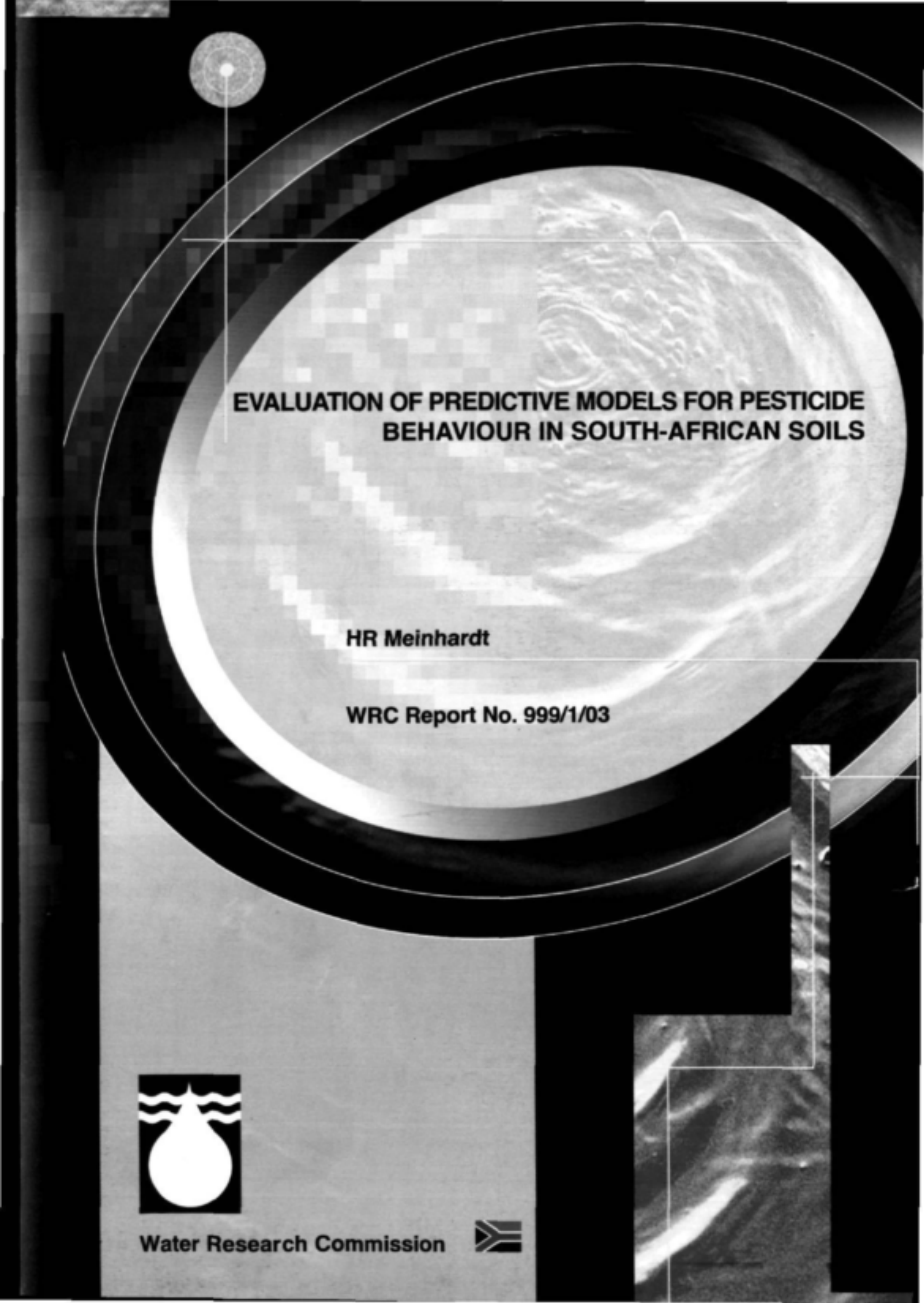

EVALUATION OF PREDICTIVE MODELS FOR PESTICIDE BEHAVIOUR IN SOUTH-AFRICAN SOILS

HR Meinhardt

WRC Report No. 999/1/03

Water Research Commission

Evaluation of predictive models for pesticide behaviour in South-African soils

By

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EVALUATION OF PREDICTIVE MODELS FOR PESTICIDE BEHAVIOUR IN SOUTH-AFRICAN SOILS

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EXECUTIVE SUMMARY

INTRODUCTION

The environmental behaviour of pesticides and other environmental pollutants has in recent years received much attention both from regulators and researchers. Specific aspects that have received attention are, the persistence of pollutants, their bioaccumulation, toxicity, soil mobility and long-range transport as well as the identification of Persistent Organic Pollutants (POP's) in accordance with the Geneva Convention on POP's. Pressure from environmental groups and the public at large has led to regulatory authorities paying special attention to the pesticides in the environment.

When considering persistence of chemicals, it differs of course between different media such as air, soil, water and biota, but also due to climatic and physical factors. With regards to POP's, it has been proposed that if a substance's half-life is longer than six months in soil and sediment, it should be considered to qualify as a POP, if criteria for bioaccumulation and long-range transport potential are also met. Geographical variable climatic and physical conditions affect the half-lives of substances. Substances will tend to have longer half-lives under colder conditions. Arctic conditions for example have resulted in an accumulation of compounds in the biota, including humans, and its effects are becoming evident (Letcher *et. al.* 1995). There might however be other conditions that could prolong the half-lives of substances under warm and arid conditions.

South African soils are generally deemed as having developed from aged geomorphic structures (Partridge and Maud, 1987). The presence of organic topsoil horizons on South African soils is limited (Soil Classification Working Group, 1991), leading to them being characteristically low in organic carbon, and often having low microbial activity. These factors are believed to contribute to higher leaching characteristics and prolonged persistence of certain pesticide residues in soil. If this aspect is considered for the South African situation, many of the high-use pesticides in South Africa could be considered for classification as POPs. This aspect is of importance where compounds are used at high dosage rates and are designed to resist environmental degradation.

Prolonged persistence of pesticides combined with high soil mobility, are indicators of high pollution potential of a pesticide, an aspect that has been the subject of numerous studies. Persistence- and mobility-related problems of pesticides are however not confined purely to classic persistent pesticides, but also to the newer generation compounds. Pesticides have been implicated in causing adverse environmental and health effects for some time. So also the fate and behaviour of pesticides in the environment has been of concern for many decades internationally (Weber, 1991). Low level effects of pesticides and other environmental pollutants on the environment and human health such as endocrine disruption is also of importance. Here we see effects on immune systems and reproductive systems from organic compounds, including pesticides, at extremely low environmental concentrations (parts per trillion). Although much research is done on lowering analytical detection limits for pesticides, the level of interest is becoming even lower. Added to this aspect is that of pesticide development with higher activity at lower applied rates. When regulations have to be evaluated, variability in the properties of the chemical as well as variations in field sites must be taken into account (Flurry, 1996). It is thus obvious that the process of quantifying pollution potential and incorporating this into a regulatory process has been a difficult and slow one.

Under ideal conditions, regions or a country should be mapped according to soil units, thus according to the risk of pesticide loss in the "soil region". This is however a difficult task if the important parameters governing the loss are not clearly understood. It is this aspect which has gained some attention within the realms of modelling pesticide behaviour in the environment as a whole, but especially in soil. The field of modelling pesticide behaviour is especially important when one considers potential pesticide effects at low environmental concentrations such as found with endocrine disruption.

Models are used in developed countries as part of a pesticide screening process for registration and regulation of pesticide use. Models are used despite their accuracy sometimes being dubious. Nevertheless the model gives an indication of how a new compound may behave in the environment, thus serves as a tool for decision making by regulators. The accuracy of the model should not necessarily discourage a regulator from using it. From an environmental and human health perspective, it is important that the model rather over-estimates the pollution potential of a compound rather than under-estimate it. This is a similar scenario to the use of lysimeters packed with sandy soils being used for screening leaching potential. Both these systems provide the worst case scenario for pesticide mobility in soil.

Current South African legislation requires testing under local conditions only of the efficacy and phytotoxicity of a pesticide. Although the environmental and toxicity data are required for registration, the environmental data as produced in overseas countries are accepted for registration locally. This includes data on field soil leaching, persistence, ecotoxicology, effects on environmental indicator species etc. The registration process does not require leaching studies being conducted locally.

It is however internationally accepted that leaching and persistence requirements are essential to safeguard primarily groundwater. In South Africa, such requirements are crucial to safeguard groundwater as well as surface water of especially rural areas. Rural communities carry the highest risk from the use of pesticide-contaminated water. In addition most irrigated agricultural fields are irrigated from untreated water sources, which are at high risk of being contaminated with agrochemicals. It is believed that there is an urgent need for the implementation in South Africa of leaching and persistence evaluation of pesticides as part of the registration process. The time has arrived for this type of environmental screening of pesticides to be done in South Africa. There are approximately 180 pesticide active ingredients on the South African market, available in 400 formulated products. The registration of pesticides in South

Africa is controlled by the provisions of Act No. 36 (1947), and revisions of this Act. The Act is administered and implemented by the Directorate Agricultural Input Productions through the Registrar Act 36 of 1947. The country thus does have a system through which additional screening could be implemented.

AIMS

The primary goal of the project was to evaluate existing computer based - mathematical models, developed Europe and the USA for their efficiency for in predicting pesticide behaviour under South African conditions. The evaluation was aimed at recommending implementation of the use of the most suitable model by pesticide registration authorities. It is believed that this will lead to reduced risk of pesticide contamination of ground and surface waters form pesticide application and thus lead to improved water quality of water used especially in rural communities. In order to attain the aims of the project, the following objectives were set:

1) Collect field leaching data for pesticides and compare to model predictions.
2) Compare results on three field soils, representing a range of soil characteristics.
3) Select pesticides to represent a range of chemical characteristics with regards to their published persistence and soil mobility.
4) Determine parameters for the half-life and adsorption of the pesticides used for field trials.

The evaluation of the models was aimed at recommending implementation of the use of the most suitable model by pesticide registration authorities. It is believed that this will lead to reduced risk of pesticide contamination of ground and surface waters form pesticide application and thus lead to improved water quality of water used especially in rural communities.

MATERIALS AND METHODS

In this study field leaching data for pesticides was collected and compared to model predictions. The study was conducted on three field soils, representing a range of soil characteristics. The soils used were a sandy loam soil, a sandy clay loam and a clay soil. The pesticides used were so chosen as to represent a range of chemical characteristics with regards to their published persistence and soil mobility. The compounds selected were the herbicides tebuthiuron and azifenidin and the insecticide fenthion.

In order for model runs to be conducted, parameters for the half-life and adsorption of the pesticides used to the field soils tested had to be determined. Also meteorological data for the trial sites were required. The sites were all located within a 15 km radius of the Pretoria central weather station. The trial sites were selected in such a way that they were in close proximity to a functioning weather station. Although there are weather stations in the vicinity of each of the trial site, the data from these sites were incomplete, mainly due to poor upkeep at the stations. It was therefore decided to use the Pretoria central weather station data for all three the trial sites.

RESULTS

Adsorption study

Results of laboratory adsorption experiments indicate that the adsorption coefficients for fenthion decreased with soil depth, for both the formulations tested. This data indicates that the extent of adsorption will decrease with soil depth. However the K_{oc} values were all higher than 100, indicating limited mobility. The K_{oc} values were the highest on the clay soil. Data further indicates a trend of lower K_{oc} values for the Queletox formulation, which would indicate that fenthion as the oil-based formulation may be more mobile than when it is formulated as a emulsifiable concentrate formulation.

Results for azafenidin indicate no significant difference in the adsorption due to soil depth or soil type. The data indicates that the compound will have similar leaching characteristic in all three these soils. Similar results were obtained for tebuthiuron.

Half-life study

Results of half-life determinations shows a high degree of variability in analysis results, especially where tebuthiuron is concerned. Results for fenthion and azafenidin indicate no difference in half-life between the sandy clay loam soil and sandy loam soil. The half lives for these two compounds were however significantly higher on the clay soil. The half-life for fenthion of 4 to 7 days is longer than the published and accepted 1 day half-life.

Where tebuthiuron is concerned, no significant differences were found in half-life due to soil type. Data indicates the half-life for tebuthiuron in excess of 500 days irrespective of soil type. This half-life is longer than the generally accepted published value 365 days. The half- lives determined for azifenidin were within the published range of 10 to 45 days.

Field leaching study

Results of field leaching studies indicate that all three the compounds tested leached with ease in all three soils. Comparison of tebuthiuron leaching patterns found in the three field soils tested showed that tebuthiuron leaching patterns were similar in the sandy loam soil and the sandy clay loam soil during the initial time intervals. During the following time intervals up to the end of the trial period, the leaching profiles for the sandy clay loam and clay soils were similar. However a more rapid decrease in tebuthiuron residues from the top soil layer was found on the clay soil as compared to the sandy clay loam soil.

There are also indications of build-up of the compound in the deeper soil and the possibility of to leaching past the deepest soil layer sampled (120 cm).

Residue data for fenthion indicates that fenthion may be highly mobile in all three soils tested. The mobility of the compound is not only limited to leaching, but also to upward movement 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 compound. Data further indicates that fenthion mobility is affected by soil type only during the initial time period where after the soil type seems to have a limited affect on fenthion mobility.

The observed leaching patterns for azafenidin were similar for the sandy loam soil and sandy clay loam soil during the initial time period with similar proportions of applied compound remaining in these two soils. A higher degree of leaching is however apparent in the sandy clay loam soil. After 30 days, azafenidin distribution was similar for the clay and sandy loam soils. In the case of the sandy loam soil, this could be due to extensive movement of the compound whereas very little movement was apparent on the clay 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.

MODEL EVALUATIONS

Linear regression analysis was performed on the observed (measured) data versus model predicted concentrations. This test was performed to test the fit of $y = x$ or measured concentrations over depth for each time interval. A zero constant or intercept and a slope of 1 for the fitted curve would thus indicate a perfect fit. In such a situation, the model predictions fit the actual measured values exactly. An indication of the extent of fit is given as a percentage fit.

The analyses performed for the day 0 data showed that all the models accurately predicted the situation at day 0, rendering a 100 % fit of observed values to model predictions. This is not unexpected, as at day 0 no leaching would have occurred and the initial application rates are given.

Ideally, the model of choice should renders an exact fit of predicted values to those measured. This was not found with any of the three models evaluated. Also the models could not predict upwards movement of the compounds. The Pelmo model is not sensitive to a change in degradation rate entered and for all the compounds and all three soils not only predicted limited leaching, but also limited degradation or dispersion of the compounds. The only model that could predict the leaching as observed, although with limited accuracy is Pestan. Pestan does not allow for more than one soil profile to be entered, and is useful only where the soil profile is homogenous. Also Pestan tends to over-predict the pesticide concentrations especially in the deeper soil layers. However, the model may be useful as a screening tool for predicting the worst case scenario with regards to leaching potential of a pesticide. Pestan does not use input of weather data for calculating leaching and leaching rates. The model uses hydraulic conductivity, re-charge rate and the dispersion ability of the compound in a particular soil to calculate leaching rates. In this evaluation, the dispersion was estimated from the field leaching studies as an average over the trial period. This parameter can however not be changed over the time period for which the model is run. It is believed that a change in the dispersion parameter with time to allow for changes in meteorological conditions may counter the over prediction that the model renders. Also the dispersion parameter will have to be estimated from leaching trials conducted on the compound of interest.

In this study, the model Pestan was run using published hydraulic conductivity values for soils with similar characteristics as the trial soils. This was done because local laboratories no longer do these determinations (ISCW pers. comm). The re-charge rates were set equal to the hydraulic conductivity as suggested by ISCW after tedious deliberations. If this model is to be further investigated, it will be necessary to determine these parameters more accurately.

Future research needs

The project only considered three leaching models in the evaluation of the predictive capacity of the models. It could be valuable to test alternative models such as those used in the Australian pesticide registration system for their efficacy under South African conditions. These model can be run without having to redo the field leaching phase as this data is already available.

As an alternative to the further evaluation of existing models it may be more relevant if the existing water movement models which were developed for South African conditions are modified to include a pesticide leaching module.

The model PESTAN should be evaluated in more detail and the potential use of conversion factors for hydraulic conductivity as well as running the model consecutively for different soil layers should be considered.

The leaching evaluations in this study were done using un-cropped fields. It will be valuable to conduct leaching studies using cropped fields, of the same soil types. This will render data on the effects of cropping on the leaching potential of the pesticides. Such trials can be conducted using only a single pesticides, instead of all three tested in the current study.

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STORAGE OF DATA

All raw data used for the purposes of this study will be kept in archive at the Agricultural Research Council, Plant Protection Research Institute archive facilities at the Roodeplaat –East campus.

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). The convention is aimed at promoting international action to protect human health and the environment by reducing or eliminating releases of POPs. Initially the focus of the INC was to focus on pesticides such as aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene, industrial chemicals such as hexachlorobenzene, and polychlorinated biphenyls and the unintended byproducts dioxins and furans. The identification of additional POPs on science based criteria remains one of the committee's priorities. Specific criteria for persistence, bioaccumulation, toxicity and long-range transport are under consideration (UNEP, 1998a). One of the criteria is persistence. Persistence of chemicals differs of course between different media such as air, soil, water and biota, as well as climatic and physical factors. The Criteria Expert Group (CEG) advising the INC, has proposed that if a substance's half-life is longer than six months in soil and sediment, it should be considered to qualify as a POP, if other criteria, for bioaccumulation and long-range transport potential is met. Geographical variable climatic and physical conditions affect the half-lives of substances. Substances will tend to have longer half-lives under colder conditions. Arctic conditions for example have resulted in a accumulation of POPs in the biota, including humans, and effects are becoming evident (Letcher *et. al.* 1995). There might however be other conditions that could prolong the half-lives of substances under warm and arid conditions.

South African soils are generally deemed as having developed from aged geomorphic structures (Partridge and Maud, 1987). The presence of organic topsoil horizons on South African soils is limited (Soil Classification Working Group, 1991), leading to them being characteristically low in organic carbon, and often having low microbial activity. These factors are believed to contribute to higher leaching characteristics and prolonged persistence of certain pesticide residues in soil. If this aspect is considered for the South African situation, many of the high-use pesticides in South Africa could be considered for classification as POPs. Reclassification of compounds as POPs is especially important where most industrial herbicides are concerned. These compounds are used at high dosage rates and are mostly designed to resist environmental degradation.

Prolonged persistence of pesticides combined with high soil mobility, are indicators of high pollution potential of a pesticide, an aspect which has been the subject of numerous studies. Persistence- and mobility-related problems of pesticides are however not confined purely to classic persistent pesticides, but also to the newer generation compounds. Pesticides have been implicated in causing adverse environmental and health effects for some time. So also the fate and behaviour of pesticides in the environment has been of concern for many decades internationally (Weber, 1991).

Pressure from environmental groups and the public at large has led to regulatory authorities paying special attention to the pesticides in the environment. The process of quantifying pollution potential and incorporating this into a regulatory process has however been a difficult and slow process. When regulations have to be evaluated, variability in the properties of the chemical as well as variations in field sites must be taken into account (Flurry, 1996). Under ideal conditions, regions or a country could be mapped according to soil units, thus according to the risk of pesticide loss in the "soil region". This is however a difficult task if the important parameters governing the loss are not clearly understood. It is this aspect which has gained some attention within the realms of modelling pesticide behaviour in the environment as a whole, but especially in soil.

Researchers in the field of weed science have made the most input into this field. The field of modelling pesticide behaviour is especially important when one considers potential pesticide effects at low environmental concentrations such as found with endocrine disruption. Here we see effects on immune systems and reproductive systems from organic compounds, including pesticides, at extremely low environmental concentrations (parts per trillion). Although much research is done on lowering analytical detection limits for pesticides, the level of interest is becoming even lower. Added to this aspect is that of pesticide development with higher activity at lower applied rates. Examples of these are the sulphonyl urea herbicides and synthetic pyrethroid insecticides. These compounds are applied at dosage rates of between 7 and 30 g/ha. A compound such as the pyrethroid deltamethrin, which has a maximum application rate of 17 g/ha, is a known endocrine disrupter. Detection of a compound such as deltamethrin is difficult enough post-application due to dilution of the compound. Once the compound has entered the soil environment, it is further diluted, but may remain at a concentration where it could cause environmental and health effects. Detection of compounds such as these in environmental samples is made more difficult due to environmental samples being "dirty", with many co-elluents present in the samples.

In such situations, the use of bioassays is useful, as they will indicate whether a water source is contaminated. The identity of the contaminant will however remain unknown, and will still require chemical analysis. Ideally the contaminant should not be allowed to enter the water source in the first place. It is here where regulatory authorities and the use of pesticide fate modelling play important roles.

Models are used in developed countries as part of a pesticide screening process for registration and regulation of pesticide use. Models are used despite their accuracy sometimes being dubious. Nevertheless the model gives an indication of how a new compound may behave in the environment, thus serves as a tool for decision making by regulators. The accuracy of the model should not necessarily discourage a regulator from using it. From an environmental and human health perspective, it is important that the model rather over-estimates the pollution potential of a compound rather than under-estimate it. This is a similar scenario to the use of lysimeters packed with sandy soils being used for screening leaching potential. Both these systems provide the worst case scenario for pesticide mobility in soil.

The time has arrived for this type of environmental screening of pesticides to be done in South Africa. There are approximately 180 pesticide active ingredients on the South African market, available in 400 formulated products. The registration of pesticides in South Africa is controlled by the provisions of Act No. 36 (1947), and revisions of this Act. The Act is administered and implemented by the Directorate Agricultural Input Productions through the Registrar Act 36 of 1947.

Current South African legislation requires testing under local conditions only of the efficacy and phytotoxicity of a pesticide. Although the environmental and toxicity data are required for registration, the environmental data as produced in overseas countries are accepted for registration locally. This includes data on field soil leaching, persistence, ecotoxicology, effects on environmental indicator species etc. The registration process does not require leaching studies being conducted locally.

It is internationally accepted that leaching and persistence requirements are essential to safeguard primarily groundwater. In South Africa, such requirements are crucial to safeguard groundwater as well as surface water of especially rural areas. Rural communities carry the highest risk from the use of pesticide-contaminated water. In addition most irrigated agricultural fields are irrigated from untreated water sources, which are at high risk of being contaminated with agrochemicals. It is believed that there is an urgent need for the implementation in South Africa of leaching and persistence evaluation of pesticides as part of the registration process. Field leaching and persistence trials are costly, the cost to the producer, who passes these costs to the consumer.

These additional costs of pesticide registration should be minimised in order to avoid a negative impact on crop production. However, pesticide leaching to ground water and entrance to surface waters cannot be ignored, and impacts on the environment and human health must be considered. The impact on human health is especially important in rural areas where water used by communities does not undergo treatment and potential contaminant synergistic effects on health could occur. Predictive models may provide the balance in the registration process between essential environmental screening and reduced cost.

1.2 Aims

The primary goal of the project was to evaluate existing computer based - mathematical models, developed Europe and the USA for their efficiency for in predicting pesticide behaviour under South African conditions. The evaluation was aimed at recommending implementation of the use of the most suitable model by pesticide registration authorities. It is believed that this will lead to reduced risk of pesticide contamination of ground and surface waters form pesticide application and thus lead to improved water quality of water used especially in rural communities.

1.3 Approach to the study

In this study field leaching data for pesticides was collected and compared to model predictions. The study was conducted on three field soils, representing a range of soil characteristics. The pesticides used were so chosen as to represent a range of chemical characteristics with regards to their published persistence and soil mobility. In order for model runs to be conducted, parameters for the half-life and adsorption of the pesticides used to the field soils tested had to be determined. Also meteorological data for the trial sites were required. The sites were all located within a 15 km radius of the Pretoria central weather station. The trial sites were selected in such a way that they were in close proximity to a functioning weather station. Although there are weather stations in the vicinity of each of the trial site, the data from these sites were incomplete, mainly due to poor upkeep at the stations. It was therefore decided to use the Pretoria central weather station data for all three the trial sites. Individual rain data from the sites were collected from the sites and manually checked against the Pretoria central data. The exercise showed no difference in rainfall pattern from the sites as compared to the Pretoria central data.

In the section on materials and methods the experimental protocol is described, for the project as a whole. Here the field leaching trials are described and details on soil types etc. given. Under the results section, the laboratory experiments are reported on first, followed by a discussion of the leaching results and finally the comparisons with model predictions are discussed.

