IMPACTS OF CO-FORMULANTS ON PESTICIDE SORPTION AND LEACHING THROUGH SOIL

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ABSTRACT

A large variety of co-formulants are added to commercial pesticide formulations to enhance their biological effectiveness, but their impacts on the behaviour of active substances are largely unknown due to lack of regulatory measures concerning their use. The overall aim of this research was to investigate the impacts of co-formulants on pesticide sorption and leaching through soil. Leaching and sorption experiments were carried out using technical grade and commercial formulations of four different pesticides at various intervals from application in two soils from the Blackwood and Bishampton associations.

The effects of formulation, residence time and soil type on the leaching behaviour of pesticides were all found to be highly statistically significant ($p<0.001$). Both solubility of the active substance and the type of formulation also influenced the effect of formulation on leaching behaviour of pesticides. The relative difference in mass leached between formulated and technical material of low solubility pesticides was less than that for pesticides with greater water solubility. Greater leaching losses of pesticide were observed from an emulsifiable concentrate (EC) formulation compared to suspension concentrate (SC) formulation for the fungicide azoxystrobin. Results from sorption and desorption experiments on propyzamide in the two soils showed that the batch-equilibrium method is not suitable to study the effect of formulation on pesticide sorption. Rather it is important to use a centrifugation technique under natural moisture conditions to characterise these interactions. The effect of formulation on sorption of propyzamide was highly significant ($p<0.001$) in sandy loam soil, but there was no effect of formulation in the sandy silt loam soil when characterised by a centrifugation technique. Results suggested that any effect of formulation on pesticide sorption was not sufficient to explain fully the effect of formulation on leaching behaviour. Two-site and three-site sorption models were applied and fitted the sorption phase of the experiment well. However, the models failed to describe the observed desorption behaviour of propyzamide.

These results highlight gaps in the existing knowledge about the formulation effects on pesticide sorption and leaching through soil and suggest that these effects should be considered during the risk assessment of environmental fate and behaviour of pesticides.

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AUTHOR'S DECLARATION

The work in this thesis was undertaken as a PhD student in the Environment department, University of York (March 2012 – February 2016). The work presented in this thesis is original to the best knowledge of the author. Where this is not the case, appropriate citations and acknowledgements have been given. This work has not previously been presented for an award of this, or any other, University.

Chapter 1

INTRODUCTION

Pesticides are widely used in agricultural practices throughout the world, particularly in European countries and are considered important environmental contaminants. A pesticide can be defined as “any substance, or mixture of substances of chemical or biological ingredients intended for repelling, destroying or controlling any pest, or regulating plant growth” (FAO, 2014). The term pesticide thus covers a wide range of substances that includes organic and inorganic or synthetic and naturally occurring compounds. Pesticides can be classified on the basis of their chemical properties, mode and period of action as well as intended target (Arias-Estevez *et al*., 2008). Pesticidal products are very effective in protecting agricultural and non-agricultural crops from harmful pests, weeds and fungal diseases and have been widely used since the 1940s. Hundreds of pesticide formulations are currently available on the market and these can be applied to arable and grassland based on specific label recommendations.

The use of pesticides in agriculture is required due to an ever-growing population and hence the pressure to boost net productivity to meet the demand for food (Navarro *et al*., 2007). Pesticides certainly play a vital role in modern agriculture and their applications have greatly improved the quantity and quality of food over the past few decades (Arias-Estevez *et al*., 2008; Abhilash and Singh, 2009). However, prolonged use and repeated applications of pesticides in agriculture have resulted in their widespread distribution in the environment (Ortiz-Hernández, *et al*., 2011). Regardless of restraining regulations and highly efficacious pesticide formulations, the use of pesticides in agricultural and non-agricultural practices still causes contamination of various environmental compartments (Chaplain *et al*., 2011). Intensive applications of pesticides to land each year may result in high residual levels in soil which can potentially contaminate surface and groundwater due to runoff and leaching. Recent studies have reported the presence of pesticides in both surface and groundwater in most European countries (Sattler *et al.*, 2007; Shriks *et al.*, 2010; Evans, 2009; Tediosi *et al*., 2012; Tediosi *et al*., 2013). Such contamination of natural resources may pose a potential risk for human health, aquatic and terrestrial life and environmental sustainability in general (Tiktak et al., 2004; Gregoire *et al*., 2009; Szekacs *et al*., 2015). In fact, only a small amount of applied pesticide reaches its intended target; the remaining pesticide enters the environment, particularly the soil compartment, where it is subjected to biological and chemical degradation, and a fraction can potentially contaminate soil, water resources and the atmosphere (Lode *et al*., 1995; Arias-Estevez *et al*., 2008). Therefore, a great deal of effort is expended to manage and reduce possible harmful effects of pesticides on the environment.

Pesticides enter the soil as a result of direct application as a spray or released from granules incorporated directly into the soil (Chaplain *et al*., 2011; Lopez-Perez *et al*., 2006; Ortiz-Hernández *et al*., 2011). They may also fall through the crop canopy during spraying or be washed off from crop surfaces by rainfall or irrigation into the soil, or incorporated into the soil with crop residue (Wauchope *et al*., 2002; Rial-Otero *et al*., 2003). Soil is a heterogeneous mixture of a wide range of mineral and organic particles with a variety of surfaces and is complex in nature (Wauchope *et al*., 2002). Various physical, chemical and hydrological characteristics of soil have a major influence on the fate and behaviour of organic chemicals (Wauchope *et al*., 2002). Soil is a major interface between different environmental compartments, acting as a receptor for polluting substances (Ortiz-Hernández *et al*., 2011) and playing a buffering role in the fate of chemicals (Chaplain *et al*., 2011). Previous studies suggest that the mobility of pesticides within the soil profile is also determined by environmental and agricultural conditions which prevail during and shortly after pesticide application (Brown *et al*., 1995). Surface preparation, soil structure, initial water content, type of irrigation and rainfall events are some of the most important agricultural and environmental factors which have been studied to date (Flury, 1996). Furthermore, in addition to spray drift and areal transport, most of the pesticides detected in surface and groundwater enter via the soil. Once in the soil, pesticide molecules tend to partition between the solid and liquid phases (Wauchope, 2002). The partitioning behaviour and hence the subsequent movement of pesticide within the soil profile is not only a function of soil properties (Cheng, 1990; Johnson *et al*., 1996); it is also strongly influenced by the physico-chemical properties of the pesticide itself and the type of formulation (Navarro *et al*., 2007). It is therefore, vital to accurately characterize the processes that influence the fate and behaviour of organic pollutants within the soil environment.

The risk of pesticide leaching may vary strongly at the field scale, mostly because of heterogeneities in soil structure and biochemistry and the strength of pesticide interaction with the soil matrix (Paradelo *et al*., 2015). Sorption is recognised as a key process that not only determines the availability of pesticides in the liquid phase and controls leaching through soils, but also reduces pesticide availability to soil microorganisms and hence limits their biodegradation (Kah and Brown, 2007; Arias Estévez *et al*., 2008; Wang and Keller, 2009; Keren *at al*., 2015; Paradelo *et al*., 2015). Considering that the groundwater represents nearly 98% of available fresh water on the earth, it is important to minimise the risk of contamination caused by pesticides in order to maintain the quality of drinking water (de Wilde *et al*., 2008; Lerner and Harris, 2009). Groundwater is the biggest source of drinking water in the majority of European countries and leaching of pesticides could easily deteriorate its quality (Fenoll *et al*., 2010). Research in the UK found pesticides in over a quarter of groundwater monitoring sites in 2004, where the levels of pesticides were in access of the admissible limits in some of the monitoring sites (Environment Agency, 2006). Recent studies have also reported the presence of pesticides in UK surface waters, which may pose problems for environmental agencies and water supply companies to comply with drinking water quality standards set within the EU regulations (Evans, 2009; Tediosi *et al*., 2012).

In Europe, a precautionary limit value of 0.1 μg L^{-1} for a single pesticide and 0.5 μg L^{-1} for a combination of pesticides in drinking water were first established by the Drinking Water Directive (80/778/EEC) in 1980 (EC, 1980). These regulations were further strengthened by the introduction of the European Water Framework Directive (2000/60/EC) in 2000 and Groundwater Directive (2006/118/EC) in 2006, which required member states to continuously monitor the levels of organic pollutants in surface and groundwater bodies and to take measures to maintain required standards for drinking water (EC, 2000; 2006).

Pesticide retention and transport through soil has been studied intensively over the past forty to forty-five years and information is available in the literature regarding the controls on pesticide leaching through soil to groundwater (Flury, 1996; Navarro *et al*., 2007; Arias Estévez *et al*., 2008). However, only limited information is available about the influence of co-formulant chemicals found in commercial pesticide products on the behaviour of active substances in soils. Pesticide formulations contain active ingredients and co-formulant chemicals, also called adjuvants, and various other additives. These co-formulants are frequently included in commercial formulations (Pose-Juan *et al*., 2009) to solublise or emulsify the active substances for better spray application (Rial-Otero *et al*., 2003) and hence to enhance their effectiveness and bioavailability (Krogh *et al*., 2003). These additives improve the performance of an active substance by modifying the physical and chemical characteristics of the spray mixture. It is important to understand how the presence of co-formulants in commercial products of pesticides will affect their natural fate and behaviour within the environment. As some of the formulations may hold the pesticide molecule in soil solution (e.g. as an emulsion), it is possible that this may retard sorption and consequently may increase the leaching of pesticides to groundwater.

Some recent studies have indicated that the presence of co-formulants in commercial products may interfere with natural fate processes of pesticides in the environment. For example, Pose-Juan *et al*. (2011) reported that the presence of adjuvants in the commercial formulation ‘Switch’ increased the concentration of the active substance fludioxonil in water suspensions and the compound dissolved up to 9 mgL^{-1}; this is about 5 times its solubility limit in water (1.8 mgL^{-1}) resulting in greater availability of pesticide in soil solution for transport. The results from a recent study indicate that at low concentrations the adsorption of active substances of the sulfonylurea herbicides chlorsulfuron and tribenuron methyl was greater for solutions containing pure active ingredients than from formulation solutions (Földényi *et al*., 2013). The same study reported that the presence of the co-formulant Supragil resulted in a decrease in adsorption of chlorosulfuron and hence increased environmental mobility of the pesticide. Metribuzin retention in an Algerian silty-clay soil showed 11% less adsorption from formulated material (Metriphar) compared to pure analytical grade material when characterised by batch-equilibrium method and as a result of this effect, the authors hypothesised an increased risk of transport of the chemical to groundwater (Oukali-Haouchine *et al*., 2013). Beigel and Barriuso (2000) suggested that the solubilisation of triticonazole above its water solubility in the suspension concentrate formulations may increase the amount of the active ingredient available in soil solution for transport. However, Cox and Walker (1999) did not observe any significant difference in sorption behaviour between technical grade material and commercial formulation of linuron. A better understanding of the interaction of co-formulant chemicals with time-dependent sorption processes of pesticides in soil over time is required in order to develop safer formulations. This is particularly important in order to minimise the risk of contamination of groundwater caused by leaching losses.

The overall aim of this PhD was to investigate the impacts of co-formulants in commercial products of pesticides on the sorption and leaching of their active substances through soils. This was achieved through a series of laboratory experiments designed to compare the leaching and sorption-desorption behaviour of analytical grade material and commercial products of pesticides over time under controlled conditions in sandy loam soil from the Blackwood association and sandy silt loam soil from the Bishampton association. The main objectives of this work were to:

i. Undertake column experiments using technical grade and commercial formulations of pesticides to study any effects of formulation on pesticide leaching through soil.

ii. Investigate the influence of pesticide solubility and type of formulation on the effects of formulation on leaching behaviour in soil

iii. Measure sorption of technical grade and commercial formulations of pesticides using a centrifugation technique to quantity changes in sorption behaviour over time and so aid interpretation of results from column experiments.

iv. Use modelling to describe the overall effects of formulation on pesticide behaviour.

This thesis comprises seven chapters. The contents in each chapter are briefly described below:

Chapter 1 provides a general introduction on the importance of pesticides, their uses and deleterious impacts on the environment. It also introduces various fate processes of pesticides within the environment and how the presence of co-formulants in commercial pesticide products may interfere with these natural fate processes.

Chapter 2 provides information on the current state of knowledge on various aspects of the fate and behaviour of pesticides within the environment. Particularly, mechanisms and measurement of sorption as well as various controlling processes on pesticides fate within the environment are discussed. The concept of time-dependent sorption is also considered. The chapter reviews current knowledge on the effect of formulations on pesticide behaviour and identifies associated research needs.

Chapter 3 presents detailed information on the test substances (pesticides and soils used). The key physico-chemical properties of studied pesticides as well as the methods used to characterize the main properties of two soils are discussed. Different analytical methods used to analyse test substances in leachate and pore water samples are also discussed in detail.

Chapter 4 reports the experimental design and methods used in the column leaching experiment on four pesticides. Key findings from the preliminary experiment on the leaching behaviour of technical grade and commercial formulation of propyzamide over time are discussed in detail. This chapter also reports the results of column leaching experiments investigating the influence of solubility and formulation type of pesticides on the effect of formulation on leaching behaviour. Effects of solubility were investigated using four pesticides in sandy loam soil. However, the effects of type of formulation were only investigated for the fungicide azoxystrobin.

Chapter 5 presents the results from a series of experiments carried out to investigate the effects of formulation and residence time on sorption and desorption behaviour of propyzamide in the two soils. The sorption and desorption behaviour of propyzamide was explored by using a standard batch-equilibrium method and a centrifugation technique. The experiments described in this chapter replicate the time intervals used in column leaching experiments in order to make comparisons between the leaching and sorption behaviour of pesticide.

Chapter 6 reports the modelling approach where the two-site and three-site sorption and desorption models were applied to data from the centrifugation experiments. The aim was to interpret the sorption behaviour of propyzamide in greater detail and to understand various mechanisms involved in sorption kinetics and describe the overall effects of formulation on pesticide behaviour. Model estimates of the time-dependent sorption behaviour of propyzamide from the two treatments were compared with the measured data and the parameters were used to understand the formulation effects.

Chapter 7 summarises the key findings and conclusions of the research and discusses the implications and research needs for future work.

Chapter 2

FACTORS AFFECTING THE RETENTION AND MOBILITY OF PESTICIDES THROUGH SOILS

2.1. Introduction

Assessment of the fate and behaviour of pesticides in the environment is vital to determine the exposure and consequently the impact of pesticides on target and non-target organisms (Chaplain *et al*., 2011). Surface and groundwater contamination resulting from an intensive use of agrochemicals has gained much attention over the past few decades (Ortiz-Hernández, *et al*., 2011). Due to growing public concerns and the possible deleterious effects of these chemicals on aquatic and terrestrial life (Chaplain *et al*., 2011), a great deal of research has been carried out on the fate and behaviour of agrochemicals in the environment. Sorption of pesticides within soil, biological and chemical degradation, leaching to groundwater, runoff to surface water, volatilization to the atmosphere and uptake by plants are the main fate processes controlled by a combination of physico-chemical characteristics of soil and chemicals (Cheng, 1990; Johnson *et al*., 1996; Navarro *et al*., 2007). It is of profound importance to understand and characterise the retention and transport mechanisms to accurately predict the fate and behaviour of pesticides within the environment. A better understanding of the interaction of co-formulants on natural fate of pesticides in soil will provide important regulatory decision-making information to set new standards in legislation. This chapter reviews the retention and transport processes of pesticides in detail and includes physical and chemical processes that influence time-dependent sorption, factors controlling pesticide sorption in soil, pesticide formulations and effects of formulation on the fate and behaviour of pesticides. It also identifies gaps in the current knowledge and future research needs.

2.2. Mechanisms of sorption

The term sorption is defined by Pignatello (2000) as: “the bulk mass-transfer phenomena in which molecules leave the fluid phase and become associated with an immobile phase and vice versa”. Interactions between organic compounds and soil constituents may arise as a result of various binding mechanisms at a molecular level. Such binding mechanisms are strongly influenced by the physico-chemical properties of solutes and the soil matrix (Calvet, 1989). The term adsorption has been defined as the attraction and accumulation of pesticide molecules at the soil-water or soil-air interface which results in the formation of molecular layers on the surface of soil constituents (Koskinen and Harper, 1990). However, it is extremely difficult to differentiate and isolate the binding mechanisms responsible for pesticide retention in a given soil system (Calvet, 1989; Kah and Brown, 2006).

Due to the lack of direct experimental evidence of a particular mechanism and difficulty in isolating specific binding mechanisms, scientists usually only propose a hypothesis and make assumptions regarding the intermolecular interactions involved (Calvet, 1989). This is also why the more generalised term sorption is used rather than either adsorption or absorption. Mechanisms of sorption and subsequent retention of pesticides in soil have been extensively explored over the past few decades and a number of scientists have reviewed the subject in detail (Hamaker and Thompson, 1972; Calvet, 1989; Koskinen and Harper, 1990; Senesi, 1992; Gevao *et al.*, 2000; Kah and

Brown, 2006). Mechanisms of binding may include van der Waals forces, hydrophobic bonding, hydrogen bonding, charge transfer, ligand exchange, covalent bonding and ionic bonding. These are briefly described below.

2.2.1. Van der Waals forces

Van der Waals interactions between sorbent and sorbate are particularly weak (2 – 4 KJ mol^{-1}) and result from short-range dipolar or induced-dipolar attractions that exist in addition to stronger binding forces (Calvet, 1989; Gevao *et al*., 2000; Delle Site, 2001; Kah and Brown, 2006). Due to the additive nature of these forces, their contribution to molecular interactions increases with the size of the interacting molecule and with its ability to adapt to the adsorbate surface (Senesi, 1992; Gevao *et al*., 2000, Kah and Brown, 2006). The effect of van der Waals interactions tends to decrease rapidly with distance; hence their contribution to sorption would be greatest for those ions which are in closest contact with the surface (Gevao *et al*., 2000). Such interactions are of particular importance in the sorption mechanisms of non-ionic and non-polar pesticides on suitable soil organic constituents (Senesi, 1992). Although the experimental evidence is sparse, binding as a result of van der Waals interactions have been reported as major sorption mechanism for dichlorodiphenyltrichloroethane (DDT) and benzonitrile (Pierce *et al*., 1971) and 2,4-dichlorophenoxyacetic acid (2.4-D) and picloram (Khan, 1973a). Atrazine retention on the surfaces of smectites has been reported to result from weak van der Waals forces or hydrogen bonding (Barrisuo *et al*., 1994).

2.2.2. Hydrogen bonding

Hydrogen bonds are formed as a result of intra- or inter-molecular dipole-dipole interactions between several oxygen- and hydroxyl-containing functional groups on soil humic substances with suitable complementary groups on pesticide molecules (Calvet, 1989; Gevao *et al*., 2000; Kah and Brown, 2006). Water molecules in the soil liquid phase may also have an affinity for such functional groups on soil organics; hence there may be a strong competition between pesticide molecules and water for binding sites within soil (Senesi, 1992; Gevao, *et al*., 2000). Hydrogen bonds are slightly stronger (2 - 40 KJ mole^{-1}) than the bonds formed as a result of van der Waals forces (Delle Site, 2001). Hydrogen bonding is suggested to play a vital role in the adsorption of several non-ionic polar pesticides, including substituted ureas and phenylcarbamates (Gevao *et al*., 2000). Some of the anionic and acidic pesticides including dicamba and asulum, and phenoxyacetic acids (2,4-D and 2,4,5-trichloropenol (2,4,5-T)), can also interact with soil organics at pH values below their pKa by H-bonding in non-ionised forms through their –COOH, -COOR groups (Senesi *et al*., 1992, Gevao *et al*., 2000). Hydrogen bonding has been suggested as the mechanism for sorption of s-triazine herbicides on soil and indicated for adsorption to clay surfaces from the study of infrared spectra of adsorbed material (Hamaker and Thompson, 1972).

2.2.3. Hydrophobic bonding

Retention of chemicals in soil as a result of hydrophobic bonding is not an active sorption mechanism; rather it involves a partitioning between soil aqueous phase and a non-specific surface of a solute introduced into the soil environment (Gevao *et al.*, 2000; Kah and Brown, 2006). Hydrophobic bonding may also be regarded as solventmotivated sorption where a hydrophobic solute is expelled from the water and becomes associated with the soil organic matrix. Such binding mechanisms play an important role in the sorption of non-polar pesticides by active hydrophobic sites of humic substance or clay (Senesi, 1992; Kah and Brown, 2006). Non-polar pesticides interact weakly with water and water molecules are not good competitors for sorption; as a result hydrophobic sites of humic substance (HS) and clay become active for the sorption of non-polar pesticides. Senesi (1992) explained that active hydrophobic sites may include aliphatic side-chains or lipid portions, lignin-derived moieties with high carbon content and a small number of polar groups of macromolecules contained within soil humic substances. Pierce *et al*. (1971) suggested that hydrophobic sorption may be the main binding mechanism for DDT and other organochlorine pesticides, as well as some ionisable pesticides in their molecular form, such as the weakly basic triazine herbicide prometryn (Khan, 1982). Binding mechanisms resulting from hydrophobic partitioning are usually independent of the pH of a medium.

2.2.4. Ion exchange

Ion exchange mechanisms are regarded as non-specific electrostatic interactions that can take place either between cationic forms of pesticides and negatively charged surfaces of soil constituents or between anionic forms of pesticides and positively charged surfaces of the soil matrix (Calvet, 1989; Kah and Brown, 2006). Both binding mechanisms are briefly explained below. According to Gevao *et al*. (2000), ionic binding involves ionised, or easily ionisable, carboxylic and phenolic hydroxyl groups of humic substances. Sorption as a result of cation exchange involves compounds which exist either in the cationic form in soil solution, or can be protonated and become cationic e.g. weak basic compounds with pK_a values between 3.0 and 8.0, allowing ionisation by protonation in the normal soil pH range when $pH < pK_a$ (Calvet, 1989; Gevao *et al*., 2000). Cation exchange takes place between cations and negatively charged sites on clay mineral surfaces occupied by a metal ion (Calvet, 1989; Kah and Brown, 2006). According to Gevao *et al*. (2000), binding of positively charged bipyridilium pesticides (e.g. diquat and paraquat) to humic substances in soil occurs by ion exchange via their cationic group which may form highly stable and unreactive bonds with the carboxyl groups of the humic substances. Senesi (1992), however, suggested that not all negative sites on organic matter are available to bind large organic cations due to the effects of steric hindrance.

Anion exchange is the binding mechanism by which anions become associated with a positively charged site on the soil surface, involving the exchange of one ion for another at the binding site (Calvet, 1989; Kah and Brown, 2006). This binding mechanism is not relevant for soils in temperate climates where clays and organic matter are generally either non-charged or negatively charged. Soils under tropical conditions provide a more favourable environment for anion exchange where significant quantities of positively charged adsorption surfaces may be present in the form of aluminium and iron (hydr)oxides (Kah and Brown, 2006).

2.2.5. Charge transfer

Binding as a result of charge transfer can occur between soil humic substances and pesticides with electron donor or electron acceptor properties (Gevao *et al*. 2000; Kah and Brown, 2006). Such mechanisms involve the formation of a donor-acceptor complex as a result of transfer of electrons from an electron-rich donor to an electron-deficient acceptor (Calvet, 1989). Structurally, soil humic substances contain both electron-deficient moieties, such as quinones, and electron-rich centres e.g. diphenols (Senesi, 1992; Gevao *et al*, 2000). Binding due to charge transfer has been reported for the bipyridilium pesticides, paraquat and diquat and the evidence of such interaction comes from infrared (IR) spectroscopy (Gevao *et al*., 2000). Experimental evidence for the formation of charge-transfer complexes between methoxytriazines and soil organic matter is also available from the IR spectroscopic studies where a shift towards lower frequencies in the IR spectrum was observed between several *s*-triazines and humic acid (Gevao *et al*., 2000). Pignatello (1989) reported that the sorption of chemicals to humic acid is most likely due to a charge transfer mechanism, while the interactions between clays and acidic pesticides are also believed to be the result of charge transfer.

2.2.6. Ligand exchange

Ligand exchange involves the replacement of relatively weak ligands, such as H_2O or other weak ligands partially holding polyvalent cations associated with soil organic matter, by suitable adsorbent molecules such as *s*-triazines and anionic pesticides (Senesi, 1992; Gevao *et al*., 2000; Kah and Brown, 2006). The substitution of a weak ligand by a pesticide molecule may also be facilitated by an entropy change if a pesticide molecule succeeds in replacing several water molecules associated with one or several complexed metal ion(s) (Gevao *et al*., 2000). This binding mechanism is also responsible for the retention of many organic acids to oxide surfaces where an organic functional group, such as carboxylate or hydroxyl, displaces a surface coordinated –OH or water molecule of a metal ion (Fe, Al) at the surface of a soil mineral (Kah and Brown, 2006).

2.2.7. Covalent bonding

Some sorption mechanisms involve significant atomic or molecular orbital overlap with the soil solid phase resulting in the formation of a covalent or coordination bond. Pignatello (2000) referred to such binding mechanisms as chemisorption which includes “inner-sphere” coordination complexes between carboxylate, phenolate, amine, or sulfhydryl groups and metal ions. The energy associated with this binding mechanism is about 60-80 KJ mol^{-1} (Delle Site, 2001). The formation of covalent bonds between pesticides (and/or their degradation products) and soil humic substances is often mediated by chemical, photochemical or enzymatic catalysts (Gevao *et al.*, 2000). Sorption accompanied by formation of a covalent bond, i.e. C-C bond, leads to stable, mostly irreversible incorporation of the adsorbed pesticide into the soil matrix (Pignatello, 2000; Gevao *et al.*, 2000). Covalent bonding is thus regarded as the principal binding mechanism responsible for the formation of bound residues. Pesticides capable of covalently binding to humic substances have similar functionalities to the components of the soil humus and structurally resemble phenolic compounds (Gevao *et al.*, 2000).

2.3. Factors controlling pesticide sorption in soil

On entry to the soil, the partitioning of a pesticide molecule between solid and aqueous phases is controlled by a variety of factors. Major factors that influence pesticide sorption processes in soil include physico-chemical properties of soil and pesticides as well as environmental conditions. This section only focuses on the soil and pesticide properties that influence the sorption behaviour of non-ionic or neutral pesticides.

2.3.1. Effects of soil properties

2.3.1.1. Soil organic matter

The significance of soil organic matter in controlling the sorption of non-ionic pesticides in soil is well established (Karickoff, 1984; Spark and Swift, 2002; Benoit *et al*., 2008; Fernandez-Bayo *et al*., 2009; Gondar *et al*., 2013). Despite the fact that the organic matter only represents a small proportion of the total dried material in most soils, it has been considered as a major sorbent for pesticides in soil (Calvet, 1989). This is attributed to its high chemical reactivity towards organic molecules, allowing various types of interactions with pesticides (Chaplain *et al*., 2011). The chemical composition of organic matter strongly influences its sorption capacity. Structurally, organic matter has a very heterogeneous composition and is made up of humic and non-humic substances. It has been demonstrated that humified matter is more chemically reactive with pesticides than non-humified matter (Senesi *et al*., 1997; Forenhorst, 2006). The humic substances contain humic acids (HAs), fulvic acids (FAs) and humin (Senesi, 1992; Pignatello, 2000). Most soils are relatively rich in HAs, which are more chemically reactive with pesticides than FAs or humin (Senesi, 1992; Senesi *et al*., 2001; Forenhorst, 2006; Chowdhury *et al*., 2014). These humic acids have unique chemical characteristics and are polyfunctional in nature. Humic acids contain various chemically reactive functional groups including hydroxyl, phenols, carbonyl, amines, amide, carboxylic acids, alkoxy and esters. These acids also contain hydrophilic and hydrophobic groups in their molecular structure which play a vital role in their interaction with organic pesticides (Senesi, 1992). The humic acids have been shown to influence the sorption of alpha and beta isomers of endosulfan (Chowdhury *et al*., 2014), imazethapyr (Senesi *et al*., 1997), s-triazines (Stevenson, 1972) and MCPA (Haberhauer *et al*., 2001).

The particle size of the organic fraction of soil also influences the sorption of pesticide. The smaller particles of organic matter contain large surface area, so a greater number of binding sites may be available for a pesticide molecule to interact with (Benoit *et al*., 2008). Organic pesticides closely associate with the organic fraction within soil due to the presence of many of the same structural units and functional groups and as a result of involvement in many of the same microbial and chemical transformations (Barraclough *et al.*, 2005). The intrinsic nature of the soil organic fraction may also have strong effects on the sorption behaviour of organic compounds (Ahangar *et al*., 2008). It has been suggested previously that soil organic matter acts as a dual-mode sorbent due to its rubbery and glassy nature (Xing and Pignatello, 1997; Farenhorst, 2006). The rubbery structures of soil organic matter are usually expanded and flexible, while the glassy structures are condensed and rigid in nature. The sorption of hydrophobic organic compounds by soil organic matter occurs through partitioning into both the flexible and rigid domains, as well as though adsorption-like interactions (micropore-filling retention) that occur at the surface (intra-matrix) of the rigid domain (Xing, 2001; Ran *et al*., 2002; Farenhorst, 2006). The flexible and rigid domains of soil organic matter are considered to have different effects on the sorption behaviour of organic pesticides. For example, the expanded and flexible domain usually generates a linear sorption isotherm due to less competition for sorption sites, whereas the rigid domain with competitive adsorption generates a nonlinear sorption isotherm (Gunasekara and Xing, 2003; Farenhorst, 2006).

2.3.1.2. Soil minerals

Retention and mobility of pesticides is often related to the mineral fractions, predominantly the clay-sized particles in soils which have low organic matter contents (Spark and Swift, 2002). The mineral fractions that are mainly involved in the sorption of organic pesticides are clays (as silicate minerals), oxides and hydroxides (Calvet, 1989). Increased proportion of clay minerals in soil has been reported to increase the retention and reduce the mobility of pesticides in soils (Spark and Swift, 2002). The surfaces of clay minerals are largely hydrophilic due to the presence of hydroxyl groups and exchangeable cations (Chaplain *et al*., 2011). The adsorption of pesticides on clay minerals is likely to occur on external surfaces of clay particles rather than in interlamellar space and increases with the specific surface of clays (Barriuso *et al*., 1994). Adsorption of napropamide has been shown to be strongly correlated to soil clay content (Walker *et al*., 1985). Due to their small particle size, large surface area per unit weight, negative surface charge and close association with soil organic matter, clay minerals play an important role in the adsorption of organic pesticides (Gilchrist *et al.*, 1993). Oxides and hydroxides are frequently associated to clays; they have a high surface activity and their charge depends on the soil pH (Calvet, 1989). For example, the adsorption of glyphosate increases as follows: kaolinite < illite < montmorillonite < nontronite (Mc Connell & Hossner, 1985). The adsorption of glyphosate on iron and aluminium oxides and hydroxides is high at intermediate pH and driven by ionic bonding between the positive surface sites of minerals and the negative acid groups of glyphosate (Morillo *et al*., 2000). However, sorption is much lower at very acid or very alkaline pH because oxides will bear the same charge as glyphosate (Chaplain *et al*., 2011). Different clay mineral species have shown different sorption capacities to thiazafluron, where the herbicide was not sorbed to kaolinite, only slightly to illite and greatly sorbed to smectite (Cox *et al*., 1995). The authors attributed this to the greater accessibility of herbicide molecules to the interlayer spaces of the smectite clays. However, owing to soil structural complexity where organic matter and clay minerals are found in intimate association, it is very difficult to isolate the individual effects of these components on pesticide sorption within soil systems (Stevenson, 1972; Cox *et al*., 1998; Kennedy *et al*., 2005).

2.3.1.3. Soil microorganisms

Soil microorganisms play a key role in biodegradation of pesticides (Gilani *et al*., 2016), and hence may influence their sorption behaviour within the soil environment. Burauel and Fuhr (2000) suggested that the metabolism of pesticides in soil is highly dependent on microbial activities. Soil microbes are able to metabolise pesticides through numerous enzymatic reactions described by Chaplain *et al*. (2011). These include; (i) functionalisation reactions involving oxidation, reduction and hydrolysis of the parent compound whereby additional functional groups such as OH, COOH and NH_2 are introduced as a result of microbial activity; this results in the formation of metabolites with modified physiological and biological properties; (ii) conjugation which is a synthetic process that results in the formation of final metabolites by linkage of the activated metabolite with cell constituents; such metabolites are subsequently distributed and sequestered by microorganisms, or excreted; (iii) synthetic reactions leading to the oligomerisation of several units of the parent compound, or secondary conjugation of the parent compound with cellular components of the cells. These transformation stages may result in metabolites which are generally more hydrophilic in nature. The main groups of microorganisms involved in pesticide transformation include prokaryotic bacteria, actinomycetes and eukaryotic fungi; however, bacteria are the main biodegraders in soils (Chaplain *et al*., 2011). Nowak *et al*. (2010) reported that soil microbes are able to integrate the derived carbon into their cellular systems which could be stabilised within the soil organic matter. Hence the biodegradation may be associated with irreversible sorption. It is generally accepted that the degradation of organic pollutants mainly occurs in the solution phase and that the sorption of pesticides to the soil matrix usually slows down such kinetics over time. Furthermore, it is also important to consider the role of co-formulants present in pesticide commercial products which may retard sorption processes and favour the microbial transformations of pesticides within soil systems.

2.3.2. Effects of pesticide properties

In addition to the soil properties, the chemical characteristics of pesticides also influence their behaviour in soil. Observed differences in adsorption between organic compounds in the same soil are because of differences in the chemical characteristics of the compounds (Koskinen and Harper, 1990). The key molecular properties that play a role in the sorption of neutral or non-ionic pesticides include their electronic structure, water solubility (or hydrophilicity) and lipophilicity (or hydrophobicity). These are briefly described below.

2.3.2.1. Electronic structure

The electronic structure mainly governs the type of interactions of pesticides with soils (i.e. hydrogen bonds, donor-acceptor electron) and is determined by the nature of their constituent atoms and of different functional groups (Calvet, 1989; Koskinen and Harper, 1990; Chaplain *et al*., 2011). The reactivity of different functional groups involved in binding mechanisms with the soil matrix is strongly influenced by different substitutions and their spatial arrangement in the molecule (Liu *et al*., 2000; Chaplain *et al*., 2011). The most important aspects of the electronic structure of pesticides that influence their sorption behaviour include: (i) polarity or their permanent dipole moments that depends on electron distribution; (ii) polarisability that represents the ease with which the electronic cloud is deformed in an electric field; and, (iii) delocalisation as a result of the presence of π electrons (Calvet, 1989). Both polarity and polarisability of a molecule fix the magnitude of its permanent and induced electric dipoles, which appear to play a role in sorption processes, especially for interactions with metallic cations (Calvet, 1989). Again the charge distribution has a significant role in the binding of pesticide molecules within soil matrix. For example, the charges in aromatic and conjugated aliphatic structures are delocalised which is important for adsorption of many protonated triazines, aromatic and pseudo-aromatic compounds (Clavet, 1989). Similarly, charge delocalisation also affects the sorption through charge transfer and hydrogen bonding. Sorption of the basic structural units (i.e. phenols and substituted phenols) of many organic pesticides (e.g. the herbicide propyzamide and its derivatives) is also correlated to the position of ring substituents and electron donor power (Calvet, 1989).

2.3.2.2. Hydrophilicity and lipophilicity

The hydrophilicity or lipophilicity of a pesticide molecule also strongly influences its binding with soil constituents. The hydrophilicity of pesticides is their affinity for water molecules and is defined by their water solubility, while the lipophilicity (or hydrophobicity) refers to the ability of a chemical compound to partition into lipids, fats and oils, and is described by their octanol-water partition coefficient (*Kow*), usually stated as log *Kow* or log *P*. Generally, hydrophilic compounds are only weakly sorbed to soil organic constituents compared to lipophilic compounds; however, this behaviour is also dependent on the hydrophilic/hydrophobic balance of the soil adsorbents (Chaplain *et al.*, 2011). Hydrophobic interactions are the primary mechanisms underlying the sorption of non-ionic compounds, however, for highly polar compounds hydrophilic interactions are more relevant (dos Reis *et al.*, 2014). Compounds that are highly soluble in water are more likely to be transported to surface and groundwater bodies.

2.4. Time-dependent sorption behaviour

The concept of time-dependent sorption of pesticides in soil has been discussed extensively over the past few decades. There is increasing evidence in the literature that sorption is not a simple instantaneous equilibrium process and that partition coefficients derived from freshly treated soil samples are inadequate and may result in false predictions in terms of mobility and retention of chemicals within the soil environment (Walker *et al.*, 1995; Pignatello and Xing, 1996; Koskinen *et al.*, 2001; Mamy and Barriuso, 2007). It is now widely accepted that sorption of pesticides in soil is a slow process that may progress over a relatively long period of time to reach equilibrium (Koskinen and Harper, 1990; Pignatello and Xing, 1996; Pignatello, 1998; Pignatello, 2000; Boivin *et al.*, 2005; Walker *et al.*, 2005; Mamy and Barriuso, 2006). As sorption influences transport of pesticides in the soil environment, it is important to consider the time-dependent aspects when assessing potential leaching and bioavailability of pesticides (Báez *et al*., 2013). The strength of sorption increases with increasing residence time in soil resulting in a decrease in the availability of pesticide for transport or uptake by soil organisms (Gevao *et al*., 2000; Koskinen *et al*., 2001; Beulke *et al*., 2004; Boivin *et al*., 2004; Renaud *et al*., 2004; Mamy and Barriuso, 2007; Ortiz-Hernández *et al*., 2011). This phenomenon is also referred to as ageing, non-equilibrium sorption, non-ideal sorption or kinetic sorption (Huang and Weber, 1997; Cox and Walker, 1999; Lesan and Bhandari, 2004; Walker *et al*., 2005; Villaverde, 2007; Shareef and Shaw, 2008).

Longer contact times between chemical and soil matrix facilitate the formation of bound residues due to physical and/or chemical non-equilibrium sorption processes. This results in greater retention of sorbed organic chemicals and hence limits their susceptibility to desorption and degradation (Boivin *et al*., 2005). As the bioavailability of pesticide and its potential for leaching through soil to groundwater bodies decreases with increasing residence time in soil (Beulke *et al*., 2004), considerations should be given to characterising and incorporating ageing effects in mathematical models for pesticide leaching (Boesten & Van der Linden, 2001; Mamy and Barriuso, 2007). It is also well understood that these processes are partially non-reversible in various cases and desorption often occurs more slowly than adsorption and is frequently hysteretic (Clay & Koskinen, 1990; Pignatello, 2000). To date there is no evidence in the literature about whether the presence of co-formulants in commercial products of pesticides have any effects on the slow sorption kinetics that proceed over a longer period of time. It is, therefore, necessary to design the appropriate laboratory experiments to explore whether the co-formulants in pesticidal products have any impacts on the natural fate and behaviour of active substances.

2.4.1. Factors responsible for time-dependent sorption

The diffusive mass transfer mechanisms responsible for time-dependent sorption of pesticides in soil include film diffusion, pore diffusion and organic matter diffusion. Due to differences in soil porosity and the fact that soil minerals are coated with organic substances, it is rather difficult to distinguish specific mechanisms involved in slow sorption kinetics in a given system. Film diffusion is potentially rate-limiting for the initial fast stage of sorption, but this mechanism is generally considered to be less important compared to pore and organic matter diffusion (Brusseau *et al.*, 1991; Pignatello and Xing, 1996). Sorption and desorption rates of neutral (non-ionic) pesticides are mainly governed by molecular diffusion through the fixed interstitial pores of particle aggregates (pore diffusion) and through the three-dimensional pseudo-phase of soil organic matter (intra-organic matter diffusion); this process is slow in soil relative to that in bulk water (Pignatello and Xing, 1995; Pignatello, 2000). Mechanisms involved in non-equilibrium sorption of pesticides in soils have been reviewed in detail by several authors (Brusseau *et al.*, 1991; Pignatello and Xing, 1996; Pignatello, 2000; Gevao *et al.*, 2000). Therefore, only the main features of the rate-limiting processes will be summarised here.

