promote free radical reactions or may directly degrade reactive substances such as sulphides and phosphines (Miller and Hebert, 1987). So it is possible that H_2O_2 could enhance the photolysis rates of herbicides in water when it is activated by other substances in water.

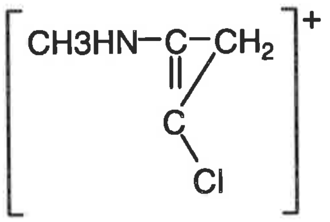
8.4 PHOTOPRODUCTS

8.4.1 Norflurazon

Four compounds were detected in the aqueous solution of norflurazon after photolysis under sunlight (Figure 8.6). Compound **3** was identified as the parent compound norflurazon with a molecular ion at m/z 303 by GC-MS (Figure 8.7). The isotopic contributions of molecular ion $[M]^+$ and its isotopic peak $[M + 2]^+$ had a ratio of 100 to 32.5 due to a chlorine atom. Norflurazon had the following two characteristic ions:



m / z 145



m / z 102

Compound **4** had a similar fragmentation pattern with a molecular weight of 303 (Figure 8.8). But the abundance of an ion at m/z 102 seems relatively lower than that in the mass spectra of norflurazon. The base peak was also at m/z 145, which was the same as in the mass spectra of norflurazon. So compound **4** was considered to be an isomer of norflurazon.

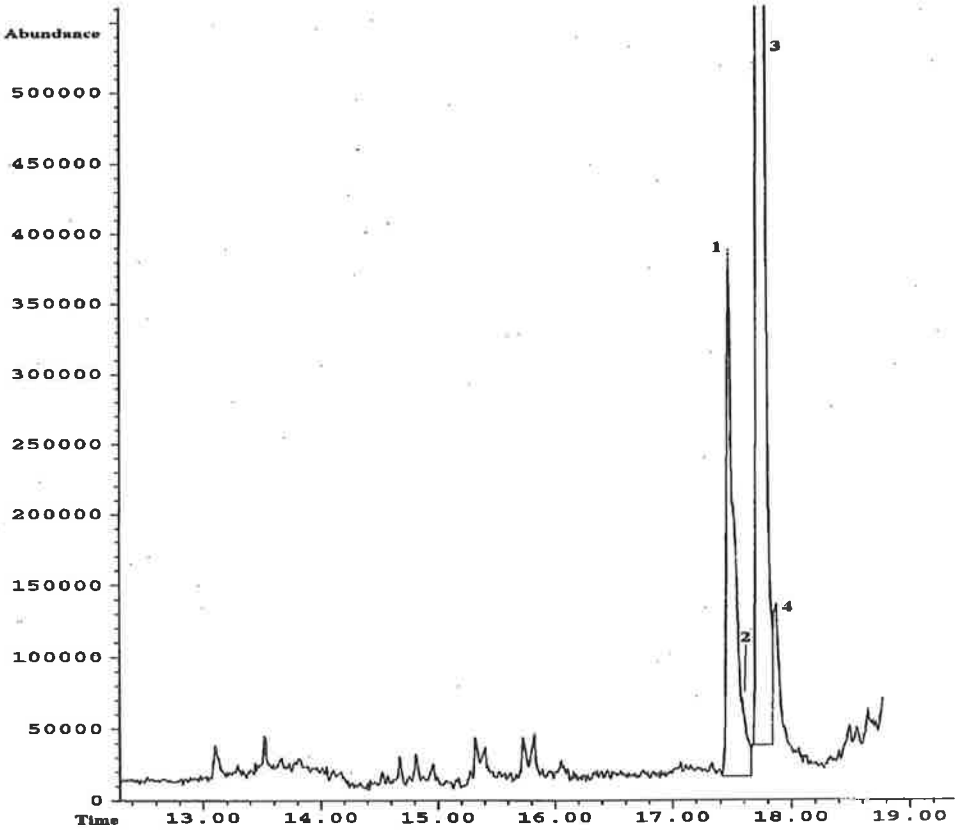


Figure 8.6 TIC of photoproducts of norflurazon.

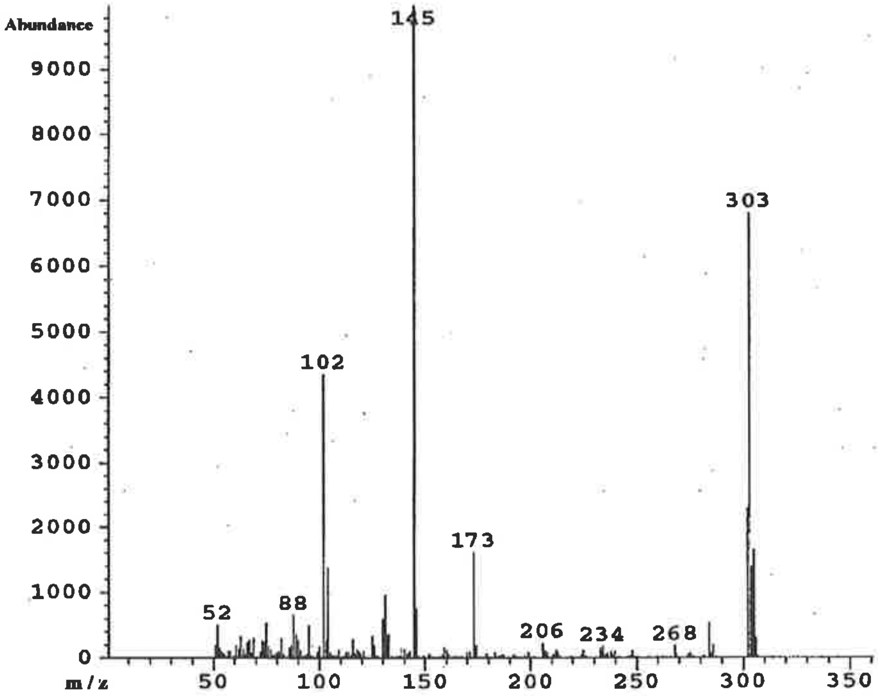


Figure 8.7 Mass spectra of compound 3 (norflurazon).

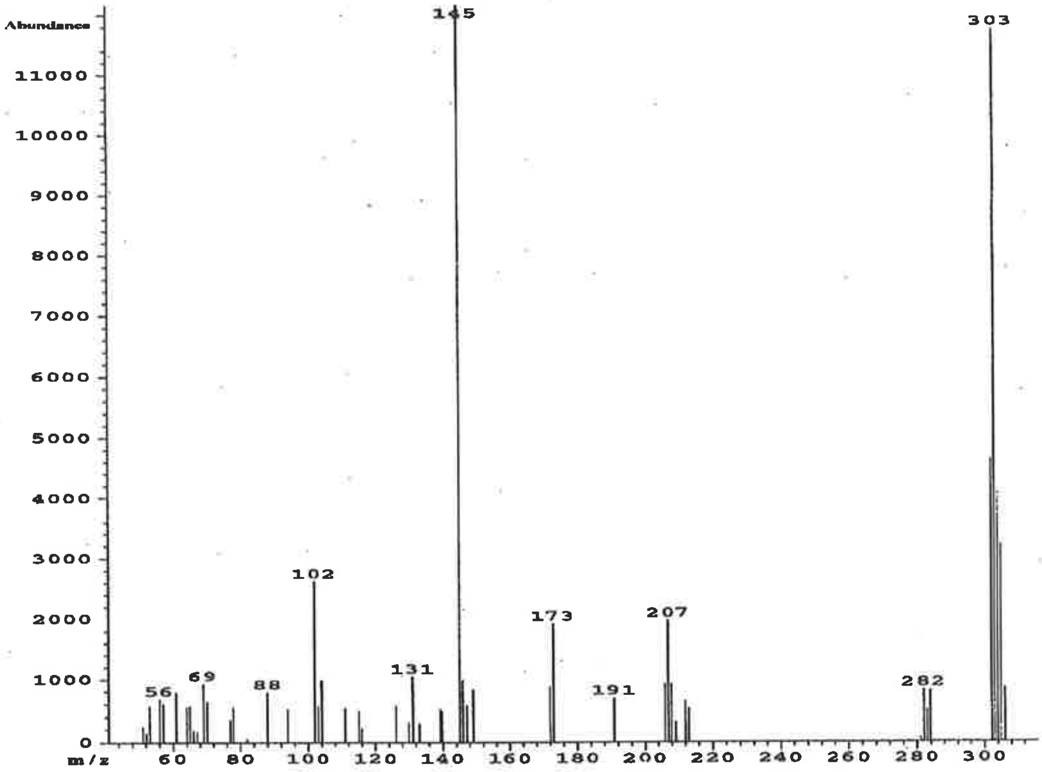


Figure 8.8 Mass spectra of compound 4 (norflurazon isomer).

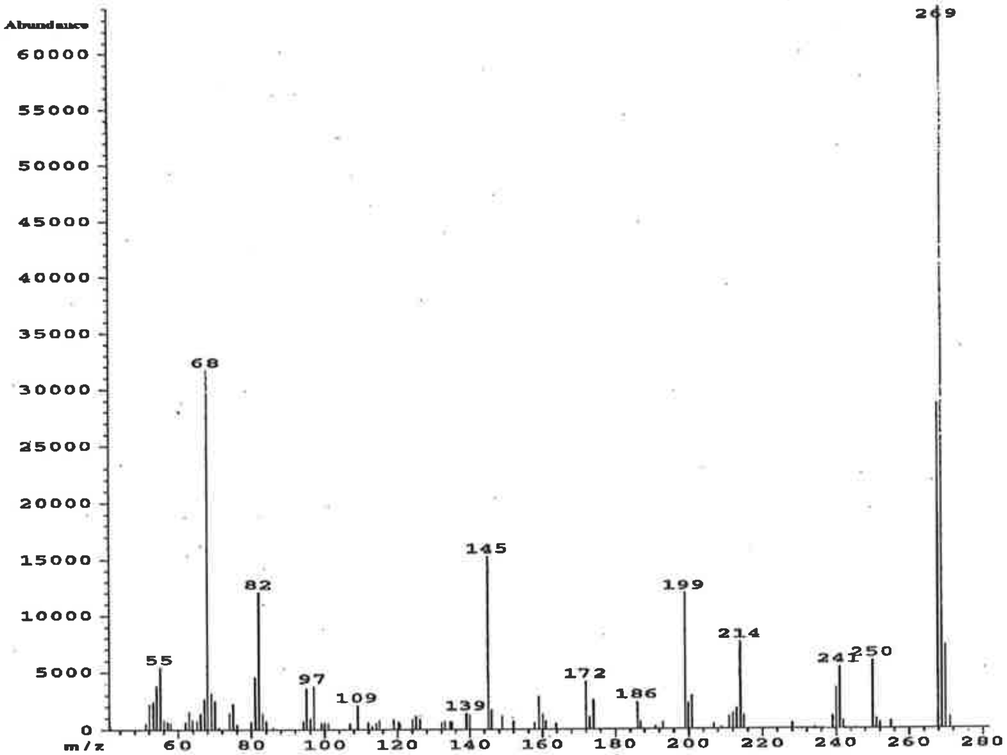


Figure 8.9 Mass spectra of compound 1 (dechlorinated norflurazon).

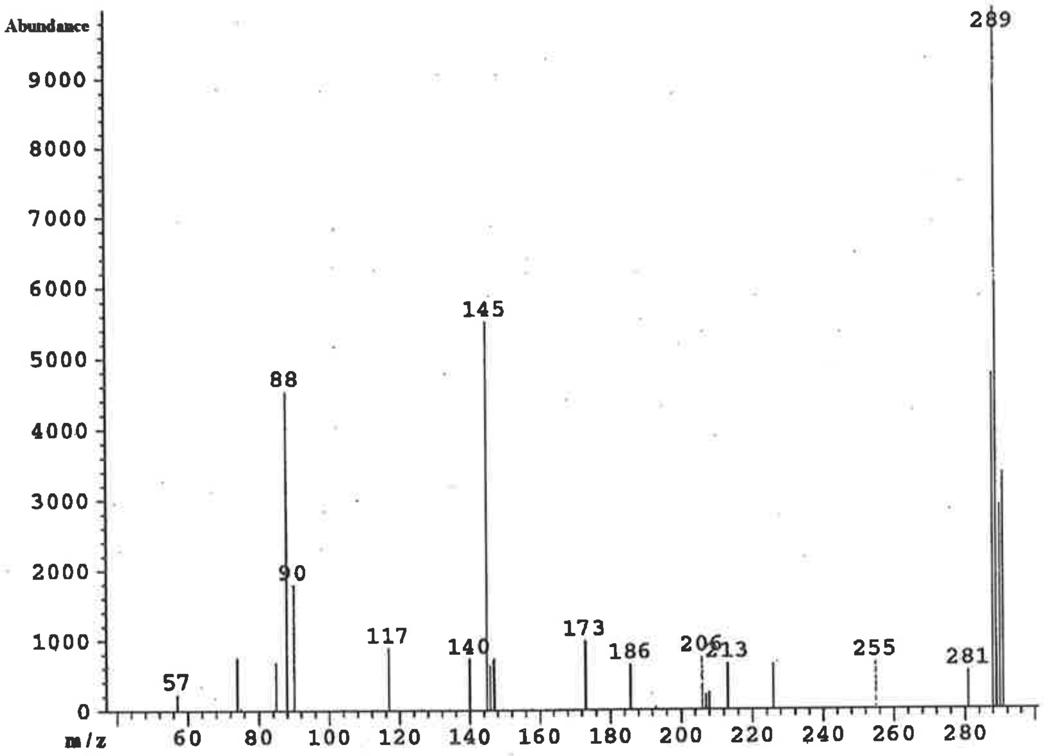


Figure 8.10 Mass spectra of compound 2 (desmethylnorflurazon).