2. LITERATURE SURVEY

2.1 Pesticides in South Africa

Approximately 400 pesticides are available commercially in South Africa. These include herbicides, insecticides and fungicides. The largest commercial market lies with herbicides. The formulated products contain approximately 180 active ingredients. The compounds are formulated in various formulations as liquids and dry materials. Before a pesticide may be placed on the commercial market they need to be registered under Act No. 36 of 1947. Registration is granted and administered by the Registrar of Agricultural and Veterinary chemicals of the National Department of Agriculture. Registration legislation requires only testing under local conditions for efficacy and phytotoxicity. Environmental and toxicity data are required for registration, but does not have to be relevant to South African conditions. The environmental data sheets of pesticides are produced in overseas countries and are accepted for registration locally as is. This includes data on field soil leaching, persistence, eco-toxicology, effects on environmental indicator species etc.. The impression is given that the registration process was designed to protect of the crop producer and the pesticide-manufacturing sector and not at protecting the environment, preventing water contamination and its effects on water sources.

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 Unites States of America differs from that is South Africa primarily in that the focus is on the potential health and environmental effects of pesticides, rather than efficacy. Registration screening is therefore focussed at the environment and human health and market forces tend to regulate efficacy requirements. Internationally legislation controlling registration of pesticides demands strict environmental impact studies as part of a package of data that must be satisfied before a pesticide can be registered and commercialised. To meet the data requirements pesticides must undergo extensive laboratory and field-testing. It is a further requirement that the laboratory and field-testing occurs in the country where the compound is to be used. Tests are focused on human health, potential environmental consequences and the compounds reaching water sources. Much of the data required is focussed on pesticide behaviour.

There is a tendency in the European Union to share data, so that a compound registered for use in one member country will automatically be eligible for use in all member countries. This process has however not come to its full conclusion. One of the matters that still requires attention is that of pesticide behaviour and especially prediction of behaviour in soil. The EU has launched an investigation into determining, which of the models used should be the standard. Currently the Pesticide Leaching Model (PELMO) is most widely used. Attempts are made to develop the PELMO screening system with a Geographical Information System (GIS) based data-base. Should such a system come into use it would enhance the potential of joint registration greatly (Klein, 1999). Due to the great variation in South African soils and variable environmental conditions this type of application could be ideal for the South African registration process. However, South Africa is not yet using an environmental screening approach for local conditions, let alone such a well-developed systems as model links to GIS. The first step in pesticide behaviour assessment for South Africa would be to select or develop appropriate models i.e. establish a validated model for South African conditions.

2.2 Pesticides and human health

Limits are set for pesticides residues that may occur in soil, water, the atmosphere, plants and in foodstuffs and are contained in legislation. In most cases critical concentrations are used on which these limits are based. Modern pesticides are developed with low toxicity and low persistence in mind whilst being highly effective, with new generation compounds being applied at low dosage rates. The applications of active ingredients at rates of <20 g ha^{-1} is not uncommon. The older more toxic and persistent compounds such as DDT are either being phased out or their use is strictly controlled. In most cases limits of pesticide residues allowed in the environment and in foodstuffs are based on toxicity data from laboratory trials. There is a tendency internationally of agencies setting pesticide residue limits on the minimum detectable residue levels of current analysis methodology.

2.3 Pesticides and water resources

Most of the environmental problems that occur due to pesticides are due to the movement of a pesticide away from the intended target location, e.g. because of spray drift, vaporisation, leaching and soil erosion through wind and water action. The discovery of pesticides residues in ground water in the agricultural areas of the USA in the mid seventies has been due primarily to monitoring, using suitable analytical techniques (Barbash and Reseck, 1996). Many further reports of incidences of pesticide in ground water have been reported internationally since (Walker and Hollis, 1994).

Levels of pesticides detected in groundwater have generally been lower than those in surface water. However the primary effort on regulating pesticide residues in water has been focussed on groundwater. The reason for this is that surface water undergoes severe chemical processing before its used as drinking water. So the primary aim behind the regulations is the protection of the larger proportion of the population (Gustafson, 1999). Groundwater on the other hand collected from wells internationally is used as is with little on no pre-treatment.

Within the South-African scenario this is especially true for rural areas, and pertains not only to ground water, but also surface water. 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. In the South African rural context, the water sources are however not only limited to ground water, but also surface water used by households.

Internationally much effort has been spent on understanding the processes that control the transport of pesticides in soil and eventually to groundwater. In parallel efforts have been made to limit the amount of pesticide, which will be allowed present in water sources. Strict limits has been placed on acceptable pesticide residue levels in water (Gustafson, 1999). The maximum permissible residue limits for pesticides are somewhat arbitrary as it is not based on toxicological properties of pesticides, but rather on the lowest level that modern technology can measure. Based on these limits, the registration process in developed countries takes into account the potential pollution by pesticides of water sources. The main motivation internationally for screening of pesticide leaching potential is the prevention of pesticide pollution of water sources but more specifically ground water sources. This aspect is not receiving much attention in South Africa. Pesticide leaching data and that of persistence used for registration are accepted as is from overseas sources.

Techniques applied to evaluate pesticide leaching include laboratory and field experimentation, monitoring studies in which the levels of pesticides are measured and movement are evaluated. However, the risk of pollution of water sources is determined by a number of variables. The amount of excess water in the soil, the depth of the water table, and adsorption of pesticide residues to soil colloids are all aspects which must be considered (Groen, 1997). To take into account all potential variables that may occur within a country in laboratory and field studies is not practical. Because of difficulties in determining long-term pesticide behaviour in soil as well as the high costs involved, much developmental effort has gone into the prediction of pesticide behaviour. Model developers have spent much effort on the development of predictive models for leaching and surface run-off from pesticide treated areas. The use of screening and simulation models in pesticide regulation has grown internationally, but has yet not been considered for use in South Africa.

Models have advantages over other methods in pesticide management. These advantages include reduced cost, extrapolation from relatively small sets of data, and the potential for establishing standard criteria for registration of both the tested chemical and similar compounds (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.

2.4 Solute transport and flow in the unsaturated zone

2.4.1 Solute transport the pesticide perspective

Water is the primary carrier of solutes in soil. The result of movement of the solutes is a result of three processes: convective transport in the liquid phase, diffusive transport in the liquid phase and diffusive transport in the gas phase. Convective solute transport in soil leads to solute dispersion in the soil profile.

Water movement is distinguished in two different systems within the soil, the unsaturated zone and the saturated zone. The two systems are a continuum with the saturated zones, the wet extreme. However, for modelling purposes these are separated. In the unsaturated zone, water movement is generally one-dimensional in a vertical direction. Here solute movement will percolate downwards due to excess water input from either irrigation or rain (Groen, 1997). Where the extraction of water from the soil is high, such as due to high evaporation rates, movement may occur upwards.

Water flow in the saturated zone is generally assumed to be in the direction of ground water movement. In soil with lateral sub-surface drainage, ground water flow is assumed to be horizontal (Groen, 1997).

This discussion will be limited to the processes in the unsaturated zone. Factors that limit the transfer of chemicals in the soil can be summarised to include adsorption to soil colloids, volatilisation and surface run-off. The extent of volatilisation is dependent primarily on the volatility of the compound, therefore chemical properties.

2.4.2 Adsorption

The rate of movement of a solute in its simplest form is dependent on its sorption capacity to the soil and so is an important process in determining the fate of pesticides in soil (Bailey and White, 1970). Adsorption of the solute in the soil is a function of chemical characteristics of the solute, but also soil characteristics. Solutes are adsorbed to soil colloids (Mora et al, 1996) which carry an electrical charge and which adsorb solutes carrying a charge. Adsorption is generally temporary as expected in as adsorption/desorption system. An equilibrium exists between the fraction of solute adsorbed and that in soil water.

The adsorption of solutes to colloids is a function of the charge that the molecule carries, and the charge on the colloid. Solutes are present in soil solution either as anions, or cations, or neutral molecules. Amphoteric compounds 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 influencial effect on the mobility of pesticides in soil.

The most important soil colloids are organic colloids or organic matter and inorganic clay minerals. The adsorption capacity of soil can be quantified and is expressed in terms of base exchange capacity or cation exchange capacity (CEC) of soil. The two main representative clay types regarding adsorption of solutes are smectite and kaolinite. Organic matter consists primarily of the humus fraction, (mainly humic and fulvic compounds) and organo-metal complexes (Sannini et al, 1996). The adsorption capacity of these colloids for pesticides is: organic matter greater than montmorilinite, greater than kaolinite.

Interactions between pesticides and the interfaces of organic and inorganic soil colloids through adsorption and desorption mechanisms influence the amount of free pesticides (Sannini et al, 1996). 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 free fraction. One of the main assumptions that is made in the modelling process is that the attainment of equilibrium is instantaneous. The sorption 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)

C_e = 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

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

Where:

Q^o = 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) give 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

The reference concentration should be at the order of magnitude at which pesticide sorption measurements are normally made. It can be assumed that the pesticide sorption system to soil is heterogeneous. Because the Langmuir isotherm assumes uniform sorption, the Freunlich isotherm is preferred as it accounts to some extent for surface heterogeneity (Boesten, 1986 in Groen, 1997).

In addition to sorption, the distribution of the solute between the gas and liquid phase will also influence leaching. This is a function of the volatility of the compound being investigated. Volatilisation is the process in which a chemical evaporates in the vapour phase to the atmosphere from a different environmental compartment. The rate of evaporation is dependent chemical properties of the compound, as well as environmental conditions. Where pesticides are applied directly to soil it is assumed that loss through volatilisation is negligible, and is thus not taken into account. The situation changes where pesticides such as fumigants are considered.

2.4.3 Preferential flow

The term preferential flow refers to a range of physical non-equilibrium flow processes in soil. The process dominates on fine textured soil and occurs through macropores such as shrinkage cracks, worm holes and root pores. In these soil macropores operate structures as high-conductivity flow paths, and by-pass the denser soil matrix (Jarvis, 1996). Preferential flow can also occur in unstructured sandy soil as a result of profile heterogeneity such as at horizon interfaces, due to texture variations and even through water repellence. Preferential flow will also occur on homogenous soils with soils with sub-surface drainage (van der Zee and Boesten, 1991). During preferential flow, solutes leach more rapidly than would be expected. 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 soil matrix. Preferential flow is important in pesticide leaching because the pesticide rapidly by-passes the top-soil, into the sub-soils. In the sub-soils, adsorption and degradation generally greatly decreases or slows down. From the available experimental data it can be concluded that preferential flow is rather the rule than the exception (Flurry *et al*, 1994). This means that the models that do not take these processes into account may not be that widely applicable. A number of models have been developed which take preferential flow into account. There are two major groups of preferential flow models, those which 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. This means that additional parameters are required for the multi-domain models. These include fractions of sorption sites per domain, the diffusion path length which regulates exchange between domains and soil hydraulic conductivity defining each domain.

2.4.4 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 from the soil. The rate of loss is determined by the combination of the degradation processes and the transfer processes. Persistence is thus a function of degradation. Degradation occurs through biological decomposition (microbes and plants), chemical degradation and / or photo-decomposition. Not all pesticides are prone to all three these degradation processes.

The persistence of a pesticide is mostly characterised by the half-life of the compound. The half-life or DT_{50} is defined as the time in days required for the concentration of a compound 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. It must be kept in mind that degradation may occur during any stage of transfer.

2.4.4.1 Biological decomposition

This includes decomposition by microbes and metabolic decomposition by plants. Some microbes have the ability to use herbicides as a food source, expending O_2 in the process releasing CO_2. The higher the microbial activity of a soil, the higher the rate of microbial degradation to be expected for those pesticides prone to microbial degradation. Generally the higher the soil organic matter content, the higher the microbial activity. Soil microbial activity is also affected by temperature, water, O_2, pH and nutrient availability. Thus if a herbicide is prone to microbial degradation, the residual activity of such a compound will also be affected by these factors.

2.4.4.2 Chemical degradation

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

2.4.4.3 Photo decomposition

Pesticide molecules absorb light energy, electrons are excited, and chemical bonds are broken. Some herbicides are more sensitive than others to light. In order to be effective, light-sensitive herbicides must be incorporated into the soil immediately after application, or be washed into the soil by means of irrigation.

2.5 Pesticide Models

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

2.5.1 Screening Models

Screening models classify pesticides for their water contamination potential. One such model is the Groundwater Ubiquity Score (GUS) index developed by Gustafson in the late 1980's (Walker and Hollis, 1994). Gustafson proposed a single index for pesticide contamination potential based on the soil/water partitioning coefficient (K_{oc}) and the soil half-life (DT_{50}). The basis of the model is that pesticides that are weakly absorbed, and have prolonged soil persistence will have a greater potential of contaminating ground water. This index was developed for data on chemicals found in well water in surveys in the USA. Gustafson estimated average K_{oc} values and field-derived half-lives for the chemicals found in the water. He then constructed a diagram which showed a grouping of groundwater contaminants in one section of the diagram. From this data Gustafson, developed the GUS index given as:

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

The half-life (DT_{50}) 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. Applying the GUS index to British data indicated a reasonably accurate transition of pesticides which are frequently detected and those that are infrequently found (Walker and Hollis, 1997). Screening models however only provide qualitative indications as to leaching potential of chemicals.

2.5.2 Predictive models

The more complex simulation models can be used to make more qualitative comparisons of pesticide leaching. A number of such models have been developed and improved upon over the last number of years. Scientists in the field of weed science developed these models for herbicides.

VARLEACH

The model VARLEACH of Walker, (1987) is a modification of the model CALF of Nicols et al, (1982). VARLEACH is a simple leaching 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 will calculate evaporation. It further requires a measurement (or estimate) of soil water content at field capacity and at 200 kPa. 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 runs off a Fortran coded file in DOS. The model output gives water content with depth, residue concentrations with depth (μg/kg), water-phase concentration with depth (μg/l), total flow across the lowest boundary (maximum 2 m depth), total leaching loss, and average "leachate" concentration over the whole simulation period. The user can specify time intervals at which the outputs are given. The calculations in the model are carried out in successive 1-cm layers, but can 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 Model:

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

Weaknesses of Model:

The model does not allow for volatilisation, cannot incorporate crop growth and uses a tipping bucket-type water flow routine (Vischetti *et al.*, 1997, Cheah-UanBoh *et al* 1997; Baer-U and Calvet-R, 1996, Giupponi, et al, 1996, Brown, CD; Baer-U; Gunther-P; Trevisan-M; Walker-A; 1996, Walker-A et al, 1996, Gottesburen B et al, 1995, Borchers-U 1995). Model inputs are done in dos format, which makes it tedious.

The Pesticide Root Zone Model (PRZM)

The model was first released in 1984 and is the most widely used leaching simulation model (Gustafson, 1993). It is used by the EPA in the pesticide screening procedure and includes a volatilization model and can model up to two metabolites during a single run. Based on this model, the German model PELMO was developed by Klein (1991).

Pelmo

PELMO was developed to estimate the leaching potential of pesticides through distinct soil horizons based on an extended cascade model. It includes the estimating potential for soil temperatures, pesticide degradation, sorption, volatilization, and estimate of potential evapo-transpiration using the Haude equation. It is viewed as an enhancement of the 1984 version of PRZM. Applications have mostly involved pesticide leaching 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 (Haude, 1952) or direct input of the potential evapo-transpiration if this data is available. PELMO calculates depth-dependent temperature in soil using daily air temperatures.

The input for PELMO includes pesticide parameters such as half-life, temperature and water content factors for half-life, organic carbon, soil partition coefficient (Kd, Kf). Freundlich exponent, limits for using Freundlich equation, rate, date 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 consists of daily precipitation, daily mean temperature, relative humidity, maximum air temperature, and potential evapo-transpiration (if available). The output is given as depth and time-dependent pesticide concentrations in the soil profile (kg/ha), the amount of pesticide in the 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 model

Default values can be used for estimation of leaching for screening purposes. Fate data which are necessary for the registration of pesticides such as sorption and degradation according to OECD standards can be considered in the model.

Model Weaknesses

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

The model suite – Waterloo Hydrogeologic Incorporated (WHI) UnSat Suite

The latest developments in pesticide fate modelling has 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 developed from Visual HELP which was the first model 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 by environmental scientists 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: VS2D/T, 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 will only allow run for its specific input types.

PESTAN

PESTAN is a U.S. EPA model for assessing contamination of soil and groundwater with pesticides. 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 organic pollutants, commonly pesticides, through homogeneous soil to groundwater. The model is based on a close-form analytical solution of the advection-dispersive-reactive transport equation. The model was developed for initial screening assessments to evaluate the potential for groundwater contamination of already registered pesticides and those newly submitted for registration. The model has been tested under field and laboratory conditions

The model simulates constant re-charge rate, agricultural application of pesticides, flow and transport of pesticides through the soil with constant velocity, sorption and decay of pesticide and leaking of the pesticide to groundwater. The vertical transport of dissolved pollutant 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. A maximum of ten applications of the active ingredients can be applied in a single calculation and for each application. The slug begins to enter the soil at the first precipitation and irrigation event at a rate equal to the pore water velocity. The pollutants stored at the soil surface before the re-charge is subject for solid-phase decay. Once the recharge starts, the remaining pollutant are considered dissolved and starts to enter the soil. In the soil, liquid-phase decay, sorption and dispersion influence the pollutant. The flow of the pollutant slug occurs with the constant velocity. The hydraulic conductivity of the soil accounts for partially saturated conditions using the Campbell's equation.

VS2DT

VS2DT (Variably Saturated 2-D Flow and Transport Model) is a basic unsaturated zone model based on the solution of Richardson's equation. This model describes the transport of contaminants with unsaturated water flow and their transformation in the heterogeneous vadose zone. The model is used by the US Geological Survey (USGS), as a finite difference model for cross-sectional, variably saturated flow and transport in porous media. This model describes the transport of different contaminants, including radioactive with unsaturated water flow and their transformation in the soil and vadose zone and leaching of contaminant to groundwater. The model simulates processes of surface storage (constant head), infiltration (constant flux), seasonal soil evaporation, plant transpiration, and vegetative plant growth. Also unsaturated vertical flow (van Genuchten, Brooks and Corey and Haverkamp functions); pollutant transport with hydraulic dispersion, pollutant decay, pollutant adsorption

(Freundlich and Langmuir isotherms), ion exchange (monovalent-monovalent, divalent-divalent, monovalent-divalent, divalent-monovalent) are simulated.

Initial conditions may be used as water content or as pressure head for water and as concentration for chemical uniformly throughout the profile or by individual layers. An equilibrium profile may be specified above a user-defined free water surface. The model allows only for multilayer heterogeneous soil profiles. This aspect makes the model seemingly an ideal tool for use in pesticide leaching predictions. The ability of the model to take only inputs for multi-layer heterogenous soil profiles was unfortunately also a major drawback in this project. The soil profiles used in the experiments reported on in this report are all single layer profiles. Although some characteristic differed between the top and sub-soil layers, the soil remains of the same type.

Unfortunately the model VS2DT does not allow for inputs of such soils. Attempts made to enter the soil data as if they were two separate horizons, and run the model, failed. Because of this, VS2DT was not included in the evaluation.

V LEACH

VLEACH is a popular U.S. EPA model for making assessments of contamination of soil and groundwater with volatile organic contaminants. The model allows for a one-layer homogeneous profile with an initially uneven distribution of a volatile contaminant. The model simulates a constant re-charge rate, constant flow and transport of a volatile contaminant through soil, sorption, volatilisation, diffusion to atmosphere and leaking of contaminant to groundwater. VLEACH is a 1-D finite difference model. The code simulates leaching in a soil polygon. The contaminant may be present in the soil as initial condition and may be introduced at the top boundary as a concentration for the recharge. A polygon is represented as a vertical stack of cells with constant depth that reach from the land surface to the groundwater table. The soil properties are considered to be uniform within the polygon. The initial contaminant concentration may vary from cell to cell.

The total mass of contaminant within each cell is partitioned among three phases: liquid (dissolved in water), vapour, and sorbed to solid surfaces. For simulation purposes, the total simulation time is divided into user-specified discrete time steps of constant length. During each time step there are three separate processes that take place. The contaminant in the liquid phase is subject to downward advection, and the contaminant in the vapor phase is subject to gas diffusion. Finally each cell is re-equilibrated according to the distribution coefficients. Gas diffusion can take place at the top and bottom boundaries. The mass flux in the liquid phase running across the bottom boundary is calculated. The model assumes a steady-state downward water flow. The processes of in-situ degradation or production, and dispersion are neglected.

The model proved to be a very efficient tool for estimates of environmental impacts of industrial sources of groundwater contamination such as leaking from underground fuel tanks or spills from the pipelines. The ability of the model to account for volatilisation and air diffusion of the volatile organic contaminants makes it a unique tool. The model does however not allow for zero volatilisation parameters. In this study, the compounds of interest are all non-volatile, and thus this specific model within the suite was rendered unusable.

HELP

HELP is a U.S. EPA model for predicting landfill hydrologic processes and testing the effectiveness of landfill designs, enabling the prediction of landfill design feasibility. HELP has become a requirement for obtaining landfill operation permits in the U.S.A. HELP is also used for assessment of groundwater recharge rates.

HELP is a quasi-two-dimensional hydrologic model and accepts input data of weather (precipitation, solar radiation, temperature, evapotranspiration parameters), soil porosity, soil field capacity, wilting point, hydraulic conductivity, and also engineering design data such as liners, leachate and runoff collection systems and surface slope.

The profile structure used is typically multi-layer, consisting of a combination of natural (soil) and artificial materials (waste, geomembranes) with an option to install horizontal drainage, and change the slope of profile parts (e.g. landfill cap, leachate collection and removal systems).

HELP was designed around a landfill site design concentrating on water percolation and flow through the landfill system. The model does not allow for determination of the flow of solutes in the system. This model is therefore not useful for the prediction of pesticide movement as was required in this project.

PRZM version 3.12.

As has been mentioned the latest developments in pesticide modelling have centred around developing software. PRZM-3 is an example of a software modelling system that links subordinate models. PRZM3 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 leaching through the plant root zone into and through the unsaturated zone in a single run. Even though the run is run as a single one, the processes distinguishing movement in the root zone from that in the unsaturated zone remain separated.

PRZM is a one-dimensional, finite-difference model that accounts for pesticide and nitrogen fate in the crop root zone. PRZM-3 includes modelling capabilities for such phenomena 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 compound and as many as two metabolites.

VADOFT is a one-dimensional, finite-element code that solves the Richard's equation for flow in the unsaturated zone. The user may make use of constitutive relationships between pressure, water content, and hydraulic conductivity to solve the flow equations. VADOFT can also simulate the fate of two parent and two daughter products.

The PRZM and VADOFT codes are linked through execution supervisor that allows for site-specific situations, in order to perform probability-based exposure assessments.

The linkage of the tow 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 is not yet complete. The model runs through an execution, which is edited using a DOS editor. A major problem with the model is that it can 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.

3 MATERIALS AND METHODS

3.1 Laboratory studies

3.1.1 Determination of adsorption coefficients (K_{oc})

The K_{oc} of the compounds was determined using the OECD batch slurry method (OECD, 1981). The 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. Soil was collected form field plots and air-dried. Soil characteristics are set out in Table 1. The tests were conducted using pesticide as the formulated product. The pesticides selected for the trial work were the herbicides tebuthiuron as the 20% granular formulation Molopo (Dow chemicals) and azifenidin as the 80 % wettable granule formulation Evolus (Du Pont) and the insecticide fenthion as a 50 % emulsifyable concentrate Lebaycid (Bayer) and the 64% ULV formulation Queletox.

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 $CaCl_2$ solution to render an active ingredient concentration of 1 mg/l. Each pesticide determination consisted of three replicates, and fortified matrices and blanks included determining recovery rates and background interference. Analyses were based on solvent extraction and analysis by Gas Chromatography.

Calculations were based on the method as described by Weber (1991), in which the concentration is expressed in nmol per g soil.

3.1.2 Determination of soil half-lives of pesticides

Pesticide soil half-lives were determined using a standardised time-lapse analysis. Soil was air dried, fortified with pesticide and placed in a controlled environment glasshouse. Average day temperature was measured as 27 °C and average night temperature as 15 °C. For each soil and each pesticide three replicate samples were used. Samples were removed and analysed at day 0 (staring 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.