2.4.1.1. Pore diffusion

Pore diffusion (retarded intra-particle diffusion) comprises hindered diffusion of molecules through the fixed intra-particle pore system (macro- and micro-pores) and can occur in pore liquids or along pore wall surfaces. Both liquid and surface diffusion occur simultaneously, so it is difficult to isolate the two mechanisms (Pignatello and Xing, 1996). Fixed pores are more or less permanent and unaffected in shape by the presence of the diffusant (Pignatello, 2000). The presence of nanopores may further hinder the diffusion of molecules and complicate the process of sorption. Slow diffusion and hence retardation in the fixed pore system in soil is primarily due to the tortuosity and increased length of flow path within soil aggregates, variations in pore diameter, the degree of pore connectivity, chromatographic adsorption to pore walls, steric hindrance in the smallest pores, and the viscosity of water near hydrophilic surfaces (Pignatello, 2000). It was also suggested that gaps in the interlayers of expandable clays (typically <1 nm) may also hinder molecular diffusion (Pignatello, 2000). Understanding factors involved in pore diffusion is important when using pore diffusion models to describe the sorption behaviour of organic chemicals.

2.4.1.2. Organic matter diffusion

Organic matter (or intra-organic matter) diffusion refers to diffusive mass transfer of sorbate within the three-dimensional pseudo-phase of soil organic matter (Brusseau *et al*., 1991; Pignatello and Xing, 1996; Pignatello, 2000). Intra-organic matter diffusion can have a predominant role in the sorption of neutral hydrophobic organic compounds (Brusseau *et al*., 1991; Pignatello, 2000; Weber *et al*., 2001). While diffusing into soil aggregates, pesticide molecules may interact with new adsorption sites and become entrapped more tightly within organic components in the soil (Koskinen and Harper, 1990; Kah and Brown, 2007). Soil organic matter has a strong affinity for most organic compounds and exist in rubbery and glassy phases; it retards sorption and desorption through its viscosity and by the presence of internal nanopores, which detain molecules and may sterically inhibit their migration (Pignatello, 2000). The rubbery and glassy phases of soil organic matter show different behaviour relating to time-dependent sorption and sorption capacity (dual mode sorption). Diffusion coefficients of small molecules in rubbery polymers compared to water are several orders of magnitude smaller and depend more strongly on the size and shape of the diffusant (Pignatello, 2000). Humic acid is believed to be a more rubbery form of organic matter in the solid state. Glassy soil organic matter offers a much greater impediment to diffusion than the rubbery form as it is more rigid and condensed and it contains holes (nanopores) in which organic molecules can momentarily be detained (Pignatello and Xing, 1996). Slow sorption is assumed to occur mainly in the glassy domain, causing non-linear sorption due to its limited sorption capacity; faster sorption predominantly occurs in rubbery-type soil organic matter, and usually exhibits linear sorption (Pignatello and Xing, 1996).

2.5. Measurement of sorption

The availability of pesticides in the soil solution and hence their fate and behaviour in the environment is strongly influenced by the extent of their sorption to soil organic matter and other constituents as a result of the various binding mechanisms discussed in Section 2.2. Sorption of pesticides and other organic chemicals has been studied extensively over the past few decades and attempts have been made to develop universally accepted partitioning parameters to express this behaviour. These parameters are expressed in terms of a soil-liquid partition coefficient (K_d) and a soil organic carbon sorption coefficient (K_{oc}). These parameters are widely used by environmental scientists and regulatory agencies to predict and compare the binding of chemicals within the soil (Wauchope *et al*., 2002).

The soil sorption coefficient or partition coefficient K_d, conventionally written with a subscript d (for 'distribution'), can be defined as a ratio of the pesticide concentration in the solid phase to that in the solution phase at equilibrium (Wauchope *et al*., 2002; Kah and Brown, 2006). Determination of K_d is commonly undertaken by the batch-equilibrium method following OECD guideline 106 (OECD, 2000), where a soil sample is shaken with an aqueous pesticide solution usually in 0.01M $CaCl_2$ (in order to minimise soil mineral balance disruption) for a specific time (equilibration step, typically 24 hours). After this, the samples are centrifuged and the supernatant is removed and analysed to determine the equilibrium solution pesticide concentration C_e. Assuming that all the pesticide removed from the solution is sorbed by the soil, sorption of a pesticide by soil (C_s) is calculated from the difference between the initial and final pesticide concentrations in an aqueous solution (Wauchope *et al*., 2002). The partition coefficient (K_d, mL g^{-1}) is then calculated as:

$$C_s = K_d C_e$$

where C_s is the concentration of pesticide in the solid phase (μg g^{-1}) and C_e is the concentration of pesticide in solution phase (μg mL^{-1}) at equilibrium and provided C_s varies linearly with C_e. K_d values are ideally determined at pesticide concentrations that would occur in soils when the compounds are applied at recommended rates followed by enough rainfall to bring the soil to field capacity (Weber *et al*., 2004). Large values of K_d (of the order of ≥100 mL g^{-1}) indicate that a pesticide is strongly sorbed to the soil particles and will be relatively immobile in soil; it may also be relatively resistant to microbial degradation (Wauchope *et al.*, 2002). When there is a non-linear relationship between sorbed and solution phase pesticide, the distribution coefficient is then expressed in terms of the empirical Freundlich relationship as:

$$C_s = K_f {C_e}^{n_f}$$

where K_f is the Freundlich distribution coefficient (mL g^{-1}) and n_f is the Freundlich exponent.

It has been generalised from the thousands of K_d and K_f measurements over the past few decades that there is often a high correlation between the organic matter content of different soils and K_d values in those soils (Wauchope *et al*., 2002). Due to this positive correlation between pesticide sorption and soil organic matter, the sorption coefficient normalized to soil organic carbon content, K_{oc} is commonly used (Wauchope *et al*., 2002). Organic matter content of a given soil is often measured by determining the amount of organic carbon present by combustion or digestion techniques (Wauchope *et al*., 2002). Due to the inconsistent ratio of soil organic matter mass to soil organic carbon mass, the organic carbon fraction itself is usually reported (Wauchope *et al*., 2002). Thus the soil organic carbon sorption coefficient (K_{oc}, mL g^{-1}) of a pesticide is calculated by dividing a measured K_d in a specific soil by the organic carbon fraction (F_{oc}, $g\ g^{-1}$) of the soil (Wauchope *et al.*, 2002):

$$K_{oc} = \frac{K_d}{F_{oc}}$$

K_{oc} values indicate the strength of sorption of pesticides to soils and are frequently used as measures of relative potential mobility of pesticides in soils and in ‘fugacity’ models describing the partitioning of pesticides in soil, water and atmospheric systems (Wauchope *et al*., 2002).

Measurement of pesticide sorption by the batch-equilibrium method has many advantages including: (i) the method can be easily used for routine laboratory analysis following OECD guideline 106 (OECD, 2000); (ii) it allows the separation of solution from the solid phase more effectively; and (iii) a large volume of solution can be obtained for analysis. However, the experimental conditions in the batch-equilibrium method raise many questions on the suitability and relevance of the technique to measure the retention of pesticides within soil. For example, some of the important experimental features including temperature, type of vessel, type of shaking, centrifugation speed and soil to solution ratios have not been completely standardised which makes the results from different studies difficult to compare (Kah and Brown, 2007).

A centrifugation technique described by Walker (2000) is currently being used by scientists as an alternative to the batch-equilibrium method for the measurement of aqueous phase concentrations of pesticides (Beulke *et al*., 2004; Yazgan *et al*., 2005: Kah and Brown, 2007). This method permits investigation of pesticide sorption at realistic soil:solution ratios over extended time periods and can also be used with structured soils. In contrast to the slurry system in the batch equilibrium method, soil is usually wetted to field capacity in the centrifugation technique and is thus more representative of field conditions. Walker and Jurado Exposito (1998) investigated the sorption behaviour of diuron, isoproturon and metsulfuron-methyl by centrifugation and standard batch-equilibrium methods. Although the results were not fully consistent, the K_d and n_f values obtained by the centrifugation technique were generally lower (indicating less sorption and greater curvature) than the corresponding values obtained by the batch equilibrium method. They concluded that the batch technique might overestimate sorption in some cases. Other methods that have been used to characterise the retention of pesticides by soils include soil thin-layer chromatography (Johnson and Sims, 1998), gel filtration chromatography methods (Madhun *et al*., 1986), supercritical fluid extraction methods (Berglöf *et al*., 2003) and transport through soil columns (Tuxen *et al*., 2000; Heistermann *et al*., 2003).

2.6. Processes responsible for pesticide transport from soil to water

The mobility of pesticides refers to their displacement from the site of application to other environmental compartments (Navarro *et al*., 2007). Pesticides are now frequently detected in surface and groundwater bodies throughout Europe, so it is vital to understand the processes responsible for their movement to water resources in order to minimise the risk of contamination. Surface runoff and leaching are the two main processes involved in pesticides transport from soil to water bodies. These are briefly discussed here.

2.6.1. Runoff to surface water

Depending on soil properties, water inputs received as rainfall or irrigation will either infiltrate the soil surface or run-off as overland flow to surface waters. Surface runoff can be a critical process, since water is in direct contact with the immediate soil surface which often contains the largest portion of applied pesticide and can result in the pesticide being transported into surface waters. The movement of pesticide through runoff is governed by various factors which include slope characteristics and structural stability of soil, physico-chemical properties of the pesticide molecule and type of formulation, type of plant cover, and irrigation or rainfall intensity (Navarro *et al*., 2007). Soil capping is also an important mechanism where the surface soil particles bind together creating an impermeable layer. This reduces the ability of soils to absorb water, leading to surface water-logging and increasing the risk of runoff and erosion. Since concentrations of pesticide can be very large in the source or 'distribution zone' close to the soil surface (Kim *et al*., 2005), and the majority of applied pesticide generally remains in the top few centimeters of the soil surface, it is important to be aware of any hydrological pathways which connect the soil surface with drainage outflow (Johnson *et al*., 1996).

Timing and intensity of irrigation and rainfall events are very important in governing pesticide losses in runoff from agricultural fields, especially the time between pesticide application and the first runoff event (Baker and Johnson, 1979, Wolfe, 2001). Severe rainfall conditions occurring shortly after pesticide application usually results in higher runoff losses. It has been reported in the literature that runoff losses for the majority of commercial pesticides generally remain in the range of 0.5% or less of the total amount applied, provided no severe rainfall conditions occur within the first few weeks after application (Wauchope, 1978). However, there are exceptions to this generalisation depending on type of formulation, slope characteristics and weather pattern. For example, pesticides that are applied to the soil surface, especially herbicides formulated as wettable powders, show the largest long-term losses of up to 5%

depending on weather condition and slope of the field (Wauchope, 1978). Water insoluble pesticides that are usually applied as emulsions are persistent in the environment and long-term run-off losses of such pesticides have been reported in the range of 1% or less regardless of weather pattern. 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 where this occurs soon after application (Wauchope, 1978).

Runoff losses largely depend on the solubility and sorption potential of pesticides. Adsorption to organic matter is one of the key processes in governing such losses (Ulrich *et al*., 2013). Pesticides with low solubility and higher adsorption coefficient (K_{oc}) are mainly lost in the sediment phase of the runoff (Huber *et al*., 1998), and hence erosion control measures can be important in minimizing losses of these compounds (Wauchope, 1978). On the other hand compounds with higher solubility and lower K_{oc} values are mainly lost in the water phase of runoff (Ulrich *et al*., 2013), and erosion control practices will have little effect on such losses (Wauchope, 1978). Overall dissolved runoff losses generally exceed solid-phase losses (Huber *et al*., 1998). Wauchope (1978) also reported that the majority of pesticides are lost in the water phase, despite the fact that pesticide concentrations are usually 2-3 orders of magnitude higher in sediments than in the water phase. This is due to the fact that sediments make up only a small fraction of overall runoff volume.

2.6.2. Leaching to groundwater

Leaching losses of pesticides through soil and subsequent contamination of groundwater bodies occur as a result of conventional use of such chemicals in agricultural practices as well as accidental spills (Flury, 1996). Pesticide leaching below the root zone largely depends on the soil and chemical properties, pesticide formulation and time of application as well as weather conditions. The rate of infiltration of water across the soil surface depends on soil properties, such as soil structural composition, texture, permeability and soil moisture content (Brown *et al*., 1995). Soil porosity and density are important physical characteristics of soil which determine the water holding or retention capacity of the soil as well as the rate of water movement within soil profiles (Brown *et al*., 1995). Hydraulic conductivity is another important physical property of soil which determines the rate that water, and thus any dissolved pesticide, moves either vertically or laterally within a soil profile.

Water flow through soil macropores is an important process (Nicholls *et al*., 1993), and this bypass flow can result in the transport of pesticide from surface layers to deeper soil layers. There is a greater potential of contamination of water sources when these macropores connect with any artificial drainage system, which has been shown to be responsible for the transport of large amounts of dissolved pesticide (Johnson *et al*., 1993; Brown *et al*., 1995), particularly when rainfall and subsequent drainage occur shortly after pesticide application (Tediosi *et al*., 2012). The risk of pesticide leaching is potentially greater under high precipitation conditions in sandy soils characterized by low organic matter content and loamy and clayey soils dominated by macropore flow (Reichenberger *et al*., 2007). Leaching is considerably reduced if the period after application is characterized by dry weather or by light rain showers which do not generate macropore flow (Walker *et al*., 2005; Lewan *et al*., 2009). However, if the pesticide is applied to wet soil, it is more prone to leaching as macropore flow can be triggered more quickly following rainfall or irrigation (Jarvis, 2007). Flury (1996) reported that overall annual leaching losses generally remain in the range of <0.1 to 1% of the total mass applied when there is no heavy rainfall within the first few weeks after pesticide application, but leaching losses can reach up to 5% of the total mass applied in extreme conditions. Pesticide losses through leaching are generally smaller than the run-off losses (Flury, 1996).

Leaching losses are also shown to be dependent on the water solubility of a pesticide molecule and type of formulation. For example, the differences in the leaching behaviour of the herbicides propyzamide and benfluralin under the same conditions have been reported to be directly related to their water solubility (Oliva *et al*. 2000). Wybieralski (1992) reported greater leaching losses of propoxur from emulsifiable formulation (EC), intermediate losses from suspension concentrate formulation and smallest losses from pure active substances in five different arable soils. Potter *et al*. (2010) reported greater leaching losses of metolachlor from EC formulation compared to granular formulation under different tillage systems.

2.7. Pesticide formulations

Pesticide formulations contain active ingredients and co-formulant chemicals also called adjuvants as well as various other additives. These co-formulants are frequently included in commercial formulations to solublise or emulsify the active substances for better spray application (Rial-Otero *et al*., 2003; Pose-Juan *et al*., 2009) and hence to enhance their effectiveness and bioavailability (Foy, 1996; Krogh *et al*., 2003). These additives improve the performance of an active substance by modifying the physical and chemical characteristics of the spray mixture.

Though the history of pesticide formulations dates back to the 18th century when simple additives such as sugar, flour, resins and molasses were used in combination with lime, copper, arsenates and sulphur to improve the biological performance of the applied mixture (Green and Beestman, 2007; Castro *et al*., 2014), research on formulation technology has advanced rapidly in recent years. Adjuvant is a broad term describing any additive to a spray tank that enhances pesticide activity. In general there are two types of adjuvants: (i) formulation adjuvants (or inerts); and, (ii) spray adjuvants (or tank mixing additives). Formulation adjuvants are part of the formulation, while the spray adjuvants are added along with the formulated product to the water in the tank of the sprayer before application (Hochberg, 1996; Krogh *et al*., 2003). Examples of adjuvants are surfactants, spreaders, stickers, crop oils, anti-foaming materials, anti-freezing agents, buffering agents, and compatibility agents. Adjuvants for pesticides therefore comprise a large and heterogeneous group of substances and can constitute up to 90% of pesticide formulations (Murphy *et al*., 2005). The co-formulants include solvents and surfactants, but the latter are the major group of adjuvants; particularly the non-ionic surfactants are mostly used in agrochemical formulations (Van Valkenburg, 1982; Foy, 1996). However, since co-formulants are considered by regulators and industry as ‘inert ingredients’, their use is largely unregulated and information regarding their composition is rarely available (Upham *et al*., 2007).

A wide variety of pesticide active substances with different physico-chemical properties are available on the market. Development of agrochemical formulations is mainly based on physical and chemical properties of the active substance (Knowles, 2008). However, intended target, crop and environment are also important considerations when these formulations are developed. Modern pesticide formulations are different from the old conventional formulations which were based on simple solutions in water, wettable powders, dust and emulsifiable concentrates in a non-aqueous petroleum-based solvent (Knowles, 2005). There is a growing pressure on manufacturers from most government and regulatory authorities to develop formulations which are safe in use and less hazardous to the environment. To meet these demands, the majority of current pesticides are formulated to use with water as a carrier. The petroleum-based formulations are now being replaced with water-based suspensions and emulsion formulations, while powders are being replaced with free flowing water dispersible granules to overcome the dust problems (Knowles, 2008). Controlled release formulations (CRFs) are being developed to reduce leaching of pesticides and contamination of groundwater (Maqueda *et al*., 2009), as well as safe handling of toxic active substances.

Suspension concentrates (SC), emulsions and suspoemulsions (SE) are water based formulations. SC formulations were developed as a substitute for wettable powders to overcome the problems associated with dust (Knowles, 2005). These formulations not only give enhanced biological activity and rainfastness but are easy to handle and are considered to be safer to the operator and environment (Mulqueen, 2003). Similarly, to eliminate volatile organic solvents in agrochemical formulations, oil-in-water emulsions (EW) were developed as alternatives to emulsifiable concentrate (EC) formulations (Mulqueen, 2003; Knowles, 2005). EW formulations contain active ingredient surrounded by oil droplets dispersed in a continuous aqueous medium. These formulations are very cost effective, safe to handle and transport (Mulqueen, 2003).

Development of EW formulations requires a careful selection of surfactant emulsifiers to prevent flocculation, creaming and coalescence of the oil droplets. Non-ionic surfactants, block copolymers and other polymeric surfactants are now being used to produce stable emulsions (Knowles, 2005). Suspoemulsion formulations (SE) are mixtures of suspension concentrates and oil-in-water emulsions with added surfactants to prevent flocculation and thickeners to prevent separation of the dispersed phases (Mulqueen, 2003). These formulations are particularly designed as a combination of different active substances in a single product, and include active substances both in solid and liquid form (Knowles, 2005). Microemulsions (ME) are also becoming increasingly popular due to their very fine droplet size and long-term thermodynamic stability (Green and Beestman, 2007; Pratap and Bhowmick, 2008). These formulations consist of oily liquid or solid dissolved in organic solvent, water and surfactant (Knowles, 2005; Faers and Pontzen, 2008). Water dispersible granules (WG) were developed as alternatives to wettable powders and suspension concentrates. They are considered to be safer and commercially attractive due to their uniform size, non-dustiness, and ease of handling and long term stability at low and high temperatures (Knowles, 2005).

2.7.1. Formulation chemistry

It is a regulatory requirement to develop commercial formulations of pesticides that not only improve the biological activity and persistence of the active substance but also meet the needs of environmental safety and hence decrease the amount of pesticides released into the environment (Castro *et al*, 2014). Many types of pesticide formulations have been developed by considering the physico-chemical properties of the pesticide, not only to maximise their efficacy but also to prevent unfavourable environmental contamination from pesticides and their degradation products (Katagi, 2008). For example, a lower water solubility of the pesticide usually leads to utilisation of a water-miscible organic solvent and adjuvants including surfactants to solubilise, suspend, or disperse the active substance of pesticide in the spray mixture applied in agricultural practices (Katagi, 2008). Different types of co-formulants used in commercial formulations of pesticides are briefly discussed below.

2.7.1.1. Surfactants

The majority of pesticides are currently formulated to use water as a carrier. The main problem associated with these water-based formulations is how to penetrate the waxy surfaces of many insects and plants (Knowles, 2008). Adjuvants have been developed to overcome this issue and to improve the efficacy of pesticide active substances and hence, the overall pesticidal effects (Castro *et al*., 2014). Surfactants are the most important group of adjuvants that are used for this purpose, especially the non-ionic surfactants which are most commonly used in agrochemical formulations (Katagi, 2008; Knowles, 2008). In addition to enhancing biological performance of the agrochemicals, surfactants are also essential for their preparation and maintenance of long-term physical stability (Castro *et al*., 2014). Surfactants are defined as “amphiphilic molecules that consist of two or more chemically different portions, each of which has a preference for a different phase or interface, e.g. oil and water” (Knowles, 2005). A surfactant molecule consists of a hydrophilic polar head and a lipophilic non-polar tail. These components of a surfactant molecule lower the surface tension of an air-water interface, allowing the pesticide to be more evenly dispersed on a surface and to reach its intended target (Katagi, 2008). The hydrophilic portion of the surfactant molecule imparts water solubility to the molecule and sodium and calcium salts of negatively charged groups such as sulphate or sulphonates are commonly used for this purpose. The hydrophobic portion of the surfactant molecule is usually a solvent-soluble lipophile which is based on aliphatic or aromatic groups (Castro *et al*; 2014; Knowles, 2005). Synthetic or natural alkanes and alkenes, alkylbenzenes, polypropylene oxide, silicones and fluorocarbons are some of the common examples of lipophiles. Synthetic surfactants represent a relatively new development to obtain surface active effects. These surfactants have been tailor-made with the introduction of amphipathic molecules with anionic properties for specific applications. The main types of pesticide formulations containing surfactants are listed in Table 1. The surfactant in these formulations generally occupies less than 10% (w/w), and the remaining consists of various additives such as oils, polymers, and carriers (Katagi, 2008).

***Table 2.1*:** Principal types of pesticide formulations containing surfactants in their typical composition

Formulation type	Active substance (%)	Surfactant (%)	Other co-formulants (%)
Suspension concentrate (SC)	20-70	2-5	Propylene glycol antifreeze (5-10), antisettling agent (0.2-2), water (to 100)
Emulsifiable concentrate (EC)	20-70	5-10	Solvent/co-solvent (to 100)
Soluble concentrate (SL)	20-70	5-10	Antifreeze agent (5-10), water miscible solvent (to 100)
Wettable powder (WP)	10-80	1-2	Dispersing agent (2-5), antifoaming agent (0.1-1)
Water dispersible granules (WPG)	50-90	1-3	Dispersing agent (3-15), disintegrating agent (0-15), Soluble or insoluble filler (to 100)
Oil-in-water emulsion (EW)	5-30	<5	Stabilizer, thickener
Granules (G)	1-40	0-5	Stabilizer (1-2), polymer or resin (0-10), binder (0-5), carrier (to 100)

Source: From Knowles (2005) and Katagi (2008).

Non-ionic surfactants are most commonly used in agrochemical formulations and are often produced by reacting a hydrophobic group with condensed molecules of ethylene oxide to impart hydrophilic properties to the surfactant. A wide range of surfactant properties can be achieved by varying the ethylene oxide chain length, which affects the fundamental functional properties of wetting, dispersion, emulsification and solubilisation in the formulation and application of pesticides (Katagi, 2008). The major classes of non-ionic surfactants are alkylamine ethoxylates, alkylphenol ethoxylates, alkanol ethoxylates and caster oil ethoxylates. The functional properties of non-ionic surfactants can be modified by changing the level of ethoxylation and, hence, the hydrophilic/lipophilic balance (Knowles, 2005). Castro *et al*. (2014) reported that the polymerised glycol ether or glucose units cause the hydrophilic behaviour of non-ionic surfactants. Such surfactants are solely produced by addition of ethylene oxide or propylene oxide to alkylphenols, fatty alcohols, fatty acids, fatty amines or fatty acid amides. The applications of non-ionic surfactants in commercial pesticide formulations are increasing as emulsifiers, wetting agents and dispersing agents (Castro *et al*. 2014).

2.7.1.2. Other co-formulants in pesticide formulations

Solvents are one of the main co-formulants in commercial pesticide products that are usually liquid based. Currently, a diverse range of solvents are available that are used in commercial products depending on the solubility of the active ingredient (Knowles, 2005). The most popular solvent is water and most of the SC formulations are water based. However, the majority of the pesticide active substances are not soluble in water, hence petroleum based aliphatic and aromatic organic solvents are used (Knowles. 2005). Inert materials such as fillers and carriers are also added to commercial pesticide products in order to maintain the required strength of the active substance so that the product can be safely used (Knowles, 2005). Carriers and fillers are mostly used in solid based formulations that include dispersible granular and wettable powder formulations. These inert substances can be of organic or inorganic nature. Anti-freezing and anti-foaming agents are also important co-formulants used in agrochemical formulations. Anti-freeze agents are usually added to water based products in order to maintain and preserve the commercial products at lower temperatures. Suspension concentrate formulations, suspo-emulsions and oil-in-water emulsions contain up to 15% of ethylene glycol and propylene glycol anti-freeze agents (Knowles, 2005). Anti-foam agents are used to counter the foam formation in the spray tank in water based formualtions (Green and Beestman, 2007). These agents are meant to reduce the surface tension in order to destabilise the foam bubble. Suspension and emulsion formulations also contain anti-settling agents (thickening and gelling agents) in order to improve their long term stability (Knowles, 2005). These are usually clay based swelling and non-swelling agents. Ultraviolet light absorbing compounds and anti-oxidants are currently being used as stabilise the complex formulations of pesticides (Green and Beestman, 2007). Some of the water based commercial products such as SC formulations, oil-in-water emulsions and solution concentrates need preservatives in order to protect them from microbial degradation (Knowles, 2005). Preservatives play an important role in preventing the gas build up and odours within the pack containing the product. They are also important in maintain the product pH, colour and viscosity (Knowles, 2005).

2.7.2. Interaction of co-formulants with fate processes of pesticides

Over the past few decades, studies concerning adjuvants only dealt with the development trends in pesticide formulations, mode of action and applications of adjuvants (Reeves, 1992). Effect studies of pesticides have also compared effectiveness of different adjuvants (Foy, 1993, Krogh *et al*., 2003) and some of the studies discuss the environmental toxicity and risk of adjuvants (Parr, 1982; Chow and Grant, 1987; Scholz, 1997; Vandepitte and Feijtel, 2000).

It is generally assumed that sprayable formulations do not have any impact on the transport of pesticide in soil (Flury, 1996), as the active substance is assumed to be released from the formulation almost instantly after application (Gückel *et al*., 1974; Furmidge, 1984). However, Ghodrati and Jury (1992) observed that atrazine, napropamide, and prometryn moved deeper into the soil profile when applied as technical grade compared to their wettable powder formulations. On the other hand, granular formulations hold the active substance on entry to the soil and release it gradually either by diffusion or by breakdown of the granule under the influence of irrigation or precipitation (Furmidge, 1984). Therefore, Flury (1996) suggested that granular formulations may affect the movement of a pesticide, especially when rainfall occurs shortly after application. Similarly, other controlled-release formulations release the active substance slowly when applied to the soil and the rate of release depends on environmental factors such as temperature and soil moisture content (Flury, 1996). Laboratory studies were also performed to compare the transport of technical grade and starch-encapsulated atrazine in undisturbed soil cores, where 13% of the applied technical grade atrazine was lost to leaching, compared to <1% for starch-encapsulated formulations after applying less than 2.3 pore volumes of irrigation water (Gish *et al*., 1991a). Schreiber *et al*. (1993) also reported that starch-encapsulated formulations of atrazine reduced the movement of atrazine by 70% compared to commercial formulations in both silty clay loam and sandy soils after application of 75 mm h^{-1} simulated rainfall. Gish *et al*. (1994) suggested that controlled-release formulations may reduce the amount of chemical available for fast leaching and thus reduce the risk from preferential flow.

A few recent studies demonstrated that co-formulants present in commercial formulations can influence the sorption behaviour of active substances in soil. These chemicals may alter the soil-liquid partition coefficient of pesticides under field conditions (Pose-Juan *et al*., 2010a). For example, the sorption of triticonazole can be increased by up to 50% in the presence of higher concentrations of non-ionic hydrophobic surfactants (Beigel *et al*., 1998). Authors argued that the additional surfactant monomers may sorb on the monolayer of hydrophilic heads of surfactants already sorbed in soil resulting in a bilayer of surfactant on the soil surfaces which would considerably enhance the sorption of triticonazole on soil surfaces. This behaviour indicates that sorption of pesticides in soil is a complex process and pesticide molecules not only interact with soil organic matter but the presence of surfactants in commercial pesticide formulations may lead to an additional sorption mechanism where some pesticide is also retained onto formulation adjuvants. Beigel *et al*. (1998) also measured the sorption behaviour of triticonazole when applied as technical grade material and formulated product with low doses of anionic surfactants using the batch equilibrium method. They reported that triticonazole sorption was not significantly affected by the presence of low concentrations of the anionic surfactant (Soprophor, FLK and ‘Supragil’ MNS90) used in the commercial formulation. Their experimental data showed that the K_f value of triticonazole from the solutions of technical grade material was 4.61 (±0.20) litre kg^{-1}, while it was 4.48 (±0.11) and 4.60 (±0.13) litre kg^{-1} in systems containing 80 mg L^{-1} of the surfactant Sonrophor, FLK and Supragil, MNS90 respectively.

Beigel and Barriuso (2000) investigated the effect of field rate applications of three SC formulations and two anionic surfactants on the solubilisation and sorption behaviour of triticonazole fungicide in a loamy clay soil using the classical batch equilibration technique. Solubilisation of triticonazole from the commercial formulation solutions was greater than its solubility in water and the authors correlated this to triticonazole association with surfactant monomers. They reported that apparent concentrations measured in the supernatants at equilibrium were 23, 24, and 30 mg L^{-1}, for Real, [Real + FLK], and [Real + MNS90] respectively, and these concentrations were almost three times larger than the solubility of triticonazole in water (8.4 mg L^{-1}). They concluded that the greater solubilisation of triticonazole from commercial formulation solutions may increase the amount available in soil solution for transport and plant uptake. However, the sorption isotherms of triticonazole applied as technical grade material and commercial product with diluted surfactants and formulation adjuvants were similar.

The impacts of commercial formulation on pesticide behaviour were also studied for metalaxyl in vineyard soils by the batch incubation method, where the formulated product (copper oxychloride-metalaxyl formulation) showed ten times higher retention values in soil compared to technical grade material (Pose-Juan *et al*., 2010a). The authors attributed this behaviour to an interaction of adjuvants and soil, contributing to an overall increase in the retention of metalaxyl in the solid phase. Furthermore, it was suggested that the mechanisms of metalaxyl retention could be related to the presence of methyl-ester based surfactants in the commercial formulation (Ridomil Gold Plus). They also suggested that when pesticides and surfactants coexist in soils, the pesticides could be adsorbed by surfactants previously adsorbed into the soil which will increase pesticide retention. The authors demonstrated experimentally that the effect of copper oxychloride colloids (40%, w/w) in the commercial fungicide formulation (100-130 mg kg^{-1}) on the retention of metalaxyl was six time higher than that of soil organic matter colloids (15-20 mg kg^{-1}). The authors also observed an increase in pH after the addition of commercial formulation to the soils and related it to a buffering effect of copper oxychloride in the commercial formulation and noted that variations in the pH can induce changes in the sorption of metalaxyl to soil.

In another study, Pose-Juan *et al*. (2010b) reported that the sorption of penconazole in the commercial formulation was greater than for the technical grade material and approximately 70% of the total penconazole retained by the solid phase was sorbed on the soil whereas the other 30% was retained by the adjuvants present in the commercial formulation. They measured this soil-water partitioning of technical grade material and commercial water-oil emulsion formulation of penconazole (WOEP) at a range of concentrations using batch experiments with an incubation time of 24 hours. The authors suggested that the solid adjuvants present in the commercial formulation, together with soil, contributed to increase the total penconazole concentration in the solid phase. The authors suggested that the oil-surfactant mixture of the commercial formulation influenced the adsorption of penconazole on soil, either by enhanced penetration of the penconazole onto the less polar sites of the soil organic matter, or by the co-adsorption of penconazole within the oil-surfactant mixture.

Pose-Juan *et al*. (2011) studied the influence of adjuvants in a commercial formulation of the fungicide 'Switch' on the adsorption of its active ingredients cyprodinil and fludioxonil on vineyard soils. They reported that the adjuvants present in the commercial formulation increased the concentration of fludioxonil in water suspensions up to 9 mg L^{-1}; this is about five times its solubility limit in water (1.8 mg L^{-1}), and this may consequently have a strong influence on the mobility of pesticide in soil. However, their fungicide batch sorption experiments showed large increases in the K_d values of both active ingredients and the authors suggested that a higher concentration of adjuvants may favour the sorption of active substances in soil. The authors reported that only 4.0-8.6% of the total amount of cyprodinil in the solid phase was adsorbed to soil, while the remaining material was either precipitated or retained on the non-soluble adjuvants of commercial formulation. They concluded that the soil-water partitioning of cyprodinil for the technical grade material and commercial product (Switch) may not differ if its concentration is below its solubility limit in water. However, additions of Switch in excess of the solubility limit of cyprodinil, may result in alternative retention mechanisms. In the case of fludioxonil, K_d was similar to the partition of pure compound when Switch concentrations were low. However, with higher additions (i.e., C_{liquid} >1 mg L^{-1}), distribution coefficients were smaller than those for technical grade material. The authors suggested that this may be due to an increased solubilisation of the compound by the co-formulant adjuvants.

Garcia-Ortega *et al*. (2006) compared the sorption/desorption (batch method), biodegradation and toxic effects of the Pestanal® grade and commercial formulation (Ectomort Centenary) of the organophosphate insecticide propetamphos in river and estuarine sediments. They did not observe any significant differences in rate of biodegradation between the two pesticide forms; however, differences were observed in their sorption behaviour. The authors reported that at low concentrations of propetamphos, sorption of the compound was greater from technical grade treatments compared with that from the commercial formulation. However, at higher concentrations of propetamphos, the commercial formulation showed a greater affinity for the sediment phase (K_d = 7-11 mL g^{-1}) compared to the Pestanal® grade (K_d = 4-10 mL g^{-1}), suggesting the Shellsol R® solvent present in commercial formulation enhances access of the pesticide to sorption sites that are not available to the Pestanal® grade material (Garcia-Ortega *et al*., 2006). The authors suggested that this may be due to the affinity of aromatic solvent (Shellsol R®) with the carbon content of sediment that resulted in enhanced sorption onto sediment organic matter. Toxicity data suggested that the commercial formulation was also more toxic to the microbial community than the technical grade material (Garcia-Ortega *et al*., 2006).

Földényi *et al*. (2013) reported that co-formulant chemicals in sulfonylurea herbicides resulted in a decrease in the extent of adsorption of active substances. They compared the sorption of technical grade and commercial formulations of chlorsulfuron and tribenuron methyl in sand, loam and clay loam soils using the batch equilibrium method. Their results indicate that at small concentrations, the extent of adsorption of the active substance was higher for solutions of pure ingredients than from formulation solutions (Földényi *et al.*, 2013). They also reported that the presence of dispersing agent 'Supragil' in commercial formulation resulted in a decrease in adsorption of the smaller concentrations of chlorosulfuron and hence increased environmental mobility of the pesticide. Their experimental data showed that for concentrations above 40 µmol L^{-1}, the adsorption of chlorsulfuron was lower in the presence of Supragil than for concentrations < 40 µmol L^{-1} in clay loam soil; however, adsorption of chlorsulfuron decreased markedly on sandy soil in the presence of forming agent. Sorption of the two compounds at higher concentrations was found to be greater from the formulated products and this behaviour was correlated with the hydrophobic interactions between the dispersant and specific surface area as well as with the total organic carbon content of soils. Cox and Walker (1999) compared the sorption behaviour of analytical grade and commercial formulation of linuron (Linuron-50, 50% active ingredient, wettable powder) using a centrifugation technique in soil samples incubated at 5°C for a period of 28 days. However, they did not observe any significant difference in sorption behaviour of linuron in soil from the two treatments and suggested that the co-adjuvants present in the herbicide formulation do not interact with the sorption behaviour of the active substance. They used wettable powder formulation of linuron and the results were only based on two replicates for each treatment which perhaps are not sufficient to justify the results.

Although Cox and Walker (1999) used the centrifugation method to study the time-dependent sorption behaviour of linuron, all other studies discussed above were based on the batch equilibrium method which may be less suitable to characterise the effect of formulation on the sorption behaviour of pesticides in soil. This may be due to the slurry conditions and continuous shaking employed in the batch system which is in contrast to centrifugation method where the experiments are carried out under realistic soil moisture conditions.

2.8. Modelling sorption behaviour of pesticides

The fate and behaviour of pesticides in the environment is dependent on a variety of factors that have been discussed earlier in this chapter. Sorption of pesticides in soil is recognised as a key mechanism that controls their availability in the solution phase for transport and uptake by plants and microorganisms. Laboratory experiments are mainly used to measure the partitioning of a pesticide between aqueous and solid phases in soil. However, in scenarios where experimental measurements are not possible, modelling approaches are used to describe and predict the fate and behaviour of pesticides released into the environment. Mathematical modelling is an important tool to generate data based on extrapolation from the existing experimental results that can be used to anticipate the behaviour of pesticides in unknown circumstances. Mathematical descriptions of time-dependent sorption may provide important estimates on the potential contamination of surface and groundwater as well as toxic effects on non-target aquatic and terrestrial organisms.

Sorption of pesticides in soil is a time-dependent mechanism that is controlled by several rate-limiting processes including pore diffusion and intra-organic matter diffusion as discussed in Section 2.4. Mathematical models that consider various types of non-equilibrium sites reacting at different rates can be used to describe the kinetics of sorption over the entire timescale (Beulke and van Beinum, 2012). Such models have been widely used to describe and predict the time-dependent sorption behaviour of pesticides (Maraqa *et al*., 2001; Heistermann *et al*., 2003; van Beinum *et al*., 2005; van Beinum *et al*., 2006; Villaverde *et al*., 2009; Suddaby *et al*., 2013). Diffusion and mass transfer models are the two most common modelling approaches that have been used to conceptualise the non-equilibrium sorption behaviour of organic molecules. Diffusion models are used to describe the behaviour in terms of intra-particle and intra-organic matter diffusion and are usually based on complex diffusion equations. Van Beinum *et al*. (2006) developed an intra-particle diffusion model and successfully applied it to describe the sorption and desorption of isoproturon on lignin. Van Beinum *et al*. (2005) used the process-based diffusion modelling to examine the rate-controlling steps in the sorption process. They reported that the time-dependent sorption on intact soil aggregates could be described by a diffusion model that accounts only for diffusion into the aggregate followed by instantaneous sorption.

Mass transfer models are usually based on the assumption that the sorbent consists of multiple sorption sites and that movement of an organic molecule between the different compartments follows first-order kinetics (Fortin *et al*., 1997; Suddaby *et al*., 2014; Beulke *et al*., 2015). The two main mass transfer modelling approaches are: (1) two-region (mobile-immobile) models, and (2) two-site and multisite models. Two-region models conceptualise non-equilibrium behaviour with the assumption that the soil water is divided into mobile and immobile regions (van Beinum *et al*., 2010; Beulke *et al*., 2015). The two-region model is complex to use due to the uncertainty in establishing the relative proportions of mobile and immobile regions (Ma and Selim, 1997). Two-site models are based on the concept that the soil matrix consists of two types of sorption sites. These are (i) equilibrium sorption sites usually the outer surfaces of soil aggregates where sorption reactions occur instantaneously; and, (ii) non-equilibrium or less accessible sorption sites situated within the soil organic matter where the sorption reactions proceed slowly and are rate-limited (Suddaby *et al*., 2014; Beulke *et al*., 2015).

