
**THE MOBILITY OF ENDOSULFAN AND
CHLORPYRIFOS IN THE SOILS OF
THE HEX RIVER VALLEY**

by

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ABSTRACT

The Department of Community Health, University of Cape Town is assessing the quality of water supplies in the rural Western Cape, South Africa, with respect to agrochemical pollutants. This study focuses on the area of the Hex River Valley where pesticides have been detected in water samples. The two pesticides, endosulfan and chlorpyrifos, were selected for the study based on their usage and toxicity. As an initial assessment a simple screening model was used to confirm that their potential to leach into groundwater, in the Hex River Valley, is low but that their potential loss attached to sediment in runoff is high. The aim of the study was to examine the mobility of these two pesticides in the soil environment. Two soils, representative of the soils in the Hex River Valley, were sampled in August 1998. A range of chemical analyses was performed on the samples including pesticide sorption experiments in which gas chromatography coupled with electron capture detection and flame photometric detection were employed.

The Hex River Valley is a sensitive area because of the intensive agricultural activities and high vulnerability of the shallow aquifer. The valley has a semi-arid climate and receives winter rainfall which averages between 240 and 329 mm per annum. The dominant soil type is sandy with a low clay and low organic carbon content. The clay fraction is dominated by mica and to a lesser extent, kaolinite as determined by X-ray diffractometry. The slightly acidic nature of the soils will retard the rate of degradation of endosulfan and chlorpyrifos and therefore endosulfan and chlorpyrifos will be more persistent than in alkaline conditions. However, the possible catalysis of hydrolysis by chelation to Fe, Al and Cu could counteract this persistence.

The phosphate sorption capacity of the sandy Hex River soils ($K_f = 15.8 \text{ L/kg}$) was compared with a clayey Shortlands soil ($K_f = 620.6 \text{ L/kg}$) as an indicator of the potential risk associated with a particular soil for contamination of water bodies by hydrophobic insecticides. The Hex River Valley soils are considered high-risk soils because of the low sorption capacity and mobility of phosphate.

The sorption coefficients of endosulfan and chlorpyrifos with the Hex River Valley soils were determined. Endosulfan was more strongly sorbed than chlorpyrifos although both endosulfan and chlorpyrifos are non-ionic, hydrophobic insecticides. However, organochlorine pesticides (e.g. endosulfan) are more persistent than organophosphates (e.g. chlorpyrifos) by design. Chlorpyrifos, as anticipated, was less strongly sorbed to the

should be determined experimentally for site specific cases. However, this depends on the use of the output and the needs of the user.

In general, GLEAMS underestimates pesticide mobility and this has been attributed to its inability to simulate: increased solubility of pesticides due to dissolved organic matter; loss of pesticides attached to suspended sediment in percolation water; pesticide and water loss via macropores; non-equilibrium sorption kinetics; and the effects of temperature and soil water content on degradation. Inaccurate curve number estimation and therefore inaccurate runoff losses, amongst other factors, are also responsible for the underestimating of runoff losses.

Overall, GLEAMS estimated that endosulfan and chlorpyrifos are highly immobile in the soil environment of the Hex River Valley. However, these pesticides are being mobilised and lost from the sites of application as they have been detected in water samples taken from certain points in the valley. The major method of transport will probably be through attachment to suspended soil material (mainly organic matter) and therefore, in order to minimise the movement of these pesticides we need to minimise losses of soil material by avoiding practices liable to cause soil instability or erosion. Spray drift during application is also a potentially significant mode of transport. Large peaks of pesticide loss are unusual and may be attributable to a single event; for example, a heavy, downpour only once a year is enough to account for the entire year's pesticide loss. A field, other than the average field used for simulations in the present studies, with a steeper slope, less cover, different management practice and lower infiltration rate could also be account for the appearance of pesticides in runoff water samples. It is recommended in future studies with GLEAMS that a worst case scenario simulation be compared to an average case scenario for the Hex River Valley, in order to meaningfully describe a range of possibilities which may provide a better explanation for actual measurements of pesticide concentration in the Hex River Valley environment. The integration of GLEAMS with GIS is also suggested for future studies. The farmer is the first line of defence against pollution and it is the responsibility of government departments and pesticide manufacturers to ensure that the farmer is informed on the risk status of the area and the relevant techniques one can use to prevent pesticide contamination of the environment.

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INTRODUCTION

The importance of pesticides to modern agriculture is well recognised. The dispersion of pesticide residues into the environment by surface runoff and percolation from agricultural lands has been a major concern, mainly in the USA, for the last 20 years. Growing evidence indicates that trace amounts of pesticides are present on non-agricultural land, in the atmosphere, and in water, both in surface bodies and underground, far from the sites of pesticide application (Cheng, 1990). Since concerns are mostly associated with the presence of pesticides in the soil environment, it is essential that the processes affecting the transport of pesticides in the soil be understood before any cause-and-effect relationship between pesticide use and contamination of the surrounding environment, causing adverse effects on environmental health, can be established. The fate of a pesticide in the soil environment is governed by the retention, transformation and transport processes and the interaction of these processes. A discussion of the research on these processes, focusing on retention, is provided in Chapter 1. World-wide, there is an extensive amount of work that has been completed on pesticides in the soil, water and air. However, the amount of research on pesticide mobility in South Africa, is very limited.

The Water Research Commission is funding The Department of Community Health, University of Cape Town, to assess the quality of water supplies in the rural western Cape with regards to agrochemical pollutants. They have focused on three areas in the Western Cape; Grabouw, Piketberg and the Hex River Valley. The following report will focus on the Hex River Valley, which is an area of intensive agriculture and use of pesticides. A preliminary survey of pesticide levels in groundwater in the Hex River Valley detected none of the target pesticides of the study even though the presence of elevated nitrate in the groundwater proves that leaching of agricultural chemicals does take place (Weaver, 1993). Weaver concludes the most probable cause of the non-detection is that the pesticides have been degraded due to hot weather and low soil pH. However, due to the high usage of pesticides and hydrogeological conditions which favour groundwater contamination by certain pesticides, it was decided that further monitoring of a wider range of pesticides, was needed.

The Department of Community Health, UCT, has collected samples from various sources in the Hex River Valley once a week from 1997. These samples have been analysed by The Peninsula Technicon and the Government Chemical Forensics Department for a range of pesticides. The following study will focus on two of the pesticides which have been

detected in these samples and which were not part of the preliminary survey of pesticides in the Hex River Valley in which no pesticides were detected.

Endosulfan is a chlorinated hydrocarbon insecticide and one of the pesticides most toxic to fish. It is registered in South Africa for control of a large spectrum of insects. It is used in the Hex River Valley to control the American Bollworm. Unlike other organochlorine insecticides, endosulfan is regarded as a "soft" organochlorine because of its chemical properties, degradation rate, and metabolism in plants and animals (Antonious and Byers, 1997). However, endosulfan tends to accumulate in the environment as it is not readily detoxified by soil micro-organisms, and residues are detectable in crops at harvest time. Furthermore, endosulfan is highly toxic to aquatic organisms (Antonious and Byers, 1997). Endosulfan has a low solubility in water and adsorbs strongly to soil particles while degrading slowly in the environment. It is a non-ionic, hydrophobic hydrocarbon and soil organic carbon is mostly responsible for its partitioning into soil from water.

In British Columbia, endosulfan residues were transported from treated farms into nearby ditches on suspended soil particles resulting from surface runoff. Concentrations in ditch water following normal agricultural use averaged 13.4 µg/L, whereas those in ditch sediments averaged 332 µg/kg, which was about one-fifth of the mean concentration of 1529 µg/kg found in crop soils in the adjacent farms (Antonious and Byers, 1997). The target water quality range for endosulfan, according to DWAF (1995), is equal to or less than 0.01 µg/L. This is the range for which no measurable adverse effects are expected on the condition and integrity of aquatic ecosystems. Davies (1997) found, in an assessment of the suitability of farms dams to waterbeds, that out of 27 Elgin dams sampled only one dam was within this range, the rest all greatly exceeded the limit. In the Hex River Valley water sampled contained 1.794 µg/L endosulfan (Water Research Commission, 1998). This value is the sum of endosulfan alpha, beta and sulphate for one particular sample site and is the maximum value out of 8 sampling occasions.

The other insecticide which has been detected in the water samples taken from the Hex River Valley, is chlorpyrifos. Chlorpyrifos is an organophosphate insecticide, also registered in South Africa for the control of a wide spectrum of insects. In the Hex River Valley it is used to control mealy bug and ants. Chlorpyrifos is less persistent than endosulfan, but also relatively immobile in the environment. Chlorpyrifos may bioconcentrate at very low levels in ecological systems (EXTOXNET¹). Chlorpyrifos

¹ Extension Toxicology Network, Pesticide Active Ingredient Profiles at <http://pmep.cce.comell.edu/profiles/endosulfan-ext.html>.

adsorbs strongly to soil particles and it is not readily soluble in water. It is considered to be a non-ionic, hydrophobic hydrocarbon and soil organic carbon is also thought to be mostly responsible for its partitioning into soil from water.

Less focus in research has been placed on the organophosphates because of their less persistent nature. Domagalski *et al.* (1997) state that organophosphate pesticides are of particular interest because of potential toxicity to some aquatic organisms at relatively low concentrations. In this study by Domagalski *et al.* (1997), chlorpyrifos was detected at only one site in the San Joaquin River Valley, at a concentration of 0.12 µg/L. These results being consistent with the pesticide use data, which show minor applications of chlorpyrifos in this area during the dormant-spray period, which was the time of sampling. No target water quality range for chlorpyrifos was available in DWAF (1995). The Australian guideline is a maximum 0.03 µg/L for chlorpyrifos. Davies (1997) found that out of the 27 Elgin dams only one exceeded the limit for chlorpyrifos. In the Hex River Valley a maximum of 19.13 µg/L (provisional results) was detected over 8 sampling sessions.

Certain types of agriculture like citrus and cotton production have become reliant on specific pesticides for economic survival. Endosulfan is one of these and it is the only insecticide available for a specific pest/crop situation and it does not kill beneficial insects, spiders and mites (Australian National Registration Authority, 1997). However, it is a highly toxic chemical and its use cannot go unregulated. Environmental monitoring and examination of use patterns should be considered just as important as its use.

It is of critical importance to understand the transport and concentrations of these pesticides in surface water and groundwater so that effective control strategies can be implemented. This research was undertaken as a contribution to this effort by: (1) determining the properties of the soil in the Hex River Valley (2) measuring the sorption capacity of the soils for the two pesticides, in a laboratory study (3) to model the mobility of the pesticides and determine possible explanations for their presence in the sampled waters using the measured soil properties, sorption coefficients and information collected on the climate, geohydrology and farming practices of the Hex River Valley.

CHAPTER 1

The Mobility of Pesticides in Soil - A Review

1.1 Introduction

Agricultural chemicals, such as pesticides, are indispensable in modern agriculture. Pesticides are beneficial to the crops being grown but only as long as they remain in the root zone of the soil. If a portion of the pesticides applied to agricultural fields leaves the target soil compartment, the pesticides may no longer complete their proposed purpose and may harm the environment.

In 1989 it was estimated that Africa accounted for 5% of the world's pesticide use (Mhlanga, 1990). Although the effect of pesticides on the environment has been studied extensively in developed countries, there is still a need to assess their impact in developing countries. In developing countries agricultural practices, climates, soil types and pesticide types all differ from those of developed countries so persistence patterns would be expected to be different (Zaranyika and Mugari, 1997).

The main problems of pesticide use are the direct effects on human health, especially for the persons applying the chemicals and the side effects on non-target organisms and the environment. A number of reviews are available on the health effects of pesticides (Igbedioh, 1991; London, 1992; Muldoon & Hodgson, 1992; British Medical Association, 1992; Dinham, 1993). A comprehensive database, EXTOTOXNET, of the toxicological effects of the most commonly used pesticides is accessible at <http://pmep.cce.cornell.edu/profiles/ext>. Contributing to the problems in Africa are farmers using pesticides without adequate knowledge about the significance of residue levels in agricultural products and the new international market rules.

The earlier persistent organochlorine insecticides, associated with well-documented ecological problems, have been progressively replaced with alternatives such as synthetic pyrethroid and

organophosphorus compounds. These insecticides are normally readily degraded in the environment but transient levels are often highly toxic to aquatic organisms. In addition to contamination of drinking water, transient levels of one of the more toxic insecticides have been shown to kill *in situ* bioassay organisms in surface waters near to agricultural applications (Matthiessen *et al.*, 1995). The longer-term ecological implications of such impacts are difficult to elucidate, but along with the intensification of agriculture and the reduction of wildlife habitats, biodiversity is likely to be under increasing threat (Turnbull *et al.*, 1997).

The main pathways and reactions of pesticides in the environment are presented in Figure 1.1. The factors which govern pesticide stability in soil and the loss of pesticide to surface waters, groundwater and air may be summarised as follows (after White, 1997):

- Volatilisation;
- Adsorption by soil minerals and organic matter;
- Chemical and biological transformations;
- Transport in the air, liquid or solid phase;
- Absorption by plants and animals.

The relative importance of each process depends very much on:

- The pesticide properties - e.g. solubility in water;
- Pesticide formulation - e.g. organic solvent, wettable powder;
- Mode of application - e.g. whether applied to crop surfaces or cultivated into the soil;
- Environmental conditions - e.g. temperature, rainfall, soil type and cropping system.

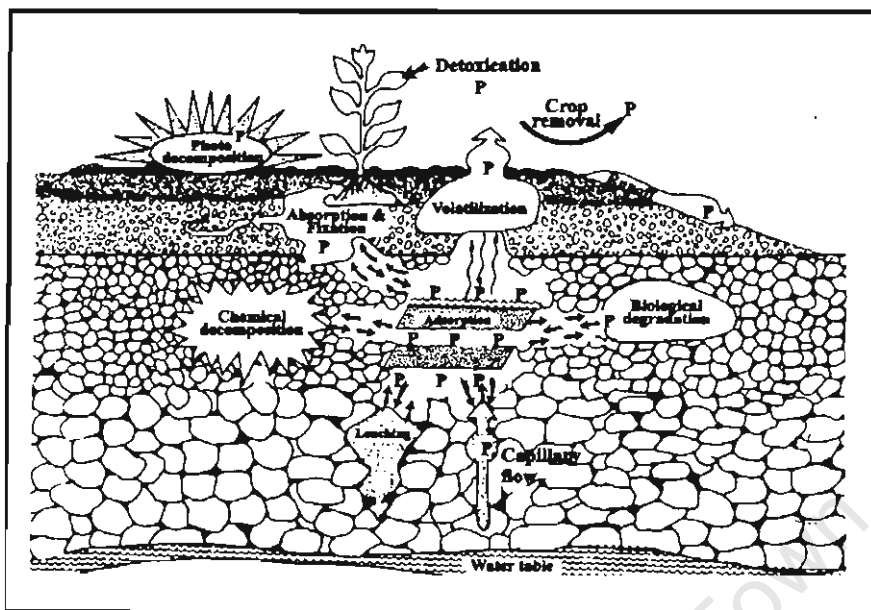


Figure 1.1: The pathways of pesticide loss. P = pesticide. (Adapted from Skrotch and Sheet, 1981; <http://hammock.ifas.ufl.edu>)

The factors and processes (listed above) which govern the fate of pesticides in the environment can be summarised further as retention, transformation and transportation. Retention refers to the ability of the soil to hold a pesticide or other organic molecule and to prevent the molecule from moving either within or outside of the soil matrix. As such, retention refers primarily to the adsorption process but also includes absorption into the soil matrix and soil organisms, both plants and micro-organisms. Retention strongly influences chemical transport to the atmosphere, groundwater and surface waters and therefore this review will focus on retention process. The retention processes discussed are mainly adsorption and the properties of the soil affecting adsorption and the parameters used to measure adsorption. According to Cheng (1990), adsorption is defined as the accumulation of a pesticide or other organic molecule at either the soil-water or the soil-air interface. In practice, adsorption is usually determined only by chemical loss from solution, thus adsorption is often replaced by the more general term, sorption. Sorption refers to a general retention process with no distinction between the specific processes of adsorption, absorption and precipitation.

Leaching and runoff are two important transport processes. This review discusses these two processes and current issues relating to them. Transformation is briefly assessed and the

important soil and pesticides properties affecting retention, transport and transformation are also reviewed.

Pesticide formulation, application and type of irrigation also need to be considered when studying the mobility and fate of pesticides in the soil environment especially if the researcher intends using a model to simulate pesticide leaching or runoff. Himel *et al.* (1990) review these factors in detail.

There is an extensive amount of literature on pesticide mobility in soils including comprehensive reviews of this literature (Flury, 1996; Linn, 1993; Cheng, 1990; Sawhney and Brown, 1989). The aim of this review is, therefore, to point out and discuss the current issues relating to pesticide mobility in soils.

In a review of the research on pesticide mobility a direct comparison of experimental results from different field studies is rather difficult because the experimental conditions such as type of soil, pesticides, type of irrigation, amount and timing of rainfall and sampling procedures vary from study to study. To provide these details for each paper reviewed would be excessive but the possible variations in experimental conditions should be kept in mind when generalisations are made about pesticide behaviour.

1.2 Retention

The extent to which a pesticide is free in a soil depends on the strength of adsorption. Leaching, capillary movement and chromatographic studies confirm that chemicals that are strongly sorbed by soils are low in mobility while those that are sorbed in low amounts are extremely mobile. Chemicals that are immobile do not pose such a great threat to groundwater but do pose a severe problem in the cleanup of accidental spills. Immobile chemicals pose a greater threat of contaminating surface water via runoff. Because most pesticide molecules are uncharged and hydrophobic they have a stronger affinity for organic matter than for other soil particles. Adsorption is also a useful indicator of availability to non-target organisms.

The main types of forces involved in the sorption of pesticides in soils can be divided into enthalpy related and entropy-related adsorption forces. The enthalpy related forces are (after Hassett and Banwart, 1989):

- london-van der Waals;
- coulombic-electrostatic;
- charge Transfer;
- π Bonds;
- hydrogen Bonding;
- ligand Exchange;
- dipole-dipole or Orientation Energy;
- induction or Dipole-induced Dipole;
- chemisorption.

The entropy-related adsorption forces are identified as hydrophobic sorption and differ from the forces outlined above in that hydrophobic sorption tends to be an entropy driven process. The enthalpy term may or may not contribute to a negative free energy, but the major contribution to sorption is the entropy term. Whether hydrophobic sorption is adsorption or the partitioning of the molecule into an organophilic phase in the humic material, is a contentious issue. The partitioning of nonpolar organics out of the polar aqueous phase onto hydrophobic surfaces in the soil is primarily due to soil organic matter, but may also include $-\text{Si-O-Si}-$ bonds at the mineral surface. The extent to which clay minerals contribute to sorption depends on both the ratio of clay minerals to organic C fractions of the soil and on the nature of the organic sorbate. The type of soil clay becomes increasingly important when soil organic C contents are low.

Hassett and Banwart (1989) review sorption of nonpolar organics extensively and they concluded that the primary force in hydrophobic sorption appears to be the large entropy change resulting from the removal of the solute from solution. The entropy change is large due to the destruction of the cavity occupied by the solute in the solvent and the destruction of the structured water shell surrounding the solvated organic solute. It is interesting to note that in adsorption studies carried out using dry soils and organic solvents instead of an aqueous phase, Hassett and Banwart (1989) found that the clay minerals controlled the extent to which sorption occurred. This suggests differences in water contents in soil are as, or even more, important than differences in soil properties with regards to the sorption of pesticides.

Pesticide sorption can be investigated in the field by core sampling. This is a laborious, time-consuming process and computer modeling of the process is now a primary tool of research. However, the parameters for input into these models must still be measured and calculated.

The partitioning of a pesticide when equilibrated between particle surfaces (the adsorbed phase) and the soil solution (the aqueous phase) is usually displayed as an adsorption isotherm. Giles *et al.* (1960) devised a classification scheme for sorption isotherms and used it to characterise the sorption mechanisms of assorted solutes by various sorbents. Figure 1.2 illustrates the major types of Giles isotherms that have been observed in the binding of organic compounds by soils and soil constituents.

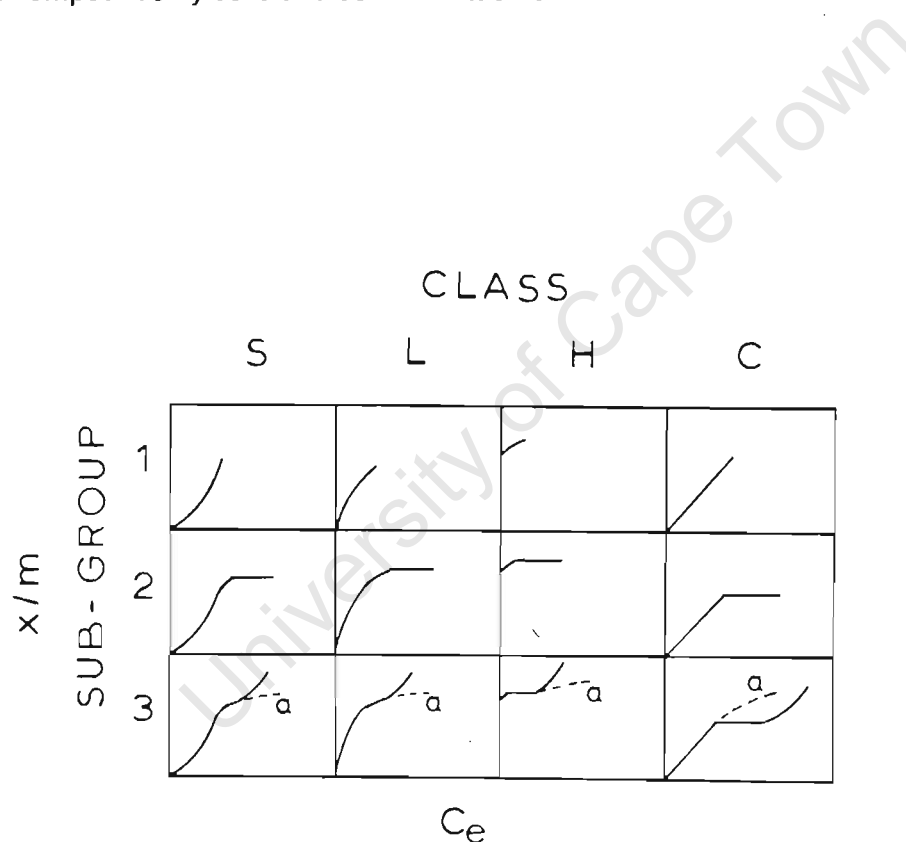


Figure 1.2: Systems of sorption isotherm classification according to Giles *et al* (1960). C_e is the equilibrium concentration (aqueous phase) and x/m is the sorbed concentration (adsorbed phase).

The S-type isotherm (S-shaped) has an initial slope that is non-linear and convex with respect to the abscissa (aqueous phase concentration) (Figure 1.2). This suggests "co-operative adsorption," which operates if the adsorbate-adsorbate interaction is stronger than the adsorbate-adsorbent interaction. The L-type isotherm (Langmuir-type) has an initial slope that is non-linear and concave with respect to the abscissa (Figure 1.2). This reflects a relatively high affinity between the adsorbate and adsorbent, and is usually indicative of chemisorption. The H-type Isotherm (high-affinity type) is a special case of the L-type isotherm indicating a very strong adsorbate-adsorbent interaction. The C-type isotherm (constant-partition), which suggests a constant relative affinity of the adsorbate molecules for the adsorbent, is usually observed only at the low range of adsorption and has a linear slope.

In an extensive review, Weber and Miller (1989), discuss sorption processes and the S, L, H and C-type isotherms with respect to organic chemicals. The authors compiled tables of solutes with likely sorbents and relevant references on the specific solute/sorbent relationships. It should be noted the classification of an isotherm using the S, L, H and C-type description is highly empirical and dependent on concentration ranges, equilibration period and numerous other variables. Weber and Miller (1989) concluded that the type of sorption isotherm involved for a given chemical characterises the capacity and intensity of the bond and reflects the relative mobility of the compound through soils.

At the small concentrations involved in pesticide use, the isotherm is normally approximated by the C-type isotherm, a straight line described by the equation:

$$C_s = K_d \times C_{aq} \quad (\text{Eq. 1})$$

where C_s is the concentration of the adsorbed pesticide ($\mu\text{g/g}$), C_{aq} is the concentration in the aqueous phase ($\mu\text{g/ml}$) and K_d is the adsorption coefficient with the units ml/g . The slope of the isotherm has the value of K_d . With increased concentrations the isotherm becomes curved and is better described by the Freundlich equation:

$$C_s = K_f C_{aq}^x \quad (\text{Eq. 2})$$

where x is a constant which can be used as an index to describe generalised adsorption mechanisms and K_f is the Freundlich adsorption coefficient. When $x = 1$, Eq. 2 approximates Eq. 1 and K_d approximates K_f . For convenience, the logarithmic form of the Freundlich equation (Eq. 2) is used:

$$\log C_s = \log K_f + x \log C_{aq} \quad (\text{Eq. 3})$$

The intercept on the $\log C_s$ axis ($\log C_{aq} = 0$) is $\log K_f$.

Adsorption coefficients are often expressed in terms of organic matter, K_{oc} , because of the importance of organic matter in the soil's capacity for adsorption. In Eq. 1, the sorbed concentration, C_s , represents pesticide sorption per unit mass of dry soil. C_s can also be adjusted to represent the amount of pesticide sorbed per unit mass of organic C in the soil, i.e.,

$$C_{oc} = K_{oc} \times C_{aq} \quad (\text{Eq. 4})$$

with K_{oc} also having units of ml per g when the mass of organic C is expressed in grams. If $f_{oc} = (\text{mass organic C}) / (\text{mass dry soil})$, K_{oc} is given by $K_{oc} = K_d / f_{oc}$ and $C_{oc} = C_s / f_{oc}$ ($f_{oc} = \text{percent organic carbon} / 100$). Thus Eq. 4 represents a linear sorption isotherm, which is referenced to organic C content and K_{oc} is a distribution coefficient that describes the distribution of a pesticide between the aqueous and the soil organic phases. This approach is most appropriate for hydrophobic pesticides, that is non-ionic pesticides with a water solubility less than about 10^{-3} M, but may be practically suitable for many pesticides that are slightly polar and too water soluble to be considered hydrophobic.

Variations in the value of K_{oc} for a given compound in a range of soils are caused primarily by differences in pH and the nature of the organic matter as shown by Table 1.1. Thus, Rowell (1996) states that there will be significant error in using a single value of K_{oc} for a pesticide as a means of predicting its K_d values from its organic carbon content.

Table 1.1: The effects of soil properties on the adsorption of atrazine [after Rowell (1996) according to data from M.Lane, Zeneca Agrochemicals].

Soil No.	pH	Organic C (%)	Texture	K_{oc} (cm ³ g ⁻¹)
1	4.6	10.9	Loamy sand	434
2	5.8	3.7	Loam	79
3	5.9	1.5	Clay	636
4	7.0	1.7	Silt loam	57
5	8.0	10.9	Silt loam	60
6	8.3	0.3	Silt	80

When it is not possible to actually measure a sorption isotherm for a given pesticide-soil combination, a simplified estimation procedure must be used. The most attractive simplification is that which can use existing or easily developed data on pesticides and soils to provide sorption estimates that are sufficiently accurate for a given modeling objective. The K_{oc} approach as described above is a widely accepted method. In the above method, however, K_d is measured and used to estimate K_{oc} . This method would be used either to compare K_{oc} values to literature values to check the reasonability of K_d or because it is the required form of the sorption coefficient for a particular model. The other method is to estimate K_{oc} and combine it with organic C content to estimate K_d . There are various methods that can be used to estimate K_{oc} without isotherm determination.

An alternative to the organic-C-referenced-sorption-approach may be desirable for some pesticide-soil combinations. For example, if the chemical is hydrophilic the relationship between K_d and f_{oc} may not be reliable. The K_{oc} approach may also be inappropriate for soils having a clay/organic C ratio which is sufficiently high (perhaps >40) for the clay contribution to pesticide sorption to be a significant part of the total sorption. Pionke and DeAngelis (1980) developed an estimation methodology, which allows one to predict K_d values for a large number of pesticides on the basis of the relationship of K_d to either the organic C content or

the specific surface of the soil. Pionke and DeAngelis (1980) calculated the specific surface (SS) from the equation:

$$SS = 100 (\% \text{ OC}) + 2.0 (\% \text{ clay}) + 0.4 (\% \text{ silt}) + 0.005 (\% \text{ sand}) \text{ (Eq. 5).}$$

For a diverse group of pesticides the equation $K_d = mSS$ gave consistently higher coefficients of determination than did the equation $K_d = m (\% \text{ OC}) + b$, in which m and b are fitted coefficients of linear regression. Thus, the authors recommended the surface area approach. This surface area calculation also weights sorption heavily toward organic C content. However, the organic C-referenced method has gained the most acceptance because organic C content is commonly measured in soils, in contrast to surface area which is usually estimated from other soil properties.

A number of simplifying assumptions are inherent in the organic C referenced method of representing sorption of pesticides (K_{oc} approach). Green *et al* (1993) investigated these assumptions and the validity of using literature values for site-specific impact assessments. One of the principal assumptions is linearity of the isotherm (Eq. 1) is assumed. Green *et al* (1993) determined the sorption isotherms and K_{oc} for four different soil types using ^{14}C radioassay. The authors determined the K_d value for Chlorpyrifos and the associated coefficient of determination for linear regression (r^2). Figure 1.3 shows the isotherm for chlorpyrifos and the coefficient of determination was 0.85. The authors considered that this was a poor fit and concluded that chlorpyrifos did not meet the requirements for calculating K_{oc} values. Another principal assumption inherent in the application of the K_{oc} calculation is a linear relationship between K_d and OC. Green *et al* (1993) plotted the K_d vs. fraction OC for all soils with each pesticide in the study and conformity of the measured data to linearity was indicated. The best fit was obtained for atrazine ($r^2=0.86$) (Figure 1.4).

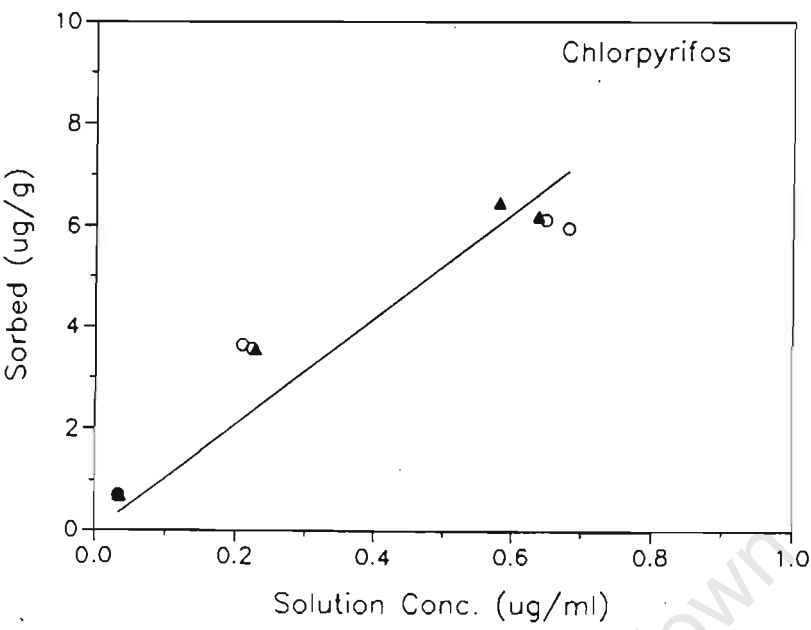


Figure 1.3: Example of a linear sorption isotherm having poor fit for chlorpyrifos. Different symbols represent two different sites within a field plot (From Green *et al*, 1993).

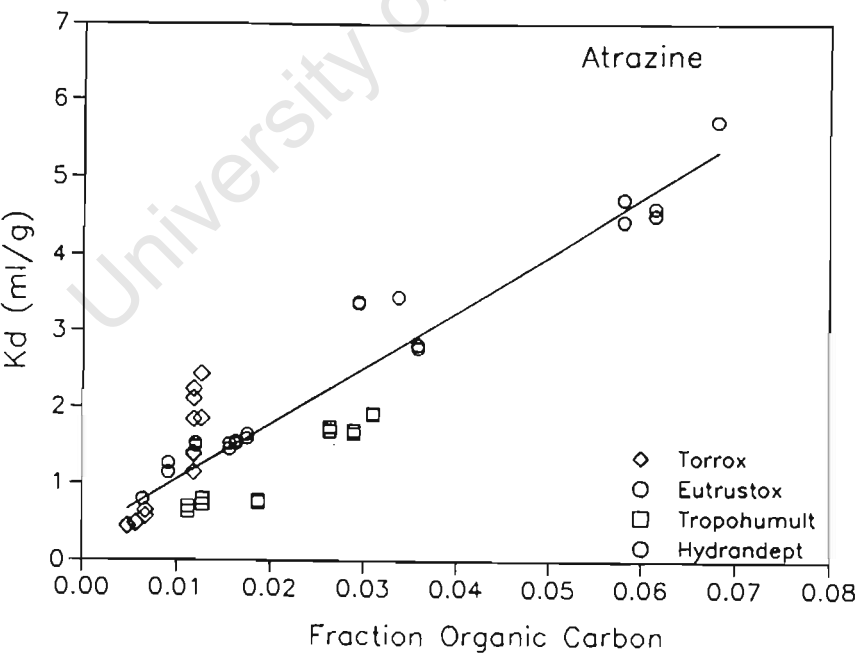


Figure 1.4: Linear plot of K_d vs. f_{oc} for four Hawaii soils: example of relatively good fit for atrazine, $r^2=0.86$. Multiple symbols for a given soil represent replicate field soil samples (From Green *et al*, 1993).

The authors fail to explain why the coefficient of determination, 0.85, for chlorpyrifos is described as a poor fit while 0.86 for atrazine is described as a good fit. Nevertheless, this research provides valuable evidence of the dependence of the sorption coefficient on the specific pesticide, soil properties and the model used to describe the sorption.

Sorption partition coefficients are most frequently needed. These values are often taken from the literature and it is widely recognised that mean values of such parameters obtained from diverse soil environments are usually associated with high standard deviation. The sorption data (K_{oc}) for the above experiment were compared to literature values from Oshiro *et al.* (1993, cited by Green *et al.* 1993) and it was concluded by Green *et al.* (1993) that mean measured K_{oc} values for all soils, except one, were generally lower than literature mean values. However, the overall ranking of pesticides, according to the K_{oc} , was the same when measured or using literature values. Green *et al.* (1993) do not advise the use of literature values in site specific investigations.

In summary, several assumptions are inherent in the computation and use of K_{oc} values:

- equilibrium exists;
- isotherms are linear and singular;
- sorption occurs on organic matter only and not on clay minerals;
- all OC in soils has similar sorption characteristics.

It is suggested by White (1997) that, if not measured directly in soil, K_{oc} for different pesticides can be estimated with reasonable confidence from the octanol-water partition coefficient, that is:

$$K_{ow} = \frac{[pesticide]_{oc \tan ol}}{[pesticide]_{water}} \quad (Eq.6)$$

Zhou *et al.* (1995), however, suggested that the quantity as well as the quality of the organic matter on particle surfaces are important in predicting contaminant transport in aquatic and soil environments. The authors concluded that it is therefore inappropriate to predict K_{oc} from K_{ow} or solubility as this does not take into consideration the composition and structure of organic matter.

Green and Karickhoff (1990) concluded that quantitative estimates of pesticide sorption on soils are now required routinely for pesticide regulation. Simple indices of pesticide mobility in soils and also more complex dynamic models, require sorption coefficients. The choice of procedure to measure or estimate sorption coefficients is dependent upon the level of accuracy required for a given use. A few potential sources of error have been identified that may result in unsatisfactory sorption estimates if stringent accuracy requirements are imposed. Presently, however, there are many environmental quality applications that require only approximate estimates of pesticide sorption, so that simplifying assumptions implicit in estimation procedures may be acceptable. On the other hand, Green and Karickhoff (1990) advised that regulators and modelers should be aware of the uncertainty associated with various types of sorption estimates. They also suggested that the determination of parameter error propagation in a model and its impact on model output is an important component of modeling in the regulatory context.

The existence of different models to estimate the adsorption coefficients is a manifestation of the uncertainty associated with the mechanisms of organic molecules' sorption to soil particles. This uncertainty is partly due to researchers attempting to classify the mechanisms of adsorption for a wide range of pesticides on a wide range of reactive soil components, into one or two groups. The heterogeneous nature of soil and the wide variety of organic chemicals preclude systematic determination of retention mechanisms. For example, adsorption processes probably involve a range of mechanisms with one mechanism predominating under a given set of conditions. To further confound the situation, the retention mechanism may change with time resulting ultimately in irreversible bonding of chemicals to soil surfaces and totally removing them from transport processes.

In order to gain a better understanding of retention of organic chemicals in soil the mechanisms of retention need to be explored further. To do this the specific type of force and specific site of retention for a particular pesticide needs to be examined. Information on the types of bonding mechanisms possible for particular chemicals on soil can be obtained by studying the adsorption of a chemical on well-defined adsorbents.

Dios Cancela *et al.* (1992) researched the adsorption of carbendazim onto montmorillonite, peat and soil. Carbendazim is a systemic fungicide. The Environmental Protection Agency of the USA has pointed to the possibility that carbendazim, under defined conditions, may promote mutagenicity, teratogenicity (causes malformations in a fetus) and has the potential to

reduce spermatogenic activity. On the other hand, because of the slow rate of degradation and low solubility in water of carbendazim, this fungicide may remain in the soil for a long time in an immobilised state due to interactions with soil colloids (Dios Cancela *et al.*, 1992). These facts emphasise the need for adsorption studies with carbendazim, since adsorption significantly affects its movement and persistence in the soil environment. It has already been pointed out that clay minerals and organic matter play a prominent role in the adsorption of pesticides by soils. Dios Cancela *et al.* (1992) state that it is the nature of the adsorption mechanism (physical or chemical) which defines the release of carbendazim from adsorption surfaces.

In order to determine the thermodynamic parameters of the adsorption process and to establish the retention mechanism, Dios Cancela *et al.* (1992) determined the effect of temperature on the adsorption process. The possible effect of the exchangeable cation on the adsorption was measured and finally the authors studied the adsorption of carbendazim on soils of different composition and a correlation with the different soil components was established.

The adsorption isotherms of carbendazim on peat, saturated with H^+ , K^+ , Mg^{2+} , Co^{2+} and Cu^{2+} at 20°C and 30°C, were determined and are presented in Figure 1.5. The linear form of the Freundlich equation (Eq. 3) described the adsorption well ($r=0.99$). All the x values were less than 1 indicating convex or L-type isotherms. From the K_f values it was deduced that carbendazim adsorption capacity follows the order H^+ -peat, $>Cu^{2+}$ -peat $> Co^{2+}$ -peat $> Mg^{2+}$ -peat = K^+ -peat, at 20°C and 30°C. The significantly higher values found for H^+ and Cu^{2+} -peat were attributed to different bonding mechanisms for these adsorbents compared to the others. The pH value of the H^+ and Cu^{2+} -peat suspensions was 6.0 but for the other samples it was 7.5. At those pH levels the authors suggested that the carbendazim molecules must be predominantly in an (uncharged) molecular state ($pK_a=4$) and so may be adsorbed by physical forces. However, they also state, it is possible that exchangeable protons on the adsorbent protonated the carbendazim molecules, which could then have been adsorbed by ion exchange. The authors suggested that this could explain the relatively high adsorption capacity of the H^+ -peat.

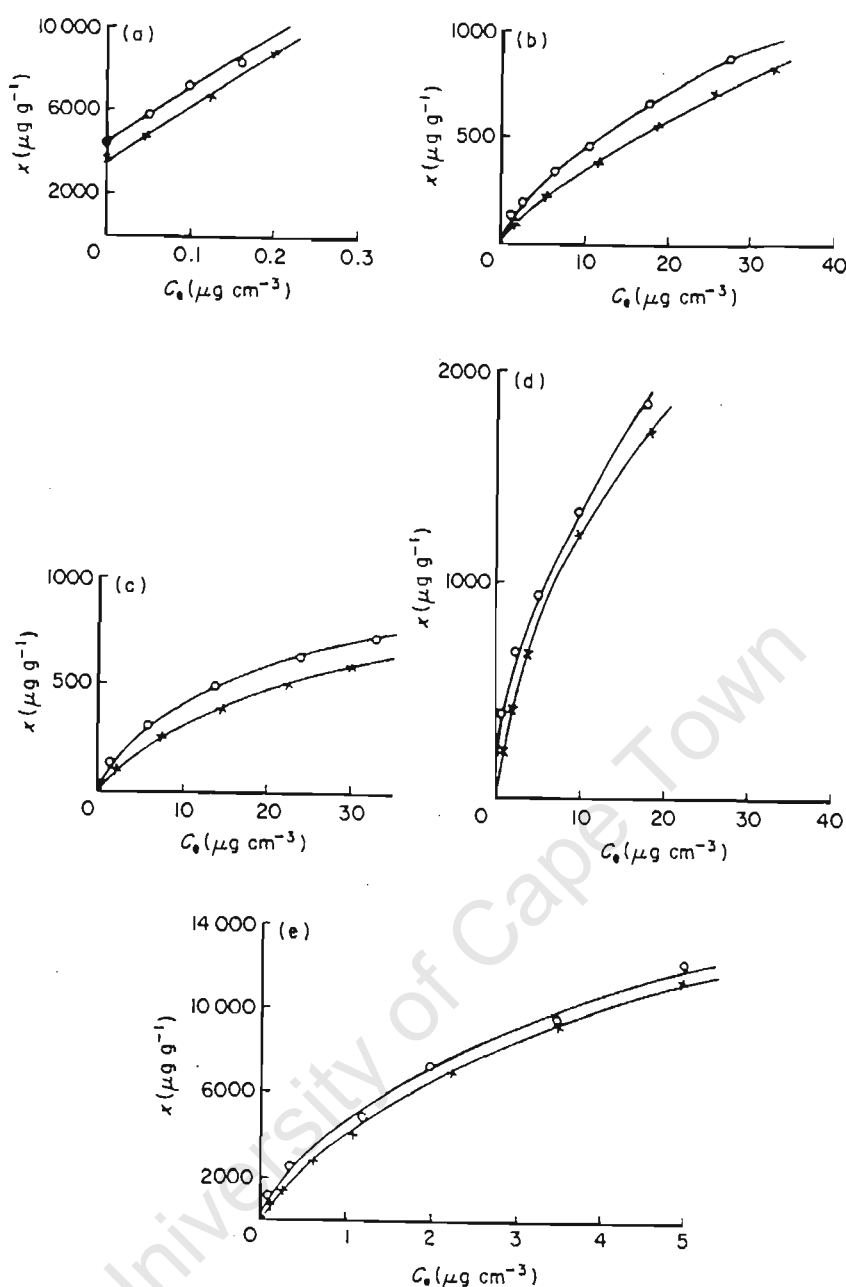


Figure 1.5: Adsorption isotherms of carbendazim on peat at 20°C (o) and 30°C (x): (a) H⁺-peat, (b) K⁺-peat, (c) Mg²⁺-peat, (d) Co²⁺-peat, (e) Cu²⁺-peat (After Dios Cancela *et al.*, 1992).

The same adsorption experiment was repeated with montmorillonite saturated with H⁺, Ca²⁺, Co²⁺ and Cu²⁺ at 20°C and 30°C. As for peat, the Freundlich equation (Eq. 3) described the adsorption well ($r=0.99$). The x values were all < 1 , indicating convex or L-type isotherms. The isotherms and K_f values demonstrated that the adsorption capacity decreased in the order H⁺-mont. $>$ Cu²⁺-mont. $>$ Ca²⁺-mont. $>$ Co²⁺-mont., with very high values for H⁺ and Cu²⁺-montmorillonite. The pH of the H⁺ and Cu²⁺-mont. suspensions was about 5.1, although the

authors reported that montmorillonite surfaces are usually more acidic. Under these conditions the authors state that some of the carbendazim molecules must have been protonated and so could have been adsorbed directly by ion exchange. The pH of the Ca^{2+} and Co^{2+} -mont. suspensions was 7.0, so the authors concluded that the number of protonated molecules would have been much smaller and ion exchange mechanisms would have been less important.

An increase in temperature resulted in a decrease in adsorption and this was used by Dios Cancela *et al.* (1992) to confirm the suspected mechanism of adsorption. The authors used the smaller effect of temperature on adsorption capacity of certain adsorbents as an expression of the main adsorption mechanism e.g. ion exchange. The authors observed no significant adsorption of carbendazim on other clay minerals, such as illite and kaolinite.

Dios Cancela *et al.* (1992) determined the adsorption isotherms of carbendazim on soils. They used a number of soil types from around southern Spain. The Freundlich equation (Eq. 3) described the adsorption well ($r=0.99$) with $x < 1$, as for montmorillonite and peat. The different types of soils sampled were ranked according to their adsorption capacities. Using the results of the clay and peat adsorption studies the authors deduced that carbendazim molecules must have been adsorbed on soil colloids mainly by physical forces. The authors suggested that the high affinity of carbendazim for organic matter accounted for the high adsorption capacity of certain of the soils that were particularly high in organic matter. To check this hypothesis, simple linear correlations were made between the K_f values and the various physico-chemical properties of the soils. The correlation coefficients and their significance levels are shown in Table 1.2.

Table 1.2: Correlation coefficients (r) between the Freundlich constant (K_f) and soil properties (After Dios Cancela *et al.*, 1992).

Soil properties	Organic matter	Nitrogen	pH	Specific surface	CEC	C/N	Clay	Free iron
Correlation coefficient, r	*** 0.920	** 0.926	0.278	* 0.616	*** 0.920	* 0.633	*** 0.847	0.218

*** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$.

Thus, the authors concluded that: carbendazim adsorption follows the Freundlich equation well, under the experimental conditions; both on montmorillonite and on peat, the absorption capacity is greater for acidic than for neutral or basic surfaces; the adsorption mechanism on acidic montmorillonite or peat is by protonation and ion exchange, whereas for neutral surfaces physical forces predominate; the adsorption of carbendazim by soils is directly proportional to their organic matter content and clay content. The correlation with the clay content of the soils ($r=0.85$) was weaker than for organic matter content which was concluded to be related to the low montmorillonite and high illite content of the soil. Illite has a low affinity for carbendazim. A strong correlation with CEC was shown as would be expected due to the close correlation between CEC and organic matter and clay content of soils.

Studies of this type using model adsorbents can be problematic when trying to relate to real soil because of the interactions that take place between soil components, particularly organic matter and organic matter-clay complexes. However, looking at specific pesticide retention mechanisms are essential as it enables researchers to decide with confidence, as Dios Cancela *et al.* (1992) did, as to the vulnerability of particular water sources to pesticide contamination. Dios Cancela *et al.* (1992) concluded that soils low in montmorillonite and organic matter like some of the southern Spanish soils have low adsorption capacity for carbendazim and the possibility of contamination of underground and surface waters is high.

Overall, there are various methods, which can be used to estimate the capacity of soils to retain pesticides. Whichever method is used the user must assess the assumptions and uncertainties associated with the method. For a rigorous understanding of retention, under specific circumstances, the mechanism of retention can be determined using model adsorbents. The particular components of soil responsible for pesticide adsorption are well known. The knowledge of these components combined with adsorption coefficients enables one to conclude that, for a given pesticide, sorption is greater in soils with larger organic matter content. Thus, pesticide leaching in soils with higher % organic matter is expected to be slower compared to soils low in % organic matter or for a given soil, pesticides with smaller K_{oc} values are sorbed to a lesser extent and are therefore more likely to be leached when compared to pesticides having larger K_{oc} values.

1.3 Transformation

Degradation and its relationship to adsorption, is covered extensively by Linn (1993). With the increase in potency of pesticides the quantity, which is needed for effective pest control, has decreased dramatically. Thus, the concentration of pesticide in the soil is very small when compared with other reactive constituents, such as clay and organic matter so that the decay of the chemical usually follows first-order kinetics (White, 1997). Transformation of pesticides can occur abiotically (hydrolysis, reduction, photolysis) or biotically (biodegradation, polymerisation) and can result in conversion to more toxic or less harmful products. Any pesticide will be metabolised or decomposed eventually but the rates of decomposition can vary enormously. The standard measurement of rate of degradation is the half-life ($T_{1/2}$) of the compound. The variation in degradation rates, according to Rowell (1996), depends on:

- the affinity of micro-organisms for the chemical;
- the susceptibility of the chemical to attack by enzymes and other chemicals in the soil;
- the accessibility of the pesticide to attack by micro-organisms which is usually dependent on the extent and strength of adsorption on soil particle surfaces, particularly organic matter; and
- soil temperature; water content and other soil properties.

1.4 Transport

1.4.1 Volatilisation

Volatilisation of pesticides has currently become an important issue with respect to the depletion of the ozone layer. Methyl bromide emission from fumigated fields is suspected to be a major source of ozone depletion in the stratosphere (Singh and Kanakidou, 1993).

Volatilisation appears to contribute to contamination of rainwater tanks by endosulfan. The 1997 State of the Environment report for NSW Australia reports trace levels of endosulfan in a rainwater tank in the Narromine area located some 11km from the nearest spraying. When responding to the draft review, the NSW EPA indicated that surveys in the Namoi valley had also found endosulfan in rainwater tanks, at peak levels of 0.27 g/L in 1996 and 0.12 g/L in

1997. Residues above 0.01 g/L were found in 61% of tanks during the 1997 survey, at up to 3.6 km from the nearest source, with a maximum concentration beyond 1.3 km of 0.02 g/L. A significant inverse relationship was found between minimum distance from spraying and endosulfan concentrations in tankwater (Australian National Registration Authority, 1997).

Volatilisation can be a major mechanism of pesticide loss from plant and soil surfaces and for very persistent chemicals such as the organochlorines, the means whereby they become widely dispersed in the environment. The dispersal of residues into the atmosphere involves two distinct processes. The first is the evaporation of pesticide molecules into the air from the residues present on soil or plant surfaces. The second is the dispersion of the resulting vapour into the overlying atmosphere by diffusion and turbulent mixing. The two processes are fundamentally different in character and are controlled by different chemical and environmental factors. Taylor and Spencer (1990) discuss these factors in an extensive review on volatilisation.

1.4.2 Leaching

Leaching through soil has been identified as a major cause of the appearance of agrochemicals in groundwater. Accidental spills are responsible for groundwater contamination in some cases but most of the pesticides in groundwater seem to result from conventional application of the chemicals to fields and their subsequent leaching through soil (U.S. Environmental Protection Agency, 1992).

Groundwater was not widely analysed for pesticides until new, very sensitive and relatively inexpensive analytical techniques became available. The occurrence of pesticides in groundwater revealed the limitations of our current understanding of transport processes in soils. Pesticides are usually thoroughly tested in the laboratory for their environmental fate. Currently, it takes about 7 to 10 years of testing, which can cost approximately 30 million dollars, before a new pesticide can be used (<http://www.epa.gov>). Leaching studies using soil columns often indicate that pesticides should be retained by the soil matrix and not be leached to groundwater to the extent found in monitoring studies. It became evident that results obtained in the laboratory may not always be applied to the field situation. In many of the studies pesticides moved deeper into the soil than expected based on laboratory measurements. Spatial variability or preferential flow phenomena have been hypothesised to

be responsible for the inconsistencies between many laboratory and field studies (Flury, 1996).

Leaching potential depends on two parameters:

- the length of time the pesticide persists in the soil measured by its half-life; and
- the strength of binding to the soil, measured by its partition coefficient.

In essence, a compound which degrades quickly will not be in the soil long enough to leach very deep even if it is free in solution, e.g. 2,4-D, and a compound which is strongly adsorbed will not be free to leach even if it is persistent, e.g. DDT. Researchers studying pesticide movement by preferential flow pathways, however, are challenging this point. Preferential flow will be discussed in Section 1.4.3.

Agricultural fields with subsurface drains are extremely well suited to pesticide leaching studies. Subsurface drains usually collect a large portion of the drainage water from a field and samples taken from drainage outflow are highly representative of the cumulative loss of a chemical through leaching. In a review on leaching by Flury (1996) a list of studies is provided where pesticides have been detected in water sampled from subsurface drains. The soils in these studies are mostly fine textured, usually loamy or clayey. The results of the studies indicate different behaviour of the chemicals within different soils. Buhler *et al.* (1993) found much more atrazine than alachlor in the drains and attributed this finding to the greater persistence (Half-life or $T_{1/2}$ is when half of the original amount of the pesticide has decayed) of atrazine ($T_{1/2} = 60$ d) in soil compared to alachlor ($T_{1/2} = 15$ d). No evidence of preferential flow was observed. On the other hand, Kladvko *et al.* (1991) found that all applied chemicals appeared at the same time in the drain. However, larger concentrations were found for more mobile pesticides than for strongly adsorbing pesticides (Kladvko *et al.*, 1991). Loss of pesticides to subsurface drains seems to be event-driven and single, heavy rainfall events can leach large amounts of chemicals through the soil (Kladvko *et al.*, 1991).