3.2 Field experiments

The field leaching evaluations were done in field studies, where plots were sprayed with the compounds of interest and leaching determined by sampling soil at various depths over at set time intervals

3.2.1 Field trial site selection

The trials were conducted on three soils in the Pretoria area. The sites are located at Roodeplaat (ARC-VOPI) and the University of Pretoria. At each site the top 0 -20 cm soil layer and 40 – 60 cm soil layer was sampled and analysed for soil characterisation. Samples were taken as composite samples with each sample consisting of five sub-samples. Results of soil analysis are given in Table 3.1.

Table 3.1 Selected soil properties of the soils used in experimental work.

Site number	Location	Soil Horizon (cm)	Clay content*	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 (Kt)	0.37	8.41

* Dominant clay mineral: Kt = Kaolinite St = Smectite

The trial sites were located at:

- University of Pretoria experimental farm, Pretoria: located at 25°5400 (S)28°15 69(E)
- ARC-VOPI Roodeplaat experimental farm, district 5 located at 5: 25°3614 (S)28°21 29(E)
- ARC-VOPI Roodeplaat experimental farm district 12 located at 25°35 78 (S)28°21 51 (E)

The soils were selected to represent a range of soil properties, with regard to clay type, clay content, organic carbon content and soil pH.

3.2.2 Pesticide selection

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

- tebuthiuron (herbicide) (Molopo – Dow chemicals: test compound UPI – com-009)
- azifenidin (herbicide) (Evolus Du Pont: test compound UPI com-007)

- fenthion (insecticide) (Lebaycid – Bayer: test compound UPI com-008).

3.2.3 Field experiments

At each of the three experimental sites, three experimental plots were set out, each plot measuring 10m X 15m (150m^2). At each trial site, the three plots were treated individually with the three compounds selected. The compounds were be applied as formulated product at an application volume equivalent of 500 l/ha. The applications were made using a standard knapsack sprayer fitted with a pressure gauge. The application dosage rates were calculated from the day 0 field residue determinations and are given in Table 3.2. The compounds were applied at an operating pressure of 3.2 bar and applied at a speed of 1m/s. All equipment was calibrated before application. The compounds were applied to bare soil. The fields were ploughed to 50 cm depth, disced and rotovated before application.

Table 3.2. Application dosage rate of pesticides applied

Compound	**Soil type**	**Active ingredient recovered (kg a.i/ha)**
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

3.2.4 Field sampling

Samples were collected at five time intervals. The first sampling event took place at time 0, i.e. day of application. Follow-up samples were collected after 18, 30, 60 and 120 days of application. At each sampling interval samples were collected of the 0 – 20 cm, 20 – 40 cm, 40 – 60 cm, 60 – 80 cm and 80 - 120 cm soil horizons separately. A composite sampling strategy was followed in which each sample was composed of five sub-samples taken across the field. Sampling was replicated three times per plot, per compound, rendering three composite samples per time interval per soil horizon for each pesticide. The sites remained undisturbed for the period of the trials. The trial sites were kept weed free through chemical control using Rounup as a 3 % (volume per volume) solution.

3.2.5 Sample analysis

Samples were by the Pesticide Analytical laboratory of PPRI. Fenthion residues in soil were analysed using the protocol PALSRAM 68 as registered in the PAL protocol registry system. Tebuthiuron residues were analysed using the protocol PALSRAM 67 as registered in the PAL protocol registry system. Azifenidin was analysed according to the protocol PALSRAM 78. For each soil and each pesticide, fortified matrix samples and blank samples were analysed for the determination of recovery as well as potential interfering peaks. In addition, pesticide residue stability in samples under storage was determined over a 12-week storage period.

3.3. Simulation Models

Models were selected after consultation with model developers and software companies that distribute the products as well as relevant literature on the subject. Presently numerous models are available for the prediction of leaching in soils. The Scientific Software Group have approximately 22 models for the prediction of organic solutes in the unsaturated zone. Discussions with researchers in the field of pesticide modelling including Allan Walker (Developer, VARLEACH), Michael Klein (Developer, PELMO), Richard Kubiak (Head of Research Saatliche Lehr- und Forschunganstalt, Neustadt, Germany) and Developers at the Scientific Software Group led to the decision on the models which could be used in this study. VARLEACH was selected as an early model for evaluation, PELMO because of its extensive use in the European regulatory system, WHI Unsat Suite due to its development to cover a range of potential applications and its extensive use by the United States Environmental Protection Agency for pesticide screening and PRZM 3 as representative of the latest version of the PRZM model used extensively in the US pesticide regulation system. Three of the models within the WHI Unsat Suite could not be included in the evaluation. These were VS2DT, Vleach and HELP. The reasons for these not being included were that VS2DT was designed for multilayer soils and attempts to enter the soil data as if they were relevant to two separate horizons instead of the single horizon of the field soils used. In the case of VLEACH, it was designed to model movement of volatile compounds, and an attempt to run this model with the compounds, which are non-volatile again, failed. HELP was designed as a tool for the design of landfill sites, and relies on water movement in its predictions. The model is not suitable for prediction of pollutant movement.

The model PRZM 3 uses outputs from the root zone model as inputs for the unsaturated zone model (VADOFT). The two are however linked and cannot be run separately. The PRZM code can however not be run for un-cropped fields. An attempt to run PRZM 3 by entering zero values for the plant related parameters, failed.

The models used in the evaluation were limited to VARLEACH, PELMO and PESTAN.

3.3.1 Model simulations

Half-life data and the adsorption data from laboratory trials were used as inputs for all the models. Metereological data sourced from the weather bureau (Appendix 1) was used as inputs for the PELMO and VARLEACH models. The weather data required included daily mean temperature, humidity, rainfall and evaporation data.

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 metereological data required are data file which contains evaporation from an open water surface (Eo, mm), daily values of Max temperature, Min temperature and rainfall.

The model outputs were given as the concentration of the pesticide (µg/kg) per soil layer for each specified time interval. This data was saved as a text file and later imported to MS Excell for statistical purposes.

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. This data was first converted to µg/kg 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.

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 compound 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 leaching data.

The outputs for the model PESTAN are pesticide soil concentrations for the profile for each cm soil layer, for specified days after application.

4. RESULTS

4.1 Laboratory experiments.

4.1.1 Soil adsorption experiments

The results for adsorption coefficient determinations are given in Table 4.1. Analysis of variance was performed on the adsorption data. The least significant difference indicated in the tables reflects the interaction of soil type, pesticides and soil depth. The calculations used to calculate the adsorption coefficient are based on that of Weber (1991), in which concentrations are expressed in nmol per g soil.

Results indicate that the adsorption coefficients for fenthion decreased with soil depth, for both the formulations tested. This data indicates that the extent of adsorption will decrease with soil depth. However the K_{oc} values were all higher than 100, indicating limited mobility. The K_{oc} values were the highest on the clay soil. Data further indicates a trend of lower K_{oc} values for the Queletox formulation, which would indicate that fenthion as the oil-based formulation may be more mobile than when it is formulated as a emulsifiable concentrate formulation.

Table 4.1. Results of adsorption coefficient determinations

	K_{oc}							
	Lebaycid		Queletox		Molopo		Evolus	
	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Sandy loam	9281	5781	2240	986	35	210	400	247
Sandy clay loam	3571	2625	3967	1155	74	581	379	1327
Clay	21206	17731	5585	2244	153	511	237	140

LSD = 1092

Results for azafenidin indicate no significant difference in the adsorption due to soil depth or soil type. The data indicates that the compound will have similar leaching characteristic in all three these soils. Similar results were obtained for tebuthiuron.

4.1.2 Soil half -life determinations

Results of half-life determinations are given in Table 4.2. The variability of analysis results were high, especially where tebuthiuron is concerned. Results for fenthion and azafenidin indicate no difference in half-life between the sandy clay loam soil and sandy loam soil. The half lives for these two compounds were however significantly higher on the clay soil. The half-life for fenthion of 4 to 7 days is longer than the published and accepted 1 day half-life.

Table 4.2. Pesticide Half-lives determined from laboratory trials

Pesticide	Sandy Clay Loam	Sandy Loam	Clay
Fenthion	4.54 ± 0.12	4.57 ± 0.47	7.20 ± 1.85
Azafenidin	12.18 ± 1.39	14.31 ± 1.25	33.46 ± 2.47
Tebuthiuron	566.35 ± 179.70	535.56 ± 312.82	576.19 ± 160.43

Where tebuthiuron is concerned, no significant differences were found in half-life due to soil type. Data indicates the half-life for tebuthiuron in excess of 500 days irrespective of soil type. This half-life is longer than the generally accepted published value 365 days. The half lives determined for azifenidin were within the published range of 10 to 45 days.

4.2 Field experiments.

4.2.1 Field leaching studies

4.2.1.1 Tebuthiuron

Results of analyses of the day 0 samples indicate that no leaching had occurred beyond the 20-cm soil horizon. These results further showed a significant difference between the actual applied field dosage rate, calculated from residue analysis data. The highest tebuthiuron concentration was found in the clay soil and the lowest concentration in the sandy loam soil. Such variability 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 makes it impossible to apply a pesticide to a field soil and effect exactly the same soil pesticide residue level. Variability of up to 20 percent is commonly found in closed spray chambers where pesticide is applied to soil in pots. The results found for each soil type tested is described below per soil separately.

Sandy loam soil

The results of tebuthiuron leaching in the sandy loam soil presented over time are given in Figure 4.1. Results show an increase in tebuthiuron concentration in the 20 – 40 cm soil horizon within 18 days of application.

Results further indicate that tebuthiuron leached into the deeper soil horizons rapidly, within this time interval. Tebuthiuron residue levels in the soil layers below 40 cm were low and were similar to the lower extreme of the profile sampled. A significant increase in tebuthiuron residue levels was found at day 30 in the 20 – 40 cm and 40 – 60 m soil layers remaining similar up to day 60. By day 120 the decrease in the residue levels was observed in the 20 – 40 cm soil layer, coinciding with an increase in the soil layers below 60 cm in the profile. The data indicate that tebuthiuron leaching had occurred to from the top soil layer (0 –20 cm) to the 20 – 40 cm soil layer rapidly within the first 30 days of application. After this initial rapid movement period, a slower percolation process is seen to the deeper soil layers up to the end of the trial period. Data further indicates limited degradation of the compound in this soil.

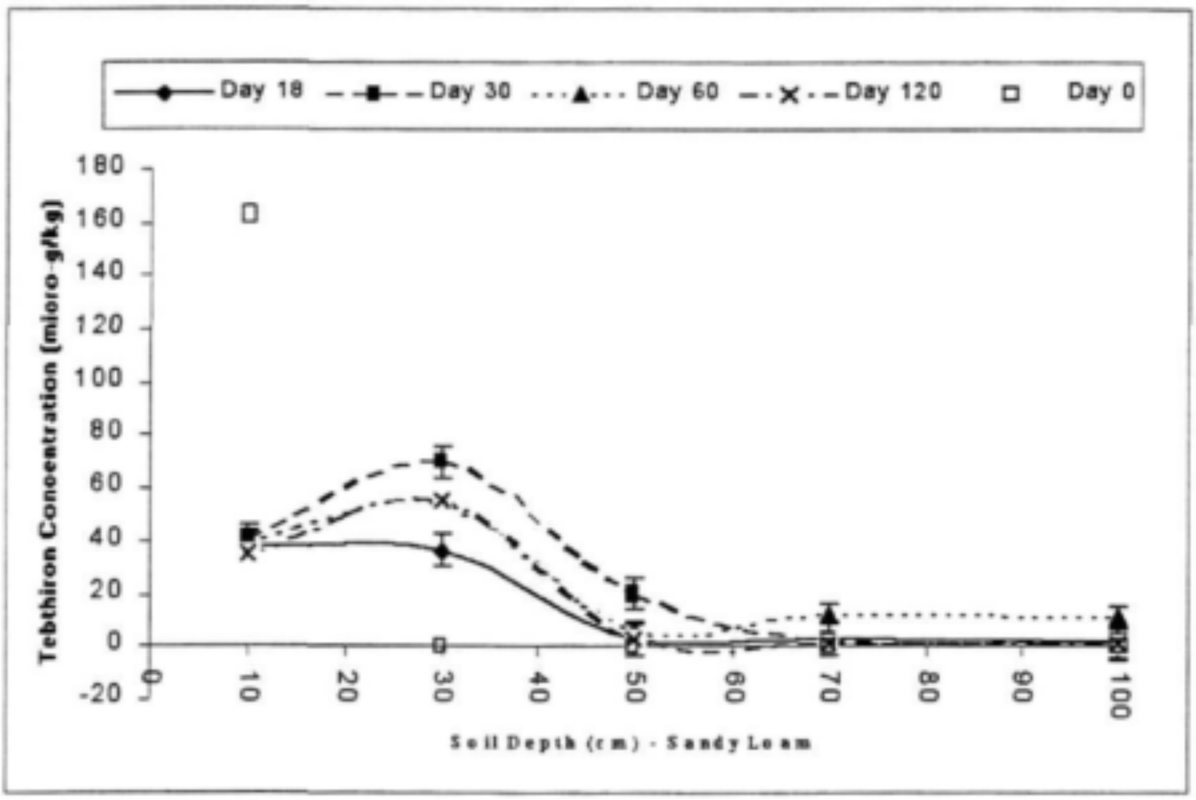

Figure 4.1. Tebuthiuron residue levels detected in the sandy loam soil for the time intervals day 1, day 30, day 60 and day 120.

Fitting an exponential regression to the mean observed values rendered a general exponential equation of tebuthiuron concentration versus soil depth.

The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

Day 18 sandy loam soil: $y = 3.958 + 111.5(0.95)^x$
Day 30 sandy loam soil: $y = 11.84 + 102.7(0.959)^x$
Day 60 sandy loam soil: $y = 16.68 + 106.6(0.939)^x$
Day 120 sandy loam soil: $y = 5.61 + 102.5(0.939)^x$

When comparing the slopes of the fitted curves for the different time intervals, it can be seen that there is limited change in the slopes with time. This indicates that the tebuthiuron leaching rates did not change with time, and that for the sandy loam soil tebuthiuron leaching will be constant over time, and almost perpetual. It is clear from Figure 1 that this is not the case. The fitted curve does not take into account the increase in tebuthiuron residue levels found in the top soil layers. It must be kept in mind that the fitted curves are based on the means of residue concentrations, and only on four points against soil depth. Although a handy tool for describing the data, this cannot be used for predictive purposes.

Sandy clay loam soil

The results of analysis of tebuthiuron leaching in the sandy clay loam soil presented over time are given in Figure 4.2. A significant increase in the tebuthiuron residue levels occurred in the soil layers below 20 cm within the first 18 days of application. The concentration profile remained the same until the end of the trial period, although a decrease in concentration in all the soil layers was observed.

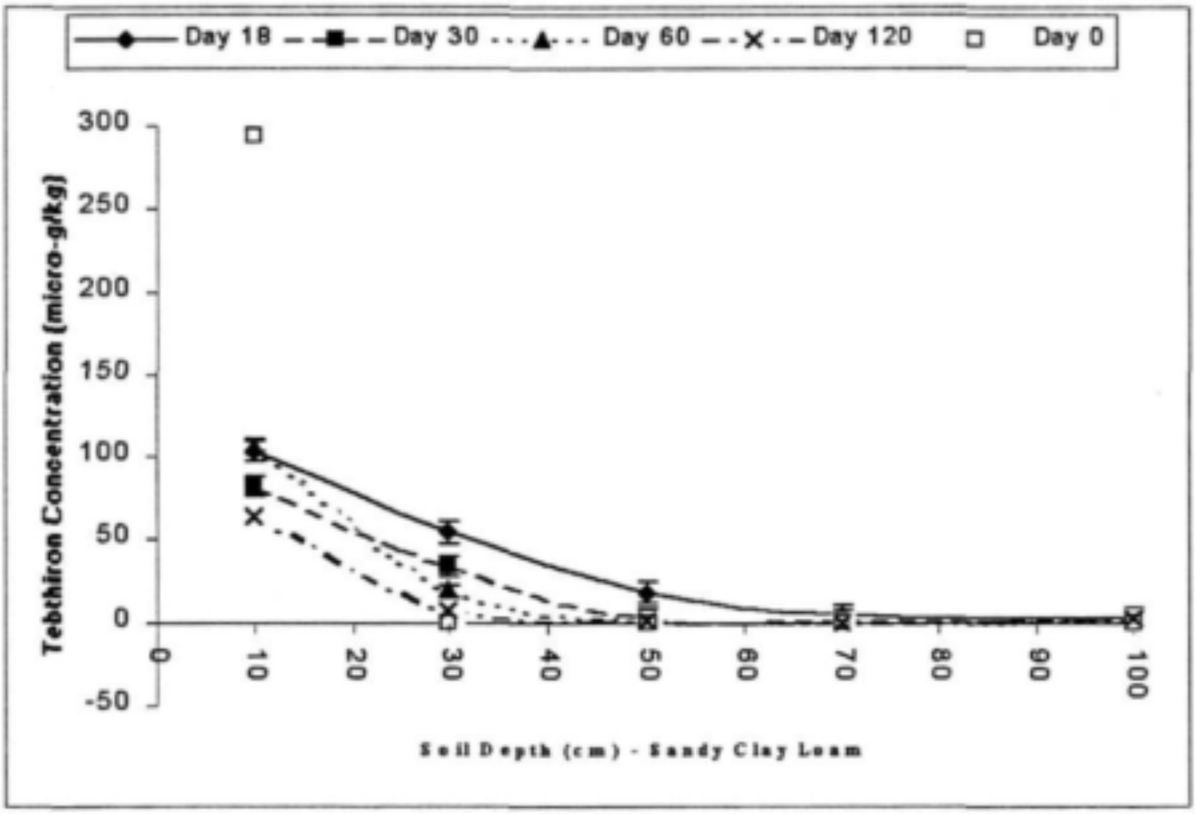

Figure 4.2. Tebuthiuron residue levels detected in the sandy clay loam soil for the time intervals, day 1, day 30, day 60 and day 120.

The data indicate that tebuthiuron is mobile in the sandy clay loam soil. The lack of a rapid increase in the second and deeper soil layers over time as found on the sandy loam soil indicates that tebuthiuron mobility is lower in the sandy clay loam soil than that observed in the sandy loam soil.

Fitting an exponential regression to the mean observed values rendered a general exponential equation of tebuthiuron concentration versus soil depth.
The general equation is given as:

$$y = a + br^x$$

Day 18 sandy clay loam soil: $y = 5.171 + 285.6(0.95)^x$
Day 30 sandy clay loam soil: $y = -5.072 + 199.7(0.959)^x$
Day 60 sandy clay loam soil: $y = -4.272 + 377.7(0.939)^x$
Day 120 sandy clay loam soil: $y = -5.8 + 160.8(0.939)^x$

A general trend of a decrease in the slope of the fitted curves is found for tebuthiuron on the sandy clay loam soil. Judging from the data given in Figure 2, this general trend predicted by the slope of the fitted curve does describe the leaching rates found to some extent. Again the curves are based of only four points and means were used, so the use of the fitted curve in predictions is somewhat dubious.

Clay soil

The results of tebuthiuron leaching in the clay soil presented over time are given in Figure 4.3. As was found with the other two soils, tebuthiuron leached into the soil horizons within the first 18 days. The residue levels detected in the deeper soil layers (although significant) were low. The tebuthiuron concentration profile at day 30 did not differ significantly from that found at day 18. During the next two time intervals a significant decrease in tebuthiuron residue levels were found in the top 20 cm soil layer. The residue levels in the soil layer below 60 cm remained unchanged until the end of the trial period.

The results indicate that tebuthiuron is mobile in the clay soil, but to a lesser extent than that found with the other two test soils. The decrease in tebuthiuron residue levels in the top soil layers at day 60, coinciding with stabilisation of residue levels in the deeper soils indicates that the decrease is due rather to field degradation of the compound than leaching.

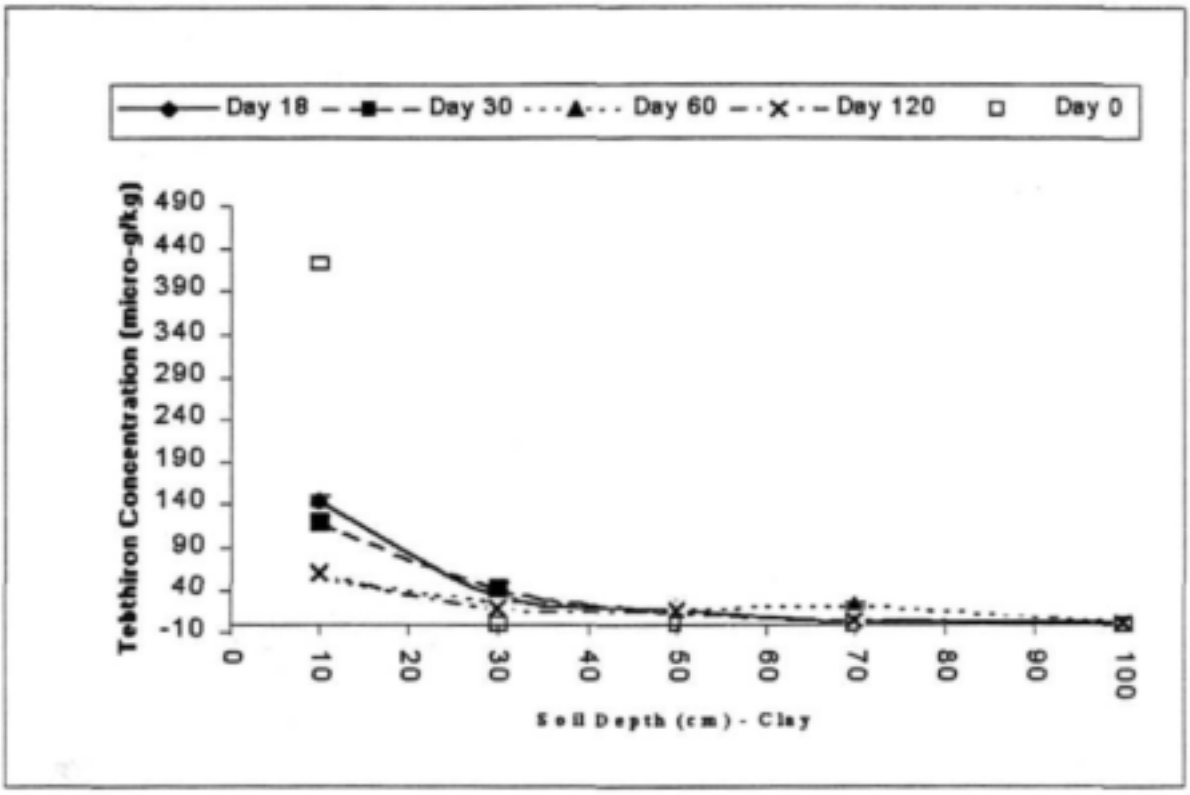

Figure 4.3. Tebuthiuron residue levels detected in the clay soil for the time intervals, day 1, day 30, day 60 and day 120.

Fitting an exponential regression to the mean observed values rendered a general exponential equation of tebuthiuron concentration versus soil depth.
The general equation is given as:

$$y = a + br^x$$

Day 18 clay soil:	$y = -5.10 + 406(0.95)^x$
Day 30 clay soil:	$y = -6.732 + 283(0.959)^x$
Day 60 clay soil:	$y = 13.49 + 146.7(0.939)^x$
Day 120 clay soil:	$y = 1.125 + 142.7(0.939)^x$

Comparison of the slopes of the regression curves fitted for tebuthiuron on the clay soil shows a decrease in the slope over time. This decrease is brought about primarily due to the decrease in the tebuthiuron residue levels in the upper soil layers, rather than increasing concentration in the deeper soil layers.

Comparison of the slopes of the fitted regression curves for the different soil types show that the slope for the clay soil was the steepest, followed by the sandy clay loam and the sandy loam soil, which rendered the shallowest slope. This data indicates that the leaching rate for tebuthiuron was highest on the sandy loam soil. The differences in the slope of the fitted curves also decline over time, i.e. the variation in leaching rates decrease over time. This indicates that under the conditions of the trials the effect of soil type on tebuthiuron leaching decreases with time. Thus the more time that elapsed, the less the difference in leaching between soils.