Compound **1** had a molecular ion at m/z 269, and some fragmental ions at m/z 250 $[M{-}F]^+$, 145, 68 $[102{-}Cl + H]^+$. The mass spectra of compound **1** shows no isotopic peaks due to loss of chlorine atom (Figure 8.9). So the compound was identified as dechlorinated norflurazon.

The mass spectrum of compound **2** (Figure 8.10) shows a molecular ion at m/z 289 with its isotopic peak $[M+2]^+$, two charateristic fragment ions at m/z 145 and 88 $[102 - CH_2]^+$. This clearly indicates that compound**2** is desmethylnorflurazon.

This study shows that the photolysis pathways of norflurazon in water under sunlight involved dechlorination and desmethylation reactions, as well as isomerization (Figure 8.11). Ring cleavage was also believed to be an important pathway. Norflurazon could be broken down easily to small fragments once the rings were cleaved.

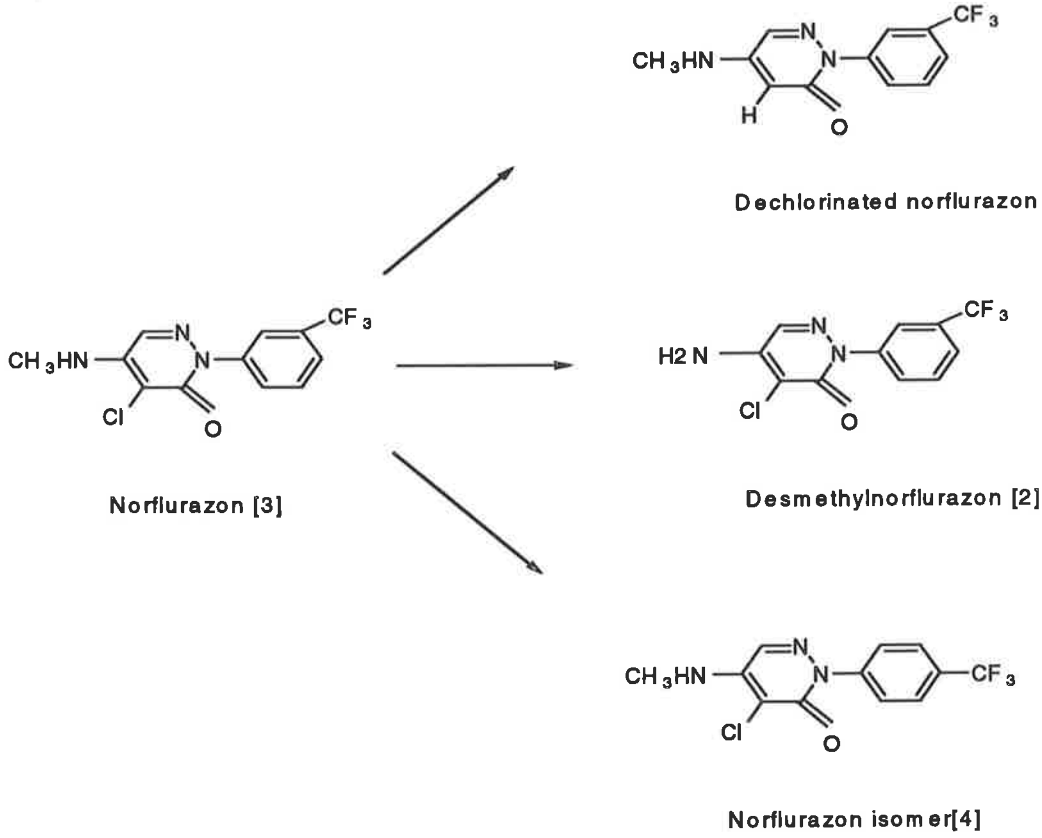


Figure 8.11 Photolysis of norflurazon in water under sunlight. Numbers in the brackets are peak numbers in TIC.

8.4.2 Oxadiazon

Four compounds were detected by GC-MS after photodegradation of oxadiazon in water under sunlight (Figure 8.12). The mass spectrum (Figure 8.13) indicates that compound **2** was the parent compound oxadiazon. In addition to the molecular ion peak at m/z 344, oxadiazon had the following fragment ions: m/z 302 $[M-(CH_3)_2C]^+$, m/z 258 $[M-(CH_3)_2C-CO_2]^+$, m/z 202 $[M-(CH_3)_3C-(CH_3)_2C-CO_2]^+$ and base peak m/z 175 $[M-HCN-(CH_3)_3C-(CH_3)_2C-CO_2]^+$. The ratio of the intensities of the isotopic ions at m/z 344, 346 and 348 was 9: 6: 1, which implied the presence of two chlorine atoms in the molecule.

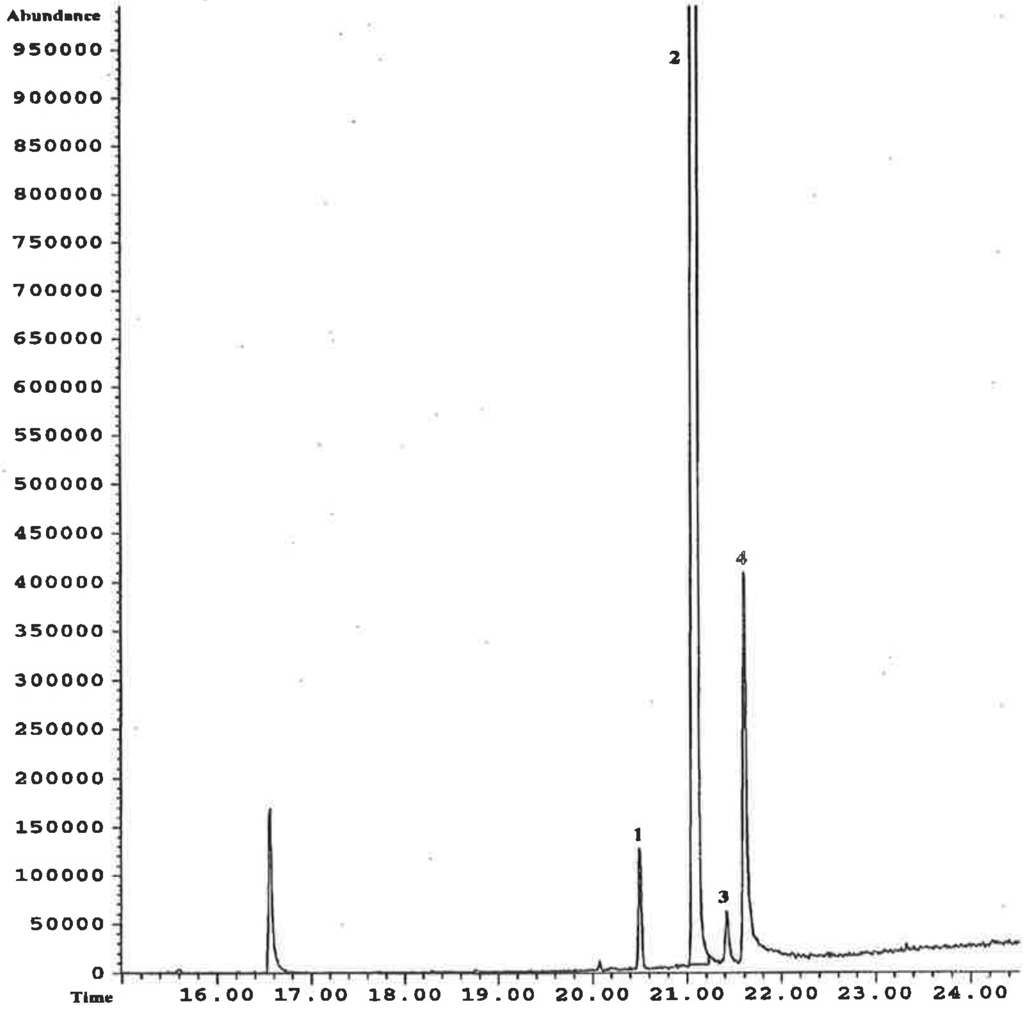


Figure 8.12 TIC of photoproducts of oxadiazon.

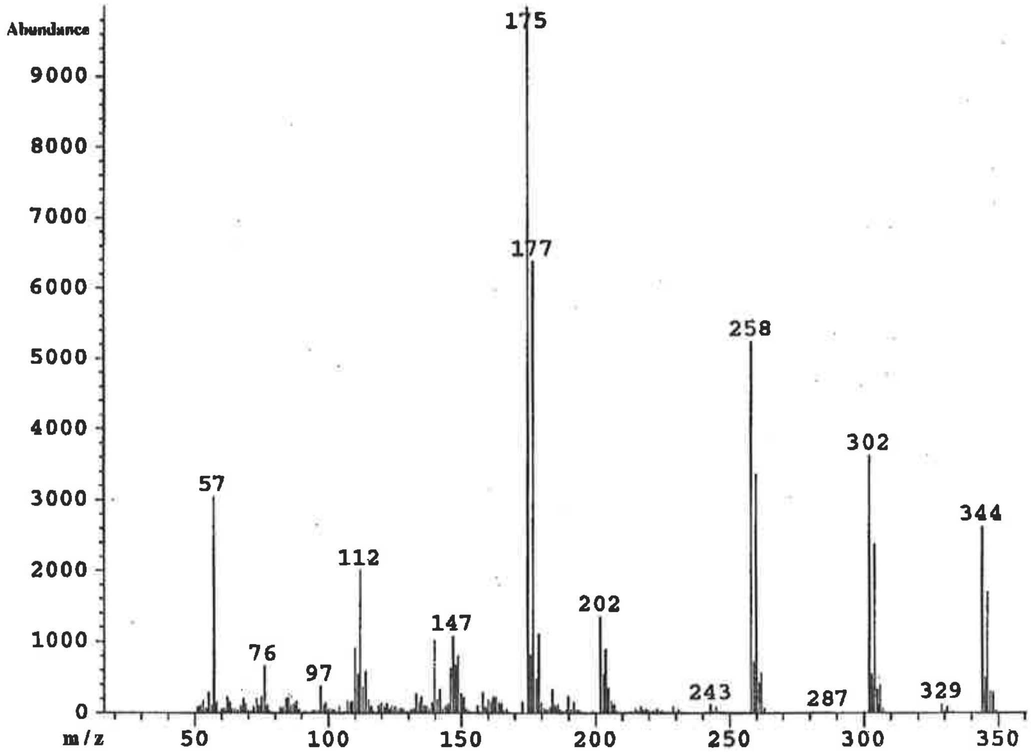


Figure 8.13 Mass spectra of compound 2 (oxadiazon).

The mass spectra of compound **1** shows a molecular ion at m/z 310 and its base peak at m/z 141 $[175\text{–}Cl]^+$ (Figure 8.14). The compound had the following fragment ions: m/z 268 $[M\text{–}(CH_3)_2C]^+$, m/z 224 $[M\text{–}(CH_3)_2C\text{–}CO_2]^+$, m/z 168 $[M\text{–}(CH_3)_3C\text{–}(CH_3)_2C\text{–}CO_2]^+$. Therefore compound **1** had a similar fragmentation pattern to oxadiazon. The 3:1 isotopic contributions of $[M]^+$ and $[M+2]^+$ suggests that compound 1 contained only one chlorine atom. So compound **1** was identified as dechlorinated oxadiazon.

Compounds **3** and **4** had the same molecular weight of 326, and their isotopic peaks indicate that there was only one chlorine atom in their molecular structures (Figures 8.15 and 8.16). So the two compounds were formed by the loss of a chlorine atom and the addition of hydroxyl from oxadiazon, but they had different fragmentations due to their different structures. In the presence of oxygen, radical oxidation of a chemical can proceed by abstraction of a hydrogen atom, followed by the addition of molecular oxygen to form hydroperoxides, hydroxyl and superoxide, all of which participate in photochemical transformations of the chemical (Miller and Hebert, 1987).

The mass spectra of compounds **3** and **4** show some characteristics of their fragmentations. The base peak for both compounds was at m/z 57, which indicates easy loss of alkyl groups. They all had an ion at m/z 157 $[175\text{–}Cl + OH]^+$, which corresponds to the ion m/z 175 in the mass spectra of oxadiazon. The compound **3** had the following characteristic fragment ions: m/z 292 $[M\text{–}Cl]^+$, m/z 250 $[M\text{–}Cl\text{–}(CH_3)_2C]^+$ and m/z 166 $[M\text{–}HCN\text{–}(CH_3)_3C\text{–}(CH_3)_2C\text{–}Cl]^+$, which suggests a preferential loss of chlorine atom from this compound. Except for m/z 129, the compound **4** had similar fragment ions to the parent compound oxadiazon: m/z 284 $[M\text{–}(CH_3)_2C]^+$, m/z 240 $[M\text{–}(CH_3)_2C\text{–}CO_2]^+$, m/z 184 $[M\text{–}(CH_3)_3C\text{–}(CH_3)_2C\text{–}CO_2]^+$. So it is believed that compound **4** should have similar structure to oxadiazon. The structures for compounds **3** and **4** were tentatively assigned as shown in the Figure 8.17.

The above study clearly shows that the photochemical transformations of oxadiazon were dominated by the loss of chlorine atoms and the participation of hydroxyl (Figure 8.17).