Flury (1996) suggested that without using conservative tracers e.g. Br^- or Cl^- , to characterise the water transport, it is difficult to interpret the transport of adsorbing solutes with respect to preferential flow phenomena. The observation made in many studies that different chemicals

occur at the same time in the drains, irrespective of their chemical properties, indicates that preferential flow phenomena are common in loamy and clayey soils.

1.4.3 Preferential Flow

There is experimental evidence that pesticides can move differently in the field than anticipated from laboratory studies. In some cases, pesticide leaching in the field was overestimated (Burgard *et al.*, 1994). However, in many cases, chemicals moved deeper than expected (Kladivko *et al.*, 1991). The researchers generally explained this behaviour by preferential flow mechanisms, where the solutes are transported through only a small portion of the soil volume. However, in the literature the term preferential flow is not used in a consistent manner. Direct evidence for preferential flow of herbicides is shown by compounds with different adsorption characteristics that have been applied simultaneously to the soil surface and appeared at the same time in drain outflow. There is no data available to quantify the relative importance of matrix flow and preferential leaching processes on pesticide mobility for an individual site.

1.4.4 Soil Structure

The structure of surface soils is closely related to surface preparation. Tillage homogenises and destroys part of the structure of the topsoil and continuous macropores are disrupted. It has been demonstrated that earthworm burrows are effective flow pathways for water and solutes (Edwards *et al.*, 1993). With respect to transport of adsorbing chemicals, earthworm burrows are very different from other macropores in soil, such as cracks or root channels. Edwards *et al.* (1993) suspected that organic and microbial lining of burrows increased the adsorption of atrazine. Stehouwer *et al.* (1993) confirmed this hypothesis by explicit determination of chemical properties of burrow linings as a function of soil depth. The implication that the soil structure, preferential flow and groundwater contamination are closely related means researchers must consider management process, e.g. conservation tillage, when examining pesticide mobility.

1.4.5 Initial Water Content

Little information is available about the effect of the initial water content of the soil on pesticide transport. Flury *et al.* (1995) indicated that the initial water content has an important influence on leaching of pesticides. The authors suspected that when pesticides are applied to air-dry aggregated soil, the chemicals are adsorbed within the aggregates by means of bulk flow of water into dry aggregates. The downward leaching of the chemicals by subsequent irrigation is then retarded compared with chemicals applied to initially wet soil.

There is evidence that the effects of water content depend on soil texture. Under dry soil conditions, sandy soils tend to show less leaching, whereas loamy and clayey soils show more leaching when exposed to heavy rainfall shortly after pesticide application. Brown *et al.* (1995) found less pesticide leaching through wet than through dry soil in heavy clay. The conclusions made by many authors appear to be contradictory on the issue of initial water content. As mentioned in the introduction, however, most of these conclusions are about site-specific experiments and comparisons may be impractical.

1.4.6 Time of pesticide application and rainfall events

Climate affects the type of crops grown, the intensity of pest problems and the persistence of pesticides used. The intensity of rainfall and its occurrence with respect to pesticide application determines how much pesticide transport occurs. While these factors are not controllable, probabilities of pesticide runoff and leaching can be estimated and avoiding pesticide application when rain is imminent is often possible (Flury, 1996).

Flury (1996) discussed the apparent increase of adsorption of pesticides in the field with increasing time which may have several reasons. For instance, chemicals may form bound residues, adsorption may be a rate-limited process, or biodegradation may decrease the concentrations in solution and thus increase apparent adsorption. It can be expected that the mass of pesticides leached is inversely proportional to the time elapsed between pesticide application and the first infiltration event (Edwards *et al.*, 1993). This inverse relationship has also been observed for the loss through runoff as will be discussed in Section 1.5. Soil

properties and topography of the field largely determine whether runoff or leaching is dominant.

1.4.7 Movement of degradation products

Pesticides degrade in soil by combined chemical and biological processes. Degradation products can have very different chemical, physical and biological properties than the parent compound. For instance, endosulfan was found to undergo enzyme catalysed epoxidation, hydrolysis, reduction and hydroxylation. The major hydrolysis product is endosulfan diol and the oxidation product, endosulfan sulfate. These degradation products have rather different mobility characteristics in soil compared to the parent product (Zaranyika and Mugari, 1997).

If endosulfan sulfate is released to the soil, it will be expected to bind to the soil based on estimated K_{oc} values and will not be expected to leach to the groundwater. There is minimal information about the environmental fate of endosulfan sulfate in water was found. If it is released to water, it will be expected to adsorb to the sediment and may bioconcentrate in aquatic organisms (Spectrum Laboratories: Chemical fact sheet - Cas # 1031078 <http://www.speclab.com/compound/c1031078.ht>). Overall, there is considerably less information on the environmental fate of the degradation products of pesticides when compared to the available information on the parent pesticide.

1.4.8 Runoff

Runoff carries chemicals from agricultural fields to surface waters such as rivers and lakes. Chemical fluxes resulting from runoff can be considerable. It has been estimated that the Mississippi River carries an annual mass of 150 t atrazine, 71 t simazine, 56 t metolachlor and 18 t alachlor into the Gulf of Mexico (Pereira, 1993). Single rainfall events can cause substantial pesticide losses to surface waters. It has been estimated for a wide range of pesticides that 1 to 2 % of the applied mass can be lost in a single runoff event (Wauchope, 1978).

Leonard (1990) has reviewed the subject of the movement of pesticides into surface waters. The mechanisms of runoff according to Bailey (1990, cited by Leonard, 1990) are (i) diffusion and turbulent transport of dissolved pesticides from soil pores to the runoff stream; (ii) desorption from soil particles into the moving liquid boundary; (iii) dissolution of stationary pesticide particulates; and (iv) scouring of pesticide particulates and their subsequent dissolution in the moving water. Pesticide is also entrained in runoff attached to suspended soil particles. Raindrop impact, in addition to suspending and dislodging soil particles, produces instantaneous pressure gradients affecting the turbulent interchange between the soil pore solution and the runoff stream.

The process of extraction of chemicals into runoff is obviously complex, with the degree of complexity increasing as the complexity of slope, drainage and soil management increases within a catchment. In the development of mathematical models, modelers have sought a definition of the "effective" surface soil mass or depth that interacts with runoff (Leonard, 1990). Leonard and Wauchope (1980), use a 10 mm depth as a predictor of pesticide available for runoff and did not assume complete mixing throughout this zone, but defined an additional parameter they called the extraction ratio. The extraction ratio approximates the effective mass ratio of the interacting soil to water in the runoff stream. Leonard (1990) emphasised that the assumption of complete mixing of the surface zone with runoff is a gross oversimplification.

Leonard (1990) discusses the role of the adsorbed phase and sediment transport with regard to organic matter and to model uncertainties and assumptions. Adsorption-desorption relationships are extremely complex and isotherms are often non-singular and not completely reversible. Adsorption isotherms, the models used to estimate sorption and the errors introduced by the model assumptions are discussed in Section 1.2.

The factors which affect runoff potential the most, are those which affect pesticide persistence in the active zone at the soil surface. These are factors that affect overall pesticide susceptibility to degradation and volatilisation, leaching below the soil surface and physical redistribution of residues. Climate, soil, pesticide and management factors interact in a complex manner to affect pesticide runoff (Leonard, 1990). There is a vast collection of references relating to each of these factors but the following discussion is a brief outline of the main factors affecting pesticide entrainment and transport in runoff.

The timing of rainfall and runoff is an important factor with respect to pesticide application. The highest concentration of pesticide in runoff occurs in the first significant runoff event after application. The pesticide concentration and availability at the soil and foliar surfaces dissipate with time thereafter. The rainfall intensity is also important as surface runoff occurs when the rainfall rate exceeds the infiltration rate. Increasing intensity increases the runoff rate and energy available for pesticide extraction and transport. The intensity may also affect the depth of surface interaction and increasing intensity reduces the time to runoff within a storm. The rainfall duration and amount affects the total runoff volumes which determine the amount of pesticide washoff from foliage and the amount of leaching below the soil surface. The time to runoff after the beginning of a rainfall event also determines the amount of runoff. Runoff amounts increase as time to runoff decreases. Pesticide concentrations and availability are greater in the first part of the storm event before significant reduction has occurred as a result of leaching and incorporation by raindrop impact.

The soil texture and organic matter are important factors affecting pesticide entrainment and transport in runoff. They both also affect infiltration rates. Runoff is usually higher on finer-textured soils. Time to runoff is greater on sandy soils reducing initial runoff concentrations of soluble pesticides. The organic matter content affects pesticide adsorption and mobility and chemical enrichment factors. Surface crusting and compaction should also be considered when looking at soil factors affecting runoff. Crusting and compaction decrease infiltration rates, reduces time to runoff and increases initial concentrations of soluble pesticides. The soil water content should also be considered when quantifying runoff. The initial soil water content when a rainstorm begins may increase runoff potential, reduce time to runoff and reduce the leaching of soluble chemicals below the soil surface before runoff starts. Increasing slope may increase runoff rate, soil detachment and transport and increase the depth of soil susceptible to surface erosion and, therefore, for chemical extraction. The degree of soil particle aggregation and stability also affects infiltration rate. The effective depth of chemical entrainment and therefore the potential for sediment to be carried by the runoff is determined by the degree of soil aggregation and stability. The deeper the entrainment depth and the greater the sediment transport potential the more, strongly adsorbed chemicals, will enrich the sediment.

The pesticide properties such as: solubility; sorption; the polar and ionic nature; persistence; formulation; the application rate and placement are, also, factors affecting pesticide entrainment and transport in runoff.

Management practices like erosion control can reduce transport of adsorbed and insoluble compounds. Crop residue can reduce pesticide runoff by increasing time to runoff, decreasing runoff volumes and decreasing erosion and sediment transport. Management options like vegetative buffer strips and type of irrigation also affect pesticide entrainment and transport in runoff. If one is using a model to predict pesticide mobility in an environment, the more details about the aforementioned factors one has, the more powerful the model will be as a predictive tool.

Research reported by Turnbull *et al.* (1997) is a field study of the factors outlined above. The silty clay soils, at Rosemaund, England, are subject to considerable and deep shrinkage cracks during the dry summer months. The work at Rosemaund has shown that considerable bypass flow through macropores leads to rapid movement of rain through to the stream via the drainage system (Turnbull *et al.*, 1997). In saturated field soil conditions, small differences in rainfall patterns can lead to significant effects on runoff characteristics with drainage derived from either sub-surface saturated flow, or rapid bypass flow through large macro-pores (e.g. earthworm burrows, root channels and incompletely closed shrinkage cracks) with a slight increase in rainfall field capacity is reached and runoff can be considerable (Turnbull *et al.*, 1997).

Soil surface pesticide concentrations are usually a good indication of runoff concentrations. Turnbull *et al.* (1997) noted that most of the pesticide residues in the runoff were transported in the water phase and a large pesticide K_d would be required to shift the primary mode of transport to sediment. However, as the time of contact with field soils increases, K_d appears to increase (Leonard and Wauchope, 1980). Turnbull *et al.* (1997) found that for low sediment loads the greater K_d values of trifluralin meant that significant movement remained associated with the suspended sediments. So persistent and highly immobile pesticides have the potential to accumulate in sediment if applied to fields that have been poorly managed with respect to erosion.

1.4.9 Leaching versus. runoff

A number of large (regional or national scale) well water quality surveys have been conducted to assess the extent of this largely invisible pollution. In the most ambitious nation-wide attempt, the U.S. Environmental Protection Agency (EPA) analysed samples from 540 community water wells and 752 rural household wells for 126 pesticides and pesticide metabolites. The wells were carefully selected to statistically represent all U.S. water supplies. Fourteen pesticides and metabolites were found and the percentage of contaminated wells, when extrapolated to the country as a whole, indicated that between 0 and 750 community systems (0-0.8%) and between 9 000 and 200 000 rural household wells (0.1-1.9%) will have at least one pesticide above a human-health-based drinking water standard, such as the maximum contaminant level (MCL) set by the EPA. As many as 14% of all wells may have detectable residues, generally in the range 0.1 to 0.2 parts per billion (one millionth of a gram per litre of water, ppb for short) of some pesticide.

Pesticide runoff, the process that may contaminate surface water directly, occurs if rain falls faster than it can infiltrate the soil, thereby generating flow across the soil surface, which picks up soluble pesticides or pesticides attached to eroding soil particles. Recently, the U.S. Geological Survey used the same analytical techniques, as mentioned above, to demonstrate that surface waters, including major rivers and lakes in the Corn Belt, also contain some of the most commonly used pesticides in the United States e.g. herbicides used in corn and soybean production, including atrazine, alachlor and cyanazine. During the 2 to 3 months in spring and early summer immediately after these herbicides are applied on farms, herbicide concentrations in surface waters can be much higher than in groundwater. In some instances, human health thresholds are exceeded and concentrations of 1 to 10 ppb are common; occasionally, concentrations exceeding 100 ppb are observed (Council for Agricultural Science and Technology, 1994).

Leaching and runoff are mutually dependent processes. During runoff, a portion of the water moves laterally to surface waters and does not contribute to leaching any longer. Increased runoff is therefore related to decreased leaching. This might not be generally true for preferential flow processes through macropores but certainly holds for the leaching of chemicals through bulk soil. The factors influencing leaching and runoff have been discussed

but the most important, when comparing the two processes, are the pesticide properties such as mobility and degradation, and soil management practices.

Pesticide residues at the topmost surface of soils are most available for runoff. The loss of water as runoff may be complete within hours of irrigation or rainfall event. The sediment in this runoff, which is a result of erosion, may remove pesticides which are otherwise immobile in the bulk soil. Thus, pesticide runoff is less dependent on pesticide properties than pesticide leaching and much more dependent on how soon runoff occurs after application. The inverse relationship between leaching and runoff leads to a dilemma when attempting to reduce overall loss of agrochemicals to surface and subsurface water. Steps taken to reduce surface runoff may lead to a potentially higher risk of loss through leaching.

There are only a few studies available in the literature where simultaneous pesticide loss through surface runoff and leaching have been compared (Gaynor *et al.*, 1992; Brown *et al.*, 1995). In all of the studies the soils were loamy to clayey and the pesticide leaching was measured from tile drains. The pesticide concentration in the runoff was consistently larger than in the leached drainage except for in the drier seasons when there appeared to be no significant difference. Brown *et al.* (1995) attributed this finding to greater preferential flow during springtime when the initial soil conditions of the clayey soil was dry. Flury (1996) states that runoff and leaching cannot be eliminated completely and strategies to minimise environmental impacts have to balance the potential risks posed by the different pathways.

1.5 Pesticide properties

The physical and chemical properties of pesticides can be considered to reflect the movement of these compounds. Observed differences in adsorption between organic compounds in the same soil are because of differences in the chemical characteristics of the compounds. As with the soil surfaces, functional groups on an organic molecule influence the strength and mechanism of chemical retention.

Pesticides can be classed as (after White, 1997):

- hydrophobic – water solubility $< 10^{-3}\text{M}$ or approximately 300 mg / L;
- sufficiently polar that the solubility $> 10^{-3}\text{M}$, but not a cation or weak acid or base;
- weak bases, i.e. RH_2^+ (RH (pesticide) + H^+);
- weak acids, i.e. RH (pesticide) (R^- + H^+); and
- cations.

For non-polar, hydrophobic compounds of low water solubility (e.g. organochlorines), soil organic matter is the most important adsorbent. For pesticides that are weak bases or weak acids, the strength of adsorption depends on soil pH because this influences the charge on the adsorbing surfaces and the charge on the molecule. Weak acids and bases are affected more by mineral surfaces than by organic matter. Pesticides that are cations are the most strongly adsorbed.

It is apparent that significant variation from expected behaviour could result from specific field and meteorological conditions in the environment. Certain generalisations can, however, be made about the class of pesticide and its expected mobility in the soil environment. Soluble pesticides may be more readily removed by runoff or leaching through the soil than hydrophobic pesticides. The polar, soluble pesticides are more easily removed from foliage by rainfall than the hydrophobic (lyophilic) compounds which are retained by leaf surfaces and waxes. Cationic pesticides are most strongly adsorbed by mineral surfaces and strongly adsorbed pesticides will generally be retained near the application site and if this is the soil surface they will be more susceptible to runoff (Leonard, 1990). The formulation, application rate and placement of the pesticide are also important factors determining the fate of the pesticide in the soil environment.

Vollner and Klotz (1997) found that the pesticide, chlorpyrifos and its degradation products moved rapidly through the sandy layers of a saturated zone (2-5m below surface) whereas in the humic layers it was strongly retained. A compilation of the pesticide properties as presented by Turnbull *et al.* (1997) in Table 1.3 was used by Vollner and Klotz (1997) to explain the behaviour of chlorpyrifos. Table 1.3 is a summary of the important physical and chemical properties of the pesticides used in the study by Turnbull *et al.* (1997) together with an approximation of their relative annual usage in the UK in 1992.

Table 1.3: Properties of the pesticides that were applied (after Turnbull *et al.*, 1997)

	Mol. weight	Log K_{ow}	Solubility (mg/l)	Vap. pressure (mPa)	Reported field T_{50} (days)	UK sprayed area (ha $\times$ 1000)	Tonnes applied in the UK
Trifluralin	335.3	5.27	0.221	9.5	57–126	336	313
Deltamethrin	505.2	4.6	$<2 \times 10^{-3}$	$<1.33 \times 10^{-2}$	10–30	290	1.7
Chlorpyrifos	350.6	4.7	1.4	2.7	60–120	32	21
Fenpropimorph	303.5	4.1	4.3	2.3	15–93	1790	511

Pesticide properties also need to be investigated when assessing the type of degradation reactions the pesticide undergoes. For example a study of the properties of endosulfan by Zaranyika and Mugari (1997), revealed that endosulfan undergoes epoxidation, hydrolysis, reduction and hydroxylation. The mobility of endosulfan would be greatly dependent on these reactions and the products.

1.6 Soil properties

In all studies of the mobility of pesticides in the soil, soil profiles are described and soil properties measured. For example, Espinosa-Ganzelez (1997), in a study of the fate and effects of pesticides, describes one of the soils studied as a volcanic soil from Cerro Punta which drains well, shows rapid permeability and has granular fine, strong structure, with many tubular and very fine pores. The author determined the percentage sand, clay, lime and organic carbon as well as the pH and macro nutrient content (P, K, Ca and Mg). The author carried out leaching experiments using lysimeters and three different soil types. Each soil was characterised by the author in the same manner as described above. The leaching experiments were conducted under the same climatic conditions and therefore Espinosa-Ganzelez (1997) concluded that the difference in dissipation rates has to be related to the soil properties.

For example, in soils with high clay content and organic matter pesticide residues are usually found in the top 10 mm layer of the soil whereas in more sandy soils greater leaching occurs and most residues are found in deeper layers. The residues in deeper layers are usually

insoluble compounds that move attached to particles under the influence of downward moving water. Low organic matter and low clay content facilitate this downward movement. Pesticides adsorbed on clay are also expected to move to deeper layers as clay particles move to deeper depths in sandy soil (Agnihottri, 1996). The pH of soils is an important property with regards to pesticide mobility. Yucel *et al.* (1997) demonstrated the influence of pH on the pesticide chlorpyrifos. The authors concluded that the high pH of the surface and subsurface soils, of their study area, increased hydrolysis and decreased the adsorption of chlorpyrifos. The clay mineralogy is another property that should be determined when studying pesticide retention. Green *et al.* (1993) suggested that chlorpyrifos may be highly adsorbed onto smectite and the authors emphasise the need to identify the clays, in soils used for pesticide studies.

The impact of pesticides seems to be less on soil systems than on aquatic systems, as they are adsorbed and degraded in soil to a greater extent than other compounds. However, the soil microflora has been shown to be significantly affected in terms of nitrification capacity and enzymatic content (Espinosa-Ganzelez, 1997). The soil also has a profound effect on microbial activity, which plays a major role in dissipation of pesticides.

Scheunert *et al.* (1997) found that the mineralization of pesticides was highest in a soil with the highest clay content and organic carbon. The authors concluded, however, that mineralization is not directly dependent on physicochemical soil properties but on the quantity and quality of soil microflora which perform the degradation. The quantity and quality of soil microflora are not constant but vary with space and time, depending not only on the soil properties but also on many other factors such as temperature, humidity, aeration status and nutrients.

1.7 Modeling of pesticide movement

A variety of physical, chemical and biological processes determine the environmental fate of pesticide. The rates at which these processes operate will determine the mobility and the persistence of a pesticide. The rates and pathways of each of the processes, in turn, are modified to a considerable extent by various environmental factors as well as the properties of the pesticide itself. Microbiologists, chemists, soil scientists and hydrologists study these processes in isolation. A more holistic approach is required, however, to understand and

forecast the interactions among the processes and their integrated impact on the environmental behaviour of pesticides.

The development of simulation models for forecasting pesticide behaviour is an attractive way of evaluating solutions to some agricultural and environmental problems. For example, guidance is needed in determining which pesticides should be used for a particular soil-crop-weather combination and to estimate the rate and timing of pesticide application such that crop protection is maximised and adverse environmental impacts are minimised.

For these reasons, and many more, modeling is increasingly being used as a tool for evaluating the fate of pesticides in soil-water systems. Sorption, leaching, degradation, volatilisation and other processes are being integrated through the use of simulation modeling techniques. Wagenet and Rao (1990) point out that the proper development, testing and responsible use of a modeling approach must be based upon a thorough, comprehensive understanding of interdependent and dynamic natural processes as well as a clear definition of the purpose for which the model will be used.

One major limitation and constraint to the widespread use of pesticide-fate models is the apparent lack of recognition that different types of models are required for different purposes. The quantity of required input data, the level of detail at which the basic processes are described, sensitivity and accuracy of the model outputs all depend upon whether the modeler intends to approach the simulation from a research or management perspective.

Simulation of the pesticide-fate processes: transport, sorption, volatilisation, degradation and plant uptake has been developed from basic theory of the physical and chemical processes affecting solutes in soils. For example, transport of solutes is the result of diffusion and convection. Diffusion and convection can be described by mathematical expressions such as Fick's law, Darcy's law and Richard's Law. The inputs for the model will then be the site-specific parameters which are needed to solve these types of expressions. This is a very simplistic explanation but Wagenet and Rao (1990) discuss the derivation and manipulation of expressions used by pesticide-fate models to describe the contents of soil-water and soil-water fluxes. They also discuss by way of example models how the pesticide-fate processes are integrated.

The major characterising parameters required by models such as LEACHM (Wagenet and Hutson, 1989) and CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems) (United States Department of Agriculture) are: the pesticide properties (K_{oc} and $T_{1/2}$); soil properties (% organic carbon, pH, CEC, field capacity and hydraulic properties); crop properties (root density distribution and maximum rooting depth); climatic properties (daily rainfall and evaporation) and management options (pesticide application rate and date, irrigation rates and soil tillage effects).

A review of approaches used to predict solute leaching in soils (Addiscott and Wagenet, 1985) identified a number of research and management models that have been reported in the scientific literature. Research models e.g. LEACHM were identified as generally intended to provide quantitative estimates of water flow and pesticide behaviour but with comprehensive and often substantial data demands regarding the system to be simulated. Management models e.g. CREAMS while less data-intensive, were identified as commensurately less quantitative in their ability to predict water and solute movement under transient field conditions.

The research model, LEACHM, is the only generally available unsaturated zone model, which solves the water balance using the classical Richard's equations. The water flow calculation enables the soil-water contents and soil-water fluxes to be calculated. These values are then used in the convective-dispersive transport equations for predicting solute transport. Thus, transient flow of water and solutes are explicitly linked. Volatilisation losses of the pesticide are also calculated in LEACHM. Another feature of this model is that it provides predictions of the transport and transformation of the parent chemical as well as up to two daughter products. Appropriate specification of surface and bottom boundary conditions will permit simulation of upward movement of soil water as a result of evaporation or because of the presence of a shallow water table. Note that LEACHM does not account for preferential flow of water and solutes in macropores (e.g. root channels and cracks) or the presence of mobile and immobile soil-water domains, as would be the case in aggregated soils (Wagenet and Rao, 1990). Although several approaches have been proposed to deal with preferential water and solute flow, none have been incorporated into research models for pesticide fate in soils.

Pearson and Inskeep (1996) used the LEACHM model (Wagenet and Hutson, 1989) for mapping the leaching potential of soil units and, therefore, predicting the fate of chemicals at specific locations. In all the studies, poor model performance is attributed to the inability of

LEACHM to simulate preferential flow. The authors state that comparison of observed and predicted solute movement under field conditions is necessary for verifying the predictive capability of solute models. The author's evaluation of LEACHM supports the use of this model based on the criteria presented by Pennel *et al.* (1990, cited by Pearson and Inskeep, 1996) that the predicted solute travel times are within 50% of the observed values.

Leonard (1990) discusses modeling and computer simulation of pesticide runoff: The author covers model selection, use and the range of runoff models that are available e.g. the CREAMS model (United States Department of Agriculture, 1980). The applications of these models are discussed in brief. Leonard (1990) concluded that the models developed to simulate pesticide runoff losses do not provide predictions in terms of absolute values to a high degree of accuracy but do provide information for relative comparisons between management alternatives, weather patterns and other variables.

Scientists of the U.S. Department of Agriculture, Agricultural Research Service, developed the CREAMS model to evaluate nonpoint source pollution from field-size areas but this simulated runoff only. Problems of pesticide in groundwater and increased emphasis on groundwater quality led to modifications of CREAMS to consider impact of agricultural management systems on groundwater loading. The GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model was developed to utilise the management-oriented physically based CREAMS model and incorporate a component for vertical flux of pesticides. Therefore the advantage of GLEAMS is that it can simulate runoff and leaching for up to ten solutes (parent pesticide and its degradation products). The model incorporates rainfall, infiltration and runoff processes. Runoff is estimated from daily rainfall using the curve number technique. Daily weather data are required but may be generated by an internal routine. The erosion components are relatively sophisticated. They include overland flow, channel flow and impoundments, as well as the effects of particle-size distribution and the specific gravity of each particle-size class. Solute transport is modeled using a storage routing procedure (i.e. it solves the transient convection-dispersive equation for solute transport using a simplified water balance). Seepage from the root zone occurs only when saturation exceeds field capacity.

GLEAMS is recommended for applications only to the root zone. GLEAMS divides the root zone into a minimum of three and maximum of twelve computational layers. Pesticide mass transport is based on a complete mix model coupled with the soil/water submodel. Other

pesticide processes considered by GLEAMS are degradation, volatilisation, plant uptake, extraction into runoff, metabolites and transport with sediments. Soil properties and degradation rates can be varied with depth. The GLEAMS model accounts for the difference between pesticide application on plant foliage and application on the soil surface. Different degradation rates also can be specified for chemicals on foliage and within the soil.

This model is, however, data intensive although the model does provide a range of estimate values for the input parameters that the modeler can use if site specific data are unavailable. However, the designers of the model (Knisel and Leonard, 1993) state in the GLEAMS model user manual, "It must be remembered that model output is no better than the input data." Leonard *et al.* (1987), discuss the theory, sensitivity and validation of GLEAMS.

The use of simulation models for describing pesticide fate in soils has gained increasing popularity. Although site-specific investigations might be preferred, the economic and scientific resources required to conduct such studies are unrealistically high given the vast number of combinations of pesticide-soil-crop-weather-management scenarios that might need to be investigated. Models also permit an assessment of the complex interrelationships among the environmental processes that affect pesticide fate in soils and groundwater.

Some models with varying levels of sophistication have been developed for a variety of applications. Limited availability of data sets from field studies, however, continues to be a major constraint in evaluating the validity of these models before they can be used with confidence for the purpose for which they were developed, i.e., management and regulatory guidance. In only a few cases have predictions of different models been compared with a single data set to examine the adequacy of the simplifying assumptions in the model developed for management purposes. Wagenet and Rao (1990) state that there is a need for conducting co-ordinated field studies to collect the required data, to compile data bases and estimation methods for the model input parameters and to develop objective criteria for assessing model validity. They concluded that much of the current research and scientific debate focuses on these important issues.

1.8 Summary and conclusions

Retention is a major factor influencing the mobility of pesticides in the soil. Currently, data intensive computer models are used for predicting the mobility of pesticides in the soil.

Adsorption isotherms and the adsorption coefficients calculated are input into these models. The success of the model is dependent on the method used to determine these parameters and the validity of assumptions associated with their calculation and interpretation. Parameters are increasingly taken from the literature because of the increase in model use but evidence is given that this is inappropriate for site specific cases. The K_d must be measured by experimentation for site specific cases and not calculated from organic matter content as not all soil-pesticide systems obey the assumptions associated with calculating adsorption coefficients, especially K_{oc} . To add meaning to the value of the adsorption coefficient and to make reliable conclusions about pesticide mobility, the mechanism of retention may be determined experimentally. Model adsorbents, temperature and pH effects are used to determine retention mechanisms.

Volatilisation is an important transport process whereby pesticides can be lost from the soil. Transport by leaching is responsible for the occurrence of pesticides in groundwater and the depth of leaching is often greater in the field than in laboratory experiments. It has been demonstrated that sandy soils are most susceptible to pesticide leaching to groundwater but loamy or clayey soils may lose pesticides by leaching via cracks and macropores. There is evidence that even strongly adsorbing chemicals can reach groundwater via preferential flow pathways such as earthworm burrows or cracks. Soil structure and management can affect pesticide mobility and there is evidence that conservation tillage increases the risk of preferential flow in structured soils. Leaching is only likely in soils, which do not show preferential pathways, once the field capacity is exceeded. The initial water content seems to have an effect on leaching; dry soils appear to show less fast leaching than wet soils but it cannot be specified what dry and wet mean quantitatively. There is less leaching the longer the period between application and rainfall or irrigation event. Degradation products, which can be more toxic than the parent chemical, have different leaching potentials to the parent pesticide.

Chemicals applied to field crops and other areas for pest control may enter surface waters by rainfall and irrigation runoff. Factors governing runoff are desorption-adsorption (especially to the sediment phase), diffusion, dissolution, scouring, entrainment, raindrop impact and erodability. Climate, soil type and pesticide management determines these factors and how they interact. An important issue is the relative importance of leaching vs. runoff. Leaching and runoff are to some degree mutually exclusive and the relative contribution, once again, depends on soil properties and the topography of the field.

The chemical and physical properties of the pesticide also determine their mobility in the soil. The reactions in the soil depends on polarity, hydrophobicity, acidity, ionic status and solubility amongst others. The soil properties (% sand, % clay, lime, pH, OC, major ions) and soil profile descriptions should always be determined before embarking on adsorption studies. The soil conditions which are conducive to high adsorption are also conducive to high microbial activity so less leaching may be due to more degradation as oppose to adsorption. However, degradation rates are dependent on the strength of adsorption and thus, the availability of pesticide.

Models can save time and money but should be used with caution. One should have good site and parameter knowledge before starting to use a model. The model LEACHM makes few simplifying assumptions and estimates of parameters but it is extremely data intensive. GLEAMS requires slightly fewer input parameters and is a field-based model that simulates both vertical and horizontal fluxes of soil-water and soil-water contents.

Roberts (1997) recommended that South African scientists need to develop more know-how in computer simulation modeling and have a multi-disciplinary approach involving chemistry, soil science, ecotoxicology and hydrogeology skills. Roberts (1997) also suggested that more South African scientists need to develop expert knowledge on organic contamination of soils, water and air to enable regulation of the standard of work being completed in this area. Viljoen (1994) advised that pesticide analysis techniques need to be standardised and validated as soil analyses, especially, are in demand by private individuals such as farmers taking decisions about planting crops or determining reasons for poor germination of seeds. It is also recommended by Espinosa-Ganzelez (1997) that research should be undertaken to develop monitoring programmes for relevant pesticides in soil and food, especially taking into consideration the local practices of farmers and the prevailing climatic conditions. The Council for Agricultural Science and Technology (Pesticides in groundwater and surface waters, Issue paper 2, April 1994, WWW.CAST\pwg_ip.htm) recommended that national and state departments and pesticide manufacturers need to make an effort to provide farmers with the information needed for pollution prevention. The farmer has considerable control over the pollution probabilities: knowledge of erosion control and of best application techniques as well as an eye on the weather are the first lines of defence against pollution.

CHAPTER 2

Characterisation of the Hex River Valley Soils

2.1 Introduction

One of the aims of this study is to determine the sorption coefficient for chlorpyrifos and endosulfan and to model their mobility in the soil environment. To be able to interpret the value of the sorption coefficient in terms of the mobility in a specific area, like the Hex River Valley, the soil properties need to be determined. The individual processes of sorption are highly complex and this is mainly due to the heterogeneity of the soil and the soil intimacy with biological, atmospheric and water systems. One of the pathways to understanding the mechanisms and the processes that control the mechanisms of retention is, therefore, to have a good understanding of the composition of the soil matrix.

It has been reported that soil organic carbon content is significantly correlated with the sorption of non-ionic and non-polar hydrocarbons. In this context, non-polar also refers to weakly polar molecules, since few organic molecules are strictly non-polar (i.e., have zero dipole moment) (McBride, 1994). The clay content and the mineralogy of the Hex River Valley soils affects their capacity to facilitate the movement of organic chemicals into water supplies and therefore these properties need to be determined. The greater the clay content, the larger the specific surface area and thus surface for adsorption and the number of reactive sites for interaction with the functional groups of the organic molecule. The mineralogy is also important since, for example, smectite and vermiculite are able to trap organic molecules in their interlayer spaces decreasing the mobility of the molecule while kaolinite has low specific surface area and the variable charge on the edges are the most reactive sites.

The pH, cation exchange capacity (CEC) and P-sorption are all indications of the type and quantity of charge in the soil components. Their significance becomes more relevant the greater the overall charge of the soil, the more nucleophilic the functional groups and the more polar the organic molecule. Even soil properties that are not directly related to sorption of pesticides need to be measured. For example, the electrical conductivity and major cations and anions are needed to determine the salinity and sodicity of the soil. Sodic soils are susceptible to compaction and poor infiltration and thus a percentage of pesticide applied to a sodic soil can be lost from the field in runoff and can pose a threat to

the environment. Runoff is defined as water and any dissolved or suspended matter it contains that leaves a plot, field, or small singlecover watershed in surface drainage. Specifically, pesticide runoff includes dissolved, suspended particulate, and sediment-adsorbed pesticide that is transported by water from a treated land surface (Leonard, 1990).

A detailed soil chemical characterisation and interpretation of their effect on pesticide mobility is provided in this chapter. These data are also needed as input parameters for the modelling of the pesticide mobility by GLEAMS (Knisel and Leonard, 1993) in Chapter 4.

Soil physical properties like hydraulic conductivity, field capacity and wilting point, which are important to the timing and amount of pesticides lost in runoff and leaching water, are also discussed in Chapter 4. The geo-chemical origin of the soil and geohydrology of the Hex River Valley is presented in this chapter not only as background to this study but to provide a basis for an entire catchment simulation, visualisation and management which would be the ultimate aims of a group effort in understanding movement and concentrations of organic molecules in a large area like the Hex River Valley.

2.2 The Hex River Valley

2.2.1 Introduction

This study site was chosen, as it is an area of intensive agriculture and pesticide use. The hydrogeology of the area is well understood as the Department of Water Affairs and Forestry (DWAF) conducted a detailed hydrogeological survey of the Hex River Valley so as to explain the observed deterioration in quality and quantity of the groundwater (Rosewarne, 1981).

The Hex River Valley is situated about 125km north-east of Cape Town. De Doorns is the town at the centre of the valley (Figure 2.1). It is a steep-sided valley surrounded by rugged mountains. The valley is 23 km long and varies from 0-5 km in width. The valley sides are quartzite of the Table Mountain Group and valley floor is alluvial overlying shale of the Bokkeveld Group. Where the mountain streams enter the valley extensive alluvial fans were developed (Weaver, 1993). Figure 2.2 shows the geo-hydrological layout of the Hex River Valley.

2.2.2 Relief

The rugged mountains surrounding the valley are the Hexriverberge, in the north and north-east, and the Kwadousberge, in the south and south-east. These mountains rise up to 1637m above the valley floor with the highest peak being the Matroosberg, in the Hexriverberge, which is 2249m above sea level. The mountains are cut by steep gorges eroded by the tributaries of the Hex River. Groothoekkloof, Rooielskloof and Sanddrifskloof are the main gorges in the Hexriverberge (Weaver, 1993).

2.2.3 Drainage

The Hex River rises near Matroosberg Station and enters the valley at Mountain Lodge in the north-east. The main tributaries are from the Hexriverberge and are perennial, although for much of the year the flow is diverted into irrigation schemes and does not reach the Hex River. There is about 4000 Ha of land irrigated in the valley and about 30 million m³ of water per annum is needed for irrigation. Sixteen and a half million being from groundwater and the rest from dams that store water from the winter rainfall (Personal communication, Christiaan from the Hex Valley Irrigation Board).

The river has a narrow flood plain and a simple regime with high flow during the winter rainfall months. The alluvial fans, where the tributaries enter the valley, were presumably built up during past periods of more active erosion and deposition. The slope of the alluvial fans varies from 2° - 6° (Weaver, 1993).

2.2.4 Climate

The Hex River Valley lies within the Southwestern Cape winter rainfall area and has a Mediterranean climate. The upper catchment area of the Hex River lies in the Karoo region and tends towards a semi-desert climate. This region has a total mean annual rainfall of

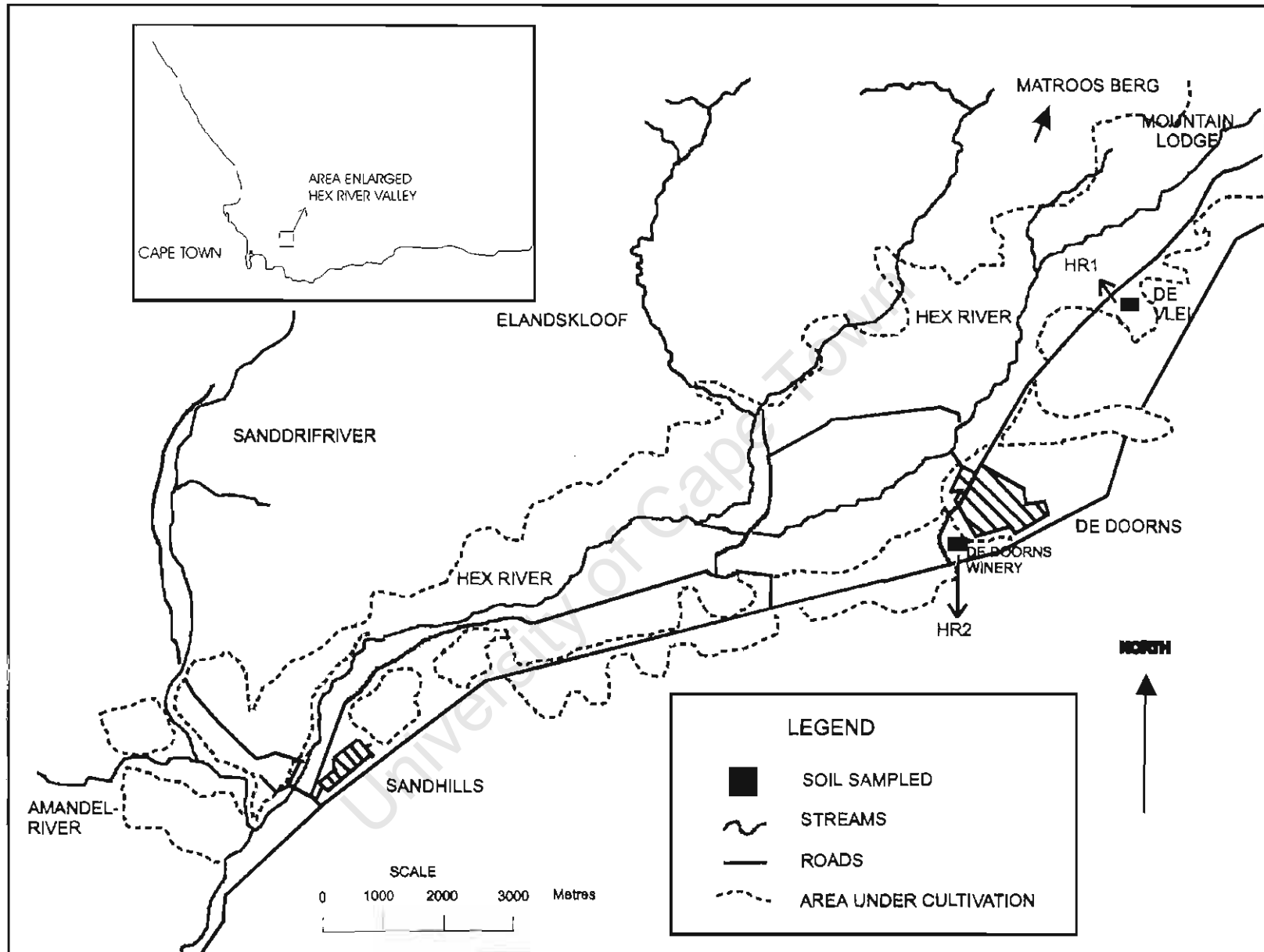


Figure 2.1 Schematic of the Hex River Valley showing the town of De Doorns and the soil sampling sites.

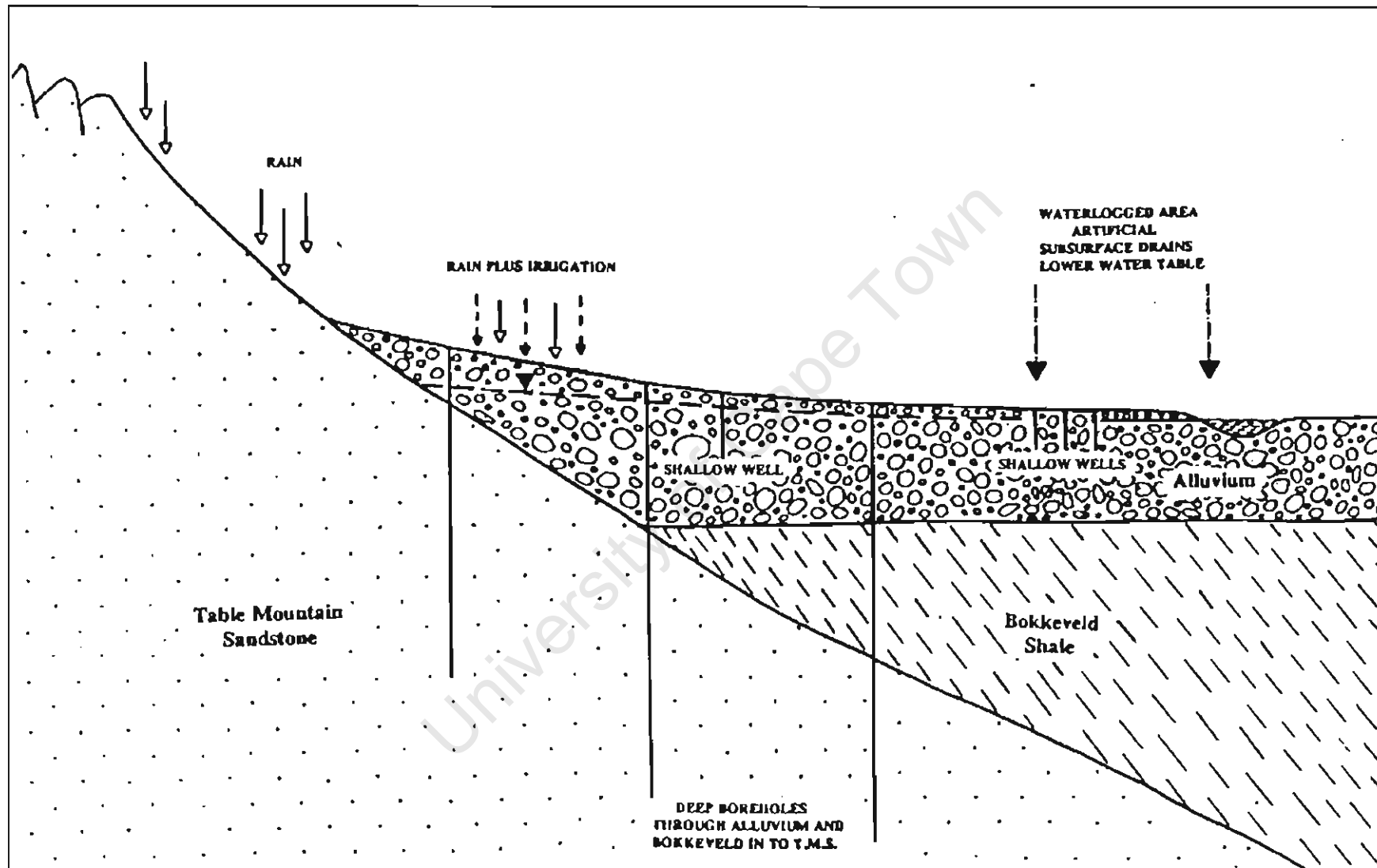


Figure 2.2 A schematic of the geo-hydrology of the Hex River Valley (Adapted from Rosewarne, 1981)

284 mm, of which only 84 mm occurs in summer, giving it a “very arid” aridity index of 640 mm, i.e. the difference between 0.4 standard USA class A pan evaporation and seasonal rainfall (Saayman and Lambrechts, 1995). Rainfall varies over the area and is largely controlled by topography. The Hexriverberge are frequently capped by snow during the winter months. The area receives winter rainfall which average between 240 and 329 mm per annum so irrigation is needed. Water applied by means of irrigation in the summer is greater than precipitation due to rainfall in the winter months. The Institute for Soil, Water and Climate at Nietvoorbij, Stellenbosch has two weather stations in the Hex River Valley. Daily rainfall, temperature, wind speed, evaporation and dew point temperature were obtained from them for June 1997 to June 1998 for the modelling chapter of this study, Chapter 4. A summary of the climatic data for the Hex River Valley is presented in Table 2.1.

Table 2.1: Average monthly temperature, total monthly rainfall and monthly evaporation (American Class) for the Hex River Valley.

MONTH	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
T (°C)	22.4	24.3	21.0	19.3	15.2	12.8	12.0	13.6	16.7	19.3	19.0	21.9
R (mm)	11.0	0.0	1.0	5.1	83.0	14.5	38.0	25.0	0.0	0.0	17.0	2.8
E _p (mm)	346	284	240	153	97	78	89	115	168	229	290	337

2.2.5 Geology

Figure 2.2 shows the geological formations bordering the valley. In the north, west and south are the sandstones, quartzities and shales of the Table Mountain Group and in the east and north-east the alternating shales and sandstones of the Bokkeveld Group. The Bokkeveld Group is only exposed to the east and north-east of De Doorns, being covered by alluvial deposits elsewhere. Evidence from boreholes indicates that the lowermost member of the Group, the Ceres Formation extends to the south-east almost as far as Sandhills (Rosewame, 1981).

The hydrological reservoir formations in the area are the sandstone and shales of the Table Mountain and Bokkeveld Groups and alluvium covering the valley floor. The Table Mountain Group is the oldest formation in the valley and consists predominantly of hard quartzitic sandstones and quartzites. Two shale horizons are present, the lower one

associated with a tillite horizon. The sandstones show massive bedding and are highly jointed. The resistance of these rocks to erosion has led to the formation of a rugged mountainous topography which significantly controls the geohydrology of the area (Rosewarne, 1981).

The Bokkeveld Group is a sequence of alternating shales and sandstones with a total thickness of up to 600m. Only the lowermost member of the Bokkeveld Group, namely the Ceres Formation, is found in the Hex River Valley. The unweathered shales are typically dark grey in colour, micaceous and may contain pyrite, calcite and vein quartz. Arenaceous horizons occur within the shales. The sandstones are generally impure, micaceous and fine to medium grained. The exposed Bokkeveld rocks are weathered to a typically reddish-brown colour presumably due to the formation of iron oxides by chemical weathering processes. The subsurface bedrock is also weathered to some extent but does not exceed 10m (Rosewarne, 1981).

Extensive alluvial deposits have been laid down over the valley floor ranging from silty and clayey sand to sand and gravel deposits of considerable thickness along the flanks of the valley where streams enter from the bordering mountains. Rosewarne (1981) used surface observations and detailed logging of exploration boreholes to sub-divide the alluvial deposits on the basis of their source rock and mode of deposition:

- Alluvium derived from the Table Mountain Group is the most extensive of the alluvial deposits and is predominantly quartzitic and typically off-white to light brown in colour. The greatest thicknesses are found in the piedmont deposits of the alluvial fans built up along the flanks of the valley at mouths of gorges cut in the Table Mountain sandstone, where up to 69m of alluvium is present. The alluvium is very coarse and poorly sorted consisting of a silty sand matrix with gravel up to boulder size. Elsewhere the alluvium consists of normal fluvial deposits comprising very fine to very coarse sand with some fine gravel. Coarse gravel is found along the channel of the Hex River. These deposits mainly occupy the central area of the valley.
- Alluvium derived from the Bokkeveld Group is less extensive and on average, is thinner. The alluvium has been derived from both shales and sandstones. The shales have given rise to a silty clay matrix with coarser grains of

sandstone up to pebble/cobble and rarely, boulder size. Appreciable quantities of mica are present and the alluvium is reddish-brown in colour.

- Alluvium of mixed origin contains material derived from both Table Mountain and Bokkeveld sources. It consists typically of a silty and sometimes clayey matrix with sand and gravel up to cobble/boulder size and is buff coloured.

2.2.6 Land Type Inventory

The Hex River Valley falls mainly into two landtypes according to Land Type Survey Staff (1984). Landtype, Ia22, covers 5320 Ha of which 30% is the soil series, Dundee (Du10), which has a depth greater than 1200 mm and a clay content in the A horizon of between 0 and 6%. The Warrington series (Fw31), with a depth of between 700 and 1200 mm and between 0 and 6% clay in the A horizon, constitutes 17.5 % of this land type. The second landtype in the valley is Hb40 which covers an area of 2630 Ha and 64% of this is the Fernwood series (Fw11) which varies between 500 and 1000 mm in depth and 0 and 6 % clay in the A horizon.

2.2.7 Soils

The Hex River Valley is dominated by a soil classified as Fernwood 11 (Soil Classification Working Group, 1991). This soil is described as having a pale, sandy topsoil, underlain by a leached, white, sandy, eluvial horizon without lamellae. The physical characteristics of the soil are summarised in Table 2.2.

Table 2.2: Mean physical properties of the Fernwood * soil at the Nietvoorbij Experimental Farm, De Doorns, Hex River Valley (Adapted from Saayman and Lambrechts, 1995).

Depth (mm)	Sand (%)			Silt(%)	Clay(%)	Bulk density (kg m ⁻³)	Water retention (Vol. %)				
	Coarse	Medium	Fine				-5 (KPa)	-10	-100	-200	-1500
0-300	18.9	52.5	23.9	2.5	2.2	1410	6.5	4.6	2.5	2.2	1.6
300-600	20.2	52.3	22.9	2.3	2.3	1438	5.6	4.4	2.6	2.3	1.7

*Soil Classification Working Group (1991).

2.2.8 Landuse

The Hex River Valley is an agricultural area. Barlinka, a late-maturing, black grape variety, brought to South Africa in 1910, is still an important cultivar in the South African range of table grapes. According to Unifruco statistics for the 1994 season, Barlinka comprised about 19% of the national export crop of 18.75 million 5kg cartons and 34% of the Hex River Valley export of 9.53 million cartons. Barlinka is mainly grown in the Hex River Valley (92% of the national Barlinka export) where table grape production is virtually a monoculture. It is a late region, with the late-ripening Barlinka maturing towards the end of March to early April, thus putting it in the high demand/low supply marketing period of the Northern Hemisphere. Additionally, during the maturation period there is a 16.1°C mean night/day temperature difference, compared to 13.7°C in the coastal Paarl region, enhancing the coloration of Barlinka, a variety known for its tendency towards inferior colouring. Consequently more than 90% of all Barlinka vineyards in the RSA are situated in the Hex River Valley, making it unique in this respect (Saayman and Lambrechts, 1995).

2.3 Material and methods

2.3.1 Soil sampling and preparation

Two soils were sampled in this study. The soils were collected as composite topsoil samples. The sampling was done to not more than 300 mm depth. Since the two pesticides being examined are known to be strongly adsorbed onto soil particles and are both applied by spraying onto the soil and plant surface, the top 0-300 mm would be the most important compartment to characterise and understand in terms of mobility in the soil environment. The soil samples would not be analysed for pesticide residues so multiple samples at different depths were not needed. The intention of the sampling was to gain a representative soil sample of the grey, sandy, Fernwood soil which is known to dominate a large majority of the Hex River Valley and a sample of the less dominant reddish-brown loamy sand which is to be found in the more north-east part of the valley. The soils were sampled from uncultivated areas of the valley so as to minimise possible pesticides contamination, which would then interfere with the adsorption test and subsequent pesticide analyses. Since the number of samples was limited to two no proper statistical analyses could be carried out but since the main objective is to obtain the adsorption coefficients for the particular soil/pesticide pair and not to measure the spatial geochemistry of the area, this was deemed acceptable. A summary of information about the

soil collection is provided in Table 2.3. The sample codes will be used as the sample names throughout the text. The sampling sites are indicated on Figure 2.1. The soils were air-dried, gently crushed to pass through a 2 mm sieve, and stored in 2 L plastic containers.

Table 2.3: Information on the sampling sites and soil sample colour.