Comparison of tebuthiuron leaching in three field soils.

In order to compare tebuthiuron leaching between the different soil types used in the field tirals, the residues detected per time interval were converted to the percentage residues remaining of the residues recovered after application. These results are shown in Figure 4.4.

Comparison of the leaching patterns found in the three field soils tested showed that tebuthiuron leaching patterns were similar in the sandy loam soil and the sandy clay loam soil during the time interval to day 18. The leaching rate in the clay soil appears slower than the other two soils within the first 18 days of application. During the following time intervals up to the end of the trial period, the leaching profiles for the sandy clay loam and clay soils were similar. However a more rapid decrease in tebuthiuron residues from the top 20-cm soil layer was found on the clay soil as compared to the sandy clay loam soil. During the same time intervals, tebuthiuron movement was the highest on the sandy loam soil. There are also indications of build-up of the compound in the deeper soil layers at day 60 which decreased by day 120 probably due to leaching past the 120 cm soil layer. The data indicated that the decrease in tebuthiuron in the upper soil layers of the clay and sandy clay loam soils might be due to degradation.

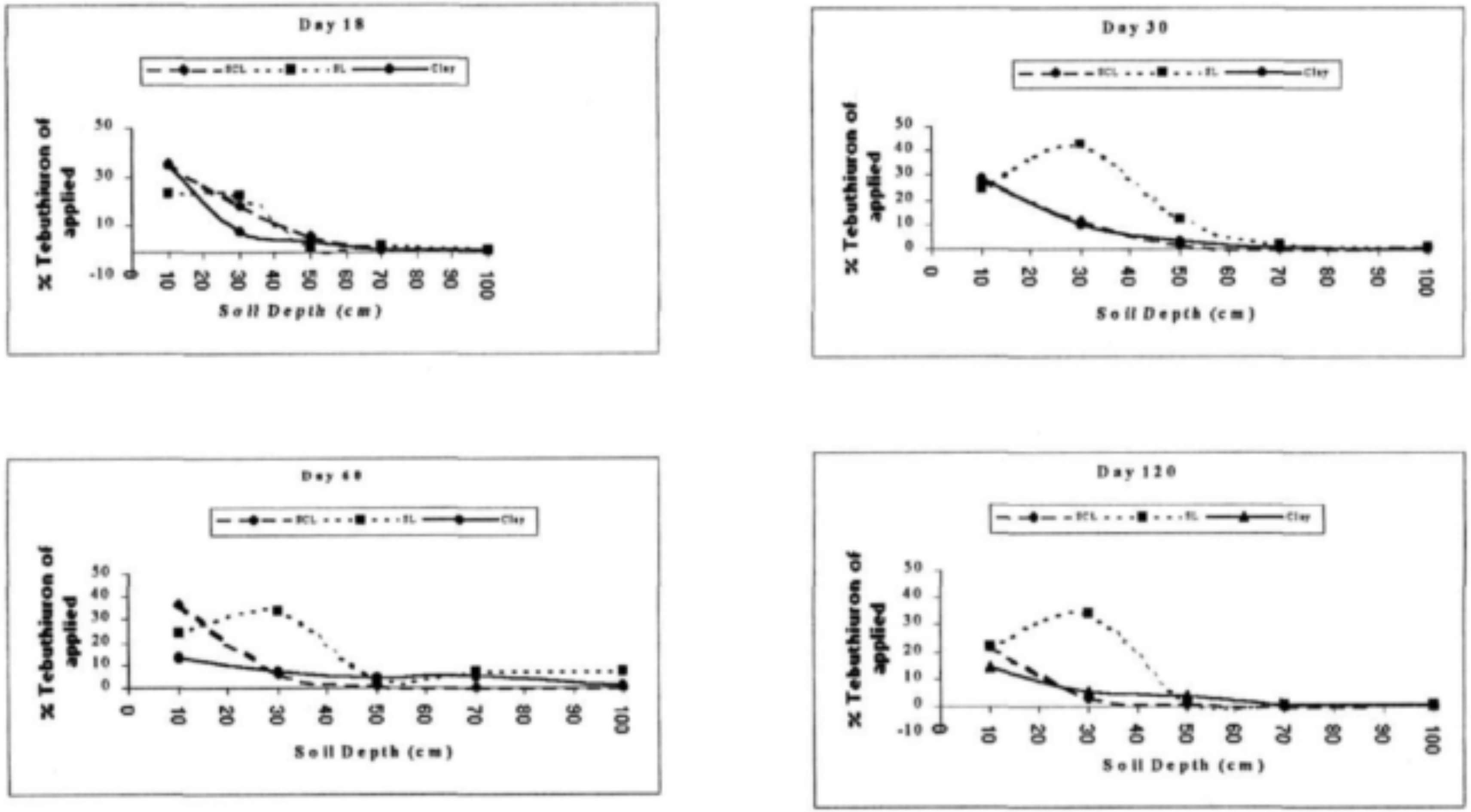

Figure 4.4. Comparison of the percentage tebuthiuron remaining in the soil profile for time interval day 18, day 30, day 60 and day 120. Legend: SCL = Sandy Clay Loam; SL = Sandy Loam; CL = Clay

4.2.1.2 Fenthion

The recoveries of fenthion were low on all three soils tested. On the sandy loam soil, the recovery of applied compound was approximately 20 %. The residue analyses did not take into account the formation of metabolites.

Sandy loam soil

The results of fenthion leaching in the sandy loam soil presented over time are given in Figure 4.5. Fenthion residues were detected in the 0 – 20 soil horizon within 18 days of application. The fenthion residue levels detected in the top 20 cm soil layer and the 20 – 40 cm soil layer were significantly higher than those found in the soil layers below 40 cm at day 18. These results indicate that fenthion had leached to the deepest soil layer sampled within the first 18 days but also that very little of the compound had reached the deeper soil layers.

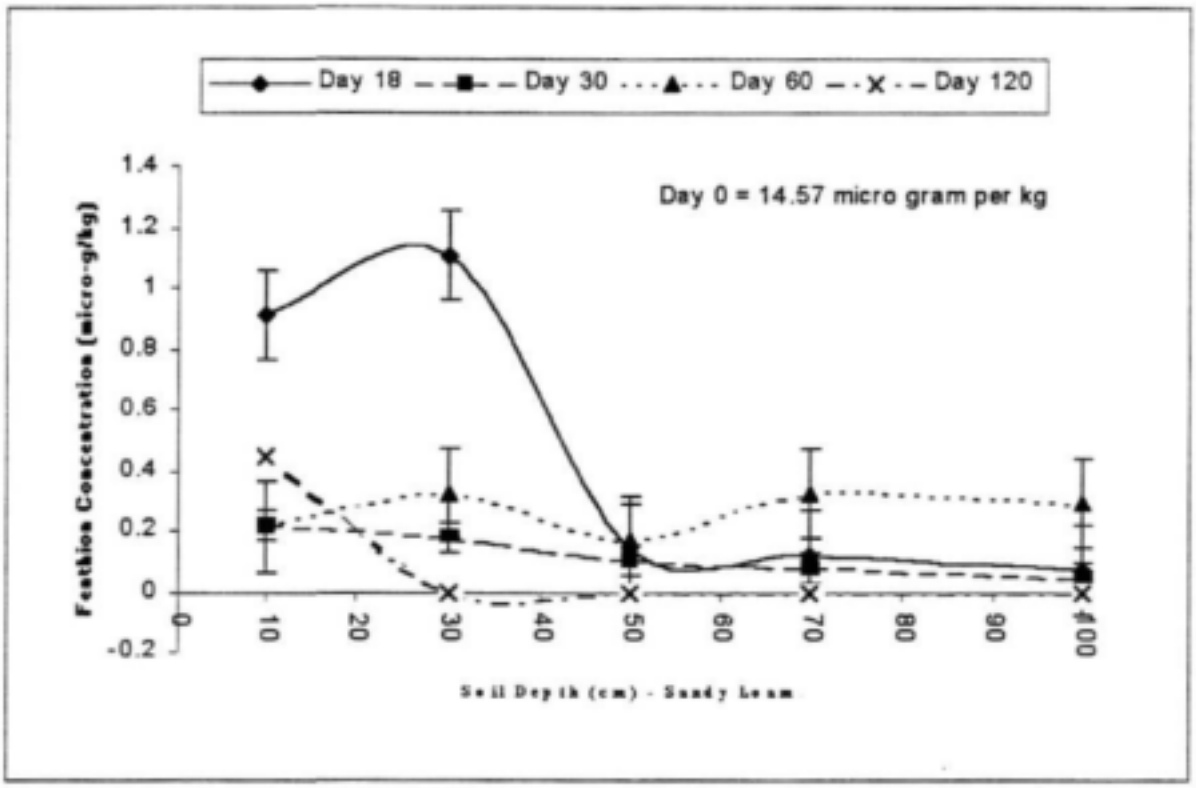

Figure 4.5. Fenthion residue levels detected in the sandy loam soil for the time intervals, day 1, day 30, day 60 and day 120.

The fenthion residue levels decreased rapidly during the duration of the trial period, as is expected with a compound with short half-life. A significant increase in the fenthion residue level was found in the top 20 cm soil layer at day 120, coinciding with the disappearance of the compound from the deeper soil layers. It is suggested that this increase may be due to upward movement of the compound during the 60 to 120 day interval.

Fitting an exponential regression to the mean observed values rendered a general exponential equation of fenthion concentration versus soil depth.

The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

Day 18 sandy loam soil: $y = -0.28 + 1.800\ (0.98)^x$
Day 30 sandy loam soil: $y = -0.020 + 0.31\ (0.98)^x$
Day 60 sandy loam soil: $y = 0.270 + -3.20\ (0.82)^x$
Day 120 sandy loam soil: $y = -0.16\mathrm{E}{-8} + 3000291\ (0.40)^x$

The slopes of the fitted regression curves for the sandy loam soil decreased over the time period day 18 to day 60 after which there is a steep incline in each slope. This indicates that the leaching rate decreased over time, and then increased sharply towards the end of the trial period. However the sharp increase in the slope for the final time period may be misleading due to the zero values recorded for the deeper soil layers.

Sandy clay loam soil

The results of fenthion leaching in the sandy clay loam soil presented over time are given in Figure 4.6. Residue analysis showed the presence of fenthion residues throughout the soil profile at day 18. An increase in fenthion residue levels was found at day 30, in the soil layers below 40 cm, coinciding with a significant decrease in residue levels in the top 40 cm soil layers. This residue profile remained to day 60 and finally at day 120 the compound was not detected at all.

The tendency of increased fenthion residues in the lower soil layers coinciding with a decrease in the upper soil layer may indicate that the compound had leached out of the 120 cm soil profile. It is however more likely that the zero levels found at day 120 was due to degradation.

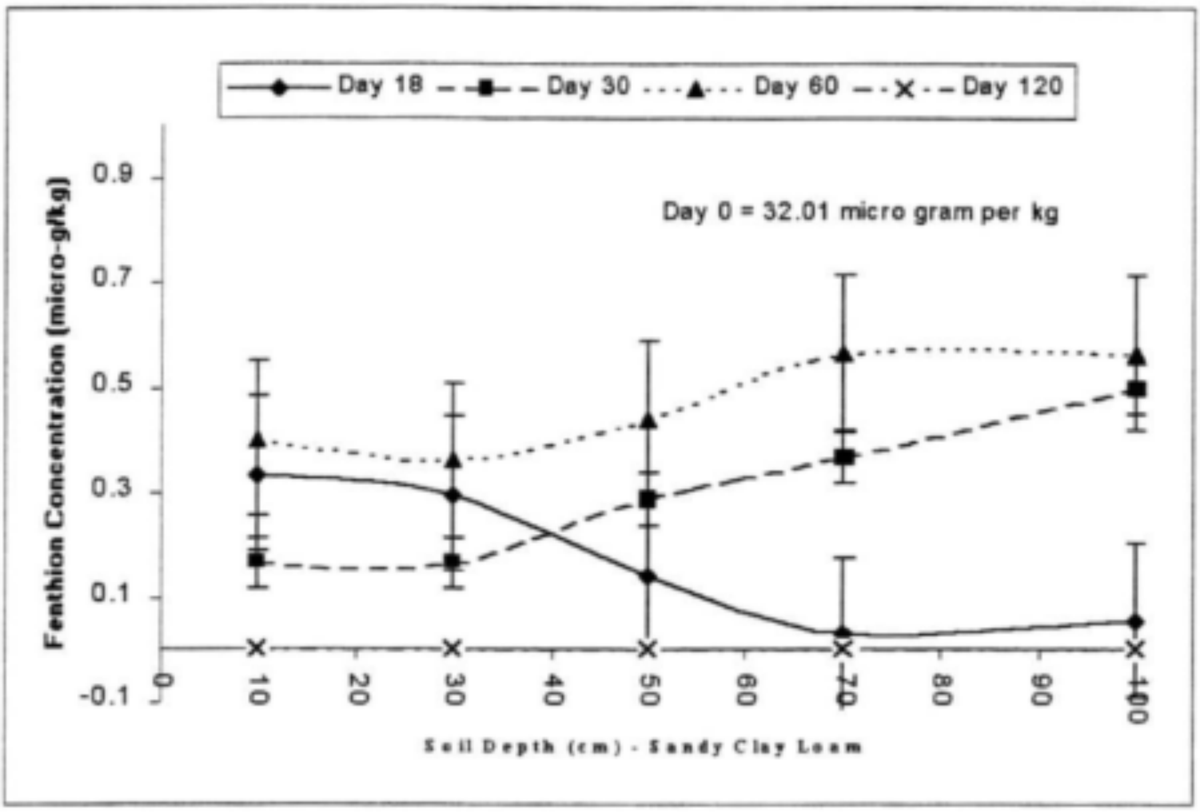

Figure 4.6. Fenthion residue levels detected in the sandy clay loam soil for the time intervals, day 1, day 30, day 60 and day 120

Fitting an exponential regression to the mean observed values rendered a general exponential equation of fenthion concentration versus soil depth.
The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

Day 18 sandy clay loam soil: $y = -0.06 + 0.570\,(0.98)^x$
Day 30 sandy clay loam soil: $y = 0.580 + -0.62\,(0.98)^x$
Day 60 sandy clay loam soil: $y = 0.480 + -4.50\,(0.82)^x$

The slope of the fitted regression curve decreased with time, becoming negative at day 30 and 60, describing the movement of the compound to the deeper soil layers. At day 120 the compound was no longer detected.

Clay soil

The results of fenthion leaching in the clay soil presented over time are given in Figure 7. As with the sandy soil and the sandy clay loam soil, residue analysis indicates that fenthion leached to the 80 – 120 cm soil layer within the first 18 days of application. The majority of the fenthion was detected in the 40 to 60 cm soil layer at this time. After 30 days fenthion was detected only in the top 40 cm of the soil, at 60 days and 120 days only in the top 20 cm soil layer.

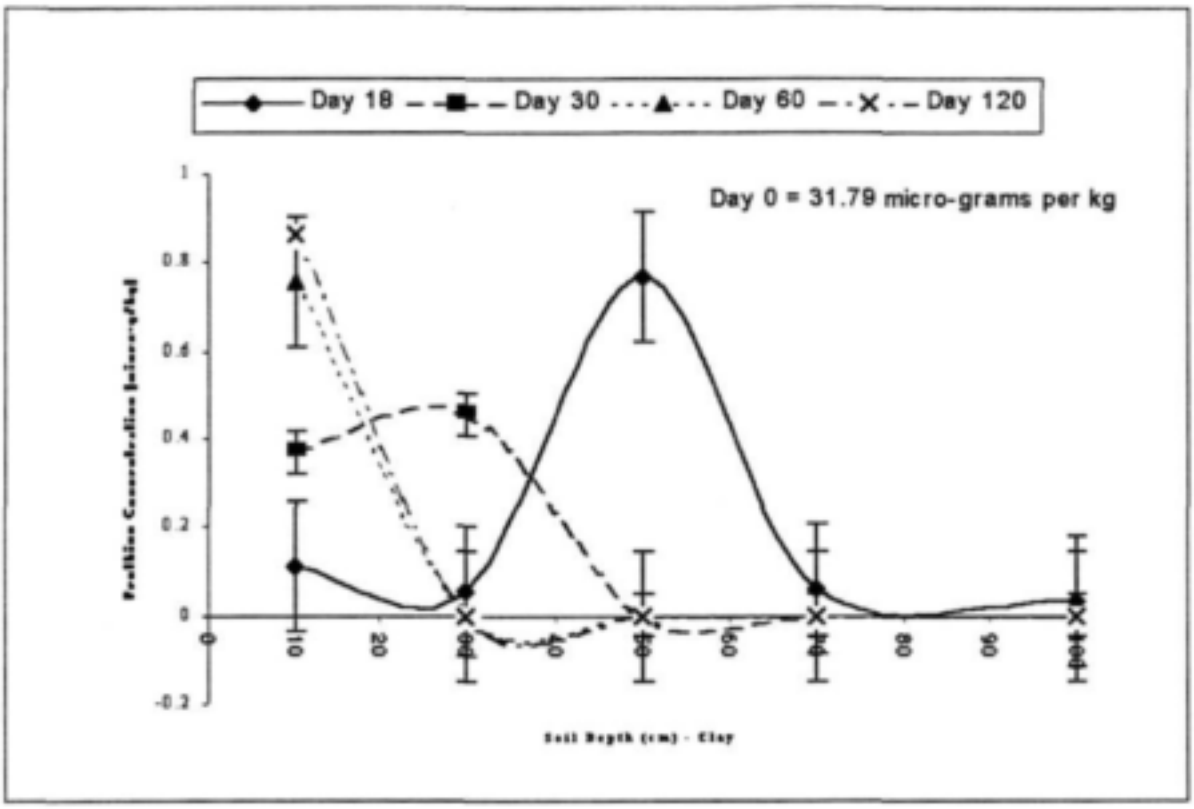

Figure 4.7. Fenthion residue levels detected in the clay soil for the time intervals, day 1, day 30, day 60 and day 120

If the fenthion flow through the soil is animated, it seems as if fenthion at first leached rapidly into the soil. This leaching movement was followed by evaporation driven movement back to the soil surface over the 30 to 60 day intervals as a much slower process, remaining in this soil layer for the remainder of the trial period.

Fitting an exponential regression to the mean observed values rendered a general exponential equation of fenthion concentration versus soil depth.
The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

Day 18 clay soil: $y = 0.204 + 0.002\,(0.98)^x$
Day 30 clay soil: $y = -0.230 + 0.86\,(0.98)^x$
Day 60 clay soil: $y = -0.0035 + 40.40\,(0.82)^x$
Day 120 clay soil: $y = -0.32\text{E-}8 + 58037817\,(0.40)^x$

The steepest slopes were found descriptive of fenthion behaviour in the clay soil. The slopes did not become negative at any of the time intervals. The slope of the fitted curve increased over time indicating a decrease in leaching with time. The decrease in leaching rate is not necessarily indicative of low mobility of fenthion in this soil, but rather a decrease in movement to deeper soil layers or because of degradation.

The increase in slope found in the sandy clay loam soil occurred sooner, indicating a higher leaching rate in this soil, reaching zero at the end of the trial period. The zero slope for day 120 is descriptive of the absence of fenthion residues rather than indicative of a high leaching rate during this time period. The almost bell-shaped curve found within the first 18 days of application indicate that fenthion is highly mobile even in the clay soil. The fitted regression curve does not take this into account.

Comparison of fenthion leaching in three field soils.

In order to compare fenthion leaching between the different soil types used in the field tirals, the residues detected per time interval were converted to the percentage residues remaining of that which was applied. These results are shown in Figure 4.8.

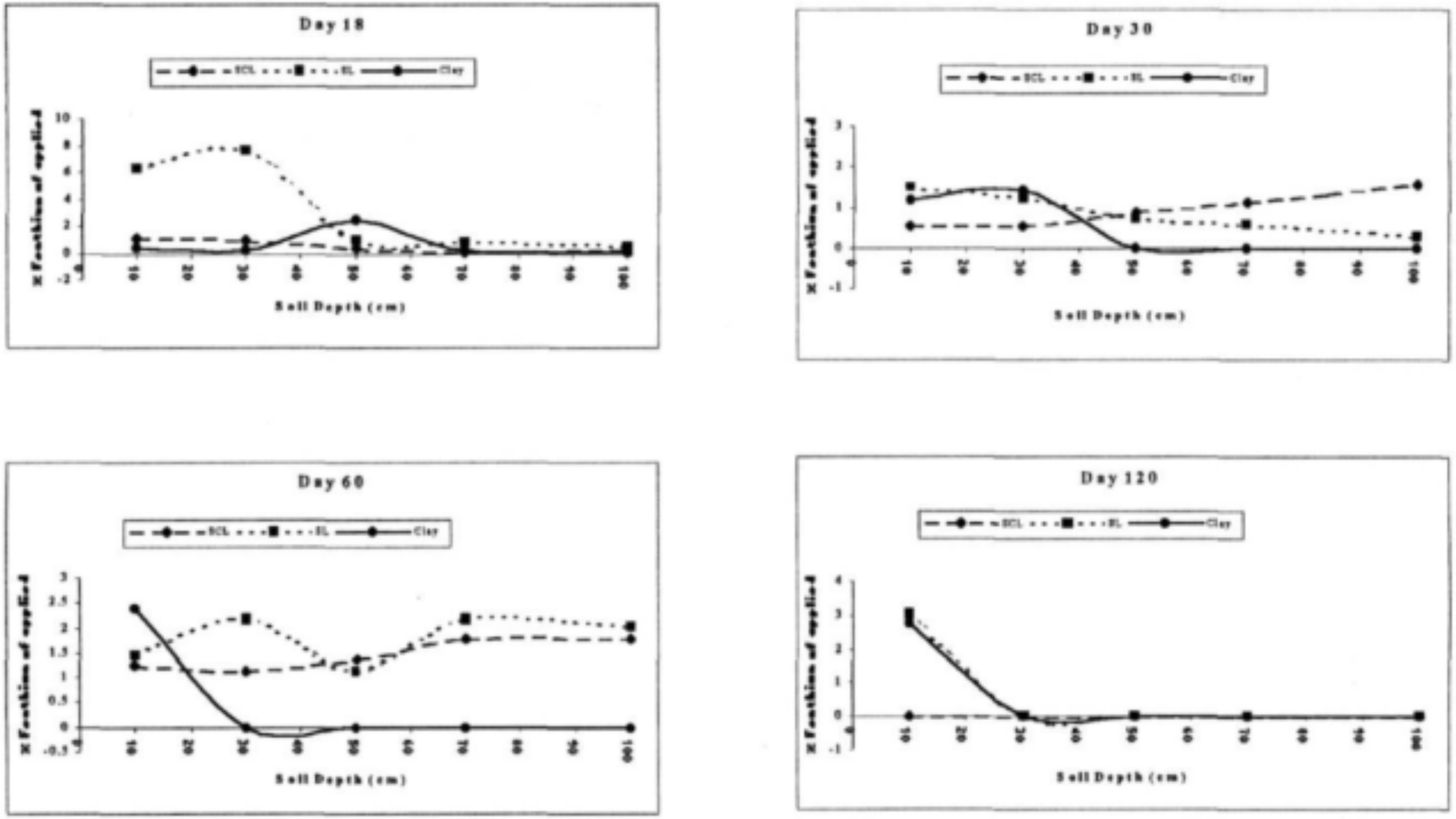

Figure 4.8. Comparison of the percentage fenthion remaining in the soil profile for time interval day 18, day 30, day 60 and day 120.

Fenthion leached into the deeper soil layers within 18 days of application on all three soil types tested. In the sandy loam soil, the fenthion residue level detected in the top 40-cm soil layer was higher than those found in the deeper soil layers within this period. In the following period, up to day 30, a decrease in fenthion residue levels was observed, remaining for the next 30 day period (day 60), where after an increase in fenthion residues occurred in the top soil layer.

Results of analysis of the sandy clay loam soil indicates that fenthion residues increased in the soil layers below 40 cm within the first 30 days of application. At day 120 no fenthion residues were detected in the soil profile on the sandy clay loam soil. The fenthion present in the soil profile had probably degraded to levels below the detectable quantities.