Two-site models are the simplified form of a multi-site model which can either describe the initial rapid increase in sorption or the long-term behaviour of sorption (Beulke and van Beinum, 2012). Such models provide a reasonable balance between the complexity of the model and the experimental efforts needed to determine the model parameters and are preferred within the regulatory context (Beulke and van Beinum, 2012). A two-site modelling approach is now integrated into FOCUS-based pesticide leaching models (i.e. PEARL, MACRO, PRZM, and PELMO). The two-site model is also implemented in the PEARLNEQ software package in order to describe long-term sorption behaviour of pesticides (Boesten *et al*., 2007; Beulke and van Beinum, 2012). The two-site model generally assumes that degradation only occurs in the equilibrium domain.

The concept of only two-sorption sites in modelling generally oversimplifies the sorption phenomenon. However, in reality, the sorption reactions occurring in soil involve multiple sites at different rates (Beulke *et al*., 2015). Some authors suggested to include three sorption sites (instantaneous sorption reaction sites, sites where sorption proceeds over a period of days and sites where sorption proceeds over a period of years) to describe the experimental results effectively (Boesten *et al*., 1989). Three-site models have also been used to account for irreversible sorption in order to better describe the non-equilibrium sorption behaviour of pesticides in soils (Selim and Amacher, 1988; Prata *et al*., 2003; Suddaby *et al*., 2013). However, irreversible sorption is not incorporated in the current regulatory mass-transfer models due to the fact that slowly reversible and irreversible sorption processes occur simultaneously and are difficult to distinguish by laboratory experimentation (van Beinum *et al*., 2010).

2.9. Conclusion

The review in this chapter summarises the current knowledge available on the processes and mechanisms that influence retention and mobility of pesticides in a given system. Sorption is recognised as the key retention mechanism that determines the availability of pesticides in soil solution, and hence strongly affects their transport processes within soil. Various binding mechanisms are known to be involved in the sorption of pesticides in soils. These include van der Waals forces, hydrogen bonding, hydrophobic bonding, ion exchange, charge transfer, ligand exchange and covalent bonding. Due to the structural complexity and intimate association of organic matter with soil minerals, it is rather difficult to isolate a specific binding mechanism responsible for pesticide retention in a given soil system. Furthermore, there is no direct experimental evidence of a particular mechanism and scientists usually only propose a hypothesis and make assumptions regarding the intermolecular interactions involved. This is also why the more generalised term sorption is used rather than either adsorption or absorption. Various factors have been reported to influence the partitioning of pesticide between liquid and solid phase within soil. Soil properties that play a significant role in the sorption behaviour of neutral pesticides include organic matter content, clay content and microbial population. In addition, pesticide properties (e.g. electronic structure and hydrophilic or lipophilic character of pesticides defined by their water solubility and octanol-water partition coefficient respectively) also strongly influence their retention and mobility within a given soil system.

It was previously thought that partitioning of pesticide between the liquid and solid phases within soil is a simple instantaneous equilibrium process. However, it is now widely accepted that sorption of pesticides in soil is a time-dependent process that may progress over a relatively long period of time before reaching equilibrium. The strength of sorption generally increases with increasing residence time in soil which results in a decrease in the availability of pesticide for transport and uptake by soil organisms. This phenomenon is also referred to as non-equilibrium sorption or ageing and is largely dependent on the molecular diffusion through the fixed interstitial pores of particle aggregates (pore diffusion) and through the three-dimensional pseudo-phase of soil organic matter (intra-organic matter diffusion). Sorption of pesticides to soils is usually measured using a standard batch-equilibrium method following OECD guideline 106 and is reported in terms of partition coefficient (K_d or K_f, ratio of pesticide concentration in the solid phase to that in the solution phase at equilibrium) and the sorption coefficient normalised to soil organic carbon content (K_{oc}). Time-dependent sorption behaviour of pesticides is best characterised by a centrifugation technique described by Walker (2000). This method allows the measurement of pesticide sorption over a relatively longer period of time and under more realistic soil moisture conditions compared to those in the batch equilibrium method.

Commercial products of pesticides are developed as formulations which, in addition to the active substance, also contain many other compounds called co-formulants or adjuvants. Co-formulants are added to pesticide formulations in order to solubilise or emulsify the active substances for better spray applications, and hence to maximise their efficacy and bioavailability. These additives improve the performance of an active substance by modifying the physical and chemical characteristics of the spray mixture. Examples of adjuvants are surfactants, spreaders, stickers, crop oils, anti-foaming materials, anti-freezing agents, buffering agents, and compatibility agents. Adjuvants for pesticides therefore comprise a large and heterogeneous group of substances and can constitute up to 90% of pesticide formulations. The co-formulants include solvents and surfactants, but the latter are the major group of adjuvants; particularly the non-ionic surfactants are most used in agrochemical formulations. However, since co-formulants are considered by regulators and industry as ‘inert ingredients’, their use is largely unregulated and information regarding their composition is rarely available.

A great deal of work has been carried out in the past concerning the retention and mobility of pesticides within soil and an extensive literature presents the knowledge of various factors that influence these processes, and hence the fate and behaviour of pesticides within the environment. However, knowledge concerning the interaction of co-formulants present in commercial formulations of pesticides with their environmental fate processes is limited and it is necessary to further investigate how the presence of co-formulants in commercial products of pesticides will affect the sorption/desorption behaviour of pesticides within soil and the impact of this interaction in the subsequent leaching losses. Particularly, in the presence of surfactants, the basic physical and chemical processes of pesticides are most likely to be modified in a commercial formulation.

Any research that has been carried out so far can only be applied to specific compounds under specific conditions. Furthermore, different studies have shown contrasting results, particularly in relation to the interaction of co-formulants with sorption behaviour of pesticides within soil and in some cases, no effects were observed. In addition to the sorption of pesticides to soil organic matter, some authors have also reported retention of pesticide molecules onto the formulation adjuvants, particularly surfactants. This may be an alternative mechanism for increased sorption of pesticides in soil. Nevertheless, this behaviour of pesticides was highly dependent on the concentrations of surfactant adjuvants in commercial formulations which were added to a given soil system.

Most of the studies discussed in section 2.7.2 were carried out using the batch-equilibrium method where the slurry conditions eliminate the porosity of soil and may also result in the separation of the active substance from the formulation in a different way than would occur in the field. Hence the standard batch-equilibrium method may not be suitable to study the effect of formulation on pesticide behaviour in soil. It is therefore, necessary to design experiments under realistic soil moisture conditions using a centrifugation method which allows us to characterise the non-equilibrium sorption behaviour of pesticides. To date there is no evidence in the literature about whether the presence of co-formulants in commercial products of pesticides have any effects on the rate of sorption kinetics (time-dependent sorption). Field-scale experiments are extremely difficult to study such interactions, so it is of profound importance to explore this behaviour with well-designed laboratory experiments under controlled experimental conditions. Long-term experiments are required in order to compare the leaching and sorption behaviour of technical grade and commercial formulations of pesticides. This would help understand the impacts of co-formulants with time-dependent fate processes of pesticides within the environment.

Chapter 3

CHARACTERISTICS OF SOILS AND TEST SUBSTANCES AND ANALYTICAL METHODOLOGY

3.1. Introduction

The laboratory studies presented in this thesis were carried out on four pesticides and two UK soils. The four pesticides were: (i) the benzamide herbicide propyzamide; (ii) the strobilurin fungicide azozystrobin; (iii) the triazole fungicide triadimenol; and (iv) the triazole fungicide cyproconazole. The two UK soils were: (i) a sandy loam from the Blackwood association; and (ii) a sandy silt loam from the Bishampton association. The experimental work focused on leaching and sorption behaviour of the test substances in the two soils. Leaching experiments were carried out on all the test substances using small soil columns where the behaviour was studied using technical grade and commercial formulations of different pesticides, whereas the sorption and desorption studies mainly focused on propyzamide. This chapter provides information on the key physico-chemical properties of test substances, methodology used to characterise various properties of the two soils and analytical methods used to analyse different chemical samples in laboratory studies.

3.2. Properties of soils

Soil samples were collected from two different locations in York, UK, grid reference 4648 4478 and 4597 4473, for the Blackwood and Bishampton association soils, respectively. The Blackwood association consists of deep permeable sandy and coarse loamy soils in glaciofluvial drift where the groundwater is controlled by ditches (SSEW, 1983). The soils in Blackwood association are mainly used to grow cereals, potatoes and sugar beet as well as areas covering some grassland and coniferous woodland. This association occurs widely throughout Northern and Eastern England, the Midlands and north Wales. The Bishampton association is dominated by deep fine loamy soils with slowly permeable subsoils which are occasionally waterlogged due to well drained fine and coarse loamy soils in an undulating landscape (SSEW, 1983). The Bishampton soils are mainly cultivated for cereals, roots, potatoes, oilseed rape, and short-term leys and some areas also cover permanent grassland. This association occurs mainly in Worcestershire and Warwickshire with small patches in Oxfordshire, Buckinghamshire and Bedfordshire. The Blackwood association covers 1219 km^2 area while the Bishampton association covers 125 km^2 area of arable and grassland in England and Wales (Cranfield University, 2016).

Study soils were collected, prepared and stored prior to use following the OECD guideline 106 (OECD, 2000). The soils were taken from the upper 5-15 cm of the surface horizon following the removal of surface vegetation and litter. Soil samples were air dried at room temperature and passed through a 2-mm mesh sieve. Soil moisture contents were determined by oven-drying triplicate samples at 105°C for 24 hours and calculating the average difference in soil mass before and after drying. The soils were then stored at 4°C in dark prior to use for soil characterization and column studies.

3.2.1. Particle size distribution

Particle size distribution of the two soils was determined using a Malvern granulometer (Mastersizer 2000). Briefly, the instrument was thoroughly cleaned following the laboratory standard operating procedures in place. The machine was also optimised for electronic background, laser intensity (ideally between 60 – 70%) and light energy and calibrated for accuracy by testing with 40 – 100 mesh (0.152 – 0.422 mm) sand. Particle size distributions of the two soils were measured by pumping 0.5 g of air-dried (<2mm) soil samples into the machine with the help of deionised water. The instrument was set to report the average of three separate measurements. As the organic matter content in the sandy silt loam soil was >3.5%, this soil was treated with 30% H_2O_2 in order to remove excess organic matter before the measurements were made.

3.2.2. Organic matter content

The organic matter content of the two soils was determined by weight loss on ignition method (Adolfo Campos, 2010). Triplicate samples of 2 g oven-dry (105°C overnight) soil were weighed into porcelain crucibles and placed in a muffle furnace. The muffle furnace was then gradually heated to 550°C for 4 hours. The ignited samples were then allowed to cool in a desiccator at room temperature, and the organic matter content was determined as the mass difference before and after ignition from the following formula:

$$LOI\ (\%) = \frac{weight_{105} - weight_{550}}{weight_{550}}\ X\ 100$$

where $weight_{105}$ is the weight of the soil sample after oven drying at 105°C and $weight_{550}$ is the weight of the soil sample after ignition at 550°C.

3.2.3. pH

pH values for the two soils were determined in 1:5 soil:liquid suspension in deionised water as well as in 0.01M $CaCl_2$ using a Thermo Orion 420A pH meter. The pH meter was calibrated before the measurements were made using buffer solutions of pH 4.01, 7.00 and 10.01. Triplicate air-dried and sieved (2-mm mesh) samples of 5 g soil were mixed thoroughly in 25 mL of either deionised water or 0.01M $CaCl_2$ solution in a glass beaker and allowed to stand for 1 hour before the measurements were recorded.

3.2.4. Water content at field capacity

Water content at field capacity was measured by filling triplicate soil samples into porous plastic containers (4 cm in height, 6 cm in diameter) with filter papers at the bottom and connected to funnels. Samples were saturated and then equilibrated at a tension of 50 cm below the soil level generated by a hanging water column. Water contents were determined by weight difference before and after oven-drying at 105^{o}C overnight.

The main physico-chemical properties of the two soils are presented in Table 3.1. The sandy silt loam soil is finer textured with larger silt content and has a greater organic matter content compared to the sandy loam soil.

Table 3.1: *Main properties of the two soils studied. The value in parentheses is the standard deviation.*

Soil texture	pH (Water)	pH (0.01M $CaCl_2$)	Sand (%)	Silt (%)	Clay (%)	Water content at field capacity (gg^{-1})	Water holding capacity (gg^{-1})	Organic matter (%)
Sandy loam	5.14 (0.03)	4.87 (0.03)	62.3 (0.39)	36.5 (0.40)	1.2 (0.01)	0.22 (0.01)	0.37 (0.02)	2.7 (0.58)
Sandy silt loam	6.71 (0.03)	6.35 (0.02)	39.4 (0.15)	56.8 (0.15)	3.8 (0.1)	0.29 (0.01)	0.42 (0.03)	4.30 (0.58)

3.3. Properties of pesticides

Pesticides used in this study were chosen to provide a range of water solubility and other chemical and environmental fate characteristics. The key physico-chemical properties of the pesticides studied are summarised in Table 3.2. The aim was to select a range of very low to moderately soluble compounds which are stable to degradation and aqueous hydrolysis and have similar sorption behaviour in soil. It was very difficult to obtain commercial formulations of pesticides with these specified properties. The four compounds studied in this thesis were therefore, selected based on their chemical properties, environmental fate and behaviour as well as the availability of their commercial formulations. These pesticides are frequently used in UK to control various pests and fungal diseases either as a single formulation or in mixtures. In particular, these pesticides have been frequently measured in surface and groundwater bodies in UK. Propyzamide is used in a wide range of crops to control annual and perennial weeds and is mostly used to control blackgrass in oilseed rape in the UK. In contrast to its physico-chemical properties, this compound has been frequently reported in surface and groundwater bodies (Evans, 2009; Tediosi et al., 2012). Propyzamide was studied in greater detail in this thesis due to its environmental fate and behaviour and subsequent implications, particularly for areas where the surface and groundwater is intercepted for drinking purposes. Similarly, azoxystrobin is also frequently used in UK to control various fungal diseases in fruits, vegetables and cereals crops and has the potential to leach to groundwater under certain conditions. Triadimenol and cyproconazole are widely used on various crops to control fungal diseases in the UK, mostly as mixtures with other low solubility compounds. These compounds are highly persistent in the environment and are moderately soluble in water; hence have the potential to contaminate soil and water resources.

Analytical grade propyzamide (purity 99.6%), azoxystrobin (purity 99.9%) and triadimenol (purity 98.7%) were purchased from Sigma-Aldrich Ltd (Dorset, UK), while the cyproconazole (racemic mixture of diastereomers A and B) was acquired from Alfa Aesar (UK). Commercial formulations Kerb Flo (suspension concentrate, 400g/L (35.3% w/w) propyzamide), Priori Xtra (suspension concentrate mixture of 200 g/L azoxystrobin and 80 g/L cyproconazole), Headway (emulsifiable concentrate mixture of 62.5 g/L azoxystrobin and 104 g/L propiconazole) and Veto F (emulsifiable concentrate mixture of 75 g/L triadimenol and 225 g/L tebuconazole) were supplied by the Food and Environment Research Agency York, UK.

Table 3.2: *Key physicochemical properties of the studied pesticides (Source: pesticide properties database, University of Hertfordshire, UK. Available at: http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm)*

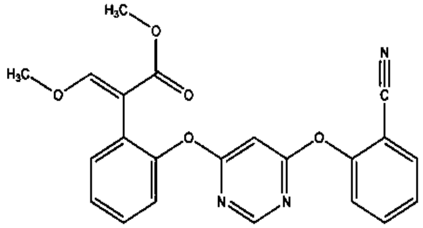
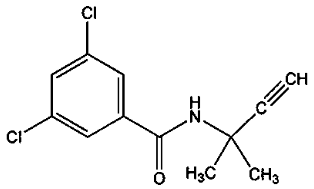
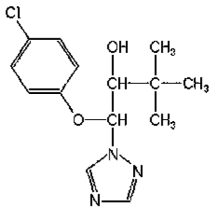
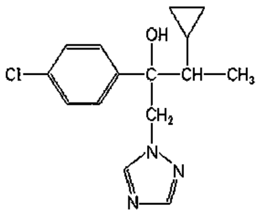
Properties	Azoxystrobin	Propyzamide	Triadimenol	Cyproconazole
Pesticide type and substance group	Fungicide, strobilurin	Herbicide, benzamide	Fungicide, triazole	Fungicide, triazole
Activity profile and mode of action	Broad spectrum, systemic translaminar and protectant action having additional curative and eradicant properties. Respiration inhibitor (QoL fungicide)	Selective, systemic absorbed by roots and translocated throughout the plant and interferes with cell division during mitosis. Microtubule assembly inhibition	Selective with curative, protective and eradicant action. Disrupts membrane function. Sterol biosynthesis inhibitor.	Broad spectrum, systemic with protective, curative and eradicant action. Disrupts membrane function. An ergosterol-biosysthesis inhibitor.
CAS number and name	[131860-33-8] methyl (αE)-2-[[6-(2-cyanopheoxy)-4-pyrimidinyl]oxy]-α-(methoxymethylene) benzeneacetate	[23950-58-5] 3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide	[55219-65-3] β-(4-chlorophenoxy)-a-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol	[94361-06-5] α-(4-chlorophenyl)-α-(1-cyclopropylethyl)-1*H*-1,2,4-triazole-1-ethanol
Chemical formula	$C_{22}H_{17}N_3O_5$	$C_{12}H_{11}Cl_2NO$	$C_{14}H_{18}ClN_3O_2$	$C_{15}H_{18}ClN_3O$
Chemical structure				

Table 3.2 *(continued)*

Properties	Azoxystrobin	Propyzamide	Triadimenol	Cyproconazole
Molecular mass (g mol^{-1})	403.4	256.1	295.8	291.8
Water solubility (mg L^{-1}) at 20°C	6.7	9.0	72.0	93.0
Log Octanol-water partition coefficient (Log P at pH 7, 20°C)	2.5	3.3	3.2	3.1
Soil organic carbon sorption coefficient (K_{oc}, ml g^{-1})	589	840	750	364 (K_{foc}*)
DT_{50}* lab at 20°C (days)	85 [persistent]	47 [moderately persistent]	137 [persistent]	142 [persistent]
Aqueous hydrolysis	Stable	Stable	Stable	Stable
Photostability in water (DT_{50} in days)	9 [moderately fast]	41 [stable]	9 [moderately fast]	40[stable]
Formulation type	Emulsifiable concentrate & suspension concentrate	Suspension concentrate	Emulsifiable concentrate	Suspension concentrate

DT_{50}* (Time for pesticide concentration to decrease 50%) classification from European Union (EU) dossier laboratory studies
K_{foc}* (Freundlich organic carbon sorption coefficient)

3.4. Analytical methods

Propyzamide and azoxystrobin samples from the leaching and sorption experiments were analysed by gas chromatography-mass spectrometry (GC-MS), while triadimenol and cyproconazole samples were analysed by high performance liquid chromatography (HPLC).

3.4.1. Processing leachate and pore water samples of propyzamide

The leachate and pore water samples of propyzamide from column leaching and sorption/desorption experiments were evaporated under nitrogen before analysis. For this purpose, a 1-mL aliquot of each leachate sample was transferred into a test tube and evaporated to dryness under a gentle stream of nitrogen on a sample concentrator at room temperature in the fume hood. The residue was then re-dissolved in 1 mL of hexane and transferred to GC-MS vials for analysis. For the pore water samples, a 0.5-mL aliquot was evaporated to dryness under nitrogen and the propyzamide residue was re-dissolved in 1.5 mL of hexane for analysis by GC-MS.

3.4.2. Processing leachate samples of azoxystrobin

Azoxystrobin leachate samples were concentrated using solid-phase extraction (SPE). The SPE method was adapted from Montagner *et al*. (2014). Oasis HLB cartridges (6 cm^3) packed with 200 mg of 30 µm sorbent material were conditioned with 5 mL of methanol followed by 5 mL of acetonitrile and 5 mL of HPLC grade water using a 12-port SPE vacuum manifold (Supelco, UK). Leachate samples were passed through the cartridges at the rate of about 1 mL per minute. After sample loading, the cartridges were dried under vacuum for 20 minutes and eluted with 4 mL of methanol followed by 4 mL of acetonitrile. After this, the solvents were evaporated to dryness under a gentle stream of nitrogen gas and the compound was re-dissolved into 2 mL of ethyl acetate. 0.5 mL of this solution was further diluted to a final volume of 2 mL in ethyl acetate and analysed by GC-MS.

3.4.3. Gas chromatography-mass spectrometry

Propyzamide and azoxystrobin were analysed by GC-MS. A PerkinElmer (Cambridge, UK) Clarus 680 gas chromatograph equipped with a Clarus 600 mass spectrometer and automatic split-splitless injector was operated in electron impact ionization mode with an ionizing energy of 70eV, scanning from m/z 50-500 at 0.2 s per scan. The ion source temperature was 180°C. The electron multiplier voltage was maintained at 323 V, and a solvent delay of 3 min was employed. An Elite-5MS fused silica capillary column (30 m x 0.25 µm i.d. and 0.25 µm film thickness) supplied by PerkinElmer was used. The oven temperature was maintained at 90°C for 1 min, followed by a ramp to 270°C at a rate of 20°C/min for propyzamide, while for azoxystrobin, the oven temperature was programmed as 45°C for 1 minute, followed by a ramp to 295°C at a rate of 25°C/min and held for 5 minutes. Helium was used as carrier gas with a flow rate of 20 mL/min for both the chemicals. Sample (1µL) was injected in splitless mode and the injector temperature was maintained at 250°C. The instrument was programmed to wash injection needle six times before and after sample injection to avoid cross contamination of the analytical samples. Analysis was performed with selected ion monitoring (SIM) mode using primary mass ions of m/z 173 and 344 for quantification of propyzamide and azoxystrobin respectively. The target and qualifier abundances were determined by injection of propyzamide and azoxystrobin standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from m/z 50-500. Compounds were confirmed by their retention times and the identification of target and qualifier ion. Retention times had to be within 0.2 min of the expected time, and qualifier-to-target ratios had to be within a 10% range for positive confirmation. The concentrations of the compounds were determined by comparing the peak area in the samples to those found for pesticide standards of known concentrations.

3.4.4. Preparation of standards for calibration curve on GC-MS

Individual stock solutions (100 µg mL^{-1}) were prepared in hexane and ethyl acetate for propyzamide and azoxystrobin, respectively. All solutions were protected from light and stored at <5°C in the fridge. Propyzamide analytical standards were prepared in hexane with a range of 0.02 to 0.5 µg mL^{-1}. Azoxystrobin analytical standards were prepared in ethyl acetate with a range of 0.1 to 3.0 µg mL^{-1}. All analytical standards were stored for a maximum of two days before replacement.

3.4.5. Determination of linearity of detector response, LOD and LOQ

Analytical standards were injected into the GC-MS to determine the linearity of detector response and the limits of detection (LOD) and limits of quantification (LOQ) for propyzamide and azoxystrobin. The response of the detector was found to be non-linear for standards of propyzamide above 0.5 µg mL^{-1}. The instrument was therefore calibrated using standards ranging from 0.02 to 0.5 µg mL^{-1} as the response of the detector was linear within this range. The linearity of detector response was tested several times. The LOD and LOQ were determined by the standard deviation of the response and the slope of the calibration curve. For this purpose, the standards of propyzamide ranging from 0.02 to 0.5 µg mL^{-1} were injected into the GC-MS several times to estimate the slope and standard deviation of the calibration curve. The LOD and LOQ were then calculated using the following equations:

$$LOD = \frac{3.3 \text{ x } \sigma}{S} \quad , \quad LOQ = \frac{10 \text{ x } \sigma}{S}$$

where σ is the standard deviation of the response and S is the slope of the calibration curve. The LOD and LOQ of propyzamide were 0.02 and 0.05 µg mL^{-1}, respectively. The coefficient of determination (r^2) derived from linear regressions varied for different sets of standards between 0.97 and 0.99.

The samples were run on GC-MS in smaller batches and each time the equipment was calibrated using a range of standards. Reproducibility of the analysis was also carried out by repeated injections of samples of known concentration. The response decreased initially for the repeated injections by about 20% and started to stabilize after about thirty injections when the standards for the calibration curve were run and the samples were analysed. The reproducibility of the analysis was also confirmed by injecting the highest concentration standard of the calibration after every 6 samples. The LOD and LOQ of azyxystrobin were 0.1 and 0.4 µg mL^{-1}, respectively.

3.4.6. Processing leachate samples of triadimenol and cyproconazole

Leachate samples containing triadimenol and cyproconazole were concentrated using solid phase extraction (SPE). Oasis HLB cartridges (6 cm^3, 200 mg, 30 µm) were pre-conditioned with 2 x 5 mL of acetonitrile followed by 2 x 5 mL of HPLC-grade water. After loading samples, the cartridges were dried under vacuum for 20 minutes and pesticides were eluted with 5 mL of acetonitrile. The solvents were then evaporated to dryness under a gentle stream of nitrogen in the fume hood and the pesticides were re-dissolved into 1 ml of methanol. Subsequent dilutions aimed to deliver all samples for analysis within the range of the calibration standards. For triadimenol, 0.25 mL of the solutions from technical grade treatments was further diluted in methanol to a final volume of 2 mL and analysed on HPLC. A 0.25 mL subsample of the solutions from commercial formulation treatments was diluted in methanol to a final volume of 7 mL and analysed on HPLC. For cyproconazole, a 0.5 mL subsample of the solutions from both treatments was further diluted in methanol to a final volume of 2.5 mL before analysis on HPLC.

3.4.7. High performance liquid chromatography

Triadimenol and cyproconazole samples were analysed on a PerkinElmer Flexar Chromera HPLC system. The analysis used a SUPELCO 516 C-18-DB (15 cm x 4.6 mm, 5µm) column for separations. The mobile phase was a mixture of methanol and water (70:30 v/v) at a flow rate of 1.0 mL min^{-1}. The injection volume was 20 µL and the oven temperature was maintained at 30°C. An isocratic elution was carried out where both the analytes were detected with good peak resolutions at 221 nm wavelength. The retention time for triadimenol was 5.4 minutes. However, the two diastereomers (A & B) of cyproconazole eluted separately and the retention times for the diastereomers A and B were 4.7 and 5.3 minutes, respectively. The instrument was calibrated using pesticide standards with a concentration range of 0.5 to 5 µg mL^{-1} prepared from the individual stock solutions (100 µg mL^{-1}) in methanol. The correlation coefficient ranged between 0.996 and 0.998. The LOD and LOQ of triadimenol were determined to be 0.3 and 0.7 µg ml^{-1}, respectively. The LOD and LOQ of cyproconazole were 0.4 and 0.9 µg ml^{-1}, respectively.

Chapter 4

INFLUENCE OF COMMERCIAL FORMULATIONS OF PESTICIDES ON LEACHING OF THEIR ACTIVE SUBSTANCES THROUGH SOILS

4.1. INTRODUCTION

The importance of various factors that influence the retention and mobility of pesticides through soils has been discussed in Chapter 2. Sorption is recognised as a key retention mechanism that controls the mobility of pesticides within the soil environment particularly leaching losses of pesticides to groundwater (Flury, 1996; Pignatello, 2000; Boivin *et al*., 2005). Furthermore, sorption of pesticides to soil constituents is a time-dependent process that increases with their increasing residence time in soil (Cox and Walker, 1999; Koskinen *et al*., 2001; Beulke *et al*., 2004; Mamy and Barriuso, 2007). Any process that affects the sorption behaviour of pesticides in soil will directly or indirectly affect their leaching potential and subsequent contamination of groundwater resources. The influence of various physico-chemical properties of soil as well as properties of pesticides on their fate and behaviour within soil is well established (Koskinen and Harper, 1990; Cox and Walker, 1999). Nevertheless, pesticides are applied as commercial formulations in agricultural and non-agricultural practices where, in addition to the active substances, different adjuvant and additives are also introduced into the environment. Developing new and effective pesticide formulations has been, and will continue to be, an essential strategy for safeguarding valuable agricultural commodities from harmful insect pests and fungal diseases (Knowles, 2005). However, the effects of co-formulant chemicals in commercial pesticide formulations on the behaviour of their active substances are largely unknown. Only a few studies have shown the interaction of co-formulants on the sorption behaviour of certain pesticides under specific conditions. The information available in the literature so far is not only limited but also conflicting and cannot be generalised. Most importantly, there is no experimental evidence that demonstrates the impact of co-formulants on the leaching behaviour of pesticides as a result of their interaction with sorption processes within soil. The experimental work presented in this chapter is explicitly focused on the impacts of co-formulants on the leaching behaviour of pesticides through soils.

An initial leaching experiment was carried out using the technical grade and commercial formulation (Kerb Flo) of the herbicide propyzamide in sandy loam and sandy silt loam soils at different times from application under controlled experimental conditions. The aim of this experiment was to better understand how the presence of co-formulants in commercial products influences the leaching behaviour of that pesticide through soil. Propyzamide has a low leaching potential through soil and is not expected to contaminate groundwater (English Nature, 2003; Dow, 2012). Irrespective of its physicochemical properties, propyzamide has been detected in surface and ground water monitoring studies (USEPA, 2008), which suggests a need to further investigate the factors which influence transport of propyzamide in the field. UK studies have reported the presence of propyzamide at high concentrations in surface waters especially during the winter season (Evans, 2009). A recent study by Tediosi *et al*. (2012) reported that the estimated losses of propyzamide and carbetamide were 1.1% and 8.6% respectively of the total amount applied in the month after application. These losses to surface water occur dominantly via subsurface drain flow. However, concentrations of carbetamide (500 – 694 µg L^{-1}) in drain flow were higher than propyzamide (24 – 55.7 µg L^{-1}), and they attributed these differences to physico-chemical properties of the two pesticides and environmental conditions at the time of application.

Solubility of pesticides in water is one of the most important physico-chemical properties that influences their fate and behaviour in the environment (Ying *et al*., 2005; Iwafune *et al*., 2010; Rojas *et al*., 2013). Low solubility hydrophobic compounds tend to be less mobile within the soil due to their strong affinity for soil organic matter compared to hydrophilic chemicals that are generally weakly sorbed to soil particles due to their high solubility in water. Leaching of high solubility chemicals could lead to the contamination of groundwater bodies resulting in serious implications for water supply companies if the water is intercepted for drinking purposes (Tediosi *et al*., 2012). In addition to the solubility of the compound, the type of formulation may also have an influence on the effect of formulation on pesticide behaviour in soil (Navarro *et al*., 2007). It was hypothesised that the effect of formulation on leaching will be more pronounced for less soluble compounds. Such compounds will normally sorb quickly out of solution and it was assumed that the formulation may change that behaviour. To test this hypothesis, further leaching experiments were carried out using the technical grade and commercial formulations of pesticides (azoxystrobin, triadimenol and cyproconazole) differing in their water solubility. The data for propyzamide from the preliminary experiment were used for comparison purposes. The aim of this experiment was to investigate the influence of water solubility of pesticides and the formulation type on the effect of formulation on their behaviour and leaching through sandy loam soil. The effects of formulation type were studied using the suspension concentrate (Priori Xtra) and emulsifiable concentrate (Headway) formulations of azoxystrobin; results were compared with the leaching of technical grade material. Complete breakthrough curves of triadimenol were developed to study whether the absolute leaching losses of the compound from columns treated with technical grade material are the same or less than the losses from columns treated with commercial product. Apart from the initial experiment on propyzamide, all other leaching experiments were carried out on sandy loam soil due to consistent behaviour of pesticide in this soil and to make the experimental design practical in terms of number of replicates.

4.2. MATERIALS AND METHODS

4.2.1. Soils

Sandy loam and sandy silt loam soils were used to study the effects of formulation on the leaching behaviour of different pesticides in this Chapter. Various physical and chemical properties and the methods used to characterise these properties are discussed in detail in Chapter 3 (section 3.2).

4.2.2. Reagents

One herbicide (propyzamide), and three fungicides (azoxystrobin, triadimenol and cyproconazle) were selected for this study. Information concerning the physico-chemical properties and formulations of these pesticides are given in detail in Chapter 3 (section 3.3).

4.2.3. Leaching studies in small soil columns

4.2.3.1. Preparation of soil columns

Leaching experiments were performed in polyvinyl chloride (PVC) columns of 2 cm (i.d.) x 10 cm length. Moisture contents (g g^{-1}) were determined for both soils after oven-drying subsamples (triplicates of 5 g) at 105°C overnight. These moisture contents were then used to calculate the mass of air-dried soil to be filled into columns. Each column was manually packed with 20 g of soil on an oven-dry weight basis with glass wool at the bottom to prevent soil losses during the experiment. Four replicate columns were prepared per treatment for each leaching event. Each column was carefully packed with exactly the same amount of soil. During packing, the soil was added to the columns in steps followed by gentle tapping of the column on a hard surface; this was to ensure that uniform packing was achieved and to maintain the same height of soil within each column. Before the application of pesticides, columns were saturated with 0.01M $CaCl_2$ solution to their maximum water holding capacity and the excess water was allowed to drain freely for 24 h under gravity in order to attain soil moisture conditions close to field capacity. The pre-wetting was done from the bottom of the columns to prevent the formation of air bubbles and to reduce the risk of channelling (Kjølholt, 1998). After 24 hours of draining, any excess water was evacuated from the glass wool at the base of the column by applying a small suction using a plastic syringe connected to the column with a plastic tube.

4.2.3.2. Experimental design and pesticide treatments

Column leaching studies were conducted in two stages. Initially, a leaching experiment was carried out on propyzamide in sandy loam and sandy silt loam soils. Further leaching experiments were carried out using the full set of study compounds in sandy loam soil only. For the preliminary experiment, a total of 80 columns were divided into two sets with 40 columns packed with each of the two soils. Pesticide was applied to the top part of the columns at a rate of 100 µg per column. There were two treatments: half of the columns in each set were treated with 0.1 mL of technical grade propyzamide solution in acetone containing 1000 µg mL^{-1} of pesticide. The solvent was allowed to evaporate before the application of 0.5 mL of deionised water to each column. The other half of the columns in each set were treated with 0.5 mL of Kerb Flo solution in deionised water containing 200 µg mL^{-1} of pesticide. The application rate for the commercial product of propyzamide (Kerb Flo) on oilseed rape is 2.1 L ha^{-1}(Dow, 2012), which equates to a maximum field application rate of 840 g ha^{-1} for the active substance. The field application rate relative to the experimental concentration was determined using the area of the column as:

$$A = \pi r^2$$

where A is the area (mm^2) and r is the radius (mm) of the column. The area of the column was found to be 314 mm^2. The area of the column was then used to calculate the field application rate for the columns. The field application rate of the column was determined to be 26.4 µg per column. The application rate in this study was about 3.8 times greater than the maximum field application rate. The higher application rate of propyzamide in the current study was used due to analytical reasons. As the experiments were designed to study the time dependent behaviour of pesticide over multiple times from application, the field application rate of 26.4 µg was too low to achieve the detectable concentrations of compound in leachate and pore water samples. The top 1 cm of each column was filled with acid-washed sand to allow the even distribution of water and to avoid the disturbance of the soil surface by irrigation during the experiment. In addition to the treated columns, ten control columns for each soil were also prepared with no pesticide treatment; two to be leached on each time event. Columns were stored in the fridge (<5^{o}C) until leaching to minimise degradation of the chemical.

The second column leaching experiment was carried out using azoxystrobin, triadimenol and cyproconazole to investigate the influence of solubility of pesticides on the effects of formulation on leaching behaviour through sandy loam soil. For this experiment, a total of 56 columns were packed with sandy loam soil and each pesticide was allocated 16 columns. A further eight columns were allocated to azoxystrobin as two different formulations (suspension concentrate, Priori Xtra and emulsifiable concentrate, Headway) were used for this chemical to study the effect of formulation type on leaching behaviour of pesticide. The columns were treated with technical grade or commercial formulations of pesticides at a rate of 100 µg per column by preparing the application solutions using the method described earlier in this section. 12 control columns (without any treatment) were also prepared with two to be leached on each leaching event.

The volume occupied by the soil within the column was calculated as

$$V = \pi r^2 h$$

where V is the volume (cm^3) of the soil column, h is the height (cm) of soil sample within the column and r is the radius (cm) of the column. The volumes occupied by sandy loam and sandy silt loam soils within the columns were found to be 16.96 and 17.90 cm^3, respectively. The porosity, Φ, of soil ($cm^3 cm^{-3}$) was determined as

$$\Phi = 1 - [\frac{\rho_b}{\rho_p}]$$

where ρ_b ($g\ cm^{-3}$) is the bulk density and ρ_p ($g\ cm^{-3}$) is the particle density of soil within the column. The values of the bulk density for the sandy loam and sandy silt loam soils were 1.18 and 1.12 $g\ cm^{-3}$, respectively. Assuming that the particle density of topsoil is 2.55 $g\ cm^{-3}$ (Avery and Bascomb, 1982), the porosities of sandy loam and sandy silt loam soils were 0.54 and 0.56 $cm^3 cm^{-3}$, respectively. The pore volumes PV (cm^3) of the two soils were then calculated as

$$PV = V\Phi$$

One pore volume (PV) of sandy loam and sandy silt loam soils was found to be 9.20 and 10.02 cm^3, respectively.

For the experiment on propyzamide, separate columns were leached on either day 1, 7, 14, 21 or 28 after pesticide application. On each leaching event one set of four replicates from each treatment together with two controls (blank columns) were irrigated with a total volume of 55.2 mL of 0.01 M $CaCl_2$ solution using a 323S Watson Marlow peristaltic pump at the rate of 23.25 mm/hour. The volumes applied correspond to six and five and half pore volumes for sandy loam and sandy silt loam soils respectively. In the second leaching experiment, the columns were only leached on days one and seven after pesticide application. The total leaching time was four hours and forty minutes. Leachate was collected as a single fraction at the bottom of each column in a labelled vial, weighed and stored in the fridge pending analysis. The leachate samples of different pesticides were processed and analysed using the methods described in Chapter 3 (section 3.4).

4.2.3.3. Triadimenol breakthrough curves

A separate column leaching experiment was carried out on triadimenol to develop complete breakthrough curves for the leaching losses of the compound from the columns treated with technical grade and formulated material. This experiment was designed to assess whether the leaching of the pesticide from the columns treated with technical grade material is the same or less than those treated with commercial product if the columns are leached with enough water over a longer period of time. For this purpose, four replicate columns were prepared for each treatment. The columns were packed with sandy loam soil using the method described in section 4.2.3.1. The columns were treated with either the technical grade or formulated material at the rate of 100 µg per column. Replicates were leached 24 hours after pesticide application with a total volume of 165.6 mL of 0.01 M $CaCl_2$ solution equivalent to 18 pore volumes for sandy loam soil, using a 323S Watson Marlow peristaltic pump at the rate of 12.56 mL/hour. The leachate was collected in fractions of 10 ml. A 1-mL aliquot of each leachate sample from the first 10 fractions was transferred into a test tube and evaporated to dryness under a gentle stream of N_2 at room temperature using a sample concentrator. The chemical was re-dissolved into 1 mL of methanol and analysed on HPLC using method described in Chapter 3 (section 3.4.7). For the remaining leachate fractions, a 2-mL aliquot was evaporated and the residue was re-dissolved in 0.5 mL of methanol before analysis.

4.2.3.4. Statistical analysis

Statistical analysis was performed using SPSS. Two- and multi-way ANOVA was carried out to test the significance of formulation, residence time and soil type on the leaching behaviour of pesticides. This was achieved by setting the mass of pesticide as dependent variable and formulation, residence time and soil type as fixed factors. Tukey post-hoc test was performed to test the variation within the individual treatments over time. Two-sided t-tests were carried out to test the differences in masses of pesticides leached from columns treated with technical grade material and commercial formulations of pesticides. The Shapiro-Wilk test was used to test the normality of the datasets.

