MODELLING THE BEHAVIOUR AND FATE OF PRIORITY PESTICIDES IN SOUTH AFRICA

Simone Maharaj

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Department of Earth Sciences
University of the Western Cape

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PREFACE

This report emanates from a project funded by the Water Research Commission (WRC), executed by the Institute for Groundwater Studies, CSIR and University of the Western Cape, entitled “Identification and prioritisation of groundwater contaminants and sources in different hydrogeological environments of South Africa” (Project No. K5/1326). The third chapter is based on the report on ‘Pesticide Modelling‘ (Jovanovic and Maharaj, 2003) for a scoping study, funded by the WRC, entitled “Modelling non-point source pollution in agriculture from field scale to catchment scale” (unpublished).

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EXECUTIVE SUMMARY

BACKGROUND

The use of pesticides poses a serious threat to the limited water resources of South Africa. The amounts which are not taken up by crop plants, are often washed away by runoff into surface waters, or leached through the soil, causing groundwater pollution. The problem of pesticide pollution is often intensified by inappropriate usage, disposal and monitoring in agriculture and predictive models have proven to be an effective tool for improving management practices. Research, however, has focused mainly on surface water contamination and groundwater impacts are largely unknown. Furthermore, pesticide registration in South Africa is largely determined by international standards and there is a need for impact assessments to be carried out under local conditions.

METHODS USED TO MEET OBJECTIVES

The aims of the study included the determination of priority pesticides in South Africa based on usage and properties, the determination of pesticide sorption in two selected South African soils, and an assessment of pesticide fate by modelling. In order to meet the objectives, the study was divided into five phases. The first phase included a literature review for (i) the identification of most detected and most widely used pesticides in South Africa, (ii) the determination of priority pesticides based on pesticide properties and site characteristics, representative of South African soils, and (iii) a review of models to predict the behaviour and fate of pesticides. The second phase involved a characterisation of two selected South African soils using standard laboratory procedures. Sampling sites, located in Bellville (non-farming) and Elgin (farming) were selected as contrasting soil types, on the basis of land-use. Soils were analysed in the laboratory for chemical and physical properties including pH, electrical conductivity, cation exchange capacity, organic matter content, particle size distribution and water retention. Emphasis was placed on the impacts of soil properties on sorption as a dominant process involving pesticides. The third phase involved sorption experiments and HPLC analysis to determine pesticide sorption behaviour, using sorption isotherms and coefficients. Simazine was selected as an example of a priority pesticide for the determination. The fourth and fifth phases included the modelling of priority pesticides in selected soils using the VLEACH and SWAP predictive models. The soil properties determined in the experimental work were used as input data for the models so that quantities and timing of leaching could be investigated.

IDENTIFICATION OF PRIORITY PESTICIDES

Most frequently encountered pesticides in the literature were chlorpyrifos (organophosphate), endosulfan (organochlorine), azinphos-methyl (organophosphate), atrazine (triazine), simazine (triazine), deltamethrin (pyrethroid) and penconazole (azole). Pesticide sales records from AVCASA also reflected high usage of triazines, organophosphates and organochlorines, but low usage of pyrethroids and azoles. The literature findings were thus considered to be an indication of pesticide usage and water contamination. To determine priority pesticides in South Africa based on pesticide properties and site characteristics, a properties database was compiled and priority pesticides were ranked according to their leaching potential, using a simple screening model (Rao et al., 1985). Simazine was identified as an example of a priority pesticide to be studied for its leaching potential under local conditions as it is extensively used in orchard and vineyards in South Africa. Despite various international studies reporting on simazine detection in groundwater systems and the associated hazard, not much research and monitoring has been done to test the impacts of simazine under local conditions.

SOIL AND PESTICIDE ANALYSIS

The chemical analysis of the two selected soils showed that the loamy sand Elgin soil has a higher cation exchange capacity and lower concentration of dissolved salts and organic carbon, than the sandy Bellville soil. The chemical properties of the Elgin soil favour the stronger mechanisms of chemisorption, while the properties of the Bellville soil favour the weaker physical forces of hydrophobic sorption. The water retention curves showed that, overall, the Elgin soil retains water better than the Bellville soil and, therefore, further enhances the potential for sorption due to an increase in the residence time of pesticides in the soil. Therefore, the Elgin soil is likely to have a greater, overall, immobilising effect on simazine.

Using the classification of Giles (1972), the sorption isotherms showed that simazine is weakly associated with water and will reach maximum adsorption on soil surfaces, forming a double homogenous layer around the particles. The linear sorption coefficient (Kd) equations were the best-fit for the sorption data and Kd values were found to be within the same order of magnitude as the literature values. Kd values were higher in the Elgin soil, than the Bellville soil, indicating a greater potential for sorption activity in the Elgin soil.

MODELLING PESTICIDE MOVEMENT THROUGH SOIL

VLEACH was used to model pesticide leaching based on typical soil conditions of the W. Cape and pesticide organic carbon partitioning coefficient (Koc) values derived from the best-fit equations of Weber et al. (2004). The model predicted the following time frames in which pesticides reach a maximum rate of leaching (or peak) under typical conditions: 12 to 48 yrs for simazine, 4 yrs for atrazine, 22 to 33 yrs for dimethoate, 4 yrs for lindane (Elgin soil), 42 to 43 yrs for 2,4-D, 12 to 28 yrs for carbofuran, 284 yrs for fenthion (Elgin soil) and 556 yrs for parathion (Elgin soil). For pesticides with extremely low mobility, leaching rate continued to gradually increase over a certain time period: 600 yrs for lindane (Bellville soil), dieldrin, fenthion (Bellville soil) and parathion (Bellville soil), and 200 yrs for carbaryl.

The experimentally determined soil properties and sorption coefficients (Kd) were used in SWAP and it was estimated that simazine is not likely to leach within one year under typical conditions and typical application rates. The sensitivity analysis of SWAP showed that leaching was generally greater for the Bellville soil, than for the Elgin soil. This outcome is in accordance with the outcomes of the soil analysis.

CONCLUSION

The results of the experimental work and the SWAP model is, therefore, in line with the hypothesis that simazine will not leach considerably in South African conditions. Furthermore, higher leaching was predicted for soils poorer in organic matter and with lower cation exchange capacity, in the presence of shallow groundwater table, and for pesticides with lower organic carbon partitioning and longer half-lives. It is recommended, however, that the results of this study be validated in leaching experiments. Furthermore, there is a need for data on pesticide degradation in local environments, requiring potentially long-term experimental studies.

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LIST OF ACRONYMS

AF	Attenuation Factor
AVCASA	Crop Protection and Animal Health Association
CEC	Cation Exchange Capacity
EC	Electrical Conductivity
EXTOXNET PIPs	Toxicology Network, Pesticide Information Profiles
GC	Gas Chromatography
GIS	Geographic Information System
HPLC	High Pressure Liquid Chromatography
ICE	Ion Composition Elucidation
LD_{50} value	the Lethal Dose that kills 50% of the test animals in a standard experiment
OC	Organic Carbon content
OM	Organic Matter content
PAN	Pesticide Action Network
RF	Retardation Factor
SCS	Soil Conservation Service
SWAP	Soil Water Atmosphere Plant model
US DA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
US NTP	United States National Toxicity Program
UWC	University of the Western Cape
VLEACH	Vadose zone LEACHing model

INTRODUCTION

Agricultural practice in South Africa is becoming increasingly dependent on the widespread use of toxic pesticide chemicals for crop protection, growth regulation and seed treatments to enhance productivity (London and Myers, 1995a & b). The use of pesticides poses a serious threat to already limited water resources, as the amounts which are not taken up by crop plants, are often washed away by runoff into surface waters, or leached through the soil, causing groundwater pollution (Aharonson, 1987). The problem of pollution is often intensified by poor management of pesticide usage, handling and disposal. Obsolete pesticides that have been banned, discarded or expired also pose a threat to the environment, examples of which are DDT and dieldrin. (Aharonson, 1987; Dalvie and London, 2001; Naidoo and Buckley, 2003). The Food and Agricultural Organisation (FAO) has recommended that chemical manufacturers should share some of the responsibility with government departments for hazardous waste management and adopt a 'cradle to grave' approach. The paradigm shift, however, has not yet occurred in South Africa (Naidoo and Buckley, 2003).

Surface water contamination by pesticides has been widely documented, particularly in agricultural areas, yet relatively little attention has been given to groundwater impacts. (Schulz et al, 2001). In general, groundwater systems are not as easily monitored and are therefore not well understood (Aharonson, 1987). Nevertheless, there is evidence to suggest that research interests in the field are growing steadily, with a wealth of monitoring, deterministic, risk assessment and multi-disciplinary investigations underway.

Modelling of pesticide processes has proven to be an effective predictive tool for the management of agrichemical usage and, internationally, is often associated with the screening of new pesticides for registration (Boesten, 1999; Vanclooster et al., 2000a). In order to model the behaviour and fate of pesticides, it is necessary to identify the multitude of processes. Furthermore, toxic effects can be hazardous to the environment and need to be included in pesticide assessments. Processes (Figure 1.1) can be broadly grouped into transfer (mobility) or transformation (degradation). Transfer can occur through runoff, volatilisation, adsorption/desorption (or simply sorption), plant uptake and soil water fluxes (leaching and preferential flow). Transformation includes chemical, microbial and photo-degradation. In general, the processes are highly sensitive to pesticide properties, site conditions (weather, soil, geohydrology etc.), and management practices (pesticide application, irrigation, soil treatments etc.).

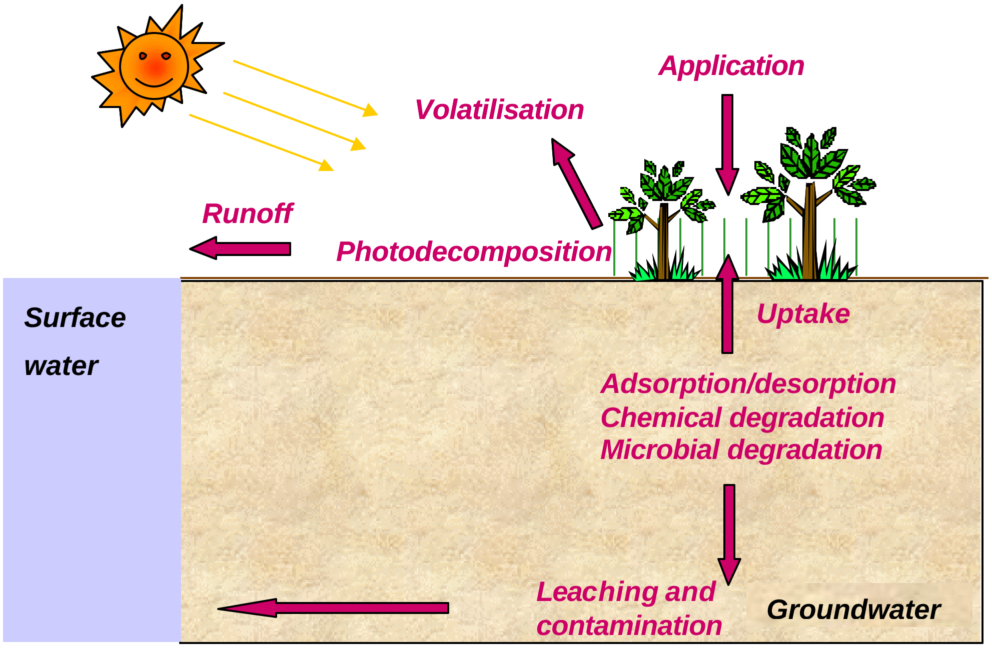


Figure 1.1. Balance of pesticide processes to be considered in modelling pesticide behaviour and fate

The objectives of this study are:

- Determination of priority pesticides in South Africa based on usage and properties
- Determination of pesticide sorption in two selected South African soils
- Modelling the behaviour and fate of priority pesticides, using VLEACH and SWAP predictive models to estimate the times and amounts of leaching

In order to meet the objectives, the study was outlined into five chapters:

Chapter 1 includes a literature review for (i) the identification of most detected and most widely used pesticides in South Africa, (ii) the determination of priority pesticides based on pesticide properties and site characteristics representative of South African soils, and (iii) a review of modelling to predict the behaviour and fate of pesticides.

Chapter 2 includes the characterisation of two selected South African soils using standard laboratory procedures. Sampling sites, located in Bellville (non-farming) and Elgin (farming) were selected as contrasting soil types, on the basis of land-use. Soils were analysed in a laboratory for chemical and physical properties including pH, electrical conductivity, cation exchange capacity, organic matter content, particle size distribution and water retention.

Emphasis was placed on the impact of soil properties on sorption as a dominant process involving pesticides.

Chapter 3 involves a set of sorption experiments and high pressure liquid chromatography (HPLC) analysis to determine pesticide sorption behaviour, using sorption isotherms and coefficients. Simazine was selected as an example of a priority pesticide for the determination.

Chapters 4 and 5 describe the modelling of priority pesticides in the selected soils using VLEACH and SWAP predictive models, respectively. The soil properties and sorption coefficients determined in the experiments (Chapters 2 and 3), were used as input data for the models, for the prediction of leaching times and quantities.

CHAPTER 1

Literature Review

1.1 Introduction

Agriculture is the primary source of water pollution by pesticides, although other sources can include forestry, domestic use and the control of vector-borne diseases. Pesticide usage associated with waste generation in South Africa can broadly be identified according to several major groupings and sub-groupings, namely, insecticides (including organochlorines, organophosphates, carbamates and pyrethroids), herbicides and fungicides. Even though the pesticide market is dominated by highly industrialized nations, it was found that inadequate pesticide management and disposal facilities in developing countries can pose a substantial risk to environmental health. The importance of adequate disposal facilities and effective management can be seen in the following case regarding obsolete pesticides (Naidoo and Buckley, 2003).

A clean-up project was carried out in 1999 involving storage at the Holfontein landfill site in Gauteng and export to an incinerator facility in Wales. At that stage, South Africa was considered to be generally clean and obsolete pesticides were not recognised as being a potential threat to the environment. However, it was then realized that not all obsolete pesticides were collected, as some farmers were unaware of the project (Dalvie and London, 2001; Naidoo and Buckley, 2003). Furthermore, certain harmful pesticides that are banned in other countries are still currently used in South Africa. These include chlorpyrifos (in products like Effekto Ant, Effekto Chlorpyrifos and Kombat Chlorpyrifos), dimethoate (in Effekto Aphicide), gamma-BHC (Lindane, found in Effekto Woodborer) and dichlorprop (newspaper article, Sunday Times, 24th August 2003).

Therefore, in light of the present climate of uncertainty regarding pesticide use and groundwater impacts in South Africa, this chapter includes a comprehensive literature review aimed at modelling pesticide impacts on local groundwater resources. Literature on pesticide usage and detection often emanated from monitoring studies and waste surveys conducting multi-residue analyses. Target analyses, however, were also reported and caution should therefore be taken when relating the priority status of a pesticide with its occurrence in the literature. To verify the literature findings, records of sales figures were also used as an indication of pesticide usage, in the absence of adequate data from farmers. The assumption is that all pesticides sold will eventually be used on farms or will potentially threaten the environment. It may, however, be over-simplistic to relate the priority of a pesticide with the volumes used, as pesticides differ considerably with respect to their level of toxicity in the environment. Agrichemicals can be standardised according to toxicity effects, such as, the biological equivalent units that are based on a chemicals oral LD_{50} value. The LD_{50} value is the lethal dose that kills 50% of the test animals in a standard experiment. London and Meyers (1995a & b) conducted a study in the southern region of South Africa, of pesticide usage and biological equivalent units. The use of such standards, however, exceeds the scope of this study and pesticide usage was considered to merely give a broad indication of the threat of a chemical. Pesticide sales figures were obtained from the Directorate of the Crop Protection and Animal Health Association, AVCASA (personal communications, Kleynhans J), a representative organisation of the pesticide chemical industry.

In determining priority pesticides based on pesticide properties and site characteristics, numerous chemical databases were consulted via the internet and a single comprehensive database of properties was compiled. Being one of the largest pesticide users world-wide, the USA has contributed much to the research, especially through the development of large-scale monitoring programmes (Weaver, 1993). As a result, many of the databases used in this study are of US origin. Key pesticides used and/or detected in South Africa were screened under typical soil and geohydrological conditions of the Western Cape. A simple screening method, using retardation and attenuation factor indices (Rao et al., 1985) was used to determine the relative groundwater impacts.

Pesticide toxicity is an important aspect in the assessment of pesticide impacts, however, there are constraints associated with quantifying toxicity. Therefore, various toxicity classifications were included in the pesticide properties database (Appendix A3), with a brief explanation given on prominent systems used internationally.

Lastly, a review of pesticide fate models was based on a progress report for a scoping study on modelling non-point source pollution in agriculture (Jovanovic and Maharaj, 2003). The main processes involved in the behaviour and fate of pesticides were theoretically reviewed and discussed. Knowledge gaps have been identified, recommendations given on future research needs, and links to other agricultural contaminants have been identified.

1.2 Identification of pesticides in South African literature

In this section, key findings of the literature review on the most widely used and detected pesticides in South Africa, as well as sales records, are discussed.

London and Myers (1995a) investigated the chemical usage patterns in specific farming sectors in the southern region of South Africa. They identified a widespread and diverse use of agricultural chemicals and that different sectors require different pesticide groups. Deciduous farming is the principal user of insecticides, herbicides, fungicides and growth regulators. Vineyards, wheat and vegetable production use primarily fungicides, herbicides and nematicides, respectively. Organophosphates are the main insecticides used, particularly azinphos-methyl, chlorpyrifos and dimethoate. Fungicides include phthalic acid derivatives, copper salts, sulphur and in particular, dithiocarbamates. Dominant herbicides include dipyridyls (particularly paraquat), chlorphenoxyacetic acids (particularly 2,4D), and triazines, particularly simazine. Widely used nematicides are ethylene dibromide and aldicarb.

A project was carried out by the United Nations Environmental Programme, involving an assessment of 30 years of available data on organochlorine residues in South Africa (Bouwman et al., 2003). Records showed that organochlorine pesticides are dominant, with DDT and dieldrin originating from past agriculture and control of Tsetse flies, and atrazine residues reflecting current agricultural use.

In January 2003, a European-Southern African conference took place in Cape Town on pesticides in non-target agricultural environments. The conference hosted a number of studies that involved pesticide detection in South African waters. Bennett et al. (2003) investigated the effects of spraydrift-airborne azinphos-methyl on a vegetated wetland at the Lourens River (Western Cape), and measured concentration levels from 0.08 µg/L to 0.7 µg/L in water. At the same site, they measured chlorpyrifos, prothiofos, endosulfan a, b and sulphate in sediment cores at concentrations ranging from 0.8 to 12 µg/kg.

Dabrowski and Schulz (2003 a & b) evaluated the loading of azinphos-methyl in the Lourens River at catchment scale and found that runoff produced a higher annual load (47.6g) than spraydrift (5.5g). Predicted values from an integrated Geographic Information System (GIS) were extrapolated for the catchment and found to be in agreement with the measured values. Dabrowski et al. (2002 b and 2003) also performed a risk assessment for subcatchments of the same river, using a GIS-based runoff model. Over the 3-year study period, the most applied and detected pesticides were azinphos-methyl, chlorpyrifos and endosulfan. Levels of detection in water samples were up to 0.2, 0.03 and 0.3 µg/L, respectively, and levels in sediment samples were up to 27.9, 43.6 and 34.75 µg/kg, respectively. Schulz et al. (2001) measured run-off related contamination at the Lourens River during the rainy season in 1999. Levels of endosulfan, chlorpyrifos and azinphos-methyl reached 0.16, < 0.01 and 0.38 µg/L in water samples, respectively, and 245, 344 and 244 µg/kg in sediment samples. Transient pesticide levels were found to be in excess of the target water quality limit proposed by the Department of Water Affairs and Forestry (Dabrowski et al., 2002 a). The two sites found to be most vulnerable were those with the least buffer strips and the presence of erosion rills and high slopes.

Solomons et al. (2003) and London et al. (2000) investigated the contamination of surface and groundwaters from 1997 to 1999, in areas of the Western Cape that are intensively used for agriculture, namely, the Hex River Valley, Grabouw and Piketberg. Endosulfan and chlorpyrifos were the dominant pesticides found in surface and groundwater samples. Out of 382 samples, 30% for chlorpyrifos and 37% for endosulfan were found to be in excess of the European Drinking Water Standard of 0.1 µg/L. Hotspots for endosulfan were found in the Hex River Valley (0.83 ± 1.0 µg/L) and a dam in Grabouw (3.16 ± 3.5 µg/L). Other pesticides detected include azinphos-methyl, fenarimol, iprodione, deltamethrin, penconazole and prothiofos.

McGregor (1999) reported on maximum levels of endosulfan and chlorpyrifos that were found at one site over 8 sampling sessions. That is, 1.794 and 19.13 µg/L, respectively. Davies (1997) also reported on endosulfan in 26 out of 27 farm dams in the Elgin area, as well as detections of chlorpyrifos (McGregor, 1999).

Fatoki and Awofulu (2003) evaluated different methods for the selective determination of persistent organochlorine pesticide residues in water and sediments. Liquid/liquid extraction and soxhlet extraction methods were used on marine and freshwater samples in the Eastern Cape and hazardous pesticide residues were found, namely, DDT, DDE, heptachlor and endosulfan.

A different approach was used in an assessment of the Crocodile River catchment in Mpumalanga (Heath et al., 2003). Pesticide concentrations in fish tissues were used and found to be positively correlated with estimations from a GIS model, based on a commercial database of actual pesticide usage values. The pesticides found include BHC, lindane, dieldrin, heptachlor and DDE.

Sereda and Meinhardt (2003) investigated water pollution levels in areas of KwaZulu-Natal and found residues of pyrethroid, organophosphate, organochlorine and carbamate insecticides. Residues were attributed to the high usage of insecticides in the area, for agriculture and the control of malaria (DDT and deltamethrin).

The following pesticides were identified in surface water samples collected near Johannesburg and analysed with the Ion Composition Elucidation (ICE) technique (Grange et al., 2003): anthracene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, camphor and atrazine. Additionally, diazinon and o-hydroxybiphenyl were identified with ICE, but their presence was not confirmed as standards were not available (Grange et al., 2003).

The role of hydrogeological and soil characteristics in pesticide leaching was highlighted by Weaver (1993) who conducted a preliminary survey of pesticide levels in groundwater and soil profiles in two areas of the Western Cape. The Hex River Valley, studied for pesticide levels in groundwater, and the Vaalharts Irrigation Scheme, studied for atrazine levels in the soil profile, are both areas of intensive agriculture and are considered to be vulnerable to contamination. However, despite the prevalence in groundwaters of the USA, none of the target pesticides, particularly atrazine, were found at the sample sites above the specified levels. It was concluded that local conditions of high temperature and low soil pH, significantly reduced the pesticide half-life's. Low soil pH, however, favours other pesticides such as aldicarb and the author recommended that these pesticides be closely monitored in the future and that further research should be done at a larger scale to confirm the findings.

1.2.1 Key pesticides identified in the literature

The frequency with which a pesticide was encountered in the literature was considered to be a good indication of its priority status, especially since strong motivation was generally given for studying particular pesticides, usually in the form of selection criteria for the likelihood of contamination. One such study was done by London et al. (2000), in which the extent and health impacts of water contamination by pesticides, were investigated. Pesticides to be intensively studied, were selected according to the following criteria, based on expert industry opinion and spray programmes recommended by the cooperative:

- Health impacts based on international standards

- Usage in the specific study area as determined from industry opinion and from published literature
- Data from farmers on local spray applications; data from commercial spray operators and cooperatives on types and concentrations of chemicals used, and methods of application; and data on weather conditions during sampling
- Likelihood of contamination based on industry opinion, US Environmental Protection Agency list of water pollutants and known groundwater ubiquity scores. The groundwater ubiquity score is based, amongst other factors, on the leachability of pesticides determined by organic sorption coefficients and half-life in soil.
- Availability and existence of methods of analysis

A summary of the literature review can be found in Appendix A1. It was found that the seven pesticides most frequently reported in South Africa are chlorpyrifos (organophosphate), endosulfan (organochlorine), azinphos-methyl (organophosphate), atrazine (triazine), simazine (triazine), deltamethrin (pyrethroid), and penconazole (azole). A summary of the literature on these key pesticides is given in Table 1.1. It should be borne in mind that many of the studies found in the literature report on target analyses rather than multi-residue analyses. In addition, many of the studies were conducted in the Western Cape, where pesticide residues originate mainly from orchards. Comparison with other areas of the country would be interesting, however, little monitoring data were found for this purpose.

From the review, it is evident and well acknowledged, that considerably more research has been done on the contamination of surface waters, and a gap exists in research on groundwater pollution. Additionally, it has been shown that pesticide impacts are strongly influenced by the nature of their physical and chemical environments, ranging from surface features to soil and hydrogeological properties. There is, therefore, a need to develop and integrate on-going monitoring systems within geohydrological studies, so that accurate assessments can be made for the management of groundwater impacts in localised environments. This will facilitate the setting of local standards and criteria by which to assess pesticide impacts, which is lacking at present in South African literature

1.2.2 Total sales figures

The sales figures from AVCASA, in kg or L of active ingredient, include those of defoliants, plant growth regulants, herbicides, fungicides, seed dressing, acaricides, nematicides and insecticides. In general, there has been an overall increase in sales from 1994 to 2000 (Figure 1.2 and 1.3) and it can be assumed that the trend will not change considerably in the near future. Figure 1.3 shows that, during this period, sales values were highest, in decreasing order for triazines (for example, atrazine and simazine), carbamates/thiocarbamates, organophosphates (for example, azinphos-methyl, chlorpyrifos, prothiofos and glyphosate), hydrocarbons, anilines/ acetanilides, and organochlorines (for example, endosulfan). Total sales figures from 1994 to 2000, can be found in Appendix A2.

Table 1.1 Summary of the seven most frequently reported pesticides in South African literature

Type of source	Examples	Reference
	Chlorpyrifos	
Agricultural peri-urban areas, orchards	1) From 0.8 µg kg^{-1} to 12 µg kg^{-1} in sediment cores of wetlands constructed along Lourens River (Western Cape).	Bennett et al. (2003)
	2) Measured predominantly in suspended particle samples.	Dabrowski et al. (2003)
	3) Measured in surface and groundwaters of Hex River Valley, Grabouw and Piketberg (Western Cape).	Solomons et al. (2003) London et al. (2000)
	4) Applied to grapevine (Western Cape).	London and Myers (1995 b)
	5) From 0 to 0.19 µg L^{-1} in water samples and from 0 to 152 µg kg^{-1} in suspended sediments from Lourens river (Western Cape)	Dabrowski et al. (2002a)
	6) From 0 to 0.03 µg L^{-1} in water samples and from 0 to 43.6 µg kg^{-1} in suspended sediments from Lourens river (Western Cape).	Dabrowski et al. (2002b)
	7) <0.01 µg L^{-1} in water samples and up to 344 µg kg^{-1} in suspended sediments from Lourens river (Western Cape).	Schulz et al. (2001)
	8) 19.13 µg L^{-1} in water samples from Hex river valley (Western Cape).	McGregor (1999)
	9) Eleventh most used pesticide in southern Africa in 1989.	London and Myers (1995a)

Type of source	Examples	Reference
	Chlorpyrifos	
	10) Detected in farm dams in Elgin (Western Cape).	Davies (1997)
	11) High usage in Hex River Valley (Western Cape).	Weaver (1993)
	Endosulfan a, b and sulphate	
Gardens and agricultural peri-urban areas, orchard	1) From 0.8 µg kg-1 to 12 µg kg -1 in sediment cores of wetlands constructed along Lourens River (Western Cape).	Bennett et al. (2003)
	2) Measured predominantly in suspended particle samples.	Dabrowski et al. (2003)
	3) 0.83 µg L-1 and 3.16 µg L -1 in surface and groundwaters of Hex River Valley, Grabouw and Piketberg (Western Cape).	Solomons et al. (2003) London et al. (2000)
	4) Applied to grapevine (Western Cape).	London and Myers (1995 b)
	5) From 0 to 0.35 µg L-1 in water samples and from 0 to 273 µg kg -1 in suspended sediments from Lourens river (W. Cape).	Dabrowski et al. (2002a)
	6) From 0 to 0.3 µg L-1 in water samples and from 0 to 34.75 µg kg -1 in suspended sediments from Lourens river (W. Cape). 7) Up to 0.16 µg L-1 in water samples and up to 245 µg kg-1 in suspended sediments from Lourens river (Western Cape).	Dabrowski et al. (2002b) Schulz et al. (2001)
	8) 1.794 µg L-1 in water samples from Hex river valley (Western Cape). 9) Nineteenth most used pesticide in southern Africa in 1989.	McGregor (1999) London and Myers (1995a)
	10) Detected in 26 out of 27 farm dams in Elgin (Western Cape).	Davies (1997)

Type of source	Examples	Reference
	11) Low usage in Hex River Valley (Western Cape).	Weaver (1993)
	Azinphos-methyl	
Agricultural peri-urban areas, orchards	1) From 0.08 µg L-1 to 0.7 µg L-1 in water of constructed wetlands at Lourens river (Cape Town).	Bennett et al. (2003)
	2) Loads of 27.8 g via runoff and 0.69 g via spray drift from 400 ha per event.	Dabrowski and Schulz (2003a and b)
	3) Measured predominantly in water samples.	Dabrowski et al. (2003)
	4) 0.2 µg L-1 in Western Cape streams.	Schulz and Dabrowski (2003)
	5) Detected in surface and groundwaters of Grabouw (Western Cape).	Solomons et al. (2003) London et al. (2000)
	6) 0 to 0.6 µg L-1 in water samples and 0 to 245 µg kg-1 in suspended sediments from Lourens river (Western Cape).	Dabrowski et al. (2002a)
	7) From 0 to 0.2 µg L-1 in water samples and from 0 to 27.9 µg kg-1 in suspended sediments from Lourens river (W. Cape).	Dabrowski et al. (2002b)
	8) Up to 0.38g L-1 in water samples and up to 244µg kg-1 in suspended sediments from Lourens river (Western Cape). 9) Thirteenth most used pesticide in southern Africa in 1989.	Schulz et al. (2001) London and Myers (1995a)
	10) Detected in farm dams in Elgin (Western Cape).	Davies (1997)
	11) High pollution likelihood.	London et al. (2000)

Type of source	**Examples**	**Reference**
	Atrazine	
Gardens and agricultural peri-urban areas	1) Identified in surface water samples (Johannesburg).	Grange et al. (2003)
	2) Measured residues in water and fish.	Bouwman et al. (2003)
	3) Between 0.1 and 11.6 µg L-1 of atrazine and related triazines, depending on the season, in northern and central part of S.A.	Du Preez et al. (2003)
	4) Regularly detected in surface and groundwaters of the Vaalharts Irrigation Scheme.	Weaver (1993)
	Deltamethrin	
Malaria mosquito control, gardens and agricultural peri-urban areas	1) Measured residues in surface waters in the Ubombo and Ingwavuma districts in KwaZulu-Natal.	Sereda and Meinhardt (2003)
	2) Detected in surface and groundwaters of Hex River Valley (Western Cape).	Solomons et al. (2003) London et al. (2000)
	3) 0 to 1.43 µg L-1 in water samples from Lourens river (Western Cape).	Dabrowski et al. (2002a)
	4) High usage in Hex River Valley (Western Cape).	Weaver (1993)
	Penconazole	
Gardens and agricultural peri-urban areas, vineyards	1) Detected in surface and groundwaters of Grabouw (Western Cape).	Solomons et al. (2003) London et al. (2000)
	2) Applied to grapevine (Western Cape).	London and Myers (1995 b)
	3) Detected in farm dams in Elgin (Western Cape).	Davies (1997)
	4) High usage in Hex River Valley (Western Cape).	Weaver (1993)

Type of source	Examples	Reference
	Simazine	
Gardens and agricultural peri-urban areas	1) Seventh most used pesticide in southern Africa in 1989. 2) High usage and pollution likelihood in the Western Cape.	London and Myers (1995a) London et al. (2000)
	3) High usage in the Hex River Valley (Western Cape).	Weaver (1993)
	4) Triazines most commonly used pesticide in South Africa	Naidoo and Buckley (2003)

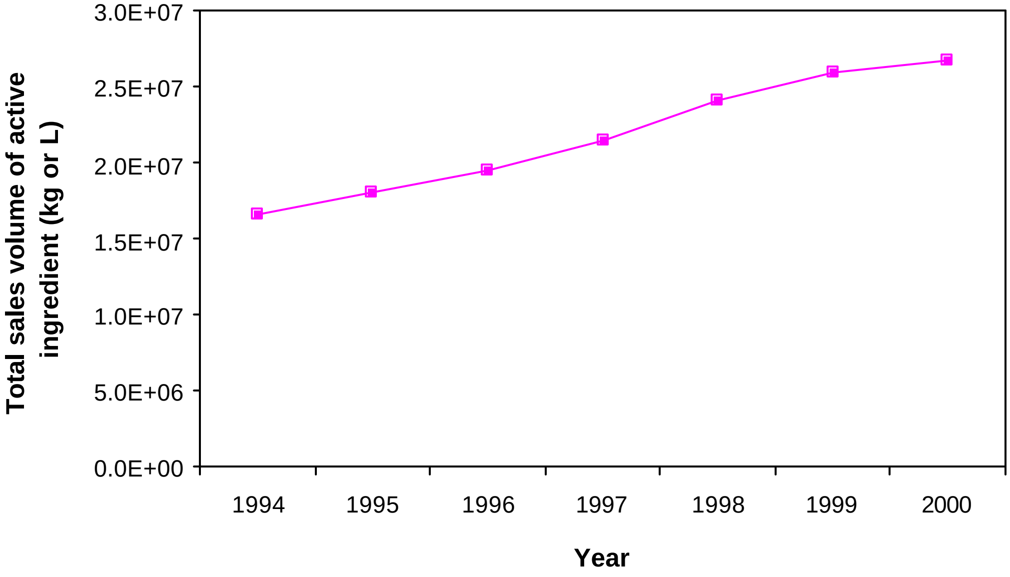


Figure 1.2 Total sales of pesticides from 1994 to 2000 (AVCASA, after Naidoo and Buckley, 2003)

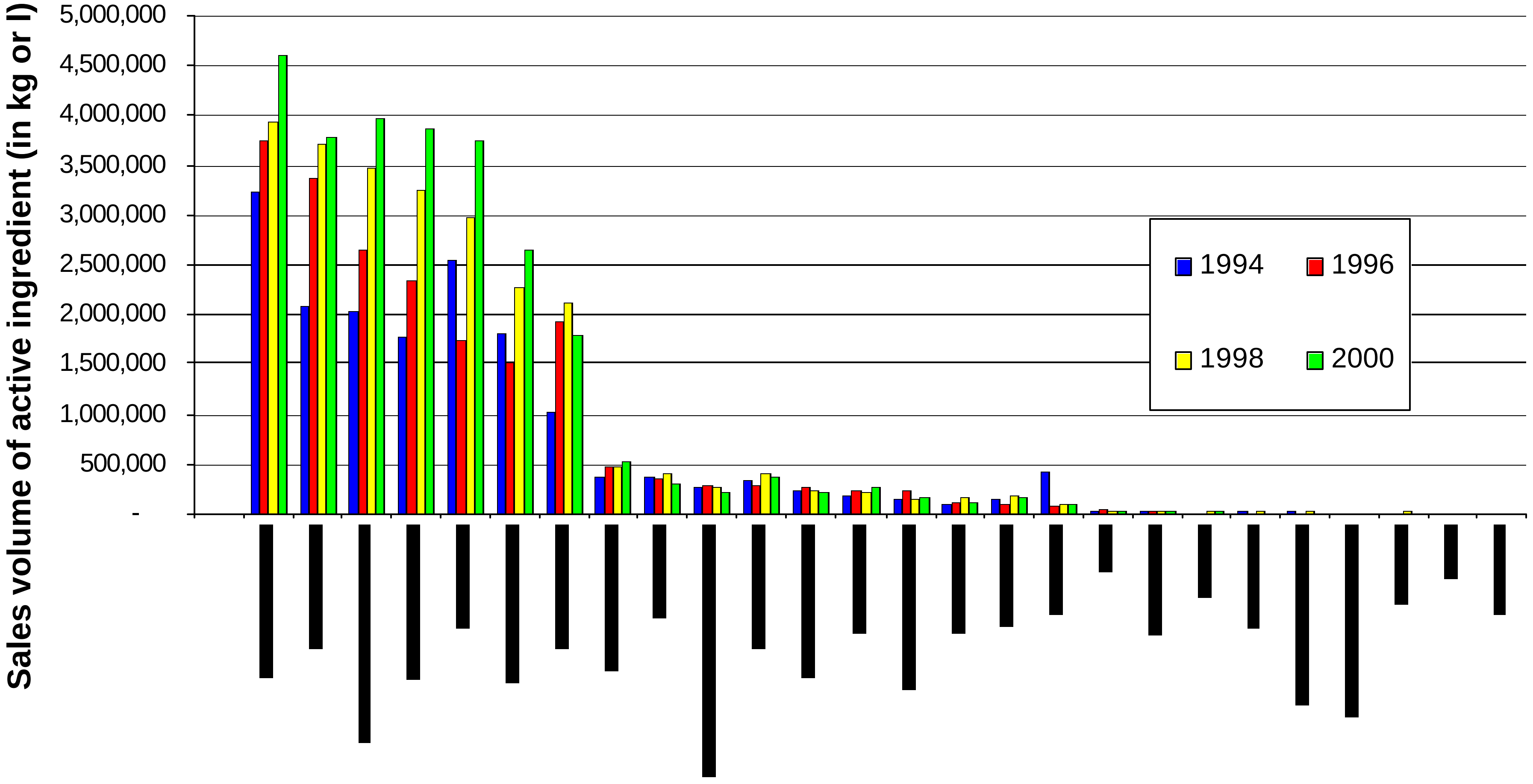


Figure 1.3 Sales for various groups of pesticides for 1994, 1996, 1998 and 2000 (AVCASA after Naidoo and Buckley, 2003).

The sales figures are generally in accordance with the identification of pesticides in the literature as key pesticides identified were also found to be characterised by high sales values. Deltamethrin and penconazole, however, were reported frequently in the literature, yet sales values reflect low usage. This could be due to the fact that some compounds may be dominant in localized areas where studies have been done and usage elsewhere may be minimal. For example the use of deltamethrin is concentrated in the Western Cape and KwaZulu-Natal, and penconazole is concentrated in the Western Cape. Alternatively, factors other than usage, for example pesticide properties, could be the reason why these pesticides have received research attention. According to the United States Environmental Protection Agency (US EPA) toxicity classification, deltamethrin is moderately toxic and small levels of usage may be hazardous. Penconazole however is 'unlikely to be hazardous' according to the World Health Organisation standards but little data is available for leaching potential. Pesticide properties are outlined in section 1.3.

As reflected by the sales figures, triazine herbicides are the most widely used class of pesticides. This is probably since the two most common examples, namely atrazine and simazine, are used extensively for maize, and orchards and vineyards, respectively. These crops form a particularly large portion of South Africa's agricultural market and their prevalence has also been confirmed by one of the primary chemical manufacturers, Makhteshim-Agan (personal communications, Jan van Graan).

It should be borne in mind that, besides volumes of compounds used, their specific effects on health and the environment need to be considered.

1.3 Determination of priority pesticides based on properties and site characteristics

In this section, the main factors that determine potential groundwater impacts are discussed. These primarily include pesticides properties related to toxicity, mobility (water solubility, sorption, etc) and degradation (half-life), and site characteristics (depth to groundwater, recharge rate, etc.). A comprehensive database was compiled for the review of pesticide properties (Appendix A3.1 and A3.2) and a summarised version for selected pesticides (identified in the literature as priority in SA) is given in Table 1.2. The full database contains type of usage, grouping/class, toxicity classification, molecular weight, density, boiling point, vapour pressure, soil half-life, hydrolysis half-life, water solubility, soil adsorption coefficient, organic carbon sorption coefficient and a description of mobility, based on properties and levels of leaching detected (Appendix A3). Only prominent properties are included in the summary, that is, toxicity, water solubility, vapour pressure, organic carbon sorption coefficient and soil half-life (Table 1.2). The use of a screening model for the prioritisation of pesticides, based on pesticide properties and site characteristics, is also discussed, however, toxicity effects are not included in the screening model. The importance of toxicity classifications is discussed separately and the reader is referred to the section on pesticide modelling for a discussion on mobility and degradation factors.

The major sources of information used in compiling the properties database include the Extension Toxicology Network, Pesticide Information Profiles (EXTOXNET PIPs, Online: http://www.ace.orst.edu/info/ extoxnet/ pips.htm), personal communication with Ingrid Dennis of the Institute for Groundwater Studies in Bloemfontein, the Spectrum Laboratory Chemical Fact Sheets (Online: http://www.speclab.com/search.html), and the Pesticide Action Network Databases of Chemicals (Online: http://data.pesticideinfo.org/Index.html). The toxicity categories are mainly from the US EPA classification for acute toxicity, unless otherwise indicated, as this was the dominant source of information. Other categories are from the World Health Organisation (WHO), United States National Toxicity Program (NTP) and the Pesticide Action Network Acute Toxicity Descriptions.

1.3.1 Prioritisation of pesticides using screening models and indices

Screening models and indices are often used as a preliminary evaluation of the relative potential for pesticides to leach under certain hydrogeological conditions. These methods are generally more simple and affordable than the use of more complex and highly deterministic models. One such method is DRASTIC (Aller et al., 1987), more simply the DAS index, which ranks different hydrogeological settings according to the relative vulnerability to groundwater contamination (Aharonson, 1987). The model is based on the following hydrogeological factors that are included in the acronym, that is, <u>d</u>epth to groundwater, <u>r</u>echarge of groundwater by precipitation and irrigation, <u>a</u>quifer media (sand and gravel, etc.), soil media (sandy loam, etc.), topography (slope), impact of the vadose zone, and hydraulic <u>c</u>onductivity of the aquifer. The parameters are weighted and scores are assigned for different hydrogeological environments. The model, however, does not adequately account for specific pesticide-related processes.

Table 1.2 Summary of important pesticide properties of the seven most common pesticides in South African literature (extract of database in Appendix A.3)

Pesticide	**Toxicity classification**	**Water solubility (mg/L)**	**Vapor pressure (mPa)**	**Koc* (mL/g)**	**Soil half-life (approx. days)**
Atrazine[1]	III – slight[3]	28 at 20 °C	0.04 at 20 °C	100	60 – 100
Azinphos-methyl[1]	I - high[3]	30 at 25 °C	<1 at 20 °C	1000	5 (sandy loam), 355 (sterile soil)
Chlorpyrifos[1]	II – moderate[3]	2 at 25 °C	2.5 at 25 °C	6070	60-120, or 14-365+
Deltamethrin[1]	II – moderate[3]	<0.1	2×10^{-12} at 25 °C	438[6]	7 - 14
Endosulfan[1]	I – high[3]	0.32 at 22 °C	1200	12400	< 9.1[5], ca. 50, 35 (Endos. a), 150 (Endos. b)
Penconazole[2]	IV – unlikely to be hazardous[4]	-	-	-	-
Simazine[1]	IV – practically non-toxic[3]	5 at 20 °C	8.1×10^{-4} at 20 °C	130	28 – 149, Ca. 60 (residual activity up to a year at high pH)

Note: The references for each pesticide is cited in the first column and additional sources are cited for individual values

* Organic carbon sorption coefficient

[1] Extension Toxicology Network (EXTOXNET), Pesticide Information Profiles (See: http: ace.orst.edu/info/extoxnet/pips.htm)

[2] Pesticide Action Network Databases - Chemicals, North America, 2000-003

[3] US EPA Acute Toxicity Classification: I – high, II – moderate, III – slight, IV - practically non-toxic

[4] WHO acute hazard ranking: Ia - extremely hazardous; Ib - highly hazardous; II - moderately hazardous; III - slightly hazardous; IV - unlikely to be hazardous

[5] Ingrid Dennis, Institute for Groundwater Studies, Bloemfontein, personal communication

[6] calculated from the equation (Weber et al., 2004): Koc = (Kd*100)/%OC

Rao et al. (1985) derived a simple ranking scheme by which a range of contaminants can be screened according to their relative potential to enter groundwater. The model employs retardation and attenuation indices for contaminants in particular environments, as an indication of relative leaching potential but is not suitable as a predictive tool. Instead, it is suggested that the method is more appropriately used for ranking a large number of contaminants. With regard to pesticide leaching, the retardation factor RF is an index determined by pesticide partitioning between the solid, vapor and liquid phases. The attenuation factor AF is an index for pesticide emission downward from the vadose (root) zone and is determined by pesticide travel times and degradation rates (McGregor, 1999).

The model assumes that degradation follows first-order kinetics and the mass of pesticide that reaches groundwater (M_1 in g, kg, etc.) is given as:

$$M_1 = M_0 \exp(-tr*K)$$

Where, M_0 is the mass of pesticide applied at the soil surface (in g, kg, etc.), tr is the travel time (days) in the vadose zone, and K is the first-order degradation rate coefficient (/day) in the vadose zone, given as:

$$K = 0.693/T_{1/2}$$

Where, $T_{1/2}$ - pesticide half-life in days

tr and K have been considered for both the soil and intermediate (vadose) zone, therefore tr is essentially given by the sum of travel times in both zones. Due to complexities, however, in the nature of solute transport processes in the vadose zone, tr is calculated based on steady flow conditions characteristic of the soil. Ideally K should also be determined for each zone, however due to a lack of methods and available data on degradation in the vadose zone, K is given by rate coefficients in the soil zone.

Furthermore, the portion of applied pesticide that leaches is given as:

$$AF = (M_1/M_0) = \exp(-0.693\ tr/T_{1/2})$$

Where, $0 < AF < 1$

And the total travel time (in days) is given by:

$$tr = (Z\ RF?_{FC}/q)$$

Where, Z is the depth to groundwater and q is the net recharge rate, calculated as the difference between annual evapotranspiration and rainfall plus irrigation. $?_{FC}$ is the volumetric soil-water content at field capacity (fraction).

RF is calculated as a function of $?_{FC}$, soil bulk density ($?_b$ in kg/m^3), soil organic carbon content (f_{OC}, fraction), air/gas content ($?_g$, fraction), pesticide sorption coefficient (K_{oc} in m^3/kg) and Henry's constant (K_h in atm.m^3/mol), with the following equation:

$$RF = [1 + (?_b f_{OC} K_{oc})/(?_{FC}) + (?_g K_h / ?_{FC})]$$

In this study, six priority pesticides identified in the literature were ranked for their relative leaching potential in the Western Cape, using the attenuation factor indices (Rao et al., 1985). Average soil conditions at the Bellville and Elgin sampling sites were used in the screening as typical conditions representative of the Western Cape (Table 1.3). The characterisation of these two soils can be found in Chapter 2. Air content, depth to groundwater and net recharge rate, however, were estimated for typical conditions. Penconazole was not included in the ranking, as insufficient data was available, particularly with respect to Henry's constant.

Table 1.3 Average soil properties of the Bellville sampling site in the Western Cape, used in the screening of pesticides

Soil Property	**Average values for two sample sites**
Field Capacity (FC)	0.24 (-)
Air Content (AC)	0.5 (-)
Bulk Density (BD)	1520 kg.m^{-3}
Depth to Groundwater (L)	2.0 m
Net Recharge Rate (q)	0.35 m.yr^{-1}
Organic Carbon Content (OC)	0.0075 (-)

RF and AF values were determined for the six pesticides and ranked from 1 to 6 (Table 1.5). Pesticide properties used in the calculations, can be found in Table 1.4. Penconazole was not included in the screening model as data on its properties were not available. An index of 1 indicates a high potential for leaching and is assigned to pesticides with the lowest RF and highest AF values. An index of 7 represents a low potential for contamination and corresponds with highest RF and lowest AF values. The AF value was used as the index for relative leaching potential and it has been recommended that RF values should only be used for this purpose if data on half-lives is lacking (McGregor, 1999).

According to the screening, AF indices and leaching potential are in decreasing order, for chlorpyrifos, atrazine, endosulfan, simazine, azinphos-methyl and deltamethrin. It is, however, important to note the limitations to this method in assessing priority pesticides. Firstly, it does not account for toxicity which also strongly determines whether a pesticide is hazardous or not. Secondly, RF and AF are not absolute values and the screening results can vary considerably depending on the particular study (study sites/condition, combination of pesticides selected for screening etc). This means that process modelling is not feasible and the outcomes are purely for purposes of preliminary assessment.

Table 1.4 Pesticide parameters used to calculate RF and AF indices for the ranking of pesticides

Pesticide	**K_{oc} (m^3kg^{-1})** [1]	**K_h (atm.m^3mol^{-1})**	**$T_{1/2}$ (days)**
Chlorpyrifos	6.07E+00	7.33E+03	90
Endosulfan	1.24E+01	2.87E+02	50
Azinphos-methyl	1.00E+00	3.26E+01	5
Atrazine	1.00E-01	3.45E+00	80
Deltamethrin	4.38E-01	3.10E-02	10
Simazine	1.30E-01	1.97E+00	60

[1] derived from values in Table 1.2

Table 1.5 RF and AF indices for ranking of pesticides according to leaching potential

Pesticide	**RF**	**RF Index**	**AF**	**AF Index**
Chlorpyrifos	6.82E-03	1	1.000E+00	1
Atrazine	3.64E-01	4	9.990E-01	2
Endosulfan	3.54E-01	3	9.984E-01	3
Simazine	7.40E-01	5	9.972E-01	4
Azinphos-methyl	2.64E-01	2	9.880E-01	5
Deltamethrin	2.77E+01	6	5.311E-01	6

1.3.2 Toxicity Classifications

Toxic contaminants threaten the normal functioning of aquatic ecosystems and the quality of drinking water. The potential health effects suffered by organisms, including human beings, can be acute from short-term exposure to high levels of chemical, or chronic from long-term exposure to low-levels of chemical. In general, the health effects associated with groundwater contamination are considered to be mainly chronic. Examples of chronic effects include benign or malignant tumours, mutations, reproductive and birth defects, immunological changes and endocrinological disruption (Weaver, 1993). Studies have been done in the USA to determine the causes of deaths due to cancer. It was found that even though the percentages of deaths associated with pollution are relatively low, the actual number of deaths is considerable (Gough, 1989 in Weaver, 1993). However, due to complexities in determining the causes, particularly with cancer, it is often difficult to quantify the chronic toxicity of pesticides.

Nevertheless, toxicity is an important aspect in the determination of priority pesticides and acute effects can be used qualitatively, as a precautionary guideline in this respect. Acute health effects are also a major concern in the case of farm workers directly involved in the handling and application of pesticides, associated with dermal and oral exposure to chemicals (London and Meyers, 1995b).

Various classification systems have been developed for toxicity, particularly in the USA. The classification mostly ascribed to in this study is the US EPA acute toxicity classification, outlined in Table 1.6. The categories I to IV (high, moderate, slight and practically non-toxic) are typically determined by the results of five acute toxicity studies performed with the product formulation, namely, acute oral, acute dermal, acute inhalation, primary eye irritation and primary skin irritation (EPA Label Review Manual, Online: http://www.epa.gov/oppfead1/labeling/lrm/chap-07.htm). The category that a pesticide is assigned to determines the appropriate precautionary labelling to be used by manufacturers. The signal words associated with toxicity categories are DANGER (category I), WARNING (category II) and CAUTION (category III), and none are required for category IV.

Other classification systems used in this study are the WHO acute hazard rankings, based on the lowest published oral LD_{50} values for rats. The WHO ranking also takes into account other toxic effects such as reproductive and developmental toxicity, but does not include fumigants and obsolete pesticides. The classification contains five categories of toxicity, namely, extremely hazardous (Ia), highly hazardous (Ib), moderately hazardous (II), slightly hazardous (III), and unlikely to be hazardous (IV).

The US NTP acute hazard categories include highly toxic, moderately toxic, slightly toxic and not acutely toxic and is based on the LD_{50} values for oral, dermal and inhalation exposure of a range of mammals (analogous to humans), according to US EPA guidelines (Pesticide Action Network pesticide databases). The PAN Acute Toxicity classification system is based on a summary of the WHO, NTP, US EPA Toxicity Release Inventory (TRI) categories and Material Safety Data Sheets (MSMS) and consist of the categories, extremely toxic, highly toxic, moderately toxic and slightly toxic. The categories reflect the most toxic ranking assigned by any of the organisations.