Sample code	Location	Land use	Altitude (m.a.s.l)	Parent material	Soil colour Munsell
HR1	De Vlei	Uncultivated Roadside	480	Bokkeveld shales & sandstones	5YR5/4 reddish brown 5YR4/4 reddish brown (wet)
HR2	De Doorns Winery	Uncultivated	480	TMS sandstone & shales	10YR6/2 light brownish grey 10YR4/2 dark greyish brown (wet)

2.3.2 Methods Used to Determine the soil properties related to the mobility of endosulfan and chlorpyrifos

A brief description of the methods used to analyse the Hex River Valley soil samples will be given here; details are provided in Appendix A. The analyses were performed by the author in the Department of Geological Sciences at the University of Cape Town except where otherwise stated.

2.3.2.1 Soil pH and EC

A 1:2.5 soil to solution ratio was used to determine pH of soil suspensions in distilled water and 1M KCl using a Crison micro pH 2001 instrument (Rowell, 1996). Electrical conductivity (EC) of the saturated paste extracts was determined using a Crison micro EC 2201 meter fitted with a combination electrode. ΔpH values were calculated as a difference between pH measured in water and KCl.

2.3.2.2 Mineralogy of the clay fraction

The clay minerals were identified by X-ray diffractometry (XRD) techniques, after the clay size ($<2\ \mu\text{m}$) fraction had been separated. The concentration of the separated clay suspension was determined gravimetrically and then adjusted to $\pm 20\ \text{mg/L}$. An aliquot of 2ml was withdrawn and pipetted onto a level glass slide. The glass slide was covered and kept in a stable, aerated place to dry. The slides were examined by XRD using a Philips PW 3890 diffractometer with graphite monochromator and scintillation detector with $\text{CuK}\alpha$ radiation. The scanning was over a 2θ range of $4 - 50^\circ$ (machine running at 25mA, 40KV). Results were recorded and processed with Philips PC-identity software (PW1876 Version 1.0E).

2.3.2.3 Specific surface area

The specific surface area was determined in The Particle Technology Centre, in the Chemical Engineering Department of the University of Cape Town.

The BET method (Carter *et al.*, 1989) was employed in determining specific surface area using a Micrometrics ASAP 2000 instrument with nitrogen as the adsorbing gas. The BET equation allows for the calculation of surface area based on the number of molecules adsorbed in a monolayer. Although, nitrogen gas is weakly adsorbed and cannot penetrate the interlayer space of expansible minerals (Carter *et al.*, 1989), this method was considered suitable as a reasonable approximation of the specific surface area.

2.3.2.4 Particle size distribution (PSD)

The PSD was determined at, ARC-Infruitec, Stellenbosch by sedimentation using the Pipette Method (Gee and Bauder, 1986).

2.3.2.5 Organic Carbon

Organic carbon was determined both by the author at the Geological Science Department, UCT and by a technician at ARC-Infruitec, Stellenbosch. Both labs used the same rapid dichromate oxidation-titration method of Walkley & Black (1934), as described by Nelson and Sommers (1982). The method consists of oxidising the organic material in soil with a treatment of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and sulphuric acid. This solution is titrated

with ferrous ammonium sulphate in the presence of 0.025-M ferroin indicator. Blank solutions, which were prepared by the same method, were also titrated.

2.3.2.6 Water soluble cations and anions

The saturated paste extract was prepared according to the method outlined in Appendix A.5. The pH and EC were measured before filtering the extract through 0.22 μm filters. The extracts were diluted using deionised water to ensure the EC was not higher than 100 $\mu\text{S}/\text{cm}$. This was to maintain the ion chromatograph's column efficiency. The filtered and diluted extracts were analysed for total dissolved cations and anions using a HPIC model DIONEX 3000 series (ion chromatography system).

2.3.2.7 Exchangeable cations and cation exchange capacity (CEC)

The exchangeable cations were determined by ARC-Infruitec, Stellenbosch. Exchangeable Na, K, Ca and Mg were extracted with 1M NH_4OAc solution buffered at pH7 (Thomas, 1982). The CEC was measured directly using with 1M NH_4OAc solution buffered at pH7 according to the method of Bremner and Keeney (1965) (Soil Science Society of SA Handbook, 1990). ICP-AES was used to determine the concentration of cations in the extracts.

2.3.2.8 Extractable Fe, Cu, Zn and Mn and P

ARC-Infruitec, Stellenbosch, carried out the following analyses. The micro-elements, Fe, Cu, Zn and Mn were determined using the di-ammonium EDTA method (Trierweiler and Lindsay, 1969 as modified by Beyers and Coetzer, 1971; Soil Science Society of SA Handbook, 1990). The Fe, Cu, Zn and Mn were analysed for by ICP-AAS. The Bray-2 method (Bray and Kurtz, 1945; Soil Science Society of SA Handbook, 1990) was used to extract P.

2.3.2.9 P sorption

The method for the determination of the adsorption isotherms for phosphate was adapted from Rowell (1996). A 2.5 g, <2mm, air-dried soil sample was weighed into a 50ml centrifuge tube to which 25ml of standard phosphate solution was added. The standard phosphate solutions were made up from a 100 μg P ml^{-1} stock solution made up with 10mM

CaCl₂. The initial P concentrations were 0, 0.5, 1.0, 2.0, 3.0 and 5.0 µg P ml⁻¹. The centrifuge tubes were capped with cork bungs covered with parafilm to prevent contamination, and shaken horizontally on a reciprocal shaker for 24 hours. After 24 hours the tubes were centrifuged at 6000 rpm for 2 minutes and the supernatant transferred using a cambridge pipette, to avoid visible colloids, to test tubes. The phosphate concentration in the supernatant was determined by the Murphy & Riley (1962) technique (Appendix A.10). The procedure was duplicated on each of the soil samples.

2.4 Results and discussion

A summary of the analytical results is presented in Table 2.4 and the details are listed in Appendix A, along with any data manipulation that was required in the processing of the results.

Table 2.4: A compilation of the results of the characterisation of topsoils HR1 and HR2.

	HR1	HR2
Soil Type	Reddish-brown loamy sand	Grey medium sand
% clay	9	2
% silt	16	3
% sand	76	94
% organic carbon	1.58	0.87
Specific Surface Area (m²/g)	4.61	0.59
pH (H₂O)	7.20	6.90
pH (1M KCl)	5.83	5.60
CEC (cmol_c/kg)	7.85	1.98
Clay Mineralogy	Mica, Kaolinite, Quartz	
P sorption (%)	64.5	49.7

The texture of HR1 can be classified as loamy sand and HR2 is medium sand. They have medium to low organic carbon content, low specific surface area, neutral pH (H₂O) and more acidic pH (1M KCl). The soils sampled were dominated by a sand-sized material (>50 µm). The predominance of this size fraction is a result of the dominant parent material being alluvium derived from quartzitic sandstones. The higher clay sized fraction (<2 µm) of

9% in HR1 is due to the sampling site being close to the exposed Bokkeveld shales which give rise to a silty clay matrix. These shales contain appreciable quantities of mica and possibly pyrite.

2.4.1 Mineralogy of the clay fraction

The X-ray diffraction patterns of the clay fraction of the two soils are presented in Figure 2.3 along with the mineral identity and d-spacing for each peak. The principal primary minerals of both the soils was found to be quartz and feldspars. While the dominant secondary mineral in the clay fraction was mica and kaolinite was subdominant. The predominance of mica and kaolinite in the clay fraction is characteristic of the weathering of the sandstones and shales which dominate the geology.

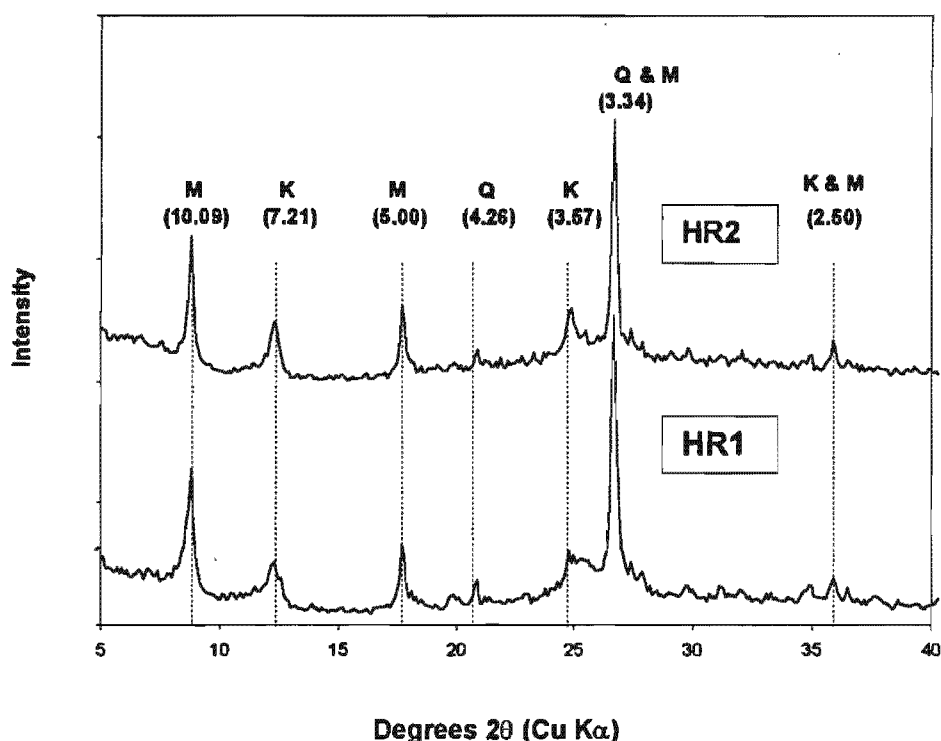


Figure 2.3 X-ray diffraction patterns of the Hex River Valley soil clays. The indicated d-spacings in Å have been interpreted as being diagnostic of the following minerals: Mica (M; 10.09, 5.00, 3.34 and 2.50); Kaolinite (K; 7.21, 3.57 and 2.50) and Quartz (Q; 4.26 and 3.34).

The identification of clay minerals presented above is tentative since no additional analyses or sample pretreatments were carried out to confirm the mineral identification.

2.4.2 Extractable iron, copper, zinc and manganese

The concentrations of EDTA extractable Fe, Cu, Zn and Mn are presented in Table 2.5. The Fe and Mn concentrations (71.2 and 64.4 mg/kg, respectively) in HR1 are considerably higher than in HR2 (18.9 and 6.3 mg/kg, respectively). The high extractable Fe and Mn in HR1 are a direct result of the weathering of the minerals in the Bokkeveld shales and contribute to the reddish-brown colour of HR1. The Munsell soil colour, 5YR5/4, for HR1, according to Schwertmann and Taylor (1989), is a suggestion of the presence of iron oxides possibly hematite. Although hematite was not identified in the XRD pattern (Figure 2.3), the quantity in the clay fraction was most likely too small to be detected. The small specific surface areas of the two soils suggests that the Fe and Mn are most likely present in the soils as crystalline oxides as opposed to non-crystalline oxides which would have contributed to a greater surface area. However, the role of the Fe and Mn oxides, which are present, in the mobility of pesticides are to increase the surface area and reactivity of the soils for adsorption and they may catalyse the degradation of pesticides.

Table 2.5: EDTA extractable Fe, Cu, Zn and Mn in the soils of the Hex River Valley.

Sample	Fe	Cu	Zn	Mn
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
HR1	71.2	1.60	5.5	64.4
HR2	18.9	0.60	2.0	6.3

2.4.3 Surface area and CEC

The mineralogical composition and organic matter content affect the specific surface area (Carter *et al.*, 1989). The relationship of the mineralogy and specific surface area in these soils may be demonstrated by a simple calculation. There is probably 5 to 6 times as much mica as there is kaolinite based on peak heights (Refer Figure 2.3). From the particle size determination (Refer Table 2.4), there is approximately 92% quartz and approximately 8% clay. If there is a 5:1 ratio of mica:kaolinite in the clay then there is about 6.6g mica and 1.4g kaolinite and 92g of quartz per 100g soil. If it is assumed that quartz has a surface

area of $2.6\text{m}^2/\text{g}$; kaolinite a surface area of $6\text{ m}^2/\text{g}$ and mica $35\text{ m}^2/\text{g}$ then these fractions will contribute 239.2m^2 ; 8.4m^2 and 231m^2 per 100g , respectively. This totals $478.6\text{m}^2/100\text{g}$ or $4.79\text{m}^2/\text{g}$ which compares well with the measured value of $4.61\text{m}^2/\text{g}$ (Refer Table 2.4). This, therefore, suggests that for this soil the BET method may actually be a good approximation of reactive surface area. The low specific surface area of 4.61 and $0.59\text{ m}^2/\text{g}$ for HR1 and HR2, respectively, is therefore a result of the principal soil mineral being quartz; the low clay content with mica and kaolinite being the dominant clay minerals as well as the low organic carbon content of the soils.

A similar calculation may be used to express the relationship between mineralogy and cation exchange capacity for these soils assuming values of 30 cmol/kg for mica; 15 cmol/kg for kaolinite; zero cmol/kg for quartz; and 200 cmol/kg for organic matter. If the same quantities, as above, of quartz, mica and kaolinite are used then the CEC calculates to 7.63 cmol/kg which is a reasonably good agreement with the measured value of 7.85 cmol/kg (Refer Table 2.4). The above calculations with CEC and specific surface area do not agree as well for soil HR2, however, when the clay and organic matter content is at such low levels as in HR2, the errors involved in the analysis and calculations is too great to expect close agreement.

Certain properties of the clay minerals contribute to the low CEC of 1.98 cmol/kg measured for HR2. Kaolinite has limited isomorphous substitution that occurs within the crystal structure and results in only a slight permanent negative surface charge. Mica has a comparatively higher cation exchange capacity and specific surface area but with little interlayer surface accessible for cation exchange or water adsorption. The slightly higher CEC of 7.85 cmol/kg of HR1 is a consequence of the greater quantity of clay and therefore mica as well as a higher organic carbon content in HR1.

Submicroscopic Fe and Mn oxide particles have high specific surface area and higher exchange capacities and can coat the kaolinite particles increasing their reactivity (Juo, 1981). The identification of such coatings would only have been possible using electron microscopy techniques. Iron oxide coatings on kaolinite, according to Parfitt (1980), can increase the net positive charge on the surface of the mineral and the anion exchange capacity (AEC) of the soil. The higher quantity of Fe and Mn oxides (Refer Table 2.5) coupled with the higher specific surface area of soil HR1 and the presence of kaolinite in the clay fraction suggests this effect may possibly be contributing to the soils properties.

This increase in AEC would increase the adsorption of organic acids on the mineral surface (kaolinite) and natural organic matter contains mainly organic acids. These organic acids adsorbed to the surface of oxides will in turn increase the sorption or partitioning of the hydrocarbon pesticides, endosulfan and chlorpyrifos.

2.4.4 pH and the micronutrients

A further indication of the status of the soil, with respect to relative amounts of positive and negative charge and the tendency for specific adsorption of ions, is the measurement of pH. The ΔpH value in Table A.3 indicates that the soils have a nett negative charge (Rowell, 1996).

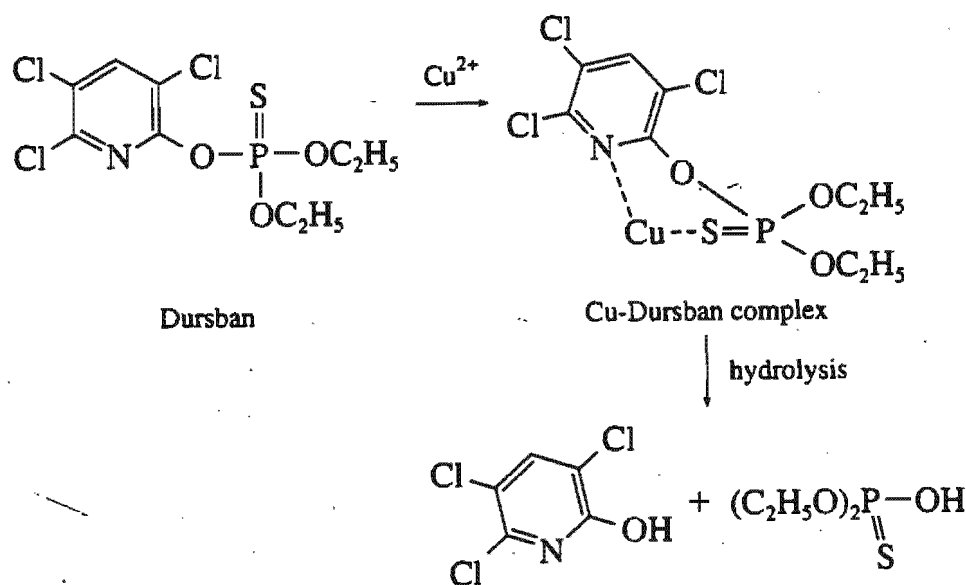
The nett negative charge and importance of electrostatic attraction in the sorption of cationic pesticides are clear. The pesticide molecule (cation) serves as a counter ion in the same way as inorganic cations satisfy excess negative charges on clay minerals. Basic pesticides, when protonated, may behave as positive counter ions in the same manner as cationic pesticides. Acidic pesticides are proton donors, and the anionic form is repelled by negatively charged surfaces in soil. The surface charge sign and magnitude, of these soils are, however, variable and dependant on the pH and ionic strength/composition of the soil solution. In these soils in which mica and to a lesser extent kaolinite are the principal clay minerals, a decrease in pH would decrease the CEC and increase the anion exchange capacity (AEC) and so anionic pesticides may be adsorbed on the positively charged clay sites. The pH of the soil solution will determine the dissociation and, therefore, the ionic character of the organic solutes. Hence, at the neutral to slightly acid pH of these soil solutions protonation and ligand exchange would most probably be the mechanism of organic ion adsorption. Chlorpyrifos and endosulfan, however, do not have ionic character and ,therefore, the hydrogen ion concentration would play a minor role in the mechanism of sorption of these pesticides.

Some organic compounds are degraded more rapidly by acidic soils or clays than by the same adsorbents in nonacidic form. For example, atrazine has a lower half-life in low pH soils. In many cases this may reflect an acid-catalysed hydrolysis reaction. However, endosulfan is hydrolytically stable at acidic pH but hydrolyses to endosulfan diol with a half-life of a few weeks at pH 7 and a few hours at pH 9 (Australian National Registration Authority, 1997) while chlorpyrifos has a constant rate of hydrolysis in acidic to neutral

waters, but this increases in alkaline waters (EXTOXONET¹). Therefore, the slightly acidic soil pH conditions of the Hex River Valley soils may contribute to longer soil half-lives and possibly increase the persistence of these two pesticides.

Conversely, the persistence may be decreased by positively charged oxide surfaces resulting in a higher OH⁻ ion activity, than was measured in the solution, which would account for increased hydrolysis of these organic molecules under acidic soil conditions.

McBride (1994), suggested that it seems rather to be the co-ordination reactions between structural Fe³⁺ or Al³⁺ (Lewis acids) and the organic functional groups which is a more probable cause of decomposition. For example, Mortland and Raman (1967), demonstrated that Cu²⁺ on exchange sites of montmorillonite is able to catalyse the hydrolysis of certain organophosphates like chlorpyrifos, a reaction that probably involves a Cu²⁺ - organic chelation step as shown (Dursban is the commercial name for chlorpyrifos):



¹ Extension Toxicology Network, Pesticide Active Ingredient Profiles at <http://pmep.cce.cornell.edu/profiles/endosulfan-ext.html>.

However, if the metal is strongly complexed it may not be free to co-ordinate with the organophosphate. It is interesting to note that the soils contained 0.16 % and 0.06% EDTA extractable Cu^{2+} for HR1 and HR2, respectively. The EDTA chelates to Cu^{2+} in the same manner as chlorpyrifos. Overall, the Lewis acid properties of metals such as Cu^{2+} , Fe^{3+} and Al^{3+} appear to be important to mineral-catalysed hydrolysis of organic molecules (McBride, 1994).

2.4.5 Water and its solutes, organic carbon and clay content

In the case of non-ionic, hydrophobic hydrocarbons like chlorpyrifos and endosulfan mechanisms, and properties of the soils, other than ion exchange, and clay content, must explain the considerable sorption. The effect of clay in the sorption of these pesticides becomes less significant due to the fact that they are non-polar, non-ionic pesticides and strongly hydrophobic. Consequently, in wet conditions the number of hydrophobic sites on clays is insignificant compared to that of organic carbon. To reiterate, McBride (1994), states that the effect of the "Edge," pH-dependent charge on the Fe oxides, Al oxides and layer silicate edges on the sorption of non-ionic, non-polar molecules especially on wet layer silicate and oxide minerals are often very low, if detectable at all. On clays weak physical forces like hydrogen bonding and ion-dipole attraction, for example, by co-ordination directly with exchange cations on the surface of the clay mineral or by hydrogen bonding to hydration water of the cations, are possible. However, they become ineffective under moist conditions in soils because the excess water can easily displace physically adsorbed organic molecules from the surfaces. Water molecules have the dual competitive advantage of usually being present in great excess of the organic molecule and have a greater polarity than most organics (McBride, 1994).

Water has an important role in the retention of pesticides by soil in that it is both a solvent for the pesticide and a solute that can compete for adsorption sites (Koskinen and Harper, 1990). The soil solution from which pesticides are adsorbed is composed of water and some dissolved components – inorganic salts, organic compounds, and gases. The major cations and anions were measured in the saturated paste extract by ion chromatography and the results are presented in Table 2.6.

In the saturated paste extracts of both soils, the predominant inorganic anions are sulphate and chloride. These two anions usually become more important in arid areas such as the Hex River Valley. Nitrate and phosphate are present in the HR2 extract. The dominant cations in HR1 are calcium and magnesium. In HR2 potassium as well as calcium and

magnesium are dominant. The presence of phosphate and ammonium in the soils is most likely due to their proximity to cultivated soils to which phosphate and ammoniacal fertilisers are added. A small portion of the soil organic matter is also soluble but this was not measured. The endosulfan and chlorpyrifos must compete with the water molecules, anions, cations and hydrophobic solutes for adsorption sites. The affinities of dissolved solutes for soil surfaces and for water in some cases will control the degree of adsorption and the type of adsorption sites available. In general, this means a polar surface will adsorb the more polar component of a solution and nonpolar surface will adsorb the more nonpolar component (Stumm and Morgan, 1981). In the soil system, hydrophobic organic molecules like endosulfan and chlorpyrifos will tend to have greater affinity for the surface than the solution and that surface will be the more nonpolar or hydrophobic surface which is the soil organic matter. The anions and cations will compete for charged, polar sites more strongly than endosulfan and chlorpyrifos. The sorption sites on clays are more

Table 2.6: Water soluble cations and anions in saturated paste extract

	HR1	HR2
Cation	mmol _c L ⁻¹	mmol _c L ⁻¹
Na ⁺	1.746	0.546
NH ₄ ⁺	0.074	0.128
K ⁺	0.442	0.895
Mg ²⁺	2.710	0.749
Ca ²⁺	2.473	0.777
Σcations	7.445	3.095
Anions		
Cl ⁻	1.009	0.712
SO ₄ ²⁻	2.005	0.360
NO ₃ ⁻		0.012
NO ₂ ⁻		0.031
PO ₄ ³⁻		0.105
Σanions	3.014	1.220
EC μS/cm	448	206
pH	7.65	6.53

accessible to the smaller inorganic ions than the larger organic molecules. Generally speaking, chlorpyrifos and endosulfan dislike water and, therefore, distribute into another component of the soil environment but water. The inorganic ions, however, prevent the clay minerals from being this component. The organic matter, similar in nature, is therefore the component endosulfan and chlorpyrifos distribute into.

Despite this preference for organic matter, the clay minerals may still contribute to the sorption of the pesticides. Gubevu (1997) reported a negative correlation with surface area and organic carbon and the author suggested that this was due to the interaction of organic matter with clay minerals, which thus reduce the surface reactivity of the minerals. Figure 2.4 shows a depiction of this interaction. However, with respect to endosulfan and chlorpyrifos, this reduction in surface reactivity of the minerals in this manner (Figure 2.4) means an increase in "reactivity" of the soils toward the pesticides. It is in this respect that the greater clay content of HR1 becomes significant to the sorption of endosulfan and chlorpyrifos. The increased surface area of the clay provides a greater surface for natural soil organic matter to coat and, therefore, a greater surface for the sorption of the non-ionic, hydrophobic molecules.

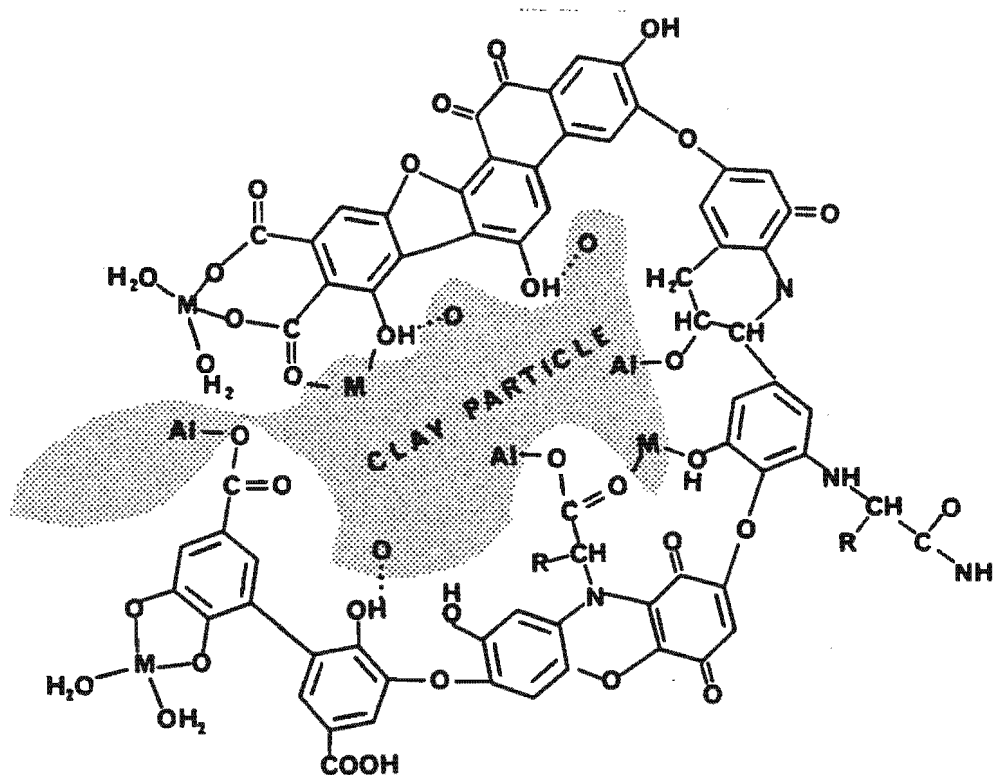


Figure 2.4 Interaction of a clay particle and an organic molecule (After Cheng, 1990).

It is, also, possible for clays to have hydrophobic sites and according to Yaron *et al.* (1967), many non-ionic organic chemicals may adsorb extensively on the clay fraction of soil due to hydrophobic interactions. According to Hassett and Banwart (1989), the -Si-O-Si bonds of minerals are hydrophobic in nature and are potential sites for the sorption of nonpolar compounds. They point out that there is a potential for soil minerals to contribute to the sorption of non-ionic, hydrophobic molecules particularly in soils with low organic matter and even more so in soils with low organic matter and high clay contents. This research, reported by Hassett and Banwart (1989), demonstrated that adsorption of water relative to hydrocarbon oils increased with increasing isomorphous substitution and decreased with decreasing amounts of isomorphous substitution. Therefore, kaolinite, which has low isomorphous substitution and is the sub-dominant clay mineral in the Hex River Valley soils, may contribute to the sorption of non-ionic organic molecules more than other clays with higher isomorphous substitution. This may result in higher sorption coefficients than expected if organic matter was considered to be the only hydrophobic surface. The value of the sorption coefficients and the implications thereof will be discussed further in Chapter 3.

There are numerous mechanisms and forces involved in the sorption of non-ionic pesticides due to the heterogeneous nature of soils, but it is known from previous studies that sorption of non-ionic organic compounds by soil in aqueous systems is controlled mainly by the organic matter content of the soil (Chiou *et al.*, 1979; Karickhoff *et al.*, 1979; Means *et al.*, 1982). It is important to note, however, that sorption of non-ionic organic compounds in dry and unsaturated soils from nonpolar organic solvents is determined mainly by the mineral type and content (Chiou *et al.*, 1985). The different sorption behaviour of organic chemicals with dry and wet soils can thus, be reconciled by the postulate that the soil behaves as a dual sorbent, in which the mineral matter functions as a conventional solid sorbent and the organic matter as a partition medium. In aqueous solution, adsorption of organic compounds by minerals is suppressed by water and hence, the soil uptake consists mainly of solute partitioning into soil organic matter (Chiou *et al.*, 1985). In fact, Koskinen and Rochette (1996) state that it appears the differences in water content may have a greater effect on strength of sorption than differences in soil properties.

In the Hex River Valley, despite the arid climate, there is enough water to irrigate the fields well and endosulfan and chlorpyrifos are made up and applied in aqueous solutions. Hence, hydrophobic partitioning would be the factor controlling sorption on organic matter. This concept of different sorption mechanisms due to initial moisture of soils is more relevant when one is using laboratory sorption test results to explain field conditions. In

laboratory sorption experiments the soil becomes saturated, whereas in the field soils do not necessarily get saturated, especially in the months of pesticide application, September and October, which are often the driest months of the year because irrigation has not started yet. This can result in the over-estimation of the retention of the pesticides in the soil. This and the concepts of partitioning will be further discussed in Chapter 3.

It is interesting to note that before pesticide formulation had become what it is today, the application of pesticides with very low solubilities was often carried out using organic solvents. If this practice were used in an area like the Hex River Valley contamination of the groundwater would be a large threat because retention of the pesticides in soil due to partitioning into organic matter would be inhibited by its solubility in the organic solvent.

The organic components of the soil include polymeric organic solids, decomposing plant and animal residues, and soil organisms. A variety of organic functional groups are present in the humic substances of soil. The exact structure of humic substances is largely unknown, but it has been theorised that they are large aromatic polymers made up of N heterocycles, quinones, phenols, and benzoic acids. The functional groups of humic substances are known to include carboxyl, carbonyl, phenylhydroxyl, amino, imidazole, sulfhydryl, and sulfonic groups. Thus the variety of functional groups in soil organic matter and the steric interactions between functional groups leads to a continuous range of reactivities in soil organic matter. The organic carbon content measured in the soils was low, 1.58% and 0.87% for HR1 and HR2, respectively. However, it has been shown that endosulfan and chlorpyrifos adsorb strongly to soils so the weak physical forces and entropic energies between the pesticides and humic functional groups must be numerous and powerful as they dominate the mobility of endosulfan and chlorpyrifos in the soil environment.

2.4.6 Electrical conductivity, exchangeable cations and the physical properties of the soil affecting runoff and leaching

The saturated paste extract of sample HR1 had a higher EC (Table 2.6) value and the soluble cations and anions were at correspondingly higher concentrations. Gubevu (1997) demonstrated an inverse relationship between EC and pH, confirming the effect of ionic strength on pH as reported by Rowell (1988). However, HR1 has a higher EC than HR2 but its pH is also higher than HR2's. In this case the high EC of HR1 seems to be more a consequence of salt accumulation than to an increased hydrogen ion concentration.

The low EC and ion concentrations of HR2's saturated paste extract agree with the measured low CEC, low clay content and low organic carbon content character of the dominant soil type in the Hex River Valley. The higher EC and ion concentrations of the less dominant reddish-brown soil is a consequence of its higher clay content, organic carbon content, CEC and its parent material being mostly from Bokkeveld shales as compared to Table Mountain sandstone.

The water soluble ions were discussed in Section 2.4.5. The exchangeable cations concentrations are reported in Table A.5, Appendix A. One of the roles these ions play in pesticide mobility is competition for adsorption sites; another is facilitating adsorption of organics by hydrogen bonds and ion-dipole type physical forces; and thirdly they influence the structural characteristics of the soil which contributes to the susceptibility of the soil to runoff and leaching.

The accumulation of soluble salts in soils is called salinization and the sodium saturation of soils exchange complex is called sodication. Salinity and sodicity play an important role in the swelling and dispersion of clays and it is the swelling and dispersion of clays which results in compacted surfaces that prevent infiltration and immobilisation of pesticides in the soil compartment.

Soils with well developed structure have enough high-cation exchange (bi-valent) cations and high electrolyte concentrations in solution to promote flocculation and thereby avoiding compaction, surface crusting, sealing and erosion which are all factors that promote pesticide loss in runoff or leaching to groundwater via cracks. Crusting and compaction decrease infiltration rates, reduces time to runoff, and increases the initial concentrations of soluble pesticides. Kutilek and Nielsen (1994) report it is the nature of the prevalent exchangeable cation which plays an important role relative to the value of the saturated hydraulic conductivity (K_s).

The parameters used to identify the conditions of salinity and sodicity are the sodium adsorption ratio (SAR), the exchangeable sodium percentage (ESP), and electrical conductivity (EC). The SAR and ESP were calculated using the following equations taken from McBride (1994):

$$SAR = \frac{[Na^+]}{\sqrt{([Ca^{2+}] + [Mg^{2+}])/2}} \quad Eq. 1$$

(Calculated using the water soluble cations in Table 2.6)

$$ESP = \left[\frac{\text{Exchangeable Na}^+ \text{ ions}}{\sum \text{Exchangeable cations}} \right] \times 100\% \quad \text{Eq. 2}$$

(Calculated using the exchangeable cations in Table A.5, Appendix A)

(All solution concentrations expressed as mmol/L)

The SAR for HR1 and HR2 is 1.08 and 0.62, respectively and the ESP is 3.2 % and 1.5%, respectively. McBride (1994) suggested that it is only in sodic soils (i.e. pH>9.0; ESP>15 and EC < 4mS/cm) that the Na⁺/(exchangeable cations) ratio on exchange sites, defined by the ESP, controls particle size, arrangement and dispersability. HR1 and HR2 have comparatively low EC, low ESP and about neutral pH. They are neither sodic nor saline.

Wild (1973) states that the permeability of a profile depends not only on the ESP of the soils, but on the concentration of soluble salts in the percolating water. Furthermore, the ESP at which swelling or deflocculation and dispersion processes become important in a given concentration of solution depends, on the type of clay, the content and distribution of the sesquioxide films as well as the amount and type of organic matter. Wild (1973) also advised that alluvial soils, containing much fine sand and silt with micaceous-type clays and small amounts of organic matter, with low ESP will lose permeability in a dilute salt solution. Hex River Valley soils are alluvial with similar properties to the soil described above and they have low ESP. They are, therefore, vulnerable to clay dispersion. But, as long as the irrigation water has a high enough ionic strength and low enough SAR, the soils should have good permeability.

The structure of the Hex River Valley soils is a direct consequence of the clay content, sand content and organic carbon content. Both soils have poor aggregation, high sand content and low organic carbon content and, if irrigated with the appropriate water, will have moderate to high infiltration and they are not expected to be predisposed to runoff problems. K is the hydraulic conductivity, a constant that serves as a measure of the permeability of the porous medium. K_s is the hydraulic conductivity when the medium is saturated (Todd, 1980). HR1 has a higher clay content and is underlain by an

impermeable layer so the K_s will be lower than HR2. HR2 has a high K_s , according to Todd (1980), high is defined when K_s is between 10^{-5} and 10^{-4} m.s $^{-1}$). The relationship between leaching, runoff and hydraulic conductivity is by no means this straightforward, but it provides a first approximation as to which water sources are potentially vulnerable to pesticide contamination.

Some of the farmers in the Hex River Valley have installed sub-surface drains to lower the high watertable which would otherwise cause the soil to become waterlogged which would be detrimental to grapevine performance. These areas of the valley where the watertable is so high would be more vulnerable to runoff problems and groundwater contamination.

Runoff is not just a consequence of soil aggregation but is also dependent on rainfall intensity, rainfall amount and slope. Wauchope (1978) states that it becomes obvious that single-storm losses can be very important. Wauchope (1978) concluded that except for one study, maximum losses of pesticides in runoff were always a result of a single runoff event that produced losses which dwarfed those during the rest of the season. Therefore, although the soils are not predisposed to runoff, one intense rainfall event on the slopes of the valley may cause a unique runoff event which may be responsible for the pesticides that have been detected in concentrations which exceed the acceptable limits.

Another characteristic of the soils, which may result in more runoff than expected, is water repellancy. Soil water repellancy reduces agricultural production on sandy soils of south-western Australia (McKissock *et al.*, 1998). These authors state that water repellancy is caused by plant and fungal residues consisting of waxes and other hydrophobic compounds that coat soil particles. They reported that a low clay (< 2 μ m) content is probably the most important soil condition for the natural occurrence of water repellancy. The consequence of water repellancy is that in the first 20 – 30 minutes of precipitation the soil will not absorb the water as well as expected and instead would pool at certain points in a field. Thus, given enough precipitation and slope the loss of pesticides from fields to ditches and channels in runoff may be a definite problem if the soils are water repellent.

It should also be noted that for contamination of water sources by runoff, the volume of runoff does not always have to be high. In fact, according to Wauchope (1978), low-volume events on large watersheds typically resulted in the highest concentrations of pesticides in the runoff for the studies reviewed. Besides the volume of runoff, the solubility of the pesticides is also an important issue. The endosulfan and chlorpyrifos are very

insoluble and will be lost mostly attached to sediment in runoff. The volumes of runoff as well as the effective depth for chemical entrainment, sediment transport potential, and adsorbed chemical enrichment in sediment, are all important issues to be considered when investigating the runoff of pesticides.

Pesticides that are strongly adsorbed, like endosulfan and chlorpyrifos, will be retained near the application site, i.e. the soil surface, and be more susceptible to runoff. The pesticides are applied before irrigation starts in the valley and they are sprayed onto the foliage and soil surface so that the effective depth of soil available for runoff interaction will also be the layer of soil where chlorpyrifos and endosulfan are the most concentrated. However, endosulfan and chlorpyrifos have very low solubilities and for them to be lost in runoff the enrichment ratio of the runoff needs to be fairly high and especially organic matter needs to be suspended and transported in the runoff. The enrichment ratio is the ratio of the total specific surface area for the sediment in runoff to that for the original soil (Foster *et al.*, 1981). A high percentage of the sediment yield from these soils will be organic matter, fine silt and clay. These are also the surfaces to which the two pesticides will be strongly adsorbed. But, if there is no runoff, there will be no sediment yield and the enrichment ratio will be zero. Thus, the loss of pesticides to water bodies can be prevented by erosion control management practices.

Hesketh *et al.* (1998) found that for a sandy soil (8% clay, 0.95% OC and pH 7.14) the transport of chlordane (organochloride pesticide) was unequivocally facilitated by suspended soil material and none occurred independently of it. The same authors concluded that the contamination of groundwater by chlordane in this soil was only a very small risk even when abnormally large amounts of pesticide were applied. However, conservation tillage is practised in the Hex River Valley and thus macropores due to root channels and worm burrows are quite common. Pesticides attached to suspended particles would not be subject to the same retention if the water movement were via these macropores and not the bulk soil (personal communication with Aqiel Dalwie, Dept. of Community Health, UCT).

In summary, if erosion is controlled then sediment in runoff should be minimal and pesticide loss negligible. However, the loss of pesticides attached to sediment in water moving via preferential flow could still be a problem. The type of tillage used can control preferential flow. In this chapter the conditions under which runoff will occur in the Hex Valley soils, which intuitively seem more prone to leaching of agrochemicals, have been investigated. This is because the source of the water at sites where the highest pesticide levels have

been found, in the Hex River Valley, are ditches at the sides of fields where runoff would collect.

Another pathway by which water is lost from a field is by interflow. Ahuja *et al.* (1981) suggested that on a field scale, where the interests will be in the interflow that may occur in the near-surface soil horizons, there is experimental evidence that this water may significantly contribute to baseflow, stormflow, or both, on sloping lands with surface soil horizons of high permeability underlain by a horizon of much lower permeability or bedrock. This condition exists in certain parts of the Hex River Valley where the sandy soils are underlain by the impermeable weathered shales. However, for chlorpyrifos and endosulfan to be transported via interflow, the interflow would have to carry sediment or suspended organic matter. The shorter the pathway from application site to the point at which the interflow enters the water body (channel) the more likely the interflow water is to carry significant quantities of pesticides attached to suspended soil particles.

If significant levels of pesticides are detected in a water body and one is trying to identify the source as being either the loss of pesticides in runoff to surface waters or by leaching to groundwater, it should be noted, that this division is a gross simplification of a very complex interaction of processes. Depending of the hydraulic gradients, surface water may recharge groundwater or be replenished by groundwater (Hicks *et al.*, 1987). Therefore, levels of pesticides in surface water may affect groundwater or be affected by groundwater.

2.4.7 P Sorption

The results of the P sorption experiment are presented in Table 2.7. The details of the results and the calculations are available in Appendix A. 10.

Table 2.7: Phosphorus sorption results for the Hex River Valley soil samples, HR1 and HR2.

Sample Label	Sorbed P (mg P kg ⁻¹)	Log Sorbed P (mg P kg ⁻¹)	Equilibrium P (mg P L ⁻¹)	Log Equilibrium P (mg P L ⁻¹)
HR1	-0.728	*	0.073	-1.14
	3.360	0.526	0.164	-0.785
	6.653	0.823	0.335	-0.475
	12.169	1.085	0.783	-0.106
	16.071	1.206	1.393	0.144
	32.725	1.515	1.728	0.237
HR2	-2.249	*	0.225	-0.648
	2.950	0.470	0.246	-0.609
	4.444	0.650	0.556	-0.255
	10.590	1.025	1.231	0.090
	14.762	1.169	1.524	0.183
	30.833	1.489	1.917	0.283

* These points could not be plotted on the Freundlich isotherm as the log of a negative number is invalid.

The first points of the isotherm data have a negative amount P sorbed as this is the amount of phosphate desorbed from the soils. HR2 desorbed more phosphate than HR1 which corresponds to the water-soluble ions measured in the saturated paste extract (Table 2.6). Phosphate was detected at a concentration of 0.105 mmol/L in HR2 while none was detected in HR1.

There are various models used to describe sorption behaviour and to differentiate quantitatively between the P sorption characteristics of the soils. A compilation of the indices used to describe the sorption capacity of the soils is provided in Table 2.8 along with the indices for a Shortlands soil for comparison. The P sorption isotherms plotted in Figure 2.5 can be classified as a C-type (constant-partitioning) isotherm. The C-type isotherm has a straight line slope and is described by the equation:

$$C_s = K_d \times C_{aq} \quad (\text{Eq. 3})$$

Where C_s is the amount of P sorbed to the soil; K_d is the linear partition coefficient and C_{aq} is the aqueous equilibrium concentration. Simple regression analysis can be used to fit a straight line to the isotherm and the slope of the line estimates the sorption coefficient (K_d ; $K_d = [\text{sorbed concentration}] / [\text{equilibrium concentration}]$). The better the fit the more reliable K_d is at describing the soils sorption capacity. Figure 2.6 shows the best-fit line for the sorption data of soil HR1 and HR2. The K_d value, the standard error of the slope and the coefficient of determination (r^2) for the linear regression are provided in Table 2.8.

According to McBride (1994), the C-type isotherm is a constant relative affinity of the adsorbate molecules for the adsorbent and is usually observed at low range adsorption. With increased ranges and longer equilibration periods the C-type isotherm would become curved because the sorption sites of the soil becomes saturated, however, this point of saturation was not reached in the time of the sorption experiment presented here. Phosphate is usually relatively immobile in the soil environment and isotherms which have a steeper initial slope, curve and then flatten out are commonly seen for the same experimental conditions as those used in this study. Sposito (1989) suggested that P sorption is most often described by the H- and L- curve isotherm which are explained by the fact that at low adsorbate concentrations, the soil has a high adsorptive capacity but as the concentration of the adsorbate in solution increases, the soil surfaces become swamped and the amount of adsorbing surface therefore decreases. An example of this is provided in Figure 2.7. Figure 2.7 is a comparison of the sorption behaviour of a clayey (65% clay) Shortlands soil to the sandy (2% clay) soil of the Hex River Valley (HR2). Identical conditions were used for both experiments except the range of initial concentrations for the Shortlands soil was 0-80 mg/L and for the Hex River soil it was 0-5 mg/L. Although much higher quantities of P were added to the Shortlands soil, the range for the equilibrium concentrations for both soil were almost the same. The Shortlands soil demonstrates faster sorption and higher amounts sorbed at low initial concentrations

compared to the HR2 soil isotherms, which are relatively linear over the whole range. According to Lanyon (1996) the Shortlands soil sorbed 53% of the added P and was classified as a medium-sorbing soil. In comparison, HR2 is classified as being a low sorbing soil.

Since P sorption isotherms are often non-linear and, therefore, the K_d is a poor description of the sorption capacity, the Freundlich isotherm equation is used to describe the sorption of P in soils (Rowell, 1996)

$$C_s = K_f C_{aq}^x \quad (\text{Eq. 4})$$

where K_f is the Freundlich sorption coefficient and x a constant which describes the linearity of the isotherm. The linear form of the Freundlich equation ($\log C_s = \log K_f + x \log C_{aq}$) is plotted in Figure 2.8 from the data presented in Table 2.7. Linear regressions are fitted to the data and the intercept is equal to $\log K_f$. The K_f value, the standard error of the intercept and the coefficient of determination (r^2) for the linear regression are provided in Table 2.8. The Shortlands soil is a good example of the applicability of the Freundlich isotherm. The coefficient of determination is 0.47 for the linear isotherm and thus the K_d value of 359.4 L/kg would be an unreliable estimate of the sorption coefficient where as the r^2 for the linear Freundlich isotherm is 0.99 and K_f is, therefore, a reliable estimate of the sorption coefficient for the Shortlands soil.

The percentage P sorption can be used as an indication of the soils capacity to sorb phosphate. The % adsorbed was calculated for each data point and the mean and standard error are presented in Table 2.8 along with the results of the other models used to describe the sorption.

Sorption indices are also used to describe the sorption capacity. The indices are determined by using the amount of P sorbed at a chosen P equilibrium concentration. The chosen P equilibrium concentration was 1 mg/L as this is middle of the range. This approach is limited as it describes the isotherm at one particular concentration only and does not allow further interpretation at other concentrations.

Table 2.8: Results of four different methods used to describe the P sorption capacity of HR1, HR2 and Shortlands soil, including standard errors and coefficients of determination.

	Shortlands ¹			HR1		HR2		
		(r ²)		(Std. Error)	(r ²)		(Std. Error)	(r ²)
K _d (L/kg)	359.4	0.47	16.5	2.72	0.90	16.3	2.64	0.90
K _f (L/kg)	620.6	0.99	15.8	1.11	0.95	10.6	1.16	0.91
Percentage (%)	53.0	na	64.5	2.50	na	49.7	4.74	na
Sorption indices (mg/kg)	645	na	13.5	0.67	na	8.0	0.25	na

¹ Lanyon (1996)

* The standard deviations (SD) for the % and sorption indices for HR1 are 5.6 and 1.5 respectively and 10.6% and 0.56 for HR2. Std error = SD/ $\sqrt{5}$

na – not applicable

The HR1's parameters have a consistently greater value than HR2 for all the methods therefore HR1 has a greater P sorption capacity. The K_d value for HR1 is only marginally higher than HR2 and this is a consequence of the fit of the regression analysis. The coefficient of determination for the linear distribution isotherm is 0.90 for HR1 and therefore for HR1 (r²=0.95) the linear Freundlich equation describes the sorption better. The standard error for K_f is, also, less for HR1 and HR2, than for K_d. The K_f (15.8 and 10.6 for HR1 and HR2, respectively) is, therefore, the best estimate of the adsorption capacity of the soils.

The sorption coefficients for the Shortlands soil are considerably higher than the coefficients for the Hex River Valley soils substantiating the greater sorption capacity of the Shortlands soils. The sorption index of 645 mg/kg (Table 2.8) for the Shortlands soil suggests that larger quantities of phosphate could be applied to this soil before the equilibrium concentration or soil water concentration increased. The isotherm for the

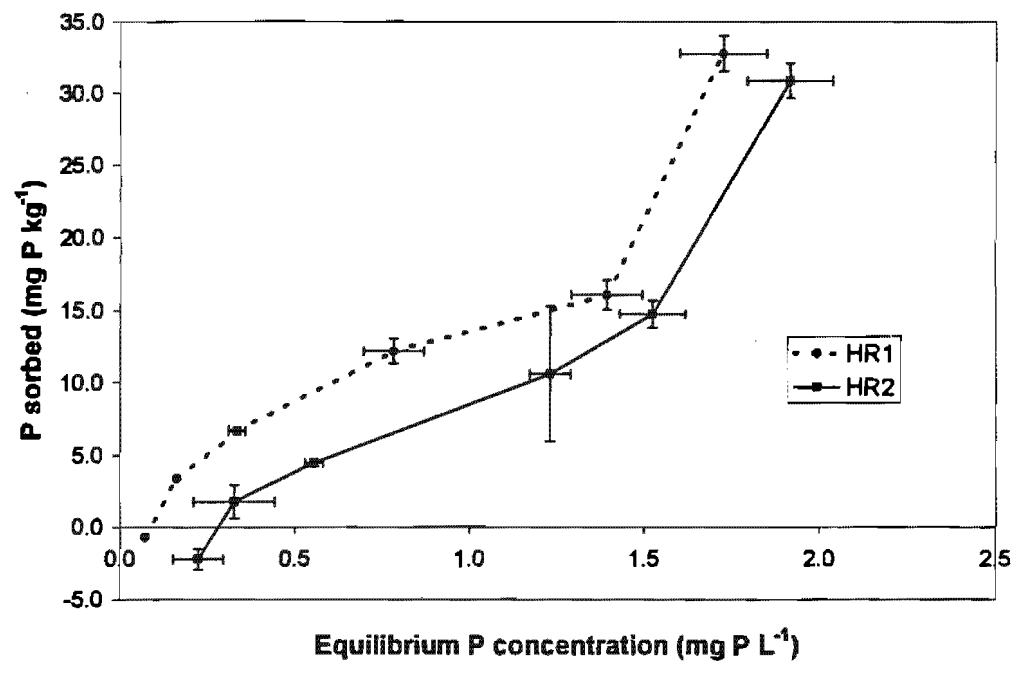


Figure 2.5: Phosphorus sorption isotherms for HR1 and HR2 including error bars.

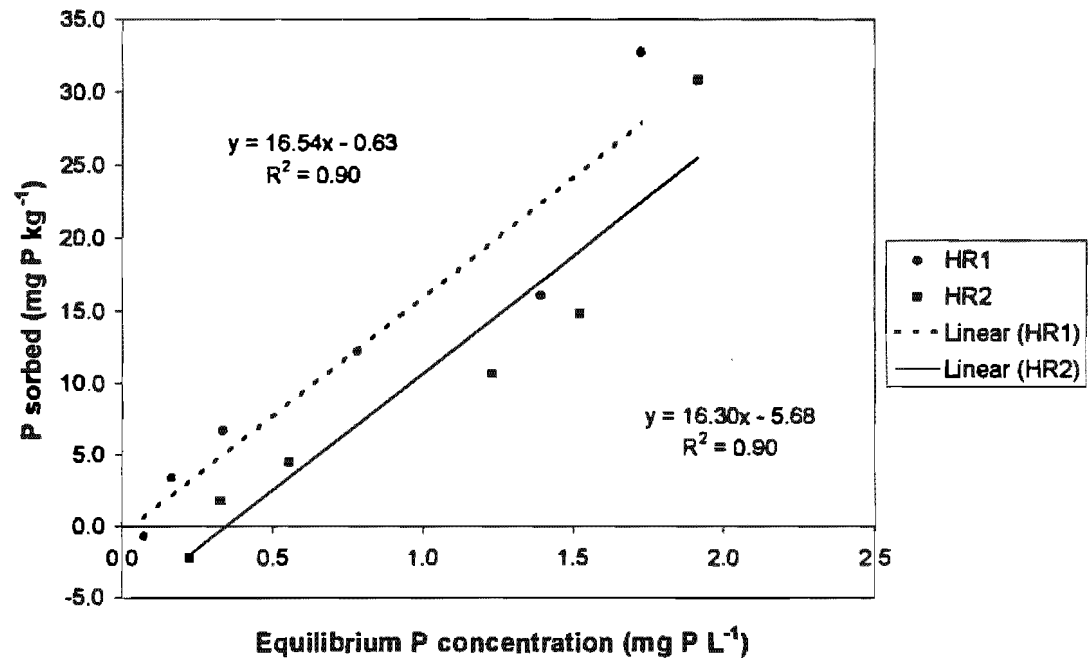


Figure 2.6: Phosphorus sorption isotherm for HR1 and HR2 with straight-line regression analysis.

