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Evaluation of predictive models for pesticide behaviour in South African soils

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February 2009

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CHAPTER 1.

INTRODUCTION

1.1 Background

In 1997, the United Nations Environment Programme (UNEP) convened an International Negotiating Committee (INC) to prepare a convention on Persistent Organic Pollutants (POPs) (Stockholm Convention, 2002). The convention is aimed at promoting international action to protect human health and the environment by reducing or eliminating releases of POPs. The initial focus of the INC was on the pesticides; aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene, the industrial chemicals; hexachlorobenzene (HCB), and the polychlorinated biphenyls (PCBs) and their unintended by-products; dioxins (PCDDs) and furans (PCDFs) (Stockholm Convention, 2002). However, the identification of additional POPs, on science-based criteria, remains one of the committee's priorities, under Article 8 and Annexes D, E and F (Stockholm Convention, 2002). In order to aid this process, the committee decided on specific evaluation criteria for persistence, bioaccumulation, toxicity and long-range transport to be used in determining the potential of a chemical to be considered as a POP (Stockholm Convention, 2002).

In their consideration of the persistence of an active ingredient, the Criteria Expert Group (CEG) advising the INC, proposed that a substance should be considered as a POP if its soil and sediment half-life (the period of time it takes for one-half of the amount of pesticide in a soil to degrade) exceeds six months. The CEG further propose that such consideration should be given, irrespective of whether the criteria for bioaccumulation and long-range transport potential are met (Stockholm Convention, 2002). This proposal emphasises the importance of persistence of a chemical when considering its potential impacts on human and environmental health.

The extent of persistence of a chemical varies between different media such as air, soil,

water and biota. Persistence is also affected by climatic conditions and physico-chemical factors within the environment (Helling *et al.*, 1971). It has been shown that the half-life of most chemical substances will tend to be longer under colder conditions. An example is that of POPs such as DDT which have been detected in biota under Arctic conditions, and in regions where the active ingredients had been withdrawn from use (Letcher *et al.*, 1995). Prolonged soil half-lives of substances considered to be short-lived may also be found under warm and arid climates such as in certain South African soils (Meinhardt, 2003).

This may be particularly relevant to industrial herbicides that are used at high dosage rates and are mostly designed to resist environmental degradation. Prolonged pesticide persistence, combined with high soil mobility, is an indicator of high pollution potential, an aspect that has been the subject of numerous studies (Weber, 1991a). Pesticide persistence and mobility related problems may not be confined to older pesticides such as the organo-chlorines, but also to modern pesticides that were designed to be short-lived and bio-degradable.

Pesticides have been implicated in causing adverse environmental and human health effects for many decades (Sereda and Meinhardt, 2005a; Sereda and Meinhardt, 2005b; Rahman, 1989; Weber, 1991b). As a result, regulatory authorities have been under pressure to pay special attention to pesticide residues in the environment. The process of predicting pollution potential and incorporating this into a regulatory process has, however, been difficult and slow. One of the reasons for the slow progress is that the variability in the properties of the chemical as well as variations within field sites and between field sites must be taken into account (Flurry, 1996; Lee *et al.,* 1998; Ma *et al.*, 2000; Müller, 2003) and this variability is difficult to define.

Within the European Union (EU), a process is under development in which the "Pesticide Migration Model" (PELMO) is to be used in conjunction with Geographical Information

System (GIS) based databases for the purposes of screening pesticides with regards migration. The aim of this combined system to is overlay migration potential information onto areas of similar soil and environmental conditions. Should such a system come into use, it would allow authorities to identify geographic areas of concern where the use of certain pesticides could be restricted (Klein, 1999).

The ability to model pesticide behaviour in soil is especially important when one considers their potential impacts at low environmental concentrations. A relevant example is that of endocrine disruption, where mammalian and reptilian immune and reproductive systems are affected at extremely low environmental concentrations (parts per trillion) by active ingredients such as DDT and deltamethrin (Letcher *et al.*, 1995).

Monitoring for pesticide residues in the environment is no longer sufficient. Although much research has been conducted on decreasing the analytical sensitivity of pesticides, the concentration level at which effects are expected, remain below the current detection limits of most modern analytical techniques (Ferrer *et al.*, 2005).

This is because the trends in pesticide development lean towards development of active ingredients that are active at low dosage rates. As a result pesticide application rates are decreasing. Examples of such developments are the sulphonyl urea herbicides and synthetic pyrethroid insecticides that are applied at dosage rates ranging from 7 to 30g of the active ingredient per hectare. Post-application detection of these active ingredients is difficult because of the dilution of the pesticide active ingredient in the application solution. The active ingredient is further diluted once it has entered the soil environment. Detection is made more difficult due to environmental samples being "dirty", and the many co-eluting active ingredients present in the extracts interfere with the analyses (Anastassiades and Lehotay, 2003).

It may be possible to use a suitable bioassay for the detection of the presence of pesticide contamination (Rahman, 1989). An example of such bioassay system is the floating

Pseudoaegerita matsushimae propagules used for detection of fungicides in water developed by Premdas and Kendrick (1992). Once its presence has been shown, the absolute identity of a contaminant will remain unknown. Identification of contaminants, and therefore their origin, unfortunately remains dependent on specialised chemical analyses.

In the EU and United States of America (USA), the pesticide regulatory authorities emphasise the protection of human- and environmental health, and the protection of groundwater resources. Pesticide migration potential and persistence are therefore scrutinised before a pesticide is approved for use (Gustafson, 1999) through the use of predictive models. Pesticide fate modelling allows regulatory authorities to evaluate the migration potential and persistence of a pesticide, before it reaches the market (Gustafson, 1999).

Pesticide behaviour prediction has been integrated in the registration process in the USA and the EU. Because the governing processes for pesticide behaviour are not all clearly understood, the models are at times inaccurate (Cowan *et al.*, 1995; Gustafson, 1993; Muller *et al., 2003*). From an environmental and human health perspective, it is important that the model rather over-estimates the pollution potential of an active ingredient than under-estimate it (Gustafson, 1999). This is a similar scenario to the use of standardised sandy soils in lysimeters during pesticide screening for migration potential.

Current South African (SA) legislation requires that residue decline, efficacy and phytotoxicity are tested under local conditions. Although environmental and toxicity data are required for registration, data produced in overseas countries are accepted for South African registration (Khelawanlall, Technical Advisor to the Registrar Act 36 of 1947, personal communication). The data accepted includes those for field migration, persistence and ecotoxicology.

Within the South African context, most irrigated agricultural fields are irrigated from

untreated water sources; these may be at a high risk of carrying agrochemical contaminants with (Sereda and Meinhardt, 2003). In addition pesticide migration to ground water and contamination of surface waters cannot be ignored, and impacts on the environment and human health must also be considered. The impact on human health is especially important in rural areas where water used by many communities does not necessarily undergo treatment (London *et al.*, 2000). It is therefore essential that pesticides comply with pre-determined migration and persistence regulatory specifications in order to safeguard such water sources (London *et al.*, 2000). There is an urgent need for the evaluation of pesticide migration potential and persistence within the South African pesticide registration process. Field migration and persistence studies *per se* are, however, costly and these additional costs may prove too high for the agricultural industry to absorb. These additional costs could however, be minimised to some extent, if a validated screening system was available and validated for South African conditions. In my opinion pesticide evaluation should be based, amongst others, on screening for migration potential and persistence using suitably validated modelling tools.

1.2 Aims

The primary aim of this study is to evaluate the mobility of selected pesticides in South African soils. In addition, the study investigated the potential use of existing predictive models as screening tools for determining the mobility of pesticides in local soils. This investigation was further aimed at recommending the implementation of a suitable screening process for use in the local pesticide registration process. This should reduce the risk of pesticide contamination of ground and surface waters once a product is in use (Klein, 1999).

In order to attain the aims of the study, the following objectives were set:

1) Collect herbicide mobility data from selected from case studies.
2) Determine the extent of phytotoxicity, if any, resulting from the movement in soil, of

selected soil applied herbicides.

3) Assess the need for migration evaluations based on results from case studies.
4) Determine whether pesticide half-life and adsorption coefficients for South African soils differ from internationally published values.
5) Determine pesticides field-migration behaviour for South African soils.
6) Evaluate current use models for their ability to predict field migration potential of selected pesticides in selected South African soils.
7) Optimise model inputs for promising models, so that these could be proposed for use, under South African conditions, as screening tools for local soils.
8) Make recommendations regarding the implementation of a suitable screening model(s) for use within the existing local registration process.

1.3 Approach to the study

In this thesis a number of case studies regarding off-target herbicide damage will be assessed in order to establish whether trends could be identified with regard to off-target migration and non-target vegetation damage. Case studies involving herbicides will be used, as herbicide damage is generally easily identified and it leads to immediate financial losses. These cases are thus more easily reported and investigated by farmers and affected parties. The herbicide case studies will be examined as examples of potential pesticide soil behaviour in general.

In order to establish the biological significance of migrated herbicide residues, greenhouse experiments were conducted to establish potential phytotoxicity. Specific attention was given to whether low levels of herbicide could damage non-target vegetation at residue levels detected in the case studies. These studies are discussed in Chapter 4.

The results of these studies indicated a need for the evaluation of pesticide mobility potential in South Africa. It was decided to attempt the validation of internationally used models for use under South African conditions. In order to validate these models field-migration studies were conducted in which migration data was generated for selected pesticides on selected soils. The data generated in this way were compared to model

predictions. Model predictions were made using input parameters either generated under laboratory conditions, or gathered from local literature.

Data from model predictions show that the models evaluated were not suitable for use under South African conditions, as the predictions did not render an acceptable approximation of the experimental data from field trials. These results led to an investigation into determining and setting specific model parameters that could be used as model inputs to the model PESTAN.

CHAPTER 2.

LITERATURE SURVEY

2.1 Pesticides in South Africa

Approximately 180 pesticide active ingredients are commercially available in South Africa, formulated as approximately 400 registered trade names (Nel *et al.*, 2000). These formulations include herbicides, insecticides and fungicides. The largest commercial market in terms of product volume sold, lies with herbicides (Crop Life South Africa, 2004). The active ingredients are formulated in various formulations as both liquids and/or dry materials.

2.1.1 The South African Pesticide Registration Process in Brief

Before a pesticide is released into the South African market, it has to be registered under the Agricultural and Veterinary Remedies act, Act No. 36 of 1947, administered by the Registrar, under the National Department of Agriculture. Registration legislation requires that testing be done under local conditions for efficacy and phytotoxicity of a new pesticide. Pesticide residue trials are required to be performed in order to set maximum residue limits (MRL) for the active ingredient as it is applied to a particular crop. The MRL is set using toxicity data generated by the active ingredient's mother company, and is based on the South African diet. Environmental and toxicity data are required for registration, but do not have to be generated under South African conditions. The environmental and toxicity data for pesticides are normally generated on other continents (Khelalwanlall, Technical Advisor to the Registrar Act 36 of 1947, personal communication), and are generally accepted for local registration as is, as long as the local testing requirements are met.

The general impression is that the registration process does not place much emphasis on

the potential environmental variations that are experienced within South Africa. It would appear as if aspects such as prevention of contamination of water sources are not considered in sufficient detail, and that local authorities rely heavily on overseas data.

2.1.2 Comparing South African and international pesticide registration perspectives

Within the perspective that pesticides and other standard agricultural practices may have a negative impact on the environment, there is growing international interest in this field. Pesticide registration legislation in European countries and the USA differs from that in South Africa, primarily in that the focus within the EU and USA, is on the potential health and environmental effects of pesticides, rather than crop safety. In these regions, legislation controlling registration of pesticides demands that strict environmental impact criteria are met and that data proving this is submitted before a pesticide can be registered and commercialised. To meet these requirements, companies are required to conduct extensive laboratory and field-testing on new active ingredients. It is a further requirement that laboratory and field-testing occurs in the country of origin. As most of the multinational companies that develop the products are based in the EU and USA the requirements for these are fulfilled during initial development of the products. Thus, much of the data required is focussed on pesticide behaviour in the environment.

Since the early 1990s, with the introduction of EC Directive 91/414, a process of data sharing among European Union member states has been developing (European Commission – Director General Health and Consumer Protection, 1991). This process has, however, not been fully implemented. One of the main issues that still requires harmonisation is the prediction of pesticide migration and persistence in soil. The EU launched an investigation into determining which of the models currently in use in different countries, should become the standard (Klein, 1999). Currently the Pesticide Migration Model (PELMO) is most widely used. A development is underway in which the use of

PELMO in conjunction with a Geographical Information System (GIS) based database is proposed as a screening tool. The aim of this interactive system is to identify areas of similar soil and environmental conditions where similar pesticide behaviour could be expected. Should such a system come into use, it would greatly enhance the potential of joint registrations within the EU (Klein, 1999).

Due to the great variation of South African soils and variable environmental conditions, the modelling approach to pesticide screening, could be an ideal solution for use within the South African registration system. However, South Africa is not yet using an environmental screening approach for local conditions, let alone well-developed systems such as GIS linked model. The first step towards implementing a pesticide behaviour assessment system for South Africa could be to select or develop appropriate models validated for South African conditions. It is this aspect that makes up a partial aim of this thesis.

2.2 Pesticide safety, health and the environment

Internationally, limits are set for pesticide residues allowed to occur in soil, water, the atmosphere, plants and in foodstuffs. These limits are stated in legislation and mostly critical concentrations are used to determine these limits. In most cases, limits of pesticide residues allowed in the environment and in foodstuffs are based on toxicological data. There is, however, a tendency internationally (especially in Europe) of agencies setting pesticide residue limits at the minimum detectable residue levels of current analytical methodology (Gustafson, 1999).

Modern pesticides are developed with low mammalian and environmental toxicity as well as low persistence, whilst being highly effective. New generation active ingredients are applied at low application dosage rates and the application rates of active ingredients at <20 g ha^{-1} are common. The older toxic and persistent active ingredients such as aldicarb

and DDT are either being phased out, or their use heavily restricted.

Most of the environmental problems caused by pesticides are due to the movement of a pesticide away from the intended target site, through spray drift, vaporisation, migration and surface run-off including the movement of both dissolved and sediment associated pesticides (Walker and Hollis, 1994; Meinhardt and van der Walt, 2005). The initial discovery of pesticide residues in ground water of major agricultural areas of the USA, during the mid seventies, was due to the implementation of monitoring programmes, using suitable sampling and analytical techniques (Barbash and Reseck, 1996). Many further reports on pesticide residues in ground water have since been reported internationally (Walker and Hollis, 1994). Pesticides contamination of groundwater is largely the result of migration through the soil profile.

Levels of pesticides detected in groundwater have generally been lower than those in surface water. However, the primary regulatory effort on reducing pesticide residues in water has been focussed on groundwater. The reason for this is that surface water undergoes processing before it is used as potable water. International general practice is that groundwater collected from wells is used as is, with little or no pre-treatment. Within South-African this is especially true for rural areas, and pertains not only to ground water, but also surface water (London *et al.*, 2000). It is also the rural communities where little development has taken place in respect of water provision that carries the highest risk from pesticides in water sources. This aspect is highlighted for the African context in a recent publication of Kylin *et al.* (2005).

2.2.1 Pesticides in South African freshwaters

Table 2.1 below summarises incidences of pesticide residues detected in South African freshwaters, likely to have entered the water sources through migration and surface run-off. The majority of the data was reported on at the *Joint European-Southern African*

International Conference on Pesticides in non-target agricultural environments – Environmental and economic implications, Cape Town (January 2003). The data provided does not stem from an organised pesticide monitoring programme, as South Africa does not have such a national programme as of yet, although it is planned (Jooste, Sebastian, 2006, Department of Water Affairs, Personal Communication). The data was mainly generated from *ad hoc*, project-based investigations into pesticides in the environment. The data thus provides a problem base for pesticides that may be present in our water sources.

Table 2.1. Incidence of pesticides detected during *ad hoc* monitoring actions.

Active ingredient	Area and Source
2,4 Dichloro -phenoxyacetic acid	Eastern Cape - fresh water sediment (Fatoki and Awofulu, 2003)
Aldicarb	Hex river valley – surface water (Weaver, 1993)
Aldrin (banned)	Eastern Cape - fresh water sediment (Fatoki and Awofulu, 2003)
Atrazine	Johannesburg - surface water (Grange *et al.*, 2003) Vaalharts irrigation scheme - surface water and groundwater (Weaver, 1993) Kwazulu Natal - surface water and fish (Bouwman *et al.*, 2003) Central South Africa – surface water (Du Preez *et al.*, 2003)
Azinphos-methyl	Lourens river wetland - surface water (Bennett *et al.*, 2003) Western Cape – surface water (Dabrowski *et al.*, 2002) Western Cape - surface water and groundwater (London *et al.*, 2000) Western Cape - suspended sediments and surface water (Dabrowski *et al.*, 2002)
Benomyl / Carbendazim	Hex river valley – surface water (Weaver, 1993)
BHC	Crocodile river, Mpumalanga - fish (Heath *et al.*, 2003) Eastern Cape - freshwater sediment (Fatoki and Awofulu, 2003)
Bromopropylate	Hex river valley – surface water (Weaver, 1993)
Carbofuran	Vaalharts Irrigation Scheme - surface water and groundwater (Weaver, 1993)

Active ingredient	Area and Source
Chlorpyrifos	Western Cape – surface water and groundwater (London *et al.*, 2000; Solomons *et al.*, 2003) Lourens river wetland - sediment (Bennett *et al.*, 2003) Western Cape - surface water and suspended sediment (Schulz *et al.*, 2001) Hex river valley – surface water (Weaver, 1993)
DDT and metabolites	Crocodile river, Mpumalanga - fish tissue (Heath *et al.*, 2003) Johannesburg - surface water (Grange *et al.*, 2003) Kwazulu Natal - surface water and fish (Bouwman *et al.*, 2003) Ubombo and Ingwavuma districts in KwaZulu-Natal - surface water and sediment (Sereda and Meinhardt, 2003)
Deltamethrin	Ubombo and Ingwavuma districts in KwaZulu-Natal - surface water and sediment (Sereda and Meinhardt, 2003) Hex river valley – surface water (Weaver, 1993) Western Cape - surface water and ground water – (London *et al.*, 2000; Solomons *et al.*, 2003)
Diazinon	Johannesburg – surface water (Grange *et al.*, 2003) Kaal-spruit river, Midrand - surface water (Papo and Mathebula, 2003).
Dichlorovos	Hex river valley – surface water (Weaver, 1993)
Dieldrin	Kwazulu Natal - surface water and fish (Bouwman *et al.*, 2003) Crocodile river, Mpumalanga - fish tissue (Heath *et al.*, 2003)
Dinocap	Hex river valley – surface water (Weaver, 1993)
Diquat	Hex river valley – surface water (Weaver, 1993)
Endosulfan a, b and sulphate	Lourens river, Western Cape – surface water (Dabrowski *et al.*, 2002) Lourens river wetland - sediments (Bennett *et al.*, 2003) Western Cape - surface water and groundwater – (London *et al.*, 2000; Solomons *et al.*, 2003)
EPTC	Vaalharts irrigation scheme - surface water and groundwater (Weaver, 1993)
Fenarimol	Western Cape - surface water and ground water – (London *et al.*, 2000; Solomons *et al.*, 2003)
Fenthion	Hex river valley – surface water (Weaver, 1993)
Fenamiphos	Hex river valley – surface water (Weaver, 1993)
Fenvalerate	Hex river valley – surface water (Weaver, 1993)
Folpet	Hex river valley – surface water (Weaver, 1993)
Formothion	Hex river valley – surface water (Weaver, 1993)
Glyphosate	Hex river valley – surface water (Weaver, 1993)
Heptachlor	Crocodile river, Mpumalanga - fish tissue (Heath *et al.*, 2003)

Active ingredient	Area and Source
Hexaconazole	Hex river valley – surface water (Weaver, 1993)
Iporodione	Western Cape - surface water and groundwater – (London *et al.*, 2000; Solomons *et al.*, 2003) Hex river valley – surface water (Weaver, 1993)
Lindane	Crocodile river, Mpumalanga - fish tissue (Heath *et al.*, 2003)
Mancozeb	Hex river valley – surface water (Weaver, 1993)
MCPA	Hex river valley – surface water (Weaver, 1993)
Methidathion	Hex river valley – surface water (Weaver, 1993)
Methiocarb	Hex river valley – surface water (Weaver, 1993)
Mevinphos	Hex river valley – surface water (Weaver, 1993)
Omethoate	Hex river valley – surface water (Weaver, 1993)
Penconazole	Hex river valley – surface water (Weaver, 1993)
Pirifenox	Hex river valley – surface water (Weaver, 1993)
Procymidone	Hex river valley – surface water (Weaver, 1993; Dabrowski *et al.*, 2002)
Profenofos	Hex river valley – surface water (Weaver, 1993)
Prometamphos	Hex river valley – surface water (Weaver, 1993)
Propineb	Hex river valley – surface water (Weaver, 1993)
Propoxur	Hex river valley – surface water (Weaver, 1993)
Prothiofos	Hex river valley – surface water (Weaver, 1993; Bennett *et al.*, 2003; Solomons *et al.*, 2003)
Simazine	Hex river valley – surface water (Weaver, 1993; London *et al.*, 2000)
Triademifon	Hex river valley – surface water (Weaver, 1993)
Vinclozolin	Hex river valley – surface water (Weaver, 1993)

The studies show the presence of a variety of pesticides in water sources from a range of environments. Because the data was generated whilst targeting specific pesticides, it cannot be determined, on a comparative basis, what the major types of pesticides may be that would prove to be a problem for local water sources. The data does, however, show that where a pesticide has been targeted due to its high use rates, it is likely to be present in water sources.

2.2.2 Pesticide behaviour in soil

Internationally, the techniques applied to evaluate pesticide migration potential include laboratory and field experimentation, as well as monitoring programmes in which the levels of pesticides are measured and thus the movement evaluated. The potential for pollution of water sources, and especially ground water, is determined by a number of variables. These variables include the amount of excess water in the soil, the depth of the water table, and the extent of pesticide adsorption to soil colloids (Groen, 1997). Because of difficulties in determining long-term pesticide behaviour in soil, as well as the high costs involved, much development has been focused on the prediction of pesticide behaviour (Groen, 1997).

Models have advantages over other pesticide evaluation methods including reduced cost, the potential to extrapolate from relatively small data sets, and the potential for establishing standard criteria for registration of both chemicals tested as well as those with similar charateristics (Gustafson, 1993). The advantages of the use of models have become evident with their use over the last 10 years in Europe and the USA. Models will be further discussed in section 2.6.

2.3 Solute transport and flow in the unsaturated zone: understanding the process

Pesticide surface runoff is responsible primarily for the contamination of surface water, whereas pesticide migration leads primarily to groundwater contamination. The movement of the contaminant is also reliant on the movement of water in soil. Therefore, water and solute fluxes in the soil profile require accurate description to allow accurate migration and persistence predictions. This section will be limited to discussions of the processes involved in migration occurring in the unsaturated zone.

Water is the primary carrier of solutes in soil. The resultant movement of solutes is due to: convective transport in the liquid phase, diffusive transport in the liquid phase and

diffusive transport in the gas phase. Convective solute transport in the soil profile then leads to solute dispersion in the soil profile.

Modellers generally distinguish between two flow systems within soil, the unsaturated zone and the saturated zone. The two systems are viewed as a continuum, with the saturated zone a wet extreme. In the unsaturated zone, water movement is generally one-dimensional and vertical i.e. in the simplest terms water will flow into soil once applied. The solute will percolate into the soil profile as a result of water input from irrigation or rain (Groen, 1997). Where the extraction of water from the soil is high, such as during high evaporation, the solute may move upwards towards the soil surface (Groen, 1997).

In the saturated zone, water flow is assumed towards ground water. In soil with lateral sub-surface drainage, ground water flow is assumed to be horizontal (Groen, 1997). The extent of mobility of a pesticide is indicative of its migration potential, defined as the amount of pesticide percolating through the bottom boundary of the active root zone (Weber, 1991b).

The major factors that govern transfer of chemicals include:

- Adsorption to soil colloids
- The extent of preferential flow
- Pesticide residual activity (persistence) in soil
- Degradation processes
- Soil water content
- Mineral element interactions

What follows is a discussion on each of these factors.

2.3.1 Adsorption

The rate of movement of a solute in its simplest form is dependent on its retention in the soil, and the extent of water flow through the soil (Bailey and White, 1970). Adsorption of

a solute to soil colloids is a function of the chemical characteristics of the solute and those of the soil. Solutes are adsorbed to soil colloids (Mora *et al.*, 1996) which carry an electrical charge. Adsorption is a function of the charge that the solute molecule carries, and the charge on the soil colloid. Solutes are present in soil solution as anions, cations, or neutral molecules. Amphoteric active ingredients carry a positive and negative charge. Clay minerals carry a negative charge and attract mainly cations, whereas organic material has an affinity for anions, cations and neutral molecules. This is why the organic matter content of the soil has such a large influence on the mobility of pesticides in soil (Eagle, 1976; Hance, 1967; Nel and Reinhardt, 1984; Reinhardt and Nel, 1989; Singh *et al.*, 2001).

Water is added to the soil solution through rain or irrigation and then either infiltrates the soil or runs off the surface. The ratio of the water fraction that infiltrates the soil to that fraction which runs off is dependent on the intensity of precipitation and the infiltration capacity of the soil.

High rainfall rates onto a compacted clay loam soil will result in minimal water infiltration, and most of the water will be expended as surface run-off. Similarly, surface run-off is expected on a non-compacted, water logged (saturated) soil. Surface runoff carries pesticides in solution as well as pesticides adsorbed to eroding soil particles. If this mixture flows into surface water, it would lead to surface water contamination.

Water infiltrating the soil will be either be stored in the soil profile or will add to the percolation stream moving towards groundwater. The extent of this water movement is dependent on the soil water conditions. When the soil is dry, water infiltrating the soil will add to the stored water fraction. This soil water is available for uptake by plants, evaporation from the surface and use by soil organisms. Only when the water-holding capacity of the soil is exceeded will the excess water percolate further toward the

groundwater. If the rain water volume exceeds that of plant consumption and soil storage, the water will percolate to deeper soil layers, possibly reaching the groundwater.

The addition of small amounts of water to a system containing organic contaminants in a hexane/soil system (i.e. a soil system free of water) will lead to reduced adsorption of the active ingredients to soil colloids (Jene,1998). Jene (1998) concludes that the soil behaves as a dual sorbent in which soil organic matter functions as a partitioning medium and the mineral fraction as conventional adsorbents. Jene (1998) further conclude that adsorption of the active ingredients to mineral fractions is restrained by ambient moisture because the water molecules will preferentially occupy the adsorptive sites on the mineral surfaces.

In the case of moderately and strongly polar active ingredients, multiple sorption mechanisms are expected. These mechanisms may include solute partitioning into soil organic matter as well as specific interactions with clay minerals. Where ion-dipole mechanisms occur, this could involve either direct interactions of organic active ingredients with exchangeable cations or, as indirect interactions via water molecules surrounding the cations. Increasing the concentration of salts in a soil solution will also increase pesticide sorption.

The adsorption capacity of soil is quantified and is expressed in terms of its base exchange capacity or cation exchange capacity (CEC). The two main adsorptive inorganic clay minerals are smectite (montmorilinite) and kaolinite. Organic matter consists primarily of a humus fraction, (mainly humic and fulvic active ingredients) and organo-metal complexes (Wagenet and Rao, 1990). The adsorption capacity of the colloids for pesticides is higher for organic matter than for montmorilinite clay, which is higher than that of kaolinite clay (Riley and Morrod, 1976; Walker, 1987; Weber, 1991a; Weber, 1991b).

The free pesticide fraction is that fraction which is available for uptake by plants and for

breakdown by microbes. The sorption process is a dynamic one in which the main interaction between chemical and sorption surfaces are London-Van der Waals forces, electrostatic bonding by ion exchange, hydrogen bonding, and dipole-dipole bonding. The interactions are not necessarily separate, but are usually a combination of two or more bonding interactions (Bailey and White, 1970). The bound fraction is in equilibrium with the free fraction and one of the major assumptions made for the modelling process is that the attainment of equilibrium is instantaneous. The adsorption process can be described by the linear Langmuir and Freundlich equations.

The Freundlich equation is used most often and given as:

$$q_e = \frac{x}{m} = KC_e^{\frac{1}{n}}$$

Where:

q_e = mass of solute absorbed per mass of adsorbent (soil) (mg adsorbent per mg soil)

x = mass of solute absorbed (mg)

m = mass of adsorbant (mg)

Ce = equilibrium concentration of solute (mg/l)

K = experimental constant

n = experimental constant

The Langmuir isotherm can be derived, by assuming that the solute forms a mono-layer of atoms on the adsorbant

$$q_e = \frac{x}{m} = \frac{KQ^{\circ}C_e}{1+KC_e}$$

Where:

Q° = constant representing the mass of solute adsorbed per mass of adsorbant at saturation on a mass per mass basis

K = experimental constant

Boesten and Van der Linden, (1991) gives the Freundlich equation as:

$$X = K_F c_{l,ref} \left[\frac{c_l}{c_{l,ref}} \right]^{\frac{1}{n}}$$

Where:

$C_{1,ref}$ = reference concentration in the liquid phase

K_F = Freundlich coefficient

L/n = Freundlich exponent

Boesten and van der Linden (1991), assume that sorption is heterogeneous and non-uniform. Because the Langmuir isotherm assumes uniform sorption, the Freundlich isotherm is preferred as it accounts to some extent for surface heterogeneity (Groen, 1997).

In addition to the extent of adsorption, the distribution of the solute between the gas and liquid phase will also influence migration, which is a function of the volatility of the pesticide. Volatilisation is the process in which a chemical evaporates to the atmosphere from different environmental compartments. The rate of evaporation is dependent on the chemical properties of the active ingredient, as well as environmental conditions. Where pesticides are applied to soil, it is assumed that loss through volatilisation is negligible, and is not taken into account (Jene, 1998).

2.3.2 Preferential flow

The term preferential flow refers to a range of physical non-equilibrium flow processes in soil. The process is dominant on fine textured soil and occurs through macro-pores such as shrinkage cracks, worm burrows and root pores. The macro-pores function as high-conductivity flow paths, and a by-pass the to denser soil matrix (Jarvis, 1996). Preferential flow can also occur in unstructured sandy soil as a result of profile heterogeneity, such as at the interfaces of different soil layers. At these interfaces, preferential flow occurs due to soil texture variations, and water repellency. Preferential flow will also occur in homogenous soils with sub-surface drainage (Van der Zee and

Boesten, 1991). During preferential flow, solutes leach more rapidly than would be expected when compared to soils lacking preferential flow paths. This is because the solutes in the fast flowing water do not have sufficient time to equilibrate with the slow moving or stagnant water contained in the bulk of the soil matrix. Preferential flow is important in pesticide migration because the pesticide rapidly bypasses the topsoil and quickly reaches the sub-soils. In the sub-soils, adsorption and degradation generally is greatly reduced (Flurry and Fluhler, 1994).

Available experimental data shows that preferential flow may be the rule rather than the exception (Flurry and Fluhler, 1994). This means that the models that do not take preferential flow into account may not be that widely applicable. A number of preferential flow models have, however, been developed. There are two major groups of preferential flow models; those that use microscopic approaches to calculate transport at the pore scale, and those that follow the macroscopic continuum approach. The continuum approach divides the soil into flow domains, each characterised by a water flow rate and solute concentration (Groen, 1997).

2.3.3 Pesticide residual activity (persistence) in soil

The length of time that a pesticide remains active in soil is a function of the dosage rate and the rate of loss of the pesticide from the soil (Eagle and Caverly, 1981; Gottesburen *et al.*, 1992). The rate of loss is determined by a combination of the degradation and transfer processes. Degradation occurs through biological degradation (microbes and plants), chemical degradation and / or photo-degradation, although not all pesticides are prone to all three these degradation processes.

The persistence of a pesticide can be quantified in terms of its half-life. The half-life or (DT_{50}) is defined as the time in days required for the concentration of a pesticide active ingredient to be halved, under a given set of environmental conditions. Pesticide half-life

is sensitive to environmental conditions such as soil temperature, soil water content, air temperature, ultra-violet radiation and microbial activity of the soil.

The ideal agronomic pesticide should persist for a sufficient time to provide season-long control of the target pest, whilst not harming sensitive follow-up crops or non-target organisms. Carry-over problems occur when soil and weather factors exists which favour reduced degradation post application. Excessive persistence tends to occur more frequently in some seasons than in others (Gojmerac *et al.*, 1996), reflecting the influence of climatic factors on rates of loss. Extended persistence may be exacerbated by overdosing during application. Most of the studies on carry-over have been conducted on herbicides, as carry-over problems are frequently a problem with follow-up crops. In the case of systemic persistent pesticides, excessive residues could remain in the harvested produce. This could have significant implications during the sale or export of such produce.

The persistence of pesticides is the overriding factor determining their potential to reach groundwater sources in detectable amounts (Gustafson, 1999). A highly mobile, non persistent pesticide will be unlikely to pose a threat to deep lying groundwater because its limited persistence will likely render it less hazardous. On the other hand, a highly persistent, immobile pesticide may accumulate to unacceptable levels in groundwater given sufficient time (Walker and Hollis, 1994). Thus, both persistence and migration characteristics of pesticides must be considered when assessing their potential to contaminate groundwater. Due to the influences of various factors and their interactions, the persistence of a pesticide may vary considerably between soils, between sites and seasons (Kubiak, *et al.*, 1990). Because of this variance, computer models have been used to screen the potential persistence and mobility of pesticides. A prerequisite for accurate predictions of pesticide fate, is the validation of these models against field generated data, reflecting these variances (Walker and Barnes, 1981; Nicholls *et al.*,

1982a; Nicholls *et al.*, 1982b).

2.3.4 Biological degradation

Biological degradation is the process by which microbes and plants metabolise pesticides. Some microbes have the ability to use pesticides as a food source, using O_2 and in the process releasing CO_2. The higher the microbial activity of a soil, the higher the expected rate of microbial degradation for pesticides prone to microbial degradation. Soil microbial activity is also affected by organic matter content, temperature, water, O_2, pH and nutrient availability. Therefore the residual activity of a pesticide that is prone to microbial degradation will also be affected by these factors (Bollag *et al.*, 1992).

Most pesticides are prone to microbial breakdown in soil (Bollag *et al.*, 1992). Kauffmann (1992) has shown a large number of micro-organisms that have the ability to degrade active ingredients such as atrazine in pure culture; most of those reported on being fungi. There are, however, reports of bacteria including *Arthrobacter* sp., *Bacillus* sp. and *Pseudomonas* sp. capable of degrading pesticides (Kauffmann, 1992).

2.3.5 Chemical degradation

This is brought about by chemical reactions involving oxidation, reduction and hydrolysis. As in the case of microbiological degradation, this is an important route of loss of activity for certain pesticides.

2.3.6 Photolysis

Excessive activation by sunlight of electrons in pesticide molecules may cause loss of structural integrity and inactivation (Weber, 1991). The pesticide molecules absorb light energy, electrons are excited, and chemical bonds are broken. This route of degradation is only important for pesticides that remain on the soil surface for a extended periods, or

those that are exposed to sunlight in clear water. Where such pesticides are used in crop protection, it is generally advised that they be mechanically incorporated into the soil, or alternatively rain or irrigation is required after application in order to leach the pesticide out of the light zone. Photolysis may only be important in relation to migration and soil persistence, for the period of time that the active ingredient is applied and retained on the soil surface.

2.4 Modelling Pesticide Behaviour in Soil

Models can be divided into two groups, namely the simple screening models and the more detailed predictive models.

2.4.1 Screening Models

Screening models classify pesticides according to their water contamination potential. One such model is the Groundwater Ubiquity Score (GUS) index, developed by Gustafson in the late 1980s (Walker and Hollis, 1994). Gustafson proposed a single index for groundwater contamination potential based on the soil/water partitioning coefficient (K_{oc}) and its half-life (Walker and Hollis, 1994). The principal of the model is that pesticides that are weakly absorbed, and are persistent in soil have a greater potential for contaminating ground water. This model was developed using chemical characteristics of chemicals found during well water surveys in the USA. Gustafson estimated average K_{oc} values and field-derived half-lives for these chemicals and then constructed a diagram that separates groundwater contaminants and non-contaminants.

Using this data, Gustafson developed the GUS index given as:

$$GUS = \log (DT_{50}) \times [4 - \log (K_{oc})]$$

The half-life is given in days and the K_{oc} in L/kg. Gustafson further suggests that if the

GUS index exceeds 2.8, a high pollution potential exists, and where the index falls below 1.8, a low pollution potential exists. Extrapolation of the GUS index to British data indicated a reasonably accurate transition of pesticide that were frequently detected and those that were infrequently detected in groundwater (Walker and Hollis, 1994). Screening models, however, only provide qualitative indications as to the migration potential of chemicals.

2.4.2 Predictive models

The more complex simulation models are used for qualitative comparisons of pesticide migration and persistence. A number of predictive models have been developed and improved upon over a number of years and these are discussed below.

2.4.2.1 VARLEACH

The model VARLEACH of Walker (1987) is a modification of the Nicolls model CALF (Nicholls *et al.*, 1982a; Nicholls *et al.*, 1982b). VARLEACH is a simple migration model that incorporates sub-routines to allow for effects of temperature and soil water on pesticide degradation rates. The model requires input of daily weather data of maximum and minimum air temperatures, rainfall and potential evaporation. Where evaporation data are not available, the model can calculate evaporation. It further requires a measurement (or estimate) of soil water content at field capacity. It requires a half-life for the pesticide at a known temperature and soil water content. Also, an adsorption distribution coefficient (K_d) is an essential input. These soil parameters can be varied with soil profile depth with a maximum of three soil layers.

The model output provides water content, residue concentrations (mg kg^{-1}), water-phase concentration (mg/l), total flow across the lowest boundary (maximum 2 m depth) and total

migration loss, and average "leachate" concentration over the a set simulation period. The user can specify time intervals at which the outputs are given. The model calculates parameters in successive 1-cm layers, but these can also be specified at other increments for output. Output is in tabular form as a text file, which can be imported to spread sheet software.

Strengths of VARLEACH:

The model requires few input parameters; it has a rapid run time and provides a detailed simulation of temperature and water content effects on degradation.

Weaknesses of VARLEACH:

The model does not allow for volatilisation, cannot incorporate crop growth and uses a tipping bucket-type water flow routine (Baer and Calvet, 1996; Borchers *et al.*, 1995; Brown *et al.*, 1996; Cheah *et al.*, 1997; Giupponi *et al.*, 1996; Gottesburen *et al.*, 1995; Vischetti *et al.*, 1997). Model inputs are done in DOS format, which makes it tedious. The model does not take into account physical and chemical properties of the soil into account except to assume that these will be covered within the parameters for persistence and mobility.

VARLEACH was included in the evaluations, as it is a simple model, which makes provision for meteorological conditions. Also, most of the modern models in use are based on the codes and concepts of this model.

2.4.2.2 PELMO

PELMO was developed to estimate the migration potential of pesticides through distinct soil horizons based on an extended cascade model. It includes the estimating potential for soil temperatures, pesticide degradation, sorption, volatilisation, and estimate of potential evapo-transpiration using the Haude equation (Trevisan, *et al.*, 1995). It is viewed as an enhancement of the 1984 version of PRZM. Applications have mostly involved pesticide

migration scenarios on German soils. Similar to PRZM, PELMO has two major components; a water and a chemical transport component. The water transport component for calculating run-off and erosion is based on the USDA Soil Conservation Curve Number technique, and the Modified Universal Soil Loss Equation as for PRZM. The calculation of evapo-transpiration is estimated using the Haude equation (Trevisan *et al.*, 1995). Alternatively, direct input of evapo-transpiration can be used if this data is available. PELMO calculates depth-dependent temperature in soil using daily air temperatures (Klein, 1991).

The input for PELMO includes pesticide parameters such as half-life, temperature and water content, factors for half-life, organic carbon, soil partition coefficient (K_d and K_f), application rates and depth of application, volatilisation estimates, vapour pressure, water solubility, and molecular mass.

Soil parameters include depth, organic carbon, sand, and clay content and biodegradation factors for each horizon. The model also makes provision for crop parameters such as plant emergence, maturation, and harvest dates, although it can be run for non-cropped fields. Meteorological inputs consist of daily precipitation, daily mean and maximum temperature, relative humidity and potential evapo-transpiration. The output is given as depth and time-dependent pesticide concentrations in the soil profile (kg ha^{-1}), as well as the amount of pesticide contained in leachate. The output files are automatically saved to a sub-directory on the computer. These output data files are saved as DOS text files. Data can be imported into standard spread sheet software.