Table 1.6 US EPA Acute Toxicity Categories (after the US EPA Label Review Manual, Online: http://www.epa.gov/oppfead1/labeling/lrm/chap-07.htm)

	Category I	**Category II**	**Category III**	**Category IV**
Acute Oral (mg/kg)	= 50	50 - 500	500 - 5000	> 5000
Acute Dermal (mg/kg)	= 200	200 - 2000	2000 - 5000	> 5000
Acute Inhalation[1](mg/L)	= 0.05	0.05 - 0.5	0.5 - 2	> 2
Primary Eye Irritation	Corrosive (irreversible destruction of ocular tissue) or corneal involvement or irritation persisting for more than 21 days	Corneal involvement or other eye irritation clearing in 8-21 days	Corneal involvement or other eye irritation clearing in 7 days or less	Minimal effects clearing in less than 24 hrs
Primary Skin Irritation	Corrosive (tissue destruction into the dermis and/or scarring)	Severe irritation at 72 hrs (severe erythema or edema)	Moderate irritation at 72 hrs (moderate erythema)	Mild or slight irritation at 72 hrs (no irritation or slight erythema)

[1] 4 hr exposure

1.3.3 Pesticide selection

In the determination of priority pesticides for experimental analysis in this study, a selection was made based on the outcomes of the screening model and prevalence in the literature. According to the screening, chlorpyrifos, atrazine and endosulfan have the highest leaching potential (Table 1.5) and this is well reflected in the literature. Chlorpyrifos and endosulfan were the most frequently encountered pesticides in the literature and this is probably also because they are known to be moderately and highly toxic (US EPA classification), respectively (Table 1.1). Atrazine has also been well researched in the process of its classification as a 'restricted use pesticide' in the US. Although it is still widely used in South Africa for the cultivation of maize, atrazine is generally known to be 'slightly toxic', with moderate to high leaching potential (US EPA), and has been detected frequently in surface and ground waters (Grange et al.,2003; Bouwman et al., 2003; Du Preez et al. 2003; Weaver, 1993). According to manufacturers and government departments, much research is already underway for the restriction of atrazine-use in South Africa (personal communications, Makhteshim-Agan; National Department of Agriculture).

According to the screening model, simazine was found to be the next most likely pesticide to leach after endosulfan. Simazine is a widely used herbicide in South Africa, particularly in the Western Cape for orchards and vineyards, and falls under the class of triazines, which had the highest record of pesticide sales in South Africa form 1994 to 2000 (Fig 1.2). Despite the widespread use, however, simazine has received relatively little research attention in South Africa and this is probably due to the incorporation of international standards in local registration procedures and its classification in the US, as a 'practically non-toxic', 'general use pesticide' (EPA). However, since pesticide processes are highly sensitive to site conditions, the need for local studies to be carried out provided further motivation for selecting simazine. Additional cause for concern is that simazine has been detected, above target levels, in international groundwaters and is currently under review in the US. It was, therefore, selected as an example of a priority pesticide for further analysis in this study.

1.4 Modelling pesticide-related processes

In this section, the main pesticide processes occurring at field scale, have been reviewed from the literature, in terms of pesticide fate modelling. The focus on improving pesticide management in recent years has led to the development of a wide array of models. Boesten (1999) and Vanclooster et al. (2000a) have provided comprehensive reviews of models used worldwide and one of these reviews is presented in Table 1.7.

1.4.1 Transfer Processes

1.4.1.1 Runoff

Runoff is one of the most direct processes by which water resources are contaminated. Pesticides can be transported as both solutes or adsorbed on suspended particles (Rose and Ghadiri, 1992). Gouy et al. (1999) determined sorption isotherms, which were found to be highly variable with the pesticide species. The solute component of runoff can be calculated as a function of rainfall or irrigation and is generally assumed to be proportional to the pesticide concentration in the top centimetre of the soil (Cohen et al., 1995). Adsorbed sediments are associated with sediment transport processes (Johanson, 1983). Organic matter coating suspended soil particles can considerably increase the sorption of pesticides (Zhou et al., 1995).

Several models have been developed to predict runoff and most use the semi-empirical method based on the USDA SCS runoff curve (Ma et al., 1998). The GLEAMS model (Rekolainen et al., 2000) uses the USDA SCS curve number to estimate water runoff and the Universal Soil Loss Equation (USLE) (Wischmeier and Smith, 1978) to estimate sediment loss. The concentration of pesticide available to runoff (C_{av}) is given by:

$$C_{av} = C_w / B + C_s$$

Where, C_w - Concentration of pesticide in water
B - Extraction coefficient
C_s - Concentration of pesticide in soil

Table 1.7. Review of models currently in use and their main features (after Vanclooster et al., 2000a)

Model	**Features**					**Author**
	Water flow	**Solute transport**	**Preferential flow**	**Sorption**	**Volatilisation**	
CRACK-NP	Capacity	Convection	Yes	Linear	No	Armstrong et al. (2000)
GLEAMS	Capacity	Convection	No	Linear	No	Rekolainen et al. (2000)
LEACHP	Richards	Convection-dispersion	Yes	Freundlich	Yes	Hutson and Wagenet (1992); Dust et al. (2000)
MACRO	Richards	Convection-dispersion	Yes	Linear	No	Jarvis et al. (2000)
PELMO	Capacity	Convection	No	Freundlich	No	Klein et al. (2000)
PESTAN	-	Convection	-	-	-	Cohen et al. (1995)
PESTLA	Richards	Convection-dispersion	No	Freundlich	No	Boesten and Gottesburen (2000)
PESTRAS	Richards	Convection-dispersion	No	Freundlich	Yes	Freijer et al. (1996)
PLM	Capacity	Convection	Yes	Linear	No	Nicholls et al. (2000)
POLLUTE	-	-	-	-	-	Rose and Ghadiri (1992)
PRZM2	Capacity	Convection	No	Linear	No	Trevisan et al. (2000a)
SESOIL	-	-	-	-	-	Bonazountas (1983)
SIMULAT	Richards	Convection-dispersion	Yes	Freundlich	No	Aden and Diekkruger (2000)
VARLEACH	Capacity	Convection	No	Linear	No	Trevisan et al. (2000b)
WAVE	Richards	Convection-dispersion	Yes	Linear	No	Vanclooster et al. (2000b)

The extraction coefficient B is modelled as a function of the adsorption coefficient Kd, which varies from 0.1 to 0.5 (Rekolainen et al., 2000).

The removal of pesticide from a unit area of land (N) through transport on suspended, eroded soil particles can be described using a more empirical function (Yaron et al., 1996):

$$N = ER\ M\ C_s$$

Where, ER - g chemical g^{-1} soil eroded sediment / g chemical g^{-1} original soil

M - Accumulated mass of chemical per unit area (g chemical m^{-2})

1.4.1.2 Volatilisation

Volatilisation is the process where solutes move from the medium where they are dissolved into the atmosphere. It can occur from plant and soil, but this process is generally not well understood (Boesten, 1999). Volatilisation from the plant surface is most likely a function of saturated vapor pressure (Woodrow et al., 1997; Smit et al., 1998). Volatilisation from the soil can occur from the very thin surface film after spraying and before rainfall and/or irrigation, as well as, in the case of volatile pesticides, from the soil matrix via vapor fluxes (Boesten, 1999). The top soil layer from which volatilisation occurs is generally in the order of 5 mm (Jury et al., 1983; Hutson and Wagenet, 1992). Most losses in the field occur within one week after application and a simplified correction to the application rate can be made for the expected loss (Vanclooster et al., 2000a). Volatilisation models were reviewed by Vanclooster et al. (2000a) (Table 1.7).

LEACHP (Hutson and Wagenet, 1992) makes use of Henry's law to model volatilisation:

$$C_g = K_h C_w$$

Where, C_g - Concentration of pollutant in the gas phase

K_h - Henry's constant

Henry's constant is typical for a pesticide species. Chemicals with low Henry's constant are more prone to accumulate at the soil surface. This process can then be modelled as a function of the air-boundary layer thickness and water evaporation rate. Accumulation of pesticides at the soil surface can also increase photodecomposition and runoff into surface waters, as well as change adsorption coefficients in the top soil layer.

Volatilisation can be expressed in terms of flux (Hutson and Wagenet, 1992; Klein et al., 2000):

$$J_v - -D K_h C_w / d$$

Where, J_v - Volatilisation rate
D - Diffusion coefficient in air
d - Top soil layer from which volatilisation occurs

In LEACHP, the diffusion coefficient can be modified to account for changes in soil water content, barometric pressure and temperature that may cause air flow through soil (Scotter et al., 1967). More detailed models include losses by volatilisation in the convection-dispersion equation, which is used to describe solute fluxes in the soil profile (Hantush et al., 2000). Experimental data also showed that hourly time-step models are more accurate in the prediction of volatilisation, particularly during the first day after application (Van den Berg et al., 2003), and that aerodynamic resistance should be accounted for in modelling volatilisation from soil and plant surfaces (Wolters et al., 2003).

1.4.1.3 Adsorption/desorption

Adsorption is the adhesion of pesticide molecules to soil solid particles. This process influences the pesticide fluxes by retarding or enhancing pesticide migration.

Bonazountas (1983) proposed a very simple model for cation exchange:

$$S = CEC\ MWT / VAL$$

Where, S - Maximum mass of pesticide associated with solid
CEC - Cation exchange capacity
MWT - Molecular weight of pollutant
VAL - Valence of ion

As the largest component of pesticide adsorption is generally associated with organic matter, the equilibrium partitioning between soil water and solids can be simply written as (Bomberger et al., 1983):

$$C_s = K_{oc} f_{oc} C_w$$

Where, K_{oc} - Organic carbon partition coefficient

f_{oc} - Fraction of the soil solid phase that is organic

Besides these simplified methods, adsorption/desorption can be quantified with linear or non-linear sorption isotherms (Pepper et al., 1996). The linear isotherm used, for example, in LEACHP (Hutson and Wagenet, 1992) is given by:

$$S = K_d C_w$$

K_d can be calculated as (Dust et al., 2000):

$$K_d = K_{oc} f_{oc}$$

Non-linear (Freundlich) isotherms:

$$S = K_f C_w^n$$

Where ‘n’ is a power function related to the sorption mechanism and K_f is defined as the Freundlich isotherm.

Vanclooster et al. (2000a) reviewed models the use either linear or non-linear sorption (Table 1.7). Linear or non-linear sorption can be included in the convection-dispersion equation. Alternatively, selectivity coefficients could be used to determine adsorption/desorption, but this would require more inputs. The adsorption/desorption processes are generally assumed to be instantaneous. Their dependence on time can be modelled if the kinetic process is known, but this would also require more inputs. The effect of hysteresis on adsorption/desorption was also proven and should be taken into account (Leake and Gatzweiler, 1995).

1.4.1.4 Plant uptake

Uptake of pesticides by plants is generally modelled based on the water uptake and the concentration of pesticides in the soil solution to follow a linear model (Hutson and Wagenet, 1992; Klein et al., 2000):

$$J_{UP} = F_{UP} C_w T$$

Where, J_{UP} – Uptake flux

F_{UP} – Plant uptake factor

T – Transpiration flux

The WAVE model (Vanclooster et al., 2000b) provides a mechanistic calculation of transpiration as a function of potential transpiration, root density distribution and soil matrix potential. Exudation and retention by plants can also be modelled, but these processes are not deemed to have a major effect on the total balance.

1.4.1.5 Soil fluxes

Water and solutes

The first requirement for modelling pesticide transfer in the soil profile, is reliable prediction of water fluxes. The second requirement is accurate simulation of pesticide fluxes. Heat fluxes required to predict, for example, pesticide solubility and degradation are not deemed to be relevant due to the uncertainty of the impact (Vanclooster et al., 2000a).

Water redistribution in the soil profile can be modelled using tipping bucket (cascading) models based on soil-specific field capacity levels, or finite difference models based on the solution of Richards' continuity equation. Solute redistribution can be modelled assuming complete mixing, piston flow, convection or convection-dispersion. Vanclooster et al. (2000a) reviewed the different approaches models adopt in solving water and solute redistribution (Table 1.7). Similarly, Pepper et al. (1996) classified the modelling of pesticide transport and leaching into:

- Convection or mass transport (passive movement of chemicals through the soil with water)
- Convection-dispersion flow (movement by convection, dispersion due to variations in velocity through pores of different size, and diffusion governed by Fick's law based on differences in concentration gradients over limited distances)

The state-of-the-art approach for simulating water and solute fluxes in soils makes use of a finite difference solution to Richards' continuity equation. For example, Pang and Letey (1999) developed a pesticide transport model in the convection-dispersion equation for solutes to predict pesticide movement through soils and leaching, accounting at the same time for adsorption and biochemical decay of the pesticide:

$$\partial C_P/\partial t = D_R\, \partial^2 C_P/\partial z^2 - V_R\, \partial Cp/\partial z - \mu C_P$$

Where, C_P - Pesticide concentration
RF - Retardation factor
µ - First-order decay rate constant of pesticide
z – Distance

t - Time

$D_R = D_P/R$

$\mu = \ln(2) / T_{1/2}$

Where, D_P – Combined diffusion and hydrodynamic dispersion coefficient
$T_{1/2}$ – Half-life of pesticide
R - Gas constant

$V_R = ?/RF$

$RF = 1 + ?_b K_d / ?$

Where, ? - Pore water velocity
$?_b$ – Soil bulk density
? - Volumetric soil water content
K_d – Distribution coefficient equal to the slope of linear adsorption isotherm

In their work, Pang and Letey (1999) also investigated the effect of different factors (nitrogen applications, irrigation management and soil salinity) on pesticide transport and leaching. The model was expanded by Hantush et al. (2000) by replacing D_R with the effective liquid phase diffusion coefficient and μ with the effective first-order loss rate coefficient to account for volatilisation and crop uptake.

The convection-dispersion approach has a more scientifically sound background, but it requires more inputs compared to the convection approach, in particular if processes like volatilisation, crop uptake and biochemical decay are solved simultaneously. In addition, models are required to have a sound theoretical basis of both water fluxes and pesticide processes. This can be achieved by coupling water balance and pesticide models in order to improve the overall prediction accuracy of the system. An example of coupling between the PEARL pesticide model and the SWAP hydrologic model can be found on:
www.alterra-research.nl/pls/portal30/docs/folder/pearl/pearl/pdf/pearlthe.pdf.

Leaching

Along with runoff, leaching is the most direct process involved in the contamination of water resources. Therefore, water and solute fluxes in the soil profile need to be accurately described in order to accurately predict leaching. Leaching is the amount of pesticide dissolved in the solution percolating through the bottom of the active root zone.

Preferential flow

Preferential (macropore or by-pass) flow needs to be simulated in the presence of cracking soils, but this process is generally not well understood (Boesten, 1999). Vanclooster et al. (2000a) reviewed models accounting for preferential flow (Table 1.7).

CRACK-NP is a pesticide model used to predict leaching in cracking clay soils (Armstrong et al., 2000). Mass transport of solute (pesticides) is calculated from the amount of water flowing in the cracks between the layers and the solute concentration of the crack water in each layer. Solute diffusion between crack water and aggregate water is simulated. The shortcoming is that CRACK-NP can only be used in clay soils where the dominant water flow is through cracks and fissures as it assumes that water flow in soil matrix aggregates is negligible.

On the other hand, modelling preferential flow by using the mobile/immobile approach for water and solute flow in soils is becoming more and more popular (Cote et al., 1999). For example, PLM simulates preferential flow of water and pesticides by establishing a mobile and immobile category of soil solution, where the mobile category represents the macropores in structured soils (Nicholls et al., 2000). The mobile category is also divided into “slow” and “fast”, where preferential flow occurs only when rainfall or irrigation intensity is so high to replenish the “fast” mobile phase. The model can then be used to predict preferential flow if the percentage of “fast” pores in the mobile phase is calibrated (input data). Caution should be exercised in the use of this empirical method because the percentage of “fast” pores changes with location and time.

Hantush et al. (2000) described a model combining the mobile/immobile phases with the convection-dispersion equation. SWAP employs the clay shrinkage characteristic, based on the relationship between the void ratio and the moisture ratio, for the simulation of soil crack formation and water and solute transport in the mobile and immobile phases (Huygen et al., 2000).

Besides the lack of understanding of preferential flow processes, models were also not sufficiently validated. The number of specific cases is too large and there is, therefore, a need to develop and adapt existing models for preferential flow processes.

Intermediate (vadose) zone

The intermediate (vadose) zone is increasingly becoming the topic of research investigating groundwater impact and vulnerability to contaminants. The rate of pesticide transfer and transformation in sub-soils is often unknown and difficult to establish (Vanclooster et al., 2000a). It is different from the root zone because of lack of organic matter, different temperatures, microbial activity, water content, texture and structure. Despite this, the principles of pesticide transfer in the intermediate zone, including preferential flow, are similar to those applied in the root zone (Hantush et al., 2000). There is need to expand the description of water and pesticide fluxes from the root zone to the intermediate zone.

Alternatively, models developed for vulnerability assessment of groundwater impact could be adapted and used in combination with soil water and solute flux models. The most commonly used model for this purpose is DRASTIC (Aller et al., 1987) as discussed earlier under ‘screening models and indices to rank priority pesticides’. Although DRASTIC is a powerful tool when applied at large scale, it does not describe specific pesticide-related processes. Alternatively, attenuation factor (AF) and retardation factor (RF) indices (Rao et al., 1985) may be used for pesticide-groundwater vulnerability assessments. The equations are explained in the previous section on ‘screening models and indices to rank priority pesticides’, and are as follows:

$$AF = (M_1/M_0) = \exp(-0.693\ tr/T_{1/2})$$
$$RF = [1 + (?_b\ f_{OC}\ K_{oc})/(?_{FC}) + (?_g\ K_h / ?_{FC})] \qquad \text{Eq. 4}$$

Where, M_1 – Mass of pesticide entering groundwater
M_0 – Mass of pesticide applied to the soil surface
$?_{FC}$ – Volumetric water content at field capacity
q – Net recharge rate
$?_g$ – Gas/air content

A leaching potential index (LPI) can also be used by inverting the exponential argument of AF (Meeks and Dean, 1990):

$$LPI = 1000\ T_{1/2}\ V / (0.693\ RF\ Z)$$

Where, V – Soil water velocity
Z – Depth to water table

Schlosser and McCray (2002) did a sensitivity analysis using LPI and concluded that organic carbon content, depth to groundwater and soil water velocity are the main factors affecting pesticide leaching, whilst the effect of bulk density and soil water content is less pronounced. Major factors are also the organic carbon partition coefficient and pesticide half-life. These are, however, dependent on pesticide type, site and environmental conditions.

The effects of pesticide leaching on the catchment can be simulated by combining soil water and solute flux models extended to the intermediate vadose zone with groundwater models, like for example MODFLOW (McDonald and Harbaugh, 1988). Tiktak et al. (2002a) coupled the PEARL pesticide leaching model to GIS in order to investigate the leaching potential of pesticides both into local surface waters and the regional groundwater. Tiktak et al. (2002b) also suggested a five-step procedure to upscale field models to catchment level. These steps include: (i) model selection and development, (ii) application of the field-scale model, (iii) scale transfer, (iv) application of the regional scale model, and (v) analysis of results.

1.4.2 Transformation processes

1.4.2.1 Chemical degradation

The factors controlling the degradation of pesticides are not always well understood (Boesten, 1999) as degradation is a complex process and is not an inherent property of the pesticide. It is dependent on soil properties, weather conditions and properties of pesticide (reactivity, solubility, age etc.). Aden and Diekkruger (2000) suggested several approaches to describe pesticide degradation in the SIMULAT model (O'Neill optimum curve, Michaelis-Menten kinetic, metabolic or co-metabolic degradation).

Chemical degradation and decomposition due to microbial activity and light (photodecomposition) are often expressed simultaneously by first order kinetics (Jury and Masoud, 1989; Cohen et al., 1995):

$$C_{t2} = C_{t1} \exp [-K (t_2 - t_1)]$$

Where, C_{t2} – Concentration at time t_2
C_{t1} – Concentration at time t_1
K – Degradation rate constant

Simple exponential decay can also be described in terms of field half-life $T_{1/2}$, generally expressed in days:

$$T_{1/2} = \ln(2)/K$$

The ideal pesticide and environmental conditions will induce enough activity for the pesticide to have the desired effect on pests, but short enough attenuation or persistence to limit entry into groundwater. In many instances, adsorption/desorption processes are simultaneously included with degradation to estimate leaching. For example, Cohen et al. (1995) used the following equation to estimate leaching:

$$AF = \exp(-B) = M_2/M_0$$

Where, AF – Pesticide decay

M_2 – Mass lost below the root zone

M_0 – Amount of pesticide applied to the soil surface

$$B = K(tr)$$

Where, tr – Pesticide travel in the vadose zone

$$tr = Z\ RF\ ?_{FC} / q$$

Where, RF – Retardation factor $(1 + ?_b + K_d / ?)$

Gustafson (1989) suggested the GUS (Groundwater Ubiquity Score) screening index as a function of half-life ($T_{1/2}$) and the partitioning coefficient between the soil organic carbon content and the soil solution (K_{oc}):

$$GUS = \log(T_{1/2}) * [4 - \log(K_{oc})]$$

Empirical equations of the following form can also be derived for specific sites and conditions:

Potential leaching depth = a + b * %C + c * pH of the soil
Potential leaching depth = a + b * %C + c * rainfall/irrigation

1.4.2.2 Microbial degradation

The half-life of pesticides will depend on microbial activity, determined by temperature and soil moisture. It is therefore very important to indicate the soil conditions under which biochemical degradation occurs. Similarly, pesticide transformation in groundwater depends on the biogeochemical conditions. Leistra and Smelt (2001) indicated possible approaches to quantifying transformation processes in groundwater. The microbiological activity can be predicted using base, optimal and maximum temperatures (Monteith, 1977), which will induce a temperature -degradation rate response function. The effect of soil water content on pesticides degradation can be modelled with a similar response function (Vanclooster et al., 2000a).

The soil temperature can be described as a function of air temperature (Campbell and Norman, 1998). The response of degradation to temperature can be modelled using the Arrhenius function (Aden and Diekkruger, 2000):

$$K(T) = K_0 \exp (E_a / RT)$$

Where, T – Actual ambient temperature
E_a - Activation energy
K_0 – Baseline degradation rate
R - Gas constant

Jarvis (1994) expressed the effect of soil temperature on degradation through a factor, F_T:

$$F_T = \exp[a(T - T_{ref})]$$

Where, T_{ref} – Reference soil temperature
a - Degradation rate coefficient

The influence of soil moisture can be calculated using an empirical factor b, with:

$$F_W = (? / ?_b)^b$$

Where, $?_b$ – Boundary volume fraction of water

Actual volumetric soil water content is calculated from the water balance.

LEACHM (Hutson and Wagenet, 1992) uses first-order transformation and degradation rate constants, which can be corrected for water content and temperature.

1.4.2.3 Photodecomposition

Photodecomposition is a photochemical reaction due to absorption of electromagnetic energy by a pollutant. It occurs at the plant and soil surface exposed to sunlight, before the first rainfall/irrigation event for many pesticides (Walker, 1974), and there is evidence that it can contribute considerably to the pesticide balance (Bavcon, 2003). Similar to volatilisation however, there are difficulties in micro-measurements at the soil surface, and the process has not been adequately studied. Both photodecomposition and volatilisation can be reduced or eliminated by shallow incorporation of the pesticide applied into the soil (Bromilow et al., 1999).

1.5 Conclusions and Recommendations

In the literature review for identification of priority pesticides, chlorpyrifos, endosulfan, azinphos-methyl, atrazine, simazine, deltamethrin, and penconazole, were most frequently encountered. This was used as an indication of contamination of water resources. The data were in accordance with the pesticide sales records from AVCASA. Those pesticides that are widely researched are generally also found to be widely sold on the South African market. Therefore, the literature findings are considered to be a good indication of pesticide usage and contamination. Another outcome of the literature review is the comprehensive database of pesticide properties which may serve as a reference source for future research. It contains key properties, which can be used in risk assessments of pesticides used in South Africa.

The use of a simple screening model (Rao et al., 1985) proved to be a useful tool in this study, for determining priority pesticides according to pesticide properties and site characteristics. The model enabled pesticides identified in the literature, to be ranked according to their leaching potential on the basis of pesticide properties, and soil and hydrogeological conditions.

Simazine was selected as the priority pesticide in this study based on leaching potential and widespread usage (sales) for orchards and vineyards in South Africa (particularly the W. Cape) and the fact that not much research has been done under local conditions, despite its widespread use.

Based on the literature review on pesticide-related processes, the following conclusions were drawn, knowledge gaps identified and recommendations made:

In terms of transfer processes, pesticide runoff is, generally, modelled to occur from the top centimetre of the soil and to be adsorbed on solid mineral and organic particles. Most models use the semi-empirical USDA SCS runoff curve number method to estimate dissolved pesticides and sorption isotherms to determine adsorbed pesticides. There is therefore a need to introduce a more mechanistic approach based on rainfall intensity, to accurately predict pesticide runoff. Runoff should be modelled in conjunction with sediment transport, as a portion of the transported pesticides is adsorbed onto solid particles of minerals and/or organic matter.

Volatilisation from plant and soil surface can be modelled using Henry's constant, which is specific for the pesticide species. At present, the process of volatilisation is more theoretically understood and modelling requires validation in field trials. It can be associated with losses of pesticide during spraying and, as volatilisation mainly occurs from the soil surface where pesticides accumulate, this process can also be linked to sediment transport.

Sorption of pesticides is modelled depending on pesticide species and soil properties, where the organic component is generally dominant compared to the mineral fraction. The fraction of pesticides adsorbed on soil solid particles is modelled using linear or non-linear (Freundlich) isotherms. The key parameter in this process is the sorption coefficient. This is specific to the pesticide species and needs to be determined experimentally. Pesticide sorption (as well as plant uptake and preferential flow) can be associated with sorption of nutrients (nitrogen, phosphorus) and heavy metals.

Plant uptake of pesticides is modelled as a function of water uptake and concentration of pesticide in the soil solution. In order to model plant uptake of pesticides, an accurate plant water uptake subroutine is essential and this is often neglected in pesticide leaching models.

Water redistribution in the soil profile can be modelled using tipping bucket (cascading) models based on soil-specific field capacity levels, or finite difference models based on the solution of Richards' continuity equation. Solute redistribution in the soil profile and leaching can be modelled using the complete mixing, piston flow, convection or convection-dispersion approaches. These approaches, however, require more validation work. In some instances, detailed laboratory measurements need to be extrapolated to field conditions.

Lastly, preferential (macropore or by-pass) flow can be modelled by differentiating between mobile and immobile phases. However, this process is not fully understood and validated and there is a need to develop and adapt existing models for use. There is also a need to adapt existing models to simulate fluxes and processes occurring in the intermediate vadose zone, in order to allow for extrapolation from field to catchment scale.

In terms of transformation processes, chemical degradation is, generally, modelled as a function of pesticide half-life using first-order kinetics. Microbial degradation is largely determined by soil water content and temperature, and photodecomposition can be modelled as a function of incoming solar energy and concentrations of pesticides on plant and soil surfaces. Photodecomposition, however, is only theoretically understood and needs to be validated in field trials, as there is evidence that it can contribute considerably to the pesticide balance.

In general, state-of-the-art models use the convection-dispersion equation to simulate water and pesticide fluxes in the soil profile as well as the mobile/immobile phase to account for preferential flow. This is coupled to sorption and decay of chemicals depending on temperature and soil moisture. Most validation exercises found in the literature are related to short-term experiments (Diekkruger et al., 1995). In developing models for groundwater and catchment management, however, model validation needs to be done for a number of years. Alternatively, mechanistic models validated over the short term could be used to run scenario simulations. Spatial variability and preferential flow should be taken into account under certain conditions, particularly depending on the soil type and research needs (Bergstrom and Jarvis, 1994). Vanclooster et al. (2000a) recommended that simulations be made for worst, average and best case scenarios, in order to overcome uncertainties.

In order to improve regional pesticide management, on-farm management tools need to be refined. It is important that groundwater models include processes occurring in the soil profile and intermediate vadose zone in estimating impacts of management practices on the catchment.

CHAPTER 2

Soil Properties of Selected Sampling Sites

2.1 Introduction

In order to understand the complex nature of pesticide behaviour and fate in soils, it is necessary to know the soil conditions that impact on solute mobility and degradation within the soil profile. Important pesticide chemical processes that affect leaching are volatilisation, sorption and microbial degradation. The most pertinent of such processes are adsorption of molecules onto soil colloids and microbial breakdown. Pesticide mobility is also largely determined by soil water balances and properties. Furthermore, soil properties are usually required as input in predictive models, as in the case of VLEACH and SWAP (Chapters 4 and 5).

pH, electrical conductivity (EC) and cation exchange capacity (CEC) all determine the nature and strength of ionic charges present in the soil and therefore drive most pesticide chemical reactions. CEC can be used as a measure of available sorption sites and, conversely, dissolved salts measured through EC can impede adsorption by competing for sorptive sites in the soil. The presence of certain ions can also impact adversely on soil structure, as in the case of sodium ions. High sodium and/or low calcium and magnesium ion concentrations present in clay soils can cause dispersion of soil aggregates and crusting of the surface. The result would be a reduction in hydraulic conductivity and infiltration, and increased surface runoff of contaminants. Nevertheless, most pesticides, including simazine, are often hydrophobic, have weak charges and are mostly attracted to the organic components of the soil, which have slightly negative charges. Pesticide sorption is therefore greatly determined by the organic matter content (OM) of soils. Furthermore, organic matter improves pore structure, thereby enhancing water retention and the residence time of pesticides in the soil for adsorption (McBride, 1994).

Organic contaminants are transported mainly by convection and soil-water retention properties, determined strongly by texture and pore-size distribution. Furthermore, retardation of pesticide mobility is favoured by soils that retain moisture well, by enabling a greater contact time for sorption onto soil surfaces. Microbial degradation is also favoured by increased residence-time of contaminants in the root zone. Water retention curves, plotting volumetric water content against matrix potential (applied suction force), are generally used to determine hydraulic conductivity, the nature of water fluxes, infiltration, and swelling and shrinking in the case of clay soils (Carter, 1993). Particle size distribution affects water retention in terms of pore-spaces and surface area. This can be clearly seen in the case of sandy soils that have greater hydraulic conductivity than clay soils when saturated, but lose conductivity faster when unsaturated. More simply, when a suction is applied, sandy soils will lose water faster due to larger pore spaces, whereas moisture loss from clay soils is more gradual owing to the effect of a larger surface area for water molecules to adsorb to (Rowell, 1994).

In certain cases, however, texture can impact adversely on water retention. For example, the presence of clays (or layers formed by sand and clay) can impede infiltration. Swelling and shrinking of clay soils, and surface crusting when impacted by raindrops and/or high sodium content, can also impede infiltration. In this way, low permeability can lead to enhanced transport of solutes via surface runoff. Conversely, cracks and macro-pores often present in clays can cause large amounts of contaminated water to infiltrate the soil, leading to unexpectedly higher levels of leaching (Rowell, 1994). Nevertheless, clay-rich soils generally provide a greater surface area for sorption, thereby retarding pesticide mobility (Sililo et al., 1999). Clay minerals and organic components of the soil usually carry negative charges and simazine, being a weakly basic molecule, is known to adsorb onto these surfaces (Taya and Ashtamkar, 2000).

The objectives of this section include the analysis of key chemical and hydraulic properties of two South African soils, so that they can be used as input in a modelling exercise with VLEACH and SWAP, as outlined in Chapters 4 and 5. Sampling sites, located in Bellville (soil A) and Elgin (soil B), were selected on the basis of differences in land-use, for the sake of comparison (Table 2.1). The UWC soil can be described as a non-farming, light grey sandy soil, while the Elgin soil is reddish brown and originates in a farming region. One may therefore expect soil B to contain more clay and organic matter, and have better moisture retention capabilities, than soil A.

This chapter includes a description of the methods used in the sample collection, preparation and analysis. The soil properties included in the analysis are pH, EC, CEC, OM, texture, and water retention curves. Results are summarised in the form of a comparison between the two Western Cape soils and discussed in terms of the potential impacts on simazine transport. Of the important pesticide-related processes, the discussion on chemical properties focuses mainly on sorption, and not on volatilisation and degradation. Impacts of soils on degradation is not emphasised as it can be a complex process, often requiring lengthy bio-experiments, which is outside the scope of this study. Volatilisation is also not expected to be considerable for simazine, which has a low vapour pressure of 0.000810 mPa at 20 °C (EXTOXNET PIPs). Details of methods used and data collected can be found in Appendix B.

Table 2.1 Characteristics of the two Western Cape sampling sites selected for the study

Sampling site	**A**	**B**
Location	UWC, Bellville	Elgin
Depth (cm)	0 - 10	0 - 10
Land-use	Uncultivated	Uncultivated
Vegetation	Patchy grasses	Patchy grasses
Soil colour	Light grey	Reddish brown

2.2 Materials and Methods

2.2.1 Soil sampling

Disturbed samples were collected from the top 10cm soil layer at each site, as pesticides are generally applied to the soil surface and are mostly found in this layer. Both sites were sampled in the same manner, with four samples weighing approximately 1kg collected at each site and placed in plastic bags for transport to the laboratory. Prior to storage at room temperature, soil aggregates were gently loosened and separated from visible gravel, stone and plant material, and air-dried overnight.

2.2.2 pH and electrical conductivity

The method involved an equilibration of 1:2.5 soil solutions containing water and 0.01M $CaCl_2$, separately. Electrical conductivity of the solutions was measured using an EC-meter to give an indication of the total dissolved ions in the soil solution. pH was measured with a pH-meter for the standard water and saline solutions and the difference was calculated to determine the total charge of the soil (McBride, 1994; Rowell 1994).

2.2.3 Organic matter content

The organic content of the soil was determined by loss-on-ignition. Weight losses of the samples were measured after organic material was oxidised in a furnace at approximately 900 °C for 2 days. It should be noted that the Bellville soil is likely to contain free lime and could cause the organic matter content to be slightly over estimated.

2.2.4 Exchangeable cations and CEC

The method involved the use of an extraction agent containing an "exchange cation" to displace cations present in the soil. The neutral salt solution, ammonium acetate, was used as the extraction agent, which is a standard method used for soil testing, especially in the United States. Exchangeable ions in the extract were identified and measured with a spectrophotometer. Sodium acetate was also used in the determination of total cation exchange capacity (Soil Analysis Handbook of Reference Methods, Soil and Plant Analysis Council Inc, 1999; Rowell, 1994).

2.2.5 Particle size distribution

A standard method was used for the particle size analysis, involving sieving and then sedimentation using the pipette sampling technique (Rowell, 1994). The Soil Textural Classification, of the US Department of Agriculture, was used as the reference for grain size limits.

2.2.6 Water retention

The method involved the use of a sand/kaolin box with hanging water column and regulated vacuum to control the matrix potential and extraction of water from sample cores (Carter, 1993). As the original samples were disturbed, sample cores were reconstructed in the laboratory to resemble the field bulk density. The saturated soil cores were brought into hydraulic contact with the saturated medium (a very fine sand and kaolin clay) and the matrix potential (suction) was increased to a selected value. Time was given to allow water to flow in response to the new matrix potential, until equilibration, and the soil water content was measured. The above process was repeated for each successive matrix potential (kPa) selected and water-retention curves were plotted using the measured volumetric water content (m/m) of the soil at each potential (Carter, 1993).

2.3 Results and discussion

A summary of the soil properties can be found in Table 2.2.

Table 2.2 Summary of mean soil properties for sites A and B with standard deviations given in parentheses

Soil properties	**Site A**	**Site B**
pH_w	7.2 (0.3)	7.5 (0.1)
pH_{CaCl2}	6.9 (0.2)	7.1 (0.1)
? pH	-0.3	-0.4
EC_w ($\mu S.cm^{-1}$)	142 (0.1)	117 (0.1)
[Ca^{2+}] ($cmol.kg^{-1}$)	0.42 (0.2)	0.46 (0.2)
[Mg^{2+}] ($cmol.kg^{-1}$)	1.15 (0.2)	1.33 (0.2)
[K^+] ($cmol.kg^{-1}$)	0.12 (0.1)	0.10 (0.1)
[Na^+] ($cmol.kg^{-1}$)	0.24 (0.2)	0.22 (0.2)
CEC ($cmol.kg^{-1}$)	1.93 (0.7)	2.12 (0.8)
% organic carbon	1.05 (0.8)	0.45 (0.2)
% sand	92.8 (13.4)	82.8 (6.8)
% silt	6.0 (4.6)	15.6 (6.4)
% clay	1.20 (1.5)	1.6 (1.3)
Dry bulk density ($g.cm^{-3}$)	1.62 (0.02)	1.42 (0.09)
Porosity (ratio)	0.39 (0.01)	0.42 (0.02)

? pH = pH $CaCl_2$ – pH H_2O

2.3.1 Effects of acidity on sorption

The change in pH that occurred when a salt was added indicates that both soils have a slight tendency to be negatively charged (Rowell, 1994). Sorption of basic molecules, such as simazine, to soil colloids has been shown to increase in acidic soils. The availability of hydrogen ions enables protonation of the basic molecule to form a conjugate acid, which is then expected to adsorb strongly onto the negative surfaces of soil particles and organic matter (McBride, 1994). Furthermore, sorption has been identified as occurring due to either strong chemisorptive forces, as described for the conjugate acid or by weaker physical forces. The latter may occur due to polar functional groups that enable attraction to soil surfaces by hydrogen bonding and ion-dipole attraction. In this manner, simazine is expected to also adsorb weakly by physical forces, however this interaction is not pH-dependent.

In negatively charged soils, chemisorption will dominate and organic bases will be adsorbed at an optimum pH that is generally close to the pH at which dissociation of the conjugate acid occurs. For most bases, this occurs below the soil pH and simazine is expected to be less mobile in acidic soils. In more neutral soils, sorption will occur mainly due to weaker physical forces as mentioned above (McBride, 1994).

2.3.2 Effects of salinity and exchangeable cations on soil structure and sorption

The EC measurements for both sites (A: 142, B: 117 µS cm^{-1}) indicate non-saline conditions, when considered in relation to the effect on plants. Carter (1993) states that an EC between 0 and 200 µS cm^{-1} at 25 °C is considered to have negligible effects. The measurement of total dissolved salts is most important in the context of plant growth, however salinity can also increase the osmotic potential between water and soil surfaces, despite the absence of a semi-permeable membrane and water retention may, thus, be enhanced (McBride, 1994).

To determine the potential dispersive effects of salinity on soil structure, the Sodium Adsorption Ratio (SAR) was determined. The SAR is an index for sodicity that indicates the presence of highly soluble Na^+ cations relative to less soluble Ca^{2+} and Mg^{2+} cations in solution. As ion activities often differ from their absolute concentrations, the Exchangeable Sodium Percentage (ESP) was calculated as a measure of the proportion of exchangeable sodium ions (Na^+_{exch} relative to the total cation-exchange capacity). The equations for SAR and ESP are taken from Carter (1993) and the cation concentrations and exchange capacities from Table 2.2. were used in the calculations:

$$SAR = [Na^+] / [Ca^{2+} + Mg^{2+}]^{0.5} \qquad \text{Eq.1}$$

$$ESP = [Na^+_{exch}] / CEC \times 100 \% \qquad \text{Eq.2}$$

The outcomes indicate that both soils are not sodic as SAR values (A: 0.97, B: 0.90) are well below 13 and ESP values (A: 12%, B: 10%) are below 15%, which are considered to be the critical values for sodic soils (Carter, 1993). It was concluded that neither of the soils are sodic or highly saline and dispersion of the soil structure is not likely to occur.

Soil A has a slightly higher concentration of dissolved salts (EC) and lower total cation exchange capacity (CEC for A: 1.93 cmol.kg^{-1}, B: 2.12 cmol.kg^{-1}) than soil B (Table 2.2). The higher EC value for soil A could enhance water retention by increasing the osmotic potential of the soil, thereby increasing the contact-time for adsorption. The impacts of osmotic potential on sorption activity, however, are not well documented and osmotic potential is not considered to play a major role in this study. CEC involves a process occurring at soil particle surfaces and is therefore dependent on the particle size distribution. A lower CEC at site A can be attributed to the higher sand content and hence, smaller effective surface area for cation exchange (Table 2.2.). The difference in CEC's thus implies that sorption involving cation exchange may be greater at soil B where there are also fewer dissolved salts present to compete with organic cations for sorption sites. Soil B is therefore expected to impede simazine mobility slightly more than soil A on the basis of its affinity for cation exchange.

2.3.3 Organic matter content and sorption

Both soils have a relatively low percentage of organic carbon content (A: 1.05 %, B: 0.45 %) and this is expected to reduce the soil's ability to immobilise simazine in the soil profile. As simazine is a weak base, it may be useful to consider the sorptive mechanisms of basic chemicals in conjunction with more neutral chemicals. In addition to the weaker forces of hydrogen bonding and ion-dipole attraction to negative soil surfaces, most organics and in particular non-polar, non-ionic organics are, generally, more strongly attracted to organic components of the soil than to mineral elements. This is largely due to a physical hydrophobic attraction where large organic molecules in water often have a greater affinity for organic matter than for water (the solvent). This relationship between hydrophobic sorption and organic matter content is often described with a linear isotherm (Sililo, 1999). Simazine has a low water solubility (6.2 – 7 ppm @ 25 °C) and hydrophobic attraction could normally play a major role in simazine sorption, especially since it is known to be sorbed to organic matter and clay (Taya and Ashtamkar, 2000). However, the low organic content of both soils is not expected to impact considerably on sorption.

2.3.4 Texture and sorption

Using the USDA classification of soil texture, soil A was found to be sand and soil B, loamy sand. The relationship between soil organic matter content and hydrophobic sorption is strongly dependent on the surface area available for organic coatings. Therefore clay and silt soils often adsorb more organic pollutants than larger sand particles. As both sites are predominantly sandy in texture (A: 92.8, B: 82.8 %), hydrophobic sorption may thus be limited. Similarly, the stronger forces of chemisorption to negatively charged organic matter and clay may be inhibited by the low surface area of both soils. In comparing the two sites, however, there is a marked difference in texture. Soil B contains considerably larger fractions of silt and clay combined (A: 17.2, B: 7.2 %) and thus, would have a greater surface area, than soil A. Therefore, on the basis of texture, it is expected that soil B will be more favourable to sorption. Nevertheless, infiltration of contaminants with soil water is expected to be relatively rapid due to the sandy texture of both soils.

2.3.5 Water retention curves

Figure 2.1 depicts the water retention curves based on 4 sample determinations for soil A and 3 determinations for soil B. The fourth replicate of soil B was omitted as some data were not available. Overall, the curves indicate that soil B retains water better at suction levels > 6.3 kPa, and soil A retains water better at suction levels < 6.3 kPa (Fig 2.1). Soil B (sandy) retains moisture better in the high suction range, due to a larger fraction of clay and silt-sized particles, lower dry bulk density (A: 1.62 g/cm^3, B: 1.42 g/cm^3) and higher effective porosity (A: 0.39, B: 0.42), than soil A (loamy sand), which has better water retention in the low suction range. The higher surface area of soil B also favours adhesive forces that govern water fluxes in unsaturated soils. Generally, soils with a lower bulk density will have a greater porosity and, therefore, better overall water retention in field conditions (Rowell, 1994). The water retention curves, therefore, support the assertion that soil B will limit simazine mobility to a greater extent than soil A, and thus, increase the residence-time for sorption of simazine. The two soils, both predominantly sandy in texture, differ only slightly with respect to porosity. This may be due to the higher organic matter content in the sandier soil (A) compared to soil B. Organic matter is known to generally enhance the porosity of soils (Rowell, 1994).

Additionally, moisture is a key requirement for the uptake of solutes by microbes. Degradation of organic molecules, however, could result in metabolites that are much more soluble in water and thus easily transported by convection (Hassall, 1982). Simazine is such a molecule whose metabolites, namely 2-chloro-4-amino-6-ethylamino-1,3,5-triazine and 2,4-dihydroxy-6-amino-1,3,5-triazine, are highly water soluble and this may lead to greater mobility. However, unavailability of the parent compound due to sorption on soil surfaces and extremely low water solubility could be a limitation to the assimilation by microbes. Therefore, the water content of the soil is not expected to have a considerable effect on simazine degradation but this aspect is generally worth investigating further, especially, with respect to pesticide registration.

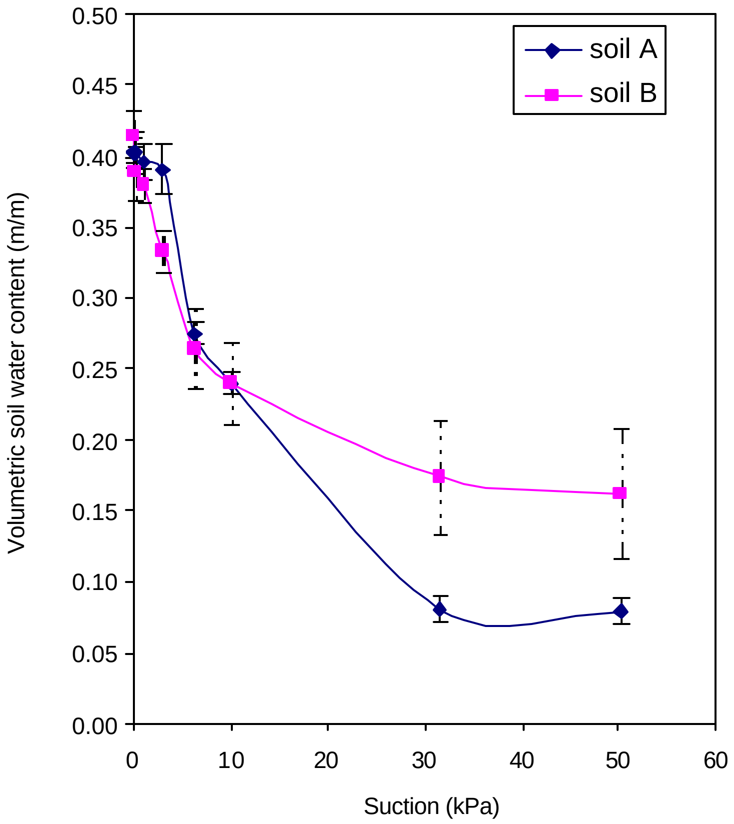


Figure 2.1 Water retention curves for soils A and B, depicting the change in soil water content with the change in applied suction or matrix potential. The standard deviation of 4 determinations from soil A and 3 determinations from soil B are shown using error bars.

2.4 Conclusion

Instead of the various soil properties operating in isolated systems within the soil, broad inter-relationships were found. The pH is neutral for both soils, however, the slight tendency to be acidic in the presence of a salt may favour the stronger cation-exchange mechanisms of chemisorption. The higher CEC of soil B, owing probably to a greater surface area associated with smaller particles, implies a greater overall affinity for sorption. The smaller concentration of dissolved salts also implies that there will be less competition with organic molecules for sorption sites than in soil A. Conversely, the higher percentage of organic content at soil A will favour the weaker physical forces resulting in hydrophobic sorption, however these bonds are often temporary and easily detached by water molecules that are more polar.

The water retention curves showed that at higher suction levels, analogous to matrix potential, soil B will retain water better than soil A, and this was expected from the differences in texture. Therefore the moisture retention capabilities of soil B further enhances the potential for sorption as it will increase the residence time of pesticides in the soil.

In summary, the chemical analysis indicates that soil B may favour a stronger sorption mechanism than soil A, which is enhanced by the physical properties of smaller particle sizes and greater effective surface area for sorption, and ultimately greater water retention. The results therefore indicate that the reddish Elgin soil (B) may have a greater overall affinity for simazine sorption, than the grey, sandy Bellville soil (A), and may have a greater immobilising effect on the compound.

Furthermore, soil texture may be the most important driving force behind both the chemical and hydraulic status of the soil, as it determines hydrophobic sorption, chemisorption and water retention. Therefore, it should be noted that despite the differences between the two soils, the texture of both is ultimately dominated by sand and not silt and clay. The actual retardation of simazine by both soils may therefore be more subtle than what is implied in this discussion, which highlights the differences between soils. This uncertainty forms the basis of investigation for the chapters to follow. The retardation capabilities of the two soils will be quantified in relation to simazine properties using sorption experiments, outlined in Chapter 3, and modelling, in Chapters 4 and 5.

CHAPTER 3

Sorption Characteristics of Simazine as an Example of a Priority Pesticide

3.1 Introduction

Sorption to soil colloids is a dynamic process in the partitioning of contaminants between the liquid, solid and gas phases of soil. It determines the availability of most pesticides for volatilisation, runoff, uptake by plants, biodegradation and leaching (Aharonson, 1987; London et al. 2000; Meinhardt, 2003). As soils are generally made up of organic and inorganic complexes varying in capacity for ion exchange, sorption of pesticides can vary greatly depending on the site conditions. In addition, various factors such as temperature and incubation time can play a role in sorption, and pH has been proven to impact on the behaviour of simazine (McBride, 1994). Nevertheless, organic matter which is concentrated in the root zone, has been shown to have the greatest impact on adsorption and is widely considered to be the best method for measuring sorption potential (Aharonson, 1987).

Sorption isotherms are commonly used to describe sorption behaviour under varying conditions. The classification of isotherms provided by Giles (1972) provides a useful system by which to standardise and interpret graphical data, in terms of their shapes. It was suggested that isotherms can be grouped into four main classes, namely S, L, H and C-types, with some variation occurring within each group depending on the particular solid/solute system. Typically the S class represents a stronger intermolecular attraction between solutes than between solutes and the surface. The L class is the most common and represents solutes with weaker intermolecular attraction with a uniform layer of solutes forming around the solid surface. The H class indicates an extremely strong sorption affinity usually by large molecules, and the C class represents sorption of molecules that penetrate the surface better than the solvent and therefore have a more linear shape (Giles, 1972). According to McGregor (1999), most pesticides are characterised by the C or L class.

Alternatively, simple mathematical equations may be used to model sorption, as outlined in Chapter 1 (review of models). The most common and simplest of these are the linear partition (Kd) and non-linear Freundlich equations (Kf). Although numerous studies have shown that pesticide sorption is a complex process, it is usually described by the simple linear partition equation at very low concentrations that typify their occurrence in the environment.

A study was done by Weber et al (2004) which entailed a compilation of globally published Kd values for a range of commonly used pesticides under specific soil conditions, such as organic matter and clay content, and pH. The result was a host of equations relating Kd values to the relevant soil properties, as well as mean values for many pesticides. These equations may be useful in characterising sorption behaviour for a range of soil types. As organic matter is generally considered to be the dominant sorbent in soils, the resulting sorption coefficients can be related to organic matter content to yield a more versatile carbon-referenced parameter that is applicable to various soil types.

Several methods varying in complexity can be used in the determination of sorption data. Some of the most widely used include field leaching experiments and monitoring, undisturbed field lysimeters, laboratory soil leaching columns, and batch equilibration experiments, which are used in this study (Albarran, 2004; Aharonson, 1987; London et al. 2000; Meinhardt, 2003; Rae, 1998; Weaver, 1993). Water samples are generally analysed using gas chromatography (GC) or high pressure liquid chromatography (HPLC). According to the comparative study done by Li (1996), no particular preference has been shown for either method and both can produce highly accurate results. It was found that HPLC is generally used for polar, non-volatile compounds, while GC allows for measurement of a wide range of compounds.

The primary aims of this experimental work was to determine the sorption behaviour of simazine in selected South African soils using isotherms and coefficients. Much of the research on leaching has generally been done in the context of pesticide registration and has received great international attention, particularly in the USA. The trend in SA, however, is that pesticide registration depends on these international findings and there is a growing need for independent fate studies to be carried out in local environments (Meinhardt, 2003). From the available literature, it is shown that simazine generally has low mobility and is adsorbed onto organic matter and clay. However, this has not been sufficiently proven for the Western Cape and traces of simazine have been found in several water bodies. Therefore, this study aims to test the assertions made in the literature, about simazine sorption behaviour. Furthermore, the coefficients will be used as input for the models, selected to predict the leaching potential of simazine in local soils. Owing to the time constraints of the study, only the simplest, albeit effective, laboratory method was selected and no leaching or field experiments were carried out.

The following chapter includes a brief description of the batch experiments and HPLC analysis used in determining sorption isotherms and coefficients, with reference made to experimental guidelines and equations used. Details are provided in Appendix C. The samples were water-based and HPLC was therefore selected as the best method for analysis as it would reduce the time needed for sample preparation characteristic of GC that typically separates chemicals from organic solvents. The sorption isotherms are discussed in terms of Giles' classification and regression analysis was used to derive linear (Kd) and non-linear (Kf) coefficients. The most suitable coefficients were compared with literature values so as to assess the integrity and reliability of the experimental methods. The implications of the study for future research and simazine use have been considered in relation to the limitations inherent in the methods, possible sources of error, and to what extent these may be mitigated.