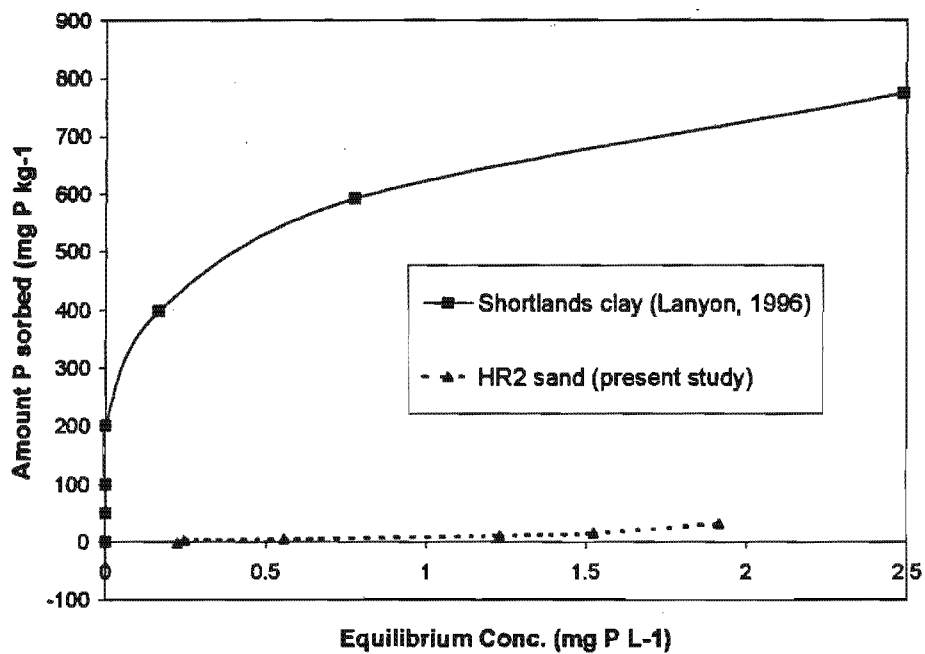


Figure 2.7: A comparison of the P sorption isotherms for HR2, a sandy soil, with a Shortlands clay soil (Data taken from Lanyon, 1996)

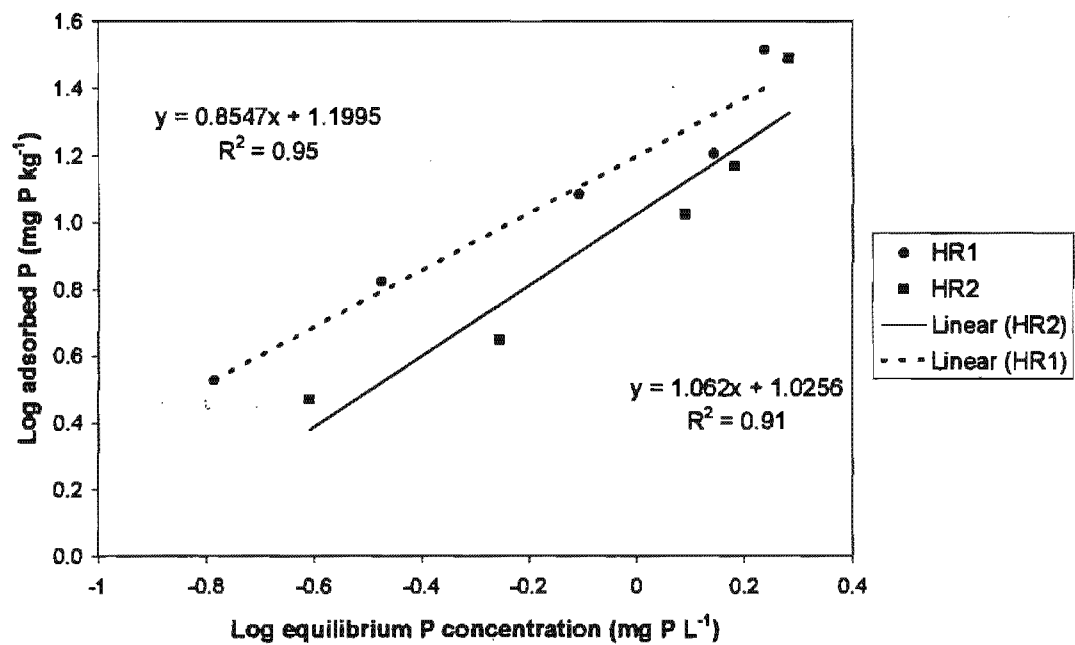


Figure 2.8: Linear expression of the Freundlich equation for P sorption data derived from HR1 and HR2.

Shortlands soil shows saturation (Figure 2.7; point of curving) at which point the solubility of phosphate increases considerably and anions are more likely to leach out of the soil. However, this point is reached only after the soil has sorbed about 400 mg/kg P, whereas for the Hex River Valley soils the equilibrium concentration at this amount sorbed (400 mg/kg) would be infinitely high and a significant amount of phosphate would leach out of the soil.

There are two aspects of P sorption, with respect to the Hex River Valley soils, which are apparent. The soils have low P sorption capacity and HR1 has a greater sorption capacity than HR2. The low sorption capacity is a result of the low clay content especially in HR2. Mott (1988) suggests that the mechanism of P sorption is one of ligand exchange whereby phosphate displaces hydroxyl ions from sorbing surfaces. The clay fraction minerals would provide the sorbing surface on which the hydroxyl ions would be displaced by ligand exchange. This surface would be greater in HR1 due to the higher clay content.

The soils also have an overall negative charge confirmed by the markedly lower pH (1M KCl) than pH (H₂O). The degree of repulsion of the P anion would depend on the major species present of P, PO₄³⁻ or H₂PO₄⁻. However, the speciation of P was not determined but the sorption would be less the greater the valency. The clay fraction is dominated by mica and kaolinite to a lesser extent both have low specific surface area. Kaolinite, however, has shown high P sorption at low P solution concentrations. This is related to the presence of two different types of sorption sites on the crystal structure, both of which differ energetically and correlate with different regions of an adsorption isotherm (Dixon, 1989). The first type, correlated with the steep initial slope of a P sorption isotherm, is a protonated hydroxyl site associated with Al at the edge of the octahedral sheets of the kaolinite crystal structure. These sites have a very high affinity for phosphate ions and result in largely irreversible sorption. Although the second type of sorption site, correlated with the point at which the sorption isotherm becomes convex to the y-axis, is also a protonated hydroxyl site, it is associated with the Al at the exchange sites in kaolinite. Sorption at these sites is still high, but it is also reversible.

Overall, the low clay content of the Hex River Valley soil and its dominance by mica and subdominance by kaolinite contributes to the low affinity of the soils for P. The sorption that does occur in HR1 and HR2, at the initial concentration range used, is mainly due to the kaolinite edge effects and Fe oxides.

In addition, the higher P sorption capacity of HR1 is a result of the higher clay content as well as the Fe oxide content. Fe oxide coatings on kaolinite increase the surface area and positive charge on the surface. Le Mare (1981) discusses a number of studies in which the BET surface area of a range of soils was correlated with P sorption. However, the soil leaching experiments of Korte *et al.* (1976) indicated that the attenuation of elements present in their leachates as anions was more strongly correlated with Fe oxide content than with surface area. Elkhatab *et al.* (1984a) observed that whereas Fe oxide content was correlated with the sorption at high initial anion concentrations, total clay content was correlated with sorption at low initial concentrations. The concave (to y-axis) nature of the HR1 isotherm (Figure 2.8), at high initial concentrations, is further supported by the x value in the linear Freundlich equation which is less than 1. The x value is a constant that describes the linearity of the isotherm. The concave shape of the HR1 isotherm at high initial concentrations implies an increase in adsorption for HR1 which may be attributed to the Fe oxide presence in this soil.

The concentration of extractable P for HR1 and HR2 was 15 and 14 mg/Kg, respectively. This is an indication of low available P and therefore although major soil type, HR2, in the Hex River Valley desorbed phosphate at zero initial concentration and phosphate was detected in the saturated paste extract, this was not due to saturation of the soil with phosphate but rather due to a low capacity to sorb phosphate.

In conclusion, the soils in the Hex River Valley do not adsorb P strongly. This along with the low clay content and coarse texture of the soils suggests that these soils are susceptible to the leaching of anions. It is interesting to note that Weaver (1993) concluded that the presence of elevated nitrate in the groundwater of the Hex River Valley proves that leaching of agricultural chemicals does take place and therefore the concern that pesticides could be contaminating the groundwater. However, Fey (personal communication) suggested that elevated concentrations of nitrate in groundwater could be attributed to processes other than leaching of agricultural chemicals. The findings in this study, therefore, that the soils have a low capacity to sorb phosphate, is more conclusive evidence that the Hex River Valley is a high-risk area with regards to potential mobility of pesticides and contamination of water sources. A comparison of the sorption of inorganic molecules, phosphate, and the sorption of organic molecules, non-ionic pesticides, by the Hex River Valley soils, is provided in Chapter 3

2.5 Conclusions

The dominant soil type in the Hex River Valley is sandy with a low organic carbon and low clay content. Quartz is the dominant soil mineral while mica and kaolinite, to a lesser extent, are the principal clay minerals. The slightly acidic nature of the soils may slow the rate of degradation of endosulfan and chlorpyrifos down which would make endosulfan and chlorpyrifos more persistent than in alkaline conditions. However, the possible catalysis of hydrolysis by chelation to Fe, Al and Cu and increase in hydroxyl ions due to the presence of iron oxides could counteract this persistence.

The soil in the Hex River Valley is not prone to runoff and loss of water via leaching through the soil profile would be more common. In contrast the endosulfan and chlorpyrifos, according to the literature, are strongly sorbed and are most likely to be lost attached to suspended soil particles in runoff rather than by leaching into the groundwater.

One would expect with this combination of conditions that the pesticides would be highly immobile and retained in the soil. However, the process of extraction of chemicals into runoff is obviously complex, the degree of complexity increasing as the complexity of slope, drainage and management increases within a catchment. The potentially risky conditions which would mobilise the pesticides are: intense, heavy storms on sloping fields; water repellancy; poor infiltration due to dispersion as a result of irrigating with very dilute electrolyte concentrations; small volumes of runoff with high suspended organic matter and loss to groundwater via preferential flow.

Finally, phosphate can be used as an indicator of the potential risk associated with a particular soil for contamination of water bodies by pesticides. The Hex River Valley soils are considered high-risk soils because of the low sorption capacity and mobility of phosphate.

CHAPTER 3

The Sorption Characteristics of Endosulfan and Chlorpyrifos

3.1 Introduction

When a chemical is applied to the soil, it comes into contact with a variety of surfaces upon which adsorption can occur. Because adsorption can influence the translocation, volatility, persistence and bioactivity of a pesticide, it probably is the major process that affects the behavior of a pesticide in soil. Adsorption is measured in this study by difference so the processes of retention are not differentiated. The term sorption, therefore, is used to include adsorption, absorption and precipitation.

The pesticides chlorpyrifos and endosulfan were chosen for the study as they have been detected in water samples taken from the Hex River Valley (Water Research Commission, 1998). Also, endosulfan represents the older, more persistent organochlorine type pesticides, while chlorpyrifos represents the newer, less persistent organophosphates. Indices were derived, using a screening type model, to determine if they are likely to contaminate water under the conditions in the Hex River Valley and these indices were used to decide whether further investigation was needed.

Institutions such as the United States EPA have been regulating the use of pesticides for about the past twenty years. The issue of pesticide contamination in the environment is a sensitive subject and because of the huge legal and economic controversies, which have and can result from the use or non-use of pesticides, the EPA has had to rigorously document adsorption study methods and analyses. These guidelines, although desirable, are time consuming, expensive and require specialized equipment. This study did not, therefore, follow these guidelines rigorously. However, the steps that were omitted are discussed and the implications for the accuracy of the results are pointed out.

The objectives of this chapter are to measure the degree to which the Hex River Valley soils sorb chlorpyrifos and endosulfan, to derive indices that estimate the capacity of the soils for sorption of endosulfan and chlorpyrifos and identify the sources of error in the methods used to calculate these indices. In addition, it was decided to compare these indices with other well documented values so as to make decisions about the reliability of

the results and mobility of the pesticides. The relationship between the sorption by soil and the soil physicochemical properties, presented in Chapter 2, has also been examined.

3.2 Physico-chemical properties and environmental fate

3.2.1 Chlorpyrifos

Chlorpyrifos is one of a class of insecticides referred to as organophosphates. These chemicals act by interfering with the activities of cholinesterase, an enzyme that is essential for the proper working of the nervous systems of both humans and insects. Figure 3.1 shows the chemical structure of chlorpyrifos.

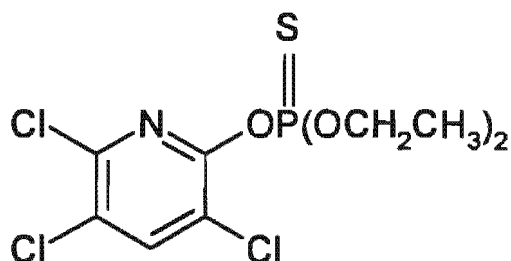


Figure 3.1 O, O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphorothioate (Mol. Wt. 350.6; common name: chlorpyrifos; IUPAC name: O, O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphorothioate; principal tradenames: Dursban and Lorsban; solubility: 1.4 mg/L in water (25°C); formulation type: GR; EC; WP; DP; UL; Microcapsule)

Environmental Fate: According to EXTtoxNET¹, chlorpyrifos adsorbs strongly to soil particles and is not readily soluble in water. It is therefore immobile in soils and unlikely to leach or to contaminate groundwater. It is not mobile in sandy loam and loamy sand soils. It is incompatible with alkaline materials. The rate of hydrolysis increases with pH and in the presence of copper and possibly of other metals that can form chelates. In soil, chlorpyrifos is slowly degraded, with a half-life of c. 60-120 days, to 3, 5, 6-trichloropyridin-2-ol (TCP), which is subsequently degraded to organochlorine and carbon dioxide. TCP, the principle metabolite, adsorbs weakly to soil particles and appears to be moderately

¹ Extension Toxicology Network, Pesticide Active Ingredient Profiles at <http://pmep.cce.cornell.edu/profiles/endosulfan-ext.html>.

mobile and persistent in soils. Soil texture or organic matter does not affect the soil half-life. Adsorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis and by soil microbes. Slow desorption from sediments can maintain low (ppb) residual concentrations of chlorpyrifos in open waters for long periods of time. It enters freshwater and saltwater ecosystems primarily as spray drift and carried on eroded soil particles from treated areas. In water, chlorpyrifos readily adsorbs to suspended sediment and bottom materials. Volatilization is probably the primary route of loss of chlorpyrifos from water.

3.2.2 Endosulfan

Endosulfan is a chlorinated hydrocarbon insecticide of the cyclodiene subgroup which acts as a contact poison in a wide variety of insects and mites. The commercial product is made up of a mixture of two separate parts (isomers): α - and β -configurations. Endosulfan will be considered as a single (homogeneous) product unless otherwise stated. Figure 3.2 shows the chemical structure of endosulfan. The cyclodiene insecticides such as dieldrin have largely been withdrawn from use because of persistent and bioaccumulation properties but the structural features of endosulfan moderate these tendencies significantly.

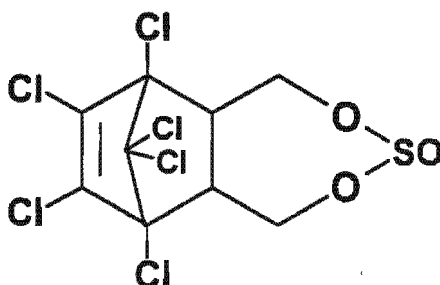


Figure 3.2 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide (Mol. Wt. 406.9; common name: endosulfan; IUPAC name: 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide; principal tradenames: Thiodan and Thioflo; solubility: 0.33 mg/L in water (22°C); formulation type: GR; EC; WP; DP; UL; DP; FT; SC; EO; Powder concentrate)

Environmental Fate: According to EXTOWNET¹, endosulfan is strongly sorbed and immobile in soils. It does not easily dissolve in water. Transport of this pesticide is most likely to occur if endosulfan is attached to soil particles in surface runoff. Large amounts of endosulfan can be found in surface waters near areas of application. It is not expected to pose a threat to groundwater. The two isomers have different degradation times in soil. These two isomers will persist longer under more acidic conditions. It is hydrolytically stable

at acidic pH but hydrolysis to endosulfan diol with a half-life of a few weeks at pH 7 and a few hours at pH 9. The breakdown in water is faster (five weeks) under neutral conditions than at more acidic conditions (five months). Endosulfan is incompatible with strongly alkaline materials. It is stable to sunlight. The compound is broken down in soil by fungi and by bacteria. Endosulfan ($-\alpha$ and $-\beta$) is degraded in soil with DT_{50} 30 to 70 days. The main metabolite is endosulfan sulfate, which degrades more slowly and is for this reason the most important metabolite. DT_{50} for total endosulfan ($-\alpha$, $-\beta$ and sulfate) in the field is 5-8 months. After 11 weeks 90% of residues will be endosulfan sulfate. Endosulfan sulfate bioaccumulates in aquatic organisms and may be more toxic than endosulfan.

3.3 Choice of Pesticides

3.3.1 Usage

According to Weaver (1993), Chlorpyrifos is classed in the high usage category. The high usage means that the pesticide is generally used throughout the Hex River Valley. Endosulfan, on the other hand, is classed as low usage meaning that it is used in an irregular and localized manner to control outbreaks of unusual pests. According to representatives of the pesticide companies chlorpyrifos is applied at 8.83 kg/ha once at about the end of September (pre-bud break) and again a week later. However, another representative stated an application rate of 3.84 kg/ha is used. Endosulfan is applied at a rate of 0.475 kg/ha according to the instructions supplied by AGREVO with the product. However, according to Leonard (1990), application rates for grapes and citrus range from 1.66 – 5.96 kg/ha across the United States.

3.3.2 Toxicity

Bot *et al.* (1988) divided pesticides into four groups according to toxicity. The toxicity of the group 1 pesticides is the highest while group 4 is the lowest. Chlorpyrifos is placed in toxicity group 2 and endosulfan into group 1.

3.3.2.1 Chlorpyrifos

According to EXTOWNET, the US EPA requires precautionary language on products containing chlorpyrifos, warning of the hazard that this insecticide poses to birds, wildlife and aquatic organisms as well as to humans. They must bear the signal word "Warning" or "Caution" depending on the toxicity of the formulation. Chlorpyrifos acts on pest primarily as a contact poison, with some action as a stomach poison. It is a nonsystemic contact

chemical, meaning that it acts only where it comes into direct contact with plant tissues and is not transported to other plant parts. It should not be applied directly to water and drift and runoff from treated areas may be hazardous to aquatic organisms in adjacent aquatic sites.

Chlorpyrifos is moderately toxic to humans. Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system and the respiratory system. The organophosphate insecticides are cholinesterase inhibitors which may be absorbed through all routes of exposure.

The amount (dose) of material that causes death in one-half (50%) of the test population, when it is given on a short-term basis by mouth is referred to as its oral lethal dose (LD50). The oral LD50 for chlorpyrifos in rats is 82 to 270 mg/kg. In sheep it is 800 mg/kg. The lethal concentration fifty, or LC50, is that concentration of a chemical in air or water that kills half of the experimental animals exposed to it for a set time period. The 4-hour inhalation LC50 for chlorpyrifos is greater than 200 mg/m³.

Research indicates that chlorpyrifos does not build up or persist in body tissues. It does not have a significant bioaccumulation potential. When formulated chlorpyrifos (Dursban) was fed to cows, unchanged pesticide was found in the faeces, but not in the urine or milk. Chlorpyrifos was detected in the milk of cows for 4 days following spray dipping with a 0.15% emulsion. The maximum concentration in the milk was 0.304 ppm.

Chlorpyrifos is moderately to very highly toxic to birds. Its oral LD50 in pheasants is 8.41 mg/kg and 112 mg/kg in mallard ducks. The LD50 for a granular product in bobwhite quail is 108 mg/kg. Bird deaths have not been observed in repeated mosquito control efforts, but it has more of an effect on the quantity and quality of eggs laid.

Chlorpyrifos is very highly toxic to freshwater fish, aquatic invertebrates and estuarine and marine organisms. Cholinesterase inhibition was observed in acute toxicity tests of fish exposed to very low concentrations of this insecticide. To decrease potential hazards, the US EPA, is imposing precautions and restrictions. Application of concentrations as low as 0.011 kg of active ingredient per hectare (0.01 pounds/acre) may cause fish and aquatic invertebrate deaths. Chlorpyrifos is extremely poisonous to wildlife and honeybees (EXTOXNET).

3.3.2.2 Endosulfan

Endosulfan is a highly toxic substance and carries the signal word DANGER on the label. Toxicity is partly dependent on the manner with which the pesticide is administered. Undiluted endosulfan is slowly and incompletely absorbed into the body whereas absorption is more rapid in the presence of alcohols, oils and emulsifiers. EXTOKNET notes several chronic effects for animals exposed to endosulfan. The pesticide is most likely to affect kidneys, liver, blood chemistry and the parathyroid gland. Endosulfan is rapidly degraded and eliminated in mammals with very little absorption in the gastrointestinal tract. Cattle fed 0.15 mg/kg for 60 days had no residues in the fat. The metabolite, endosulfan sulfate, seems to show similar toxicity to the parent compound. Most of the endosulfan seems to leave the body within a few days to a few weeks.

Birds in general are fairly sensitive to endosulfan poisoning. The oral LD50 is 33 mg/kg for young ducks and 205-243 mg/kg for mature mallards. The oral LC50 is 805 mg/kg for bobwhite quail. Male mallards from three to four months old exhibited wings crossed high over their backs, tremors, falling and other symptoms as soon as ten minutes after an acute, oral dose. The symptoms persisted for up to a month in a few animals.

Several fish species are quite susceptible to endosulfan. The 96-hour LC50 is 1.2 ppb for bluegill and 1.44 ppb for rainbow trout. In an accidental fish kill, the initial water level was 30.9 ppb which dropped to 0.01-6.5 ppb in four days. Endosulfan is also quite toxic to shellfish. It is moderately toxic to bees and is relatively non-toxic to beneficial insects such as parasitic wasps, ladybird beetles and some mites (EXTOKNET).

3.3.3 Preliminary evaluation – screening models and indices

A preliminary estimate of the potential a pesticide has to contaminate water sources is desirable due to the high cost associated with obtaining data for a large number of soil-crop-pesticide combinations. Models have been developed to describe the various environmental processes that influence pesticide dynamics in soils. Such models are usually data intensive and require knowledge of a number of soil, environment, crop and pesticide parameters. In a majority of the cases, such parameters are neither available nor likely to be available in the near future. As an alternative, simple screening approaches are being developed for assessing the relative potential of various pesticides to leach beyond the crop root zone and reach groundwater.

Weaver (1993) recommended that the numerical rating scheme, DRASTIC (Aller *et al.* 1985, cited by Weaver, 1993), be used to evaluate the potential for groundwater contamination at a specific site given its geohydrological setting. The acronym, DRASTIC, is derived from the seven factors considered in the scheme: (1) depth to groundwater, (2) recharge rate, (3) aquifer media, (4) soil media, (5) topography, (6) impact of the vadose zone and (7) conductivity of the aquifer. A combination of weights and ratings are assigned to each of these factors and a numerical rating, called the DRASTIC index, is calculated for each site or an area. This index is then used to prioritize various areas with respect to their vulnerability for groundwater contamination. The DRASTIC scheme, however, does not explicitly take into account the pesticide properties and the United States Environmental Protection Agency (1997) recommended that DRASTIC be used by individuals with a high level of experience in local hydrogeology, soils, and contaminant fate and transport. For these reasons using DRASTIC, for the screening of chlorpyrifos and endosulfan in the Hex River Valley, was regarded inappropriate.

Rao *et al.* (1985) developed a simple scheme for ranking the relative potentials of different pesticides to intrude into groundwater. The Attenuation and Retardation factors are calculated to assess groundwater contamination potential. The authors assumed that pesticide degradation follows first-order kinetics and therefore the total amount (M_1) of pesticide leaching past the root zone was given by:

$$M_1 = M_0 \exp(-tr_1 k_1) \quad \text{Eq. (1)}$$

where M_0 is the amount of pesticide applied at the soil surface, and tr_1 and k_1 are the travel time and the first-order degradation rate coefficient in the root zone, respectively. The pesticide amount leaving the root zone is further degraded as it travels through the intermediate vadose zone. Thus, the amount (M_2) entering the groundwater was defined as:

$$M_2 = M_0 \exp(-tr_2 k_2) \quad \text{Eq. (2)}$$

where M_2 , tr_2 and k_2 are as defined for Eq. (1) except that the subscript 2 designates the values for the intermediate vadose zone. Substituting Eq. (1) in Eq. (2) yields:

$$M_2 = M_0 \exp - [(tr_1 k_1) + (tr_2 k_2)] \quad \text{Eq. (3)}$$

From Eq. (3) it is evident that computation of pesticide mass emission from the vadose zone (i.e., M_2) requires the estimates of the travel times (tr_1 , tr_2) and the rate coefficients

(k_1 , k_2) in the root zone and the intermediate vadose zone. Water and solute transport processes within the root zone are transient in nature and the travel time (tr_1) is a complex function of rainfall, irrigation, evapotranspiration and rooting patterns. Thus, it is difficult to obtain a simple estimate of tr_1 . Rao *et al.* (1985) suggested that the difference between annual evapotranspiration and rainfall plus irrigation could be used to estimate tr_2 because the flow processes in the intermediate vadose zone are essentially steady. According to Rao *et al.* (1985), a considerable amount of data exists for estimating pesticide degradation rates in the root zone based on measurements with surface soils. In contrast, the authors state that there is a paucity of data for estimating degradation rates in the intermediate vadose zone. In the absence of better information, the authors were then faced with the need to assume that $k_1 = k_2 = k$. The total travel time (tr) required for a pesticide to travel through the root zone and intermediate vadose zone was determined as the sum of the respective travel times in each of these zones; thus, $tr = (tr_1 + tr_2)$.

With the above simplifying assumptions, Eq. (2) was restated as:

$$M_2 = M_0 \exp (-tr k) \quad \text{Eq. (4)}$$

The pesticide half-life, $t_{1/2} = (0.693/k)$ and Eq. (4) simplifies to:

$$M_2 = M_0 \exp (-B) \quad \text{Eq. (5)}$$

$$B = (0.693 tr/t_{1/2}).$$

Finally, the authors defined the fraction of surface-applied pesticide that reaches the groundwater as being equal to:

$$AF = (M_2/M_0) = \exp (-B) \quad \text{Eq. (6)}$$

where AF is defined as the Attenuation Factor and serves as an index for pesticide mass emission from the vadose zone. It should be noted that $0 < AF < 1$.

The total travel time (tr) in Eq. (4) was approximated by:

$$tr = (L RF FC/q) \quad \text{Eq. (7)}$$

where

$$RF = [1 + (BD \cdot OC \cdot K_{oc})/(FC) + (AC \cdot K_h/FC)] \quad \text{Eq. (8)}$$

L is the distance from the soil surface to groundwater, AC is the air-filled porosity, FC is the volumetric soil-water content at field capacity, BD is the soil bulk density, OC is the soil organic carbon content, K_{oc} is the sorption coefficient and K_h is the Henry's constant. The authors assumed that the net recharge rate (q) was the same in both the root zone and the intermediate vadose zone. The term RF in Eqs. (7) and (8) is known as the Retardation Factor and represents the retardation of pesticide leaching through soils due to sorption and pesticide partitioning between the vapor and liquid phases.

The AF and RF were calculated for the soils for endosulfan and chlorpyrifos as well as for six other pesticides which are priority listed in the Hex River Valley. DDT and dieldrin are included as, although their usage has been banned, they have long half-lives and residual traces may still be present. It should be noted that the AF and RF are indices and therefore are meaningless without comparisons. The pesticide parameters needed for the calculation are presented in Table 3.1 and the soil properties are provided in Table 3.2.

Table 3.1: Pesticide parameters needed for RF and AF calculation (adapted from Rao *et al.*, 1985) and the indexing of the pesticides based on the RF and AF .

Pesticide	K_{oc} ($m^3 \text{ kg}^{-1}$)	K_h	$t_{1/2}$ (days)	RF	AF
Aldicarb	1.900E-01	1.300E-06	7	3	5
Chlorpyrifos	6.070E+00	1.800E-04	60	5	7
Carbaryl	2.290E-01	1.400E-03	22	4	2
DDT	2.400E+02	2.000E-03	3837	8	6
Dieldrin	1.200E+01	6.700E-04	868	6	3
Endosulfan	12.4E+00	1.700E-04	120	7	8
Fenamiphos	1.710E-01	2.400E-08	10	2	4
Simazine	1.400E-01	3.400E-08	75	1	1

Table 3.2: Soil properties used in calculating the AF and RF

Soil property	HR1	HR2
Porosity (P) $\text{m}^3 \text{m}^{-3}$	0.40	0.43
Field Capacity (FC) $\text{m}^3 \text{m}^{-3}$	0.19	0.18
Air Content (AC) $\text{m}^3 \text{m}^{-3}$	0.095	0.285
Bulk Density (BD) kg m^{-3}	1600	1480
Depth to Groundwater (L) m	1.5	1.5
Net Recharge Rate (q) m yr^{-1}	0.03	0.03
Organic Carbon Content (OC)	0.0158	0.0087

The retardation factor (RF) represents the retardation of pesticides leaching through soils due to sorption and pesticide partitioning between the vapor and liquid phases. For non-volatile and non-adsorbed pesticides, K_{oc} and $K_h = 0$ and $RF = 1$. Larger values of the Attenuation Factor (AF) and smaller values of B imply that a larger fraction of the pesticide is likely to arrive at the groundwater. Conversely, pesticides with low aqueous solubility (large K_{oc}) and/or those that degrade readily to nontoxic forms (small $t_{1/2}$) would have large B values and a small AF value and the fraction of the applied amount leaching to groundwater is likely to be small. Thus, the AF value was used as a simple index for ranking the eight pesticides. The index 1 – 8 was used, 1 being the pesticide with the most potential to contaminate groundwater (highest AF, lowest RF) and 8 has the lowest potential to contaminate groundwater (highest RF, lowest AF) but poses a greater threat to contaminating surface water bodies via runoff (Rao *et al.* 1985).

The ranking orders based on the AF and RF are presented in Table 3.1. The ranking order based on the RF is different to the order based on the AF and the orders were the same for both soils HR1 and HR2. Rao *et al.* (1985) suggested that the RF should only be used for ranking in the absence of any information on pesticide half-lives and provides the most conservative estimate of the potential for groundwater contamination.

Rao *et al.* (1985) discussed the limitations of using such indices. The AF index is not designed to be a predictive tool but rather a simple method for ranking a number of pesticides in terms of their relative potential to intrude into groundwater. It was designed for the comparison of a large number of pesticides being used in a large area but it has still been useful for these eight pesticides in the Hex River Valley. It has provided a preliminary evaluation of these pesticides without experimentation, using pesticide properties reported in the literature.

Chlorpyrifos and endosulfan are ranked seventh and eighth (AF index) suggesting that, within this group of pesticides, they are least likely to contaminate groundwater but they are the most likely to be lost in runoff to surface waters. The actual value of the RF and AF can also be used as an indication of the need for further study of a particular pesticide at a specific site. The highest RF, 31770, was for DDT while the second highest, 1654, was for endosulfan and the third highest, 1599, was for dieldrin. The almost twenty times higher RF for DDT is cause for attention and interestingly, DDT and dieldrin are banned.

In summary, chlorpyrifos is used extensively in the Valley and has the capacity to be hazardous to aquatic organisms at low concentrations and endosulfan is generally highly toxic. According to RF and AF factors, both pesticides have low potential to contaminate groundwater but high potential to be lost in runoff to surface waters. It is, therefore, concluded that further investigation into the mobility of chlorpyrifos and endosulfan in the Hex River Valley soil is justified.

3.4 Materials and methods

The sorption experiment was performed by the author in the Department of Geological Sciences, University of Cape Town. The Pesticide Division of the Government Forensic Chemistry Department performed the extraction and analysis of the pesticides. Appendix B contains the details of the experiment, the results and calculations. It should be noted that for both soils sorption experiments were conducted in which only water was added to the soil and no pesticide. This was used as a check to ensure the soils were not previously contaminated in the field.

3.4.1 Sorption measurements

Sorption of the pesticides from aqueous CaCl_2 (0.01M) solution was determined at ambient laboratory temperature (22 ± 2 °C) in a batch suspension with a solution ratio of 5:1 and 24 hour equilibration. Two sets of measurements were made: a sorption isotherm determination with each surface soil sample, HR1 and HR2, and five solution concentrations (0.00192, 0.0384, 0.192, 0.96 and 4.8 mg/L for chlorpyrifos and 0.00019, 0.0038, 0.019, 0.095 and 0.475 mg/L for endosulfan); the second set, also for sorption isotherm determination, was on soil samples, HR1 and HR2 and five solution concentrations (0.0096, 0.048, 0.24, 1.20 and 6.00 mg/L for chlorpyrifos and 0.00038, 0.019, 0.095, 0.475 and 2.375 mg/L for endosulfan).

The pesticides were extracted from the equilibrium solution by solid phase columns (Chromabond C18ec/ 6ml / 500 mg) evaporated with N₂ and rewetted with hexane. The hexane extracts were analysed on a Hewlett Packard 5890 series II gas chromatograph equipped with a ⁶³Ni electron-capture detector (ECD) and a flame photometric detector (FPD). The following conditions were used for the extracts from the sorption experiments: column, fused-silica, open-tubular, capillary, 15m x 0.32 mm ID (J & W DB1), 0.25µm film thickness; carrier gas, N₂ at 3 mL/min; temperatures, column 170°C, injection port 230°C, detector 300°C.

3.5 Results and discussion

3.5.1 Models for interpreting experimentally determined pesticide sorption data

The experimental results are presented as sorption isotherms. The approach in this chapter is to focus on estimates of sorption from solution at equilibrium as a first step in defining sorption quantitatively. There are various sorption equations which can be used to describe sorption and directly estimate the sorption coefficient. Only the simplest of equilibrium models are used in this study. The two equations used are the linear partition equation,

$$C_s = K_d C_{aq}$$

and the linear Freundlich equation,

$$\log C_s = \log K_f + x \log C_{aq}.$$

A complete description of these equations were presented in Chapter 1 and in Chapter 2 they were used to determine the phosphate sorption capacity of the soils from the Hex River Valley.

3.5.2 Models for indirectly estimating sorption

The sorption of nonpolar organic compounds by soils has been shown to be highly correlated with soil organic matter content (Hassett and Banwart, 1989). The organic C-referenced sorption coefficient (K_{oc}) was, therefore, determined for comparison with the experimentally determined sorption coefficients. The K_{oc} was determined using the K_d or K_f value from the experimental isotherms combined with the organic carbon content ($K_{oc} = K_d /$

f_{oc}). However, K_{oc} , for non-polar organics, is a compound property and should be an average for a particular pesticide over a range of soils with variable organic carbon content. Thus, the ultimate procedure for estimating K_{oc} is from the regression of K_f against % organic carbon for a number of soils. Only two soil types were sampled so the range of organic carbon contents was limited and this method, therefore, could not be used. Instead, the average of the K_{oc} values calculated from the individual isotherms (K_d or K_f) were determined. Values of K_{oc} were also taken from the literature and used to calculate K_d . The octanol-water partition coefficient (K_{ow}) is, also, a compound property and was used to approximate K_{oc} (Green and Karickhoff, 1990). The surface area-referenced sorption coefficient (K_{ds}) was estimated on the basis of the relationship of K_d to the specific surface of soil (Pionke and DeAngelis, 1980). These indirect estimates of the sorption coefficient are discussed in Chapter 1 and the calculations are provided in Appendix B.

3.5.3 Chlorpyrifos isotherms and sorption coefficients

The sorption isotherms for the first sorption experiment (initial conc. range 0.00192 – 4.8 mg/L) are presented in Figure 3.3.a. The experiment was repeated at a higher range of initial concentrations (0.0096 – 6.00 mg/L) as it was more convenient, at these concentrations, to handle the numerous dilutions needed and the quantitative results for the low range of concentrations are more reliable at the slightly higher initial concentration. The sorption isotherms for the second experiment are presented in Figure 3.3.b.

Both the sorption isotherms appear to be of the L-type. According to Weber and Miller (1989), this suggests that at low initial concentration sorption is strong and at the higher initial concentration the soil is saturated, the amount sorbed is less, and the isotherm curves flatten out. The L-type of classification is dependent on the range of concentrations being analysed. At the low range concentrations the isotherms are more linear (C-type) which is due to constant partitioning and a stronger affinity of the chlorpyrifos molecules for the soil particles than for water. The difference between the two sets of isotherms is that Figure 3.3.b has a different range of initial concentrations and at the high initial concentration of 6.00 mg/L (last point on Figure 3.3.b) the soils had sorbed more than the first experiment at initial concentration of 4.8 mg/L (for the last point, Figure 3.3.a). At this higher initial concentration the soil, HR1, had become less extensively saturated and the isotherm does not flatten off as much as with HR2. This is because HR1 has a higher surface area and organic-C content than HR2 and therefore a greater capacity to retain the chlorpyrifos.

An alternative method for the comparison of the sorption capacity of soils is to determine the sorption coefficients. The simplest way to do this is to fit a straight line to the data ($C_s = m C_{eq}$). The slope of the line (m) is equal to the K_d . The linear regression lines, and associated equations, fitted to the sorption data are presented in Figure 3.4.a and b. A compilation of the sorption coefficients obtained by these linear equations and the associated coefficients of determination and standard error of the slopes are detailed in Table 3.3.

Table 3.3: The directly (experimentally) determined K_d for chlorpyrifos on HR1 and HR2 including literature values (from Green *et al.*, 1993) of K_d for a given soil.

HR1			HR2		
Linear K_d (ml/g)	r^2	Std. error	Linear K_d (ml/g)	r^2	Std. error
First Set					
4.90	0.81	0.83	3.29	0.86	0.48
Second Set					
25.02	0.97	1.60	5.92	0.92	0.65
Literature Values*					
9.43	0.84	0-20 cm; 1.30 %OC; pH _{H2O} 6.7 (soil type 1)			
10.4	0.85	0-20 cm; 1.63 %OC; pH _{H2O} 6.4 (soil type 2)			
19.0	0.92	0-20 cm; 2.88 %OC; pH _{H2O} 5.3 (soil type 3)			
49.1	0.82	0-20 cm; 6.22 %OC; pH _{H2O} 5.3 (soil type 4)			

*After Green *et al.* (1993)

The results can be compared to the literature values as a means of checking their reliability. The soil, in the literature reviewed, closest to HR2 on which chlorpyrifos sorption experiments had been performed, was soil type 1 (Table 3.3). The clay content was not specified and the organic carbon content is twice the organic carbon content of HR2 and the sorption coefficient, 9.43 ml/g, is almost twice that determined for HR2 (5.92 and 3.29 ml/g). It was concluded that the reliability of the results is satisfactory.

The high r^2 values for HR1 and HR2 (Table 3.3) are, however, misleading and this is evident from the line fit plots determined by the regression analyses and presented in Figures 3.5.a and b. The line fit plot uses the linear regression equation to generate y-values (predicted amount sorbed) and compares these to the real, measured amount sorbed. As can be seen in Figure 3.5 the generated y-values do not correspond closely to

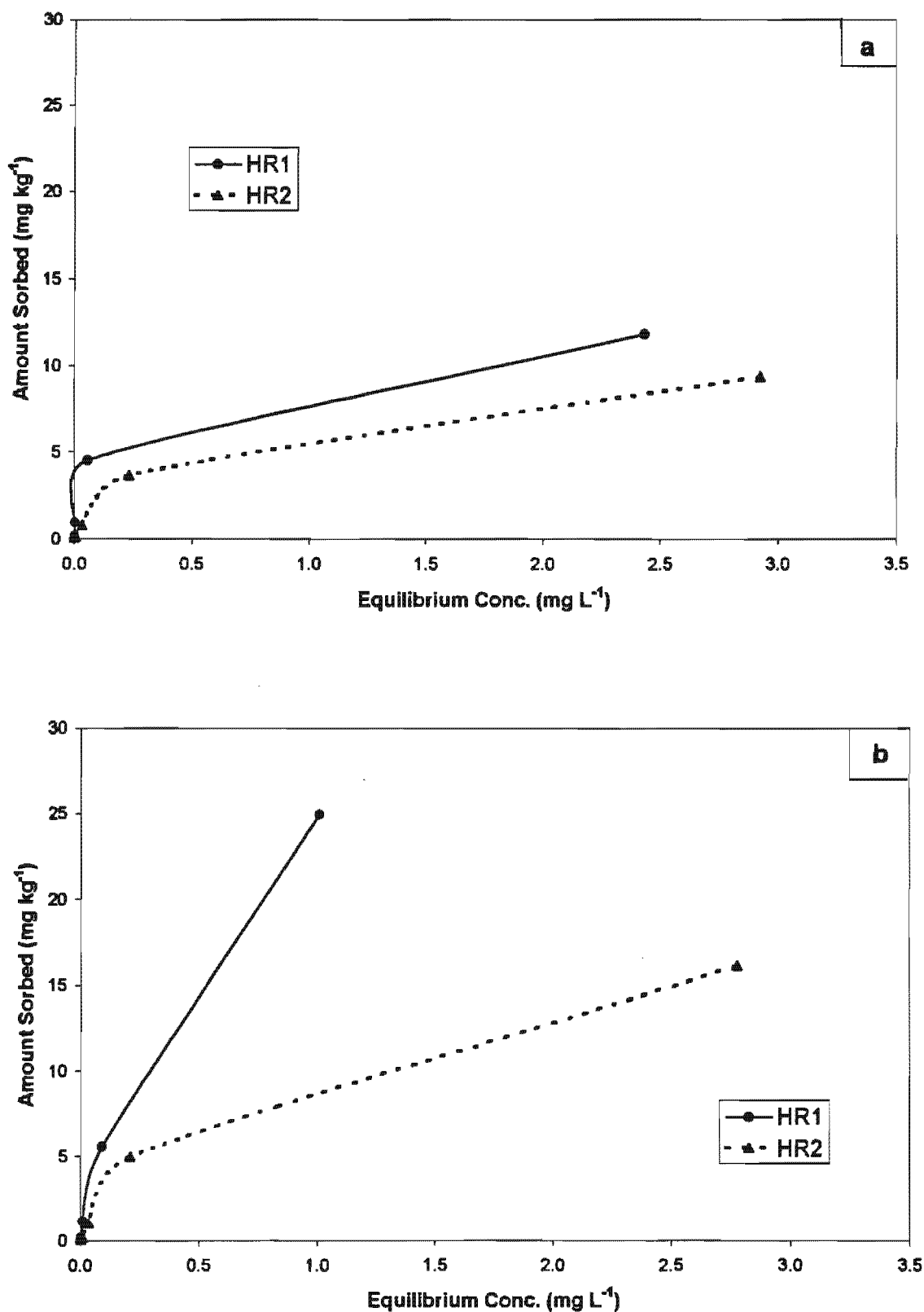


Figure 3.3 a) First set of sorption isotherms for chlorpyrifos on HR1 and HR2 (initial conc. range 0.00192 – 4.8 mg/L). b) Second set of sorption isotherms for chlorpyrifos on HR1 and HR2 (0.0096 – 6.00 mg/L).

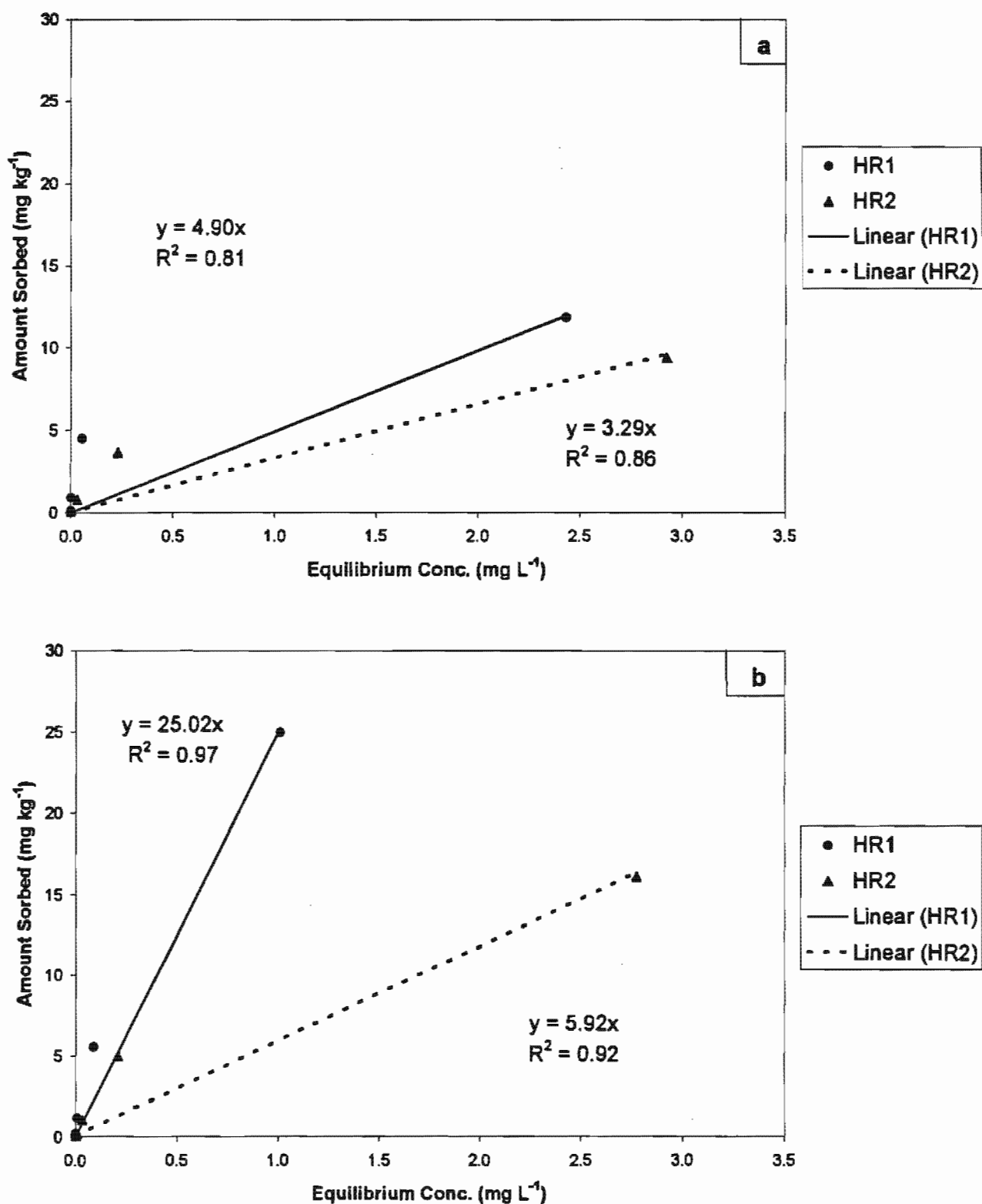


Figure 3.4 Linear regression of a) the first set of sorption data (initial conc. range 0.00192 – 4.8 mg/L) and b) the second set of sorption isotherms (0.0096 – 6.00 mg/L) for chlorpyrifos on HR1 and HR2.

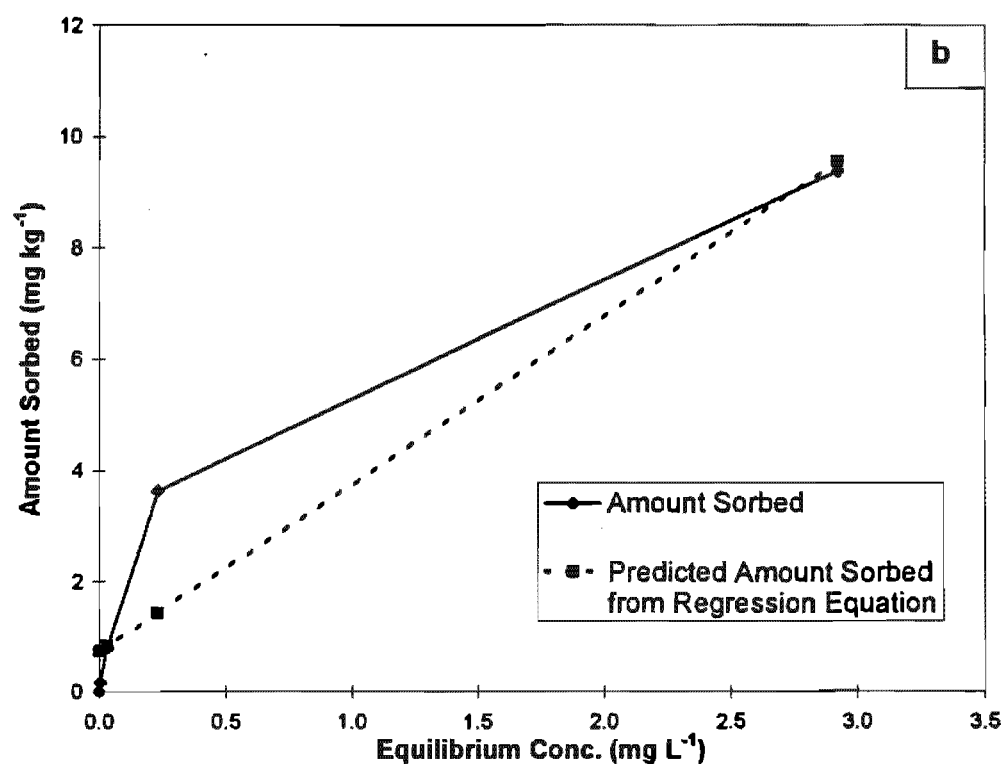
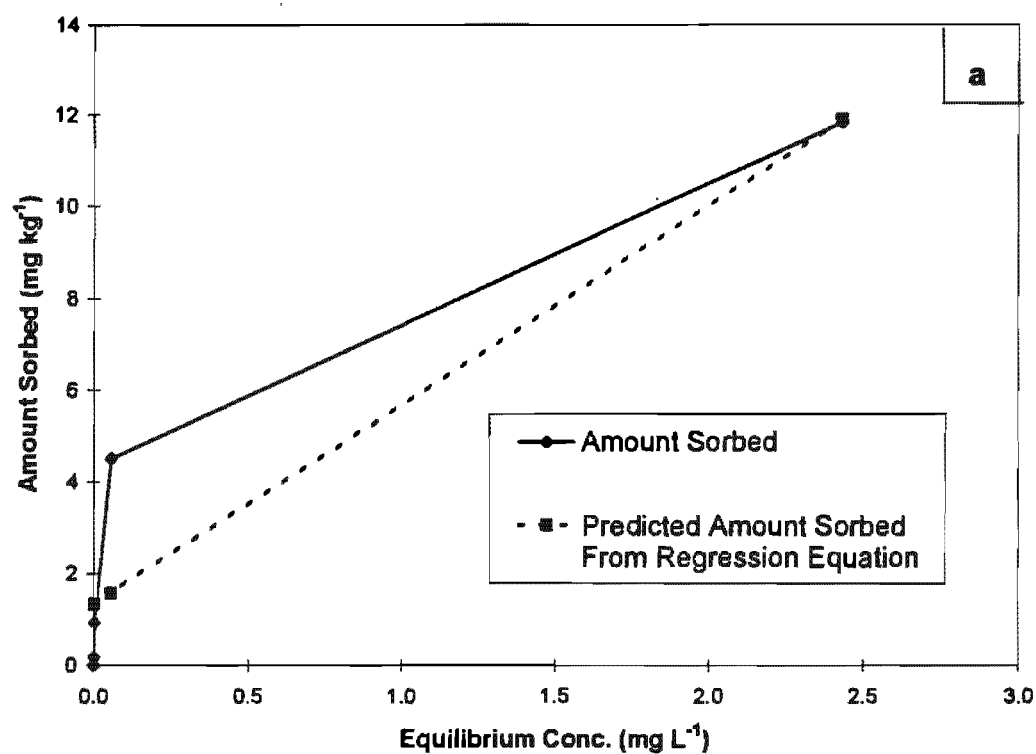


Figure 3.5 The line-fit plots from regression analysis on the first set of sorption data (initial conc. range 0.00192 – 4.8 mg/L) for a) HR1 and b) HR2 with chlorpyrifos.