Strengths of the PELMO:

Default values can be used for estimation of migration for screening purposes. Fate data that are necessary for the registration of pesticides, such as sorption and degradation according to OECD standards, can be used as inputs to the model.

Weaknesses of PELMO

The estimation of water flow through a cascade model is simple. The model cannot estimate preferential flow such as through macro-pores.

The model was included in the evaluation as it is widely used in the EU as screening tool for pesticide migration evaluations. Also, PELMO was the first model to be linked with a GIS system in order to differentiate between areas with different soils.

2.4.2.3 Waterloo Hydrogeologic Incorporated (WHI) UnSat Suite - model suite

The latest developments in pesticide fate modelling have revolved around the development of software and software packages. Software companies such as the Scientific Software Group (SSG) and WHI have taken existing models and grouped them into more streamlined software packages. These packages are designed to link different models so that input data can be shared. One such model is the WHI UnSat Suite. The model was the first in a series of leading-edge environmental protection models designed for use by regulators with regard to the unsaturated zone. The development stems from a need for easy-to-use modelling tools for landfill design, well-head protection, contaminant clean-up, and agrochemical application.

WHI developed interfaces for models such as: VS2DT, PESTAN, VLEACH and HELP, forming them into a suite of models. A major advantage of a system like this is that input data can be exchanged between models. A major drawback, however, is that each model can only be run for its specific input types.

2.4.2.4 PESTAN

PESTAN is run as a module within the WHI UnSat Suite. PESTAN is used by the US EPA model for assessing contamination of soil and groundwater with pesticides (Waterloo

Hydrogeologic, 2003). It is used for evaluating the environmental impacts of potential non-point agricultural sources of groundwater contamination. It simulates the one-dimensional vertical transport of pesticides through a homogeneous soil to groundwater. A draw-back of the homogenous layer used is that multiple runs are required for heterogeneous soil layers.

The model is based on a close-form analytical solution of the advection-dispersive-reactive transport equation. The model was developed as a first tier assessment of the potential for groundwater contamination of already registered pesticides and those submitted for new registration.

The model simulates constant recharge, agricultural application of pesticides, flow and transport of pesticides through the soil with constant velocity, sorption and decay of pesticide and migration of the pesticide to groundwater. The vertical transport of dissolved pesticide through the vadose zone is simulated in PESTAN as a 'slug' of contaminated water that migrates in homogeneous, partly saturated soil. The concentration of the chemical slug is set as equal to its water solubility. The slug enters the soil at the first precipitation or irrigation event at a rate equal to the pore water velocity. The further flow of the pesticide slug is assumed to occur at constant velocity.

The pesticide is assumed stored at the soil surface, before the recharge is subjected to solid-phase decay. Once recharge is initiated, the remaining pesticide is considered dissolved and assumed to enter the soil at this point.

Strengths of the PESTAN:

The model is set up in windows format, which makes the input of data and running the model simple. Outputs can be given in tabular form or as graphs. Simple reports can be generated using the model report generator. Default values for soil parameters can be used for model runs allowing quick simple initial evaluations.

Weaknesses of PESTAN

The model does not consider macro-pore flow. The model can only be run for a single soil type in a profile, as soil profiles cannot be layered in a single run. The model does not provide for inputs of weather data, but rather uses a combination of soil dispersion ability (weather dependant) and recharge rate to calculate flow.

PESTAN was included in the evaluation as it is used as screening tool for groundwater contamination by the US EPA as part of their tiered approach to pesticide evaluation.

2.4.2.5 The Pesticide Root Zone Model (PRZM) version 3.12.

The model was first released in 1984 and remains the most widely used migration simulation model (Gustafson, 1993). The model is used by the US EPA in the pesticide screening procedure as a second and third tier pesticide evaluation. It includes a volatilisation model, and can model up to two metabolites during a single run.

PRZM-3 is an example of a software package that links two subordinate models, PRZM and VADOFT in order to predict pesticide transport and transformation through the crop root zone and unsaturated zone. This development has enabled predictions of pesticide migration through the plant root zone into and through the unsaturated zone in a single run. Even though the run is a single run, the processes distinguishing movement in the root zone from that in the unsaturated zone, remain separated.

PRZM is a one-dimensional model that accounts for pesticide and nitrogen fate in the crop root zone. PRZM-3 includes modelling capabilities for phenomena such as soil temperature simulation, volatilisation and vapour phase transport in soils, irrigation simulation, and microbial transformation. PRZM is capable of simulating transport and transformation of the parent active ingredient and up to two metabolites. VADOFT simulates flow in the unsaturated zone.

Strengths of PRZM

In order to perform probability-based exposure assessments, the PRZM and VADOFT

codes are linked through an execution supervisor that allows for site-specific situations. The linkage of the two models makes PRZM 3 a powerful model for use in predicting pesticide fate. The version acquired for use in this project is version 3.1. The model is still DOS based, as the development of the Windows version, at the time of the study, was not yet complete. The model runs through an execution, which is edited using a DOS editor.

Weaknesses of PRZM

A major problem with the model was that in the manner it is set up, it could only be run for cropped fields. The model uses outputs from the root zone as inputs for the unsaturated zone modelling (VADOFT). An attempt was made to run PRZM 3 by entering zero values for the plant related parameters, but this failed. The model simply ends the run stating that errors had occurred. Thus this model could not be used for the evaluations as planned.

The models selected for further evaluation were therefore VARLEACH, PELMO and PESTAN.

CHAPTER 3.

HERBICIDE PHYTOTOXICITY ON NON-TARGET PLANTS DUE TO HERBICIDE MOBILITY.

3.1 Introduction

Chapter 1 of this thesis referred to many South African soils being characterised by low organic carbon content (below 1 %), and thus expectedly low microbial activity (Chapter 1). These factors are believed to contribute to increased ease of pesticide migration and prolonged pesticide soil persistence. The assessment of the case studies that follow showed that where high dosage rates of persistent pesticides are applied, a high potential might exist for severe impacts on human and environmental health (Chapter 1). The case studies confirm this, at least for herbicides and non-target plants.

The control of annual and perennial weeds under industrial conditions is conducted primarily by the application of soil applied pre-emergence herbicides. Industrial weed control includes the control of weedy invaders in security areas, rights-of-way, under and over utility supply areas etc. The efficacy of this application is determined by the application rate, the rate of degradation and the extent of movement of these active ingredients once delivered to soils (Bingeman *et al.*, 1962). The herbicides used in industrial weed control are generally applied at high dosage rates and are mostly designed to resist environmental degradation. The degradation of these herbicides relies on the presence of soil microbes in the soil system to which they are applied (Weber and Whitare, 1982). The detection of atrazine in groundwater during the late 1980s was the first South African evidence of pesticides reaching groundwater. These findings led to the identification of the industrial application of atrazine as being a point source for groundwater contamination. Subsequently, this had led to the banning of industrial applications of atrazine in South Africa in 1990 (Vermeulen *et al.*, 1998).

If the soil has as a rule, low microbial activity, it follows that reduced degradation will occur. Soil microbial activity is measured and expressed as soil respiration per unit time. The average microbial activity for European forest soils is 1.02 g CO_2 $m^{-2}H$. On Sub-Saharan soils respiration rates of approximately 0.5 g CO_2 m^{-2} H and lower have been measured (Grimsby, 2005). A soil respiration rate of 1.02 g CO_2 m^{-2} H is viewed as average, and therefore microbial activity ranging from 0 to 0.5 g CO_2 m^{-2} H may be viewed as low. By inference the sub-Saharan soils are low in microbial activity.

There have been numerous unpublished reports on alleged herbicide damage to non-target crops and natural vegetation, after their application to road verges, under power lines, within rights-of-way, etc (Khelalwanlall, Technical Advisor to the Registrar Act 36 of 1947, personal communication). Often the applications cause growers great financial losses. These incidences are usually investigated as a result of lawsuits made by the affected growers. The ultimate objective of such investigations would be to provide evidence to prove or dismiss allegations of damage, and where relevant, determine the extent of the damage caused.

Four such incidences of alleged herbicide damage, led to investigations to determine the cause and extent of damage allegedly caused by the application of industrial herbicides. During these investigations, the four study sites were monitored after the development of non-target phytotoxicity. The herbicides implicated were representative of the substituted ureas, uracils and triazines.

The herbicides were all applied over a number of years, for purposes of industrial weed control, prior to visual and tangible damage developing. The four case studies selected all involved the application of herbicides for the industrial control of weeds. In all four cases, the patterns of damage found were typical of soil applied herbicides as described by Skrotch and Sheets (1979).

Because the areas of damaged vegetation were all somewhat removed from the areas of herbicide application, the cases provided an indication that the herbicides may move readily in the soil. The data collected during the original investigations were re-evaluated in order to determine whether they would provide data and information as to whether South African soil conditions are such that pesticides may pose an enhanced risk with regard to human and environmental health.

The main objectives of this chapter were to:

1. To evaluate collected data on mobility of selected herbicides from case studies.
2. To determine the potential impacts of the herbicides on South African soils.
3. To assess the need for migration evaluations based on results from case studies.

3.2 Materials and methods

Soil typing analyses indicated that all the soils under investigation contained kaolinitic clay. In the studies, detailed soil characteristics were not determined, and soils data from generalised analyses for the areas were used (Land Type Survey Staff, 1997).

The herbicides under investigation were all photosynthetic inhibitor herbicides. These herbicides give rise to chlorosis of leaf tissues, progressing to necrosis and eventually leading to plant death. In the case of trees being damaged, the symptoms may initially only be observed on one half of the tree nearest the applied zone (Skroch and Sheets, 1979). The herbicides that were of particular interest in the investigations were the substituted ureas tebuthiuron, ethidimuron and diuron, the uracil bromacil as well as the triazine, simazine.

3.2.1 Case study 1 - Limpopo River Valley.

The site is located in the Limpopo River Valley, Limpopo Province, RSA, between the Nwadedzi and Njelele rivers (22°19 S 30°28 E). Soil analyses showed that the soil is a sandy loam soil, containing 17 % kaolinitic clay. The soil of the area is described as soils with minimal development, usually shallow on hard weathering rock, with or without intermittent diverse soils. The soils are characterised as having a high base status and lime is generally present (Land Type Survey Staff, 1997).

During the late 1970's a sisal barrier hedge was erected parallel to the Limpopo River, in the area east of Messina in the Limpopo River Valley in the Limpopo Province, for border control. The hedge was constructed between a strip of cultivated fields and the Limpopo River riparian zone at distances of 10 to 50 m from the river bank. As part of hedge maintenance, residual herbicides were applied, between the sisal plants and fences on either side of the hedge for the control of invasive plants. The residence time, soil infiltration, migration and off-target movement of the herbicide's active ingredient, tebuthiuron, were investigated, which was applied at a dosage rate of 4000 - 6400 g ha^{-1} (active ingredient), annually for nine years.

Deterioration of the riparian vegetation between the applied zone and the river was first reported six years after the initial tebuthiuron applications. The damage observed was chlorosis and necrosis of leaf tissues on trees and scrubs, typically associated with photosynthetic inhibitor herbicides, leading to massive die-back of branches and plants as a whole (Beste,1983).

A monitoring programme was initiated in the area, through which soil was sampled and analysed for tebuthiuron residues to establish the possible movement of the applied herbicide. Samples were collected on a transect running from cultivated fields through the applied area and riparian zone and ending in the riverbed. Figure 3.1 illustrates the

relative location of 3 of the sampling points. Sampling points were located in the applied zone, 3 m out of the applied zone, between the riparian zone and the applied zone, and 10 m from the applied zone, within the damaged riparian vegetation. At each sampling point, the 0 – 300-mm and 301- 600-mm soil horizons were sampled separately. These samples were also analysed separately. Sampling and analyses were conducted in 1994, one year after the last application of tebuthiuron in the area.

3.2.2 Case study 2 – Nelspruit

The second case study was investigated at a site in Mpumalanga Province, near Nelspruit (25°27 S 30°57 E), on soils described as red, sandy, well-drained soils with low to medium base status (Land Type Survey Staff, 1997). Soil analyses showed that the soil is a sandy clay loam soil, containing 35 % kaolinitic clay.

Herbicides were applied to the soil around a utility installation adjacent to a fruit orchard. Herbicides containing the active ingredient ethidimuron were initially applied for six years, and then substituted with tebuthiuron containing herbicides for a further eight years. Damage to trees in the rows nearest to the site of application developed eight years after the ethidimuron applications were stopped. In order to establish whether the herbicides caused the observed damage, samples from four sampling points were collected in September 1994, on a transect starting in the applied zone and at 5, 8.5 and 12.5 m from this zone, into the orchard. Figure 3.2 illustrates the relative locations of these sampling points. At each of these points, the 0 - 300, 301 - 600 and 601 - 900 mm soil horizons were sampled. The samples were analysed individually for the presence of tebuthiuron and ethidimuron residues.

3.2.3 Case study 3 - Hluhluwe.

The third case study investigated is located at a site outside Hluhluwe (28°01 S 32°16 E), KwaZulu-Natal, on yellow sandy soils, which are well drained and have a high base status (Land Type Survey Staff, 1997). Soil analyses showed that the soil is a sandy loam soil, containing 15 % kaolinitic clay

The application of bromacil- and diuron-based granular herbicides was the preferred practice for the control of invasive vegetation, on linear transport infrastructure in the Hluhluwe area, KwaZulu Natal, for an unknown number of years. Approximately 6 years after the initial application of this herbicide, damage to eucalyptus forests, 20 km south of Hluhluwe, adjacent to the treated areas, was reported. In order to establish whether herbicide had caused the observed damage, soil was sampled and analysed for the presence of bromacil in 1996. Bromacil was chosen as a surrogate for the presence of the herbicide mixture. At this site, four sampling points were identified on a transect running from the applied zone (transport line), through the damaged forest, and into an undamaged section of the forest (Figure 3.3). The 0 - 450-mm soil horizon and 451 - 900 mm horizon were sampled separately, in accordance with client requirements.

3.2.4 Case study 4 - Pretoria

The fourth case study was investigated at a site located in Pretoria (25°46 S 28°15 E), on a soil with plinthic catena red soils with low base status. These soils are characterised as being vesicular with iron and manganese oxide accumulates (Land Type Survey Staff, 1997). Soil analyses showed that the soil is a loamy sand soil, containing 17 % kaolinitic clay.

This site is a perimeter security fence, located in the eastern part of Pretoria. Herbicides were applied to a perimeter security fence over an eight-year period. Off-target damages

to garden plants in adjacent gardens were reported approximately eight years after the initial herbicide applications. The herbicides applied contained the active ingredients diuron, bromacil and tebuthiuron. Two years before the onset of off-target damage, these herbicides were substituted with glyphosate and simazine containing herbicides. It was believed that simazine was the causal agent of non-target damage. Soil samples were collected in 1997, from the applied zones as well as from areas where trees were observed with phytotoxic symptoms, or where plant deaths were evident. Soil was analysed for residues of tebuthiuron, bromacil, diuron and simazine. Figure 3.4 illustrates the relative locations of three sampling points. The 0 - 450 mm and the 451 - 900 mm soil horizons were sampled. Only the samples taken in the 451 - 900 mm soil layer of the damaged zone were analysed, as the area had been land filled prior to sampling.

3.2.5 Analytical techniques

Herbicides were extracted and analysed using modified analytical methods incorporating solvent extraction and gas-chromatographic analyses (Fillion *et al.*, 1995; Jarczyk, 1979; Loh *et al.*, 1980).

Analyses were based on duplicate sample extractions and triplicate analyses per sample. All residue results provided are expressed on a soil dry mass basis.

3.3 Results

3.3.1 Case study 1 - Limpopo River Valley.

Results of analyses of the soil samples collected in the Limpopo river valley site showed that tebuthiuron was present in all the soil samples collected (Figure 3.1). The levels ranged between 1 and 54 $\mu g\ kg^{-1}$ soil. The active ingredient was present in the applied zone at levels up to 44 $\mu g\ kg^{-1}$ in the 0 – 300-mm horizon and 54 $\mu g\ kg^{-1}$ in the 301 - 600-mm horizon.

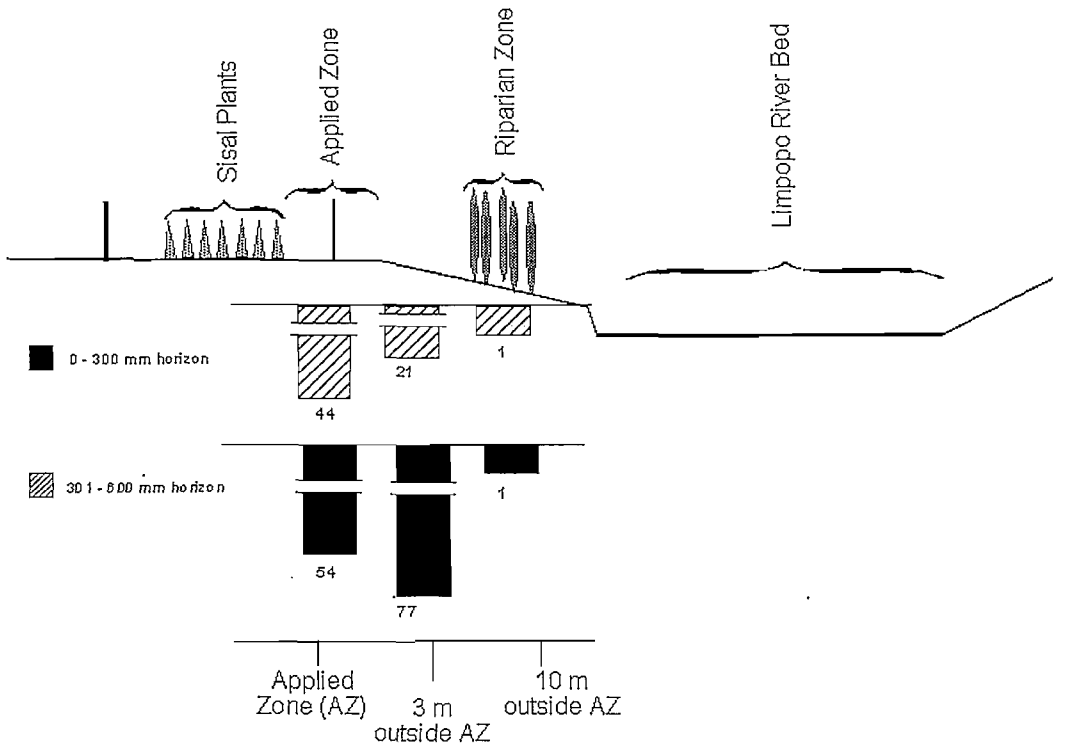


Figure 3.1. Graphic representation of tebuthiuron residue levels (μg kg^{-1}) detected in two soil horizon samples from the Limpopo River Valley (AZ – applied zone)

Tebuthiuron was also detected in both soil horizons sampled, 3 m outside the applied zone (Figure 3.1). At this point, the tebuthiuron was present at 21 and 77 μg kg^{-1}, in the 0 – 300 and 301 – 600 mm horizons, respectively. Analyses also showed the presence of tebuthiuron among damaged riparian vegetation, 10 m from the applied zone. Here the levels were low, present at 1 μg kg^{-1} in both the horizons sampled.

This data indicates that tebuthiuron had moved downwards at least 600 mm into the soil, and also that a high degree of movement out of the applied zone occurred. The generally high tebuthiuron levels in the bottom 301 – 600 mm horizon indicated that both downward movement into the soil as well as vertical movement had occurred. The presence of tebuthiuron in the riparian zone indicated that the damage observed was most likely due to the tebuthiuron, which had moved out of the applied zone, probably both from migration and surface run-off.

Also indicative that the damage was caused by herbicides, was that the riparian vegetation in the Zimbabwean riparian zone, where there was no herbicide applications, was undamaged. The soil has low clay and organic content (8 – 15 % kaolinitic clay; 0.3 – 0.7 % organic matter) and a high base status (Land Type Survey Staff, 1997). The soil thus has a high base saturation, indicating that most of the exchangeable negative charges are saturated. Introduction of a cationic organic active ingredient such as tebuthiuron into the system is therefore expected to result in little of the active ingredient being bound by clay and organic matter and should therefore be able to move in the soil with relative ease.

3.3.2 Case study 2 - Nelspruit.

Analyses showed that tebuthiuron residues were only present in two of the samples collected in the applied zone (Figure 3.2), and not in the damaged zone. Ethidimuron on the other hand, was present in the applied zone as well as in all the samples collected within the damaged zone. The levels detected ranged between 40 and 900 $\mu g\ kg^{-1}$ in the damaged zone, and between 700 and 4200 $\mu g\ kg^{-1}$ in the applied zone. The highest ethidimuron levels were detected in the upper 0 – 300-mm horizon sampled in the applied zone. Similar results were obtained within the damaged zone, 5 and 12.5 m from the applied zone. Only a small portion of the ethidimuron moved downward and there seemed to have been substantial horizontal movement of the active ingredient, probably through surface flow.

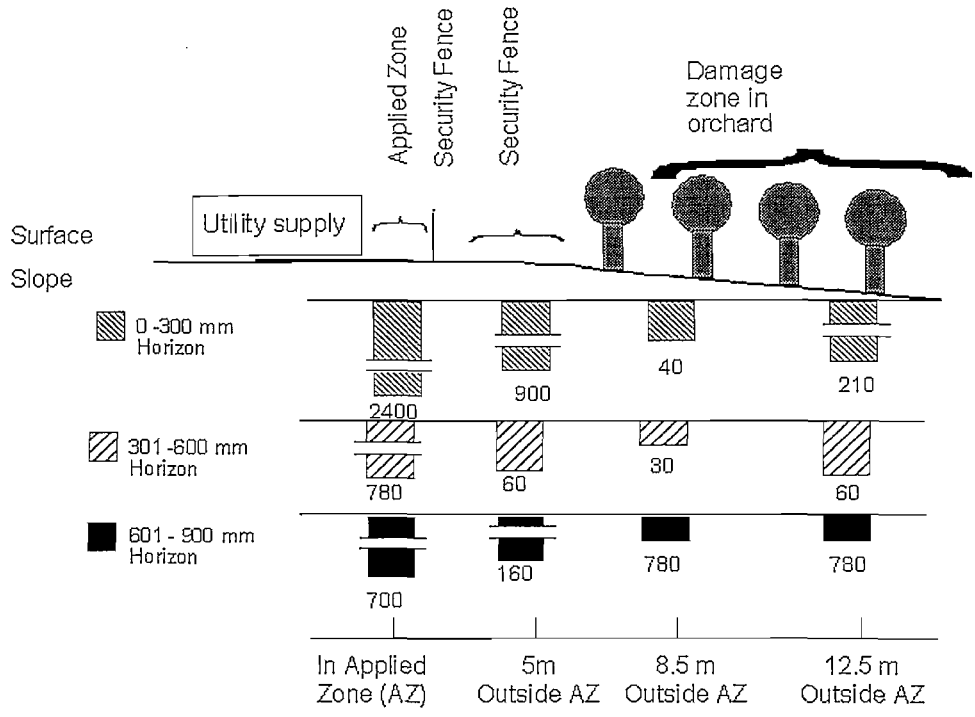


Figure 3.2. Graphic representation of ethidimuron residue levels (μg kg^{-1}) detected in Nelspruit soils sampled. (AZ – applied zone)

When comparing the residue levels in the application zones of the Limpopo and Nelspruit sites, residue levels in the upper soil horizon at Nelspruit were high. This may be explained by higher clay content (35 % clay soil) in the Nelspruit area, where soils characteristically have clay contents ranging between 25 and 66 % (Land Type Survey Staff, 1997). The soils are also characterised as having a low to medium base status, which means that the soils are relatively unsaturated. Thus the Nelspruit soils can be expected to have a higher capacity for binding herbicide. Herbicide movement through the soil is therefore expected to be slow via chromatographic movement with water as the mobile phase. It must also be considered that the sampling and analyses were done eight years after the final ethidimuron application. Even after such a prolonged period, high levels were present in the applied zone. This indicates that prolonged persistence of these active ingredients may be expected in the Nelspruit soils.

3.3.3 Case study 3 - Hluhluwe.

Results showed the presence of bromacil residues in the samples from the applied zone as well as the damaged zone (Figure 3.3). The bromacil levels in the applied zone ranged between 0.329 and 8.095 μg kg^{-1} soil, whereas those in the damaged zone ranged between 0.006 and 0.009 μg kg^{-1} (Figure 3.3).

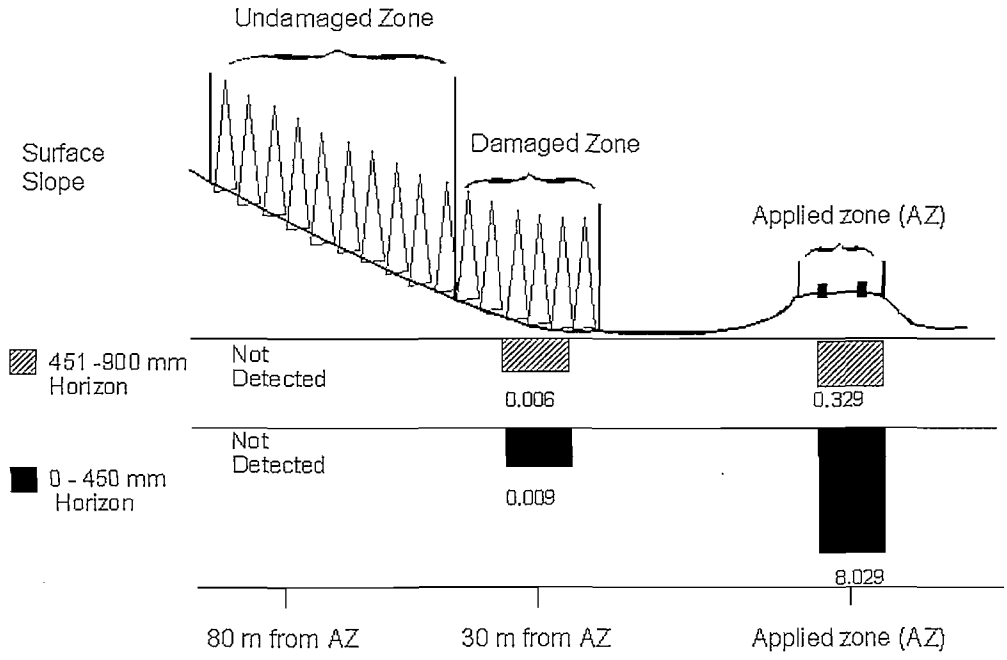


Figure 3.3. Graphic representation of bromacil residue levels (μg kg^{-1}) detected in Hluhluwe soils sampled.

Herbicide residues could not be detected in the samples from the undamaged zone. At both the sampling sites, where herbicide residues were detected, the bottom 450 – 900 mm horizon contained the highest residues. The results thus indicate that the active ingredient had moved downward into the soil profile.

This downward movement was not unexpected, as the soils are well drained. In addition, the soils are expected to be saturated, thus little binding of the active ingredient is

expected and the potential for movement is good. The presence of bromacil residues in the damaged zone indicated that the damage observed was likely due to the presence of the herbicide. As with the Limpopo soils, downward movement seems apparent as well as horizontal movement. Horizontal movement likely primarily due to surface run-off, but horizontal chromatographic flow cannot be excluded.

3.3.4 Case study 4 - Pretoria

Diuron, bromacil, simazine and tebuthiuron were present in the applied zones (Figure 3.4). Only simazine and tebuthiuron were detected in the damaged zone. Within the applied zone, the upper 0 – 450 mm soil horizon contained higher herbicide residues than the lower 451 – 900 mm horizon.

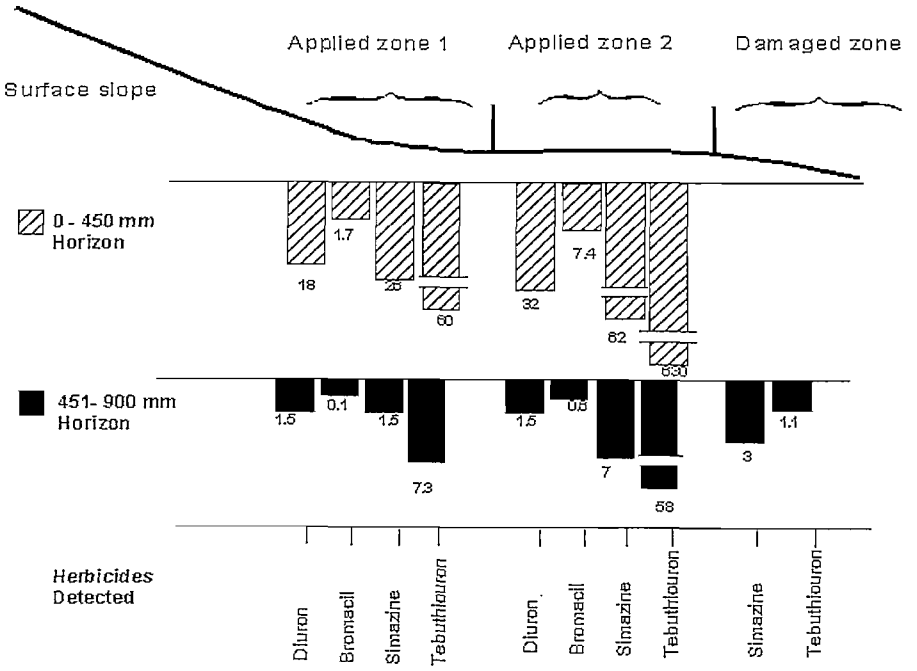


Figure 3.4. Graphic representation of herbicide residue levels (µg kg^{-1}) detected in Pretoria soils.

The presence of tebuthiuron, diuron and bromacil at relatively high levels in the applied zones indicated prolonged persistence of these active ingredients, especially when taking into account that they were last applied at least three years before sampling. The presence of tebuthiuron and simazine in the damaged zone indicated that these two active ingredients could have been the cause of damage.

3.4 Discussion

The removal of most modern pesticides from soil is primarily via microbial degradation (Larson and Cowan, 1995). Similarly, the herbicides that were investigated also depend primarily upon microbial degradation as their main path of degradation (Ahrens *et al.*, 1994). Studies have shown that the half-lives of the substituted ureas, uracils and triazine herbicides in soil vary from five to fifteen months in high rainfall areas (Beste,1983; Tomlin, 1994). It is further known that the half-lives may increase considerably in low rainfall areas (Tomlin, 1994). General trends of low annual rainfall, high temperatures and low organic carbon content are expected to lead to low microbial activity within local soils (Killham, 1995). This may increase herbicidal half-lives. It therefore seems obvious that low microbial activity in soils will lead to an increase in the half-lives of herbicides, which rely on microbial degradation or organic matter.

The fate of pesticides in soil is determined by the extent of adsorption to and desorption from soil colloids. A strong positive association has been shown between herbicide activity and organic matter content (Bollag *et al.*, 1992; Carringer *et al.*, 1975; James and Lauren, 1995; Khan, 1980; Weber *et al.*, 2004). The organic matter has been shown to be the principal sorbent for organic active ingredients (Koskinen *et al.*, 1996). The only fraction of applied herbicide, which is available for plant uptake, is the non-bound, bio-available fraction. It thus follows that low organic matter content of soils will contribute significantly towards enhanced migration rates, when compared with soils with higher organic content.

As the soils in the areas of the case studies, are generally low in organic carbon (Land Type Survey Staff, 1997), high migration rates of applied pesticides may be expected. Organic matter is, however, not the only contributing factor. At all the sites investigated, a surface slope (15° – 30°) was present from the applied zone to the damaged zone. The movement of free water across the surface of the soil, and through the soil profile is believed to have moved the unbound herbicides out of the applied zones to areas where damage occurred. Similar behaviour has previously been found (Hubbs and Lavy, 1990; Spencer and Cliath, 1973).

The investigations also showed that in such situations, movement following chromatographic flow might be of great importance. In addition, the herbicides were applied in a linear manner at all the sites. Greater ease of migration could lead to the contamination of ground and surface water sources, as has been found with triazines in South Africa and other countries, such as has been shown in Tasmania, Australia (Davies *et al.*, 1994).

The case studies were conducted to establish cause of damage to vegetation, be it natural or cropped. In these studies the sampling and analyses for herbicide residues were limited to 900mm soil depth. These case studies thus do not provide an indication of the threat to ground water sources, but provides information on the mobility of the herbicides. The data from the case studies show that the herbicides that were applied are persistent and mobile under the conditions they were applied.

At all the sites investigated, the damage observed was prominent on tree species, even though herbicide soil concentrations were relatively low. Because of the extensive root systems of trees (Palgrave, 1994), trees are exposed to a large reservoir of bio-available herbicide residues, even though the concentration may be low. In addition, trees take up and transport large volumes of water per unit time and therefore the herbicide concentration in the tree may increase rapidly over time (Nieuwoudt, 1986). This type of

damage to non-target trees is not unique to South Africa, and has also been described by Allender (1991), where the application of the herbicide bromacil and hexazinone in a non-crop situation led to deaths of surrounding native trees.

The application rate for most soil applied herbicides ranges between 3000 g ha^{-1} to 6500 g ha^{-1} or 300 mg m^{-2} to 650 mg m^{-2}. This amount is roughly 0.65 mg dm^{-3}, or 0.65 mg kg^{-1} (650 μg kg^{-1}) soil depending on the density of the soil. At this concentration, death of sensitive plants may be expected. The concentration detected in the soil where case studies were conducted was 10 to 10 000 fold lower than these levels.

The presence of the herbicides in the areas where damage was observed had been established in all four case studies. The symptomology for the herbicides also could be related to with those observed on damaged vegetation. In the case studies the herbicide were applied at high dosage rates for total weed control in security areas and under fences. This type of application is known as industrial weed control. The case studies therefore indicate that industrial weed control actions could lead to the herbicide movement out of the areas of application. In addition the case studies indicate that the herbicides may also cause damage to sensitive vegetation. The concentrations of herbicides detected in some instances were as much as 10 000 fold lower than those expected to be effective after application. In order to determine the lowest levels at which industrial herbicides may damage sensitive vegetation, it was however necessary to conduct glass-house phytotoxicity trials. It is this subject that is dealt with in Chapter 4.

CHAPTER 4.

EFFECTS OF SELECTED HERBICIDES ON GROWTH OF TOMATO (*LYCOPERSICON ESCULENTUM*)

4.1 Introduction

It is evident from Chapter 3 that industrial weed control actions could lead to herbicide migration out of the areas where they were applied to other potentially sensitive areas. Furthermore, indications are that the mobility of these herbicides could lead to damage of susceptible vegetation, including crops in close proximity to the applied areas. These effects are likely to occur at extremely low soil concentrations (up to 10 000 fold of applied rate) (Chapter 3). The active ingredients could also end up in ground water at diluted residue levels.

The biological significance of low residue levels of herbicides in soil is virtually unknown. It is the aim of this Chapter to determine the potential phytotoxicity of the primary herbicides investigated and reported on in Chapter 3. To this end, the effects of ethidimuron, tebuthiuron and bromacil on tomatoes were investigated under controlled environmental conditions at the concentrations found in the case studies described in Chapter 3. The study was undertaken in order to establish differential effects of these active ingredients on tomato seedlings, should they exist.

The main objectives of the study were:

1. To determine the extent of phytotoxicity, if any, of sub-lethal concentrations of selected soil applied herbicides.

4.2 Materials and methods

4.2.1 Test system

The test system consisted of six-weeks old tomato seedlings of the cultivar Hygrotech HTX 14. The cultivar is an indeterminate growing field tomato. The seedlings were cultivated from seed in 300 plug seedling trays using a Hygrotech seedling mixture. Seedlings were cultivated under controlled environmental conditions in the seedling trays, for a period of six weeks after emergence.

Six-week old seedlings were transferred into sterilised silica sand rooting medium contained in 2 litre plastic pots. The planting system used was a closed system with the soil being irrigated with nutrient rich water to 60 % of field capacity by mass. Irrigation was performed using a custom-made balance watering system.

4.2.2 Test items

The herbicides used in the trials were commercial formulated material of:

- Bromacil (as the 80% wettable powder, formulated product Hyvar X®, Agricura)
- Ethidimuron (as the 70% wettable powder formulated product Ustilan 70WP®, Bayer)
- Tebuthiuron (as the 80% wettable powder formulated product Spike 80WP®, Dow Life Sciences)

The active ingredients used are primarily soil-applied herbicides that are used in pastures, natural veld and in non-crop situations such as industrial sites. The active ingredients control broad-leaved species and woody species at low application rates. They will also control grasses and brush species (total weed control), at higher dosage rates. The active ingredients are photosynthetic inhibitors that block electron transport. The end result of the action of the herbicide is the loss of the pigments chlorophyll and carotenoids and leakage of lipid membranes.

4.2.3 Herbicide Treatments

Herbicide solutions were made up using ultra pure water as carrier. Herbicide solutions were then poured into separate plastics bags each containing 2 kg of the sterilised silica sand-rooting medium. The rooting medium and herbicide were then added to the soil, mixed using a mechanical shaker for 3 hours, and placed into pots. One bag of treated rooting medium was placed into one pot. Each treatment consisted of 5 replicate pots.

The herbicide treatments used were (μg kg^{-1} herbicide active ingredient):

- control (no herbicide)
- 1
- 5
- 10
- 20
- 40
- 80
- 160
- 320
- 640
- 1280

Plants were grown in the treatment mixture for a three-week trial period. A fully randomised experimental design was used in which the plants were randomly placed on tables in the glass-house. Plant positions were changed every two days to ensure that potential varying light effects in the glass-house were eliminated. Fertilisation was provided using a Chemicult hydroponics fertigation solution at the label-recommended dosage and application rates, ensuring that no deficiencies develop. Plants were grown under controlled environmental conditions of 15°C night temperature, 25°C day temperature and 30% relative humidity.

4.2.4 Visual phytotoxicity evaluations

The seedlings were evaluated daily for symptom development over the three-week trial period. The plants were evaluated according to typical photosynthetic inhibitor herbicide symptoms, a discussion of which follows.

Symptom development for the ureas and uracils is similar. The most common symptoms are foliar chlorosis and necrosis as well as reduced growth (stunting). Foliar chlorosis is generally concentrated around the veins but sometimes extends to interveinal regions (Figure 4.1.).

Figure 4.1. Leaf veinal chlorosis caused by application of the uracil herbicide, bromacil.

Chlorosis is followed by necrosis of the affected areas and death of plant tissues and organs (Ahrens *et al.*, 1994; Gage and Munro, 1987) (Figure 4.2).

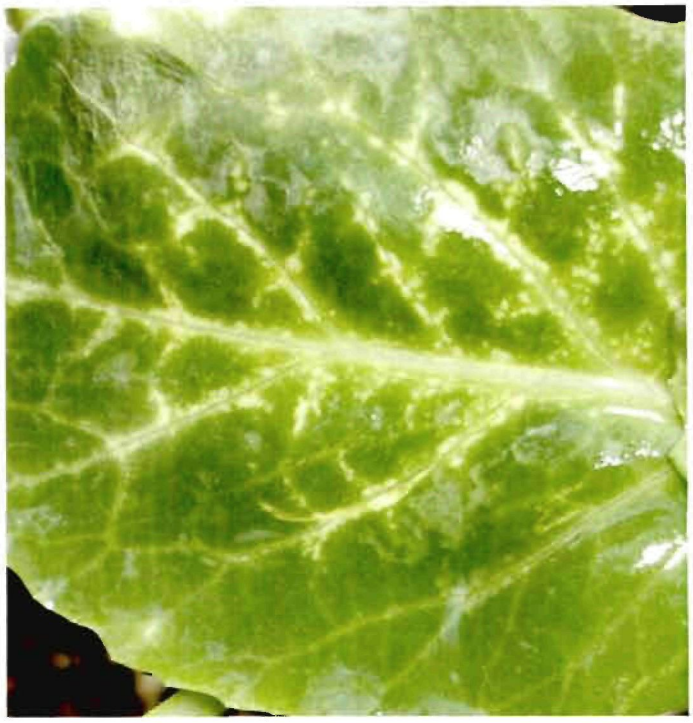


Figure 4.2. Leaf veinal necrosis caused the by application of bromacil.

At relatively low doses, veinal chlorosis is found which becomes more extensive with time and increased concentration (Eagle and Caverly, 1981). As the concentration is increased, chlorosis is followed by necrosis, the severity of which increases over time, leading to eventual plant death (Skroch and Sheets, 1979) (Figure 4.3). Where concentration levels are extreme (10 – 100 μg kg^{-1}), the transition from chlorosis to necrosis occurs over a short period of hours rather than days after application.

5 µg kg^{-1} bromacil in sand > 10 µg kg^{-1} bromacil in sand > 1 µg kg^{-1} bromacil in sand

Figure 4.3. Increase in symptom severity caused by the application of increasing concentrations of bromacil.