3.2 Materials and Methods

3.2.1 Sorption experiment

The sorption determination of simazine was carried out at the UWC Earth Sciences department. The method has been adapted from the EPA Fate, Transport and Transformation Test Guidelines for determining sediment and soil adsorption/desorption isotherms (US EPA, 1998). The method involved an equilibration of sieved air-dried soil samples with the pesticide product, Simanex 50 SC, containing 490 g/L of simazine, and centrifugation for separating the mixture.

A soil mass of 15g was added to 75ml of the pesticide solutions in centrifugation test-tubes to yield a 1:5 ratio. 0.01M $CaCl_2$ was added to the samples to improve sedimentation during centrifugation and minimise cation exchange. The concentrations used were within the range recommended by the manufacturers for use (4 to 6 L/ha). Depending on whether simazine is applied with irrigation and how much water is used in the actual application, concentrations can range between 0.5 and 4.9 mg/L. A single stock solution of 10ppm was used to prepare the seven concentrations (0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0 mg/L or ppm) by means of dilution, so as to avoid potential error while weighing the product. Three replicas were used for each concentration and standards were prepared for the calibration so that the response curve could be quantified in terms of concentration. Controls with no soil were included for each concentration to determine whether pesticides were degraded during the sample preparations. Blanks were not included as the sample sites have not been used for agriculture and is known to contain no traces of simazine. The samples and controls, were shaken for 24 hours immediately after preparation, after which they were centrifuged for approximately 5 minutes at a speed of 1300 rpm (359 RCF, relative centrifugal force). The liquid was extracted into plastic vials and stored in the refrigerator for no longer than 4 days prior to HPLC analysis.

3.2.2 HPLC extraction and analysis

The liquid chromatography equipment and facilities of the UWC Chemistry Department were utilised for this phase of the experiments. The reference method used is that published by Agilent Technologies (Ricker, 2000). The Hewlett Packard 1090(50) HPLC was used with ZORBAX SB-C18 column, 4.6 x 150 mm. The mobile phase contained 33% acetonitrile and 67% 0.1 M sodium acetate buffer at pH 6.0. The UV-wavelength best suited to detect simazine under the current conditions was 245 nm as opposed to the 210 nm stipulated by the reference method. A flow rate of 1.5 mL/min and injection volume of 5 µL was used.

The detection limits of the HPLC were relatively high and the samples were spiked with 1ml of exactly 10ppm of the simazine product prior to analysis so that it could be detected with reasonable certainty and still be within the limits of water solubility (6.2 – 7 ppm at 25°C). The spiking of samples, however introduced a potential source of error as discussed below. The samples and spikes were measured using a 2500 µL glass syringe with disposable plastic syringe filters or a 2ml pipette and added to 2ml glass vials. After allowing the samples to equilibrate with room temperature, they were placed in the HPLC for analysis.

3.2.3 Potential sources of error and mitigation

Due to the use and analysis of the pesticide at very low concentrations, it was important to consider all possible routes of error that may have been incorporated in the methods. Firstly, the experiments were done in two parts, separated by a few days taken for a preliminary analysis of the results before proceeding with further experiments. During this time, the stock solution was stored in a dark refrigerator so as to prevent photolysis.

The syringes used for measuring and adding samples to the 2ml vials for the HPLC were limited in the department. When experiments resumed, they had to be replaced with pipettes. This change in instrumentation could have caused a change in the level of accuracy of the measurements, as well as discrepancies between samples prepared with different instruments. All other procedures, however, remained consistent throughout the experiments. Furthermore, it is noted that there is always a degree of subjectivity involved in sample measurements, especially at low concentrations. This could be pertinent to the dilution process and the spiking of samples.

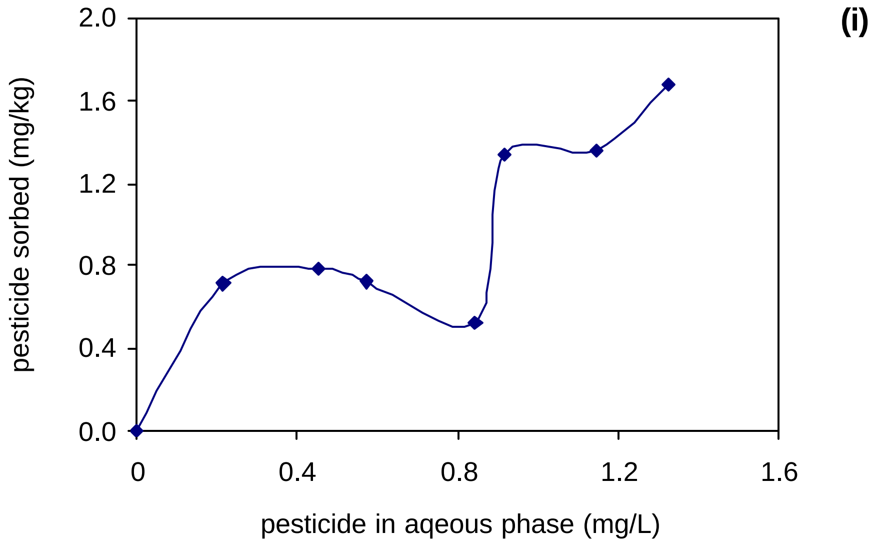
Lastly, as a result of availability, the Simanex formulation was used instead of the pure simazine compound. It is, therefore, possible that other triazines present in the product could have affected the rate of simazine sorption by competing for sorptive sites. Sorption rates would thus be underestimated in the experiments, leading to an overestimation of leaching by the models. Alternatively, the formulation additives could generally enhance the sorption rates, leading to an underestimation of leaching. Irrespective, sorption results may vary depending on the specified product and more research should be done in this area before such experiments are conducted, using formulated products. Testing a product, however, may be beneficial as it is pertinent to field conditions in which pesticide products are used as opposed to the pure chemicals.

3.3 Results and Discussion

3.3.1 Sorption isotherms

The HPLC results and calculations that were used to plot the isotherms can be found in Appendix C, as well as a typical chromatograph for simazine. Concentrations of simazine detected in the extracted solutions or aqueous phase (mg/L) are included, as well as the derived concentrations of sorbed pesticide (mg/kg). Average values for the replicas were used in order to reduce the variance of the data and standard deviations are included.

Referring to Giles's classification, the sorption isotherms for simazine in both soils, appear to be of the L class, indicating relatively weak intermolecular attraction and a more uniform yet loosely packed layer forming around the substrate (Fig 3.1 i & ii). This is attributed to the fact that solutes require energy to detach from solvent molecules and to replace those that form around the substrate. Therefore the maximum rate of sorption can vary depending on the nature of the solution from which sorption occurs. The simazine isotherms in Figure 3.1 resemble a variety of L-curves representing a maximum level of adsorption due to solutes forming a second layer around the substrate (Giles, 1972). This could be due to the fact that simazine is a weak base, which protonates somewhat under the correct pH, thus being more strongly attracted to the negative charges on soils by cation-exchange. However, the soils were found to be fairly neutral in pH (Chapter 2) and an alternative explanation is that the low water solubility of simazine causes it to be readily pushed out of water and onto soil surfaces, particularly towards the organic matter. For a more detailed discussion on the mechanisms of simazine sorption in relation to the soil environment, the reader is referred to Chapter 2.



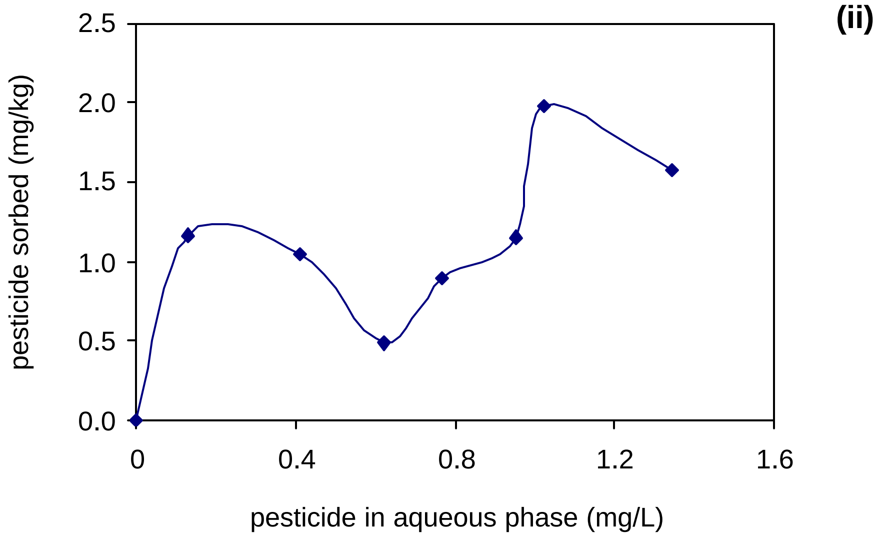
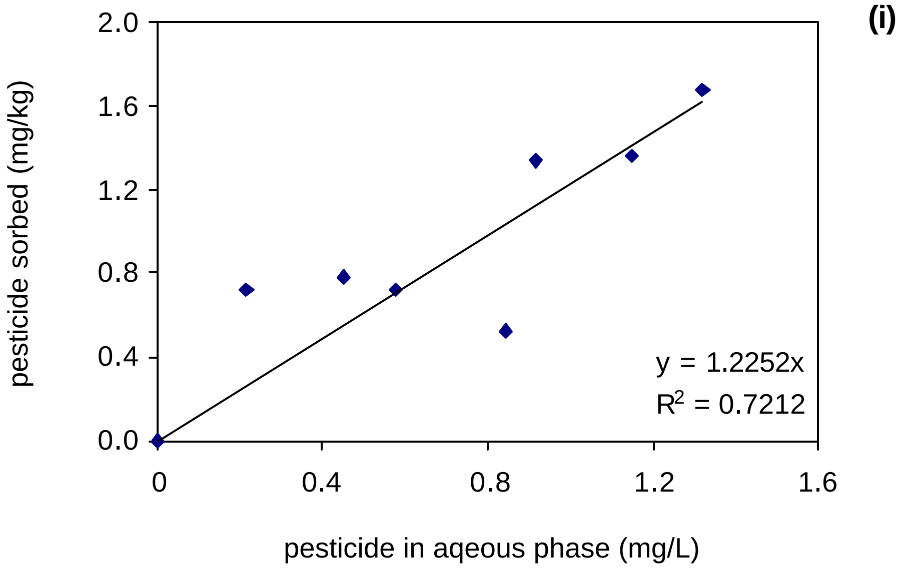


Figure 3.1 Sorption isotherms of simazine applied at concentrations ranging between 0.5 and 2.0 mg/L for soils A (i) and B (ii)



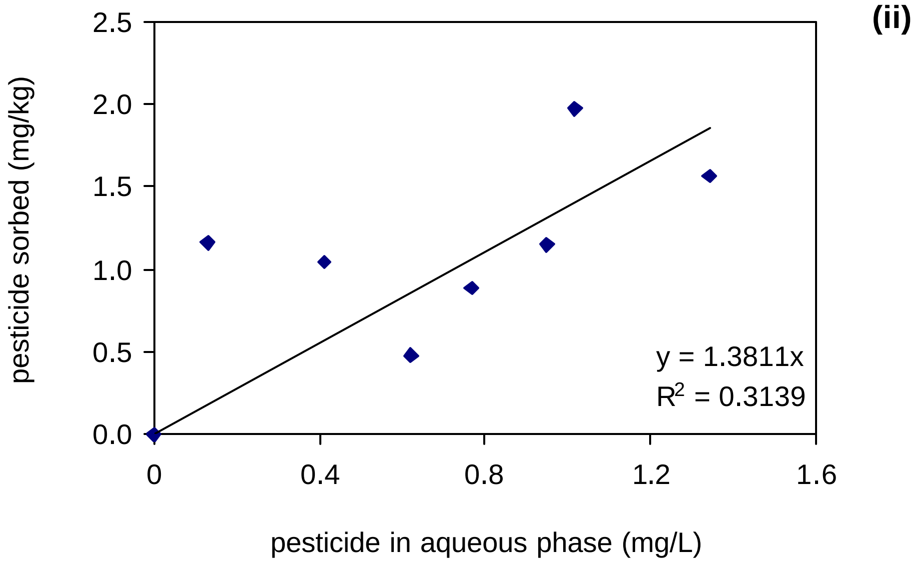


Figure 3.2 Linear regression using the average values of replicas for soils A (i), and B (ii)

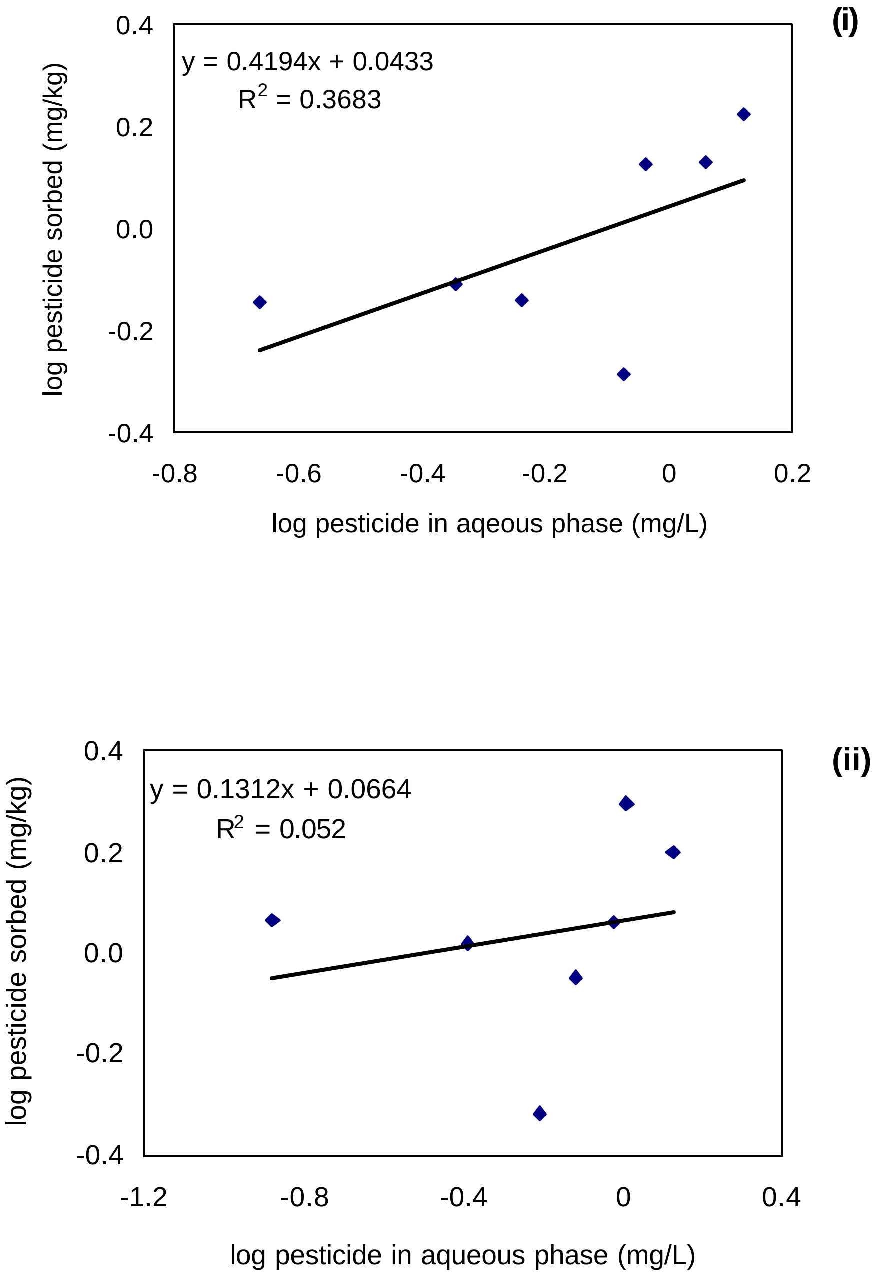


Figure 3.3 Linear regression of the Freundlich isotherms (using logarithms) of simazine applied at concentrations ranging between 0.5 and 2.0 mg/L for soils A (i) and B (ii)

3.3.2 Sorption coefficients

Regression analysis was used to determine sorption coefficients. The Kd values were determined by fitting a straight line through the measured data:

$Cs = Kd\ Caq$

Also written as $y = Kd\ x$

Soil A (Fig 3.2 i): $y = 1.23\ x$

Therefore $Kd = 1.23$

Soil B (Fig 3.2 ii): $y = 1.38\ x$

Therefore $Kd = 1.38$

The non-linear Freundlich equation was converted into a linear form by using logarithms and fitting a straight line through the data:

$Cs = Kf\ Caq^n$

Using logarithms: $\log Cs = \log Kf + n \log Caq$

Also written as: $y = n\ x + \log Kf$

Soil A (Fig 3.3 i): $y = 0.4194x + 0.0433$

therefore $\log Kf = 0.0433$

and $Kf = 1.11$

Soil B (Fig 3.3 ii): $y = 0.1312x + 0.0664$

Therefore $\log Kf = 0.0664$

and $Kf = 1.17$

The coefficients derived from the regression analysis (Figs 3.2 and 3.3) are summarised in Table 3.1. In comparing the R^2-values for the Kd (A: 0.72, B: 0.31) and Kf (A:0.37, B: 0.05) equations, it was concluded that the simple linear partition model of Kd provides the best-fit for the sorption data. Kd values were then compared to the values derived using the equation provided by Weber et al (2004), as well as the mean Kd for a range of soil types (Table 3.1). The Kd values determined experimentally (A: 1.23, B: 1.38) were found to be in accordance with the values derived from the equation of Weber (mean: 2.19, A: 0.42, B:

0.04), which accounts for organic matter content, clay content and pH. The values are within the same order of magnitude, or within the same range when considering the error margins. Furthermore, the difference in Kd values between soils, is expected due to differences in texture. Soil B is a loamy sand with a higher effective surface area for sorption and greater water retention capacity, than soil A.

Table 3.1 Simazine sorption coefficients determined experimentally and coefficients reported in or derived from Weber et al (2004)

Coefficient	**Source**	**Soil A**	**R^2**	**Soil B**	**R^2**
Kd Kf	Experimental Experimental	1.23 1.105	0.72 0.37	1.38 1.17	0.31 0.05
Kd[1]	Weber et al., 2004	0.42	0.49	0.04	0.49
Kd[2]	Weber et al., 2004	2.19			

[1] calculated from the best-fit equation for simazine: Kd = 5.3 +0.2 (OM) + 0.03 (Cl) – 0.73 (pH), where Cl is clay content

[2] mean value of 194 different international findings

3.4 Conclusions

Graphs plotted from the sorption data for both soils, were found to resemble an L class of isotherms. The L class indicates that simazine is relatively weakly associated with water and will adsorb readily onto the soil surfaces, forming a somewhat homogenous layer around the particles. Additionally, the particular type of L curve found for simazine falls into a subcategory that describes a maximum rate of sorption due to a second layer forming around the soil particles. These outcomes support the theory discussed in Chapter 1, that simazine behaves as a basic molecule with a strong affinity for negatively charged soils, particularly under slightly acidic conditions (chemisorption). Moreover, the low water solubility of simazine could also be responsible for high sorption rates, by causing the hydrophobic solutes to be attracted away from water molecules and onto more hydrophobic soil surfaces, such as organic matter (physical sorption).

The linear Kd equations were the best-fit for the sorption data and this is probably due to the very small concentrations used in the experiments. Also, hydrophobic sorption is often characterised by linear isotherms. The fact that the Kd values are within the same order of magnitude as the literature values is a positive outcome as model-users are often faced with time constraints and rely heavily on existing data. Similarly, the scope of this study did not include leaching experiments to validate the experimental findings and, instead, reliable published data was used.

As outlined in Chapter 1, the selected soils could limit the potential for both chemisorption and physical sorption as they are generally neutral in pH, have low salinity and cation exchange capacity, low organic matter content, and are predominantly sandy in texture. Therefore, under more contrasting soil conditions, simazine might have a stronger sorption affinity. Nevertheless, the isotherms indicate strong sorption activity in these soils. The difference in Kd values between soils, albeit small, are to be expected from the outcomes of the soil analysis and the effect due to soil properties. Soil B is, to some extent, more favourable for sorption than soil A and this is mostly due to a larger fraction of silt and clay-sized particles, and greater surface area and moisture retention. These differences are reflected in the higher Kd value for soil B than soil A.

Despite the relatively high R^2-value for the Kd equations of soil A (0.72), there is considerable data variance for both soils. By evaluating the data during the course of the experiments, it was found that increasing the number of samples did not improve the data variance. Instead, an emphasis is placed on the importance of accuracy of measurements and avoidance of error that can be introduced throughout the experiments, particularly during the weighing, diluting and spiking of samples. The interruption in experiments may have increased the potential for errors and it is recommended that experiments of this nature be done using consistently standard methods. Increasing the sample numbers may improve the quality of the results but only if the data is highly accurate. Other triazines present in the Simanex product may have interfered with simazine sorption. However, the potential or extent of such interactions is unaccounted for in this study and is considered to be negligible in light of the relatively small constituencies of other triazines in the product. Spatial variability of soils is another reason for data variance.

Nonetheless, the results indicating low simazine mobility are reasonably well supported by the outcomes of the soil analysis, as well as the literature values. The sorption coefficients will be used as key input parameters for selected models, namely VLEACH and SWAP, and this is dealt with in Chapters 4 and 5. Additionally, they can be used as a general guideline for further research and can be further validated using field leaching experiments. The importance of these findings is highlighted by the fact that few sorption studies have been done for simazine in South African soils and such data is generally limited for many pesticides.

CHAPTER 4

Modelling Pesticide Fate using the Vadose Zone Leaching Model (VLEACH), version 2.2b - Sensitivity Analysis

4.1 Introduction

The aims of this section include an assessment of groundwater vulnerability to pesticide leaching in the Western Cape. VLEACH and SWAP (Chapter 5) were selected for the study on the basis of their differences in functionality and detail, and so that comparisons may be drawn. VLEACH is a one-dimensional, steady-state model that simulates linear partitioning of a contaminant between the different phases of the soil (gaseous, sorbed and dissolved) as well as solute transport. However, VLEACH does not account for solute dispersion and degradation. Conversely, SWAP is a comprehensive mechanistic model that simulates water, solute and heat fluxes, as well as crop-growth, evapotranspiration, drainage and management factors at field and regional scales. Water fluxes are calculated based on Richard's continuity equation for one-dimensional water flow. Solute-related processes including convection, diffusion, dispersion, non-linear adsorption, first-order decay and root uptake are simulated. Furthermore, soil heterogeneity is simulated using soil hydraulic functions and preferential flow input data.

In this chapter, VLEACH version 1.0 (US EPA, 1990) is evaluated for its capabilities in simulating a simple hypothetical soil-groundwater-contaminant system. The model was originally developed for the US Environmental Protection Agency, primarily for estimating groundwater impacts of volatile organic contaminants. It was subsequently modified until version 2.2b (US EPA, 1998).

A sensitivity analysis was performed to evaluate the effects of certain input parameters on the model output, using a range of pesticides and site conditions. Certain hydrogeological input parameters, namely recharge rate, water content and depth to groundwater, were estimated for typical local conditions. Experimentally determined soil properties (Chapter 2) and contaminant information from the literature (Chapter 1) were used as inputs to the model. Special emphasis is placed on predictions for simazine and the extent to which pesticide leaching can be modelled with VLEACH. It should be noted that the two sites used in the study, are not necessarily used for agriculture and the following analysis is predominantly a conceptual one.

4.1.1 VLEACH model concepts, assumptions and limitations

VLEACH simulates instantaneous equilibration of a contaminant between the aqueous, gaseous and solid phases of the root zone, by means of advection, diffusion and adsorption, respectively. The model uses coefficients defined by the user to describe the transport mechanisms. Liquid advection is simulated based on the principles governing infiltration and soil water content, while diffusion is based on differences in concentration gradients. User-defined polygons are representative of homogeneous soil and hydrological conditions and consist of cell layers which may differ in terms of initial contaminant concentration only. VLEACH is therefore limited with regard to vertical heterogeneity. The total impact of the contaminant mass on the defined area is calculated in time-steps based on a finite difference (Ravi & Johnson, 1997).

Contaminant mobility is simulated within homogeneous polygons and soil moisture conditions are assumed to be uniform within a polygon over the simulation period. Steady-state conditions are unlikely to occur in the field, however, corrections can be made by referring to simulations based on a likely range of soil/hydrological conditions. Also, the fact that the model does not account for solute dispersion and degradation can lead to conservative estimates of contamination.

4.2 Model parameters

4.2.1 Input parameters

Simulations were run for ten pesticides, namely, atrazine, simazine, carbofuran, carbaryl, dieldrin, lindane, dimethoate, fenthion and parathion, for the two W. Cape soils characterised in Chapter 2. The model was assessed for variation of pesticide leaching with depth to groundwater, recharge rate, depth of pesticide application, as well as individual pesticide and soil properties. In addition, simulations were run for pesticide impacts based on specifically recommended or used application rates, as reported by manufacturers or in the literature. Simulations were run for once-off applications (initial) and for continuous applications (through recharge). The model does not include an input option to simulate pesticide application at yearly time intervals, and application via recharge water was the closest alternative to simulate yearly pesticide applications. An example of an input file can be found in Appendix D.

Contaminant information

The organic carbon distribution coefficient Koc in mL/g is defined as 'the partitioning of the contaminant with organic carbon'. Henry's constant Kh is dimensionless and given as an empirical value based on solubility and partial vapour pressure, used to describe the vaporisation of the contaminant at a given temperature (Ravi & Johnson, 1997).

The ten pesticides selected for the study, are those that have been identified in Chapter 1 as priority pesticides in South Africa and for which best-fit equations or mean values have been provided by Weber et. al. (2004). The Koc values used in the model input, were derived using the equation Kd = (Koc)(%OC)/100 (Weber et. al., 2004). For the sake of uniformity, these values were also used for simazine, rather than the experimentally derived coefficients from Chapter 3. Furthermore, the experimentally determined sorption isotherms for simazine are non-linear and they are, therefore, incompatible with VLEACH, which models sorption as a linear function. Henry's constant Kh and water solubility were taken from the literature. The input parameters used, including Kd values and pesticide families, can be found in Table 4.1.

Site information

Measurements of length are required by VLEACH in the US metric system and conversions have been made where necessary. Baseline data used in the analysis include: once-off applications (recommended 4L/ha/yr), polygon area (1m^2), net recharge rate (estimated 1.15 ft/yr or 350 mm), volumetric water content (estimated 20%), and experimentally determined dry bulk density, effective porosity and organic carbon content. For the sake of comparison, all pesticide applications are based on the average recommended rate of 4 L/ha/yr for the simazine product, Simanex 50 SC. Pesticides are often sprayed onto the surface of bare soil and the initial concentration of the pesticide in the top 3cm of the soil, was calculated to be 5030 ug/kg.

Table 4.1 Input parameters taken from the literature, for the 10 pesticides used in the sensitivity analysis, including soil distribution coefficients Kd and derived organic carbon distribution coefficient Koc (from best-fit equations), Henry's constant Kh and water solubility

Family	**Pesticide**	**Kd (mL/g)**		**Koc (mL/g)**		**Water solubility (mg/L)**[1]	**Kh (-)**[3]
		A	**B**	**A**	**B**		
COOH acid	2,4 D (2,4 DDD)	0.46	0.41	43	90	900	7.35E-11
Weak base	Atrazine	0	0	0	0	28	1.20E-07
	Simazine	0.42	0.04	40	9	5	3.96E-08
Carbamate/ Nonionizable	Carbofuran	0.22	0.05	21	10	320	2.10E-08
	Carbaryl (mean)	1.63	1.63	155	360	40	5.30E-06 [4]
Organochlorine/ Nonionizable	Dieldrin	135.60	99.99	12919	22102	193 [2]	2.65E-05
	Lindane	7.02	0	669	0	7.3	7.42E-05
Organophosphate /Nonionizable	Dimethoate	0.27	0.18	26	40	25,000	5.61E-10
	Fenthion	15.01	2.03	1429	448	2	1.00E-04 [4]
	Parathion	14.83	3.09	1413	683	12.4	4.98E-06

[1] Extension Toxicology Network (EXTOXNET), Pesticide Information Profiles

[2] personal communication, Ingrid Dennis of the Institute for Groundwater Studies, Bloemfontein

[3] Illinois General Assembly

[4] International programme on chemical safety, 1994

4.2.2 Output files

The output data of groundwater impact and soil contamination profiles were used to plot the graphs which are presented in Appendix D. Total groundwater impact is expressed as either the leaching/contamination rate (g/yr), or cumulative mass that enters groundwater (g). The soil impact is represented by the soil contamination profiles, expressed as contaminant mass (g) per square meter in each soil layer that is specified by the user as 'vertical thickness of a cell'.

4.3 Results and Discussion

4.3.1 Depth to groundwater

For all pesticides and both soils, groundwater contamination was found to be inversely related to depth to groundwater (2 to 10 m), as this relates to the travel-time of pesticides through the soil. For example, simazine leaching occurs sooner and at a higher rate when depth to groundwater equals 2m, in comparison to the other groundwater depths (Figs 4.1 & 4.2). The graphical output for each pesticide at each site can be found in Appendix D2.1 and a summary is given in Table 4.2. Results for an average depth (6m) were used for the summary table so that pesticides can be compared.

It was found that the rate of contamination depends on the pesticide and site conditions. With the exception of atrazine and lindane, pesticides leached more rapidly at site B than at site A. This can be attributed to the lower organic carbon content at site B (0.5%) compared to site A (1%), which limits the retention of pesticides by sorption. The trend can be seen for simazine at a depth of 6m where a peak in contamination of 1.43e–2g/yr occurs after 15 yrs at site A, and 1.53e –1g/yr at site B after 5.2 years (Fig 4.1). The cumulative mass at site A is 0.2558g after 50 yrs, while at site B a mass of 0.225g accumulates after 10 yrs (Fig 4.2). The soil profile indicates that, with a once-off initial application, simazine concentration in the soil is very small and increases considerably towards the deeper layers, after 50 yrs at site A and 10 yrs at site B. With a depth to groundwater of 20 ft or approximately 6m, the predicted maximum concentration in the soil profile is just above the groundwater table. This is 7.09e–11g/m^2 after 50 yrs at site A and 6.13e–17g/m^2 after 10 yrs at site B (Fig 4.3).

Atrazine and lindane were assumed to have Koc equal to zero for both soils, as negative values of Koc were derived from the best-fit equations of Weber et al. (2004). The values suggest that these pesticides will leach rapidly, having a similar overall impact. With a groundwater depth of 6m, atrazine reaches a maximum rate of contamination of 0.32641 g/yr after 3.8 yrs at site A, 0.287 g/yr after 3.8 yrs at site B and lindane reaches 0.287g/yr after 3.8 yrs at site B (Table 4.2).

The similarity in behaviour of pesticides with equal Koc emphasises the role of organic carbon and sorption coefficients in leaching. It should, however, be noted that there is a margin of error in the method of Weber et al. (2004), due to a range of confidence limits used to determine the best-fit equations. Experimentally determined Kd values (Chapter 3) also imply that soil B has a greater sorption capacity than soil A.

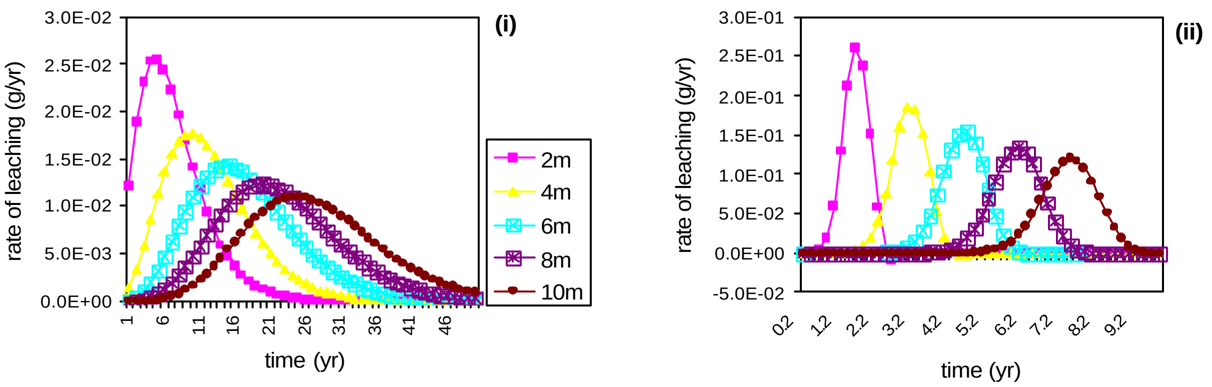


Figure 4.1. Leaching rate of simazine at (i) site A, over 50 yrs, and (ii) site B over 10 yrs, with varying depth to groundwater and once-off initial application

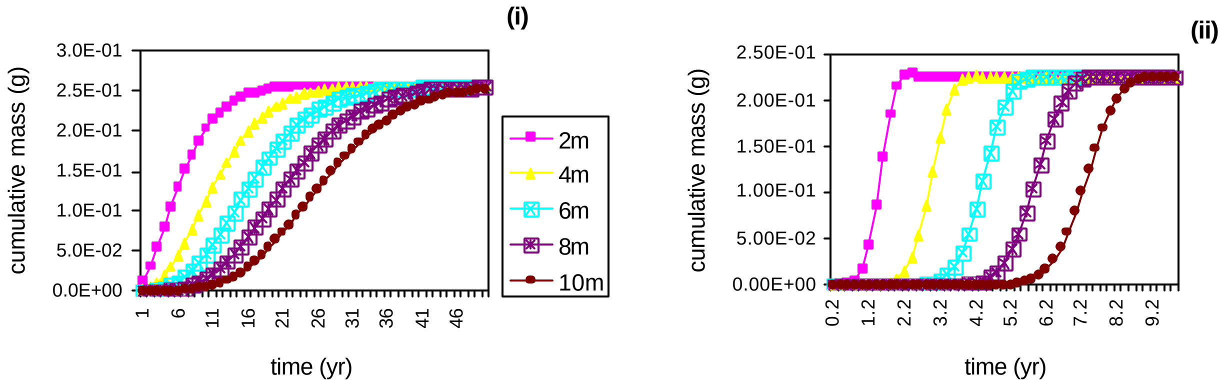


Figure 4.2. Cumulative groundwater impact of simazine at (i) site A over 50 yrs, and (ii) site B over 10 yrs, with varying depth to groundwater and once-off initial application

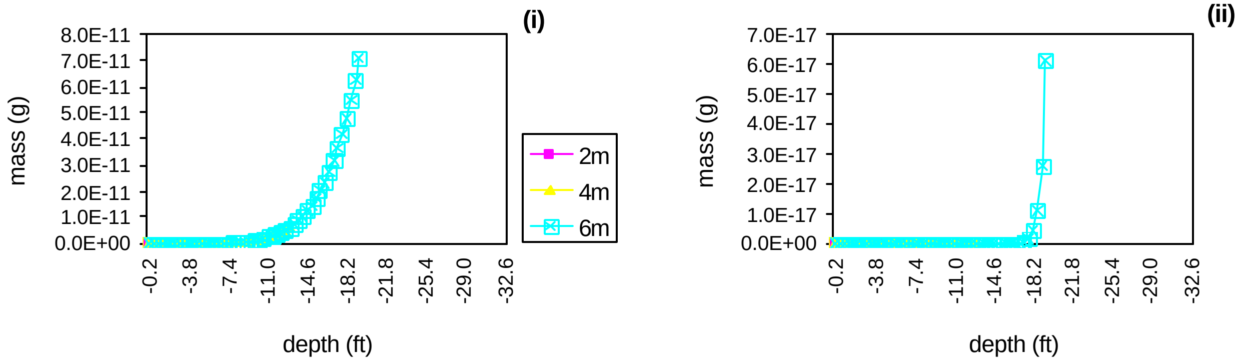


Figure 4.3. Soil profile of simazine at (i) site A after 50 yrs, and (ii) site B after 10 yrs, with varying depth to groundwater and once-off initial application

Table 4.2 Peaks in the rate of leaching, with depth to groundwater of approx. 6m, and the time needed to reach the peak

	Site A		Site B	
Pesticide	**Peaks in leaching rate (g/yr)**	**Time (yr)**	**Peaks in leaching rate (g/yr)**	**Time (yr)**
Atrazine	3.2641e-1	3.8	0.2870	3.8
Simazine	1.4300e-2	15	1.5300e-1	4.6
Dimethoate	2.0800e-2	11	2.83e-2	8
Lindane *	gradual decrease	500	2.87e-1	3.8
2,4-D	1.34e-2	15, 16	1.46e-2	13
Carbofuran	2.47e-2	10	1.4e-1	4.8
Carbaryl	2.21e-3	32	2.96e-3	38
Dieldrin *	gradual increase	600 yrs	gradual increase	600 yrs
Fenthion	2.51e-4	240-280	2.4e-3	46
Parathion	2.54e-4	244-268	1.59e-3	62-72

* A gradual increase occurs when the rate of leaching is very low and a peak is not reached.

4.3.2 Recharge rate

For the analysis of the model sensitivity to recharge rate, simulations were run under varying rates of recharge between 0 and 700mm, for a standard depth of water table equal to 20 ft or approximately 6m and the recommended application rate of 4L/ha in the top 3cm soil layer. The graphs are shown in Appendix D2.2.

The model predicts for all pesticides that the rate of contamination will be strongly determined by the net recharge rate. This relationship can be seen in Figures 4.4 and 4.5 for simazine, where the effect of site conditions on contamination is also evident. Leaching is generally faster at site B than at site A due to a lower organic matter content. A maximum of 0.2559 g simazine accumulates at site A after about 40 yrs for 300-700mm recharge, while 0.2252g accumulates at site B after about 23 yrs for all rates of recharge. The effect of recharge rate can also be seen in the soil profiles where higher rates of recharge and/or leaching result in lower soil concentrations of the contaminant as pesticides enter groundwater. The soil profile for simazine at site A shows a decrease in concentration with increased recharge rate (Fig 4.6).

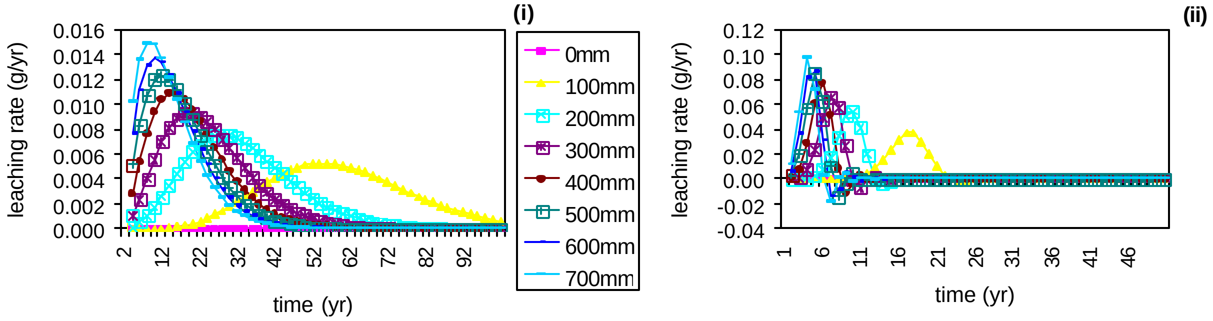


Figure 4.4. Leaching of simazine at (i) site A over 100 yrs, and (ii) site B over 50 yrs, with varying recharge rate and once -off initial application

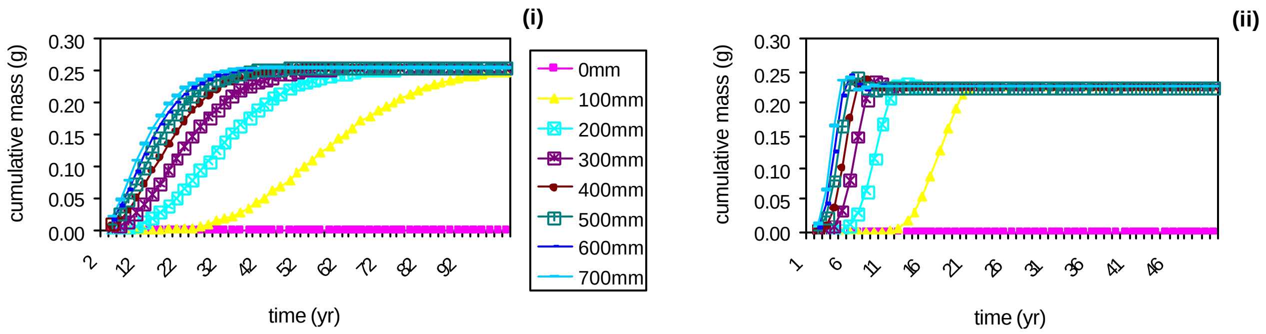


Figure 4.5. Cumulative groundwater impact of simazine at (I) site A over 100 yrs, and (ii) site B over 50 yrs, with varying recharge rate and once-off initial application

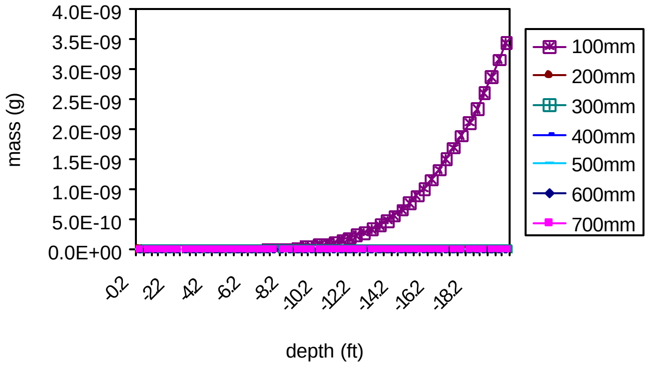


Figure 4.6. Soil profile of simazine at site A after 100 yrs, with varying recharge rate and once-off initial application

4.3.3 Initial contaminant concentration

The initial concentration was derived from the application rate of the pesticide (2-8 L/ha/yr), applied once to the top 3cm soil layer. Simulations were run with depth of water table and net recharge rate kept constant. Variation in initial pesticide concentration in the soil affects the total contaminant mass entering groundwater and hence the soil profile (Fig 4.7). By observing the peaks in leaching rate (Fig 4.2), it was found that the greater the concentration, the greater will be the overall impact on groundwater and soil environments. Graphs illustrating the effects of varying initial concentration on the peaks in leaching rate can be found in Appendix D2.3 and a summary is given in Table 4.3. The effect of site conditions and sorption coefficients are also evident. Leaching is generally faster at site B, with the exception of Atrazine, which has Koc equal to zero at both sites.

The effect of varying initial concentration can also be seen in the cumulative mass leached and the soil profiles, as in the case of simazine (Figs 4.8 & 4.9). Increasing the concentration of simazine causes the cumulative groundwater impact to increase from 0.12778g to 0.51105 g after about 40 yrs at site A, and from 0.1125g to 0.44995 g after about 10 yrs at site B. After 50 yrs the pesticide mass in the soil (just above the groundwater table increases from 4.29e –11g to 1.72e –10g at 19.8ft at site A, depending on the application amount.

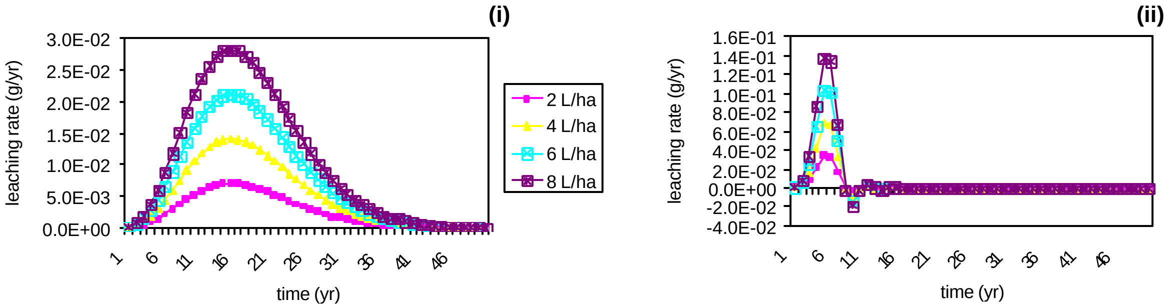


Figure 4.7. Leaching rate of simazine at (i) site A and (ii) site B over 50 yrs, with varying initial contaminant concentration and once-off initial application

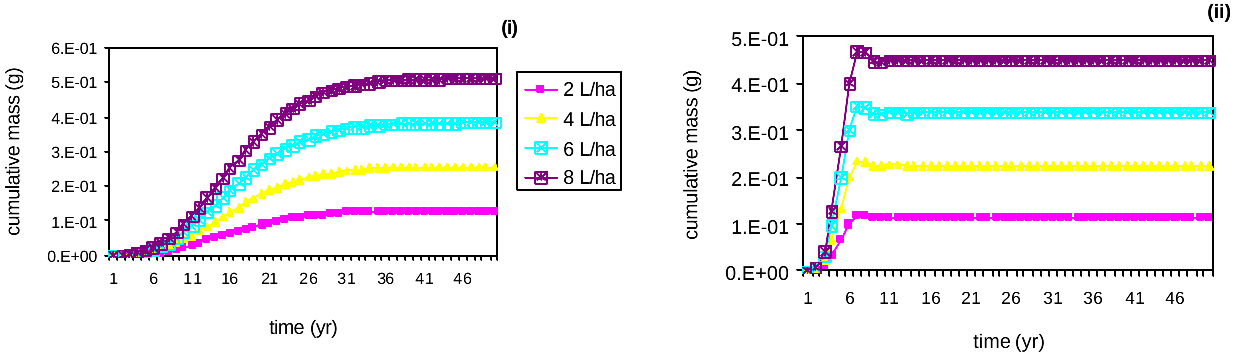


Figure 4.8 Cumulative groundwater impact of simazine over 50 yrs at (i) site A and (ii) site B, with varying initial contaminant concentration and once-off initial application

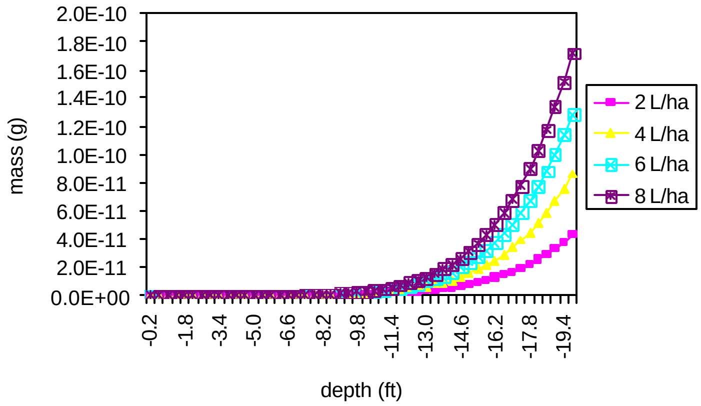


Figure 4.9 Soil profile of simazine at site A, after 50 yrs, with varying initial contaminant concentration and once-off initial application

Table 4.3 Change in the peaks of leaching rate with initial contaminant concentration varied between 2 and 8 L/ha, and the time taken to reach the peak (see Appendix D2.3)

Pesticide	**Site**	**Change in peaks of leaching rate (g/yr)**	**Time (yrs)**
Simazine	A	7.07e–3 to 2.83e–2	15
	B	3.44e–2 to 1.38e–1	5
Atrazine	A	1.62e–1 to 6.5e–1	3.8
	B	1.43e–1 to 5.72e–1	3.8
Dimethoate	A	1.03e–2 to 4.12e–2	11
	B	1.4e–2 to 5.61e–2	8
Lindane *	A	minimum: 4.75e–5 to 1.9e–4 (declining)	1000
	B	1.43e–1 to 5.71e–1	3.8
2,4-D	A	6.67e–3 to 2.67e–2	16
	B	7.22e–3 to 2.89e–2	13
Carbofuran	A	1.23e–2 to 4.9e–2	10
	B	7.04e–2 to 2.82e–1	4.8
Carbaryl	A	1.1e–3 to 4.38e–3	36
	B	1.09e–3 to 4.38e–3	32
Dieldrin	A	1.2e–5 to 4.8e–5	600
	B	1.72e–5 to 6.9e–5	600
Fenthion	A	1.24e–4 to 4.96e–4	248-288
	B	8.88e–4 to 3.55e–3	36
Parathion	A	1.25e–4 to 5.02e–4	256-276
	B	5.91e–4 to 2.37e–3	52

* A minimum rate of leaching occurs for lindane as it has a very low rate of leaching and a peak is not visible on the graphical output.

The effect of varying time-steps and total simulation times on the model

For different simulation times and different time-steps, the pesticide concentrations display different patterns in the soil. To quantify this effect, simulations were run for simazine, by way of example, with 400mm of recharge, and varying time-steps and total simulation times.

Increasing the time-step for simazine from 1 to 6 yrs leads to an increase in the soil impact. The soil profile at site A shows an increase in concentration at the lowest soil layer, from 5.36e –18g to 9.61e –11g with an increase in the time-step from 1 to 6 yrs (Fig 4.10). The cumulative graph shows that increasing the time-step, may cause an over-estimation of the time needed for the pesticide to leach completely and an under-estimation of the cumulative impact. When increasing the total simulation time from 6 to 36 yrs, the soil concentration decreases in the shallower layers and increases in the deeper layers, until leaching starts to decline and the concentration in the deeper layers begins to decrease again.

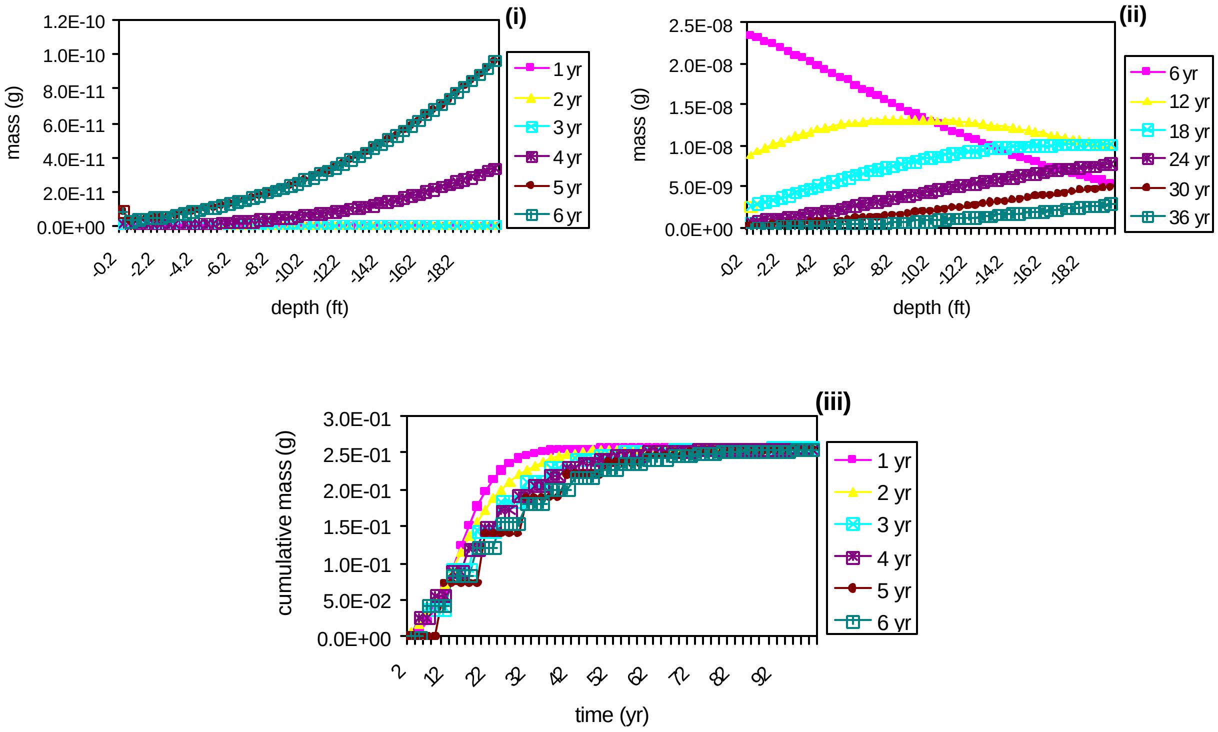


Figure 4.10. Soil profile of simazine at site A with 400mm recharge, once-off initial application and (i) with varying time-steps and (ii) total simulation times, and (iii) the cumulative groundwater impact of simazine with varying time-steps over 100 yrs.