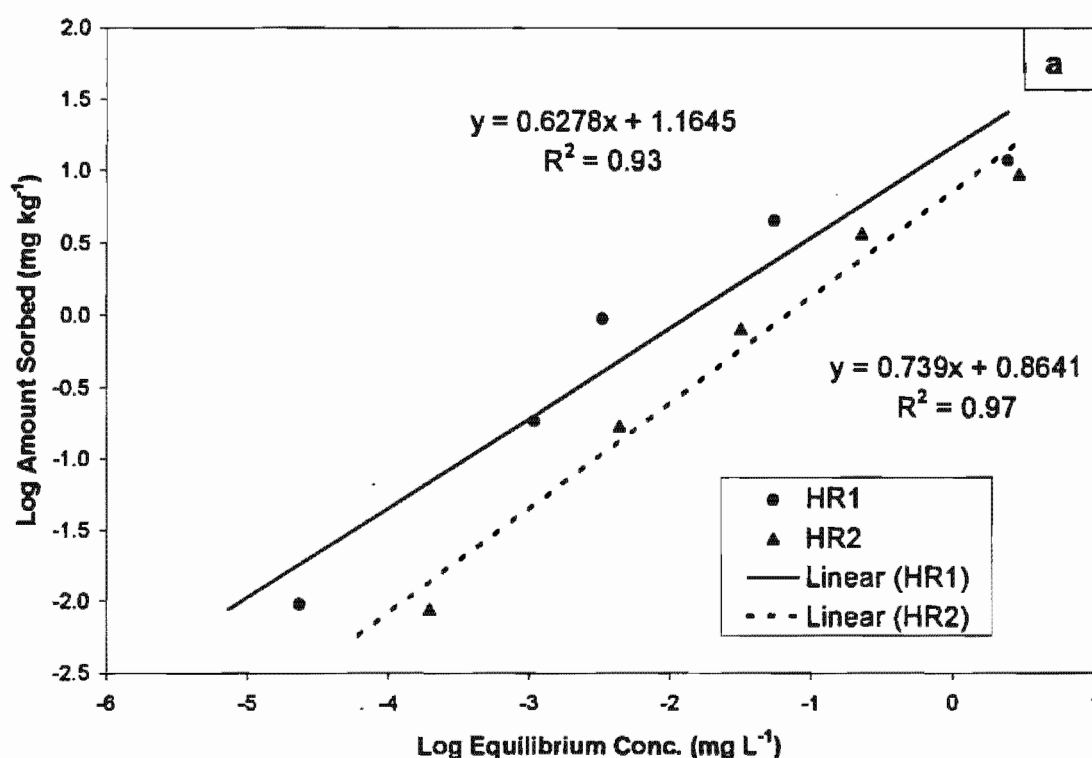
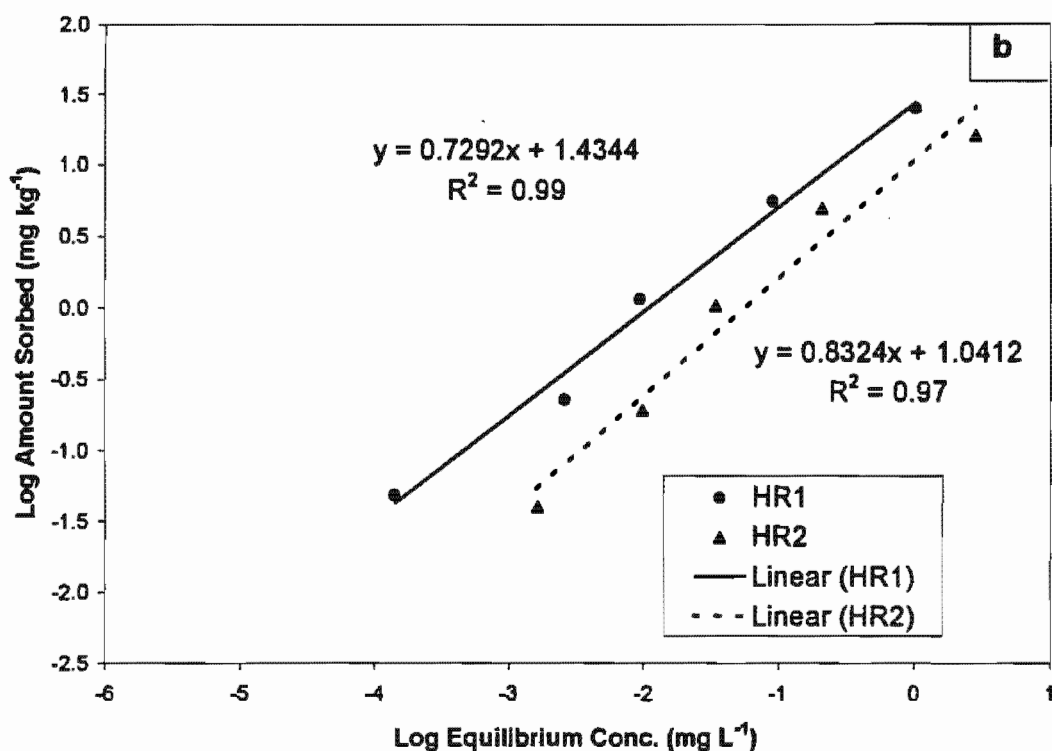


Figure 3.6 Linear Freundlich isotherms for a) the first set of sorption data (initial conc. range 0.00192 – 4.8 mg/L) and b) the second set of sorption isotherms (0.0096 – 6.00 mg/L) for chlorpyrifos on HR1 and HR2.

the real y-values and therefore these were considered a poor fit. This simple method ($C_s = m C_{aq}$) of determining the K_d value was, therefore, considered unsuitable and the more mathematical linear Freundlich equation was used to determine the sorption coefficient. Figure 3.6 shows the linear Freundlich sorption isotherms for the two sets of data for chlorpyrifos on soils HR1 and HR2.

The Freundlich sorption coefficients and corresponding estimations of associated error are compiled in Table 3.4. For comparison, Table 3.4 includes Freundlich coefficients taken from the available literature as well as the properties of the soils used to determine these coefficients.

Table 3.4: Freundlich sorption coefficients, coefficients of determination and standard error of K_f for chlorpyrifos including coefficients taken from the literature

HR1			HR2		
Linear K_f (ml/g)	r^2	Std. Error ¹	Linear K_f (ml/g)	r^2	Std. Error ¹
First Set					
14.60	0.93	1.85	7.31	0.97	1.40
Second Set					
27.19	0.99	1.29	10.96	0.97	1.43
Literature Values ²					
28.38	0.98	Soil type 1			
46.88	0.98	Soil type 2			
161.19	0.91	Soil type 3			
397.19	0.98	Soil type 4			

¹ This is the standard error of the intercept since $\text{Log } K_f = \text{intercept}$

² After Felsot and Dahm (1979). Soil type 1: pH 7.30; CEC 5.71 cmol/kg; 0.51 %OC; 77/15/8 (sand/silt/clay). Soil type 2: pH 6.83; CEC 6.10 cmol/kg; 1.07 %OC; 83/9/8 (sand/silt/clay). Soil type 3: pH 5.00; CEC 21.02 cmol/kg; 2.64 %OC; 37/42/21 (sand/silt/clay). Soil type 4: pH 7.30; CEC 37.84 cmol/kg; 3.80 %OC; 21/55/24 (sand/silt/clay).

The second set of data obtained from the sorption experiment has a higher r^2 value for HR1 and the r^2 values for HR2 are the same for the first and second set of data. The soils, for which Freundlich sorption coefficients had been determined and were reported in the literature, that were most similar to HR1 and HR2 were soil type 2 and 1, respectively

(Table 3.4). Considering that organic carbon content is most significant in the sorption of these particular pesticides, the closest soil type was based on first, the OC content and secondly, on the texture. The reported coefficients (Table 3.4) are higher than the K_f results determined in the present study but they are still within an order of magnitude. The higher literature values are possibly due to the mineralogy of the soils used in the sorption experiments reported in the literature, which was not specified, for example, smectite has a greater capacity to adsorb non-polar organics than kaolinite. The higher values reported in the literature (Table 3.4) could also be as a result of different experimental conditions, for example, the equilibration time used in the sorption experiments reported by Felsot and Dahm (1979) for chlorpyrifos was 2 hours compared to the 24 hours used in the present study. The very high K_f values reported in the literature are for soils with two or three times the organic carbon content, clay content and exchange capacity. It was concluded that the sorption coefficient for chlorpyrifos on soils HR1 and HR2 was best determined by the second set of sorption data using the linear Freundlich equation (Table 3.4).

The slope of the Freundlich isotherm (x in $\log C_s = \log K_f + x \log C_{eq}$) is a constant which is an index of the sorption intensity (Weber and Miller, 1989). Weber and Miller (1989) state that for L-type isotherms the slope will always be less than 1 which is the case for the Freundlich isotherms in Figure 3.6 (Figure 3.6.b: slope = 0.73 for HR1 and 0.83 for HR2). When $x < 1$ the resulting isotherm is curvilinear, with the sorbed quantity increasing rapidly as concentration is increased at low concentrations; sorption approaches a maximum slowly at high solution concentrations. Weber and Miller (1989) suggest that over short-range, low initial concentrations C-type isotherms are observed for organic chemicals and as the range widens and concentrations increase the isotherm becomes the L-type. The L-type isotherms are the most common for organic chemical sorption by soils and soil materials, probably because soils are heterogeneous mixtures of adsorbents, each of which may sorb the solute at least to some extent. The result is a composite isotherm that reflects the sorption of the solute by several different surfaces. These authors found that an L-type isotherm was repeatedly observed for sorption of organics in studies using only organic matter as the adsorbent. The organic matter in soils HR1 and HR2 would probably be the major adsorbent responsible for retention.

Since organic carbon is so important to the sorption of non-ionic hydrophobic pesticides the organic C-referenced sorption coefficients (K_{oc}) were determined. As mentioned there are different methods available to calculate K_{oc} . K_{oc} is also the most common form in which sorption coefficients are reported in the literature and input into simulation models. The K_{oc} for chlorpyrifos on soils HR1 and HR2 determined from the experimental K_d and K_f as well

as estimates using K_{ow} and the surface area (SS) are presented in Table 3.5. Literature values are also included for comparison.

Table 3.5: A compilation of the organic C-referenced (K_{oc}) and surface area referenced (K_{ds}) sorption coefficients, for chlorpyrifos, estimated by direct and indirect methods. The values in parenthesis are the standard deviations.

HR1 K_{oc} (ml/g)	HR2 K_{oc} (ml/g)	Mean K_{oc} (ml/g)	Soil Properties
K_{oc} from K_f ¹			
1721 (668)	1260 (1101)	1490 (1288)	HR1: pH 5.8; %OC 1.58; 76/16/9 ⁵ HR2: pH 5.6; %OC 0.87; 94/3/2 ⁵
K_{oc} from K_d ²			
1583 (897)	680 (324)	1131 (954)	as above
K_{oc} from K_{ow} ³			
45211	45211	45211	as above
K_{ds} ⁴			
11882	6025	8953	as above
Literature Values ^{1,2,3,4}			
K_{oc} from K_f ¹			
5549	6630		Soil type 1 (Table 3.4)
4381			Soil type 2 (Table 3.4)
6139			Soil type 3 (Table 3.4)
10452			Soil type 4 (Table 3.4)
K_{oc} from K_d ²			
1010 (75)	922 (256)		Soil type 1 (Table 3.3)
765 (61)			Soil type 2 (Table 3.3)
673 (187)			Soil type 3 (Table 3.3)
1241 (143)			Soil type 4 (Table 3.3)

- ¹ Organic C-referenced sorption coefficient calculated using K_f (second set, Table 3.4) and the fraction organic carbon (%OC / 100) in soils HR1 and HR2 (Table 2.4). Literature values from Felsot and Dahm (1979).
- ² Organic C-referenced sorption coefficient calculated using K_d (second set, Table 3.3) and the fraction organic carbon (%OC / 100) in soils HR1 and HR2 (Table 2.4). Literature values from Green *et al.* (1993).
- ³ Organic C-referenced sorption coefficient calculated using K_{ow} (50 000) for chlorpyrifos (Appendix B.5.1)
- ⁴ Surface area referenced sorption coefficient calculated from SS (Appendix B.5.2) and the constant m .
- ⁵ Sand/silt/clay (%)

The general trend for chlorpyrifos is that the K_f values are higher than the k_d values. The K_{oc} from K_f is higher than the k_{oc} from K_d . They are, however, within an acceptable range.

The most reliable results based on goodness of fit (linearity of the isotherm) is the K_{oc} determined from the K_f . The average experimental K_{oc} from K_f is 1490 ml/g and is considerably less than the literature value, 6630 ml/g (Table 3.5), even though the soil properties of HR1 and HR2 fit into the range of soils reported in the literature and used for the sorption experiments. This disparity emphasizes the need to determine site-specific sorption coefficients and that even if the soils being studied are similar to those reported in the literature, using the literature value of the sorption coefficient could lead to misinterpretation and significant model errors. The standard deviation for the K_{oc} results (Table 3.5) are high because of the large standard deviation associated with the % organic carbon (Appendix A.2). The K_{oc} values calculated from K_{ow} and SS are extremely high compared to the experimentally determined K_{oc} values and no reported literature values could be found for comparison. The reasons for the discrepancy between the experimentally determined and indirectly calculated K_{oc} will be discussed in Section 3.5.7 and 3.5.8.

3.5.4 Endosulfan isotherms and sorption coefficients

The sorption isotherms for the first sorption experiment (initial conc. range 0.00019 – 0.475 mg/L) and second sorption experiment (0.00038 – 2.375 mg/L) are presented in Figures 3.7 and 3.8, respectively. The sorption isotherms are of the C-type with HR1 tending toward the L-type due to its larger available area for sorption. This implies that at low initial concentration sorption is strong and at the higher initial concentration HR1 sorbs less as the soil becomes saturated and the isotherm curves slightly and flattens out. While at the higher initial concentration HR2 maintains a constant partitioning in which endosulfan has a stronger affinity for the soil particles than for water. In the second set of data the point of highest amount sorbed, and initial concentration of 2.375 mg/L, is excluded. This is because at this high concentration the solubility of endosulfan is greatly exceeded and artifacts of emulsions complicate the sorption data. Sorption coefficients can no longer be determined by convenient methods and the soil is saturated to an extent that is highly unlikely to be found due to normal field applications.

Endosulfan is a mixture of two isomers, endosulfan- α and - β . In the GLEAMS model (Knisel and Leonard, 1993), the isomers of endosulfan are not taken into account and a single sorption coefficient is entered as the sorption parameter for endosulfan. However, the more recent literature (Tomlic, 1994 and Australian National Registration Authority, 1997) reports separate sorption coefficients for endosulfan- α and - β and they suggest that the two isomers exhibit different environmental behaviour. The sorption coefficients for endosulfan, endosulfan- α and - β have, therefore, been determined and are presented in

the following discussion. Figures 3.7 and 3.8 shows the linear regressions fitted to the sorption data for endosulfan, endosulfan- α and - β , for the first and second set of data. Table 3.6 is a compilation of the sorption coefficients (K_d) obtained from these linear equations ($C_s = m C_{aq}$ and $m = K_d$) with the associated coefficients of determination and standard error of the slopes.

Table 3.6: The directly (experimentally) determined K_d for endosulfan, endosulfan- α and - β , on HR1 and HR2.

	HR1			HR2		
Pesticide	Linear K_d (ml/g)	r^2	Std. error	Linear K_d (ml/g)	r^2	Std. error
	First Set					
Endosulfan	208	0.99	12.2	107	1.0	1.22
Endosulfan- α	95	0.99	3.88	45	1.0	0.94
Endosulfan- β	513	0.98	36.0	308	1.0	4.5
	Second Set					
Endosulfan	245	0.99	18.06	166	0.98	14.0
Endosulfan- α	224	0.97	26.78	159	0.98	13.21
Endosulfan- β	277	0.99	16.38	182	0.98	15.58
	Literature Values ¹					
Endosulfan- α	63	na		pH 5.4; %OC 0.62; 16/66/18 ²		
	102	na		pH 5.9; %OC 1.28; 59/31/10 ²		
	521	na		pH 5.8; %OC 2.45; 80/10/10 ²		
	364	na		pH 5.8; %OC 2.66; 80/11/9 ²		
Endosulfan- β	74	na		pH 5.4; %OC 0.62; 16/66/18 ²		
	178	na		pH 5.9; %OC 1.28; 59/31/10 ²		
	566	na		pH 5.8; %OC 2.45; 80/10/10 ²		
	378	na		pH 5.8; %OC 2.66; 80/11/9 ²		

¹ Australian National Registration Authority (1997). The K_d values were not reported in this literature but they were calculated from the K_{oc} and organic carbon content provided. It was assumed the K_{oc} was calculated from K_d although this was not specified in the report.

² Sand/silt/clay (%)

na – not available

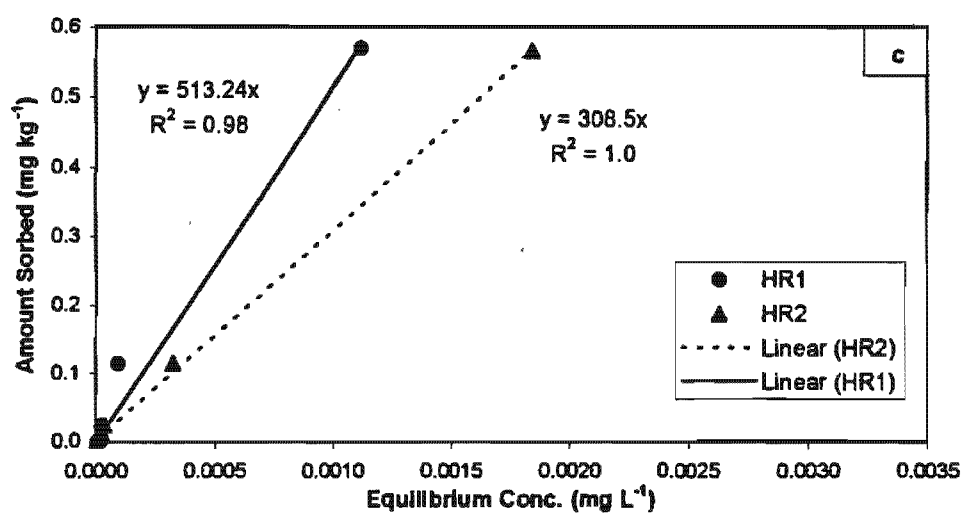
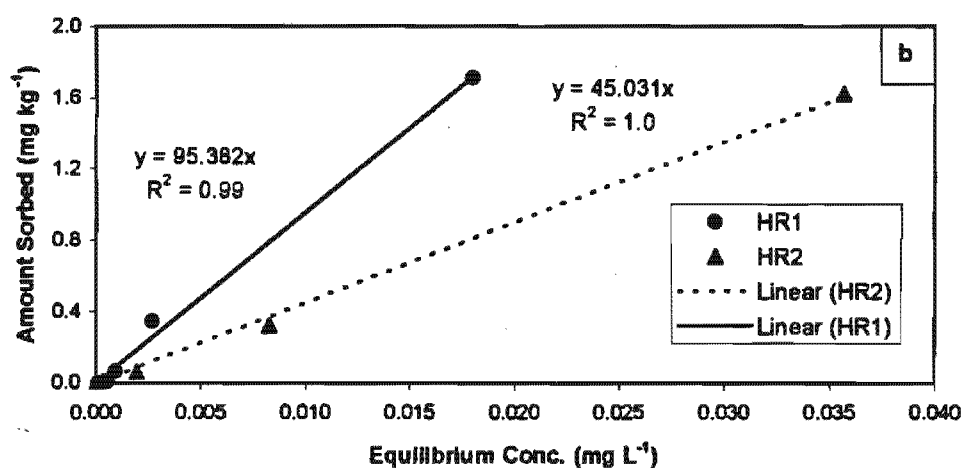
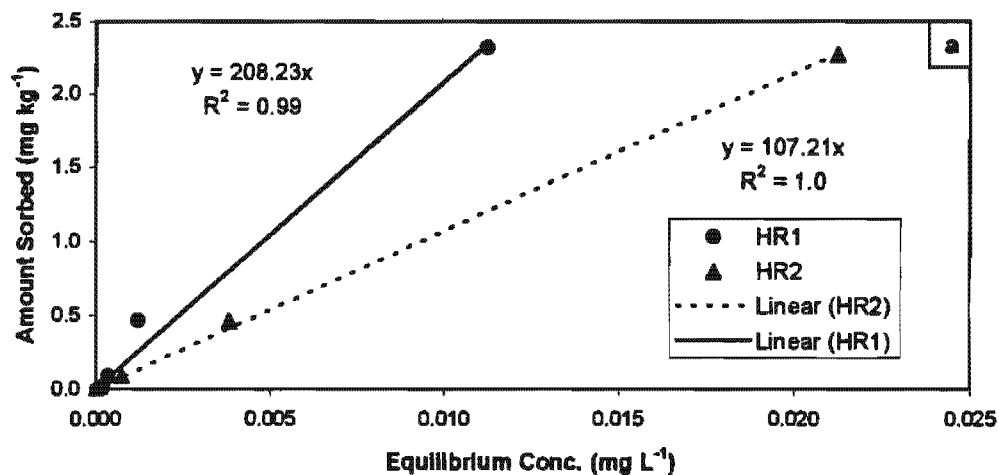


Figure 3.7 Sorption isotherms with linear regressions of the first set of data (initial conc. range 0.00019 – 0.475 mg/L) for a) endosulfan b) endosulfan- α and c) endosulfan- β , on HR1 and HR2.

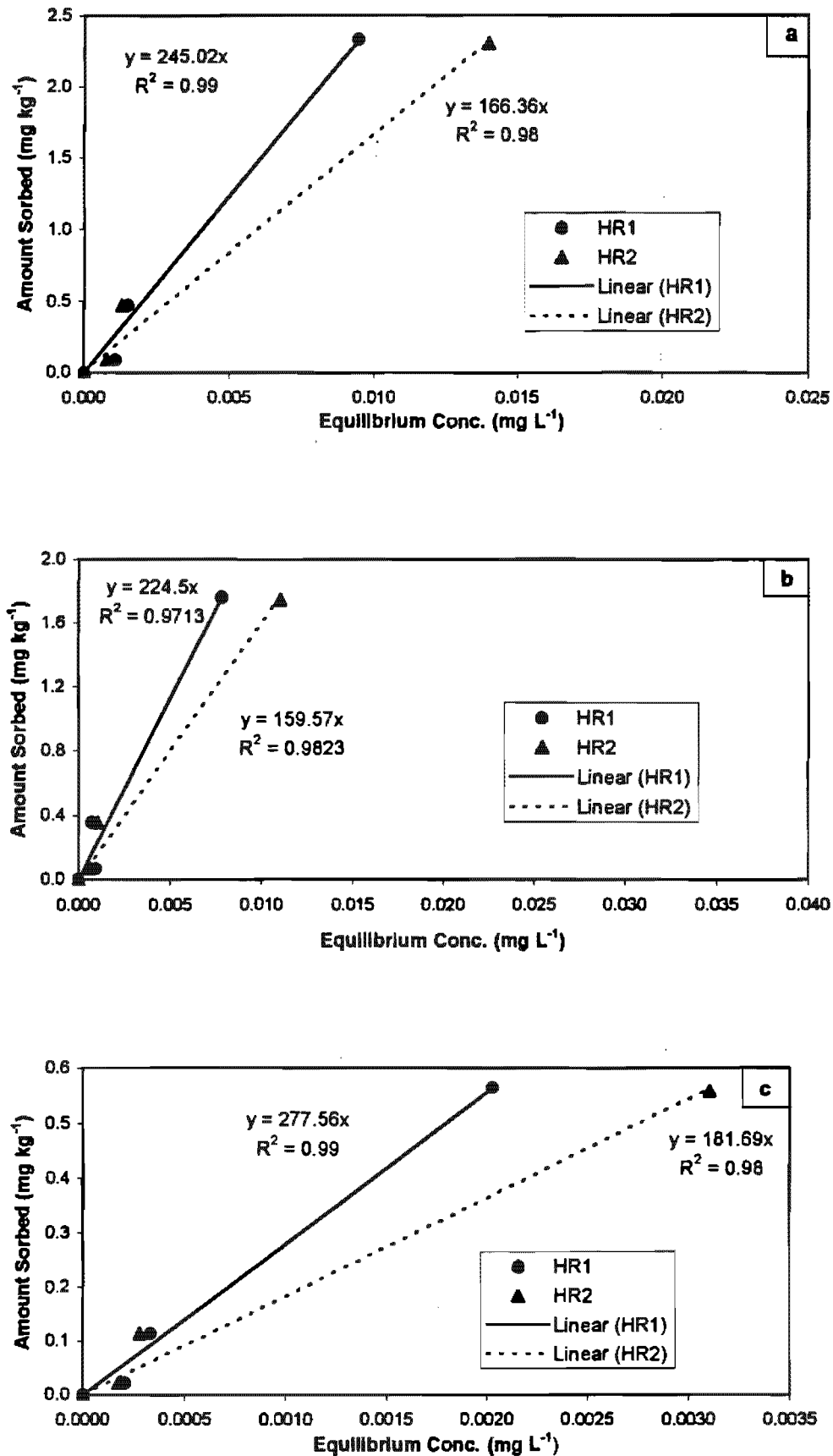


Figure 3.8 Sorption isotherms with linear regressions of the second set of data (initial conc. 0.00038 – 2.375 mg/L) for a) endosulfan b) endosulfan-α and c) endosulfan-β, on HR1 and HR2.

The linear sorption isotherm ($C_s = mC_{aq}$) described the isotherms for endosulfan well. All the coefficients of determination were greater than 0.97. This is, therefore, a good method for determining K_d . The literature K_d (Table 3.6) for endosulfan- α (63 ml/g) for the soil with 0.62 % organic carbon is in the middle of the range for the experimentally determined K_d for endosulfan- α (45 and 159 ml/g) for HR2 (0.87 % organic carbon). Slightly higher values would be expected for HR2 as it has a higher organic carbon content however it should be noted that the variability in organic carbon content for the soils is high. Overall, there is good agreement between experimentally determined sorption coefficients and the literature values (Table 3.6). The values of K_d for endosulfan for the two sets of data were within reasonable agreement. However, the K_d for endosulfan- α and - β for the two sets of data did not agree. The Australian National Registration Authority (1997) state that the sorption coefficients for endosulfan- α and - β are fairly similar with the - β K_d usually being slightly higher than the - α K_d . This was used as a basis for deciding which set of data to use.

The linear Freundlich isotherms for endosulfan, endosulfan- α and endosulfan- β , with HR1 and HR2, for the two sets of data are presented in Figures 3.9 and 3.10. The Freundlich sorption coefficients and corresponding estimations of associated error are compiled in Table 3.7. No literature reporting Freundlich sorption coefficients for endosulfan was available for comparison.

Table 3.7: Freundlich sorption coefficients, coefficients of determination and standard error of K_f for endosulfan, endosulfan- α and endosulfan- β .

	HR1			HR2		
	Linear K_f (ml/g)	r^2	Std. Error ¹	Linear K_f (ml/g)	r^2	Std. Error ¹
	First Set					
Endosulfan	5720	0.88	11.22	159	0.99	1.73
Endosulfan- α	4559	0.93	6.40	123	0.97	2.20
Endosulfan- β	18663	0.84	33.88	71	0.99	1.56
	Second Set					
Endosulfan	824	0.97	2.94	346	0.97	2.70
Endosulfan- α	1096	0.92	7.42	374	0.97	2.81
Endosulfan- β	427	0.98	3.01	288	0.97	3.05

¹This is the standard error of the intercept since $\text{Log } K_f = \text{intercept}$

Weber and Miller (1989) explain that for C-type isotherms the slope of the linear Freundlich isotherm (or x in $\log C_s = \log K_f + x \log C_{aq}$ or $C_s = K_f C_{aq}^x$) is close to 1 and the Freundlich expression becomes simply a distribution expression given by

$C_s = K_d C_{aq}$, where $K_d = K_f$ (if $x = 1$). This was used as the basis for deciding which set of data estimated the sorption coefficients more closely since there is no significant difference in the coefficients of determination and standard errors between the sets of data.

The slopes of the linear Freundlich isotherms (x in $\log C_s = \log K_f + x \log C_{aq}$) in Figure 3.10 for the second set of data are closer to one than the first set (Figure 3.9) and the K_f values are closer to the K_d values than for the first set. It was therefore decided the second set of data's sorption coefficients would be used in following calculations and discussions. Since $x > 1$ for the Freundlich isotherms, the isotherm is curvilinear. It curves downwards towards the x-axis. Hassett and Banwart (1989) explain that at aqueous concentrations above 60 to 80 % of the sorbate's water solubility the equilibrium concentration of the sorbing species increases rapidly, while the amount apparently sorbed either does not increase or increases gradually. This causes the

isotherms to turn down sharply and this has been explained by either the formation of a discrete phase or because of inadequate techniques used to measure adsorption.

Assuming that the organic matter fraction in the soils is the material primarily responsible for sorbing endosulfan, the organic C-referenced sorption coefficients (K_{oc}) were determined. The K_{oc} value was also the only coefficient for which literature values for endosulfan, endosulfan- α and - β could be found. The K_{oc} for endosulfan, endosulfan- α and - β on soils HR1 and HR2 determined from the experimental K_d and K_f (using the second set of results in Tables 3.6 and 3.7) is presented in Table 3.8 as well as estimates using K_{ow} and the surface area (SS). Literature values (Australian National Registration Authority, 1997) are also included for comparison. It should be noted that the K_{oc} values in Table 3.8 are reported in L/g and not ml/g, for convenience.

Since both the linear distribution and linear Freundlich equations describe the data well, the K_{oc} values from both K_f and K_d should be suitable to enter into models and to explain endosulfan's mobility. However, the K_{oc} values based on K_f appear too high and the possible explanations for this will be discussed in Section 3.5.5. The K_{oc} values, based on K_d , are the most reasonable and are comparable to values reported in the literature. Once again the standard deviation (values in parenthesis in Table 3.8) for the K_{oc} results are high because of the large standard deviation associated with the % organic carbon (Appendix A.2). In all cases the variability in organic carbon content accounted for more than 75% of the error. The K_{oc} values calculated from K_{ow} and SS are much more reasonable and closer to the experimental sorption coefficients than was the case for chlorpyrifos. It is possible that endosulfan is sorbed to a greater extent by the mineral phases than chlorpyrifos and so the SS method is more appropriate for endosulfan. A different equation was used for calculating K_{oc} from K_{ow} for endosulfan and this equation probably describes the sorption of endosulfan better than the equation used to describe sorption of chlorpyrifos (Appendix B.5.1).

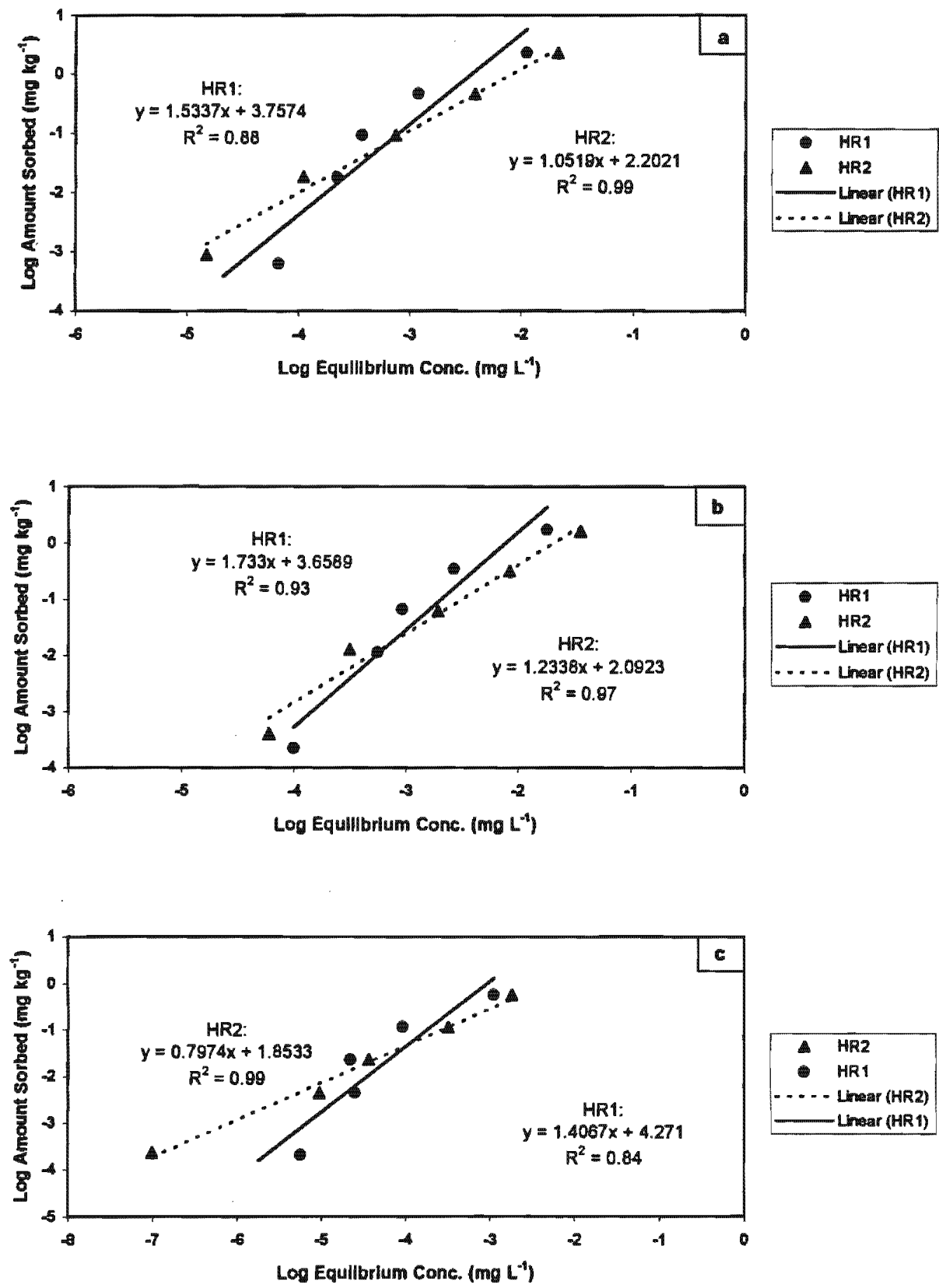


Figure 3.9 The first set of Linear Freundlich isotherms fitted by linear regression for a) endosulfan, b) endosulfan-α and c) endosulfan-β, for HR1 and HR2.

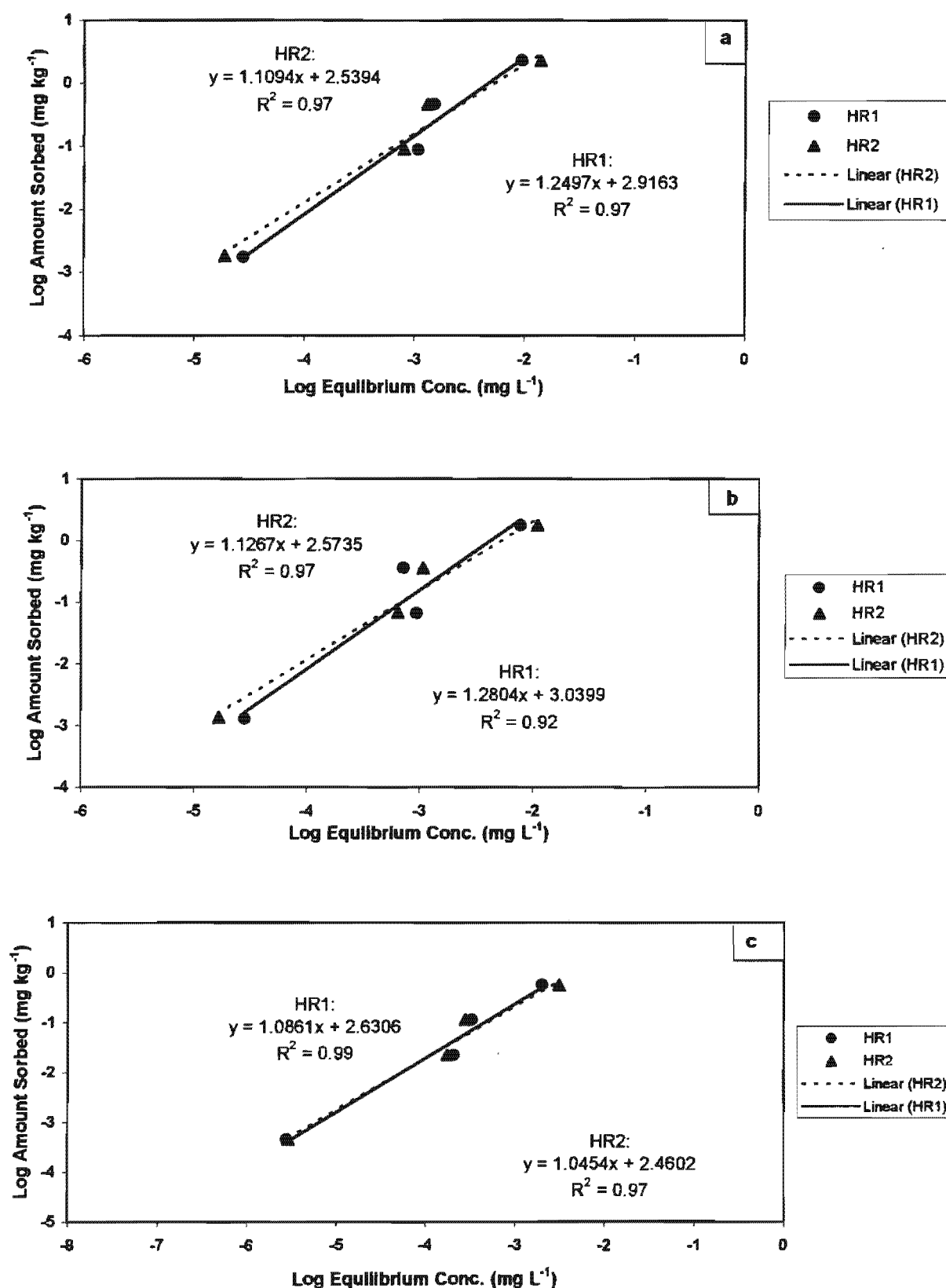


Figure 3.10 The second set of Linear Freundlich isotherms fitted by linear regression for a) endosulfan, b) endosulfan- α and c) endosulfan- β , for HR1 and HR2.

Table 3.8: A compilation of the organic C-referenced (K_{oc}) and surface area referenced (K_{ds}) sorption coefficients estimated by direct and indirect methods. The values in parenthesis are the standard deviations.

Pesticide	HR1 K_{oc} (L/g)	HR2 K_{oc} (L/g)	Mean K_{oc} (L/g)	Soil Properties
K_{oc} from K_r ¹				
Endosulfan	52.15 (27.02)	40.70 (24.32)	46.43 (36.35)	HR1: pH 5.8; %OC 1.58; 76/16/9 HR2: pH 5.6; %OC 0.87; 94/3/2
Endosulfan- α	69.37 (35.30)	44.00 (26.50)	56.68 (44.14)	as above
Endosulfan- β	27.02 (14.11)	33.88 (14.64)	30.45 (20.34)	as above
K_{oc} from K_d ²				
Endosulfan	15.51 (5.26)	19.53 (6.44)	17.52 (8.32)	as above
Endosulfan- α	14.18 (4.67)	18.71 (5.21)	16.44 (6.70)	as above
Endosulfan- β	17.53 (6.01)	20.92 (5.86)	19.22 (8.39)	as above
K_{oc} from K_{ow} ³				
Endosulfan	26.48	26.48	26.48	as above
Endosulfan- α	na	na		as above
Endosulfan- β	na	na		as above
K_{ds} ⁴				
Endosulfan	18.28	9.27	13.77	as above
Endosulfan- α	na	na		as above
Endosulfan- β	na	na		as above
Literature Values ^{1,2,3,4}				
K_{oc} from K_r ¹				
Endosulfan			12.40	No soil properties specified (GLEAMS, Knisel and Leonard, 1993)
K_{oc} from K_d ²				
Endosulfan			12.40	No soil properties specified (GLEAMS, Knisel and Leonard, 1993)
Endosulfan- α	10.20		13.30	pH 5.4; %OC 0.62; 16/66/18 ⁵
	8.00			pH 5.9; %OC 1.28; 59/31/10 ⁵
	13.70			pH 5.8; %OC 2.66; 80/11/9 ⁵
	21.30			pH 5.8; %OC 2.45; 80/10/10 ⁵
Endosulfan- β	11.90		15.77	pH 5.4; %OC 0.62; 16/66/18 ⁵
	13.90			pH 5.9; %OC 1.28; 59/31/10 ⁵
	14.20			pH 5.8; %OC 2.66; 80/11/9 ⁵
	23.10			pH 5.8; %OC 2.45; 80/10/10 ⁵

¹ Organic C-referenced sorption coefficient calculated using K_r (second set, Table 3.7) and the fraction organic carbon (%OC / 100) in HR1 and HR2.

² Organic C-referenced sorption coefficient calculated using K_d (second set, Table 3.6) and the fraction organic carbon (%OC / 100) in HR1 and HR2.

- ³ Organic C-referenced sorption coefficient calculated using K_{ow} (54954) for endosulfan (Appendix B.5.1). No literature values were available.
 - ⁴ Surface area referenced sorption coefficient (K_{as}) calculated from SS (Appendix B.5.2) and the constant m .
 - ⁵ Sand/silt/clay (%); Australian National Registration Authority (1997).
- na – literature values not available

3.5.5 Choosing the best estimate of the organic C-referenced sorption coefficient

When sorption isotherms are measured in the laboratory, the decision of whether to use $C_s = K_f C_{aq}^x$ or $C_s = K_d C_{aq}$ may be dictated by the model in which the sorption expression is to be used. Essentially, a partition coefficient (K_d) is needed and this can be taken from the literature, calculated or estimated using the Freundlich equation. The equation for K_d ($C_s = K_d C_{aq}$) is a simplification of the Freundlich equation ($C_s = K_f C_{aq}^x$) where $x = 1$ and K_f is the Freundlich coefficient. Strictly speaking, it is only when x is equal to unity, i.e. the isotherm is linear, that K_f can be used to approximate the partition coefficient. The sorption of many, if not most nonpolar organics on soils produces linear isotherms for up to 60 to 80 % of the aqueous concentration of the sorbing species water solubility (Hassett and Banwart, 1989). Green and Karickhoff (1990) suggested that the values of x (in $C_s = K_f C_{aq}^x$) commonly range between 0.75 and 0.95. They suggested that for many modeling purposes a linear isotherm could be used in lieu of the Freundlich isotherm with acceptable error. The error introduced by this approximation depends on the value of the x and the solution concentration. Green and Karickhoff (1990) suggested that for $0.7 < x < 1$ and concentrations less than 1 mg/L this approximation is acceptable.

In the present study, K_f and K_d were determined. The K_f value was considered the best estimate of the partition coefficient as long as the x value was between 0.7 and 1.0. If this was not the case a linear regression, fitting the plot C_s against C_{aq} well, was considered the best estimate of the partition coefficient.

Use of the GLEAMS model in Chapter 4 requires the K_{oc} value as an input parameter. The equation $K_{oc} = (K_d/OC) 100$ is then used to calculate the K_d using the % organic carbon in the soil layer. The K_{oc} value is used, as it is considered a compound parameter and is, therefore, not dependent on the soil characteristics. K_{oc} is the slope of a line fitted to a plot of K_d data to % organic carbon for a range of soils or K_f (if the

0.7 < x < 1.0) to % organic carbon. However, Knisel and Leonard. (1993), point out that for a given pesticide where experimental values are tabulated from different sources, the K_{oc} may vary over a range of 1 to 3 times the mean value. Therefore, when the model is applied for site-specific purposes, particularly when comparing simulated results with field data for validation, site-specific values of K_{oc} and its spatial variability within the site are desirable. The mean of the K_{oc} values for the two soils (HR1 and HR2) was, therefore, used as the site-specific organic C-referenced sorption coefficient. The best estimate of K_{oc} was chosen by comparing and minimizing the various assumptions and approximations associated with using K_f and K_d to calculate K_{oc} .

The Freundlich isotherms for chlorpyrifos have x values (slope) that are in the range of 0.75 to 0.95 and comparing Tables 3.3 and Table 3.4 an acceptable approximation of K_f for K_d is evident. This can also be seen in the similarity of the K_{oc} values calculated from K_f or K_d (Table 3.5). One could safely be used in lieu of the other. However, linearity of the isotherm ($C_s = K_d C_{aq}$) is assumed when calculating K_{oc} from K_d and for chlorpyrifos this assumption is invalid. The line fit plots (Figure 3.4) demonstrate this by way of comparing the predicted y -values from the regression equation to the real y -values. Therefore, the K_{oc} values calculated from the K_f values were considered the best estimate of K_{oc} .

It is interesting to note that when the isotherms curve ($x < 1$) at higher equilibrium concentrations like those for chlorpyrifos the equilibrium concentration increases while the sorption coefficient decreases. At the higher concentrations encountered in surface soils soon after application of chlorpyrifos to the soil, the assumption of linearity of the Freundlich isotherm (i.e. $x = 1$) may result in sorption estimates that are too high, depending on the degree of non-linearity and the concentration of solute in solution.

The x values for the endosulfan Freundlich isotherm are greater than 1 and go as high as 1.7 for the first set of data. The K_f values (Table 3.7) are much higher than the K_d values (Table 3.6) and especially the K_{oc} values (Table 3.8) calculated from K_f are higher than the K_{oc} values calculated from K_d . The disparity between the K_{oc} results is attributed to the $x > 1$ and the assumption that K_f can approximate the partition coefficient is invalid. Since the linear partition isotherm from which K_d was derived is linear, the use of K_d to calculate K_{oc} is valid for endosulfan. The K_{oc} values based on K_d were considered the most acceptable estimate of the organic C-referenced sorption coefficient.

3.5.6 The assumptions made when using the K_{oc} approach

The K_{oc} approach was used in this study because the organic carbon in the soils is the dominant sorbent; it is the primary form in which sorption coefficients are reported in the literature and the model used in this study, GLEAMS, requires K_{oc} as an input parameter. Several assumptions, however, are inherent in the computation and use of K_{oc} values (Green and Karickhoff, 1990): (i) equilibrium exists; (ii) isotherms are linear and singular; (iii) sorption occurs on organic carbon only and not on clay minerals; (iv) all organic carbon in soils has similar sorption characteristics. The first two assumptions (equilibrium, linearity and reversible sorption) are inherent in the use of $C_s = K_d C_{aq}$. Adoption of $K_{oc} = K_d / f_{oc}$ is a further simplification and introduces additional assumptions, which if invalid, will introduce more error. The errors encountered in predicting pesticide distribution are caused by the violation of these assumptions in actual field situations and are difficult to assess. The impact and importance of such errors will depend on the objective of the modeling effort and the sensitivity of model output to variation in sorption parameters (This aspect is developed further in the chapter on modeling, Chapter 4). Clearly, none of these assumptions is valid in the strict sense so the use of organic C-referenced sorption will introduce errors, the magnitude of which, depends on how severely the assumptions are violated. The application of the K_{oc} concept has been proposed and also questioned repeatedly since its introduction relative to pesticides in the early 1960's. Acceptance of its approach has been encouraged by the increasing need for calculation procedures applicable to hundreds of organic chemicals in hazard assessments for a wide range of environmental conditions. Green and Karickhoff (1990) suggested that the importance and urgency of developing a generalized procedure justifies some sacrifices in scientific rigor and accuracy.

The calculation of K_{oc} from K_d for chlorpyrifos (Table 3.5) assumes the distribution isotherm is linear, but if one examines the line fit plots (Figure 3.4) it is evident that the assumption of linearity is not obeyed and this increases the error associated with the K_{oc} value. Although, the K_{oc} value, 1131 g/ml (from K_d), is within the range of literature values provided, it was, therefore, not considered as a useable estimate of K_{oc} . Green *et al.* (1993) found that chlorpyrifos did not conform well to the assumption of isotherm linearity and this further supports the decision to not use this value.

The potential causes of irreversibility or non-singularity are according to Pignatello (1989): Artifacts due to method; chemical or biological transformations; competitive adsorption from natural adsorbents; "irreversible" or "resistant" fractions of sorbed compounds and failure to establish equilibrium. All of which have been discussed elsewhere in this study except for the "irreversible" or "resistant" fractions. Resistant is defined by Pignatello (1989) to mean the compound under study has not desorbed during the time of the experiment, but will eventually desorb in its original form. Irreversible is defined, by the author, as that fraction that cannot be recovered in its original form. This area of study has barely been explored and Pignatello (1989) discusses the effects on the value of the partition coefficient and the mobility of pesticides.

The complex nature of colloidal surfaces in soil, which defies exact identification of mechanisms, undoubtedly contributes to a suite of sorption rates for each soil, depending upon the specific interaction of the sorbate with each sorbent component (Green and Karickhoff, 1990). Soil organic matter tends to dominate the sorption process for many pesticides in most soils and sorption of non-ionic pesticides on organic matter generally requires hours to days to achieve apparent equilibrium. For practical application, the 24 hour equilibration period used in the present study probably produced sorption coefficients that represent macroscale equilibration quite well, even though equilibrium may not be reached at the internal sorbent sites. The assumption of equilibration when using K_{oc} has therefore acceptable error.

A more significant issue is the question of whether or not equilibrium is reached in the field? In other words is the use of K_{oc} realistic with regards to field applications. This question is difficult to answer in a general sense because the field systems being simulated may or may not be near equilibrium. In general, the assumption of equilibrium results in an over prediction of retardation of pesticides in the field and the K_{oc} values for endosulfan and chlorpyrifos may, therefore, be too high as a result of the assumption of equilibrium.

The last two assumptions that sorption occurs on organic matter only and all organic matter is similar can result in as many errors as the first two. This can be seen in the variability in the K_{oc} for HR1 and HR2 values before they were averaged. The K_{oc} for HR2 is higher than for HR1 for endosulfan (Table 3.8) although HR1 has a higher organic carbon content. This could be due to other mechanisms and forces being involved in the sorption process than hydrophobic partitioning. It also explains why

sorption of pesticides on soils with the same organic carbon content do not necessarily result in the same K_{oc} . For example, the K_{oc} values from the present study are not the same as the literature values for soils with the same organic carbon content. The type of clay and nature of the organic matter is probably contributing to the sorption and therefore different values were obtained.

Green and Karickhoff (1990) suggested that a reasonable estimate of sorption is better than no estimate at all. They concluded that as long as the errors are analyzed and attempts are made to quantify them then the K_{oc} approach is acceptable. This was achieved in the present study by calculating the standard deviations for each K_{oc} (Values in parenthesis in Tables 3.5 and 3.8) as well as by the qualitative analysis which has been provided above.

3.5.7 Effects of dissolved organic matter on the sorption coefficient

Chiou *et al.* (1986) found that the presence of high-molecular weight material in water even at trace quantities can significantly enhance the apparent water solubility of some otherwise extremely insoluble organic compounds by partition-like interactions with the microscopic organic environment of the dissolved humic material. As a result, the authors suggested that the apparent concentration (or solubility) of a solute in water containing high-molecular weight organic matter may be greater than that in pure water. The authors provide an expression that relates the solubility enhancement to the K_{oc} or K_{DOM} (dissolved organic matter, DOM). The authors concluded that if this effect is not taken into account, the K_{oc} value could be significantly enhanced.

Gschwend and Wu (1985) demonstrated that if precautions are taken to either eliminate or account for the nonsettling microparticles in water, the calculated true K_{oc} values remain constant for all the compounds used in the study over a wide range of sediment-to-solution ratios. The authors concluded that it would thus seem that the relatively large variation of the K_{oc} values as commonly observed, and observed in the present study, for highly water-insoluble organic compounds with different soils and sediments, could be partly related to their different extents of water solubility enhancement by dissolved and suspended organic matter. This is also a possible explanation for the variation of the sorption coefficients determined in the present study

and in the literature values. This effect of DOM is dependent on the size and polarity of the DOM.

The water of the Hex River Valley has the typical brown colour of Western Cape waters due to high amounts of dissolved organic matter. It is possible that if the sorption experiment had been carried out using the water which is used for irrigation instead of the de-ionised water which was used, the sorption coefficients would have been lower.

3.5.8 K_{oc} - K_{ow} approach

The K_{oc} values (Tables 3.5 and 3.8) calculated indirectly from K_{ow} were high for endosulfan and chlorpyrifos compared to the experimental values. The K_{ow} method, for chlorpyrifos, was not suitable and over-estimated K_{oc} by almost forty times. This is because chlorpyrifos is partitioned to a greater extent into the solvent, octanol, than it is in the polar high-molecular weight amorphous solid material of organic matter. This is an artifact of the K_{oc} - K_{ow} approach not being able to take into account the quantity and quality of organic matter (Hassett and Banwart, 1989). In addition, materials such as the surfactants and other additives in the formulation of the commercial grade chlorpyrifos alter the aqueous chemistry of the sorbing species and according to Hassett and Banwart (1989), result in inaccurate predictions derived from K_{oc} - K_{ow} relationships. The K_{oc} from K_{ow} for endosulfan was 26.48 L/g while the experimental K_{oc} was an average of 17.52 L/g and although this is a better prediction it still overestimates the hydrophobic contribution to sorption probably for the same reasons as discussed above. Therefore, while the K_{oc} – K_{ow} relationship has proven to be adequate for many uses, in this case and for these pesticides the relationship is neither accurate enough nor does it encompass enough chemistry to be used indiscriminately.

3.5.9 Mechanisms and the surface area sorption coefficient (K_{ds})

The complexity of the solid matrix of soils prevents clear definition of sorption mechanism for most soil-pesticide combinations. The mechanisms responsible for the sorption of the pesticides cannot be determined from the isotherms presented in this study. Aspects of the mechanisms can be investigated by carrying out the sorption experiments at different temperatures and by using model adsorbents. A detailed analysis of the possible reactions between the functional groups of the soil components and that of the pesticides is beyond the scope of this study.