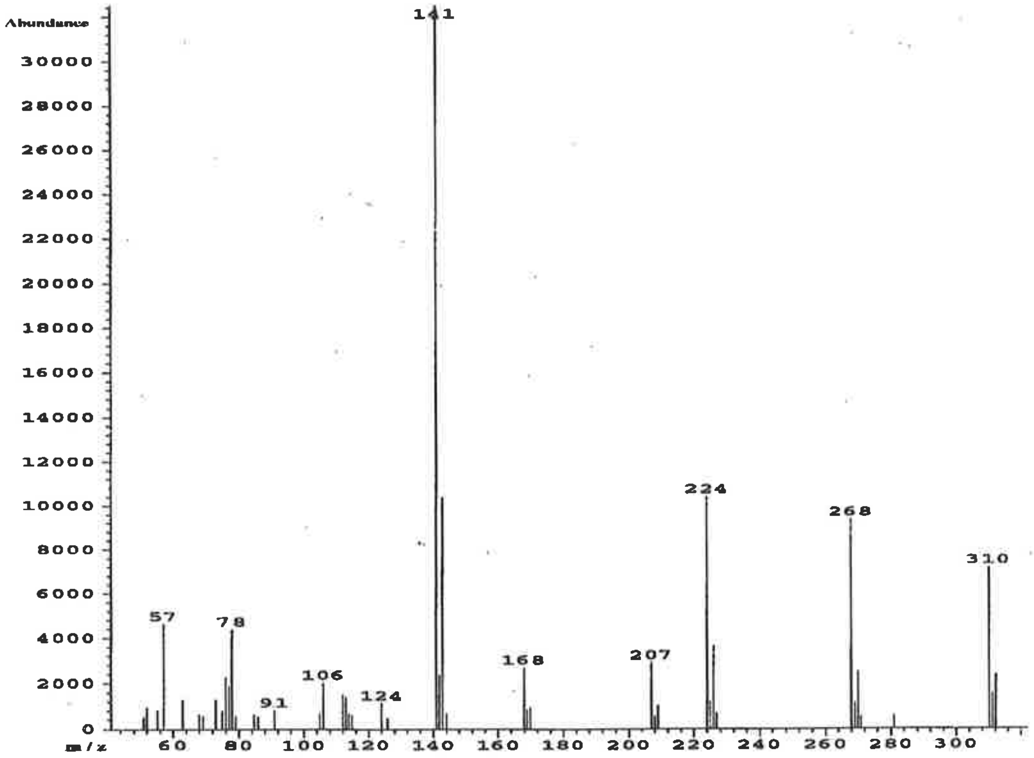


Figure 8.14 Mass spectra of compound 1 from the photolysis of oxadiazon (dechlorinated oxadiazon).

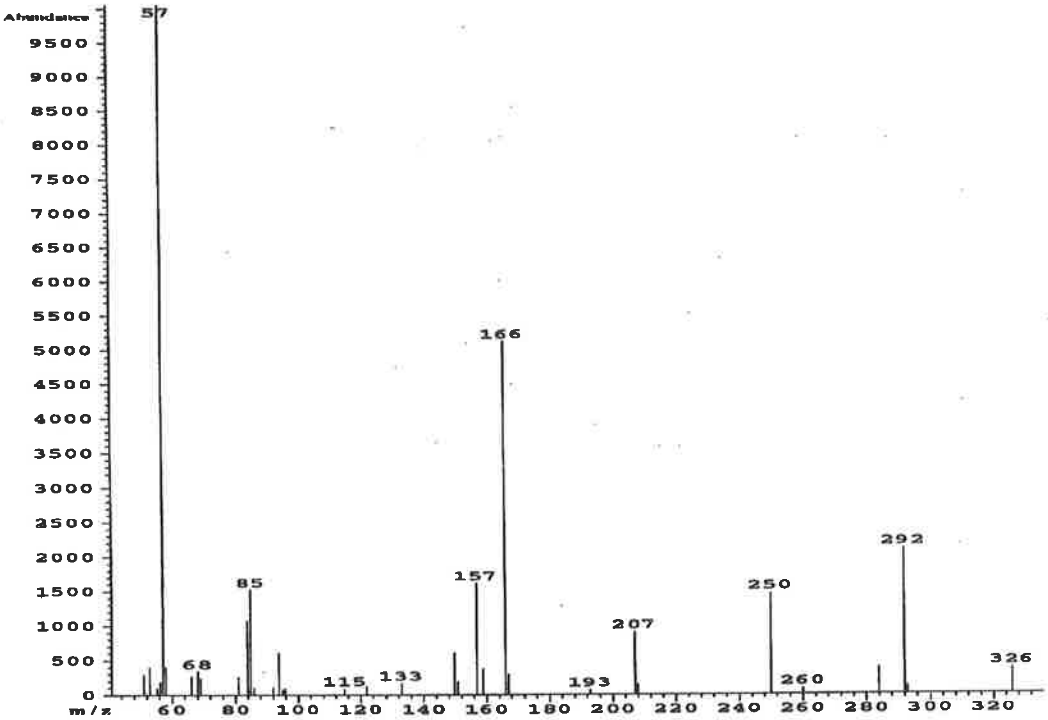


Figure 8.15 Mass spectra of compound 3 from the photolysis of oxadiazon.

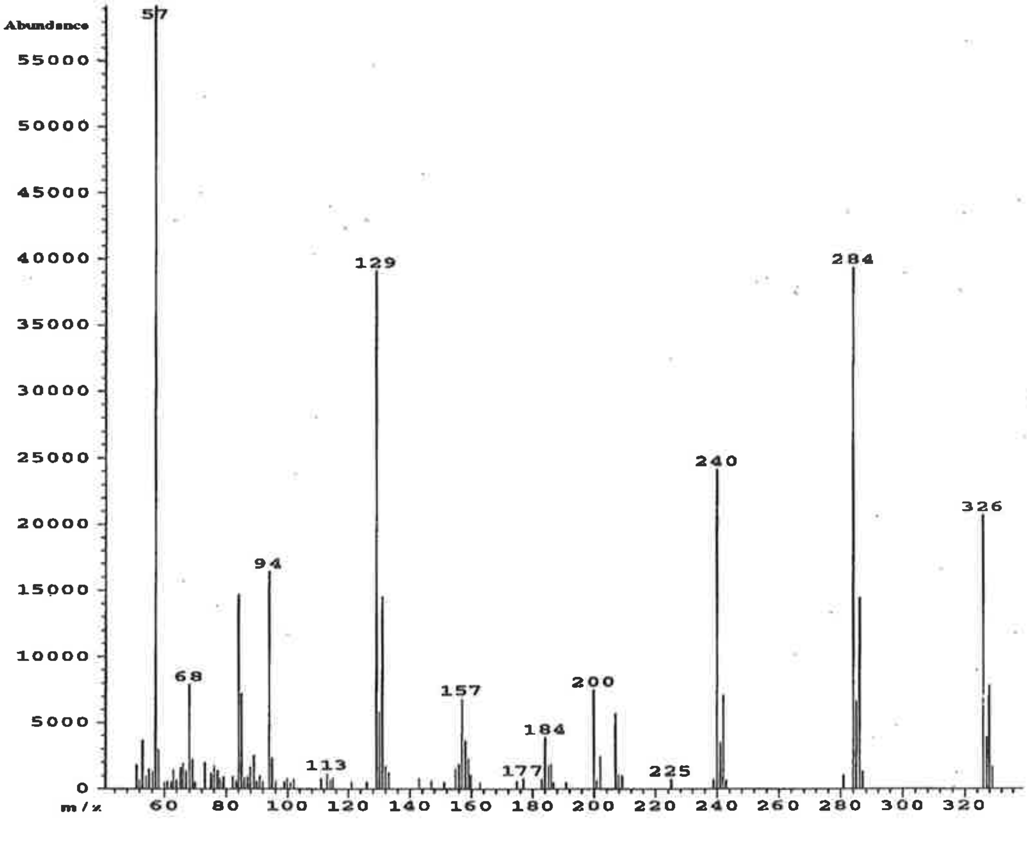


Figure 8.16 Mass spectra of compound 4 from the photolysis of oxadiazon.

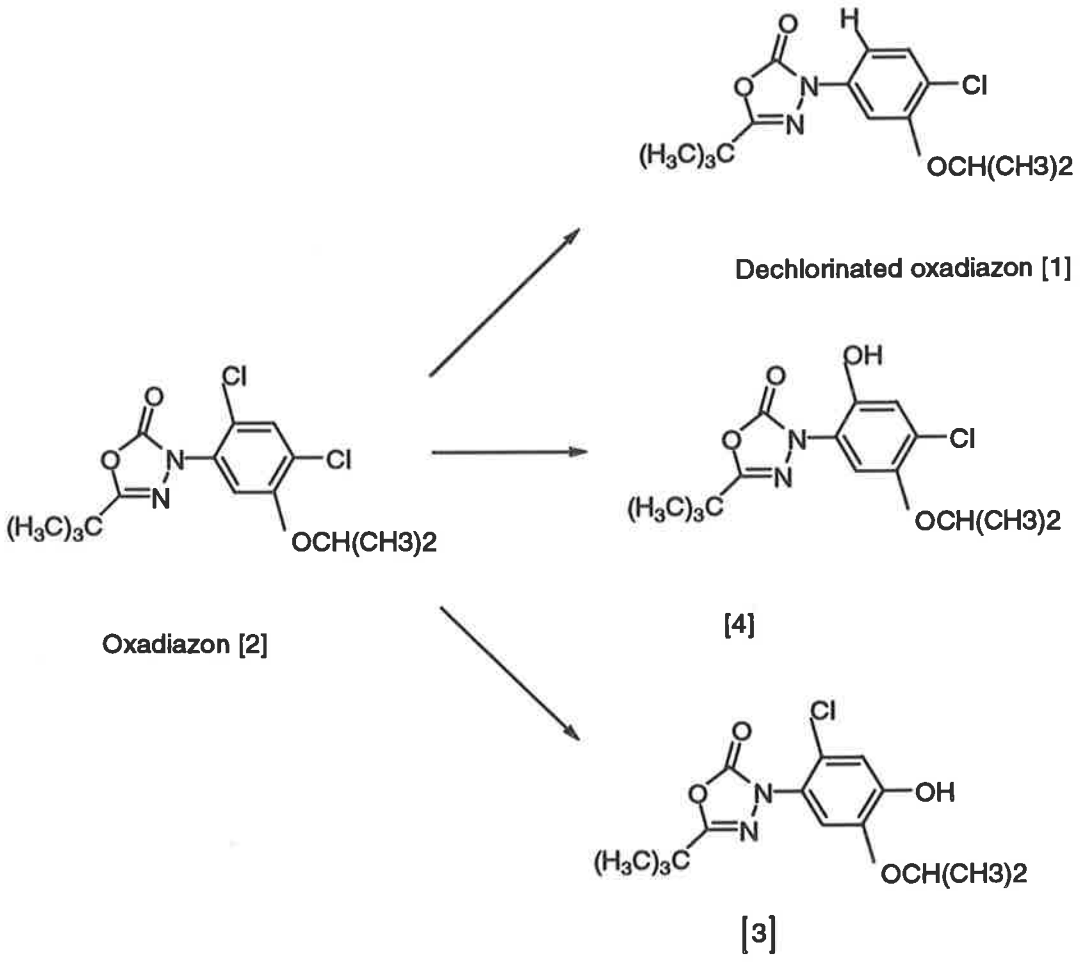


Figure 8.17 Photolysis of oxadiazon in water under sunlight. Numbers in the brackets are peak numbers in TIC.

8.4.3 Oxyfluorfen

GC-MS analysis shows that there were four compounds in the aqueous solution after photolysis of oxyfluorfen in water under sunlight (Figure 8.18). Compound **4** was oxyfluorfen, which has a molecular weight of 361. Oxyfluorfen had a base peak at m/z 252 due to the loss of Cl, CH_2CH_2 and NO_2 from the molecular ion. The m/z 280 $[M-81]^+$ points to the loss of Cl and NO_2 (Figure 8.19).

The even-numbered molecular weight (m/z 332) of compound**1** clearly indicates the loss of NO_2 from oxyfluorfen (Figure 8.20).The NO_2 position in oxyfluorfen structure was replaced by OH in this compound. Compound 1 had the following fragment ions: m/z 304 $[M-CH_2CH_2]^+$, m/z 251 and m/z 223 $[M-CH_2CH_2]^+$.

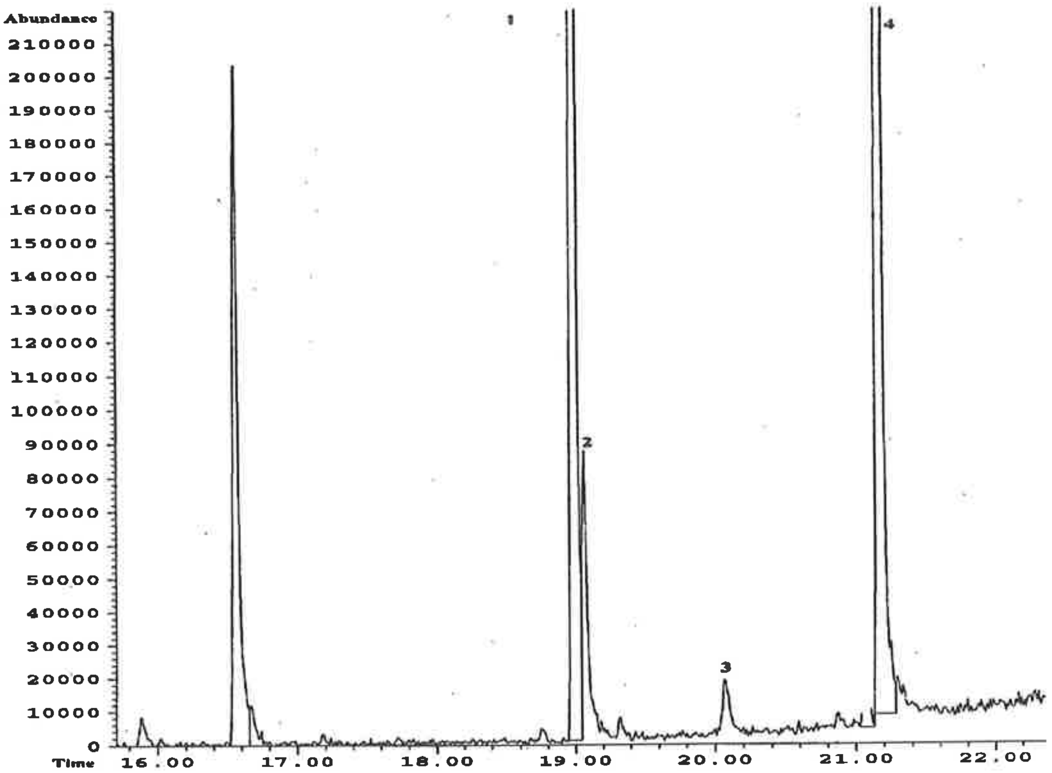


Figure 8.18 TIC of photoproducts of oxyfluorfen.