4.2.5 Dry mass determinations

Plant dry mass was determined at the end of the three-week exposure period. Plants were harvested and the roots and shoots separated. Plants were placed into paper bags and dried at 84°C for 48 hours. After the drying period, plant roots and shoots were separately weighed.

4.3 Results

4.3.1 Bromacil

Symptom development

The visual phytotoxic effects of the bromacil treatments found are summarised in Table 4.1.

No visual damage symptoms were observed on control treatments. The degree of damage as was assessed by observation, increased with the concentration applied. Severe symptoms developed four to six days after treatment at 20 - 1280 µg kg^{-1} bromacil. Severe symptoms developed 10 – 14 days after treatment at 10 µg kg^{-1}.

Symptoms include severe chlorosis leading to necrosis of leaves and ending up in total death of tissue areas, or the whole plant.

Veinal and marginal chlorosis developed 14 days after treatment at 5 μg kg^{-1}.

Table 4.1. Symptom development as observed on tomato seedlings treated with bromacil.

Treatment concentration	Time	Symptoms observed
20 – 1280 μg kg	3-4 days	Initial venial chlorosis and chlorosis of leaf edges.
	6 days	Severe chlorosis leading to necrosis of entire leaf surface
10 μg kg^{-1}	6 days	Initial veinal chlorosis and chlorotic leaf edges.
	10-14 days	Severe chlorosis leading to necrosis of entire leaf surface
5 μg kg^{-1}	14 days	Veinal chlorosis and chlorosis of leaf edges
1 μg kg^{-1}	21 days	No visual symptoms
Control (no herbicide)	1 –21 days	No phytotoxicity observed

Dry mass

Results of dry mass determinations are given in Figure 4.4. Results indicate that the bromacil treatments had a similar effect on both root and shoot dry mass. However, the 5 μg kg^{-1} treatment caused a significant decrease in dry mass of shoots, whereas the 10 μg kg^{-1} treatment was required for a similar effect on the roots of tomato seedlings. Significant differences due to treatments were determined by Anova and Dunnett's T test at 5% significance level on mass data.

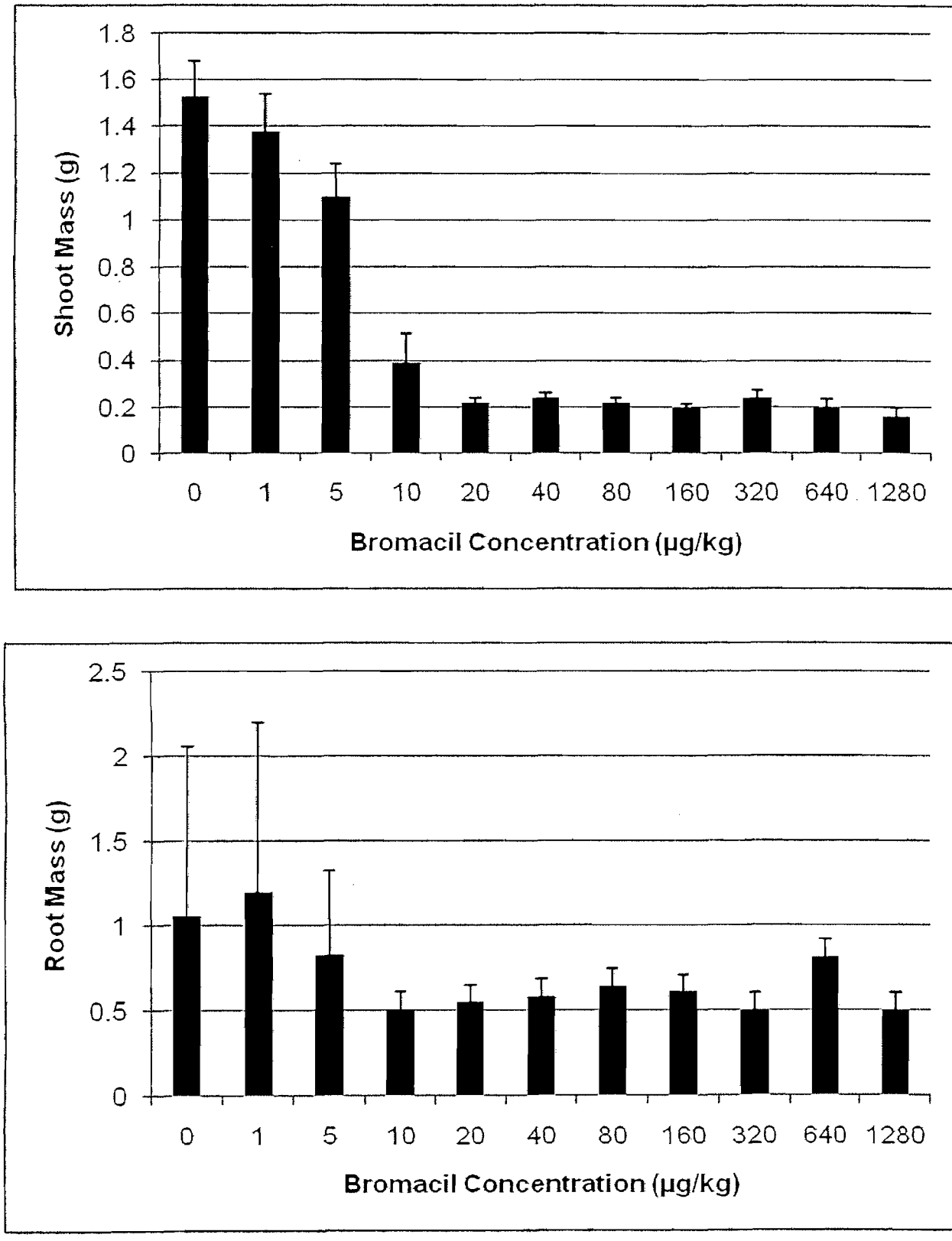


Figure 4.4. Results of dry mass determinations of roots and shoots of tomato seedlings treated with the herbicide bromacil (lines on bars indicate standard deviation).

A significant halving of the dry mass of both shoots and roots was found with the 10 µg kg^{-1} bromacil treatment. No significant difference in root dry mass was found when comparing the effects on root dry mass of the 10 to 1280 µg kg^{-1} bromacil treatments.

4.3.2 Tebuthiuron

Symptom development

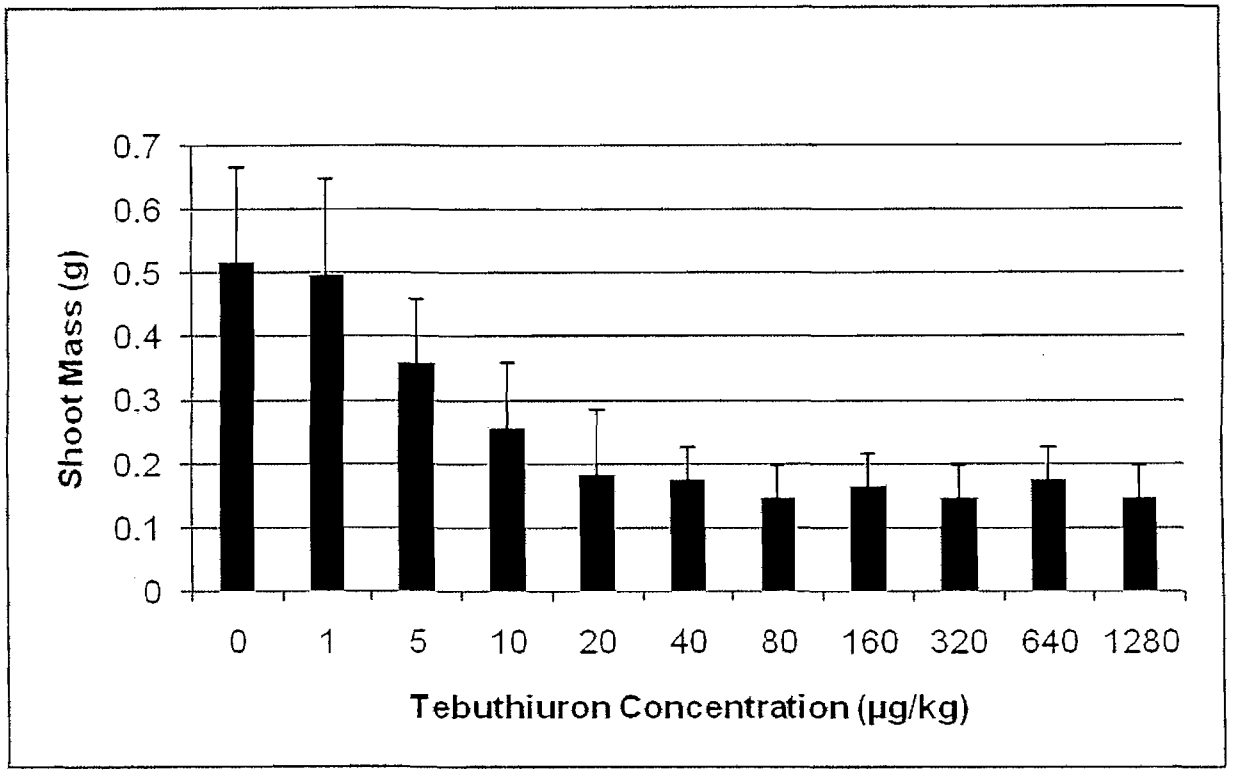
The visual phytotoxic effects of the tebuthiuron treatments are summarised in Table 4.2. No symptom development was observed on the control treatment. The degree of damage as assessed purely by observation, increased with the concentration applied. Initial veinal chlorosis developed four days after treatment at 20 to 1280 µg kg^{-1} tebuthiuron. This tendency was also observed over time, i.e. the degree of damage increased over time to the extent where these symptoms became very clear on plants treated with 10 µg kg^{-1} tebuthiuron seven days after treatment. In addition, plants treated with 80 to 1280 µg kg^{-1} tebuthiuron started dying seven days after treatment. Death of all plants treated with 40 to 1280 µg kg^{-1} tebuthiuron was found 11 days after treatment.

Table 4.2. Symptom development as observed on Tomato seedlings treated with tebuthiuron.

Treatment concentration	Time	Symptoms observed
20 – 1280 µg kg^{-1}	4 days 7 days	Initial venial and interveinal chlorosis and chlorosis on leaf edges. Severe chlorosis leading to necrosis of entire leaf surface
10 µg kg^{-1}	6 days 10-14 days	Initial veinal and interveinal chlorosis and chlorosis on leaf edges. Severe chlorosis leading to necrosis of entire leaf surface
5 µg kg^{-1}	14 days	Veinal chlorosis and chlorotic leaf edges
1 µg kg^{-1}	21 days	No visual symptoms
Control (no herbicide)	1-21 days	No phytotoxicity observed

Dry Mass

Results of dry mass determinations are given in Figure 4.5. Results indicate that the lowest concentration of tebuthiuron used, that caused a significant decrease ($p<0.05$) in dry mass, was 5 µg kg^{-1} for shoots and 10 µg kg^{-1} for roots. A significant halving of dry mass was found with the 10 µg kg^{-1} application of tebuthiuron for both shoots and roots. All other tebuthiuron concentrations applied (20 to 1280 µg kg^{-1}) had a similar or more severe effect on the dry mass of the tomato seedlings, than that caused by the 10 µg kg^{-1} treatment. The plants treated at this concentration range had no living plant tissue at the time of harvest.



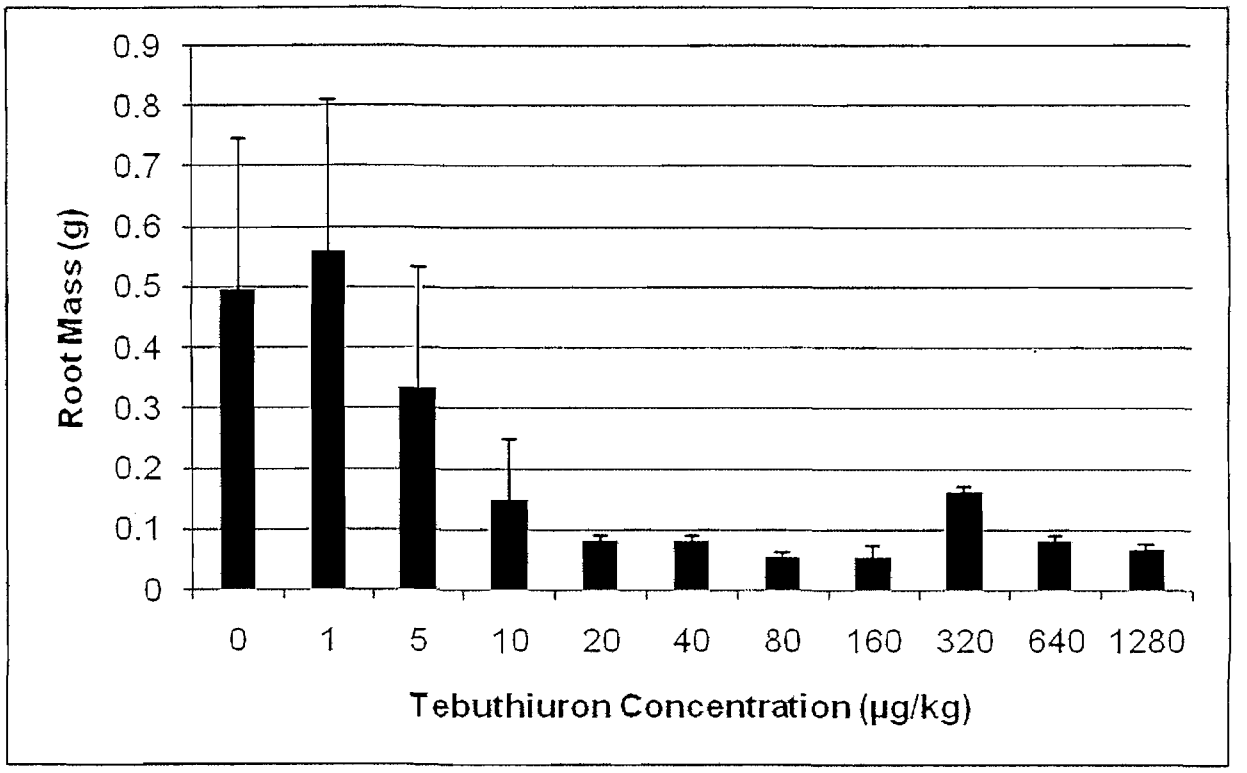


Figure 4.5. Results of dry mass determinations on roots and shoots of tomato seedlings treated with the herbicide tebuthiuron (lines on bars indicate standard deviation).

4.3.3 Ethidimuron

Symptom development

The visual phytotoxic effects of the ethidimuron treatments are summarised in Table 4.3. No symptom development was observed on control treatments or 1 to 10 µg kg^{-1} ethidimuron treatments four days after treatment. However, plants treated with 40 to 1280 µg kg^{-1} ethidimuron showed typical photosynthetic herbicide damage four days after treatment. These included chlorosis and necrosis of leaves and tissue areas. The observed degree and extent of necrosis was higher than that of the tebuthiuron treatments.

As with the tebuthiuron treatments, the degree of symptom development also increased with increased concentration. The degree of damage increased to the extent where the symptoms developed on plants treated with 10 µg kg^{-1} seven days after treatment. In addition, plants treated with 80 to 1280 µg kg^{-1} died seven days after treatment.

Table 4.3. Symptom development as observed on Tomato seedlings treated with ethidimuron.

Treatment concentration	Time	Symptoms observed
40 – 1280 µg kg^{-1}	4 days	Initial venial and interveinal chlorosis as well as chlorosis leaf edges.
	6 days	Severe chlorosis leading to necrosis of entire leaf surface
10 µg kg^{-1}	6 days	Initial veinal chlorosis and chlorosis on leaf edges.
	10-14 days	Severe chlorosis leading to necrosis of entire leaf surface
5 µg kg^{-1}	14 days	Veinal chlorosis and chlorotic leaf edges
1 µg kg^{-1}	21 days	No visual symptoms
Control (no herbicide)	1-21 days	No phytotoxicity observed

Dry Mass

Results of dry mass determinations are given in Figure 4.6. Results indicate a significant decrease in dry mass of shoots with the application of 5 μg kg^{-1} and of roots with the 10 μg kg^{-1} treatment.

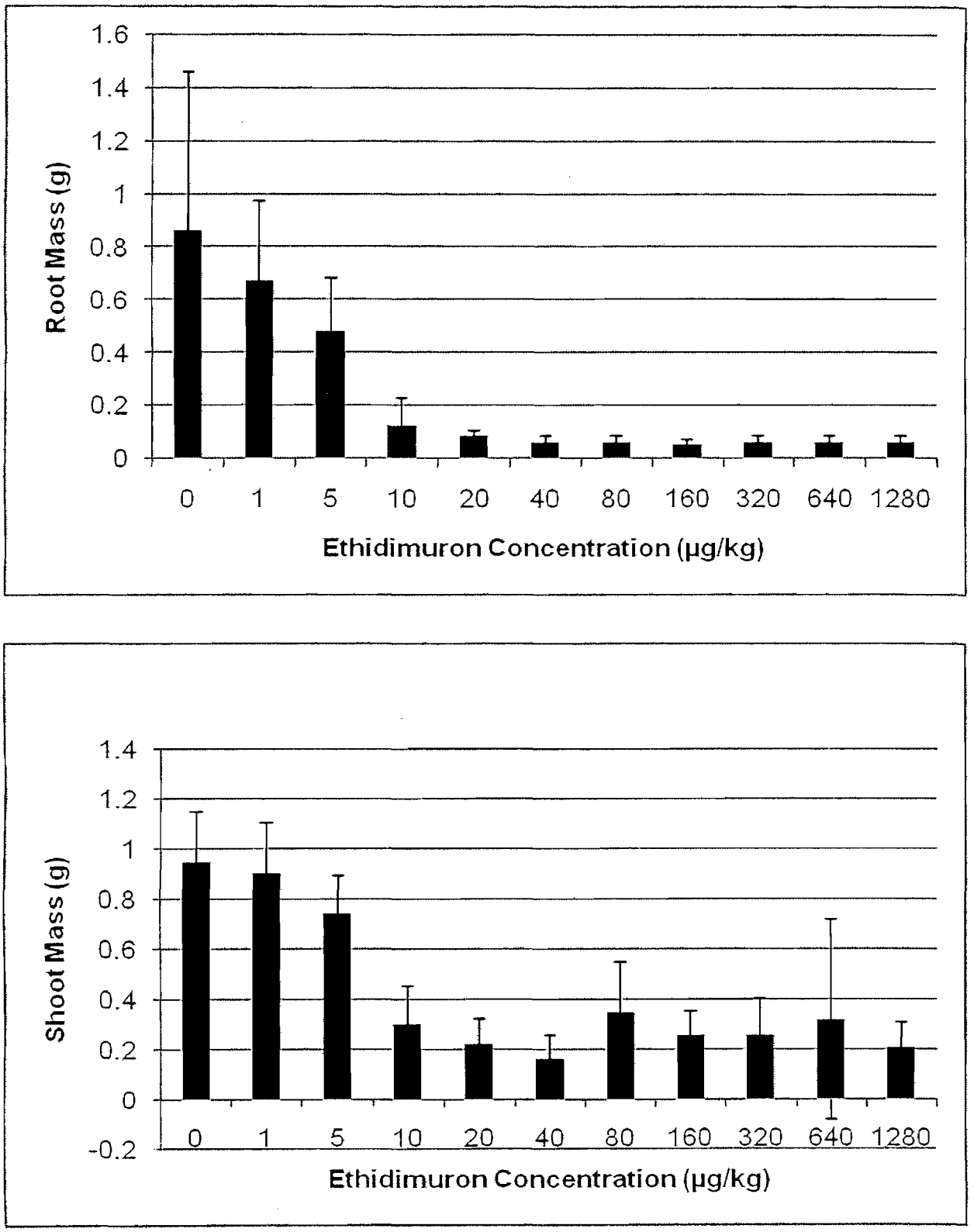


Figure 4.6. Results of dry mass determinations on roots and shoots of tomato seedlings treated with the herbicide ethidimuron (lines on bars indicate standard deviation).

4.4 Discussion and Conclusions

The symptoms that were found to develop on the treated seedlings are typical photosynthetic inhibitor herbicide symptoms. A significant decrease in dry mass of the plants is found with the application of concentrations at 5 μg kg^{-1}. These are low concentrations, and within the limit of detection for this active ingredient (1 μg kg^{-1}). This was also the level at which herbicide damage symptoms were observed in tomato plants. Although the symptoms are not severe (Tables 4.1 to 4.3), a significant effect is exerted on plant growth which establishes as an effect on dry mass (Figures 4.4 – 4.6). This indicates that where these herbicides are present in soil within the range of the level of determination, negative effects may be exerted on plant growth.

Glass-house experiments conducted by Myburgh (1999) showed significant effects on tomato growth at 10 μg $kg^{-1}$of the herbicides tebuthiuron, bromacil and ethidimuron. In this work Myburgh determined the 10 and 50 % growth reduction concentrations for these active ingredients. The work shows that a 10% reduction in mass of sensitive plants occurred at levels as low as 1 μg kg^{-1}. An interesting aspect of this work was that at the level of 10% growth reduction no visible symptoms were observed. This indicates that not only can damage be expected on vegetation at the levels detected at the case study sites, but that damage may be expected even though visible symptoms are not observed.

The presence of herbicides in non-target soils, in the proximity where industrial weed control has taken place, were discussed in Chapter 3. The case studies discussed, indicate that the herbicides used in industrial weed control have a tendency to migrate in soils low in Organic carbon and microbial activity such as the majority of soil types in SA. This is also seen in other experiments from literature. The experimental work discussed in Chapter 4 indicates that even though the active ingredients may enter non-target soils at low levels, these low levels may be of biological significance for sensitive seedlings grown under the experimental conditions. Migration of such pesticides to cropped areas,

be they field or tree crops, may have serious financial implications for a farmer in the proximity of rights of way etc., in that crop losses may be suffered. The possible synergistic effects of combinations of low levels of more than one of these contaminants should not be ignored. It has been shown for example that the herbicides ethidimuron, tebuthiuron and bromacil have an additive effect concerning phytotoxicity on sensitive crops (Myburgh, 1999).

The analyses methods used for the active ingredients analysed in Chapter 3, were non exhaustive, thus the bound fraction of the active ingredients were not extracted. The glass-house trials conducted showed that significant biological effects could be expected on sensitive vegetation at the residue levels found in the non-target areas. The biologically-significant effects of herbicides at low soil residue levels, as identified here, highlight the potential toxicity of pesticides at extremely low levels where the active ingredients enter non-target areas after application under conditions found in South Africa. The case studies described in Chapter 3 are but a few examples where litigation was served and where the farmers and individuals suffering damage sued the institutions that had applied the active ingredients. If this type of damage is found with the selected herbicides discussed, it can be expected that other pesticides with similar characteristics would show similar soil behaviour. The effects may, however, not be as obvious as trees and crops dying, the effects could be of a more long-term deterioration of eco-systems, or long-term health effects on humans such as effects of reproductive systems such as observed for endocrine disruptors including the pesticides DDT and deltamethrin (Burger, 2005).

The movement of insecticides, such as the organophosphate azinphos methyl, to surface water resources has been shown in South Africa (Dabrowski and Schulz, 2003a; Dabrowski and Schulz, 2003b; Dabrowski *et al.*, 2002; Dabrowski *et al.*, 2003). The presence of organochlorine, organophosphate and pyrethroid insecticides in water

resources in South Africa has also been shown (Sereda and Meinhardt, 2003; Sereda and Meinhardt, 2005a; Sereda and Meinhardt, 2005b). Although the source of these contaminants is not clear, it is likely that their presence in the water sources originated surface run-off as well as infiltration into and migration through the soil. Furthermore, the presence of such active ingredients in breast milk (Bouwman *et al.*, 1990; Bouwman *et al.*, 2006) has been shown. The potential effects of these active ingredients on human and environmental health are the subject of numerous studies (Burger, 2005; Sereda and Meinhardt, 2003; Van Wyk *et al.*, 2005). The studies all conclude that the presence of pesticides in the environment poses a serious risk.

If migration of pesticides from applied zones is a principal route of pesticides entering non-target zones, then this aspect requires evaluation when decisions are taken as to whether to allow pesticides onto the South African market. Results of studies discussed in Chapters 3 and 4 indicate that pesticide infiltration and migration into the soil profile is a potential pathway for pesticides to enter non-target environmental compartments.

In order to allow the local registration authority to evaluate migration potential of pesticides, they may require field migration evaluation to be conducted under locally relevant conditions. Field migration studies are, however, extremely costly. Adding such evaluations, and the concurrent costs, to local registration requirements is likely to force the agricultural chemical industry to abandon the local registration of many of the newer generation active ingredients.

An alternative to conducting field studies could be the use of predictive models within the evaluation system. The models will, however, have to be able to predict pesticide mobility reasonably accurately. In order to ensure that a model is available to local authorities, it will have to be developed locally, or existing models could be used that have been developed in the EU or USA. However, existing models will require evaluation and validation to ensure that they are suitable for use under local conditions. The evaluation

of existing models is likely cheaper and faster than re-inventing the modelling wheel. This approach has been followed internationally; as for example the modifications to PELMO from evaluations of PRZM.

In the case of South Africa, where funds are not necessarily freely available for model development, models could be evaluated against actual migration data, allowing the estimation of the accuracy of such models. Once this step has been taken, model developers could adapt existing models to more accurately predict migration under local scenarios, should this be required.

Chapter 2 discusses the input data requirements for some pesticide migration models. The pesticide adsorption parameters and soil degradation rates are two important input parameters for migration models. Before models are evaluated, it is critical to establish whether these two parameters will be similar to those from published sources. The next chapter (Chapter 5) describes laboratory experiments aimed at determining adsorption coefficients and half lives for selected pesticides on selected soil types.

CHAPTER 5.

DETERMINATION OF PARAMETERS INDICATIVE OF PESTICIDE SOIL BEHAVIOUR IN SOUTH AFRICAN SOILS.

5.1 Introduction

Many factors determine the rate of dissipation or loss of a pesticide from soil (Reinhardt and Nel, 1989; Riley and Morrod, 1976). The major processes occurring at field scale that are important for modelling the behaviour and fate of pesticides can be placed in two groups namely 1) transfer and 2) transformation processes (Meinhardt and van der Walt, 2005). Transfer processes involve the movement of an active ingredient from point A to point B, without its biological activity necessarily being affected. Transfer processes include, runoff, volatilisation, adsorption/desorption and plant uptake (Bollag *et al.*, 1992; Leeds-Harrison, 1995; Wolfe *et al.*, 1990). The adsorption/desorption of the pesticide to soil constituents describes the extent to which an active ingredient will be retained in various soil layers (Bailey and White, 1970). A parameter that describes the extent of adsorption is the adsorption coefficient (K_d). When the K_d is normalised to take into account the organic carbon content of the soil, the K_{oc} is rendered. The K_{oc} for an active ingredient is dependent on chemical characteristics of the pesticides, and on soil properties (Mora *et al.*, 1996). It thus follows that the K_{oc} for an active ingredient may differ depending on the soil characteristics. In general, the higher the K_{oc}, the less mobile an active ingredient will be. Also the higher the clay or organic fraction, the higher the K_{oc} (Weber, 1991a).

Transformation, the second major process, entails the changing of the chemical structure of molecules, which usually, but not always, results in the reduction or loss of biological activity. Transformation of an active ingredient may occur at any stage during its transfer from one location to another (Rose and Ghadiri, 1992). The three major transformation

processes are chemical-, microbial- and photo-transformation. Pesticide transformation is a process taken into account in most migration models (Guoy *et al.*, 1999). As has been mentioned the descriptive parameter used for degradation rates in most models is the half-life or Deterioration Time at which the initial concentration is decreased by 50% (DT_{50}).

This study was conducted in order to determine pesticide soil half life and adsorption coefficients for three pesticides, on three different South African soils.

It has been discussed that selected South African soils may be low in organic matter and microbial activity (Chapter 1) and the hypothesis was thus set that:

1. the K_{oc} for pesticides are likely lower for certain South African soils than the K_{oc} for soils containing higher organic matter and having higher microbial activity.
2. the DT_{50} for pesticides are likely longer for certain South African soils than the DT_{50} for soils containing higher organic matter and having higher microbial activity.

5.2 Materials and Methods

5.2.1 Soil types

The laboratory experiments were conducted on three field soils, representing a range of typical South African, agricultural soils. The experiments were done on the top 20 cm soil layer and lower 40-60 cm soil layer separately. Selected soil characteristics are presented in Table 5.1. The soils were selected to represent a range of soil characteristics, with particular reference to clay and organic carbon content, prevalent in South African agricultural soils.

Table 5.1. Soil characteristics of the soils selected for determination of K_{oc} and DT_{50}.

Soil type	Soil Horizon (cm)	Percentage Clay content*	Carbon %	pH (Water)
Sandy loam soil	0 - 20	19.7 (Kt)	0.48	4.16
	40 – 60	29.2 (Kt)	0.49	4.94
Clay soil	0 - 20	38.5 (St)	1.26	7.56
	40 – 60	53.2 (St)	0.86	8.18
Sandy clay loam	0 - 20	22.3 (Kt)	0.63	7.68
	40 – 60	32 (Kt)	0.37	8.41

* Dominant clay mineral: Kt = Kaolinite, St = Smectite

5.2.2 Determination of adsorption coefficients

Soil was collected from field plots (Table 5.1) and air-dried. Soil was sampled from the 0-20 cm "top soil" layer and the 40-60 cm "sub-soil" layer separately, and determinations conducted on these soils separately. The tests were conducted on the active ingredient applied as the formulated product. The pesticides selected for the trial work were two herbicides and one insecticide. The herbicides were tebuthiuron as the 20% granular formulation Molopo (Dow Chemicals), and azafenidin as the 80% wettable granular formulation Evolus (Du Pont). Two formulations of the insecticide fenthion were used; a 50% emulsifiable concentrate (EC) Lebaycid (Bayer), and the 64% Ultra Low Volume (ULV) formulation Queletox. The two formulation types were tested separately to establish whether the formulation would affect the adsorption of the active ingredient.

The adsorption coefficient (K_{oc}) of the active ingredients was determined using the OECD batch slurry method (OECD, 2006). This procedure measures the decrease in concentration of a pesticide when the chemical is in contact with soil at room temperature. The determinations were conducted at ARC-PPRI laboratories, Roodeplaat, at an average temperature of 22°C.

The determination was carried out using a 1:5 soil to solution ratio on a mass-per-mass basis. Pesticides were made up in a 0.01 mol l^{-1} $CaCl_2$ solution to render an active ingredient concentration of 1 mg l^{-1}. Each pesticide determination consisted of three replicates, and fortified matrices and blanks were included, to determine recovery rates and background interference. Analyses were based on solvent extraction (liquid – solid) and analysed with gas-chromatography (as described in Chapter 4). Calculations were based on the method described by Weber (1991a), in which the concentration is expressed in nmol g^{-1} soil.

5.2.3 Determination of soil half-lives of pesticides

Pesticide soil half-lives were determined using a standardised time-lapse analysis (Alexander and Scow, 1989; Hance, 1967). Soil was air dried, fortified with pesticide and placed in a controlled-environment glasshouse. Average day temperature was 27°C, and average night temperature was 15°C. For each soil and each pesticide, three replicates were used. Sub-samples were removed and analysed at day 0 (starting concentration), day 5, 11, 22, 88 and 120. Half-lives used for model predictions were derived using the equation:

$$DT_{50} = \frac{0.30103(t - t_0)}{\log\left(\frac{m(t_0)}{m(t)}\right)}$$

Where:

m(t) = amount of pesticide at time t (g)

$m(t_0)$ = amount of pesticide at an earlier time (g)

t and t_0 = time at which pesticide amounts were determined measured in days.

5.3 Results and Discussion

5.3.1 Adsorption coefficients

The results for adsorption coefficient determinations are given in Table 5.3. Analysis of variance (ANOVA) was performed on the adsorption data. Mean adsorption coefficients and standard deviations are summarised in Table 5.2.

Table 5.2. Results of adsorption coefficient determinations.

Pesticide	Soil type	Soil Horizon	K_{oc} (ml g^{-1})	Mean published K_{oc} (ml g^{-1})
Fenthion as Lebaycid (EC)	Sandy Loam	Top Soil	3571 (± 565)	1500
		Sub Soil	2625 (± 1235)	
	Sandy Clay Loam	Top Soil	9281 (± 323)	
		Sub Soil	9193 (± 2689)	
	Clay	Top Soil	23276 (± 2981)	
		Sub Soil	17731 (± 1658)	
Fenthion as Queletox (ULV)	Sandy Loam	Top Soil	2240 (± 617)	
		Sub Soil	1002 (± 431)	
	Sandy Clay Loam	Top Soil	4057 (± 468)	
		Sub Soil	2254 (± 211)	
	Clay	Top Soil	9331 (± 2895)	
		Sub Soil	9282 (± 1323)	
Azafenidin	Sandy Loam	Top Soil	313 (± 102)	298
		Sub Soil	400 (± 130)	
	Sandy Clay Loam	Top Soil	379 (± 96)	
		Sub Soil	1327 (± 336)	
	Clay	Top Soil	237 (± 60)	
		Sub Soil	1400 (± 354)	
Tebuthiuron	Sandy Loam	Top Soil	20.5 (± 8)	56
		Sub Soil	210 (± 47)	
	Sandy Clay Loam	Top Soil	74 (± 19)	
		Sub Soil	581 (± 117)	
	Clay	Top Soil	153 (± 18)	
		Sub Soil	511 (± 95)	

Fenthion

Results of K_{oc} determinations for Fenthion using an EC and ULV formulation are provided in Figure 5.1 and Figure 5.2 respectively.

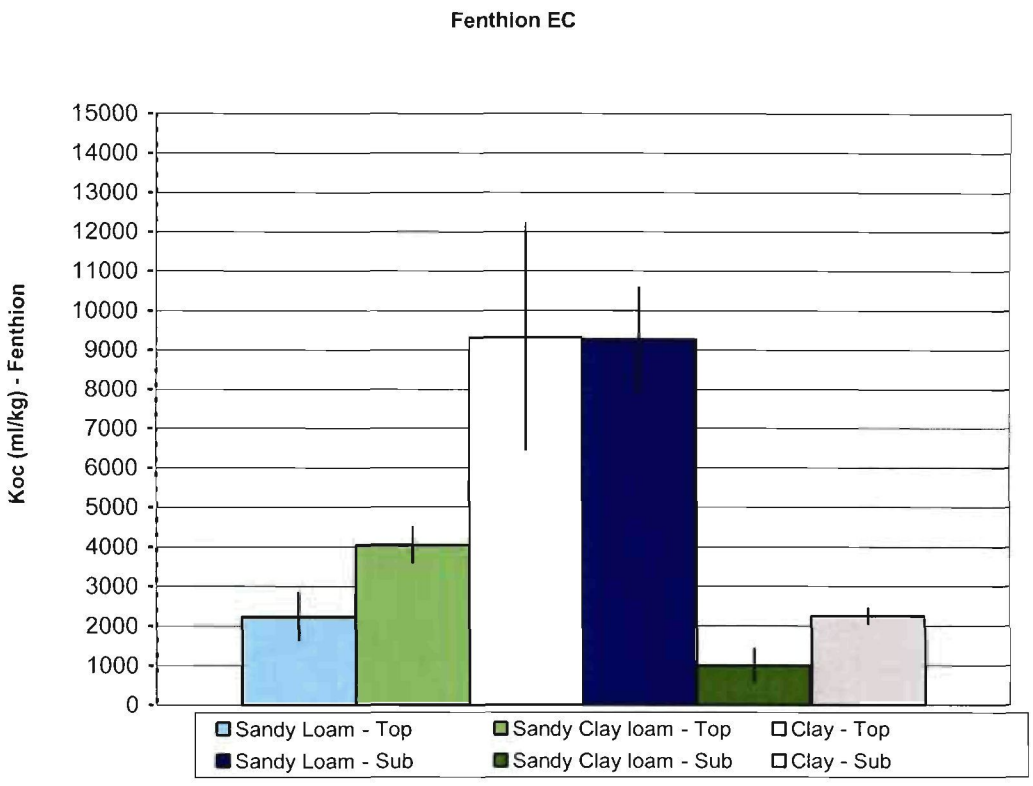


Figure 5.1. Mean adsorption coefficients and standard deviations (indicated by lines on bars) for fenthion as tested using an EC formulation.

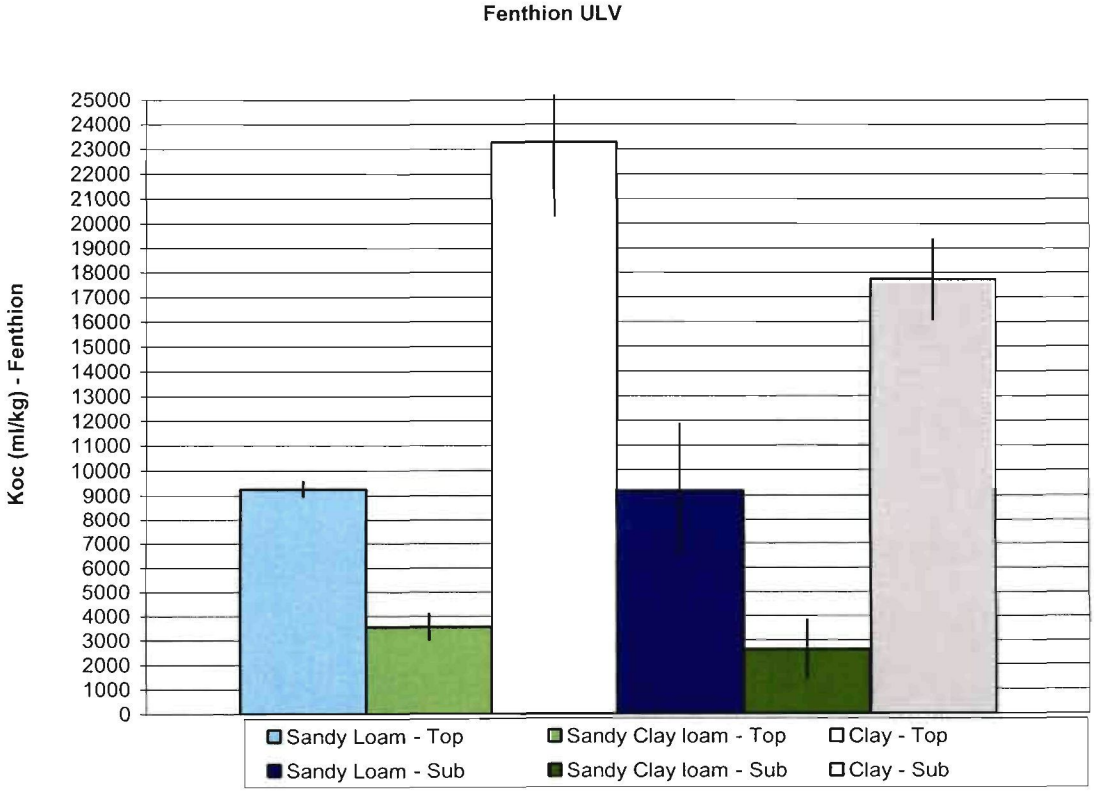


Figure 5.2. Mean adsorption coefficients and standard deviations (indicated by lines on bars) for fenthion as tested using a ULV formulation.

The K_{oc} values determined for fenthion tested as using a ULV formulation (Queletox®) were higher than those for the EC (Lebaycid) formulation. This trend was found for both the top soil and sub soils tested. The K_{OC} for the EC formulation indicates that this formulation will be more mobile than the ULV formulation. It must however be kept in mind that in general terms, a K_{OC} in excess of 200 indicates that limited mobility might be expected (Gustafson, 1999). If one considerers the K_{OC} values determined for fenthion on local soils, these were all above 1000 ml g^{-1}. The mean K_{OC} for fenthion calculated using all data points, across all soils is 7820 (±6831) ml g^{-1}. This mean value is considerably higher than the published mean value of 1500 ml g^{-1} for a variety of soil types, (Ahrens *et. al.,* 1994) (Table 5.2). It can therefore be deduced that fenthion is not likely to migrate when applied to these local soils. The fact that the ULV formulation provided higher K_{OC} may thus have no real effect on actual adsorption and decreased migration potential of fenthion. This is because the active ingredient is "released" almost immediately from the formulation after application (Flurry, 1996). Where the fenthion is applied as an EC, the formulation is diluted in water (approximately 200 ml formulation per 300 l of water), and the mixture is applied to crops and the soil. If the ULV formulation is used in a similar way and also diluted in water a similar effect would result. Where the fenthion is applied to a crop or soil directly as the ULV formulation (this is not likely due to phytotoxicity), the fenthion could be expected to migrate less than an EC. But because the K_{oc} for fenthion determined is very high irrespective of formulation used, fenthion is not likely to migrate anyway, at least under conditions where preferential flow does not occur. On soils prone to preferential flow movement of a part of the pesticide applied will migrate following this route, but again this will be independent of the formulation type.