4.3. Results

4.3.1. Column leaching experiment on propyzamide

4.3.1.1. Volumes of water generated by leaching soil columns

Volumes of leachate (cm^3) generated during the column leaching experiment are given in Table 4.1. Values are the average of four replicates together with standard deviation for the two soils treated with technical grade and commercial formulation of propyzamide. Two-sided t-tests revealed that there were no significant differences in leachate volumes generated at each sampling interval for all treatments with p-values of 0.128 and 0.153 in sandy loam and sandy silt loam soils, respectively. Leachate volumes for the individual replicates are given in the Appendix A, Tables A1 and A2.

Table 4.1: *Volumes (cm^3) of water collected during leaching from sandy loam and sandy silt loam soils treated with technical grade and formulated propyzamide on different irrigation events. Values are average of four replicates and the value in parentheses is the standard deviation*

Soil type	Formulation	Day 1	Day 7	Day 14	Day 21	Day 28
Sandy loam	Technical grade	54.22 (0.53)	54.65 (0.75)	54.59 (0.26)	53.79 (0.40)	53.34 (0.64)
Sandy loam	Commercial product (Kerb Flo)	53.90 (0.25)	54.12 (0.27)	53.12 (0.52)	53.45 (0.83)	52.70 (0.46)
Sandy silt loam	Technical grade	53.33 (0.44)	53.90 (0.72)	53.45 (0.35)	52.30 (0.31)	53.06 (0.28)
Sandy silt loam	Commercial product (Kerb Flo)	53.68 (0.22)	54.75 (0.69)	53.60 (0.56)	53.43 (0.28)	53.44 (0.22)

4.3.1.2. Leaching behaviour of propyzamide over time in soils

Figure 4.1 presents the results obtained from leaching columns treated with technical grade and commercial formulation of propyzamide over time for the two study soils. Overall, the masses of propyzamide found in leachate from columns treated with technical grade material were smaller than those observed in leachate from columns treated with commercial formulation in both sandy loam and sandy silt loam soils, respectively. These differences were statistically significant (two-sided t-tests, $p<0.001$) for all sampling dates in the two soils. The individual and average masses (µg) of both the treatments of propyzamide found in the leachate from the two soils are given in Appendix A, Tables A3 to A5. The data sets of propyzamide in the sandy loam and sandy silt loam soils were normally distributed with p-values of 0.072 and 0.976, respectively. A multi-way ANOVA was performed to test the effects of formulation, residence time and soil type on the leaching behaviour of propyzamide on different irrigation events (Appendix A, Table A6). Overall, there was a significant effect of formulation on the leaching behaviour of propyzamide in soil ($p<0.001$). The effects of time and soil type were also observed to be statistically significant on the leaching behaviour of pesticide ($p<0.001$). The interactions between time and formulation, time and soil type and formulation and soil type were also found to be statistically significant ($p<0.05$).

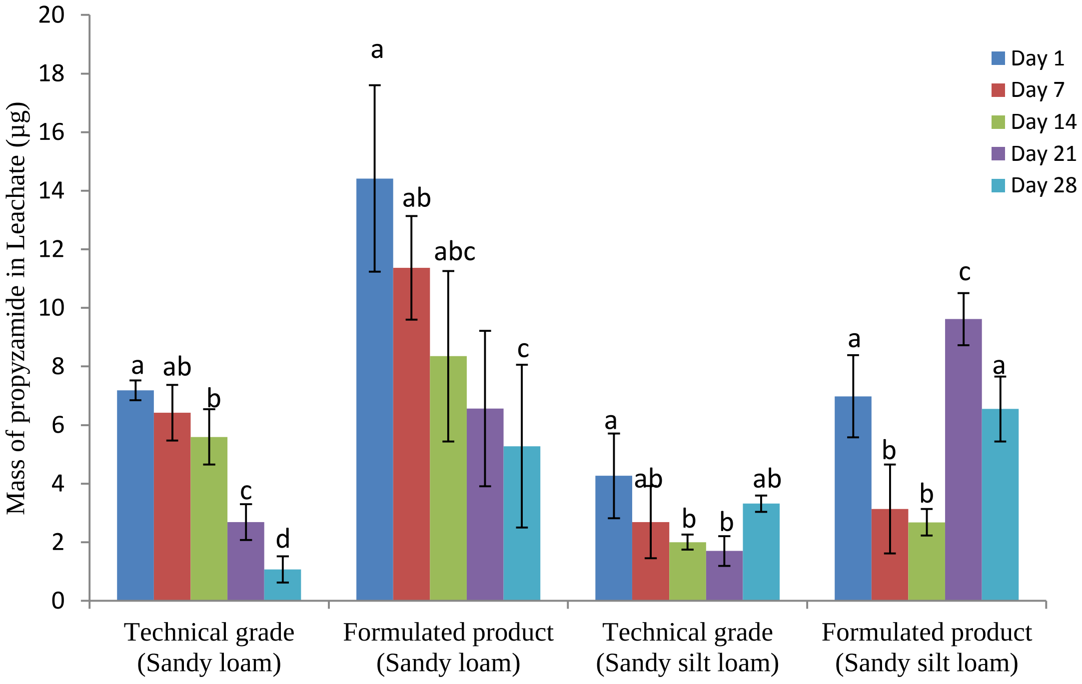


Figure 4.1. *Mass of propyzamide leached through sandy loam and sandy silt loam soils treated with technical grade and commercial formulation of propyzamide (Kerb Flo). The error bars are ± 1 standard deviation (four replicates). Letters on the bars show significant differences within the treatments (Tukey post-hoc test).*

Between 1.1% and 7.2% of the applied propyzamide was leached from sandy loam soil treated with technical grade material during irrigation events up to 28 days after treatment, while the corresponding losses for the commercial formulation of propyzamide were between 5.3% and 14.4% of the applied amount. Similarly, between 1.7% and 4.3% of the applied propyzamide was leached from sandy silt loam soils treated with technical grade propyzamide compared to sandy silt loam soils treated with commercial product where the pesticide leached between 2.7% and 9.6% over intervals up to 28 days after application. There was a trend of decreasing loss for the later sampling intervals and this was very consistent for both the treatments in sandy loam soil. Leaching losses also decreased up to 14 days after treatment in the sandy silt loam soil, but there was a marked increase in leaching at the final (technical grade) or final two (formulation) sampling intervals. The availability of propyzamide for leaching was different for the two soil types. The masses of propyzamide observed in leachate from sandy loam soil for both treatments were larger than those found in leachate from sandy silt loam soil (Fig. 4.1).

The relative change in mass was calculated as a ratio between the average masses of propyzamide leached on different time intervals after treatment as well as between the different treatments on the same time interval in the two soils. Overall, the relative change in mass of propyzamide leached between day 1 and 28 decreased by a factor of 6.7 and 2.7 from sandy loam soil treated with technical grade and commercial formulation of propyzamide respectively. The relative change in mass leached from the columns treated with technical grade material between day 1 and 7 and between day 7 and 14 was identical where the mass leached decreased by factors of 1.1. The availability of propyzamide declined faster between the sampling intervals of 14 and 21 days and between 21 and 28 days after application of technical grade propyzamide where the relative change in mass decreased by a factor of 2.1 and 2.5 respectively. The relative change in mass leached from sandy loam soil treated with commercial product of propyzamide between day 1 and 7, day 7 and 14, day 14 and 21, and day 21 and 28 decreased by factors of 1.3, 1.4, 1.3, and 1.2 respectively. The losses of propyzamide from sandy loam soil treated with commercial formulation were greater than the technical grade material by factors of 2.0, 1.8, 1.5, 2.4, and 4.9 on 1, 7, 14, 21, and 28 days after treatment, respectively (Fig. 4.1).

The masses of propyzamide found in the leachate from sandy silt loam soil treated with technical grade material decreased by factors of 1.6, 1.3, and 1.2 between the sampling intervals of day 1 and 7, day 7 and 14, and day 14 and 21, respectively. However, the mass in the leachate increased by factor of 1.9 between the sampling intervals of 21 and 28 days after treatment with technical grade material. The relative change in the mass of propyzamide leached from sandy silt loam soil treated with formulated product decreased by factors of 2.1 and 1.2 between the sampling intervals of day 1 and 7 and day 7 and 14, respectively. However, the relative change in mass between sampling intervals of day 14 and 21 increased by a factor of 3.6, while it decreased between the last sampling intervals by a factor of 1.5. The losses of propyzamide from sandy silt loam soil treated with commercial formulation were greater than the technical grade material by factors of 1.6, 1.2, 1.3, 5.6, and 2.0 on sampling intervals of 1, 7, 14, 21, and 28 days after treatment (Fig. 4.1).

4.3.2. Leaching experiment with full set of pesticides

4.3.2.1. Volumes of water

Average volumes of water along with standard deviation for four replicates collected over different irrigation events are given in Table 4.2 for sandy loam soil treated with technical grade and commercial formulations of different pesticides. As the propyzamide data were used from the previous leaching experiment, volumes of leachate for the technical grade and commercial formulation of propyzamide for the two time intervals presented in Table 4.2 are taken from Table 4.1. There were no significant differences in leachate volumes (two-sided t-tests, p=0.691) across all treatments of pesticides and sampling dates. Volumes of water for individual replicates leached from columns treated with technical grade and commercial products of pesticides are presented in Appendix A, Table A7 and A8, respectively.

Table 4.2: Volumes *(cm^3) of water collected during leaching from sandy loam soil treated with technical grade material and commercial products of pesticides on different irrigation events. Values are average of four replicates and the value in parentheses is the standard deviation*

Pesticides	Technical grade Day 1	Commercial product Day 1	Technical grade Day 7	Commercial product Day 7
Azoxystrobin	54.06 (0.05)	54.11 (0.11)	53.88 (0.12)	54.07 (0.12)
Propyzamide	54.22 (0.53)	53.95 (0.25)	54.65 (0.75)	54.12 (0.27)
Triadimenol	53.93 (0.02)	53.93 (0.14)	53.98 (0.05)	53.91 (0.08)
Cyproconazole	54.07 (0.08)	54.12 (0.21)	53.63 (0.27)	53.74 (0.28)

4.3.2.2. Leaching behaviour of pesticides

Figure 4.2 presents the results obtained from leaching columns on day one and seven after treatment with technical grade and commercial formulations of pesticides for sandy loam soil. Overall, the masses of pesticides found in leachate from columns treated with technical grade solutions of pesticides were smaller than those observed in leachate from columns treated with commercial formulations. These differences were statistically significant (two-sided t-tests, p<0.001) for all pesticides and sampling dates. Masses of pesticides detected in water leached from sandy loam soil on day one and seven after treatment for all the replicates are presented in appendix A, Table A9 and A10. Average masses of all the pesticides are given in appendix A, Table A11.

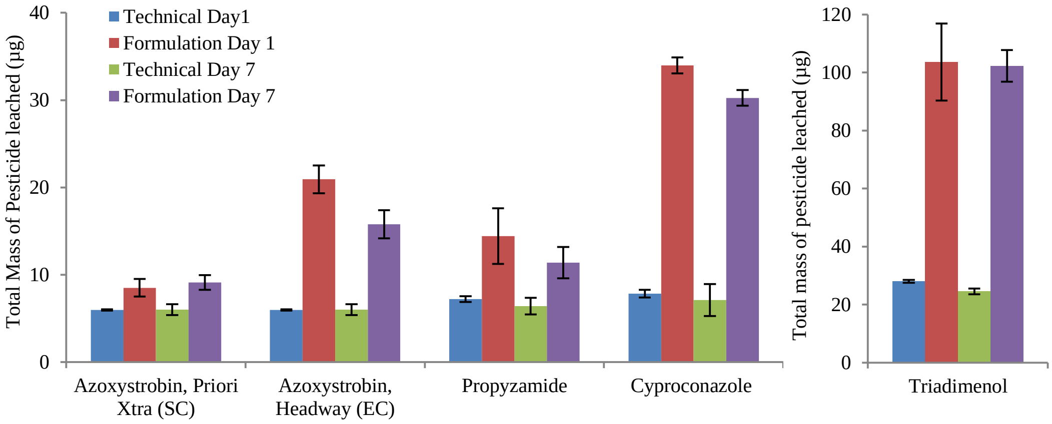


Figure 4.2: *Mass of pesticides leached through sandy loam soil treated with technical grade and commercial formulations of different pesticides. Error bars show ± 1 standard deviation for four replicates.*

Azoxystrobin and cyproconazole datasets were normally distributed with p-values of 0.182 and 0.897, respectively. However, the triadimenol data failed the normality test ($p<0.05$) due to very high variability in the commercial formulation data. Triadimenol data was then tested separately for days one and seven using t-test and it passed the test of normality. The p-values for the day one and seven datasets were found to 0.053 and 0.073, respectively. Hence the data can be assumed to be normally distributed for ANOVA test. Two-way analysis of variance was performed to test the effects of formulation and residence time on the leaching of individual pesticides through sandy loam soil (Table 4). The effect of formulation was found to be statistically significant with p-values of <0.001 for all pesticides. The effect of residence time was found to be statistically significant for azoxystrobin EC formulation and cyproconazole with p-values of <0.001 and 0.002, respectively. However, non-significant effects of residence time were observed for azoxystrobin

SC formulation, propyzamide and triadimenol with p-values of 0.400, 0.221 and 0.515 respectively (Table 4). Interaction between formulation and residence time was found to be statistically significant for azoxystrobin EC formulation and cyproconazole with p-values of <0.001 and 0.021 respectively. The interaction between formulation and residence time was non-significant (p >0.05) for all other chemicals (Table 4).

Table 4.3: *P-values from two-way ANOVA for the effects of formulation, residence time and interaction between formulation and residence time on the leaching behaviour for the studied pesticides*

Pesticides	Formulation	Residence time	Formulation x Residence time
Azoxystrobin SC	<0.001	0.400	0.438
Azoxystrobin EC	<0.001	<0.001	<0.001
Propyzamide	0.001	0.221	0.526
Triadimenol	<0.001	0.515	0.771
Cyproconazole	<0.001	0.002	0.021
- Diastereomer A	<0.001	0.001	0.028
- Diastereomer B	<0.001	0.018	0.031

A multi-way ANOVA was carried out to compare the combined effects of formulation, residence time and different pesticides on the masses of pesticides leached in water after the two irrigation events for the full dataset (Appendix A, Table A12). Overall, there was a significant effect of formulation on the leaching behaviour of the four pesticides under study (p<0.001). Also, the leaching behaviour of four pesticides was significantly different from each other (p<0.001). There was no effect of residence time on leaching for the two irrigation events (p=0.096), and no interaction effect of formulation and residence time on leaching (p=0.584). However, the interaction of formulation and pesticides was highly statistically significant with p-value of <0.001 (Appendix A, Table A12).

4.3.2.3. Influence of solubility of pesticides on the effects of formulation on leaching

The influence of solubility of pesticides on the effect of formulation was studied. It was hypothesised that the effect of formulation would be more pronounced for low solubility chemicals. Although the effect of formulation was significant in all cases, it was more pronounced for chemicals with greater water solubility compared to those that are less soluble in water (Fig. 4.3). Two-way ANOVA was carried out to test the influence of solubility of pesticides and residence time on the leaching behaviour of all pesticides (Appendix A, Table A13). The effect of solubility of pesticides on their leaching behaviour was highly significant with p value of <0.001. This effect of solubility is the reverse of the relationship that was initially hypothesised. There was no effect of residence time on the leaching behaviour of all pesticides (p = 0.788) for the two time intervals.

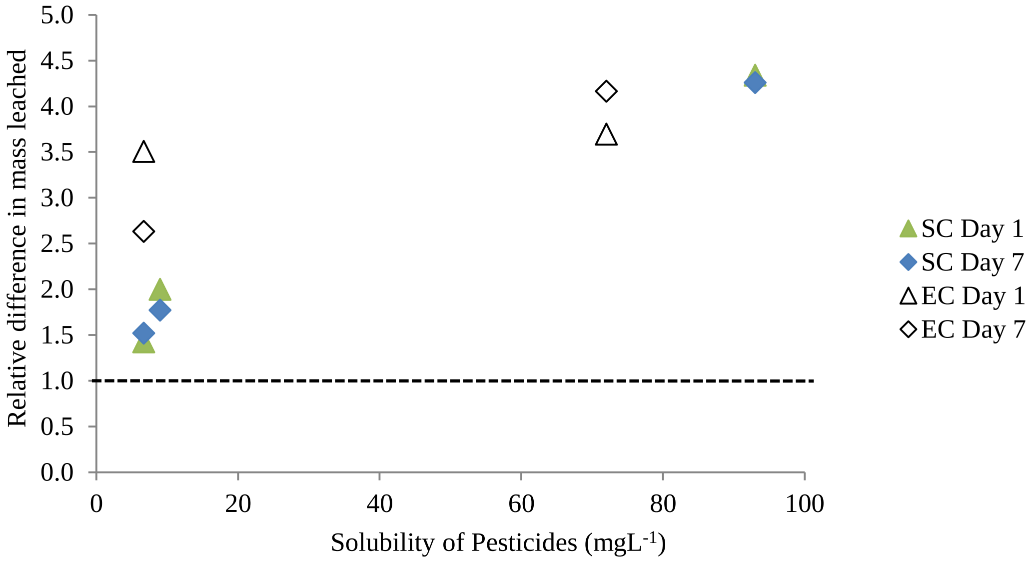


Figure 4.3: *Comparison of the relative difference in mass of pesticide leached between technical grade and commercial products of pesticides with different water solubility. Closed symbols (▲ and ♦) represent the relative difference between SC formulations and technical grade material of pesticides, while the open symbols (Δ and ◊) represent the relative difference between EC formulations and technical grade material of pesticides on day 1 and 7 respectively.*

Greater masses of pesticides were leached for triadimenol and cyproconazole with water solubility of 72 and 93 mg L^{-1} compared to azoxystrobin and propyzamide which have very low solubility in water (solubility of 6.7 and 9 mg L^{-1} respectively). Figure 4.3 presents the relative difference in mass of technical grade and commercial formulations of pesticides with different water solubility leached on day one and seven after treatment. Values above the dotted line indicate that the formulated material leached more than the technical material which also shows that there was an effect of formulation on pesticide behaviour. The relative difference in mass of chemicals leached from columns treated with technical grade pesticides versus commercial formulations of azoxystrobin (SC) and propyzamide (SC) on day one was 1.43 and 2.0 respectively, while on day 7, it was 1.52 and 1.77 respectively. However, the relative difference in mass of chemical leached from columns treated with technical grade and EC formulation of azoxystrobin on day 1 and 7 was 3.51 and 2.63 respectively (Fig. 2). For moderately soluble compounds triadimenol and cyproconazole, the relative difference in mass between commercial product and analytical grade chemical leached on day 1 was 3.70 and 4.34 respectively, while on day 7 the difference was 4.17 and 4.26 respectively for the two compounds (Fig. 4.3).

4.3.2.4. Effect of formulation type on pesticide leaching

The effects of type of formulation on the behaviour of azoxystrobin within the soil environment were also studied (Fig. 4.4). For this purpose, two different formulations of azoxystrobin (Priori Xtra (SC) and Headway (EC), Syngenta) together with its technical material were compared under the same set of experimental conditions. Around 6% of the applied pesticide was leached from columns treated with technical material of azoxystrobin on day one and seven, respectively. The total amount of pesticide that was leached from columns treated with the suspension concentrate formulation of azoxystrobin on day one and seven varied between 8 and 9% of the applied dose. The corresponding losses of the compound from an EC formulation on day one and seven varied between 15 and 21% of the applied dose. These leaching losses of azoxystrobin from EC formulation were significantly higher (p<0.001) than those from SC formulation on both leaching events. The raw data for masses of azoxystrobin in leachate from different treatments is given in Appendix A, Table A14.

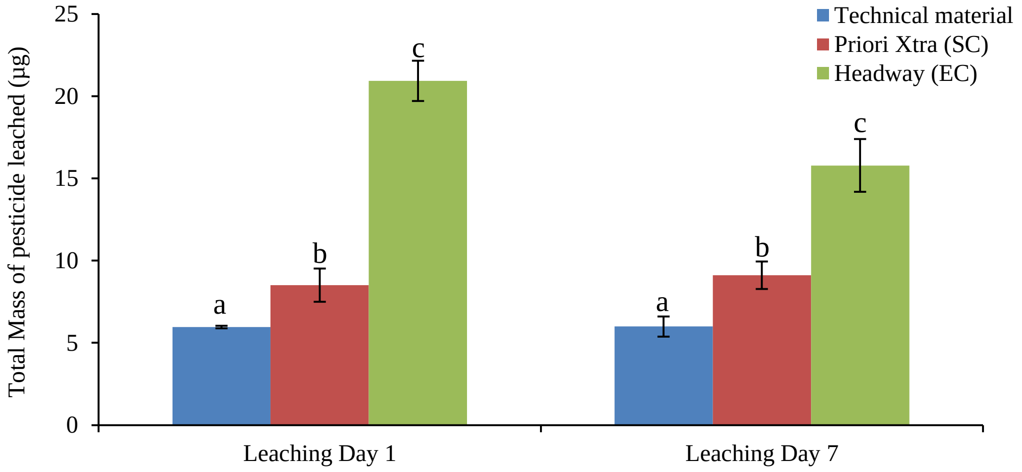


Figure 4.4: *Leaching behaviour of technical material, SC and EC formulations of azoxystrobin in sandy loam soil on day 1 and day 7 after treatment. Error bars represent ± 1 standard deviation for four replicates. Letters on the bars show significant differences between treatments (Tukey post-hoc test).*

Two-way ANOVA was also performed to test the effect of type of formulation on the leaching behaviour of azoxystrobin through soil (Appendix A, Table A15). The effect of formulation type was found to be statistically significant (p <0.001). The combined effect of residence time was also significant (p = 0.002). The interaction between residence time and formulation type was also highly statistically significant (p <0.001). A Tukey post-hoc test revealed that the masses of pesticide leached from technical material, SC and EC formulations of azoxystrobin were significantly different from each other (p <0.001) on both sampling intervals (Fig. 4.4).

4.3.2.5. Leaching behaviour of cyproconazole

In addition to the overall leaching behaviour of cyproconazole (Fig. 4.2), the two diastereomers (A & B) were also studied separately for both treatments to investigate any differences in their leaching behaviour. Figure 4.5 presents the results of the leaching behaviour of the two diastereomers (A & B) of cyproconazole. These results are presented in terms of percentage of the initially applied mass due to the differences in the starting mass of the two diastereomers in technical grade material and commercial formulation. The ratio of diastereomer A to B in analytical grade material was 1:2, while in the commercial product the two diastereomers were present in the ratio of 1:1. The technical grade and commercial product of cyproconazole were applied at the same rate of 100 µg per column which means that the applied doses of technical materials of diastereomers A and B were 33 and 67 µg per column respectively, while for commercial product the two diastereomers were both applied at the rate of 50 µg per column. The average mass of diastereormer A leached from columns treated with technical material varied between 15.6 and 17.6% of the applied dose for the two leaching intervals, while for the commercial product it varied between 41.6 and 46.9% for the two leaching intervals. The average mass of diastereomer B leached from columns treated with technical material was around 3% of the applied dose for both the leaching intervals, while it varied between 18.9 and 21.1% of the applied dose of the commercial product. These differences in the masses of diastereomers A and B from the technical grade material and commercial formulation treatments of cyproconazole were statistically significant (p<0.001) on both leaching events. Two-way analysis of variance revealed that the effect of formulation was highly significant ($p<0.001$) for both the diastereomers (Appendix A, Tables A16 and A17). The effect of residence time was also found to be statistically significant for both diastereomers with p-values of 0.001 and 0.018, respectively. The interaction between formulation and residence time was also found to be statistically significant for both the diastereomers A and B with p-values of 0.028 and 0.031 respectively.

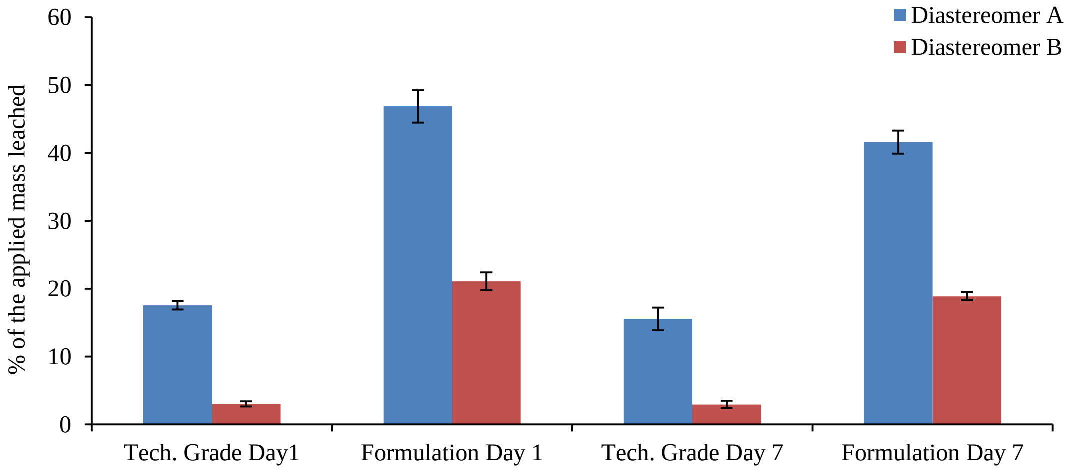
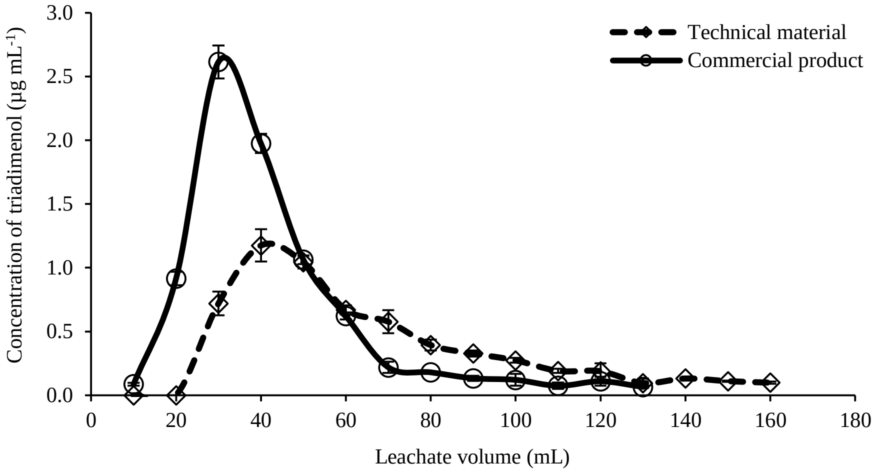


Figure 4.5: *Leaching behaviour of diastereomers A and B of cyproconazole for technical grade material and commercial formulation through sandy loam soil on day 1 and day 7 after treatment. Error bars represent ± 1 standard deviation for four replicates.*

4.3.2.6. Triadimenol breakthrough curves

Relative and cumulative breakthrough curves (BTCs) of triadimenol following applications of technical grade or commercial product to soil columns are shown in Figure 4.6. The results indicate that the technical grade material leached less than the commercial product even when the leaching was carried out with large volumes of water over a long period of time. Cumulative breakthrough curves (Fig. 4.6b) show that at the end of the experiment, the total leaching losses of triadimenol from columns treated with the technical grade material were around 60%, while the corresponding losses were around 80% from the columns treated with the commercial product. In addition to this, relative breakthrough curves show that triadimenol applied as commercial formulation started to leach out of soil columns earlier than the compound applied as technical grade material. Triadimenol leached rapidly after breakthrough from columns treated with commercial formulation where peak concentrations of the compound reached up to 2.6 µg mL^{-1} in the leachate. For the columns treated with technical material, peak concentrations of triadimenol in the leachate were recorded as 1.2 µg mL^{-1}.

(a)



(b)

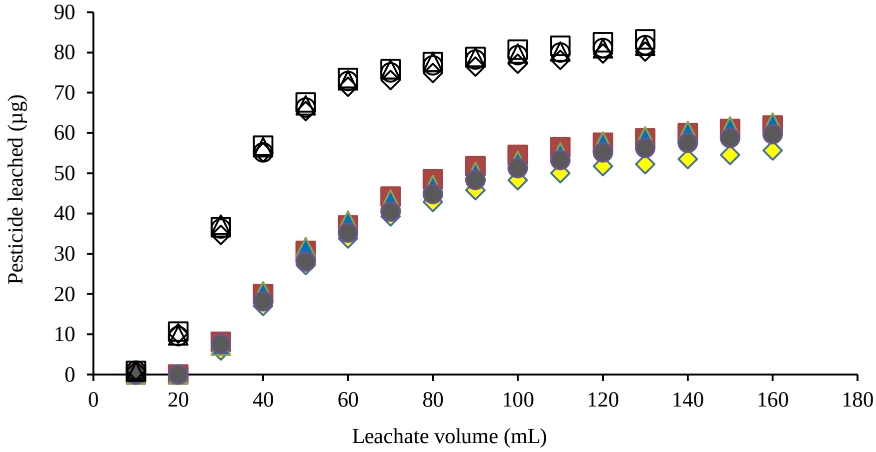


Figure 4.6: *Relative (a) and cumulative (b) breakthrough curves of triadimenol following application of technical grade or commercial formulation to soil columns. The error bars in the relative breakthrough curves represent ±1 standard deviation of the four replicates. Closed and open symbols in the cumulative breakthrough curve represent the data for the four replicates from technical grade and commercial formulation treatments respectively.*

4.4. Discussion

The fate and behaviour of pesticides in the environment is controlled by a combination of physico-chemical properties of chemicals and soil as well as the prevailing environmental conditions. The literature is abundant in knowledge about the controlling and transport mechanisms that affect the fate and behaviour of xenobiotics introduced into the soil environment. Information on the interaction of co-formulants with the fate of organic chemicals is very limited and different studies have shown contrasting results as discussed in Chapter 2 (Section 2.7.2). This study specifically focused on the influence of co-formulants, residence time, solubility of pesticides and type of formulation on the leaching behaviour of pesticides through soils. Observed masses of propyzamide in leachate from solutions of commercial formulation were larger than those measured in leachate from technical grade solutions of propyzamide for the two soils investigated. Although the application rates for both the treatments as well as the experimental conditions were the same, this greater availability of propyzamide for leaching from commercial formulations may be attributed to the presence of co-formulants and additives that would favour maintaining pesticide molecules in the solution **(**Beigel and Barriuso, 2000; Oukali-Haouchine *et al*., 2013).

The chemical nature of co-formulant materials used in pesticide formulations may greatly affect the interaction between the pesticide and the constituents of soil systems (Bailey and White, 1964). In particular, the presence of surfactants in the commercial products may prevent the immediate separation of pesticide active substance from the formulation. The slow separation of the pesticide molecule from the surrounding co-formulants within soil may prevent the sorption process from occurring in the same way as would happen for the technical grade material (Pose-

Juan *et al*., 2011). This may result in greater availability of pesticide from formulated products in soil solution which can potentially be leached to groundwater bodies under the influence of irrigation or rainfall events. Földényi *et al*. (2013) reported that at small concentrations, the extent of adsorption of chlorsulfuron and tribenuron methyl in sand, loam and clay loam soils was higher for solutions of pure ingredients than from formulation solutions. They also reported that the presence of the forming agent Supragil (anionic dispersant) resulted in a decrease in adsorption of chlorosulfuron and hence increased environmental mobility of the pesticide. Pose-Juan *et al*. (2011) reported that the adjuvants present in a commercial formulation of the fungicide 'Switch' increased the concentration of the active substance fludioxonil in water suspensions up to 9 mg L^{-1}; this is five times its solubility limit in water (1.8 mg L^{-1}). They carried out soil batch experiments with the fungicide and showed that with higher additions of Switch (i.e. fludioxonil concentration, $C_{Liquid} > 1$ mgL^{-1}), K_d values were smaller than those found for the adsorption of the technical grade material and suggested an increased solubilisation of fludioxonil by the adjuvants.

Time between application and first rainfall event is also one of the most important factors that influences the fate of pesticide within soil and hence the leaching losses of pesticide and subsequent groundwater contamination. The importance of timing of rainfall events relative to pesticide application in controlling leaching losses of pesticides was also suggested by Walker *et al*. (2005). Propyzamide is poorly soluble in water (9 mg L^{-1} at 20^{o} C) and readily bound to the soil matrix (K_{oc} ranges from 548 to 1340 mL g^{-1}), and hence moderately to slightly mobile in soil depending on organic carbon and clay contents (USEPA, 2008). It has a low leaching potential through soil and is not expected to contaminate groundwater (English Nature, 2003; Dow, 2012). However, despite its physico-chemical properties, this chemical has been identified in surface and groundwater monitoring studies (Evans, 2009; USEPA, 2008). Rapid movement of propyzamide to subsurface drains under the influence of rainfall soon after application was reported in a small clay headwater tributary of the Upper Cherwell catchment in the UK (Tediosi *et al*., 2012). Rainfall soon after application may also result in higher leaching losses of pesticides from soil to groundwater bodies (Balogh and Anderson, 1992; Lewan *et al*., 2009). This may be due to pesticide that is available in the liquid fraction of soil and has not yet moved to sorption sites. As the adsorption of pesticides in soil increases with increasing contact time (Cox and Walker, 1999; Beulke *et al*., 2004; Mamy and Barriuso, 2007), strongly sorbing chemicals like propyzamide will move from liquid phase to solid phase resulting in their limited availability for leaching and degradation. A longer period of time between application and rainfall or irrigation event results in less leaching losses of pesticides (Flury, 1996).

Generally, the mass of propyzamide in leachate from sandy loam soil was greater than that found in leachate from sandy silt loam soil (Fig. 4.1). The leaching of propyzamide through soil was observed to be highly time dependent where the availability of pesticide in the leachate decreased over time and this behaviour was very consistent in the sandy loam soil, but much less consistent in the sandy silt loam soil. Leaching losses of propyzamide during the later sampling intervals of 21 and 28 days after pesticide applications in sandy silt loam soil were larger than those in the earlier leaching event (Fig. 4.1). This may be attributed to the differences in the physico-chemical properties of the two soils. Sandy silt loam soil is finer textured with much larger silt content resulting in different structures and pore sizes compared to sandy loam soil. Furthermore, it also has more organic matter and one possibility is that there might be some more facilitated transport through dissolved organic matter if the soil starts to breakdown under the incubation conditions later in the experiment. Despite the increase in transport at later time intervals, the formulated material leached more than the technical grade material indicating that the patterns of leaching are consistent between the technical grade and formulation treatments. Sharma *et al*. (2013) compared the leaching behaviour of analytical grade hexaconazole and its EC formulation in light and heavy textured soils under saturated conditions in soil columns. They reported that the herbicide was more mobile in sandy loam soil compared to clay soil. However, they observed no differences in leaching behaviour of the herbicide for the two treatments in various soils.

Fate processes like sorption to the soil matrix and leaching to groundwater are also thought to be generally influenced by the solubility of chemicals (Delle Site, 2001; Fernández-Pérez *et al*., 2011; Langeron *et al*., 2014). Hydrophilic chemicals tend to be more mobile within the soil environment and available for leaching to groundwater compared to hydrophobic chemicals with low water solubility. In this chapter, the influence of solubility of pesticides on the effects of formulation on their leaching behaviour was also investigated. Leaching experiments were conducted in small soil columns using analytical grade and commercial formulations of pesticides of very low to moderate solubility. Effects of formulation were observed in all the cases, with leaching losses of pesticides from commercial formulations greater compared to their technical grade materials.

Chemicals with low solubility often exhibit high K_{oc} values and are more likely to sorb strongly to soil organic matter compared to highly soluble compounds (Shabeer and Gupta, 2011; Sakaliene *et al*., 2007; De Wilde *et al*., 2008). It was expected that the effect of formulation would be higher for pesticides with low water solubility compared to pesticides with moderate to high water solubility. However, the effect of formulation was more pronounced for high solubility chemicals (Fig. 4.3), which is the reverse of what was hypothesised for this study. These results suggest that the solubility of a compound has an influence in controlling the effects of formulation on pesticide behaviour and leaching through soil. It can be postulated that this opposite behaviour may be due to the combined effect of formulation, water solubility and other environmental fate properties of pesticides. Firstly, there is an effect of formulation where the co-formulant chemicals present in pesticide formulation may favour maintaining pesticide molecules in solution and inhibit the chemical from interacting with soil particles. The commercial formulation of triadimenol applied to soil columns was a mixture of triadimenol with a low solubility triazole fungicide (tebuconazole; water solubility 36 mg L^{-1}), while the cyproconazole formulation was a mixture of cyproconazole with a low solubility strobilurin fungicide (azoxystrobin; water solubility 6.7 mg L^{-1}). Thus, individual columns treated with 100 µg of triadimenol and cyproconazole with commercial formulation solutions also received nearly 300 µg and 166 µg of tebuconazole and azoxystrobin, respectively. It can be argued that there may be competition for the sorption sites within the soil columns and most of the sorption sites in soil may be occupied by low solubility hydrophobic compounds (azoxystrobin and tebuconazole) which were added to the soil columns at very high proportions when the pesticides were applied to soils. This behaviour may exacerbate greater leaching losses of pesticides from commercial products compared to their technical grade materials.

Furthermore, when higher solubility compounds separate from their formulation, they tend to remain in the liquid phase and may only be weakly sorbed to soil particles. As a result more leaching losses may occur under the influence of irrigation or rainfall. For the chemicals with lower water solubility and larger K_{oc}, the presence of co-formulants may temporarily delay their interaction with the soil constituents. However, as the chemical separates from the formulation, it may strongly associate to the soil matrix with time. Filipe *et al*. (2009) compared adsorption and desorption of pure and formulated thiram onto humic acid and observed lower hysteresis for the formulated material which suggests that the adsorption is more reversible in the presence of co-formulants making the pesticide more susceptible to be leached.

For the less soluble compound azoxystrobin (water solubility of 6.9 mg L^{-1}), the effect of type of formulation on the leaching behaviour was also studied. For this purpose, separate columns were treated with technical material, suspension concentrate (Priori Xtra) and emulsifiable concentrate (Headway) formulations of azoxystrobin. The observed masses of azoxystrobin in the leachate were in the order of technical material < suspension concentrate < emulsifiable concentrate. An emulsifiable concentrate (EC) formulation is usually a solution of pesticide with emulsifying agents in a water insoluble organic solvent (oil) which is designed to form an oil-in-water emulsion upon dilution. (Knowles, 2008; Mulqueen, 2003). The presence of oily water-insoluble organic solvents (lipophilic molecules) in EC formulations may affect the behaviour of pesticide active substance in two ways. First, they may restrict the pesticide molecule from dissolving in water and secondly, the oily organic solvents surrounding the pesticide molecule may prevent or slow down the sorption process for a longer time compared to SC formulations. The suspension concentrate (SC) formulation, also called flowables, usually consists of particles covering a wide size range (0.1 – 10 µm) dispersed in a liquid medium, generally water, at high solid volume fractions (up to 60%) and usually contain suspension agents, wetting agents and thickeners (Luckham, 1989). Perhaps the separation of the active ingredient from EC formulation may be slower than that from SC formulations due to the presence of surfactants emulsifiers and water insoluble organic solvents. Consequently, greater leaching losses of pesticides may occur if rainfall or irrigation follows soon after application of pesticides in EC formulations. Wybieralski (1992) carried out column leaching experiments on propoxur and reported greater leaching losses of the compound from an emulsion form, intermediate losses from suspension form and smallest losses from pure active substances in five different arable soils. He also reported that in addition to the effect of type of formulation, there was an effect of soil properties on the patterns of leaching and on the amount of propoxur residues retained in the soil where the greater losses were observed from loamy sand and sandy loam soils compared to clay loam soils.