Compound **2** had a molecular ion at m/z 327 with a base peak at m/z 251 (Figure 8.21). The ion m/z 308 was due to the loss of F while m/z 223 was due to the loss of CH_2CH_2. Compound **2** was believed to be dechlorinated oxyfluorfen. Compounds **1** and **2** both had the same base peak at m/z 251. The structure of the ion m/z 251 remains to be determined.

Compound **3** gave an odd numbered molecular ion at m/z 331 and fragment ions at m/z 302 and 274 (Figure 8.22). This indicates existence of a nitrogen atom in the molecule of compound **3**. This compound probably has the structure as shown in Figure 8.23, which was identified as one of the possible photoproducts from methanolic solution by Brodsky *et al.* (1992). Therefore, the photodegradation pathways of oxyfluorfen in water involved the loss of nitro group, dechlorination and photocyclisation.

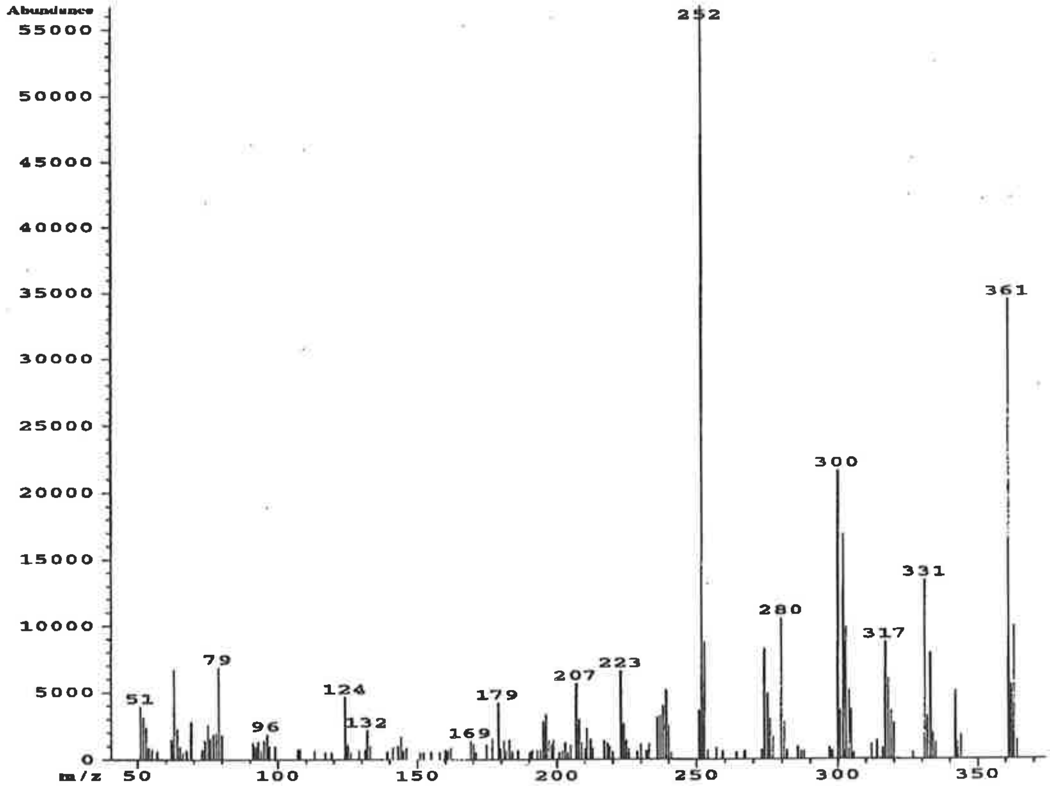


Figure 8.19 Mass spectra of compound 4 (oxyfluorfen).

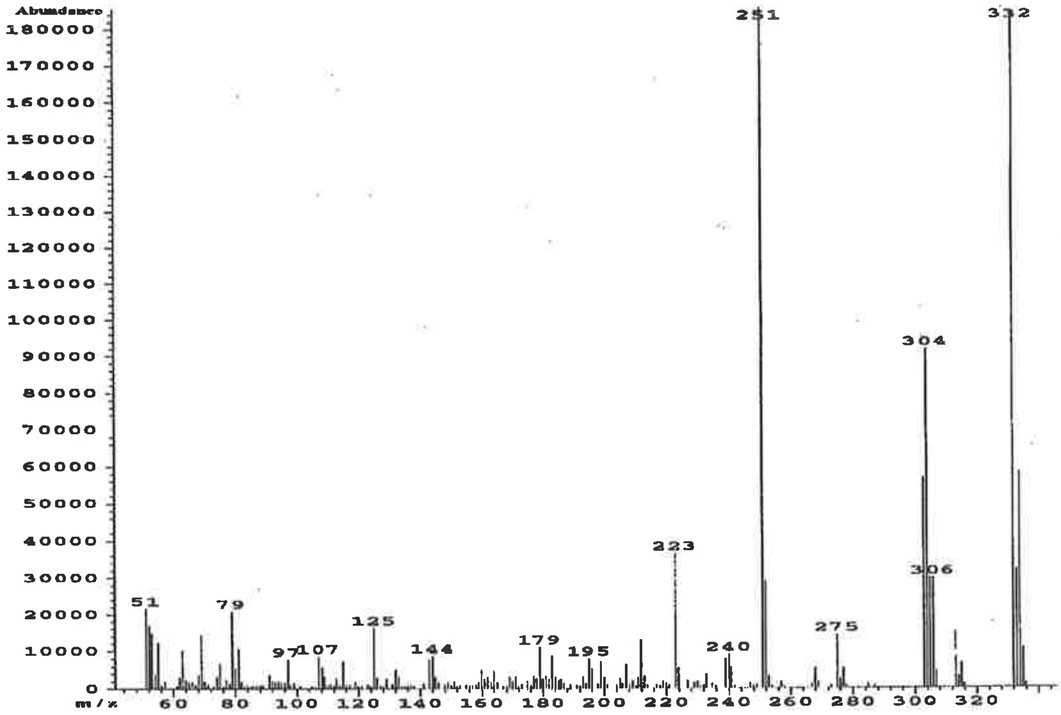


Figure 8.20 Mass spectra of compound 1 from the photolysis of oxyfluorfen.

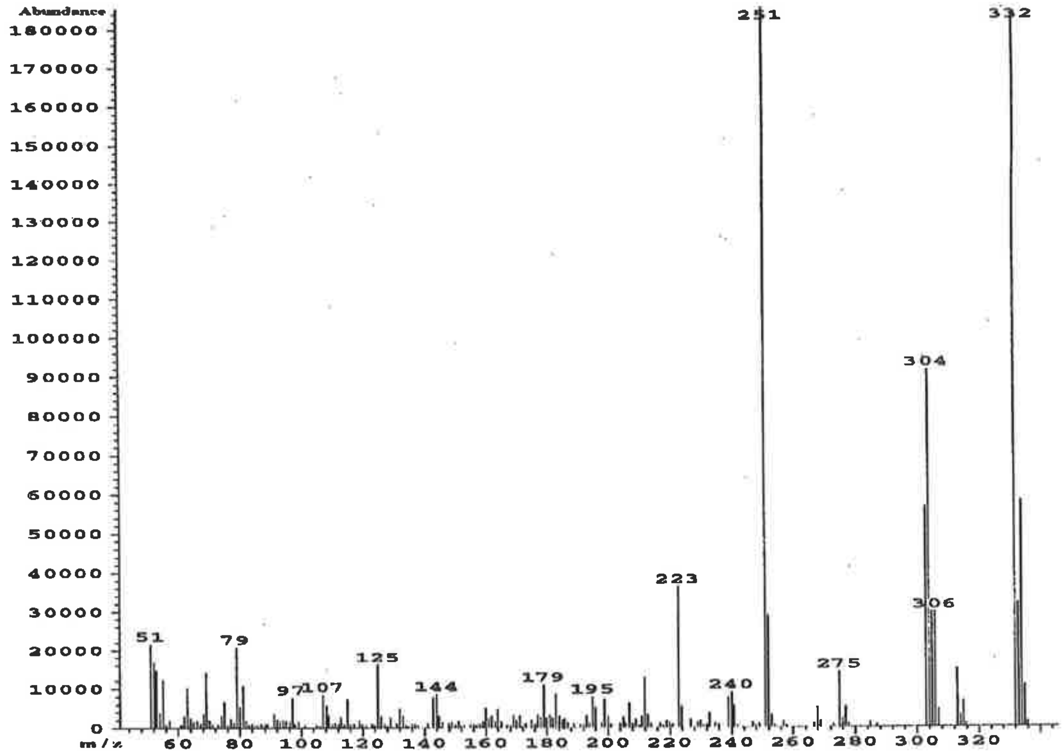


Figure 8.21 Mass spectra of compound 2 from the photolysis of oxyfluorfen.

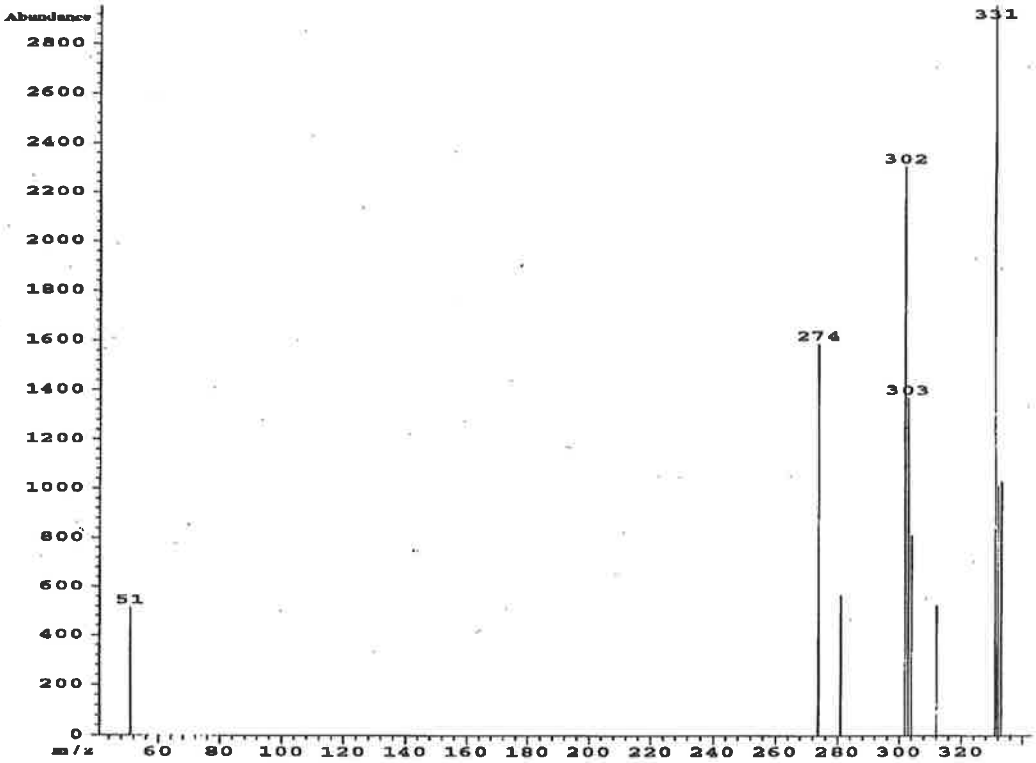


Figure 8.22 Mass spectra of compound 3 from the photolysis of oxyfluorfen.

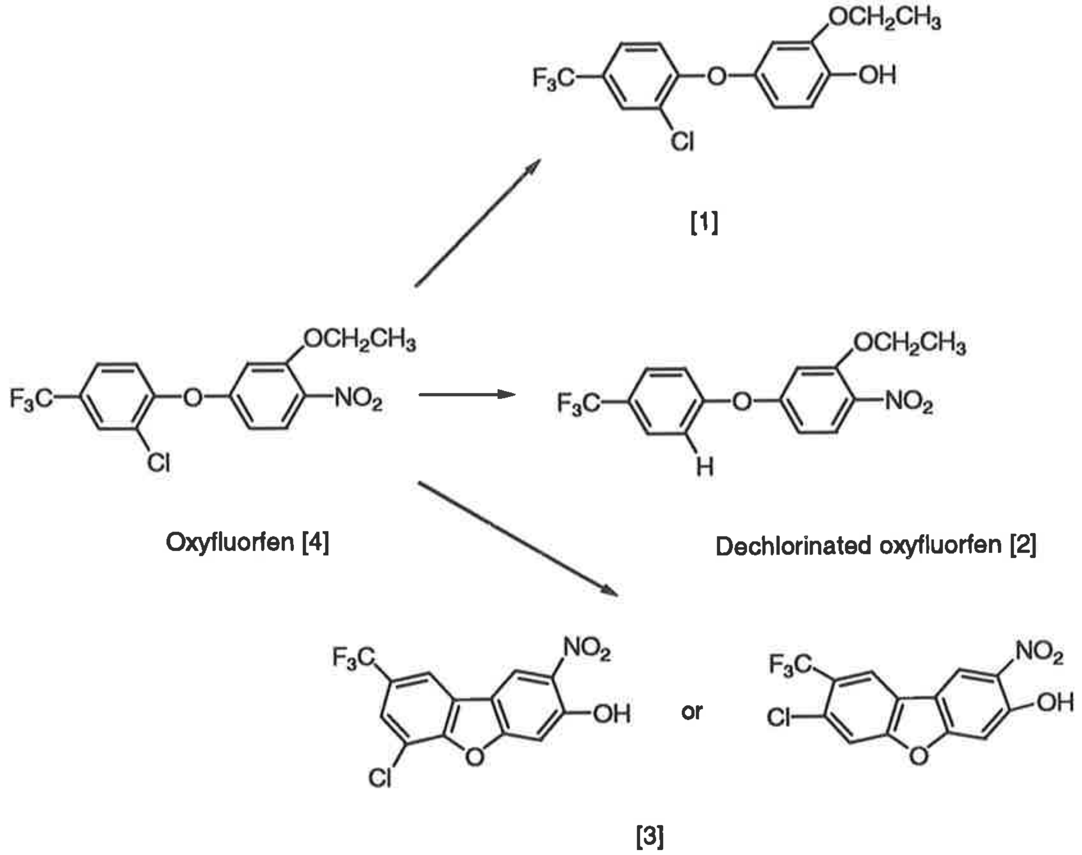


Figure 8.23 Photolysis of oxyfluorfen in water under sunlight. Numbers in the brackets correspond to peak numbers in the TIC.