In the clay soil, fenthion leached rapidly into the soil profile within the first 18 days of application, to the extent where significantly higher residues were found in the 40 – 60 cm horizon, compared to the other soil horizons sampled. After this period the concentrations in the upper soil layers increased whilst those in the deeper horizons decreased. This data indicates that fenthion residues leached rapidly into the soil, where after the compound moved to the upper soil horizons probably through evaporative processes.

Data indicates rapid leaching of fenthion into the deeper soil layer of the sandy loam soil within the first 18 days continuing up to day 60. In the period from days 60 to 120, upward movement of fenthion is observed. This upward movement is probably due to evaporative mechanisms occurring during the dry period. The low levels of the compound detected throughout the trial period indicate rapid degradation process of the compound in the sandy loam soil. Data further indicates that fenthion is highly mobile in the sandy loam soil.

The fenthion present throughout the sandy clay loam soil profile had probably degraded to levels below the detectable quantities by day 120. It is however also possible that the compound had leached to soil layers below 120 cm. This is however unlikely in view of the high degree of upward movement found in the two other soil types tested.

The residue data on fenthion collected indicates that fenthion may be highly mobile in all three soils tested. The mobility of the compound is not only limited to leaching, but also to upward movement 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 compound. Data further indicates that fenthion mobility is affected by soil type only during the first 30 days of application, where after this soil type seems to have a limited affect on fenthion mobility.

4.2.1.3 Azafenidin

Azafenidin leached throughout the soil profile on all three soils within the first 18 days of application.

Sandy loam soil

Residue analyses indicated that the applied azafenidin had leached below the 0 – 20 cm soil horizon within the first 18 days after application. The azafenidin soil concentration decreased from 134 µg/kg to 6.13 µg/kg in the top 20 cm soil layer over the 120 day time period. Significant azafenidin leaching had occurred in the first 18 days after application. No significant differences were found in concentration in the soil layers below 60 cm. The azafenidin residue levels were significantly higher in the top 20 and 40 cm soil layers as compared to the deeper soil layers. At the end of the trial period no detectable levels of azafenidin were found in the soil below 20 cm soil depth.

The data indicates that the majority of the applied azafenidin had remained in the top 20-cm soil layer of the sandy loam soil.

The data indicates that azafenidin had leached to the 120 cm soil horizon, but that the leaching process was not sustainable, likely due to the compound being degraded during the 120-day trial period. The data indicates a high rate of degradation of azafenidin in the sandy loam soil.

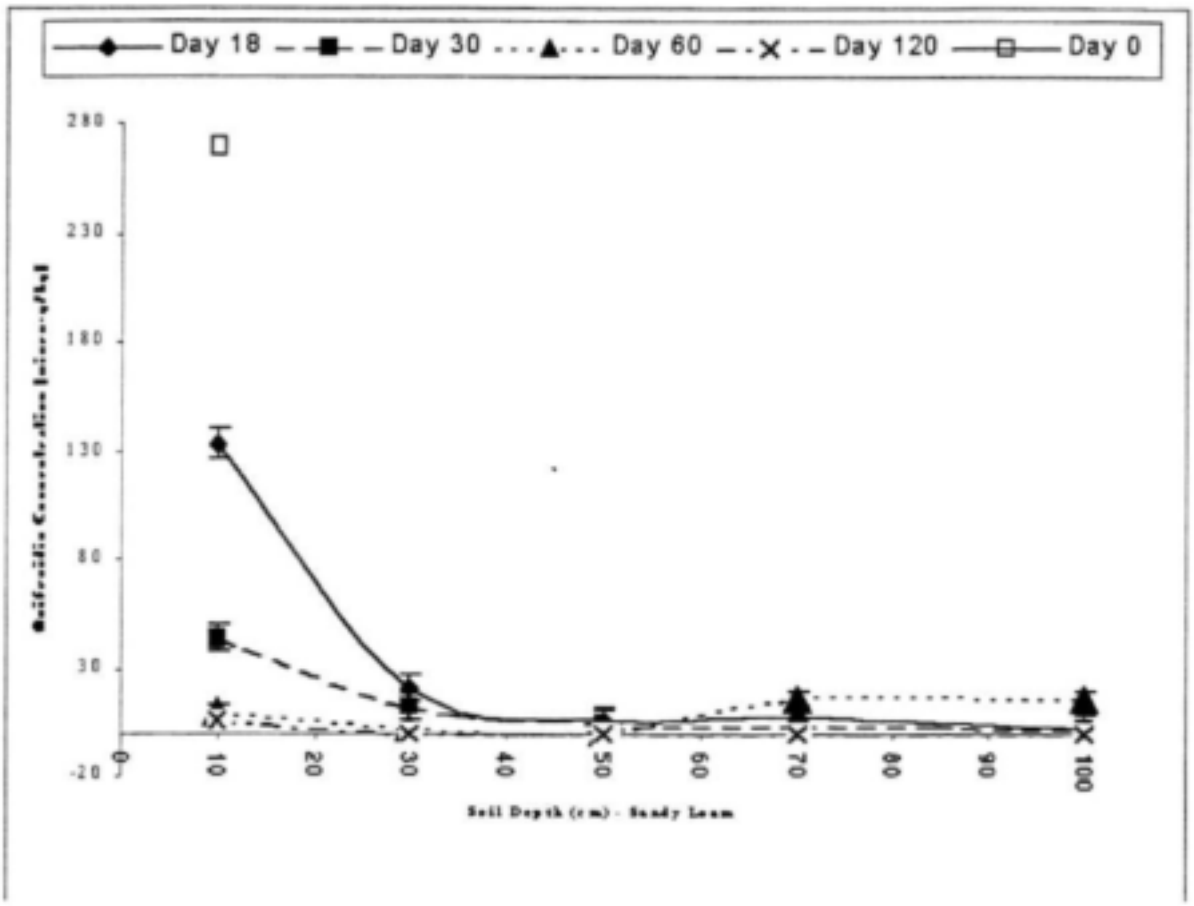

Figure 4.9. Azafenidin residue levels detected in the sandy loam soil for the time intervals, day 1, day 30, day 60 and day 120

Fitting an exponential regression to the mean observed values rendered a general exponential equation of fenthion concentration versus soil depth.
The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

Day 18 sandy loam soil: $y = -1.378 + 520.9 \ (0.933^x$
Day 30 sandy loam soil: $y = 3.38 + 239.4 \ (0.99)^x$
Day 60 sandy loam soil: $y = 690.7 + -688.5 \ (0.99)^x$
Day 120 sandy loam soil: $y = -0.23 + 44.59 \ (0.91)^x$

Comparison of the slopes of the fitted regression curves for the azafenidin leaching on the sandy loam soil indicates a decrease in the slope with time to day 60, where the slope becomes negative. This indicates an increase in the soil concentration in the deeper soil layers and a decrease in the upper soil layers in this soil. The shallow slope for day 120 relates to the absence of azafenidin from the deeper soil layers.

Sandy clay loam soil

Residue analysis indicates a high proportion of azafenidin present in the 0 – 20 and 20 – 40 cm soil layers within the first 18 days of application. No significant differences were found in azafenidin concentration for the 18 and 30 day analyses. Residue analysis indicates a decrease in azafenidin in the 0 – 20 cm soil layer between day 30 and 120. A significant increase in azafenidin soil concentration was found in the soil layers below 60 cm in the period from 30 to 60 days after treatment. Hereafter a significant decrease in residue levels was found.

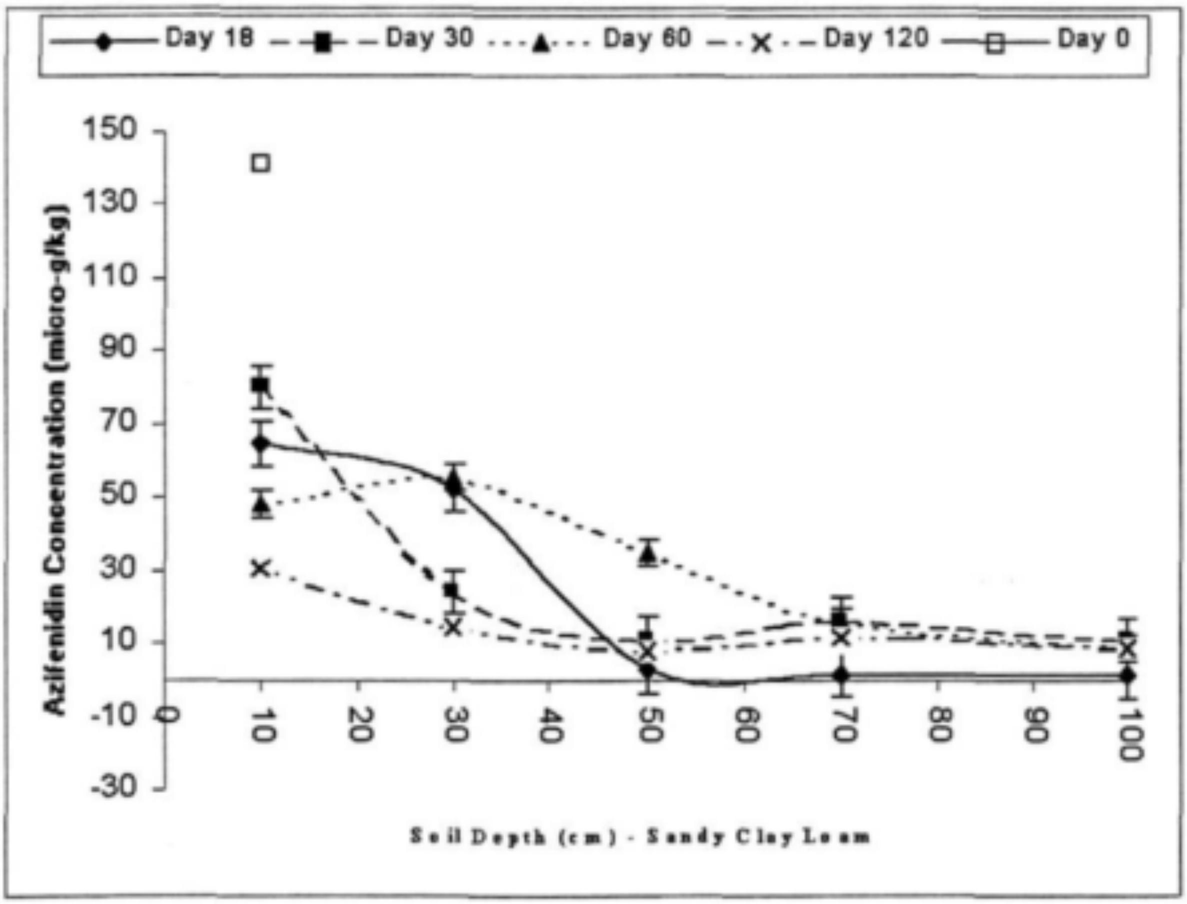

Figure 4.10. Azafenidin residue levels detected in the sandy clay loam soil for the time intervals, day 1, day 30, day 60 and day 120

The azafenidin proportion in the soil layers below 60 cm did not change over the rest of the trial period.

Residue analysis further showed that the compound is mobile in the sandy clay loam soil. The compound is more persistent than in the sandy loam soil.

Fitting an exponential regression to the mean observed values rendered a general exponential equation of fenthion concentration versus soil depth.

The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

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

On the sandy clay loam soil the slope of the fitted curve increases to day 60. This may indicate a decrease in leaching rate over this time period, but may rather relate to a rapid decrease in azafenidin residue levels in the deeper soil layer, and little change in that in the upper soil layer.

Clay soil

Azafenidin residue analysis conducted on the clay soil indicates the azafenidin had leached to the deeper soil layers within 18 days of application (Figure 4.11). No significant differences in azafenidin residue levels were found at the different depths tested throughout the trial period up to day 60. A significant increase in residue levels was found at day 120, in the deeper soil layers. This increase at the end of the trial period indicates slow migration of the compound through the clay soil. The initial leaching rate appears to have been higher within the first 18 days, after which the rate of leaching decreases toward the end of the trial period, but does not cease entirely. The data further indicates that the compound may have leached past the 120 soil layer sampled.

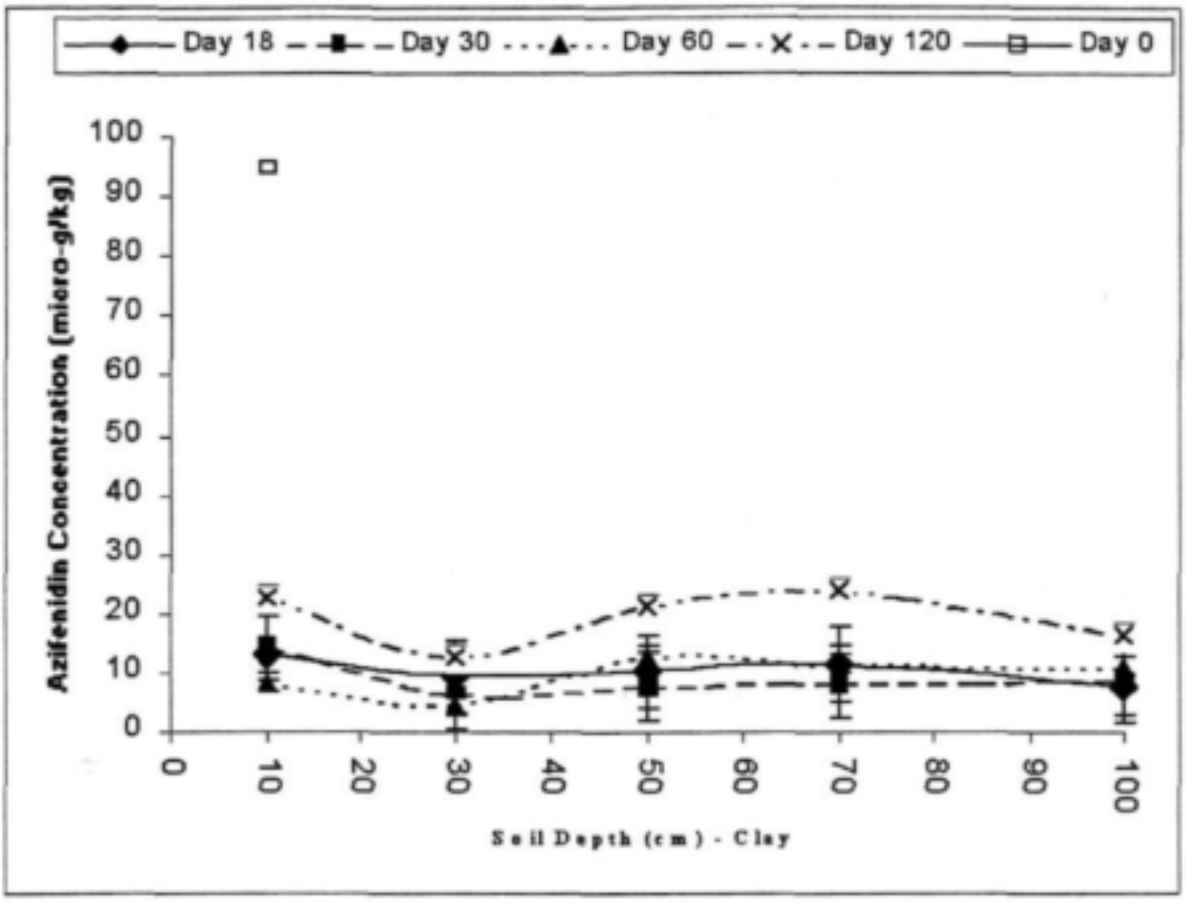

Figure 4.11. Azafenidin residue levels detected in the clay soil for the time intervals, day 1, day 30, day 60 and day 120

Fitting an exponential regression to the mean observed values rendered a general exponential equation of fenthion concentration versus soil depth.

The general equation is given as:

$$y = a + br^x$$

The fitted regression then renders the following for the various time intervals:

Day 18 clay soil: $y = 9.305 + 14.68\,(0.933)^x$

Day 30 clay soil: $y = 7.52 + 37.6\,(0.99)^x$

Day 60 clay soil: $y = 307.2 + -300.6\,(0.99)^x$

Day 120 clay soil: $y = 18.79 + 21.62\,(0.91)^x$

On the clay soil the slope is extremely shallow at day 18. The slope increases slightly by day 30, indicating a loss in herbicide in the deeper soil layers. By day 60, the slope becomes negative due to the azafenidin moving into the deeper soil layers, levelling off towards the end of the trial period.

Comparison of azafenidin leaching in three field soils.

In order to compare azafenifdin leaching between the different soil types used in the field tirals the residues detected per time interval was converted to the percentage residues remaining of that which was applied. These results are shown in Figure 4.12.

The observed leaching patterns for azafenidin were similar for the sandy loam soil and sandy clay loam soil during the initial 18 days after application. Also similar proportions of applied compound remained in these tow soils. A higher degree of leaching is however apparent in the sandy clay loam soil. After 30 days, azafenidin distribution was similar for the clay and sandy loam soils. In the case of the sandy loam soil, this could be due to extensive movement of the compound whereas very little movement was apparent on the clay 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.

The herbicide distribution patterns for the clay and sandy clay loam soil are similar toward day 120, with the exception that in the clay soil azafenidin seems to build up in the deeper soil layers. In the case of the sandy loam soil the compound disappears for the soil profile whereas a higher degree of retention is seen on the sandy clay loam soil.

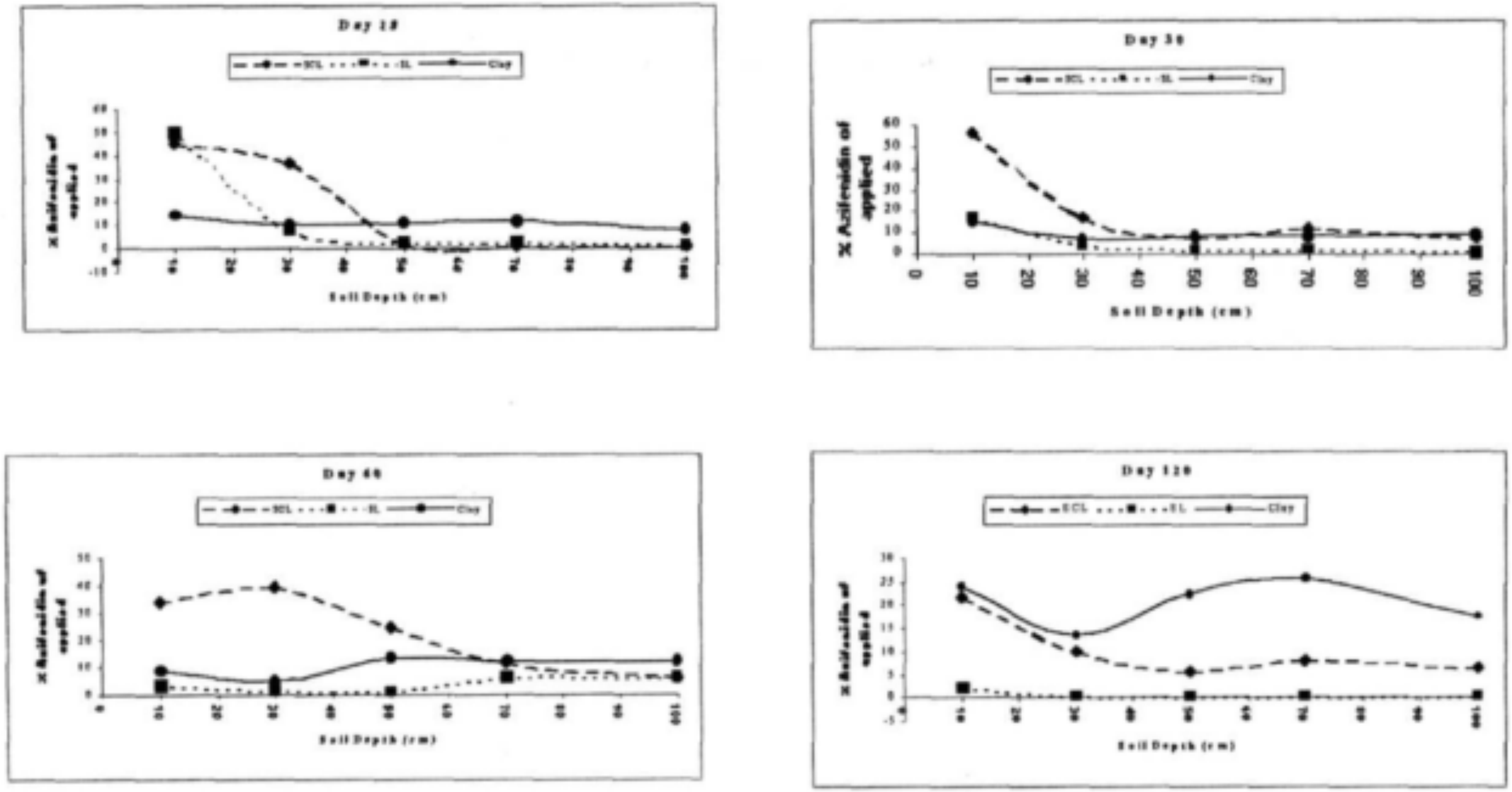

Figure 4.12. Comparison of the percentage azafenidin remaining in the soil profile for time interval day 18, day 30, day 60 and day 120.

4.3 Model Evaluation

Linear regression analysis was performed on the observed (measured) data versus model predicted concentrations. This test was performed to test the fit of y = x or measured concentrations over depth for each time interval. A zero constant or intercept and a slope of 1 for the fitted curve would thus indicate a perfect fit. In such a situation, the model predictions fit the actual measured values exactly. An indication of the extent of fit is given as a percentage fit.

In the graphs that follow the y = x curve is shown as a dotted line. The curve was generated by plotting measured values against themselves rendering a straight. In the figures that follow the plot of observed values (y) against predicted values (x) are shown as a cross (Varleach), open triangle (Pelmo) and an open circle (Pestan).

In general terms, the analyses performed for the day 0 data showed that all the models accurately predicted the situation at day 0, rendering a 100 % fit of observed values to model predictions. This is not unexpected, as at day 0 no leaching would have occurred and the initial application rate is given. These data are shown in Figures 4.13 to 4.16.

Although the analyses performed on the day 0 data indicate that the models all predict the leaching in the local soils for day 0 with some accuracy, this did not take any leaching into account at all. Thus analyses of samples taken at the further time intervals is of more importance. This aspect will be treated below, for each pesticide individually, per soil type.

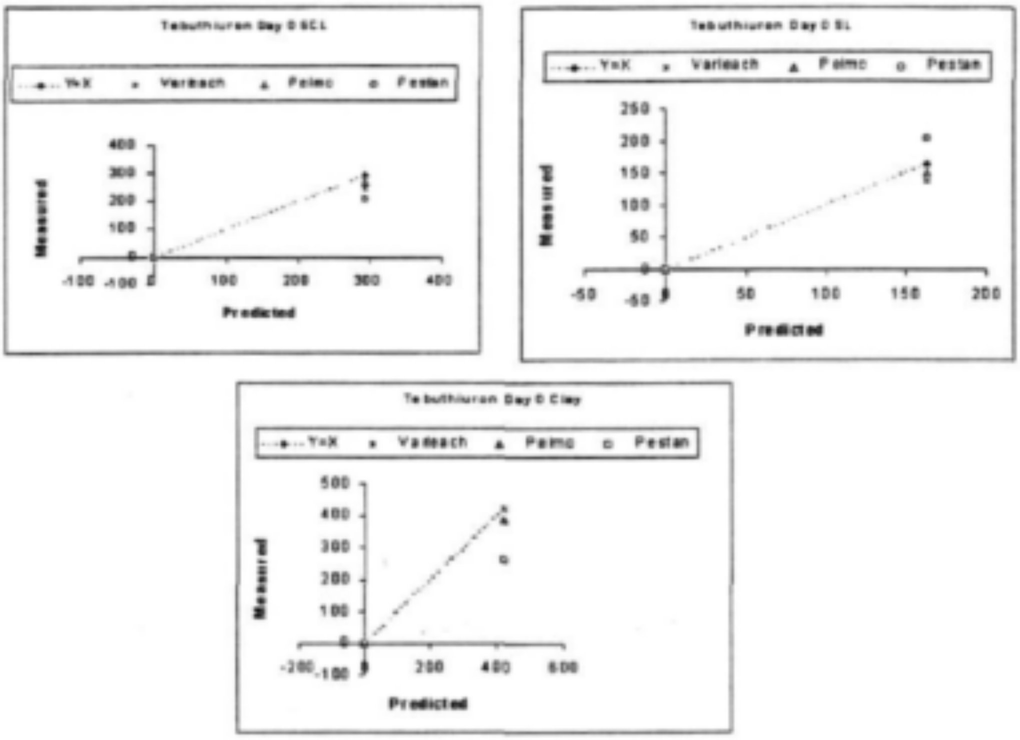

Figure 4.13. Comparison of measured tebuthiuron concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan at day 0 for the sandy clay loam (SCL), sandy loam (SL) and clay soils.