A general trend was observed of fenthion adsorption coefficients decreasing with soil depth, despite an increase in clay content. With the exception of the sandy loam soil the

percentage carbon content was lower in the sub soil as compared to the top soil. The observed decrease in K_{OC} corresponded with a decrease in organic matter of the soil. There was however no correspondence with the change in clay contents when considering data per soil type individually. This would indicate that organic matter content rather than clay content governs the adsorption of azafenidin.

When considering K_{OC} values across the soil types, the K_{OC} values were the highest on the soil containing the highest clay content, as might be expected for pesticides in general (Gustafson, 1993).

Azafenidin

Results for azafenidin adsorption coefficient determinations are provided in Figure 5.3.

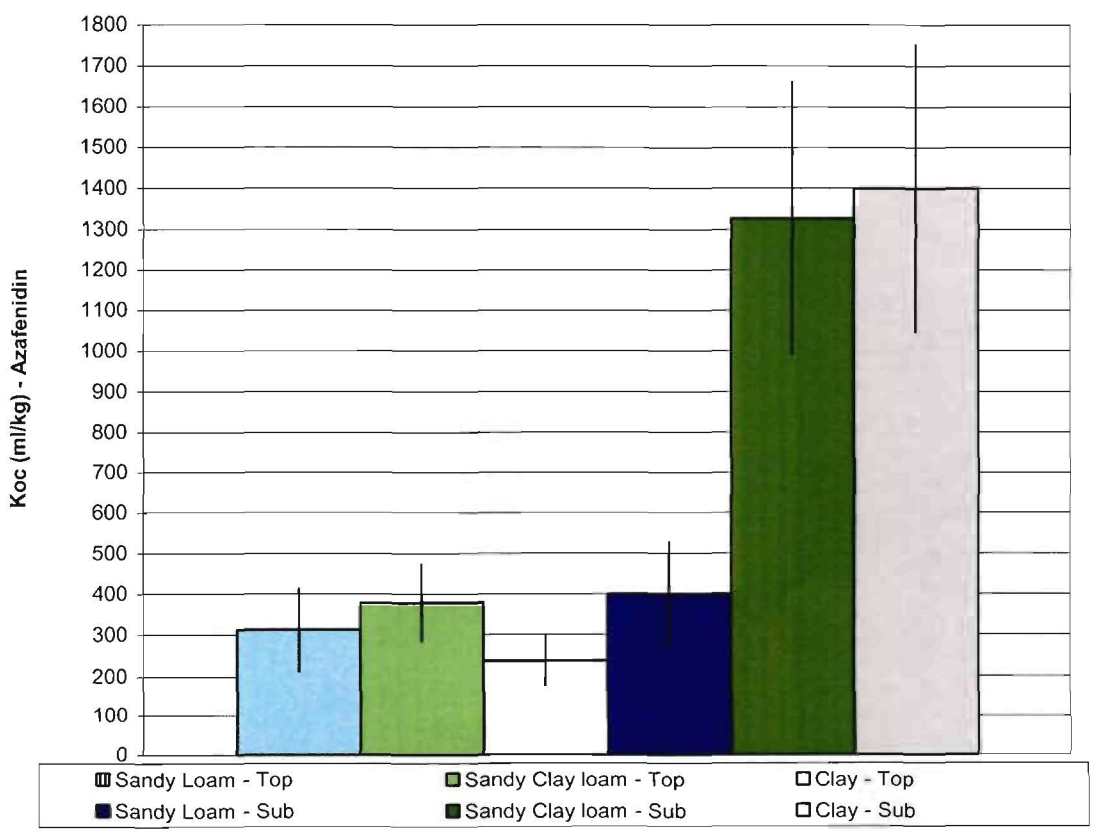


Figure 5.3. Mean adsorption coefficients and standard deviations (indicated by lines on bars) for azafenidin.

The K_{OC}'s determined for the topsoil layers, are similar to published values (mean of 298 ml g^{-1} (Ahrens *et. al.,* 1994). The values determined for the sub soils were however higher than would be expected, judging from published values. As in the case with fenthion, the values determined were above 200 ml g^{-1}, which indicated that migration should be minimal. Where movement would occur, the active ingredient is not expected to move past the sub-soil layer.

Comparison of the K_{oc} determined for top and sub soils, showed a trend of higher K_{oc} values for the sub soils, when compared with the top soils, corresponding to a to higher clay content in the deeper soil layer. Similar results have been found for DDT by Lalah *et. al.* (2001). This was somewhat unexpected as it is generally accepted that organic carbon is the main determining factor for pesticide adsorption (Reinhardt and Nel, 1989).

As in the case with fenthion, the K_{oc} values determined were above 100 ml g^{-1}, which indicates that migration should be minimal. Where movement will occur, the active ingredient should not move past the sub-soil layer.

Tebuthiuron

Results for tebuthiuron adsorption coefficient determinations are provided in Figure 5.4.

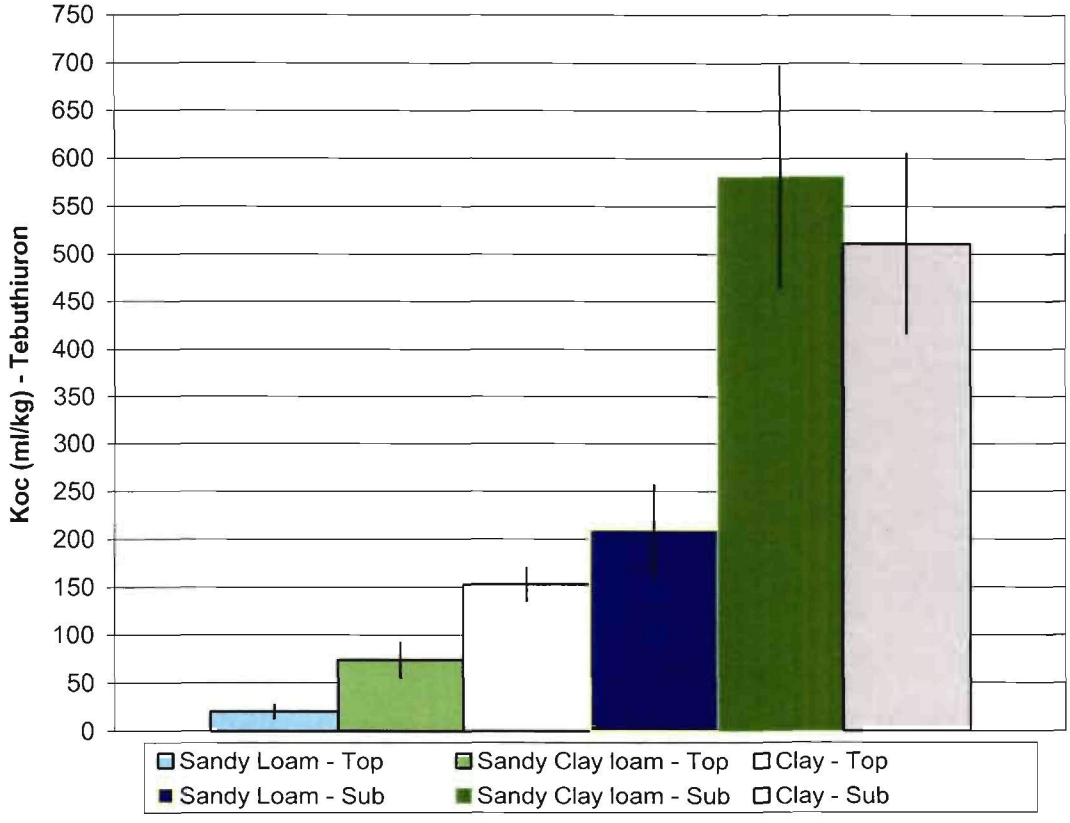


Figure 5.4. Mean adsorption coefficients and standard deviations (indicated by lines on bars) for tebuthiuron.

Adsorption coefficients for tebuthiuron were lower for the top soils than the sub soil. A lower K_{OC} is indicative of lower adsorption, and thus higher migration potential (Weber and Whitare, 1982) indicating the active ingredient will tend to move through the topsoil and then become retained in the subsoil. This was found for all three of the soils tested, including the sandy loam soil. If one thus uses this data as indication of migration potential, tebuthiuron should only be expected to migrate on sandy loam soils, and then no deeper than approximately 40 cm.

The adsorption coefficients determined for all the active ingredients used in the experiments are similar to published values (Ahrens *et al.*, 1994). This indicates that the

published values for active ingredients should provide a reasonable approximation for use in migration predictions in South African soils. The values determined in local experiments were not lower than those determined in other countries, as was hypothesised (Chapter 1).

The experiments did however show that formulation type may have an effect of the adsorption of an active ingredient. The implications of the results of experiments is that the adsorption of pesticides will be higher if its carrier is a less polar, oily type formulation, such as in the case of the fenthion ULV formulation. Although no literature could be sourced investigating the effects of formulation type on migration and adsorption to corroborate these findings, it is generally accepted that the polarity of an active ingredient will affect its adsorption (Gerber *et al.*, 1970). In general terms lower water solubility, or lower the polarity of an active ingredient, the higher it is expected to be adsorbed to soil constituents, and the higher the K_{oc} is likely to be for the active ingredient. What this indicates is that the formulation type, or the carrier of the active ingredient, may affect its adsorption, and therefore probably its migration capacity. An EC formulation would be applied in a volume of water whereas the ULV formulation would be applied as is. However, once the active ingredient reaches the ground, it is likely to be significantly diluted either by rain or irrigation water after application. This water is of course critical to the migration of a pesticide. The rain or irrigation water would then dilute the active ingredient to such a degree that the formulation additives may have no affect on its adsorption. If there is such dilution of agricultural pesticides, the formulation type is not likely to further effect the adsorption and migration thereof. Therefore, the effect of the formulation type on migration may be short lived, and it may make more sense to consider the solubility and polarity of the active ingredient.

It should be kept in mind that the experiments on formulation types were conducted using fenthion as a candidate pesticide. Fenthion has a high K_{oc} indicating a high degree of

adsorption. The fact that a difference was found between the two formulation types may bear no real consequence for fenthion migration. The measured values for the EC were between 2000 and 11000 ml g^{-1}. In the case of the ULV formulation the values were between 4000 and 23 000 ml g^{-1}. All values were well above 150 ml g^{-1}, indicating high adsorption and thus limited migration

5.3.2 Determination of pesticides soil half -life

Published half-lives are provided in Table 5.3.. Results of half-life determinations are provided in Table 5.4. The variability of analysis results was high, approximately 50%, between replicate samples analysed. Pesticide residue analyses regularly provide high variability and a relative standard deviation of 30 - 50% is considered acceptable (Anastassiades and Lehotay, 2003). What this shows is that much attention needs to be placed on the residue analyses phase when determining soil half-lives.

Table 5.3. Published DT_{50} for the active ingredients tested (Ahrens *et al.*, 1994; Tomlin, 1994)

Pesticide	DT_{50} min	DT_{50} max
Fenthion	1.5 days	
Azafenidin	24 days	40 days
Tebuthiuron	365 days	450 days

Table 5.4. Pesticide half-lives determined from laboratory trials

Pesticide	Soil type	DT_{50} (days)
Fenthion	Sandy Loam	4.57 ± 2.7
	Sandy Clay Loam	4.53 ± 1.2
	Clay	7.20 ± 1.85
Azafenidin	Sandy Loam	12.07 ± 5.40
	Sandy Clay Loam	49.29 ± 4.6
	Clay	20.34 ± 9.5
Tebuthiuron	Sandy Loam	117.95 ± 80.1
	Sandy Clay Loam	119.17 ± 70.5
	Clay	576.19 ± 160.43

Fenthion half-life exceeded the published values (Metcalf, *et al.* 1963; Tomlin, 1994), for all three the soils tested. The azafenidin half-lives determined were similar to those from literature. Tebuthiuron half-lives were shorter than published half-lives for the sandy loam and sandy clay loam soils, whereas in clay soil the half-lives were longer compared to the published values. For all the soil types tested, the half-lives were the longest where the adsorption coefficients were the highest. This was not surprising, as a pesticide would have to be unbound for breakdown to occur, especially where the active ingredient in prone to microbial degradation.

5.4 Conclusions

The laboratory half-life and adsorption studies were aimed at determining whether the model input parameter for soil adsorption and persistence could be sourced from published data or whether it would have to be generated under local conditions.

The results of laboratory experiments indicated that the adsorption coefficients determined using selected South African soils did not differ from published values for this parameter. This indicated that the published data on this subject would suffice as input for running predictive migration models for South African soils.

The experiments, however, did show that the half-lives might be longer than those published, this was especially for the tebuthiuron and fenthion results generated on clay soils. The pesticides may thus persist longer in South African soils when compared with published expectations. However one also needs to consider the high variances found during analyses.

The study indicated that when pesticide behaviour is to be predicted for South African soils, the model input for soil persistence needs to be determined for local soils.

It was anticipated that pesticide adsorption would be lower in South African soils, due to the soils older geomorphic age, together with the lower organic content and microbial

activity. The experiments conducted indicated that the adsorption coefficients varied greatly. The values determined were however, all within the published ranges for adsorption coefficients.

CHAPTER 6.

FIELD MIGRATION STUDIES OF SELECTED PESTICIDES IN SELECTED RSA SOILS

6.1 Introduction

The data generated in laboratory studies (Chapter 5) on determining the soil migration parameters for South African soils indicated that the soil half-lives of pesticides tend to be longer than those from published data. This would indicate that should a model be used to predict soil behaviour under South African conditions, the data for this parameter would have to be generated under local conditions. Therefore, models should predict longer residence times for pesticides.

In this Chapter, experimental work will be discussed in which pesticide migration patterns were determined for selected pesticide / soil combinations, as well as soil characteristics that are known to influence soil behaviour of pesticides. This data will then be compared to modelled data in order to determine whether existing soil migration models can be used in South Africa.

The work for this chapter was conducted at selected trial sites, using selected pesticides, in order to cover a wide range of chemical and physical characteristics of soils and pesticides. The soils were selected to be representative of the many of South African soils. The pesticides selection was based on both chemical characteristics as well as South African use patterns.

The specific aims of the experiments were to:

- determine field migration characteristics for selected pesticides
- determine soil characteristics of selected soils
- evaluate selected models for their ability to predict the migration of selected pesticides

6.2 Materials and methods

Pesticide migration evaluations were undertaken in field studies, where plots were sprayed with selected pesticides, and migration determined by sampling soil at pre-determined depths and time intervals (section 6.2.1 to section 6.2.4). The soils were selected to represent a range of soil properties, with regard to clay type, clay content, organic carbon content and soil pH. Details of the study protocols are provided below.

6.2.1 Soil characterisation

The trials were conducted on three soil types located at sites in the Pretoria area. Two of the trial sites were located at the Roodeplaat, Agricultural Research Council (ARC) experimental farm north-east of Pretoria. The third trial site was located at the University of Pretoria experimental farm, Pretoria. The coordinates for each of the trial sites are provided in Table 6.1.

Table 6.1. Trial site locations and coordinates

Site number	Area – description	Coordinates
1	Pretoria Central - University of Pretoria experimental farm section 4	25°54 00 (S) 28°15 69(E)
2	NE-Pretoria ARC-VOPI Roodeplaat experimental farm, district 5	25°36 14 (S) 28°21 29(E)
3	NE-Pretoria ARC-VOPI Roodeplaat experimental farm, district 12	25°35 78 (S) 28°21 51 (E)

At each of the three sites, soil samples were collected from the 0 -20 cm and 40 – 60 cm soil layers and analysed for soil typing, soil pH (water), clay content and percentage total carbon content (determined by furnace ignition). Samples were taken as composite samples, with each sample consisting of five sub-samples. Soil analyses were performed by the ARC Institute for Soil Climate and Water, Pretoria. Specific soil characteristics are provided in Table 6.2.

Table 6.2. Selected soil properties for the soils used for soil migration experiments.

Site number	Soil type	Soil Horizon (cm)	Percentage Clay content*	Percentage Organic Carbon	pH (Water)
1	Sandy loam soil	0 - 20	19.7 (Kt)	0.48	4.16
		40 – 60	29.2 (Kt)	0.49	4.94
2	Clay soil	0 - 20	38.5 (St)	1.26	7.56
		40 – 60	53.2 (St)	0.86	8.18
3	Sandy clay loam	0 - 20	22.3 (Kt)	0.63	7.68
		40 – 60	32.0 (Kt)	0.37	8.41

* Dominant clay mineral: Kt = Kaolinite; St = Smectite

6.2.2 Pesticide selection

The pesticides were selected to represent a range of partitioning coefficients and half-lives, which would influence soil behaviour. The pesticides selected for the field trials were:

- Tebuthiuron (herbicide) (Molopo® – Dow chemicals)
- Azifenidin (herbicide) (Evolus® - Du Pont)
- Fenthion (insecticide) (Lebaycid® – Bayer)

Table 6.3. Mean adsorption coefficients and half lives for pesticides used in field migration studies.

Pesticide	Mean Published K_{oc} (ml g^{-1})	Mean Published DT_{50} (days)
Fenthion	1500	1.5
Azafenidin	298	32
Tebuthiuron	56	405

Fenthion was selected as an insecticide with a short half-life and high K_{oc}, indicating the active ingredient is short-lived in soil, and also relatively immobile in soil. Tebuthiuron was selected as an herbicide with the opposite characteristics of fenthion. The active ingredient has an extended half-live and low K_{oc}, indicating that the active ingredient will likely migrate in soils, and persist for extended periods of time (Ahrens *et al.*, 1994).

Azafenidin was selected as a herbicide with intermediate characteristic, i.e. relatively immobile and with intermediate persistence (Hatzios *et al.*, 1998).

6.2.3 Field experiments

At each of the three experimental sites, three experimental plots were set out, each plot measuring 10m X 15m (150 m^2). The fields were ploughed to 50 cm depth, rotovated and disked before application to ensure a flat, even surface (Brown, 1996; Walker, 1991). All applications were made to bare soil, with no vegetation present.

At each trial site, the three plots were treated individually with the three active ingredients selected. The active ingredients were applied as a single application of commercial formulated product at an application volume equivalent to 500 l ha^{-1}. The applications were made using a pressurised knapsack sprayer fitted with a pressure gauge. The application rates are provided in Table 6.4. Applications were made at an operating pressure of 3.2 bar and application speed of 1 m s^{-1}. All equipment was calibrated before application.

Weed management took place by applying a three % Roundup® solution (volume per volume), to the weeds in the sites at three-monthly intervals. Weed coverage was low, not exceeding 5% of the area of trial sites. The weeds that did develop were primarily grasses. The Roundup applications were made as spot applications, where the active ingredient was applied directly to the weeds, rather than a full cover application of the site as a whole. Because the applications were directed target sprays to the weeds, it is not expected that these applications would have an effect on the migration patterns for the pesticides under investigation.

In order to calculate the amount of pesticide active ingredient applied, the application dosage rates (active ingredient (AI) per hectare (ha)) were calculated from the residue concentrations determined at day 0 (directly after application). For this purpose, soil

samples were collected from the top 10 cm soil layer and residue analyses conducted. The analytical methodology used is set out below in section 6.2.5 "Sample Analyses".

Table 6.4. Pesticide application dosage rates.

Active ingredient	Soil type	Application dosage rate (kg ha^{-1} a.i.)
Tebuthiuron	Sandy loam	0.3965
	Sandy clay loam	0.6659
	Clay	0.9459
Azifenidin	Sandy loam	0.611
	Sandy clay loam	0.321
	Clay	0.215
Fenthion	Sandy loam	0.016
	Sandy clay loam	0.079
	Clay	0.0319

Meteorological data were sourced from the South African Weather Service. The sites selected were all located within a 15 km radius of the Pretoria central weather station.

6.2.4 Field sampling

Samples were collected at five time intervals. The first sampling event took place at day 0, i.e. on the day of application (1 March 2003). Follow-up samples were collected 18, 30, 60 and 120 days after application. At each sampling event, samples were collected of the 0 – 20 cm (horizon 1), 20 – 40 cm (horizon 2), 40 – 60 cm (horizon 3), 60 – 80 cm (horizon 4) and 80 - 120 cm (horizon 5), soil horizons. A composite sampling strategy was followed in which each sample was composed of five sub-samples taken across the field, and combined for analyses. Sampling was replicated three times per plot, per active ingredient, providing three composite samples per time interval per soil horizon for each pesticide. The sites were undisturbed for the duration of the trials.

6.2.5 Sample Analysis

Soil samples collected were analysed by the Pesticide Analytical laboratory of the ARC - Plant Protection Research Institute. Residue analyses were conducted using solvent extraction and Gas Chromatography according to in-house ARC-PPRI analytical methods. Fenthion residues in soil were analysed using the PALSRAM 68 protocol, as registered in the PAL protocol registry system. Fenthion analyses were conducted for the active ingredient only, and metabolites were not analysed. Tebuthiuron residues were analysed using the PALSRAM 67 protocol as registered in the PAL protocol registry system. Azifenidin was analysed according to the PALSRAM 78 protocol.

Analytical method validation and active ingredient residue stability under storage was conducted for each soil / pesticide combination. Details are provided in section **6.5.1**. of this **Chapter**.

6.2.6 Model selection

A large number of models are available for the prediction of migration in soils. Many of these are used in the pesticide evaluation programmes within the European Union and US – EPA as has been discussed in Chapter 2. The models used in this study were selected after consultation with model developers and software distribution companies, as well as relevant literature on the subject.

The institutions and individuals that were consulted included:

- The Scientific Software Group, which has approximately 22 models for the prediction of organic solutes in the unsaturated zone
- US EPA – model end users
- Dr D Gustavson – Model developer – US EPA
- Allan Walker (developer, VARLEACH)
- Michael Klein (developer, PELMO)
- Richard Kubiak (Head of research, Staatliche Lehr- und Forschunganstalt, Neustadt, Germany).

A brief description of the models selected is provided in Table 6.5.

Table 6.5. *Main characteristics of models selected for evaluation.*

Model	Use	Description	Operating system and model inputs
VARLEACH	Research	Early model – first true predictive tool for modelling herbicide behaviour in soil	▪ DOS Basic ▪ depth of soil profile, set to 120 cm and divided into 20 cm soil layers ▪ soil parameters; soil moisture content, soil bulk density and organic carbon content ▪ pesticide parameters; adsorption coefficients, water solubility, half-life and application rates ▪ output provided as concentration (µg/kg) per soil depth layer
PELMO	EU – pesticide screening	Simulations for regularity purposes	▪ Windows ▪ pesticide parameters of half-life, adsorption coefficients, application rate, water solubility, molecular mass and vapour pressure. ▪ soil parameters for core depth, soil bulk density, soil hydraulic conductivity ▪ cropping parameters (set to zero) ▪ model defaults 10 cm soil layers up to 120 cm depth, ▪ concentration is calculated by adding the concentrations per 10 cm soil layer for the relevant soil thickness. ▪ output given as a pesticide concentration in g/ha. This data needs first to be converted to µg/kg soil taking the soil bulk density into account.
WHI Unsat Suite – PESTAN module	USEPA – Tier 1 pesticides screening	Pollutant behaviour prediction in the Unsaturated zone	▪ Windows-based integrated model engine ▪ pesticide parameters for pesticide solubility, adsorption and half-life. ▪ soil parameters for saturated water content, bulk density, hydraulic conductivity, recharge rate and a parameter describing the ability of the dispersion of the pesticide in the soil. ▪ outputs as soil concentration (µg/kg) per cm soil layer.
WHI Unsat Suite - VS2DT	USEPA – Tier 1 pesticide screening	Designed for multilayer soils	▪ Windows ▪ integrated model engine
WHI Unsat Suite - VLEACH	USEPA – tier 1 pesticide	Predicts behaviour of Volatile organics – not included, as pesticides	▪ Windows ▪ integrated model engine

Model	Use	Description	Operating system and model inputs
	screening tool	are not volatile.	
WHI Unsat Suite - HELP	Landfill design	Designed to aid in the design of Landfill	▪ Windows ▪ integrated model engine
PRZM 3	USEPA – tier 1 pesticide screening tool	Predictive tool for cropped fields – does not run for uncropped situations	▪ BASIC

6.2.7 Model input parameters

Half-life data and adsorption data generated during laboratory trials (Chapter 5) were used as inputs for all the models. Meteorological data, sourced from the South African Weather Services, was used for PELMO and VARLEACH. The weather data included daily temperature, humidity, rainfall, and evaporation data.

Measured soil hydraulic conductivity data could not be obtained, as these analyses are no longer done in South Africa. The lack of availability of these analyses in South Africa created a potential gap information gap. The options to gain such data were to develop the infrastructure to do these analyses particularly for this project, to have these samples analysed overseas, or to make use of data derived from existing data. The funding for this project was limited, as in any funded research project. After extensive deliberation with the experts in the field, it was decided to use hydraulic conductivity data derived from published data of South African soils with similar characteristics. The reasons for that existing data had been generated by the Agricultural Research Council, Institute for Soil Climate and Water, Pretoria for the particular purpose of providing hydraulic conductivity reference data for South Africa. The data was reflective of a range of South African soil types, including those used in the pesticide migration study. In addition the costs of setting up the infra-structure or using overseas laboratories were prohibitively high. Also the variation within results obtained for hydraulic conductivity analyses varies greatly, within one soil type, and even within a specific field. Because of these factors the

decision was taken to make use of data published data rather than generating data at high cost.

The Hydraulic conductivity data was derived from published data of South African soils with similar characteristics. These data were generated and published by the ARC, Institute for Soil Climate and Water, Pretoria (Barnes, 1976; Cass, 1980).

VARLEACH

The model VARLEACH required inputs on the depth of the soil profile, which was set to 120 cm. The profile was divided into six 20 cm soil layers. For calculation of concentration, the concentration outputs for the bottom two soil layers were added. Further inputs required for soil parameters were soil moisture content, soil bulk density and organic carbon content.

Pesticide parameters required were adsorption coefficient water solubility, half-life and original application rate. The meteorological data required are data file which contains evaporation from an open water surface (E_o, mm), daily values of maximum temperature, minimum temperature and rainfall.

The model outputs were given as the concentration of the pesticide ($\mu g\ kg^{-1}$) per soil layer for each specified time interval. These data were saved as a text file and later imported to MS Excell for statistical purposes.

PELMO

The model PELMO was run using pesticide inputs on half-life, adsorption coefficient, application rate, water solubility, molecular mass, vapour pressure and pKa. Soil data required were core depth, soil bulk density, soil hydraulic conductivity and crop information (set to zero). The model defaults on soil layers 10 cm thick, so the soil

horizon was set at 120 cm depth, divided into 10 cm layers. For calculation purposes, the predicted concentrations in the relevant soil layers were added. Output data is given as a pesticide concentration in g ha^{-1}. This data was first converted to µg kg^{-1} soil taking soil bulk density into account, for statistical purposes. The data output for PELMO is given as daily data, from which the time intervals of interest are selected.

PESTAN

The model PESTAN requires the inputs for pesticide solubility, adsorption and half-life. Soil inputs required are saturated water content, bulk density, hydraulic conductivity, recharge rate and a parameter describing the ability of the active ingredient to be dispersion by the soil. Data on hydraulic conductivity could not be analysed for. This data was derived for known soils with similar characteristics. The recharge rate was set as the same as the hydraulic conductivity. The dispersion parameter was derived for the field migration data. The recharge rate was set to the same values as the hydraulic conductivity as is suggested in the model manual (Waterloo Hydrogeologic, 2003).

6.3 Results and Discussion

Results of field migration studies are presented in this section. The residue levels are expressed in µg kg^{-1} on a dry mass basis.

6.3.1 Fenthion migration under field conditions

The result of residue analyses for fenthion in samples collected directly after application indicates that no migration had occurred below horizon 1 within the first hours of application. The highest fenthion concentration detected was in the clay soil and the lowest concentration in the sandy loam soil. The residue levels detected on all three soils were low (3 – 8 % of that applied). It is generally known that fenthion degrades rapidly in

soil, which explains the low recovery found. The residue analyses also did not take into account the formation of metabolites, which would also explain low recoveries.

6.3.1.1 Fenthion migration in sandy loam soil

The migration pattern for fenthion in the sandy loam soil (Figure. 6.1) shows a 10-fold reduction in fenthion soil concentration in horizon 1 during the first 18 days after application (DAA) sign. The initial decrease in fenthion concentration in the upper soils layers is followed by an increase in fenthion concentrations in the deeper soil layers. This profile shows fenthion had migrated into the soil. The profile further indicates limited retention of the active ingredient. The drastic decrease in fenthion residue levels is more or less what could be expected, judging from the half-life for this soil (Chapter 5).

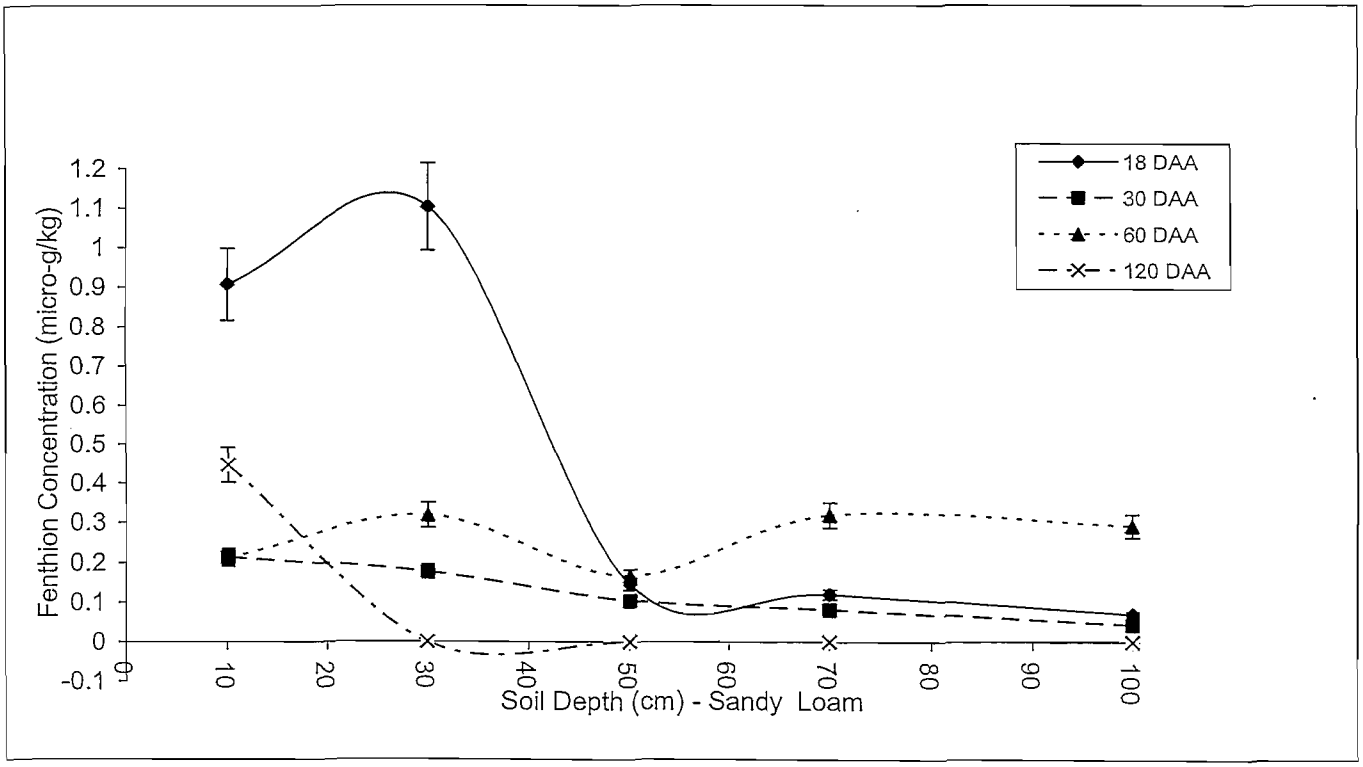


Figure 6.1. Mean fenthion residue levels (µg kg^{-1}) detected in the sandy loam soil 0, 18, 30, 60 and 120 DAA. Initial concentration (0 DAA) = 14.6 µg kg^{-1}. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

The fenthion residue levels decreased rapidly during the duration of the trial period, as would be expected for an active ingredient with a short half-life. An increase in the fenthion residue levels was found in horizon 1, 120 DAA. This increase in the upper soil horizon coincided with an apparent removal of the active ingredient from the deeper soil layers. This data indicates that the active ingredient had moved upward from the deeper soil horizons to the upper soil horizons.

6.3.1.2 Fenthion migration in sandy clay loam soil

The fenthion migration pattern observed in the sandy clay loam (Figure 6.2) showed the presence of fenthion residues throughout the soil profile 18 DAA. An increase in fenthion residue levels was found 30 DAA, in the soil below horizon 2, coinciding with a decrease in residue levels in horizon 1 and 2. This residue profile remained the same to 60 DAA and finally at 120 DAA the active ingredient was not detected at all.

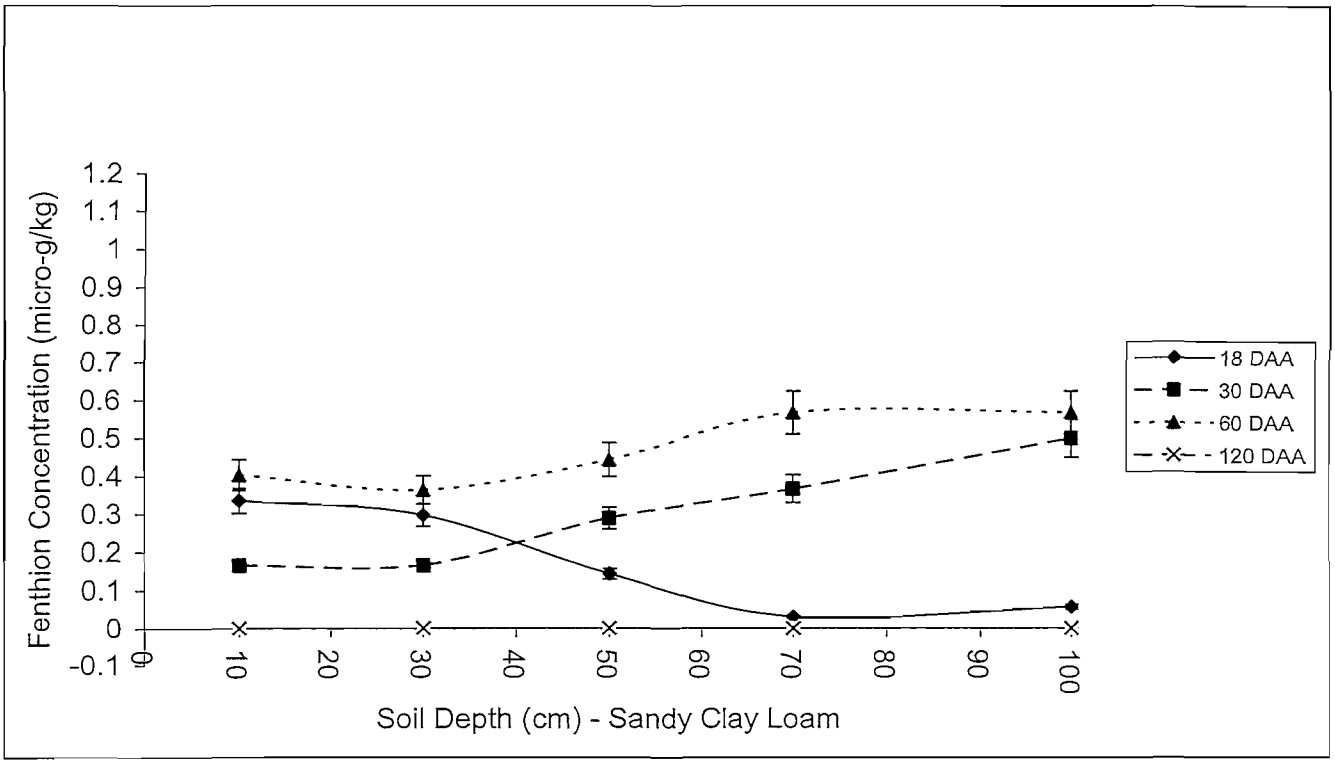


Figure 6.2. Mean fenthion residue levels (µg kg^{-1}) detected in the sandy clay loam soil 0, 18, 30, 60 and 120 DAA. Initial concentration (0 DAA) = 32.01 µg kg^{-1}. The 0 – 20 cm horizon 1 is indicated at 10cm, the 20 – 40 cm horizon at 30 cm, the 40 – 60 cm horizon indicated at 50 cm, the 60 – 80 cm horizon at 70 cm, and the 80 - 120 cm horizon at 100 cm. Standard deviations are shown.

6.3.1.3 Fenthion migration in clay soil

The fenthion migration pattern observed in the clay (Figure 6.3) showed fenthion reached horizon 5 within 18 DAA. The majority of the fenthion residues were detected in horizon 3. Fenthion residues were detected only in horizons 1 and 2, 30 DAA and only in horizon 1 60 and 120 DAA.

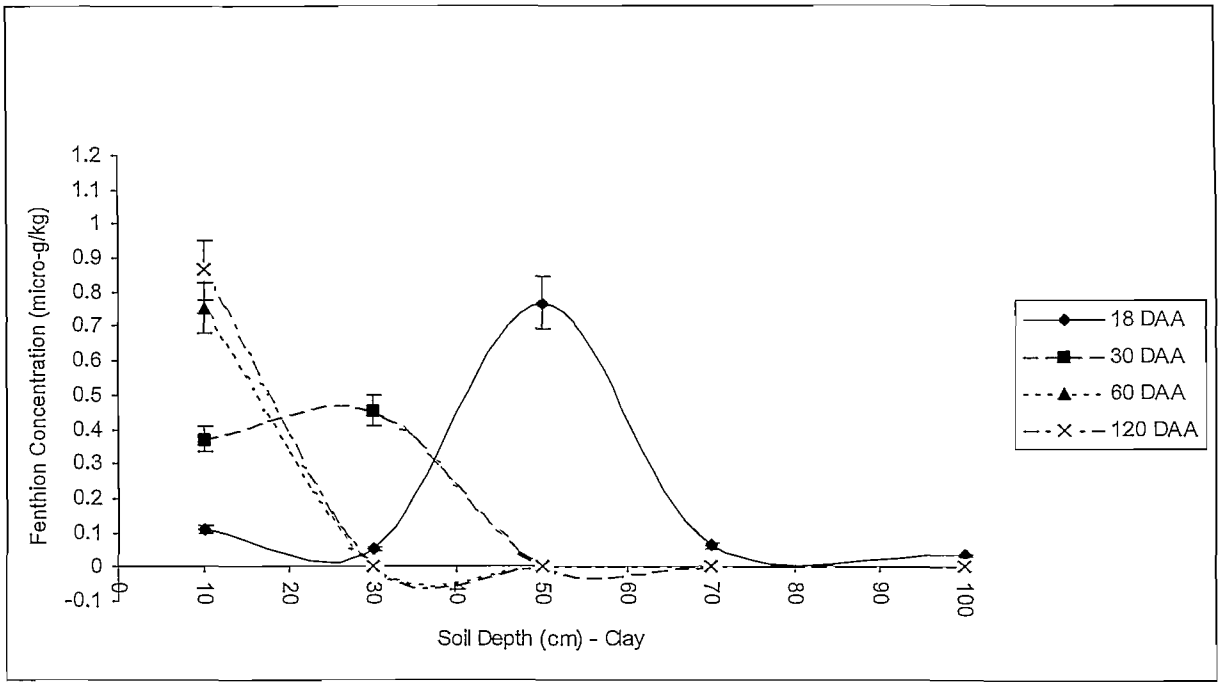


Figure 6.3. Mean fenthion residue levels (µg kg^{-1}) detected in the clay soil 0, 18, 30, 60 and 120 DAA. Initial concentration (0 DAA) = 31.8 µg kg^{-1}. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.1.4 Comparison of fenthion migration in three field soils.

In order to compare fenthion migration between the different soil types used in the field trials, the residues detected per time interval were converted to the percentage residues remaining of that which was applied.

The following exponential equation of percentage pesticide detected versus soil depth was rendered.

The following exponential equation of percentage pesticide detected versus soil depth was rendered.

$$y = a + br^x$$

Where *b* is the slope, *a* the intercept, and *r* is base of the natural logarithm.

The equations describing fenthion distribution 18, 30, 60 and 120 DAA, are provided for each soil type in the section below.