At the end of the leaching experiments, complete breakthrough curves were developed for the leaching losses of triadimenol through sandy loam soil in columns treated with technical grade material and EC formulation. The aim of this experiment was to show whether the absolute leaching of a pesticide from technical grade material is the same as or less than that from the commercial product. The results show that there was less leaching of triadimenol from the columns treated with technical grade material (around 60% of the applied amount) than from those treated with the commercial product (around 80% of initially applied). Triadimenol not only started to leach earlier from the formulation treatments but also the peak concentrations in leachate were larger compared to those from technical grade material. Fenoll *et al*. (2011) also developed breakthrough curves to study the leaching behaviour of different pesticides from a clay loam soil in columns treated with their technical grade material. They reported that triadimenol behaved as a "leacher" compound because 60-65% of its initial amount was found in leachate and that was similar to atrazine (68%), which is a compound with known leaching behaviour.

4.5. Conclusion

Laboratory studies were carried out to investigate the effects of formulation on pesticide leaching through soil at different times from application. Leaching experiments used technical grade and commercial formulations of four different pesticides (propyzamide, azoxystrobin, triadimenol and cyproconazole) in sandy loam soil and propyzamide was also studied in sandy silt loam soil. In the first experiment, the effects of formulation, residence time and soil type on the leaching behaviour of propyzamide were all found to be highly statistically significant ($p<0.001$). However, the pattern of behaviour was more consistent in the sandy loam soil compared to the sandy silt loam soil. Further experiments were carried out to determine whether solubility of the active substance influences the effect of formulation on leaching and to investigate the effect of formulation type on leaching. The effect of formulation was highly significant ($p<0.001$) for all the pesticides. The relative difference in mass leached between formulated and technical material for low solubility pesticides was less than that for pesticides with greater water solubility. These results suggest that the solubility of a compound has an influence in controlling the effect of formulation on pesticide behaviour. However, the effect of formulation was more pronounced for high solubility chemicals which is the reverse of what was hypothesised for this study. It may be possible that the presence of co-formulants in commercial products may favour maintaining the pesticide in solution resulting in greater leaching losses compared to the technical grade material. Greater leaching losses of azoxystrobin were observed from the EC formulation compared to the SC formulation. The results indicate that there was a combined effect of solubility and formulation type on the effect of formulation on pesticide behaviour. Furthermore, enhanced leaching losses of high solubility pesticides (triadimenol and cyproconazole) from commercial formulations may also be due to competition for sorption sites with low solubility hydrophobic compounds (azoxystrobin and tebuconazole) which were added to the soil columns at relatively high rates when the pesticides were applied to soils as commercial products. These results suggest that more detailed studies are needed to further investigate effects of formulation on sorption behaviour of pesticides to aid interpretation of the results from column experiments.

In chapter 5, standard batch-equilibrium and centrifugation techniques were used to isolate the effect of formulation on sorption and desorption behaviour of propyzamide in the two soils. Most importantly, the soil moisture content in the centrifugation technique was maintained at field capacity throughout the experiment to maintain conditions similar to those representative of the field.

Chapter 5

EFFECTS OF FORMULATION AND RESIDENCE TIME ON THE SORPTION BEHAVIOUR OF PROPYZAMIDE IN SANDY LOAM SOIL

5.1. INTRODUCTION

Chapter 4 revealed that presence of co-formulants in commercial pesticide products has an impact on the leaching behaviour of their active substances through soils. Water solubility and formulation type of pesticides were also shown to influence the effects of formulation on leaching behaviour of pesticides in laboratory column experiments. It was argued that the co-formulants present in formulated products may favour maintaining the pesticide molecule in the solution phase resulting in greater leaching losses compared to the technical grade material. It was also suggested that this behaviour may interfere with the sorption behaviour of pesticides due to slow separation of the active substance from the formulation. This chapter specifically focuses on the effects of formulation on the sorption behaviour propyzamide in the two soils to investigate further the findings from Chapter 4.

A huge amount of research has been carried out over the past forty to fifty years to study the sorption behaviour of pesticides in the environment (Karickhoff, 1984; Calvet, 1989; Koskinen and Harper, 1990; Beulke *et al*., 2004; Kah and Brown, 2007). Sorption of pesticides to soil constituents often increases with increasing residence time in soil (Cox and Walker, 1998; Koskinen *et al*., 2001; Beulke *et al*., 2004; Boivin *et al*., 2004; Mamy and Barriuso, 2007). Sorption and desorption rates are governed mainly by molecular diffusion through the fixed interstitial pores of particle aggregates and through the three-dimensional pseudo-phase of soil organic matter (discussed in detail in Chapter 2). Such non-equilibrium sorption due to physical non-equilibrium and intra-organic matter diffusion have been suggested to be the two major factors responsible for the time-dependent sorption of non-ionic or hydrophobic compounds (Pignatello and Xing, 1995).

The aim of the present work was to study the influence of formulation and residence time on the sorption and desorption behaviour of propyzamide in a sandy loam and a sandy silt loam soil. Standard batch-equilibrium experiments were carried out to develop sorption isotherms for various initial concentrations of propyzamide in solution, whilst subsequent desorption was investigated for the single highest concentration to study possible effects of formulation. Sorption experiments were also carried out using a centrifugation technique where the sorption behaviour of analytical grade propyzamide was compared with commercial formulation. The availability of pesticide in soil pore water was measured at various time intervals that matched with those in the leaching experiment in Chapter 4, in order to compare and interpret the leaching and sorption behaviour of propyzamide in the two soils. The purpose was to compare patterns in leaching of the formulated and technical material with patterns in sorption of the formulated and technical material over time. It was hypothesised that it may be the desorption process that is controlling the enhanced leaching of formulated material from soil columns (Chapter 4). To confirm this hypothesis, desorption experiments were carried out over three successive steps using a centrifugation technique under realistic soil water conditions that involved the same incubation conditions as in the sorption experiment and then by adjusting the water content up to one pore volume in the two soils and spinning them again to extract the pore water.

5.2. MATERIAL AND METHODS

5.2.1. Soils

Information concerning the collection and characterisation of various physico-chemical properties of the two study soils (sandy loam and sandy silt loam) for the experimental work is given in Chapter 3 (section 3.2).

5.2.2. Chemicals

Details of the sources of technical grade and commercial formulation of propyzamide, as well as its different physico-chemical and environmental fate properties are given in Chapter 3 (section 3.3).

5.2.3. Measurement of sorption and desorption by standard batch equilibrium method

5.2.3.1. Preparation of application solutions

A standard application solution of propyzamide (1000 µg mL^{-1}) was prepared by weighing 5 mg of technical grade propyzamide in a glass weighing tub and dissolving in HPLC grade methanol into a 5 mL volumetric flask. A stock solution of formulated product of propyzamide (Kerb Flo) was prepared by dissolving 28.33 mg of suspension concentrate of propyzamide in 50 mL of 0.001M $CaCl_2$ solution which gave an initial concentration of 200 µg mL^{-1} of the active substance. A working application solution of 20 µg mL^{-1} was prepared by diluting 1 mL of stock solution in 10 mL of 0.001M $CaCl_2$ solution. Low molarity $CaCl_2$ solution was used in sorption experiments compared to leaching experiments (where the molarity of $CaCl_2$ solution was 0.01M) due to the difficulties in re-dissolving the propyzamide residues in hexane after evaporating the extracted pore water.

5.2.3.2. Experimental methodology

Sorption of propyzamide was determined at five different concentrations and with three replicates in sandy loam and sandy silt loam soils using a standard batch equilibrium method following OECD guideline 106 (OECD, 2000). A preliminary study was carried out to determine the appropriate soil to solution ratio, the equilibration time for sorption, and the amount of propyzamide sorbed at equilibrium. A soil to solution ratio of 1:5 and equilibration period of 24 hours were selected for both soil types based on the findings of the preliminary studies (results in Appendix B, Tables B4 and B5 and Fig. B1).

In the main experiment, the sorption of propyzamide was determined at initial concentrations of 0.2, 0.3, 0.4, 0.5 and 1.0 µg mL^{-1} using technical grade and formulated materials of propyzamide in the two soils. For this purpose, 2 g dry weight of soil in triplicate was transferred into 50 mL PTFE centrifuge tubes and was pre-equilibrated with 9.5 mL of 0.001M $CaCl_2$ solution by shaking on an orbital shaker at 250 rpm for a period of 15 hours overnight. After pre-equilibration, the soil suspensions were spiked with 2 to 10 µL of propyzamide solution in methanol containing 1000 µg mL^{-1} of technical material to achieve the required concentrations of propyzamide in soil suspensions. Volumes of formulated product of propyzamide (Kerb Flo) applied ranged from 0.1 to 0.5 mL containing 20 µg mL^{-1} of active substance. The volume of 0.001M $CaCl_2$ solution was adjusted by weighing the contents to achieve the required soil to solution ratio of 1:5 and the centrifuge tubes were returned to shaking for a period of 24 hours. After shaking, the soil suspensions were centrifuged at 4000 g for 15 minutes to separate the two phases. For the replicates with initial concentrations of 0.2 and 0.3 µg mL^{-1} of propyzamide in soil solutions, a 1-ml aliquot of the supernatant was evaporated to dryness under a gentle stream of nitrogen. Pesticide residue was then re-dissolved into 1 mL hexane for analysis by GC-MS using the method described in Chapter 3 (Section 3.4.3) to determine the concentration of propyzamide remaining in the solution at equilibrium (C_e, µg mL^{-1}). For replicates with initial concentrations of 0.4, 0.5 and 1.0 µg mL^{-1} of propyzamide in soil solutions, a 0.5-mL aliquot of the supernatant was evaporated under a gentle stream of nitrogen and residue was re-dissolved into 1 mL hexane before analysis. Assuming that all pesticide removed from the solution is sorbed by the soil, the concentration of pesticide in the solid phase C_s (µg g^{-1}), was calculated as:

$$C_s = \frac{V\,(C_i - C_e)}{m_s}$$

where V (mL) is the volume of solution in the suspension, C_i (µg mL^{-1}) is the initial concentration of propyzamide in solution and m_s is the mass of soil (g). Two control samples with only propyzamide in 0.001M $CaCl_2$ solution without soil were subjected to exactly the same experimental conditions to check the stability of the compound in $CaCl_2$ solution and sorption to the walls of centrifuge tubes. Blank runs for each soil (without propyzamide) were also carried out under the same experimental conditions to check for artefacts in the analytical method.

Sorption coefficients (K_d, mL g^{-1}) were obtained by plotting the equilibrium concentration of the pesticide in the aqueous phase (C_e) versus the concentration of pesticide sorbed on the soil samples (C_s) for each concentration:

$$K_d = \frac{C_s}{C_e}$$

The K_d values were then used to calculate the organic carbon normalised coefficients (K_{oc}, mL g^{-1}) using the organic carbon content of each soil as:

$$K_{oc} = \frac{K_d}{F_{oc}}$$

where F_{oc} (g g^{-1}) is the organic carbon fraction of the soil. Sorption isotherms were also expressed using the non-linear form of the Freundlich equation:

$$C_s = K_f C_e^{n_f}$$

where K_f is the Freundlich sorption coefficient, and n_f is the Freundlich exponent.

Samples spiked with the highest initial concentrations in the sorption experiment (1 mg L^{-1} for technical grade and commercial formulation of propyzamide) were used for the desorption study. There were five replicates for the desorption study. Desorption was carried out after sorption equilibrium and the supernatant was removed as much as possible by weight and replaced by an equivalent volume of 0.001M $CaCl_2$ solution by weight. The soil was re-suspended and the suspensions were shaken for 24 hours. After this, the soil suspensions were centrifuged and an aliquot of the supernatant was analysed to quantify the amount of propyzamide desorbed. The supernatant in the system was then replaced with herbicide-free solution of 0.001M $CaCl_2$ and this desorption process was carried out over three successive steps for both technical grade and formulation treatments.

Desorption isotherms were described using the non-linear form of the Freundlich equation:

$$C_s = K_{fd} C_e^{n_{fd}}$$

where K_{fd} and n_{fd} are parameters related to the capacity to desorb and to the intensity of desorption, respectively. The hysteresis index, HI was then calculated as the ratio of the slope of the desorption curve and the slope of the sorption curve.

5.2.4. Measurement of time-dependent sorption by a centrifugation technique

5.2.4.1. Experimental methodology

Sorption studies were carried out on sandy loam and sandy silt loam soils using technical grade and commercial formulation of propyzamide. Individual replicate samples of 10 g oven dry weight of soil were transferred into 60 mL glass jars. Separate samples were prepared for each treatment and time interval. A total of 40 samples were prepared for each soil together with two blank samples without any treatment for each time interval. Moisture content at field capacity was determined to be 0.22 and 0.29 g g^{-1} for sandy loam and sandy silt loam soils, respectively. The moisture contents in soil samples were adjusted to 0.25 mL below the field capacity level to account for the water content in application solutions and pre-incubated for 24 hours at 4°C in the dark. After pre-incubation, the soil samples were treated with solutions of either technical grade or commercial formulation of propyzamide (Kerb Flo) at the rate of 50 µg active substance per 10 g of soil (the same pesticide to soil ratio as in the leaching experiments). Technical grade application solution was prepared in acetone (500 µg mL^{-1}) and 0.1 mL of this solution was applied dropwise to soil samples in each container. The application solution of formulated product was prepared in 0.001M $CaCl_2$ solution at the rate of 200 µg mL^{-1} and 0.25 mL of this solution was applied dropwise to soil samples. To ensure homogeneous application, the soil samples were thoroughly mixed with a spatula for a few minutes. After this the soils were incubated at 4°C in the dark for a period of 28 days. Water contents were checked between sampling intervals and re-adjusted by weight for any water losses every 2 – 3 days. Water contents were also checked and re-adjusted for any losses before each sampling interval and mixed carefully. The soil samples were transferred from glass jars to centrifugation tubes on day 1, 7, 14, 21 or 28 after pesticide application to extract soil pore water by centrifugation.

5.2.4.2. Extraction of soil pore water by centrifugation

For each soil type, the entire incubated soil sample was transferred into the insert of a 50-ml centrifuge tube (Vivaspin 20 polypropylene, 0.2 µm PES, Sartorius UK limited). Before transferring the soil sample to the centrifuge tube, a glass microfibre filter (Whatman GF/F, 25 mm diameter, 0.45 µm pores, GE Healthcare UK limited) was placed inside the insert. At each sampling interval, four replicate samples for each treatment were centrifuged for 30 minutes to collect an aliquot of soil pore water. Samples were centrifuged at 1500 g corresponding to a pressure of ca. 200 kPa following the protocol proposed by Kah and Brown (2007). The pressure of 200 kPa was also proposed by Walker and Jurado-Exposito (1998) to extract soil solution as this corresponds to the boundary between mobile and immobile water according to Addiscott (1977). 0.5 mL of the extracted soil solution was evaporated to dryness under a gentle stream of nitrogen at room temperature and the pesticide was re-dissolved into 1 mL hexane for the time intervals of 1 and 7 days after treatment. For the remaining time intervals 0.5 mL of pore water was evaporated and the residue was re-dissolved in 0.7 mL of hexane. The contents were transferred into vials and analysed by GC-MS (method given in Chapter 3, section 3.4.3) to determine the concentration of propyzamide (C_e, µg mL^{-1}) remaining in the soil solution. Concentrations of propyzamide obtained from analysis on GC-MS were converted into masses of propyzamide in soil solution based on the respective field capacity moisture content for the two soils.

The solid phase concentration of propyzamide (C_s, µg g^{-1}), sorption coefficient (K_d, mL g^{-1}), and organic carbon normalised coefficients (K_{oc}, mL g^{-1}) were calculated using the equations provided in section 5.2.3.

5.2.4.3. Measurement of desorption by centrifugation

After extracting the soil pore water by centrifugation, desorption was carried out on all soil samples. The compressed soil sample inside the centrifuge tube was loosened with a spatula and the centrifuge tube was gently tapped on a hard surface to ensure uniform packing of the soil. The water retained in each soil sample was calculated by weight difference of the extracted pore water. The water content in each soil sample was adjusted to exactly one pore volume by adding 0.001M $CaCl_2$ solution after accounting for the water already held in each soil sample. One pore volume of sandy loam and sandy silt loam soil was equivalent to 4.58 and 5.01 cm^3 respectively. The samples were then allowed to stand for 30 minutes and this time was equivalent to the time it took the same volume of water to leach through soil columns during leaching experiments described in Chapter 4. The replicates were centrifuged at 1500 g for 30 minutes to extract the pore water. The whole desorption process was repeated over three successive steps. 0.5 mL of the extracted water sample from each desorption step was evaporated under a gentle stream of nitrogen and the contents were re-dissolved into 1 mL of hexane and transferred to GC-MS vials for the analysis using the method described in Chapter 3, section 3.4.3.

5.2.5. Measurement of total pesticide and degradation check

A separate degradation experiment was carried out with sampling intervals 0, 1, 7, 14, 21 and 28 days after pesticide application to study the persistence and degradation behaviour of propyzamide under the experimental conditions. A preliminary test was performed to study propyzamide extraction from wet and dry soils and separate tests were carried out by extracting the soils with acetonitrile and methanol to test the extraction efficiency of the two solvents. Greatest recoveries were achieved from dry soils extracted with acetonitrile (results not shown). Based on the findings from the pre-test, a drying step was introduced in the main experiment and the soils were then extracted with acetonitrile.

For the degradation check, 5 g oven-dry soil was transferred into 30 mL glass bottles. 0.001M $CaCl_2$ solution was applied to each sample to bring the water level close to field capacity moisture content. Replicates were then pre-incubated for 24 hours at 4°C in the fridge. After this, replicates from each soil were treated with solutions of technical grade and commercial formulation of propyzamide at a rate of 25 µg per sample. At sampling, four replicates were taken from each treatment and air-dried in a fan oven at 20°C for 24 hours. The herbicide residues were then extracted in three steps using 10 mL of acetonitrile each time for the sampling intervals up to day 14. For the later sampling intervals of day 21 and 28, pesticide residues were extracted in four steps using 9 mL of acetonitrile each time. The suspension was vigorously shaken on a platform shaker at 300 rpm for one hour. After shaking, the contents were allowed to stand until the soil had settled and the supernatants from the three steps were combined and centrifuged at 4000 g for 20 minutes. 0.3 mL of the supernatant was evaporated under a gentle stream of nitrogen and the chemical was re-dissolved in 2 mL of hexane. The samples were then directly analysed on GC-MS using the method described in Chapter 3 (Section 3.4.3) to determine the total residues of propyzamide in soil at each sampling interval.

5.2.6. Statistical analysis

Statistical analysis was performed using SPSS. Two- and multi-way ANOVA was carried out to test the significance of formulation, residence time and soil type on the sorption behaviour of propyzamide. This was achieved by setting the mass of pesticide as dependent variable and formulation, residence time and soil type as fixed factors. Tukey post-hoc tests were performed to test the variation within the individual treatments over time. The Shapiro-Wilk test was used to test the normality of the datasets.

5.3. Results

5.3.1. Sorption studies by batch-equilibrium method

Sorption and desorption behaviour of technical grade and commercial formulation of propyzamide was studied using standard laboratory batch experiments and characterised through sorption isotherms in sandy loam (Fig. 5.1a) and sandy silt loam soil (Fig. 5.1b). Sorption parameters K_f and n_f, r^2 values and partition coefficients are given in Table 5.1. Sorption isotherms were relatively well described by the Freundlich equation with regression coefficients (r^2) ranging between 0.93 and 0.95.

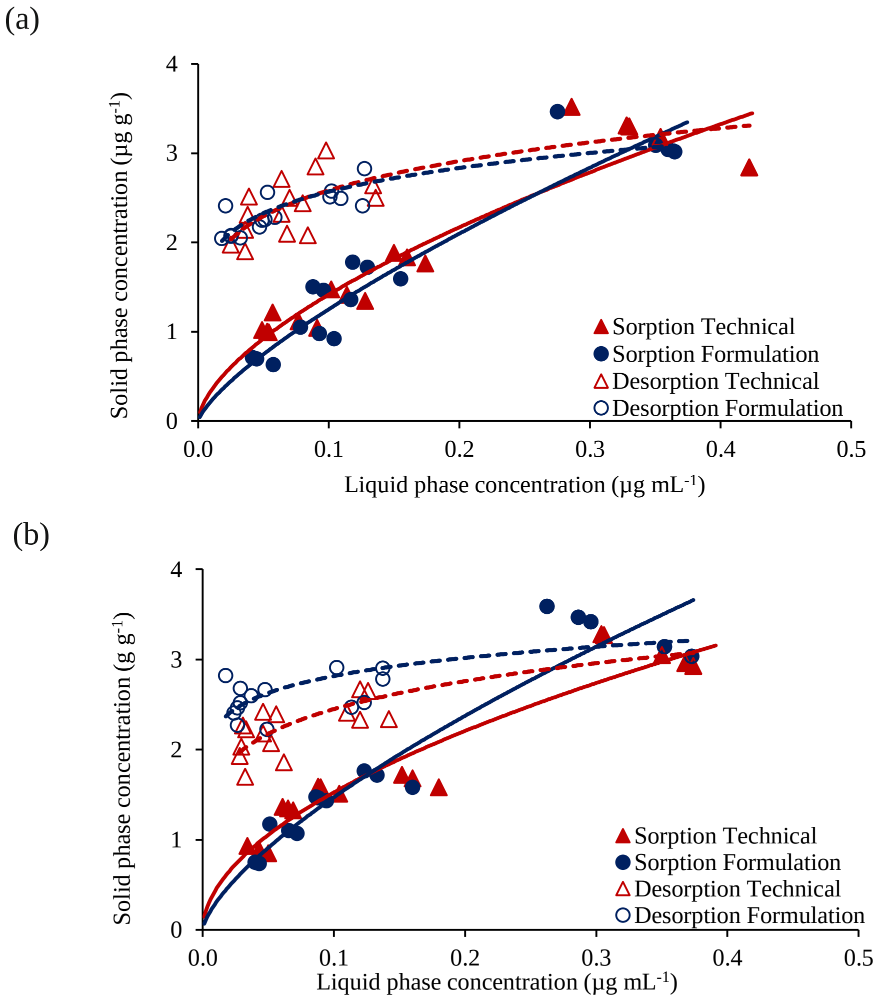


Figure 5.1: *Batch sorption (closed symbols) and desorption (open symbols) isotherms of technical grade (triangles) and commercial formulation (circles) of propyzamide in sandy loam soil (a) and sandy silt loam soil (b). The red and blue solid and dotted lines represent the sorption and desorption isotherms from the technical grade material and formulated product.*

The sorption behaviour of propyzamide from the technical grade material and commercial formulation treatments in the sandy loam soil was similar. The differences in the values of Freundlich sorption coefficients (K_f) for the two treatments were not real as the standard errors associated with the model fit were identical (Table 5.1). However, the K_f value of propyzamide from technical grade material was lower than the corresponding value from the commercial formulation treatment in the sandy silt loam soil and the standard errors associated with the model fit for the two treatments were also significantly different from each other

(Table 5.1). The calculated Freundlich exponent (n_f) values for technical grade and formulated product were ≤0.70 in both soils indicating that the sorption behaviour of propyzamide was highly nonlinear for the two treatments. However, there were no significant differences in the n_f values for the technical grade material and formulated product of propyzamide in the sandy loam soil as the standard errors associated with the values were identical (Table 5.1). The n_f value for the formulated product was greater than the corresponding value for the technical grade material of propyzamide as the standard errors associated with the values were significantly different. The K_d and K_{oc} values of the propyzamide from the technical grade material and formulated product were also given for the comparison in Table 5.1 (Charts in Appendix B, Figures B2 and B3). The calculated K_{oc} values of propyzamide in the sandy loam and sandy silt loam soils were very low compared to the K_{oc} value of 840 mL g^{-1} for propyzamide given in Chapter 3 (Table 3.2).

Table 5.1: *Freundlich sorption coefficients and partition coefficients calculated for technical grade and commercial formulation of propyzamide. Values in parentheses are the standard errors associated with the model fit.*

Soil & formulation type	K_d (ml/g)	r^{2*}	K_{oc}	K_f (ml/g)	n_f	r^2
Sandy loam						
Technical grade material	7.2 (0.70)	0.88	450	6.13 (0.61)	0.64 (0.06)	0.93
Formulated product	7.6 (0.67)	0.90	475	6.50 (0.63)	0.70 (0.06)	0.94
Sandy silt loam						
Technical grade material	6.6 (0.53)	0.91	264	5.54 (0.44)	0.55 (0.05)	0.95
Formulated product	8.4 (0.78)	0.89	336	6.91 (0.71)	0.66 (0.06)	0.94

(where * indicate r^2: correlation coefficient)

Desorption isotherms were hysteretic for the technical material and commercial formulation of propyzamide in both soils (Fig. 5.1a and 5.1b). Desorption parameters of propyzamide are shown in Table 5.2. The regression coefficients (r^2) ranged between 0.62 and 0.87 in the two soils. The Freundlich desorption coefficients for the technical grade material and formulated product in the two soils were identical as the standard errors associated with the K_{fdes} values were not significantly different from each other (Table 5.2). However, the calculated n_{fdes} value for the technical grade material was greater than that for the formulated product in the sandy silt loam soil. The hysteresis index (HI) was calculated as the ratio of the Freundlich desorption exponent (n_{fdes}) and sorption exponent (n_f). Hysteresis indices were less than one for both treatments in both soils. However, the hysteresis was greater for the formulated product compared to the technical material in both soils.

Table 5.2: *Freundlich desorption coefficients, hysteresis index, H and cumulative amount of propyzamide desorbed after three successive desorption steps (expressed as % of the amount initially adsorbed after 24 hours). Values in parentheses are the standard errors associated with the model fit.*

Soils and treatments	K_{fdes}	n_{fdes}	r^2	HI	Desorbed proportion %
Sandy loam					
Technical grade material	3.83 (0.23)	0.168 (0.03)	0.68	0.26	32.9
Formulated product	3.60 (0.14)	0.146 (0.02)	0.87	0.22	31.9
Sandy silt loam					
Technical grade material	3.62 (0.20)	0.170 (0.02)	0.74	0.31	34.5
Formulated product	3.61 (0.19)	0.104 (0.02)	0.62	0.16	30.6

The amounts of propyzamide desorbed after three successive desorption steps are expressed as a percentage of the amount adsorbed after 24 hours. The amounts of propyzamide desorbed form sandy loam and sandy silt loam soils treated with solutions of technical grade material were 32.9 and 34.5 %, respectively. The corresponding proportions of propyzamide desorbed from sandy loam and sandy silt loam soils treated with solutions of commercial formulation were 31.9 and 30.6 %, respectively.

5.3.2. Sorption studies by centrifugation method

The results from the degradation checks under the same experimental conditions as in the sorption experiments are shown in Figure 5.2. The extraction method used in the experiment gave between 97.8 and 103.5% recoveries across all time intervals. The results indicate that propyzamide was persistent over the duration of the experiment and no degradation losses occurred under the controlled experimental conditions where the samples were incubated at 4°C in the dark.

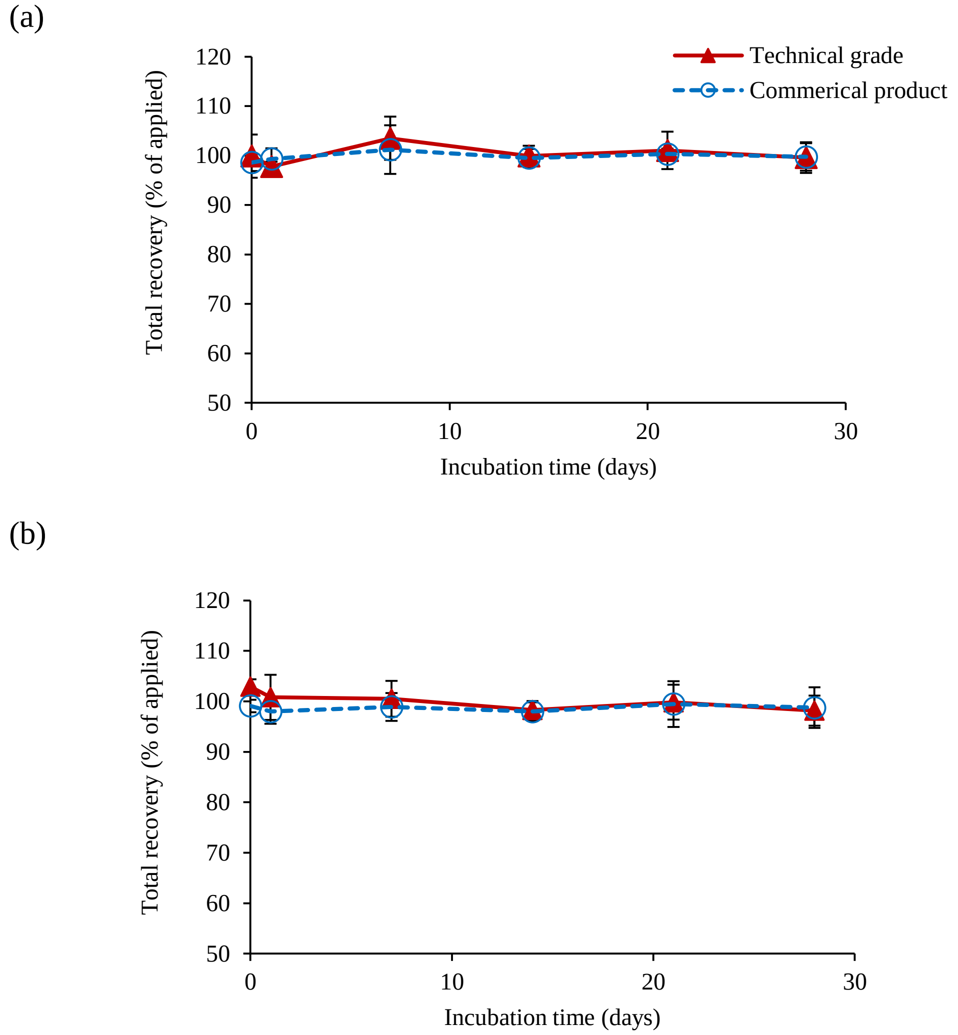


Figure 5.2: *Degradation check for the analytical grade material and formulated product of propyzamide under controlled experimental conditions (4°C and field capacity) in (a) sandy loam, (b) sandy silt loam soils. The values are the average of the four replicates and error bars show ±1 standard deviation.*

The changes in the availability of propyzamide in pore water over time in sandy loam and sandy silt loam soils treated with technical grade and commercial formulation of propyzamide are shown in Fig 5.3. The detailed results for all the replicates are presented in the Appendix B, Tables B1 to B3. Generally, the mass of propyzamide available in soil pore water from treatments with technical grade material were smaller than those observed in pore water from treatments with commercial formulation of propyzamide in sandy loam soil. The average mass of propyzamide in soil pore water in sandy silt loam soil on various sampling intervals was found to be almost identical for the two treatments. Two-sided t-tests also confirmed that there were no significant differences in the masses of propyzamide (p=0.854) available in pore water from the two treatments in sandy silt loam soil.

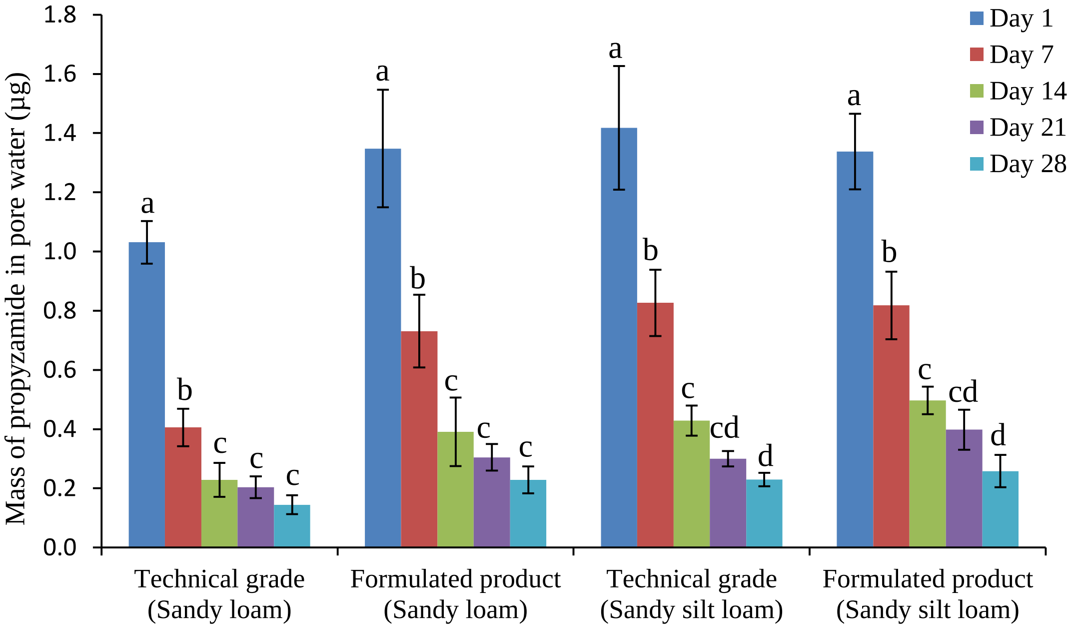


Figure 5.3: *Mass of propyzamide found in pore water in sandy loam and sandy silt loam soils treated with technical grade and commercial formulation of propyzamide (Kerb Flo). Values are means ± standard deviations. Letters on the bars show significant differences between time intervals within the treatments (Tukey post-hoc test).*

The mass of propyzamide in pore water decreased with time for both treatments in both soils. There was a rapid decrease in the mass of propyzamide in pore water from day 1 to 14 after treatment compared to the later sampling intervals in the two soils. The availability of propyzamide in pore water varied between 2.06% and 0.29% of the applied amount in sandy loam soil treated with technical material from day 1 to 28 after treatment, while it varied between 2.70% and 0.46% for the replicates treated with commercial product over a similar period of time. Similarly, between 2.84% and 0.46% of the applied propyzamide was available in pore water in sandy silt loam soil treated with technical grade propyzamide compared to the commercial product where the pesticide availability in pore water varied between 2.68% and 0.52% over a period of 28 days after application. The relative change in the availability of chemical in pore water over time was very consistent for all treatments in both soils (Fig.5.3). The availability of propyzamide in pore water was different for the two soil types where the masses of chemical found in pore water from sandy silt loam soil were larger than those found in sandy loam soil for both treatments (Appendix B, Table B1 and B2).

The Shapiro-Wilk test of normality showed that the data was normally distributed ($p>0.05$ for all combinations). The results of the multi-way ANOVA to test the effects of pesticide formulation, residence time and soil type on the availability of propyzamide in pore water during various sampling events over time are presented in the Appendix B, Table B6. The results show that the effects of formulation, residence time and soil type on the availability of propyzamide in pore water were highly statistically significant with p values of <0.001. The interactions between formulation and soil type was significant ($p<0.001$). However, there was no interaction between residence time and formulation ($p = 0.713$) or residence time and soil type ($p = 0.079$).

Changes in distribution coefficients over time measured using the centrifugation technique are shown in Fig. 5.4. Sorption of propyzamide was expressed as distribution coefficient (K_d, mL g^{-1}), i.e. concentration sorbed (per unit dry weight of soil) divided by the concentration in the soil solution.

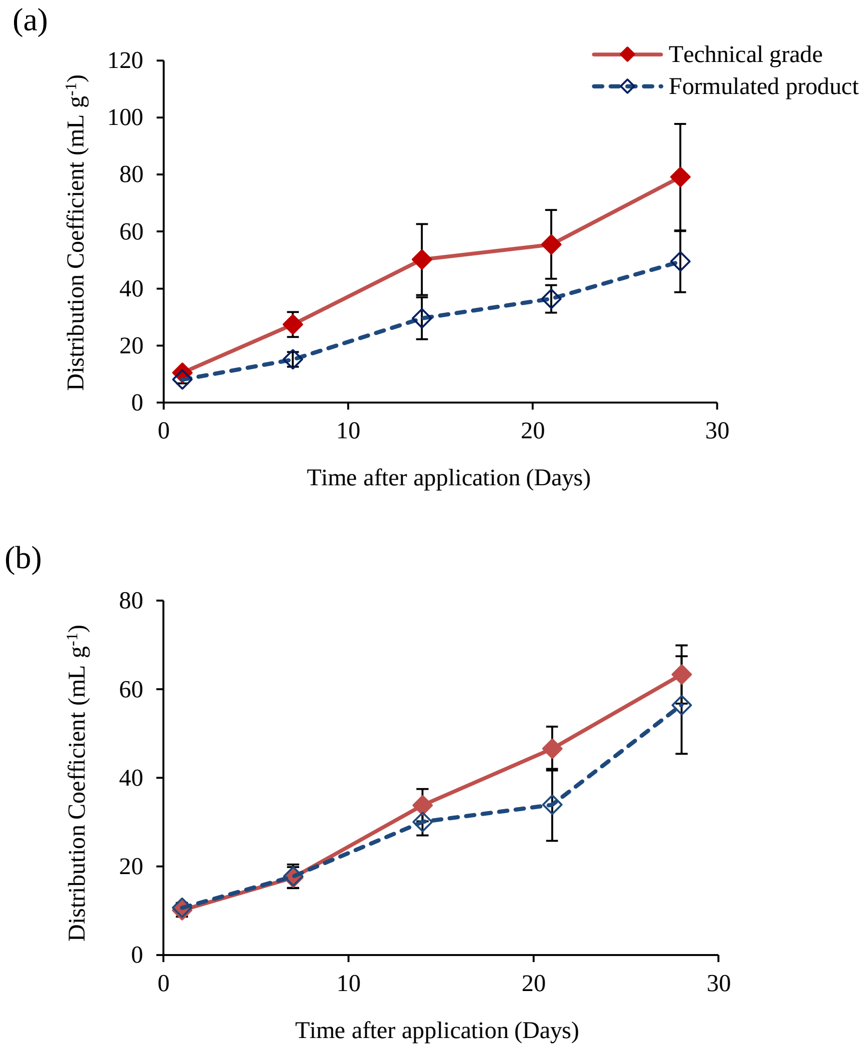


Figure 5.4: *Change in distribution coefficients of technical grade and commercial formulation of propyzamide over time in sandy loam soil (a) and sandy silt loam soil (b). The values are the average of the four replicates and error bars show ±1 standard deviation.*

The results indicate that there was a large and progressive increase in the value of K_d over time for both treatments and in both soils. K_d values for technical grade and commercial formulation of propyzamide in sandy loam soil increased by a factor of 7.5 and 6.1, respectively. The corresponding increases in sandy silt loam soil were factors of 6.3 and 5.3, respectively. The distribution coefficients obtained for the technical material were significantly different from those for commercial formulation in sandy loam soil for all sampling intervals from 7 days onwards. Table 5.3 gives the partition coefficients obtained by batch ($K_d b$) and by centrifugation methods after one and seven days ($K_d c1$ and $K_d c7$, respectively) for technical grade and commercial formulation of propyzamide in the two soils.

Table 5.3: *Distribution coefficients (ml g^{-1}) of technical grade and commercial formulation of propyzamide obtained with batch (means of five replicates) and centrifugation methods (means of four replicates) for initial concentration of 5 µg g^{-1} of soil after one and seven day equilibrium in sandy loam and sandy silt loam soils. Values in parentheses are the standard deviations.*

Soils	Technical Grade material			Commercial formulation		
	K_db	K_dc1	K_dc7	K_db	K_dc1	K_dc7
Sandy Loam	9.62 (2.02)	10.49 (0.77)	27.39 (4.41)	9.31 (1.84)	8.09 (1.34)	15.15 (2.59)
Sandy silt loam	9.21 (1.43)	10.10 (1.49)	17.49 (2.34)	10.88 (2.30)	10.63 (1.12)	17.72 (2.68)

The K_d values for the technical grade material and commercial formulation of propyzamide obtained by batch and centrifugation methods after one day of equilibrium were generally similar in the two soils. The distribution coefficients of technical grade propyzamide obtained by centrifugation after seven day equilibration exceeded the distribution coefficients obtained by the batch method by a factor of 2.9 and 1.9 in sandy loam and sandy silt loam soil, respectively. The corresponding increase in the distribution coefficients of the commercial formulation of propyzamide in both sandy loam and sandy silt loam soils was a factor of 1.6 in both soils.