4.3.4 Depth of the pesticide application

Simulations were run to determine the effect of varying application depth while keeping the application rate constant. In other words, the total mass of pesticide applied to the area remained constant while depth of application was varied. The results reveal that change in depth while keeping the overall application rate constant does not have any effect on the overall mobility of pesticide in the soil, as in the example for simazine (Fig 4.11). VLEACH does not simulate photolysis, or any form of enhanced degradation that may occur in the surface layers of the soil.

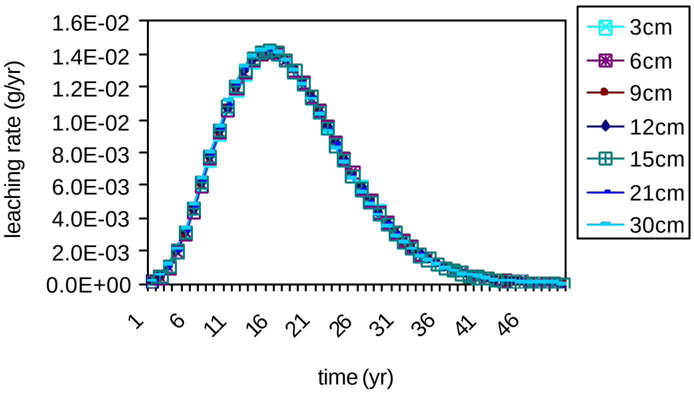


Figure 4.11 Leaching rate of simazine at site A over 50 yrs, with varying depth of once-off initial application

4.3.5 Pesticide properties

The effect of varying contaminant input parameters, such as Koc (10-640 mL/g), Kh (1e-10 - 1e+2 dimensionless), water solubility (10-10,000 mg/L) and free air diffusion coefficient (0-160 m^2/day), were assessed independently for a generic pesticide at both sites. The model output suggests that increasing the Koc by a factor of 2 will cause a considerable decline in the maximum rate of leaching (Figs 4.12). The relationship is best described by the following power functions: $y = 0.8924x^{-1.1597}$ ($R^2 = 0.9528$) for site A and $y = 0.5396x^{-0.8346}$ ($R^2 = 0.9865$) for site B (Fig 4.13). There is no considerable change in the contamination rate when Kh is increased by factors of 200, when water solubility is increased by factors of 2 and 10, and when free air diffusion coefficient is increased by a factor of 2 (Appendix D2.4).

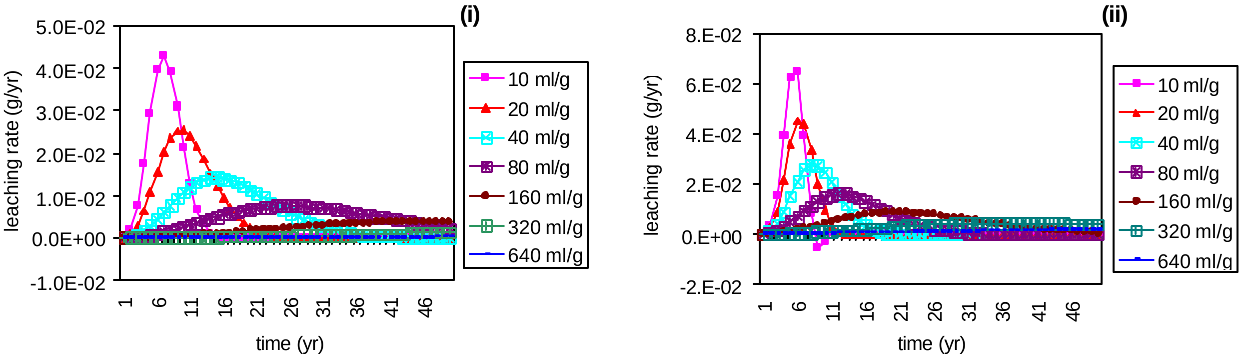


Figure 4.12 Leaching rate of a generic pesticide over 50 yrs, with varying organic carbon distribution coefficient, Koc and once-off initial application at (i) site A and (ii) site B

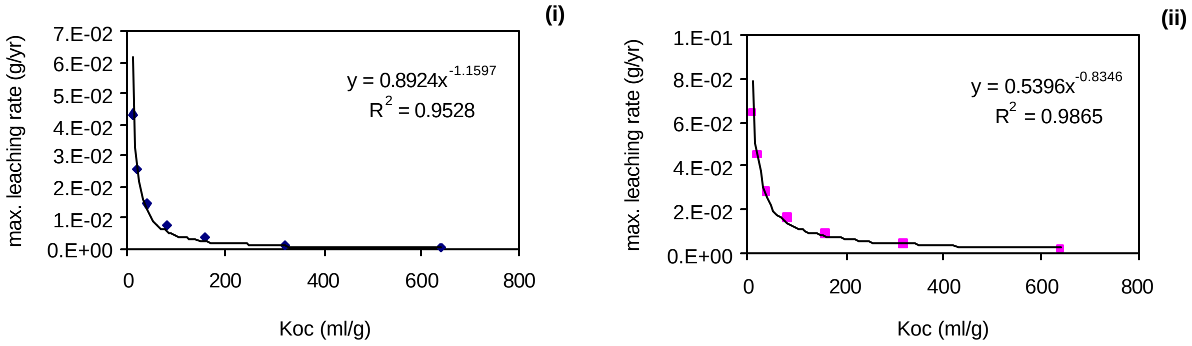


Figure 4.13 Change in the maximum leaching rate of a generic pesticide with varying Koc and once-off initial application. The power function and R^2–values are used to describe the relationships.

4.3.6 Soil properties

The model sensitivity to soil input parameters was tested for dry bulk density (1.0 - 2.0 g/cm3), effective porosity (0.3 - 0.55 dimensionless), volumetric water content (0 - 40 %) and organic carbon content (0.000 - 0.012 dimensionless) for a generic pesticide at site A. Leaching was correlated with bulk density, water content and carbon content (Appendix D2.5), whereas change in effective porosity was found to have no major effect on the model output (Fig 2, Soil Properties, Appendix D). Contamination rate and bulk density is correlated as $y = 0.0132x^{0.1319}$ ($R^2 = 0.9937$), and contamination rate and water content is correlated as $y = 0.0049x^{0.3488}$ ($R^2 = 0.9976$). Increasing the carbon content causes a considerable decline in the peaks of contamination and is described by $y = 0.0004x^{0.778}$ ($R^2 = 0.9973$).

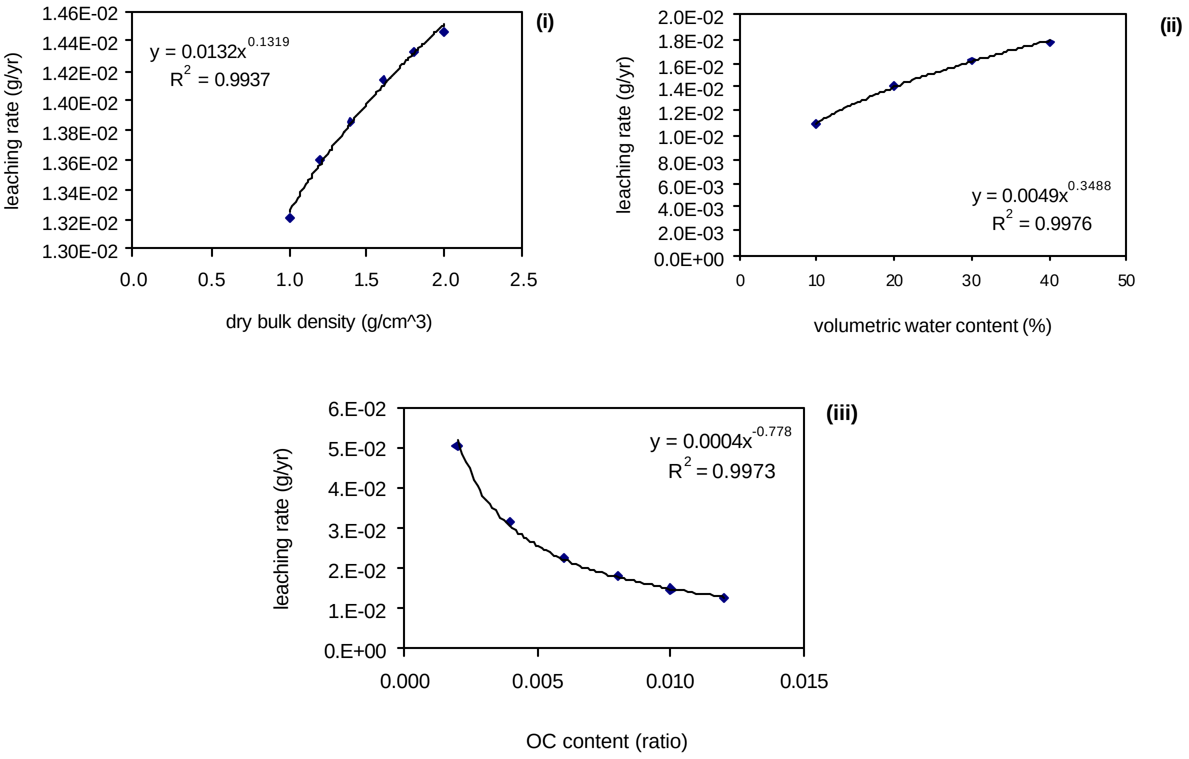


Figure 4.14 Peaks in leaching rate of a generic pesticide at site A, with once-off initial application and varying (i) dry bulk density, (ii) volumetric water content, and (iii) organic carbon (OC) content. The power function and R^2-values are included.

4.3.7 'Real-life' scenarios

Lastly, simulations were run at the specific application rates recommended for pesticides, as found in the literature, in order to depict a more 'realistic' scenario. The simulations were programmed for once-off applications and applications through recharge. A summary of the peaks in leaching rate are presented in Table 4.4 and the graphs are displayed in Appendix D2.6. As VLEACH does not account for biodegradation, soil half-lives reported in the literature are included in the table.

For all pesticides except for atrazine and lindane (at site B), contamination rates are significantly increased with yearly applications (Fig 4.15). A maximum rate of leaching is generally sustained as opposed to the decline that occurs with a once-off application. Due to the zero-Koc values of atrazine at both sites and lindane at site B, peaks in leaching rates are lower for yearly applications but the rate then fluctuates and stabilises (Fig 4.15 and Table 4.4). For pesticides with low mobility, such as carbaryl, dieldrin, lindane (site A), fenthion and parathion, the leaching rate continues to increase gradually when applied every year. Simazine is expected to leach at 1.42e –2 g/yr after 15 yrs at site A and 6.65e-2 g/yr after 5 yrs at site B, for a single application. When applied through recharge (yearly) simazine will leach at a rate of 2.03e –1 g/yr after 48 yrs at site A and 2.03e –1 g/yr after 12 yrs at site B (Fig 4.16 and Table 4.4). Furthermore, leaching of most pesticides is greater at site B than site A, due to the presence of more organic matter at site A and hence, greater organic sorption activity at site A than site B.

With reference to the soil half-lives, the rate of pesticide leaching is considerably lower than the rate of biodegradation in most cases (Table 4.4). Therefore simazine, along with other pesticides, will probably not have a major impact on groundwater, as biodegradation may prevent pesticides from reaching the water table. This highlights the important relationship between persistence and mobility in the overall assessment of groundwater impacts.

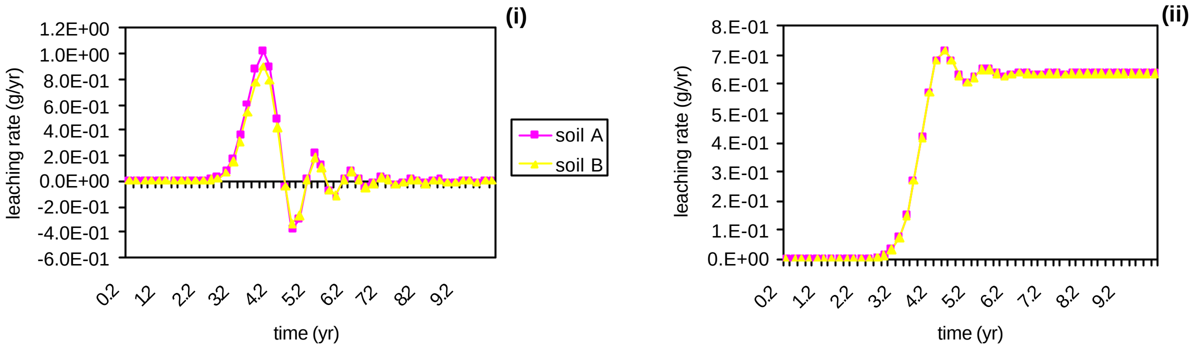


Figure 4.15 Leaching rate of atrazine over 10 yrs at both sites, applied (i) once-off and (ii) yearly

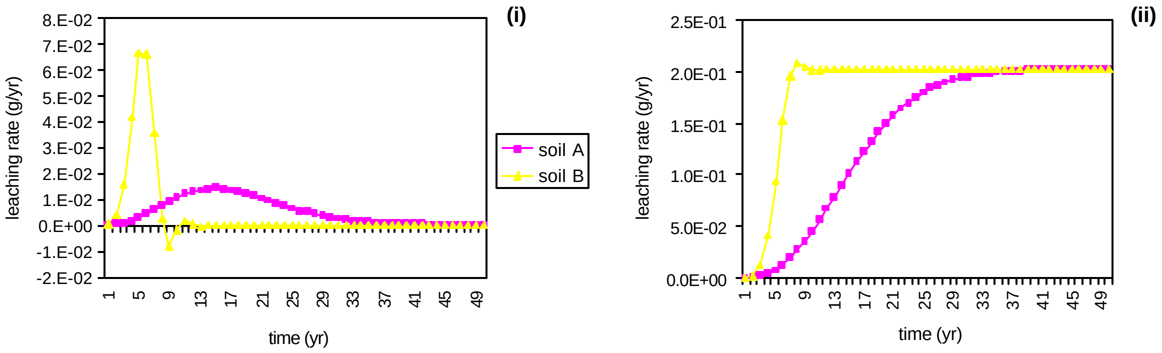


Figure 4.16 Leaching rate of simazine over 50 yrs at both sites, applied (i) once-off and (ii) yearly

Table 4.4 Peaks in the rate of leaching of pesticides applied at recommended rates (1) once and (2) through recharge, with the time taken to reach the peak (T_{peak}), the trend afterwards, the total simulation times in parentheses, and the pesticide-soil half-life's

Pesticide	**Site**	**Peak in leaching rate (g/yr)**	**T_{peak} (yr)**	**Trend after peak in leaching is reached**	**$T_{1/2}$ (days)**
Simazine	A1	1.42e –2	15	declines (50)	60 [1]
	A2	2.03e -1	48	constant	
	B1 B2	6.65e -2 2.03e -1	5 12	declines (50) constant	
Atrazine	A1	1.0216	3.8	declines (10)	60 [1]
	A2	7.14e -1	4.4	fluctuates until 8.6 yrs and constant at 6.37e –1 g/yr	
	B	Refer to site A		(10)	
Dimethoate	A1	5.83e -3	11	declines (50)	7 [1]
	A2	5.79e -2	33	constant	
	B1	7.91e -3	8	declines (50)	
	B2	5.79e -2	22	constant	
Lindane	A1	1.78e -4	116-144	declines (600)	690 [3]
	A2	6.47e -2	600	gradually increases	
	B1 B2	9.66e -2 7.71e -2	3.8 4.4	declines (10) fluctuates slightly until 6.87e –2g/yr at 10 yrs	
2,4-D	A1	1.63e -2	15, 16	declines (50)	10 [1]
	A2	2.49e -1	43	constant	
	B1	1.77e -2	13	declines (50)	
	B2	2.50e –1	42	constant	
Carbofuran	A1	7.36e -2	10	declines (50)	50 [1]
	A2	6.08e -1	28	constant	
	B1	1.94e -1	6	declines (50)	
	B2	6.08e -1	12	constant	
Carbaryl	A1	4.34e -3	32, 36	declines (200)	38 [2]
	A2	3.95e -1	200	gradually increases	
	B1	4.33e -3	32	declines (200)	

Pesticide	Site	Peak in leaching rate (g/yr)	T_{peak} (yr)	Trend after peak in leaching is reached	$T_{1/2}$ (days)
	B2	3.98e -1	200	gradually increases	
Dieldrin	A1	2.74e -5	600	gradually increases (600)	1000 [1]
	A2	5.98e -2	600	gradually increases	
	B1	3.94e -5	600	gradually increases (600)	
	B2	6.97e -2	600	gradually increases	
Fenthion	A1	1.27e -4	252-280	gradually declines (600)	34 [1]
	A2	7.63e -2	600	gradually increases	
	B1	9.06e -4	36	increases (600)	
	B2	1.05e -1	284	constant	
Parathion	A1	3.07e -8	240-288	gradually declines (600)	14 [1]
	A2	1.82e -5	600	gradually increases	
	B1	1.45e -7	52-56	declines (600)	
	B2	2.5e -5	556	constant	

1. Oregon State University Extension. Pesticide Properties Database, 1994
2. US EPA, National Pesticide Information Centre
3. US EPA, Office of Prevention of Pesticides and Toxic Substances, Re-registration Eligibility Decision for Lindane, Case 315 (See: http://www.epa.gov/oppsrrd1/REDs/lindane_red.pdf)

4.4 Conclusion & Recommendations

In summary, contamination tends to have a strongly inverse relationship with soil carbon content and pesticide Koc. The effect of Koc is also evident in the behaviour of atrazine and lindane, where a value of zero results in a distinctive change in the modelled pesticide behaviour. One can postulate from the model output that in the absence of sorption, atrazine and lindane will leach rapidly. It is important to note that Koc input values, taken from best-fit equations, cover a range of confidence levels (Weber at al., 2004), which may not be applicable to all conditions. Furthermore, these values are different from the experimental values obtained for simazine in Chapter 3. Comparisons of output between sites should, therefore, be made with caution, while a greater emphasis is placed on the determination of model sensitivity to Koc values, independent of site conditions. Experimental Kd values for simazine are used in SWAP and this may provide a more accurate basis for comparison between sites (Chapter 5).

Kh, water solubility and free air diffusion coefficient do not have any major impact on the results and the model is only slightly sensitive to soil water content and bulk density, and not at all sensitive to porosity.

Changes in depth to groundwater and recharge rate affect contamination as these factors are directly involved in the mechanism of leaching and water flux. Increasing initial contaminant concentrations by increasing the application rate, and applying pesticides as a concentration in recharge, has a considerable impact. However, changing the concentration by changing the depth of the application, has no effect at all as photolysis and other forms of degradation in the top soil layer are not simulated with VLEACH.

The major factors determining pesticide impact on groundwater and soil environments, as portrayed by the model, are therefore the pesticide sorption coefficient, soil organic carbon content, depth of water table and recharge rate, and the rate and frequency of pesticide applications. Aside from organic content, Koc values are also dependent on clay and pH in some cases, according to Weber et al. (2004). These relationships have been broadly categorised according to the different pesticide families. For example, Simazine and Atrazine are both weak bases and are the two pesticides to be related with clay and pH also. It is important to note that increasing the time-step of a simulation affects the model sensitivity, by underestimating the overall groundwater impacts.

Lastly, biodegradation, although it is not incorporated in VLEACH, is potentially a major determinant of groundwater contamination. When soil half-lives from the literature are considered in conjunction with the model estimates, one is inclined to question whether these chemicals pose any significant threat to groundwater at all. Thus, a good understanding of the relationship between persistence and mobility is central in the assessment of leaching by organic chemicals. The model assumes that pesticide sorption to organic carbon is the dominant chemical process taking place in the soil and the suitability of VLEACH should therefore be questioned on the basis that it does not account for biodegradation. Even though it is possible to achieve a broad estimation by considering half-lives in the data analysis, there remains a significant margin of error as this method cannot account for biodegradation occurring throughout the ‘lifespan’ of the chemical. Thus, for practical and effective management requirements, it is necessary for comprehensive models to be used, that integrate all the dominant processes playing a role in the contamination of pesticides. VLEACH gives a good indication of the role of sorption and is therefore a powerful tool to be used in preliminary and theoretical studies.

CHAPTER 5

The Soil-Water-Atmosphere-Plant (SWAP) Model, version 3.0.3, for Pesticide Transport in the Unsaturated Zone – Sensitivity Analysis

5.1 Introduction

SWAP is a sophisticated, mechanistic model designed to simulate the vertical transport of water, solutes and heat in variably saturated soils at both field and regional scales. The simulation of evapotranspiration, crop-growth and multi-level drainage are included in the functionality. Thus, SWAP enables the interaction between field balances and surface water management to be simulated, thus providing a valuable tool for the sustainable management of agricultural systems (Kroes and Dam, 2003).

This study entails an investigation into the basic functionality of SWAP from a groundwater-quality perspective. A sensitivity analysis of key input parameters was performed in order to assess the model capabilities in simulating pesticide transport in the unsaturated zone. This chapter includes a brief theoretical description of the model focusing on solute transport, a summary of the criteria used in selecting the input data, as well as key findings with regard to the major transport processes that determine the leaching of pesticides, with an emphasis on simazine. Recommendations have been made as to the practical uses of SWAP in the management of water-quality.

5.2 Theoretical background to the model

The reader is referred to the Reference Manual, SWAP version 3.0.3 by Kroes and Dam (2003) for a more comprehensive and mathematical description of the model. SWAP was developed on the premise that the unsaturated zone is central in global hydrological and energy cycles, as well as in the distribution of solutes within. Water fluxes are described by Richard's continuity equation, based on Darcy's principles of one-dimensional, vertical movement of water in soil due to spatial differences in soil water potential. Water fluxes are therefore determined by the soil water pressure head and hydraulic conductivity. Furthermore, the water balances are considered within infinitely small soil volumes and allow for the uptake of water by roots, built in the continuity equation used in SWAP.

Despite a certain degree of homogeneity in land-use and soil characteristics at the field scale, in reality, most soils are heterogeneous. SWAP accounts for soil heterogeneity due to spatial variation in soil hydraulic functions and preferential flow, in the case of macro-pores and water-repellent soils. Soil hydraulic functions are specified by the user for each soil layer and can be determined experimentally or obtained from existing data sets of similar soil types. Alternatively, field experiments can be conducted to determine the effective transport parameters that can be used for calibration and inverse modelling.

Root uptake is determined largely by crop growth, which is simulated based on the amounts of incoming solar radiation, crop-leaf area and photosynthetic leaf characteristics, taking into account, also, the effects of water-stress and salinity. SWAP accounts for diffusion of solutes due to concentration gradients, and solute dispersion caused by the variation of soil water velocity through pores of different shapes and sizes. The continuity and transport equation is therefore used to describe one-dimensional solute transport by convection, diffusion and dispersion, including also non-linear adsorption, first-order decomposition and root uptake. Initial boundary and top boundary conditions are specified by the user, in terms of solute concentrations in soil water, groundwater, irrigation and rainwater. The bottom boundary conditions are then determined by the fluxes occurring from the bottom compartment of the soil profile. SWAP integrates the principles that govern water and solute balances, with land-use management practices. The user is able to regulate the timing and amounts of sprinkler and irrigation systems, pesticide applications, as well as the design of drainage systems.

5.3 Input parameters

The primary input data file is given in Appendix E1. Additional input files used in this study include typical crop factors for a hypothetical orchard and three-year daily weather data for Stellenbosch. Key input parameters were analysed using simple baseline data, which were kept constant as far as possible. Such values include a standard groundwater level at 200cm depth and irrigation amounts of 60mm per year. Each parameter (pesticide application, drainage, etc.) was assessed independently, so as to provide a full understanding of the impacts on the model. Functions considered to be outside the scope of the study, were excluded from the simulations, like the simulation of crop growth, mobile-immobile transport, heat transport, lateral drainage, snow and frost, etc.

Parameters assessed were rate of pesticide application through irrigation and initial concentration, drainage of rainfall and irrigation, groundwater level, pesticide properties and soil hydraulic properties. The SWAP User Manual includes a Dutch nomenclature that links soil type with soil hydraulic functions (Kroes and Dam, 2003). As soil hydraulic functions were not included in the soil analysis in Chapter 2, the properties of the two W. Cape soils were not used as input data. Instead, three different soil types from the Dutch nomenclature, as well as the default soil type (Hupsel, Netherlands), resembling typical soil types occurring in the Western Cape, were used in the assessment of soil hydraulic properties.

In general, solute properties (dispersion length, diffusion coefficient, etc.) for a generic pesticide were used in the sensitivity analysis. However, experimentally determined Kd values from Chapter 3 were used in order to make predictions about the behaviour and fate of simazine under different soil conditions.

The primary output files used can be found in Appendix E2 and include (1) the cumulative solute balance components, (2) the overview of actual water and solute balance components, and (3) the final state variables. The data contained in these files and used for the analysis include the total flux of solutes from the bottom boundary and the total amount of solutes remaining in the soil (mg/cm^2) after the simulation period, as well as, the final soil profile of the solute (mg/cm^3). The bottom flux data in the second file mentioned above was used as a direct indication of pesticide leaching.

5.4 Results and Discussion

The output data included in this section have been summarised in graphs and tables. Table 5.1 includes the impact of initial and irrigation pesticide concentrations, drainage, groundwater level, key pesticide parameters and soil type, on the pesticide balance components. The data in Table 5.2 indicate some of the effects on the final soil profile of the solute.

5.4.1 Pesticide application and initial concentration

Increasing the irrigation and initial concentrations from 0.001 to 1.0 mg/cm^3 caused an increase in leaching and in the final pesticide mass remaining in the soil (Fig 5.1 and 5.2). Weather data were obtained from a weather station in Stellenbosch (W. Cape) and simulations were run for 1996. The irrigation concentration had a greater impact, as the quantities of irrigation are typically greater than the soil water content in the soil layer containing any initial pesticide. Initial pesticide in the soil can generally be attributed to residues from previous applications and would thus also be present in small quantities in the field. Furthermore, different patterns are evident for these two inputs. A greater proportion of pesticide leached to pesticide remaining in the soil, occurred for variations in initial pesticide concentrations, as compared to variations in pesticide applied through irrigation. This trend is also evident in the peaks and dips in concentration along the soil profile (Fig 5.2). For all irrigation concentrations of pesticide (C_{ir}), a major peak in concentration resulted in the shallower layers as pesticide application through irrigation occurs at regular intervals. When only initial concentrations of pesticide was present (C_{in}), smaller peaks occurred in the shallower layers, followed by a considerable increase toward the bottom of the soil profile. This indicates a greater proportion of pesticides leached, although the absolute levels of leaching with irrigation applications is greater.

5.4.2 Drainage

Increasing the irrigation amount from 1 to 20 cm per year caused an increase in pesticide leaching and a decline in the total pesticide remaining in the soil (Fig 5.3 and 5.4). The individual peaks and dips along the soil profile also dropped in concentration and increased in depth, with increased irrigation. This trend is visible for both total irrigation pesticide inputs of 0.6 and 6 mg/cm^3, with the output data differing by a factor of 10. Thus, solute leaching and solute amounts remaining in the soil are directly proportional to the amount of irrigation.

The effect of rainfall amount was evaluated by comparing the results of yearly simulations for 1996 (97 cm rainfall), 1997 (58 cm rainfall) and 1998 (63cm rainfall). Similar to the effect of irrigation and for both total irrigation inputs of 6 and 0.06 mg/cm^3, the highest rate of leaching and least total pesticide remaining in the soil, occurred in 1996 which had the highest rainfall (Fig 5.5). For 6 mg/cm^3, there was no leaching during 1997, while for 0.06 mg/cm^3, there was no leaching during 1997 and 1998. Hereafter, all simulations were run for 1996 only and the irrigation concentration of 6 mg/cm^3 was retained as a baseline value for most of the simulations, so that leaching rates may be substantial enough to allow for comparisons to be drawn.

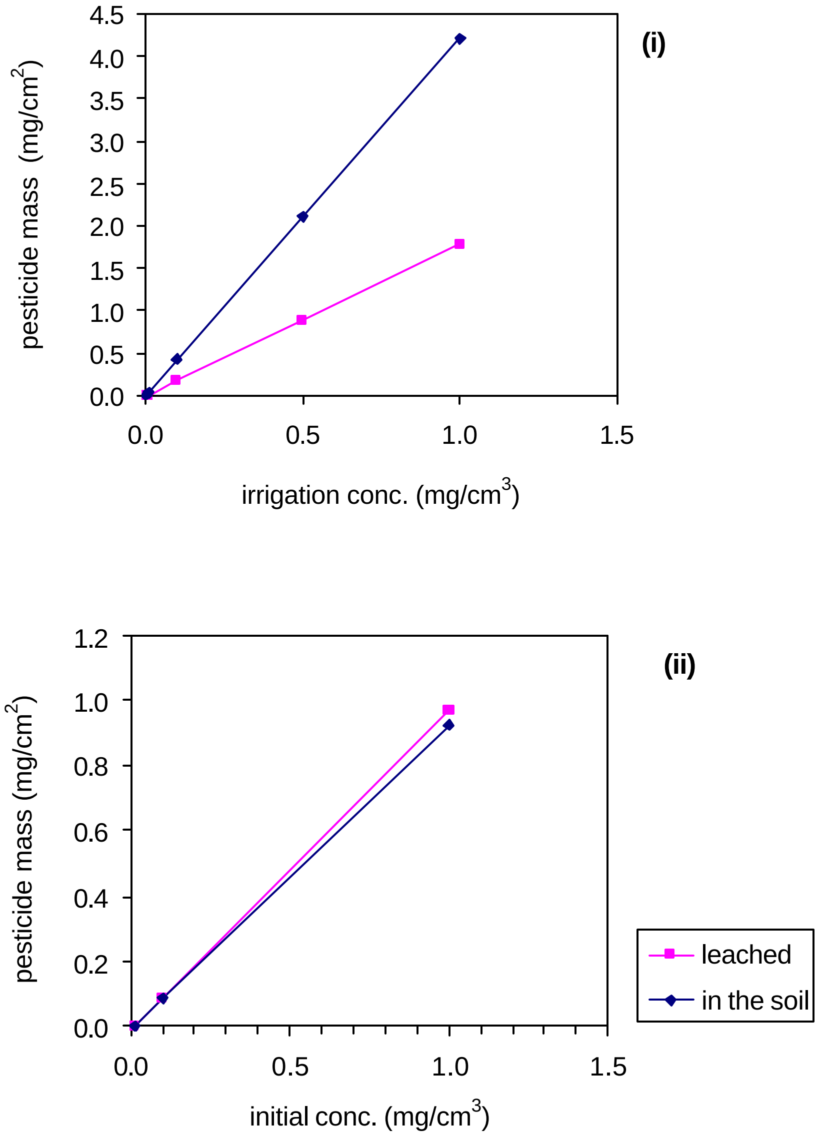


Figure 5.1 Total amounts of pesticide leached and pesticide remaining in the soil at the end of 1996, with varying (i) irrigation concentration and (ii) initial concentration, between 0.001 and 1.0 mg/cm^3.

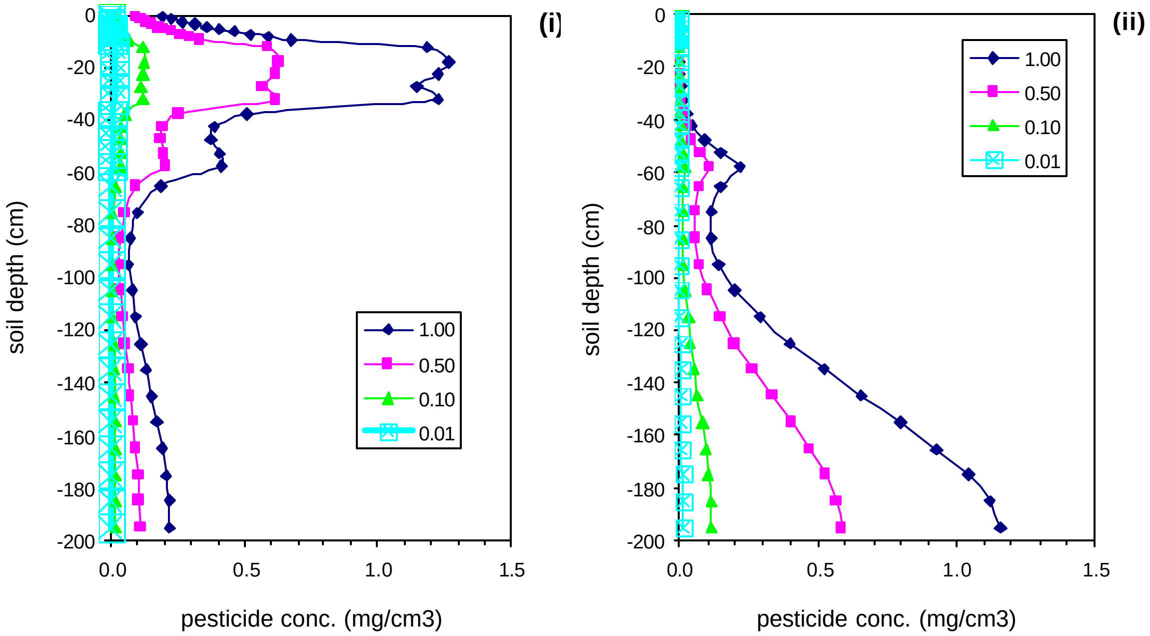


Figure 5.2 Soil profiles of pesticide at the end of 1996 with varying (i) irrigation concentration and (ii) initial concentration, between 0.01 and 1 mg/cm^3

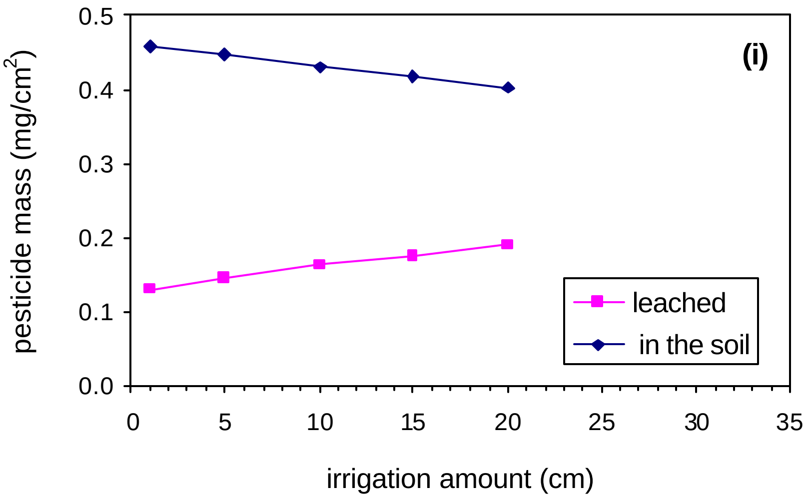


Figure 5.3(i) Total amounts of pesticide leached and pesticide remaining in the soil in 1996, when a total of 0.6 mg/cm^2 of pesticide was applied through varying amounts of irrigation (1-20 cm)

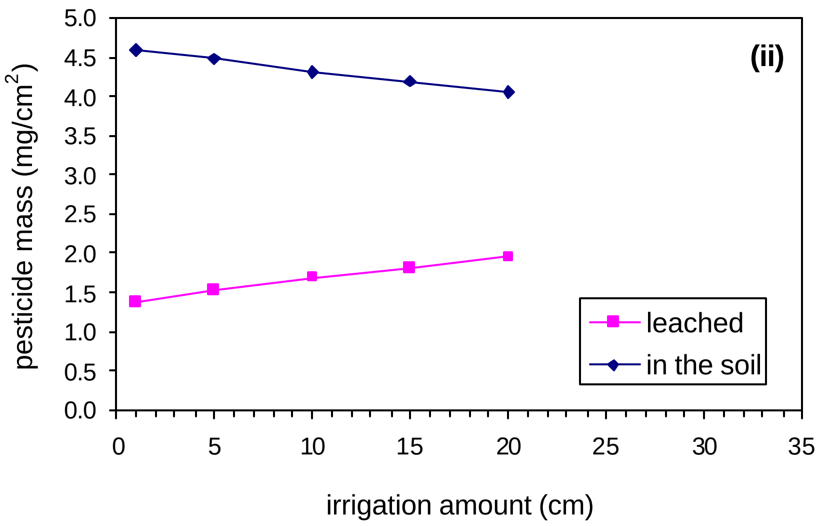


Figure 5.3(ii) Total amounts of pesticide leached and pesticide remaining in the soil in 1996, when a total of 6 mg/cm^2 of pesticide was applied through varying amounts of irrigation (1-20 cm)

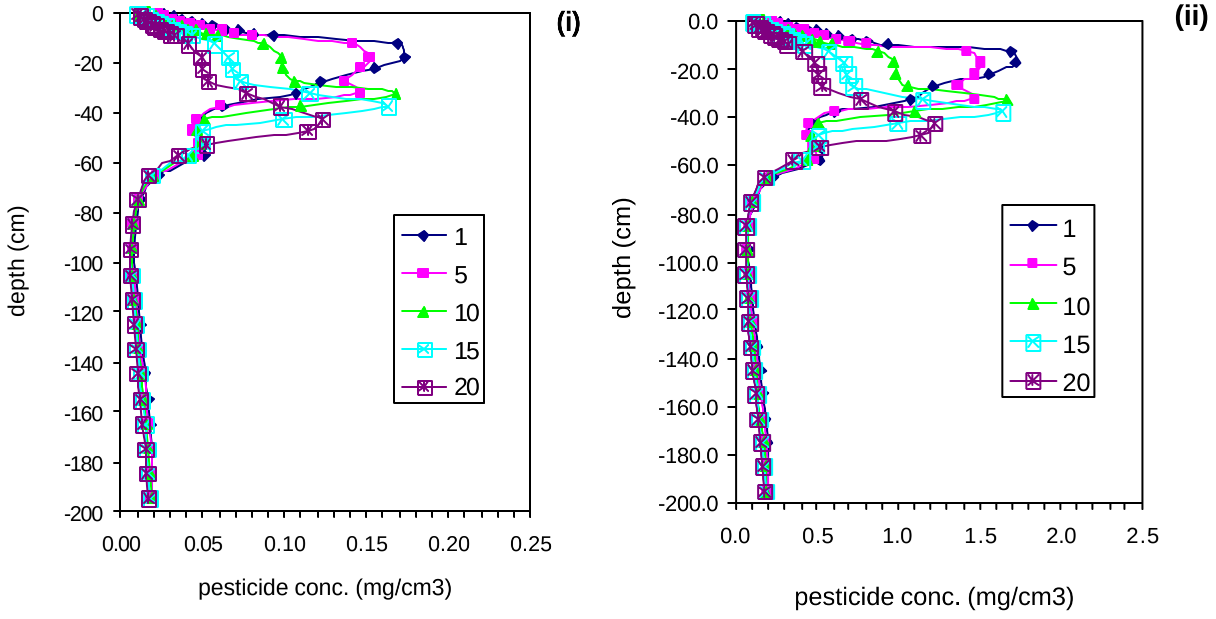


Figure 5.4 Final soil profiles of pesticide in 1996, with varying amounts of irrigation (1 –20 cm) for total pesticide applications of (i) 0.6 and (ii) 6 mg/cm^2

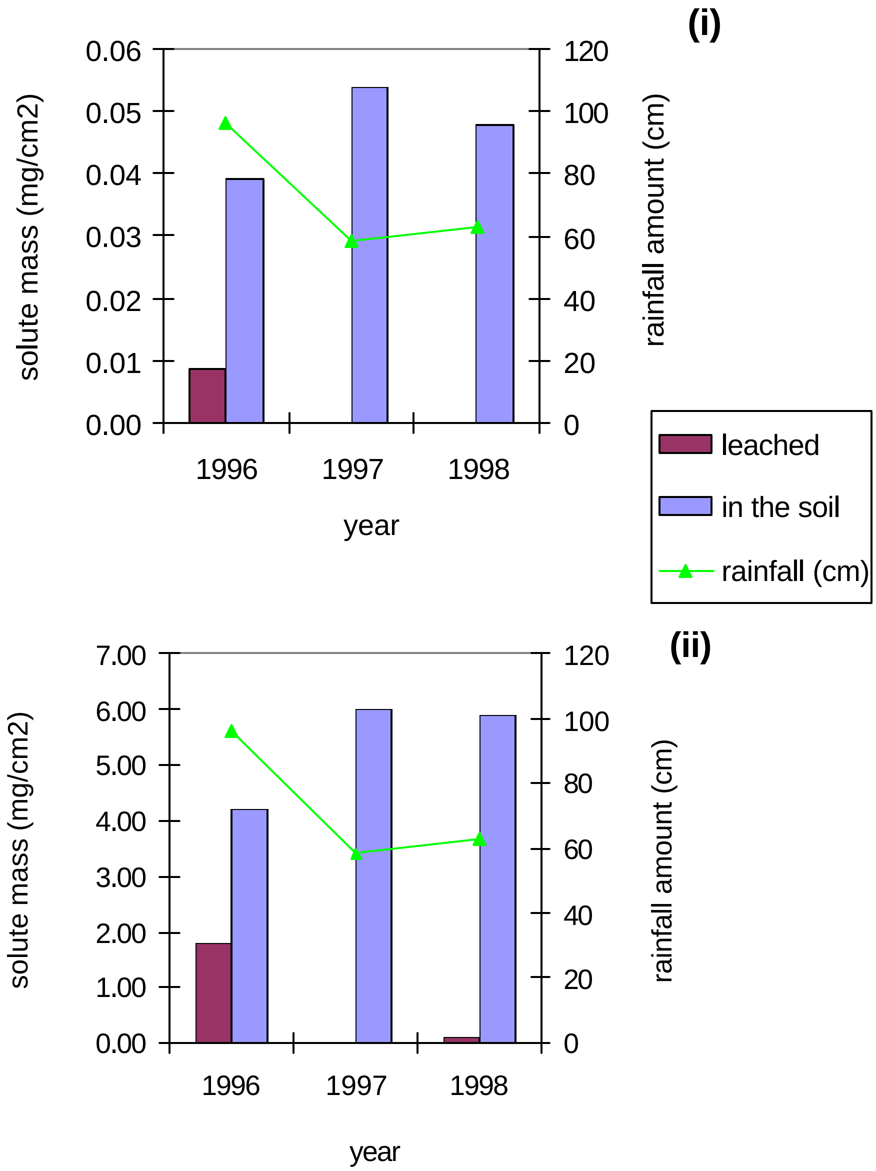
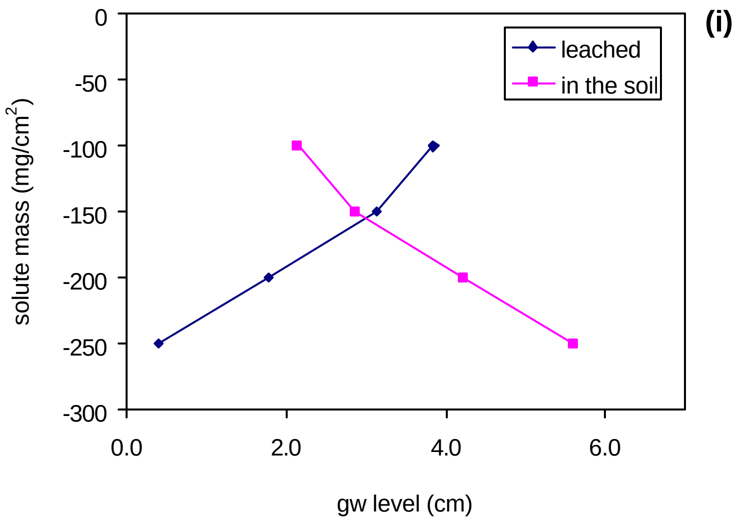


Figure 5.5 Total amounts of pesticide leached and pesticide remaining in the soil when a total of (i) 0.06 and (ii) 6 mg/cm^2 of pesticide was applied, with varying amounts of rainfall between 1996 and 1998

5.4.3 Groundwater level

Increasing the depth to groundwater from 100 to 250 cm caused a decline in leaching and an increase in pesticide remaining in the soil. However, the trends of concentrations along the soil profile do not change considerably with an increase in groundwater depth (Fig 5.6). On this basis, it can be assumed that variation in groundwater level does not impact considerably on the mechanisms of solute transport. Only at the highest groundwater level of 100cm, was the peak in solutes considerably higher than that of other groundwater levels.



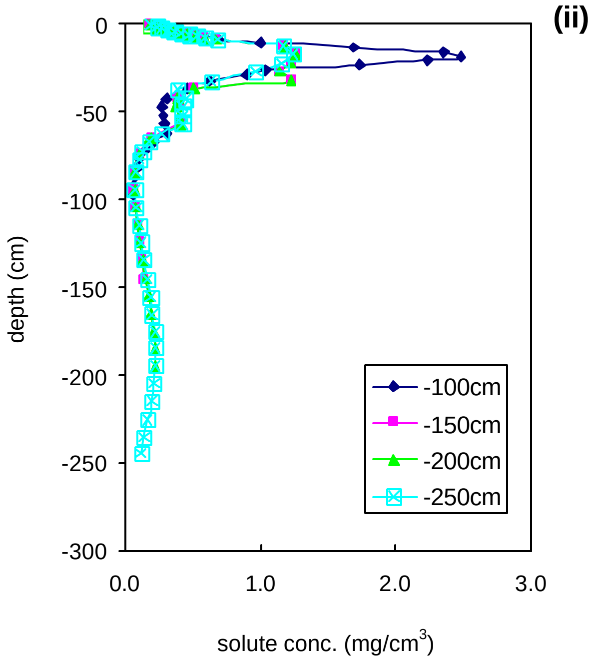


Figure 5.6 (i) Total amounts of pesticide leached and pesticide remaining in the soil, and (ii) the final soil profile in 1996, with an irrigation concentration of 1 mg/cm^3 and variation in groundwater level

5.4.4 Pesticide properties

Changing the parameters of solute diffusion and dispersion had little effect on the model output. Increasing the dispersion length from 2 to 37.5 cm while keeping the molecular diffusion coefficient constant at the default value of 0 cm^2/day, caused a gradual decline in leaching. This change occurs mainly between a length of 2 and 12.5 cm. Increasing the diffusion coefficient from 0 to 10 cm^2/day, with a default constant dispersion length of 5cm, did not have a considerable impact on the results (Fig 5.7(ii)).

Relative root uptake, defined by the root uptake preference factor (dimensionless), accounts for the selection of pesticide ions relative to the amount of extracted soil water. Increasing the root uptake factor of a generic pesticide, from 0 to 9, caused a dramatic reduction in both leaching and pesticide remaining in the soil (Fig 5.8). The results indicate there will be no leaching and only trace amounts of chemical in the soil once root uptake reaches a value of 3.

Increasing the pesticide decomposition potential from 0 to 10 per day caused a rapid increase in decomposition and decline in pesticide leaching and soil concentration (Fig 5.9), especially at low values of decomposition. According to the model, there would be no leaching above a value of 0.1 and most of the pesticide would be completely degraded for values greater than 1.

5.4.5 Soil hydraulic functions

When considered along a continuum of soil types, from silt-poor sandy soil, to silt-rich sandy soil, to clay soil types, leaching decreases and solutes remaining in the soil increase (Fig 5.10). In addition to the impact on convective transport, variation in soil texture is also expected to impact on sorption.

Simazine mobility was simulated for different soil conditions, using experimentally determined Kd values (Chapter 3) as a linear form of the Kf coefficient. Thus, Kd values of 1.2 and 1.4 were used for the silt-poor and silt-rich sand, respectively. No leaching occurred one year after application with a rainfall level of 100 cm (Fig 5.11) and soil concentrations are also relatively low (< 0.005 mg/cm^2). It was, therefore, concluded that the balance of simazine was adsorbed by the soil matrix and that the difference in the amount of simazine remaining in the soil, between sites, is due to the difference in simazine Kd values.

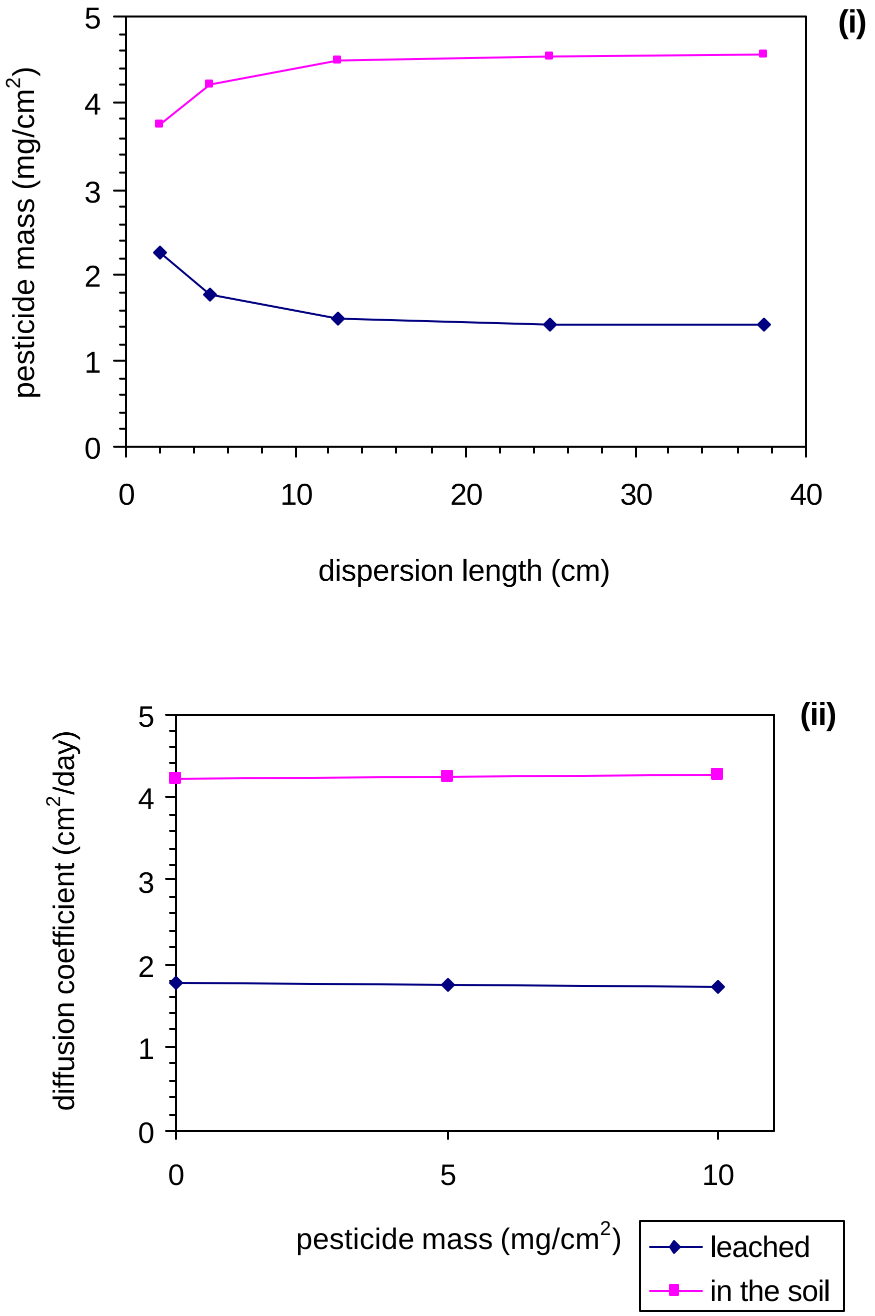


Figure 5.7 Total amounts of pesticide leached and pesticide remaining in the soil in 1996, with variation in the (i) dispersion length, and (ii) molecular diffusion coefficient of the pesticide

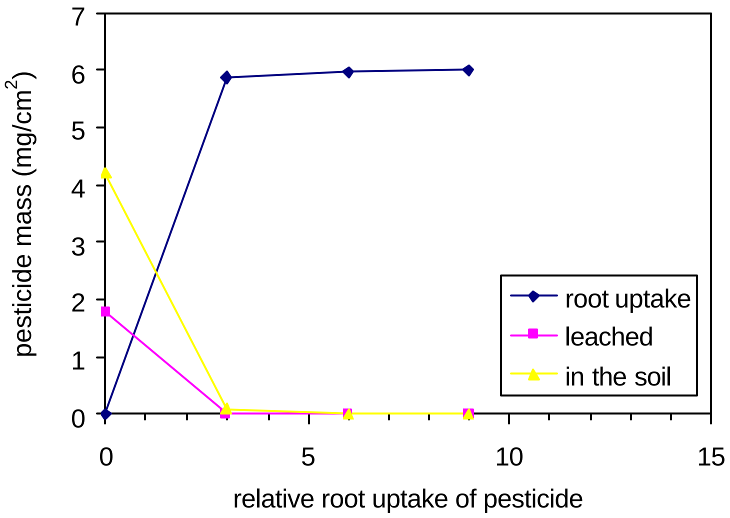


Figure 5.8 Total amounts of pesticide leached and pesticide remaining in the soil in 1996, with variation in the relative root uptake of pesticide

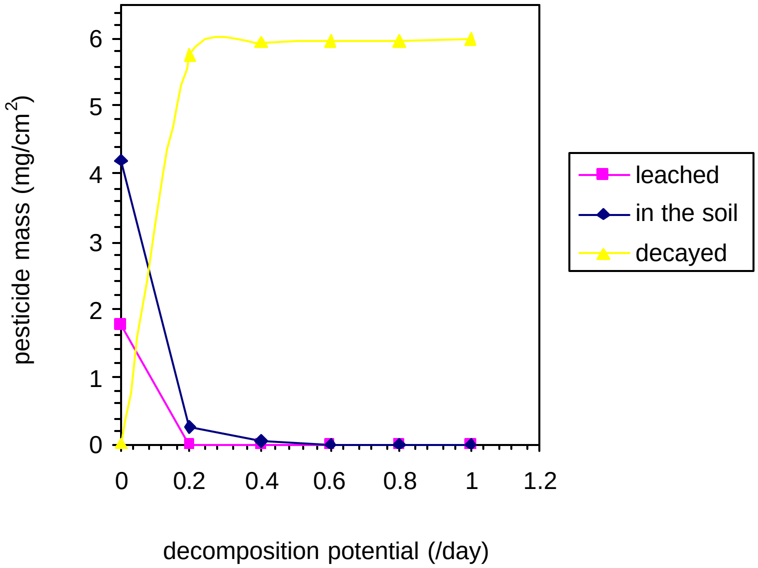


Figure 5.9 Total amounts of pesticide leached and pesticide remaining in the soil in 1996, with variation in the pesticide decomposition potential

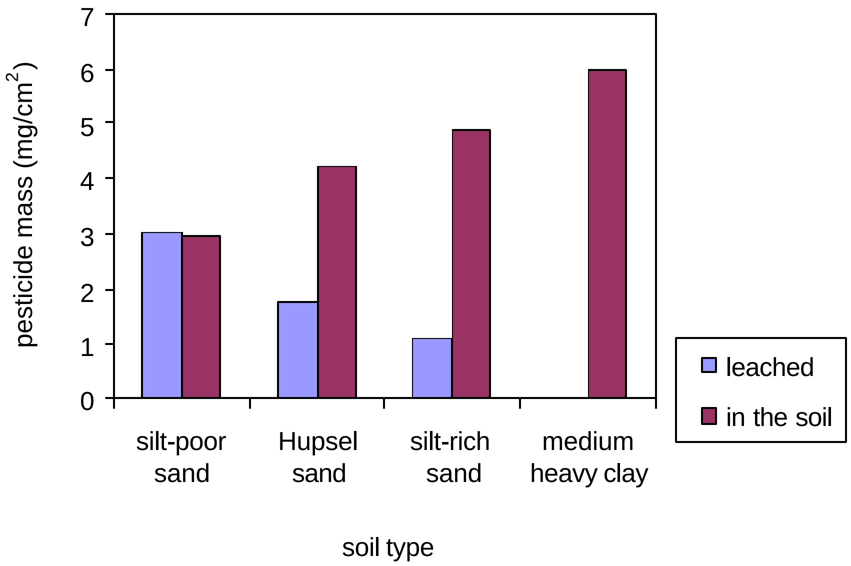


Figure 5.10 Total amounts of pesticide leached and pesticide remaining in the soil in 1996, for different soil types / hydraulic properties

Nevertheless, the silt-rich sand was found to retain more pesticide than the silt-poor sand and these soil types can be equated with the W. Cape soils, with the former representing soil B and the latter, soil A. Furthermore, the soil profile shows that simazine remains in the top soil layer (approx. 50 cm) and this is generally a favourable condition for root uptake and degradation of solutes, further reducing the leaching potential of simazine.