Sandy Loam
18 DAA: $y = -0.28 + 1.80\ (0.98)^x$
30 DAA: $y = -0.02 + 0.31\ (0.98)^x$
60 DAA: $y = -0.27 + -3.20\ (0.82)^x$
120 DAA: $y = -0.16E\text{-}8 + 1.50\ (0.40)^x$

Sandy Clay loam
18 DAA: $y = -0.06 + 0.570\ (0.98)^x$
30 DAA: $y = 0.58 + -0.62\ (0.98)^x$
60 DAA: $y = 0.48 + -4.50\ (0.82)^x$

Clay
18 DAA: $y = 0.20 + 0.002\ (0.98)^x$
30 DAA: $y = -0.23 + 0.86\ (0.98)^x$
60 DAA: $y = -0.01 + 40.40\ (0.82)^x$
120 DAA: $y = -0.32E\text{-}8 + 58.04\ (0.40)^x$
The slopes of the curves (b) generated are summarised in Table 6.6.

Table 6.6. Comparison of the slopes for curves generated on percentage fenthion remaining 18, 30, 60 and 120 DAA.

Soil type	Slope (b)			
	18 DAA	30 DAA	60 DAA	120 DAA
Sandy Loam	1.8	0.31	-3.2	1.5
Sandy clay Loam	0.5	0.62	-4.5	0
Clay	0.002	0.86	40.40	58.04

Sandy Loam

The slope of the fitted regression curve (Table 6.6) decreased with time, becoming negative 60 DAA, corresponding with the decreasing residue levels in horizon 1 over the first 60 DAA. At 120 DAA the slope is similar to that at 18 DAA, mimicking the upward

movement of the active ingredient in this soil. The slopes curves describe what was observed in the field trials.

Sandy Clay Loam

As in the case of the sandy loam soil, the slope of the fitted regression curve decreased with time, becoming negative 60 DAA. Thereafter the slope was reduced to 0 at 120 DAA, indicating an even distribution of the active ingredient in the soil. The curves describe the rapid dispersal yet even distribution of fenthion in the sandy clay loam soil.

Clay

The steepest slopes were found for fenthion distribution behaviour in the clay soil. These slopes (descriptive of high levels of the active ingredient in the upper layer) were found 60 and 120 DAA. The slope of the fitted curve increased over time indicating a decrease in migration with time. The decrease in the migration rate is not necessarily indicative of low mobility of fenthion in this soil, but rather a decrease in movement into deeper soil layers, due to upward movement of the active ingredient.

In all three the soils tested, low levels of fenthion were detected. These low levels indicate rapid degradation of the active ingredient. Data indicates migration of fenthion into the deeper soil layer in all three the soils. Some fenthion retention was found in the sandy loam soil, indicating percolation of the active ingredient through the soil layers, rather than a bolus type movement (where a pesticide front moves through the soil). Bolus type movement was observed only in the clay soil, which occurred from either macropore flow or a charge induced preferential flow.

Fenthion migrated into the deeper soil layers within 18 DAA all three soil-types tested. The changes in the slopes of the curves fitted to the data describe the changes in distribution of the pesticide over time.

Upward movement of fenthion was observed in both the sandy loam soil as well as the clay soil. In both cases this is probably due to evaporative mechanisms occurring during the dry period.

Fenthion was mobile in all three soils tested. The mobility of the active ingredient is not only limited to downward migration, but also to upward migration probably following evaporative mechanisms. Fenthion seemingly has a short residence time in all three the soils. This is probably due to rapid degradation of the active ingredient. Fenthion mobility was affected by soil type only during the first 30 days of application, where after this soil type seems to have a limited effect on its mobility.

6.3.2 Azafenidin migration under field conditions

The mobility patterns observed for azafenidin (Figures 6.4, 6.5, 6.6) showed that the active ingredient had migrated in all three soils. The migration had occurred had migrated to at least horizon 5 within the initial 18 DAA.

6.3.2.1 Azafenidin migration in sandy loam soil

The migration pattern for azafenidin in the sandy loam soil, shown in Figure 6.4, shows a ±50 % reduction in azafenidin residues in horizon 1 during the first 18 DAA. This reduction is more or less expected when considering a half-life of 12 days as determined for this soil (Chapter 5). The migration pattern further showed that azafenidin had migrated to at least horizon 5 within 18 DAA.

The migration pattern (Figure 6.4) further indicates that the applied azafenidin migrated below horizon 1 within 18 days of application. A steady decline in azafenidin residues is observed in horizon 1 from 18 to 60 DAA. This decline coincides with an increase in azafenidin residue levels in horizon 4 and 5 during the same time period. Some retention of the active ingredient in the upper soil horizons is observed (Figure 6.4).

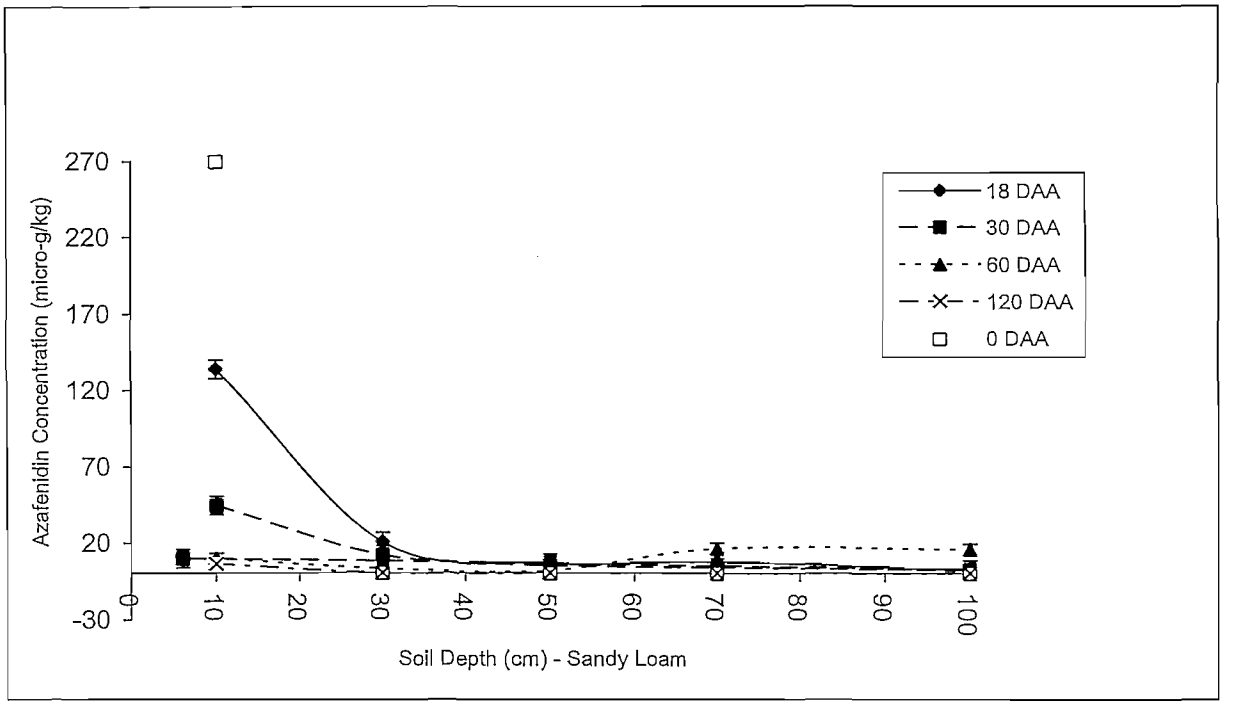


Figure 6.4. Mean azafenidin residue levels (µg kg^{-1}) detected in the sandy loam 0, 30, 60 and 120 DAA. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.2.2 *Azafenidin migration in sandy clay loam soil*

The migration pattern observed for azafenidin in the sandy clay loam soil (Figure 6.5) indicates an approximate 50 % reduction in azafenidin residue levels in horizon 1 during the first 18 DAA. The migration pattern observed in the sandy clay loam soil is similar to that found in sandy loam soil (Figure 6.4), with the exception that a higher degree of retention is observed in the sandy clay loam soil (Figure 6.5), probably due to adsorption to clay components.

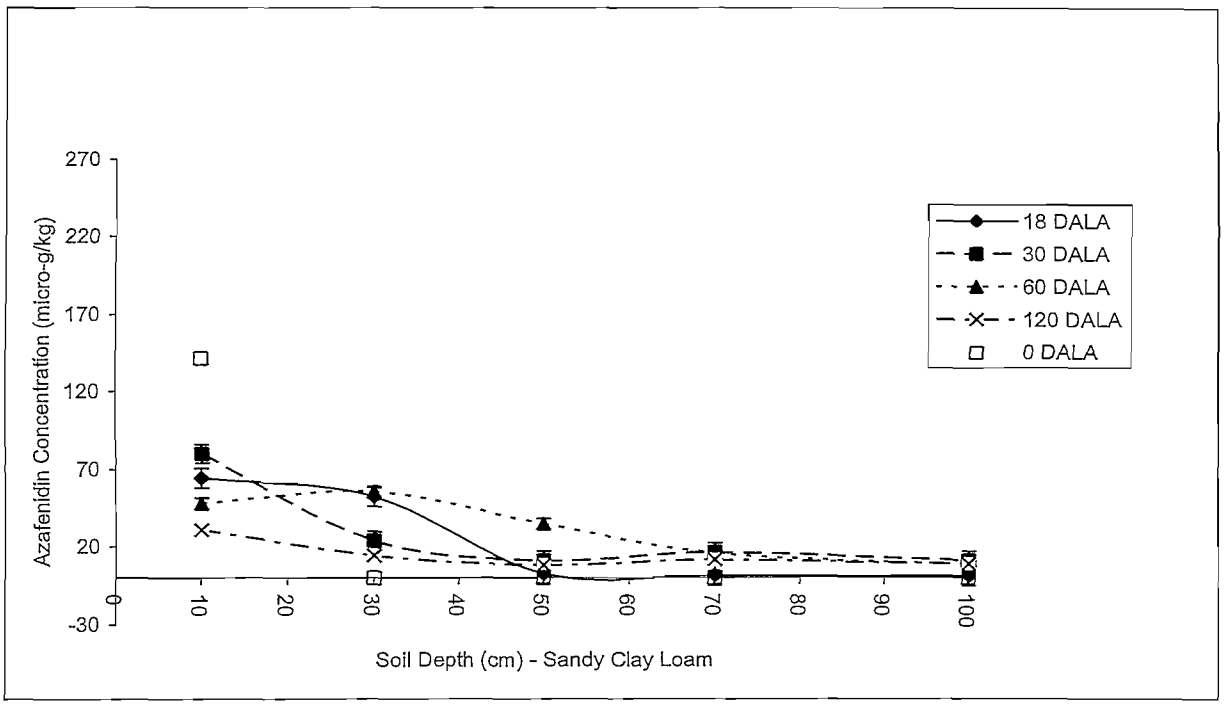


Figure 6.5. Mean azafenidin residue levels (µg kg^{-1}) detected in the sandy clay loam 0, 18, 30, 60 and 120 DAA. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.2.3 Azafenidin migration in clay soil

The migration pattern observed for azafenidin in the clay soil (Figure 6.6) indicates an approximate 80 % reduction in azafenidin residue levels in horizon 1 during the first 18 DAA. This migration pattern further indicates that azafenidin migrated to the deeper soil horizons within 18 days of application (Figure 6.6). An increase in residue levels was

observed in the horizons 3-5, coinciding with a decrease in the residue levels in horizon 1 and 2, during the initial 60 DAA. This migration pattern indicates that the azafenidin moved unhindered through the soil profile. This indicates that the active ingredient is not retained in the clay soil, contrary to that indicated by adsorption data determined in Chapter 5. The migration pattern (Figure 6.6) indicates that macropore flow of azafenidin may have occurred in the clay soil.

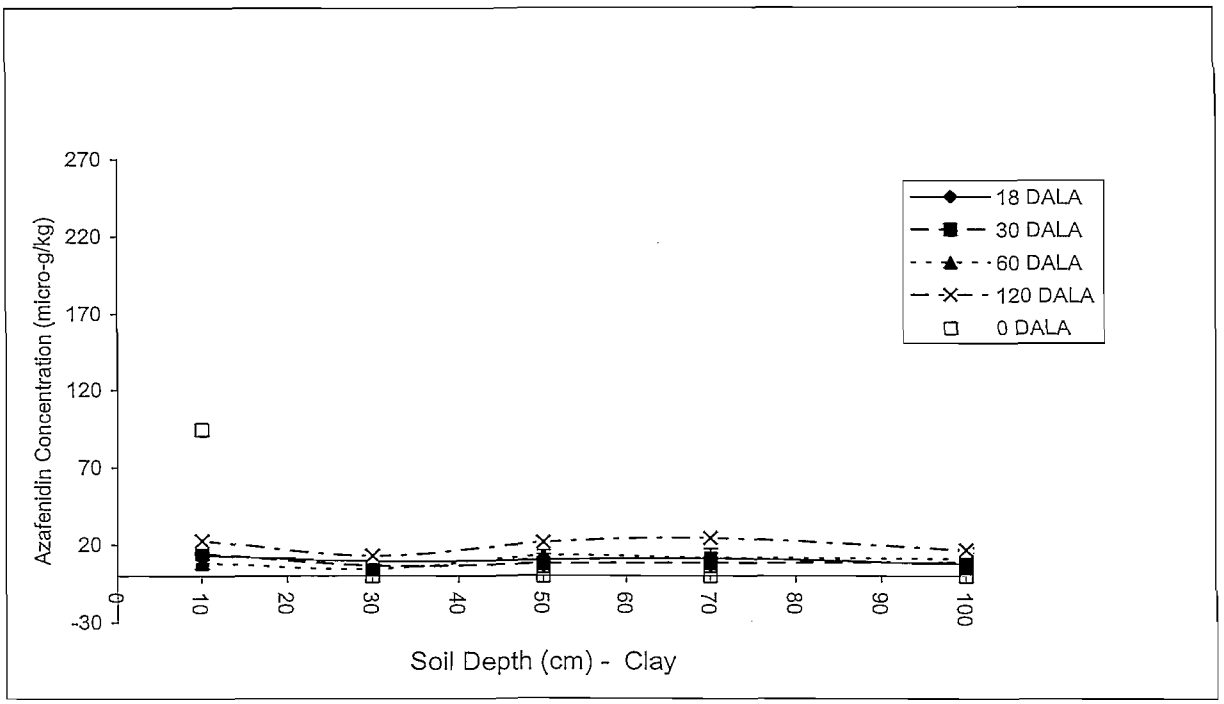


Figure 6.6. Mean azafenidin residue levels (µg kg^{-1}) detected in the clay soil 0, 18, 30, 60 and 120 DAA. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.2.4 Comparison of azafenidin migration in three field soils.

In order to compare azafenidin migration between the different soil types, regression functions were fitted to the mean measured values. The following exponential equation of pesticide concentration versus soil depth was rendered.

$$y = a + br^x$$

Where *b* is the slope, *a,* is the intercept, and *r* is base of the natural logarithm.

The distribution patterns for azafenidin 18, 30, 60 and 120 DAA are provided for each soil type in the section below.

Sandy loam

18 DAA: $y = -1.37 + 520.90\ (0.93)^x$
30 DAA: $y = 3.38 + 239.40\ (0.99)^x$
60 DAA: $y = 690.70 + -688.50\ (0.99)^x$
120 DAA: $y = -0.23 + 44.59\ (0.91)^x$

Sandy Clay Loam

18 DAA: $y = 7.44 + 250.7\ (0.933)^x$
30 DAA: $y = 12.02 + 392.7\ (0.99)^x$
60 DAA: $y = -3035 + 3099\ (0.99)^x$
120 DAA: $y = 9.749 + 150.9\ (0.91)^x$

Clay soil

18 DAA: $y = 9.30 + 4.68\ (0.933)^x$
30 DAA: $y = 7.52 + 37.6\ (0.99)^x$
60 DAA: $y = 307.20 + -300.6\ (0.99)^x$
120 DAA: $y = 18.79 + 21.62\ (0.91)^x$

Table 6.7. Comparison of the slopes of the equations for curves generated on the mean azafenidin concentrations versus soil depth 18, 30, 60 and 120 DAA.

Soil type	Slope (b)			
	18 DAA	30 DAA	60 DAA	120 DAA
Sandy Loam	520.9	239.4	-688.5	44.29
Sandy clay Loam	250.7	392.7	3099	150.9
Clay	14.68	37.6	-300.6	21.62

Sandy Loam

A decrease in the slope of the regression lines is observed over time, as the azafenidin residue levels decrease in the upper soil horizons. The active ingredient is mobilised out of the upper soil horizons, into the deeper soil horizons to such an extent that a negative slope is observed 60 DAA. The migration pattern thus shows that azafenidin had migrated into the soil profile over time, but that some retention did occur albeit short lived.

Sandy clay loam

The slopes of the fitted lines for the azafenidin residue level in the soil profile increase over time. The migration profile provided in Figure 6.5 shows that migration had occurred and comparison of slopes indicates that azafenidin may be retained in the soil. The general trend of an increasing slope over the trial period indicates a decrease in azafenidin movement to the deeper soil horizons, and an increase in retention in horizon 1 and 2.

Clay

The slope of the fitted line (Table 6.7) remains similar for the entire trial period, indicating that the distribution of azafenidin in the soil profile remained similar. A decrease in the slope is however observed at 60 DAA, indicating that at this time the movement of the active ingredient to the deeper soil horizons

General

The slope of the fitted line for the sandy loam soil decreases from 18 DAA through to 60 DAA, to the extent that the slope becomes negative at 60 DAA. This drastic decline in slope is only observed in the sandy loam soil and shows that azafenidin retention is limited in this soil.

In the sandy loam soil, on the other hand an increase in the slope is observed over time, indicating that the azafenidin is retained in the sandy clay loam. An increase in clay content is expected to lead to increased azafenidin retention in the soil. It then follows that the azafenidin retention be even higher in the clay soil. This was however not observed. In the case of the clay soil, the slope becomes negative 60 DAA, indicating that the azafenidin migrated with ease through the clay soil. The adsorption coefficients determined in Chapter 5 were similar for azafenidin on all three soils.

Similar proportions of the azafenidin applied remained in sandy clay loam and clay soils. A higher degree of migration is, however, apparent in the sandy clay loam soil. A large proportion of the applied azafenidin remained in the upper soil layer on the sandy clay loam soil, decreasing with time to proportions similar to that found in the other two soil types.

6.3.3 Tebuthiuron migration under field conditions

The migration patterns observed for tebuthiuron in all three soils are presented in Figures 6.7, 6.8 and 6.9. The migration patterns show that tebuthiuron migrated to at least horizon 5 within the initial 18 DAA.

6.3.3.1 Tebuthiuron migration in sandy loam soil

The migration pattern for tebuthiuron in the sandy loam soil, shown in Figure. 6.7, shows a ±75 % reduction in tebuthiuron residue concentration in horizon 1 during the first 18 DAA. A significant increase in residue concentrations was found at 30 DAA in the soil horizons 2 and 3, where after these concentrations declined to the end of the trial period. A similar migration pattern is observed in horizon 4 and 5, but the increase in tebuthiuron concentration is only seen 60 DAA, followed by a decline 120 DAA.

The decrease in tebuthiuron concentration in the 2nd horizon, with a concomitant increases in the next horizons, shows that migration occurred. After an initial rapid migration from horizon 1 to horizon 2 within the first 30 days after application, a slower percolation process of tebuthiuron occurred to the deeper soil layers.

The migration patterns (Figure 6.7) indicate that a transition layer exists at around 40 cm soil depth, which is not readily penetrated. This may explain why the herbicide remained predominantly in the soil horizons 1 and 2.

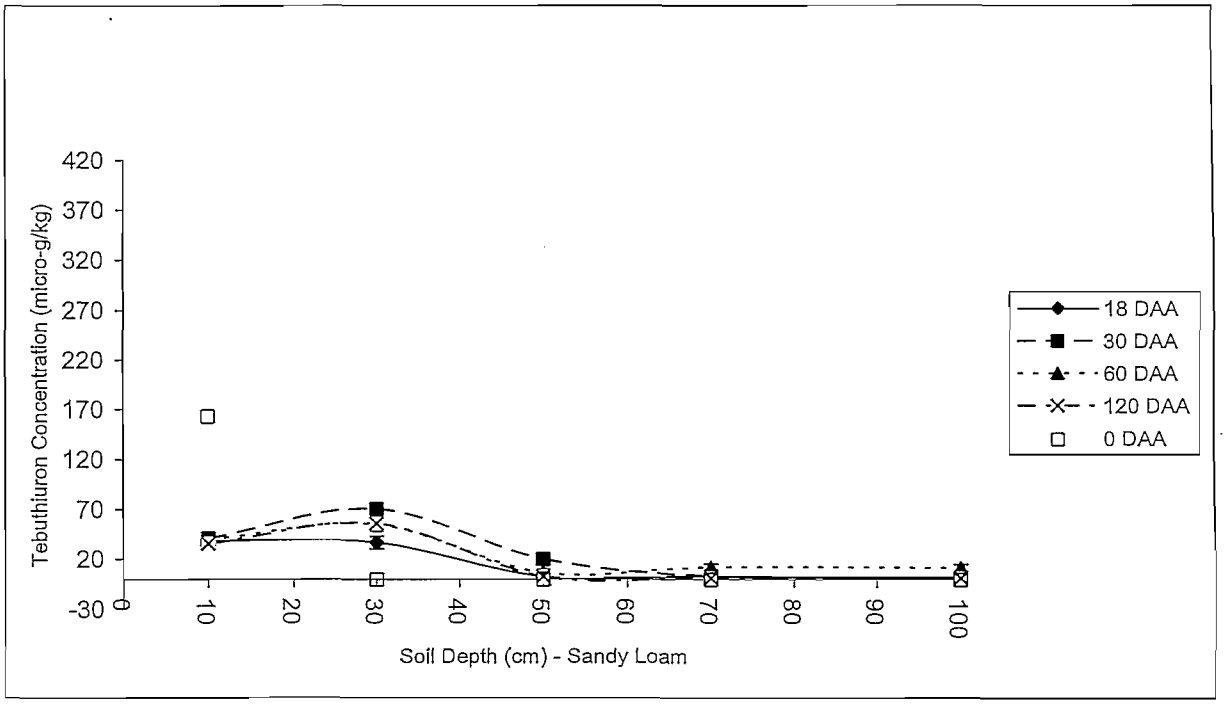


Figure 6.7. Mean tebuthiuron residue levels (µg kg^{-1}) in sandy loam soil 0, 18, 30, 60 and 120 DAA. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.3.2 *Tebuthiuron migration in sandy clay loam soil*

The migration pattern for tebuthiuron in the sandy clay loam soil, shown in Figure 6.8, shows a drastic reduction (±60 % reduction) in tebuthiuron residue concentration in horizon 1 during the first 18 DAA.

A decrease in tebuthiuron residue levels was observed over time in the soil horizons 1 to 3, coinciding with an increase in residue levels in soil horizons 4 and 5 during the initial 18 DAA (Figure 6.8). There after a steady decline in tebuthiuron residue concentration is found in horizon 1-4. The tebuthiuron concentration in horizon 5 remained constant throughout the trial period.

The migration pattern for tebuthiuron in sandy clay loam soil (Figure 6.8) shows that the tebuthiuron percolated to the deeper soil layers. Some tebuthiuron retention was, however, observed in horizons 1 and 2.

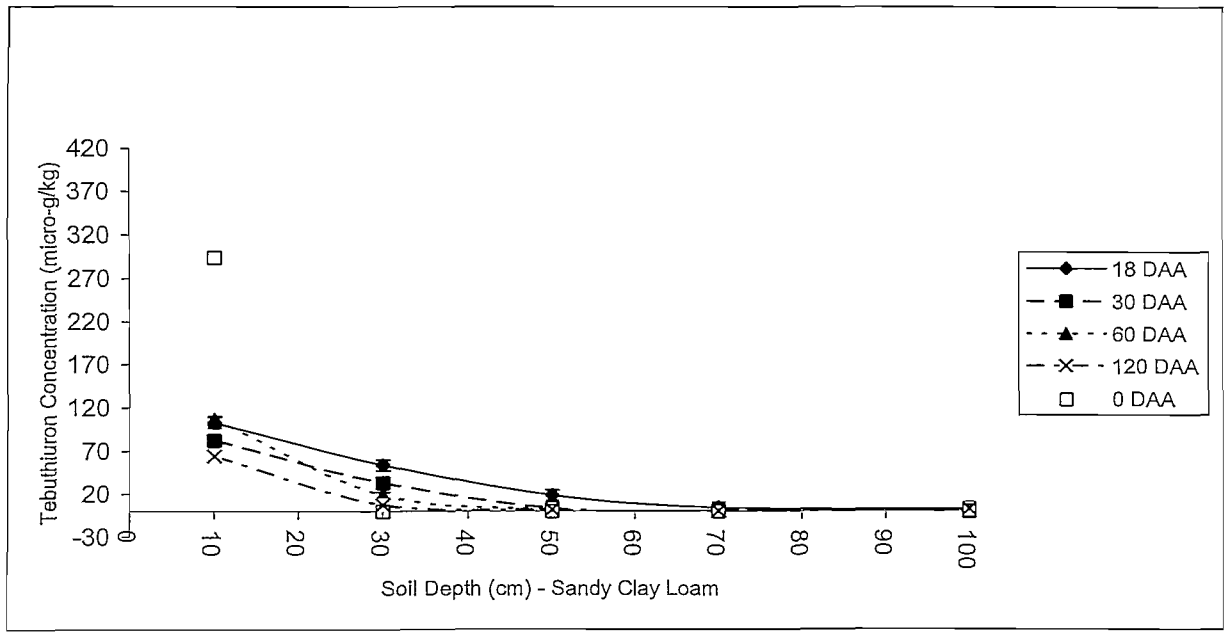


Figure 6.8. Mean tebuthiuron residue levels (µg kg^{-1}) detected in the sandy clay loam soil 0, 18, 30, 60 and 120 DAA. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.3.3 Tebuthiuron migration in clay soil

The migration pattern for tebuthiuron in the clay soil, shown in Figure 6.9, shows a drastic reduction (±60 % reduction) in tebuthiuron residue concentration in horizon 1 during the first 18 days after application (DAA).

A decrease in tebuthiuron residue levels was observed over time in the soil horizons 1 and 2 within the initial 30 DAA. This decrease in the upper 2 soil horizons, during the first 30 DAA, is followed by an increase in the concentrations in horizon 4 between 30 and 60 DAA.

The tebuthiuron migration profile 30 DAA did not differ significantly from that found 18 DAA. During the following two time intervals, a decrease in tebuthiuron concentration is observed in soil horizon 1.

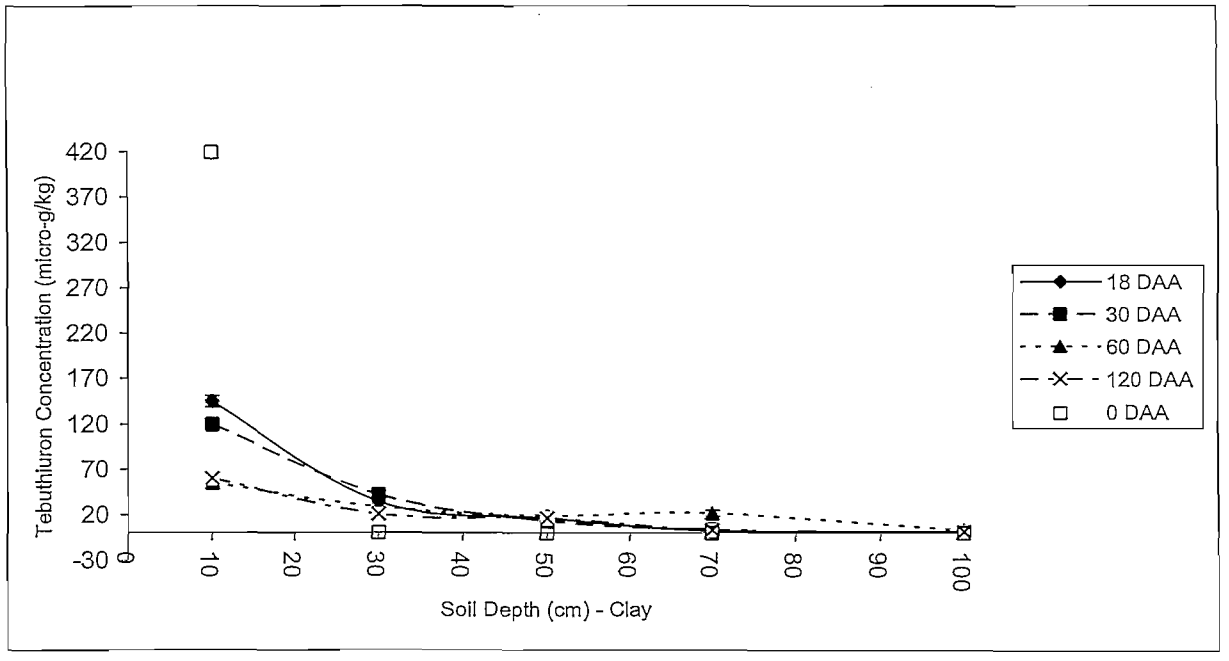


Figure 6.9. Mean tebuthiuron residue levels (µg kg^{-1}) detected in the clay soil 0, 18, 30 60 and 120 DAA. Horizon 1, 0 – 20 cm is indicated at 10 cm, horizon 2, 20 – 40 cm is indicated at 30 cm, horizon 3, 40 – 60 cm is indicated at 50 cm, horizon 4, 60 – 80 cm is indicated at 70 cm, and horizon 5, 80 - 120 cm at 100 cm. Standard deviations are shown.

6.3.3.4 Comparison of tebuthiuron migration in three field soils.

In order to compare tebuthiuron migration between the different soil types, regression functions were fitted to the mean measured values. The following exponential equation of pesticide concentration versus soil depth was rendered:

$$y = a + br^x$$

Where *b* is the slope, *a* the intercept, and *r* is base of the natural logarithm.

The curve describing the distribution of tebuthiuron 18, 30, 60 and 120 DAA are provided per soil type below.

Sandy loam soil

18 DAA: $y = 3.95 + 111.5(0.95)^x$
30 DAA: $y = 11.84 + 102.7(0.95)^x$
60 DAA: $y = 16.68 + 106.6(0.93)^x$
120 DAA: $y = 5.61 + 102.5(0.93)^x$

Sandy Clay Loam

18 DAA: $y = 5.17 + 285.6(0.95)^x$
30 DAA: $y = -5.07 + 199.7(0.95)^x$
60 DAA: $y = -4.27 + 377.7(0.93)^x$
120 DAA: $y = -5.80 + 160.8(0.93)^x$

Sandy Clay Loam

18 DAA: $y = -5.10 + 406(0.95)^x$
30 DAA: $y = -6.73 + 283(0.959)^x$
60 DAA: $y = 13.49 + 146.7(0.93)^x$
120 DAA: $y = 1.12 + 142.7(0.93)^x$

Table 6.8. Comparison of the curve slopes generated on mean tebuthiuron residue levels detected versus soil depth for the time intervals 18, 30, 60 and 120 DAA.

Soil type	Slope (b)			
	18 DAA	30 DAA	60 DAA	120 DAA
Sandy Loam	111.5	102.7	106.6	102.5
Sandy clay Loam	285.6	199.7	377.7	160.8
Clay	406	283	146.7	142.7

Sandy Loam soil

When comparing the slopes of the fitted curves for the different time intervals, it is clear limited changes had occurred in the slopes (b) with time. This lack of change in the slopes leads to the conclusion that tebuthiuron migration rates did not change with time, and that for the sandy loam soil, tebuthiuron migration is likely to be fairly constant over time. Further it is likely that the tebuthiuron distribution observed within the first 18 day of application will remain.

Sandy Clay Loam

A general trend of a decrease in the slope of the fitted curves over time was found for tebuthiuron on the sandy clay loam soil. There was however an increase in the slope, which is also observed in the field migration patterns. It is deduced that the active ingredient moved to deeper soil layers, and was not retained in any specific layer, but at 60 DAA upward movement of tebuthiuron is observed.

The organic carbon content in these two horizons were higher than of the deeper horizons. The indication of retention of the active ingredient in the field migration studies is not corroborated by the results of the adsorption coefficient studies in Chapter 5. The results presented in Chapter 5 would indicate that the active ingredient will not be retained in the topsoil and should thus flow through these layers.

Clay

Comparison of the slopes of the curves fitted for tebuthiuron on the clay soil shows a decrease in the slope over time. This decrease is slope is seen as a decrease in tebuthiuron residue levels in the upper soil horizons and an increase in the deeper soil layer. It is deducted that tebuthiuron moves with ease into the deeper soil horizons.

General

Tebuthiuron movement was the highest in the sandy loam soil. There are also indications of limited retention of the active ingredient in the deeper soil layers 60 DAA, which had decreased by day 120, probably due to migration having occurred below horizon 5. Excessive migration in the sandy loam soil is not unexpected, as tebuthiuron has been shown to have an adsorption coefficient of as low as 20 ml g^{-1} (Chapter 5).

Similar tebuthiuron migration patterns are observed on the clay and sandy clay loam soils. The extent of retention observed is however higher on the sandy clay loam soil as

compared to the clay soil. The K_{oc} determined for tebuthiuron in the clay soils were higher than those for the sandy clay loam soil (Chapter 5). One would therefore expect higher tebuthiuron retention on the clay soil. The higher retention observed in the sandy clay loam therefore provides a contradiction.

The lower degree of tebuthiuron retention in the clay soil may be due to the higher organic carbon content (Table 5.1), which would indicate higher microbial activity, and thus higher degradation rates in the clay soil. However, the tebuthiuron DT_{50}'s determined in these soils (Chapter 5) indicate a DT_{50} in clay soil of 576 days. This indicates that the decrease in tebuthiuron concentration observed in the upper horizons of the clay soil is not likely due to degradation. The decrease in tebuthiuron concentration observed in the upper horizons of the sandy clay loam soil are comparable with the half-life of 119 days determined (Chapter 5).

Percolation movement, as observed on the sandy loam soil leads to higher retention than that found where preferential flow is observed. The higher retention observed in the sandy clay loam, may therefore be due to a combination of percolation flow and preferential flow and that the flow on the clay soil is primarily preferential flow. Thus the higher degree of retention may be purely due to slower movement rather than higher adsorption. It is therefore suggested that the lower degree of tebuthiuron retention on the clay soil is due to preferential flow occurring in the clay soil.

The migration pattern for tebuthiuron on the three soils tested (Figure 6.1 – Figure 6.3), indicates that tebuthiuron is mobile in all three the soils. The lack of a rapid increase in residues, in soil horizons 2 to 5 over time on the clay and sandy clay loam soils, as found on the sandy loam soil, indicates that tebuthiuron mobility is lower in these two soils as compared to the sandy loam.

6.3.4 Model Evaluation

In this section the experimental work will be discussed in which the pesticide migration patterns determined were compared to data generated during model runs. The models selected and their input parameters are provided in Section 6.2.6.

The models were run using the input data generated in Chapter 5. In order to determine the extent to which the model predicted data corresponds with actual field migration data generated in field trials (Section 6.3.1), predicted active ingredient concentrations per soil depth were plotted against measured values. Where a zero constant (intercept) is found and a slope of 1, this would indicate a perfect fit. Where a perfect fit is found, it means that the model predictions and the measured values were the same. An indication of the extent of fit is provided as the percentage fit. This approach is similar to that followed by Brown (1996) and Walker (1991).

In the graphs that follow, the X=Y line or ideal fit, is shown as a dotted line. Any points that fall above the X=Y line, indicates that the model is over-predicting migration, whereas Points that fall below the X=Y line indicate under-prediction of the model.

6.4 Comparison of model prediction and field migration data

6.4.1 Fenthion migration predictions

6.4.1.1 Fenthion – sandy loam soil

Results of comparisons for fenthion migration against the models VARLEACH, PELMO and PESTAN are shown in Figure 6.10. Both VARLEACH and PELMO predicted that fenthion would not be dispersed in the sandy loam soil beyond horizon 1. VARLEACH predicted a high rate of degradation of fenthion in the sandy loam soil, whereas PELMO predicted limited degradation. Because of the high concentrations predicted in the topsoil layer by these two models, the percentage correlation with measured values is low. This is especially relevant to the PELMO predictions.

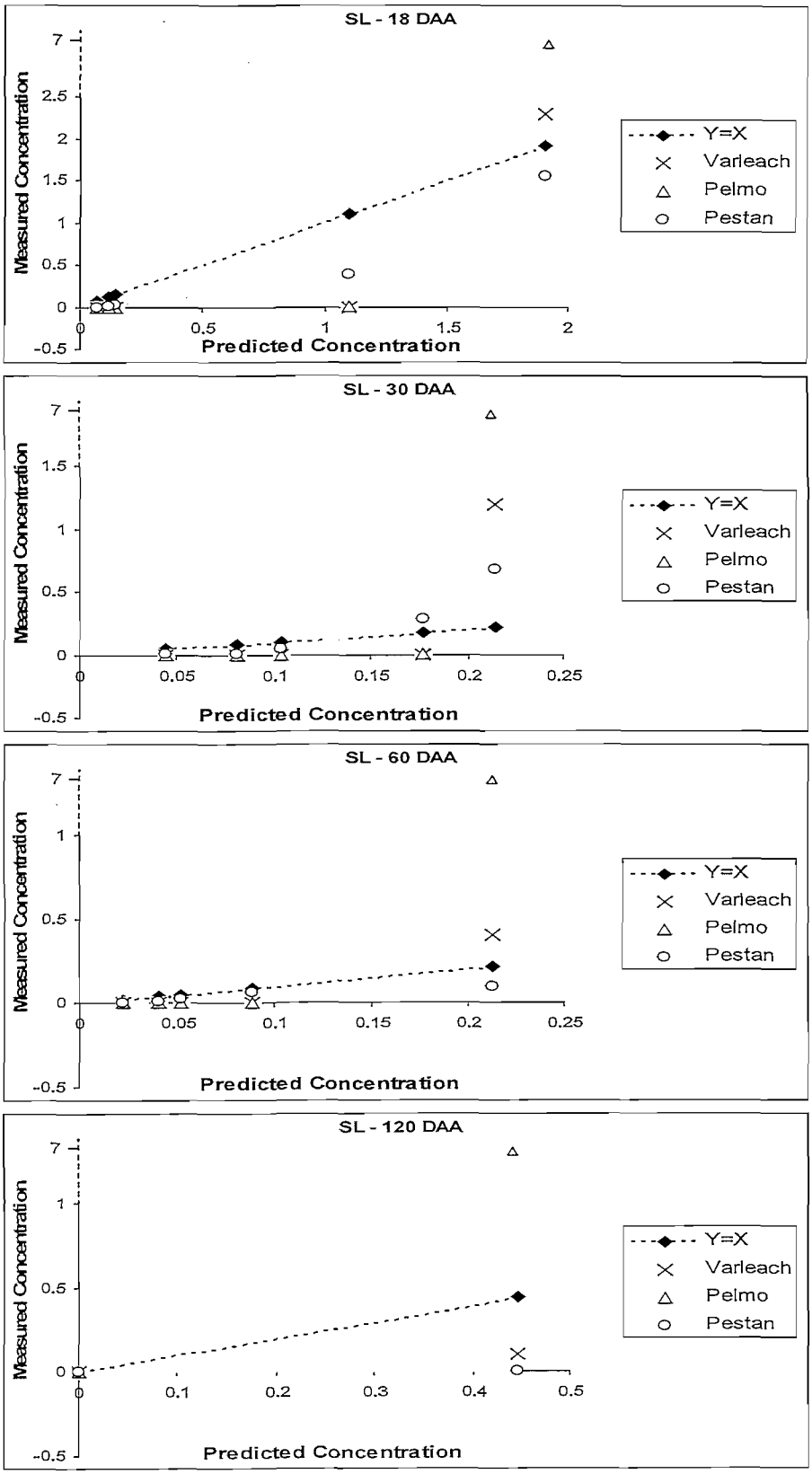


Figure 6.10. Comparison of measured fenthion concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for sandy loam soil (SL), 18, 30, 60 and 120 DAA.

PESTAN predicted fenthion migration only up to horizon 4 within 18 DAA. PESTAN, under-predicted the extent of fenthion dispersion through the soil horizon. Even so, the PESTAN predictions did follow the observed values satisfactorily.

6.4.1.2 Fenthion – sandy clay loam soil

Results of comparisons for fenthion migration against the models VARLEACH, PELMO and PESTAN are shown in Figure 6.11. The VARLEACH and PELMO models predicted that fenthion would not migrate out of horizon 1 of the sandy clay loam soil, even after 120 days. VARLEACH predicted rapid degradation of the active ingredient over the trial period with only approximately 1 % of the applied active ingredient remaining at the end of the trial period. PELMO on the other hand predicted almost no degradation of the active ingredient.