In summary, several degradation products were identified by GC-MS after photolysis of each herbicide(norflurazon, oxadiazon and oxyfluorfen) in water under sunlight. The photochemical pathways mainly involved the loss of small functional groups such as chlorine atom, methyl, nitro group. The photodegradation of norflurazon, oxadiazon, oxyfluorfen and trifluralin were quite different in the various media studied. Oxyfluorfen and trifluralin degraded at higher rates than norflurazon and oxadiazon in water and on soil. The herbicides degraded more slowly on soil than in water due to light attenuation by soil media. This study shows that suspended particulates (organic matter and sediments) in natural water could retard the photolyses of the herbicides, hence causing slower degradation in natural water than in pure water.

CHAPTER 9

HERBICIDES IN GRAPES AND WINE

9.1 INTRODUCTION

The use of persistent herbicides has become an essential practice in the control of weeds in Australian vineyards. In South Australia, herbicides are often sprayed in the vineyards from November to May. During this period, grapes ripen and are picked. Due to the persistence of the herbicides, there is a possibility that grapes could be contaminated with the applied herbicides. Although most herbicides are applied on soil, they can drift onto grapevines and thus contaminate grapes. Contamination of the wine may result.

Unfortunately, there has been little information available up to now on the fate of herbicides from vine to wine. There are some studies on the fate of insecticides and fungicides in grapes and wine (Monk, 1985; Cabras *et al.*, 1987; Cabras *et al.*, 1995a and b). Lemperle *et al.* (1982) studied the degradation behaviour of vinclozolin, iprodione and procymidone for three years and found that the residues 28 days after the last spraying were in the range of 0.6 to 1.5 ppm for vinclozolin, 0.7 to 2.0 ppm for iprodione, and 1.7 to 3.8 ppm for procymidone. They also found that 60 % of these three fungicides in the grapes passed from grapes into the must. Cabras *et al.* (1987) have reviewed the fate of some fungicides *i.e.* ethylenebisdithiocarbamates, acylalanines, cymoxanil, triadimefon, thiophthalimides and dichlofluanid, benzimidazoles and thiophanates, and dicarboximides in soil, grapes and wine. Some fungicides (*e.g.*, phthalimides and dichlofluanid) in grapes can inhibit fermentation in winemaking (Monk, 1985; Cabras *et al*, 1987). Cabras *et al.* (1997) studied the persistence and metabolism of folpet in grapes and wine, and found that folpet degraded in must, giving 80 % its degradation product phthalimide. The presence of folpet in grapes inhibited the alcoholic fermentation of *Saccharomyces cerevisiae* and *Kloeckera apiculata* completely (Cabras *et al.*, 1997).

The fate of five insecticides (chlorpyrifos methyl, fenthion, methidathion, parathion methyl and quinalphos) from the treatment on the vine to the production of wine was studied by Cabras *et al.* (1995b). The insecticides on grapes showed high loss rates after treatment, with half lives ranging from 0.97 to 3.27 days. The winemaking process caused considerable residue reduction for chlorpyrifos methyl, parathion methyl and quinalphos, moderate reduction for methidathion, and almost no reduction for fenthion (Cabras *et al.*, 1995b).

It has been reported that grapes contained insecticides (*e.g.* DDT, captan, chlorpyrifos) and fungicides (*e.g.* diazinon, vinclozolin, iprodione) and wines contained fungicides (methiocarb, procymidine, iprodione and vinclozolin) and insecticides (azinphos-methyl, carbaryl, and dimethoate) in some countries such as UK, Australia, Sweden, Italy or Canada (Watterson, 1991). Cabras *et al.* (1995a) investigated 64 wine samples from 6 Italian regions and detected residues of 5 active ingredients (a.i.), which were benomyl, dimethoate, iprodione, metalaxyl and vinclozolin with a concentration ranging from 0.02 ppm to 0.14 ppm in wine.

The aim of this chapter is to investigate the fate of the herbicides norflurazon, oxadiazon, trifluralin and oxyfluorfen from vine to wine. This chapter looks at the degradation of these herbicides in grapes after exposure, and the effect of the wine making process and wine clarification on the herbicide residues.

9.2 MATERIALS AND METHODS

9.2.1 Chemicals

Herbicides used in this study were all analytical standards. Norflurazon, oxadiazon, trifluralin and oxyfluorfen were obtained from Chem Service (USA). Acetonitrile and methanol were HPLC grade solvents (BDH, Victoria, Australia) while ethyl acetate and ethanol were analytical grade solvents. Stock solutions for each herbicide were prepared in HPLC grade methanol at a concentration of 500 ppm.

9.2.2 *Treatment*

The experiments were carried out on vines at Nuriootpa Research Station, Barossa Valley in 1997, and also on the Roseworthy campus vineyard, the University of Adelaide in 1998. The Shiraz grapes in the Nuriootpa vineyard were used to make the red wine used in the study, while the red grapes (Tarrango) and white grapes (Doradillo) from the Roseworthy campus vineyard were used to study the degradation of herbicides in grapes.

The red grapes in the Nuriootpa vineyard were dipped in the herbicide solution with a concentration of 100 ppm each of norflurazon, oxadiazon and trifluralin on March 26, 1997. The samples of the treated grape were randomly collected: one sample about 1 hour after treatment, and the other one week after treatment.

The white and red grapes in the Roseworthy campus vineyard were also dipped in the herbicide solution of 100 ppm of each herbicide (norflurazon, oxadiazon, trifluralin and oxyfluorfen) on February 9, 1998. Grape samples were randomly picked from bunches and mixed at 1 hour, 1 day, 2 days , 4 days, 7 days, 14 days, 21 days and 28 days after treatment. For the last sample, grape skin and flesh were separated by hand and then analysed separately.

9.2.3 *Winemaking*

Treated and untreated red grapes (Shiraz) were harvested from the Nuriootpa vineyard on April 2, 1997, one week after treatment. The grapes were crushed into fermentation vessels using a microscale crusher in the Roseworthy campus winery immediately after harvest. The untreated grapes were separated into two vessels, one of which was then spiked with 20 ppm of each herbicide (norflurazon, oxyfluorfen and trifluralin). The resulting three vessels were as follows: one contained treated grapes, the second one contained spiked grapes, and the third one contained untreated grapes as the control. The wines were labelled as ‘treated wine’, ‘spiked wine’ and ‘clean wine’.

The small-lot winemaking procedure was simply conducted as follows. Active yeast (EC-118) was added into each vessel. All treatments were fermented on skins at about 20 °C. The ferment in each vessel was plunged at least once daily. After primary fermentation, the must was pressed off skins and the wine racked into several 2 litre bottles 5 days after the yeast was added. The bottles were covered with cling-wrap and foil, and allowed to settle for 3 days. Then potassium metabisulphite ($K_2S_2O_5$) (about 1 gram) was added into each bottle. All bottles were covered and stored at 2 °C.

Samples (20 ml each time) were taken at the following times following the addition of yeast: 1, 3, 4, 5, 7, 24, 84, 170 days. The first four samples were taken during the fermentation on skins. The other four samples were taken after pressing off skins. The skins, which were pressed off from treated and spiked vessels 5 days after fermentation, were also analysed.

9.2.4 Wine clarification

The impact of clarifying filters on residue levels was studied using cellulose pad, charcoal and diatomaceous earth. Clarification tests were carried out on 100 ml samples of 'clean wine'. Wine was spiked with these four herbicide (norflurazon, oxadiazon, oxyfluorfen and trifluralin) to a concentration of 1 ppm for each chemical in the wine. The clarifying agents used were as follows: cellulose pad; 5 g of diatomaceous earth (diatom); 4 g of diatom and 1 g of charcoal; 2.5 g of diatom and 2.5 g of charcoal; 5 g of charcoal. Wine was filtered through the clarifying agents supported on a Whatman No.42 filter paper. After filtration, the clear wine and the control samples were extracted and analysed for herbicide residues.

9.2.5 Extraction and analysis

Grapes (about 100 g) were crushed and mixed using a Ronson mixer, then extracted with 50 ml acetonitrile. The mixture was centrifuged at 6000 rpm for 15 minutes. The upper liquid phase was filtered sequentially through glass fibre and millipore filter papers. The filtrate was diluted with distilled water and passed through a C_{18} cartridge (6 cc) which was pre-conditioned by using acetonitrile and

20 % ethanol in water. The herbicide residues in the cartridge were eluted with ethyl acetate.

Wine (20 ml) was directly extracted by passing through a C_{18} cartridge (6 cc) which was pre-conditioned by using acetonitrile and 20 % ethanol in water. Herbicide residues were then analysed by GC-NPD.

GC analyses were performed using Hewlett Packard 5890 gas chromatograph, equipped with a nitrogen-phosphorus detector. The column used in this study was an HP fused silica capillary column coated with crosslinked methyl silicone (column length 25 m, column ID 0.31 mm, film thickness 0.52 micron). Nitrogen (N_2) was used as the carrier gas and the make-up gas at the flow rate of 30 ml/min for NPD. Hydrogen was used at the flow rate of 3.5 ml/min and air at a flow rate of 110 ml/min. Oven temperature was programmed from 200 °C (1 min) to 300 °C (5 min) at a rate of 10 °C/min, with injector temperature at 250 °C and detector temperature at 300 °C.

9.3 RESIDUES IN GRAPES

Residues of the herbicide active ingredients were found in grapes after treatment in the Nuriootpa vineyard and Roseworthy campus vineyard (Figures 9.1 and 9.2). The concentrations of norflurazon, oxadiazon and trifluralin in red grapes from the Nuriootpa vineyard were 1.313, 0.054 and 0.099 µg/g respectively one hour after treatment, and 1.015, 0.042 and 0.073 µg/g respectively 7 days after treatment (Figure 9.1). This indicates a slow degradation or dissipation of herbicides on Shiraz grape surfaces in the Nuriootpa vineyard.

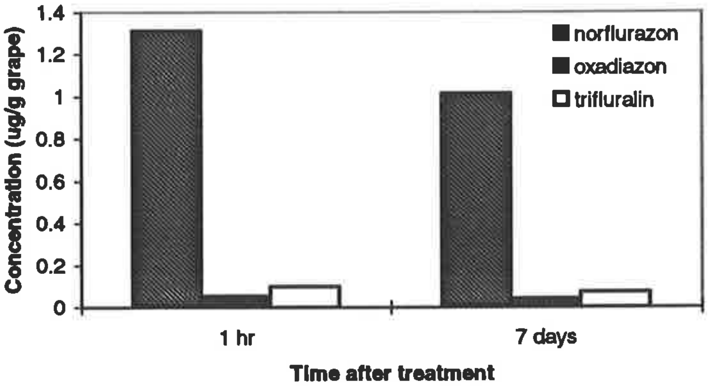


Figure 9.1 Residues of norflurazon, oxadiazon and trifluralin in red grapes from the Nuriootpa vineyard.

The study of herbicide residues on the red and white grapes from the Roseworthy campus vineyard showed that norflurazon and oxadiazon dissipated much more slowly than oxyfluorfen and trifluralin on grape surfaces (Figure 9.2). Trifluralin and oxyfluorfen were not detected in grapes from Roseworthy campus vineyard 4 days after treatment. However, norflurazon and oxadiazon residues remained in grapes for as long as one month following treatment. So the dissipation of the four herbicides was different on grapes.

The dissipation rate of a chemical on grape surfaces depends on many factors such as the inherent ability of the chemical to adhere to the grape surface, the physiochemical properties of the chemical, the texture of the grape surface including surface waxes and the climatic conditions. During the experiments in the Nuriootpa vineyard and Roseworthy campus vineyard, there were no rainfall events. so the environmental (climatic) factors operating in this study were wind and sunlight. The decay rates of herbicides on grapes in the Roseworthy campus vineyard were higher than in the Nuriootpa vineyard. This was partly due to abundant vine leaves in the Nuriootpa vineyard, because the vine canopy protects grapes from exposure to sunlight. Whereas in the Roseworthy campus vineyard, the grapevines were well pruned and canopy thinned and hence the grapes were directly exposed to sunlight.