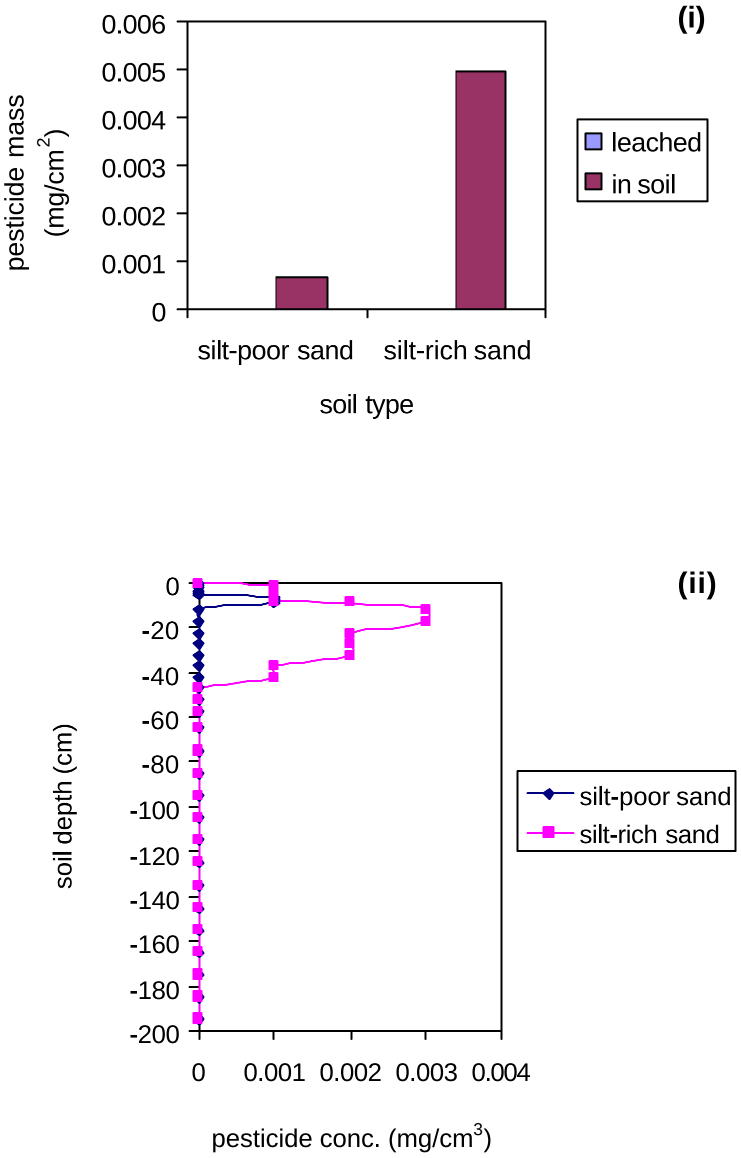


Figure 5.11 (i) The amounts of simazine leached and remaining in the soil and (ii) the final soil profile of simazine applied to a silt-poor and a silt-rich sandy soil in 1996

Table 5.1 A summary of the graphs depicting the total changes in pesticide leaching and pesticide remaining in the soil, with changes in pesticide applic. rate, initial conc., recharge rate, groundwater level, key pesticide properties and soil types

Input parameter	**Change in input parameter**	**Change in leaching (mg/cm^2)**	**Change in pesticide remaining in the soil (mg/cm^2)**
Application through irrigation (mg/cm^3)	0.001 - 1	0 - 1.78	2.97e-4[1] – 4.22e+0
Initial conc. (mg/cm^3)	0.01 – 10	0 - 9.84	2.34e-3[1] – 9.14e+0
Total irrigation (cm), C_{ir} = 0.6 Total irrigation (cm), C_{ir} = 6	1 - 20 1 – 20	1.3e-1 – 1.9e-1 1.39 – 1.96	4.57e-1 – 4.03e-1 4.61 – 4.04
Total rainfall (cm), C_{ir} = 6	‘96: 97 ’97: 58 ’98: 63	1.78 0 1.01e-1	4.22 5.99 5.89
Total rainfall (cm), C_{ir} = 0.06	‘96: 97 ’97: 58 ’98: 63	8.71e-3 0 0	3.93e-2 5.39e-2 4.77e-2
Depth to groundwater (cm) [2], C_{ir} = 6	100 - 250	3.84 – 0.39	2.15 – 5.60
Dispersion length (cm) Molecular diffusion coefficient (cm^2/day)	2 – 37.5 0 - 10	2.26 – 1.41 1.78 – 1.72	3.74 – 4.55 4.22 – 4.26
Relative uptake by roots	0 – 9	1.78 – 0.0	4.22 – 1.08E-03
Decomposition potential (per day)	0 – 10	1.78 – 0.0	4.22 – 0
Soil types	Silt-poor sand Hupsel sand Silt-rich to poor sand Medium heavy clay	3.02 1.78 1.10 0.0	2.98 4.22 4.89 5.99

C_{ir} – application through irrigation (mg/cm^3)

[1] negligible as there is no trace of pesticide in the soil profile at this irrigation concentration

[2] depth is represented here as increasing vertically downwards

Table 5.2 A summary of the graphs depicting changes in the final soil profiles of a generic pesticide, with changes in key input parameters. Soil depth (cm) is given in parentheses.

Input parameter	**Change in input parameter**	**Change in peaks concentration (mg/cm^3)**	**Change in dips in concentration (mg/cm^3)**
Irrigation concentration (mg/cm^3)	1 – 0.01	1.26 (17.5)[1] – 0.013 (17.5), 0 when Cir = 0.001	0.07 (95) – 0.001 (95)
Initial concentration (mg/cm^3)	10 – 0.1	2.2e-1(57.5) – 2e-3 (57.5)	1.15e-1 (85) – 1e-3 (85)
Total irrigation (cm), C_{ir} = 0.6	1 - 20	0.173 (17.5) – 0.123 (42.5)[2]	0.008 (95) – 0.006 (95)
Total irrigation (cm), C_{ir} = 6	1 – 20	1.73 (17.5) – 1.23 (42.5)	0.08 (95) – 0.06 (95)
Groundwater level (cm)[1], C_{ir} = 6	150 – 250 100	3.26 (17.5) – 1.24 (17.5) 2.48 (18.8)	0.07 (95) – 0.08 (95) 0.06 (92.5 – 97.5)

C_{ir} – application through irrigation (mg/cm^3)

[1] depth is represented here as increasing vertically downwards

5.5 Conclusions and Recommendations

In general, groundwater contamination predicted with SWAP, is sensitive to initial and irrigation concentrations, drainage, groundwater level, soil hydraulic properties and pesticide properties. Irrigation concentrations of pesticide have a greater impact on the output, than typically smaller initial concentrations. These two inputs also vary in terms of the patterns formed in the soil profile. The model also depicts the flushing action of drainage water that enhances the potential for leaching and reduces pesticide accumulation in the soil. Deeper groundwater levels are shown to decrease the leaching of solutes, yet do not cause any changes to the solute patterns in the soil profile. Soil types characterised by different soil hydraulic properties had a considerable effect on the output. As one might expect, the silt-rich and clay soil types were shown to limit leaching. The impact of soil hydraulic properties is mainly due to the effect on convection, as the major transport mechanism for solutes. However, soil properties could also impact on sorption mechanisms that determine the amount of pesticide available for leaching. Furthermore, in simulating the behaviour of simazine under different soil conditions, the model was sensitive to differences in simazine Kd values. The silt-rich sand, with a higher Kd value, was shown to retain considerably more pesticide than the silt-poor sand, with a lower Kd value. Pesticide decomposition and uptake by roots were also found to be dominant parameters affecting pesticide transport. However, diffusion and dispersion are shown to have little or no considerable impact.

The model predicts that simazine is not likely to leach within a year during which the pesticide is applied through irrigation, using an input data set that typically resembles conditions in the W. Cape. This outcome supports the assumption that simazine is not very mobile due to sorption onto organic matter and clay particles.

In conclusion, SWAP is a flexible tool that can simulate complex natural systems. By differentiating between initial and top pesticide boundary conditions, irrigation schedules and weather data, for example, it enables the use of detailed and accurate data relevant to a particular case study. Incorporation of the weather files as input data, further serves to enhance the accuracy of the model, making it possible to assess the soil and water impacts over a yearly basis, as well as over the long-term. Once the model has been validated for a study area, SWAP can be used to predict future impacts based on meteorological projections. Volatilisation, however, is not included in SWAP.

It is suggested by the authors that SWAP be used in combination with pesticide fate models such as PESTLA and PEARL, in order to account for more advanced mechanisms of solute transfer and transformation (Huygen et. al., 2000). The level of detail to be used, however, depends on the purposes of the study. It is thus important to perform a sensitivity analysis, calibration and validation, prior to selecting a model for use.

CONCLUSIONS

A literature review was done for the identification of priority pesticides in South Africa based on usage, pesticide properties and site characteristics. Most frequently encountered pesticides in the literature were chlorpyrifos (organophosphate), endosulfan (organochlorine), azinphos-methyl (organophosphate), atrazine (triazine), simazine (triazine), deltamethrin (pyrethroid), and penconazole (azole). Pesticide sales records from AVCASA also reflected high usage of triazines, organophosphates and organochlorines, but low usage of pyrethroids and azoles. The literature findings were thus considered to be an indication of pesticide usage and water contamination. In order to determine priority pesticides according to pesticide properties and site characteristics, properties of South African pesticides were reviewed and included in a database. Priority pesticides were ranked according to their leaching potential using a simple screening model (Rao et al., 1985). Leaching potential was found to be in decreasing order for chlorpyrifos, atrazine, endosulfan, simazine, azinphos-methyl and deltamethrin.

From the ranking, simazine was shown to have a moderate potential to leach, in comparison to other pesticides, such as, chlorpyrifos, atrazine and endosulfan. Nevertheless, simazine was identified as an example of a priority pesticide, based on the widespread use (sales) in orchards and vineyards in South Africa (particularly the W. Cape). Simazine is known to have relatively low mobility in soils, however, not much research has been done under local conditions, despite its widespread use.

From the review of models to predict pesticide leaching, it was found that state-of-the-art models, generally use the convection-dispersion equation to simulate water and pesticide fluxes in the soil profile, as well as the mobile/immobile phase to account for preferential flow. This is often coupled to sorption and decay of chemicals depending on temperature and soil moisture. Volatilisation from plant and soil surfaces can be modelled using Henry's constant, which is specific for the pesticide species.

For the determination of simazine sorption in selected soils of the W. Cape, soils were tested for physical and chemical properties, and pesticide sorption experiments were carried out to determine simazine sorption coefficients. The chemical analysis showed that soil B (Elgin) is a loamy sand with a higher cation exchange capacity and lower concentration of dissolved salts and organic carbon, than the sandy soil A (Bellville). The chemical properties of soil B tend to favour the stronger mechanisms of chemisorption, while the properties of soil A favour the weaker physical forces of hydrophobic sorption. The water retention curves showed that overall, soil B retains water better than soil A and, therefore, further enhances the potential for sorption due to an increase in the residence time of pesticides in the soil. Therefore, in summary, the Elgin soil is likely to have a greater immobilising effect on the compound.

The sorption isotherms were found to resemble a type of L class, for both soils. According to the classification system used, simazine is relatively weakly associated with water and will reach maximum adsorption on soil surfaces, forming a double homogenous layer around the particles. The linear Kd equations were the best-fit for the sorption data and Kd values were found to be within the same order of magnitude as the literature values. As expected from the outcomes of the soil analysis, Kd values were higher in the Elgin soil, than the Bellville soil.

The one-dimensional steady-state VLEACH model and the mechanistic, field and regional scale SWAP model were assessed for their capabilities in predicting pesticide leaching. VLEACH is highly sensitive to pesticide sorption coefficients and soil organic carbon content but does not simulate pesticide degradation, which is a dominant pesticide-related process. SWAP focuses on pesticide sorption and decomposition coefficients, and soil hydraulic properties, but does not simulate pesticide volatilisation.

VLEACH was used to model pesticide leaching based on typical soil conditions of the W. Cape and pesticide Koc values derived from the best-fit equations of Weber et al. (2004). The model predicted that simazine will leach at a rate of 2.03e –1 g/yr after 48 yrs at site A and 2.03e –1 g/yr after 12 yrs at site B, when applied through recharge. Leaching rates for most of the pesticides were greater at site B, than site A, due to the larger organic matter content of site A. This highlights the fact that VLEACH output is strongly determined by organic carbon content and sorption coefficients (Koc).

The experimentally determined soil properties and sorption coefficients (Kd) were used in SWAP and it was estimated that simazine is not likely to leach within one year during which the pesticide is applied through irrigation, for a typical data set of the W. Cape. In this case, however, SWAP may be limited by the duration of the simulations (maximum of 3 years). A longer series of weather data would be required to make predictions for a longer time period. However, biodegradation of simazine is likely to prevent further leaching after a period of one year. In the sensitivity analysis of SWAP, leaching was generally shown to be greater at soil A, than soil B. This outcome, in contrast to that of VLEACH, is in accordance with the outcomes of the soil analysis and sorption experiments. The results of the experimental work and the SWAP model is, therefore, in line with the assumption that simazine will not leach considerably in South African conditions. It is recommended, however, that the results of this study be validated with future leaching experiments. These outcomes do not imply that local studies regarding other priority pesticides in South Africa will necessarily be in accordance with international findings. Instead, validation studies should be carried out for all priority pesticides registered for use.

The lack of data on pesticide degradation in local environments was found to be a major obstacle in quantifying pesticide impacts, as it is known to play a strong role in pesticide balance. Herein lies a need for potentially long-term experimental studies that are well controlled to represent field environmental conditions. In general, there is a need for monitoring programmes to collect reliable data, so that all pesticide processes may be quantified, including those occurring in sub-soils.

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APPENDIX A

Outcomes of the literature review

A1 Pesticides identified in the literature review for South Africa

Type of source	Pesticide	Examples	References
Gardens and agricultural peri-urban areas	1,2-dichlorobenzene	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	1,4-dichlorobenzene	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	2-methylnaphtalene	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Garden and agricultural peri-urban areas	2,4 D (2,4 DDD)	1) 5.5 ng L^{-1} in marine water and 0.6 ng g^{-1} in freshwater sediments in Eastern Cape. 2) Twenty-first most used pesticide in southern Africa in 1989.	Fatoki and Awofulu (2003) London and Myers (1995a)
Gardens and agricultural peri-urban areas	4-chloro-3,5-dimethylphenol	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Aldicarb	1) Twenty-second most used pesticide in southern Africa in 1989. 2) High usage in Hex River Valley (Western Cape).	London and Myers (1995a) Weaver (1993)
Garden and agricultural peri-urban areas	Aldrin (banned)	0.6 ng g^{-1} in freshwater sediments in Eastern Cape.	Fatoki and Awofulu (2003)
Gardens and agricultural peri-urban areas	Alphamethrin	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Agricultural peri-urban areas and vineyards	Amitrole	Used until 20 years ago in southern Africa	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Anthracene	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Atrazine	1) Identified in surface water samples (Johannesburg). 2) Measured residues in water and fish. 3) Between 0.1 and 11.6 µg L^{-1} of atrazine and related triazines, depending on the season, in northern and central part of South Africa.	Grange et al. (2003) Bouwman et al. (2003) Du Preez et al. (2003) Weaver (1993)

Type of source	Pesticide	Examples	References
Gardens and agricultural peri-urban areas	Atrazine	4) Regularly detected in surface and groundwaters of the Vaalharts Irrigation Scheme.	
Agricultural peri-urban areas and orchards	Azinphos-methyl	1) From 0.08 µg L^{-1} to 0.7 µg L^{-1} in water of constructed wetlands at Lourens river (Cape Town).	Bennett et al. (2003)
		2) Loads of 27.8 g via runoff and 0.69 g via spray drift from 400 ha per event.	Dabrowski and Schulz (2003a and b)
		3) Measured predominantly in water samples.	Dabrowski et al. (2003)
		4) 0.2 µg L^{-1} in Western Cape streams.	Schulz and Dabrowski (2003)
		5) Detected in surface and groundwaters of Grabouw (Western Cape).	Solomons et al. (2003), London et al. (2000)
		6) 0.6 µg L^{-1} in water samples and 152 µg kg^{-1} in suspended sediments from Lourens river (Western Cape).	Dabrowski et al. (2002a)
		6) From 0 to 0.2 µg L^{-1} in water samples and from 0 to 27.9 µg kg^{-1} in suspended sediments from Lourens river (Western Cape).	Dabrowski et al. (2002b)
		7) Up to 0.38g L^{-1} in water samples and up to 244µg kg^{-1} in suspended sediments from Lourens river (Western Cape).	Schulz et al. (2001)
		8) Thirteenth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
		9) Detected in farm dams in Elgin, Western Cape.	Davies (1997)
		10) High pollution likelihood.	London et al. (2000)
Agricultural peri-urban areas and pome fruit trees	Azocyclotin	Eighth most used pesticide in the pome fruit industry in Western and Eastern Cape in 1989.	London and Myers (1995b)
Gardens and agricultural peri-urban areas	Benomyl	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Garden and agricultural peri-urban areas	BHC	1) Measurement in fish tissue in Crocodile River, Mpumalanga.	Heath et al. (2003)
	ß - BHC	2) 450 ng L^{-1} in marine water and 184 ng g^{-1} in freshwater sediments in Eastern Cape.	Fatoki and Awofulu (2003)
Gardens and agricultural peri-urban areas	Bromopropylate	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Bromoxynil	Eighteenth most used pesticide in southern Africa in 1989.	London and Myers (1995a)

Type of source	Pesticide	Examples	References
Gardens and agricultural peri-urban areas	Camphor	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Captab	Tenth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Captan	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Carbaryl	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Carbofuran	Detected in surface and groundwaters of the Vaalharts Irrigation Scheme.	Weaver (1993)
Agricultural peri-urban areas and orchards	Chlorpyrifos	1) From 0.8 µg kg^{-1} to 12 µg kg^{-1} in sediment cores of wetlands constructed along Lourens River (Western Cape). 2) Measured predominantly in suspended particle samples. 3) Measured in surface and groundwaters of Hex River Valley, Grabouw and Piketberg (Western Cape). 4) Applied to grapevine (Western Cape). 5) 0.19 µg L^{-1} in water samples and 245 µg kg^{-1} in suspended sediments from Lourens river (Western Cape). 6) From 0 to 0.03 µg L^{-1} in water samples and from 0 to 43.6 µg kg^{-1} in suspended sediments from Lourens river (Western Cape). 7) <0.01 µg L^{-1} in water samples and up to 344 g kg^{-1} in suspended sediments from Lourens river (Western Cape). 8) 19.13 µg L^{-1} in water samples from Hex river valley (Western Cape). 9) Eleventh most used pesticide in southern Africa in 1989. 10) Detected in farm dams in Elgin, Western Cape. 11) High usage in Hex River Valley (Western Cape).	Bennett et al. (2003) Dabrowski et al. (2003) Solomons et al. (2003), London et al. (2000) London and Meyers (1995b) Dabrowski et al. (2002a) Dabrowski et al. (2002b) Schulz et al. (2001) McGregor (1999) London and Myers (1995a) Davies (1997) Weaver (1993)
Gardens and agricultural peri-urban areas	Citrus bands	Sixth most used pesticide in southern Africa in 1989.	London and Myers (1995a)

Type of source	Pesticide	Examples	References
Agricultural peri-urban areas, orchards and vineyards	Copper oxychloride	1) Commonly applied as fungicide in South African vineyards and orchards. 2) Copper salts are the fourth most used pesticides in southern Africa in 1989. 3) High usage in Hex River Valley (Western Cape).	Snyman et al. (2003), London et al. (2000) London and Myers (1995a) Weaver (1993)
Gardens and agricultural peri-urban areas	Cyfluthrin	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Cyhalothrin	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Agricultural peri-urban areas, vineyards and sugarcane	Cypermethrin a – cypermethrin	1) High usage in Hex River Valley (Western Cape). 2) Effect on non-target organisms.	Weaver (1993) Leslie and Baxter (2003)
Garden and agricultural peri-urban areas	DDE	Measurement in fish tissue in Crocodile River, Mpumalanga.	Heath et al. (2003)
Malaria mosquito control	DDT (use restricted to malaria mosquito control)	1) Measured residues in water and fish. 2) Measured residues in surface waters in the Ubombo and Ingwavuma districts in KwaZulu-Natal.	Bouwman et al. (2003) Sereda and Meinhardt (2003)
Malaria mosquito control, gardens and agricultural peri-urban areas	Deltamethrin	1) Measured residues in surface waters in the Ubombo and Ingwavuma districts in KwaZulu-Natal. 2) Detected in surface and groundwaters of Hex River Valley (Western Cape). 3) 1.4 µg L^{-1} in water samples from Lourens river (Western Cape). 4) High usage in Hex River Valley (Western Cape).	Sereda and Meinhardt (2003) Solomons et al. (2003), London et al. (2000) Dabrowski et al. (2002a) Weaver (1993)
Gardens and agricultural peri-urban areas	Diazinon	Tentatively identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Diazonin	Detected in KaalSpruit river (Midrand).	Papo and Mathebula (2003)
Gardens and agricultural peri-urban areas	Dibutylphthalate	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Dichlorovos	High usage in Hex River Valley (Western Cape).	Weaver (1993)

Type of source	**Pesticide**	**Examples**	**References**
Tsetse fly control	Dieldrin (banned)	1) Measured residues in water and fish. 2) Measurement in fish tissue in Crocodile River, Mpumalanga.	Bouwman et al. (2003) Heath et al. (2003)
Gardens and agricultural peri-urban areas	Diethylphthalate	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Dimethoate	1) Fifteenth most used pesticide in southern Africa in 1989. 2) High usage in Hex River Valley (Western Cape).	London and Myers (1995a) Weaver (1993)
Gardens and agricultural peri-urban areas	Dimethylphthalate	Identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Dimethylpyridine	Tentatively identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Dinitro-ortho-cresol (DNOC)	Twentieth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Dinocap	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Diquat	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Dithiocarbamate	Extensively used fungicide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	EDB	Ninth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Endosulfan a, b and sulphate	1) From 0.8 µg kg^{-1} to 12 µg kg^{-1} in sediment cores of wetlands constructed along Lourens River (Western Cape). 2) Measured predominantly in suspended particle samples. 3) 0.83 µg L^{-1} and 3.16 µg L^{-1} in surface and groundwaters of Hex River Valley, Grabouw and Piketberg (Western Cape). 4) Applied to grapevine (Western Cape). 5) 0.35 µg L^{-1} in water samples and 273 µg kg^{-1} in suspended sediments from Lourens river (Western Cape). 6) From 0 to 0.3 µg L^{-1} in water samples and from 0 to 34.75 µg kg^{-1} in suspended sediments from Lourens river (Western Cape).	Bennett et al. (2003) Dabrowski et al. (2003) Solomons et al. (2003), London et al. (2000) London and Meyers (1995b) Dabrowski et al. (2002a) Dabrowski et al. (2002b) Schulz et al. (2001)

Type of source	Pesticide	Examples	References
		7) Up to 0.16 µg L^{-1} in water samples and up to 245 µg kg^{-1} in suspended sediments from Lourens river (Western Cape). 8) 1.794 µg L^{-1} in water samples from Hex river valley (Western Cape). 9) Nineteenth most used pesticide in southern Africa in 1989. 10) Detected in 28 out of 29 farm dams in Elgin, Western Cape. 11) Low usage in Hex River Valley (Western Cape).	McGregor (1999) London and Myers (1995a) Davies (1997) Weaver (1993)
Gardens and agricultural peri-urban areas	EPTC	Detected in surface and groundwaters of the Vaalharts Irrigation Scheme.	Weaver (1993)
Gardens and agricultural peri-urban areas	Ethylene dibromide	Extensively used nematicide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Fenamiphos	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Fenarimol	Detected in surface and groundwaters of Hex River Valley (Western Cape).	Solomons et al. (2003), London et al. (2000)
Gardens and agricultural peri-urban areas	Fenthion	1) Detected in thorn bush ecosystems. 2) High usage in Hex River Valley (Western Cape).	Van der Walt and Badenhorst (2003) Weaver (1993)
Gardens and agricultural peri-urban areas	Fenvalerate	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Folpet	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Formothion	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Glyphosate	1) Fifth most used pesticide in southern Africa in 1989. 2) High usage in Hex River Valley (Western Cape).	London and Myers (1995a) Weaver (1993)
Gardens and agricultural peri-urban areas	Heptachlor (banned)	Measurement in fish tissue in Crocodile River, Mpumalanga.	Heath et al. (2003)
Gardens and agricultural peri-urban areas	Hexaconazole	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Isobutylphthalate	Tentatively identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Iprodione	1) Detected in surface and groundwaters of Grabouw (Western Cape).	Solomons et al. (2003), London et al. (2000)

Type of source	Pesticide	Examples	References
		2) Extensively used in Western Cape. 3) High usage in Hex River Valley (Western Cape).	London et al. (2000) Weaver (1993)
Gardens and agricultural peri-urban areas	Lindane	Measurement in fish tissue in Crocodile River, Mpumalanga.	Heath et al. (2003)
Agricultural peri-urban areas and vineyards	Mancozeb	1) Second most used pesticide in southern Africa in 1989. 2) High usage in the Hex River Valley (Western Cape).	London and Myers (1995a) Weaver (1993)
Gardens and agricultural peri-urban areas	MCPA	1) Eighth most used pesticide in southern Africa in 1989. 2) High usage in Hex River Valley (Western Cape).	London and Myers (1995a) Weaver (1993)
Gardens and agricultural peri-urban areas	Metaldehyde	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Agricultural peri-urban areas and pome fruit trees	Methidathion	1) Sixth most used pesticide in the pome fruit industry in Western and Eastern Cape in 1989. 2) High usage in Hex River Valley (Western Cape).	London and Myers (1995b) Weaver (1993)
Gardens and agricultural peri-urban areas	Methiocarb	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Metiram	Sixteenth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Mevinphos	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas, carrier of other pesticides	Mineral oil	Third most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Nuarimol	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	o-hydroxybiphenyl	Tentatively identified in surface water samples (Johannesburg).	Grange et al. (2003)
Gardens and agricultural peri-urban areas	Omethoate	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Oryzalen	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Paraquat	High usage in Hex River Valley (Western Cape).	Weaver (1993)

Type of source	**Pesticide**	**Examples**	**References**
Gardens and agricultural peri-urban areas	Parathion	1) Used until 20 years ago in southern Africa. 2) Detected in farm dams in Elgin, Western Cape.	London and Myers (1995a) Davies (1997)
Gardens and agricultural peri-urban areas	Paraquat	Fourteenth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas, vineyards	Penconazole	1) Detected in surface and groundwaters of Grabouw (Western Cape). 2) Detected in farm dams in Elgin, Western Cape. 3) High usage in Hex River Valley (Western Cape).	Solomons et al. (2003), London et al. (2000) Davies (1997) Weaver (1993)
Gardens and agricultural peri-urban areas	Pirifenox	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Prochloraz	Seventeenth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Procymidone	1) 9 µg L^{-1} in water samples from Lourens river (Western Cape). 2) Low usage in Hex River Valley (Western Cape).	Dabrowski et al. (2003) Weaver (1993)
Gardens and agricultural peri-urban areas	Profenofos	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Propetamphos	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Propineb	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Propoxur	High usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas, orchards	Prothiofos	1) From 0.8 µg kg^{-1} to 12 µg kg^{-1} in sediment cores of wetlands constructed along Lourens River (Western Cape). 2) Detected in surface and groundwaters of Hex River Valley (Western Cape). 3) High usage in Hex River Valley (Western Cape).	Bennett et al. (2003) Solomons et al. (2003), London et al. (2000) Weaver (1993)
Gardens and agricultural peri-urban areas	Simazine	1) Seventh most used pesticide in southern Africa in 1989. 2) High usage and pollution likelihood in the Western Cape. 3) High usage in the Hex River Valley (Western Cape). 4) Triazines most commonly used pesticide in South Africa	London and Myers (1995a) London et al. (2000) Weaver (1993) Naidoo and Buckley (2003)

Type of source	Pesticide	Examples	References
Gardens and agricultural peri-urban areas	Sulphur	Most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Tartar emetic	Twelfth most used pesticide in southern Africa in 1989.	London and Myers (1995a)
Gardens and agricultural peri-urban areas	Triadimefon	Low usage in Hex River Valley (Western Cape).	Weaver (1993)
Gardens and agricultural peri-urban areas	Vanmidothion	1) Fourth most used pesticide in the pome fruit industry in Western and Eastern Cape in 1989. 2) High usage and pollution likelihood in the Western Cape.	London and Myers (1995b) London et al. (2000)
Gardens and agricultural peri-urban areas	Vinclozolin	High usage in Hex River Valley (Western Cape).	Weaver (1993)

A2 Total sales of pesticides in South Africa

Including major groups of pesticide used for crop protection from 1994 to 2000, excluding exports (personal communication, Jan Kleynhans, AVCASA)

DEFOLIANTS	Active ingredient (kg or L)						
	1994	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**
UNCLASSIFIED	1,832	2,106	3,846	2,544	288	0	0
INORGANIC / ORGANOMETALLIC	1,942	1,980	11,243	7,484	14,304	16,976	3,156
UREA / THIONYLUREA	55	6	64	144	659	125	0
BENZOIC ACID DERIVATIVE	47	218	0	192	0	0	0
ORGANOPHOSPHOROUS	1,356	74	89	0	0	0	0
TOTAL	**5,232**	**4,385**	**15,243**	**10,364**	**15,251**	**17,101**	**3,156**

PLANT GROWTH REGULANTS	Active ingredient (kg or L)						
	1994	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**
ALIPHATIC ACID	4,222	13,964	12,377	6,901	6,691	8,107	5,784
HYDROCARBON	1,058,940	1,071,630	1,283,328	1,298,736	1,211,891	1,408,788	1,937,080
UNCLASSIFIED	31,389	24,289	15,504	36,855	105,930	74,897	78,771
ALIPHATIC AMINE / AMIDE	23,261	29,590	20,171	42,784	85,163	108,795	114,648
HETEROCYCLIC DERIVATIVE	578	2,965	3,362	3,356	5,911	4,539	3,872
ORGANOPHOSPHOROUS	5,932	11,782	15,714	12,463	21,773	33,596	34,858
BENZOIC ACID DERIVATIVE	7,832	2,770	2,434	4,336	3,026	509	4,313
INORGANIC / ORGANOMETALLIC	791	11,350	11,115	8,935	40,198	53,304	24,754
ANILINE / ACETANILIDE	2,522	1,159	2,292	1,464	4,525	4,705	1,770
FENOLIC	39,710	40,186	48,125	48,703	43,069	49,697	59,284
TOTAL	**1,175,177**	**1,209,686**	**1,414,422**	**1,464,533**	**1,528,176**	**1,746,938**	**2,265,132**

HERBICIDES	Active ingredient (kg or L)						
	1994	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**
TRIAZINE	3,140,263	2,800,653	3,611,219	3,454,238	3,823,982	3,083,363	2,809,251
ANILINE / ACETANILIDE	1,805,250	1,684,775	1,509,342	2,230,840	2,250,696	3,537,081	2,635,976
ORGANOPHOSPHOROUS	594,327	790,424	819,260	1,480,278	1,524,090	1,937,042	1,965,452
ALIPHATIC ACID	192,934	209,918	233,665	227,487	205,216	289,582	249,077
PYRIDINE DERIVATIVE	246,865	279,009	269,713	412,721	236,187	215,782	202,098
UREA / THIONYLUREA	316,246	282,626	263,711	312,330	374,221	443,737	357,367
HYDROXYBENZONITRILE	144,680	190,075	231,994	192,811	133,942	168,393	165,202
UNCLASSIFIED	89,773	97,69	78,802	97,260	67,791	70,945	55,677
FENOLIC	310,083	371,801	402,708	454,225	406,803	269,279	440,701
IMIDAZOLE	9,325	10,410	8,734	17,152	24,183	14,200	23,150
CARBAMATE / THIOCARBAMATE	548,457	435,462	404,570	274,057	285,142	278,131	333,979
ALIPHATIC AMINE / AMIDE	89,590	80,068	20,952	48,113	64,603	88,071	39,801
HETEROCYCLIC DERIVATIVE	14,607	15,750	7,513	13,507	18,292	11,746	9,997
INORGANIC / ORGANOMETALLIC	84,755	105,764	53,680	190,343	227,943	231,614	176,900
BENZOIC ACID DERIVATIVE	24,542	31,159	4,666	22,826	11,476	3,191	1,515
TOTAL	**7,611,697**	**7,287,894**	**7,920,528**	**9,428,189**	**9,654,566**	**10,642,156**	**9,466,144**

FUNGICIDES	Active ingredient (kg or L)						
	1994	1995	1996	1997	1998	1999	2000
TRIAZINE	84,338	89,341	120,851	150,359	100,577	104,477	1,794,521
CARBAMATE / DITHIOCARBAMATE	975,432	1,513,408	1,669,435	2,651,093	2,488,899	2,325,391	2,914,972
INORGANIC ORGANOMETALLIC	1,898,671	3,109,300	3,143,195	3,503,251	3,371,273	3,382,832	3,531,944
BENZIMIDAZOLE	56,156	67,240	80,782	106,034	131,627	110,291	119,098
PYRIMIDINE / PYRIDINE	11,854	13,694	18,948	29,453	19,386	19,022	20,712
UNCLASSIFIED	96,916	101,700	131,792	141,444	126,938	115,580	95,798
DICARBOXIMIDE	20,841	27,210	12,263	27,738	27,443	27,392	20,743
ORGANOCHLORINE	148,533	220,408	230,073	172,852	190,587	159,399	243,854
ORGANOPHOSPHOROUS	30,296	33,166	42,580	101,793	62,181	24,588	28,003
AMINE / AMIDE	12,974	18,579	32,870	17,911	17,685	7,875	8,230
PHENOLIC	5,107	5,898	5,645	6,882	5,993	7,357	8,374
UREA	3,552	5,404	8,396	9,335	16,877	9,795	11,276
ACYLALANINE	2,602	1,589	2,765	3,909	771	1,865	1,423
TRIAZOLE	4,426	4,194	8,949	4,560	4,007	2,523	1,122
MINERAL OIL	0	743	225	2,025	0	3,749	1,674
BIOLOGICAL	0			0	91	0	0
STROBY	0	0	0	0	9,398	8,041	7,141
	3,351,696	**5,211,875**	**5,508,769**	**6,928,639**	**6,573,732**	**6,310,177**	**8,808,883**

SEED DRESSING	Active ingredient (kg or L)						
	1994	1995	1996	1997	1998	1999	2000
TRIAZINE	4,060	3,597	3,181	4,402	3,356	1,446	2,055
CARBAMATE / DITHIOCARBAMATE	63,918	47,891	39,745	49,465	42908	42908	32159
BENZIMIDAZOLE	47,690	29,418	27,885	28,236	25228	468	907
AMINE / AMIDE	502	568		616	816	306	603
UNCLASSIFIED	34,752	28,442	11,814	9,471	18,069	17,571	727
TOTAL	**150,922**	**109,916**	**82,625**	**92,190**	**90,377**	**62,699**	**36,451**

ACARACIDES	Active ingredient (kg or L)						
	1994	1995	1996	1997	1998	1999	2000
INORGANIC / ORGANOMETALLIC	36,249	43,179	35,276	30,130	25,891	20,729	13,951
ANTIBIOTIC	132	81	15	153	460	898	1,216
UREA / THIO-UREA	65	1,262	1,082	882	946	1,167	1,117
PHENYL DERIVATIVES	12,791	15,910	12,330	4,558	11,900	20,885	18,183
UNCLASSIFIED	17,613	22,167	9,721	5,651	16,109	25,055	29,389
ORGANOCHLORINE	1,770	1,712	4,005	5,599	6,709	5,671	7,167
TRIAZINE / TETRAZINE	380	360	323	161	227	256	246
OXIME / OXIME ETHER	146	109	67	90	72	29	31
PYRETHROID	14	7	0	4	0.45		
	69,160	**84,785**	**62,817**	**47,227**	**62,315**	**74,690**	**71,300**

NEMATICIDES	Active ingredient (kg or L)						
	1994	1995	1996	1997	1998	1999	2000
CARBAMATE / THIOCARBAMATE	137,142	202,820	203,410	238,031	218,438	200,726	196,477
ORGANOPHOSPHATE	77,440	89,769	104,561	100,149	110,426	105,078	87,187
ORGANOCHLORINE	660,613	798,220	1,497,246	539,920	1,711,549	1,759,256	1,410,544
OXIME / OXIME ETHER	9,613	13,080	33,216	16,743	20,645	19,607	31,131
UNCLASSIFIED	2,619	6,286	11,809	25,816	25,530	0	0
	887,426	**1,110,175**	**1,850,241**	**920,659**	**2,086,587**	**2,084,667**	**1,725,338**

INSECTICIDES	Active ingredient (kg or L)						
	1994	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**
ORGANOPHOSPHATE	1,066,880	1,200,882	1,341,846	1,367,792	1,537,874	1,436,117	1,744,527
PYRETHROID	66,303	62,518	81,760	84,720	87,583	77,255	101,038
CARBAMATE / THIOCARBAMATE	297,639	318,218	323,848	376,127	423,396	454,086	479,264
AMINE	15,436	17,637	22,287	20,601	27,209	28,494	9,908
ORGANOCHLORINE	211,758	203,276	202,342	214,872	220,156	181,043	133,080
HYDROCARBON	1,481,385	1,092,773	459,675	457,243	1,764,879	2,719,228	1,815,375
TRIAZINE / TETRAZINE	7,297	8,867	6,806	5,486	4,722		
UREA / THIO-UREA	5,195	11,254	3,513	5,643	4,007	5,408	2,893
PHENOLIC / PHENOXY	2,078	1,462	965	2,086	1,527	2,273	3,769
INORGANIC / ORGANOMETALLIC	60,267	78,867	129,436	65,275	20,531	24,464	26,382
BIOLOGICAL					19,455	76,949	6,913
UNCLASSIFIED	113,544	94,447	79,381	12,639	48,956	52,967	40,222
	3,327,782	**3,090,199**	**2,651,859**	**2,612,484**	**4,160,294**	**5,058,285**	**4,363,371**

A3 Database of pesticide properties

A3.1 Properties include class, toxicity, molecular weight, density, boiling point and melting point

Detected pesticides	Usage type	Grouping/Class	Toxicity	Molecular Weight (g/mol)	Density (g/mL)	Boiling Point (°C)	Melting Point (°C)
1,2-Dichlorobenzene [3]	herbicide, insecticide & soil fumigant	chlorinated aromatic	eyes & respiratory disturbance	147.01	1.3048 at 20 °C/4 °C	180.5 °C at 760 mmHg	-17.0 °C
1,4-Dichlorobenzene [3]	insecticide & fumigant	chlorinated aromatic	vapours irritating to skin, eyes & respiratory organs	147.01	1.2475 g/mL at 20 °C/4 °C	174 °C at 760 mm Hg	53.1 °C
2,4 D (2,4 DDD) [1]	herbicide, GUP (acid form)	phenoxy compound	diethylamine salt, orally: III, eye exposure: I	221.04			140.5 °C
Aldicarb[1]	Insecticide, RUP	carbamate	Ia (WHO)	190.27			99-100 °C
Aldrin (HHDN)[3]	insecticide (banned in US or converted to dieldrin)	organochlorine	eye, skin & respiratory irritation, high bioconcentration expected	0.01; 27-180 ppm [2], 364.93	1.6 g/mL at 20 °C/4 ° C (solid)	145 °C at 2 mm Hg	104 °C
Alphamethrin[5]	insecticide	pyrethroid	II				
Amitrole[1]	non-selective herbicide, RUP	triazole	III	84.08			157 °C
Anthracene[3]	pesticide	aromatic	respiratory, eye & skin disturbance	178.22	1.25 g/mL at 27 °C/4 °C	342 °C	218 °C
Atrazine[1]	selective herbicide, RUP	triazines	III	215.69	1.187 g/mL at 20 °C [3]		176 °C, 171-174 °C

Detected pesticides	**Usage type**	**Grouping/Class**	**Toxicity**	**Molecular Weight (g/mol)**	**Density (g/mL)**	**Boiling Point (°C)**	**Melting Point (°C)**
Azinphos-methyl[1]	broad-spectrum synthetic insecticide (Restricted Use for concentrations >13.5%)	OP insecticide	I	317.33			65-68 °C (technical), 73-74 °C (pure form)
Azocyclotin[4]	insecticide	organotin, heavy metal	moderate (PAN)				
Benomyl[1]	systemic fungicide, GUP	benzimidazole	IV	290.62			decomposes without melting above 300 °C
BHC (alpha)	insecticide (formerly used in US [3])	organochlorine	slight (NTP) [3], possible carcinogens [4]	290.85 [3]	1.87 g/mL at 20 °C [3]	288 °C [3]	159-160 °C [3]
ß – BHC	insecticide (formerly used in US [3])	organochlorine	not acutely toxic (NTP) [3], possible carcinogen [4]	290.85 [3]	1.89 g/mL at 19 °C [3]	60 °C at 0.5 mmHg [3]	
Bromopropylate [4]	insecticide		unlikely				
Bromoxynil [1]	Herbicide, RUP	nitrile	II	276.93			194-195 °C
Camphor [4]	insecticide, fungicide, microbiocide	essential oil					
Captan/Captab[1]	Fungicide, GUP (most uses cancelled in the US)	phthalimide	IV	300.61	1.74 g/mL [3]		178 °C
Carbaryl[1]	broad-spectrum insecticide, GUP	carbamate	I for Tercyl, III for other products	201.23	1.232 g/mL at 20 °C/20 °C		142 °C
Carbofuran[1]	broad-spectrum insecticide, nematicides, RUP	carbamate	I to II	221.25	1.180 g/mL at 20 °C/20 °C [3]		153-154 °C

Detected pesticides	**Usage type**	**Grouping/Class**	**Toxicity**	**Molecular Weight (g/mol)**	**Density (g/mL)**	**Boiling Point (°C)**	**Melting Point (°C)**
Chlorfenapyr [4]	insecticide	pyrazole	II (WHO)				
Chlorpyrifos[1]	broad-spectrum insecticide, GUP	organophosphate	(II)	350.62	1.398 at 43.5 °C (liquid) [3]		41.5-44 °C
Copper oxychloride[2]					8.96 g/mL		
Cyfluthrin[1]	synthetic insecticide, RUP & GUP, subject to change)	pyrethroid	I to II	434.3			
Cypermethrin[1] **(alpha)**	synthetic insecticide, RUP	pyrethroid	II to III, endocrine disruption [4]	416.3			60-80 °C (pure isomers)
4,4-DDE[3]	(not used commercially in US)	breakdown product of DDT	II [1], bioconcentration in aquatic organisms	318			88.4 °C
DDT[1]	insecticide (restricted to malaria mosquito control)	organochlorine	II	354.51	1.54 g/mL (2)	260 °C	108.5-109 °C
Diazinon[1]	non-systemic insecticide, RUP	organophosphate	II to III	304.35	1.116-1.118 g/mL at 20 °C/4°C [3]	83-84 °C at $2x10^{-3}$ mmHg [3]	decomposes at > 120 °C
Deltamethrin [1]	synthetic broad-spectrum insecticide, GUP	pyrethroid (powerful)	II	505.24 (high)			98-101 °C
Dichlorvos (DDVP)[1]	insecticide fumigant, RUP (household & public health)	organophosphate	I, carcinogenic	220.98	1.415 g/mL at 25 °C/4 °C [3]	140 °C at 20 mmHg	

Detected pesticides	**Usage type**	**Grouping/Class**	**Toxicity**	**Molecular Weight (g/mol)**	**Density (g/mL)**	**Boiling Point (°C)**	**Melting Point (°C)**
Dieldrin[3]	broad-spectrum insecticide (controlling disease vectors, banned for general use	organochlorine	bio-concentration in fish	380.93	1.75 g/mL [2]		175-176 °C
Dimethoate[1]	insecticide & GUP	organophosphate	II	229.28	1.277 g/mL at 65 °C [3]	107 °C at 0.05 mmHg	43-45 °C (technical) [1], 51-52 °C [3]
Dinitro-ortho-cresol (DNOC)	growth regulant	Dinitro-ortho-cresol					
Dinocap[1]	Contact fungicide, acaricides, GUP	dinitrophenyl	III	364.41	1.1 g/mL	138-140 °C at 0.05 mmHg	
Diquat (dibromide) [1]	broad spectrum, non-residual herbicide, plant regulator, desiccant, GUP	dibromide	II	344.07 (3)	1.22-1.27 g/mL at 20 °C/20 °C		335-340 °C
Endosulfan a, b and sulphate[1]	broad spectrum insecticide, acaricides, RUP	chlorinated hydrocarbon (cyclodiene sub-group	I	a & b: 406.96 , sulphate: 422.95 [3]		a & b: 106 °C at 0.7 mmHg [3]	70-100 °C (technical), a & b: 106 °C, sulphate:181°C [3]
EPTC [1]	selective herbicide, GUP	thiocarbamate	III	189.32	0.955 g/mL at 30 °C	232 °C at 760 mmHg	
Ethylene dibromide (EDB) [1]	crop fumigant, insecticide	dibromide	I	187.9	2.172 g/mL (liquid)	131-132 °C	9.8 °C
Fenamiphos [1]	broad-spectrum nematicides, RUP	organophosphate	I	303.4			46 °C (technical)
Fenarimol [4]	fungicide	pyrimidine	III				

Detected pesticides	Usage type	Grouping/Class	Toxicity	Molecular Weight (g/mol)	Density (g/mL)	Boiling Point (°C)	Melting Point (°C)
Fenthion [1]	insecticide, bird control, RUP (not for food crops)	organophosphate	II	278.33			7.5 °C
Fenvalerate [4]	insecticide	pyrethroid	III				
Folpet [1]	leaf-fungicide (no longer sold in the US)	carboximide		296.6			177-180 °C
Formothion[1]	Insecticide, RUP	organophosphate	II	257.3			25-26 °C
Fosetyl-Al [4]	fungicide	(unclassified)	I				
Glyphosate[1]	non-selective herbicide, GUP		II	169.08			200 °C
Heptachlor [1]	insecticide (banned)	organochlorine cyclodiene	II	373.34	1.57 g/mL at 9 °C	145 °C at 1.5 mmHg	95-96 °C (pure); 46-74 °C (technical)
Hexaconazole [4]	fungicide	azole	IV				
Iprodione [1]	non-selective fungicide, mostly GUP	dicarboximide	III	330.17			136 °C
Lindane (gamma-BHC)[1]	insecticide, fumigant, rodenticide, RUP, (certain products banned)	organochlorine	II, probable carcinogen, endocrine disruption [4]	290.85 [3]	1.85 g/mL	323.4 °C at 760 mmHg [3]	ca. 113 °C
Mancozeb[1]	non-selective fungicide, seed treatment, GUP	ethylene (bis) dithiocarbamate	IV	266.31			decomposes without melting at 192 °C

Detected pesticides	Usage type	Grouping/Class	Toxicity	Molecular Weight (g/mol)	Density (g/mL)	Boiling Point (°C)	Melting Point (°C)
MCPA[3]	herbicide	chlorophenoxy acid or ester	I, possible carcinogen [4]	200.6	1.56 g/mL at 25 °C/15.5 °C		120 °C
Metaldehyde [1]	broad-spectrum molluscicide, RUP		III to II	176.2			sublimes at ca 112 °C
Methidathion [4]	insecticide	organophosphate	I, cholinesterase inhibitor & possible carcinogen				
Methiocarb[3]	insecticide, molluscicide	N-methyl carbamate	I [4]	225.3			119 °C
Metiram [1]	broad-spectrum fungicide, GUP	ethylene (bis) dithiocarbamate	IV	1088.7			decomposes at 140 °C
Mevinphos [1]	broad-spectrum insecticide, acaricides, RUP	organophosphate	I	224.15	1.25 g/mL at 20 °C/4 °C [3]	106-107.5 °C at 1 mmHg [3]	21 °C (E-isomer); 6.9 °C (Z-isomer)
Mineral oil [4]	insecticide, adjuvant	petroleum derivative	III				
Nuarimol [4]	fungicide	pyrimidine	III				
o-hydroxybipheny [4]	microbiocide	phenol	I, probable carcinogen & developmental toxin				
Omethoate [4]	insecticide, breakdown product	organophosphate	I (WHO), cholinisterase inhibitor	213.18786			
Oryzalen[1]	selective herbicide, GUP		IV	346.36			141-142 °C

Detected pesticides	Usage type	Grouping/Class	Toxicity	Molecular Weight (g/mol)	Density (g/mL)	Boiling Point (°C)	Melting Point (°C)
Paraquat[1]	widely used, quick-acting, non-selective herbicide (and aquatic) & RUP	quaternary nitrogen compound	I	257.2			decomposes at 300 °C
Parathion[3]	broad-spectrum insecticide, RUP (to be cancelled by US Environmental Protection Agency[1])	organophosphate	I (very high) [1], possible carcinogen, endocrine disruption [4]	291.3	1.26 g/mL at 25 °C/4 °C	375 °C at 760 mmHg	6 °C
Penconazole[4]	fungicide	azole	IV (WHO)				
Prochloraz [4]	fungicide	azole	III (WHO), possible carcinogen				
Procymidone[4]	fungicide		IV (WHO classification), probable carcinogen				
Profenofos[4]	insecticide	organophosphate	II (WHO), cholinesterase inhibitor				
Propetamphos[1]	insecticide, mostly non-agricultural GUPs	organophosphate	II	281.3			not
Propineb [4]	fungicide, microbiocide (banned in some countries)	dithiocarbamate, inorganic-zinc	IV (WHO)				
Propoxur[1]	broad-spectrum insecticide & GUP	carbamate	I, different formulations vary	209.25			84-87 °C , 91.5 °C [3]
Prothiofos [4]	insecticide	organophosphate	II (WHO), cholinesterase inhibitor				

Detected pesticides	**Usage type**	**Grouping/Class**	**Toxicity**	**Molecular Weight (g/mol)**	**Density (g/mL)**	**Boiling Point (°C)**	**Melting Point (°C)**
Simazine[1]	selective herbicide & GUP (under review)	triazine	IV	201.7	1.302 g/mL at 20 °C [3]		225-227 °C
Sulphur[1]	insecticide, fungicide, rodenticide, secondary acaricide & mostly GUP		low toxicity for humans & animals (chronic exposure: eye & respiratory disturbances	32.064	1.80046 g/mL at 255 °F [3]	444.6 °C [3]	114.5-115 °C
Tartar emetic [4]	insecticide	antimony	I				
Triadimefon[1]	fungicide & GUP (92.6% in Bayleton)	triazole	II	293.76	1.22 g/mL at 20 °C [3]		82.3 °C
Vinclozolin[1]	broad-spectrum fungicide & GUP	dicarboximide	III	286.11			108 °C

Note: - For pesticide data that have a single reference source, citations are given as superscripts in the column labelled 'Detected Pesticides', whereas data from multiple sources have citations provided in each column.
- The US EPA Acute Toxicity Classification is the primary classification used in this database, unless otherwise stated.