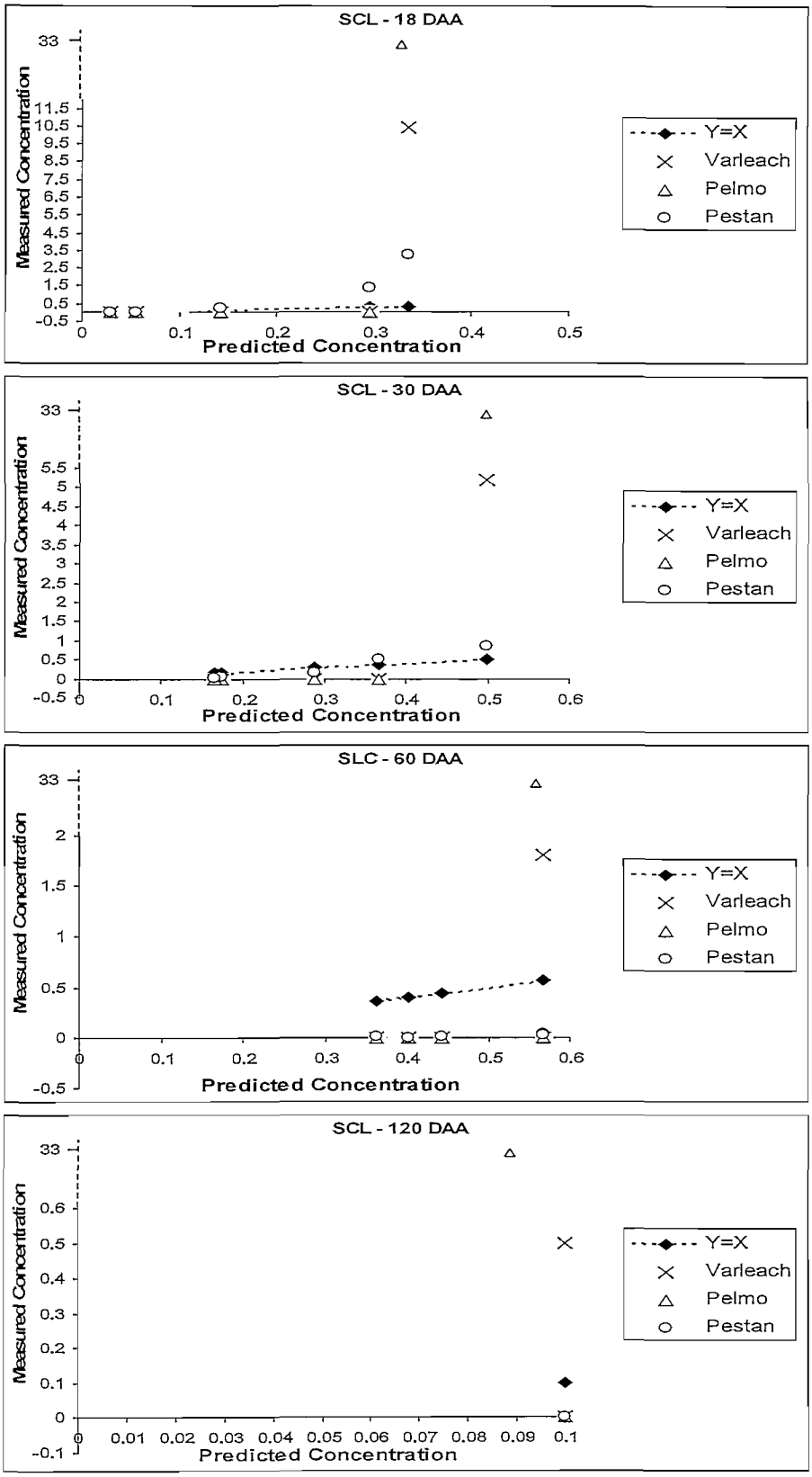


Figure 6.11. Comparison of measured fenthion concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for sandy clay loam 18, 30, 60 and 120 DAA.

PESTAN predicted fenthion migration to horizon 5 within 18 DAA. The model overestimates the fenthion concentration dispersed through the soil profile, which is probably related to the manner in which the model takes degradation into account. Overall, the PESTAN model gives a relatively reliable indication of fenthion dispersion in the soil profile with time.

6.4.1.3 Fenthion – clay soil

Results of comparisons for fenthion migration against the models VARLEACH, PELMO and PESTAN are shown in Figure 6.12. The models VARLEACH and PELMO predicted that fenthion would not migrate beyond horizon 1 for the entire trial period. The percentage correlation for the periods 60 and 120 DAA was 100 %. The high correlation is likely due to the models predicting that no fenthion movement would occur, rather than the model being able to simulate the upward mobility observed.

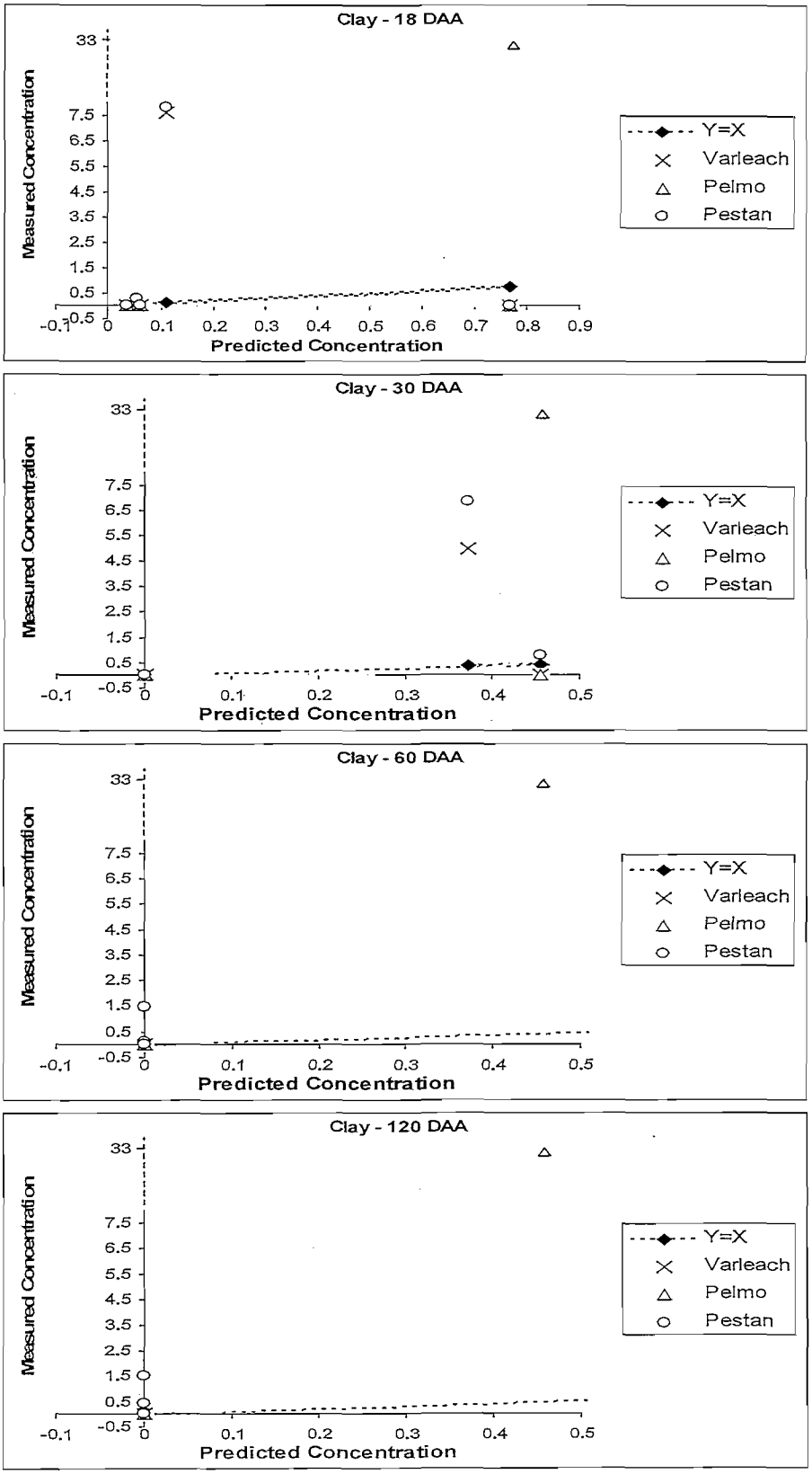


Figure 6.12. Comparison of measured fenthion concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for the clay soil 18, 30, 60 and 120 DAA.

PESTAN predicted slow movement of fenthion to the deeper soil layers, reaching horizon 5 120 DAA. The model over-predicts the fenthion concentrations in soil for all time intervals.

The models evaluated did not simulate the upward mobility observed in the clay and sandy loam soils where fenthion was applied. As was found with tebuthiuron migration predictions, VARLEACH and PELMO rendered migration predictions for fenthion on all three soils, which vastly under-estimate the observed migration potential. PESTAN tended to over-estimate the fenthion migration potential on all three-soil types tested. None of the models evaluated gave an exact fit for fenthion observed concentrations versus model predicted concentrations.

6.4.2 Azafenidin migration predictions

6.4.2.1 *Azafenidin – sandy loam soil*

Results of comparisons for azafenidin migration against the VARLEACH, PELMO and PESTAN models for sandy loam soil are shown in Figure 6.13. As was found on the sandy clay loam soil, both the VARLEACH and PELMO models predicted that azafenidin would not be dispersed in the sandy loam soil beyond horizon 1. As with fenthion, the VARLEACH model predicted a high rate of degradation of azafenidin in the sandy loam soil, whereas the PELMO model predicted limited degradation.

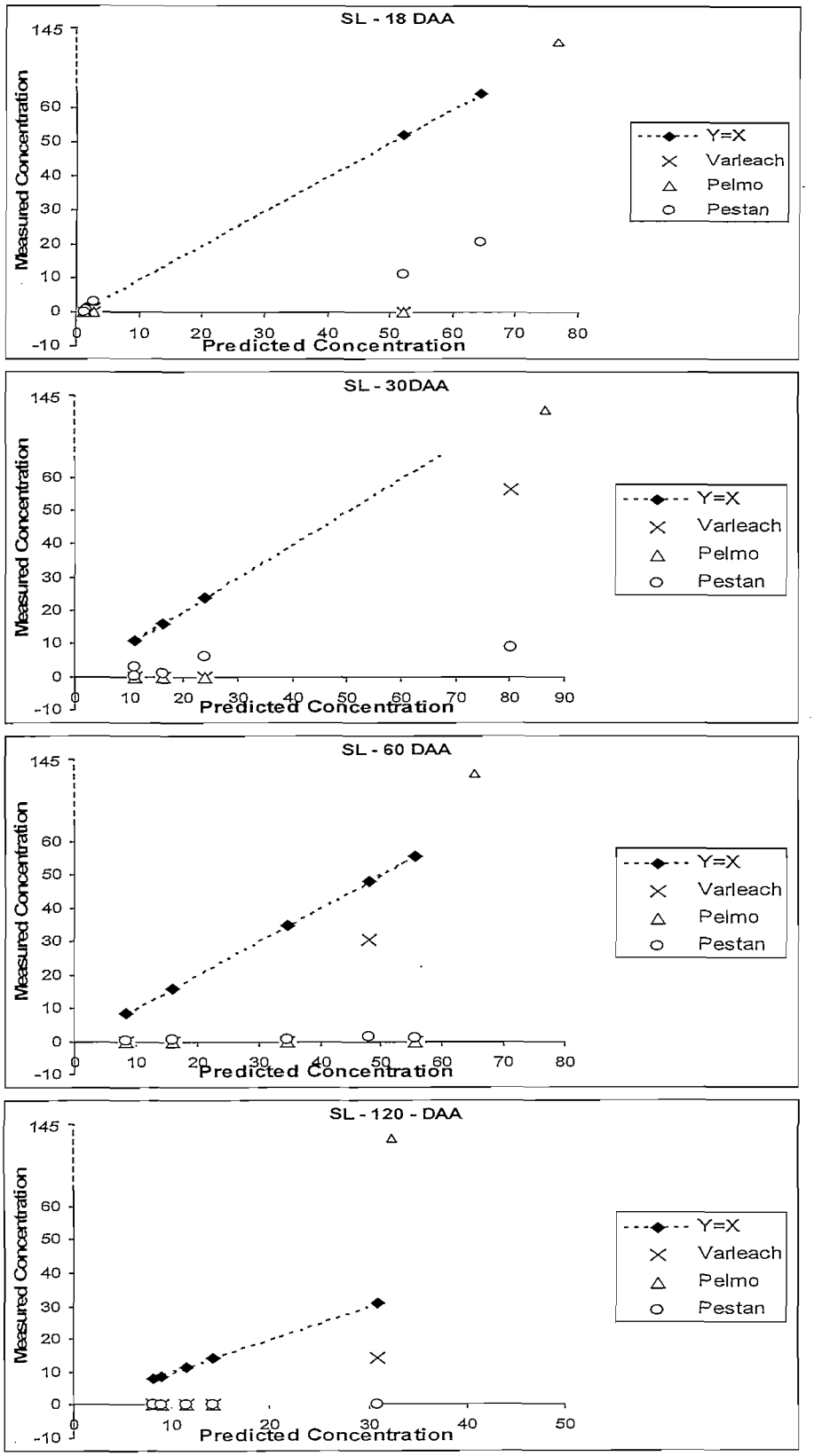


Figure 6.13. Comparison of measured azafenidin concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for the sandy loam soil 18, 30, 60 and 120 DAA.

PESTAN predicted azafenidin migration to horizon 5 within 18 days of application. PESTAN over-predicted the azafenidin levels in all soil horizons. PESTAN does, however, follow the azafenidin dispersion pattern observed in field trials to some extent.

6.4.2.2 *Azafenidin – sandy clay loam soil*

Results of comparisons for azafenidin migration against the models VARLEACH, PELMO and PESTAN are shown in Figure 6.14. Similarly to the predictions for fenthion, the VARLEACH and PELMO models predicted that azafenidin would not migrate out of horizon 1 of the sandy clay loam soil at all. VARLEACH predicted azafenidin degradation over the trial period with approximately 18 % of the applied active ingredient remaining at the end of the trial period. PELMO, on the other hand, predicted almost no degradation of the active ingredient.

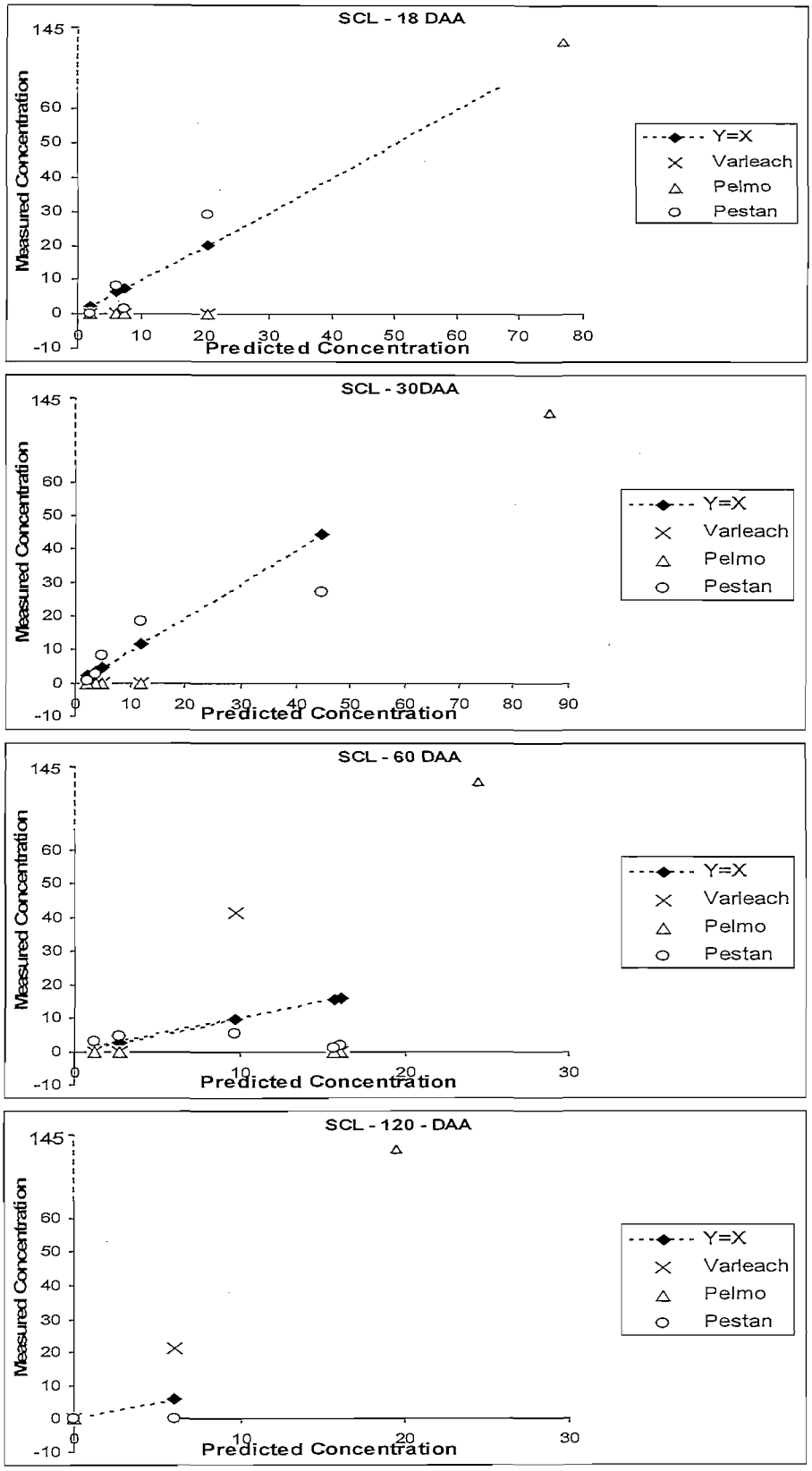


Figure 6.14. Comparison of measured azafenidin concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for the sandy clay loam (SCL), 18, 30, 60 and 120 DAA.

PESTAN predicted azafenidin migration to horizon 5 within the first 18 days of application to the sandy clay loam. The model renders a correlation of above 60% throughout. However, PESTAN under-estimated the azafenidin concentration dispersed through the soil profile. It seems as if the model over-estimated the rate of azafenidin degradation.

6.4.2.3 *Azafenidin – clay soil*

Results of comparisons for azafenidin migration against the models VARLEACH, PELMO and PESTAN are shown in Figure 6.15.

The VARLEACH and PELMO models predicted that azafenidin would not migrate beyond horizon 1. The percentage correlations of predicted values versus measured values were low for both these models. As with fenthion and tebuthiuron, PELMO seems to underestimate the rate of degradation of azafenidin.

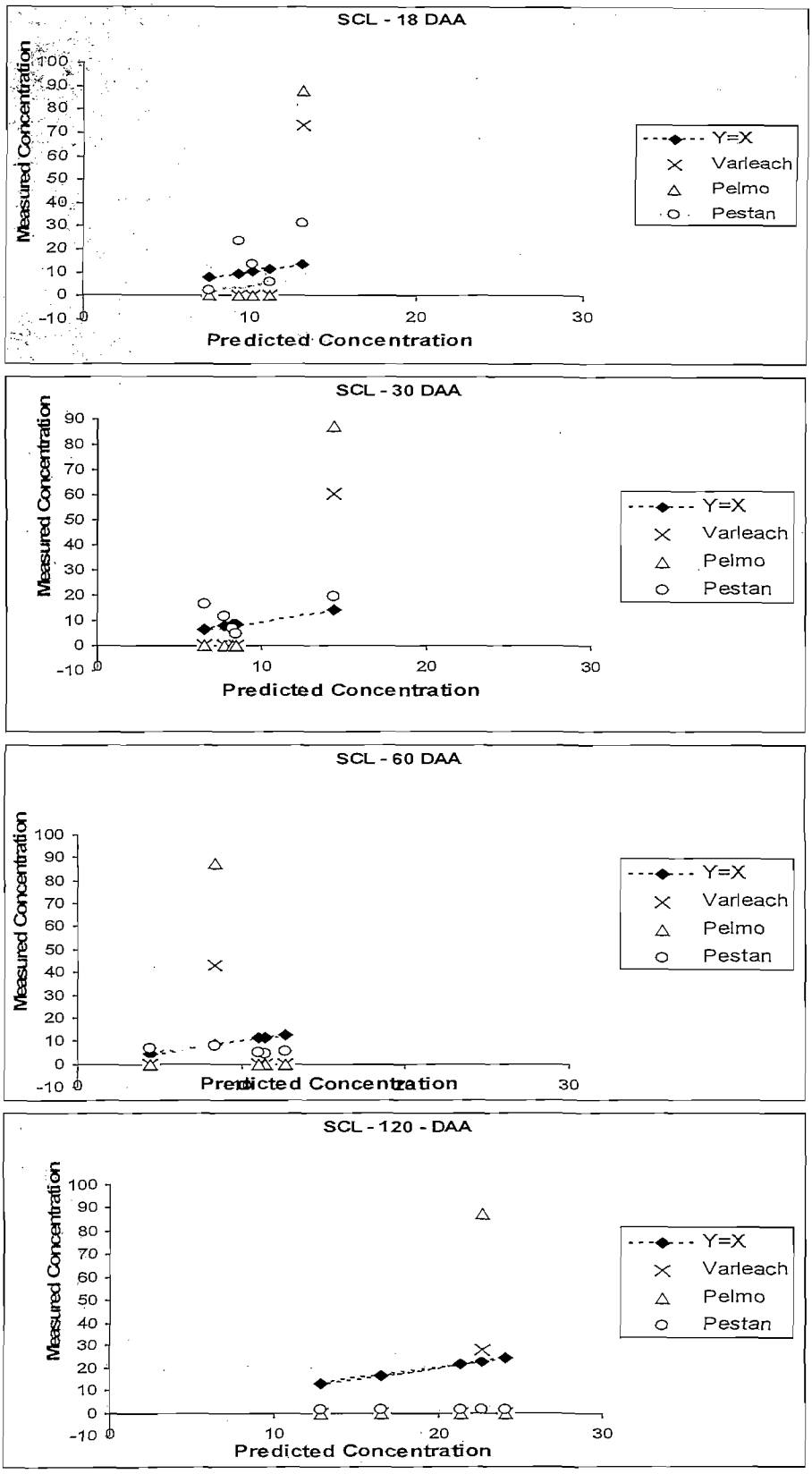


Figure 6.15. Comparison of measured azafenidin concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for the clay soil (clay), 18, 30, 60 and 120 DAA.

PESTAN predicted that azafenidin would reach horizon 5, 30 DAA. The model over-predicts the azafenidin concentration in the soil profile up to 60 DAA, but under-predicts the concentration expected 120 DAA. The percentage correlation rendered for this model was generally low. However, of the three models evaluated, PESTAN gave the more satisfactory predictions as to the migration potential of azafenidin.

As was found with the other two active ingredients, migration predictions by the VARLEACH and PELMO models rendered migration predictions for azafenidin on all three soils which vastly under-estimated the observed migration potential. The PESTAN model tended to over-estimate the azafenidin concentrations in deeper soil layers on all three soil types tested.

6.4.3 Tebuthiuron migration predictions

6.4.3.1 *Tebuthiuron – sandy loam soil*

Results of comparisons for tebuthiuron migration against the VARLEACH, PELMO and PESTAN models are shown in Figure 6.16.

The VARLEACH and PELMO models predicted only minor migration of tebuthiuron within the trial period. The models predict movement only up to horizon 2. The percentage fit gained from the correlation analysis, however, indicates a fit of 70 - 89 % over the time period. This would indicate that the model predictions fit the measured values well. However, the correlation is based on two points only, and should be considered with care. PESTAN on the other hand predicted migration up to horizon 5, although the concentrations were over-predicted. PESTAN predictions were constantly closer to those measured in the field study.

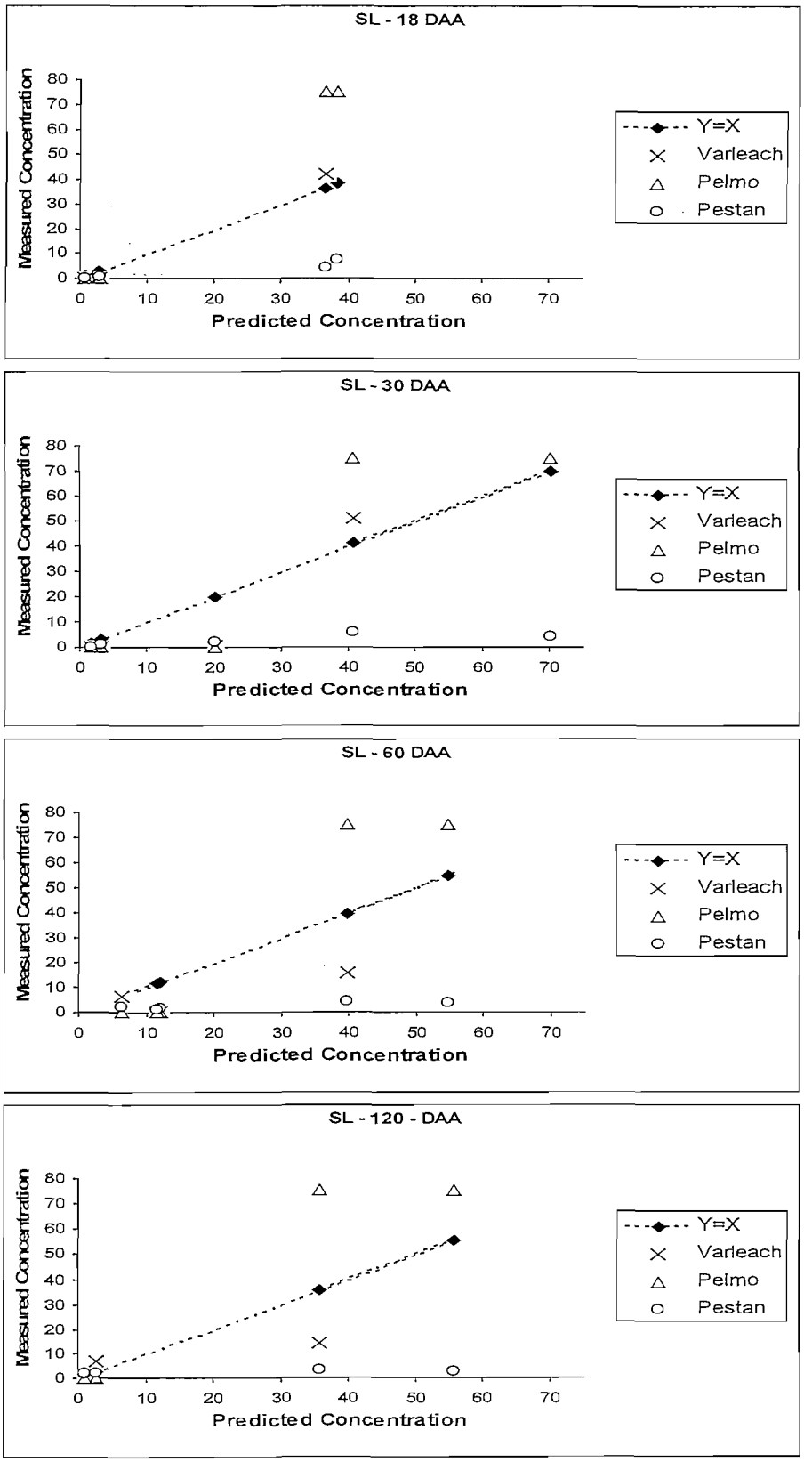


Figure 6.16. Comparison of measured tebuthiuron concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for sandy loam soil, 18, 30, 60 and 120 DAA.

6.4.3.2 Tebuthiuron – sandy clay loam soil

Results of comparisons for tebuthiuron migration based on the models VARLEACH, PELMO and PESTAN are shown in Figure 6.17.

The VARLEACH model predicted only minor migration of tebuthiuron within the trial period. The model predicts that tebuthiuron will not migrate past horizon 2 in the sandy clay loam soil. The percentage fit gained from the correlation analysis, however, indicates a fit of 70 - 89 % over the time period. This would indicate that the model predictions fit the measured values well. However, the correlation is based on two points only, and should be considered with care.

PELMO migration predictions were more conservative than that predicted by VARLEACH. The PELMO model predicted that no migration would occur beyond horizon 1. The migration pattern from the PELMO predictions for tebuthiuron on the sandy clay loam soil was similar to those predicted by the VARLEACH model. Again the percentage fit was high (>80 %), but here based only on one correlating data point.

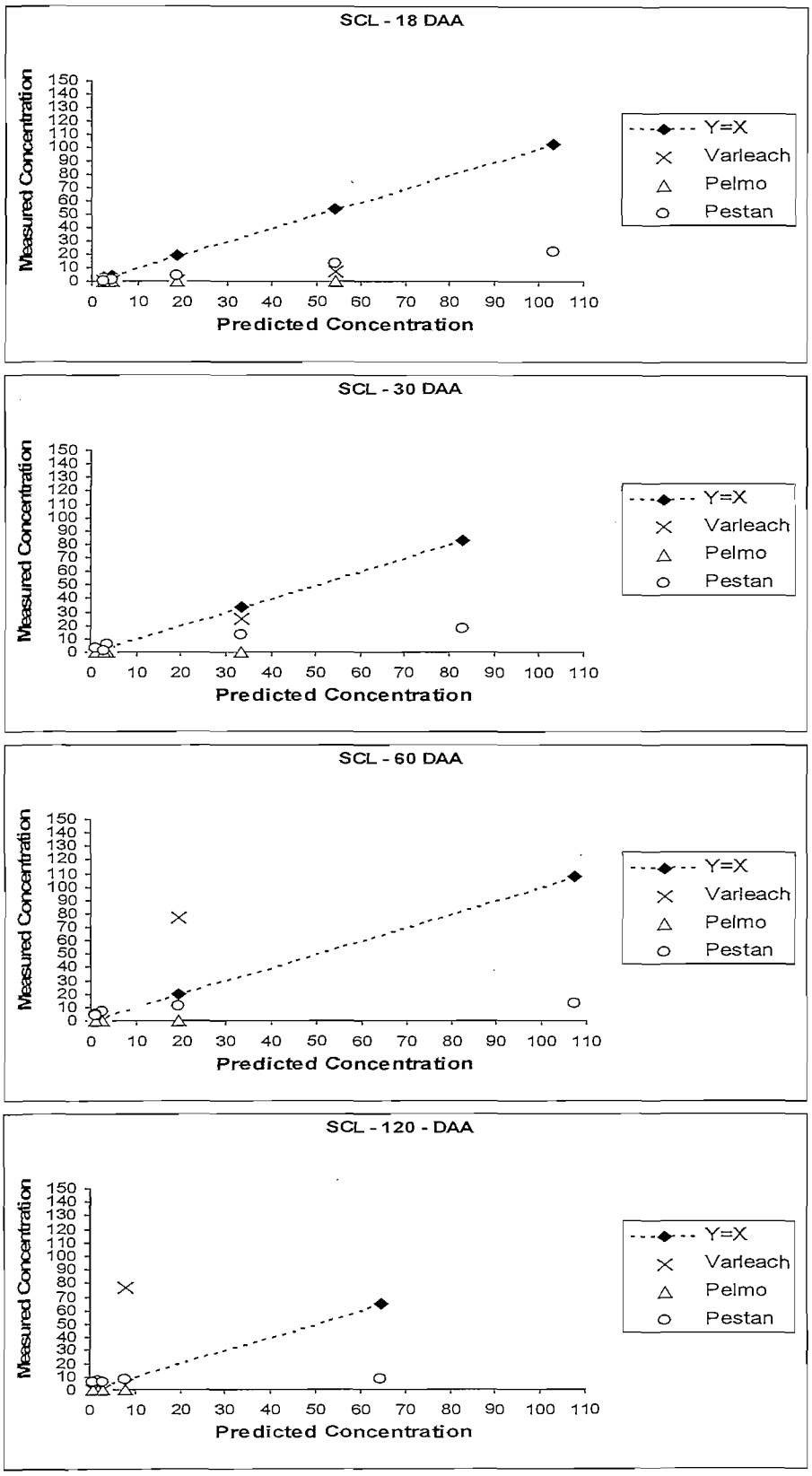


Figure 6.17. Comparison of measured tebuthiuron concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for the sandy clay loam (SCL), 18, 30, 60 and 120 DAA.

The PESTAN model predicted tebuthiuron migration to the 120 cm soil depth within the first 18 days of application to the sandy clay loam soil with a percentage correlation of 82 %, remaining up to 30 DAA. The percentage correlation decreased to 42 % by 120 DAA. The decreased fit is due to the model PESTAN over-estimating the extent of tebuthiuron migration on this soil, i.e. higher concentrations predicted in the deeper soil layers than those measured.

6.4.3.3 Tebuthiuron – clay soil

Results of comparisons for tebuthiuron migration against the models VARLEACH, PELMO and PESTAN are shown in Figure 6.18.

The VARLEACH and PELMO models predicted that no tebuthiuron would migrate beyond horizon 1 throughout the trial period. Despite this agreement for both models at all time intervals were high, indicating a good fit of measured versus predicted values. The correlation is, however, misleading as it is based only on a single correlation point. The models both predict high tebuthiuron concentrations remaining in horizon 1 for the entire time.

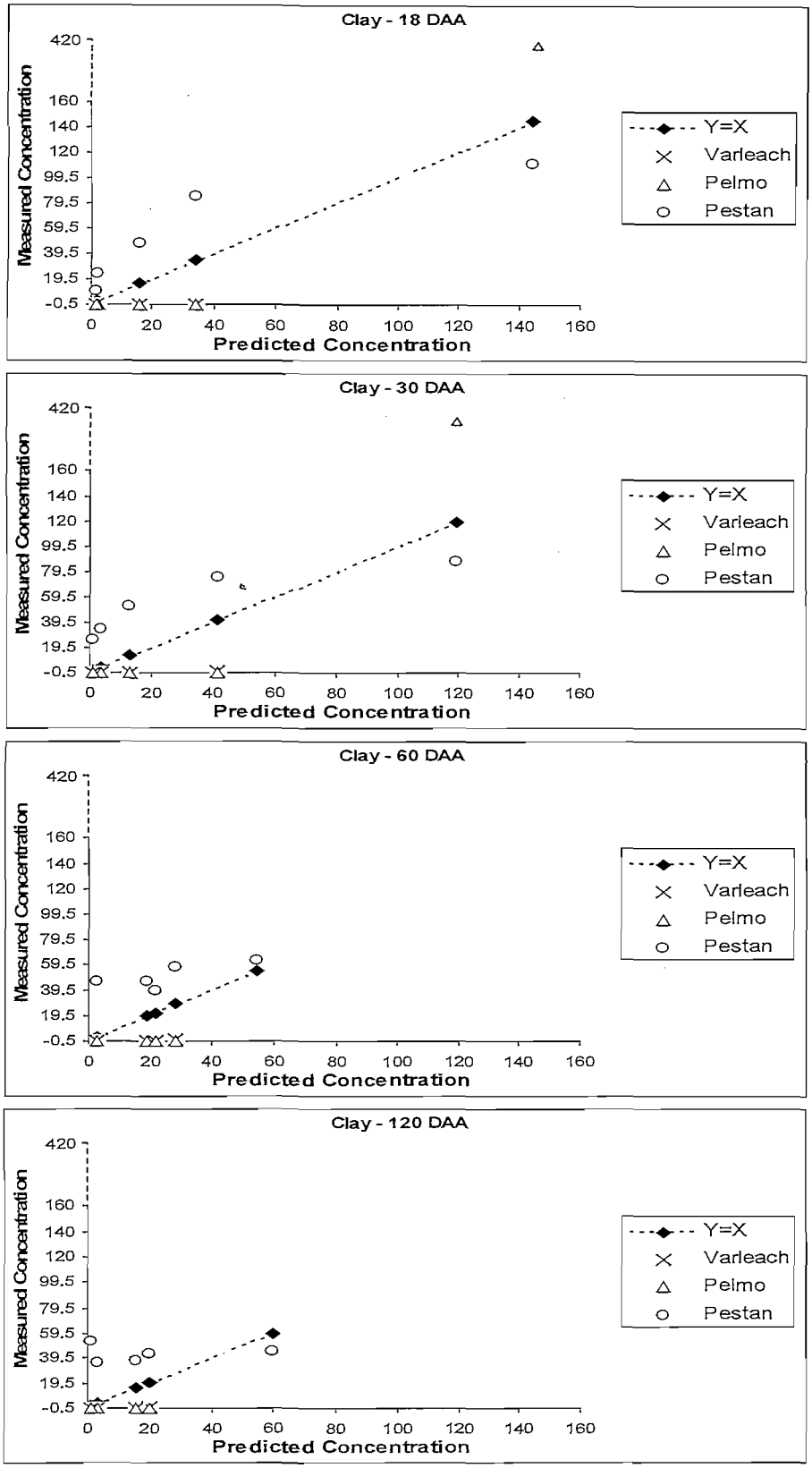


Figure 6.18. Comparison of measured tebuthiuron concentrations (µg kg^{-1}) from migration trials and model predicted concentrations (µg kg^{-1}) from the VARLEACH, PELMO and PESTAN models for the clay soil, 18, 30, 60 and 120 DAA.

The predicted tebuthiuron migration for the model PESTAN correlated well with observed migration. PESTAN predicted tebuthiuron migration to the deepest soil layer within 18 days of application as was observed. The percentage correlation was above 70 % for the 18 DAA and 30 DAA events, but decreased to below 50 % for the remaining two time periods. The reduced prediction correlation is due to PESTAN predicting a more even spread of tebuthiuron through the soil profile i.e. higher concentrations in the deeper soil layers than those that were measured.

The VARLEACH and PELMO models rendered migration predictions for tebuthiuron on all three soils, which vastly underestimate the migration potential observed. PESTAN tended to overestimate the migration potential of this active ingredient on all three soil types tested. None of the models evaluated gave a close fit for tebuthiuron observed concentrations versus model predicted concentrations.

6.5 General discussion

6.5.1 Assumptions and uncertainties

Analyses validation

Extensive analytical method validation was done for each soil / pesticide combination. In addition fortified matrix samples and blank samples were included for the determination of recovery, as well as potential interfering peaks. Pesticide residue stability in samples under storage was determined over a 12-week storage period. All active ingredients were found stable over the 12-week period when kept in storage at temperatures not exceeding –18°C.

Soil hydraulic conductivity

Soil hydraulic conductivity could not be determined for the soils. The values used as model inputs were therefore derived from soils with a similar composition and type. It is

thus possible that the hydraulic conductivity values used in the model runs were not exactly the same as for the soils tested. This is probably not of major concern, because the PESTAN model uses similar generic data, which was generated for soil from the United States.

Variability of pesticide residue analytical results.

Variability in analyses results is not uncommon and can be expected in field trials such as these described. Varying environmental conditions at the time of application and soil variability make it impossible to apply a pesticide to a field soil and obtain exactly the same soil pesticide residue level. In trials conducted in closed spray chambers variability in delivery rate of up to 20 % was commonly found (Meinhardt unpublished data).

Weed free environment

The pesticides were applied to a flat, even, weed free surface. The applications of glyphosate for weed management were directed target sprays to the weeds, and these are not expected to have an effect on the migration patterns for the pesticides under investigation, as minimal interaction of the glyphosate with soil is expected. The weed free or vegetation free environment, under which the trials were conducted, is representative of an uncropped situation (Brown, 1996; Walker, 1991; Weber and Whitare, 1982). The migration patterns observed may therefore be different from a cropped situation. In a cropped situation the presence of plant material may lead to uptake of the pesticides, which is not taken into account in an uncropped situation. In addition the presence of roots and root channels in the soil may lead to increased preferential flow.

6.5.2 Pesticide migration in local soils

The field migration data generated shows that all three the active ingredients tested are likely to migrate into the soil horizon, irrespective of the soil type. The data further shows, that it is likely that certain pesticides may migrate deeper than 120 cm into the soil over a short period of time. This is especially the case where sandy and clay soils are implicated. The ease of movement in these soils is likely due to uninterrupted percolation on sandy soils, and preferential flow on the clay soils. In addition to the relative ease of migration into the soil, a trend of upward movement of pesticides was observed in these soils.

Indications are therefore that in sandy soils and clay soils, pesticides are likely to move freely between the soil layers.