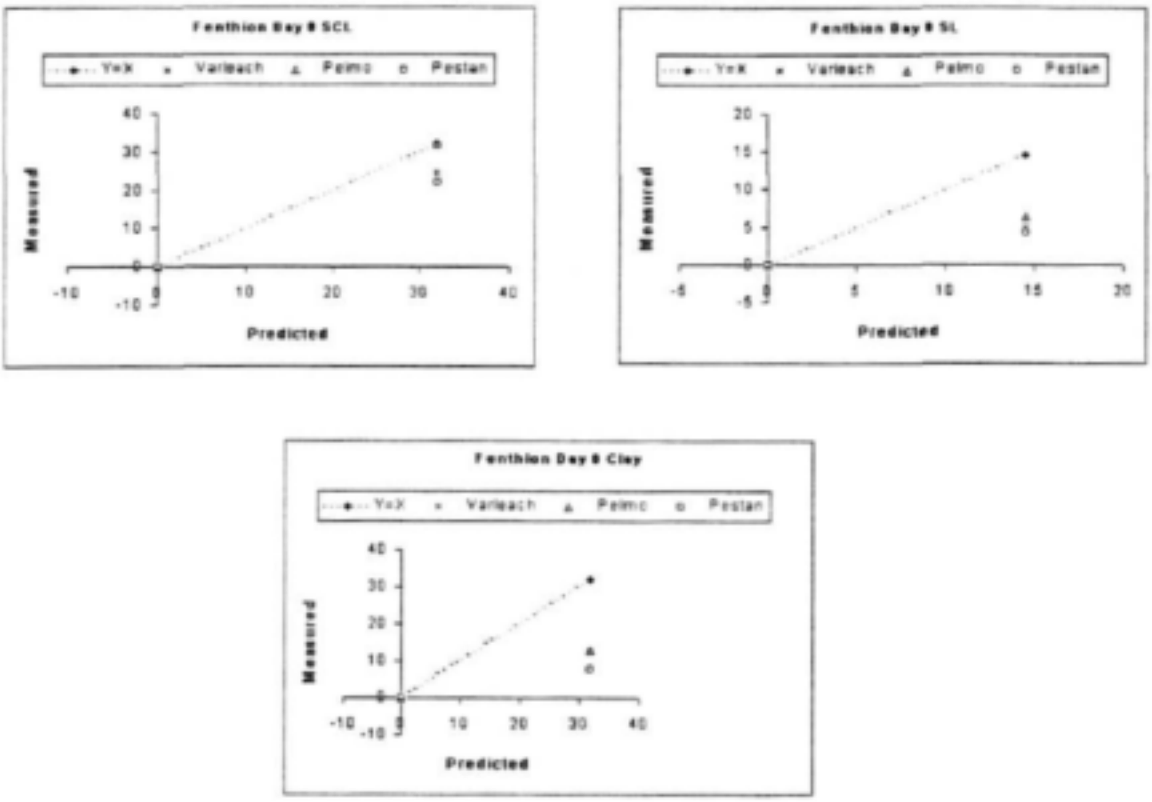

Figure 4.14. Comparison of measured fenthion concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan at day 0 for the sandy clay loam (SCL), sandy loam (SL) and clay soils.

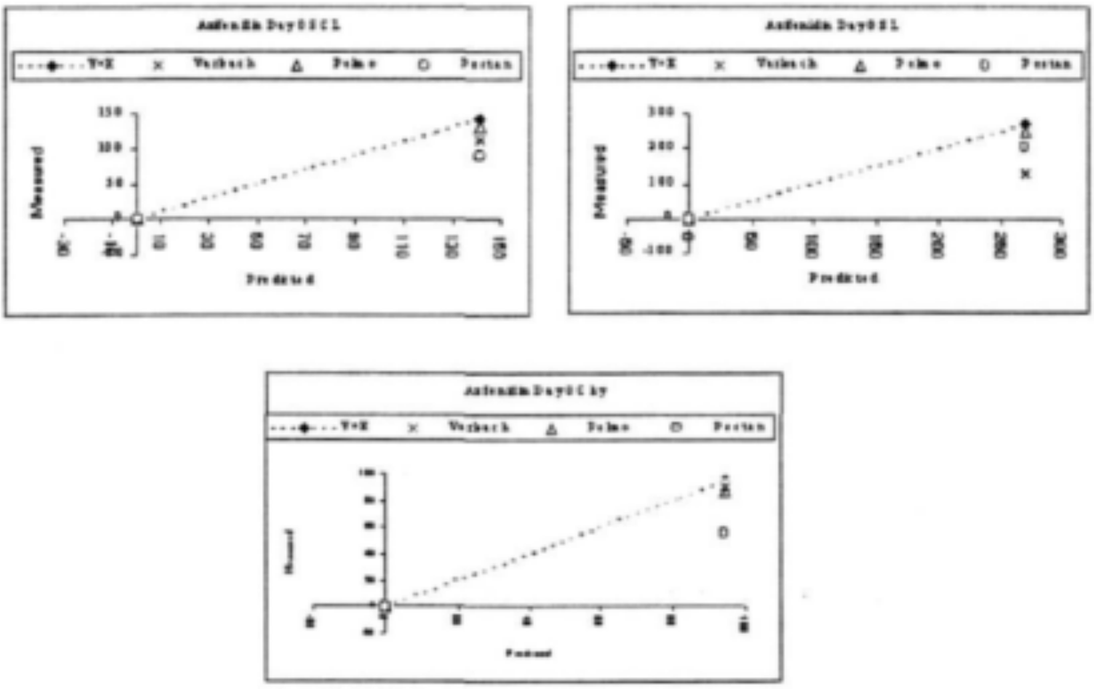

Figure 4.15. Comparison of measured azafenidin concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan at day 0 for the sandy clay loam (SCL), sandy loam (SL) and clay soils.

Tebuthiuron – sandy clay loam soil

Results of regression analyses and comparisons for tebuthiuron leaching based on the models Varleach, Pelmo and Pestan are shown in Figure 4.16.

The model Varleach predicted only minor leaching of tebuthiuron within the trial period. The model predicts that tebuthiuron will not leach past 40 cm in the sandy clay loam soil. The percentage fit gained from the regression correlation analysis however indicates a fit of 70 % to 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 renders it unreliable.

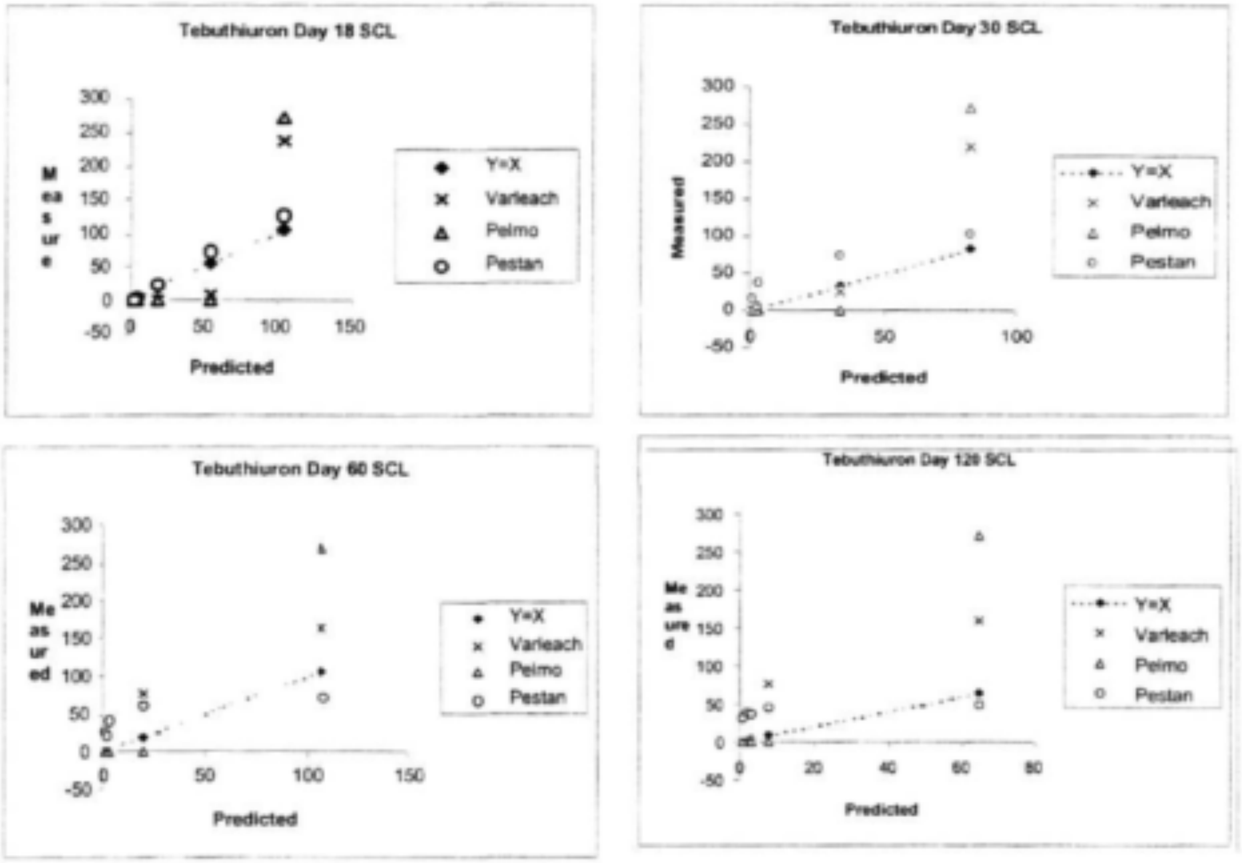

Figure 4.16. Comparison of measured tebuthiuron concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the sandy clay loam (SCL), 18, 30, 60 and 120 days after application.

Pelmo leaching predictions were more conservative that that predicted by the model Varleach. The Pelmo model predicted that no leaching would occur beyond 20 cm soil depth. The leaching 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 (above 80 %), but here based only on one correlating data point.

The model Pestan predicted tebuthiuron leaching 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 day 30. The percentage correlation decreased to 42 % by day 120. The decreased fit to is due to the model Pestan overestimating the extent of tebuthiuron leaching on this soil i.e. higher concentrations predicted in the deeper soil layers than those measured.

Tebuthiuron – sandy loam soil

Results of regression analyses and comparisons for tebuthiuron leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.17.

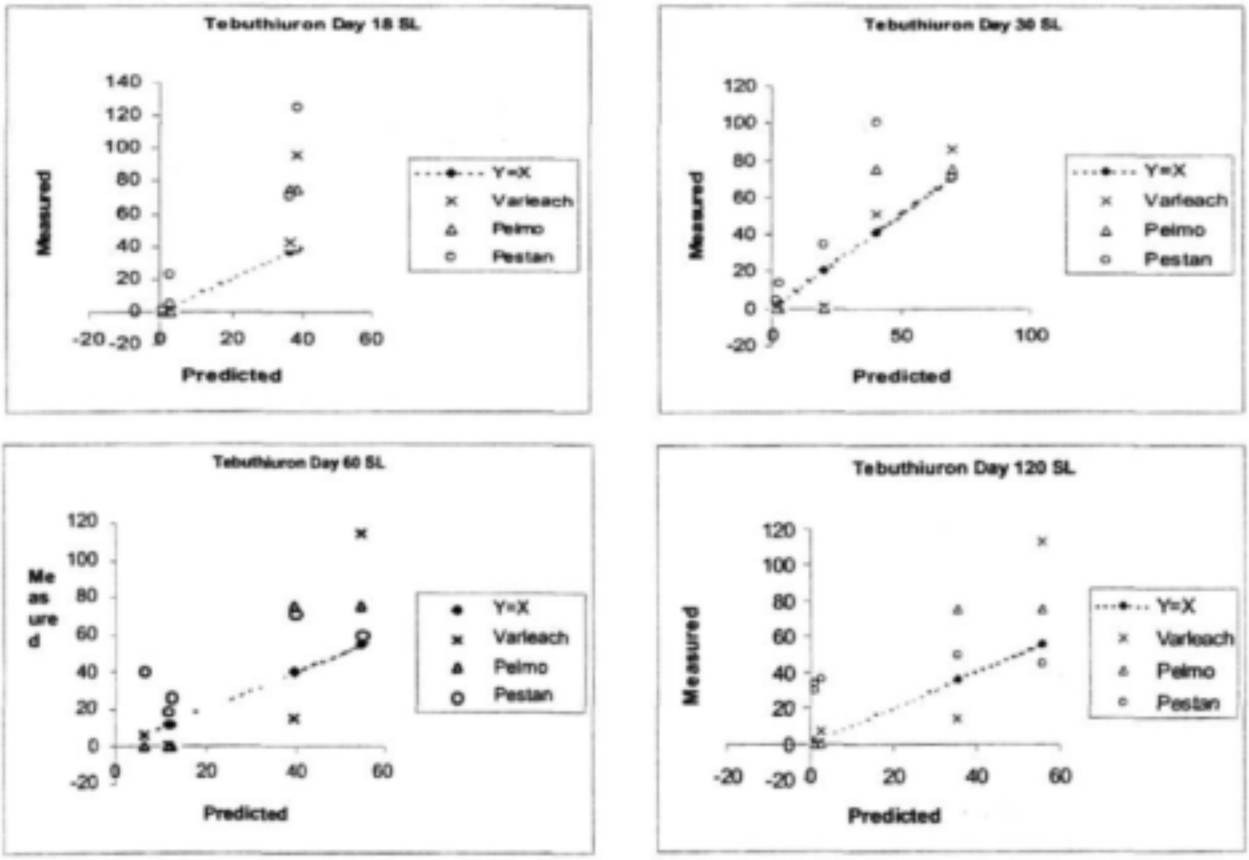

Figure 4.17. Comparison of measured tebuthiuron concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the sandy loam soil (SL), 18, 30, 60 and 120 days after application.

As with the sandy clay loam soil, the Varleach model predictions indicate mobility of tebuthiuron only in the top 40 cm soil layer. Varleach predicted higher tebuthiuron mobility in the sandy loam soil in that a higher proportion of tebuthiuron is predicted to leach to the 20 – 40 cm soil layer than that found in the sandy clay loam soil. Varleach however still does not predict movement past the 40 cm soil layer. Pelmo predictions were similar to those for Varleach, except that Pelmo predicts even distribution of the compound in the 40 cm soil horizon rather than higher proportions in the lower part of this soil layer.

The model Pestan predicted tebuthiuron leaching to the 120 cm soil layer within 18 days of application. The Pestan model over-predicted the extent of leaching found, in that higher proportions of the tebuthiuron were predicted entering the deeper soil layers as was observed.

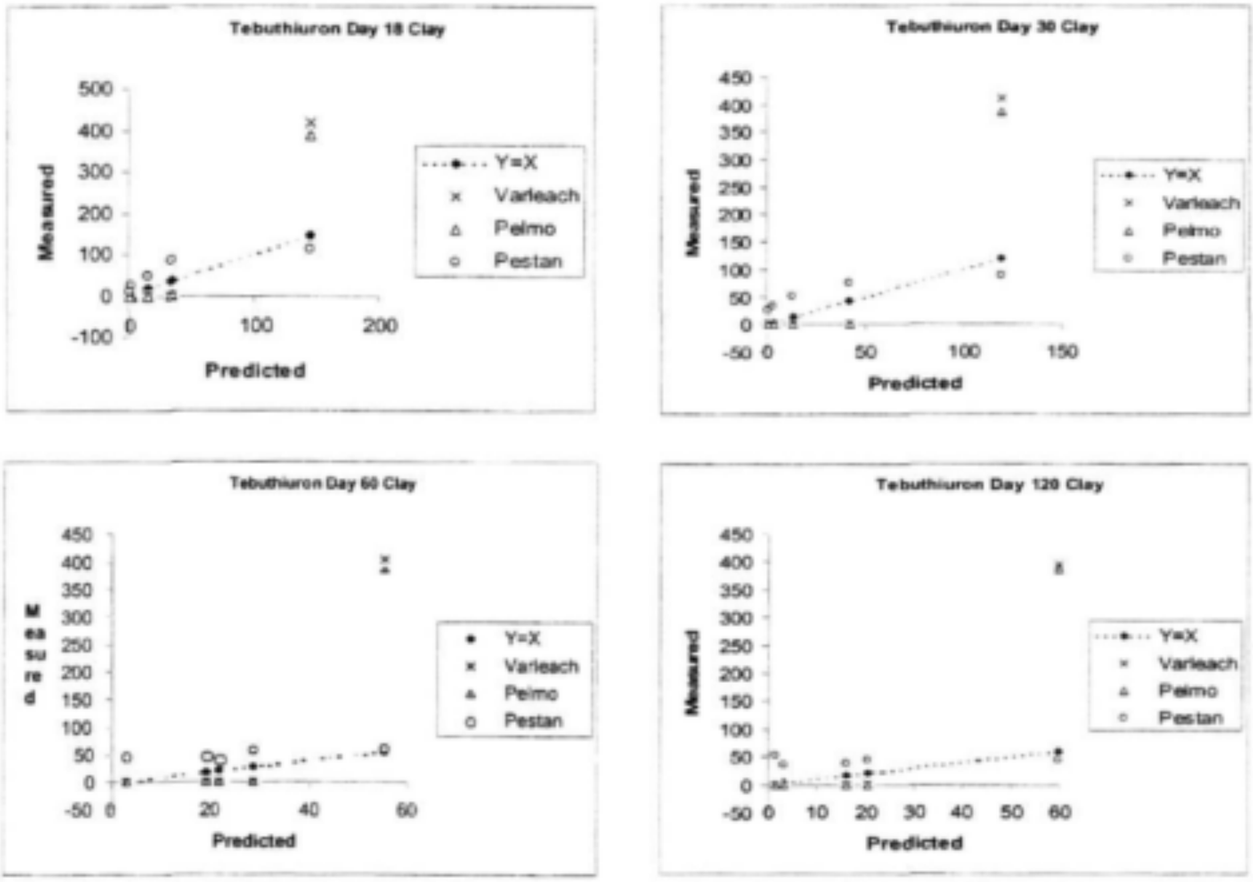

Figure 4.18. Comparison of measured tebuthiuron concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the clay soil (clay), 18, 30, 60 and 120 days after application.

Tebuthiuron – clay soil

Results of regression analyses and comparisons for tebuthiuron leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.18.

The models Varleach and Pelmo predicted that no tebuthiuron would leach to soil layers deeper than 20 cm throughout the trial period. Despite this, the percentage correlation for both models at all time intervals was high, indicating a good fit of measured versus predicted values. The correlation is however misleading as it is based only on one correlation point. The models both predict high tebuthiuron concentrations remaining in the top 20 cm soil layer for the entire time period. The percentage correlation did however decrease with time, as is expected.

The predicted tebuthiuron leaching for the model Pestan correlated well with observed leaching. Pestan predicted tebuthiuron leaching to the deepest soil layer within 18 days of application as was observed. The percentage correlation was above 70 % for day 18 and 30, but decreased to below 50 % for the remaining two time periods. The reduced 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 models Varleach and Pelmo rendered leaching predictions for tebuthiuron on all three soils, which vastly underestimate the leaching potential observed. Pestan tended to overestimate the leaching potential of this compound on all three soil types tested. None of the models evaluated gave an exact fit for tebuthiuron observed concentrations versus model predicted concentrations.

Fenthion – sandy clay loam soil

Results of regression analyses and comparisons for fenthion leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.19.

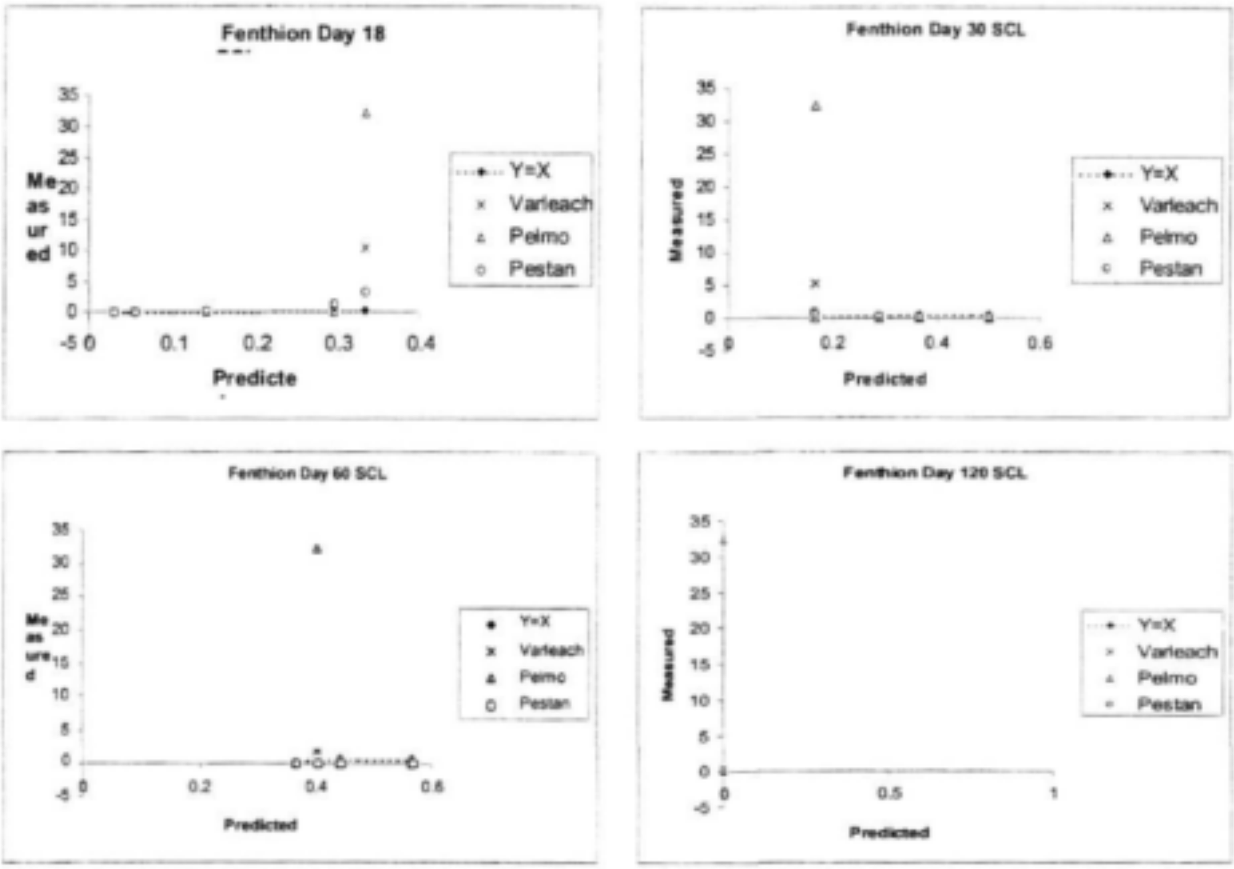

Figure 4.19. Comparison of measured fenthion concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the sandy clay loam (SCL), 18, 30, 60 and 120 days after application.

The models Varleach and Pelmo predicted that fenthion would not leach at all the top 20 cm soil layer of the sandy clay loam soil, even 120 days after application. Varleach predicts rapid degradation of the compound over the trial period with only approximately 1 % of the applied compound remaining at the end of the trial period. Pelmo on the other hand predicts almost no degradation of the compound. The correlations for all the models for day 120 were weak, due to the actual values being zero.

The model Pestan predicted fenthion leaching to the 120 cm soil depth within the first 18 days of application to the sandy clay loam soil with a percentage correlation of 74 %. The model overestimates the fenthion concentration dispersed through the soil profile, which 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.

Fenthion – sandy loam soil

Results of regression analyses and comparisons for fenthion leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.20.