1. Extension Toxicology Network (EXTOXNET), Pesticide Information Profiles
2. personal communication, Ingrid Dennis, Institute for Groundwater Studies, Bloemfontein
3. Spectrum Laboratory Chemical Fact Sheets
4. Pesticide Action Network Databases
5. Weaver, 1993
6. Cooperative Extension Service, University of Illinois
7. London & Meyers, 1995b
8. London & Meyers, 1995a

Toxicity Classifications: US Environmental Protection Agency (EPA) acute toxicity rankings, World Health Organisation (WHO) acute hazard rankings, National Toxicology Program (NTP) acute hazard rankings. US EPA rankings are used in the table unless otherwise stated.
EPA Registered Use: GUP = General Use Pesticide, RUP = Restricted Use Pesticide
US EPA Acute Toxicity Classification: I – high, II – moderate, III – slight, IV - practically non-toxic
WHO acute hazard ranking: Ia- extremely hazardous, Ib- highly hazardous, II- moderately hazardous, III- slightly hazardous, IV- unlikely to be hazardous
PAN Acute Toxicity Description: Extremely toxic, Highly toxic, Moderately toxic, Slightly toxic

A3.2 Properties include vapour pressure, half-life, water solubility, and sorption coefficients

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in $\text{cm}^3\ \text{g}^{-1}$)**	**Partition Coefficient (Kd in $\text{cm}^3\ \text{g}^{-1}$)**	**Description of Mobility**
1,2-Dichlorobenzene[3]	1 mmHg [2], low	24 days (estimated, vapor-phase)	rivers: 0.3-3 days, lakes: 3-30 days, groundwaters: 300 days	100; 133 ppm[2], low hydrolysis expected	100 [2]		leaching detected
1,4-Dichlorobenzene[3]	0.6 mmHg [2]	56-365 days[2]	4.3 hours (estimated for flowing river)	49ppm [2], low hydrolysis expected	moderate to strong	high: 63,000-100,000	leaching detected
2,4 D (2,4 DDD)[1]	150.014 mmHg at 25 °C (acid)	< 7days	1-several weeks (oxygenated conditions)	900 (25 C, acid)	20 (acid)	2.81	leaching detected
Aldicarb[1]	97509 mmHg at 20 °C	moderate depending on moisture & pH	1 day to a few months, pond water (rapid): 5-10 days	very high: 6000 mg/L at room temperature	30	0.0531	very high, leaching detected
Aldrin (HHDN) [3]	6 E-6 [2]	1 day to 3.2 years [2], 20-100 days (varies with soil type)	high volatility	0.01, 27-180 ppm [2]	expected to be significant		leaching with rainwater detected
Amitrole[1]	in soil: <7500.7 mmHg at 20 °C	14 days, 21 days in warm, moist soils	40 days	280,000 mg/L at 23 °C	100		moderate
Anthracene [3]	1.95 E^{-4} mmHg[2], evaporation half-life range: 4.3-5.9 days for flowing river	3.3-139 days	photolysis near surface & biodegradation	1.29; 0.075 ppm [2], hydrolysis not expected	very strong (expected)		significant leaching not expected

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in $cm^3\ g^{-1}$)**	**Partition Coefficient (Kd in $cm^3\ g^{-1}$)**	**Description of Mobility**
Atrazine[1]	300 mmHg at 20 °C	60 to 100+; 365+ (dry, cold)	rapid in acidic water & slower at neutral pH	28 mg/L at 20 °C	100	2.3404	moderate to high
Azinphos-methyl[1]	<7500 mmHg at 20 °C	Variable: 5 (sandy loam) to 355 (sterile soil)	ponds: up to 2 days	30 mg/L at 25 °C	1000		low leaching potential
Benomyl[1]	<7500mmHg at 20 °C	6-12 months in bare soil	several hours	2 mg/L	1900		
BHC (alpha)[3]	slow	slow degradation expected in aerobic soil	92-771 hours in natural water (volatility not expected)				
ß - BHC		13.8 to 248 days[2]					
Bromoxynil[1]	<7500mmHg at 20 °C	10 days (sandy soil) to 14 days at 25 °C (clay)		130 mg/L at 25 °C			
Captan/Captab[1]	9750.9 mmHg at 25 °C	1-10 days, aerobic: 6.93, anaerobic: 1.0 [4]	2 weeks, 0.49 [4]	3.3 mg/L at 25 °C	200	2.7853	
Carbaryl[1]	<39753.7 mmHg at 25 °C	7-14 days (sandy loam), 14-28 days (clay loam)	10 days at neutral pH (varies with acidity)	40 mg/L at 30 °C	300		leaching detected
Carbofuran[1]	20251.9 mmHg at 33 °C	30-120 days	690 weeks (at 25 °C, pH 6), 8.2 weeks (pH 7), 1 week (pH 8)	320 mg/L at 25 °C	22	1.2304 - 1.4150	varies according to texture, small amounts detected
Chlorfenapyr [4]		aerobic: 1.37	30	0.13		104.9	

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in cm^3 g^{-1})**	**Partition Coefficient (Kd in cm^3 g^{-1})**	**Description of Mobility**
Chlorpyrifos[1]	2.5 mPa at 25 °C,	60-120 days, or 14-365+ (depending on soil type, pH, climate, etc.),	varies according to formulation, photolysis half-life: 3-4 weeks; 35-78 days at pH 7 & 25 °C	2 mg/L at 25 °C	6070	4.699	immobile
Cyfluthrin[1]	1.62 x 10^{-8} mmHg	48-72 hours on soil surface; 56-63 days in anaerobic & and German loam & sandy loam soils	1 day (sunlight)	0.002 mg/ml at 20 °C	5.62		very immobile, no leaching expected
Cypermethrin[1] **(alpha)**		4 days - 8 weeks (aerobic), 2.5 weeks (sandy soil), 8-16 days (due to light & bacteria)	Hydrolysis: >50 days, photolysis: >100 days in normal conditions	0.01 mg/L at 20 °C	100,000	6.602	unlikely
4,4-DDE	6.5 E-^{6} mmHg(2), high potential evaporation[3]	slow[1]	5.6-6.4 hours in flowing river (high evaporation), half life: 15 hours - 1.1 days[3]	0.0013[2]		high[1]	slight mobility[1]
DDT[1]	187.5 mmHg at 25 °C (volatility varies)	2-15 years	lakes: 56 days, rivers: 28 days	< 1mg/L at 20 °C	100000	high	immobile or very slight
Deltamethrin[1]	2 x 10^{-8} mbar at 25 °C	1-2 weeks	evaporation in pond water	<0.1 mg/L		4.6 (25 C)	

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in $cm^3 g^{-1}$)**	**Partition Coefficient (Kd in $cm^3 g^{-1}$)**	**Description of Mobility**
Diazinon[1]	727.57 mmHg at 20 °C	2-4 weeks	12 hours in highly acidic waters & 6 months in neutral waters	40 mg/L at 20 °C	1000 (estimated)		low expected, but leaching detected
Dibutylphthalate	1 E-5 mmHg (di-n-butylphthalate) [2]	66 & 98% degradation in 26 weeks reported [3]	biodegradation: 90-100% reported 2-17 days [3]	13 ppm (for di-n-butylphthalate) [2]	moderate [3]		leaching detected with high input levels[3]
Dichlor(o)vos (DDVP)[1]	290 mPa at 20 °C, slow from soils (expected)	rapid: 7 days, ranges form 4.5-50 hours (hydrolysis & biodegradation, depending on pH)	4 days in lakes & rivers (mainly due to hydrolysis), range of 20-80 hours depending on pH	10,000 mg/L (estimated)	30 (estimated)		likely to contaminate groundwater
Dimethoate[1]	8250.7 mmHg at 25 °C, not significant for open waters	20 days, range of 4-122 days	8 days in rivers	25g/l at 21 °C	20	0.699	high
Dinocap[1]	39.7 mmHg at 20 °C	4-6 days (high photosensitivity)		<1 mg/L	top soils: 550 (estimated)	4.5366	unlikely
Diquat (dibromide)[1]		>1000 days		700,000 mg/L at 20 °C	1,000,000 (estimated)	-4.6021	low
Endosulfan a, b and sulphate[1]	9E+06 mmHg, 1 E-5 [2]	< 9.1 days [2]; ca 50 days, 35 (a), 150 (b) in neutral conditions	in raw water at room temperature, disappearance in 4 weeks, depending on pH	sulphate: 0.117-0.22 ppm, a: 0.26-0.6 ppm & b: 0.06-0.1 ppm [2]; 0.32 mg/L at 22 °C	12400		
Ethylene dibromide (EDB)[1]	11.25E-03 mmHg	100 days (estimated)	rivers: >1 day, lakes: ca 5 days	4300 at 20 °C	34 (estimated)	53.7-61.7 (calculated)	slow mobility for ions, leaching detected,

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in $cm^3 g^{-1}$)**	**Partition Coefficient (Kd in $cm^3 g^{-1}$)**	**Description of Mobility**
Fenamiphos[1]	9E+02 mmHg at 20 °C	ca 50 days	neutral water: 4 hours (depending on light)	700 mg/Lat 20 °C	100		not detected in groundwater
Fenarimol [4]		aerobic: 1.1, anaerobic: 1.622	28 days	15		757	potential
Fenthion[1]	3E+04mmHg at 20 °C; 75E+03 mmHg at 30 °C	moderate: ca 34 days (can range 4-6 weeks),	2 weeks, more rapid under alkaline conditions	2 mg/L at 20 °C	1500	4.091	unlikely
Fenvalerate [4]		aerobic: 178.8 days, anaerobic: 155 days	30 days	0.0013		13	
Folpet[1]	<1.3 x 10^{-9} mbar at 20 °C	(chemical hydrolysis)		1			
Formothion[1]	84.76E+01 mmHg at 20 °C	1-14 days in loamy soil, no accumulation				(octanol/water) ca. 30	
Fosetyl-Al [4]		aerobic: 0.04, anaerobic: 2	30	136,000		325	potential
Glyphosate[1]	negligible	ca 47 days (estimated), range 1-174 days	pond water: 12 days - 10 weeks	12,000 mg/L at 25 °C	24,000 (estimated)	-3.2218 - -2.7696	low
Iprodione[1]	<99.76E+01 mmHg at 20 °C	ca 14 days (estimated), range of <7 to >60 days	rapid under aerobic conditions	13 mg/L at 20 °C	700	3.1004 (20 °C)	low
Lindane (gamma-BHC)[1]	42E+03mmHg at 20 °C	ca 15 months, aerobic: 980 days, anaerobic: 0.0037 days	172.8 days [4]	7.3 mg/L at 25 °C , 46.8 mg/L [4]	1100	1.161 [6], 22.1 [4]	widely detected

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in cm^3 g^{-1})**	**Partition Coefficient (Kd in cm^3 g^{-1})**	**Description of Mobility**
Mancozeb[1]	negligible at 20 °C	1-7 days, range up to 5-10 weeks	1-2 days in slightly acidic to slightly alkaline conditions	6 mg/L	>2000		unlikely but metabolites can be mobile, low levels detected
MCPA [4]				160,149			
Metaldehyde [1]	negligible at room temperature	several days	rapid	260 mg/L at 30 °C	240		unlikely
Methidathion [4]		3 days	26 days	221 mg/L		341	potential
Methiocarb [4]		64 days	24	27 mg/L		655	potential
Metiram[1]	75 mmHg at 20 °C	rapid to moderate for bi-products	rapid	<1 mg/L	500,000 (estimated)	0.301	slight (bi-products)
Naphthalene[2]	362 mmHg	1 to 258 days, slow: >80 days[3]		16,700; 20,200 ppm	0.12, low to moderate[3]		(leaching detected)
Oryzalen[1]	<97.5 mmHg at 30 °C	20 days, range from 20-128 days	expected to be slow due to low levels of oxygen for bacterial activity	2.5 mg/L at pH 7, 25 °C	600	3.734 (pH7)	potential
Paraquat[1]	negligible at room temperature (paraquat dichloride)	>1000 days, range from 16 months to 13 years	range of 13.1 hours to 23 weeks	700,000 mg/L at 20 °C	1,000,000 (estimated)	4.4683	insignificant, very low levels detected
Parathion[1]	8.9 x 10^{-6} mmHg at 20 °C or 4 x 10^{-5} mmHg at 20 °C	130 days[2], degrades within several weeks	1-10 days; 209.5 days [4]	12.4 mg/L at 25 °C or 24 ppm	strong	3.83, 11.2 [4]	little or no potential for leaching, potential[4]
Propetamphos[1]	142.5+02 mmHg at 20 °C		rapid only at extreme pH or in sunlight	110 mg/L at 24 °C			

Detected pesticides	**Vapour Pressure (Volatility)**	**Soil half-life / Degradation (Avg)**	**Hydrolysis half-life / Degradation (Avg)**	**Water Solubility (mg/L or ppm)**	**Adsorption Coefficient (Koc in $cm^3 g^{-1}$)**	**Partition Coefficient (Kd in $cm^3 g^{-1}$)**	**Description of Mobility**
Propoxur[1]	2.25E+06 mmHg at 120 °C	rapid to moderate: 14-50 days	hydrolysis at 1.5% per day in a 1% aqueous solution, pH 7	2000 mg/L at 20 °C	30	0.14	high potential
Simazine[1]	6.075 mmHg at 20 °C	ca 60 days, range of 28-149 days or 1 year (at high pH),	ponds: 30 days but varies acc. to presence of algae & weeds, hydrolysis at low pH	5 mg/L at 20 °C	130	1.96	detected at low levels
Sulphur[1]	5.3 x 10^{-6} mbar at 30.4 °C; 8.6 x 10^{-5} mbar at 59.4 °C; 1 mmHg at 184 °C & 3.96 x 10^{-6} mmHg at 30.4 °C	slow mainly by bacteria, natural cycles of oxidation & reduction		practically insoluble			significant leachability detected at low rates (sulphate)
Triadimefon[1]	<750.07mmHg at 20 °C	6-60 days (varies with soil type), ca 26 days	very stable, at pH 3, 6 & 9 days (almost 95% remained after 28 weeks)	260 mg/L at 20 °C	300	3.179	moderate
Vinclozolin[1]	120.01mmHg at 20 °C	3 days to >3 weeks	potential for & hydrolysis, esp. at neutral pH	3.4 mg/L at 20 °C		100 (estimated)	unlikely

Note: For pesticide data that have a single reference source, citations are given as superscripts in the column labelled ‘Detected Pesticides’, whereas data from multiple sources have citations provided in each column.

1. Extension Toxicology Network (EXTOXNET), Pesticide Information Profiles
2. personal communication, Ingrid Dennis, Institute for Groundwater Studies, Bloemfontein
3. Spectrum Laboratory Chemical Fact Sheets
4. Pesticide Action Network Databases
5. Weaver, 1993
6. Cooperative Extension Service, University of Illinois
7. London & Meyers, 1995b
8. London & Meyers, 1995a

APPENDIX B

Soil analysis: methods and results

pH and electrical conductivity

1:2.5 soil solution slurries were prepared in triplicate by adding 5g of each soil separately to vials containing 12.5ml of distilled water and 12.5ml hydrated 0.01M $CaCl_2$. The addition of salts for measuring pH is a standard method for improving the reliability of pH results, especially in the case of agricultural soils (McBride, 1994; Rowell 1994). The vials were shaken vigorously by hand and left to stand for several hours to allow for equilibration between soil and solution. Electrical conductivity (EC) of the water samples was determined as an indication of total dissolved ions, using an EC-meter. The sample pH was then determined for all samples using a pH-meter, with glass electrode and potentiometer that was calibrated with buffer solutions of pH 4, 7 and 10.

Exchangeable cations and CEC

For the determination of exchangeable ions 25 ml of 1M ammonium acetate at pH = 7, was added with a measuring cylinder to 5 g air-dry soil particles (< 2mm) in 100 ml centrifuge tubes. This was also done for blanks containing no soil. Samples were shaken with a mixer for 10 minutes to detach particles and then centrifuged for 10 min to allow particles to settle. The clear extract was poured into 100 ml volumetric flasks. This process was repeated twice more to ensure that all ions were displaced into solution and ammonium acetate was added until 100 ml and mixed well. Test-tubes were filled with this extract and Na^+, K^+, Mg^{2+} and Ca^{2+} ions in solution were determined with a spectrophotometer. CEC was calculated as the sum of the cations in cmol(+) kg^{-1}.

Particle size distribution

Three soil samples were sieved to separate the particles > 2000 μm (gravel) and the separated fractions were weighed. 25 g of each sample without the gravel was then treated with 25 ml H_2O_2 (20%) to burn the organic matter and 5 ml HCl (30%) to break down the soil structures. The samples were boiled with HCl quietly for 10 min and allowed to stand overnight in H_2O_2. After cooling in an extraction cabinet, samples were washed with water to remove excess HCl and filter paper was used to collect the soil. A fine sieve was used to wash through and separate the particles < 45 μm (silt & clay). The remaining particles >45 μm (sand) were oven dried for approximately 7 hours at 105 °C and weighed.

The particles < 45 μm were then added to distilled water in cylinders and separated using the sedimentation method, based on Stokes' Law for streamlined flow:

$$v = (2r^2 / 9?) \cdot g\, (?_s - ?_l)$$

After t sec, the particles fall a distance s:

$$s = v \cdot t = (2r^2 / 9?) \cdot g\, (?_s - ?_l) \cdot t$$

Where,
v – sedimentation velocity
r – particle radius
g – gravitational force per unit mass (9.81 N kg^{-1})
$?_s$ – density of the particle (2650 kg m^{-3})
$?_l$ - density of the liquid (998 kg m^{-3} at 20 °C for water)
? – viscosity of the liquid (1.002 x 10^{-3} N s m^{-2} at 20 °C for water)

The cylinders were shaken and using the above equation, it was calculated that after 16 hours, particles < 2 μm (clay) will have moved a distance of 8.2 cm down the cylinder. 25 ml of the clay fraction was thus extracted from each sample using a pipette, oven-dried for approximately 2 hours at 105 °C and weighed.

Water retention

Four sample cores from each sample site were saturated in steel rings with tap water, at room temperature for approximately one week. This was done by immersing sample cores and rings, with gauze underneath, in a plastic bucket of water raised just below the upper rim of the ring. When samples were saturated and water forming on top of the ring, they were removed, allowed to leak for a few minutes on the gauze and patted dry on top. Samples cores were weighed in their rings and placed in the Eijkelkamp saturated sand box. The water column was adjusted to provide a matrix potential of 0 kPa and left to equilibrate for a few days. Samples were weighed and then placed back in the sand box. This procedure was repeated for suction levels of 0.3, 1.0, 3.2 and 6.3 kPa. For determinations at suctions of 31.6 and 50.1 kPa, an

Eijkelkamp sand/kaolin box was used, containing a top layer of kaolin clay in addition to the sand, and connected to a vacuum pump with which to apply suction. In completion, samples were oven-dried and weighed to determine the bulk density and the volumetric water content for each reading.

Weight measurements from the analysis of soil organic matter content

Sample	Empty cup (g)	Cup and soil before drying (g)	Soil used (g)	Cup and soil after drying (g)	Organic Matter (%)	Mean % Organic Matter	Std. Dev
A 1	24.07	39.15	15.08	38.99	1.06	1.81	0.83
A 2	23.85	43.34	19.49	43.02	1.64		
A 3	21.82	37.95	16.13	37.70	1.55		
A 4	23.97	43.4	19.43	42.82	2.99		
B 1	24.86	42.29	17.43	41.67	0.62	0.78	0.20
B 2	19.40	33.20	13.80	32.6	0.60		
B 3	22.36	36.05	13.69	35.17	0.88		
B 4	23.53	38.21	14.68	37.21	1.00		

Summary of the volumetric soil water content at different suction levels applied to 4 samples of soil A and 3 samples of soil B. Standard deviations are given in parentheses.

Suction (kPa)		**0.0**	**0.3**	**1.0**	**3.2**	**6.3**	**31.6**	**50.1**
Volumetric SWC (m/m)	**Soil A**	0.40 (0.01)	0.40 (0.01)	0.40 (0.01)	0.39 (0.02)	0.28 (0.01)	0.08 (0.01)	0.08 (0.01)
	Soil B	0.41 (0.02)	0.38 (0.02)	0.37 (0.01)	0.33 (0.02)	0.25 (0.03)	0.15 (0.04)	0.14 (0.05)

Results of the sieve and sedimentation analysis for gravel, sand, silt and clay fractions. Standard deviations are in parentheses.

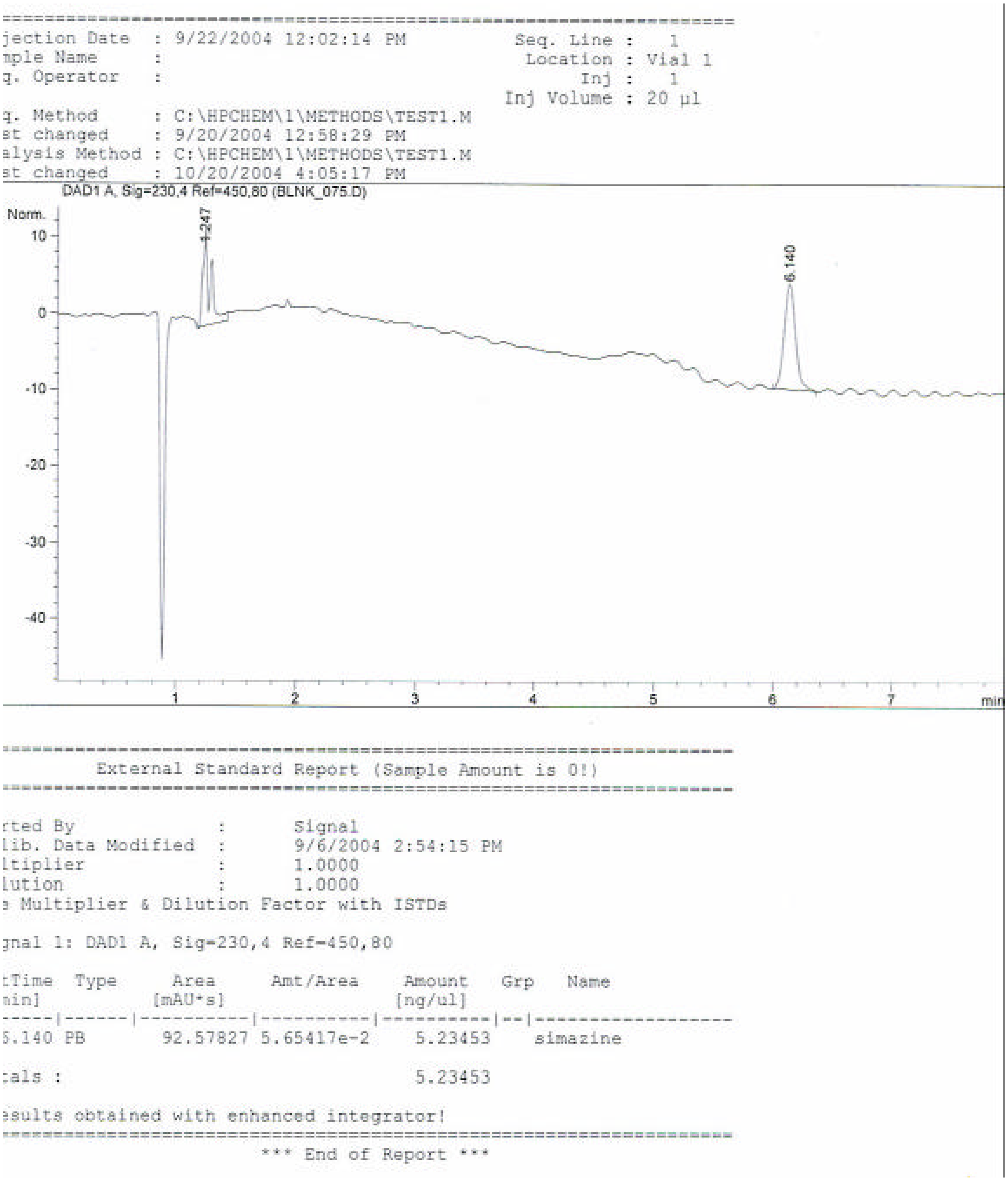
Sample	**A1**	**A2**	**A3**	**A4**	**Mean**	**B1**	**B2**	**B3**	**B4**	**Mean**
tot. sample (g)	**403.57**	**511.52**	**459.93**	**433.91**		**474.49**	**462.22**	**471.37**	**447.46**	
gravel (g)	**6.83**	**15.34**	**15.61**	**21.15**		**58.5**	**61.89**	**92.4**	**106.8**	
balance (g)	**396.74**	**496.18**	**444.32**	**412.76**		**415.99**	**400.33**	**378.97**	**340.66**	
% gravel	**1.69**	**3.00**	**3.39**	**4.87**	**3.24 (1.3)**	**12.33**	**13.39**	**19.60**	**23.87**	**17.30 (5.4)**
subset*: tot. sample (g)	**25**	**25**	**25**	**25**		**25**	**25**	**25**	**25**	
sand (g)	**24.01**	**23.65**	**23.08**	**22.07**		**22.83**	**19.74**	**19.02**	**21.22**	
% sand	**96.04**	**94.60**	**92.32**	**88.28**	**92.81 (3.39)**	**91.32**	**78.96**	**76.08**	**84.88**	**82.81 (6.75)**
clay (g)	**0.4**	**0.8**	**0**	**0**		**0**	**0.4**	**0.4**	**0.8**	
% clay	**1.60**	**3.20**	**0**	**0**	**1.20(1.53)**	**0**	**1.6**	**1.6**	**3.2**	**1.60 (1.31)**
silt (g)	**0.59**	**0.55**	**1.92**	**2.93**		**2.17**	**4.86**	**5.58**	**2.98**	
% silt	**2.36**	**2.20**	**7.68**	**11.72**	**5.99 (4.59)**	**8.68**	**19.44**	**22.32**	**11.92**	**15.59 (6.36)**

* subset refers to the 25g of soil collected from the original sample that was sieved for gravel

Appendix C

Results of sorption experiments and HPLC analysis

Printout of a typical HPLC chromatograph for simazine



```
=====================================================================
jection Date   : 9/22/2004 12:02:14 PM          Seq. Line :   1
mple Name      :                                 Location : Vial 1
q. Operator    :                                      Inj :   1
                                               Inj Volume : 20 µl
q. Method      : C:\HPCHEM\1\METHODS\TEST1.M
st changed     : 9/20/2004 12:58:29 PM
alysis Method  : C:\HPCHEM\1\METHODS\TEST1.M
st changed     : 10/20/2004 4:05:17 PM
```

```
=====================================================================
        External Standard Report (Sample Amount is 0!)
=====================================================================

rted By              :       Signal
lib. Data Modified   :       9/6/2004 2:54:15 PM
ltiplier             :       1.0000
lution               :       1.0000
e Multiplier & Dilution Factor with ISTDs

gnal 1: DAD1 A, Sig=230,4 Ref=450,80

tTime  Type     Area      Amt/Area     Amount   Grp   Name
min]           [mAU*s]                [ng/ul]
-----|------|----------|----------|----------|--|------------------
5.140 PB      92.57827 5.65417e-2    5.23453    simazine

tals :                               5.23453

esults obtained with enhanced integrator!
=====================================================================
                         *** End of Report ***
```

Terminologies used:

Std.:	standards used in the calibration and spiked with 10 ppm (mg/L)
C_{is}:	initial conc. spiked (mg/L), equal to the conc. of the std.
Spike:	10 mg/L
C_i:	initial conc. before spiking (mg/L)
C_b:	conc. of the blanks (mg/L)
b:	error correction due to the conc. of the blanks, given by $C_{is} – C_b$ (mg/L)
A:	mass of pesticide detected in the spiked solution/aqueous phase (mg/L)
S:	mass of sorbed pesticide per unit volume of solution calculated as $C_{is} – C_{aq} – b$ (mg/L)
m:	mass of soil per unit volume of solution equals 0.2 kg/L for all samples
C_s:	mass of sorbed pesticide per mass of soil calculated as S/m (mg/kg)
C_{aq}:	aqueous conc. before spiking calculated as $C_i – S - b$
Log C_s:	logarithm of pesticide sorbed (mg/kg)
Log C_{aq}:	logarithm of pesticide in solution (mg/L)

Data used to plot sorption isotherms for simazine in soil A. Standard deviations are given in parentheses for Cs and Caq

Parameters	**Sample labels**						
	A1	A2	A3	A4	A5	A6	A7
Std and C_{is} (mg/L)	5.25000	5.37500	5.50000	5.62500	5.75000	5.87500	6.00000
C_i (mg/L)	0.50000	0.75000	1.00000	1.25000	1.50000	1.75000	2.00000
C_b (mg/L)	5.10793	5.23453	5.21759	5.31751	5.43393	5.54288	5.00367
A (mg/L)	4.96707	5.07835	5.07718	5.21870	5.16609	5.27142	5.32375
S (mg/L)	0.14086	0.15618	0.14041	0.09881	0.26784	0.27146	0.33625
C_s (mg/kg)	0.71788 (0.885)	0.78088 (0.050)	0.72162 (0.731)	0.52222 (0.512)	1.33922 (0.111)	1.35730 (0.410)	1.68127 (0.354)
C_{aq}	0.21707 (0.180)	0.45335 (0.010)	0.57718 (0.152)	0.84370 (0.111)	0.91609 (0.022)	1.14642 (0.082)	1.32375 (0.071)
Log C_s	-0.14395	-0.10741	-0.14169	-0.28215	0.12685	0.13268	0.22564
Log C_{aq}	-0.66340	-0.34356	-0.23869	-0.07381	-0.03806	0.05934	0.12181

Data used to plot sorption isotherms for simazine in soil B. Standard deviations are given in parentheses for Cs and Caq.

Parameters	**Sample labels**						
	B1	B2	B3	B4	B5	B6	B7
Std and C_{is} (mg/L)	5.25000	5.37500	5.50000	5.62500	5.75000	5.875	6.00000
C_i (mg/L)	0.50000	0.75000	1.00000	1.25000	1.50000	1.75000	2.00000
C_b (mg/L)	5.10793	5.23453	5.21759	5.31751	5.43393	5.54288	5.00367
A (mg/L)	4.87486	5.03632	5.12108	5.14305	5.20417	5.14715	5.34517
S (mg/L)	0.23307	0.19821	0.09651	0.17446	0.22976	0.39573	0.31483
C_s (mg/kg)	1.16533 (0.661)	1.04207 (1.061)	0.48253 (0.168)	0.89323 (0.789)	1.14882 (0.096)	1.97863 (0.281)	1.57417 (0.466)
C_{aq}	0.13243 (0.120)	0.41132 (0.227)	0.62108 (0.034)	0.76805 (0.165)	0.95417 (0.019)	1.02215 (0.056)	1.34517 (0.093)
Log C_s	0.06645	0.01790	-0.31647	-0.04904	0.06025	0.29637	0.19705
Log C_{aq}	-0.87803	-0.38582	-0.20685	-0.11461	-0.02038	0.00952	0.12878

APPENDIX D

VLEACH 2.2b data files and graphical output

D1. Data files

Typical input file

The example provided is for simazine applied once at site A, at a concentration of 1256 µg/kg, to the top 12cm soil layer. The simulation was run for 3 years.

```
==============GENERAL PROJECT INFORMATION============================
project title............................TCE penetration at the SORI site
number of polygons.......................1
timestep [years].........................1
total time of simulation [years]........3
gw impact output interval [years].......1
profile output interval [years].........1
===============CONTAMINANT INFORMATION===============================
org.C distrib. coeff., Koc [ml/g].......40.25
Henry's constant [dimensionless]........3.96e-8
water solubility [mg/l].................5
free air diffusion coef.[sq.m/d]........0
===============Polygon #1============================================
title.....................................East-Yard
surface area [sq.ft].....................11.11
vertical thickness of a cell [ft].......0.4
net recharge rate [ft/year].............1.15
dry bulk density [g/cm3]................1.617
effective porosity [dim.less]...........0.39
volumetric water content [percent]......0.2
organic carbon content [dim.less].......0.0105
contaminant conc. in recharge [mg/l]....0.0
upper BC for vapour [mg/l]...............0
lower BC for vapour [mg/l]...............0.0
number of cells..........................50
plot variable [y/n]......................y
plot time [years].......................3.0
======repeat the following line until all cells are assigned=========
top #, bottom #, init. conc. [ug/kg]....1,1,1256.0
top #, bottom #, init. conc. [ug/kg]....2,50,0.0
```

Typical output file containing mass balances and groundwater impact data

```
Polygon   1
At time =       .00, total mass in vadose zone =    .23003E-01g/sq.ft.
Mass in gas phase    =      .19593E-09g/sq.ft.
Mass in liquid phase  =     .52080E-02g/sq.ft.
Mass sorbed          =      .17795E-01g/sq.ft.


Polygon   1
At time =      1.0000, total mass in vadose zone =    .22988E-01g/sq.ft.
Mass in gas phase    =      .19579E-09g/sq.ft.
Mass in liquid phase  =     .52045E-02g/sq.ft.
Mass sorbed          =      .17783E-01g/sq.ft.

Since last printout at time =       .0000
            Change in Total Mass =    -.15458E-04g/sq.ft.
                Advection in from atmosphere =      .00000    g/sq.ft.
                Advection in from water table =    -.15454E-04g/sq.ft.
                Diffusion in from atmosphere =      .00000    g/sq.ft.
                Diffusion in from water table =     .00000    g/sq.ft.
            Total inflow at boundaries =    -.15454E-04g/sq.ft.
            Mass discrepancy =    -.45384E-08g/sq.ft.

Since beginning of run at time = 0.0
            Change in Total Mass =    -.15458E-04g/sq.ft.
                Advection in from atmosphere =      .00000    g/sq.ft.
                Advection in from water table =    -.15454E-04g/sq.ft.
                Diffusion in from atmosphere =      .00000    g/sq.ft.
                Diffusion in from water table =     .00000    g/sq.ft.
            Total inflow at boundaries =    -.15454E-04g/sq.ft.
            Mass discrepancy =    -.45384E-08g/sq.ft.


Polygon   1
At time =      2.0000, total mass in vadose zone =    .22937E-01g/sq.ft.
Mass in gas phase    =      .19536E-09g/sq.ft.
Mass in liquid phase  =     .51929E-02g/sq.ft.
Mass sorbed          =      .17744E-01g/sq.ft.

Since last printout at time =      1.0000
            Change in Total Mass =    -.51199E-04g/sq.ft.
                Advection in from atmosphere =      .00000    g/sq.ft.
                Advection in from water table =    -.51189E-04g/sq.ft.
                Diffusion in from atmosphere =      .00000    g/sq.ft.
                Diffusion in from water table =     .00000    g/sq.ft.
            Total inflow at boundaries =    -.51189E-04g/sq.ft.
            Mass discrepancy =    -.10015E-07g/sq.ft.
```

```
Since beginning of run at time = 0.0
          Change in Total Mass =     -.66657E-04g/sq.ft.
             Advection in from atmosphere =       .00000    g/sq.ft.
             Advection in from water table =     -.66642E-04g/sq.ft.
             Diffusion in from atmosphere =       .00000    g/sq.ft.
             Diffusion in from water table =      .00000    g/sq.ft.
          Total inflow at boundaries =     -.66642E-04g/sq.ft.
          Mass discrepancy =     -.14552E-07g/sq.ft.


Polygon   1
At time =       3.0000, total mass in vadose zone =     .22825E-01g/sq.ft.
Mass in gas phase     =       .19441E-09g/sq.ft.
Mass in liquid phase  =       .51676E-02g/sq.ft.
Mass sorbed           =       .17657E-01g/sq.ft.

Since last printout at time =       2.0000
          Change in Total Mass =     -.11165E-03g/sq.ft.
             Advection in from atmosphere =       .00000    g/sq.ft.
             Advection in from water table =     -.11166E-03g/sq.ft.
             Diffusion in from atmosphere =       .00000    g/sq.ft.
             Diffusion in from water table =      .00000    g/sq.ft.
          Total inflow at boundaries =     -.11166E-03g/sq.ft.
          Mass discrepancy =      .62573E-08g/sq.ft.

Since beginning of run at time = 0.0
          Change in Total Mass =     -.17831E-03g/sq.ft.
             Advection in from atmosphere =       .00000    g/sq.ft.
             Advection in from water table =     -.17830E-03g/sq.ft.
             Diffusion in from atmosphere =       .00000    g/sq.ft.
             Diffusion in from water table =      .00000    g/sq.ft.
          Total inflow at boundaries =     -.17830E-03g/sq.ft.
          Mass discrepancy =     -.82946E-08g/sq.ft.


GROUNDWATER IMPACT OF POLYGON   1

 Time       Mass flux (g/yr/sq.ft.)      Total Mass(g/yr)
    1.00        .15454E-04              .17169E-03
    2.00        .51189E-04              .56870E-03
    3.00        .11166E-03              .12405E-02
***************************************************
***************************************************
TOTAL GROUNDWATER IMPACT

 Time (yr)         Mass (g/yr)    Cumulative Mass (g)
    1.00        .17169E-03       .17169E-03
    2.00        .56870E-03       .74039E-03
    3.00        .12405E-02       .19809E-02
```

Typical output file containing soil impact data

Mass (g)	Depth (ft)
2.125017E-07	-2.000000E-01
5.137027E-08	-6.000000E-01
4.923546E-08	-1.000000
4.696700E-08	-1.400000
4.461579E-08	-1.800000
4.222398E-08	-2.200000
3.982609E-08	-2.600000
3.745010E-08	-3.000000
3.511835E-08	-3.400000
3.284843E-08	-3.800000
3.065377E-08	-4.200000
2.854441E-08	-4.600000
2.652747E-08	-5.000000
2.460762E-08	-5.400000
2.278755E-08	-5.800000
2.106827E-08	-6.200000
1.944949E-08	-6.600000
1.792979E-08	-7.000000
1.650694E-08	-7.400000
1.517801E-08	-7.800000
1.393961E-08	-8.200000
1.278796E-08	-8.600000
1.171904E-08	-9.000000
1.072868E-08	-9.400001
9.812630E-09	-9.800000
8.966634E-09	-10.200000
8.186470E-09	-10.600000
7.468000E-09	-11.000000
6.807193E-09	-11.400000
6.200160E-09	-11.800000
5.643164E-09	-12.200000
5.132634E-09	-12.600000
4.665175E-09	-13.000000
4.237571E-09	-13.400000
3.846787E-09	-13.800000
3.489968E-09	-14.200000
3.164437E-09	-14.600000
2.867689E-09	-15.000000
2.597387E-09	-15.400000
2.351357E-09	-15.800000
2.127576E-09	-16.200000
1.924170E-09	-16.600000
1.739404E-09	-17.000000
1.571675E-09	-17.400000
1.419502E-09	-17.800000
1.281524E-09	-18.200000
1.156486E-09	-18.600000
1.043234E-09	-19.000000
9.407118E-10	-19.400000
8.479481E-10	-19.800000

D2. Graphical output of the sensitivity analysis

Graphs represent leaching rate, cumulative groundwater impacts and/or soil profiles of 10 pesticides, in the sensitivity analysis of depth to groundwater, recharge rate, initial concentration, pesticide and soil properties, and 'realistic' scenarios with VLEACH. Pesticides include simazine, atrazine, dimethoate, lindane, 2,4-D, carbofuran, carbaryl, dieldrin, fenthion and parathion.

D2.1. Depth to groundwater

Figure D1. Leaching rate of atrazine at site A, over 10 yrs

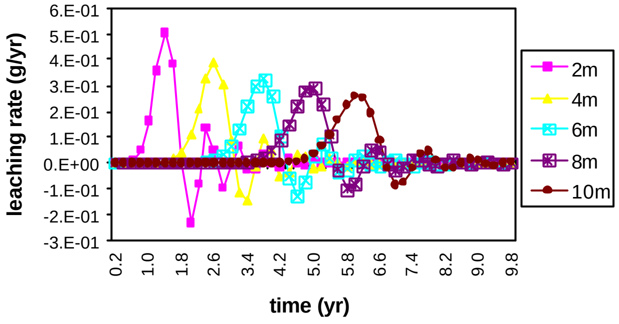


Figure D2. Leaching rate of atrazine at site B, over 10 yrs

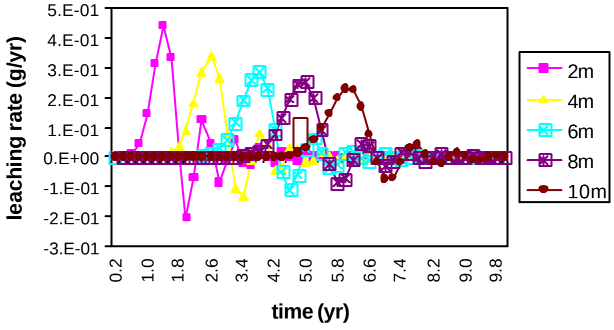


Figure D3. Cumulative mass of atrazine leached at site A, over 10 yrs

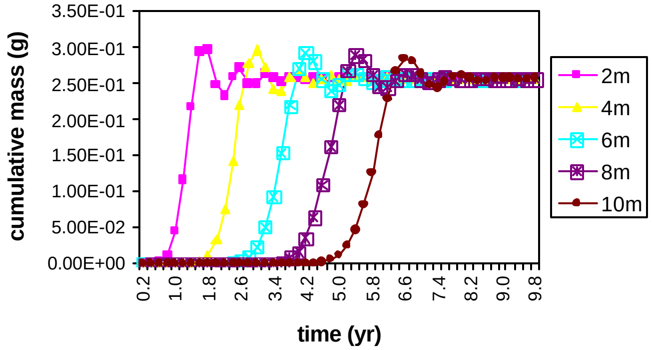


Figure D4. Leaching rate of dimethoate at site A, over 50 yrs

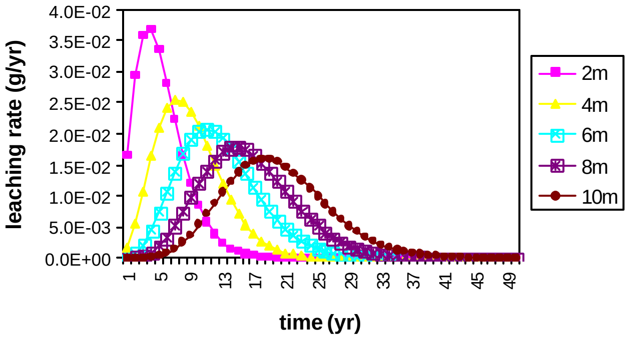


Figure D5. Leaching rate of dimethoate at site B, over 50 yrs

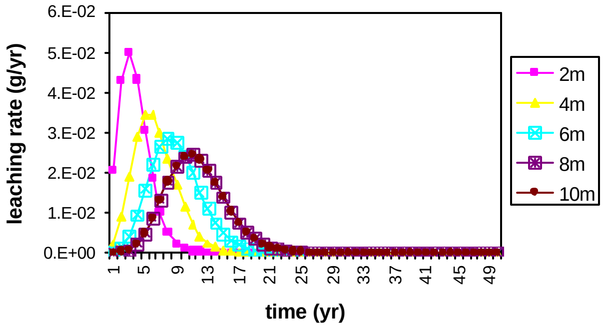


Figure D6. Leaching rate of lindane at site A, over 500 yrs

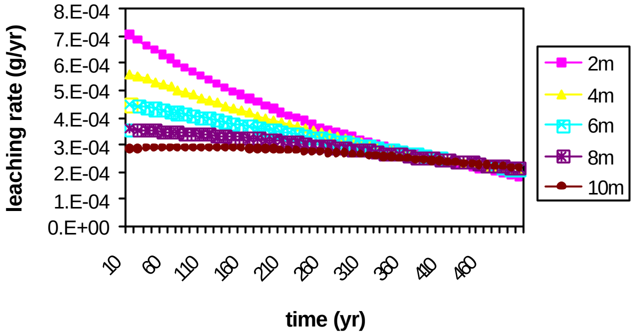


Figure D7. Leaching rate of lindane at site B, over 10 yrs

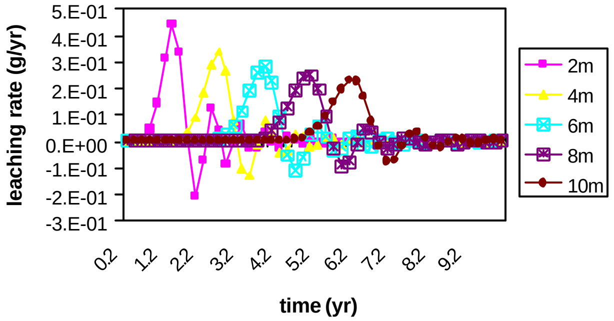


Figure D8. Soil profile of lindane at site A after 500 yrs

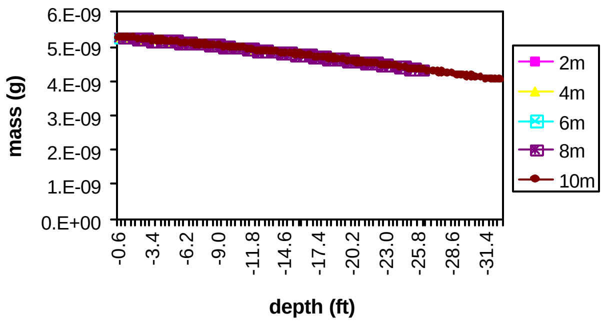


Figure D9. Leaching rate of 2,4-D at site A, over 50 yrs

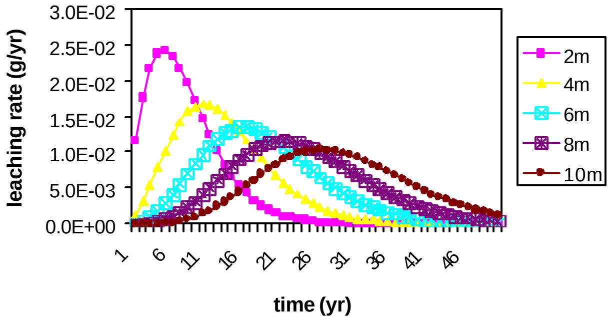


Figure D10. Leaching rate of 2,4-D at site B, over 50 yrs

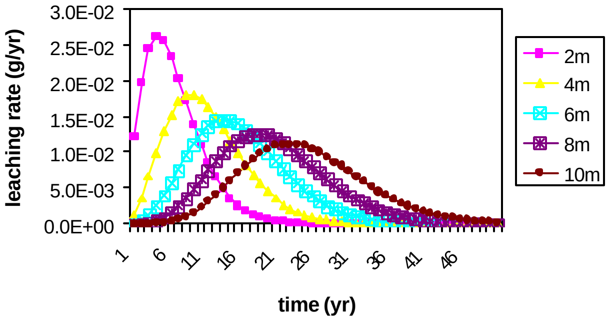


Figure D11. Leaching rate of carbofuran at site A, over 50 yrs

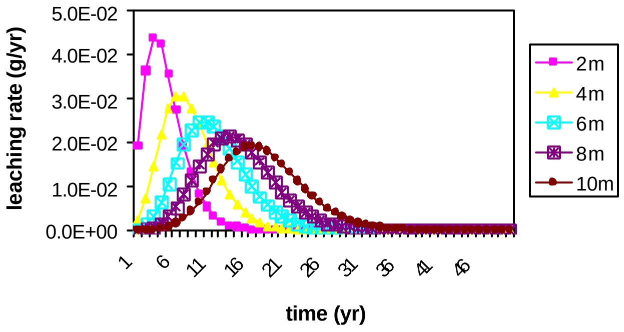


Figure D12. Leaching rate of carbofuran at site B, over 10 yrs

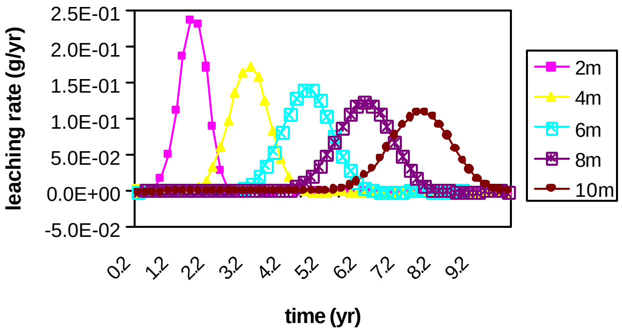


Figure D13. Leaching rate of carbaryl at site A, over 200 yrs

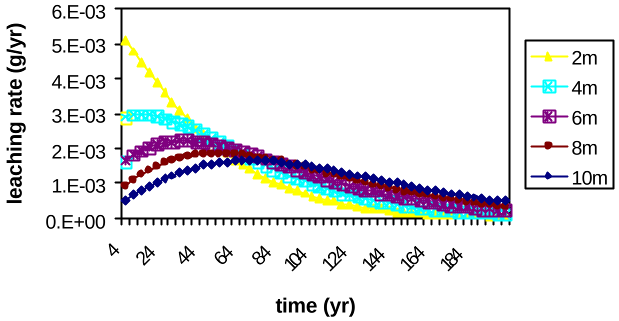


Figure D14. Leaching rate of carbaryl at site B, over 200 yrs

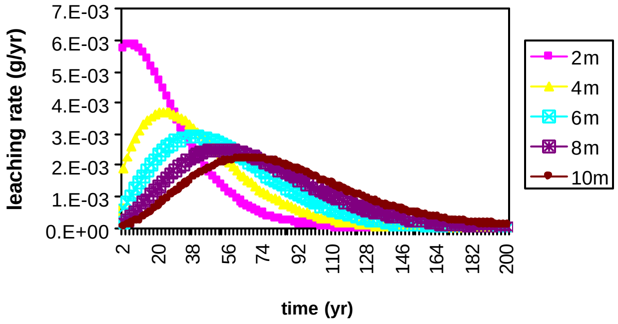


Figure D15. Leaching rate of dieldrin at site A, over 300 yrs

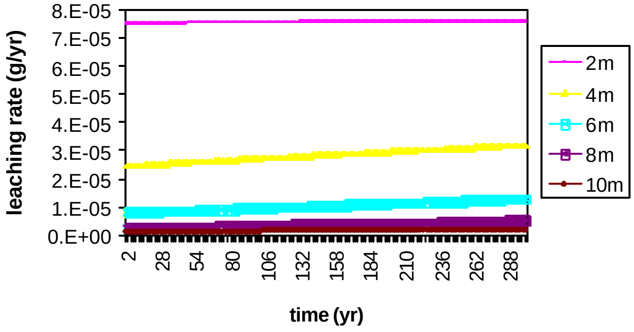


Figure D16. Leaching rate of dieldrin at site B, over 600 yrs

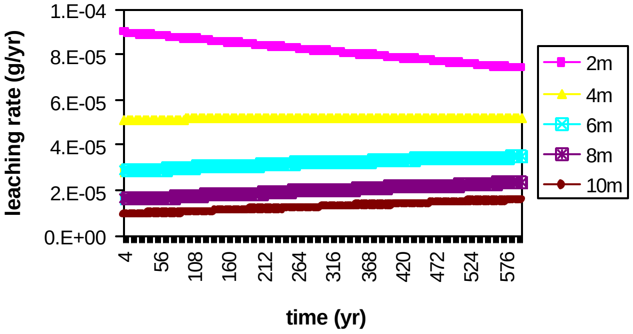


Figure D17. Leaching rate of fenthion at site A, over 600 yrs

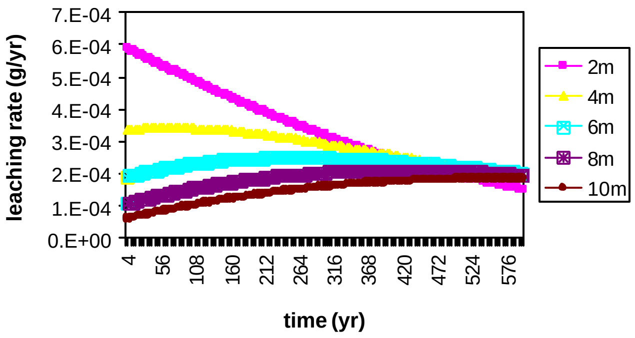


Figure D18. Leaching rate of fenthion at site B, over 200 yrs

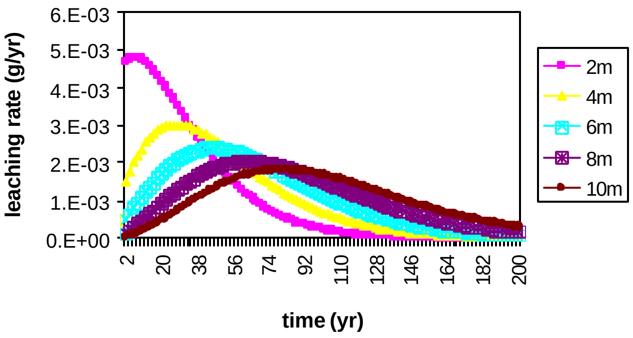


Figure D19. Leaching rate of parathion at site A, over 600 yrs

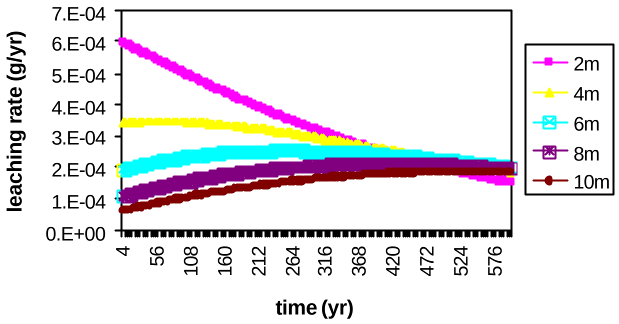
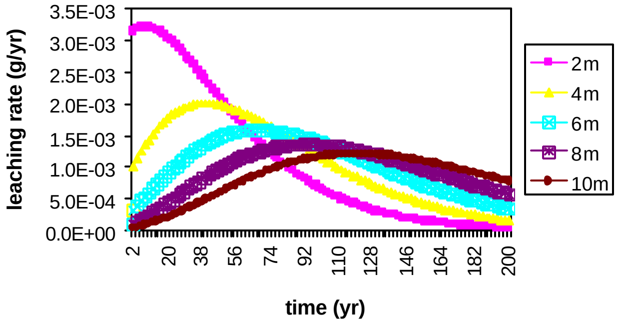