5.3.3. Comparison of leaching and sorption behaviour of propyzamide

Figure 5.5 presents the comparison of the leaching and sorption behaviours of propyzamide in the two study soils. The mass of propyzamide available in pore water was different from the mass of pesticide leached from soil columns for both treatments in the two soils. This behaviour is discussed in greater detail in Section 5.5.

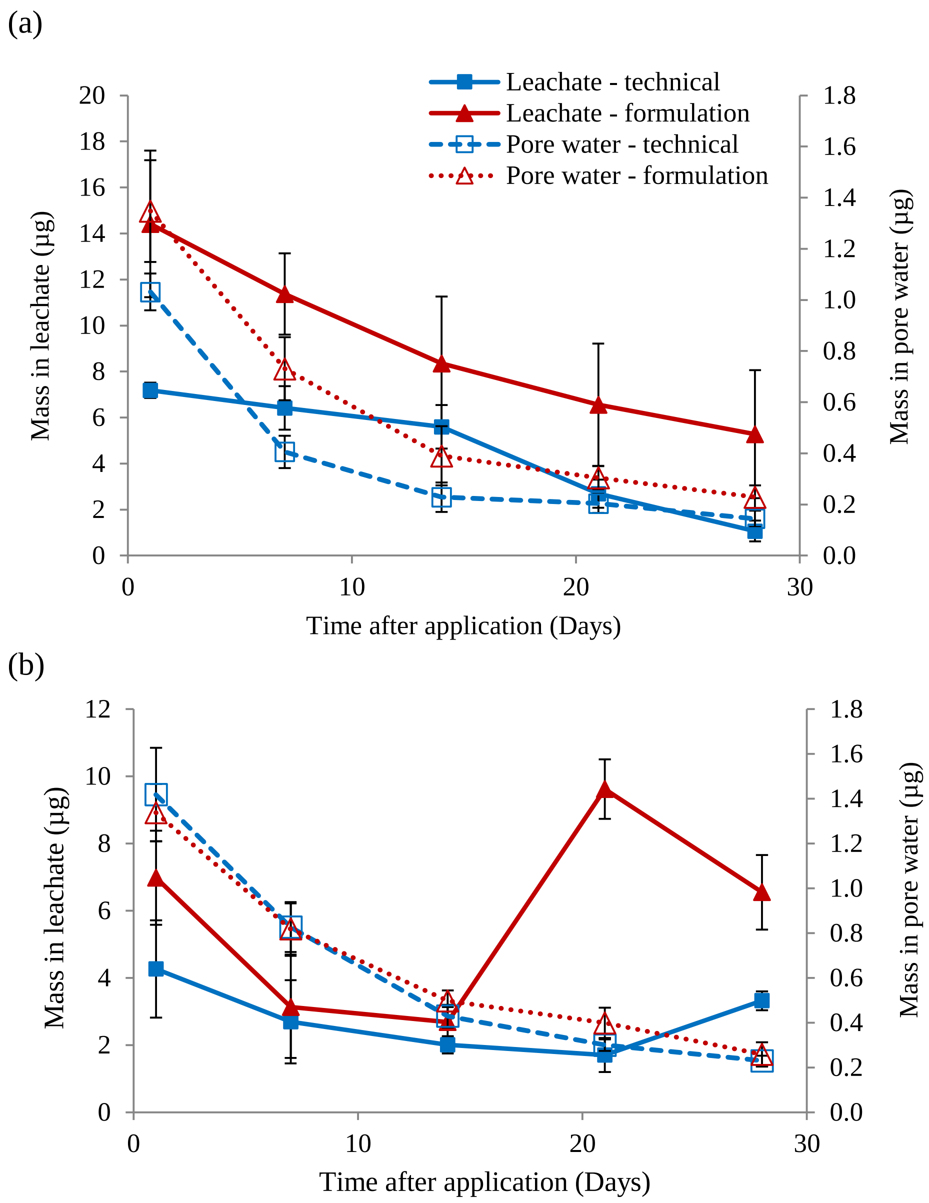
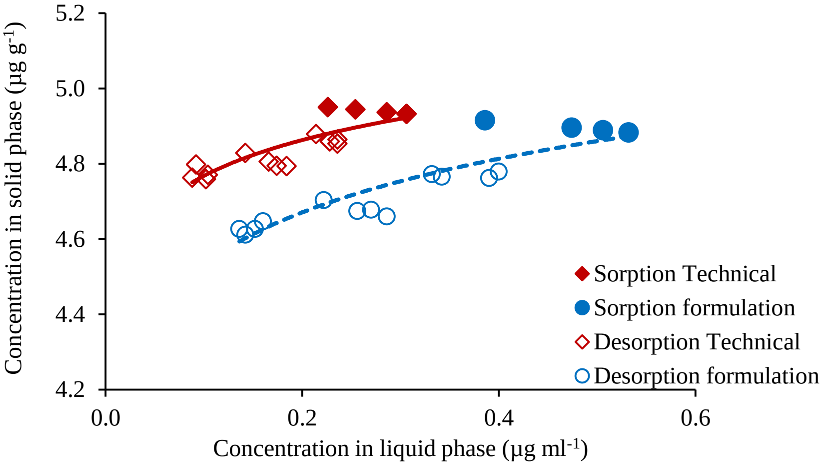


Figure 5.5: Masses of technical grade and commercial formulation of propyzamide in leachate and soil pore water extracted by centrifugation (means and standard deviations of four replicates) over several time intervals in (a) sandy loam soil and (b) sandy silt loam soil. The values are the average of the four replicates and error bars show ±1 standard deviation.

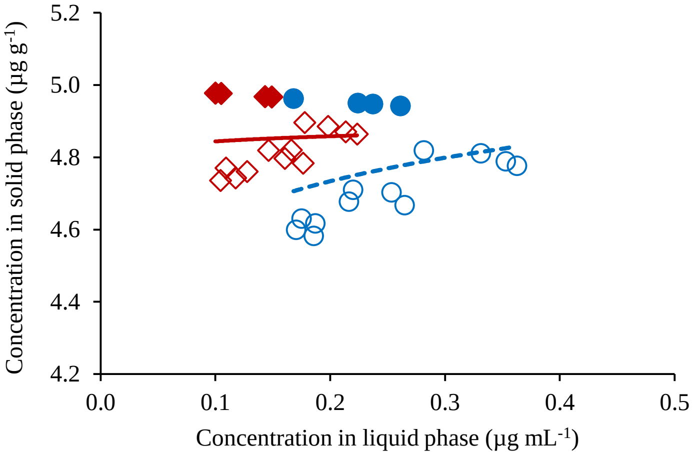
5.3.4. Desorption of propyzamide by centrifugation

Desorption behaviour of technical grade and commercial formulation of propyzamide was studied using the centrifugation method and characterised through desorption isotherms in sandy loam (Fig. 5.6) and sandy silt loam soil (Fig. 5.7), respectively. These isotherms were developed by plotting the desorbed concentrations of propyzamide in the liquid phase against the concentrations in the solid phase produced over the three successive desorption steps. This enabled characterisation of the overall sorption behaviour of propyzamide and its reversibility in the two soils. Desorption isotherms are presented separately for each time interval together with the adsorption data of propyzamide in the two soils (Figures 5.6 and 5.7).

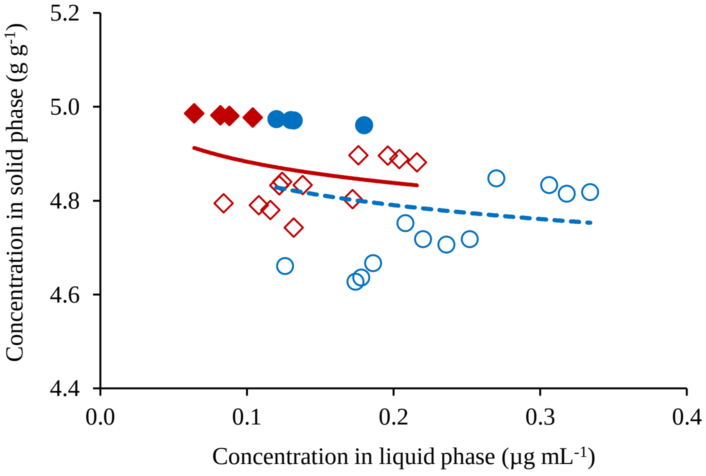
(a)


Concentration in solid phase (μg g-1)
5.2
5.0
4.8
4.6
4.4
4.2
0.0
0.2
0.4
0.6
Concentration in liquid phase (μg ml-1)
◆ Sorption Technical
● Sorption formulation
◇ Desorption Technical
○ Desorption formulation

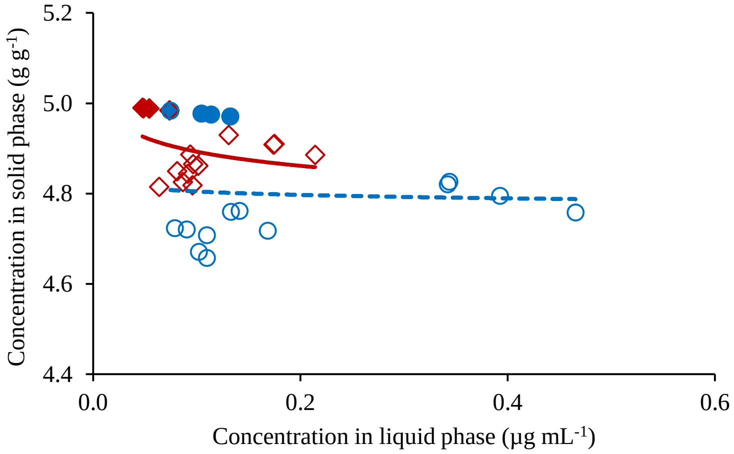
(b)


Concentration in solid phase (μg g-1)
5.2
5.0
4.8
4.6
4.4
4.2
0.0
0.1
0.2
0.3
0.4
0.5
Concentration in liquid phase (μg mL-1)

(c)


Concentration in solid phase (g g-1)
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
0.4
Concentration in liquid phase (μg mL-1)

(d)



(e)

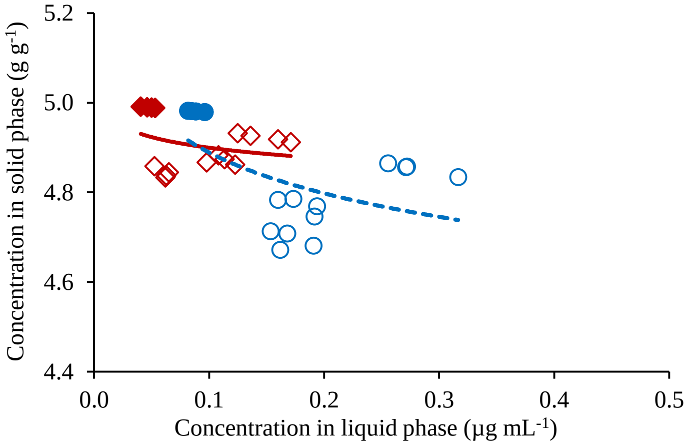
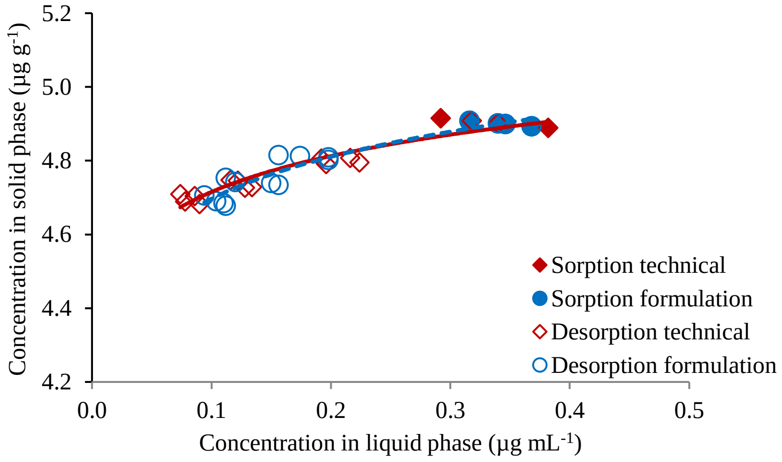
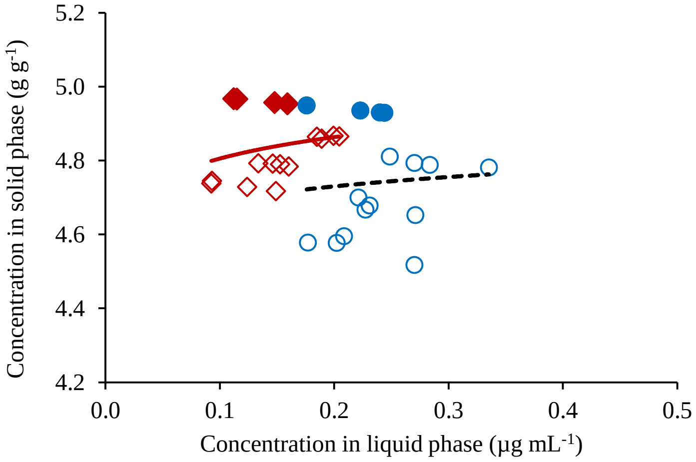


*Figure 5.6***:** *Desorption isotherms of technical grade and commercial formulation of propyzamide developed using a centrifugation method in sandy loam soil (a) day 1, (b) day 7, (c) day 14, (d) day 21 and (e) day 28. Note that the scale of the x and y-axis changes between the individual figures.*

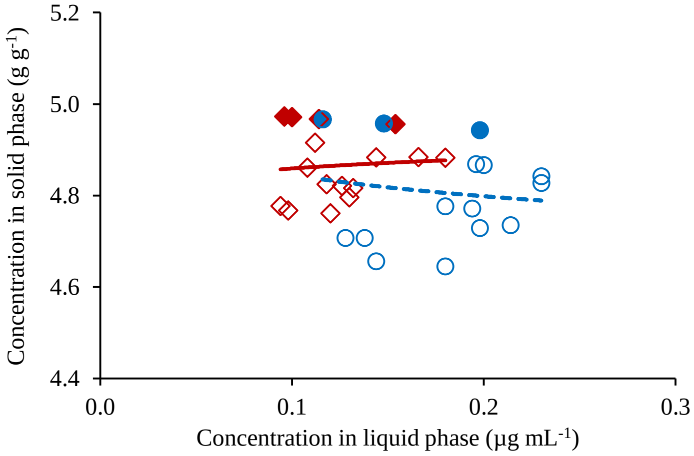
(a)


Concentration in solid phase (µg g^{-1})
5.2
5.0
4.8
4.6
4.4
4.2
0.0
0.1
0.2
0.3
0.4
0.5
Concentration in liquid phase (µg mL^{-1})
◆ Sorption technical
● Sorption formulation
◇ Desorption technical
○ Desorption formulation

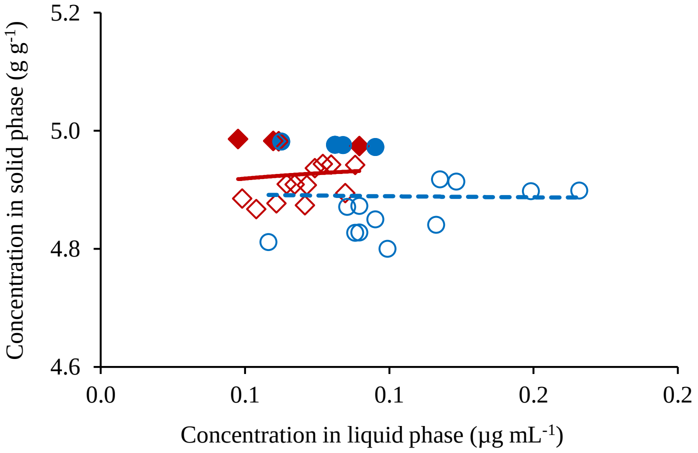
(b)


Concentration in solid phase (g g^{-1})
5.2
5.0
4.8
4.6
4.4
4.2
0.0
0.1
0.2
0.3
0.4
0.5
Concentration in liquid phase (µg mL^{-1})

(c)


Concentration in solid phase (g g^{-1})
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
Concentration in liquid phase (µg mL^{-1})

(d)



(e)

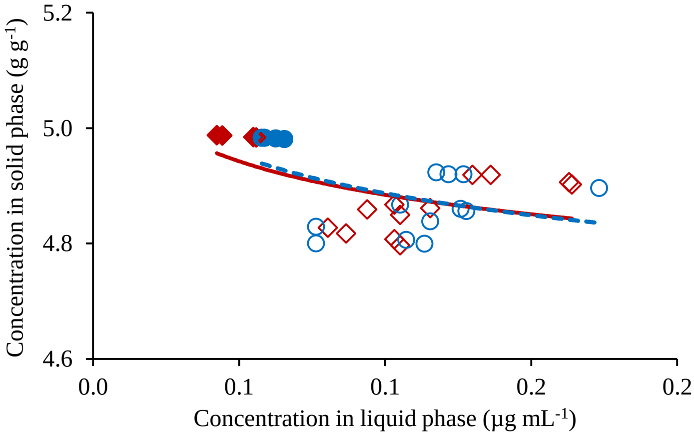


*Figure 5.7***:** *Desorption isotherms of technical grade and commercial formulation of propyzamide developed using a centrifugation method in sandy silt loam soil (a) day 1, (b) day 7, (c) day 14, (d) day 21 and (e) day 28. Note that the scale of the x and y-axis changes between the individual figures.*

Desorption isotherms were developed by non-linear fittings of the data to the Freundlich equation and the results for the sandy loam and sandy silt loam soils are shown in Tables 5.4 and 5.5, respectively. Overall, the values of Freundlich desorption coefficients (K_{fdes}) for technical grade and commercial formulation of propyzamide were very similar in the two soils. There was a large decrease in the n_{fdes} values over time for both the technical grade material and formulated product in the two soils which indicates that there was a massive hysteresis in desorption of propyzamide from both the technical grade material and formulated product in the two soils.

Table 5.4: *Freundlich desorption coefficients, desorption exponents and r^2 values for technical grade and commercial formulation of propyzamide over various time intervals in sandy loam soil determined using a centrifugation method*

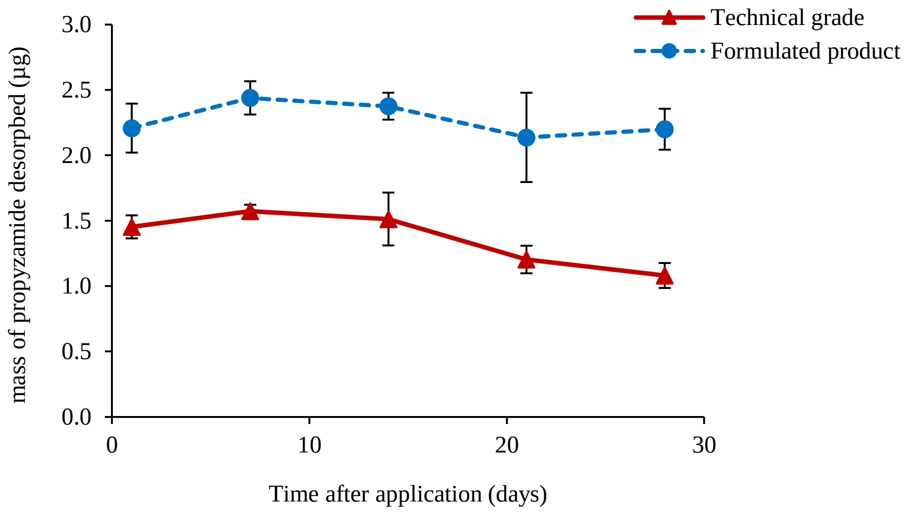
Time interval	Technical grade material		Formulated product	
	K_{fdes}	n_{fdes}	K_{fdes}	n_{fdes}
1	5.034	0.017	4.957	0.024
7	5.041	0.017	4.976	0.024
14	4.991	0.011	4.959	0.019
21	4.957	0.005	4.821	0.003
28	4.979	0.006	4.960	0.015

Table 5.5: *Freundlich desorption coefficients, desorption exponents and r^2 values for technical grade and commercial formulation of propyzamide over various time intervals in sandy silt loam soil determined using a centrifugation method*

Time intervals	Technical grade material		Formulated product	
	K_{fdes}	n_{fdes}	K_{fdes}	n_{fdes}
1	5.048	0.030	5.086	0.035
7	4.990	0.011	4.982	0.022
14	4.998	0.010	5.087	0.024
21	5.032	0.006	4.974	0.005
28	4.993	0.008	5.024	0.010

The total masses of technical grade and commercial formulation of propyzamide desorbed over three successive desorption steps are shown in Fig. 5.8. The total masses of pesticide desorbed were obtained after accounting for the mass left in the water retained in soil after sorption and desorption steps. Overall, the desorption from the formulated material was greater than the technical material in the two soils; however, the behaviour was more consistent in the sandy loam soil compared to the sandy silt loam soil.

(a)



(b)

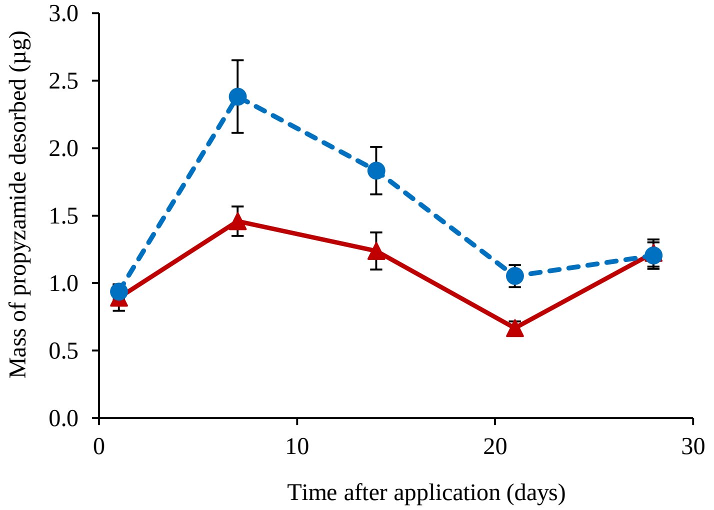


Figure 5.8: Total mass of technical grade and commercial formulation of propyzamide desorbed from sandy loam (a) and sandy silt loam (b) soils over three successive desorption steps during various time intervals

5.4. Discussion

Overall, the sorption behaviour of technical grade and commercial formulation of propyzamide was similar in sandy loam soil compared to sandy silt loam soil where the K_f value for the technical material was lower than the corresponding value for the formulated material when measured by the classic batch-equilibrium method. This may be explained by experimental conditions where the pesticide soil suspensions were vigorously shaken with an excess amount of water which may result in the early separation of pesticide from the formulation compared to the technical grade material of pesticides. Beigel and Barriuso (2000) also reported that the Freundlich sorption parameters K_f and n_f of pure triticonazole were very close to the corresponding values for three different commercial formulations when characterised by batch equilibrium method. Although they did not attribute the finding to the experimental conditions, the method used and the type of formulation were similar to the ones used in the present study. However, metribuzin retention in an Algerian silty-clay soil showed 11% less adsorption from formulated material (Metriphar) compared to pure analytical grade material when characterised by batch-equilibrium method and as a result of this effect the authors hypothesised an increased risk of transport of the chemical to groundwater (Oukali-Haouchine *et al*., 2013). Földényi *et al.* (2013) recently investigated the effects of co-formulants on the sorption of sulfonylurea herbicides (chlorsulfuron and tribenuron methyl) in sand, loam and clay loam soils with a static batch-equilibrium method. Their results indicate that at small concentrations, the extent of adsorption of the active substance was higher for solutions of pure ingredients than from the commercial formulation solutions (Földényi *et al*., 2013). They also reported that the adsorption of chlorosulfuron decreased markedly on sandy soil in the presence of forming agent Supragil and hence increased environmental mobility of the pesticide.

However, Pose-Juan *et al.* (2010) reported greater sorption of penconazole from the commercial formulation (water-oil emulsion formulation of penconazole (WOEP)) compared to the technical grade material in batch experiments. About 70% of the total penconazole retained in the solid phase of diluted commercial formulation/soil suspension was sorbed by soil. They concluded that the presence of oil-surfactant mixture in the commercial formulation may have influenced the adsorption of penconazole on soil, by either enhanced penetration of the penconazole onto the less polar sites of the soil organic matter, or by the co-adsorption of the penconazole within the oil-surfactant mixture.

The calculated n_f values were ≤0.7 for both technical grade material and formulated product indicating that the sorption behaviour of propyzamide in both soils was highly non-linear. Also, the slopes of isotherms were L-shaped with respect to the concentration in the aqueous phase. This is the most observed type of isotherm for pesticide sorption in soils (Yazgan *et al*., 2005; Singh and Singh, 2012; Kumar *et al*., 2015; Kandil *et al*., 2015). Lower n_f values indicate the greater curvature of the isotherms and hence less sorption with increasing pesticide surface concentration (Delle Site, 2001; DeSutter *et al*., 2003). This is mainly attributed to less availability of free binding sites with increasing concentration of pesticide in the solution phase. This also implies that specific binding sites may be involved in the sorption process (Kennedy, 2002; DeSutter *et al*., 2003). Similar sorption behaviour has been reported for tricyclazole in Ultisol and Vertisol soils (Kumar *et al*., 2015). Singh and Singh (2012) also reported highly non-linear adsorption of metsulfuron-methyl and sulfosulfuron in various Indian soils with n_f values <0.7 in most soils. Nemeth-Konda *et al*. (2002) carried out laboratory studies on the sorption behaviour of several pesticides in Hungarian agricultural soil and also reported non-linear sorption behaviour with $\mathrm{n_f}$ values in a similar range for most of the studied pesticides as in this study. The calculated n_f values for the commercial formulation of propyzamide was greater than the corresponding value for the technical material in the sandy silt loam soil. Although, there is no direct evidence available in the literature, the differences may be due to the presence of co-formulants in the commercial formulation of propyzamide which could affect the specific adsorption process compared to the technical grade material. When n_f values are lower than 1 the mobility of a compound in soil columns can be significantly greater at higher concentrations (Delle Site, 2001).

The effect of formulation on the sorption behaviour of propyzamide was significant ($p<0.001$) when characterised by the centrifugation technique in sandy loam soil but there was no effect of formulation on sorption in sandy silt loam soil. Using the centrifugation technique, sorption behaviour was characterised under natural moisture conditions and the water content was maintained at field capacity throughout the experiment with minimal disturbance to the soil structure. The results from the centrifugation method are generally of greater relevance to field soils due to the experimental conditions being closer to the field situation (Kah and Brown, 2007). Observed concentrations of propyzamide in soil pore water were greater from commercial formulation treatments compared to the technical grade material indicating that there was less sorption of propyzamide from the formulated material. This may be attributed to the presence of co-formulants and additives that would favour maintaining pesticide molecules in the solution **(**Beigel and Barriuso, 2000; Oukali-Haouchine *et al.*, 2013). Furthermore, the pesticide molecule may only slowly separate from the surrounding co-formulants within soil which would prevent the sorption process to occur at the same rate as for the technical material. Cox and Walker (1999) also compared the sorption behaviour of analytical grade and 50% wettable powder formulation of linuron by incubating treated soil samples for 28 days at 5°C and characterising the fraction of chemical available in soil solution by using a centrifugation technique. They reported no significant differences in the sorption behaviour of the two treatments and suggested that there was no interaction in sorption studies from the co-adjuvants present in the herbicide formulation. However, the wettable powders are dry formulations whereas the suspension concentrate formulations are mainly water based and the nature of the co-formulants used in the two formulation types may also be different. It may be possible that the effects of co-formulants from the wettable powder formulations may be different compared to those in the SC formulations.

The partition coefficients (K_d) values for the technical grade and commercial formulation of propyzamide obtained by the centrifugation method after one day of equilibration were similar to partition coefficients obtained after 24 hours by the batch method (Table 5.3). Previous studies suggest that the partition coefficients obtained by batch method are generally greater than those from extraction using centrifugation (Walker and Jurado-Exposito, 1998; Yazgan *et al*., 2005; Kah and Brown, 2007; Folberth *et al*., 2009). It has been suggested that shaking may be the main factor for greater sorption observed with the batch method as soil is disaggregated, resulting in a higher availability of sorption sites to interact with pesticide molecules (Kah and Brown, 2007; Folberth *et al*., 2009). Kennedy *et al*. (2002) suggested that the discrepancy between the two methods appeared to be related to soil physico-chemical properties, particularly organic carbon content and pH. However, the K_d values obtained by centrifugation method exceeded the corresponding values obtained by batch method after an incubation period of seven days (Table 5.3).

The distribution coefficients plotted as a function of time indicate that there was a large increase in the strength of sorption over time for both soils and for both technical and formulated material (Fig. 5.4). This may be due to the concentration of pesticide molecules being greater in the outer regions of soil particles and in the macropores soon after application (Beulke *et al*. 2004). Soil is a heterogeneous mixture of a large variety of porous particles which are structured in a complex way and thus all the sorption sites are not immediately available to the pesticide. With time, these molecules slowly move into the complex micropore structure of soil constituents mainly as a result of advection and/or diffusion where the chemical may be strongly bound to soil organic constituents resulting in greater sorption coefficients for the compound over time (Beulke *et al*. 2004). Thus the kinetic control of time-dependent sorption is mainly the physical process of migration to the binding site. Cox and Walker (1999) reported that the distribution coefficient of linuron in soil from Cottage Field 1 increased by a factor of 1.7 under similar experimental conditions as in the current experiment (incubated at 5°C for a period of 28 days). They also reported that the distribution coefficients of isoproturon in the Hunts Mill soils increased by a factor of 1.6 and in soils from Cottage Field 1 and Cottage Field 2 by a factor of 1.4, respectively. However, they observed greater values of distribution coefficients at 20°C for the two compounds in all soils and suggested that there was an interaction between sorption and degradation. Kah and Brown (2007) also reported that the adsorption coefficients measured by centrifugation after seven days incubation were significantly larger than those after one day incubation ($p<0.001$) for various pesticides. However, the differences were not as great as in the current study. Walker and Jurado-Exposito (1998) reported a progressive increase in the value of distribution coefficient of metsulfuron-methyl over time, with greater changes in the samples incubated at 25°C than at 5°C. However, the change in the distribution coefficients over-time was very small compared to the corresponding change in distribution coefficients for propyzamide in the present study. Metsulfuron-methyl is highly soluble in water (2790 mg L^{-1} at

20°C, PPDB) and only weakly sorbing compound with the overall K_f value of 0.77 mL g^{-1} (EU dossier, 2015) compared to propyzamide which is a strongly sorbing compound with low water solubility. Therefore, the strength of sorption for propyzamide is more likely to increase over time. Oi (1999) characterised the sorption behaviour of imidacloprid in sandy loam and silt loam soils incubated for 100 days after treatment. He used a batch method by employing desorption and solvent extraction techniques to determine the levels of imidacloprid in soil compartments. He reported that K_d values of imidacloprid increased by a factor of 3.2 and 3.8 in sandy and loamy soils, respectively. He further verified the time-dependent sorption results by a column leaching experiment with aged soils over identical time intervals and reported a decrease in leaching potential of imidacloprid with residence time in soil. Imidacloprid is also a high solubility compound (610 mg L^{-1}, PPDB) and moderately mobile in soil systems (K_f range between 0.956-4.18 mL g^{-1}, EU dossier, 2015), hence may behave differently compared to propyzamide. In a study on the effect of aging on the sorption-desorption of weak acid sulfonylaminocarbonyltriazolinone herbicides, Koskinen *et al*. (2002) reported that K_d values of sulfonylaminocarbonyltriazolinone increased by a factor of 4.5 in the clay loam soils and by 6.6 in the loamy sand after a 12 week incubation at -33 kPa as compared to freshly treated soils.

The results from the column study in Chapter 4 showed enhanced leaching of propyzamide from columns treated with commercial formulation compared to the columns treated with technical grade material and this behaviour was independent of time and soil type. However, the pattern of behaviour was more consistent in the sandy loam soil than in the sandy silt loam soil. Time-dependent sorption experiments discussed above were carried out under static conditions using the same time intervals and experimental conditions as in leaching experiments to characterise the sorption behaviour of technical grade and formulated material of propyzamide and the availability of pesticide in pore water. The comparison of the amount of propyzamide available in pore water for leaching from the sorption experiment with the actual amount of herbicide leached from soil columns on various time intervals is shown in Figure 5.5. The mass of propyzamide available in pore water was different from the mass of pesticide leached from soil columns for both treatments in the two soils. The initial mass of propyzamide available in pore water from sandy loam soil was 1.03 µg and 1.35 µg from the technical grade and formulated product treatments, respectively. However, the total mass of propyzamide leached from the soil columns 24 hours after treatment was 7.2 and 14.4 µg from the technical grade material and formulated product, respectively (Fig. 5.5a). While in sandy silt loam soil the mass of propyzamide that was initially available in pore water for leaching corresponded to 1.42 µg and 1.34 µg from the technical grade and formulated product treatments, respectively. However, the total mass of propyzamide leached from the soil columns 24 hours after application was 4.3 µg and 7 µg, from the technical grade and formulation treatments, respectively (Fig. 5.5b).

The results indicate that the amounts of propyzamide in leachate and in pore water decreased with time for both treatments in sandy loam soil. However, the decrease in the availability of herbicide in pore water was much faster compared to the amounts of propyzamide found in leachate, where a steady decline in the mass of herbicide was observed over time (Fig. 5.5a). The amounts of propyzamide in leachate and in pore water were always smaller for samples treated with technical material compared to the samples treated with formulated material at all time intervals in sandy loam soil. However, the effect of formulation was greater on the leaching behaviour of propyzamide compared to the sorption behaviour (Fig. 5.5a). Leaching of propyzamide from sandy silt loam soil showed an inconsistent behaviour, where the amounts of chemical in the leachate initially decreased for the first few time intervals and increased leaching was observed during the later time events for both treatments (Fig. 5.5b). However, the amounts of propyzamide in pore water decreased very rapidly over time for the two treatments. Although, the effect of formulation on the leaching behaviour of propyzamide was statistically significant ($p<0.001$), there was no effect of formulation on the sorption behaviour of propyzamide in sandy silt loam soil. Thus patterns in leaching of the formulated and technical material were different from the patterns in sorption of the formulated and technical material over time and the effect of pesticide formulation on sorption was not sufficient to fully explain the enhanced leaching of propyzamide from commercial formulation in soil columns.

It was then hypothesised that desorption may be an additional mechanism that is controlling the enhanced leaching of the formulated material in soil columns. During the leaching process, most of the chemical in the soil pore water will be leached out of the soil columns and the pesticide sorbed to soil matrix may be subject to desorption to restore the equilibrium between the two phases. The presence of co-formulants in commercial formulations of pesticides may serve as a control on the diffusion and physical migration to the binding site due to the slow separation of pesticide from the formulation over time. Hence, it may be possible that during the leaching process that was carried out for nearly five hours, enhanced losses of pesticide from formulated material may have occurred due to desorption processes.

The results from the desorption study by standard batch equilibrium method suggest that the desorption behaviour of propyzamide was similar for technical grade and commercial formulation treatments as there were no apparent differences in desorption coefficients (K_{fdes}) for the two treatments in either soil (Table 5.2). However, hysteresis was observed in the desorption behaviour of propyzamide in both soils and the hysteresis index (HI) for the formulated material was smaller than the HI for the technical grade propyzamide. In practice desorption of a chemical is hysteretic when hysteresis index (HI) < 0.7 (Olvera-Velona *et al*. 2008). The smaller the HI value, the greater the hysteresis, and hence a more irreversible sorption for a given compound (Olvera-Velona *et al*. 2008). The lower values of hysteresis index (HI) for formulated material suggest that sorption irreversibility was higher in both soils for the formulated material compared to the technical grade propyzamide. This may be due to the differences in the specific adsorption behaviour between the two treatments.

Desorption of propyzamide investigated by the centrifugation method showed that values of the Freundlich desorption coefficients (K_{fdes}) for the technical grade material and formulated product were very similar for all time intervals in the two soils. The n_f values were ≤ 0.035 suggesting that there was a very large hysteresis in the desorption of propyzamide from the two treatments. However, the desorption isotherms of propyzamide from the two treatments showed an unexpected behaviour for all time intervals longer than 1 day where isotherms shifted towards the right due to greater masses of propyzamide extracted during the desorption steps compared to those found in pore water during the adsorption steps (Figures 5.5 and 5.6). This unexpected behaviour could not be readily explained. To date there is no evidence in the literature where a similar method has been used to investigate the desorption behaviour of pesticides and it may be possible that this unexpected desorption behaviour is an experimental artefact. However, the desorption data suggest that there was very slow release of pesticide out of the soil whereas this was observed to proceed much faster under the leaching conditions. Currently, the results from the sorption experiments discussed here do not provide a clear link to the behaviour of pesticide observed during the leaching experiments. Hence, further experimental work is required to explore the impacts of co-formulants on sorption under natural soil moisture conditions. Furthermore, detailed experiments are needed to improve the centrifugation method used to characterise desorption behaviour of propyzamide so that it is applicable in future research to investigate the desorption behaviour of pesticides at natural soil water contents. It is recommended that longer desorption steps should be used in order to generate more robust desorption data.

5.5. Conclusion

Standard batch-equilibrium method and centrifugation techniques were used to characterize the sorption and desorption behaviour of technical grade and commercial formulation of propyzamide in sandy loam and sandy silt loam soils. The results from the batch method indicate that the sorption behaviour of propyzamide from the technical grade material and commercial formulation treatments was generally similar in both soils (Tables 5.1 & 5.3). The results from the centrifugation study show that the effect of formulation on sorption of propyzamide was highly significant ($p<0.001$) in sandy loam soil, but there was no effect of formulation on sorption of propyzamide in the sandy silt loam soil. There was a large increase in the strength of sorption over time in both soils and for both technical grade and formulated materials. This indicates that the sorption of propyzamide in soil was a time dependent process. Enhanced leaching of formulated material was observed from column experiments which was independent of time and soil type. However, the patterns in leaching of the formulated and technical material were different than the patterns in sorption of the formulated and technical material over time and the effect of pesticide formulation on sorption was not sufficient to fully explain the enhanced leaching of propyzamide from commercial formulation in soil columns. Despite the differences in hysteresis indices, there were no apparent differences in the Freundlich desorption coefficients of technical grade and commercial formulation of propyzamide in both soils. These results suggest that the standard batch-equilibrium method is not suitable to characterise the differences in the sorption and desorption behaviour of technical grade and commercial formulation of propyzamide. Alternatively, the centrifugation technique is the most appropriate method to characterise the sorption and desorption behaviour of pesticides in soil, particularly to interpret the differences in the behaviour of active substance due to the effect of formulation. Desorption of propyzamide by the centrifugation method revealed an unexpected behaviour in desorption which could not be explained readily. However, the desorption data suggest that there was very slow release of pesticide out of the soil whereas this was observed to proceed much faster under the leaching conditions. The unexpected behaviour in desorption may be due to an experimental artefact as the method employed has not been used previously. Detailed experiments are needed to improve this method so that it is applicable in future research.

Chapter 6

MODELLING SORPTION BEHAVIOUR OF PROPYZAMIDE

6.1. INTRODUCTION

Many studies report that the sorption of pesticides in soil is a slow process that may proceed over a relatively long period of time. Mathematical models provide an excellent tool to describe and predict the time-dependent sorption behaviour of pesticides. The results of the sorption and desorption experiments of propyzamide from the technical grade and commercial formulation treatments in the two study soils characterised by batch and centrifugation method have been presented in Chapter 5. In this chapter, a two-site and a three-site mathematical model were tested in order to describe the sorption and desorption data of propyzamide in greater detail, and hence to understand various processes that are responsible for equilibrium and non-equilibrium sorption of pesticides within soil systems. A two-site model with equilibrium and non-equilibrium sorption sites was first applied to the adsorption phase of the studies. A three-site model that also considered irreversible sorption was also tested. Two models were then applied to attempt to describe the desorption phase of the experimental data.