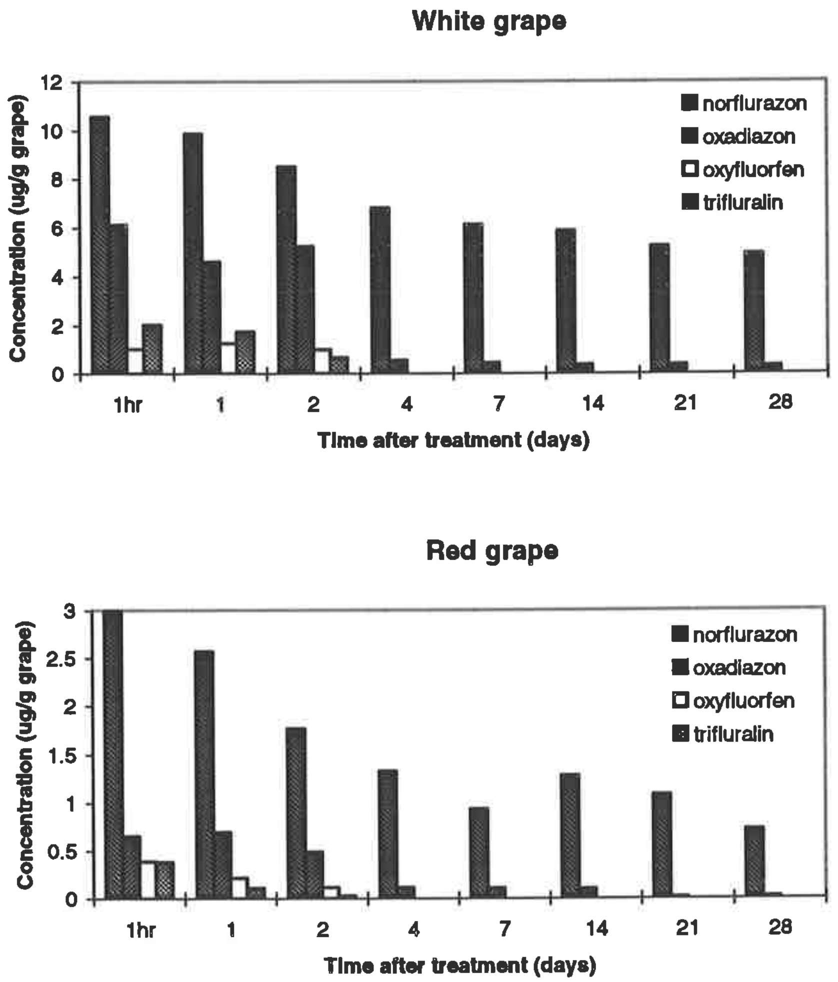


Figure 9.2 Residues of herbicides in grapes from the Roseworthy campus vineyard.

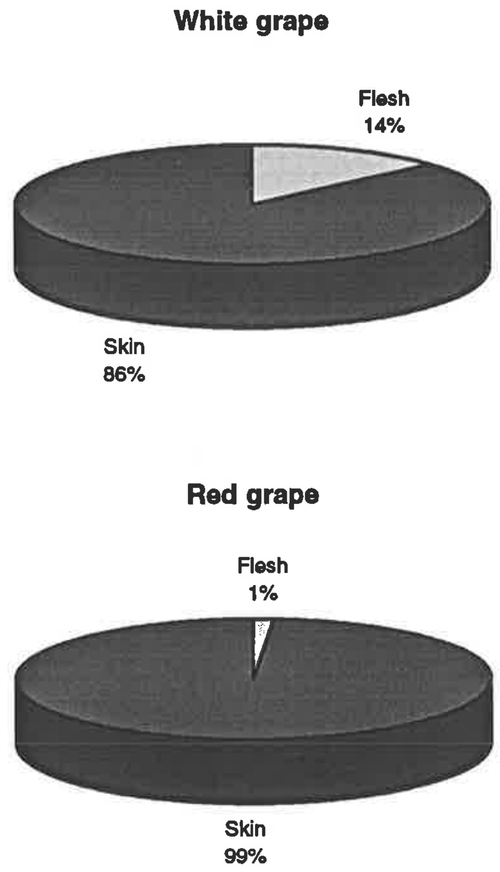


Figure 9.3 Distribution of norflurazon in the grape skin and flesh of red and white grapes from the Roseworthy campus vineyard.

An interesting finding in this study is that white grapes retained more of the herbicides on their surfaces than red grapes did following the initial application. This was believed due to the different wax composition and thickness on red and white grape surfaces. In addition, norflurazon was highest in concentration among these herbicides in both red and white grapes, although the concentrations of each herbicide in aqueous solutions were the same. This indicates that norflurazon was significantly more persistent on grape surfaces than the other herbicides. The grape skins and flesh were separately analysed 28 days after their treatment in the Roseworthy campus vineyard. The proportion of the herbicides which penetrated into grapes was different between red grapes and white grapes (Figure 9.3). About 14 % of norflurazon and 0.24 % of oxadiazon have penetrated into grape flesh in the white grapes. Only 1.47 % of norflurazon and no oxadiazon has penetrated into the grape flesh in the red grapes. The skin of the Tarrango red grape is thicker than that of the Doradillo white grape, so the herbicides can more easily penetrate into the white grapes. However, most of the chemical residues in all cases remained on the grape skins.

The residues of the herbicides were also found in the grape skins which were pressed off during wine making. The concentrations of the herbicides in the treated grape skins were: 0.644 µg/g for norflurazon, 0.008 µg/g for oxadiazon and 0.029 µg/g for trifluralin. The concentrations of the herbicides in the grape skins from the spiked vessel were: 4.111 µg/g for norflurazon, 0.023 µg/g for trifluralin and < 0.5 ppb for oxyfluorfen. This further demonstrates that grape skins adsorbed substantial percentages of herbicides in grapes and as well as the must. Herbicides in wine could be reduced by pressing off grape skins during the wine making.

9.4 RESIDUES IN WINE

9.4.1 Effects of wine making on residues

The small-lot winemaking experiments show that herbicide residues in grapes had no obvious effects on the fermentative microflora. Tests on sugar and alcohol contents during wine making indicated similar fermentation rates in the three vessels including the treated wine, the spiked wine and the clean wine.

The effects of wine making on herbicide residues in must and wine are shown in Figures 9.4 and 9.5 respectively. Norflurazon was higher in concentration than other herbicides in both treated and spiked wines. For the wine and must made from treated grapes, this concentration difference was due to the fact that on the treated grapes the residual norflurazon level was higher than that for oxadiazon and trifluralin. The same phenomena in the must and wine of the herbicide spiked treatment indicates that these herbicides, except for norflurazon, degraded quickly in must and wine. In Figures 9.4 and 9.5, the data for the first five days were measured on grape juices from the must during “first fermentation”. Residues of herbicides in the must degraded more quickly during “first fermentation”. Oxyfluorfen had disappeared completely by the second day and trifluralin had degraded 24 days later in the spiked wine. However, trifluralin had disappeared after "first fermentation" and oxadiazon had disappeared 24 days later in the case of treated wine. But norflurazon degraded very slowly in wine and it was the only residue found in the finished wines.

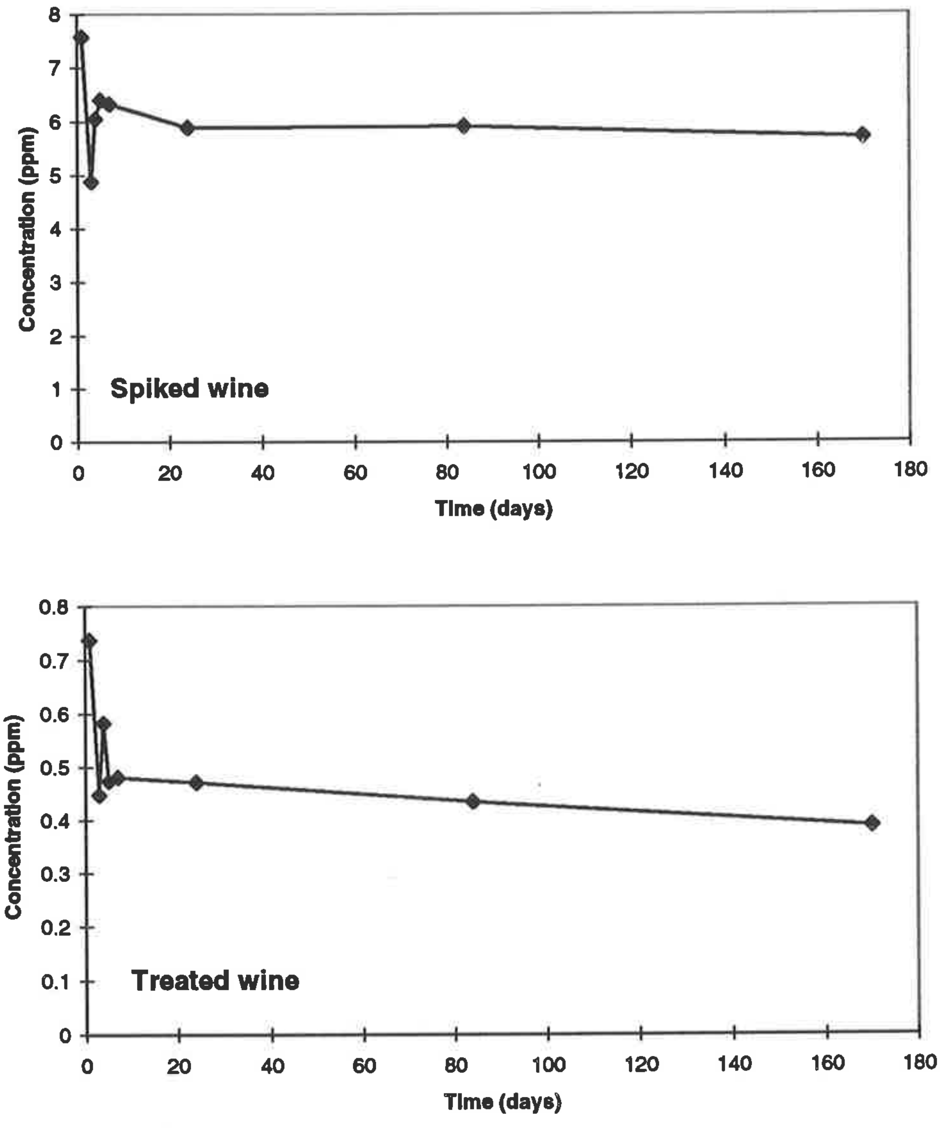


Figure 9.4 Changes of norflurazon concentrations in wines during wine making.

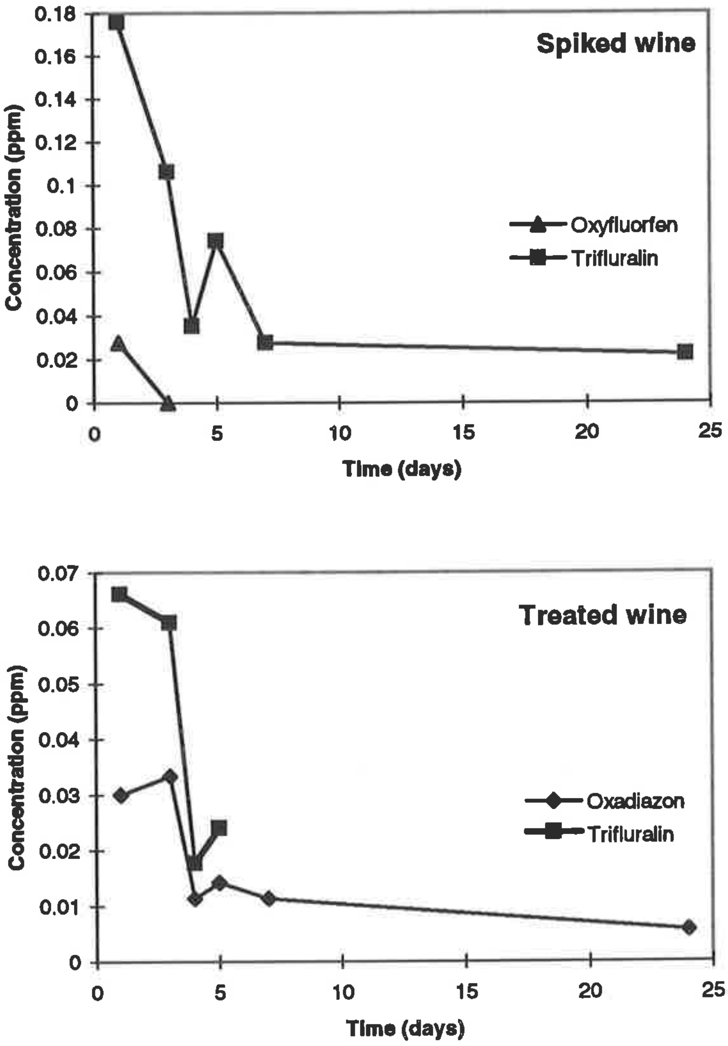


Figure 9.5 Concentrations of oxadiazon, oxyfluorfen and trifluralin in wine.

9.4.2 Wine clarification

The wine clarification study shows that the clarifying agents (cellulose pad, diatomaceous earth, and charcoal) used in this study had different effects on the residues in wine before bottling (Table 9.1). The cellulose pad and diatomaceous earth (diatom) showed no influence on norflurazon and oxadiazon, but moderate influence on trifluralin and oxyfluorfen in red wine. The cellulose pad reduced trifluralin and oxyfluorfen residues to 23.5 % and 59.0 % of their initial concentrations in wine, while diatomaceous earth only reduced these two residues to 55.2 % and 74.2 % of their initial concentrations in wine (Table 9.1). The mixture of diatomaceous earth and charcoal significantly decreased the residue contents in red wine.