Figure D20. Leaching rate of parathion at site B, over 200 yrs



D2.2. Recharge rate

Figure D21. Soil profile of simazine at site A, after 50 yrs

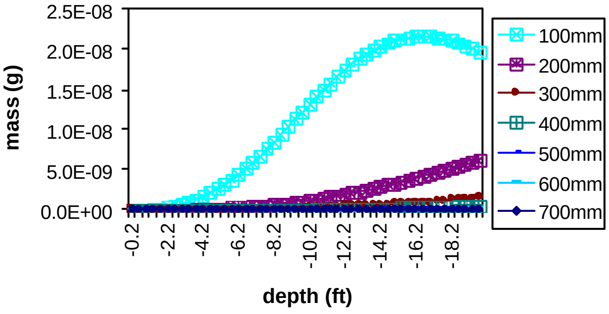


Figure D22. Soil profile of simazine at site A, after 100 yrs

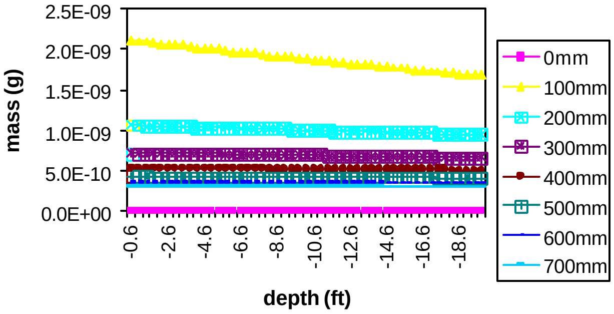


Figure D23. Leaching rate of atrazine at site A, over 10 yrs

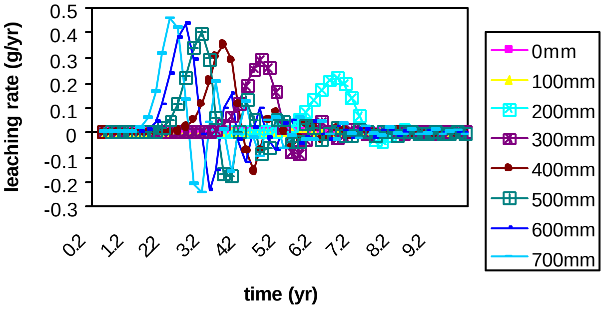


Figure D24. Leaching rate of atrazine at site B, over 10 yrs

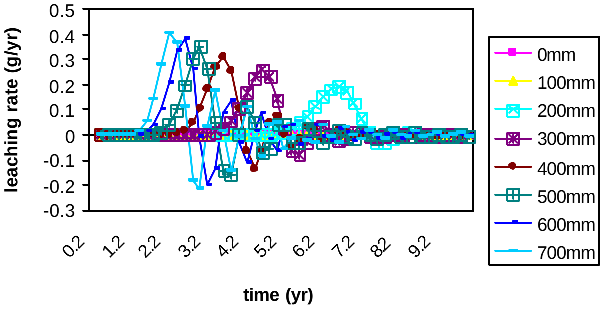


Figure D25. Cumulative mass of atrazine leached at site A, over 10 yrs

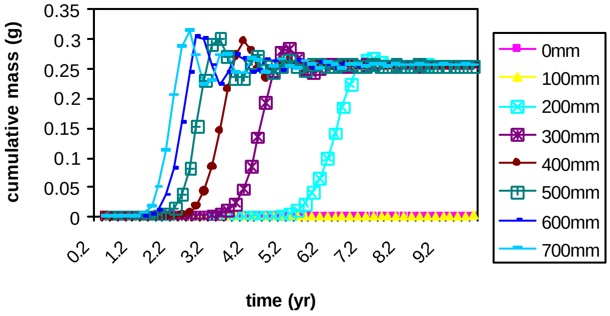


Figure D26. Cumulative mass of atrazine leached at site B, over 10 yrs

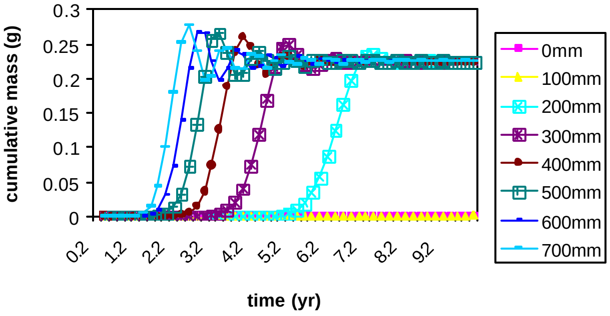


Figure D27. Leaching rate of dimethoate at site A, over 50 yrs

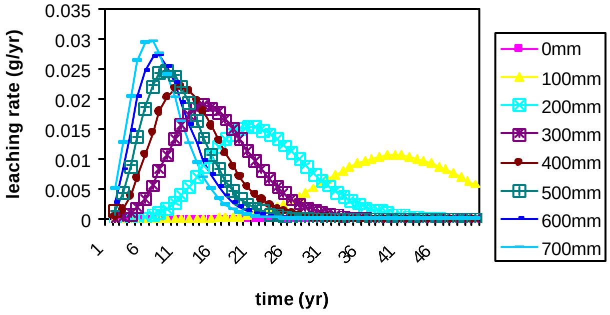


Figure D28. Leaching rate of dimethoate at site B, over 50 yrs

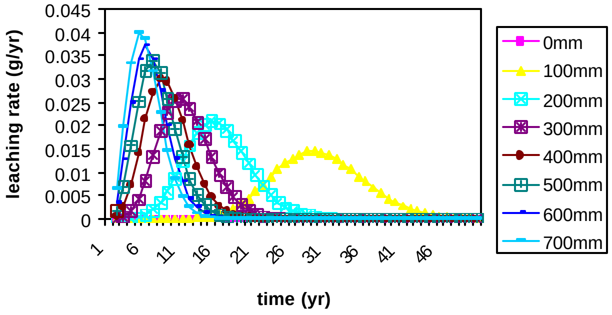


Figure D29. Soil profile of dimethoate at site A, after 50 yrs

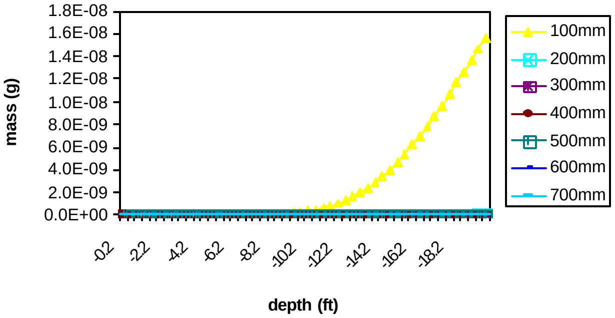


Figure D30. Soil profile of dimethoate at site B, after 50 yrs

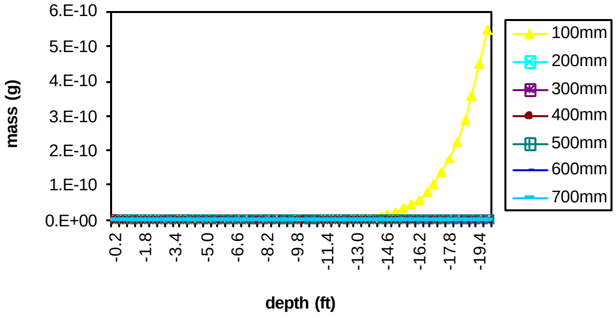


Figure D31. Leaching rate of lindane at site A, over 500 yrs

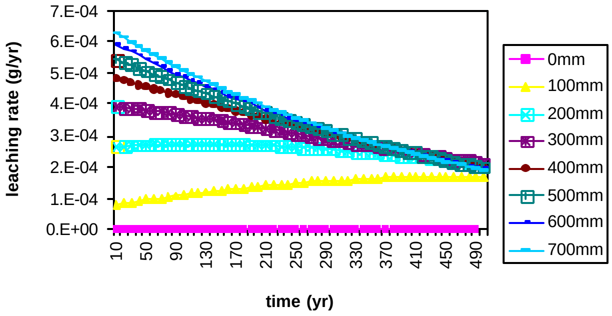


Figure D32. Leaching rate of lindane at site B, over 10 yrs

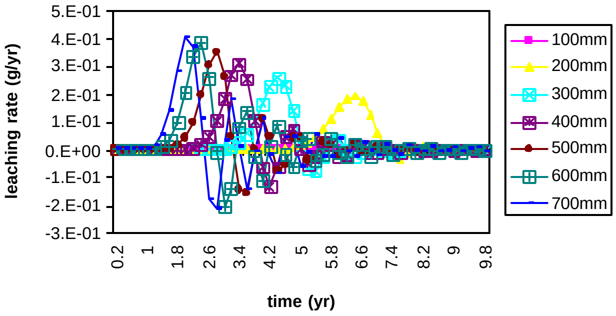


Figure D33. Cumulative mass of lindane leached at site A, over 500 yrs

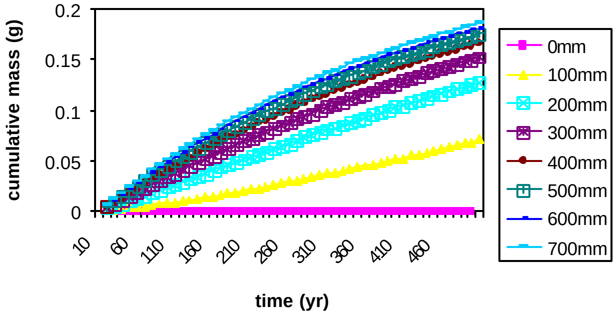


Figure D34. Cumulative mass of lindane leached at site B, over 500 yrs

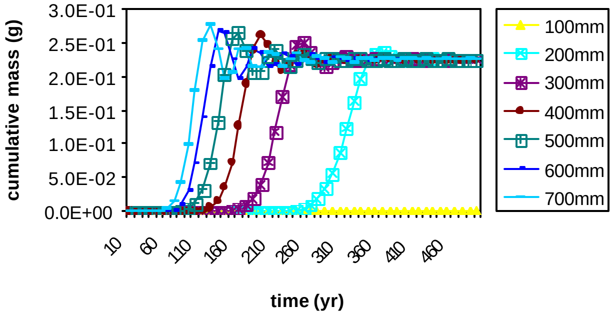


Figure D35. Soil profile of lindane at site A, after 500 yrs

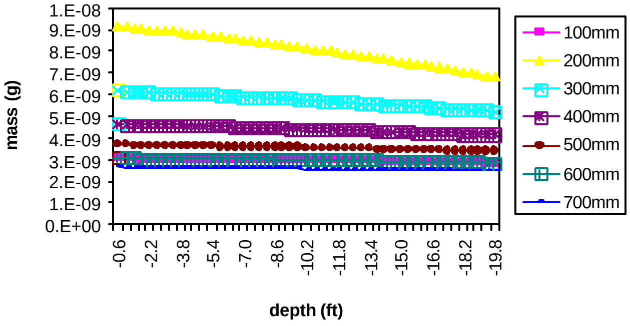


Figure D36. Leaching rate of 2,4-D at site A, over 50 yrs

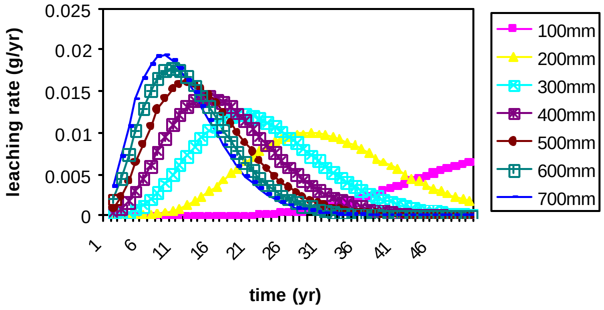


Figure D37. Leaching rate of 2,4-D at site B, over 50 yrs

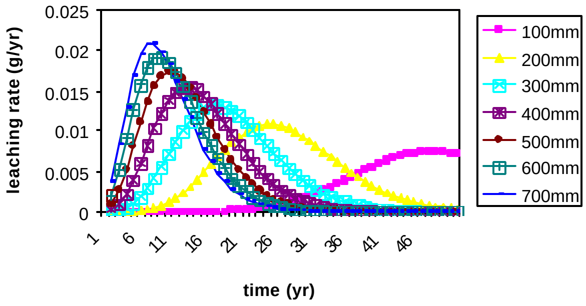


Figure D38. Leaching rate of carbofuran at site A, over 50 yrs

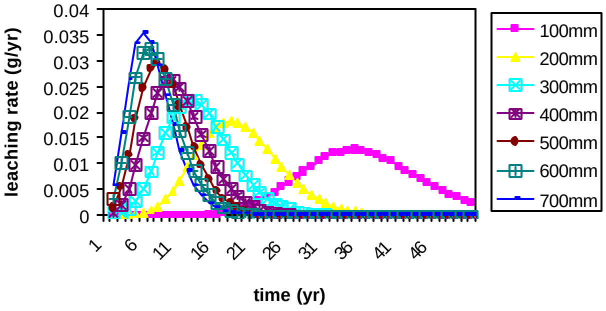


Figure D39. Leaching rate of carbofuran at site B, over 10 yrs

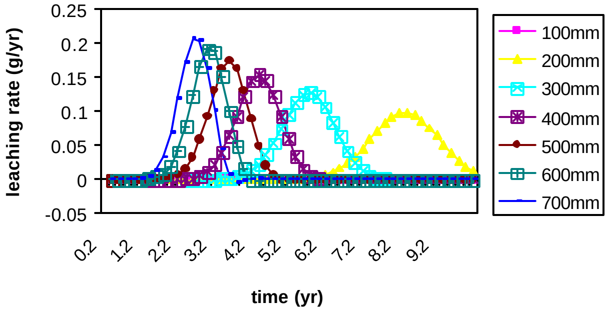


Figure D40. Leaching rate of carbaryl at site A, over 200 yrs

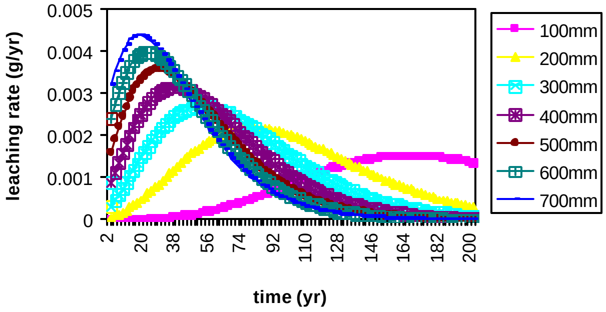


Figure D41. Leaching rate of carbaryl at site B, over 200 yrs

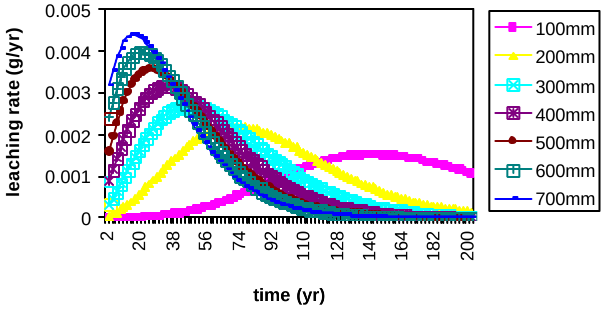


Figure D42. Leaching rate of dieldrin at site A, over 600 yrs

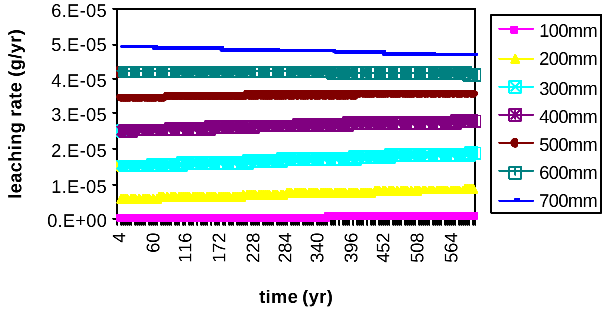


Figure D43. Leaching rate of dieldrin at site B, over 600 yrs

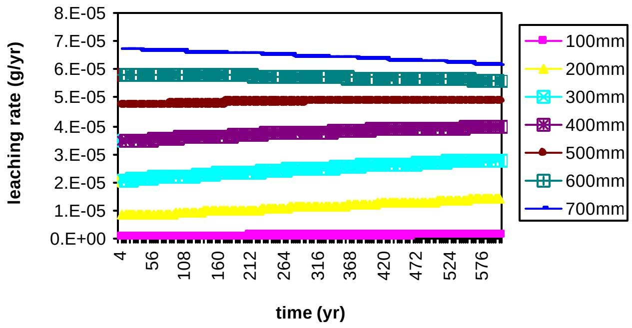


Figure D44. Leaching rate of fenthion at site A, over 600 yrs

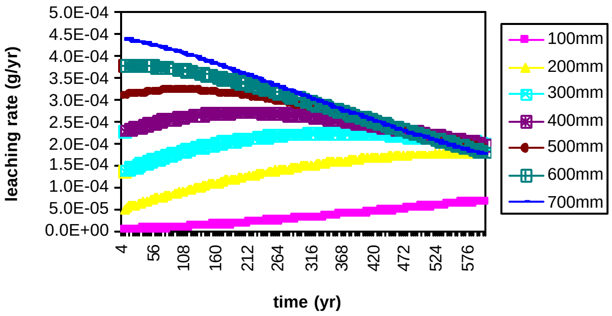


Figure D45. Leaching rate of fenthion at site B, over 200 yrs

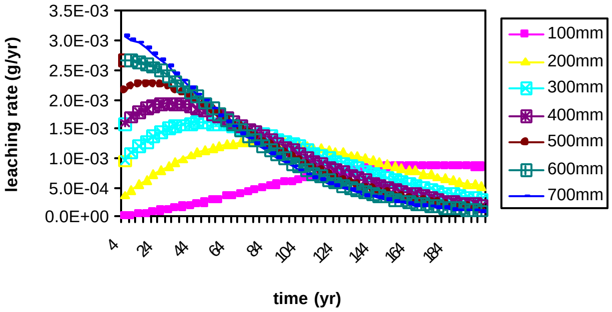


Figure D46. Leaching rate of parathion at site A, over 600 yrs

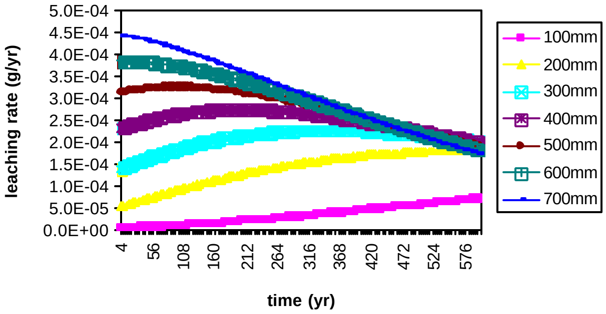
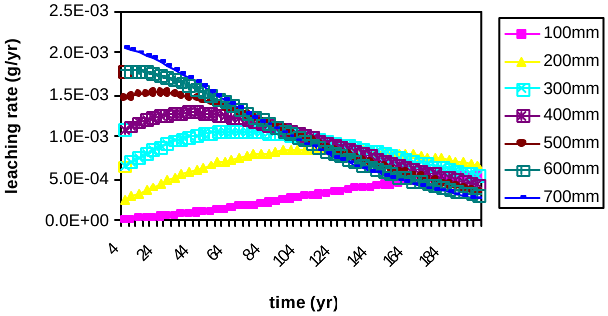


Figure D47. Leaching rate of parathion at site B, over 200 yrs



D2.3 Initial concentration

Figure D48. Leaching rate of atrazine at site A, over 10 yrs

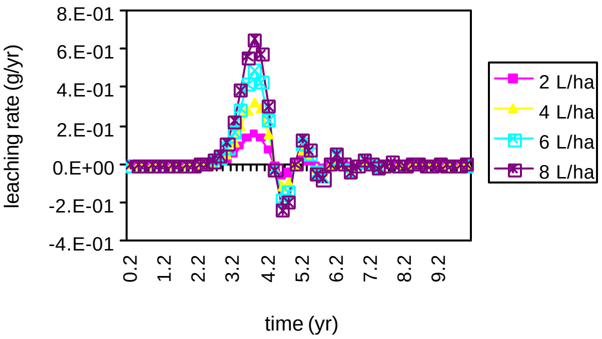


Figure D49. Leaching rate of atrazine at site B, over 10 yrs

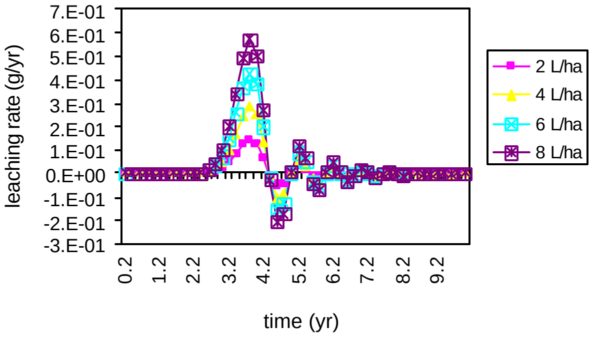


Figure D50. Leaching rate of dimethoate at site A, over 50 yrs

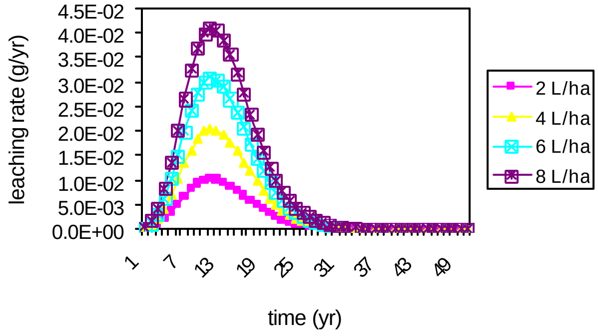


Figure D51. Leaching rate of dimethoate at site B, over 50 yrs

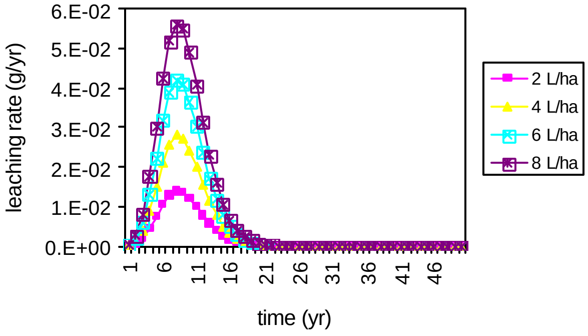


Figure D52. Soil profile of dimethoate at site A, after 50 yrs

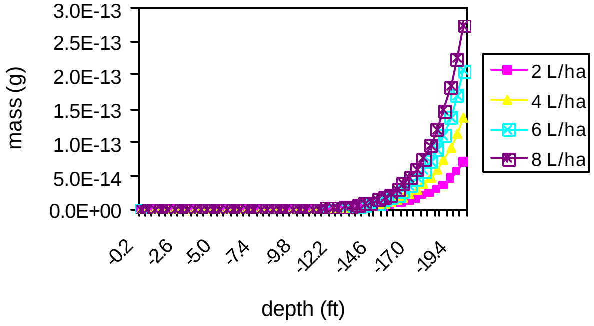


Figure D53. Soil profile of dimethoate at site B, after 50 yrs

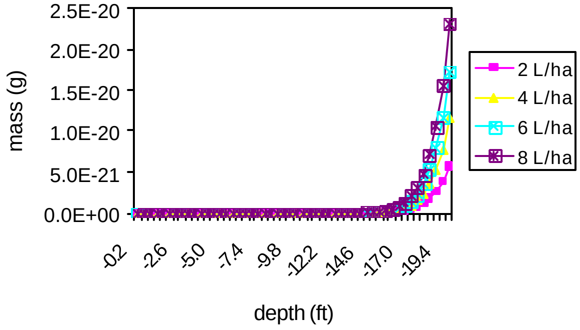


Figure D54. Leaching rate of lindane at site A, over 1000 yrs

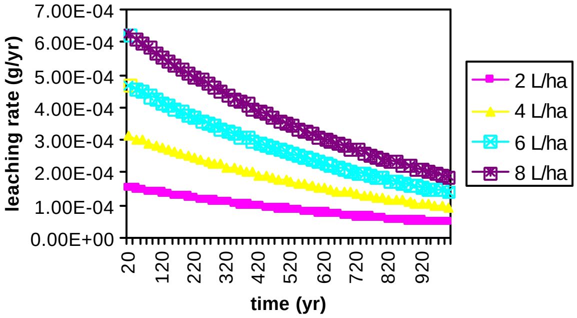


Figure D54. Leaching rate of lindane at site B, over 10 yrs

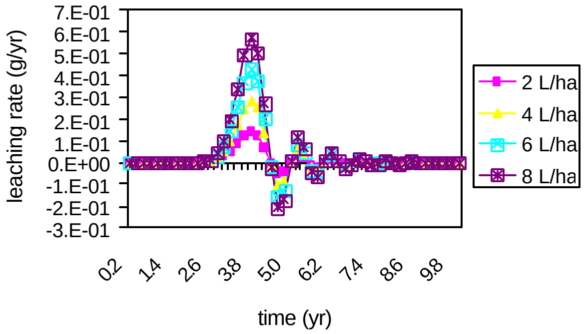


Figure D56. Leaching rate of 2,4-D at site A, over 50 yrs

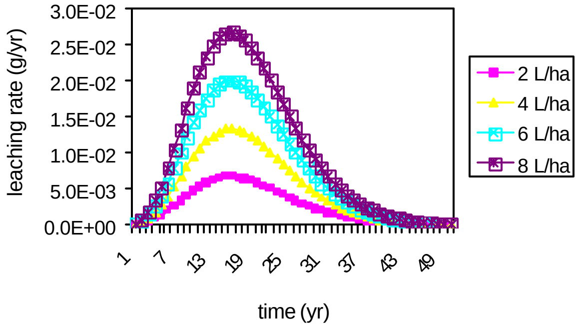


Figure D57. Leaching rate of 2,4-D at site B, over 50 yrs

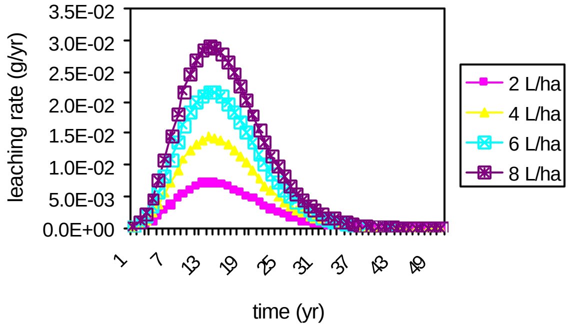


Figure D58. Leaching rate of carbofuran at site A, over 50 yrs

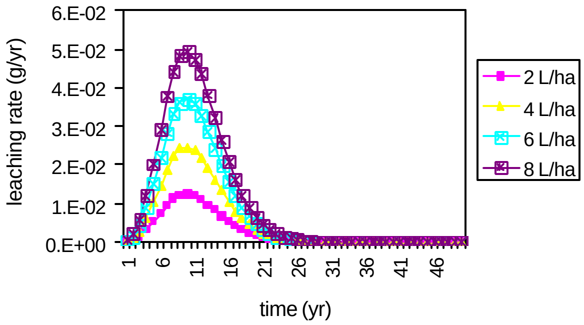


Figure D59. Leaching rate of carbofuran at site B, over 10 yrs

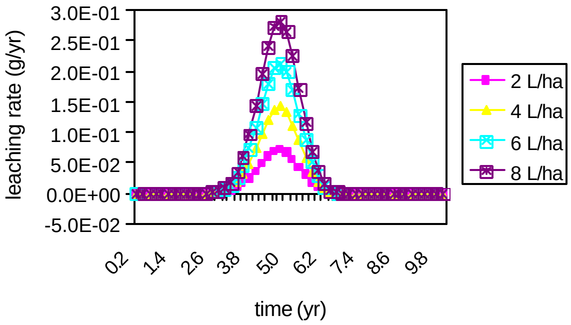


Figure D60. Leaching rate of carbaryl at site A, over 200 yrs

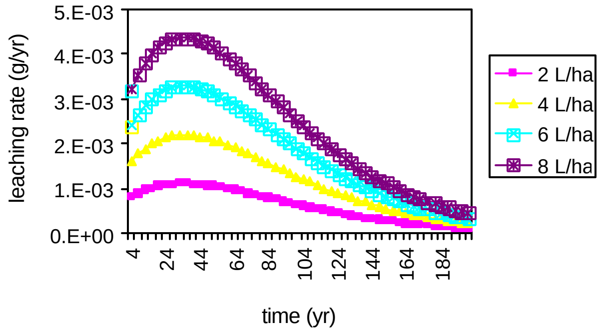


Figure D61. Leaching rate of carbaryl at site B, over 200 yrs

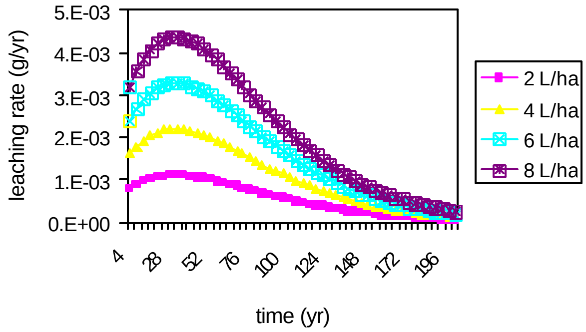


Figure D62. Leaching rate of dieldrin at site A, over 600 yrs

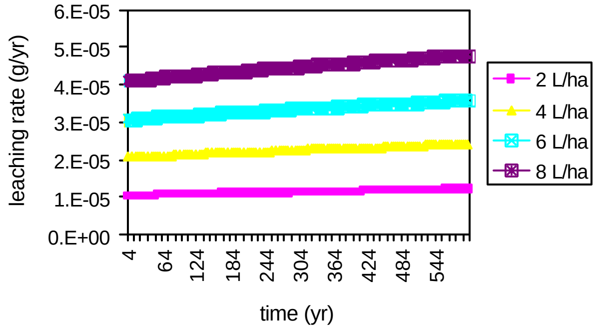


Figure D63. Leaching rate of dieldrin at site B, over 600 yrs

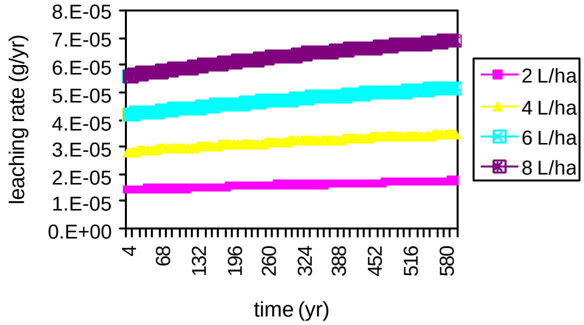


Figure D64. Soil profile of dieldrin at site A, after 600 yrs

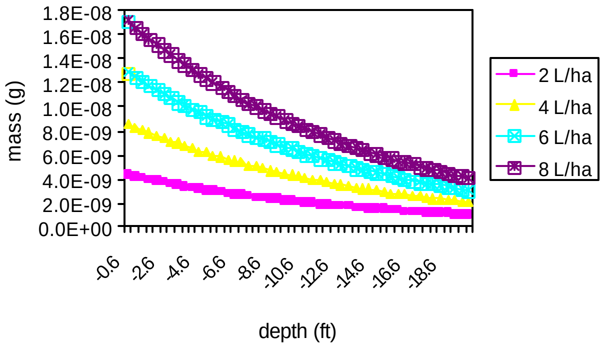


Figure D65. Soil profile of dieldrin at site B, after 600 yrs

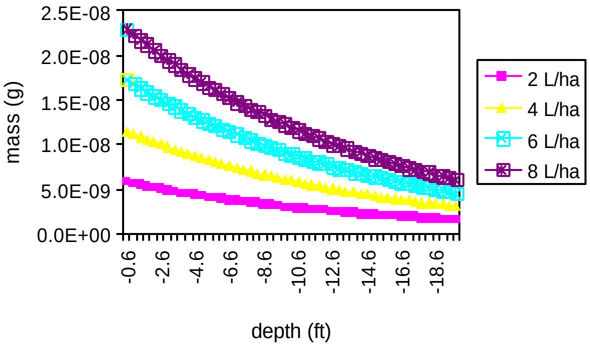


Figure D66. Leaching rate of fenthion at site A, over 600 yrs

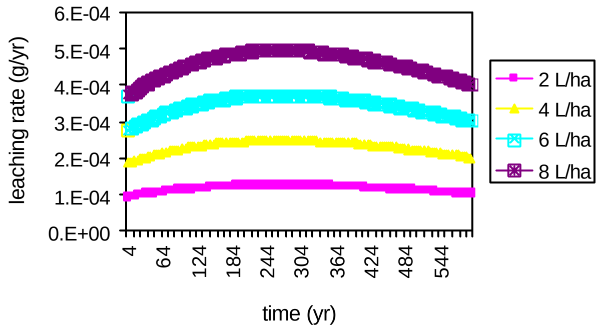


Figure D67. Leaching rate of fenthion at site B, over 200 yrs

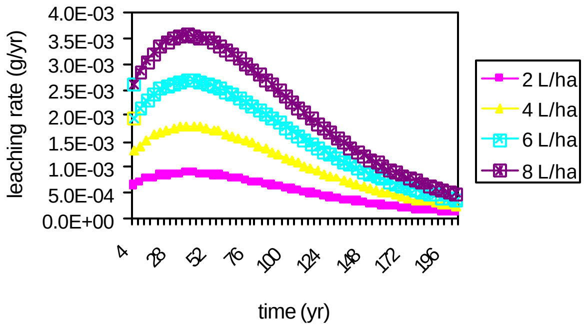


Figure D68. Soil profile of fenthion at site A, after 600 yrs

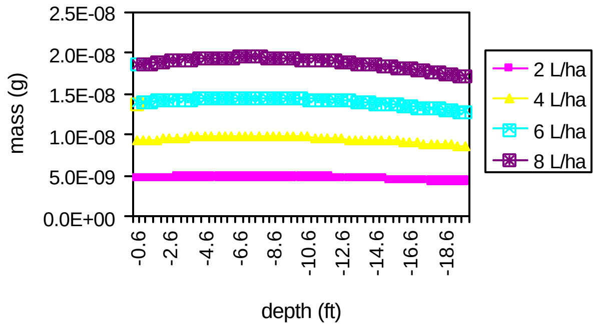


Figure D69. Soil profile of fenthion at site B, after 200 yrs

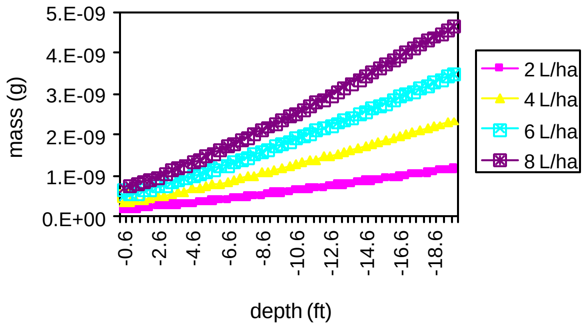


Figure D70. Leaching rate of parathion at site A, over 600 yrs

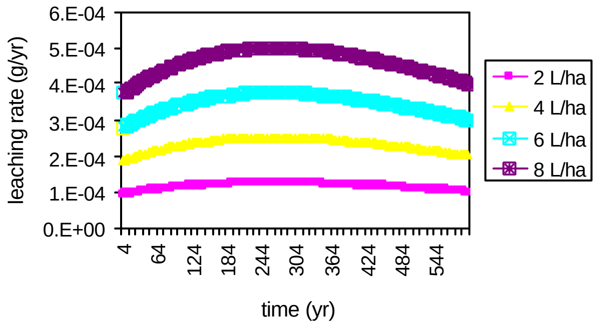
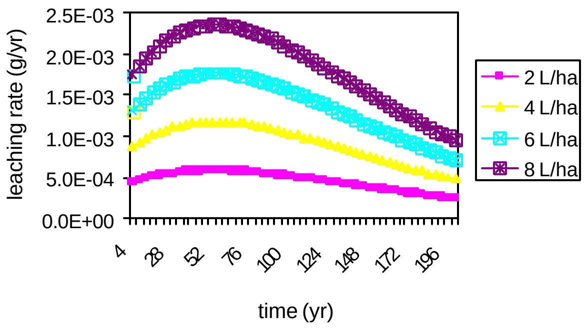


Figure D71. Leaching rate of parathion at site B, over 200 yrs



D2.4 Pesticide properties

Figure D72. Leaching rate of a generic pesticide at site A over 50 yrs, with varying Kh

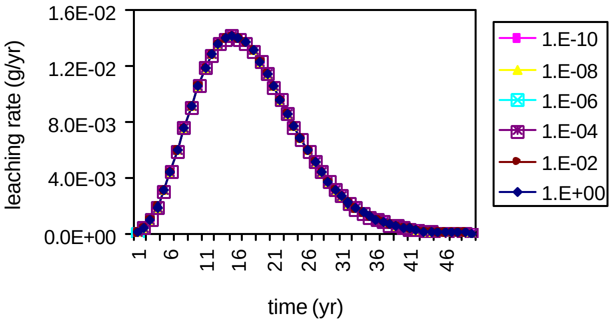


Figure D73. Leaching rate of a generic pesticide at site A over 50 yrs, with varying water solubility (mg/L)

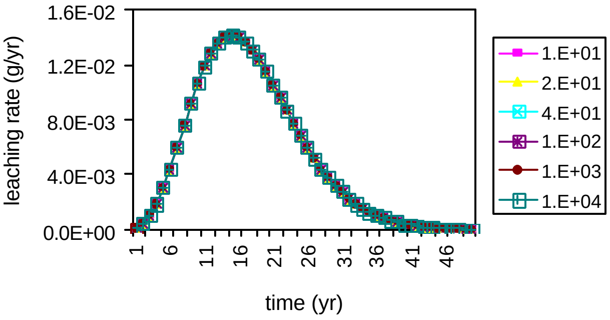
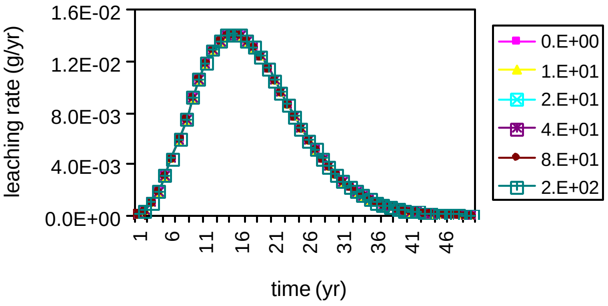


Figure 74. Leaching rate of a generic pesticide at site A over 50 yrs, with varying free air diffusion coefficient (m^2)



D2.5 Soil properties

Figure D75. Leaching rate of simazine at site A, with varying dry bulk density (g)

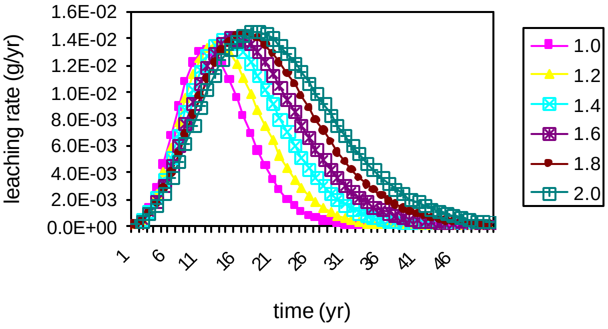


Figure D76. Leaching rate of simazine at site A, with varying effective porosity (fraction)

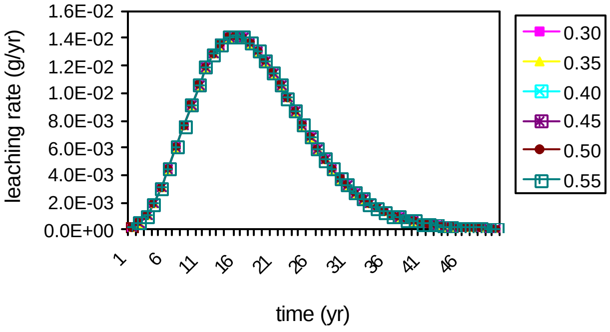


Figure D77. Leaching rate of simazine at site A, with varying volumetric water content (%)

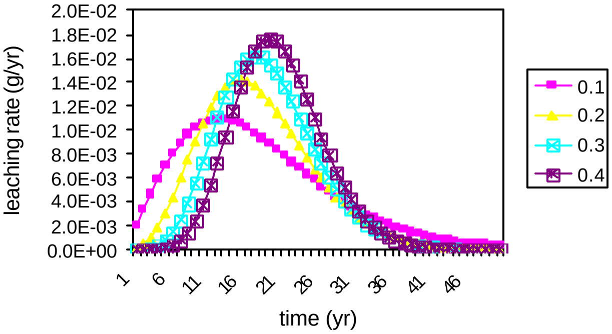
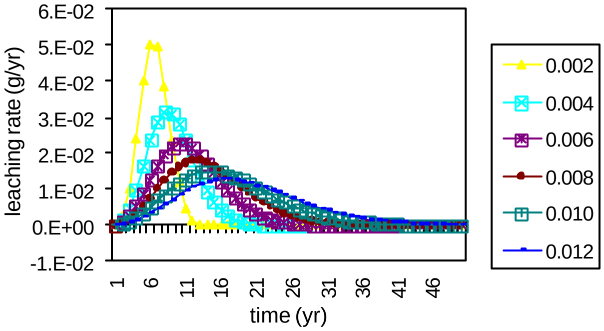


Figure D78. Leaching rate of simazine at site A, with varying organic carbon content (fraction)



D2.6 ‘Realistic’ scenarios run for once-off and yearly applications

Figure D79. Leaching rate of simazine applied once over 50 yrs at both sites

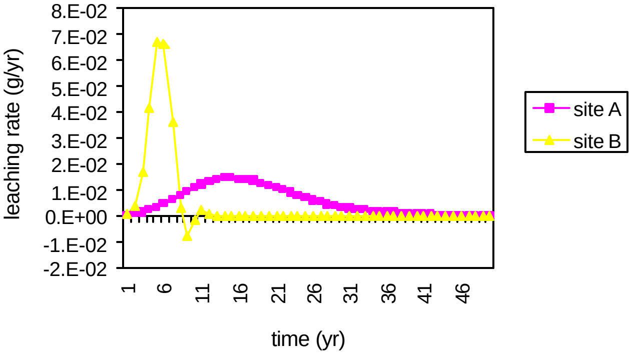


Figure D80. Leaching rate of simazine applied through recharge over 50 yrs at both sites

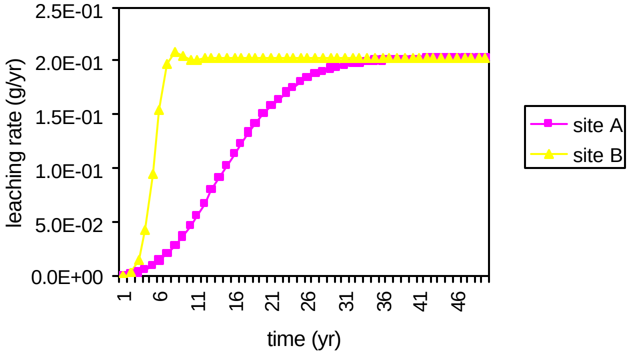


Figure D81. Leaching rate of atrazine applied once over 10 yrs at both sites

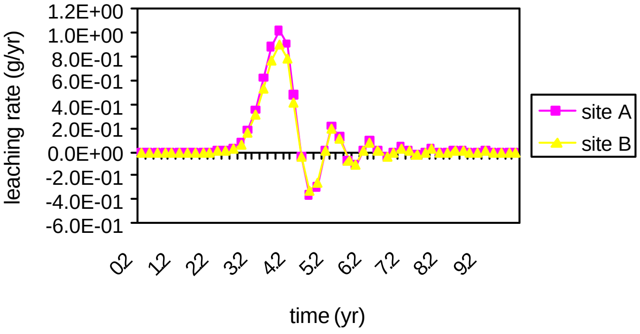


Figure D82. Leaching rate of atrazine applied through recharge for 10 yrs at both sites

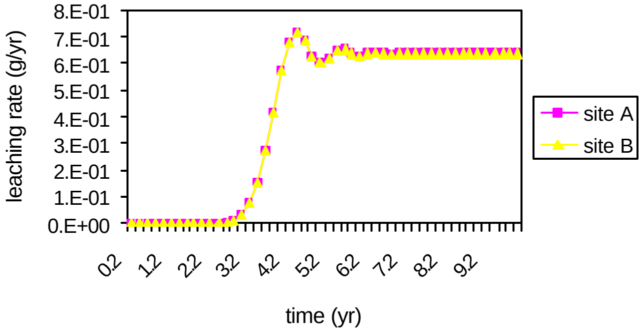


Figure D83. Leaching rate of dimethoate applied once over 50 yrs, at both sites

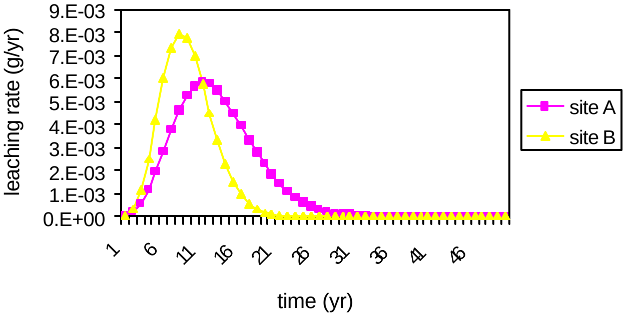


Figure D84. Leaching rate of dimethoate applied through recharge over 50 yrs, at both sites

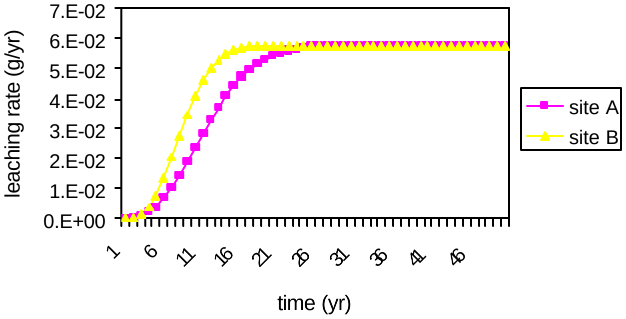


Figure D85. Leaching rate of lindane applied once over 600 yrs, at site A

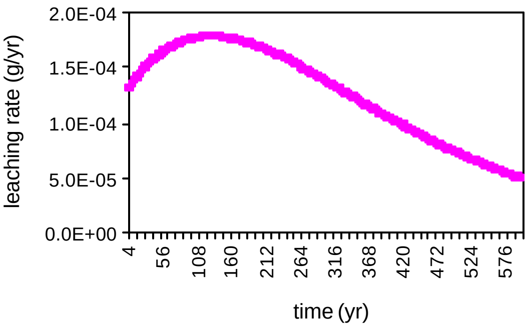


Figure D86. Leaching rate of lindane applied through recharge over 600 yrs, at site A

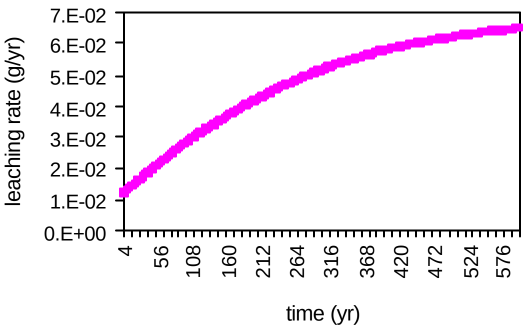


Figure D87. Leaching rate of lindane applied once over 10 yrs, at site B

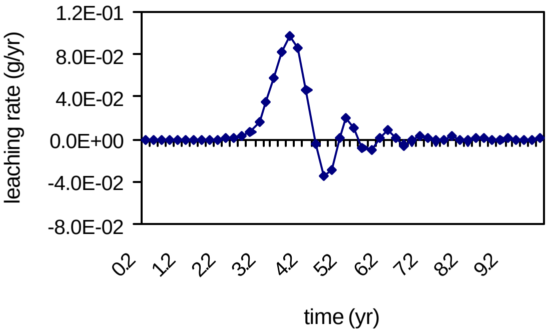


Figure D88. Leaching rate of lindane applied through recharge over 10 yrs, at site B