6.2. Methods

6.2.1. Two-site sorption model

Initially, a two-site model was applied to describe the sorption data of propyzamide from Chapter 5. The schematic representation of the model is given in Figure 6.1 and is adopted from Suddaby *et al*. (2013). The model used two different sorption sites to simulate the sorption behaviour of propyzamide from technical grade material and formulated product in the two study soils over time. These were (i) equilibrium sorption sites representing the instantaneous exchange between the solid and liquid phases and (ii) non-equilibrium sorption sites conceptualising slow but reversible sorption processes. Pesticide in the equilibrium domain (indicated by the dashed line in Figure 6.1) is subject to degradation. Sorption processes in the non-equilibrium phase were characterised by a first-order adsorption and desorption reaction with the same rate constant K_{des}. Degradation of the pesticide was set to zero based on the degradation check on propyzamide in Chapter 5.

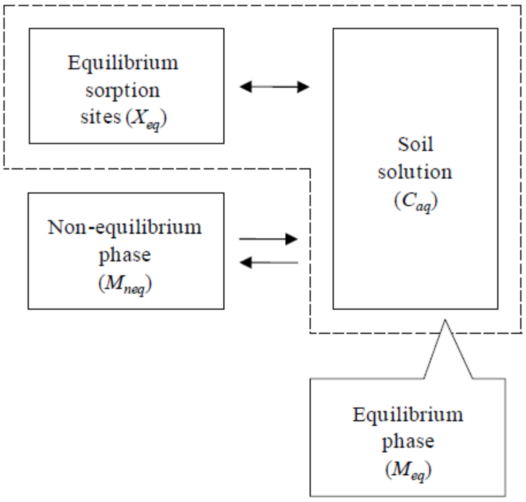


Figure 6.1: *Schematic representation of the two-site model with soil solution on the right and the equilibrium and non-equilibrium sorption sites on the left. The equilibrium phase indicated by the dashed line includes both the concentration of pesticide in the soil solution* (C_{aq}; µg mL^{-1}) *and the pesticide sorbed at equilibrium sites* (X_{eq}; µg g^{-1})*. Where* M_{eq} *and* M_{neq} *represent the mass of pesticide in the equilibrium and non-equilibrium phases respectively. (Source: Suddaby et al., 2013).*

The two-site model was then applied to the adsorption data from the centrifugation experiment described in Chapter 5 (Section 5.3.2), that involved the incubation of soil samples treated with technical grade and formulated product of propyzamide for a period of 28 days and centrifuging samples over various intervals during this time to extract the soil pore water.

The concentration of pesticide sorbed in the equilibrium domain (X_{eq}, µg g^{-1}) was calculated using the following mathematical equation:

$$X_{eq} = K_{feq} \cdot C_{aq}{}^{n_f}$$

where the K_{feq} is the Freundlich sorption distribution coefficient at equilibrium, C_{aq} (µg mL^{-1}) is the concentration of chemical in the solution phase at equilibrium and n_f is the Freundlich exponent (-).

The total mass of chemical in the equilibrium domain (M_{eq}) was then determined using the following expression:

$$M_{eq} = (V_{sol} \cdot C_{aq} + \left(M_{soil} \cdot X_{eq}\right)$$

where V_{sol} is the volume of solution (mL) and M_{soil} is the mass of soil (g) used in the sorption experiments by centrifugation method. The mass of the chemical in the non-equilibrium (M_{neq}) sorption site was derived by using the following differential equation:

$$\frac{dM_{neq}}{dt} = \left(k_{des} \cdot F_{ne} \cdot C_{aq}{}^{n_f}\right) - \left(k_{des} \cdot M_{neq}\right)$$

where k_{des} is the desorption rate coefficient (d^{-1}) and F_{ne} is the ratio between the non-equilibrium and equilibrium Freundlich coefficients (-).

6.2.1.1. Model parameters for the two-site sorption model

The fixed parameters in the model are given in the Table 6.1. K_{omeq} and n_f were determined separately by Freundlich sorption studies using the batch-equilibrium method (see chapter 5, section 5.2.3) for the propyzamide/soil systems studied in this thesis. The unknown parameters in the model were: (i) the desorption rate coefficient (K_{des}) and (ii) the ratio between the non-equilibrium and equilibrium sorption (F_{ne}). F_{ne} was initially allowed to optimise but found to always return value of 1, so then set as a fixed value thereafter.

Table 6.1: *Fixed parameter values in the model measured by laboratory batch equilibrium sorption studies of propyzamide from technical grade and commercial formulation treatments in the two soils*

Parameters	**Sandy loam**		**Sandy silt loam**	
	Technical grade	*Formulated material*	*Technical grade*	*Formulated material*
Freundlich exponent ((-); n_f)	0.64	0.70	0.55	0.66
Freundlich organic carbon sorption coefficient (K_{omeq}; $mL\ g^{-1}$)	383	406	222	276
Mass fraction of organic matter (CntOm; g g^{-1})	0.016	0.016	0.025	0.025
Mass of soil (MasSol; g)	10	10	10	10
Mass of pesticide (MasIni; µg)	50	50	50	50
Volume of water (Volliq; mL)	2.2	2.2	2.9	2.9
Degradation half-life ($DegT_{50}$; days)	0.0	0.0	0.0	0.0

6.2.2. Three-site sorption model

The three-site model not only considered equilibrium and non-equilibrium sorption sites but also included irreversible sorption sites to simulate the behaviour of propyzamide over time in the two study soils. The schematic representation of the model given in Figure 6.2 is adopted from Suddaby *et al.* (2013).

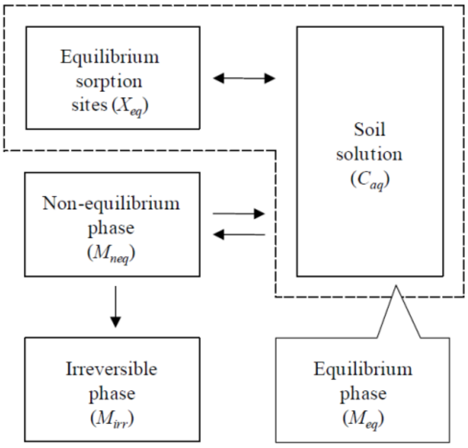


Figure 6.2: *Schematic representation of the three-site model with soil solution on the right and the equilibrium and non-equilibrium sorption sites on the left. The equilibrium phase* (M_{eq}) *indicated by dashed line includes both the concentration of pesticide in the soil solution* (C_{aq}; $\mu g\ mL^{-1}$) *and the pesticide sorbed at equilibrium sites* (X_{eq}; $\mu g\ g^{-1}$)*. (Source: Suddaby et al., 2013)*

The irreversible sorption sites presented the fraction of chemical that was irreversibly sorbed to soil organic matter as a result of very slow sorption kinetics from the non-equilibrium domain. Irreversible sorption from the non-equilibrium phase was characterised using the rate constant k_{irr} and degradation of the chemical was set to zero based on the degradation check on propyzamide in Chapter 5.

The model derived X_{eq} and M_{eq} using the mathematical equations given in section 6.2.1. However, with the introduction of irreversible sorption sites, the model determined the mass of pesticide in the non-equilibrium (M_{neq}) and irreversible (M_{irr}) domains using the following mathematical expressions:

$$\frac{dM_{neq}}{dt} = \left(k_{des} \cdot F_{ne} \cdot C_{aq}{}^{n_f}\right) - \left(k_{des} \cdot M_{neq}\right) - \left(k_{irr} \cdot M_{neq}\right)$$

$$\frac{dM_{irr}}{dt} = k_{irr} \cdot M_{neq}$$

where k_{irr} is the coefficient controlling the rate of irreversible sorption (d^{-1}).

6.2.2.1. Model parameters for the three-site sorption model

The measured and fixed parameters in the model are given in Table 6.1. The unknown parameters in the model were: (i) K_{des}; (ii) F_{ne}; and, (iii) the coefficient controlling the rate of irreversible sorption (K_{irr}). The model was optimised against the adsorption data obtained from the centrifugation experiment described in Chapter 5 (Section 5.3.2).

6.2.3. The two-site desorption model

The model contained the same sorption processes as the two-site sorption model discussed in Section 6.2.1 as well as three independent events to define different steps and time intervals during desorption process. Sorption processes in the non-equilibrium phase were characterised by a first-order adsorption and desorption reaction with same the rate constant K_{des}. Degradation of the pesticide was set to zero based on the degradation check on propyzamide in Chapter 5.

The three independent events were added to the model to define different steps and time intervals used to extract the pore water from soil samples during the adsorption step and subsequent three desorption steps. These were: (i) extraction of soil pore water to measure the concentration of chemical in pore water and concentration of chemical adsorbed to the soil. This was triggered by a non-periodic event after 30 minutes on the day of sampling. The mass remaining in the system was calculated by the model after this event by the following equation:

$$Mequ = Mequ - [Vol_{removed} \cdot C_{aqsus}]$$

where C_{aqsus} is the concentration in the extraction solution (µg mL^{-1}) and $Vol_{removed}$ is the volume (mL) of pore water removed from the soil sample during the adsorption step; (ii) the saturation of soil samples inside the centrifugation tube during the desorption steps. This was triggered after one hour (i.e. the time taken to spin and process the samples during the adsorption step) using a non-periodic event that accounted for the addition of 0.001M $CaCl_2$ solution to bring the water level to exactly one pore volume; and, (iii) extraction of soil pore water to remove chemical during the desorption step triggered every two hours (i.e. the time taken to spin and process the samples during desorption steps) by a non-periodic event.

The parameters from the two-site sorption model were transferred over to the two-site desorption model to describe the desorption behaviour of propyzamide observed by laboratory desorption experiments.

6.2.4. The three-site desorption model

The three-site desorption model contained the same sorption processes as the three-site sorption model discussed in Section 6.2.2 as well as three independent events to define different steps and time intervals used to extract the pore water from soil samples during the adsorption step and subsequent three desorption steps. The model used the same independent events as described in Section 6.2.3. The parameters from the three-site sorption model were transferred over to the three-site desorption model to describe the desorption behaviour of propyzamide observed by laboratory desorption experiments.

6.2.5. Model optimisation

The ModelMaker© software (version 4.0) used the Marquardt method and weighted least squares to optimise the unknown parameters. The optimisation method was the same for all the models discussed above. The default settings were a convergence change of 1×10^{-7} and five convergence steps; initial lambda of 10000; minimum change of 1×10^{-200}; and fractional change of 0.01. Individual weighting was used with a data error fraction of 1. The model was optimised against the adsorption data (measurements of the total mass of pesticide in the soil and concentrations of pesticide in soil solution over-time) of technical grade and commercial formulation of propyzamide obtained from the centrifugation experiment described in Chapter 5 (Section 5.3.2). Fixed and optimised parameters used to fit two-site and three-site sorption and desorption models during different simulations are given in Table 6.2. When n_f and k_{omeq} were allowed to optimise, the initial values were set to those measured in the batch sorption experiment given in Table 6.1.

Table 6.2: *Fixed and optimised parameters used during different simulations to fit two-site and three-site sorption and desorption models*

Simulation set	Model	Fixed parameters	Optimised parameters
A	Two-site sorption	n_f, K_{omeq}	K_{des}
B	Two-site sorption		n_f, K_{omeq}, K_{des}
C	Three-site sorption	n_f, K_{omeq}	k_{des}, k_{irr}
D	Three-site sorption		n_f, K_{omeq}, K_{des}, k_{irr}
E	Two-site desorption	n_f, K_{omeq}, F_{ne}, K_{des}	
F	Three-site desorption	n_f, K_{omeq}, F_{ne}, K_{des}, k_{irr}	

6.3. Results

6.3.1. Two-site sorption model

The two-site model was initially applied to describe only the adsorption data of propyzamide obtained from the centrifugation experiment (Chapter 5, section 5.3.2). The data values measured were concentrations (µg mL^{-1}) of propyzamide in solution during the adsorption phase over time. The data in the adsorption phase included concentrations of propyzamide measured in solution after all five time intervals of adsorption (1, 7, 14, 21, and 28 days). Initially the measured values of n_f and K_{omeq} given in Table 6.1 were used to fit the model to the data, however, the model did not match the measured behaviour (data not shown). It was then decided to allow the Freundlich parameters n_f and K_{omeq} as well as the unknown parameters F_{ne} and K_{des} to optimise. The parameter values returned by the optimisation are given in Table 6.3.

Table 6.3: *Optimised parameter values for the two-site model used to describe the sorption behaviour of propyzamide.*

	Sandy loam		Sandy silt loam	
	Technical grade	*Formulated product*	*Technical grade*	*Formulated product*
Optimises Values				
n_f	0.30 (0.014)	0.31 (0.019)	0.28 (0.016)	0.28 (0.044)
K_{omeq}	363 (12.13)	342 (9.32)	230 (3.61)	238 (7.17)
k_{des}**	0.066 (0.008)	0.045 (0.007)	0.035 (0.004)	0.026 (0.007)
Goodness of fit				
r^2	0.97	0.98	0.99	0.98

*Value in bracket is optimised error (standard deviation) of parameter generated by ModelMaker©

** Desorption rate constant

The optimised model fit is plotted against the measured data for the two soils in Figure 6.3. Visually, the model fitted the measured data of propyzamide well in the two soils. The optimised values of n_f generated by the model were very small for all treatments (≤ 0.31) compared to the measured values given in Table 6.1, while the optimised values of K_{omeq} were reasonably close to the measured values. Furthermore, the optimisation errors for individual parameters generated by the model were very small and the r^2 values (model weighted sum of squares / total weighted sum of squares) were all ≥0.97 (Table 6.3). Model fit to the change in K_d values over time is given in Figure 6.4.

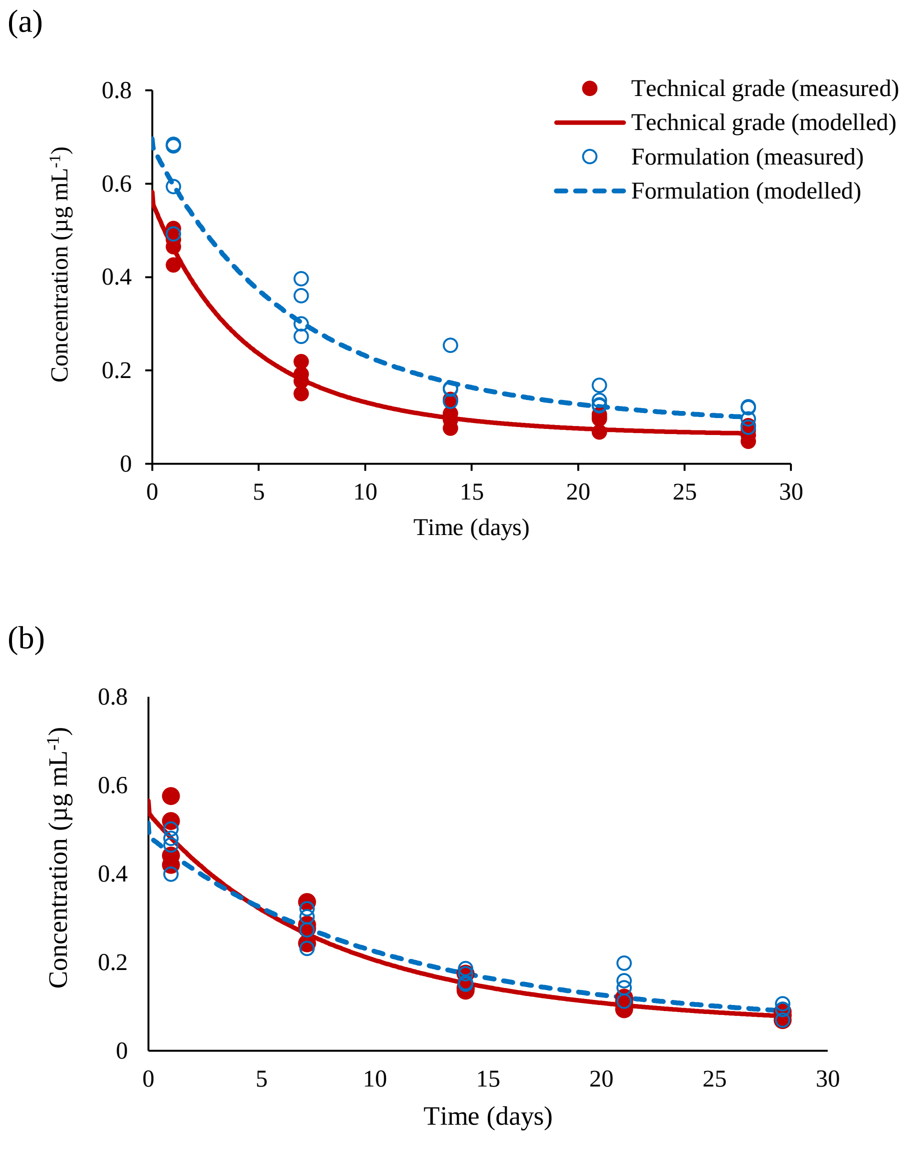
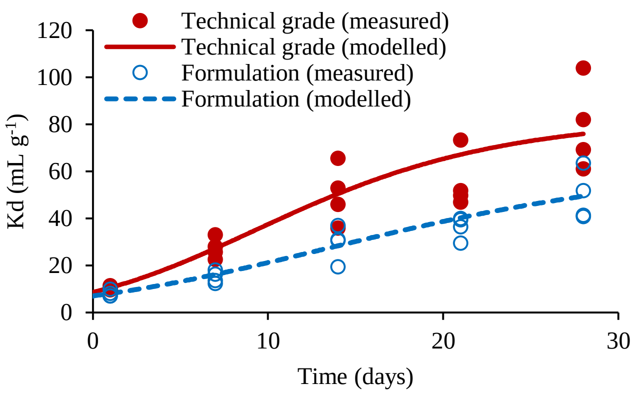


Figure 6.3: *Model fit to the propyzamide adsorption data in (a) sandy loam and (b) sandy silt loam soils over time.*

(a)



(b)

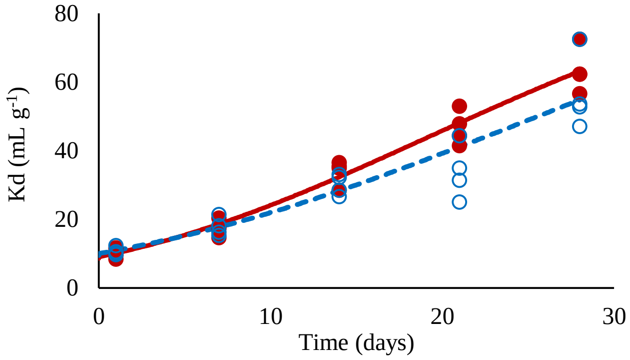


Figure 6.4: *Two-site model fitted to the change in distribution coefficients of propyzamide over time in (a) sandy loam and (b) sandy silt loam soils.*

6.3.2. Three-site sorption model

Although, the two-site model with optimised parameters fitted the data well, the values for n_f generated by the model were smaller than those measured experimentally. Hence a three-site model that considered irreversible sorption in addition to the equilibrium and non-equilibrium phases was also applied to the data. The three-site model was initially applied to describe only the adsorption data obtained from the centrifugation experiment. The parameters n_f and K_{omeq} were set to measured values from the batch studies given in Table 6.1. The optimised values for K_{des} *and* K_{irr} are given in Table 6.4. The model fit is plotted against the measured data for the two soils in Figure 6.5. Visually, the model described the adsorption data well and r^2 values were ≥ 0.96. The parameter errors for K_{des} generated by the ModelMaker© with the three-site model were larger than those observed in the two-site model.

Table 6.4: *Optimised parameter values from the three-site model used to describe the sorption behaviour of propyzamide in the two soils.*

Parameters	Sandy loam		Sandy silt loam	
	Technical grade	*Formulated product*	*Technical grade*	*Formulate product*
optimised values				
k_{des}*	0.409 (0.087)	0.132 (0.018)	0.214 (0.027)	0.115 (0.012)
k_{irr}*	0.081 (0.0052)	0.080 (0.0105)	0.055 (0.0035)	0.069 (0.008)
Goodness of fit				
r^2	0.96	0.97	0.98	0.98

* Value in bracket is the optimised error of parameter generated by ModelMaker©

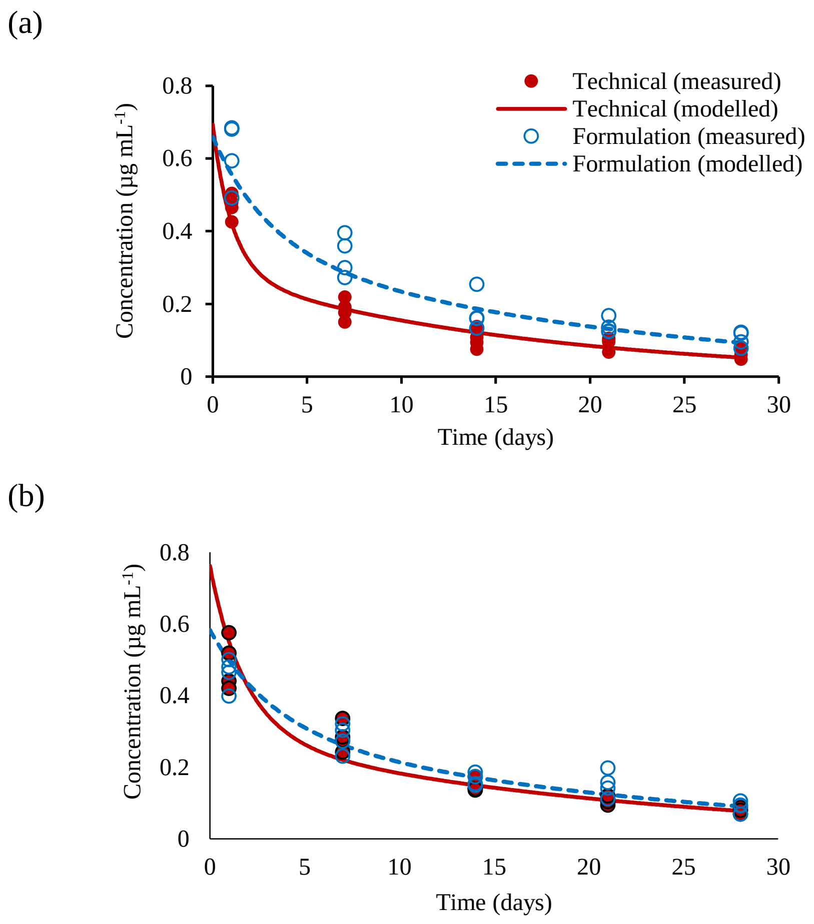


Figure 6.5: *Three-site model fitted to the adsorption data of propyzamide over time in (a) sandy loam and (b) sandy silt loam soils.*

Model fit to the change in K_d values over time is given in Figure 6.6.

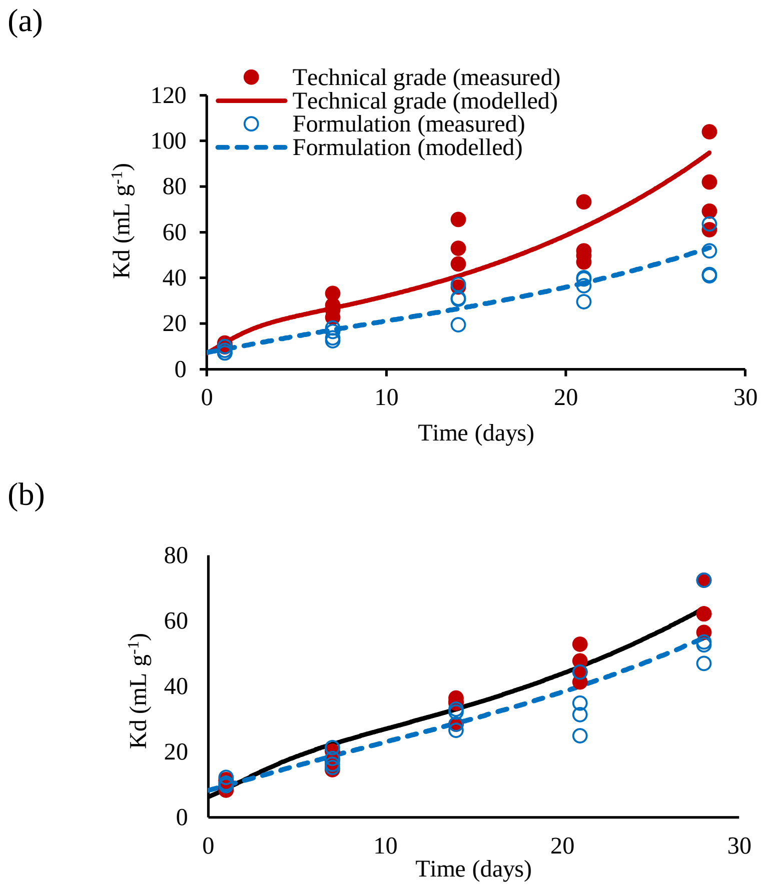


Figure 6.6: *Three-site model fitted to the changes in distribution coefficients of propyzamide over time in (a) sandy loam and (b) sandy silt loam soils.*

The three-site model was also applied to the adsorption data by allowing the n_f, K_{des}, K_{irr} and K_{omeq} to optimise. The optimised parameters are given in Table 6.5. Visually the model fitted the data well and (Figure 6.7) and r^2 values were all ≥ 0.97. Overall, the optimised values of n_f, K_{omeq} returned by the three-site sorption model (Table 6.5) were generally similar to those generated by the two-site model given in Table 6.3. The optimisation errors were also larger than those for the two-site model due to the large number of parameters included in optimisation. Model fit to the change in K_d values over time is given in Figure 6.8.

Table 6.5: *Optimised parameter values for the three-site model used to describe the sorption behaviour of propyzamide in the two soils.*

Parameters	**Sandy loam**		**Sandy silt loam**	
	Technical grade	*Formulated material*	*Technical grade*	*Formulated material*
optimised values				
n_f	0.38 (0.059)	0.35 (0.153)	0.23 (0.119)	0.28 (0.134)
K_{omeq}*	371 (17.50)	345 (17.96)	224 (15.60)	318 (18.2)
k_{des}*	0.105 (0.037)	0.053 (0.034)	0.028 (0.017)	0.055 (0.012)
K_{irr}	0.022 (0.015)	0.009 (0.039)	0.015 (0.041)	0.018 (0.046)
Goodness of fit				
r^2	0.97	0.98	0.99	0.98

* Value in bracket is the optimised error of parameter generated by ModelMaker©

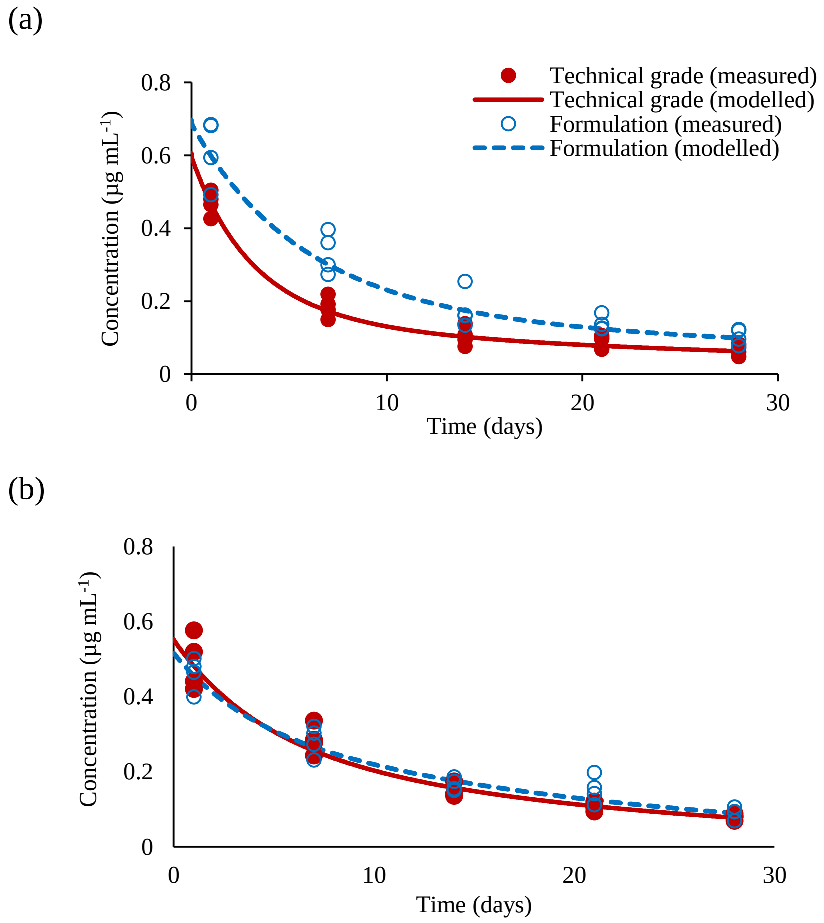
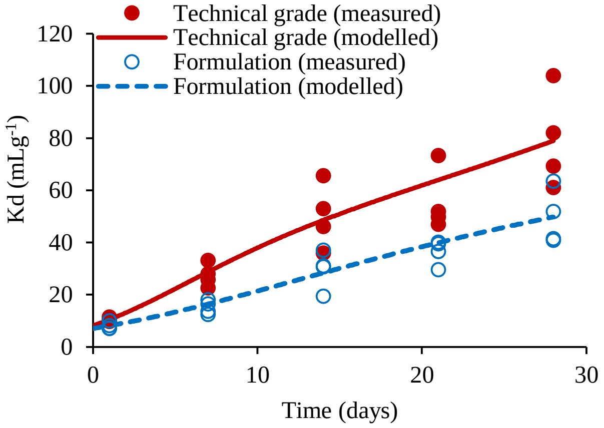


Figure 6.7: *Model fit to the propyzamide adsorption in (a) sandy loam and (b) sandy silt loam soils over time with optimised parameters*

(a)



(b)

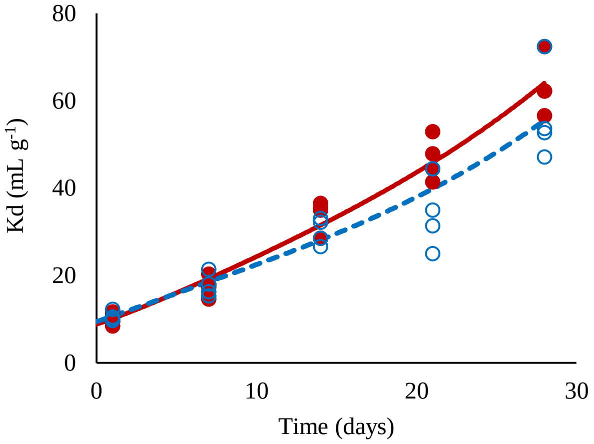
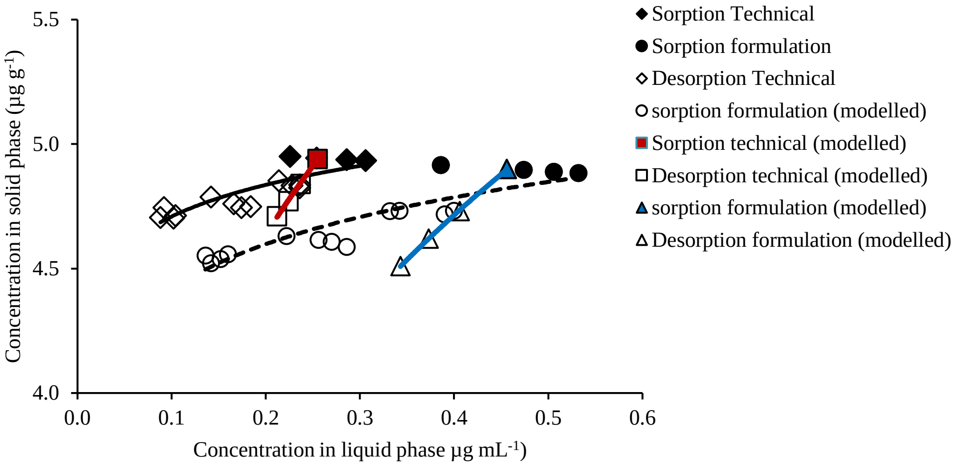


Figure 6.8: *Three-site model fitted to the changes in distribution coefficients of propyzamide over time in (a) sandy loam and (b) sandy silt loam soils.*

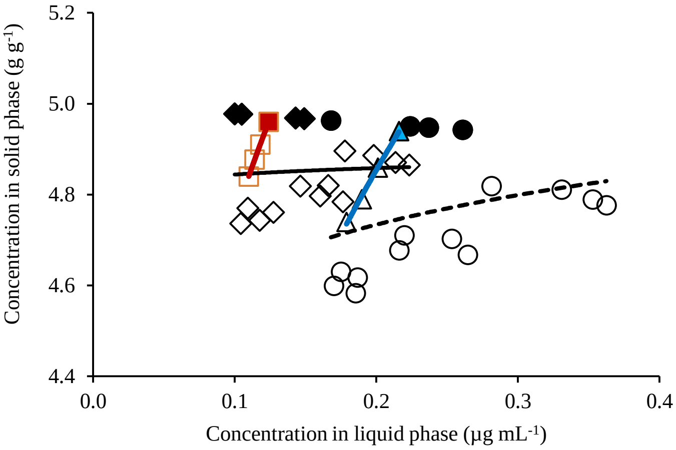
6.3.3. Two-site desorption model

The two-site desorption model was applied to data from the desorption experiment by centrifugation (Chapter 5, section 5.3.3). The model fit was implemented step-wise, by first fitting the parameters to the adsorption data and then transferring those parameter values over to two-site desorption model to assess fit to the desorption data without optimisation. The modelled behaviour has been plotted against the observed data from the sandy loam and sandy silt loam soils in Figures 6.9 and 6.10, respectively. The two-site desorption model failed to describe the desorption behaviour of propyzamide measured during the laboratory incubation experiments using a centrifugation method. The model generated the classical desorption behaviour where the concentrations of the desorbed pesticide in the solution were lower than the modelled concentrations during the adsorption steps. In contrast to this, the measured desorbed concentrations of propyzamide for all sorption intervals greater than 1 day were generally greater than those measured during the adsorption steps in both soils.