It is, however, well known that organic matter is primarily responsible for the sorption of non-ionic, hydrophobic molecules and the mechanism of this sorption has been investigated extensively. According to Chiou (1989), the mechanism of sorption into organic matter is one of a partitioning uptake. The less exothermic reaction between these pesticides and organic matter is suggested by the author to be because it is entropy driven and more a result of the dislike of the pesticide for water and the like of the mineral surfaces for water than any strong bonding forces. An implication of this partitioning mechanism, on the mobility of these pesticides, is if there is no water the pesticide does not partition into the organic matter. However, this is inconsequential because if there is no water the pesticides cannot be transported by runoff or leaching to water bodies.

The contribution of the mineral surfaces becomes more important the lower organic carbon content and higher the clay content. It is interesting to note that the sorption coefficients calculated from the surface area contribution (SS) of the organic matter and mineral surfaces gave much more reasonable sorption coefficients than the K_{ow} – K_{oc} method which considered hydrophobic interactions only. The sorption coefficient based on SS (K_{ds}) for endosulfan was 18.28 L/g for HR1 and 9.27 L/g for HR2 while the experimentally determined K_{oc} was 17.50 L/g. The higher experimentally determined K_{oc} value for HR2 than the K_{ds} suggests that the hydrophobic partitioning in HR2, due to the organic matter, is greater than anticipated by the SS equation. The K_{ds} for chlorpyrifos is 11882 ml/g for HR1 and 6025 ml/g for HR2. The higher K_{ds} values than K_{oc} values are expected since the mineral fractions have been taken into consideration in calculating K_{ds} but not in K_{oc} . They are, however, not as excessively high as the K_{ow} – K_{oc} estimates and the HR2 value for chlorpyrifos, 6025 ml/g, is the same value as the K_{oc} suggested by the model GLEAMS as the sorption coefficient for chlorpyrifos.

In general, if literature values for sorption coefficients are much greater than the experimentally determined sorption coefficients of interest as is the case with the literature values for K_{oc} (calculated from K_f) for chlorpyrifos (Table 3.5) despite the same organic carbon content, this is usually because of the contribution of clay, like smectite, to the sorption of the pesticide (Green and Karickhoff, 1990).

3.5.10 Sorption measurement techniques

The previous discussion demonstrates how isotherm shapes and the interpretation of them are highly variable. This variability depends on the equilibration time; concentration range and various other technique related parameters. Sorption measurement is considered an estimation procedure in this study because laboratory-derived sorption parameters constitute estimates of sorption in field soils. Certain techniques used in the sorption experiment can result in the over-estimation or under-estimation of the sorption coefficients.

Sorption methods can be divided into two principal categories: direct and indirect measurements. Both require equilibration of a soil sample with an aqueous pesticide solution of known initial concentration. Direct methods involve measurement of both solution concentration and adsorbed concentration; after equilibration the sorbed pesticide is displaced from the soil by an appropriate solvent and measured directly. Indirect methods determine the quantity of sorbed pesticide by measuring the change in solution concentration resulting from sorption of pesticide from solution onto the soil; in this case, the quantity of sorbed solute is assumed to equal the quantity lost from solution.

The method used in this study, the indirect batch-suspension measurement, is the most common and consists of agitating soil and pesticide in a closed vessel for a sufficient time to achieve apparent equilibrium in the system. Experimental variables include the solution/soil ratio, temperature, antecedent condition of the soil, type of vessel and nature of agitation. Green and Karickhoff (1990) warn that not all these variables have been standardized and can have a significant effect on the results. The United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (1998) provides standardized and regulated methods for sorption experiment with pesticides and the present study followed these guidelines as closely as possible.

A problem that plagues all sorption methods is the chemical or biological transformations of pesticides during the period of equilibration. A variety of procedures designed to attenuate microbial activity have been evaluated but such treatments often have other adverse effects on the accuracy of sorption measurements (Green and Karickhoff, 1990). Autoclaving has been used to sterilize soils, but this destroys the structure of the soil which is vital to the sorption procedure. Toluene has also been

used but this would interfere with the chemistry of the pesticides. Gamma-irradiation is commonly believed to have the least impact on soil properties (Scow, 1993). The apparatus needed for irradiation was unobtainable so the soils in this experiment were not sterilized.

Besides biological degradation, chemical degradation also affects the results. Chemical degradation is more easily quantified. The US EPA, Office of Prevention, Pesticides and Toxic Substances (1998) guidelines suggested that for each initial concentration/soil sample there should be a duplicate to which no soil is added. This resultant concentration of the soilless blank is then used as the initial concentration when calculating the amount sorbed by difference. This would, however, have doubled the number of samples, time and expense of the experiment and was therefore not an option. One soilless blank with a chosen pesticide concentration for each sorption experiment was, however, included in the present study as a check to ensure degradation was not excessive. This could not, however, be extrapolated to all the samples because chemical degradation follows first-order kinetics and is dependent on the initial concentration. Eight soilless blanks were included in the sorption experiment for each pesticide and for all the soilless blanks chemical degradation was less than 10% of the initial concentration. The highest values being for chlorpyrifos which is expected as it is specifically designed to be more degradable. Chemical degradation refers to hydrolysis, oxidation and photolysis. Endosulfan is stable in light whereas chlorpyrifos is sensitive to light nevertheless all equilibration and storage excluded light and the samples were stored at below 5°C. Endosulfan and chlorpyrifos are both sensitive to alkaline conditions but chlorpyrifos is more easily hydrolyzed. They both degrade faster at neutral to high pH. However, the soils HR1 and HR2 are slightly acidic as reported in Chapter 2 and this may slow degradation down. Hydroxyl ions from solvents used in the experiment and the C₁₈ extraction column may also have contributed to degradation. The additive effect of biological degradation to chemical degradation may be significant and this emphasizes the importance of considering degradation affects on sorption results.

An alternative procedure designed to attenuate microbial activity could have been used. Dao *et al.* (1982) suggested that the use of initially air-dry soil, a brief equilibration period and a low temperature minimizes transformation. Air-dry soil was used in the sorption experiments of the present study. However, the most commonly used 24 hour equilibration period was used. Felsot and Dahm (1979) demonstrated that chlorpyrifos reached equilibration within two hours. The United States

Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (1998) advise, however, that the equilibration time is soil specific and should be determined in an experiment prior to the sorption test. Once again this would have increased the time and expense of the experiment and 24 hour were considered acceptable for the two pesticides.

Ultimately, the lack of account for the degradation of the pesticides results in over-estimated sorption coefficients. The amount sorbed is calculated from the difference of the initial concentration and the equilibrium concentration. A low equilibrium concentration could be due to degradation and not sorption. The sorption coefficients (K_d) for chlorpyrifos (Table 3.4) do not appear to be high when compared to literature values. Thus, either degradation was minimal or the sorption coefficients are even lower. For endosulfan, however, the sorption coefficients (Table 3.7) do seem over-estimated in comparison to the literature. This may be the result of degradation. Endosulfan is also volatile and one of the major pathways of distribution in the environment is dissipation from the soil surface and leaves. The seemingly over-estimated sorption coefficients for endosulfan may, therefore, be due to the volatilization of the pesticide during centrifugation and extraction.

Isotherm singularity is an assumption made when using and calculating K_{oc} . Pignatello (1989) suggested that the sorption of pesticides to dissolved colloids and suspended matter could contribute to non-singularity of sorption isotherms. The author states that the sorption of compounds to dissolved and colloidal (nonfilterable, nonsettling) particles in the aqueous phase can inflate actual concentrations. The author continues that this is only important for compounds with high sorption tendency like chlorpyrifos and endosulfan, which are also highly hydrophobic compounds. The samples were not filtered before extraction. The supernatants were transferred to sample bottles using a Cambridge pipette to avoid visible organics. A small amount of organic colloidal material may have been transferred and the pesticide sorbed to this would have been extracted. This would have increased the equilibrium concentration and decreased the amount sorbed. However, this amount was considered negligible compared to the loss which would have occurred by volatilization, and sorption to apparatus, during filtration.

Sharpley *et al.* (1981) reported that the assumption that the mixing process in the laboratory is the same as in the field, i.e. the shaking of a small soil sample with a certain volume of water is the same as the interaction of the surface soil layer with precipitation, results in the over-estimation of the sorption coefficient. Different degrees

of turbulence, as a result of different rainfall, runoff and soil-surface characteristics, influence the mass of soil layer that is involved in the field.

The percentage recoveries for extraction and GC analysis reported in Appendix B, Table B.5, are low, however, these were corrected for by making the area of the peak of the standard equivalent to the expected concentration (i.e. the concentration calculated based on the label concentration of the commercial grade product). Thus, the equilibrium concentration calculated from this peak is automatically corrected for recovery losses. If greater accuracy and precision are required for example in regulatory and legal issues, a series of standards made up to the same range of concentrations as the samples should be used to construct a calibration line for quantification. Also, the pH of the samples should be determined and the possibility of hydrolysis on the C18 cartridge investigated. The samples should be sufficiently diluted to avoid saturation of the cartridge.

3.5.11 Formulation

In an extensive review of field measured pesticide concentrations, Wauchope (1978), concluded that pesticides that are water insoluble and, therefore, usually applied as emulsions show the second worst (after highly soluble wettable powders) long-term losses which may amount to 1% or less of the amount applied.

In The United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (1998) guidelines it is advised that technical grade pesticide be used in the experiments and in the literature many researches use analytical grade pesticides. A contentious issue between scientists researching pesticide mobility and the companies producing the pesticides is that scientists do not always use the commercial grade product in laboratory experiments. The formulation of the pesticide affects its sorption and mobility (Dannie Fourie, Sanachem, personal communication). The commercial grade chlorpyrifos (480 g/L EC) and endosulfan (475 g/L SC) were therefore used in the sorption experiments, although this introduces more uncertain variables, it is more environmentally realistic.

EXTOXNET state that in open waters, the concentration and persistence of chlorpyrifos will vary depending on the type of formulation and this will be the case for all pesticides. For example, immediately after entering open waters, emulsifiable concentrates tend to produce a large increase in chlorpyrifos concentrations in water.

As the pesticide adheres, or sorbs to sediments and suspended organic matter, however, concentrations rapidly decline. The chlorpyrifos used in this study is the same as that used in the Hex River Valley and is formulated as an emulsifiable concentrate. This, coupled with the less persistent nature of chlorpyrifos, implies that any water samples collected in which a high peak of chlorpyrifos is found, are most likely from a recent application or spillage of chlorpyrifos.

The endosulfan is formulated as a suspension concentrate, which like the emulsifiable concentrate has additives to increase the pesticides solubility in water. The effects of formulation on sorption were accounted for in the present study by using the formulated product in the experiments. The effects in the field due to formulation are complex and beyond the scope of this study.

3.5.12 The interpretation of the value of the sorption coefficient with respect to leaching and runoff

The K_f and K_d sorption coefficients are the most directly descriptive and site specific coefficients. The Freundlich isotherm described the sorption of chlorpyrifos the best. The K_f for chlorpyrifos on HR1 (27.19 ml/g) was higher than for HR2 (10.96 ml/g) which is a result of the higher organic carbon content, clay content, iron oxide and specific surface area of HR1 compared to HR2. Both 27.10 and 10.96 ml/g are low compared to literature values for similar soils and it is most likely that they are actually lower if the over-estimation, due to method artefacts, is taken into consideration. The K_{oc} value (1490 ml/g) for chlorpyrifos was best estimated using K_f and is also much lower than reported literature values (6630 ml/g). It is interesting to note that in the screening model (Section 3.3.3) used to derive indices for leaching probability, a value of 6070 ml/g for K_{oc} was suggested and used. In conclusion, therefore, for the site-specific case, the Hex River Valley, the use of general literature values to describe sorption is not valid. Thus, although, chlorpyrifos is sorbed more strongly than a number of other pesticides, it is less strongly sorbed than expected.

Knisel and Leonard (1993) state that pesticide runoff potential is sensitive to the K_{oc} value and that for most soils pesticides in surface runoff decreases as the K_{oc} decreases for K_{oc} values in the range 0 to 500 ml/g. This decrease occurs because for high mobility compounds the initial infiltrating rainfall reduces the concentration in the 0-1 cm surface soil layer and thereby the runoff source. For K_{oc} values greater than 1000 ml/g, pesticide adsorption to sediments reduces concentrations in the water

phase of runoff so that total surface transport is strongly influenced by erosion and sediment transport. Thus, the major pathway of loss of chlorpyrifos would be attached to eroded particles in runoff.

It is important to remember these sorption coefficients were determined in an isolated laboratory environment and in the field the influence of climate, management practices and geohydrology would have dramatic effects on the mobility of the pesticides. For example, the lower laboratory determined sorption coefficient of chlorpyrifos combined with the sandy soils with high water tables in the Hex River Valley means the potential for chlorpyrifos to leach to groundwater is greater than expected.

The sorption of endosulfan (including the isomers) was best described by the linear partition sorption coefficient (K_d). The K_d (245, 224, 277 ml/g for endosulfan, endo- α and endo- β respectively) are higher for HR1 than for HR2 (166, 159, 182 ml/g for endosulfan, endo- α and endo- β respectively) which is due to the soils properties as described above for chlorpyrifos. These values are high compared to the literature values for similar soils, but are middle of the range of the values reported. The K_{oc} values (17.52, 16.44, 19.22 L/g for endosulfan, endo- α and endo- β respectively) were best estimated using the K_d and are also higher than the literature values (12.40, 13.30, 15.77 L/g for endosulfan, endo- α and endo- β respectively). These data also prove that the use of a single sorption coefficient value for endosulfan- α and - β is relatively valid. The endo- β sorption coefficients are generally greater than for just endosulfan meaning it is more highly sorbed and the two isomers will most likely be distributed in the environment in similar proportions. However, the predominant metabolite of endosulfan, endosulfan sulphate, is the major environmental contaminant which both isomers form indiscriminately. It should be noted that if the sorption data were corrected for method artefacts such as degradation and assumptions like equilibration, the values of the coefficients would decrease. Nevertheless, the results show that endosulfan is strongly sorbed in the soil of the Hex River Valley as expected. The value used in the initial screening method (Section 3.3.3) was 12.40 L/g, for K_{oc} , compared to the experimentally determined 17.52 L/g. In the soil of the Hex River Valley the most likely pathway of endosulfan loss would be attached to eroded particles in runoff. These soils are not particularly susceptible to runoff and so this would have to be coupled with an intense rainfall event and enough slope, amongst other factors.

3.5.13 Variability of organic matter in soils

The soils sampled in this study were from the surface horizon and sorption of most pesticides in surface soil is usually measurable with acceptable precision by the batch method. However, precision is often poor on subsoil or underlying materials where sorption is low. The current and future public and scientific interest in contamination of groundwater by pesticides will undoubtedly be accompanied by attempts to measure sorption of pesticides on low organic matter horizons below the plow layer (Green and Karickhoff, 1990). Green *et al.* (1993) found that for chlorpyrifos sorption on a surface soil (0-20 cm; 1.30 %OC; pH_{H_2O} 6.7; type 1 in Table 3.3) the K_d was 9.43 ml/g while for the subsoil sample (60-80 cm; 0.55 %OC; pH_{H_2O} 6.8) the K_d was 0.67 ml/g. It is very likely that the subsoil layers of the Hex River Valley have very low organic carbon and if the pesticides did reach these layers sorption would be low and contamination of the groundwater possible. Scow (1993) reviewed evidence for the eventual mobility of sorbed chemicals including the findings that many groundwater aquifers are contaminated with pesticides and organic chemicals that have relatively high-sorption partition coefficients.

The % organic carbon measured in the soil of the Hex River Valley was associated with high standard deviation and this accounted for most of the variability in the K_{oc} values. One of the shortcomings of laboratory sorption experiments performed on only two soil samples which represent an area like the Hex River Valley is the lack of consideration for the spatial variability of organic matter. Oliver *et al.* (1998) concluded that it is the variation in soil organic matter which is much more likely to be associated with significant 'hot spots' of leaching whereas that in the hydrodynamic dispersivity of solutes flowing through the matrix is of much less consequence. The authors suggested that 'expensive' hydrodynamic properties need to be measured at much fewer locations while the easy, 'inexpensive' measurement of organic carbon content is the most important parameter and should be measured at more locations. Future studies of pesticide mobility in the Western Cape could be achieved by simple measurements of organic carbon content variation in the soils and subsequent visualisation with geo-statistics and kriging could identify points of potential vulnerability.

3.5.14 Inorganic versus organic sorption

A comparison of the sorption coefficients determined for phosphate to those determined for chlorpyrifos and endosulfan reveals that the difference in sorption capacity between the two soils HR1 and HR2 is minimal for phosphate compared to the pesticides. The K_d for phosphate on the two soils is 16.5 and 16.3 ml/g while for chlorpyrifos it is 27.19 and 10.96 ml/g and for endosulfan it is 245 and 166 ml/g. The effects of the variability of clay content in the two soils seem to have less effect on the sorption of the anions than the variability of organic carbon content on the pesticides. Also the sorption capacity for chlorpyrifos on the soil, HR2, which is the dominant soil type in the Hex River Valley, is less than or equal to the soil's sorption capacity for phosphate. The K_d for chlorpyrifos is 5.92 ml/g for HR2 while for phosphate it is 16.3 ml/g and the K_f for chlorpyrifos is 10.96 ml/g for HR2 while for phosphate it is 10.6 ml/g. Thus, the conclusion in Chapter 2 that phosphate sorption is a good, preliminary indicator of soils which are likely to be susceptible to pesticide leaching or runoff, is quite valid with regards to chlorpyrifos even though the one molecule is an inorganic anion while the other is organic and non-ionic. Endosulfan is sorbed to a considerably greater extent in the soils than phosphate is. This is a good indication of the power organic matter has to sorb non-ionic, organic molecules.

3.6 Conclusions

In Chapter 2 the properties of the Hex River Valley soil were defined and related to the expected behaviour of the pesticides as reported in the literature. On the most simplistic level the soils were defined as being more vulnerable to the leaching of pesticides to groundwater than to runoff. However, non-ionic, hydrophobic pesticides are sorbed strongly by soil and are known to be more susceptible to loss attached to sediment in runoff. The Hex River Valley soils have low organic carbon and low clay content, and it was anticipated that the sorption capacity of the soils for the pesticides would be less than expected.

This chapter experimentally defined the interaction of these soils with the pesticides. Endosulfan was more strongly sorbed than chlorpyrifos which was expected. Organochlorine pesticides are more persistent than organophosphates by design. Chlorpyrifos, as anticipated, was less strongly sorbed to the soils than suggested by the literature, an organic C-referenced sorption coefficient of 1490 ml/g was determined

compared to the literature values of 6630 ml/g for a similar soil. Endosulfan (endo- α + endo- β) was more strongly sorbed than expected with an organic C-referenced sorption coefficient of 17.52 L/g compared to the literature values of 12.40 L/g. These coefficients were estimated using the simplest, most valid methods. The model assumptions and artefacts of the experimental design are, however, most likely to have resulted in the over-estimation of the sorption coefficients. The findings of this chapter demonstrate that the pesticides are strongly sorbed to soil but the potential for the pesticides to move deeper into the soil and to be more mobile is greater than expected especially for chlorpyrifos.

As was reported in Chapter 2 predicting the mobility of pesticides is not as simple as defining soil properties and there are numerous complications and exceptions to expected behaviour. In the present chapter we saw that looking at the soil and pesticide properties only was still not enough. Only a limited number of the many factors influencing pesticide mobility and complications with respect to sorption experiment were discussed. Issues like the kinetics of sorption and desorption, and the relationship between degradation and sorption are highly significant to pesticide mobility, but are beyond the scope of this study. Geohydrology, climate and management practices also add to the complexity of interpreting sorption coefficients in terms of pesticide mobility.

The main objectives of this chapter were achieved. The sorption coefficients were determined and compared to literature values. The final objective of this study is to use the site-specific sorption coefficient, determined in this chapter, in the GLEAMS model which uses the sorption coefficient along with hydrology, erosion and pesticide related parameters to simulate pesticide interaction in a particular field environment. Thus, the sensitivity of the GLEAMS model, to the site-specific sorption coefficient compared to the default literature value provided by the model can be assessed as well as achieving a better understanding of the vast array of factors affecting pesticide mobility.

CHAPTER 4

Modelling the Mobility of Endosulfan and Chlorpyrifos with GLEAMS (Groundwater Loading Effects of Agricultural Management Systems)

4.1 Introduction

A variety of physical, chemical and biological processes determine the environmental fate of pesticides. The rates at which these processes operate will determine the mobility and the persistence of a pesticide. The rates and pathways of each of the processes, in turn, are modified to a considerable extent by various environmental factors as well as the properties of the pesticide itself. The experimental measurement of these processes, in the laboratory and field, is an expenditure few can afford, especially in Africa.

Therefore, mathematical models designed to simulate the fate and transport of agrichemicals in runoff, attached to sediments, and/or in soil percolate (LEACHM, Wagenet and Hutson, 1986 and GLEAMS ,Groundwater Loading Effects of Agricultural Management Systems, Leonard *et al.*, 1987) were developed. These models were designed for such specific purposes as management alternative comparisons, screening new chemicals for potential problems and environmental risk assessments. According to Truman (1998) all models, however, are approximations of natural hydrological/chemical fate and transport systems. Where measured data are available, most models can be calibrated to fit or represent observations within confidence intervals of the data. However, for prospective model application in different systems and climates, little confidence can be placed in absolute numerical outputs. As a result, the defensible and usual application/purpose of simulation is for comparative analysis among scenarios such as different soils, chemicals, climates and management alternatives (Truman, 1998).

In this chapter, the GLEAMS model is used to simulate the coupling and feedback of the numerous factors and processes affecting pesticide mobility. No attempt is made to calibrate the model, as no field data are available. GLEAMS has already been extensively validated (Leonard *et al.*, 1987) and so no validation of the model is attempted in the present study. The sensitivity of the model to the organic-referenced sorption coefficient

(K_{oc}) and to different soil properties is examined. No absolute prediction is intended in using the model, but rather an attempt is made to obtain a general estimate of the mobility of the pesticides while gaining a better understanding of processes and emphasising the likely pathways of pesticide movement in the Hex River Valley. Furthermore, the data collected and model set-up for the Hex River Valley could also be used as a basis for future, more in-depth and extensive modeling in the Western Cape.

In Chapter two of this study the properties of 2 soils from the Hex River Valley were characterised. In Chapter three the soil and pesticide properties in conjunction and in isolation, i.e. in the laboratory keeping other variables constant, were characterised and site-specific sorption coefficients were determined. In this chapter the results of Chapter two and three are combined with climatic data, field description data, erosion information and management data. The simulation results are compared to the observed concentrations of pesticide in Hex River Valley water and the shortcomings of the model are discussed.

4.2 Model Background

Scientists of the U.S. Department of Agriculture, Agricultural Research Service, developed the CREAMS (Chemical Runoff Erosion Agricultural Management Systems) model (Knisel, 1980) to evaluate nonpoint source pollution from field-size areas. The CREAMS model was state-of-the-art and represented physical processes (Leonard *et al.*, 1987). The model had the capability of reflecting differences in water, sediment and chemical responses from different management practices. Data available from diverse physiographic and climatic regions were used to validate CREAMS (Knisel and Leonard, 1983).

Problems of pesticides in groundwater and increased emphasis on groundwater quality led to modification of CREAMS to consider the impact of agricultural management systems on groundwater loading (Leonard *et al.*, 1987). The GLEAMS model was developed to utilise the management-oriented, physically-based CREAMS model (Knisel, 1980) and incorporate a component for vertical flux of pesticides.

GLEAMS consists of a single computer program of interactive processes. Separate hydrology, erosion and pesticide parameter files and output files are maintained. Description of the model and the input set-up for the Hex River Valley will be given by major component.

The simulation, which will be described in each component, is for a 40 ha field. This is a hypothetical field which has similar qualities to the average field in the Hex River Valley. The simulation is for one year from July 1997 to July 1998. The climatic data used for the simulation were the observed data for this period. This period also includes the time of pesticide and irrigation application in the Hex River Valley as well as the vine growing season and period in which water sampling has taken place. All input data were experimentally determined or measured in the field when possible, or taken from literature of previous studies in the Hex River Valley. If literature values were not available best estimates were made based on the GLEAMS guidelines and tables of data (Knisel and Leonard, 1993).

4.3 Hydrology Component

The 40 ha field that was used for the simulation was at an elevation of 425m above sea level and latitude of 33° 30' 00" S. The details of the input parameters are in the Hydrology component output provided in Appendix C.2. The leaf area indices for a grapevine canopy used in the input and repeated in the output were taken from Lascano *et al.* (1992). The Hydrology output is for half of 1997 and the whole of 1998 and therefore the quantities for 1998 are twice those of 1997. The input parameters in Table 4.1 are the parameters which are not provided in the output, but are no more important than the input parameter provided in the output in Appendix C.2. The data in Table 4.1 are for the Fernwood soil (HR2) which is the dominant soil type in the Hex River Valley.

The precipitation data used for the simulation are input as a separate file and are provided in Appendix C.1. The rainfall data were provided by the ARC, Institute for Soil, Climate and Water at Nietvoorbij, Stellenbosch which has two weather stations in the valley. These data, in the precipitation file, are the rainfall for the period July 1997 to July 1998 plus the estimated amount of daily irrigation. An average of 0.49 cm of irrigation water is applied per ha per day during the period October 1st to April 30th of the following year (Hexvalley Irrigation Board). Farmers in the valley suggested that irrigation water would not necessarily be applied every day during this period so the irrigation water was summed and applied only every 3 or 4 days. GLEAMS does have the option to simulate irrigation based on plant water needs but fairly accurate irrigation information was available for the Hex River Valley so this option was not used.

Table 4.1: Input parameters for the Hydrology component of the GLEAMS simulation for the Hex River Valley soil HR2.

Input parameter	Field in Hex River Valley
Effective Saturated Conductivity (cm/hr):	
Soil Horizon ¹ 1	0.86
Soil Horizon 2	2.00
Organic Carbon (%)²:	
Soil Horizon 1	1.7
Soil Horizon 2	0.89
Clay Fraction (%)³:	
Soil Horizon 1	2
Soil Horizon 2	2
Silt Fraction (%)⁴:	
Soil Horizon 1	5
Soil Horizon 2	5

¹ GLEAMS provides the option to input five different soil horizons

² The organic carbon content was increased, compared to the measured value for HR2, in order to take into account that HR2 was sampled from an off field site whereas GLEAMS is for an agricultural field site. Crop residue would contribute to OC % especially in the top 1cm layer.

³ Less than 0.002 mm

⁴ Greater than 0.0020 mm but less than 0.05 mm

The root zone is divided into nine computational layers for the water balance calculations. The input of water for each layer is the output from the layer immediately above and is based on a tipping bucket concept. Soil profile description and crop data are used to estimate effective rooting depth. Soil data are input by soil horizon (Table 4.1) and the model distributes values for porosity, water retention characteristics and organic matter into the appropriate computational layers. The surface layer is set at 1 cm thick and the thickness of layer 2 is adjusted such that the total thickness of layers 1 and 2 is 1/6 of the effective rooting depth. This provides for consistent thickness between the hydrology and pesticide components. Although a surface layer of fixed thickness is assumed, it is recognised that infiltration control and interaction of runoff and chemical extraction occurs over some depth that varies with tillage, time since last tillage, rainfall, soil texture, soil water content and soil cover among other things. According to Leonard *et al.* (1987), these

relationships have not been established so the surface layer is considered constant at 1 cm.

The water balance computations in GLEAMS, are the same as those in CREAMS (Knisel, 1983). The storage-routing technique used to simulate percolation from layer-to-layer in CREAMS is used in GLEAMS but the volume of percolation by layer is retained for routing pesticides which will be described in that component.

Soil evaporation and plant transpiration are calculated layer-by-layer and their respective identities retained also for pesticide movement. GLEAMS provides the option to simulate potential evapotranspiration. The model users can select between the Priestly-Taylor or Penman-Monteith methods (Knisel and Leonard, 1993). The Penman-Monteith method was selected as it is best for arid climates. However, it requires additional input data (mean sea level, mean monthly wind movement and dewpoint temperature) which are provided in Appendix C.2.

4.4 Erosion Component

The input file for the erosion component is provided in Appendix C.3. This is the format for all the component input files. In the output for the erosion component various input parameters are interpreted and described. Table 4.2 is a compilation of the input parameters for which there is no definition given in the output.

The erosion component of GLEAMS is essentially the same as that in CREAMS (Foster *et al.*, 1981). The only significant change is in the calculation of sediment particle characteristics. Foster *et al.* (1985) used additional data to better define aggregate sizes and their respective fractions in the detached soil. Specific gravity of the small and large aggregates, 1.8 and 1.6 g/cm³, respectively, were used. The equivalent sizes of the small and large aggregates were related to the fraction of clay in the soil matrix. The diameter and specific gravity for a certain fraction of detached sediment calculated by GLEAMS are provided on Appendix C.3.

The simplest options for field description and management were chosen. The slope of the field was considered uniform and all parameters e.g. soil erodibility, soil loss ratio and tillage, were considered constant throughout the year. GLEAMS does provide the option to divide the slope into 6 segments and describe each segment of the slope differently as well

as dividing the year into 10 parts with different management options for each part of the year.

The field, or natural drainage area, is represented by a combination of such elements as overland flow, channel and temporary impoundment. Card 4 FLGSEQ, in Table 4.2, ensures the proper sequences of these elements and determines the order in which data are read and combinations made in the model.

Table 4.2: The input parameters for the erosion component for the GLEAMS simulation

Input parameter	Field in Hex River Valley
Card 4 FLGSEQ ¹	2 (overland – impoundment)
Specific surface area for clay particles ²	20 m ² /g
Organic matter surface area active in pesticide adsorption ³	2000 m ² /g
Soil erodibility factor	0.148 t.ha.h/ha.MJ.mm
Intake rate or saturated hydraulic conductivity of the pond bottom	2.00 cm/hr
Soil loss ratio	0.35
Management practice factor	1.0
Manning's "n"	0.038

¹ The flag to indicate the execution sequence of erosion–sediment submodels: 1 indicates overland and the option extends to 6 which is the most complex: overland-channel-channel-impoundment.

² The value suggested by GLEAMS for kaolinite was used.

³ This value is automatically input by GLEAMS and no option is given to change it.

The soil erodibility factor, 0.148, was estimated by using the average particle size distribution data from the textural classification and the relationship:

$$\text{Soil erodibility} = \text{TF} (12 - \text{OM}) + \text{SF} + \text{PF}$$

where SF and PF are approximate generalised structure and permeability factors, respectively, and are taken from tables in Knisel and Leonard (1993) and the textural factor (TF) is defined as:

$$\text{TF} = (\text{SI} + \text{VFS}) (100 - \text{CL})$$

where SI is percent silt, VFS is percent very fine sand and CL is percent clay.

The soil loss ratio in Table 4.2 represents the crop factor in the universal soil loss equation (Wischmeier and Smith, 1978) for a specific part of a year. The soil loss ratio is externally defined. The crop factor was defined according to Saayman and Lambrechts (1995) as 0.3 for the months October, March and April and 0.4 for the remaining months. A value of 0.35 was, therefore, used. The soil loss factor depends upon the overland flow profile and flow sequence. Management factors like crop and tillage practices affect the soil loss ratio. The same is true for the Management practice factor (Table 4.2) which has a value of 1.0, estimated using the land slope % and maximum slope length.

The hydraulic roughness or soil cover and roughness slow overland flow and reduce its sediment transport capacity. The reduction in velocity depends upon the depth of flow, the type of material on the surface and its density. Manning's "n" value is a measure of the resistance to flow, that is, the higher the "n" value the greater the resistance and lower the flow velocity. The Manning's "n" was provided by GLEAMS (Knisel and Leonard, 1993) and was based on $n = 0.01$ for overland flow over bare soil. It represents a smooth bare surface over which flow has occurred following tillage. The value increases according to the type of cover. The Barlinka vines grow like small trees and the foliage does not rest on the soil surface but grass is grown between the rows and the value suggested by GLEAMS for a moderate grass cover is 0.038 (Table 4.2).

4.5 Pesticide Component

The basic concepts simulated with the pesticide component of GLEAMS are the same as those in CREAMS (Knisel, 1983) with some additions that enable the estimation of movement within and through the root zone. The user can examine both surface and subsurface response for all pesticides without requiring a model for surface and another model for subsurface responses.

A simple representation of the complete system is illustrated in Figure 4.1. Pesticides may be aerially applied with some fraction intercepted by foliage and some fraction reaching the soil. Aerially-applied pesticides include herbicides, insecticides, acaricides, fungicides and defoliantes which have diverse chemical characteristics affecting sorption/desorption onto soil and organic carbon, sorption and washoff from living and dead plant tissue and degradative characteristics. Degradation differs from foliage, surface soil and root zone. It is a function of soil water, temperature, soil water gradients and chemical characteristics.

Methods of application may vary from ground equipment to aircraft, and the material may be applied as solids, dispersions, emulsions and solutions.

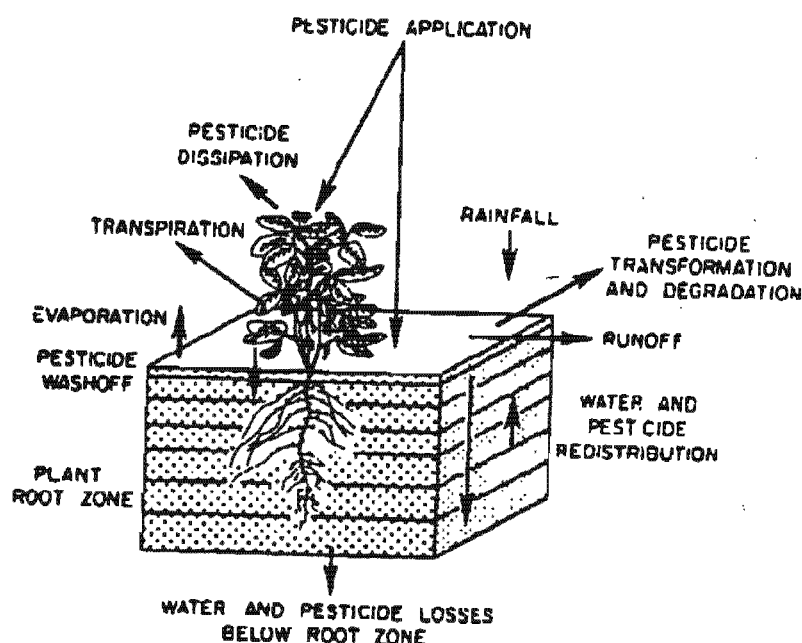


Figure 4.1 The physical system and processes represented in GLEAMS (after Leonard *et al.*, 1987)

Exact representation of pesticide application and agricultural management practices is nearly impossible. However, depth of pesticide placement is necessary to properly account for location and magnitude of the processes (Leonard *et al.*, 1987). The CREAMS model only considered surface processes and any injection below the surface 1 cm of soil was not considered. It is necessary in the GLEAMS model to specify the depth of incorporation or injection to obtain correct initial distribution among the soil layers.

Pesticides washed from the plant imply changed concentrations in the surface soil. Concentrations in the surface determine the amount that is available for extraction into surface runoff and/or movement into the soil profile.

Certain pesticide-input parameters are provided in the output of Appendix C.4. The commercial name of the pesticides chlorpyrifos and endosulfan, lorsban and thiodan, respectively, are used in the pesticide database which is provided with the GLEAMS model. The pesticide properties used in the input were a combination of data from the database provided and information provided by EXTTOXNET¹. The K_{oc} value was experimentally determined (Chapter 3).

4.5.1 Pesticide Degradation

The degradation rate of the pesticides is defined in terms of the half-life and different values are used for foliage and soil half-lives (Appendix C.4), the degradation on the foliage being faster than in the soil. Soil degradation can be specified according to soil horizon. The relationship used for pesticide degradation is, according to Leonard *et al.* (1987),

$$C_s(t) = C_{s(0)} \text{EXP} (-0.693t/S_{1/2})$$

where $C_{s(0)}$ is the pesticide concentration in the soil or foliage on the day of application in ppms, $C_s(t)$ is the pesticide concentration (ppm) in the soil or foliage at time t , and $S_{1/2}$ is the pesticide half-life in the soil or foliage.

GLEAMS operates with a daily time step since pesticide redistribution caused by water evaporation and transpiration are considered. Pesticide degradation must be calculated daily in order to adequately assess concentrations for evaporation and transpiration fluxes from the appropriate soil layers (Leonard *et al.*, 1987). The foliage concentration at the beginning of the simulation was considered to be zero for the two pesticides, since approximately 11 months passes before the next series of applications and the foliage half-life is only about 3 days.

GLEAMS can simultaneously simulate the movement of 10 pesticides and these can include parent compounds and their metabolites. The major metabolite of chlorpyrifos is 3,5,6-trichloropyridin-2-ol (TCP) and for endosulfan it is endosulfan sulphate. These metabolites were not in the GLEAMS database and the required parameters were not available so they were not included in the simulation. Endosulfan sulphate can be highly

¹ Extension Toxicology Network, Pesticide Active Ingredient Profiles at <http://pmep.cce.cornell.edu/profiles/endosulfan-ext.html>.

toxic and more persistent than endosulfan and future modeling should therefore incorporate it.

4.5.2 Pesticide extraction into runoff

The pesticide runoff component of the CREAMS model (Leonard and Wauchope, 1980) was not changed in GLEAMS. Leonard and Wauchope (1980) described pesticide distribution between the solution phase and solid phase in terms of a simple linear adsorption isotherm

$$K_d = \frac{C_s}{C_w} \quad (1)$$

where, at equilibrium, C_s is the concentration in the solid phase, mg/kg, and C_w is the concentration in the solution phase in mg/L. The distribution coefficient, K_d , is dependent upon pesticide characteristics such as the water solubility and soil properties like organic carbon among others, as discussed in Chapter 3. Since organic carbon is soil or site specific and it is desirable to use only pesticide-specific data as input, the K_{oc} is used as input for GLEAMS. The K_d is calculated in GLEAMS from the relation

$$K_d = K_{oc} (OC/100) \quad (2)$$

where K_{oc} is the linear sorption coefficient for organic carbon and OC is the organic carbon content of the soil expressed as a percent of the soil mass and input in the hydrology component by soil layer. The K_{oc} values of 1490 ml/g and 17517 ml/g for chlorpyrifos and endosulfan, respectively, were determined experimentally in Chapter 3 and were used in the simulation.

The rate of change of pesticide mass, Z , in the soil surface is, according to Leonard *et al.* (1987),

$$-dZ = C_w f dt \quad (3)$$

where f is defined as the water flux and the other terms were previously defined. Ultimately an extraction coefficient is determined via derivations detailed in Leonard *et al.*

(1987) which include soil porosity, soil specific gravity, rainfall depth, surface runoff depth, soil water storage capacity calculated in the hydrology component, and pesticide concentration in the soil after time t , amongst others.

4.5.3 Vertical flux of pesticide

The foregoing discussion of pesticide extraction into runoff provides the basis for pesticide movement through the soil surface layer and into and through the root zone.

Pesticide concentration in solution, C_w , in equation (1), is the concentration in the water that is available for percolation into soil layer 2. The pesticide mass, PERCM, transported from layer 1 becomes (according to Leonard *et al.*, 1987)

$$PERCM_1 = PERC_1 (C_{w(1)}) \quad (4)$$

where $PERC_1$ is the water mass percolated from soil layer 1. Using a simple pesticide accounting procedure, the pesticide mass percolated from layer 1 ($PERCM_1$) is subtracted from the pesticide mass in layer 1 and added to the pesticide mass in layer 2 after degradation and so on for each layer. The water mass percolated from each layer is calculated in the hydrology component using field capacity and initial soil water content. Leonard *et al.* (1987) state the potential loadings to the vadose or groundwater zone are calculated by the product of the concentration (C_w) and percolated water mass, PERC, for the last computational soil layer.

4.5.4 Pesticide transport with sediment

An enrichment ratio is calculated in the erosion component based upon the specific surface area of the sediment leaving the field and the specific surface area of the matrix soil. This ratio is a measure of the enrichment of the clay and organic matter fractions in the sediment that enables the estimation of the transport of the total sediment mass leaving the field. The enrichment ratio calculated in GLEAMS is a function of the size and composition of the large and small aggregates as given earlier in the erosion component of GLEAMS (Leonard *et al.*, 1987).

The pesticide mass transported with sediment is the product of sediment mass, enrichment ratio and concentration of pesticide in the sediment phase as given by C_s in equation (1). The pesticide concentration in the surface soil layer is used in the calculation of equation (1).

4.5.6 Pesticide evaporation and uptake

According to Leonard *et al.* (1987) pesticides that move readily with water (low K_d) may have significant quantities that move up in the soil profile as a result of evaporation or are taken up by plants. Leonard *et al.* (1987) provide a detailed discussion of the algorithms used to describe this aspect of pesticide movement. Because the two pesticides being considered in this simulation are strongly sorbed, however, and are not taken up by plant roots, no further discussion of this aspect is provided here.

4.5.7 Pesticide application

Chlorpyrifos and endosulfan are sprayed onto fields from tanks on the back of tractors or from tanks carried on farm workers' backs. The method of application stipulated in GLEAMS was therefore surface application. The details of application are provided in the output, Appendix C.4, when the model gets to the particular date (given as Julian date). Chlorpyrifos is applied as a pre-bud insecticide. This is around the last week of August for Barlinka vines in the Hex River Valley and it is applied again a week later. The rate for both applications was input at the prescribed concentration of 8.832 kg/ha. If chlorpyrifos is used effectively during these first two applications there should be no need to reapply it for the growing season. Although it is occasionally used to control outbreaks of ants, this was not considered in the simulation. Endosulfan is applied in the third week of September. AGREVO representatives advised that endosulfan is applied only once a year and at the very most twice a year and it is not used by all farmers. Due to the fact that it was being detected in the water sampled in the Hex River Valley a worst case scenario was assumed. Endosulfan was applied twice and at twice the suggested rate which amounted to 0.95 kg/ha.

4.6 Results of GLEAMS simulation

4.6.1 Hydrology and Erosion components

The output results are presented in the original format in Appendix C. The hydrology and erosion output will be discussed briefly, as the main focus of the present study is the pesticide mobility and therefore the pesticide component. The pesticide component is also intricately dependent on the hydrology and erosion output and so a discussion of the pesticide component output also encompasses a discussion of the other components. In the hydrology component no runoff was expected and 3.59 cm of percolation from the root zone was predicted for the second half of 1997, while for the whole of 1998 no runoff was predicted and 24.30 cm of percolation from the root zone was predicted (Appendix C.2).

The erosion component output estimated that the second half of 1997 had 51 storm events and 42.04 cm of precipitation (rainfall and irrigation) and no runoff. The whole of 1998 was estimated to have had 115 storm events from 94.11 cm of precipitation (rainfall and irrigation) which produced zero runoff. No loss of sediment in runoff was predicted and therefore the enrichment ratio calculated was zero. These results support the conclusions of previous chapters that the conditions in the Hex River Valley are such that the soils are not prone to runoff and that the soil is more susceptible to leaching or groundwater contamination. Russell *et al.* (1988) suggested that GLEAMS has the tendency to underestimate runoff but they state that in sand or loamy sand soils, where potential for downward movement is the highest, precise estimation of runoff is usually not needed since runoff (and chemical losses in runoff water) are typically quite small.

It is interesting to note that Dilshad *et al.* (1996) researched grey, sandy soils in north-west Australian semi-arid tropics, and found that the potential for these soils to be degraded by highly erosive rainfalls, common to the region, is high. They also found that farming practices strongly influence the soil surface characteristics (vegetation cover, roughness, soil strength), which in turn control surface runoff and sediment detachment and transport. Although highly erosive rainfalls are not common to the Hex River Valley, they do occur occasionally and as suggested by these authors could result in pesticide loss by erosion. The same authors also pointed out that soil conservation banks and no-tillage practices resulted in the least amount of soil loss.

4.6.2 Pesticide component

In the pesticide component output, Appendix C.4, lorsban and thiodan are referred to as pesticide 1 and 2, respectively. In agreement with the hydrology and erosion component GLEAMS estimated that none of the applied pesticides would be lost in runoff or attached to sediment. Despite the 24.3-cm of percolation predicted for one year, GLEAMS estimated that there would be no pesticides in this percolation and that the pesticides would not move beyond the top 20 cm of the 100 cm root zone.

The results of the simulation are presented graphically in Figure 4.2. In this Figure the change in concentration of the pesticides with time since pesticide application is depicted for each layer into which the pesticide moves. The concentrations used in Figure 4.2 are the concentrations after a storm event. GLEAMS provides the option of having the concentrations before and after each storm event but this was deemed unnecessary. Chlorpyrifos moves as far as the third computational layer (i.e. 10 – 20 cm) and the concentration in the top layer (0 – 1cm) decreased fairly rapidly due to the relatively short half-life and lower sorption coefficient compared to endosulfan. Chlorpyrifos is also more soluble than endosulfan. The second and third layers initially increase in concentration as the layers slowly fill up with overflow from the previous layer.

Endosulfan only moves as far as the second layer (1 – 10 cm) which is expected, since endosulfan has a high sorption coefficient and the decrease in concentration of endosulfan with time is slower as a result of its greater persistence and longer half-life than chlorpyrifos.

It is interesting to note that when the same input parameters were used for a five year simulation, the pesticides still only moved as far as the 33 – 46 cm layer. This is because, if the pesticides are applied according to label instructions or even in the case of endosulfan at double the rate suggested, by the time the next year's application comes the previous years application has degraded to zero or extremely low levels. Therefore, no accumulation occurs over time and subsequent slow movement of bands of pesticides is predicted by GLEAMS.

It should also be noted that the pesticide concentrations only start on about the 55th day after application. This is because, in this simulation, the concentrations in the soil layers were given, by GLEAMS, only after a storm event and storm events only occurred at

around this time. The months in which the pesticides are applied are dry. September 1997 had no rain at all and irrigation would not yet have started in the valley.

4.6.3 Sensitivity analysis

In Chapter 3, the site-specific sorption coefficients were determined and it was suggested that it was inappropriate to use sorption coefficients from the literature for modeling purposes. In the following section we will see whether GLEAMS produces significantly different results when using the site-specific sorption coefficient (calculated in Chapter 3) or the literature value suggested by GLEAMS. The output results discussed in Sections 4.6.1 and 4.6.2 are for the sandy soil (HR2) which dominates the Hex River Valley (See soil input parameters in hydrology component, Section 4.3). The effects on pesticide mobility, when changing the soil properties in the hydrology component to those of the loamy sand (HR1), will be examined in the following section.

The change in pesticide concentration up to 100 days after application date for chlorpyrifos is presented in Figure 4.3. Three simulations are compared. For simulation A (Figure 4.3) the same structure and input parameters as described in Section 4.5 were used and Figure 4.3 is a repeat of Figure 4.2.A (for simulation A) except only the first 100 days after application date are plotted and each soil layer is plotted separately. Simulation B is the same as A except the K_{oc} in the pesticide component was changed from the site-specific value of 1490 ml/g to the value suggested by GLEAMS of 6020 ml/g. Simulation C is the same as A except the soil properties in the hydrology component have been changed and Table 4.3 is a list of the properties that were changed and the substitute values which were employed.

The results presented in Figure 4.3 suggest that for the lower, site-specific sorption coefficient (simulation A) the concentration is less in the top layer and subsequently higher in the lower layers compared to the higher, literature sorption coefficient (simulation B). Simulation B results in a higher concentration in the top layer and lower concentrations in the lower layers. This is expected because as the sorption coefficient decreases so the concentration in the water phase increases and the quantity of pesticide available for movement to deeper layers is greater. Thus, GLEAMS supports the suggestion that site-specific sorption coefficients are needed as there was a greater potential for groundwater contamination or less likelihood of runoff contamination at the lower site-specific coefficient value.

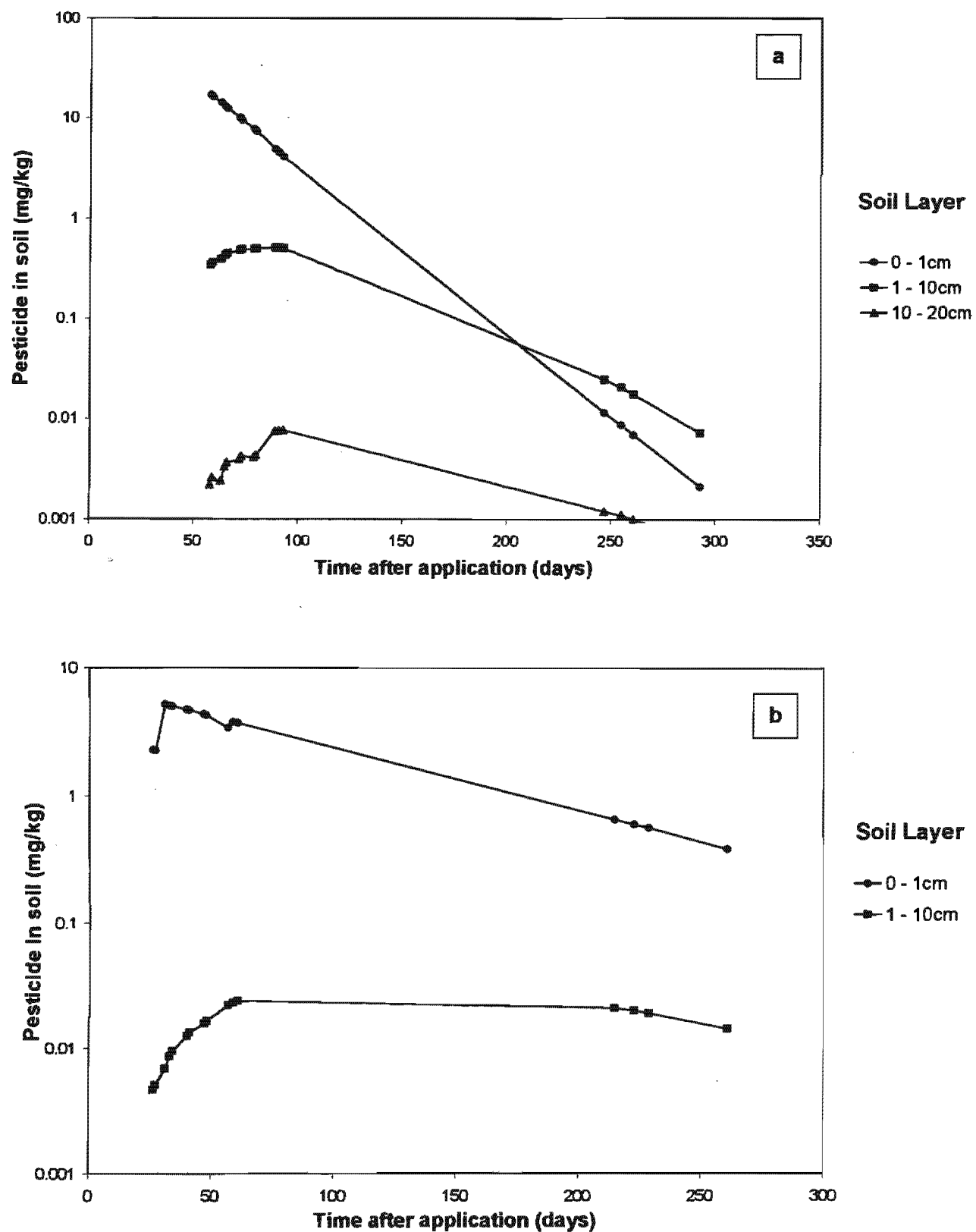


Figure 4.2 Pesticide concentration in topsoil layers after a storm event with time after application, as determined by GLEAMS. a) Chlorpyrifos and b) Endosulfan

Table 4.3: The input parameters, used for the hydrology component, for simulation C to describe the soil HR1, a loamy sand.

Soil Property	Soil Horizon 1 (0 – 20 cm)	Soil Horizon 2 (20 – 100 cm)
Porosity (cm ³ /cm ³)	0.4	0.4
Field capacity (cm/cm)	0.19	0.11
Wilting point (cm/cm)	0.05	0.04
Saturated conductivity (cm/hr)	0.66	1.00
Organic matter ¹ (%)	2.9	2.4
Clay content (%)	9.0	9.0
Silt content (%)	16.0	16.0

¹ – GLEAMS requires organic matter input even though it is converted to organic carbon internally. Organic matter was calculated by multiplying organic carbon by 1.724 g (Kniesel and Leonard, 1993)

GLEAMS uses K_{oc} instead of the K_d as a means of by-passing the necessity to determine the site-specific sorption coefficient because K_{oc} is a compound property. The difference in the results for simulation A and B are not dramatic and amount to about 0.007 mg/kg more chlorpyrifos in the 10 – 20 cm layer about 90 days after application and therefore it is suggested that the use of site-specific coefficients is dependent on the user's sensitivity needs. However, if a model that requires the K_d (partition coefficient) is being used, site-specific values would definitely be preferred.