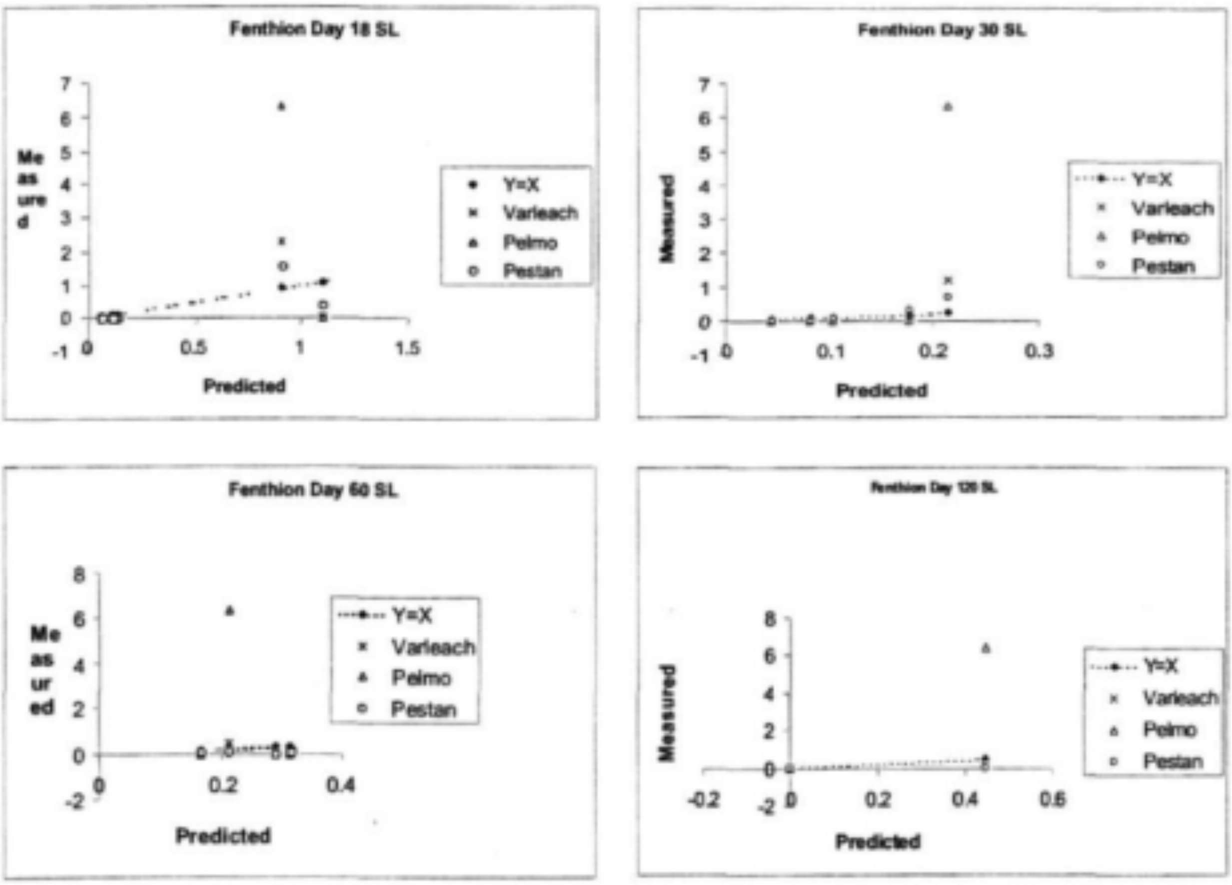

Figure 4.20. Comparison of measured fenthion concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the sandy loam soil (SL), 18, 30, 60 and 120 days after application.

As was found on the sandy clay loam soil, both the models Varleach and Pelo predict that fenthion would not be dispersed in the sandy loam soil beyond the 20 cm soil layer. Varleach predicted a high rate of degradation of fenthion in the sandy loam soil, whereas Pelmo predicts limited degradation. Because of the high concentrations predicted in the topsoil layer by these two models, the percentage correlation was low. This is especially relevant to the Pelmo predictions.

The model Pestan predicted fenthion leaching only to the 80 cm soil layer within 18 days of application, Pestan under-predicted the extent of fenthion dispersion through the soil horizon. Even so the Pestan predictions did follow the observed values satisfactorily.

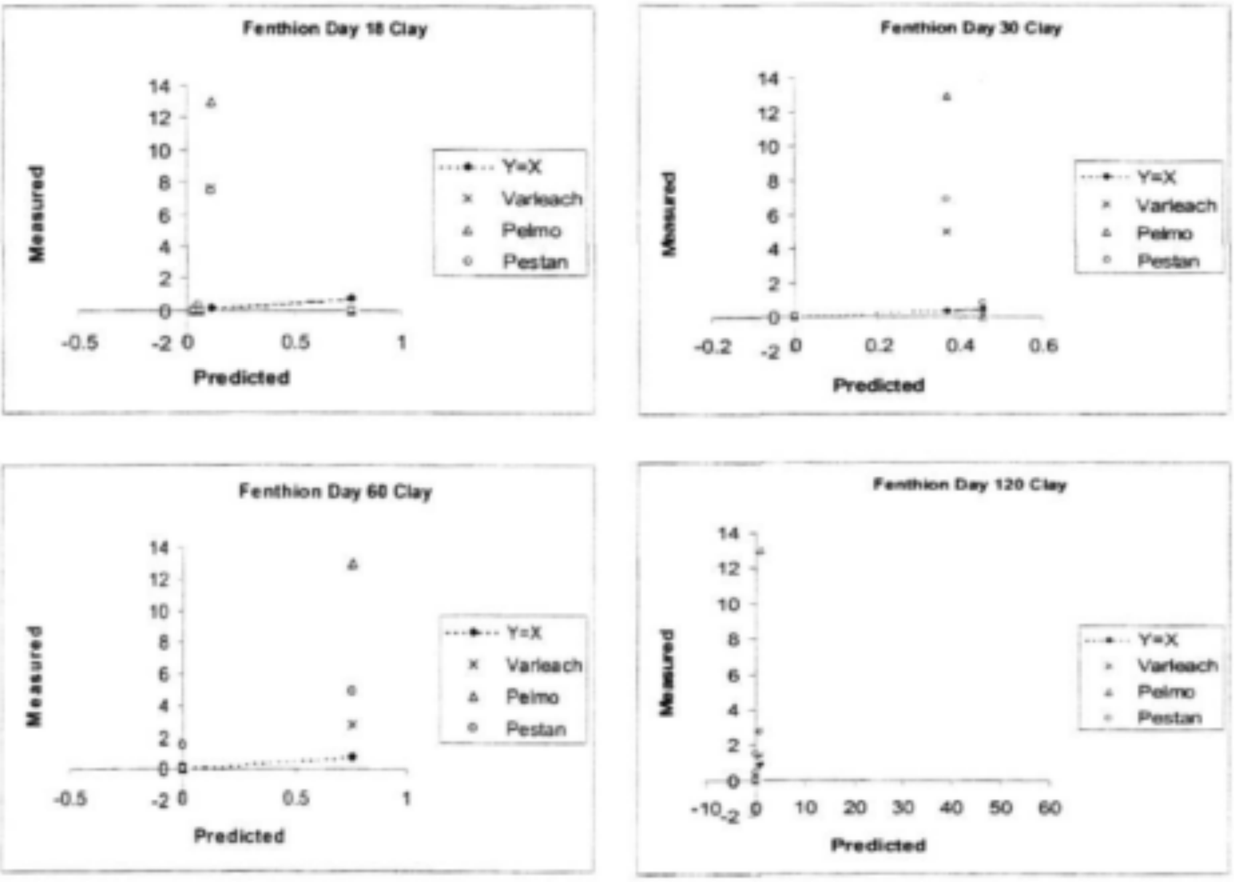

Figure 4.21. Comparison of measured fenthion concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the clay soil (clay), 18, 30, 60 and 120 days after application.

Fenthion – clay soil

Results of regression analyses and comparisons for fenthion leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.21

The models Varleach and Pelmo predicted that fenthion would not leach below 20 cm for the entire trial period. Both models rendered low correlation's for day 18 and 30, but for days 60 and 120 the correlation was an exceptional 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 believed to have been observed.

Pestan predicted slow movement of fenthion to the deeper soil layers, reaching the 120 cm soil layer only after 120 days. The model over-predicts the fenthion concentrations in soil for all time periods. The correlation for the clay soil were generally low, with the exception of day 120 where a 88 % correlation was rendered. This was probably due to the prediction of low levels of fenthion in the deeper soil layers correlating with zero levels detected.

The models evaluated did not simulate the upward mobility believed to have been observed on the clay and sandy loam soils where fenthion was applied.

As was found with tebuthiuron leaching predictions, Varleach and Pelmo models rendered leaching predictions for fenthion on all three soils which vastly underestimate the observed leaching potential. Pestan tended to overestimate the fenthion leaching potential on all three soil types tested. None of the models evaluated gave an exact fit for fenthion observed concentrations versus model predicted concentrations.

Azafenidin – sandy clay loam soil

Results of regression analyses and comparisons for azafenidin leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.22.

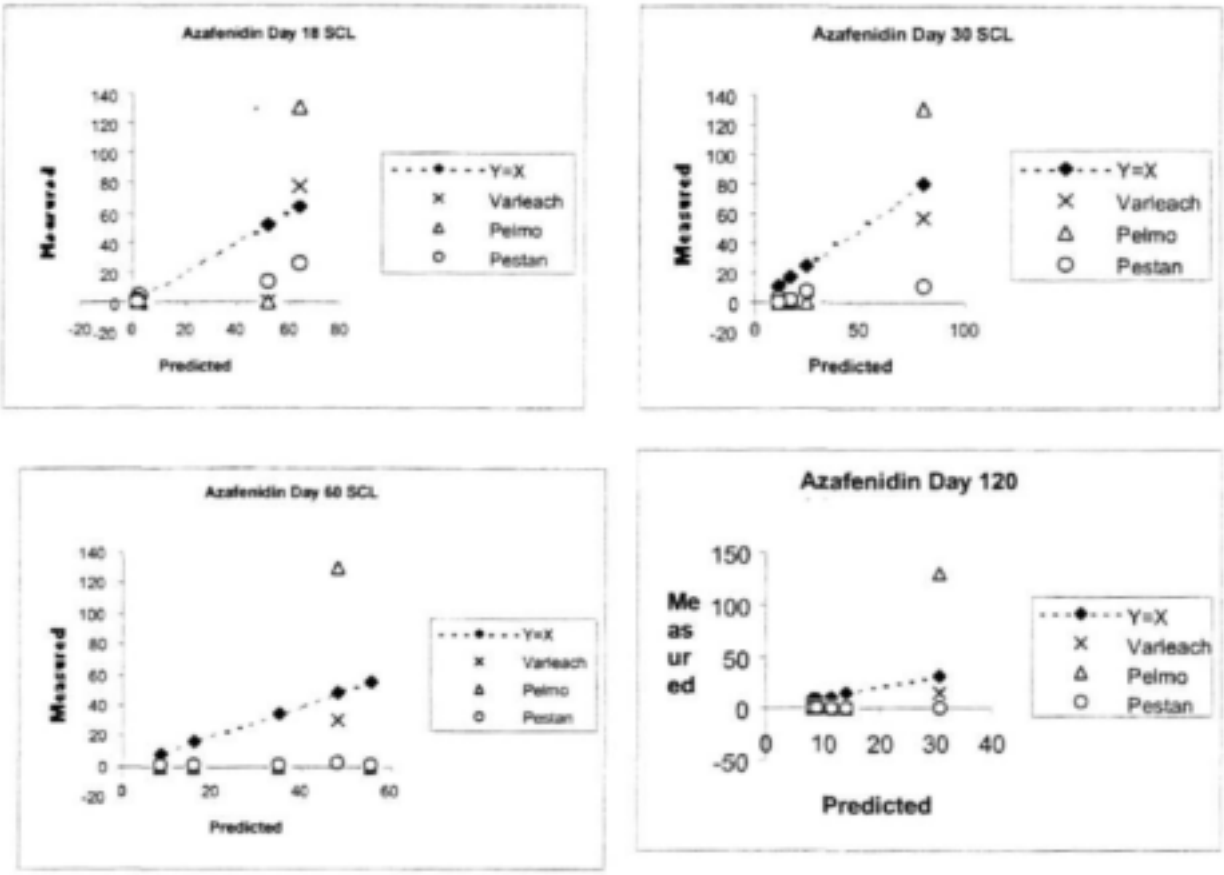

Figure 4.22. Comparison of measured azafenidin concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the sandy clay loam (SCL), 18, 30, 60 and 120 days after application.

Similarly to the predictions for fenthion, the Varleach and Pelmo models predicted that azafenidin would not leach out of the top 20 cm soil layer of the sandy clay loam soil at all even to day 120 after application. The Varleach model predicts azafenidin degradation over the trial period with approximately 18 % of the applied remaining at the end of the trial period. The Pelmo model on the other hand predicts almost no degradation of the compound. Although the correlation for these two models were good the predicted values did not fit the x = y curve due to no leaching being predicted.

The model Pestan predicted azafenidin leaching to the 120 cm soil depth within the first 18 days of application to the sandy clay loam. The model renders a correlation of above 60 % throughout. However, the Pestan model under-estimated the azafenidin concentration dispersed through the soil profile. It seems as if the model over estimated the rate of azafenidin degradation.

Azafenidin – sandy loam soil

Results of regression analyses and comparisons for azafenidin leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.23.

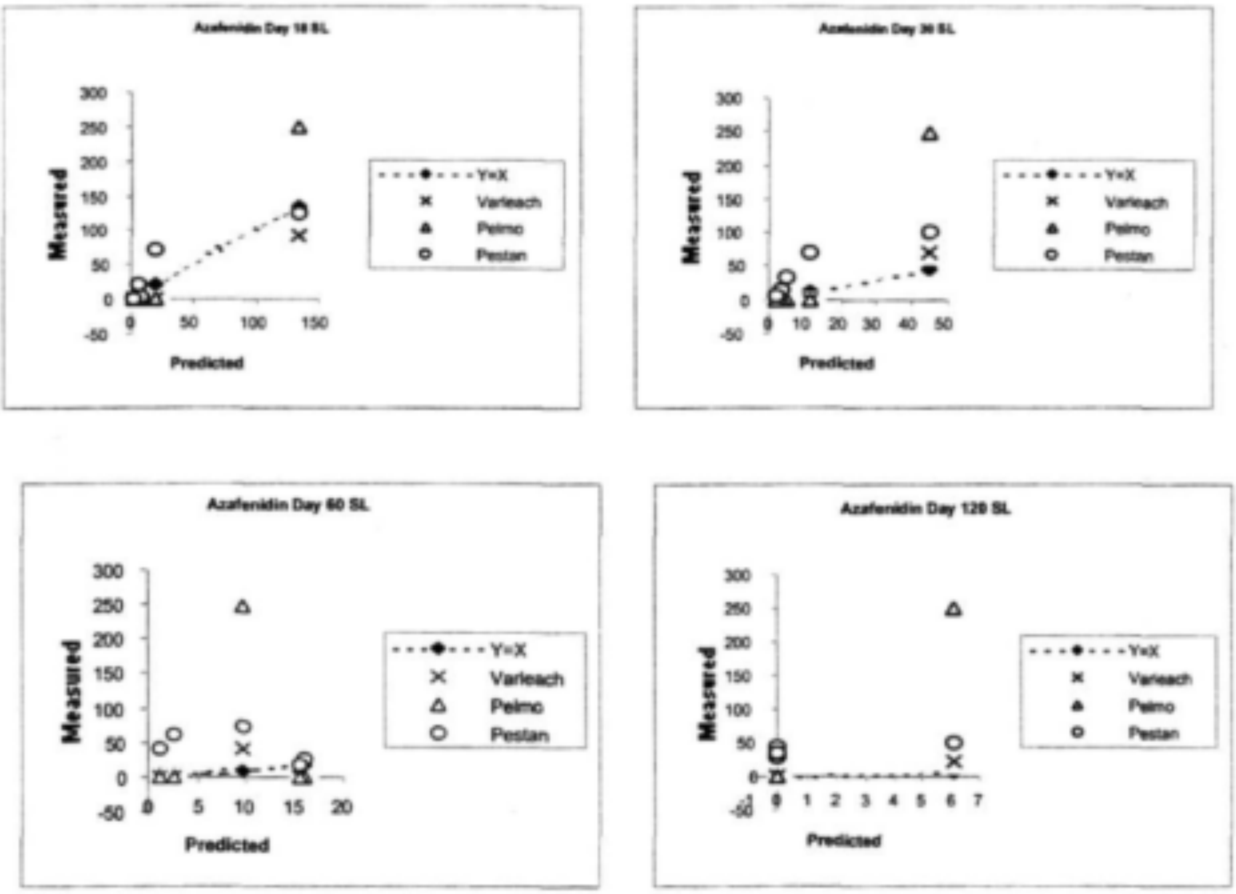

Figure 4.23. Comparison of measured azafenidin concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the sandy loam soil (SL), 18, 30, 60 and 120 days after application.

As was found on the sandy clay loam soil, both the models Varleach and Pelmo predict that azafenidin would not be dispersed in the sandy loam soil past the 20 cm soil layer. As with fenthion, the Varleach model predicted a high rate of degradation of fenthion in the sandy loam soil, whereas the Pelmo model predicts limited degradation. Because of the high concentrations predicted in the topsoil layer by these two models, the percentage correlation was low. This is especially relevant to the Pelmo predictions.

The model Pestan predicted azafenidin leaching to the 120 cm soil layer within 18 days of application. Pestan over-predicts the azafenidin levels in all soil layers through the soil horizon. Pestan does however follow the azafenidin dispersion pattern observed in field trials to some extent.

Azafenidin – clay soil

Results of regression analyses and comparisons for azafenidin leaching against the models Varleach, Pelmo and Pestan are shown in Figure 4.24.

The models Varleach and Pelmo predicted that azafenidin would not leach beyond 20 cm. The percentage correlation of predicted values versus measured values were low for both these models. As with fenthion and tebuthiuron, the model Pelmo seems to underestimate the rate of degradation of azafenidin.

The Pestan model predicted that azafenidin will reach the 120 cm soil layer only after 30 days. The model over-predicts the azafenidin concentration in the soil profile up to day 60, but under-predicts the concentration expected by day 120. The percentage correlation rendered for this model was generally low. However, of the three models evaluated, Pestan gave the most satisfactory predictions as to the leaching potential of azafenidin.

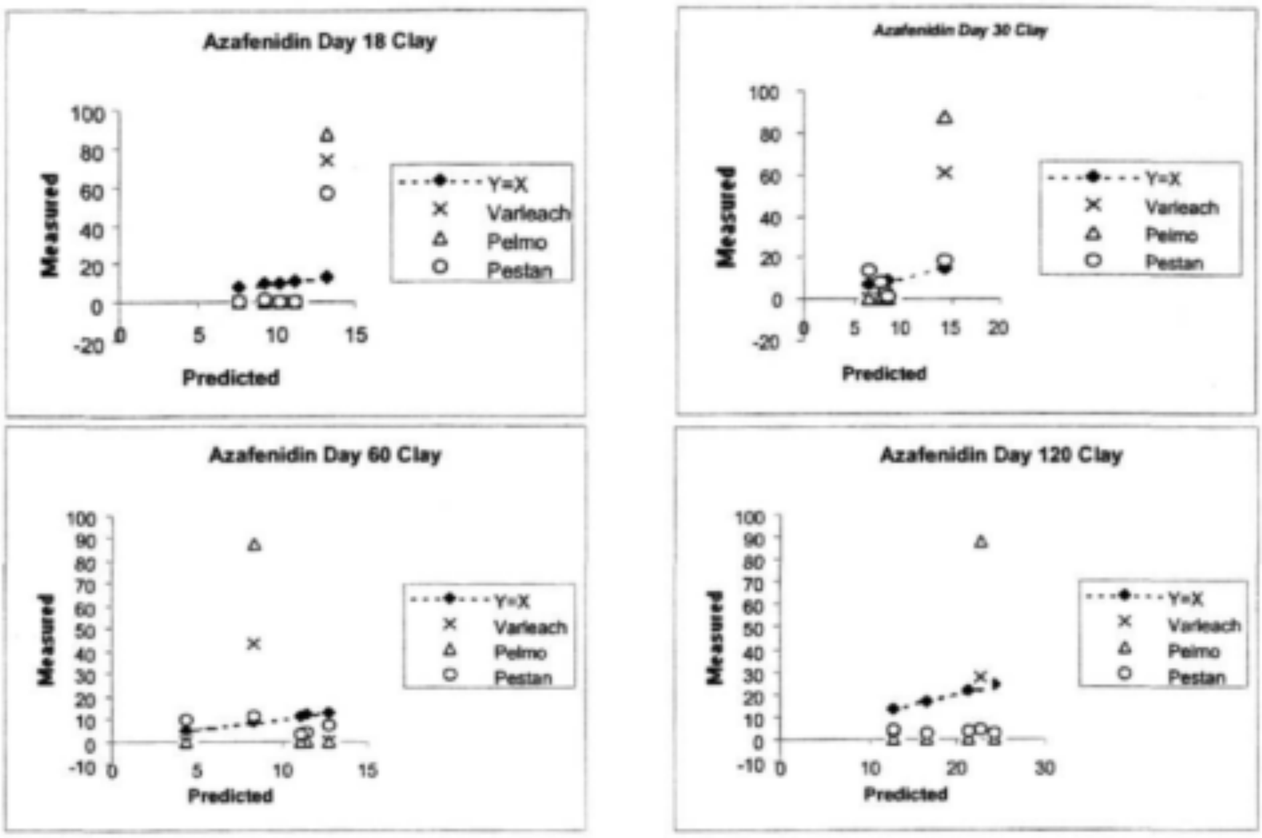

Figure 4.24. Comparison of measured azafenidin concentrations from leaching trials with predicted concentrations using the models Varleach, Pelmo and Pestan for the clay soil (clay), 18, 30, 60 and 120 days after application.

As was found with the other two compounds, leaching predictions by the Varleach and Pelmo models rendered leaching predictions for azafenidin on all three soils which vastly under-estimate the observed leaching potential. The Pestan model tended to over-estimate the azafenidin leaching potential on all three soil types tested. As was found for the other two compounds evaluated none of the models evaluated gave an exact fit for azafenidin observed concentrations versus model predicted concentrations.

Ideally, the model of choice should be one that renders an exact fit of predicted values to those measured. This was not found with any of the three models evaluated. Also the models could not predict upwards movement of the compounds. The Pelmo model is not sensitive to a change in degradation rate entered and for all the compounds and all three soils not only predicted limited leaching, but also limited degradation or dispersion of the compounds. The only model that could predict the leaching as observed, although with limited accuracy is Pestan. Pestan does not allow for more than one soil profile to be entered, and is useful only where the soil profile is homogenous. Also Pestan tends to over-predict the pesticide concentrations especially in the deeper soil layers. However, the model may be useful as a screening tool for predicting the worst case scenario with regards to leaching potential of a pesticide. Pestan does not use input of weather data for calculating leaching and leaching rates. The model uses hydraulic conductivity, re-charge rate and the dispersion ability of the compound in a particular soil to calculate leaching rates. In this evaluation, the dispersion was estimated from the field leaching studies as an average over the trial period. This parameter can however not be changed over the time period for which the model is run. It is believed that a change in the dispersion parameter with time to allow for changes in meteorological conditions may counter the over prediction that the model renders. Also the dispersion parameter will have to be estimated from leaching trials conducted on the compound of interest.

In this study, the model Pestan was run using published hydraulic conductivity values for soils with similar characteristics as the trial soils. This was done because local laboratories no longer do these determinations (ISCW pers. comm). The re-charge rates were set equal to the hydraulic conductivity as suggested by ISCW after tedious deliberations. If this model is to be further investigated, it will be necessary to determine more accurately these parameters.

5. DISCUSSION

The results of adsorption coefficient determinations indicated that soil depth did not affect the adsorption of the compounds tebuthiuron and azafenidin. In the case of fenthion however this was not the case. Here the tendency was observed of lower adsorption in the deeper soil layer of all three soils tested. The data further indicated that the leaching potential of tebuthiuron and azifenidin does not differ on the three soil types tested, despite differences in soil composition. Fenthion on the other hand showed increased adsorption potential with increased clay content, as expected. A decrease in adsorption with depth as found with fenthion indicates that fenthion may become more mobile as it enters the deeper soil layers. If this is the case, the compound will not be retained in the deeper soil layers and its mobility will be largely dependent on the extent of adsorption in the top soil layer. Thus the mobility of fenthion and similar compounds will be dependent on the soil composition in the top soil layer and the composition of the deeper soil layers may be irrelevant.