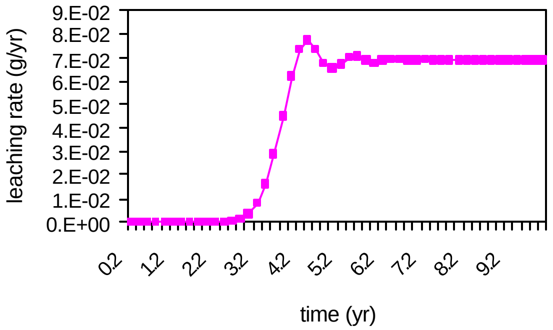


Figure D89. Leaching rate of 2,4-D applied once over 50 yrs at both sites

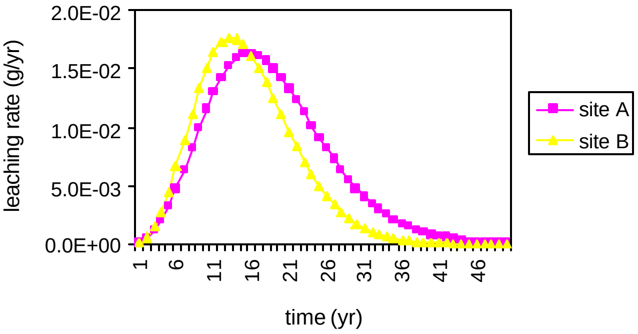


Figure D90. Leaching rate of 2,4-D applied through recharge for 50 yrs at both sites

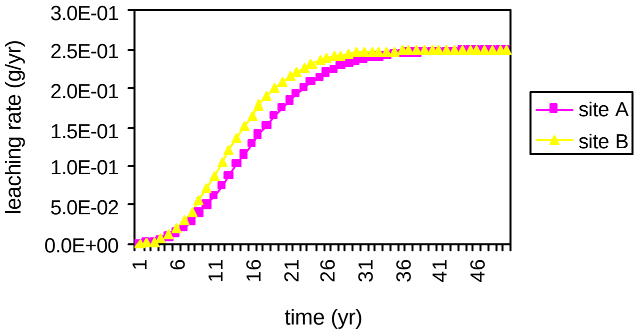


Figure D91. Leaching rate of carbofuran applied once over 50 yrs at both sites

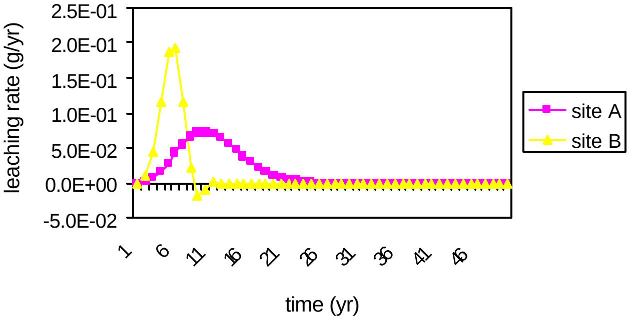


Figure D92. Leaching rate of carbofuran applied through recharge over 50 yrs at both sites

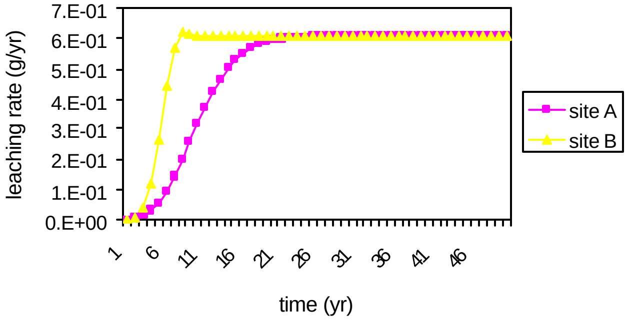


Figure D93. Leaching rate of carbaryl applied once over 200 yrs at both sites

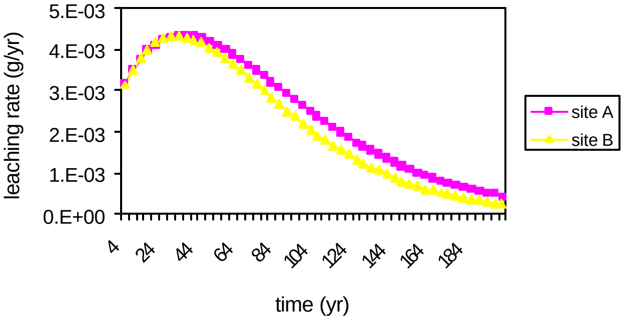


Figure D94. Leaching rate of carbaryl applied through recharge over 200 yrs at both sites

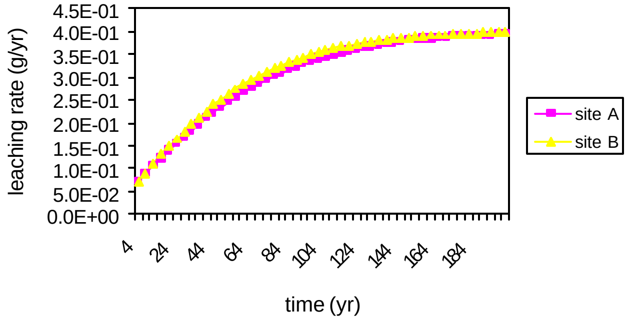


Figure D95. Leaching rate of dieldrin applied once over 600 yrs, at both sites

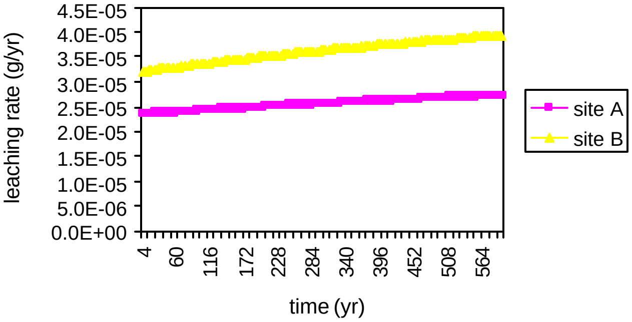


Figure D96. Leaching rate of dieldrin applied through recharge over 600 yrs, at both sites

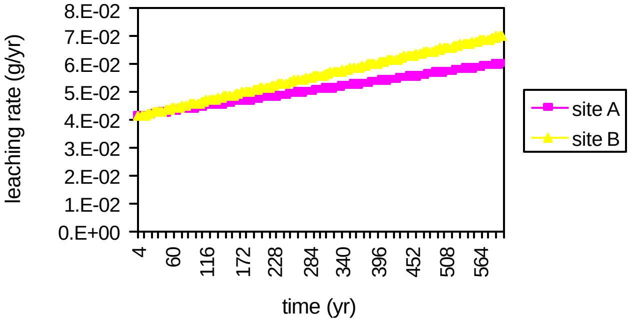


Figure D97. Leaching rate of fenthion applied once over 600 yrs, at both sites

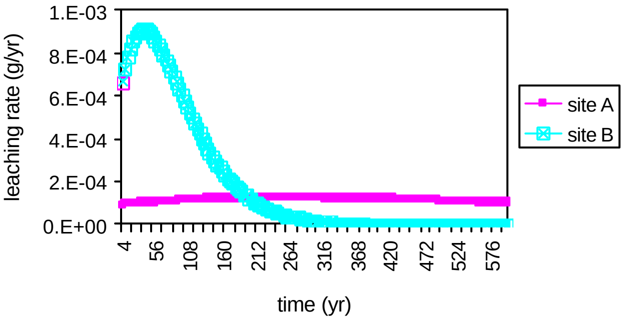


Figure D98. Leaching rate of fenthion applied through recharge over 600 yrs, at both sites

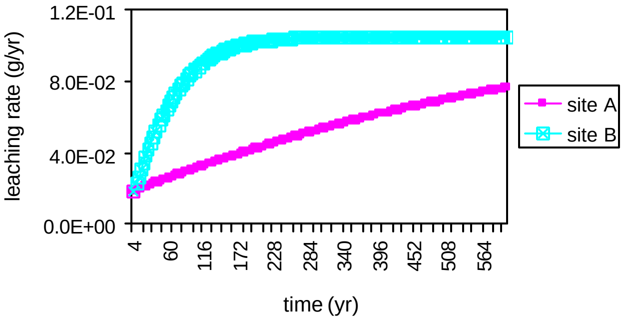


Figure D99. Leaching rate of parathion applied once over 600 yrs, at both sites

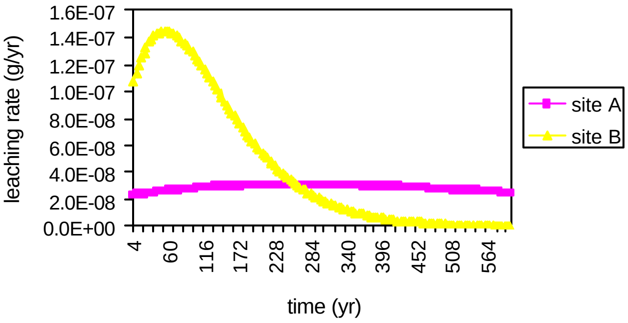
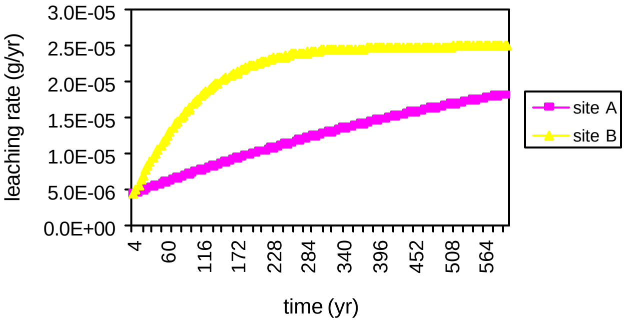


Figure D100. Leaching rate of fenthion applied through recharge over 600 yrs, at both sites



APPENDIX E

Typical input and output files used in the sensitivity analysis of SWAP, version 3.0.3. The example is based on experimentally determined sorption coefficients (Kd) for simazine, simulated for a silt-rich sandy soil, in 1996.

1. Input file

```
********************************************************************************
* Filename: Hupsel.swp
* Contents: SWAP 3 - Main input data
********************************************************************************
* Comment area:
*
* Case: Water and solute transport in the Hupsel area,
*      a catchment in the eastern part of the Netherlands
*
*      This case is described as example in the User's Guide
********************************************************************************

*   The main input file .swp contains the following sections:
*          - General section
*          - Meteorology section
*          - Crop section
*          - Soil water section
*          - Lateral drainage section
*          - Bottom boundary section
*          - Heat flow section
*          - Solute transport section


*** GENERAL SECTION ***

********************************************************************************
* Part 1: Environment

  PROJECT   = 'Hupsel'           ! Project description, [A80]
  PATHWORK  = ' '                ! Path to work directory, [A80]
  PATHATM   = 'Data\Weather\'     ! Path to directory with weather files, [A80]
  PATHCROP  = 'Data\Crops\'       ! Path to directory with crop files, [A80]
  PATHDRAIN = 'Data\Drainage\'    ! Path to directory with drainage files, [A80]
  SWSCRE    = 1          ! Switch, display progression of simulation run:
                    !   SWSCRE = 0:  no display to screen
                    !   SWSCRE = 1:  display waterbalance to screen
                    !   SWSCRE = 2:  display daynumber to screen
  SWERROR   = 1  ! Switch for printing errors to screen [Y=1, N=0]
********************************************************************************


********************************************************************************
* Part 2: Simulation period
*
  TSTART  = 01-jan-1996 ! Start date of simulation run, give day-month-year, [dd-mmm-yyyy]
  TEND    = 31-dec-1996 ! End   date of simulation run, give day-month-year, [dd-mmm-yyyy]
```

```
********************************************************************************


********************************************************************************
* Part 3: Output dates

* Output times for water and solute balances
  SWYRVAR = 0         ! Switch, output at fixed or variable dates:
                      ! SWYRVAR = 0: each year output of balances at the same date
                      ! SWYRVAR = 1: output of balances at different dates

* If SWYRVAR = 0 specify fixed date:
  DATEFIX = 31 12     ! Specify day and month for output of yearly balances, [dd mm]

* If SWYRVAR = 1 specify all output dates [dd-mmm-yyyy], maximum MAOUT dates:
  OUTDAT =
  31-dec-1997
  31-dec-1998
* End of table

* Dates for intermediate output of state variables and fluxes
  SWMONTH = 1         ! Switch, output each month, [Y=1, N=0]
  PERIOD = 0          ! Fixed output interval, ignore = 0, [0..366, I]
  SWRES  = 0          ! Switch, reset output interval counter each year, [Y=1, N=0]
  SWODAT = 1          ! Switch, extra output dates are given in table, [Y=1, N=0]

* If SWODAT = 1, specify all intermediate output dates [dd-mmm-yyyy],
* maximum MAOUT dates:

  OUTDATINT =
31-Jan-1996
29-Feb-1996
31-Mar-1996
30-Apr-1996
31-May-1996
30-Jun-1996
31-Jul-1996
31-Aug-1996
30-Sep-1996
31-Oct-1996
30-Nov-1996
31-Dec-1996

* End of table
********************************************************************************


********************************************************************************
* Part 4: Output files

  OUTFIL   = 'Result' ! Generic file name of output files, [A16]
  SWHEADER = 0        ! Print header of each balance period, [Y=1, N=0]

* Optional output files for water quality models or other specific use

  SWAFO  = 0        ! Switch, output file with formatted hydrological data
```

```
                 ! SWAFO = 0: no output
                 ! SWAFO = 1: output to a file named *.AFO
                 ! SWAFO = 2: output to a file named *.BFO

  SWAUN  = 0        ! Switch, output file with unformatted hydrological data
                 ! SWAUN = 0: no output
                 ! SWAUN = 1: output to a file named *.AUN
                 ! SWAUN = 2: output to a file named *.BUN

* if SWAFO = 1 or 2,   or if SWAUN = 1 or 2 then specify SWDISCRVERT and  CritDevMasBalAbs
  SWDISCRVERT = 0   ! Switch to convert vertical discretization   [Y=1, N=0]
                 !   only when SWAUN=1 or SWAFO=1 the generated output
                 !   files (*.afo,*.bfo,*.aun,*.bun) are influenced
                 ! SWDISCRVERT = 0: no conversion
                 ! SWDISCRVERT = 1: convert vertical discretization,
                 !                 numnodNew and dzNew are required
* Critical Absolute Deviation in water balance
* (when exceeded: simulation continues, but file with errors is created (file-extension *.DWB))
  CritDevMasBalAbs = 0.1  ! Critical Absolute Deviation in water balance [1.0d-30..1.0 cm, R]
*
* Only If SWDISCRVERT = 1 then numnodNew and dzNew are required
*  NUMNODNEW = 6    ! New number of nodes [1...macp,I,-]
*                ! (boundaries of soil layers may not change, which implies
*                !  that the sum of thicknesses within a soil layer must be
*                !  equal to the thickness of the soil layer.  See also:
*                !  SoilWaterSection, Part4: Vertical discretization of soil profile)
*  DZNEW = 10.0 10.0 10.0 20.0 30.0 50.0 ! thickness of compartments [1.0d-6...5.0d2, cm, R]
*
*
  SWVAP  = 1        ! Switch, output profiles of moisture, solute and temperature, [Y=1, N=0]
  SWATE  = 0        ! Switch, output file with soil temperature profiles, [Y=1, N=0]
  SWBLC  = 1        ! Switch, output file with detailed yearly water balance, [Y=1, N=0]

* Required only when SWMACRO= 1 or 2 (see Soil Water section, Part 10: macropore flow)
  SWBMA  = 0        ! Switch, output file with detailed yearly water balance Macropores, [Y=1, N=0]

* Required only when SWDRA=2 (see lateral section): input of SWDRF and SWSWB
  SWDRF  = 0        ! Switch, output drainage fluxes, only for extended drainage, [Y=1, N=0]
  SWSWB  = 0        ! Switch, output surface water reservoir, only for extended drainage, [Y=1, N=0]
**********************************************************************************


*** METEOROLOGY SECTION ***

**********************************************************************************
* General data

  METFIL = 'Stellenbosch' ! File name of meteorological data without extension .YYY, [A16]
                   ! Extension equals last 3 digits of year number, e.g. 2003 has extension .003
  SWETR  =  0           ! Switch, use reference ET values of meteo file [Y=1, N=0]

* If SWETR = 0, then LAT,ALT and ALTW must have realistic values
  LAT    =   -34.0       ! Latitude of meteo station, [-60..60 degrees, R, North = +]
  ALT    =   70.0       ! Altitude of meteo station, [-400..3000 m, R]
  ALTW   =    2.0       ! Altitude of wind speed measurement (10 m is default) [0..99 m, R]
*
```

```
  SWRAIN =  0          ! Switch for use of actual rainfall intensity:
                       ! SWRAIN = 0: Use daily rainfall amounts
                       ! SWRAIN = 1: Use daily rainfall amounts + mean intensity
                       ! SWRAIN = 2: Use daily rainfall amounts + duration

* If SWRAIN = 1, then specify mean rainfall intensity RAINFLUX [0.d0..1000.d0 cm/d, R]
* as function of time TIME [0..366 d, R], maximum 30 records

   TIME    RAINFLUX
    1.0       2.0
  360.0       2.0
* End of table
**********************************************************************************


*** CROP SECTION ***

**********************************************************************************
* Part 1: Crop rotation scheme during simulation period

* Specify information for each crop (maximum MACROP):
* CROPSTART = date of crop emergence, [dd-mmm-yyyy]
* CROPEND = date of crop harvest, [dd-mmm-yyyy]
* CROPNAME = crop name, [A16]
* CROPFIL = name of file with crop input parameters without extension .CRP, [A16]
* CROPTYPE = type of crop model: simple = 1, detailed general = 2, detailed grass = 3

  CROPSTART      CROPEND       CROPNAME   CROPFIL     CROPTYPE
  01-jan-1996    30-dec-1996   'Tree'     'Tree'       1

* End of table
**********************************************************************************


**********************************************************************************
* Part 2: Fixed irrigation applications

  SWIRFIX = 1    ! Switch for fixed irrigation applications
                 ! SWIRFIX = 0: no irrigation applications are prescribed
                 ! SWIRFIX = 1: irrigation applications are prescribed

* If SWIRFIX = 1:

  SWIRGFIL  = 0  ! Switch for file with fixed irrigation applications:
                 ! SWIRGFIL = 0: data are specified in the .swp file
                 ! SWIRGFIL = 1: data are specified in a separate file

* If SWIRGFIL  = 0 specify information for each fixed irrigation event (max. MAIRG):
* IRDATE   = date of irrigation, [dd-mmm-yyyy]
* IRDEPTH  = amount of water, [0.0..100.0 cm, R]
* IRCONC   = concentration of irrigation water, [0.0..1000.0 mg/cm3, R]
* IRTYPE   = type of irrigation: sprinkling = 0, surface = 1

      IRDATE   IRDEPTH    IRCONC   IRTYPE
 15-jan-1996      1.5      0.003       1
 15-feb-1996      1.0      0.003       1
```

```
 15-mar-1996      0.5       0.003       1
 15-apr-1996      0.2       0.003       1
 15-may-1996      0.2       0.003       1
 15-jun-1996      0.2       0.003       1
 15-jul-1996      0.2       0.003       1
 15-aug-1996      0.2       0.003       1
 15-sep-1996      0.2       0.003       1
 15-oct-1996      0.2       0.003       1
 15-nov-1996      0.6       0.003       1
 15-dec-1996      1.0       0.003       1
* --- end of table

* If SWIRGFIL  = 1 specify name of file with data of fixed irrigation applications:
  IRGFIL = 'testirri'      ! File name without extension .IRG [A16]
**********************************************************************************


*** SOIL WATER SECTION ***

**********************************************************************************
* Part 1: Initial moisture condition

 SWINCO = 2 ! Switch, type of initial moisture condition:
           ! 1 = pressure head as function of depth is input
           ! 2 = pressure head of each compartment is in hydrostatic equilibrium
           !     with initial groundwater level
           ! 3 = read final pressure heads from previous Swap simulation

* If SWINCO = 1, specify initial pressure head  H [-1.d10..1.d4 cm, R] as function of
* soil depth ZI [-10000..0 cm, R], maximum MACP data pairs:
      ZI         H
   -0.5     -92.831
 -195.0      99.591
* End of table

* If SWINCO = 2, specify:
  GWLI   = -200.0  ! Initial groundwater level, [-10000..100 cm, R]

* If SWINCO = 3, specify:
  INIFIL = 'result.end'   ! name of final with extension .END [a200]
**********************************************************************************


**********************************************************************************
* Part 2: Ponding, Runoff and Runon
*
 PONDMX  = 0.2  ! Maximum thickness of ponding water layer, [0..1000 cm, R]
*
 RSRO    =  0.5 ! drainage Resistance of Surface RunOff [0.001..1.0 d, R]
 RSROEXP =  1.0 ! exponent in relation of surface runoff [0.1....10.0, R]
*
*
* Specify whether runon from external source (fiel) should be included
*
  SWRUNON = 0  ! Switch, input of runon:
           ! 0 = No input of runon
```

```
          ! 1 = runon as input
*
* If SWRUNON = 1 specify name of file with runon input data
*        - this file may be an output-*.inc-file (with only 1 header) of previous Swap-simulation):
*        - from this file 2 columns are read, with column-headers  'date' and 'Runoff'
*        - the column 'date' must have dates that correpond to the current simulation period (dates are
compared)
  RUFIL = 'runon.inc' ! File name (with extension) with input data, must have extension (e.g..INC) [A80]
********************************************************************************


********************************************************************************
* Part 3: Soil evaporation
*
  SWCFBS = 0   ! Switch for use of coefficient CFBS for soil evaporation [Y=1, N=0]
           ! 0 = CFBS is not used
           ! 1 = CFBS used to calculate potential evaporation from potential
           !     evapotranspiration or reference evapotranspiration

* If SWCFBS = 1, specify coefficient CFBS:
  CFBS   = 1.0 ! Coefficient for potential soil evaporation, [0.5..1.5 -, R]

  SWREDU = 1   ! Switch, method for reduction of potential soil evaporation:
           ! 0 = reduction to maximum Darcy flux
           ! 1 = reduction to maximum Darcy flux and to maximum Black (1969)
           ! 2 = reduction to maximum Darcy flux and to maximum Bo/Str. (1986)

 COFRED = 0.35 ! Soil evaporation coefficient of Black, [0..1 cm/d1/2, R],
           ! or Boesten/Stroosnijder, [0..1 cm1/2, R]
 RSIGNI =  0.5 ! Minimum rainfall to reset models Black and Bo/Str., [0..1 cm/d, R]
********************************************************************************


********************************************************************************
* Part 4: Vertical discretization of soil profile

* Specify the following data (maximum MACP lines):
* ISOILLAY = number of soil layer, start with 1 at soil surface, [1..MAHO, I]
* ISUBLAY  = number of sub layer, start with 1 at soil surface, [1..MACP, I]
* HSUBLAY  = height of sub layer, [0.0..1000.0 cm, R]
* HCOMP    = height of compartments in this layer, [0.0..1000.0 cm, R]
* NCOMP    = number of compartments in this layer (= HSUBLAY/HCOMP), [1..MACP, I]

 ISOILLAY ISUBLAY  HSUBLAY    HCOMP    NCOMP
    1      1      10.0     1.0      10
    1      2      20.0     5.0       4
    2      3      30.0     5.0       6
    2      4     140.0    10.0      14

* --- end of table
********************************************************************************


********************************************************************************
* Part 5: Soil hydraulic functions
```

```
* Specify for each soil layer (maximum MAHO):
* ISOILLAY1 = number of soil layer, as defined in part 4 [1..MAHO, I]
* ORES   = Residual water content, [0..0.4 cm3/cm3, R]
* OSAT   = Saturated water content, [0..0.95 cm3/cm3, R]
* ALFA   = Shape parameter alfa of main drying curve, [0.0001..1 /cm, R]
* NPAR   = Shape parameter n, [1..4 -, R]
* KSAT   = Saturated vertical hydraulic conductivity, [1.d-5..1000 cm/d, R]
* LEXP   = Exponent in hydraulic conductivity function, [-25..25 -, R]
* ALFAW  = Alfa parameter of main wetting curve in case of hysteresis, [0.0001..1 /cm, R]

  ISOILLAY1  ORES    OSAT      ALFA    NPAR     KSAT      LEXP    ALFAW
      1     0.02    0.43    0.0234   1.801     23.41   -0.000   0.0454
      2     0.01    0.36    0.0224   2.286     15.22    0.000   0.0428
* --- end of table
************************************************************************************


************************************************************************************
* Part 6: Hysteresis of soil water retention function

  SWHYST = 0   ! Switch for hysteresis:
               ! 0 = no hysteresis
               ! 1 = hysteresis, initial condition wetting
               ! 2 = hysteresis, initial condition drying

* If SWHYST = 1 or 2, specify:
  TAU = 0.2    ! Minimum pressure head difference to change wetting-drying, [0..1 cm, R]
************************************************************************************


************************************************************************************
* Part 7: Maximum rooting depth

  RDS  = 200.0   ! Maximum rooting depth allowed by the soil profile, [1..5000 cm, R]
************************************************************************************


************************************************************************************
* Part 8: Similar media scaling of soil hydraulic functions

  SWSCAL = 0 ! Switch for similar media scaling [Y=1, N=0]; no hysteresis is allowed
             ! in case of similar media scaling (SWHYST = 0)

* If SWSCAL = 1, specify:
  NSCALE = 3 ! Number of simulation runs, [1..MASCALE, I]

* Supply the scaling factors for each simulation run and each soil layer:

  RUN     SOIL1       SOIL2
   1      0.5         2.0
   2      1.0         1.0
   3      2.0         0.5
   4      1.0         1.0
   5      3.0         3.0
* End of table
************************************************************************************
```

```
**********************************************************************************
* Part 9: Preferential flow due to water repellency

  SWMOBI = 0  ! Switch for preferential flow due to immobile water, [Y=1, N=0]; hysteresis
            ! or scaling are not allowed in case of preferential flow (SWHYST = 0; SWSCAL = 0)

* If SWMOBI = 1, specify mobile fraction as function of log -h for each soil layer:
*
* ISOILLAY2 = number of soil layer, as defined in part 4 [1..MAHO, I]
* PF1    = first datapoint,  log -h (cm), [0..5, R]
* FM1     = first datapoint,  mobile fraction (1.0 = totally mobile), [0..1, R]
* PF2    = second datapoint, log -h (cm), [0..5, R]
* FM2     = second datapoint, mobile fraction (1.0 = totally mobile), [0..1, R]
* THETIM = specify volumetric water content in immobile soil volume, [0..0.3, R]

  ISOILLAY2    PF1    FM1    PF2    FM2   THETIM
      1       0.0    0.4    3.0    0.4    0.02
      2       0.0    1.0    3.0    1.0    0.02
* End of table
**********************************************************************************


**********************************************************************************
* Part 10: Preferential flow due to macropores
  SWMACRO = 0     ! Switch for macropore flow, [0..2, I]:
                ! 0 = no macropore flow
                ! 1 = simple macropore flow
                ! 2 = advanced macropore flow

* If SWMACRO = 1, specify parameters for simple macropore flow:
  SHRINA = 0.53   ! Void ratio at zero water content, [0..2 cm3/cm3, R]
  MOISR1 = 1.0    ! Moisture ratio at trans. residual --> normal shrinkage [0..5 cm3/cm3, R]
  MOISRD = 0.01   ! Amount of structural shrinkage, [0..1 cm3/cm3, R]
  ZNCRACK = -5.0  ! Depth at which crack area of soil surface is calculated [-100..0 cm, R]
  GEOMF = 3.0     ! Geometry factor (3 = isotropic shrinkage), [0..100, R]
  DIAMPOL = 40.0  ! Diameter soil matrix polygon, [0..100 cm, R]
  RAPCOEF = 10.1  ! Rate coef. bypass flow from cracks to surface water [0..10000 /d, R]
  DIFDES = 0.2    ! Effective lateral solute diffusion coefficient, [0..10000 /cm, R]
* critical water content of each soil layer (max. MAHO), [0..1, R];
* if actual water becomes smaller than critical water content, cracks are formed
  THETCR = 0.49  0.40  0.38 0.38  0.38 0.39  0.39

* End of input for simple macropore flow, advance to next part

* If SWMACRO = 2, specify parameters for advanced macropore flow:
  Z_AH = -35.0    ! Depth bottom A-horizon [-1000..0 cm, R]
  Z_IC = -70.0    ! Depth bottom Internal Catchment (IC) domain [-1000..0 cm, R]
  Z_ST = -35.0    ! Depth bottom Static macropores [-1000..0 cm, R]
  VLMPSTSS = 0.05 ! Volume of Static Macropores at Soil Surface [0..1 cm3/cm3, R]
  PPICSS = 0.5    ! Proportion of IC domain at Soil Surface [0..1 -, R]
  NUMSBDM = 5     ! Number of Subdomains in IC domain [0..MaDm -, I]
  POWM = 1.0      ! Power M for frequency distribut. curve IC domain (OPTIONAL, default 1.0) [0..100 -,
R]
  RZAH = 0.0      ! Fraction macropores ended at bottom A-horizon [OPTIONAL, default 0.0] [0..1 -, R]
```

```
  SPOINT = 1.0    ! Symmetry Point for freq. distr. curve [OPTIONAL, default 1.0] [0..1 -, R]
  SWPOWM = 0      ! Switch for double convex/concave freq. distr. curve (OPTIONAL, Y=1, N=0; default:
0) [0..1 -, I]
  DIPOMI = 10.0   ! Minimal diameter soil polygones (shallow) [0.1..1000 cm, R]
  DIPOMA = 50.0   ! Maximal diameter soil polygones (deep)    [0.1..1000 cm, R]

*Start of Tabel with shrinkage characteristics
* ISOILLAY3 = number of soil layer, as defined in part 4 [1..MAHO, I]
* SWSoilShr = Switch for kind of soil for determining shrinkage curve: 0 = rigid soil, 1 = clay, 2 peat [0..2 -,
I]
* SWSoilShr = Switch for determining shrinkage curve [1..2 -, I]:  1 = parameters for curve are given;
*                                                    2 = typical points of curve are given
* GeomFac   =  Geometry factor (3 = isotropic shrinkage), [0..100, R]
* ShrParA to ShrParE = parameters for describing shrinkage curves,
*                  depending on combination of SWSoilShr and SwShrInp [-1000..1000, R]:
*                  SWSoilShr = 0              : 0 variables required (all dummies)
*                  SWSoilShr = 1,  SwShrInp 1 = : 3 variables required (ShrParA to ShrParC) (rest dummies)
*                  SWSoilShr = 1,  SwShrInp 2 = : 2 variables required (ShrParA to ShrParB) (rest dummies)
*                  SWSoilShr = 2,  SwShrInp 1 = : 4 variables required (ShrParA to ShrParD) (rest dummies)
*                  SWSoilShr = 2,  SwShrInp 2 = : 5 variables required (ShrParA to ShrParE)
  ISOILLAY3  SWSoilShr  SwShrInp  ThetCrMP  GeomFac ShrParA ShrParB ShrParC ShrParD ShrParE
      1       1         2       0.41      3.0    0.343   0.520   0.0      0.0     0.0
      2       1         2       0.40      3.0    0.343   0.520   0.0      0.0     0.0
      3       1         2       0.38      3.0    0.415   0.642   0.0      0.0     0.0
      4       1         2       0.38      3.0    0.400   0.659   0.0      0.0     0.0
      5       1         2       0.38      3.0    0.412   0.650   0.0      0.0     0.0
      6       1         2       0.39      3.0    0.406   0.700   0.0      0.0     0.0
      7       1         2       0.39      3.0    0.496   0.700   0.0      0.0     0.0
*End of Tabel with shrinkage characteristics

 ZnCrAr = -5.0  ! Depth at which crack area of soil surface is calculated [-100..0 cm, R]

*Start of Tabel with sorptivity characteristics
* ISOILLAY4   = number of soil layer, as defined in part 4 [1..MAHO, I]
* SWSorp      = Switch for kind of sorptivity function [1..2 -, I]:
*             1 = calculated from hydraulic functions according to Parlange
*             2 = emperical function from measurements
* SorpFacParl = factor for modifying Parlange function (OPTIONAL, default 1.0) [0..100 -, R]
* SorpMax     = maximal sorptivity at theta residual [0..100 cm/d**0.5, R]
* SorpAlfa    = fitting parameter for emperical sorptivity curve [-10..10 -, R]
  ISOILLAY4  SwSorp   SorpFacParl  SorpMax  SorpAlfa
      1       2        1.0        5.0       0.5
      2       2        1.0        5.0       0.5
      3       2        1.0        5.0       0.5
      4       2        1.0        5.0       0.5
      5       2        1.0        5.0       0.5
      6       2        1.0        5.0       0.5
      7       2        1.0        5.0       0.5
*End of Tabel with sorptivity characteristics

 SwDrRap = 1   ! Switch for kind of drainage function TEMPORARY: TEST option [1..2 -, I]:
 RapDraResRef = 1 * 0.1  ! Reference rapid drainage resistance [0..10000 /d, R]
                         ! an array with a single element must be indicated using a multiplier asterix
                         ! (see TTUTIL-manual, par. 5.2  Defining arrays)
 RapDraReaCof = 2.0 ! reaction coefficient for rapid drainage [0..100 -, R]
```

```
**********************************************************************************


**********************************************************************************
* Part 11: Snow and frost
*
  SWSNOW = 0   ! Switch, calculate snow accumulation and melt. [Y=1, N=0]
*
* If SWSNOW = 1, then specify initial snow water equivalent and snowmelt factor
  SNOWINCO = 22.0      ! the initial SWE (Snow Water Equivalent), [0.0...1000.0 cm, R]
  SNOWCOEF = 0.3       ! calibration factor for snowmelt, [0.0...10.0 -, R]
*
  SWFROST = 0  ! Switch, in case of frost: stop soil water flow, [Y=1, N=0]
**********************************************************************************


**********************************************************************************
* Part 12 Numerical solution of Richards' equation
*
 DTMIN     = 1.0d-7  ! Minimum timestep, [1.d-8..0.1 d, R]
 DTMAX     =    0.2  ! Maximum timestep, [ 0.01..0.5 d, R]
 THETOL    =  0.001  ! Maximum dif. water content between iterations, [1.d-5..0.01 cm3/cm3, R]
 GWLCONV   =  100.0  ! Maximum dif. groundwater level between iterations, [1.d-5..1000 cm, R]
 CritDevMasBalDt = 0.01  ! Critical Deviation in water balance of timestep [1.0d-5..100.0 cm, R]
 MSTEPS    = 100000  ! Maximum number of iteration steps to solve Richards', [ 2..100000 -, I]
 SWBALANCE =     0   ! Switch to allow compensation of water balance, [Y=1, N=0]
*            (use of SWBALANCE=1 is not recommended in this version, not tested yet !)
**********************************************************************************


*** LATERAL DRAINAGE SECTION ***

**********************************************************************************
* Specify whether lateral drainage to surface water should be included
*
  SWDRA = 0  ! Switch, simulation of lateral drainage:
           ! 0 = No simulation of drainage
           ! 1 = Simulation with basic drainage routine
           ! 2 = Simulation with extended drainage routine (includes surface water management)

* If SWDRA = 1 or SWDRA = 2 specify name of file with drainage input data:
  DRFIL = 'Hupsel' ! File name with drainage input data without extension .DRA, [A16]
*
**********************************************************************************



*** BOTTOM BOUNDARY SECTION ***

**********************************************************************************
* Bottom boundary condition

  SWBBCFILE  = 0    ! Switch for file with bottom boundary conditions:
                 ! SWBBCFILE = 0: data are specified in the .swp file
                 ! SWBBCFILE = 1: data are specified in a separate file
```

```
* If SWBBCFILE = 1 specify name of file with bottom boundary conditions:
  BBCFIL = ' '      ! File name without extension .BBC [A16]

* If SWBBCFILE = 0, select one of the following options:
            ! 1  Prescribe groundwater level
            ! 2  Prescribe bottom flux
            ! 3  Calculate bottom flux from hydraulic head of deep aquifer
            ! 4  Calculate bottom flux as function of groundwater level
            ! 5  Prescribe soil water pressure head of bottom compartment
            ! 6  Bottom flux equals zero
            ! 7  Free drainage of soil profile
            ! 8  Free outflow at soil-air interface

 SWBOTB = 7  ! Switch for bottom boundary [1..8,-,I]

* Options 1,2,3,4,and 5 require additional data as specified below!
********************************************************************************


********************************************************************************
* SWBOTB = 1  Prescribe groundwater level

* specify DATE [dd-mmm-yyyy] and groundwater level [cm, -10000..1000, R]

       DATE1    GWLEVEL         ! (max. MABBC records)
  01-jan-1996     -100.0
  31-dec-1998     -100.0
* End of table
********************************************************************************


********************************************************************************
* SWBOTB = 2   Prescribe bottom flux

* Specify whether a sine or a table are used to prescribe the bottom flux:
  SW2    = 2      ! Sine function = 1,  table = 2

* In case of sine function (SW2 = 1), specify:
  SINAVE =  0.1   ! Average value of bottom flux, [-10..10 cm/d, R, + = upwards]
  SINAMP =  0.05  ! Amplitude of bottom flux sine function, [-10..10 cm/d, R]
  SINMAX =  91.0  ! Time of the year with maximum bottom flux, [1..366 d, R]

* In case of table (SW2 = 2), specify date [dd-mmm-yyyy] and bottom flux QBOT2
* [-100..100 cm/d, R, positive = upwards]:

       DATE2     QBOT2          ! (maximum MABBC records)
  01-jan-1980       0.1
  30-jun-1980       0.2
  23-dec-1980      0.15
* End of table
********************************************************************************


********************************************************************************
* SWBOTB = 3    Calculate bottom flux from hydraulic head in deep aquifer
```

```
* Specify:
  SHAPE  =   0.79  ! Shape factor to derive average groundwater level, [0..1 -, R]
  HDRAIN =  -110.0 ! Mean drain base to correct for average groundwater level, [-10000..0 cm, R]
  RIMLAY =   500.0 ! Vertical resistance of aquitard, [0..10000 d, R]

* Specify whether a sine or a table are used to prescribe hydraulic head of deep aquifer:
  SW3    = 1       ! 1 = Sine function,  2 = table

* In case of sine function (SW3  = 1), specify:
  AQAVE  =  -140.0 ! Average hydraulic head in underlaying aquifer, [-10000..1000 cm, R]
  AQAMP  =    20.0 ! Amplitude hydraulic head sinus wave, [0..1000 cm, R]
  AQTMAX =  120.0  ! First time of the year with maximum hydraulic head, [1..366 d, R]
  AQPER  =  365.0  ! Period hydraulic head sinus wave, [1..366 d, I]

* In case of table (SW3  = 2), specify date [dd-mmm-yyyy] and average hydraulic head
* HAQUIF in underlaying aquifer [-10000..1000 cm, R]:

       DATE3    HAQUIF          ! (maximum MABBC records)
  01-jan-1980     -95.0
  30-jun-1980    -110.0
  23-dec-1980     -70.0
* End of table

* An extra groundwater flux can be specified which is added to above specified flux
  SW4   = 1        ! 0 = no extra flux, 1 = include extra flux

* If SW4 = 1, specify date [dd-mmm-yyyy] and bottom flux QBOT4 [-100..100 cm/d, R,
* positive = upwards]:

       DATE4     QBOT4          ! (maximum MABBC records)
  01-jan-1980       1.0

  30-jun-1980     -0.15
  23-dec-1980       1.2
* End of table
**********************************************************************************


**********************************************************************************
* SWBOTB = 4     Calculate bottom flux as function of groundwater level

* Specify coefficients of relation qbot = A exp (B*abs(groundwater level))
  COFQHA =  0.1  ! Coefficient A, [-100..100 cm/d, R]
  COFQHB =  0.5  ! Coefficient B  [-1..1 /cm, R]
**********************************************************************************


**********************************************************************************
* SWBOTB = 5     Prescribe soil water pressure head of bottom compartment

* Specify DATE [dd-mmm-yyyy] and bottom compartment pressure head HBOT5
* [-1.d10..1000 cm, R]:

       DATE5     HBOT5          ! (maximum MABBC records)
  01-jan-1980     -95.0
  30-jun-1980    -110.0
```

```
  23-dec-1980     -70.0
* End of table
**********************************************************************************


*** HEAT FLOW SECTION ***

**********************************************************************************
* Part 1: Specify whether simulation includes heat flow

  SWHEA  = 0 ! Switch for simulation of heat transport, [Y=1, N=0]
**********************************************************************************

**********************************************************************************
* Part 2: Heat flow calculation method

  SWCALT = 1     ! Switch for method: 1 = analytical method, 2 = numerical method
**********************************************************************************

**********************************************************************************
* Analytical method

* If SWCALT = 1 specify the following heat parameters:
  TAMPLI = 10.0 ! Amplitude of annual temperature wave at soil surface, [0..50 C, R]
  TMEAN  = 15.0 ! Mean annual temperature at soil surface, [5..30 C, R]
  TIMREF = 90.0 ! Time in the year with top of sine temperature wave [1..366 d, R]
  DDAMP  = 50.0 ! Damping depth of temperature wave in soil, [0..500 cm, R]
**********************************************************************************

**********************************************************************************
* Numerical method

* If SWCALT = 2 list initial temperature TSOIL [-20..40 C, R] as function of
* soil depth ZH [-1d5..0 cm, R]:
* When SWINCO = 3, dummy values can be present for ZH and TSOIL, because real values
* are read from file INIFIL (see this file:  Soil Water section, Part 1)

     ZH    TSOIL          ! (maximum MACP records)
   -10.0     15.0
   -40.0     12.0
   -70.0     10.0
   -95.0      9.0
* End of table

* If SWCALT = 2 specify for each soil type the soil texture (g/g mineral parts)
* and the organic matter content (g/g dry soil):

  ISOILLAY5  PSAND    PSILT    PCLAY    ORGMAT          ! (maximum MAHO records)
     1        0.80     0.15     0.05     0.100
     2        0.80     0.15     0.05     0.100
     3        0.78     0.14     0.08     0.012
* End of table
**********************************************************************************


*** SOLUTE SECTION ***
```

```
*****************************************************************************************
* Part 1: Specify whether simulation includes solute transport

  SWSOLU = 1 ! Switch for simulation of solute transport, [Y=1, N=0]
*****************************************************************************************


*****************************************************************************************
* Part 2: Top boundary and initial condition

  CPRE = 0.0    ! Solute concentration in precipitation, [1..100 mg/cm3, R]

* List initial solute concentration CML [1..1000 mg/cm3, R] as function of soil depth ZC
* [-10000..0 cm, R], max. MACP records:
* When SWINCO=3, then dummy values must be present for ZC and CML, because real values
* are read from file INIFIL (See this file:  SOIL WATER SECTION, part 1)
      ZC       CML
   -10.0       0.00
   -11.0       0.00
* End of table
*****************************************************************************************


*****************************************************************************************
* Part 3: Diffusion, dispersion, and solute uptake by roots

  DDIF = 0.0    ! Molecular diffusion coefficient, [0..10 cm2/day, R]
  LDIS = 5.0    ! Dispersion length, [0..100 cm, R]
  TSCF = 0.0    ! Relative uptake of solutes by roots, [0..10 -, R]
*****************************************************************************************


*****************************************************************************************
* Part 4: Adsorption

  SWSP = 1      ! Switch, consider solute adsorption, [Y=1, N=0]

* In case of adsorption (SWSP = 1), specify:
  KF    = 1.2    ! Freundlich coefficient, [0..100 cm3/mg, R]
  FREXP = 1.0     ! Freundlich exponent, [0..10 -, R]
  CREF  = 1.0   ! Reference solute concentration for adsorption, [0..1000 mg/cm3, R]
*****************************************************************************************


*****************************************************************************************
* Part 5: Decomposition

  SWDC = 1      ! Switch, consideration of solute decomposition, [Y=1, N=0]

* In case of solute decomposition (SWDC = 1), specify:
  DECPOT = 0.008  ! Potential decomposition rate, [0..10 /d, R]
  GAMPAR = 0.0  ! Factor reduction decomposition due to temperature, [0..0.5 /C, R]
  RTHETA = 0.3  ! Minimum water content for potential decomposition, [0..0.4 cm3/cm3, R]
  BEXP   = 0.7  ! Exponent in reduction decomposition due to dryness, [0..2 -, R]
```

```
* List the reduction of pot. decomposition for each soil type, [0..1 -, R]:

  ISOILLAY6  FDEPTH           ! (maximum MAHO records)
      1       1.00
      2       0.65
* End of table
****************************************************************************************************


****************************************************************************************************
* Part 6: Transfer between mobile and immobile water volumes

  SWPREF = 0     ! Switch, consider mobile-immobile water volumes, [Y=1, N=0]

* If SWPREF = 1, specify:
  KMOBIL = 100.0   ! Solute transfer coefficient between mobile-immobile parts, [0..100 /d, R]
****************************************************************************************************



****************************************************************************************************
* Part 7: Solute residence in the saturated zone

  SWBR = 0       ! Switch, consider mixed reservoir of saturated zone [Y=1, N=0]

* Without mixed reservoir (SWBR = 0), specify:
  CDRAIN = 0.0   ! solute concentration in groundwater, [0..100 mg/cm3, R]

* In case of mixed reservoir (SWBR = 1), specify:
  DAQUIF = 110.0 ! Thickness saturated part of aquifer, [0..10000 cm, R]
  POROS  = 0.4   ! Porosity of aquifer, [0..0.6, R]
  KFSAT  = 0.2   ! Linear adsorption coefficient in aquifer, [0..100 cm3/mg, R]
  DECSAT = 1.0   ! Decomposition rate in aquifer, [0..10 /d, R]
  CDRAINI = 0.2  ! Initial solute concentration in groundwater, [0..100 mg/cm3, R]
****************************************************************************************************

* End of the main input file .SWP!
```

2. Output files

```
* Project:       Hupsel
* File content:  cumulative solute balance components
* File name:     Result.sba
* Model version: swap_3_0_3
* Generated at:  19-Oct-2004 11:44:06

*      DATE DAY  DCUM      SQTOP      DECTOT      ROTTOT      SAMPRO      SAMCRA       SQBOT       SQDRA       SQRAP       SAMAQ       SQSUR    SOLBAL      DATE*
*dd-mmm-yyyy  nr   nr     mg/cm2      mg/cm2            mg/cm2      mg/cm2      mg/cm2      mg/cm2      mg/cm2      mg/cm2      mg/cm2      mg/cm2    mg/cm2 dd-mmm-yyyy
*<=========><==><====><==========><==========><==========>  <==========><==========><==========><==========><==========>
<==========><==========><=========><==========>
 30-Jan-1996  31     31  0.4500E-02  0.0000E+00   0.0000E+00  0.3175E-02  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.13E-02 30-Jan-1996
 28-Feb-1996  60     60  0.7500E-02  0.0000E+00   0.0000E+00  0.2927E-02  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.46E-02 28-Feb-1996
 30-Mar-1996  91     91  0.9000E-02  0.0000E+00  0.0000E+00  0.2571E-02  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.64E-02 30-Mar-1996
 29-Apr-1996 121    121  0.9600E-02  0.0000E+00  0.0000E+00  0.1127E-02  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.85E-02 29-Apr-1996
 30-May-1996 152    152  0.1020E-01  0.0000E+00  0.0000E+00  0.1366E-02  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.88E-02 30-May-1996
 29-Jun-1996 182    182  0.1080E-01  0.0000E+00  0.0000E+00  0.2528E-03  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.11E-01 29-Jun-1996
 30-Jul-1996 213    213  0.1140E-01  0.0000E+00  0.0000E+00  0.1859E-03  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.11E-01 30-Jul-1996
 30-Aug-1996 244    244  0.1200E-01  0.0000E+00  0.0000E+00  0.2054E-04  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.12E-01 30-Aug-1996
 29-Sep-1996 274    274  0.1260E-01  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.13E-01 29-Sep-1996
 30-Oct-1996 305    305  0.1320E-01  0.0000E+00   0.0000E+00  0.5455E-04  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.13E-01 30-Oct-1996
 29-Nov-1996 335    335  0.1500E-01  0.0000E+00  0.0000E+00  0.3213E-03  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.15E-01 29-Nov-1996
 30-Dec-1996 366    366  0.1800E-01  0.0000E+00  0.0000E+00  0.6887E-03  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  -0.17E-01 30-Dec-1996
```

```
* Project:      Hupsel
* File content:  overview of actual water and solute balance components
* File name:     Result.bal
* Model version: swap_3_0_3
* Generated at:  19-Oct-2004 11:44:38

Period            :  01-Jan-1997 until  31-Dec-1996
Depth soil profile :  200.00 cm

          Water storage        Solute storage
Final   :        12.96 cm      0.6887E-03 mg/cm2
Initial :        34.70 cm      0.0000E+00 mg/cm2
          =============      ================
Change           -21.74 cm      0.6887E-03 mg/cm2



Water balance components (cm)
In                        Out
=========================  ============================
Rain          :   96.54    Interception     :    0.00
Runon          :    0.00    Runoff           :    0.00
Irrigation    :    6.00    Transpiration    :   72.37
Bottom flux   :   -33.53    Soil evaporation  :   18.38
                         Crack flux       :    0.00
=========================  ============================
Sum           :   69.01    Sum              :   90.75



Solute balance components (mg/cm2)
In                        Out
=========================  ============================
Rain        :  0.0000E+00    Decomposition  :  0.0000E+00
Irrigation  :  0.1800E-01    Root uptake    :  0.0000E+00
Bottom flux :  0.0000E+00    Cracks         :  0.0000E+00
                         Drainage       :  0.0000E+00
=========================  ============================
Sum         :  0.1800E-01    Sum            :  0.0000E+00
```

```
* Project:       Hupsel
* File content:  final state variables
* File name:     Result.end
* Model version: swap_3_0_3
* Generated at:  19-Oct-2004 11:44:38

*  snow layer (Ssnow in cm)
 Ssnow =      0.000

*  ponding layer (Pond in cm)
 Pond =      0.000

*  soil water pressure heads  (z in cm, h in cm)
    z_h        h
   -0.5     -98.003
   -1.5    -104.679
   -2.5    -112.877
   -3.5    -123.216
   -4.5    -136.731
   -5.5    -155.279
   -6.5    -182.584
   -7.5    -227.290
   -8.5    -314.107
   -9.5    -538.477
  -12.5   -3669.030
  -17.5   -5999.838
  -22.5   -7567.853
  -27.5   -7980.718
  -32.5   -7999.770
  -37.5   -8000.000
  -42.5   -8000.000
  -47.5   -8000.000
  -52.5   -7999.956
  -57.5   -7421.986
  -65.0   -1366.627
  -75.0    -395.324
  -85.0    -240.700
  -95.0    -192.895
 -105.0    -170.682
 -115.0    -157.267
 -125.0    -147.985
 -135.0    -141.068
```

```
-145.0    -135.702
-155.0    -131.473
-165.0    -128.172
-175.0    -125.719
-185.0    -124.139
-195.0    -123.577

*  solute concentrations cml (z in cm, Cml in mg/cm3)
  z_Cml        Cml
   -0.5       0.000
   -1.5       0.000
   -2.5       0.000
   -3.5       0.000
   -4.5       0.000
   -5.5       0.001
   -6.5       0.001
   -7.5       0.001
   -8.5       0.001
   -9.5       0.001
  -12.5        0.000
  -17.5        0.000
  -22.5        0.000
  -27.5        0.000
  -32.5        0.000
  -37.5        0.000
  -42.5        0.000
  -47.5        0.000
  -52.5        0.000
  -57.5        0.000
  -65.0        0.000
  -75.0        0.000
  -85.0        0.000
  -95.0        0.000
-105.0       0.000
-115.0       0.000
-125.0       0.000
-135.0       0.000
-145.0       0.000
-155.0       0.000
-165.0       0.000
-175.0       0.000
-185.0       0.000
-195.0       0.000
```

* soil temperatures (z in cm, Tsoil in C)

z_Tsoil	Tsoil
-0.5	-99.900
-1.5	-99.900
-2.5	-99.900
-3.5	-99.900
-4.5	-99.900
-5.5	-99.900
-6.5	-99.900
-7.5	-99.900
-8.5	-99.900
-9.5	-99.900
-12.5	-99.900
-17.5	-99.900
-22.5	-99.900
-27.5	-99.900
-32.5	-99.900
-37.5	-99.900
-42.5	-99.900
-47.5	-99.900
-52.5	-99.900
-57.5	-99.900
-65.0	-99.900
-75.0	-99.900
-85.0	-99.900
-95.0	-99.900
-105.0	-99.900
-115.0	-99.900
-125.0	-99.900
-135.0	-99.900
-145.0	-99.900
-155.0	-99.900
-165.0	-99.900
-175.0	-99.900
-185.0	-99.900
-195.0	-99.900