Table 9.1 Recoveries (%) of herbicide residues in wine after clarification

Clarifying agents	Norflurazon	Oxadiazon	Trifluralin	Oxyfluorfen
Cellulose pad	96.1	94.8	23.5	59.0
Diatomaceous earth	106.5	118.1	55.2	74.2
Diatom (4 g) + charcoal (1 g)	8.8	22.7	15.0	trace
Diatom (2.5 g) + charcoal (2.5 g)	5.4	19.0	6.5	trace
Charcoal (5 g)	3.6	5.4	0.5	trace

The more charcoal used in clarification, the cleaner the wine. Charcoal almost completely removed the herbicide residues in wine. Previous studies (Cabras *et al.*, 1987; Cabras *et al.*, 1995b) also found that among the commonly used clarifying agents (bentonite, K-caseinate, colloidal silica + gelatin, and charcoal) only charcoal readily decreased the residues of some fungicides and insecticides in wine. Therefore, charcoal supported by a cellulose pad could be used to clean up contaminated wine before bottling.

9.5 CONCLUSION

The degradation of herbicides on grape surfaces is influenced by many factors such as climatic conditions, grape textures and surface waxes and herbicide properties. Trifluralin and oxyfluorfen degraded more quickly than norflurazon and oxadiazon on grapes. Norflurazon and oxadiazon penetrated into white grapes more easily than red grapes due to the thin skin of white grapes, but the majority of the chemical remained on the grape skins in each case. Except for norflurazon, the herbicides (oxadiazon, oxyfluorfen and trifluralin) degraded very quickly during fermentation. Norflurazon concentrations were high in the finished wines. It is clearly shown from the clarification tests in this study that charcoal filtration could effectively remove the herbicide residues in wine.

CHAPTER 10

GENERAL DISCUSSION AND CONCLUSIONS

10.1 GENERAL DISCUSSION

10.1.1 Mobility of herbicides in soils

The mobility of herbicides is influenced by many factors such as the herbicide's physiochemical properties, soil properties, rainfall or irrigation, landscape and farm management. The relative leaching potential of herbicides can be obtained through laboratory and field studies. Laboratory leaching tests on packed soil columns clearly show that the leaching potential of the herbicides used in this study in decreasing order were as follows: norflurazon > oxadiazon > trifluralin > oxyfluorfen in soils from the Mountadam, Nuriootpa, Lyndoch and Tanunda vineyards. A field study conducted in the Mountadam vineyard also showed that norflurazon was the most leachable herbicide among the four herbicides applied in the vineyard because much more norflurazon was detected in the shallow ground water in the first year than any of the other herbicides. And, in the following year, only norflurazon was found in groundwater in the same plot. All the herbicides applied to the plot were detected in the soil from this plot, which means that the other herbicides except norflurazon were strongly adsorbed on soil and resisted leaching. As expected, all herbicides persisted over a 12 month period.

Leaching tests on intact soil columns from the Barossa Valley showed that norflurazon and simazine were the only two chemicals detected in leachates. The amounts of simazine in the leachates from intact soil columns were higher than those of norflurazon. This confirms that simazine is the most mobile chemical among the herbicides tested in this study. This is consistent with previous studies on packed soil columns by Reddy and Singh (1993) and Gomez de Barreda *et al.* (1993). Reddy and Singh (1993) found that bromacil completely leached followed by simazine (82 %), norflurazon (67 %) and diuron (62 %) from a packed soil column (8 cm long and 7 cm inner diameter) in a total of five pore volumes. Stearman and Wells (1997) found that simazine leached down to the 60-90 cm soil depth in a red maple nursery plot with a silt loam soil after the first rainfall event. Simazine has been widely found in ground water in European countries (Funari *et al.*, 1991).

Laboratory leaching tests of herbicides in different soils show differences in leaching extent of the herbicides. More of the herbicides (norflurazon, oxadiazon, oxyfluorfen and trifluralin) leached out from packed sandy-soil columns than from packed clay-soil columns. Water flowed faster in sandy soils than in clay soils. Similarly, these herbicides also leached down faster in sandy soils from the Mountadam and Nuriootpa vineyards than in clay soils from the Lyndoch, Tanunda, Koonunga, Kalimna and Koonunga Hill vineyards due to textural differences among these soils. Textural differences were indirectly related to soil physical parameters such as hydraulic conductivity, bulk density and porosity. In these soils from the Barossa Valley, the organic matter contents are low and similar (Tables 5.1 and 6.1). So soil physical parameters, especially hydraulic conductivity are the important factors governing the movement of herbicides in soils; and herbicides are expected to move deeper into coarse-textured sandy soils than in medium-textured silt loams or fine-textured clay soils.

The movement of herbicides through soil and into groundwater can be modified by other processes including sorption, degradation, volatilisation, runoff and plant uptake. Among these processes, sorption is of great importance in determining the mobility of herbicides in soil. The sorption coefficient or organic carbon sorption coefficient is often measured in the laboratory and used to express the sorption of a herbicide on soil. The organic carbon sorption coefficients of norflurazon, oxadiazon and trifluralin have been measured in this study. The K_{oc} values measured on the soils from the Barossa valley ranged from 447 to 669 for norflurazon, from 1795 to 3090 for oxadiazon, and from 25689 to 36467 for trifluralin. The K_{oc} values found in literatures ranged from 40 to 159 for simazine (Carsel, 1989; Karickhoff, 1981 and Wauchope, 1992), and 100,000 for oxyfluorfen (Wauchope, 1992). The sorption values suggest that the sorption of the herbicides on soil in decreasing order was: oxyfluorfen > trifluralin > oxadiazon > norflurazon

> simazine. This reflects the fact that an inverse relationship exists between sorption of herbicides and their tendency to leach in soils.

Sorption of herbicides on soil was measured in the laboratory with dilute suspensions and the equilibrium between herbicide and soil was reached within 24 hours. But sorption of herbicides in natural soils under field conditions may require more time to reach equilibrium due to aggregated nature and low proportion of water to soil. Several weeks may be required to reach equilibrium between solution and adsorbed phases for soils at field moisture contents (Graham-Bryce, 1981; Pignatello *et al.*, 1993). Two stage kinetics models for sorption and diffusion can be used to explain this long equilibrium between herbicide and soil (Pignatello *et al.*, 1993; Brusseau and Rao, 1989; Hamaker *et al.*, 1996). An initially fast sorption or diffusion of herbicides is followed by a second slower and irreversible stage. Herbicides slowly diffuse into interior of the soil particles. Leaching tests of herbicides on three packed Nuriootpa soil columns showed that less norflurazon leached from the packed soil columns with water applied 2 and 4 weeks later after herbicide application than from the packed soil column with water applied in the following day after herbicide application. The longer the time interval between herbicide application and watering or rainfall, the less the herbicide leached down the soil columns. The results of laboratory experiments by Graham-Bryce (1981) with disulfoton could be explained by this non-equilibrium phenomenon. He found that adsorption and desorption isotherms were virtually identical and adsorption appeared completely reversible when desorption took place immediately after adsorption while soils were wet. However, when the soils were dried in air at 20 °C for 48 hours after uptake, the subsequently determined desorption was more difficult (Graham-Bryce, 1981). This phenomenon also occurred in runoff process. Gerstl (1991) found that as the time between pesticide application and irrigation increased the amount of pesticide found in the runoff greatly decreased.

In addition to non-equilibrium effects, preferential flow (or by-pass flow) can have serious impacts on the movement of herbicides in soils. Preferential flow can occur due to large variations in the pore size distribution and results in the movement of herbicides through macropores in soil profiles. Macropores ($> 30\ \mu$ m) are created by roots, earthworms and cracking. Stearman and Wells (1997) found that all chemicals studied (simazine, 2,4-D and bromide) leached down to more than 60-90 cm after first rainfall event in red maple nursery plots in Cookeville, TN. They believed that preferential flow or chemical channelling accounted for this rapid downward movement of chemicals. Leaching experiments with intact soil columns indicated that more herbicide (norflurazon and simazine) could leach down from the Koonunga and Kalimna clayey soils than from the Mountadam and Nuriootpa sandy soils with the same amounts of water applied. Bergstrom and Stenstrom (1998) also found in the lysimeter studies that more of the herbicides (chlorsulfuron, metsulfuron methyl and bentazon) leached from the lysimeters that were filled with a clay soil than from the corresponding sand-filled lysimeters. These examples could be taken as clear evidence of preferential flow. But generally speaking, sandy soils are believed to be the worst soils as far as contamination of the groundwater by herbicides is concerned, because water and its associated herbicides flow much faster in sandy soil than in clay soil. Ritter *et al.* (1994) found that simazine had moved through the entire top 150 cm of the soil profile 15 days after it was applied. The herbicides (atrazine, simazine, cyanazine and metolachlor) were leached to the ground water nine days after they were applied when 31.5 mm of rainfall occurred (Ritter *et al.*, 1994). This research demonstrated that herbicides may move through shallow ground water by macropore flow in the sandy soils of the Mid Atlantic states if sufficient rainfall occurs shortly after they are applied.

The field study in the Mountadam vineyard shows that herbicides (norflurazon, oxadiazon, trifluralin and oxyfluorfen) were found in groundwater in the first year after herbicide application but only norflurazon was detected in groundwater in the second year after herbicide application. Trifluralin, oxyfluorfen and oxadiazon were very low in concentration and were not detected in any lysimeter on any sampling occasion. The leaching of trifluralin, oxadiazon and oxyfluorfen into shallow groundwater could result from non-equilibrium effects. These herbicides might also move with fine soil particles by water. The soil in the Mountadam vineyard is a sandy soil with a high amount of gravel in it. Rain water not only moved down the soil profiles but also flowed laterally down to the dam near the vineyard. The groundwater table was near the surface during the rain season. This also facilitates movement of these herbicides via this shallow groundwater. Preferential flow through macropores might also be responsible for the leaching of these herbicides in the Mountadam sandy soil.

10.1.2 Degradation of herbicides

The degradation of a herbicide is dependent on the environmental conditions and chemical nature of the herbicide. Degradation of herbicides can reduce the persistence of herbicides in the environment. Herbicides can be transformed or degraded by chemical, photochemical and biochemical means. The importance of each degradation process in soil, water and plants is quite different.

10.1.2.1 Soil

Soil is the main media that herbicides occupy in the environment, so degradation of herbicides in soil is an important process that occurs after herbicide application. Soil provides an appropriate environment for certain chemical reactions. In soil, chemical attack by oxidation and hydrolysis can be expected. Photodegradation of herbicides on soil surfaces can result directly from absorption of solar radiation or indirectly by reaction with another chemical such as humic acid which is in turn activated by absorbed solar radiation. The half lives of the herbicides on soil surfaces in summer were respectively 5.53 days for norflurazon, 4.65 days for oxadiazon, 3.53 days for trifluralin and 5.19 days for oxyfluorfen. However, photolysis of herbicides in soil is limited due to light attenuation by soil by which sun light may only penetrate no more than several millimetres in depth.

However, the predominant means of degradation is microbial or enzymatic. Soil contains a wide variety of living organisms, in particular, a very versatile microbial population capable of attacking a very wide range of different substrates. The degradation of herbicides in soil is affected by the concentration and availability of the herbicides, the population of the microorganisms capable of degrading the herbicides, and the soil environmental conditions such as temperature, moisture and nutrients. There have been many studies on the biodegradation of the herbicides (norflurazon, simazine, oxadiazon, oxyfluorfen and trifluralin) as outlined in previous chapters. Biodegradation of norflurazon has been found to be a slow process in a bog soil (Savin and Amador, 1998) and in a sandy soil (Rahn and Zimdahl, 1973). Desmethyl norflurazon was the metabolite reported in soils (Savin and Amador, 1998; Rahn and Zimdahl, 1973). The biodegradation of simazine in soils has also been widely reported (Wang, *et al.*, 1995; Ahonen and Heinonentanski, 1994; Behki and Khan, 1994). In this study, the dissipation of the herbicides in the Mountadam vineyard soil has been monitored. The dissipation half lives in the vineyard soil varied from 2 weeks for oxadiazon to 16 weeks for oxyfluorfen. The persistence of norflurazon, oxadiazon and trifluralin in the soil is much lower than that of oxyfluorfen. Oxyfluorfen is the most persistent among these herbicides in soil and is dissipated through very slow microbial degradation and evaporation and as well as photodegradation on soil surfaces (Weed Science Society of America, 1994). Simazine could persist in soil profiles for several months with a half life of 8-10 weeks (Stearman and Wells, 1997; Wauchope, 1992).

10.1.2.2 Water

Once herbicides were applied onto the soil, they could move to water systems by processes such as runoff, leaching and drifting. All degradation processes (microbial, chemical and photochemical) can occur in water. Chemicals can degrade faster in water than in soil. Laboratory studies on the degradation of norflurazon, oxadiazon and trifluralin in water indicated that the half lives in water under laboratory conditions were respectively 8.96 days for norflurazon, 7.38 days for oxadiazon and 1.84 days for trifluralin. The laboratory degradation of herbicides in water is characterised by an initial fast loss followed by a very slow loss. The mechanisms involved in the degradation of these herbicides were believed to be biotic as well as abiotic. This study also indicated that suspended particles in natural water could retard the degradation of herbicides due to adsorption of the herbicides onto the particles. The average half-life of simazine in ponds where it has been applied is 30 days, with the actual half-life dependent on the level of algae present, the degree of weed infestation, and other factors (Weed Science Society of America, 1994). Vink and Vanderzee (1997) observed a large variation in biotransformation half lives ranging from 1 day to 139 days in surface water. Simazine may undergo hydrolysis at lower pH. It does not readily undergo hydrolysis in water at pH = 7 (Weed Science Society of America, 1994). Among the herbicides studied in this thesis, only oxyfluorfen is not subject to hydrolysis.