The results in Figure 4.3, representing a change in soil properties for simulation C, lie between those of simulations A and B, which suggests that GLEAMS was less sensitive to the change in soil properties than to the change in the sorption coefficient. Once again this demonstrates the model's dependence on the sorption coefficient to predict pesticide mobility. Overall, in the loamy soil with higher clay and organic matter content (simulation C) than that of the sandy soil (simulation A), GLEAMS estimates that chlorpyrifos would be less mobile and retained more in the top layer and that less would move into the lower layers. The trend suggested by GLEAMS is that the higher the clay and organic matter contents, and the more strongly sorbed the pesticide, the more the pesticide will be retained in the surface layer. These soils would also be subject to less infiltration and greater runoff and would, therefore, pose more of a threat of contamination of water by

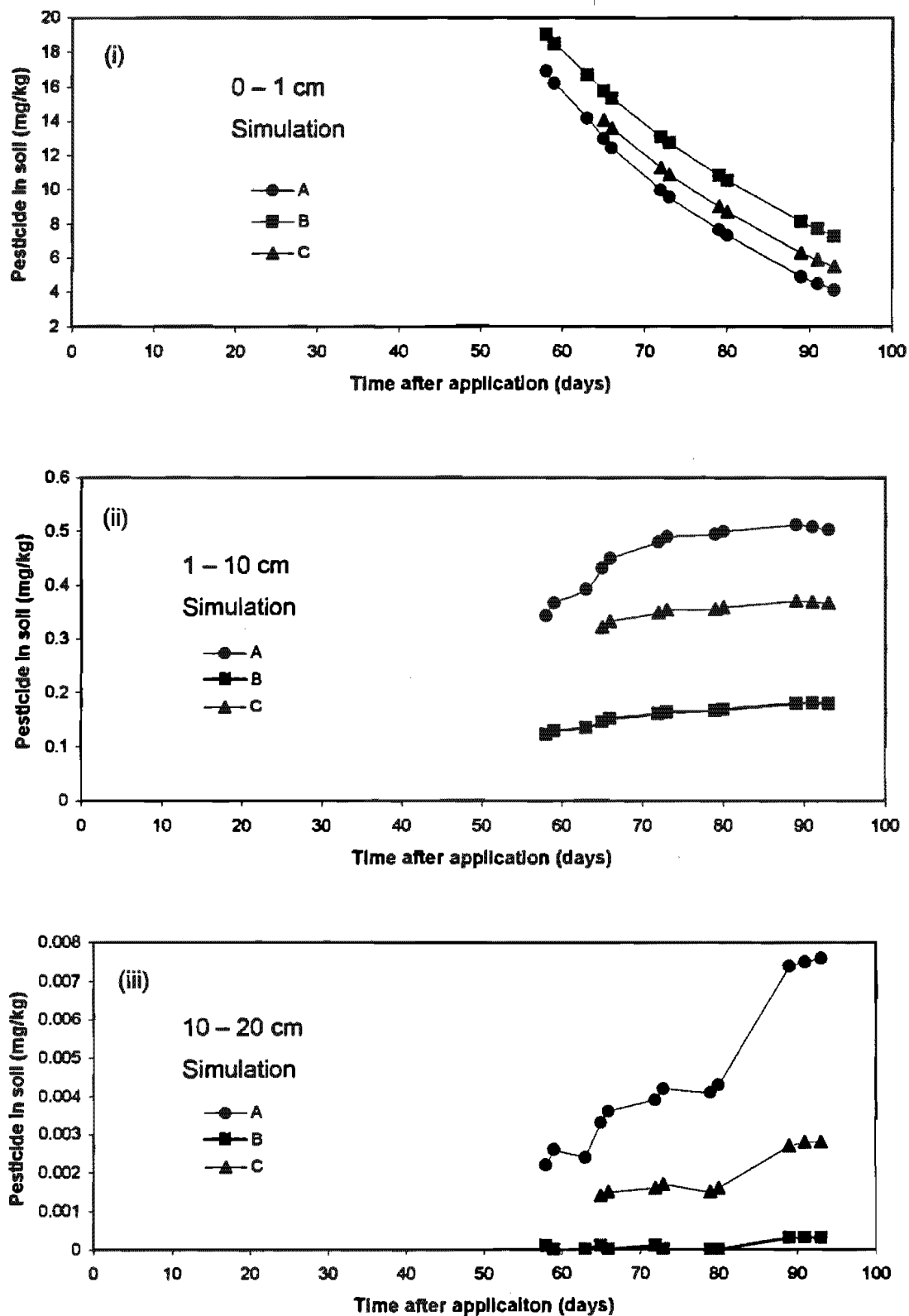


Figure 4.3 Chlorpyrifos concentrations up to 100 days after application for simulations with A) K_{oc} equal to 1490 ml/g B) K_{oc} equal to 6020 ml/g C) K_{oc} equal to 1490 ml/g and loamy sand (Table 4.3). Figure (i) is for the 0 – 1 cm layer Figure (ii) the 1 – 10 cm layer and Figure (3) the 10 – 20 cm layer.

strongly sorbed pesticides such as chlorpyrifos and endosulfan. Simulation C only begins reporting pesticide concentrations 10 days after the other two simulations because in the more loamy soil, there will be less infiltration and more time and precipitation is therefore needed to produce percolation to the next soil layer.

The results of the sensitivity analysis for endosulfan are provided in Figure 4.4 which shows that endosulfan only moved as far as the second soil layer. The site-specific sorption coefficient of 17517 ml/g was used for simulation A, 12 400 ml/g for simulation B and the same soil properties as presented in Table 4.3 were used for simulation C. In Figure 4.4 (i) the sharp increase in concentration results from the second application of endosulfan which occurred 30 days after the first application. The results of the three simulations are very similar as can be seen in Figure 4.4 (i) and it is possible that at the very high value of the sorption coefficient, coupled with the high organic matter for the loamy soil, the aqueous phase concentration (C_w in Eq. 1 of Section 4.5.2) becomes so small that the differences are not noticeable. The higher sorption coefficient value of simulation A results in lower concentrations in layer 2 and higher concentrations for the lower, literature coefficient used in simulation B. GLEAMS estimates that the loamy soil, in simulation C, would immobilise endosulfan the most and this is as a result of the higher organic matter combined with the high sorption coefficient value which results in the highest partition coefficient (K_d) value according to Eq. 1

Leonard *et al.* (1987) observed that in model applications, values selected for K_{oc} and the half-life may have pronounced effects on simulation results. They state that values for these parameters are generally not known within a factor of 2 or 3 for specific sites without conducting extensive field studies and that calibrating models with site-specific data does not overcome this inherent uncertainty if the model is to be applied at other sites.

4.6.4 Model short-comings

GLEAMS estimates that endosulfan and chlorpyrifos are highly immobile in the environment of the Hex River Valley. Despite this, contamination of water has been detected. The following discussion of the shortcomings of GLEAMS, therefore, also provides possible explanations for this observed loss of pesticide from the areas of application. Global literature abounds with discussions of model shortcomings, advantages, disadvantages, assumptions and recommendations. The following discussion focuses on selected issues only.

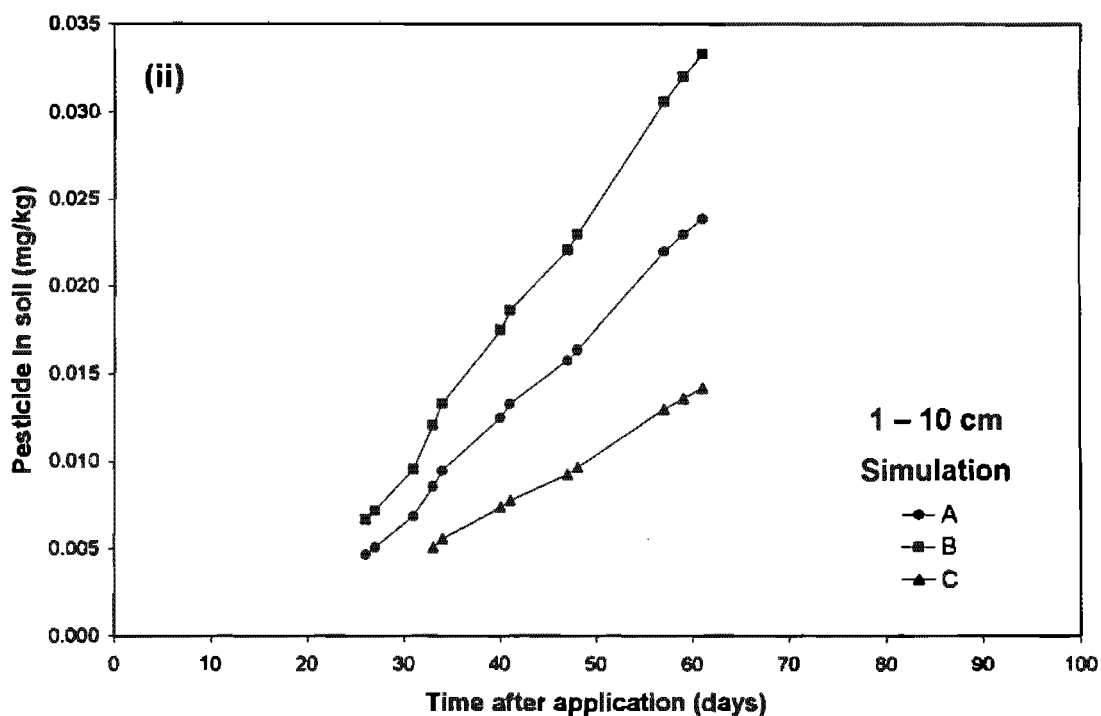
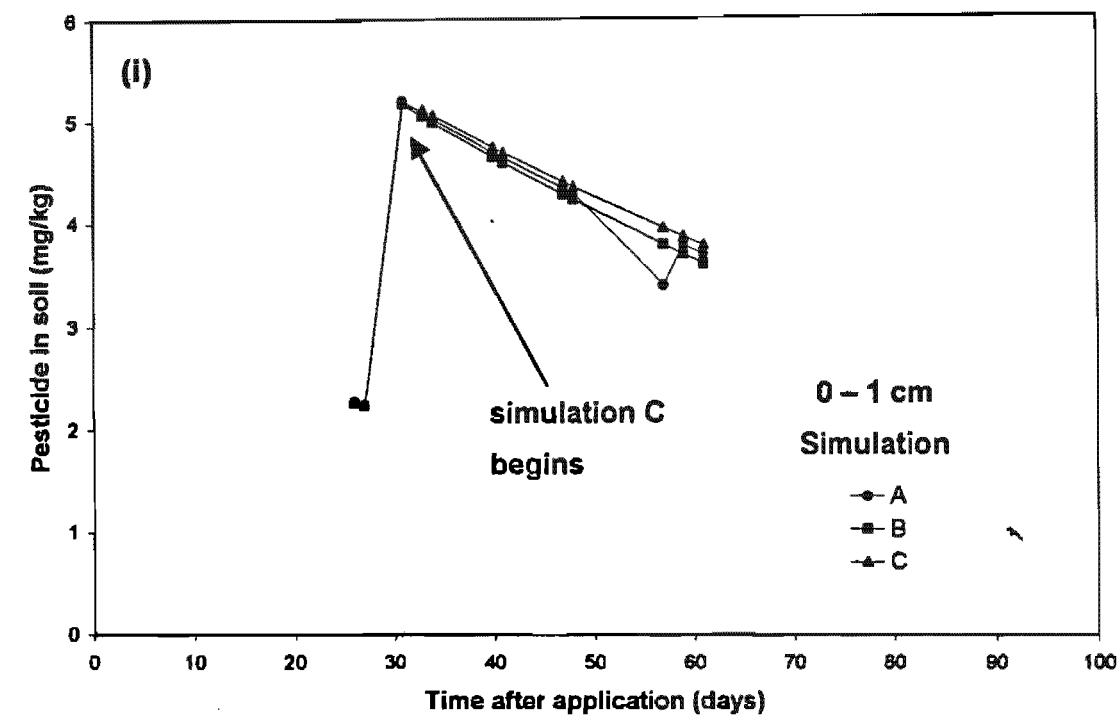


Figure 4.4 Endosulfan concentrations up to 100 days after application for simulations with A) K_{oc} equal to 17517 ml/g B) K_{oc} equal to 12 400 ml/g C) a loamy sand. Figure (i) is for the 0 – 1cm layer and Figure (ii) the 1 – 10cm layer.

4.6.4.1 Suspended soil material

In Chapter 3 (Section 3.5.7), the research by Chiou *et al.* (1986) was discussed and it was suggested that the dissolved organic matter-rich water of the Hex River Valley could be enhancing the solubility of the strongly sorbed pesticides. More recently, Hesketh *et al.* (1998) reported a study on facilitated transport of chlordane by suspended soil material from a sandy soil containing $\approx 8\%$ clay, 0.95% OC and pH 7.14. The authors concluded that transport of chlordane from the lysimeters was unequivocally facilitated by suspended soil material; none occurred independently of it. They state that this facilitation was so effective that chlordane emerged in drainage at the base of the deep lysimeters clearly in advance of bromide, which is a non-sorbed anion and thus leached from the soil. These authors concluded that although colloidal matter has usually been thought to be the most probable facilitator of pesticide movement (as suggested by Chiou *et al.* (1986) - Section 3.5.7) there was little evidence that this was so for chlordane transport. It was the largest class of suspended soil material ($> 1.2\mu\text{m}$) that was most closely associated with the transport of chlordane and the authors suggested that this was possibly because it was the fraction that contained the most organic matter.

If endosulfan and chlorpyrifos are lost from the soil it will be attached to suspended soil material. GLEAMS estimates that there will be no loss of soil in runoff. It does not consider, however, the possibility of the loss of the pesticides attached to suspended material in percolating water. Although suspended material is most likely to be trapped in the soil profile as it moves downwards, if the watertable is high and the soil sandy and porous, the effect could be significant especially if the water does not move through the bulk soil and is lost via cracks or faunal burrows in the soil.

4.6.4.2 Macropore flow

The recent emphasis given to macropore flow has resulted from the many observed cases of groundwater pollution caused by preferential movement of water and solutes through unsaturated parts of the soil, a result not predicted by classical theories of flow dynamics in porous media. Many studies have documented the presence of chemicals in drainage water only a few hours or a few days after their application on the soil surface (Morari and Knisel, 1997). This has been observed for a range of pesticides and is independent of their different adsorption coefficients. Therefore, macropore flow often results in groundwater

pollution of soil with shallow aquifers, because most of the adsorptive capacity of the matrix is not exploited (Morari and Knisel, 1997). The GLEAMS model was not formulated to represent rapid movement of water and solutes through macropores. Zacharias and Heatwole (1994) have noted that GLEAMS underestimated percolation losses of bromide, atrazine and metolachlor in sandy soils of the coastal plains of Virginia, USA, and ascribed this to the non-representation of preferential flow of chemicals.

Although the soils in the Hex River Valley are not clayey and are unlikely to be subject to major cracking, conservation tillage is commonly practised which results in a greater amount of channels and faunal burrows than other tillage practices. The Hex River Valley has a shallow aquifer in areas, sandy soils and conservation tillage is commonly practised therefore it is possible GLEAMS has underestimated the loss of pesticides by percolation.

Morari and Giupponi (1997) have modified the version 2.10 of GLEAMS, used in the present study, to simulate the movement of water and solutes through cracks which they called GLEAMS-CrackFlow.

4.6.4.3 Temperature and soil water content effects

Many pesticide fate and transport models, including the GLEAMS model, overestimate degradation during its later stages of residence in soil (Truman *et al.* 1997). According to Truman *et al.* (1997) except for runoff events shortly after pesticide application, models using equilibrium sorption kinetics often underestimate sediment-transported pesticides. To address concerns about transport of low levels of pesticides by runoff to sensitive ecosystems over annual or longer time cycles, GLEAMS was modified using a two-compartment pesticide-state model and algorithms for adjustment of degradation rates for temperature and soil water contents. This model is called GLEAMS-TC and Truman *et al.* (1997) compared model predictions with observed data. GLEAMS-TC successfully simulated observed pesticide sediment transport, whereas GLEAMS underestimated the observed data by a factor of 4.

4.6.4.4 Curve number procedures to predict runoff

The runoff curve number procedure developed by the U. S. Department of Agriculture, Soil Conservation Service (USDA-Soil Conservation Service, 1972) uses a curve number (CN)

value which is based on soil infiltration characteristics, land use and cover, agricultural management and conservation practices to estimate storm runoff volumes. The method also adjusts curve number values to represent the five-day antecedent rainfall conditions. The overall impacts of land use, management and cover conditions, and antecedent moisture are represented by the initial abstraction in SCS-curve number procedure. The parameter S defines the soil retention characteristics. Increases or decreases in this parameter reflect the decrease or increase in the estimated runoff volumes, respectively.

According to Shirmohammadi *et al.* (1997) selecting an appropriate curve number value and therefore proper initial abstraction to reflect the effect of surface cover, management, land use and antecedent moisture conditions in estimating the storm runoff volume is a crucial task. They reported that using an average CN value was inappropriate and that "a major professional judgement in applying the method is needed" in the selection of a curve number.

In general, it was concluded by Shirmohammadi *et al.* (1997) that GLEAMS under-predicts both runoff and erosion due to internal conversions of curve numbers and/or poor judgement by inexperienced users.

For the simulations in the present study a SCS curve number of 60 was used. This value was arrived at by considering the hydrological soil groups, according to USDA-SCS (1972) and taken from Knisel *et al.* (1993):

- A. (low runoff potential) Soils having high infiltration rates even when thoroughly wetted and consisting chiefly of deep, well to excessively drained sands or gravels. These soils have a high rate of water transmission.
- B. Soils having moderate infiltration rates when thoroughly wetted and consisting chiefly of moderately deep to deep, moderately coarse textures. These soil have moderate rate of water transmission.
- C. Soils having slow infiltration rates when thoroughly wetted and consisting chiefly of soils with a layer that impedes downward movement of water, or soils with moderately fine to fine texture. These soils have a slow rate of water transmission.
- D. (High runoff potential) Soils having very slow infiltration rates when thoroughly wetted and consisting chiefly of clay soils with a high swelling potential, or soils with a permanent high water table, soils with a claypan or clay layer at or near the surface and shallow soils over nearly impervious material. The soils have a very slow rate of water transmission.

GLEAMS then provides an expanded table of curve numbers relating hydrological soil group, hydrological condition, land use, treatment and practice. The Hex River Valley soils were placed in hydrological group A, with straight row crops and conservation tillage and a poor hydrological condition. This resulted in three numbers: 60, 67 and 73. Since the input value of CN2 is used only to estimate the maximum available soil water storage, the lowest value was of 60 used.

4.7 Conclusions and recommendations

It should be noted that GLEAMS is not a predictive model in the sense of providing absolute quantities, and that simulated concentrations can therefore not be interpreted as absolute values; only relative differences between management practices should be assessed.

GLEAMS estimated that there would be no runoff, no sediment loss and some percolation but that none of the applied pesticide would be lost in either runoff or percolation. This was, overall, a conservative simulation (not a worst case) which was as representative of the average field in the Hex River Valley as possible. Although, a worst case scenario was used for the pesticide application quantities, all other parameters were conservative values. Observed climatic data, measured soil properties, pesticide properties and a uniform slope with moderate steepness along with the most common management practices were used.

The results of this investigation indicate that GLEAMS is sensitive to changes in the sorption coefficient (K_{oc}) and, to a lesser extent, to soil properties. Sorption coefficients should be determined experimentally for site specific cases. However, this depends on the use of the output and the needs of the user. Determining sorption coefficients experimentally can defeat the purpose of modeling which is to inexpensively and efficiently incorporate all the factors and multidisciplinary aspects of pesticide mobility to facilitate decision-making. The determination of sorption coefficients can be expensive and laborious. However, it should be remembered that a model's output is only as good as its input.

In general, GLEAMS underestimates pesticide mobility and this has been attributed to its inability to simulate: (i) increased solubility of pesticides due to dissolved organic matter; (ii) loss of pesticides attached to suspended sediment in percolation water; (iii) pesticide and water loss via macropores; (iv) non-equilibrium sorption kinetics and (v) effects of temperature and soil water content on degradation. Inaccurate curve number estimation

and therefore inaccurate runoff losses, amongst others, are also responsible for underestimating runoff losses.

Overall, GLEAMS estimated that endosulfan and chlorpyrifos are highly immobile in the soil environment of the Hex River Valley. However, these pesticides are being mobilised and lost from the sites of application as they have been detected in water samples taken from certain points in the valley. The major method of transport will probably be through attachment to suspended soil material (mainly organic matter) and therefore, in order to minimize the movement of these pesticides we need to minimise losses of soil material by avoiding practices liable to cause soil instability or erosion. Large peaks of pesticide loss are unusual and may be attributable to a single event; for example, a heavy, downpour only once a year is enough to account for the entire year's pesticide loss. A field, other than the average field used for simulations in the present studies, with a steeper slope, less cover, different management practice and lower infiltration rate could also account for the appearance of pesticides in runoff water samples. It is recommended for future studies with GLEAMS that a worst case scenario simulation (for all hydrology, erosion and pesticide parameters) be compared to an average case scenario for the Hex River Valley, in order to meaningfully describe a range of possibilities which may provide a better explanation for actual measurements of pesticides concentrations in the Hex River Valley environment.

In an area as large as the Western Cape, field sampling and pesticide control with respect to water quality is expensive, complicated and time consuming. However, modeling provides an inexpensive, fairly rapid alternative especially if the model, such as GLEAMS, is integrated with GIS. This would enable the identification of high-risk areas as well as facilitate the identification of the optimal strategy which may be used to prevent contamination.

This study was an investigation into the sorption properties of endosulfan and chlorpyrifos and how these relate to the processes of leaching and runoff in the soil of the Hex River Valley. Leaching and runoff are nonpoint pollution processes that depend on certain factors, some of which are controllable and some not. Despite their expected immobility, certain aspects of these factors are most probably responsible for the detection of endosulfan and chlorpyrifos in water sampled from the Hex River Valley.

The application factors: These include the application site, the formulation and the application amount and frequency. These factors have not been examined in detail in the

present study but the movement of these pesticides from fields into near-by water bodies by spray drift is potentially highly significant and needs to be investigated further. The pesticide concentrations in the water sampled exceeded the stipulated limit at a time of year and by an amount that suggests farmers could possibly be applying the pesticides more frequently and at higher concentrations than stated by representatives of pesticide manufacturing companies.

Pesticide persistence and mobility factors: The pesticide-soil combinations, of the present study, resulted in such strong binding of the pesticide to soil particles that the pesticide is most probably moved only if the soil is moved, i.e., if erosion occurs. Chlorpyrifos is degraded more quickly on soil and crop surfaces than endosulfan and thus rainfall, which occurs within a few days after application, would result in the most significant transport. Pesticides must be relatively persistent and mobile to leach to ground water because the travel time for water to percolate to deep aquifers can range from months to years. Endosulfan is persistent but immobile. Chlorpyrifos is moderately persistent, and based on the finding of Chapter 3, more mobile than expected. Therefore, their leaching potential is low. However, once a pesticide has leached into subsurface soils, the biological activity and binding capacity there are often less than in soils near the surface. Thus, the pesticide becomes more persistent and mobile which is of particular concern in an area like the Hex River Valley which has a shallow aquifer and intensive agriculture.

The two pesticides are more of a threat for runoff. However, that part of pesticide residues which is most available for runoff, the part at the topmost surface of soils, is the part most rapidly dissipated by evaporation and photodegradation. Moreover, runoff transport can be complete in hours, and erosion can transport immobile pesticides attached to soil. Thus, pesticide runoff is less dependent on pesticide properties than pesticide leaching, and much more dependent on how soon runoff occurs after application. Management practices which control erosion and faunal burrows are extremely important with respect to these pesticides.

Soil and field topography factors: Soils differ greatly in their capacity to absorb water. The slope and drainage pattern of a field or a watershed greatly affect its potential to generate runoff water. Fast-draining soils like the sands and sandy loams of the Hex River Valley have the greatest leaching potential while slow-draining clays and silty clays have the greatest runoff potential. The organic matter content of soils in the Western Cape have seldom been measured yet it is probably the major factor determining pesticide mobility. It is suggested, based on the results of this study, that organic matter content be measured

throughout the Western Cape and these results be used in a geo-statistical analysis (Kriging) to guide regulators to areas of concern. Watershed size has an important effect on runoff pesticide concentration patterns: small streams adjacent to treated fields can have very high peak concentrations of hundreds of ppb, but concentrations decrease quickly to low values. In large rivers, peak concentrations are much lower but concentrations may be elevated longer.

Weather and climate factors: Climate affects the type of crops grown, the intensity of pest problems, and the persistence of pesticides used. The Hex River Valley has warm weather and low rainfall both factors which support high degradation and low mobility. However, the intensity of rainfall and its timing with respect to pesticide application determines how much pesticide transport occurs. While these factors are not controllable, probabilities of pesticide runoff and leaching can be estimated, and avoiding pesticide application when rain is imminent is often possible.

Farmer decision making factors: It is the responsibility of government departments and pesticide manufacturers to ensure the farmer is informed on the risk status of the area and the relevant techniques one can use to prevent pesticide contamination of the environment. The farmer has considerable control over the pollution probabilities: knowledge of erosion control and of best application techniques, and an eye on the weather, are the first lines of defence against pollution.

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APPENDIX A

Methods and Calculations Used in the Characterisation of the Hex Valley Soils

A.1 Mineralogy of the clay fraction

Approximately a 100g of soil was placed into 250ml plastic bottle. The bottle was filled with de-ionised water and shaken to form a slurry. The pH of the slurry was adjusted with drop-wise addition of 1M NaOH until it had stabilised at approximately 9. The pH-adjusted slurry was placed onto a reciprocal shaker overnight. The solution was then placed into a large plastic bucket and the volume made up with tap water. The suspensions were stirred vigorously and the dispersed suspension was separated after the sedimentation of the $>2\mu\text{m}$ fraction by siphoning to a depth of 15 cm after 13 hours at $\pm 20^\circ\text{C}$, based on Stoke's Law of sedimentation. The 3L containers were then filled with Na_2CO_3 solution adjusted to pH 10, stirred again and left to settle for another 13 hours before the dispersed clay was siphoned off. This procedure was repeated until enough clay was collected.

The separated clay was flocculated by adjusting the pH to between 5 and 7 by 1:1 HCl and adding excess NaCl. Excess water was removed by siphoning and then centrifugation. To remove excess salt the clay suspension was then dialysed by leaving in tap water once over night and twice overnight in double distilled water, after which the presence of chloride was tested using silver nitrate. The concentration of the dialysed clay was determined gravimetrically and was adjusted to 20 mg/ml. A 2 ml aliquot of the clay suspension was air-dried on a glass slide and used for X-ray diffraction.

A.2 Organic carbon

Organic carbon was determined by the Walkley-Black rapid dichromate oxidation-titration method of (Nelson and Sommers, 1982).

The soil was ground to pass a 0.35 mm sieve, using a porcelain mortar and pestle. 0.5g air-dried soil was transferred to a 500 ml Erlenmeyer flask. To this 10 ml $\text{K}_2\text{Cr}_2\text{O}_7$ solution was added (by pipette), and the flask was then swirled to disperse the soil in solution. 20 ml concentrated sulphuric acid was rapidly added to this, and the flask was again swirled until the soil and reagents were mixed. The flask was allowed to cool on a protected surface for about 30 minutes, before 150 ml de-ionised water and 10 ml concentrated ortho-phosphoric acid was added to it. 1 ml indicator was then added and the excess dichromate titrated with iron (II) ammonium sulphate solution in the presence of 0.025M ferroin indicator. The colour change at the end point was violet to green. The experiment at the University of Cape Town was performed in triplicate and the results are presented in Table A.1 along with the ARC-Infruitec results.

Table A.1: Soil organic C content results obtained with the Walkley - Black (1934) method.

Sample	% Organic Carbon	Mean	Std. Deviation
HR1	0.799	1.58	0.97
HR1	0.790		
HR1	1.94		
HR1*	2.8		
HR2	0.327	0.85	0.78
HR2	0.413		
HR2	0.654		
HR2*	2.1		

* Results of Walkley -Black determination by ARC-Infruitec, Stellenbosch

A.3 Particle-Size Distribution (PSD)

The PSD was determined at ARC, Infruitec, Stellenbosch by sedimentation using the Pipette Method (Gee and Bauder, 1986). No pretreatments for the removal of organic matter, Al, Fe and Mn oxides were carried out before the soils were dispersed for particle-size distribution. The dried, sieved soil was placed into a 250 ml bottle, containing 10 ml of Calgon solution. The volume of the bottle was made up to 150 ml with de-ionised water and the bottle was placed onto a reciprocal shaker overnight. Calgon addition and shaking was carried out to ensure the complete dispersion of the sample.

The dispersed sample was transferred to a 1L cylinder and the volume was made up to the 1000 ml mark with de-ionised water. The suspension was stirred a hand stirrer for 1 minute, the time when stirring stopped was recorded. A Lowy pipette was lowered into the suspension to a depth determined by the ambient temperature and the size fraction which was being determined (as relates to Stoke's Law). A 25 ml sample was drawn at each depth and emptied into a tared crucible which was placed into a 105°C oven overnight. The mass of the dried sample was determined and recorded. The sand fraction of the sediment was determined by washing the remaining suspension, after pipetting, through a 0.053 mm sieve and drying the sediment retained on the sieve (105°C overnight) and weighing. The results of the % clay, silt and sand, provided by the ARC, Infruitec, Stellenbosch are presented in Table A.2.

Table A.2: Particle Size distribution of Hex River Valley soil.

Sample	Particle size (%)				
	Clay	Silt	Fine sand	Medium sand	Coarse sand
HR1	8.8	15.6	49.5	16.2	9.9
HR2	2.3	3.4	26.4	36.5	31.4

A.4 pH measurement

The soil samples were dried and crushed before being sieved through a 2 mm sieve. Ten grams of soil was then mixed with 25 ml of MQ water to obtain 1:2.5 soil:water ratio. After mixing, the solution was allowed to settle for about 30 minutes. The pH measurements were taken on a Crison pH meter. The procedure was then repeated using 25 ml 1M KCl solution instead of 25 ml water. The results are presented in Table A.3. The pH values in Table A.3 are the mean of three readings and the values in parenthesis are the standard deviations.

Table A.3: Soil pH determined in water and 1M KCl

Sample	pH H ₂ O	pH 1M KCl	ΔpH^1
HR1	7.2 (0.01)	5.8(0.02)	-1.4
HR2	6.9(0.03)	5.6(0.01)	-1.3

$$^1\Delta\text{pH} = \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$$

A.5 Electrical Conductivity and pH on saturated paste extract

Distilled water was added to 250 ml air-dried, sieved soil, in small quantities and the resultant paste was stirred and mixed continuously. Distilled water was added until 1) the resulting paste moved slightly as a unit when the polystyrene container was tilted and 2) the paste had attained a moist, shiny outward appearance. The amount of water added was recorded. The paste was then sealed and left to equilibrate overnight. The paste was emptied into the funnel cups of a vacuum line and filtered through filter paper into centrifuge tubes (Rowell, 1996). The pH and electrical conductivity of the filtrate was measured at room temperature (20.9°C). Major cations and anions were measured on the saturated paste extract. The extracts were stored at <5°C. The results are presented in Table A.4. The pH and EC values in Table A.4 are the mean of three readings and the values in parenthesis are the standard deviations.

Table A.4: Electrical conductivity (EC) and pH measurements on the saturated paste extract

sample	Temp (°C)	pH	EC $\mu\text{S/cm}$
HR1	20.9	7.65(0.08)	448(21.5)
HR2	20.9	6.53(0.06)	206(6.43)

A.6 Water Soluble Cations and Anions

The filtered and diluted saturated paste extracts were analysed for total dissolved cations and anions using a HPIC model DIONEX 3000 series (ion chromatography system). Results are tabulated in Section 2.4.5, Chapter 2 (Table 2.6).

A.7 Exchangeable Cations and Cation Exchange Capacity (CEC)

ARC-Infruitec, Stellenbosch using the Ammonium Acetate Method, determined the exchangeable cations Na, K, Ca and Mg. Five grams of <2 mm air-dried soil was placed in a 50 ml centrifuge tube and 25 ml of 1N NH₄OAc was added. The tube was stoppered and shaken for 30 min. The tube was centrifuged for 10 min at a speed of 2000 rpm. The supernatant was poured into a 50 ml volumetric flask and the process was repeated adding an additional 25 ml, and finally bringing up to a volume of 50 ml with 1N NH₄OAc (Thomas, 1982). The concentrations of the cations in the supernatant were determined by ICP-AES. The ammonium acetate method was considered suitable for the soil samples due to the absence of excess CaCO₃ or high amounts of mica and vermiculite that give low or excessively high results. The concentrations of the exchangeable cations are presented in Table A.5.

The CEC was determined as the effective CEC (ECEC) calculated as the addition of the exchangeable base (Na, K, Ca, Mg) concentrations and extractable acidity according to the summation method of Rhoades (1982), shown as the total in Table A.5.

Table A.5: Results of exchangeable cations for Hex River Valley soils extracted using the ammonium acetate method and determined by ICP-AES.

Sample	Exchangeable Cations (cmol _c kg ⁻¹)					Total
	Na	K	Ca	Mg	H	
HR1	0.19	0.38	3.38	1.68	0.31	5.94
HR2	0.04	0.19	1.62	0.56	0.31	2.72

A.8 Extractable Fe, Cu, Zn , Mn and P

ARC-Infruitec, Stellenbosch, carried out the following analyses. Extractable Fe, Cu, Zn and Mn were determined using the EDTA method (Trierweiler and Lindsay, 1969 as modified by Beyers and Coetzer, 1971; Soil Science Society of SA Handbook, 1990). 5 g air-dried soil was shaken horizontally for 60 min. with 0.02 mol dm⁻³ (NH₄)₂EDTA solution. The samples were centrifuged and filtered. The extracts were analysed for Fe, Cu, Zn and Mn by ICP-AAS. The results are presented in Table 2.5, Chapter 2, Section 2.4.2.

Extractable phosphorus was determined according to the BRAY-2 method (Bray and Kurtz, 1945; Soil Science Society of SA Handbook, 1990). 8 g of soil was added to an extraction bottle with 60-ml Bray-2 solution and agitated for 40 seconds by hand, filtered immediately. One gram phosphorus free charcoal was added to the filtrate and agitated for another 40 seconds by hand. 2 drops of flocculent was added. The solution was filtered and P determined within 24 hours by the Murphy & Riley (1962) method (according to Rowell, 1996) detailed in Section A.10.

A.9 Specific Surface Area

The BET method was employed to determine the specific surface area using a Micrometrica ASAP 2000 instrument with nitrogen gas as the adsorbing gas in the

Particle Technology Centre, in the Chemical Engineering Department of the University of Cape Town. The results for the specific surface area are summarised in Table A.6.

Table A.6: Summarised results of specific surface area determinations of Hex River Valley soils.

Sample	BET surface area (m ² .g ⁻¹)	Single Point surface area (m ² .g ⁻¹)	Average pore diameter (Å)
HR1	4.61	4.45	78.89
HR2	0.59	0.54	95.61

A.10 P determination

Standard P solutions were made up at 0, 2.5, 5, 10, 15, 25 µg P for calibration. The Murphy & Riley (1962) method (according to Rowell, 1996) is a colorimetric technique which relies on the fact that a solution containing P and molybdate will form a blue colour in the presence of antimony. A spectrophotometer was used to measure light absorption. A 5 ml sample was withdrawn from the standards and supernatant samples for colour development by adding 1 ml of reagent. The reagent was made up from sulphuric acid (5 N), ammonium molybdate, ascorbic acid (which is made up daily), and potassium antimonyl tartrate. The intensity of the blue colour which formed depends on the concentration of P in the samples. The samples were shaken and allowed to stand for 20 minutes for full colour development. The Absorbance was measured at 880 nm. The results of the Absorbance readings were compared to those of standards by constructing a calibration graph (figure A.1). All the samples were diluted sufficiently to fall within the range of the standards. Duplicate analyses indicated that the method gives excellent reproducibility. The Absorbance and corresponding P concentrations, from the calibration line, in the solutions are presented in Table A.7.

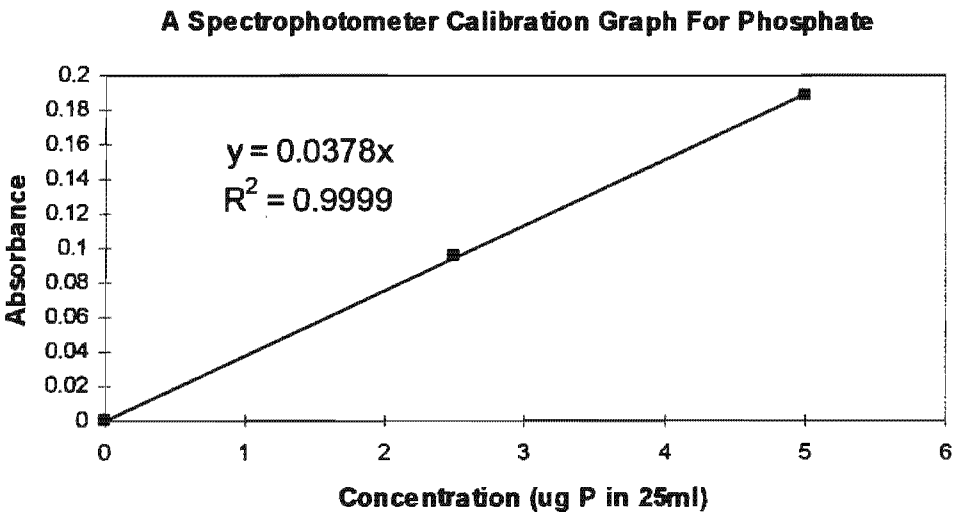


Figure A.1 Absorbance vs. concentration for standard P solutions. The two highest concentrations were removed to improve the calibration ($r^2=0.9999$). This is permissible at these higher concentrations, as the line becomes concave according to the Beer Lambert Law.

Table A.7: Absorbance and corresponding concentration of phosphorus as determined from the equation of the calibration line.

Sample label	Absorbance	Final concentration from calibration ($\mu\text{g P}$ in 25 ml)
HR1A*	0.0135	0.357
HR1A	0.031	0.820
HR1A	0.06	1.587
HR1A	0.1365	3.611
HR1A	0.2495	6.601
HR1A	0.31	8.201
HR1B*	0.014	0.370
HR1B	0.031	0.820
HR1B	0.0665	1.759
HR1B	0.1595	4.220
HR1B	0.277	7.328
HR1B	0.343	9.074
HR2A*	0.052	1.376
HR2A	0.031	0.820
HR2A	0.1015	2.685
HR2A	0.225	5.952
HR2A	0.2755	7.288
HR2A	0.346	9.153
HR2B*	0.033	0.873
HR2B	0.0465	1.230
HR2B	0.1085	2.870
HR2B	0.2405	6.362
HR2B	0.3005	7.950
HR2B	0.3785	10.013

*Phosphate adsorption was determined on soil HR1 and HR2.
A and B are replications of the analyses on the same soil.

Adsorption Isotherms

- results and calculations (taken from Rowell, 1996)

- The final concentration (From Table A.7): $X \mu\text{g P}$ was in 5 ml of filtered solution. Therefore its concentration was $X/5 = Y \mu\text{g P ml}^{-1}$ (Table A.8).
- The amount of P initially in 25 ml of solution was:
 $(\text{Initial stock solution conc.}) \times 25 \text{ ml} = A \mu\text{g P}$
 The amount finally present was $Y \times 25 = Z \mu\text{g P}$.
- The amount of P removed from solution was $A - Z = Q \mu\text{g P}$. This had been adsorbed on to 2.5g of soil. Therefore

$$\text{Adsorbed P (F } \mu\text{g P g}^{-1}\text{)} = Q/2.5$$

The results of these calculations are given in Table A.8. Negative results indicate desorption.

Table A.8: Results of each step of the calculation of the amount P sorbed

Sample label	Conc. stock soln. ($\mu\text{g P ml}^{-1}$)	Initial P in 25ml added to soil ($\mu\text{g P}$) A	Final conc. from calibration ($\mu\text{g P in 25ml}$) X	In 5ml taken for colour dev. $X / 5 = Y$ $\mu\text{g P ml}^{-1}$	Amount present after shake $Y \times 25 = Z$ $\mu\text{g P}$	P removed from soln $A - Z = Q$ $\mu\text{g P}$	P adsorbed on 2.5g soil $Q/2.5 = F$ $\mu\text{g P g}^{-1}$
HR1A	0	0	0.357	0.071	1.786	-1.786	-0.714
HR1A	0.5	12.5	0.820	0.164	4.101	8.399	3.360
HR1A	1	25	1.587	0.317	7.937	17.063	6.825
HR1A	2	50	3.611	0.722	18.056	31.944	12.778
HR1A	3	75	6.601	1.320	33.003	41.997	16.799
HR1A	5	125	8.201	1.640	41.005	83.995	33.598
HR1B	0	0	0.370	0.074	1.852	-1.852	-0.741
HR1B	0.5	12.5	0.820	0.164	4.101	8.399	3.360
HR1B	1	25	1.759	0.352	8.796	16.204	6.481
HR1B	2	50	4.220	0.844	21.098	28.902	11.561
HR1B	3	75	7.328	1.466	36.640	38.360	15.344
HR1B	5	125	9.074	1.815	45.370	79.630	31.852
HR2A	0	0	1.376	0.275	6.878	-6.878	-2.751
HR2A	0.5	12.5	2.050	0.410	10.251	2.249	0.899
HR2A	1	25	2.685	0.537	13.426	11.574	4.630
HR2A	2	50	5.952	1.190	29.762	34.762	13.905
HR2A	3	75	7.288	1.458	36.442	38.558	15.423
HR2A	5	125	9.153	1.831	45.767	79.233	31.693
HR2B	0	0	0.873	0.175	4.365	-4.365	-1.746
HR2B	0.5	12.5	1.230	0.246	6.151	6.349	2.540
HR2B	1	25	2.870	0.574	14.352	10.648	4.259
HR2B	2	50	6.362	1.272	31.812	18.188	7.275
HR2B	3	75	7.950	1.590	39.749	35.251	14.101
HR2B	5	125	10.013	2.003	50.066	74.934	29.974

The final concentrations (equilibrium concentration; **X** from Table A.8) were plotted against the amounts sorbed (**F** in Table A.8) and presented as isotherms in Figure A.2. The mean and standard deviation for the results of HR1 and HR2 were calculated and are presented in Table A.9. The results in Table A.9 were used in the final presentation of the P sorption isotherms presented in Figure 2.5, Section 2.4.7, Chapter 2.

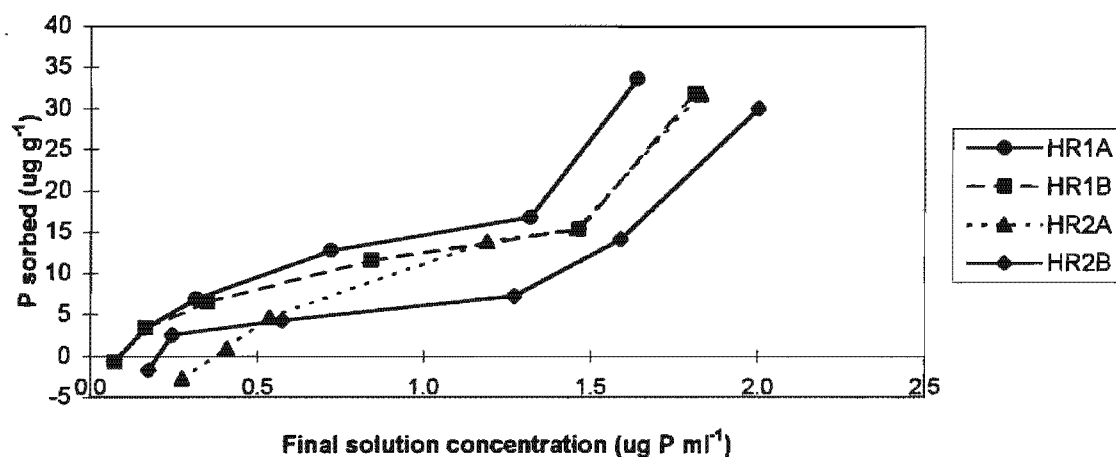


Figure A.2 Adsorption isotherms for phosphate adsorption on soils HR1 and HR2.

Table A.8: The means and standard deviations of the results of the P sorption determination for HR1 and HR2

Sample Label	Mean F ($\mu\text{g P g}^{-1}$)	Standard Deviation	Mean Y* ($\mu\text{g P ml}^{-1}$)	Standard Deviation
HR1	-0.728*	0.019	0.073*	0.002
HR1	3.360	0.000	0.164	0.000
HR1	6.653	0.243	0.335	0.024
HR1	12.169	0.860	0.783	0.086
HR1	16.071	1.029	1.393	0.103
HR1	32.725	1.235	1.728	0.123
HR2	-2.249**	0.711	0.225**	0.071
HR2	2.950	1.160	0.246	0.116
HR2	4.444	0.262	0.556	0.026
HR2	10.590	4.688	1.231	0.058
HR2	14.762	0.935	1.524	0.093
HR2	30.833	1.216	1.917	0.122

*The mean of HR1A and HR1B.

**The mean of HR2A and HR2B

APPENDIX B

Methods and Calculations Used for the Sorption Experiment and Pesticide Concentration Determination

B.1 Sorption

Commercial grade chlorpyrifos, Dursban EC (480 g/L chlorpyrifos), obtained gratis from Sanachem (PTY) LTd., Kempton Park and endosulfan, Thioflo SC (475 g/L endosulfan) obtained gratis from AgrEvo, Stellenbosch, were diluted with 0.01 M CaCl_2 to yield five different concentrations. These solutions were the initial concentrations, C_i , added to the soils to examine the sorption of the pesticides. These concentrations were representatives of the field application rates. The application rate of Dursban EC in the field is on average 8L of the 480-g/L chlorpyrifos product per ha, which is 3840g per ha. The volume of a hectare of soil is 2500m^3 and using a soil density of 1.5 g.cm^{-3} (Rowell, 1995) the mass of a hectare was calculated as $3.75 \times 10^9\text{ g}$ soil per ha. Therefore, it was calculated that the field application rate is $1.02\text{-}\mu\text{g}$ chlorpyrifos per gram of soil. Using the same calculation for endosulfan, which is applied on average at 1L of the 475g/L endosulfan product per ha, the field application rate is $0.127\mu\text{g}$ endosulfan per gram of soil. The range of initial concentrations made up were calculated to ensure similar pesticide to soil ratios in the laboratory adsorption experiment.

Fourteen grams of air-dried, sieved soil (HR1 and HR2) were shaken, with 70 ml (1:5 soil:solution) solutions (C_i) of chlorpyrifos (0.00192, 0.0384, 0.192, 0.96 and 4.8 mg/L) and endosulfan (0.00019, 0.0038, 0.019, 0.095 and 0.475 mg/L) in 100 ml glass bottles with Teflon-lined, plastic lids, for 24 hour at room temperature ($24 \pm 2^\circ\text{C}$). The bottles were shaken horizontally on a reciprocal shaker. All treatments were performed in duplicate, but the repeat experiment was at higher concentrations of chlorpyrifos (0.0096, 0.048, 0.24, 1.20 and 6.00 mg/L) and endosulfan (0.0038, 0.019, 0.095, 0.475 and 2.375 mg/L). The appropriate blanks of no soil, (Using one of the initial concentrations made up), and no pesticide (only soil and the CaCl_2 solution), were also shaken. The solutions were transferred into 25 ml glass jars and centrifuged at 3500 rpm for ± 1.5 min. The supernatants were transferred to glass sample bottles using a 10 ml Cambridge Pipette to avoid visible organics and this was repeated until at least 50 ml supernatant had been collected. The residues were retained in the centrifuge jars for later desorption studies. The extracts were stored at 5°C and in the dark. This method was adapted from the United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Fate, Transport and Transformation Test Guidelines (1998) (<http://www.epa.gov/epahome/research.htm> under heading "Researchers and Scientists/Test Methods and Guidelines/OPPTS Harmonized Test Guidelines.").

B.2 Pesticide Extraction

The pesticides were extracted from the equilibrium waters and initial concentrations (C_i) using solid phase columns, (Chromabond C18ec/ 6ml / 500 mg). The solid phase extraction column was conditioned with two column volumes of ethyl acetate,

one column volume of methanol and one column volume of distilled water. The samples were shaken well before taking an aliquot for extraction. The volume of sample used for extraction varied according to *Ci* (Table B.1 – B.4). All extracts were made up to 20 ml and were then passed slowly through the column, the rate of flow through the column was controlled by connecting the cartridge to a vacuum manifold. The column was washed to remove any non-pesticide material by flushing one column volume of distilled water through it and then dried thoroughly for 15 minutes under a vacuum. The pesticides were eluted from the column with two aliquots each of 1ml ethyl acetate. The ethyl acetate was then evaporated in a stream of nitrogen at room temperature. The residue was reconstituted in a volume of hexane. The first set of samples were made up in different volumes of hexane according to the *Ci* concentration while the second set of samples were all made up to 0.5 ml hexane (Table B.1 – B.4). The extracts were analysed by capillary gas chromatography.

Table B.1: First set of sorption test samples for Chlorpyrifos on soil HR1 and HR2

Sample label	Initial conc. added to soil before shaking (mg/l)	Aliquot taken For extraction (ml)	Volume added To C ₁₈ cartridge (ml)	Volume made up to after blowing down (ml)	Dilution factor
HR1A	4.8	1	20	10	10
HR1B	0.96	5	20	10	2
HR1C	0.192	10	20	10	1
HR1D	0.0384	10	20	1	0.1
HR1E	0.00192	10	20	1	0.1
HR1K (no soil) ¹	0.192	10	20	10	1
HR1KA ²	0.00	10	20	10	1
HR2F	4.8	1	20	10	10
HR2G	0.96	5	20	10	2
HR2H	0.192	10	20	10	1
HR2I	0.0384	10	20	1	0.1
HR2J	0.00192	10	20	1	0.1
HR2L (no soil) ¹	0.192	10	20	10	1
HR2LA ²	0.00	10	20	10	1
Standards:	<i>Ci</i>				
1	4.8	1	20	10	10
2	0.96	5	20	10	2
3	0.192	10	20	10	1
4	0.0384	10	20	1	0.1
5	0.00192	10	20	1	0.1

¹ No soil was added to this sample.

² No pesticide was added to this sample.

Table B.2: Second set of sorption test samples for Chlorpyrifos on soil HR1 and HR2

Sample label	Initial conc. added to soil before shaking (mg/l)	Aliquot taken For extraction (ml)	Volume added to C ₁₈ cartridge (ml)	Volume made up to after blowing down (ml)	Dilution factor
HR11	6.00	1	20	0.5	0.5
HR12	1.2	2	20	0.5	0.25
HR13	0.24	5	20	0.5	0.1
HR14	0.048	10	20	0.5	0.05
HR15	0.0096	20	20	0.5	0.025
HRCLO (no soil) ¹	1.2	20	20	0.5	0.025
HR16 ²	0.00	20	20	0.5	0.025
HR27	6.00	1	20	0.5	0.5
HR28	1.2	2	20	0.5	0.25
HR29	0.24	5	20	0.5	0.1
HR210	0.048	10	20	0.5	0.05
HR211	0.0096	20	20	0.5	0.025
HRCLO (no soil) ¹	1.2	20	20	0.5	0.025
HR212 ²	0.00	20	20	0.5	0.025
Standards:	Ci				
1	6.00	1	20	0.5	0.5
2	1.2	2	20	0.5	0.25
3	0.24	5	20	0.5	0.1
4	0.048	10	20	0.5	0.05
5	0.0096	20	20	0.5	0.025

¹ No soil was added to this sample.² No pesticide was added to this sample.

Table B.3: First set of sorption test samples for Endosulfan on soil HR1 and HR2

Sample label	Initial conc. added to soil before shaking (mg/l)	Aliquot taken For extraction (ml)	Volume added to C ₁₈ cartridge (ml)	Volume made up to after blowing down (ml)	Dilution factor
HR1M	0.475	10	20	10	1
HR1N	0.095	10	20	2	0.2
HR1O	0.019	10	20	1	0.1
HR1P	0.0038	20	20	1	0.05
HR1Q	0.00019	20	20	1	0.05
HRW (no soil) ¹	0.095	10	20	2	0.2
HRWA ²	0.00	10	20	2	0.2
HR2R	0.475	10	20	10	1
HR2S	0.095	10	20	2	0.2
HR2T	0.019	10	20	1	0.1
HR2U	0.0038	20	20	1	0.05
HR2V	0.00019	20	20	1	0.05
HRK (no soil) ¹	0.095	10	20	2	0.2
HRKA ²	0.00	10	20	2	0.2
Standards:	C_i				
1	0.475	10	20	10	1
2	0.095	10	20	2	0.2
3	0.019	10	20	1	0.1
4	0.0038	20	20	1	0.05
5	0.00019	20	20	1	0.05

¹ No soil was added to this sample.² No pesticide was added to this sample.