Comparison of the leaching patterns found in the tree field soils tested showed similar leaching patterns for tebuthiuron in the sandy loam soil and the sandy clay loam soil during the time interval to day 18. A lower leaching rate was found for tebuthiuron rate in the clay soil as compared to the other two soil types. During the following time intervals up to the end of the trial period, the leaching profiles for the sandy clay loam and clay soils were similar. However a more rapid decrease in tebuthiuron residues from the top 20-cm soil layer was found on the clay soil as compared to the sandy clay loam soil. During the same time intervals, tebuthiuron movement was the highest on the sandy loam soil. There are indications of build-up of the compound in the deeper soil layers and the compound leaching past the 120 cm soil layer. The differences in tebuthiuron leaching found between the three soil types was not reflected by the adsorption data.

Results indicate a high rate of fenthion degradation. This is corroborated by a relatively short half-life found in laboratory studies. Field leaching data further indicates that fenthion may be highly mobile in all three soils contrary to the belief that the compound is relative low in soil mobility. The high fenthion mobility was not corroborated by laboratory adsorption studies. The adsorption coefficients determined in laboratory studies for fenthion indicated extremely high adsorption coefficient for this compound indicating limited leaching to be expected.

From adsorption data it is expected that no differences would occur in the leaching pattern of azafenidin in the three soils. However leaching patterns for this compound did appear to differ.

Result from this study indicates that adsorption data cannot be used to characterize pesticide leaching potential in South African soils. Thus simple models which use adsorption as a major input for screening pesticide such as the GUS index are thought not suited for use in screening pesticide leaching potential.

It may be possible to derive a pesticide adsorption coefficients for South African conditions using an alternative method based on leaching, as the mini column lysimeter method developed by Kubiack.

Ideally the pesticide leaching model of choice for use in pesticide screening locally should be one that renders an exact fit of predicted values to those measured. This was not found with any of the three models evaluated. Also the models could not predict upwards movement of the compounds as was apparent with fenthion. The Models PELMO and VARLEACH model are not sensitive to changes in degradation rate and for all the compounds. The models also predicted limited leaching, degradation and dispersion of the compounds in the soils. The only model predicted leaching more or less as observed in field studies, although with limited accuracy is PESTAN. PESTAN however does not allow for more than one soil profile to be entered at one time i.e. for a single run. PESTAN is thus useful only where the soil profile is homogenous. PESTAN also over-predicts the expected pesticide concentrations, especially in the deeper soil layers. However, the model may still be useful as a screening tool for predicting the worst case scenario for pesticide leaching potential. PETAN does not make use of weather data as an input for the calculation of leaching rates. The model uses hydraulic conductivity, re-charge rate and the dispersion ability of the compound in a particular soil to calculate this. In this study, the dispersion was estimated from the field leaching studies as an average over the whole of the period. This parameter can not be altered over the time period for which the model is run. It is believed that a change in the dispersion parameter with time to allow for changes in meteorological conditions may counter the over prediction of the model. Should the model be run for predictions of pesticide mobility, the dispersion parameter will have to be estimated from actual leaching trials conducted on the compound of interest. It may be possible to do this using small-scale lysimeters, similar to those mentioned above regarding adsorption determinations. It may thus be possible to determine both a more accurate adsorption coefficient as well as a dispersion parameter from a single set of laboratory experiments. This could limit costs for screening trials thereby adding to cost effective environmental screening.

In this study, the model Pestan was run using published hydraulic conductivity values for soils with similar characteristics as the trial soils. This was done because local laboratories no longer do these determinations (ISCW personal communication). The re-charge rates were set equal to the hydraulic conductivity as suggested by ISCW after tedious deliberations. If this model is to be considdered for use in pesticide screening, it will be necessary to determine these parameters more accurately, or develop an alternative using a conversion factor. It may be possible to develop such factors for each soil type in the country. In this way the model could be used as a primitive tool for screening pesticides and delimit areas where a specific compound should not be used. This possible application of the model requires further investigation.

Although non of the models fit the leaching pattern observed, it is believed that the PESTAN model gave a good indication of the leaching potential of the three compounds tested. The model PESTAN may serve as a screening tool in predicting pesticide leaching under South African conditions. The model tends to over-predict leaching potential, and may be a useful tool for use as an indicator of the worst case scenario leaching test. If this model can be optimised, it may be possible to run the model consecutively for different soil layers, where heterogeneous soil layers are investigated. Further investigations are however required. The leaching data collected for the three compounds and three soil types could be used in further model evaluations using alternative models or newly developed models.

6. CONCLUSIONS

The integration of a pesticide leaching screening programme into the current South African pesticide registration scheme remains an urgent need for safeguarding water-, natural- and agricultural resources. Sustainable crop production, agricultural development and eco-tourism are all reliant on minimally polluted water. Leaching models can play an important role in preventing pesticide pollution especially where pesticides cause effects, at level residue levels, on human and environmental health. The

This study showed that none of the models evaluated accurately predict the leaching potential of the three compounds tested, as applied to three different soil types. The prediction accuracy of the models were measured against field leaching study data. The only model that could close predict pesticide leaching potential was the model PESTAN which shows some promise for use as a screening tool. The model will however require some form of optimisation.

The research showed that the compounds used in the field leaching studies were more mobile in local soils than expected. Expected mobility extrapolated from adsorption data indicates that the compounds tested will be low in mobility. This was not found in the study. The adsorption coefficients determined from laboratory trials all fell within the published limits for the compounds.

Studies on the half lives of the compounds showed that the compounds may be more persistent under local conditions as compared to published half lives for these compounds.

Results of the study thus shows that the standard batch slurry method for adsorption characterisation of a pesticides cannot be extrapolated to soil mobility. It is believed that an alternative adsorption characterisation method such as the lysimeter based adsorption coefficient, may be more suited to local conditions. It is believed that additional research is required before pesticide leaching screening can be introduced into the pesticide registration system.

Future research needs

The project only considered three leaching models in the evaluation of the predictive capacity of the models. It could be valuable to test alternative models such as those used in the Australian pesticide registration system for their efficacy under South African conditions. These model can be run without having to redo the field leaching phase as this data is already available.

As an alternative to the further evaluation of existing models it may be more relevant if the existing water movement models which were developed for South African conditions are modified to include a pesticide leaching module.

The model PESTAN should be evaluated in more detail and the potential use of conversion factors for hydraulic conductivity as well as running the model consecutively for different soil layers should be considdered.

The leaching evaluations in this study were done using un-cropped fields. It will be valuable to conduct leaching studies using cropped fields, of the same soil types. This will render data on the effects of cropping on the leaching potential of the pesticides. Such trials can be conducted using only a single pesticides, instead of all three tested in the current study.

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8. APPENDIX 1. - METEROLOGICAL DATA FOR THE TRIAL PERIOD

The metereological data used as inputs for the relevant models are shown in the figures that follow.

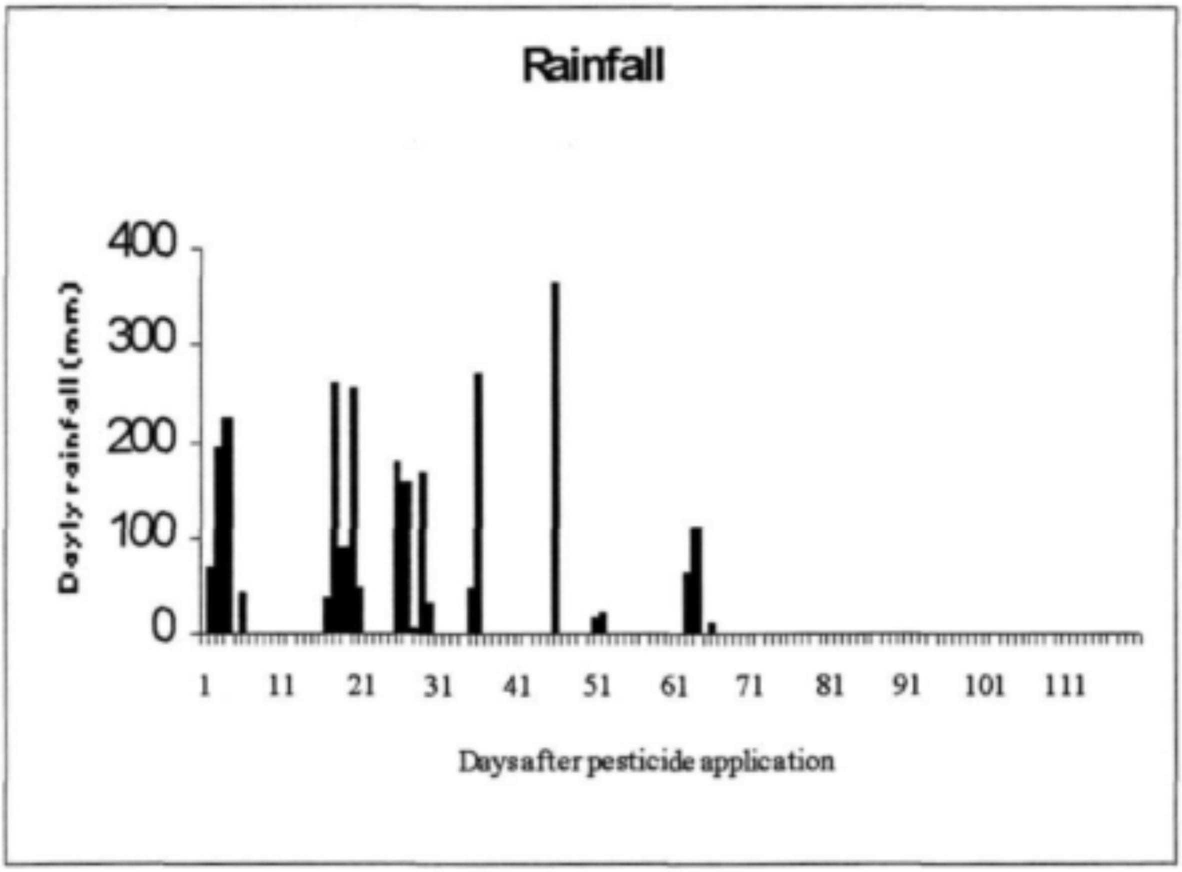

Figure 8.1. Rainfall data for Pretoria during the field leaching trial period used as model inputs.

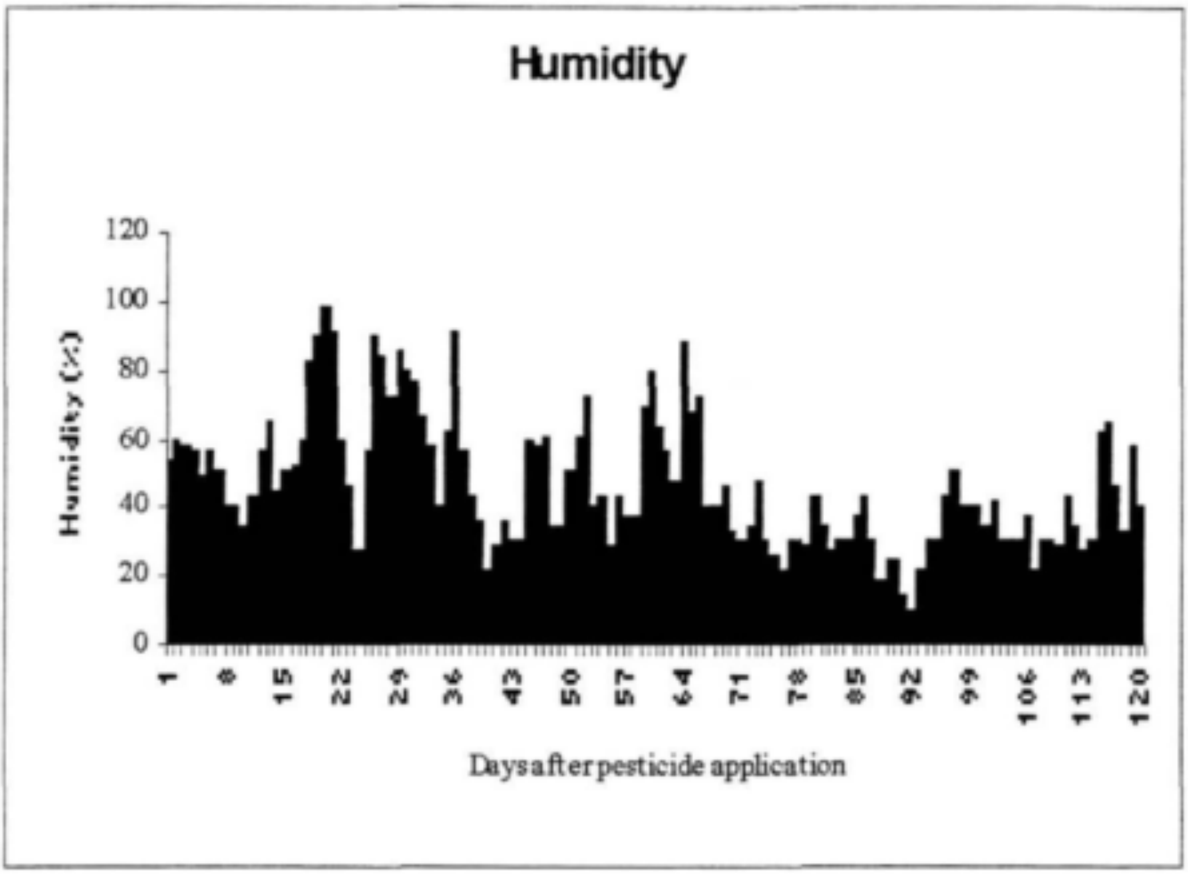

Figure 8.2. Percentage humidity data for Pretoria during the field leaching trial period used as model inputs.

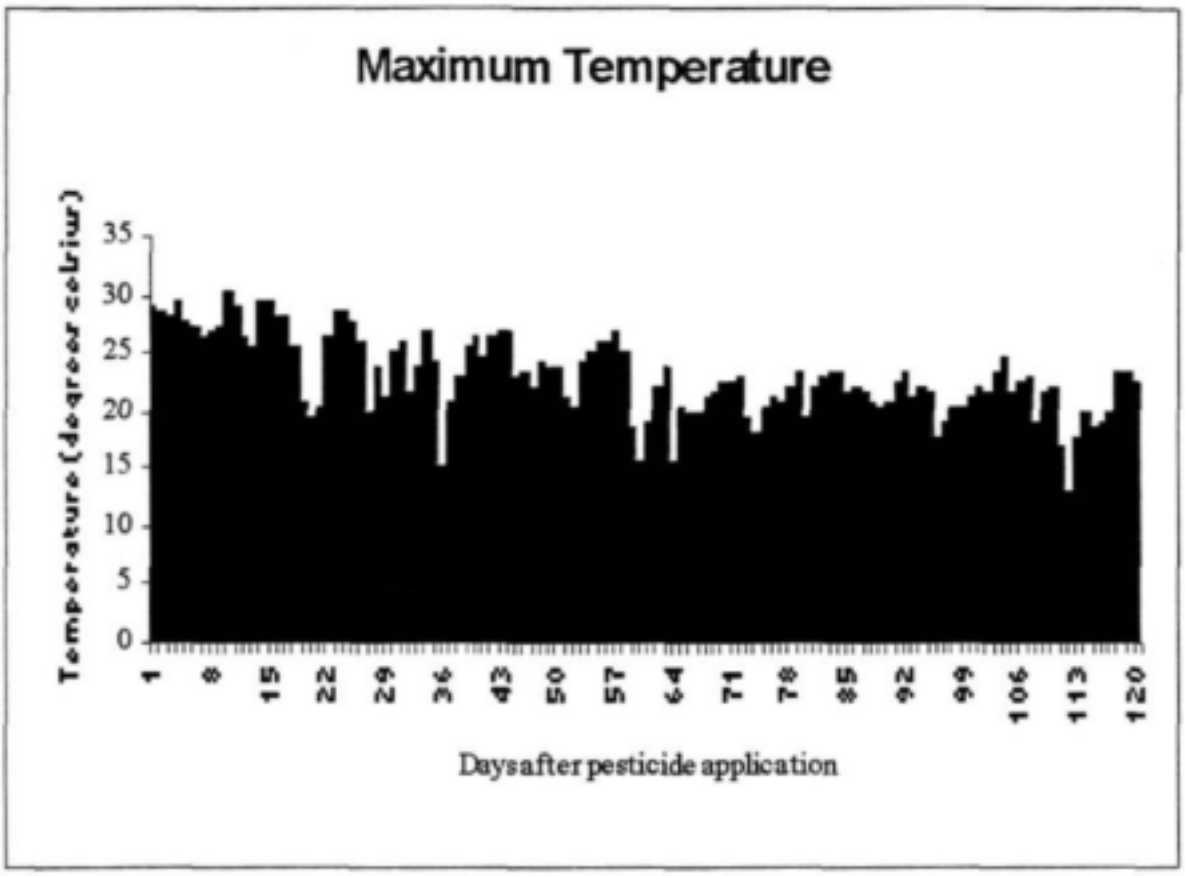

Figure 8.3. Maximum temperature (°C) data for Pretoria during the field leaching trial period used as model inputs.

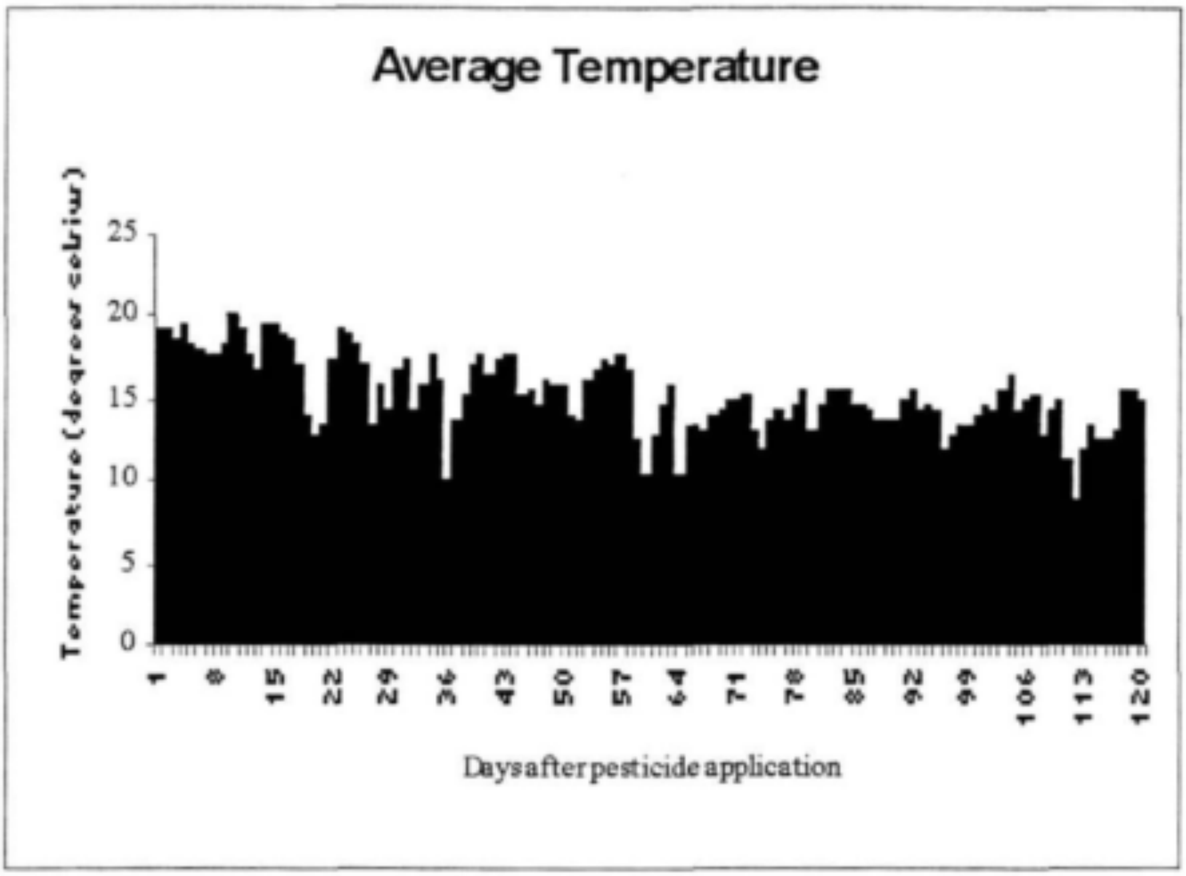

Figure 8.4. Average temperature (°C) data for Pretoria during the field leaching trial period used as model inputs.

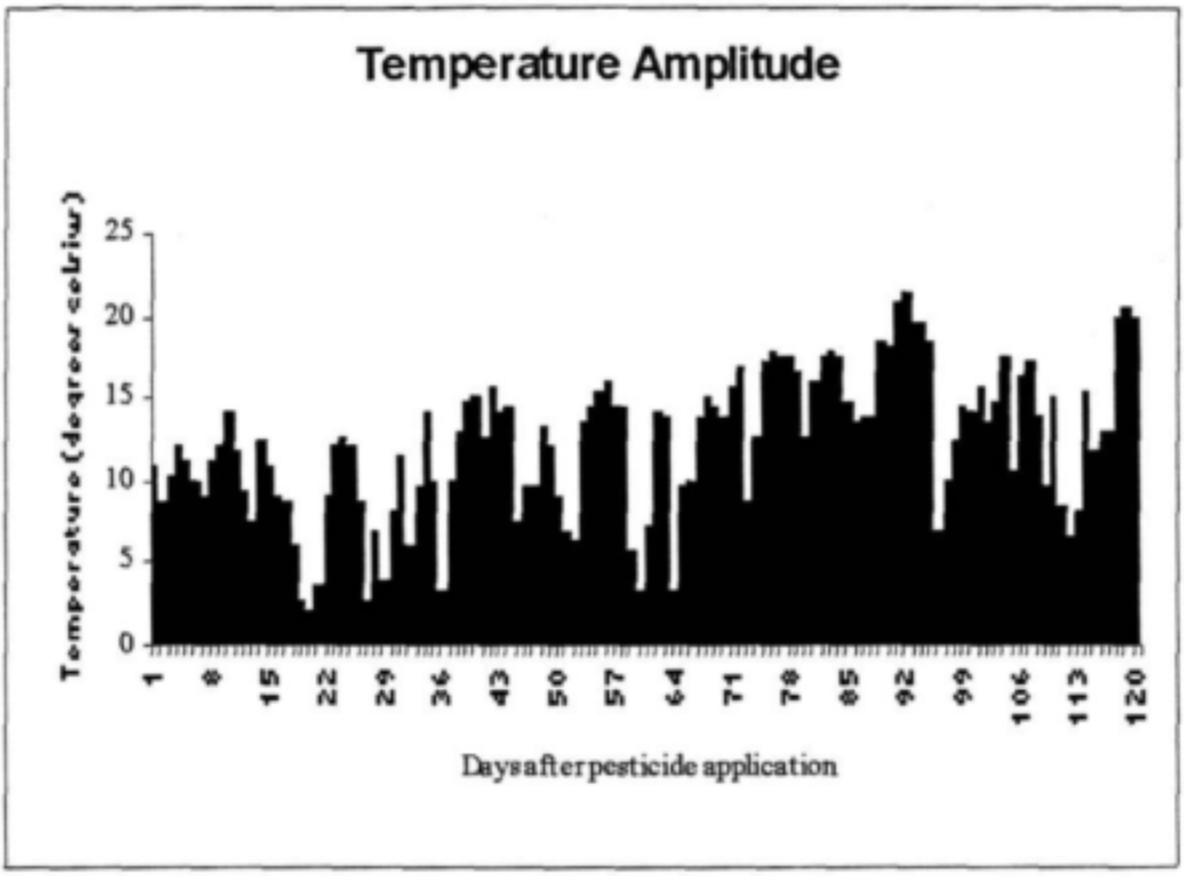

Figure 8.5. Temperature Amplitude (°C) data for Pretoria during the field leaching trial period used as model inputs.

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