However, all the herbicides are subject to photolysis in water under sunlight. During the summer in South Australia, UV irradiation is very strong during the day time. Photolysis is believed to be an important degradation process in water. Simazine was oxidised rapidly by ozone, and UV light with the formation of dealkylated and dechlorinated byproducts (Lai *et al.,* 1995). This study indicated that trifluralin and oxyfluorfen were photolysed under sunlight in water faster than oxadiazon and norflurazon in water. The half lives of photolysis for trifluralin and oxyfluorfen in water were only a few hours while those of oxadiazon and norflurazon were several days in summer. Photolysis of these herbicides in water under sunlight mainly gave rise to the loss of alkyl, nitro and chloro groups. The photolysis rates of herbicides were lower in natural water than in pure water due to adsorption of the herbicides onto suspended particles in natural water. Natural water contains many organic and inorganic materials, which can attenuate sunlight through water column thus reducing photodegradation of the herbicides in water.

10.1.2.3 Grapes and wine

The application of herbicides in vineyards may potentially contaminate grapes, so it is necessary to understand the fate of the herbicides on grapes. This study has shown that the dissipation rates of herbicides on grape surfaces were different for different herbicides. Norflurazon and oxadiazon could remain on grapes for more than one month. However, trifluralin and oxyfluorfen dissipated faster than norflurazon and oxadiazon possibly because of their high volatility. Trifluralin and oxyfluorfen disappeared on grapes in the Roseworthy campus vineyard within a week. In addition to physiochemical properties, degradation of herbicides depends on vine canopy structure, grape type and climatic conditions (wind, rain, and sunlight). Experiments in the Nuriootpa Research Station Vineyard demonstrated that trifluralin could remain on grapes for more than 7 days after treatment. This study also demonstrated different absorption and penetration of the herbicides into the grapes. Herbicides adsorbed onto and penetrated into white grapes more easily than into red grapes.

Herbicide degradation during winemaking will be discussed briefly here. The degradation of herbicides in must (grape juice) and wine during the winemaking process resulted from biological and chemical reactions. The situation was different from those in soil and water. Oxyfluorfen was the first herbicide to disappear in the must, then oxadiazon and trifluralin degraded 24 days later while norflurazon remained in wine after one year. Temperature was found to be a crucial factor for the degradation of herbicides during winemaking. The wine was made in our laboratory, where the temperature was higher than in commercial wineries. So these herbicides may degrade slower than expected in commercial wineries.

10.1.3 Minimising herbicide residues

Water is an important natural resource for human beings. Clean water is also needed for wine industry and as well as the environment. There are many dams in the Barossa Valley which are used to collect water. Widespread use of chemicals in vineyards has the potential to contaminate the dam water thus damaging the vines or affecting wine quality. This study suggests several ways to clean up the contaminated water or to reduce the levels of herbicides in water. The first method is to use clean soil or clay. The sorption study shows that soil could absorb a very large percentage of herbicides in water, especially if the soil was stirred in the water. This is a very easy and cheap way to clean up water, especially for the contaminated dam water. Soil can be obtained from nearby farms and broadcast onto the water and stirred. After sorption of herbicides onto soil, the soil will settle to the bottom of the dam. The second method is to use charcoal (activated carbon). This study indicated that charcoal was very effective in absorbing herbicides, norflurazon, oxadiazon and trifluralin from water. This method has been used in water treatment plants. Simazine and atrazine are the most commonly found herbicides in natural waters and should be removed before distribution. Ayele *et al.* (1996) found that adsorption on activated carbon was a useful method to remove triazines from natural water during treatment to produce drinking water.

The third method is to use photolysis for cleaning up water. UV light, ozone and/or hydrogen peroxide are often used in this procedure. Triazine herbicides (for example, simazine, atrazine) can be photolysed by ultraviolet radiation (UV), ozone and hydrogen peroxide with different efficiencies (Lai *et al.*, 1995; Prados *et al.*, 1995; Meijers *et al.*, 1995; Bourgine *et al.*, 1995). This study has shown that the herbicides, norflurazon, trifluralin, oxyfluorfen and oxadiazon can be degraded by sunlight in summer. This study also shows that hydrogen peroxide has no obvious effect on the photolysis rate during the summer. It might be overshadowed by the strong solar radiation in summer in South Australia. Bourgine *et al.* (1995) suggested that hydrogen peroxide improved the efficiency of UV irradiation but noted that it required high doses. It should be remembered that sunlight has limited penetration into natural water.

Wine made from chemically contaminated grapes may contain the chemicals. Cellulose pads, diatomaceous earth and charcoal were tested to clean up herbicides in wine. This study found that cellulose and diatomaceous earth had little effect while charcoal could absorb these herbicides from wine. Diatomaceous earth is used to filter wine during the pressing and racking processes, and cellulose pads are used to filter wine before bottling. So charcoal could be applied at one of the two stages in conjunction with the cellulose pad or diatomaceous earth. Charcoal can be applied with the cellulose pad as a supporter before wine bottling or mixed in a certain proportion with diatomaceous earth during wine making processes. This can effectively eliminate herbicides from the finished wine.

10.2 CONCLUSIONS

1. The leaching potential of herbicides in soil in decreasing order was: simazine > norflurazon > oxadiazon > trifluralin > oxyfluorfen. The sorption order for these herbicides on soil was the opposite of their leaching potential: oxyfluorfen > trifluralin > oxadiazon > norflurazon > simazine. Therefore, there is an inverse relationship between sorption and leaching of herbicides in soil.

2. Laboratory and field studies showed that simazine and norflurazon were more mobile than the other herbicides in soils. Simazine and norflurazon were the herbicides detected in leachates from the intact soil columns.

3. Field studies conducted in the Mountadam Vineyard, which was treated with herbicides *viz.* norflurazon, oxadiazon, trifluralin and oxyfluorfen, showed that all of them were found in shallow ground water in the first year after herbicide application, but continued monitoring indicated that only norflurazon was present in shallow ground water in the following year although all the herbicides were still present in the vineyard sandy soil. This study demonstrated that norflurazon was mobile in the soil and the other three herbicides were less mobile in the soil. However, this study also suggested that the herbicides could leach to ground water not only through soil matrix but also through macropores, or they could move due to their non-equilibrium partitioning in soil.

4. Laboratory experiments on intact soil columns showed that herbicides could leach down through macropores in clay soil. Preferential flow was believed to be responsible for the leaching of herbicides in clay soils.

5. The longer the interval between herbicide application and subsequent rainfall events, the lower the amount of herbicides leached from the soil. This study also confirmed that mixtures of norflurazon with other herbicides could retard leaching of norflurazon in soil.

6. Dissipation of a herbicide in soil depends on the environmental conditions and the physiochemical properties of the herbicides. The field dissipation half lives in the Mountadam vineyard soil varied from 2 weeks for oxadiazon to 16 weeks for oxyfluorfen. The dissipation of the herbicides in soil was believed to be caused mainly by biodegradation. In addition to biodegradation, loss of these herbicides could also have resulted from other processes such as volatilisation and photolysis. The photolysis of these herbicides on soil surfaces under summer sunlight was relatively fast with half lives of only several days. But the importance of sunlight was reduced due to limited penetration of sunlight into soil.

7. The herbicides degraded quickly in water probably due to both biotic and abiotic means. The half lives for norflurazon, oxadiazon and trifluralin were less than 10 days in water under laboratory conditions.

   Photolysis of herbicides in pure water under sunlight in summer was very fast with half lives ranging from a few hours for trifluralin and oxyfluorfen to several days for simazine , norflurazon and oxadiazon. Addition of hydrogen peroxide did not have an obvious effect on the photolysis rates of these herbicides in summer. Suspended matter in natural water could reduce photolysis rates due to attenuation of sunlight. The photoproducts of these herbicides in water under sunlight were mainly formed due to the loss of alkyl, nitro and chloro groups in the herbicide compounds.

8. The dissipation of herbicides on grapes in vineyards was dependent on their physiochemical properties as well as vine canopy and climatic conditions. Trifluralin and oxyfluorfen disappeared faster on grape surfaces than norflurazon and oxadiazon. Norflurazon and oxadiazon could remain on grape surface for more than one month. Norflurazon and oxadiazon penetrated into grape flesh in this study, and they both penetrated more easily into white grapes than into red grapes.

9. Oxyfluorfen degraded most quickly in grape juice and wine, followed by oxadiazon and trifluralin and then by norflurazon. Norflurazon could remain in wine for more than one year. The levels of norflurazon were still high in finished wine.

10. Three methods (charcoal, soil or clay, and sunlight or UV) were tried in this study to reduce herbicide levels or clean up herbicide residues in water. Charcoal could effectively absorb the herbicides from water. Soil suspended in water could also absorb a large percentage of the herbicides in the water. The herbicides studied degraded very quickly in water under sunlight.

11. Charcoal was the most effective material for cleaning up wine contaminated by herbicides, while a cellulose pad or diatomaceous earth did not have a significant cleaning effect on wine. However, charcoal could be used in combination with cellulose pad before bottling or with diatom during wine making processes.

10.3 SUGGESTIONS ON ENVIRONMENTAL MANAGEMENT OF HERBICIDES USED IN VITICULTURE

1. Choose appropriate herbicides and use minimum dosage

Choice of a herbicide depends upon the expected weed species, soil texture, and irrigation method. In most situations, a combination of two herbicides broadens the spectrum of weed control and the persistence of residual weed control. But excessive persistence is often considered as a detrimental attribute leading to the environmental problems. So in order to reduce possible residues in soil, it is better to select short-residual herbicides. Herbicide persistence has been one of the major causes of the present pesticide controversy in our society.

To avoid injuries to vines and accumulation of herbicide residues in soil, the lower of the labelled application rates should be used in vineyards. The application rate of a herbicide should be adjusted to the major soil texture of the vineyard. The necessary application rate for a soil-applied herbicide should generally be less on a sandy soil than a soil with high organic matter or clay content.

2. Proper application of herbicides

Timing of weed removal is essential for optimum effectiveness. Early weed destruction conserves soil moisture important in areas with limited water supplies. It also can reduce insects and diseases that damage grape growth. The other important factor for choosing the application time is weather conditions. It should be remembered not to apply herbicides on a windy or rainy day. The best time to apply herbicides in vineyards is when there will be no rains in the following several days after application.

Mechanical soil incorporation into the top 1 to 2 inches is recommended after herbicide application on soil. Repeated or heavy irrigation should not be used so as to avoid leaching of herbicides into the vines' root zone causing plant injury.

3. Avoid damage to vines and contamination of grapes

There have been numerous reported instances of growers increasing rates of simazine, diuron or norflurazon and causing severe vine damage and sometimes vine death. So herbicides should be applied at as low application rates as possible. Irrigation should be avoided shortly after herbicide application.

Where soil-applied residual herbicides have been used for several years down vine rows in a vineyard and it is necessary to replant a vine, use untreated soil from the row middle to backfill around the roots of the young vine. If herbicide residues are present in all vineyard soils, charcoal or humic acid can be applied on soil around the roots of the young vines to detoxify the herbicides in the soil.

Herbicide residues can occur on grapes if , (1) the crop accumulates herbicides from the vineyard soil, (2) too much herbicide is applied to the vines, (3) the herbicide is applied too close to harvest, or (4) the vineyard received herbicide drift from another area. The herbicide residues can pass from grapes into wine. Charcoal is suggested in conjunction with diatomaceous earth during wine making, or with a cellulose pad before bottling to clean up any possible residues in wine.

4. Avoid damage to the environment (water, soil and wildlife)

Water is a very important natural resource. Caution should be exercised to prevent surface and ground water contamination during storage, mixing, loading and application. Some appropriate steps are as follows:

(1) avoid spilling herbicides.
(2) whenever possible, select herbicide with low soil mobility or use ones that degrade rapidly.
(3) avoid drift of herbicides out of the vineyard by using proper application techniques and try to make applications during optimum weather conditions whenever possible.
(4) avoid excessive use of irrigation water after a herbicide application and prevent irrigation water runoff.

Mobile herbicides are not recommended for use in non-structured soils (sandy soils) because of their high mobility in the soil. Straw or humic acid can be applied into sandy soils to increase the organic matter levels in the soil thus reducing the movement of herbicides in the soil. For a structured soil, herbicides are better to be applied onto wet soils. Wet soils can reduce the chance of herbicide leaching caused by non-equilibrium or preferential flow through macropores.

Properly applied and incorporated residual herbicides can persist from a few months to a year or more. Degradation occurs much faster if soils are flooded or frequently wet. Soil tillage usually can increase degradation of herbicide residues in soil, thus reducing the levels of herbicide residues in the soil.

If a vineyard is near a wildlife area or is a habitat for non-pest wildlife, avoid using herbicides known to be highly toxic to birds and other animals.

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APPENDIX: PUBLICATIONS

Referred papers:

1. Ying Guang-Guo and Williams B., Photodegradation of norflurazon in water. *Toxicological and Environmental Chemistry* (1999) (in press)

2. Ying Guang-Guo and Williams B., Herbicide residues in grapes and wine. *Journal of Environmental Science and Health* (Part B) vol. 34, no. 3 (1999).

3. Ying Guang-Guo and Williams B., The degradation of oxadiazon and oxyfluorfen by photolysis. *Journal of Environmental Science and Health* (Part B) vol. 34, no. 4 (1999)

4. Ying Guang-Guo and Williams B., Laboratory study on the interaction between herbicides and sediments in water systems. *Environmental Pollution (Accepted).*

Posters:

1. Ying Guang-Guo and Williams B., Dissipation and Mobility of herbicides in a vineyard. *Australian Wine Industry Technical Conference, 1998, Sydney*

2. Ying Guang-Guo and Williams B., Dissipation of herbicide residues in grapes and wine. *Australian International Symposium on Analytical Science, 1999, Melbourne.*

3. Ying Guang-Guo and Williams B., The use of solid-phase extraction for the analysis of pesticides in viticulture. *Australian International Symposium on Analytical Science, 1999, Melbourne.*