Table B.4: Second set of sorption test samples for Endosulfan on soil HR1 and HR2

Sample label	Initial conc. added to soil before shaking (mg/l)	Aliquot taken For extraction (ml)	Volume added to C ₁₈ cartridge (ml)	Volume made up to after blowing down (ml)	Dilution factor
HR1AB	2.375	2	20	0.5	0.25
HR1CD	0.475	5	20	0.5	0.1
HR1EF	0.095	10	20	0.5	0.05
HR1GH	0.019	10	20	0.5	0.05
HR1IJ	0.0038	20	20	0.5	0.025
HREND (no soil) ¹	0.095	20	20	0.5	0.025
HR1KL ²	0.00	20	20	0.5	0.025
HR2MN	2.375	2	20	0.5	0.25
HR2OP	0.475	5	20	0.5	0.1
HR2QR	0.095	10	20	0.5	0.05
HR2ST	0.019	10	20	0.5	0.05
HR2UV	0.0038	20	20	0.5	0.025
HREND (no soil) ¹	0.095	20	20	0.5	0.025
HR2WY ²	0.00	20	20	0.5	0.025
Standards:	C_i				
1	2.375	2	20	0.5	0.25
2	0.475	5	20	0.5	0.1
3	0.095	10	20	0.5	0.05
4	0.019	10	20	0.5	0.05
5	0.00038	20	20	0.5	0.25

¹ No soil was added to this sample.

² No pesticide was added to this sample.

B.3 Capillary Gas Chromatography – Electron Capture Detection (GC-ECD)

USEPA Methods 8141A and 8081A are detailed documents available from <http://www.epa.gov/epaoswer/hazwaste/test/8xxx.htm>. These documents discuss the analysis of organochlorine and organophosphorus pesticides by gas chromatography. The Pesticide Division of the Government Forensic Chemistry Office, Cape Town performed the following analyses. The aim was to determine the concentration of organochlorine pesticides in extracts from liquid matrices, using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the packed columns, these columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. Endosulfan- α , endosulfan- β and endosulfan sulphate can be determined by either a single or dual column analysis system. A dual column system was used: Two 15 m (J & W DB1) x 0.32 mm ID fused-silica, open tubular columns of the same polarities were connected to an injection tee and each was connected to a detector. The two columns were utilised to facilitate a dual-detection system: one column for ECD and the other for a flame photometric detector (FPD). According to EPA method 8081A compound identification should be confirmed by a second column of a different polarity (type) to the first column, as well as by two different detection systems. Extracts suitable for analysis by this method may also be analysed for organophosphorus pesticides like chlorpyrifos. A FPD is more specific than ECD for chlorpyrifos. Both detectors were used for the pesticide analysis. The ECD

should only be used when previous analyses have demonstrated that interferences will not adversely effect quantitation, and that the detector sensitivity is sufficient to meet regulatory limits. The data system used for presenting chromatograms, retention times, and calculating peak integration was Hewlett Packard Chem. Station.

Contamination in solvents, reagents, glassware, and other sample processing hardware may have caused method interference. However, standard procedures were used to minimise interferences. Reagent grade hexane and ethyl acetate were used for extraction and injection. Stock standard solutions were prepared from pure standard materials and calibration standards prepared by dilution of these with hexane. Calibration standards especially organophosphorus should be checked for purity and replaced every two months. The EPA suggests that internal standards or surrogate standards be added to all samples and blanks to check the performance of the method. This method was checked by making up aqueous solutions of known concentration from the pure standard materials and by using the same extraction and GC method, the recoveries were checked (Table B.5)

Table B.5: Recoveries of chlorpyrifos and endosulfan by solid phase extraction

Pesticide	Recovery (%)
Endosulfan	67.6
Endosulfan α	62.2
Endosulfan β	80.3
Chlorpyrifos	50.5

The recoveries were carried out in triplicate and the values recorded in Table B.5 are the mean values. According to Tomlic (1994), technical grade endosulfan is a mixture of two stereoisomers with 64-67% endosulfan- α and 29-32% endosulfan- β . Using the standards made up for the recoveries and using the described method the ratio of α : β in the commercial grade product and the samples was 75.8%:24.2%. The similarity of the results is an indication of the accuracy of the method used.

The EPA method suggests that sample extraction should begin within 7 days of collection. This was not always the case and this delay may account for the observation of degradation products, e.g. endosulfan sulphate peak, in the extracts, and thus overestimation of adsorption coefficients.

The compounds were identified by retention times which are unique to the GC conditions and column used. The operator established retention time windows a crucial step to the identification of target compounds. Table B.6 is a compilation of the retention times, method detection limits (MDL) and estimated quantitation limits (EQL) for chlorpyrifos and endosulfan in water matrices using 15m x 32mm ID dual column system from ECD detector. Examples of the chromatographs for endosulfan and chlorpyrifos are provided in Figure B.1 and Figure B.2, respectively.

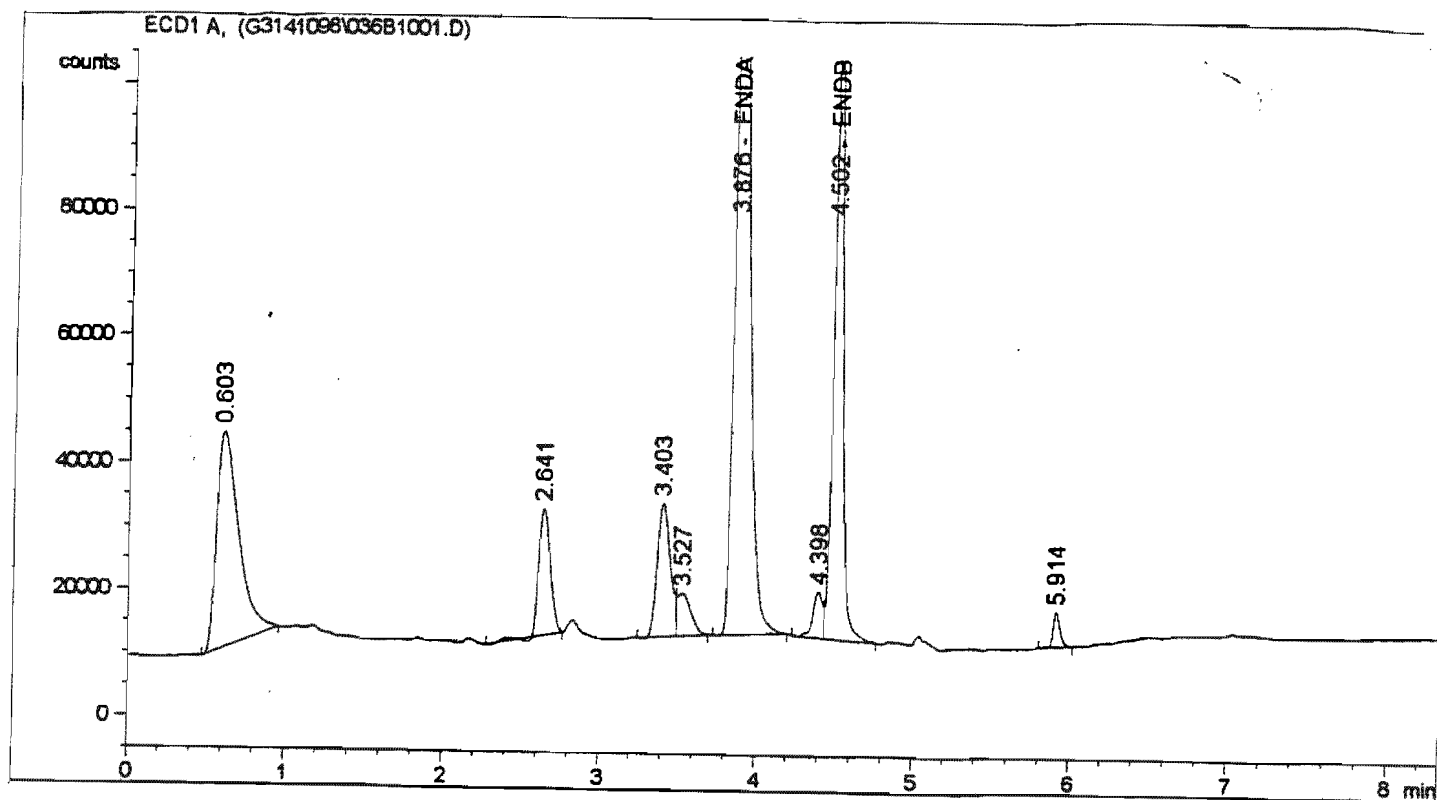


Figure B.1 Example chromatograph for endosulfan

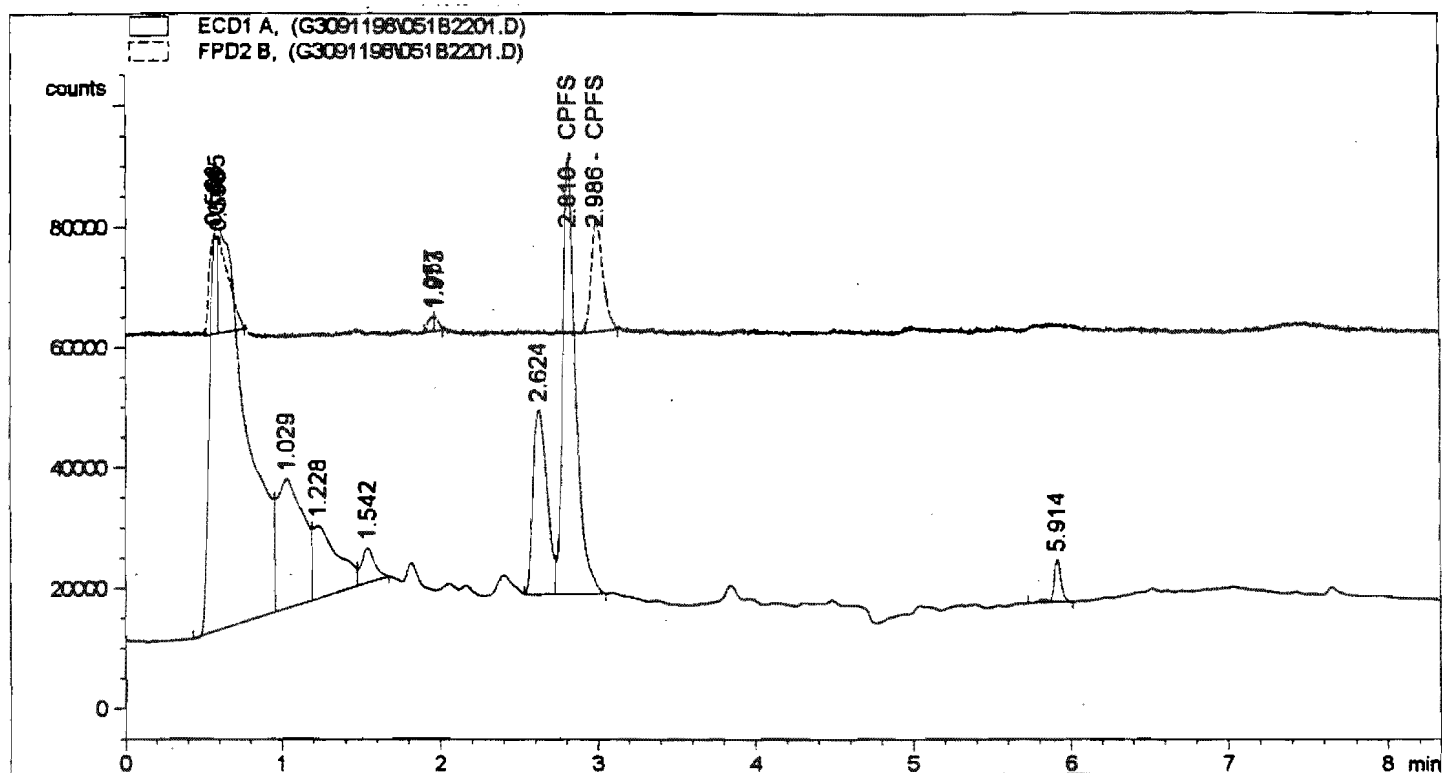


Figure B.2 Example chromatograph for chlorpyrifos

Table B.6: Retention times, method detection limits (MDL) and estimated quantitation limits (EQL) for chlorpyrifos and endosulfan in water matrices using 15m x 32mm ID dual column system from ECD detector.

Pesticide	Average Retention times (min)	MDL ($\mu\text{g/L}$)	EQL ($\mu\text{g/L}$)
Endosulfan α	3.85	1.3	13.0
Endosulfan β	4.48	0.9	9.0
Endosulfan sulphate	4.94	Unknown	Unknown
Chlorpyrifos	2.82	0.07	0.70

The operating conditions were as follows: for a 15m x 32 mm ID fused silica capillary column (J&W DB1), film thickness 0.25 μm .

Carrier gas	Nitrogen
Carrier gas pressure	20 psi
Injector temperature	230°C
Detector temperature	300°C
Initial temperature	170°C, hold 0.50 minutes
Temperature program	170°C to 195°C at 20 °C/min, followed by 195°C to 280°C at 30 °C/min
Final temperature	280°C

An injection volume of 5 μl was used for samples and standards. Calibration factors were not used to calculate the sample concentrations and therefore the error associated with quantification was not known. Quantification was based on peak area. The concentration of the sample was calculated by comparing its area with that of the area of standards made up from the commercial grade product which were also the initial concentrations added to the soils for the sorption tests. Thus, calibration was based on a single point calibration line. If peaks were 2.5 times the baseline noise levels, the validity of the quantitative result may be questionable. Performance data (accuracy and precision) for this specific method are available on request from the laboratory of interest.

B.4 Pesticide sorption test results and calculations

Definitions and abbreviations:

C_i - is the initial concentration (weight of test substance /volume solution) in mg/L. The initial concentrations used in the calculations for amount adsorbed are assumed to be the aimed at concentrations calculated from the dilution of the mass of pesticide in the commercial grade product. The equilibrium concentration (*C_e*) was determined based on this assumption. The assumption

was made in order to correct for the percent recoveries (Table b.5) and errors that could occur from the calibration being based on a single point calibration line. The RSD associated with the initial concentration was calculated to be between 2 – 6 %.

v – is the volume of the initial concentration, ***C_i***, added to the soil. It is 0.07 L in all of the experiments.

T – is the quantity of test substance in the initial solution (***C_i*** x **v**) in milligrams (mg)

C_e – is the final concentration (equilibrium concentration) after shaking and is corrected for the no pesticide blank. It is recorded in mg/L (ppm) in the tables but is plotted as µg/ml (ppm) in the adsorption isotherms.

t – is the quantity of the test substance in the final concentration (**C_e** x **v**) in milligrams (mg)

m – is the air dried, sieved quantity of soil used in the adsorption experiment in grams (g). It is 14g in each case.

X – is quantity adsorbed (**T** – **t**) in milligrams (mg)

X/m – is the quantity of test substance adsorbed per gram of soil. **X** is converted to µg and divided by 14g [(**X** × 1000)/**m**].

Table B.7: Results of first sorption experiment with chlorpyrifos at initial concentrations 4.8, 0.96, 0.192, 0.0384 and 0.00192 mg/L on soils HR1 and HR2.

Data	Sample label									
	HR1A	HR1B	HR1C	HR1D	HR1E	HR2F	HR2G	HR2H	HR2I	HR2J
Ci (mg/l)	4.8	0.96	0.192	0.0384	0.00192	4.8	0.96	0.192	0.0384	0.00192
T (Ci x 0.07L) (mg)	0.336	0.0672	0.01344	0.00269	0.00013	0.336	0.0672	0.01344	0.00269	0.00013
C _e (mg/l)	2.4326	0.0555	0.00334	0.00109	2.3E-05	2.9235	0.2307	0.03202	0.00436	1.9E-04
t (C _e x 0.07L) (mg)	0.17028	0.00388	0.00023	7.62E-05	1.6E-06	0.20464	0.01615	0.00224	0.00030	1.3E-05
X (mg)	0.16572	0.06332	0.01321	0.00261	0.00013	0.13136	0.05105	0.01119	0.00238	0.00012
X/m (µg/g)	11.837	4.52269	0.94327	0.18656	0.00948	9.3825	3.64672	0.79991	0.1702	0.00862
LOG C _e	0.3861	-1.2560	-2.4755	-2.9632	-4.6368	0.4659	-0.6370	-1.4946	-2.3605	-3.7095
LOG X/m	1.0732	0.6554	-0.0254	-0.7292	-2.0230	0.9723	0.5619	-0.0970	-0.7690	-2.0643

Table B.8: Results of second sorption experiment with chlorpyrifos at initial concentrations of 6, 1.2, 0.24, 0.048 and 0.0096 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR11	HR12	HR13	HR14	HR15	HR27	HR28	HR29	HR210	HR211
Ci (mg/l)	6	1.2	0.24	0.048	0.0096	6	1.2	0.24	0.048	0.0096
T (Ci x 0.07L) (mg)	0.42	0.084	0.0168	0.00336	0.00067	0.42	0.084	0.0168	0.00336	0.00067
C _e (mg/l)	1.0093	0.0896	0.0094	0.00260	0.0	2.77376	0.20739	0.03419	0.00980	0.00164
t (C _e x 0.07L) (mg)	0.0706	0.0063	0.00066	0.00018	0.0	0.19416	0.01452	0.00239	0.00069	0.00011
X (mg)	0.3493	0.0777	0.01614	0.0032	0.00067	0.22584	0.06948	0.01441	0.00267	0.00056
X/m (µg/g)	24.9535	5.5522	1.1529	0.2270	0.048	16.1312	4.96302	1.02903	0.1910	0.03977
LOG C _e	0.0040	-1.0479	-2.0263	-2.5850	E	0.4431	-0.6832	-1.4660	-2.0087	-2.7838
LOG X/m	1.3971	0.7445	0.0618	-0.6440	-1.31876	1.2077	0.6957	0.01243	-0.7190	-1.4004

Table B.9: Results of the first sorption experiment with endosulfan at initial concentrations of 0.475, 0.095, 0.019, 0.0038 and 0.0019 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR1M	HR1N	HR1O	HR1P	HR1Q	HR2R	HR2S	HR2T	HR2U	HR2V
Ci (mg/l)	0.475	0.095	0.019	0.0038	0.00019	0.475	0.095	0.019	0.0038	0.00019
T (Ci x 0.07L) (mg)	0.03325	0.00665	0.00133	0.00027	1.3E-05	0.03325	0.00665	0.00133	0.00027	1.3E-05
C _e (mg/l)	0.01125	0.00120	0.00037	0.00022	6.6E-05	0.02124	0.00383	0.00074	0.00011	1.5E-05
t (C _e x 0.07L) (mg)	0.00079	8.4E-05	2.6E-05	1.6E-05	4.6E-06	0.00149	0.00028	5.2E-05	7.8E-06	1.0E-06
X (mg)	0.03246	0.00657	0.00130	0.00025	8.7E-06	0.03176	0.00638	0.00128	0.00026	1.2E-05
X/m (µg/g)	2.31876	0.46900	0.09314	0.01789	0.00062	2.26886	0.45585	0.09128	0.01844	0.00088
LOG C _e	-1.9489	-2.9207	-3.4294	-3.6519	-4.1781	-1.6728	-2.4168	-3.1283	-3.9512	-4.8279
LOG X/m	0.3653	-0.3288	-1.0309	-1.7475	-3.2088	0.3558	-0.3412	-1.0396	-1.7342	-3.0576

Table B.10: Results of the second sorption experiment with endosulfan at initial concentrations of 2.375, 0.475, 0.095, 0.019 and 0.00038 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR1AB	HR1CD	HR1EF	HR1GH	HR1IJ	HR2MN	HR2OP	HR2QR	HR2ST	HR2UV
Ci (mg/l)	2.375	0.475	0.095	0.019	0.00038	2.375	0.475	0.095	0.019	0.00038
T (Ci x 0.07L) (mg)	0.16625	0.03325	0.00665	0.00133	2.6E-05	0.16625	0.03325	0.00665	0.00133	2.6E-05
C _e (mg/l)	0.16611	0.00948	0.00153	0.00109	2.8E-05	0.08217	0.01398	0.00133	0.00082	1.9E-05
t (C _e x 0.07L) (mg)	0.01163	0.00066	0.00011	7.6E-05	1.9E-06	0.00575	0.00098	9.3E-05	5.7E-05	1.3E-06
X (mg)	0.15462	0.03259	0.00654	0.00125	2.4E-05	0.16050	0.03227	0.00655	0.00127	2.5E-05
X/m (µg/g)	11.0444	2.32762	0.46733	0.08955	0.00176	11.4641	2.30509	0.46835	0.09092	0.00180
LOG C _e	-0.78000	-2.0233	-2.8139	-2.9623	-4.5483	-1.0853	-1.8544	-2.8763	-3.0885	-4.7185
LOG X/m	1.0431	0.3669	-0.3304	-1.0479	-2.7549	1.0593	0.3627	-0.3294	-1.0413	-2.7437

Table B.11: Results of the first sorption experiment for endosulfan alpha at initial concentration of 0.36005, 0.07201, 0.01440, 0.00288 and 0.00014 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR1M	HR1N	HR1O	HR1P	HR1Q	HR2R	HR2S	HR2T	HR2U	HR2V
C _i (mg/l)	0.36005	0.07201	0.01440	0.00288	0.00014	0.36005	0.07201	0.01440	0.00288	0.00014
T (C _i × 0.07L) (mg)	0.02520	0.00504	0.00101	0.00020	0.00001	0.02520	0.00504	0.00101	0.00020	0.00001
C _e (mg/l)	0.01804	0.00269	0.00093	0.00056	0.00010	0.03570	0.00830	0.00194	0.00032	0.00006
t (C _e × 0.07L) (mg)	0.00126	0.00019	0.00007	0.00004	0.00001	0.00250	0.00058	0.00014	0.00002	0.00000
X (mg)	0.02394	0.00485	0.00094	0.00016	0.00000	0.02270	0.00446	0.00087	0.00018	0.00001
X/m (μg/g)	1.71004	0.34660	0.06734	0.01158	0.00022	1.62176	0.31856	0.06232	0.01282	0.00042
LOG C _e	-1.7437	-2.5704	-3.0293	-3.2484	-4.0000	-1.4473	-2.0810	-2.7124	-3.5001	-4.2194
LOG X/m	0.2330	-0.4602	-1.1718	-1.9363	-3.6574	0.2100	-0.4968	-1.2054	-1.8921	-3.3784

Table B.12: Results of the first sorption experiment for endosulfan beta at initial concentration of 0.11495, 0.02299, 0.00460, 0.00092 and 0.00005 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR1M	HR1N	HR1O	HR1P	HR1Q	HR2R	HR2S	HR2T	HR2U	HR2V
C _i (mg/l)	0.11495	0.02299	0.00460	0.00092	0.00005	0.11495	0.02299	0.004598	0.00092	4.6E-05
T (C _i × 0.07L) (mg)	0.00805	0.00161	0.00032	0.00006	0.00000	0.00805	0.00161	0.00032	0.00006	0.00000
C _e (mg/l)	0.00112	0.00009	0.00002	0.00003	0.00001	0.00184	0.00033	0.00004	0.00001	0.00000
t (C _e × 0.07L) (mg)	0.00008	0.00001	0.00000	0.00000	0.00000	0.00013	0.00002	0.00000	0.00000	0.00000
X (mg)	0.00797	0.00160	0.00032	0.00006	0.00000	0.00792	0.00159	0.00032	0.00006	0.00000
X/m (μg/g)	0.56915	0.11448	0.02288	0.00447	0.00020	0.56554	0.11332	0.02281	0.00455	0.00023
LOG C _e	-2.9509	-4.0296	-4.6567	-4.6001	-5.2500	-2.7349	-3.4876	-4.4328	-5.0201	-7.0000
LOG X/m	-0.2448	-0.9413	-1.6405	-2.3495	-3.6951	-0.2475	-0.9457	-1.6420	-2.3420	-3.6385

Table B.13: Results of the second sorption experiment with endosulfan alpha at initial concentrations of 1.80025, 0.36005, 0.07201, 0.01440 and 0.00029 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR1AB	HR1CD	HR1EF	HR1GH	HR1IJ	HR2MN	HR2OP	HR2QR	HR2ST	HR2UV
C _i (mg/l)	1.80025	0.36005	0.07201	0.01440	0.00029	1.80025	0.36005	0.07201	0.01440	0.00029
T (C _i x 0.07L) (mg)	0.12602	0.02520	0.00504	0.00101	0.00002	0.12602	0.02520	0.00504	0.00101	0.00002
C _e (mg/l)	0.12438	0.00785	0.00072	0.00094	0.00003	0.06264	0.01103	0.00107	0.00065	0.00002
t (C _e x 0.07L) (mg)	0.00871	0.00055	0.00005	0.00007	0.00000	0.00438	0.00077	0.00007	0.00005	0.00000
X (mg)	0.11731	0.02465	0.00499	0.00094	0.00002	0.12163	0.02443	0.00497	0.00096	0.00002
X/m (µg/g)	8.37936	1.76101	0.35644	0.06731	0.00130	8.68806	1.74508	0.35471	0.06877	0.00136
LOG C _e	-0.9053	-2.1053	-3.1419	-3.0268	-4.5503	-1.2032	-1.9572	-2.9710	-3.1884	-4.7814
LOG X/m	0.9232	0.2458	-0.4480	-1.1719	-2.8863	0.9389	0.2418	-0.4501	-1.1626	-2.8673

Table B.14: Results of the second sorption experiment with endosulfan beta at initial concentrations of 0.57475, 0.11495, 0.02299, 0.00460 and 0.00009 mg/L on soils HR1 and HR2.

Data	Sample Label									
	HR1AB	HR1CD	HR1EF	HR1GH	HR1IJ	HR2MN	HR2OP	HR2QR	HR2ST	HR2UV
C _i (mg/l)	0.57475	0.11495	0.02299	0.00460	0.00009	0.57475	0.11495	0.02299	0.00460	0.00009
T (C _i x 0.07L) (mg)	0.04023	0.00805	0.00161	0.00032	0.00001	0.04023	0.00805	0.00161	0.00032	0.00001
C _e (mg/l)	0.04096	0.00203	0.00033	0.00021	0.00000	0.01562	0.00311	0.00028	0.00018	0.00000
t (C _e x 0.07L) (mg)	0.00287	0.00014	0.00002	0.00001	0.00000	0.00109	0.00022	0.00002	0.00001	0.00000
X (mg)	0.03737	0.00790	0.00159	0.00031	0.00001	0.03914	0.00783	0.00159	0.00031	0.00001
X/m (µg/g)	2.66896	0.56458	0.11328	0.02195	0.00045	2.79567	0.55922	0.11355	0.02211	0.00045
LOG C _e	-1.3877	-2.6918	-3.4753	-3.6831	-5.5494	-1.8064	-2.5078	-3.5518	-3.7561	-5.5320
LOG X/m	0.4263	-0.2483	-0.9459	-1.6585	-3.3510	0.4465	-0.2524	-0.9448	-1.6553	-3.3515

B.5 Indirect methods and calculations for estimating K_{oc}

B.5.1 Estimating K_{oc} using K_{ow}

Rao and Davidson (1982) predicted the K_{oc} for thirteen organophosphates using the following equation:

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18 \quad (r^2 = 0.91) \quad \text{Eq. B.5.1}$$

where K_{ow} is the octanol-water partition coefficient. This equation was used to estimate K_{oc} for chlorpyrifos on soils HR1 and HR2. The K_{ow} values for the pesticides were taken from Tomlic (1994). Using a K_{ow} of 50000 K_{oc} for chlorpyrifos was calculated by means of Eq. B.5.1 as follows:

$$\begin{aligned} \log K_{oc} &= 1.029 \log 50\,000 - 0.18 \\ \log K_{oc} &= 4.655 \\ K_{oc} &= 45211 \end{aligned}$$

Hassett *et al.* (1989) estimated K_{oc} using 23 organochlorines with the equation:

$$\log K_{oc} = \log K_{ow} - 0.317 \quad (r^2 = 0.98) \quad \text{Eq. B.5.2}$$

The K_{oc} for endosulfan was estimated using Eq. B.5.2. with a K_{ow} of 54954 as follows:

$$\begin{aligned} \log K_{oc} &= \log 54954 - 0.317 \\ \log K_{oc} &= 4.423 \\ K_{oc} &= 26485 \end{aligned}$$

B.5.2 Estimating K_d using specific surface area of soil

Pionke and DeAngelis (1980) estimated the sorption coefficient from the specific surface area using the equation,

$$K_d = mSS \quad \text{Eq. B.5.3}$$

In which m is a fitted coefficient of linear regression and was provided by Pionke and DeAngelis (1980) while SS is the specific surface area. SS was calculated according to the equation:

$$SS = 100 (OC) + 2.0 (Cl) + 0.4 (Si) + 0.005 (Sa) \quad \text{Eq. B.5.4}$$

Where OC is the % organic carbon and Cl , Si and Sa are the % clay, silt and sand, respectively. The % organic carbon and % particle size were taken from Table 2.4, Chapter 2.

HR1

$$SS = 100 (1.58) + 2.0 (9.0) + 0.4 (16) + 0.005 (76)$$

$$SS = 182.8$$

HR2

$$SS = 100 (0.87) + 2.0 (2) + 0.4 (3) + 0.005 (94)$$

$$SS = 92.7$$

Chlorpyrifos

HR1:

$$K_d = mSS$$

$$K_d = 65 \times 182.8$$

$$K_d = 11882$$

HR2:

$$K_d = mSS$$

$$K_d = 65 \times 92.7$$

$$K_d = 6025.5$$

Endosulfan

HR1:

$$K_d = mSS$$

$$K_d = 100 \times 182.8$$

$$K_d = 18280$$

HR2:

$$K_d = mSS$$

$$K_d = 100 \times 92.7$$

$$K_d = 9270$$

C.2 Hydrology component

The data presented in the following section are the input parameters (as discussed in Chapter 4, Section 4.3) and the output results of the GLEAMS simulation A (as discussed in Chapter 4, Section 4.6.1). The precipitation data used to generate the results of the water balance calculations, presented in the following output, are provided in Table C.1.

HYDROLOGY INPUT PARAMETER FILENAME: a:hydro4

GLEAMS 2.1 HYDROLOGY OUTPUT

HEX VALLEY, SIMULATION 4, including irrigation in precipitation file, experimentally determined Koc, one year.

MONTHLY MEAN MINIMUM TEMPERATURES, DEGREES CENTIGRADE					
14.26	13.46	11.49	8.89	6.34	4.53
3.95	4.75	6.72	9.33	11.87	13.68
MONTHLY MEAN MAXIMUM TEMPERATURES, DEGREES CENTIGRADE					
29.77	29.25	27.61	25.27	22.86	21.03
20.27	20.79	22.43	24.77	27.18	29.01
MONTHLY MEAN RADIATION, LANGLEYS PER DAY					
481.50	450.79	400.42	343.87	296.31	270.46
273.27	303.98	354.35	410.90	458.47	484.31
MONTHLY MEAN WIND MOVEMENT, KILOMETERS PER DAY					
165.44	145.42	129.81	122.81	126.28	139.31
158.39	178.42	194.02	201.03	197.55	184.53
MONTHLY MEAN DEW POINT TEMPERATURES, DEGREES CENTIGRADE					
12.60	11.52	9.88	8.11	6.70	6.01
6.24	7.32	8.96	10.72	12.14	12.83

LEAF AREA INDEX TABLE

IRFLG	YEAR	DATE	LAI	HEIGHT
0	1	274	.70	.1
0	1	313	1.50	.2
0	1	352	2.50	.3
0	1	366	3.25	.4
0	2	1	3.25	.4
0	2	65	5.00	.6
0	2	105	3.50	.6

FIELD AREA	=	40.000	HA
ROOTING DEPTH	=	100.000	CM
SATURATED CONDUCTIVITY	=	.480	CM/HR
AVG. FUL	=	.194	
AVG. FIELD CAPACITY	=	.110	CM/CM
INITIAL STORAGE FRACTION	=	.600	
EVAPORATION COEFFICIENT	=	3.300	

AVERAGE POROSITY	=	.400 CC/CC
SCS CURVE NUMBER	=	60.000
CHANNEL SLOPE	=	.490 M/M
WATERSHED LEN/WIDTH RATIO	=	2.088
PEAK FLOW RATE COEFFICIENT	=	164.440
PEAK FLOW RATE EXPONENT	=	.889
UPPER LIMIT OF STORAGE	=	36.000 CM
AVG. 15-BAR WATER CONTENT	=	.040 CM/CM
INITIAL SOIL WATER STORAGE	=	4.200 CM
FRAC. P.A.W. TO BEGIN IRR.	=	

UPPER LIMIT OF STORAGES, CM

.360	3.420	3.420	4.800	4.800	4.800	4.800	4.800	4.800
------	-------	-------	-------	-------	-------	-------	-------	-------

INITIAL PLANT AVAILABLE STORAGE, CM

.042	.399	.399	.560	.560	.560	.560	.560	.560
------	------	------	------	------	------	------	------	------

POROSITY BY LAYER (CC/CC)

.400	.400	.400	.400	.400	.400	.400	.400	.400
------	------	------	------	------	------	------	------	------

FUL BY LAYER (CM/CM)

.194	.194	.194	.194	.194	.194	.194	.194	.194
------	------	------	------	------	------	------	------	------

FEILD CAPACITY BY LAYER (CM/CM)

.110	.110	.110	.110	.110	.110	.110	.110	.110
------	------	------	------	------	------	------	------	------

FIELD CAPACITY BY LAYER (CM)

.110	1.045	1.045	1.467	1.467	1.467	1.467	1.467	1.467
------	-------	-------	-------	-------	-------	-------	-------	-------

15-BAR WATER CONTENT BY LAYER (CM/CM)

.040	.040	.040	.040	.040	.040	.040	.040	.040
------	------	------	------	------	------	------	------	------

WATER CONTENT AT WILT. PT. BY LAYER (CM)

.040	.380	.380	.533	.533	.533	.533	.533	.533
------	------	------	------	------	------	------	------	------

FOREST COVER = NONE

ANNUAL TOTALS FOR 1997

PRECIP., TOTAL = 42.040 CM
PRECIP., NET = 42.040 CM
PREDICTED RUNOFF = .000 CM
DEEP PERCOLATION = 3.595 CM
ACTUAL PLANT EVAP = 21.793 CM
ACTUAL SOIL EVAP = 18.603 CM
TOTAL ET = 40.397 CM
TOTAL INTERCEPTION= .000 CM
TOTAL INT PLUS ET = 40.397 CM
BEGIN SOIL WATER = 4.200 CM
FINAL SOIL WATER = 2.249 CM
IRRIGATION APPLIED= .000 CM
WATER BUDGET BAL. = .000 CM

ANNUAL TOTALS FOR 1998

PRECIP., TOTAL = 94.110 CM
PRECIP., NET = 94.110 CM
PREDICTED RUNOFF = .000 CM
DEEP PERCOLATION = 24.304 CM
ACTUAL PLANT EVAP = 16.769 CM
ACTUAL SOIL EVAP = 48.286 CM
TOTAL ET = 65.055 CM
TOTAL INTERCEPTION= .000 CM
TOTAL INT PLUS ET = 65.055 CM
BEGIN SOIL WATER = 2.249 CM
FINAL SOIL WATER = 7.000 CM
IRRIGATION APPLIED= .000 CM
WATER BUDGET BAL. = .000 CM

AVERAGE ANNUAL VALUES

PRECIPITATION = 68.075 CM
PREDICTED RUNOFF = .000 CM
DEEP PERCOLATION = 13.949 CM
TOTAL ET = 52.726 CM
IRRIGATION APPLIED= .000 CM

AVG. AVAL. STORAGE = 12.288 CM
FINAL AVAL. STORAGE = 11.417 CM

FINAL STORAGE FOR EACH FRACTION

.070 .665 .665 .933 .933 .933 .933 .933 .933

1997

MONTH	TOTAL RAIN	NET RAIN	RUNOFF	ET	PERC	AVG SW	IRRIGAT
-----	-----	-----	-----	-----	-----	-----	-----
	CM	CM	CM	CM	CM	CM	CM
JAN	.000	.000	.000	.000	.000	.000	.000
FEB	.000	.000	.000	.000	.000	.000	.000
MAR	.000	.000	.000	.000	.000	.000	.000
APR	.000	.000	.000	.000	.000	.000	.000
MAY	.000	.000	.000	.000	.000	.000	.000
JUN	.120	.120	.000	.106	.000	8.214	.000
JUL	4.540	4.540	.000	3.260	.000	8.776	.000
AUG	2.600	2.600	.000	2.963	.000	9.522	.000
SEP	.000	.000	.000	1.118	.000	8.482	.000
OCT	10.780	10.780	.000	6.488	1.621	10.164	.000
NOV	11.990	11.990	.000	11.332	1.973	10.448	.000
DEC	12.010	12.010	.000	15.130	.000	8.223	.000
TOT	42.040	42.040	.000	40.397	3.595	5.319	.000

1998

MONTH	TOTAL RAIN	NET RAIN	RUNOFF	ET	PERC	AVG SW	IRRIGAT
-----	-----	-----	-----	-----	-----	-----	-----
	CM	CM	CM	CM	CM	CM	CM
JAN	12.370	12.370	.000	10.989	.000	7.810	.000
FEB	9.800	9.800	.000	11.628	.000	5.947	.000
MAR	9.900	9.900	.000	9.887	.000	5.521	.000
APR	12.270	12.270	.000	4.677	2.408	8.981	.000
MAY	8.300	8.300	.000	2.855	5.775	10.722	.000
JUN	1.490	1.490	.000	2.096	.702	10.186	.000
JUL	2.600	2.600	.000	2.166	.000	10.065	.000
AUG	2.600	2.600	.000	2.572	.055	10.080	.000
SEP	.000	.000	.000	1.187	.000	9.071	.000
OCT	10.780	10.780	.000	4.426	4.118	10.523	.000
NOV	11.990	11.990	.000	5.888	6.520	10.807	.000
DEC	12.010	12.010	.000	6.685	4.725	10.805	.000
TOT	94.110	94.110	.000	65.055	24.304	9.210	.000

ANNUAL AVERAGES							
MONTH	TOTAL RAIN	NET RAIN	RUNOFF	ET	PERC	AVG SW	IRRIGAT
JAN	6.185	6.185	.000	5.495	.000	3.905	.000
FEB	4.900	4.900	.000	5.814	.000	2.973	.000
MAR	4.950	4.950	.000	4.943	.000	2.760	.000
APR	6.135	6.135	.000	2.338	1.204	4.491	.000
MAY	4.150	4.150	.000	1.427	2.887	5.361	.000
JUN	.805	.805	.000	1.101	.351	9.200	.000
JUL	3.570	3.570	.000	2.713	.000	9.421	.000
AUG	2.600	2.600	.000	2.767	.028	9.801	.000
SEP	.000	.000	.000	1.153	.000	8.777	.000
OCT	10.780	10.780	.000	5.457	2.870	10.343	.000
NOV	11.990	11.990	.000	8.610	4.247	10.627	.000
DEC	12.010	12.010	.000	10.908	2.362	9.514	.000
TOT	68.075	68.075	.000	52.726	13.949	7.264	.000

C.3 Erosion component

The data presented in the following section are the input parameters (as discussed in Chapter 4, Section 4.4) and the output results of the GLEAMS simulation A (as discussed in Chapter 4, Section 4.6.1).

EROSION INPUT PARAMETER FILENAME: a:eros4

G L E A M S NONPOINT SOURCE POLLUTION MODEL (EROSION/SEDIMENT YIELD)

VERSION 2.1, NOVEMBER 1, 1993 TIFTON GA

CARD 1:HEX RIVER VALLEY, SIMULATION 4, FOR CHLORPYRIFOS AND ENDOSULFAN ONLY,

CARD 2:ON FERNWOOD SOIL.

CARD 3:

CARD 4: 97 98 2 2 1

CARD 5: .020 .050 .930 20.0002000.000

CARD 6: 1 40.000

CARD 7: 915.000 1.500

CARD 8: 1 1.000 .148

CARD 12: 40.000 2.000 .500 2.000 .030 1 20.0 .000

CARD 14: 2

CARD 15: 1 0 0 0 0 0 0 0 0 0 0

CARD 15: 1 0 0 0 0 0 0 0 0 0 0

CARD 16: 1 1.000

CARD 17: .350

CARD 18: 1.000

CARD 19: .038

CARD 17: .350

CARD 18: 1.000

CARD 19: .038

PARTICLE SPECIFICATIONS

TYPE NO.	DIA. MM	EQSAND DIA. MM	SPGRAV. GM/CM**3	FRAC. IN DETACH. SED.
1	.002		2.60	.01
2	.010		2.65	.01
3	.030		1.80	.04
4	.300		1.60	.10
5	.200		2.65	.84

OVERLAND FLOW INPUTS

OVERLAND FLOW TOPOGRAPHY

OVERLAND AREA	40.0000 HECTARES
SLOPE LENGTH	915.00 M
AVERAGE SLOPE	1.5000

SEGMENT TYPES DEFINING THE OVERLAND FLOW PROFILE

THE PROFILE IS UNIFORM

SLOPE STEEPNESS ALONG THE OVERLAND FLOW PROFILE

DISTANCE METERS	DISTANCE NONDIM.	SLOPE
.0	.000	.832
915.0	1.000	.832

SOIL ERODIBILITY ALONG THE OVERLAND FLOW PROFILE

DISTANCE METERS	DISTANCE NONDIM.	SOIL EROD
915.0	1.000	.148

C.4 Pesticide component

The data presented in the following section are the input parameters (as discussed in Chapter 4, Section 4.5) and the output results of the GLEAMS simulation A (as discussed in Chapter 4, Section 4.6.2).

PESTICIDE INPUT PARAMETER FILENAME: a:pests4

G L E A M S NONPOINT SOURCE POLLUTION MODEL (PESTICIDES)
VERSION 2.1 NOVEMBER 1, 1993 TIFTON GA

HEX RIVER VALLEY, GLEAMS SIMULATION 4, FOR CHLORPYRIFOS AND ENDOSULFAN, 97 - 98,
FERNWOOD SOIL, USING CALCULATED K_{oc} VALUES, INCREASE ENDO RATE OF APPLICATION.

STARTING DATE FOR SIMULATION 97181 JULIAN DATE

ROOTING DEPTH 1000.00 MM

POROSITY (CC/CC) BY LAYER
1 .400 2 .400 3 .400 4 .400 5 .400 6 .400 7 .400 8 .400 9
.400

FIELD CAPACITY (MM/MM) BY LAYER
1 .110 2 .110 3 .110 4 .110 5 .110 6 .110 7 .110 8 .110 9
.110

WILTING POINT (MM/MM) BY LAYER
1 .040 2 .040 3 .040 4 .040 5 .040 6 .040 7 .040 8 .040 9
.040

ORGANIC MATTER (%) BY LAYER
1 1.70 2 1.70 3 1.70 4 .89 5 .89 6 .89 7 .89 8 .89 9
.89

PESTICIDE INPUTS

SIMULATION FOR THE PERIOD 97181 TO 98181
SIMULATION FOR 2 PESTICIDES.

PEST. NO.	PESTICIDE NAME	WATER SOL. (PPM)	FOLIAR HAFLIF (DAYS)	KOC	FOLIAR RES. (UG/G)	WSHOFF FRAC.	COEFF TRANS	COEFF UPTAKE
1	Lorsban	1.40	3.3	1490.0	.00	.65	.00	.00
	SOIL HALF-LIFE (DAYS)	1	30.00	2	60.00			
2	Thiodan	.32	3.0	17517.0	.00	.05	.00	.00
	SOIL HALF-LIFE (DAYS)	1	70.00	2	120.00			

MONTHLY SUMMARY FOR JUN 1997

1 STORMS PRODUCED	.12 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
0 STORMS PRODUCED	.00 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

MONTHLY SUMMARY FOR JUL 1997

7 STORMS PRODUCED	4.54 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
0 STORMS PRODUCED	.00 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97230	.90	.00	.00	.00	.000

NO. 1 97230 RATE 8.83 DEPTH 1.0 FOLFRFC .40 SOLFRFC .50 METHOD 0 CHEMIGATION .00

STORM SUMMARY: NO RUNOFF OR PERCOLATION -- NO PESTICIDE LOSSES

NO. 1 97237 RATE 8.83 DEPTH 1.0 FOLFRFC .40 SOLFRFC .50 METHOD 0 CHEMIGATION .00

MONTHLY SUMMARY FOR AUG 1997

4 STORMS PRODUCED 2.60 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 0 STORMS PRODUCED .00 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000	.00	.0000	.00	.0000	.00	.0000	.00

NO. 2 97262 RATE .95 DEPTH 1.0 FOLFRFC .40 SOLFRFC .50 METHOD 0 CHEMIGATION .00

MONTHLY SUMMARY FOR SEP 1997

0 STORMS PRODUCED .00 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 0 STORMS PRODUCED .00 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000	.00	.0000	.00	.0000	.00	.0000	.00

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97275	.98	.00	.00	.00	.000

STORM SUMMARY: NO RUNOFF OR PERCOLATION -- NO PESTICIDE LOSSES

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97288	.98	.00	.06	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12 DEPTH, CM 0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-			
1 AFTER	16.9047	.3427	.0022	.0000	.0000	.0000	.0000	.0000	.0000	.0000		
2 AFTER	2.2728	.0047	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000		

STORM INPUT

DATE	RAIN CM	RUNOFF CM	PERC. CM	SOIL LOSS KG/HA	ENRICH. RATIO
97289	.49	.00	.28	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12 DEPTH, CM 0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-			
1 AFTER	16.2195	.3659	.0026	.0000	.0000	.0000	.0000	.0000	.0000	.0000		
2 AFTER	2.2464	.0051	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000		

NO. 2 97292 RATE .95 DEPTH 1.0 FOLFR 40 SOLFR 50 METHOD 0 CHEMIGATION .00

STORM INPUT

DATE	RAIN CM	RUNOFF CM	PERC. CM	SOIL LOSS KG/HA	ENRICH. RATIO
97293	.98	.00	.07	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12												
DEPTH, CM	0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-		
1 AFTER	14.1922	.3928	.0024	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	5.1991	.0069	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97295	.98	.00	.49	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12												
DEPTH, CM	0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-		
1 AFTER	13.0025	.4319	.0033	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	5.0789	.0086	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97296	.49	.00	.24	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12												
DEPTH, CM	0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-		
1 AFTER	12.4451	.4490	.0036	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	5.0199	.0095	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97302	.98	.00	.30	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12												
DEPTH, CM	0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-		
1 AFTER	9.9802	.4801	.0039	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	4.6966	.0125	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97303	.49	.00	.18	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

[illegible]

MONTHLY SUMMARY FOR OCT 1997

13 STORMS PRODUCED	10.78 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
7 STORMS PRODUCED	1.62 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000	.00	.0000	.00	.0000	.00	.0000	.00

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97309	.98	.00	.01	.00	.000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

[illegible]

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97310	.49	.00	.15	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

[illegible]

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97317	.49	.00	.00	.00	.000

STORM SUMMARY: NO RUNOFF OR PERCOLATION -- NO PESTICIDE LOSSES

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97319	2.19	.00	1.40	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

[illegible]

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97331	.98	.00	.00	.00	.000

STORM SUMMARY: NO RUNOFF OR PERCOLATION -- NO PESTICIDE LOSSES

MONTHLY SUMMARY FOR NOV 1997

12 STORMS PRODUCED	11.99 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
5 STORMS PRODUCED	1.97 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
97365	.98	.00	.00	.00	.000

STORM SUMMARY: NO RUNOFF OR PERCOLATION -- NO PESTICIDE LOSSES

MONTHLY SUMMARY FOR DEC 1997

14 STORMS PRODUCED	12.01 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
0 STORMS PRODUCED	.00 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

ANNUAL SUMMARY FOR 1997

51 STORMS PRODUCED	42.04 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
12 STORMS PRODUCED	3.59 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000	.00	.0000	.00	.0000	.00	.0000	.00
Thiodan	.0000	.00	.0000	.00	.0000	.00	.0000	.00

MONTHLY SUMMARY FOR JAN 1998

15 STORMS PRODUCED 12.37 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 0 STORMS PRODUCED .00 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

MONTHLY SUMMARY FOR FEB 1998

12 STORMS PRODUCED 9.80 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 0 STORMS PRODUCED .00 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

STORM INPUT					
DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
98113	.49	.00	.37	.00	.000

STORM SUMMARY						
PEST.	RUNOFF		SEDIMENT		PERCOLATION	
NO.	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY. 12
DEPTH, CM 0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-			
1 AFTER	.0109	.0239	.0012	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	.6454	.0207	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT					
DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
98115	.98	.00	.75	.00	.000

STORM SUMMARY						
PEST.	RUNOFF		SEDIMENT		PERCOLATION	
NO.	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY. 12
DEPTH, CM 0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-			
1 AFTER	.0099	.0226	.0012	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	.6281	.0205	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
98119	.98	.00	.54	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

[illegible]

STORM INPUT

DATE	RAIN	RUNOFF	PERC.	SOIL LOSS	ENRICH.
	CM	CM	CM	KG/HA	RATIO
98120	.49	.00	.38	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC	MASS	CONC	MASS	CONC	MASS
	MG/L	G/HA	UG/G	G/HA	MG/L	G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

[illegible]

MONTHLY SUMMARY FOR APR 1998

16 STORMS PRODUCED	12.27 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
5 STORMS PRODUCED	2.41 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

DATE	RAIN CM	STORM INPUT		SOIL LOSS KG/HA	ENRICH. RATIO
		RUNOFF CM	PERC. CM		
98125	.90	.00	.57	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY. 12
DEPTH, CM	0 - 1	1 - 10	10 - 20	20 - 33	33 - 46	46 - 60	60 - 73	73 - 86	86 - 100	100 -		
1 AFTER	.0069	.0174	.0010	.0000	.0000	.0000	.0000	.0000	.0000	.0000		
2 AFTER	.5587	.0189	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000		

DATE	RAIN CM	STORM INPUT		SOIL LOSS KG/HA	ENRICH. RATIO
		RUNOFF CM	PERC. CM		
98126	1.30	.00	1.20	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11	LAY.
12												
DEPTH, CM	0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-		
1 AFTER	.0063	.0169	.0011	.0000	.0000	.0000	.0000	.0000	.0000			
2 AFTER	.5487	.0189	.0000	.0000	.0000	.0000	.0000	.0000	.0000			

STORM INPUT

DATE	RAIN CM	RUNOFF CM	PERC. CM	SOIL LOSS KG/HA	ENRICH. RATIO
98127	2.25	.00	2.15	.00	.000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11
DEPTH, CM	0 - 1	1 - 10	10- 20	20- 33	33- 46	46- 60	60- 73	73- 86	86-100	100-	
1 AFTER	.0056	.0163	.0012	.0000	.0000	.0000	.0000	.0000	.0000		
2 AFTER	.5377	.0192	.0000	.0000	.0000	.0000	.0000	.0000	.0000		

STORM INPUT

DATE	RAIN CM	RUNOFF CM	PERC. CM	SOIL LOSS KG/HA	ENRICH. RATIO
98128	1.85	.00	1.75	.00	.000

MONTHLY SUMMARY FOR MAY 1998

9 STORMS PRODUCED 8.30 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 6 STORMS PRODUCED 5.77 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

DATE	RAIN CM	STORM INPUT		SOIL LOSS KG/HA	ENRICH. RATIO
		RUNOFF CM	PERC. CM		
98157	1.45	.00	.70	.00	.000

STORM SUMMARY

PEST. NO.	RUNOFF		SEDIMENT		PERCOLATION	
	CONC MG/L	MASS G/HA	CONC UG/G	MASS G/HA	CONC MG/L	MASS G/HA
1	.0000	.0000	.0000	.0000	.0000	.0000
2	.0000	.0000	.0000	.0000	.0000	.0000

PESTICIDE CONCENTRATION (UG/G) IN 9 SOIL LAYERS AFTER THE STORM

	LAY. 1	LAY. 2	LAY. 3	LAY. 4	LAY. 5	LAY. 6	LAY. 7	LAY. 8	LAY. 9	LAY. 10	LAY. 11
DEPTH, CM 0 - 1	1 - 10	10 - 20	20 - 33	33 - 46	46 - 60	60 - 73	73 - 86	86 - 100	100 -		
1 AFTER	.0021	.0072	.0006	.0000	.0000	.0000	.0000	.0000	.0000		
2 AFTER	.3811	.0142	.0000	.0000	.0000	.0000	.0000	.0000	.0000		

MONTHLY SUMMARY FOR JUN 1998

2 STORMS PRODUCED	1.49 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
1 STORMS PRODUCED	.70 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

MONTHLY SUMMARY FOR JUL 1998

6 STORMS PRODUCED	2.60 CM. OF RAINFALL
0 STORMS PRODUCED	.00 CM. OF RUNOFF
0 STORMS PRODUCED	.00 CM. OF PERCOLATION
0 STORMS PRODUCED	.00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

ANNUAL SUMMARY FOR 1998

115 STORMS PRODUCED 94.11 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 49 STORMS PRODUCED 24.30 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000		.0000		.0000		.0000	
Thiodan	.0000		.0000		.0000		.0000	

STORM SUMMARY

166 STORMS PRODUCED 136.15 CM. OF RAINFALL
 0 STORMS PRODUCED .00 CM. OF RUNOFF
 61 STORMS PRODUCED 27.90 CM. OF PERCOLATION
 0 STORMS PRODUCED .00 T/HA OF SEDIMENT

PESTICIDE LOSSES

PESTICIDE	RUNOFF		SEDIMENT		PERCOLATION		TOTAL	
	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.	G/HA	% APP.
Lorsban	.0000	.00	.0000	.00	.0000	.00	.0000	.00
Thiodan	.0000	.00	.0000	.00	.0000	.00	.0000	.00