Curves were fitted to the residue data generated in field migration trials of concentration versus soil depth. These were done for each of the time intervals at which samples were collected. The fitted curves for the data generated, are based on the means of residue concentrations per sample depth. The curves were generated using only four points for soil depth. These curves in general describe with accuracy the behaviour of the active ingredients in soil. Although these curves are a handy tool for describing the data and isotherms (Walker *et al.*, 1996), they are not likely to be accurate enough for predictive purposes.

6.5.3 Model evaluations

The models that were used in evaluations were VARLEACH, PELMO and WHI Unsat Suite – PESTAN. None of these models could provide accurate approximations of the migration patterns found in field migration experiments for any of the three active ingredients tested (section 6.4).

PELMO and VARLEACH both predicted limited migration of all three active ingredients on all three soils with a maximum migration depth of 40 cm. The measured data on the other hand showed that for most of the pesticides and soil combinations migration up to at least 120 cm could be expected. In addition, PELMO and VARLEACH are not sensitive to a change in degradation rates entered for all three active ingredients on all three soils.

Ideally, the model of choice should be one that renders an exact fit of predicted values to those measured (Brown, 1996; Walker *et al.*, 1996). This was not found with any of the three models evaluated. VARLEACH and PELMO completely underestimated the migration potential of pesticides under South African conditions. An underestimation of migration potential is likely to allow active ingredients to be used that could carry a high risk to the environmental and human health.

PESTAN predicted soil behaviour patterns similar to those patterns found in field migration experiments. Although the prediction of behaviour showed similar trends to that of actual migration data, they are, however, limited in accuracy. PESTAN tends to over-predict the pesticide concentrations especially those in the deeper soil layers. The model thus tends to over predict the migration-ability of the active ingredients. If the model is to be used as a tool to determine risk of groundwater contamination for example, an over-estimation of migration will lead to active ingredients being disallowed unnecessarily. It is thus required that a model of choice be more accurate than that shown in the evaluations.

6.6 Conclusion

An absolute and exact fit of actual migration patterns with those predicted by the models seems difficult to achieve (Brown, 1996; Gustafson, 1993; Gustafson, 1999; Walker *et al.*, 1996). Using a model that does not give a reasonable approximation of migration patterns may not be appropriate (Brown, 1996). When used in initial screening of a

suitability of a use of a pesticide, a reasonably accurate approximation of the migration patterns may suffice (Gustafson, 1999). Although PESTAN provided an overestimation of migration potential, the model did predict similarities in pesticide behaviour. This indicates that the model lends itself to be optimised in some way, allowing for more accurate migration predictions.

PESTAN does not use input of weather data for calculating migration and migration rates. The model uses hydraulic conductivity; re-charge rate and the ability of the soil to disperse a particular pesticide to calculate migration rates. Because the model is set up in this way, these parameters could be tweaked and altered to allow for better migration predictions.

In this evaluation, the dispersion coefficient was derived from field migration studies as an average over the full trial period. If the model is to be used as a screening tool, it does not make sense to have to estimate such a parameter from actual migration data. The model should provide a first tier evaluation of migration potential. At any rate, the use of the dispersion coefficient from the field data renders inaccurate data.

The PESTAN dispersion parameter could be estimated for selected soil / pesticide combinations using the results from experiments discussed in this chapter. The parameter can be determined for each of the active ingredients investigated combined with each of the soil types investigated. Once determined, they can be used as default inputs for PESTAN for similar soil / pesticide combinations.

The published pesticide characteristics and soil data may be used as further model inputs. The coefficient to be used will have to be selected for a specific soil type and a pesticide with similar chemical characteristics described by the adsorption coefficient and half-life of the active ingredient. These two parameters can be sourced from literature on the subject

as it has been shown that the locally generated values do not vary much from those found in international literature.

In the next Chapter, the process of "fine tuning" the model PESTAN to render a more accurate migration prediction is described.

CHAPTER 7.

OPTIMISATION OF MODEL USE (PESTAN)

7.1 Introduction

Evaluations of model predictions against measured data of pesticide migration in South African soils indicated that the models VARLEACH and PELMO completely underestimated the migration potential of the pesticides (Chapter 6). Were a model to be used as registration screening tool, it would be likely to allow use of pesticides that could carry an enhanced risk to the environment and human health through an underestimation of migration (Gustafson, 1993).

The underestimation found with VARLEACH and PELMO was not restricted to underestimates of concentrations, but underestimation of the depth of migration. This underestimation was such that, in most cases, the models predicted that the tested pesticides would not migrate below 40 cm (Chapter 6).

PESTAN, on the other hand, predicted soil-migration patterns similar to those found in field migration experiments (Chapter 6). Although the migration predictions showed similar trends to that of measured data, PESTAN tended to overestimate migration. The model showed a tendency to overestimate the pesticide concentrations, especially those in the deeper soil layers.

PELMO and VARLEACH use weather and soil data to estimate rates of water movement (Walker, 1987). In contrast, PESTAN uses user-defined input parameters, such as infiltration rate of water entering the soil, conductivity dependency on moisture content, and the ability of a soil to disperse the flow of a pesticide (Waterloo Hydrogeologic, 2003). It is predicted that alterations to one or more of these parameters could result in improved migration predictions. This approach is believed to be a simpler approach to the

optimisation of the model outputs, when compared with altering source codes in PELMO and VARLEACH.

The model input parameters, using data generated in the field (Chapter 6), were altered to determine whether the simulations could more closely match the measured pesticide behaviour, but not necessarily the concentrations at different levels.

7.2 Materials and Methods

7.2.1 Model Input parameters

The model parameters investigated were the recharge rate, the characteristic curve coefficient, and the dispersion coefficient.

- Recharge rate (RR): The infiltration rate of water entering the soil.
- Characteristic curve coefficient (CCC): A parameter of the dependency of relative conductivity of the soil on the relative saturation of the soil.
- Dispersion Coefficient (DC): The characteristic ability of a soil to disperse the flow of a pollutant (pesticide) measured in cm^2 per unit time. In order to standardise, the parameter used was converted to cm^2 per hour.

The RR describes the rate of water infiltrating the soil. If pesticide movement in soil is dependent upon water flow, the recharge rate should provide an indication of the rate of movement of the pesticide through soil. It is generally accepted that the rate of movement of pesticides in soil is a function of water flow and solubility (Huygen *et al.*, 2000; McDonald and Harbaugh, 1988). It is expected that an increase in recharge rate would lead to an increase in migration rates through the soil.

The CCC provides an indication of the dependence of soil conductivity on moisture content of the soil. The parameter value may vary from 4 to 12 depending on soil type. For a sandy soil it is 4, and for clay 12. Default model values are *given in* the model for

different soil types. The characteristic curve coefficient is dependent on soil type, and it is not expected to affect migration prediction to a great extent. Also, this should be a parameter that is determined once-off for different soil types, and used as input parameter.

The DC describes the ability of the soil to disperse the pesticides. The parameter used in models as run in Chapter 6 was derived from actual migration data. It is expected that where the DC is set below optimal, the model would predict limited pesticide migration. If on the other hand the DC is set too high, the model would predict a bolus-type movement. Bolus-type movement is the movement of a concentrated cell or clump of pesticide through the soil profile, without dissipating. The higher the value, the more rapidly the active ingredient moves through the soil, and the less retention will be expected.

7.2.2 Evaluation methods

The model was run using the default soil parameters for the model prior to release. The only soil parameters that were changed were the hydraulic conductivity (estimated from literature) and organic carbon content. This was also the way it was set up during evaluations in Chapter 6. Hydraulic conductivity was set for local soils sourced from Barnes, (1976) and Cass, (1980). Soil organic carbon content values used were those from soil analyses data (Chapter 6, section 6.2).

The pesticide parameters used were those as used for all simulations on all the models (Chapter 6, section 6.2.7). The laboratory-determined values for the half-life and adsorption coefficient were used in the simulations (Chapter 5, Table 5.2 and 5.3). A summary of the published adsorption coefficient and half-lives are provided in Table 7.1.

Table 7.1. Published chemical characteristics of the pesticides used in the field experiments.

Pesticide	Water solubility (mg l^{-1})	Adsorption published K_{oc} (ml g^{-1})	DT_{50} published (days)
Tebuthiuron	2500	22 – 91	360-450
Azafenidin	16	286	25
Fenthion	55	7.7 - 38	34

The soil characteristics used for the simulations were the model defaults for the soil type specified, except that these were corrected using soil characteristics determined for the test soils. The soil parameters that were altered from the default PESTAN settings are shown in Table 7.2.

Table 7.2. Soil properties of the soils on which field experiments were conducted.

Soil type	Soil Horizon (cm)	Clay content*	Percentage Carbon Content	pH (Water)
Sandy loam soil	0 - 20	19.7 (Kt)	0.48	4.16
	40 – 60	29.2 (Kt)	0.49	4.94
Clay soil	0 - 20	38.5 (St)	1.26	7.56
	40 – 60	53.2 (St)	0.86	8.18
Sandy clay loam	0 - 20	22.3 (Kt)	0.63	7.68
	40 – 60	32.0 (Kt)	0.37	8.41

* Dominant clay mineral: Kt = Kaolinite; St = Smectite

The model parameters for each pesticide versus soil type were altered, the model run, and the simulated output compared to the original measured field data. The criteria to determine whether the changes in model parameters were successful are set out below.

- The model should approximate migration patterns in that the distribution of the pesticide though the soil profile should be similar i.e. the curves should be similar.
- The prediction of movement over time should agree.
- The concentration of the pesticide per soil horizon need not correspond (variability of 50 % may be acceptable).

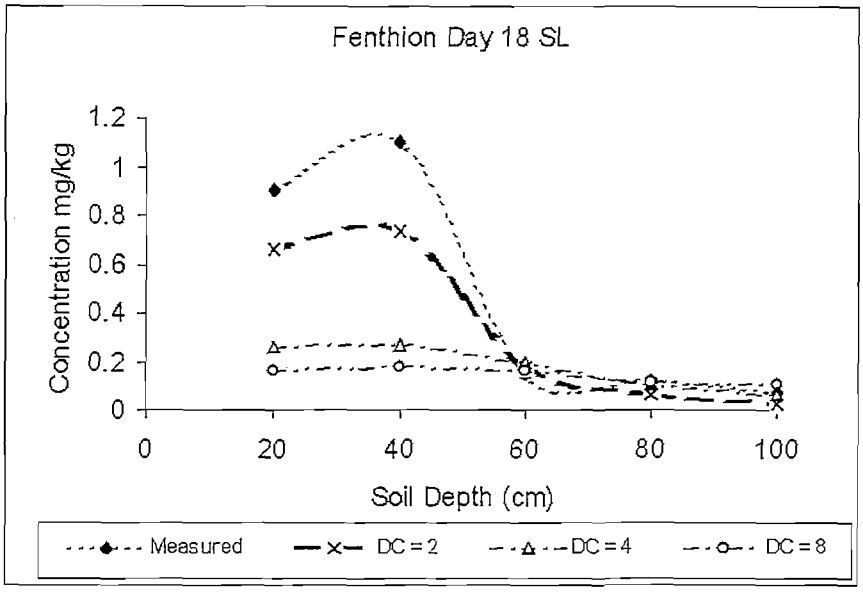
7.3 Results and Discussion

Changing the RR or CCC did not alter the simulation results with regard to the migration predictions. Changing the recharge rate only caused an increase or decrease in the simulated rate of transport of the active ingredients. The simulated migration curve did not change; it only moved the migration profile deeper or shallower in the soil profile. Similar results have been reported by Maharaj (2005). Increasing the recharge rate leads to a prediction of the pesticide soil distribution profile as a whole, being shifted deeper into the soil.

A change in the CCC did not change the predicted outputs. A decrease in the CCC simply predicted higher concentrations present at the different soil horizons, but the migration pattern or resultant shape of the plot (concentration versus depth) stayed the same.

7.3.1 Fenthion applied to sandy loam soil

Figure 7.1 provides a comparison of measured fenthion field migration on sandy loam soil compared to simulated PESTAN migration for the interval 18 and 60 DAA. The field migration pattern determined indicated that fenthion was retained in the upper soil layers effectively for the first 18 DAA, but migrated into the deeper soil layers with time (60 DAA). The simulation that provided the closest predictions was one that used a DC of 2 cm^2h^{-1}. Although the concentration predictions tended to be underestimated, the migration pattern was similar.



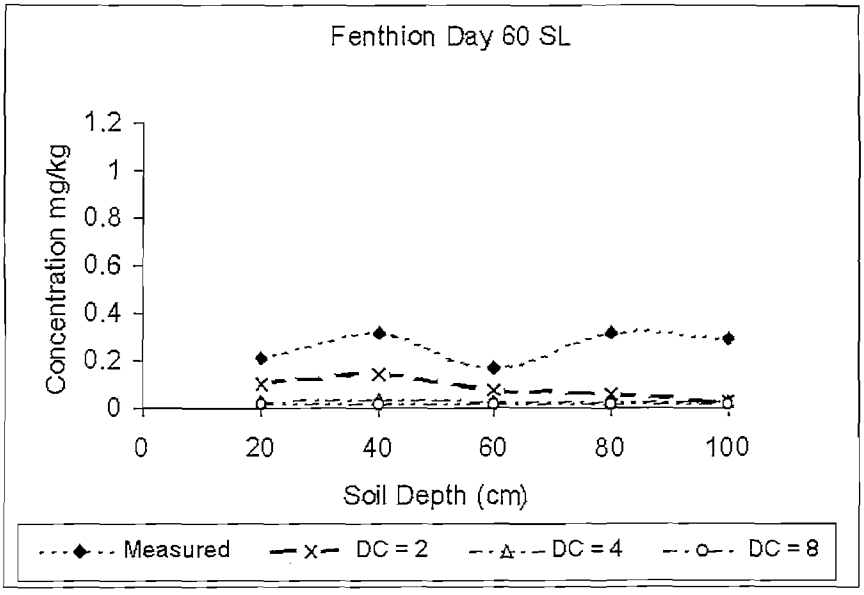


Figure 7.1. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for fenthion as applied to sandy loam soil (SL).

The field migration pattern determined indicated that the migration of an active ingredient, with chemical characteristics similar to those of fenthion, applied to a sandy loam soil, would be acceptably simulated when using a DC of 2 $cm^2 h^{-1}$.

7.3.2 Fenthion applied to sandy clay loam soil

Figure 7.2 compares measured fenthion field migration on sandy clay loam soil with simulated PESTAN migration for the 18 and 60 DAA intervals. The field migration pattern determined indicated that fenthion was retained poorly in the upper soil layers indicating some movement to the deeper soil layers in the initial 18-day period. However, little change occurred over the following 42-day period.

Applying a DC of 2 $cm^2\ h^{-1}$ resulted in little movement with most of the active ingredient being retained in the upper soil layers. Applying a DC of 10 $cm^2\ h^{-1}$ lead to simulations of a bolus-type movement of the active ingredient, which did not compare to field results. The closest fit to the measured migration trends for this soil and for fenthion was found using a DC of 5 $cm^2\ h^{-1}$. In this case, the simulation slightly over-estimated the concentrations, but the migration patterns were simulated well.

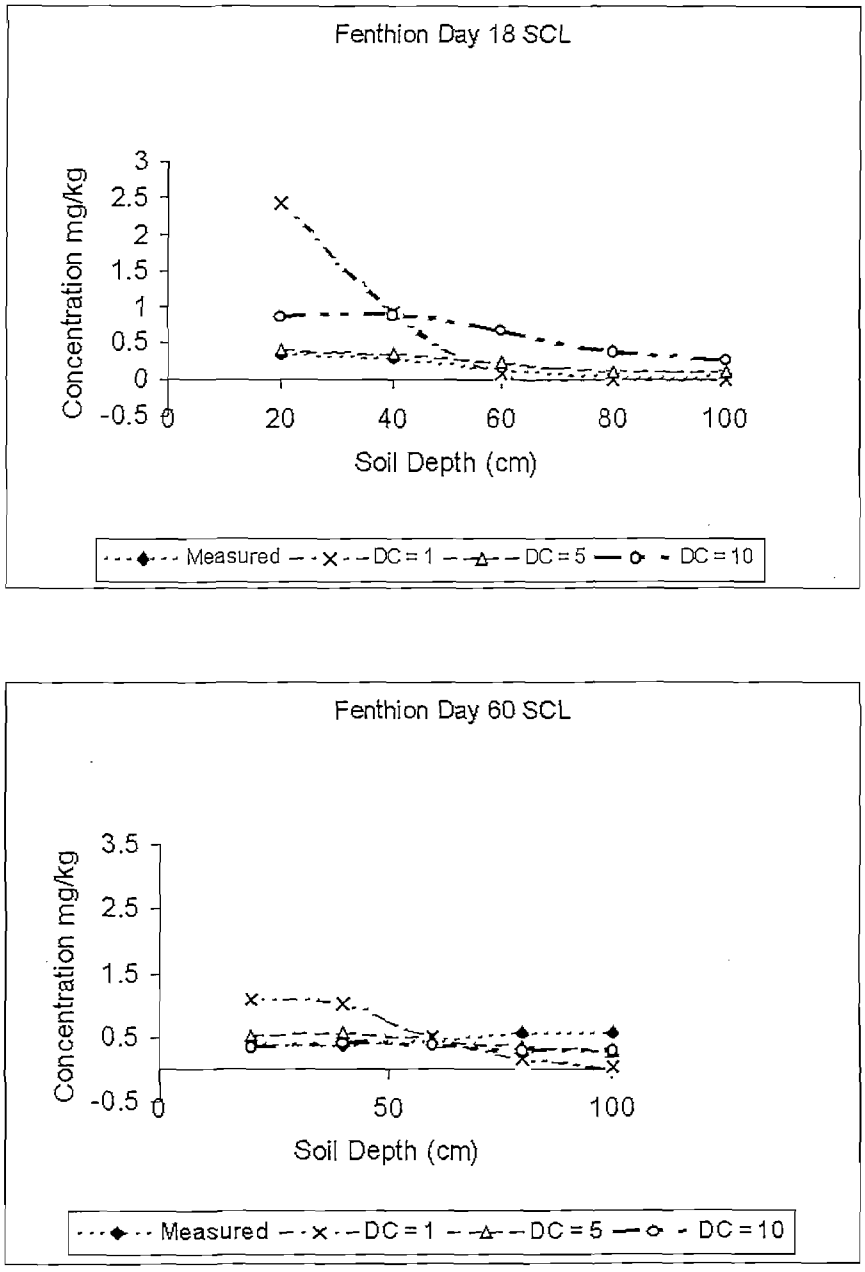


Figure 7.2. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for fenthion as applied to sandy clay loam soil (SCL).

These comparisons indicated that the migration of an active ingredient, with chemical characteristics similar to those of fenthion, applied to a sandy loam soil, will be acceptably simulated when using a DC of 5 $cm^2 h^{-1}$.

7.3.3 Fenthion applied to clay soil

Figure 7.3 provides a comparison of measured fenthion field migration on clay soil compared to simulated PESTAN migration, for the 18 and 60 DAA intervals. The field-migration pattern determined indicated that bolus-type movement occurred for fenthion in the clay soil. This may indicate an effect of preferential flow. However, measured migration patterns also indicated of the active ingredient having been moved back up to the surface with time. The model could not simulate the observed bolus-type movement. This was not surprising, as the model did not take preferential flow into account for migration predictions. Using a DC of 10 $cm^2 h^{-1}$ did predict significant migration.

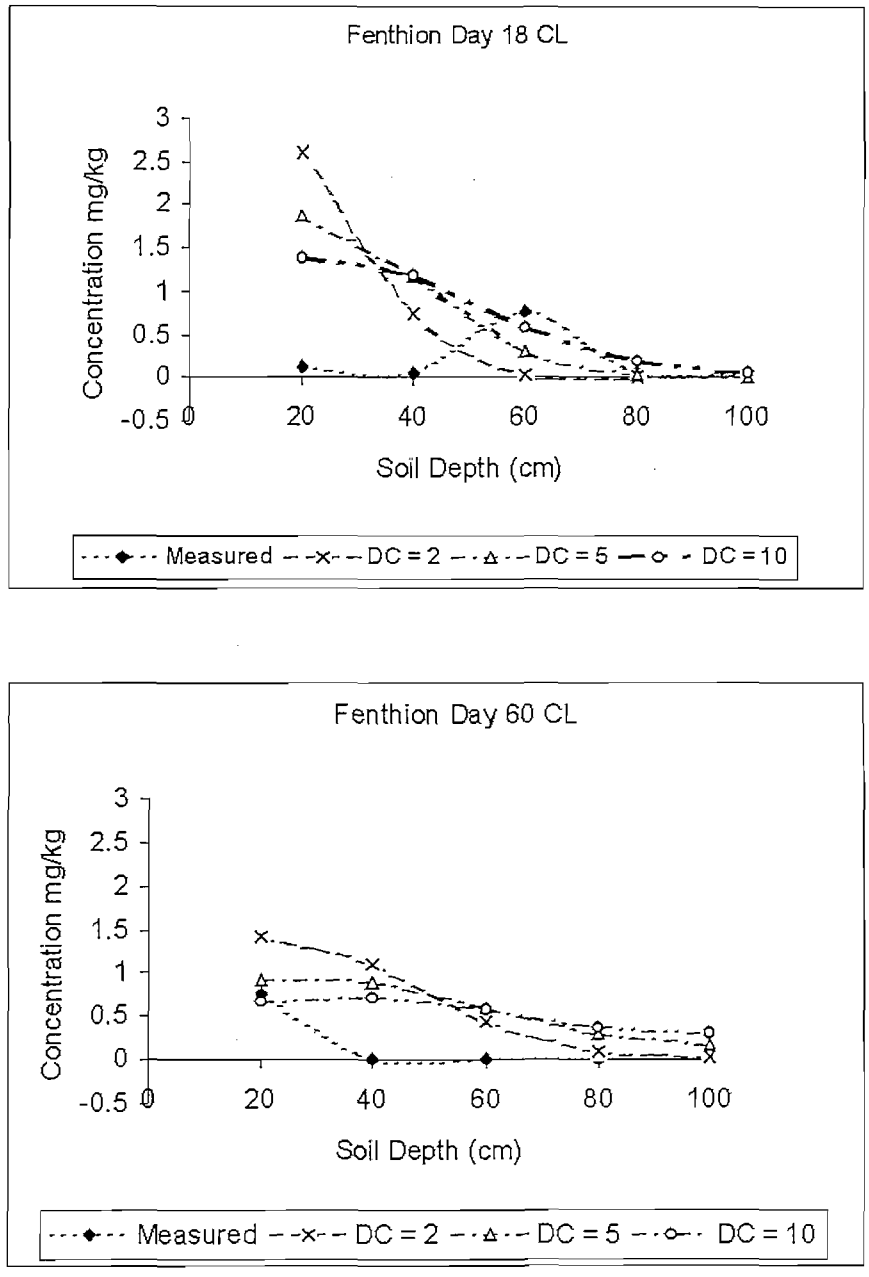


Figure 7.3. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for fenthion as applied to clay soil.

These comparisons indicated that the migration of an active ingredient, with characteristics similar to those of fenthion, applied to a clay soil, will be acceptably simulated when using a DC of 10 $cm^2 h^{-1}$.

7.3.4 Azafenidin on sandy loam soil

Figure 7.4 provides a comparison of measured azafenidin field migration on sandy loam soil compared to simulated PESTAN migration for the interval 18 and 60 DAA. The field migration pattern determined indicated that the active ingredient was retained in the upper soil layers during the initial period, but then moved as a bolus or concentrated band through the soil to the deeper layers. This lead to the upper soil concentration decreasing, with the concentration in the deeper layers increasing with time (Figure 7.4). Thus the active ingredient tended to move through the soil as a concentrated contaminant band, rather than dissipating with dilution over time. This meant that the soil did not restrict the movement of the active ingredient much. This would indicate that a higher DC would likely describe the behaviour better than a lower coefficient.

Results of simulations arising from inputs of DCs of 0.5, 1 and 5 $cm^2\ h^{-1}$ are shown in Figure 7.4. The comparisons showed a close approximation to the measured data when a DC of 0.5 $cm^2\ h^{-1}$ was used. A DC of 0.5 $cm^2\ h^{-1}$ indicated relatively low retention of the active ingredient in the upper soil layers initially, but simulated the bolus type movement that was found in field experiments during the following period. An increase in the coefficient for model runs rendered results that underestimated the extent of retention.

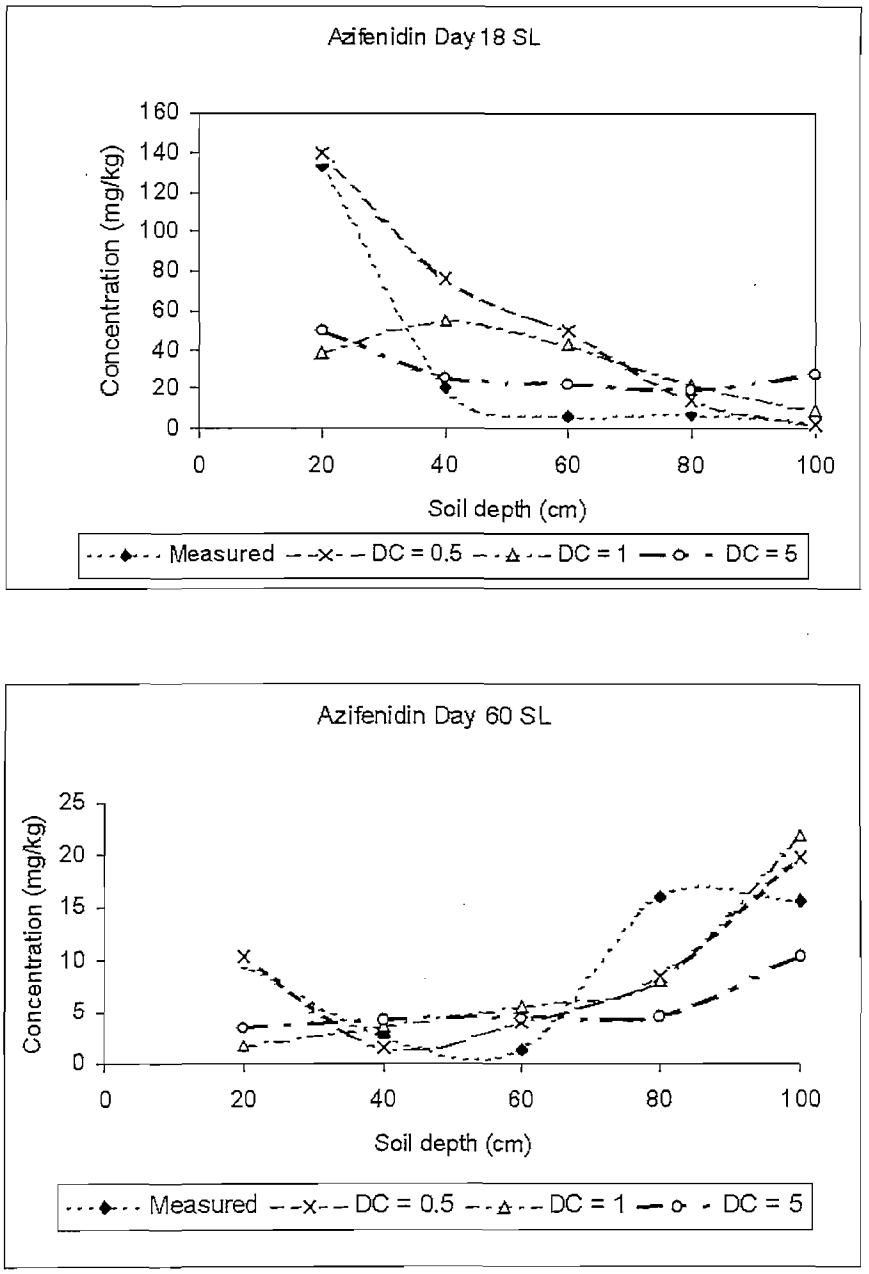


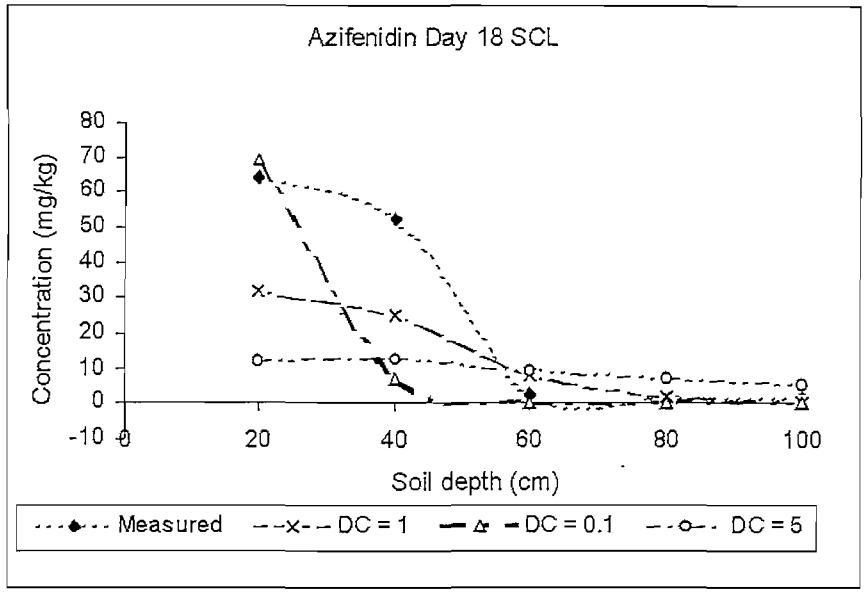
Figure 7.4. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for azafenidin as applied to sandy loam soil.

The comparisons provided in Figure 7.4 indicated that the migration of an active ingredient, with characteristics similar to those of azafenidin, applied to a sandy loam soil, would be acceptably simulated when using a DC of 0.5 $cm^2 h^{-1}$.

7.3.5 Azafenidin applied to sandy clay loam soil

Figure 7.5 shows migration behaviour results of measured data and simulations for azafenidin as applied to sandy clay loam soil. The migration patterns measured in field trials (Figure 7.5) indicated that azafenidin is effectively retained in the upper soil layers, but that migration took place to the deeper soil layers with time.

This observed field migration pattern could be simulated with the use of a DC of 1 $cm^2 h^{-1}$. An increase in the DC above this level led to a prediction of limited retention and an even dispersion of the active ingredient in the soil.



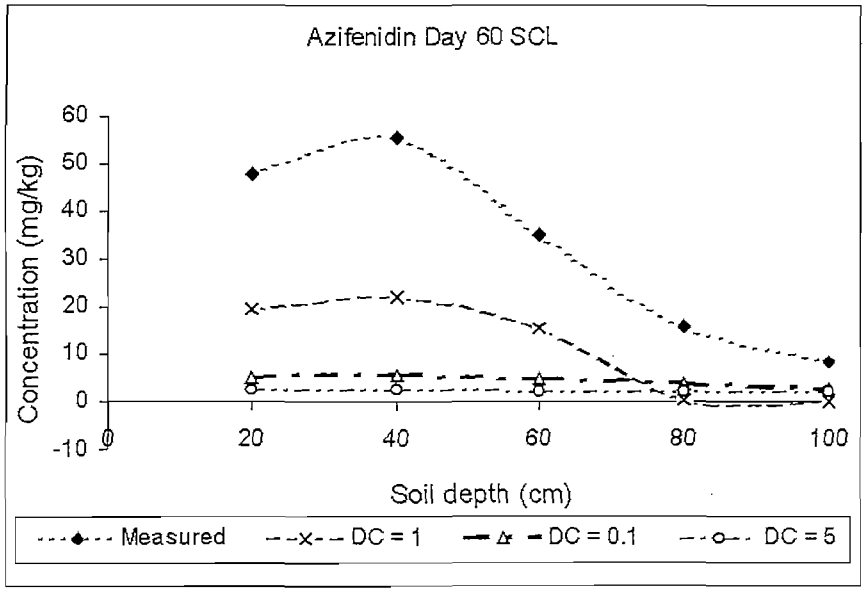


Figure 7.5. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for azafenidin as applied to sandy clay loam soil.

The comparisons of DC's indicated that the migration of an active ingredient, with characteristics similar to those of azafenidin, applied to a sandy clay loam soil, will be acceptably simulated when using a DC of 1 $cm^2 h^{-1}$.

7.3.6 Azafenidin applied to clay soil

Figure 7.6 shows the comparison of migration patterns from field experiments versus predicted migration from simulations for azafenidin applied to clay soil. Results from field migration experiments showed gradual movement of the active ingredient into the soil over time. Although the active ingredient was found to migrate into the soil, this movement was slow, indicating that the active ingredient was effectively retained in the clay soil. The DC decided upon should thus be low enough not to lead to bolus-type simulations, while not predicting a high degree of retention with minimal migration.

When running the model with a DC of 0.5 $cm^2\ h^{-1}$, a high degree of retention was predicted for both the time intervals. A DC of 5 $cm^2\ h^{-1}$ approximated the measured behaviour better, although the azafenidin concentrations in the deeper soil layers tended to be slightly underestimated.

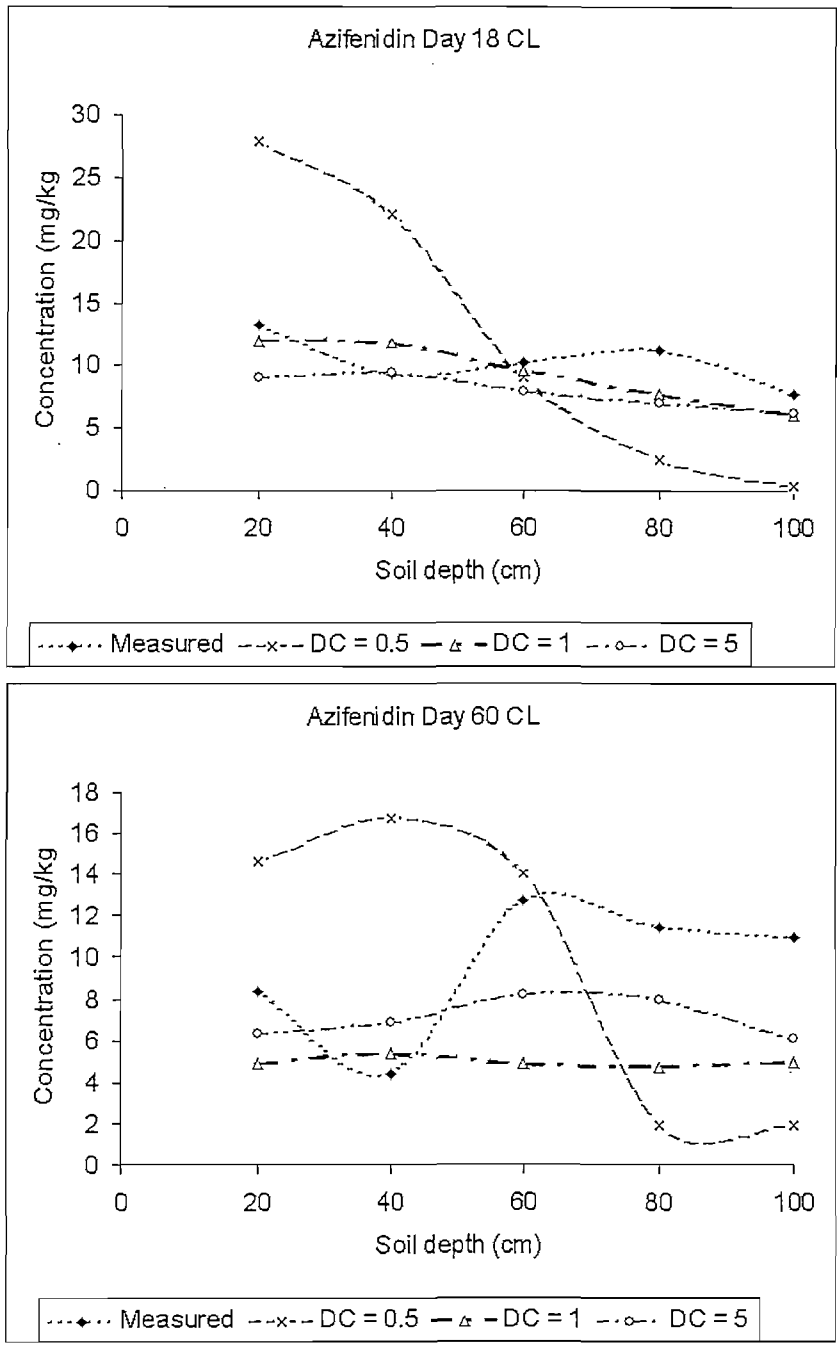


Figure 7.6. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for azafenidin as applied to clay soil.

The simulations indicated that a DC of 5 $cm^2 h^{-1}$ will provide the closest simulation result to the actual migration data. Data indicated that the migration of an active ingredient, with characteristics similar to those of azafenidin, applied to a clay soil, will be acceptably simulated when using a DC of 5 $cm^2 h^{-1}$.

7.3.7 Tebuthiuron applied to sandy loam soil

Figure 7.7 shows migration results from field experiments compared with simulations for tebuthiuron applied to sandy loam soil. Migration patterns from field migration trials showed that the active ingredient was retained in the upper 40 cm soil layers during the initial period. After this, the bulk of the active ingredient remained in the upper soil layer, but the soil concentration in the deeper layer increased, indicating even percolation of tebuthiuron to the deeper soil layers.

Running the model using a DC of 1 $cm^2 h^{-1}$ or higher, limited retention of the tebuthiuron was predicted, and the active ingredient was dispersed evenly through the soil. A DC of 0.1 $cm^2 h^{-1}$ on the other hand predicted movement to the deeper soil layers, yet retention is predicted as was found in the field experiments.

Predictions indicate that the migration of an active ingredient, with characteristics similar to those of tebuthiuron applied to a sandy loam soil, will be acceptably simulated when using a DC of 0.1 $cm^2 h^{-1}$.

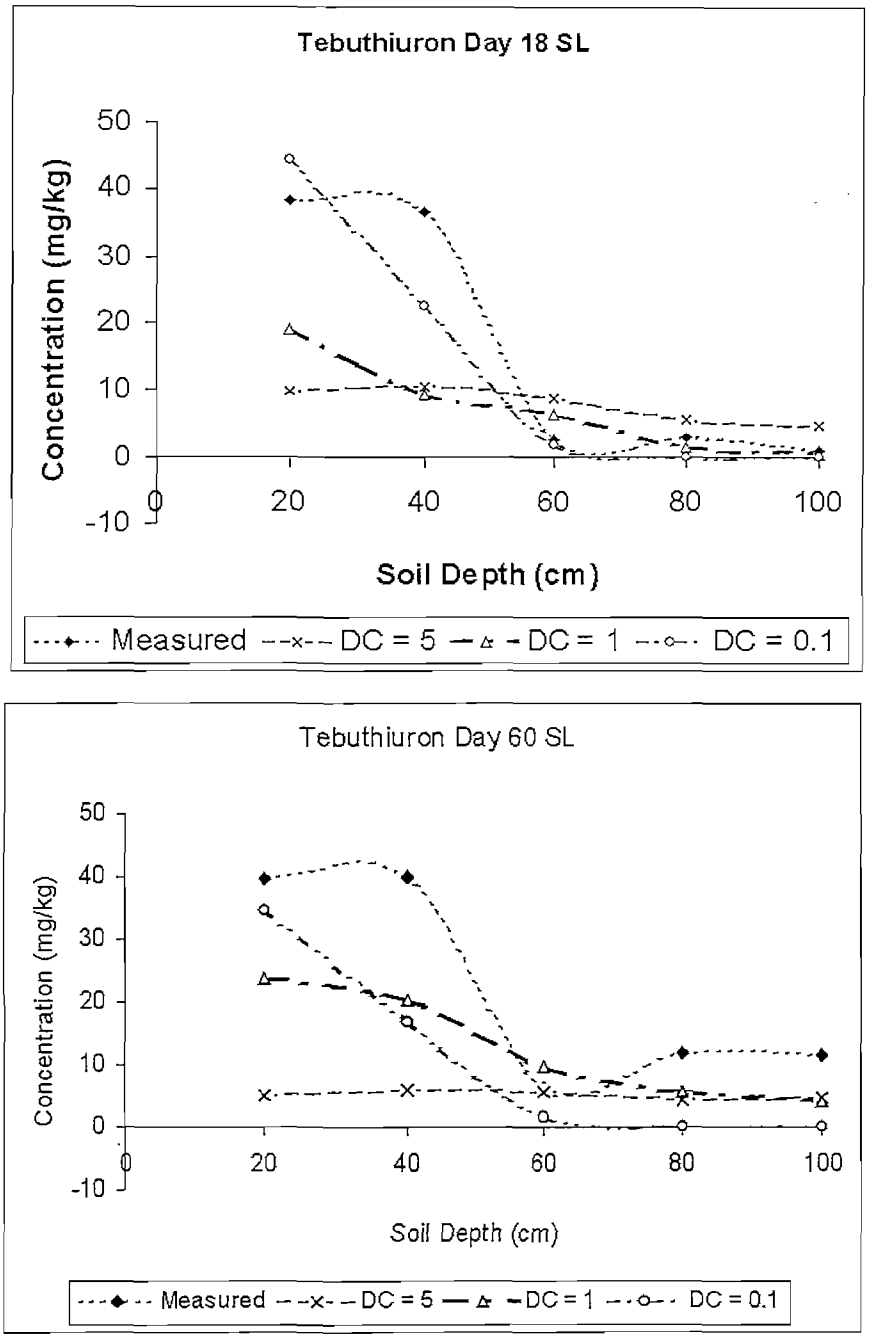


Figure 7.7. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for tebuthiuron as applied to sandy loam soil.

7.3.8 Tebuthiuron applied to sandy clay loam soil

Figure 7.8 shows migration results from field experiments compared with simulations for tebuthiuron applied to sandy clay loam soil. Measured migration patterns showed that the active ingredient reached the deeper soil layers within 18 DAA. With the model, a decrease in tebuthiuron residue levels was observed over time in soil horizons 1 to 3, coinciding with an increase in residue levels in soil horizons 4 and 5. Model predictions indicated that the active ingredient would have evenly dispersed into the soil over the trial period. Migration predictions for tebuthiuron using a DC of 2 $cm^2 h^{-1}$ closely followed the measured migration pattern.

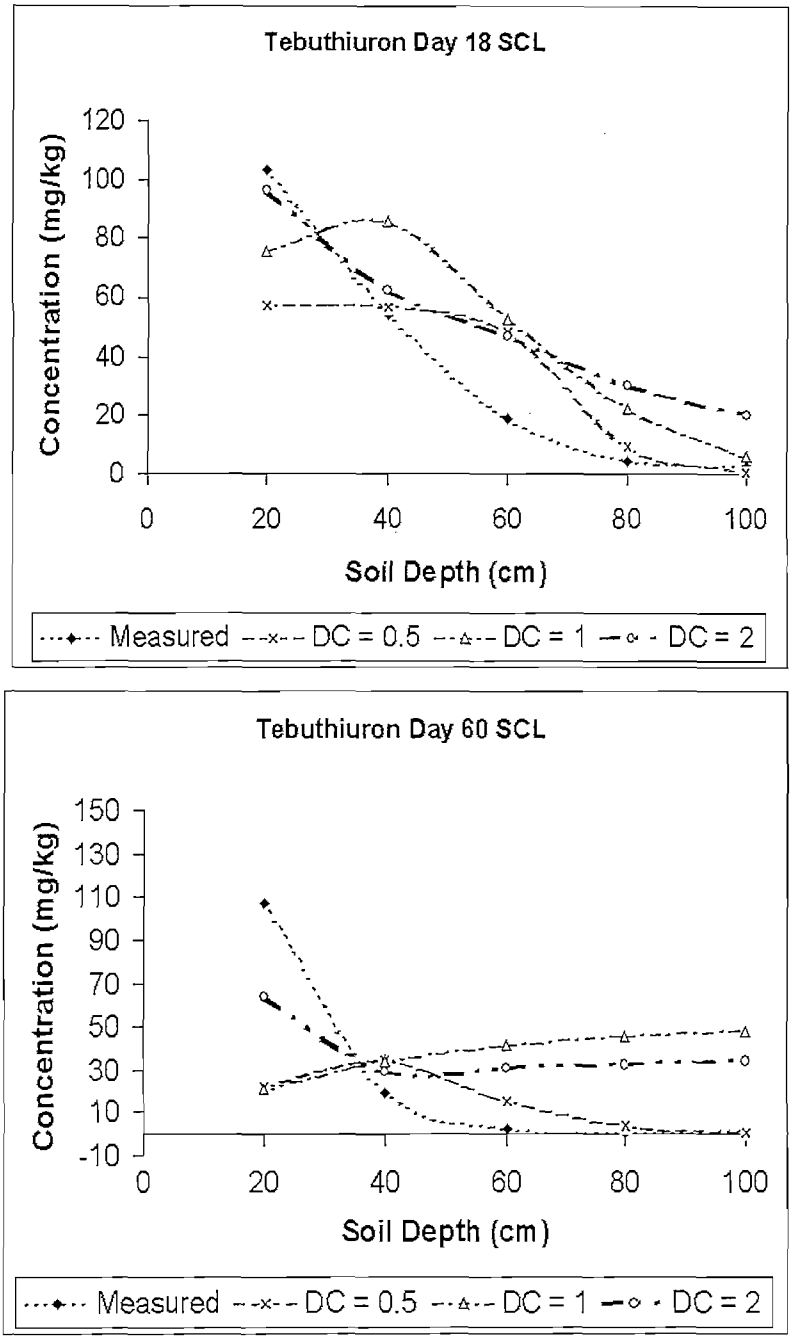


Figure 7.8. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for tebuthiuron as applied to sandy clay loam soil.

Predictions indicate that the migration of an active ingredient, with characteristics similar to those of tebuthiuron applied to a sandy clay loam soil, will be acceptably simulated when using a DC of 2 cm^2h.

7.3.9 Tebuthiuron applied to clay soil

Figure 7.9 shows migration results from field experiments compared with simulations for tebuthiuron applied to clay soil.

Measured migration patterns showed that the active ingredient was retained in the upper 40 cm soil layers during the initial period. After this, migration occurs evenly with a slow increase in concentration in the deeper soil layer. The migration predictions for tebuthiuron using a DC of 6 $cm^2\ h^{-1}$ on the clay soil closely simulated the measured migration pattern.

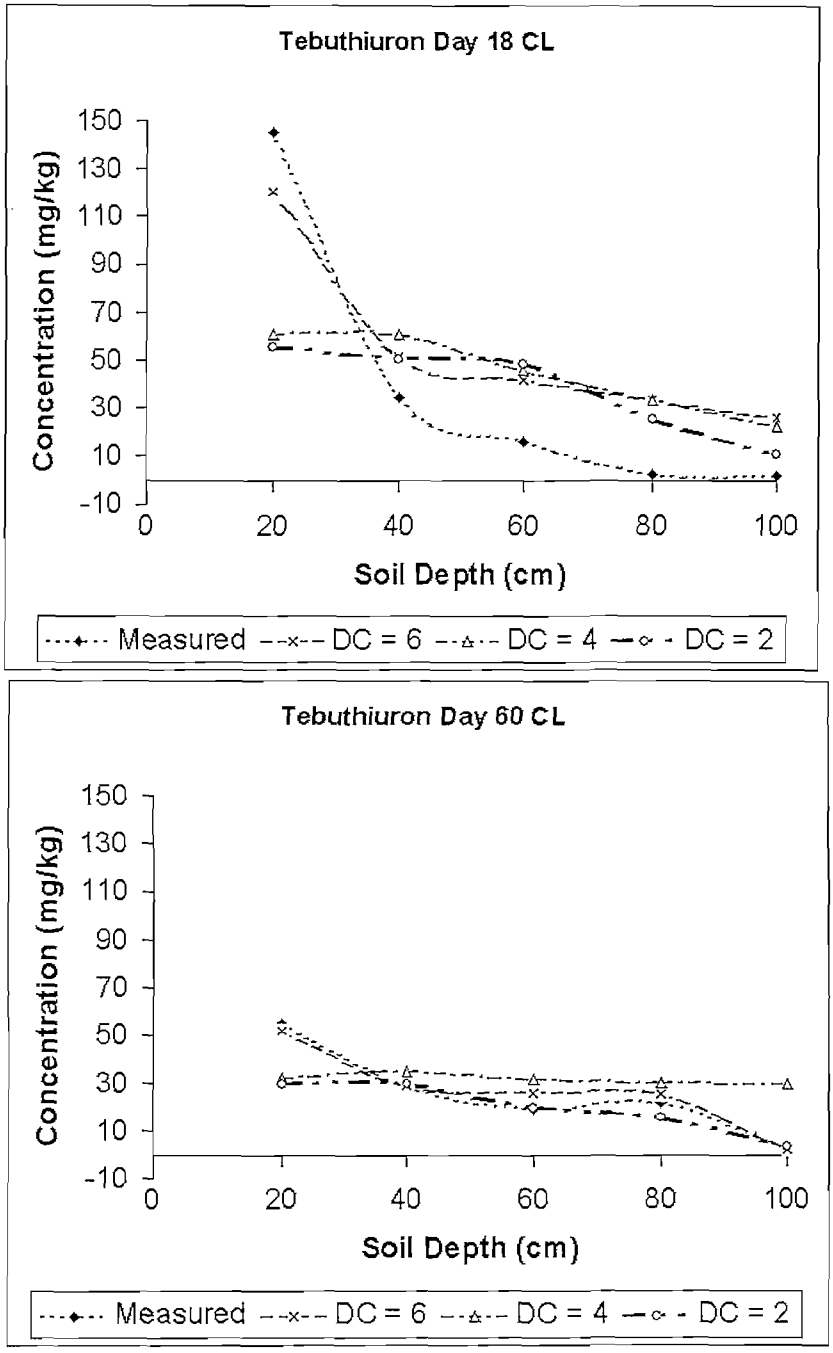


Figure 7.9. Measured migration versus predicted migration from simulations at 18 and 60 DAA, showing the effect of altering the DC for tebuthiuron as applied to sandy clay loam soil.

Predictions indicated that the migration of an active ingredient, with characteristics similar to those of tebuthiuron applied to a clay soil, would be acceptably simulated when using a DC of 6 $cm^2 h^{-1}$.

7.3.10 Default PESTAN DCs

Using the experimental active ingredients as examples, pesticides can be placed in three broad categories as described below:

A. Tebuthiuron as an example of active ingredients that are:

- Persistent (half-life exceeding 100 days), have a high water solubility and are mobile (K_{oc} less than 200) in soil.

B. Azafenidin as an example of active ingredients that are:

- Short lived (half-life less than 100 days), have low water solubility and are relatively immobile (K_{oc} exceeding 200) in soil.

C. Fenthion as an example of active ingredients that are:

- Short lived (half-life less than 100 days), have low water solubility and are mobile (K_{oc} less than 200) in soil.

The results of the simulations indicated that for these three broad pesticide categories, one could set a default DC specific to each of the soil types tested.

Table 7.3. Default DCs determined for different soil types per pesticide category.

Pesticide Category	Soil Type	DC ($cm^2.hr^{-1}$)
A	Sandy Loam	0.5
	Sandy Clay Loam	2
	Clay	6
B	Sandy Loam	0.5
	Sandy Clay Loam	1
	Clay	5
C	Sandy Loam	2
	Sandy Clay Loam	5
	Clay	10

7.4 Discussion

Model input parameters for PESTAN were modified with the aim of producing migration predictions that more accurately approximated measured field migration data. Criteria were set against which the model predictions were to be measured to determine whether such predictions could be deemed acceptable. The exercise showed that the alteration of the recharge rate and / or characteristic curve coefficient did not lead to migration simulations that met the set criteria. A decrease in the characteristic curve coefficient simply predicted higher concentrations present at the different soil horizons, but the migration pattern or resultant shape of the plot (concentration versus depth) stayed the same.

The DC describes the ability of a pesticide to move in a soil. The evaluations showed that PESTAN is sensitive to changes in the DC. The results also showed that in order to make the model outputs fit the measured data, the DC of choice should be increased with soil clay content. This is contrary to what one would expect as one would expect higher dispersion ability with lower clay content due to an expected lower degree of adsorption of the active ingredient with the clay particles. Conversely, one would expect a lower degree of pesticide dispersion with an increase in clay content.

The results of the experiments showed that the PESTAN DC could be altered in order to get an acceptable approximation of measured field migration. From the resultant data, a set of DCs could be established for each of the active ingredients used, specific for each soil type (Table 7.3).

If a distribution coefficient higher than the default model values was used, the model was manipulated into forcing dispersion of the pesticides in its simulations, which would ordinarily not be simulated. Thus by increasing the DC, the model was forced into simulating movement in the soil, rather than retention.

When a lower DC was used on more sandy soils, the predictions showed more retention of the active ingredients in such soils.

In this study, DCs were manipulated in order to render predictions that more accurately described the field migration data generated. DCs were generated for three pesticides with varying chemical characteristics on soils with varying physical characteristics.

What is proposed is that the DC values generated in this study are used as generic PESTAN DCs. With the DCs known, a DC can now be selected corresponding to the suitable pesticide and soil category. It must be kept in mind that soil parameters such as hydraulic conductivity, bulk density etc., should also be used as inputs where specific data is available. Where such data is not available, the model could be run using the default settings for the soils in the model database.

The modelling exercise should then render migration predictions that are adequate for use in a screening system for suitable pesticide behaviour on local soils.

Inputs for persistence should preferably be determined for local soils, whereas the adsorption coefficients can be taken from published data.

CHAPTER 8.
GENERAL DISCUSSION

8.1 Introduction

The Stockholm Convention promotes international action to protect human and environmental health by reducing or eliminating releases of POPs. Although the initial focus has been on chemicals such as the pesticides aldrin and DDT, the identification of additional active ingredients remains a priority.

UNEP has identified further persistent toxic substances through their programme on Regionally Based Assessment of Persistent Toxic Substances (Whylie *et al.*, 2003). In these programmes, pesticides such as hexachlorocyclohexanes (HCH) and endosulphan have been identified as possible problem active ingredients. Again these are based primarily on potential health effects and long-distance transport

One of the criteria for identification of POP's is persistence (UNEP, 1998). Persistence of chemicals differs between different media such as air, soil, water and biota, as well as climatic and physical factors (Weber, 1991). The Stockholm Convention states that where a half-life exceeds six months in soil and sediment, it could be considered a candidate POP (Annex D – Stockholm Convention, 2002). Geographical variable climatic and physical conditions however, will affect the half-lives of substances (Helling *et al.,* 1971).

Pesticides may exhibit characteristics similar to those of POPs, with the possible exception of long distance transport, under South African conditions. As an example, numerous unpublished reports of alleged herbicide damage to non-target crops have been investigated by many researchers. Often these allegations had led to court cases where the landowners who are on the receiving end, claimed damages from the owner of the herbicide or the applicator. Often the damage incurred is believed to be due to the off-target movement of the active ingredients. It appears as if many such cases were caused by soil-applied herbicides that are stable in the soil environment. These active ingredients

are also prone to movement in soil and subsequently caused damage to non-target vegetation due to the migration out of the target area.

8.2 Case studies

In this thesis, four case studies were discussed in which non-target vegetation had been damaged due to the off-target migration of herbicides (Chapter 3). In all these cases the herbicides were applied over an extended period of time (years), before the first signs of damage were observed. The active ingredients used were normally applied at relatively high rates annually. The case studies showed that the herbicides had migrated out of the applied zones over time and built up in the off-target zones where the damage was eventually incurred.

The case studies were examples of where potential off-target pesticide migration occurred, leading to negative impacts on natural vegetation and crops. These case studies were not conducted as controlled studies, in the sense that the application phases were not planned and executed as a scientific study. The statistical outlay of these was therefore post hoc, and should not be seen as a scientific study. However, application information and application methodology could be sourced from the parties supervising the application. In this way, a scenario could be sketched that represented the initial application phase of the case study. This is similar to case studies often published by the medical fraternity on diseases and disease management. In the case of medical case studies, the disease is also not induced and then studied.

All four case studies discussed showed that certain pesticides were prone to move in selected soils of South Africa. Literature revealed that this type of herbicide movement was not unique to South Africa (Bovey *et al.*, 1978; Smith *et al.*, 1975; Whisenant and Clary, 1987). The migration of the pesticide in itself may not necessarily be problematic, but when combined with extended persistence, the active ingredients build up in soil to the

point where detrimental concentrations are reached (Johnsen and Morten, 1989; Pestemer *et al.*, 1980; Stalder and Pestemer, 1980).

8.3 Glass house phytotoxicity experiments

The case studies consistently indicated that the soils at all four sites were prone to herbicide migration from the area where it was applied. In order to establish whether the migrated residues had biological significance, a set of bio-assay experiments were designed and executed, described in Chapter 4. These glasshouse experiments were conducted to determine the extent of phytotoxicity, resulting from herbicides applied at concentrations similar to those detected in damaged areas in the field. The result of these experiments indicate that although very low residue levels were detected in the case studies, significant phytotoxicity could be expected on non-target sensitive vegetation at these levels, as has been found in other studies (Whitson and Alley, 1984; Skroch and Sheets, 1979; Nieuwoudt, 1986; Myburgh, 1999).

8.4 Field migration studies

Prolonged persistence of pesticides, combined with high soil mobility, are indicators of high pollution potential (Gustafson, 1999, Walker, 1991). The case studies indicated, at least for the herbicides investigated, that persistence and mobility might play a role. Although these studies were confined to herbicides, many other pesticides have similar chemical characteristics to these active ingredients (Tomlin, 1994). It follows then that similar pesticides would undergo similar migration patterns after application. This is because the properties of the chemical determine its adsorption and retention (Ashton and Crafts, 1981).

These results led to the design and execution of field studies in which the migration of selected pesticides was evaluated, and are discussed in Chapter 6. The studies were conducted to assess the need for the evaluation of pesticide migration. The assessment

was based on field experiments, to generate pesticide migration profiles for South African soils, and compare these to model predictions. The studies were conducted using three pesticides selected to represent a range of characteristics relating to persistence and soil mobility. Fenthion was used as representing an active ingredient with a reportedly short half-life and limited soil mobility (Tomlin, 1994). Tebuthiuron on the other hand, was selected as a mobile active ingredient with extended half-life (Ahrens *et al.*, 1994). The soils were selected to provide a range of soil types and soil properties that could influence the mobility of the test active ingredients, as soil characteristics influence soil behaviour of pesticides (Weber *et al.*, 2004). Although model predictions for many models have been compared with experimental data, few reports are available on comparative evaluation exercises (Walker, 1991). This is especially relevant to the South African situation. The methodology followed was similar to that previously applied in the evaluation of predictive models (Bengtsson *et al.*, 1996; Ma *et al.*, 1999, Nicholls *et al.*, 1982; Walker, 1991).

All three the pesticides tested were detected in the deepest soil layer sampled (120 cm soil depth) within 18 DAA, probably primarily as a function of the water infiltration volume and the soil structure. The results further showed that the pesticides may migrate deeper than 120 cm into the soil over a relatively short period. This is especially the case for sandy and clay soils. The ease of movement in these soils was likely due to uninterrupted percolation in sandy soils, and preferential flow in the clay soils.

In a large-scale field study conducted on semi-arid soils in the USA, Johnsen and Morten, (1989), found tebuthiuron migration to a maximum soil depth of 105 cm. This was similar to the results of my studies, with the exception that it had taken four years of movement for the tebuthiuron to reach this depth, in the USA study. In the field experiments it was achieved within 18 to 30 DAA. Tebuthiuron is used as an example as this is the active ingredient which is most mobile of the three tested. In a laboratory migration study conducted with fenthion migration had been followed to a soil depth of 7 cm (O'Neil *et al.*,

1989). With a mean published K_{oc} of 23 000 this is not at all surprising, as one would not expect the active ingredient to migrate in soils. In my field migration experiments, patterns clearly showed migration to at least 120 cm soil depth, despite a high K_{oc} value

In addition to the relative ease of migration into the South African soil layers, a tendency was also found of upward migration of pesticides from the deeper soil layers to the surface layers. This is an aspect that has been speculated upon especially in the herbicide industry, but has not received attention in scientific studies. The processes is probably driven by evaporative forces that occur as soils dry out.

8.5 Evaluation of pesticide migration models

The results of the studies showed that the three active ingredients tested are highly likely to migrate through soil to deeper soil layers after application on the three different soil types tested. Since the three pesticides represented a range of pesticide characteristics, it is likely that similar pesticides will be more prone to migration in South African soils tested.

The migration patterns found in this study indicated that there is a need for local evaluation of migration potential of pesticides in South African soils, as part of the pesticide registration process. Curves fitted to the residue data generated in field trials of concentration versus soil depth, described with reasonable accuracy the behaviour of the active ingredients in soil. These curves are a handy tool for describing the data, but because they are based only on four points for soil depth, and on means of analysed residues, they are not likely to be suitable for predictive purposes.

Because the need for a pesticide migration screening system was identified, the migration data generated was used as a basis to evaluate the predictive abilities of three pesticide-migration models. The studies were aimed at evaluating models for their ability to predict field migration potential of selected pesticides in selected South African soils.

Before models could be run, it was necessary to determine the basic input parameters of pesticide soil half-life and adsorption for the selected pesticides on the relevant South African soils. This approach is similar to that followed internationally by Heiermann *et al.* (1995), Ma *et al.* (2000), Muller *et al.*, (2003), Walker (1987) and Walker and Zimdahl (1991). The studies described in Chapter 5 were aimed at determining whether the model input parameters for soil adsorption and persistence could be sourced from published data, or whether it would have to be generated under local conditions.

The results of these laboratory experiments indicated that the adsorption coefficients determined on South African soils (Chapter 5) did not differ significantly from published values. This showed that the published data on this subject could be used as input source for running predictive migration models for South African soils. These data must of course be matched to a soil with similar characteristics and type as that of the soils under investigation. The fact that adsorption coefficients did not differ much from published values indicated that pesticide mobility in soil may not differ from that in the countries of origin. It must be kept in mind however, that the published values for pesticide soil adsorption vary widely between soil types (Ma *et al.*, 2000, Muller *et al.*, 2003; *Weber*, 1991a, Weber, 1991b, Weber *et al.*, 2004). It may be for this reason that the adsorption values determined under South African conditions were not much different from published values. What this means is that although the adsorption data does not have to be generated for local soils, it may be preferable to run migration models using a range of adsorption coefficients, and to ensure that worst-case site or area specific scenarios are covered (Holland *et al.*, 1998; Lee *et al.*, 1998).

The experiments further showed that the pesticide half-lives determined for South African soils did differ from published data. The half-lives for the active ingredients tested tended to be longer than those reported in literature (Chapter 5). The tendency found in these experiments showed that the pesticides will probably persist significantly longer in South

African soils, when compared to published values. An extended half-life in itself would indicate that South African soils might be prone to extended pesticide persistence (Weber, 1991b). It has been shown that the use of laboratory generated incubation data may lead to overestimate modelled persistence (Ma *et al.*, 2000). The model inputs for half-lives should therefore be generated under local conditions.

8.6 Refined model outputs

The models evaluated were VARLEACH, PELMO and WHI Unsat Suite – PESTAN. The models could not provide accurate approximations of the migration patterns found in field migration experiments (Chapter 6). The results of evaluations showed that PELMO and VARLEACH both under-predicted migration in South African soils, to the extent that in most cases no migration was predicted past the 40 cm soil horizon. The field migration patterns clearly showed that migration could be expected.

PESTAN, however, predicted soil-migration patterns similar to those found in field migration experiments, yet tended to over-predict the pesticide concentrations, especially in the deeper soil layers. The model over-predicted the migration ability of the pesticides. If the model was to be used as a tool to determine the migration risk, an over-estimation of migration could lead to active ingredients being disallowed unnecessarily. It is thus required that a model of choice be more accurate than that shown in the evaluations.

PESTAN does not use weather data for calculating migration and migration rates (Waterloo Hydrogeologic, 2003). The model uses hydraulic conductivity, re-charge rate, and the ability of the soil to disperse a particular pesticide, to calculate migration rates. Because the model is set up in this way, I anticipated that these parameters could be modified in order to render better migration predictions. This could be evaluated because actual migration data was available against which to measure the accuracy of the model predictions.

These evaluations are discussed in Chapter 7. Model input parameters for PESTAN were modified with the aim of producing migration predictions that more accurately approximated measured field migration data. Criteria were set against which the accuracy of model predictions were evaluated, to determine whether such predictions would be acceptable. The exercise showed that the alteration of the recharge rate and / or characteristic curve coefficient did not lead to improved migration simulations that meet the set criteria. A decrease in the coefficient simply predicted higher concentrations present at the different soil horizons, but the migration pattern or resultant shape of the plot (concentration versus depth) stayed the same.

The DC is a parameter used to describe the ability of a pesticide to be dispersed in soil. This does not necessarily imply migration to deeper soil layers, but rather the ability of the soil to disperse the pesticide both vertically and horizontally in the soil (Waterloo Hydrogeologic, 2003). The predictions indicated that the PESTAN was sensitive to changes in the DC. The results also showed that in order to make the model outputs fit the measured data, the DC should be increased with an increase in soil clay content, in effect, forcing the model to allow for more dispersion than the increased clay content would allow for under normal predictions.

8.7 Application of refined PESTAN input parameters

The resultant predictions showed that the PESTAN DC could be altered in order to generate an acceptable approximation of measured field migration. A set of soil-type-specific DCs were then set for each of the pesticides used. In order to apply these values, pesticides were grouped into three general categories with characteristics similar to tebuthiuron, azafenidin and fenthion, respectively. These Provisional Pesticide Migration Categories (PPLC) are provided in Table 8.1.

Table 8.1. Proposed Provisional Pesticide Migration Categories for determination of the PESTAN DC.

	PPLC A	PPLC B	PPLC C
Examples	Tebuthiuron	Azafenidin	Fenthion
Half Life (days)	> 200	< 100	< 100
Water Solubility	High	Low	Low
K_{oc}	< 150	>200	>1000

It is proposed that once a pesticide has been placed in one of these three categories, the corresponding DCs provided in Table 8.2 could be used as DC input to PESTAN.

Table 8.2. Proposed DC per PPLC and soil Type

PPLC	Soil Type	DC ($cm^2.hr^{-1}$)
A	Sandy Loam	0.5
	Sandy Clay Loam	2
	Clay	6
B	Sandy Loam	0.5
	Sandy Clay Loam	1
	Clay	5
C	Sandy Loam	2
	Sandy Clay Loam	5
	Clay	10

The soil parameters such as bulk density, clay content and organic matter content etc., should be determined and used as inputs. Hydraulic conductivity can be sourced from literature. Inputs for persistence should preferably be determined for local soils, whereas the adsorption coefficients can be taken from published data. It is suggested that the model be run for each pesticide using a range of adsorption coefficients to ensure that worst-case scenarios has been covered. The model default setting for soil types can be used for the characteristic curve coefficient and recharge rates.

It is concluded therefore that modelling predictions can be made for pesticide migration under local soil conditions. The PESTAN model can be used for such predictions and it should render migration predictions that are adequate for use in a screening system for suitable pesticide behaviour on local soils.

8.8 Proposed pesticide screening system for South Africa.

This section proposes a phased approach to pesticide registration for South Africa. The suggested system is not dissimilar to that system proposed by Gustafson (1999), for use by the USEPA. The system also does not suggest a move away from the current registration system, but rather strengthening of the system with the incorporation of additional screening for migration.

The system proposes various phases of screening where, at the end of each of the phases of evaluation, a decision is made as to whether to continue to the next step or to request additional information to be generated.

- Step 1
    - Screening of the toxicological properties of the active ingredient. The screening should be based on the current system of toxicological evaluation of an expert toxicologist, who develops an independent toxicological report. The toxicological report is based on toxicological data generated by the product owner during the development of the active ingredient.
    - The criteria for such evaluations have already been set and are currently determined by Department of Health.
- Step 2
    - Evaluate eco-toxicological data of the active ingredient and determine whether the active ingredient poses a threat to the environment, making use of eco-toxicological data provided by the company. The data generated is likely to be relevant to the European or US environments, and targeted indicator species may not be relevant to South Africa.
    - It may be necessary to request data generated on relevant South African or African indicator species.

- Step 3 – Efficacy Evaluation
    - Evaluate efficacy of the pesticide in conjunction with a defined Good Agricultural Practice (GAP) for the control of the targeted organism. In most cases the target organism will be a problem on a range of field and tree crops. The suggestion is that a generic GAP be developed for similar crops, i.e. a GAP for tree crops and one for similar field crops.
    - This step will enable a pesticide to be registered with fewer efficacy valuation required. Much deliberation is currently underway regarding extrapolation of efficacy data to different crops, yet no working system is in place.
- Step 4 - Determine the target crops for the pesticide.
- Step 5 - Initial screening for mobility and persistence.
    - It is proposed that the GUS index be used during this phase. The screening should take into account different soil types found in different regions.
    - In order to do such screening, it will be necessary to have a GIS system for South Africa, dividing the country into soil regions. In addition, one should be able to overlay crops grown on these soil types as well as the relative incidence of major crop pest organisms. Also, the location of sensitive areas must be possible. This will allow initial identification of risk areas, where an active ingredient should not be used. These areas may be areas where soils are such that a selected pesticide should not be used on it due to migration risks. Also, it will identify sensitive areas where selected pesticides should be excluded. Sensitive areas do not necessarily mean ecologically sensitive, but could also include water sources, inhabited areas, and areas where sensitive crops are grown etc. It may be necessary to include neighbouring countries in the screening as potential risk areas may

fall in other countries. The result of such screening will be the reduction of risk areas from the use profile of a pesticide. Such detailed zoning of South Africa for purposes of pesticide registration has not yet been attempted.

- Step 6 – Detailed migration and persistence screening.
    - Where the GUS index identifies a high risk of migration (Gustafson, 1999), the PESTAN model can be used for more detailed evaluations of the pesticide, at the rates it is likely to be used, similar to the use of PRZM2 suggested by Gustafson (1999) and VARLEACH by Holland *et al.* (1998).
    - Adsorption, hydraulic conductivity, soils data, and other parameters can be sourced for the relevant soil type through experimental work.
    - If little or no migration is predicted the use of the product should be deemed save with regards to migration.
    - If the migration risk is high, the use of the active ingredient should be disallowed in the high-risk areas.
    - If the migration risk is dubious, allow the use of the product, but a monitoring programme should be implemented in the area at the same time.
    - Re-evaluate the data, starting at step 5
    - Klein(1999) has proposed the use of such a screening and evaluation system, linked to a GIS-based soils data base, for use in Europe. PELMO is however the proposed model of choice as it has undergone much evaluation and validation in the EU.
- Step 7 – Set maximum residue limits and generate crop safety data.
    - Where a use is allowed or deemed safe, the process of maximum residue limit setting per crop can be initiated. The process should include the use of extrapolations of residue limits to minor crops, similar to that used in the EU.

The details of such potential extrapolations are described in SANCO/D3/SI2.396179 (DG SANCO, 2004).

- This will make registrations of active ingredients on minor crops easier.

The setting of MRLs should be based on the South African food basket, as the primary aim must be to safeguard the local consumer. The way in which MRL's have been set locally and internationally to date is to ensure that the crops on which a product is to be used, a relevant food basket and toxicological properties of a pesticide are taken into account (World Health Organisation, 1997).

The system should further look at MRLs relevant to export countries. In many crops such as citrus, the majority of the local crop (70%) is exported. In these cases, the MRL of the importing country will likely be lower than the South African MRL. In order to conform to the export MRL, the GAP should therefore focus on ensuring that the export MRL will not be exceeded.

It will be necessary to develop specific criteria for each of the screening steps. These should be relevant, based on the local population, local environment, local economic conditions and development initiatives.

It is suggested that the criteria be developed through expert advisory groups, which are chaired by representatives of the relevant government departments with enforcement rights. The department must be able and willing to take a stand on crucial issues where it may become necessary.

The Department of Health should be involved in determining whether the toxicological profile of an active ingredient is acceptable, and should also approve MRL's and ensure these are based on local diets.

The advisory groups should consist of individuals deemed as local experts in their respective fields. Where environmental issues are concerned, local research

organisations involved in identification of sensitive species and have knowledge on local ecological systems should be involved in such an advisory group.

Where decisions are to be made on the suitability of GAP's and of the suitability of a pesticide for use in a crop, representatives of the crop protection companies, the growers, and the marketing organisations should be involved.

It is further proposed that institutions such as research councils, consultants and universities become involved with the process of pesticide screening, especially where expertise requires development. This will allow for reduced costs of the screening in the long term, as well as the development of centres of excellence throughout the country. The centres of excellence need not be located at a single institution; it may be necessary to develop virtual centres to which a number of institutions belong. This allows for the establishment of a pool of expertise from which to draw.

8.9 Conclusions

The re-evaluation of pesticides and pesticide use patterns for their suitability is a high priority in many countries. Pesticide re-evaluations such as those conducted under the EU directive 91/414 EEC will lead to a multitude of pesticides being withdrawn from the agricultural market. These active ingredients are being withdrawn because of their toxicity to humans, due to their persistence in the environment as well as their environmental impact.

A process of re-evaluation of the suitability of pesticides for the South African environment requires attention. In addition to re-evaluation of pesticides already in use, the way in which new pesticides introduced to the country are evaluated also requires attention.

- It was shown in Chapters 3 and 4 that applications such as soil application of herbicides for industrial weed control may lead to migration of active ingredients. It is expected that pesticides such as insecticides and fungicides with similar

characteristics, would also migrate after application, contaminating surface and groundwater sources. Where this occurs it may take several years before the disturbance or change is observed in the system. For many pesticides, these effects are only identified and studied many years after the initial use of the active ingredient is approved. An example of this is DDT, now identified as a POP as well as an EDC[Ψ] many years after initially being approved for use. Migration of pesticides from applied areas may be a possible route of pesticides entering non-target zones in South Africa. If this is the case, this aspect requires evaluation when decisions are taken as to whether to allow pesticides for use in the South African market.

- As a society, we attempt to assign a value of some kind to processes or characteristics, which allow us to compare different entities. Similarly, values that describe the mobility and persistence of pesticides in soil have been developed. We use the adsorption coefficient and the half-life to enable use to compare the mobility and persistence of various pesticides in soils. In this way we can speculate on the ability of an active ingredient to migrate in soil for example. In addition to providing a comparison between different active ingredients, such values also allow for comparisons between different soil types. I hypothesised that the mobility of pesticides would be higher for South African soils as compared to those published, and this would become evident if these values were determined locally. Laboratory experiments showed that adsorption coefficients for South African soils were in line with published values, and not lower as was expected. The variation in adsorption coefficient values for any given pesticide is high. The values determined locally all fell within the range determined by other investigators.

[Ψ] EDC = Endocrine Disruptor Active ingredient – active ingredients that have a negative effect on the endocrine system. Effects include oestrogen mimics.

- Pesticide adsorption to South African soils may thus be expected to be similar to that for soils used during the determination of published values.
- Pesticide half-lives in soil are however likely to be longer than those published. Pesticides may therefore be expected to persist for longer periods than what would be expected judging from published half-lives.
- Field migration studies were conducted to establish migration patterns for three pesticides on three soil types in South Africa (Chapter 6). The conclusions from this work were that pesticides are likely to migrate to a soil depth of up to 120 cm, irrespective of the soil type and pesticide applied. Preferential flow seems an important mechanism of transport of pesticides in clayey soils, to such an extent that migration may be more rapid in clay soils than sandy soils.
- Upward movement of pesticides from the deeper soil layers to the top layers may also be expected. With the arid South African climate, this aspect of pesticide migration could be of great importance throughout the agricultural industry. This is because it holds serious consequences for pesticide residues in crops as well as for waiting periods in establishing new crops. Both waiting periods and withholding periods may have to be revisited especially for soil-applied systemic pesticides. As such, it is necessary to take these aspects into account when pesticides are being evaluated for registration.
- Evaluation of migration and persistence is usually done for pesticides in their country of origin. The evaluations generally involve field-migration studies using state of the art lysimiters and monitoring equipment. These studies are very expensive and time consuming. Much effort has been put into the development of predictive models for the evaluation of pesticide migration in Europe and the USA. The use of models in evaluating soil behaviour of pesticides in South African soils is proposed as it is probably the more cost effective screening system available

compared to field lysimiter trials.

- The PESTAN model provided predictions of similar migration patterns to those from field trials. The model could be optimised to provide accurate predictions. The optimisation was based on altering DC for the model to the point where the prediction matched field-migration patterns (Chapter 7).
- A set of DCs could be determined for three major Provisional Pesticide Migration Categories (PPLCs) for each of the three major soil types used. This allows for the evaluation of new pesticides using the model. A requirement is however that the DC is closely matched with the general grouping suggested.
- Soil parameters such as hydraulic conductivity and bulk density etc. are also used as inputs and should ideally be determined.
- Where data is not available, the model could potentially be run using the default settings for the soils in the model database. Inputs for persistence should be determined for local soils, and adsorption coefficients can be taken from published data. The model should be run for candidate pesticides using a range of adsorption coefficients to ensure the worst-case scenarios have been covered.
- Modelling predictions can be made for pesticide migration under local soil conditions using PESTAN, which should render migration predictions that are adequate for use in a screening system for pesticide behaviour on local soils.
- A system is proposed whereby migration can be incorporated into the existing pesticide evaluation framework. If screening of migration is introduced as a part of a pesticide evaluation system, it will allow for initial identification of active ingredients that may pose risk of migration. This could in future be coupled with a GIS system to identify geographical areas where specific pesticides should ideally not be used, or other risk management strategies employed.

- Although the model is likely to provide accurate predictions for most soils, it may prove to be useless where preferential flow and "upward migration" is likely. Even though this may be the case, the current assessment and calibration of a model to evaluate migration does provide a step in the right direction. The current registration system does not take into account potential pesticide migration under South African conditions. Evaluation of pesticide migration is however considered an aspect, which requires implementation. Such evaluation of migration will however allow for better management of pesticides and the risks that pesticide migration and mobility may bring with it.
- The results of migration studies show that preferential flow and "upward migration" is important in South African soils. To date, these two aspects of predicting pesticide soil behaviour have been the most difficult to characterise and therefore to accurately model. Problems exist in describing macro-pore structures is soils and the relative flows that exist under evaporative forces. This gap in our understanding provides an opportunity for research to investigate macro-pore flow and "upward migration" under South African conditions in more detail.

ABSTRACT

The re-evaluation of pesticide use patterns is a high priority internationally. The process has led to a reduction in the numbers of pesticides allowed for use in many countries. This withdrawal of pesticides is aimed at consumer and environmental protection.

Pesticide mobility and persistence is of major importance especially when considering the protection of water sources. In order to evaluate the suitability of a pesticide for use it is essential that its environmental behaviour is understood and predictable. In this thesis several case studies in which damage to crops may have been caused as a result of herbicides migration are described.

Pesticide adsorption and persistence determinations showed that the adsorption coefficients do not differ from those published. Pesticide half lives are however likely to be prolonged in South African soils.

Field migration studies show that pesticides are vertically and horizontally mobile in South African soils, seemingly independent of soil type. Both migration as well as upward movement was found, due to the mobility of the pesticides in the test soils.

Mobility evaluation was identified as an aspect of importance for registration of pesticides under local conditions. To this end a system is proposed whereby migration can be incorporated into the existing pesticide evaluation framework. The system proposed used the migration model PESTAN as a predictive tool for pesticide migration in the evaluation process. The model is used for the evaluation of pesticides, according to Proposed Pesticide Migration Categories (PPLC). Migration evaluation should be conducted in conjunction with GPS systems to aid in determining potential risk areas where certain pesticide should not be used.

Key Words: Pesticide migration; soil behaviour; modelling; regulatory evaluation

OPSOMMING

Die evaluering van die gebruik van plaagdoders word internasionaal as hoë prioriteit beskou. Die evaluerings het al gelei tot 'n afname in die getal plaagdoders wat beskikbaar is vir gebruik, en is gemik op die beskerming van die gebruiker asook die omgewing.

Die beweeglikheid en nablywing van plaagdoders is veral belangrik wanneer die besoedeling van waterbronne beskou word. Dit is dan belangrik dat plaagdoder-beweeglikheid en -nablywing voorspel kan word sodat plaagbeheermiddels geëvalueer kan word.

So beskryf hierdie tesis gevallestudies aangaande die moontlike skade wat deur onkruiddoders veroorsaak mag word as gevolg van hul beweging in grond. Waar plaagdoder-adsopsie en -nablywing onder SA toestande getoets is, toon die resultate dat adsorpsie nie beinvloed word deur lokale gronde en toestande nie. Nablywing word dan wel beinvloed in die sin dat plaagdoders langer nably in Suid Afrikaanse gronde.

Mobiliteitstoetse dui aan dat plaagdoders beide op en af beweeglik is in die toetsgronde. Dit word gevind dat die evaluasie van plaagdoder mobiliteit en nablywing van kritiese belang is gedurende die registrasie daarvan. Daar word 'n stelsel voorgestel waarin logingsevaluasies deel sal vorm van die bestaande plaagdoderregistrasie raamwerk.

Die voorgestelde stelsel maak gebruik van die logingsmodel PESTAN as hulpmiddel. Plaagdoders word dan geplaas in bepaalde loginsklasse vir doeleindes van evaluasie.

CHAPTER 9.

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