(a)



(b)



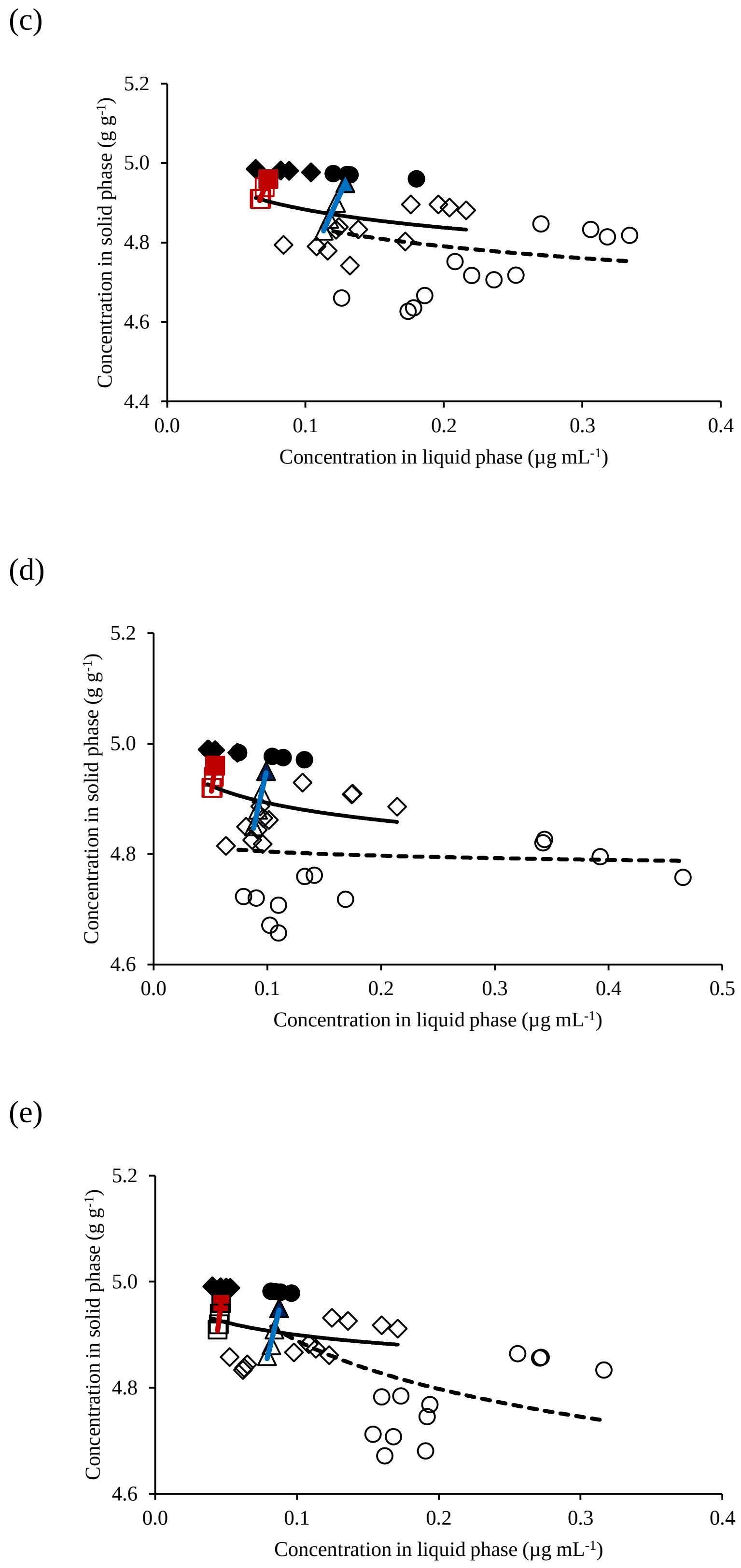
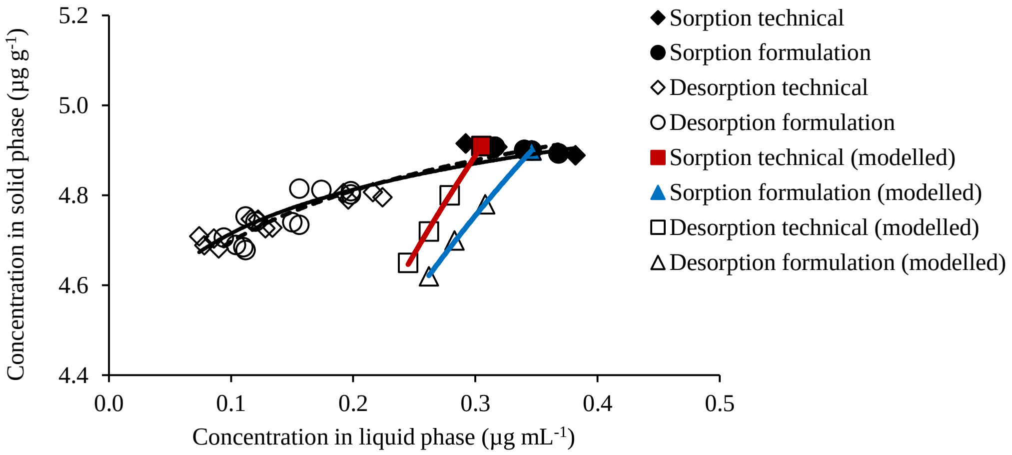
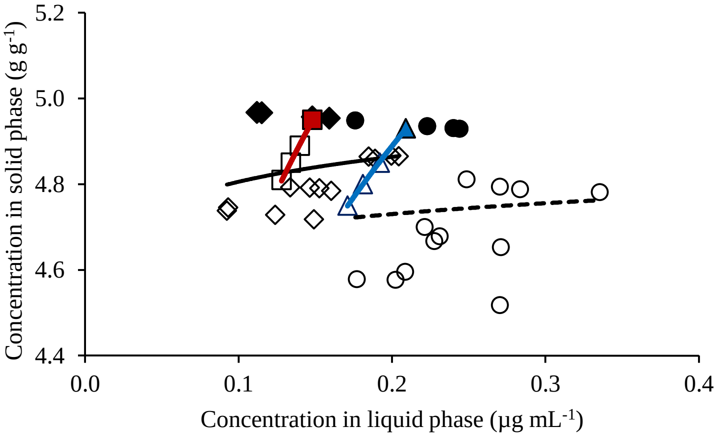


Figure 6.9. *Measured and modelled desorption isotherms of in sandy loam soil for the time intervals of (a) day 1, (b) day 7, (c) day 14, (d) day 21, and (e) day 28. The blue and red coloured lines are the modelled isotherms of formulated and technical grade material. Note that the scale of the x and y-axis changes between individual figures.*

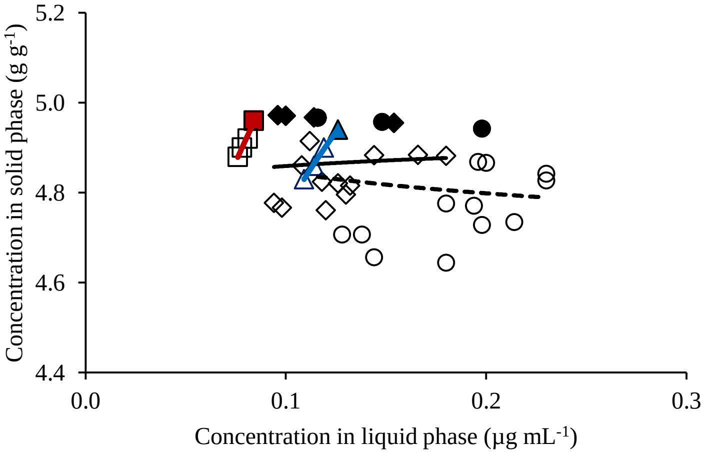
(a)


Concentration in solid phase (μg g-1)
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
0.4
0.5
Concentration in liquid phase (μg mL-1)
◆ Sorption technical
● Sorption formulation
◇ Desorption technical
○ Desorption formulation
■ Sorption technical (modelled)
▲ Sorption formulation (modelled)
□ Desorption technical (modelled)
△ Desorption formulation (modelled)

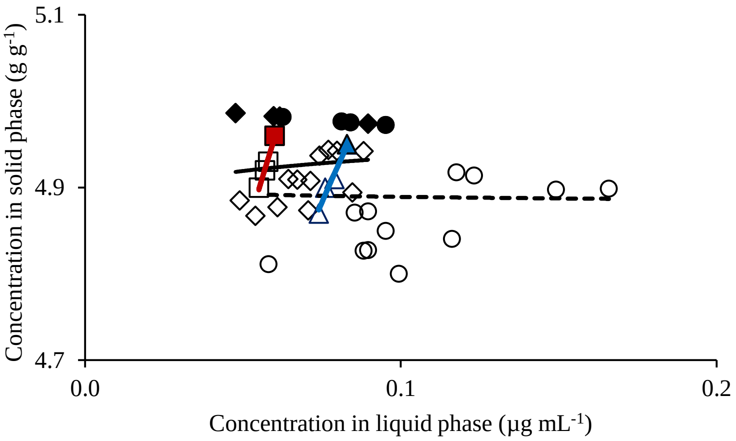
(b)


Concentration in solid phase (g g-1)
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
0.4
Concentration in liquid phase (μg mL-1)

(c)


Concentration in solid phase (g g-1)
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
Concentration in liquid phase (μg mL-1)

(d)



(e)

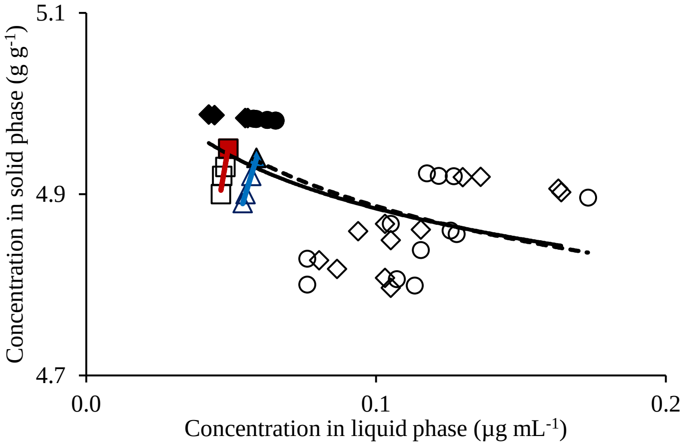
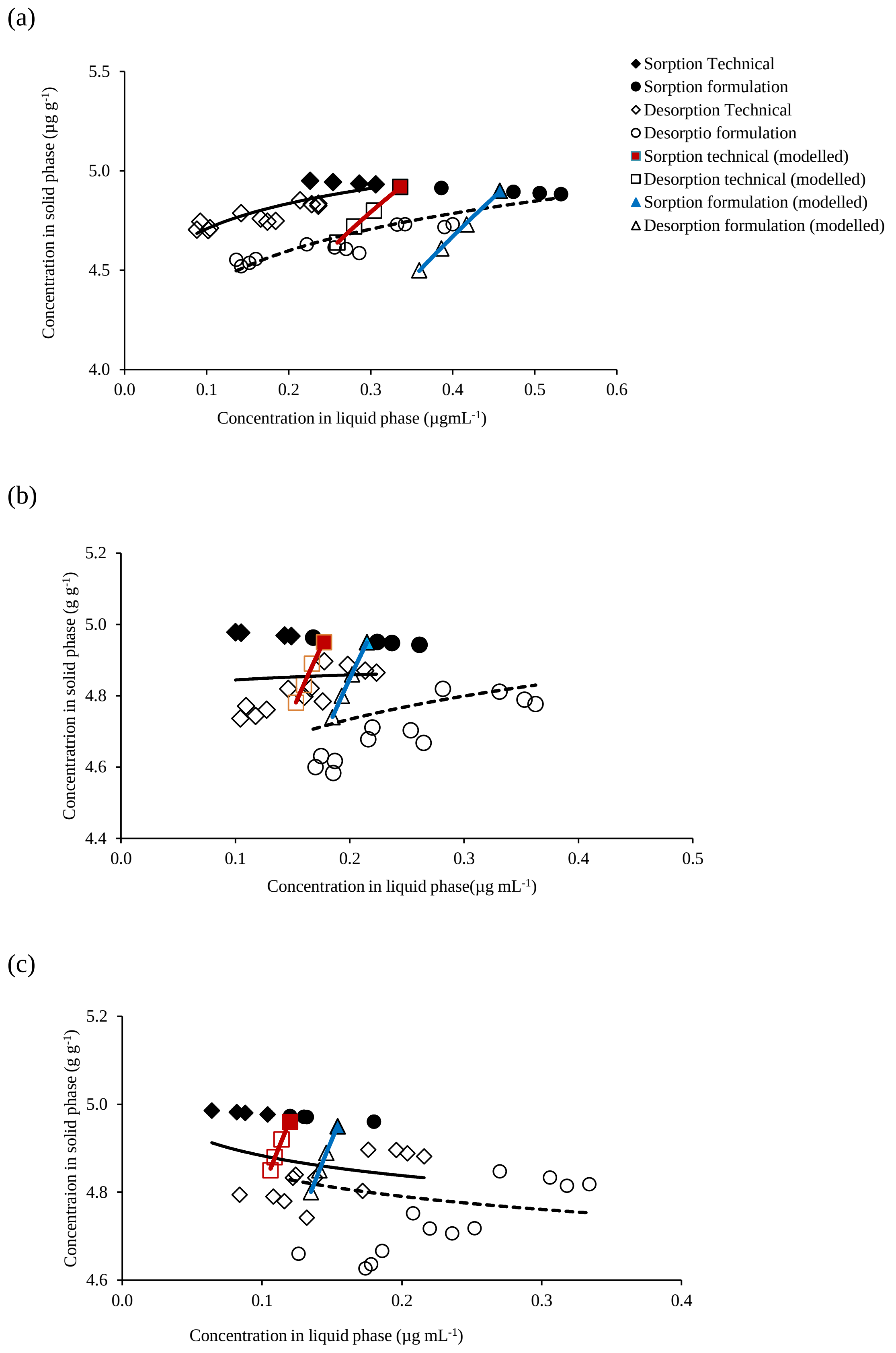


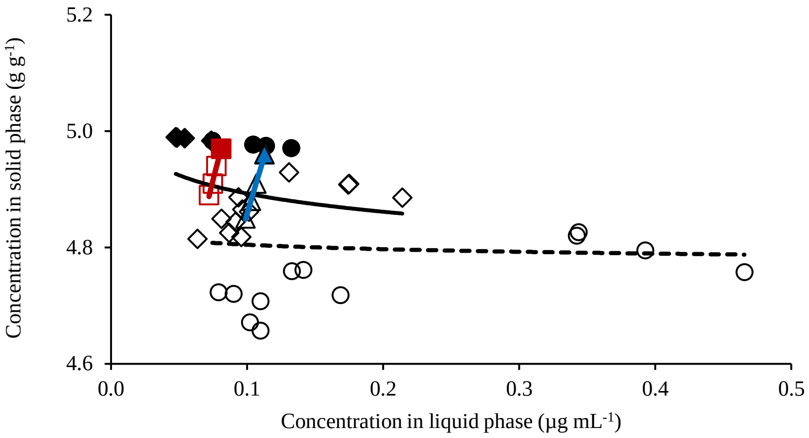
Figure 6.10: *Measured and modelled desorption isotherms of propyzamide in sandy loam silt soil for the time intervals of (a) day 1, (b) day 7, (c) day 14, (d) day 21, and (e) day 28. Blue and red coloured lines are the modelled isotherms of formulated and technical grade material. Note that the scale of the x and y-axis changes between individual figures.*

6.3.4. Three-site desorption model

The three-site desorption model was also applied to data from the desorption experiment by centrifugation (Chapter 5, section 5.3.3). The model fit was implemented step-wise, by first fitting the parameters to the adsorption data and then transferring those parameter values over to three-site desorption model to fit the desorption data without optimisation. The model failed to describe the desorption behaviour of propyzamide over-time that was measured experimentally as illustrated in Figures 6.11 and 6.12 for the sandy loam and sandy silt loam soils.



(d)



(e)

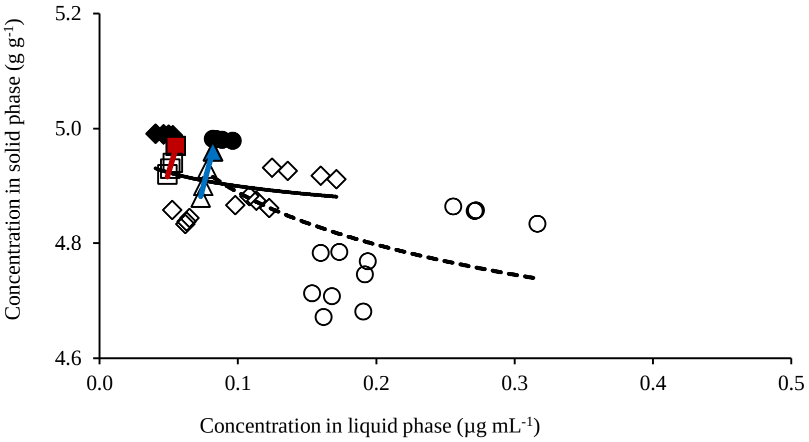
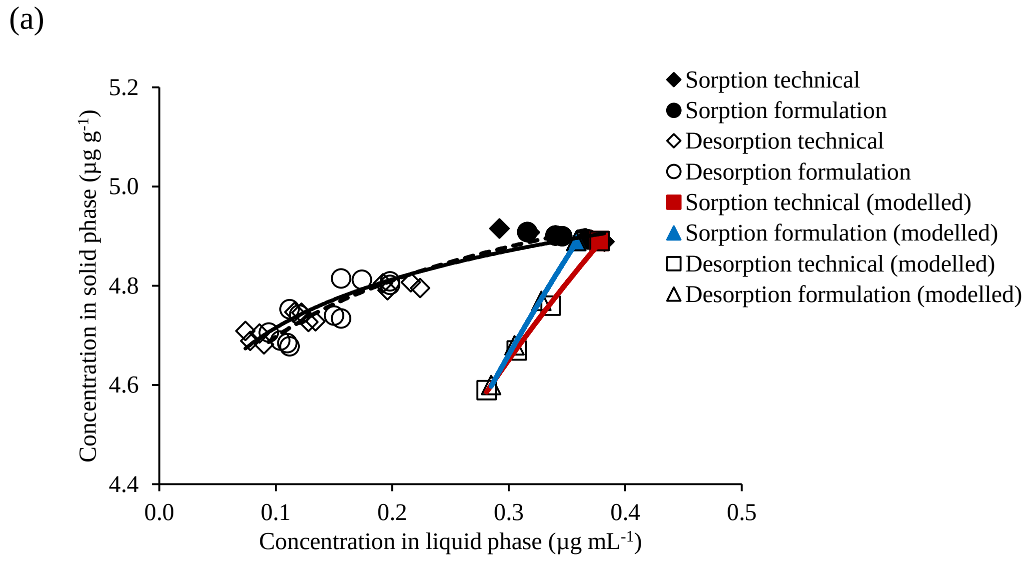
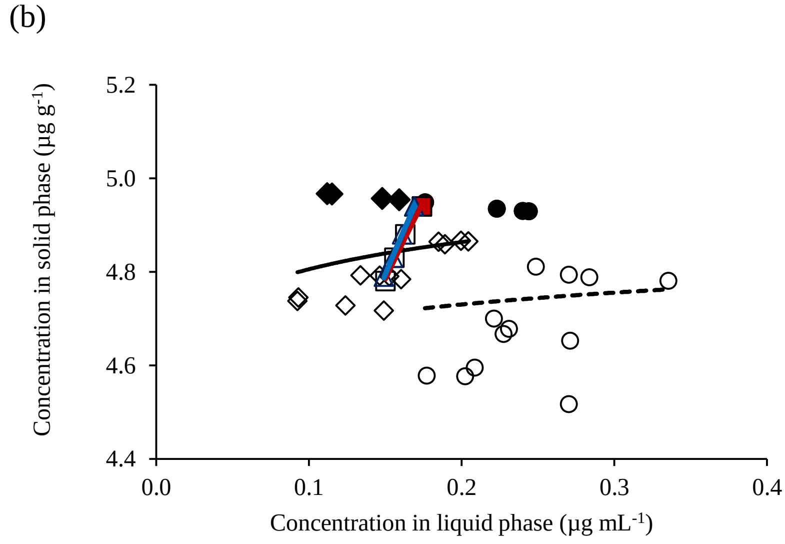
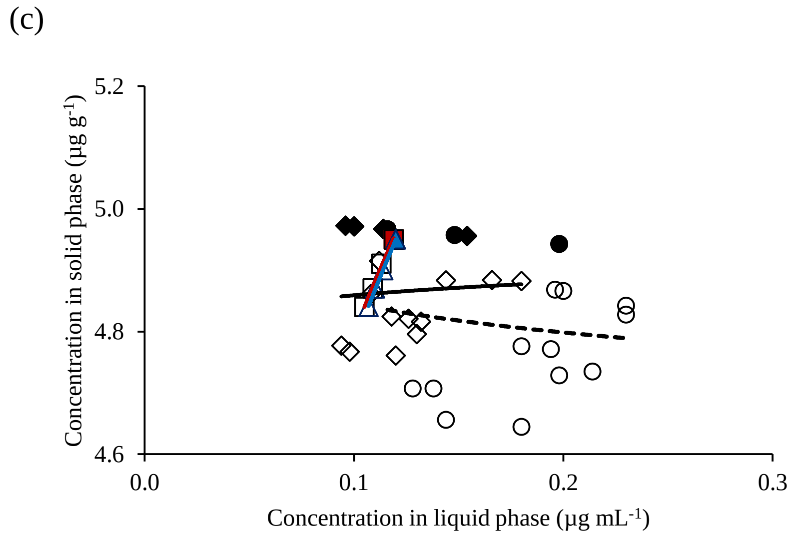


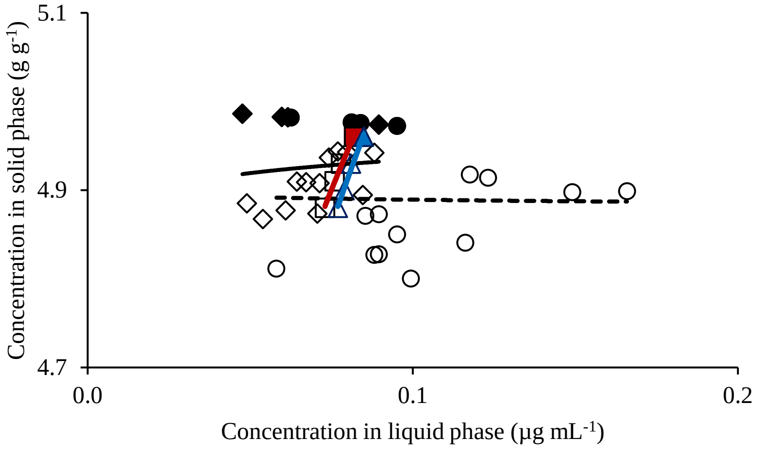
Figure 6.11: *Measured and modelled desorption isotherms of propyzamide in sandy loam soil for the time intervals of (a) day 1, (b) day 7, (c) day 14, (d) day 21, and (e) day 28. Blue and red coloured lines are the modelled isotherms of formulated and technical grade material. Note that the scale of the x and y-axis changes between individual figures.*


(a)
Sorption technical
Sorption formulation
Desorption technical
Desorption formulation
Sorption technical (modelled)
Sorption formulation (modelled)
Desorption technical (modelled)
Desorption formulation (modelled)
Concentration in solid phase (µg g-1)
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
0.4
0.5
Concentration in liquid phase (µg mL-1)


(b)
Concentration in solid phase (µg g-1)
5.2
5.0
4.8
4.6
4.4
0.0
0.1
0.2
0.3
0.4
Concentration in liquid phase (µg mL-1)


(c)
Concentration in solid phase (µg g-1)
5.2
5.0
4.8
4.6
0.0
0.1
0.2
0.3
Concentration in liquid phase (µg mL-1)

(d)



(e)

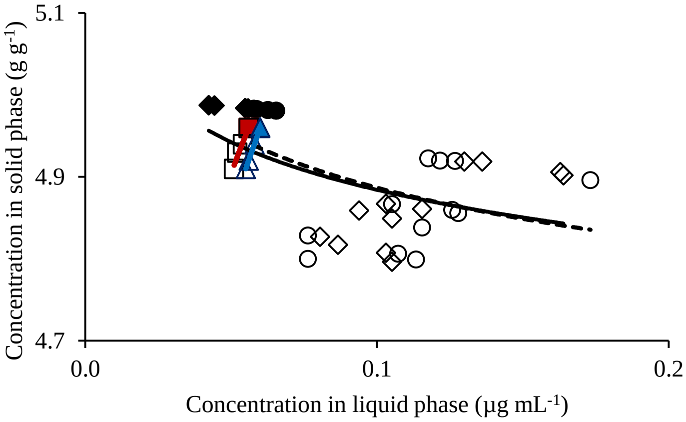


Figure 6.12: *Measured and modelled desorption isotherms of in sandy silt loam soil for the time intervals of (a) day 1, (b) day 7, (c) day 14, (d) day 21, and (e) day 28. Blue and red coloured lines are the modelled isotherms of formulated and technical grade material. Note that the scale of the x and y-axis changes between individual figures.*

6.4. Discussion

Models are currently being used to describe and predict the fate and behaviour of chemicals released into the environment. Such models use the data from experimental studies and provide important regulatory information on the behaviour of pesticides in the environment that can be used to take control measures in future scenarios. The mathematical formulations and the differences in parameters that are used to fit the experimental data from various treatments provide useful information about the differences in the data. Time-dependent sorption-desorption studies were carried out on propyzamide using a centrifugation technique (Chapter 5). In this chapter, modelling was used to describe and interpret these data.

Initially, a two-site model was applied to explore the sorption data of propyzamide over time based on slow but reversible sorption. This was important as many authors emphasised that the sorption of pesticides in soil is a slow process that progress over a relatively long period of time to reach equilibrium (Koskinen and Harper, 1990; Pignatello and Xing, 1996; Pignatello, 1998; Pignatello, 2000; Walker *et al*., 2005; Mamy and Barriuso, 2006). Initially, the attempt was made to fit the model with measured Freundlich parameters but it failed. Then the parameters n_f, K_{omeq}, and K_{des} were allowed to optimise and the model fitted the data well. The optimised values of n_f generated by the model were very small compared to the measured values. The n_f values generated by the model ranged between 0.28 and 0.31 for different treatments in the two soils (Table 6.3), while the corresponding values measured experimentally for different treatments ranged between 0.55 and 0.70 in the two soils (Table 6.1). Furthermore, the modelled n_f and K_{omeq} values were very similar for the technical grade and formulated product in either soil. The K_{des} values generated by the model for the technical grade material and formulated product in the sandy loam soil were 0.066 and 0.045, respectively, while the corresponding values in the sandy silt loam soil were 0.035 and 0.026 respectively (Table 6.3). The difference in the K_{des} values between the technical grade material and the formulated product were 32% and 25% in the sandy loam and sandy silt loam soils, respectively. The smaller values of K_{des} from the formulated product in the two soils indicate that the pesticide moves from the equilibrium phase into the non-equilibrium phase more slowly compared to that from the technical grade material. This may be due to the effect of formulation as the co-formulants may be holding the chemical in soil solution in the equilibrium domain, hence preventing the chemical from moving into the non-equilibrium phase at the same rate as for the technical grade material. The model reflected this behaviour in the form of large differences in the K_{des} values between the two treatments in both soils.

The three-site model was then applied to the data to include irreversible sorption from the non-equilibrium phase. Initially, the model fitted the data well by using the measured values for n_f and K_{omeq} and allowing K_{des} and K_{irr} to optimise (Figure 6.5). There were differences in the parameter values generated by the model when fitted to the experimental data. As for the two-site model, the K_{des} values generated by the three-site model for the formulated product were smaller than the corresponding values for the technical grade material (Table 6.4). This indicates that the kinetics of sorption process may be slower in the presence of formulation. The values for the irreversible sorption rate constant (K_{irr}) were similar for the formulated and technical grade material in the sandy loam as well as in the sandy silt loam soil (Table 6.4). However, the K_{irr} values for the sandy silt loam soil were smaller than those for the sandy loam soil suggesting that the rate of irreversible sorption was higher in sandy loam soil. Similar behaviour was also observed when the n_f and k_{omeq} were allowed to optimise together with k_{des} and k_{irr}.

Both the two-site and three-site models were able to fit the adsorption behaviour of propyzamide well with low optimisation errors, however, the n_f values returned by the two models were always very smaller than those measured experimentally. The model fit to the experimental data by the two-site model (Table 6.3) and three-site model (Table 6.5) are equally good, suggesting that the irreversible sorption was not needed to describe the sorption phase of the data. However, when the two-site and three-site desorption models were applied to the data, both the models failed to describe the desorption behaviour of propyzamide measured by centrifugation experiments. The measured desorption data showed higher concentrations of propyzamide during the desorption steps compared to the concentrations of the compound measured in the adsorption steps for all time intervals greater than 1 day and the model could not fit that behaviour (Figures 6.9 to 6.12). The desorption curves from the measured data shifted across to the right and this behaviour was completely different from the typical desorption behaviour that was expected.

Overall, the two-site and three-site sorption models were able to interpret the data well and provided valuable information about the different sorption processes and through the differences in K_{des} values, the models gave an indication that the formulation may be affecting some of the sorption processes occurring in the studied systems. At present, there are no components and controls in the models that could define the effects of formulation or suggest that the co-formulants are responsible to effect the strength of sorption or strength of irreversible binding. In order to better interpret the data and the effects the formulation may have on different sorption process, it would be more useful to develop a model with the extra processes that define the effects of formulation. For example, the extra processes that define whether the co-formulants facilitating the sorption of pesticides to the soil or holding the chemical in the solution phase need to be incorporated into the model to better describe the behaviour of pesticide in soil under the effect of formulation.

6.5. Conclusion

Modelling approach is current state of the art knowledge that is used to describe and predict the fate and behaviour of chemicals released into the environment. Such models use the data from experimental studies and provide important regulatory information on the behaviour of pesticides in the environment that can be used to take control measures in future scenarios. The mathematical formulations and the differences in parameters that are used to fit the experimental data from various treatments provide useful information about the differences in the data. Two-site and three site models were applied in order to describe the sorption and desorption data of propyzamide from Chapter 5 in greater detail, hence to understand various processes that are responsible for equilibrium and non-equilibrium sorption of pesticides within soil systems. Both the were able to fit the adsorption behaviour of propyzamide well. The model fit to the experimental data by the two-site model and three-site model were equally good, suggesting that the irreversible sorption was not needed to describe the sorption phase of the data. Overall, the models provided the useful information on the differences in the sorption processes particularly in the K_{des} values suggesting that the formulation may be affecting some of the sorption processes occurring in the studied systems. However, when the two-site and three-site desorption models were applied to the data, both the models failed to describe the desorption behaviour of propyzamide measured by centrifugation experiments. The desorption curves from the measured data shifted across to the right and this behaviour was completely different from the typical desorption behaviour that was expected. It would be more useful to develop models with extra processes that also define whether the co-formulants hold the chemical in the solution phase or facilitate sorption of active substance to the soil.

Chapter 7

GENERAL DISCUSSION AND FUTURE RESEARCH

7.1. General discussion and main findings

Continued use of pesticides in agricultural practices is vital in order to safeguard crops from harmful insect pests, fungal diseases and unwanted plants and weeds, hence to boost net productivity to meet the demand for food. However, pesticides are also important environmental contaminants which can impact on air, soil and water resources. Once in the soil, the fate and behaviour of a pesticide is strongly influenced by sorption processes. Mechanisms involved in the sorption of pesticides in soils have been extensively investigated over the past few decades (Pignatello and Xing, 1996; Reid *et al*., 2000; Barriuso *et al*., 2008). Sorption controls the availability of pesticides in soil solution and hence their uptake by plants and transport to surface and groundwater. Research focusing on the sorption behaviour of pesticides is generally aimed at developing the understanding of pesticide/soil interactions which are complex in nature and are influenced by soil and pesticide characteristics. A wide range of pesticide formulations are currently available on the market and these are used according to their specific label recommendations.

Sorption phenomena have been discussed in detail in Chapter 2. Sorption of pesticides in soil is generally measured using a standard batch-equilibrium method. This technique may be convenient when standardised measurements of the adsorption of pesticides in soil are required, however, the results may not be directly relevant to the interactions that occur under natural moisture conditions in the field.

Instead, the centrifugation method introduced by Walker (2000) is increasingly popular in terms of characterising time-dependent sorption behaviour of pesticides in soils (Beulke *et al*., 2004; Yazgan *et al*., 2005; Kah and Brown, 2007). The conditions used in the centrifugation method are realistically close to those in the field and various limiting factors on pesticide sorption such as soil moisture content, soil structure and diffusive movement of pesticide through complex pore systems are taken into account when characterising time-dependent sorption.

The overall aim of this PhD was to investigate the influence of co-formulants in commercial pesticide formulations on the sorption and leaching of their active substances in soils. The work used different experimental methods to characterise the effects of formulation on chromatographic leaching and sorption/desorption behaviour of pesticides. This was achieved by comparing behaviour of technical grade and formulated products of pesticides under controlled experimental conditions. The effects of formulation on the leaching behaviour of pesticides were investigated by carrying out a series of column leaching experiments. Sorption behaviour was characterised by batch-equilibration method as well as an *in-situ* centrifugation technique under realistic soil moisture conditions close to those in the field.

The main findings of the work carried out in this thesis were:

(i) In the experimental systems which comprised of four pesticides, two different formulation types, two different soil types and multiple times from application, in every instance the leaching of the formulated material was greater than the leaching of the technical grade material and this was highly statistically significant ($p<0.001$).

(ii) Leaching markedly decreased over time between application and irrigation and this was also very significant ($p<0.001$). Furthermore, there was also an effect of soil type on the leaching behaviour of studied chemicals. The pattern of behaviour in leaching was very consistent for the four compounds in the sandy loam soil. The sandy silt loam soil was only tested for propyzamide where the behaviour was much less consistent over time decreasing initially and then increasing during later time intervals (Chapter 4, Figure 4.1).

(iii) Solubility of the active substance influenced the effect of formulation on leaching of pesticides. The relative difference in mass leached between formulated and technical grade material for low solubility pesticides was less than that for pesticides with greater water solubility (Chapter 4, Figure 4.3). However, these findings are limited to the specific pesticide/soil systems and experimental conditions studied and the behaviour may vary for different formulations of other compounds in different soils.

(iv) The type of formulation influenced the effect of formulation on leaching behaviour of pesticides. Greater leaching losses of pesticide were observed from an EC formulation compared to the SC formulation for the fungicide azoxystrobin on day one and seven after treatment (Chapter 4, Figure 4.4). The effect of formulation type was found to be highly statistically significant ($p<0.001$). The relative difference in mass leached between technical grade material and SC formulation of azoxystrobin were factors of 1.4 and 1.5 on different time intervals, while the corresponding differences for the EC formulation were factors of 2.6 and 3.5 for different time intervals.

(v) Breakthrough curves of the fungicide triadimenol showed that the absolute leaching losses of the compound from solutions of technical grade material were smaller than those from the solutions of formulated product. Cumulative breakthrough curves (Chapter 4, Figure 4.6) show that at the end of the experiment, the total leaching losses of triadimenol from columns treated with the technical grade material were around 60%, while the corresponding losses were around 80% from the columns treated with the commercial product. These results indicate that the differences in the total mass of pesticide leached between the technical grade material and the formulated product are maintained even if the leaching is carried out for a long time and under an excess of irrigation water.

(vi) Results from the batch experiments indicate that the sorption behaviour of propyzamide from the solutions of technical grade material and formulated product was generally similar in both soils (Chapter 5, Figure 5.1, and Tables 5.1 & 5.2). Despite the differences in hysteresis indices, there were no apparent differences in the Freundlich desorption coefficients of technical grade material and commercial formulation of propyzamide in either soil. These results challenge the existing literature on the effect of formulation which is primarily based on batch studies.

(vii) There was less sorption of propyzamide from formulated product compared to the technical grade material when characterised by a centrifugation technique (Chapter 5, Figure 5.3). The effect of formulation on sorption of propyzamide in the sandy loam soil was highly statistically significant ($p<0.001$), but there was no effect of formulation on sorption in the sandy silt loam soil. Furthermore, there was a large increase in the strength of sorption of propyzamide over time in both soils and for both technical grade material and formulated product.

(viii) The availability of propyzamide in pore water rapidly decreased over time for both treatments and this behaviour was very consistent in the two soils. The effect of residence time on the availability of pesticide in pore water was highly statistically significant ($p<0.001$).

(ix) Desorption of propyzamide investigated by the centrifugation method showed that values of the Freundlich desorption coefficients (K_{fdes}) for the technical grade material and formulated product were very similar for all time intervals in the two soils. The n_f values ≤ 0.035 indicate that there was a very large hysteresis in the desorption from the two treatments in both soils. However, the desorption isotherms of propyzamide from technical grade material and commercial formulation showed an unexpected behaviour for all time intervals longer than 1 day where isotherms shifted towards the right due to greater masses of propyzamide extracted during the desorption steps compared to those found in pore water during the adsorption steps (Chapter 5, Figures 5.5 & 5.6).

(x) Two-site and three-site sorption and desorption models were applied to the sorption and desorption data from the centrifugation experiment (Chapter 5) to interpret sorption behaviour of propyzamide in greater detail and to understand various mechanisms involved in sorption kinetics. The two-site and three-site sorption models fitted the experimental data equally well ($r^2 \geq 0.96$), suggesting that the irreversible sorption was not needed to describe the adsorption phase of the data. The Freundlich parameters returned by the models were very similar, however, the K_{des} values for the formulated product were always smaller than those for the technical grade material suggesting that formulation may be influencing the rate of movement of chemical from the equilibrium phase to non-equilibrium phase. However, the two-site and three-site desorption models fail to explain the desorption behaviour of propyzamide.

The research presented in this thesis shows that the product formulation significantly influenced the leaching behaviour of pesticides in the two soils. Greater leaching losses were observed from the commercial pesticide formulations compared to their technical grade materials for all the pesticides studied. The research reported in the literature on the effects of formulation on pesticide behaviour is largely focused on the interactions of co-formulants with the strength of sorption of pesticides in soil. However, only few authors have considered the effects of formulation on leaching behaviour of pesticides. Sharma *et al*. (2013) compared the leaching behaviour of the technical grade material and EC formulation of hexaconazole in five different soils varying in texture from sandy loam to clay. Although they reported that the herbicide was more mobile in sandy loam soil compared to clay soil, they did not observe any differences in the leaching behaviour between the two treatments. Their experimental setup was totally different from that used here as they used larger soil columns and mostly studied the movement of pesticide within soil columns rather than breakthrough in leachate.

Most of the evidence on the availability for transport of pesticides in soil solution comes from sorption studies. Beigel and Barriuso (2000) and Oukali-Haouchine *et al*. (2013) have suggested through their sorption experiments that co-formulants and additives in commercial formulations may favour maintaining pesticide molecules in solution. It has also been suggested that slow separation of the pesticide molecule from the surrounding co-formulants within soil may prevent the sorption process from occurring at the same rate as would happen for the technical grade material (Pose-Juan *et al*., 2011). This may result in greater availability of pesticide from formulated products in soil solution which can potentially be leached through soil in response to irrigation or rainfall events. Földényi *et al*. (2013) reported that the presence of the forming agent Supragil (an anionic dispersant) resulted in a decrease in adsorption of chlorosulfuron and hence increased environmental mobility of the pesticide. However, there are also some confounding studies where it has been reported that the co-formulants may enhance the sorption of active substance due to a layering effect. For example, Beigel *et al*. (1998) reported that the sorption of triticonazole can be increased by up to 50% in the presence of higher concentrations of non-ionic hydrophobic surfactants. They argued that the additional surfactant monomers may sorb on the monolayer of hydrophilic heads of surfactants already sorbed in soil resulting in a bilayer of surfactant on the soil surfaces which would considerably enhance the sorption of triticonazole on soil surfaces. The retention of metalaxyl in soil was ten times higher from solutions of formulated product (copper oxychloride-metalaxyl formulation) compared to those for technical grade material (Pose-Juan *et al*., 2010a). The authors suggested that the pesticide may be adsorbed by surfactants previously adsorbed into the soil resulting in increased pesticide retention in soil. Pose-Juan *et al*. (2010b) also reported that about 30% of the penconazole retained by the solid phase was retained by the adjuvants present in the commercial formulation (water-oil emulsion formulation). Results from the current research in this thesis suggest that holding in the solution was the dominant mechanism for the studied pesticides as mobility was greater from the formulated products.

The research in this thesis identifies that both solubility of the active substance and the type of formulation also influenced the effect of formulation on leaching behaviour of pesticides. The effects of formulation were more pronounced for high solubility compounds. This study experimentally reported greater leaching losses of the fungicide azoxystrobin from an EC formulation compared to SC formulation under the same experimental conditions and with the same application rate. Enhanced leaching losses of propoxur have been reported previously from an emulsion form compared to both suspension form and pure active substance in loamy sand to sandy loam soils (Wybieralski, 1992).

Sorption of pesticides in soil is a complex process and it is very difficult to isolate the various mechanisms responsible for the retention of pesticides in soil. The sorption phenomenon and various factors that control pesticide sorption in soil have been discussed in detail in Chapter 2. It is now widely accepted that sorption of pesticides in soil is a time-dependent process that may progress over a relatively long period of time to reach equilibrium (Koskinen and Harper, 1990; Pignatello and Xing, 1996; Pignatello, 2000; Boivin *et al*., 2005; Walker *et al*., 2005; Mamy and Barriuso, 2006). The research presented in this thesis on the sorption behaviour of propyzamide by the centrifugation method showed that there was a large increase in the strength of sorption of propyzamide over time in both soils and for both technical grade material and formulated product. There is strong evidence in the literature that suggests that the strength of sorption increases with increasing residence time in soil resulting in a decrease in the availability of pesticide for transport or uptake by soil organisms (Cox and Walker, 1998; Walker and Jurado-Exposito, 1998; Koskinen *et al*., 2001; Beulke *et al*., 2004; Boivin *et al*., 2004; Renaud *et al*., 2004; Mamy and Barriuso, 2007; Ortiz-Hernández *et al*., 2011).

The research presented in this thesis on the effects of formulation on sorption and desorption behaviour of propyzamide was carried out using a standard batch-equilibrium method and a centrifugation technique in the two soils. The results from the batch study suggest that the sorption and desorption behaviour of propyzamide from the technical grade material and the formulated product was generally similar. However, significant effects of formulation were observed on the sorption behaviour of propyzamide in sandy loam soil when characterised by a centrifugation method. The literature dealing with the effect of formulation on pesticide behaviour discussed in Chapter 2 (Section, 2.7.2) is dominated by batch method (Beigel *et al*., 1998; Beigel and Barriuso, 2000; Garcia-Ortega *et al*., 2006; Pose-Juan *et al*., 2010a; Pose-Juan *et al*., 2010b; Pose-Juan *et al*., 2011; Földényi *et al*., 2013). The results from the batch experiments carried out here indicate that a batch-equilibrium method is not the best way to study the effect of formulation on pesticide sorption.

Generally, the effects of formulation on leaching behaviour of propyzamide could not be adequately linked to the effect of formulation on its sorption behaviour in the two study soils. As discussed in Chapter 4, enhanced leaching of formulated material was observed from column experiments which was independent of time and soil type. However, the patterns in leaching of the formulated and technical material were different from the patterns in sorption of the formulated and technical material over time and the effect of pesticide formulation on sorption was not sufficient to fully explain the enhanced leaching of propyzamide from commercial formulation in soil columns. Attempts were made to explain this behaviour by carrying out desorption experiments on propyzamide under more natural soil moisture conditions using a centrifugation method. However, unexpected desorption behaviour was observed which could not be explained readily. Large concentrations of propyzamide were observed in the soil solution during the initial desorption steps and this behaviour deviated from the typical desorption behaviour for organic molecules in soil. To date, there is no evidence in the literature where a similar method has been used to characterise the desorption behaviour of pesticides. Furthermore, desorption data suggest that there was very slow release of pesticide out of the soil whereas this was observed to proceed much faster under the leaching conditions. At present, the results from the sorption experiments discussed in this thesis do not provide a clear link to the behaviour of pesticides observed during the leaching experiments. Thus, further experimental work is needed to explore the effects of formulation on sorption under realistic soil moisture conditions, including the desorption behaviour using a centrifugation technique.

7.2. Implications

The implications of this research are:

(i) The existing knowledge about the formulation effects is not sufficient. To gain more valuable insight it is now necessary to carry out more detailed leaching and sorption experiments with a wide range of chemicals and formulation types in arable soils. The knowledge based on the experimental data can be applied to design effective pesticide formulations and will help to use the types of formulations that are safer for the environment.

(ii) There has been a lot of contamination of water resources by propyzamide than would expect from its physico-chemical properties and looking at the data from this research, it seems quite plausible that actually it’s the formulation effect that results in greater leaching losses of the compounds and there is an interplay between pesticide and the formulation.

(iii) The results from this research suggest that it is important to consider the effects of formulation during risk assessment of environmental fate and behaviour of pesticides. It is important to generate more data on the fate and behaviour of pesticides under the effect of formulation, particularly the leaching and sorption behaviour of pesticides and whether it has any effects on water quality, air and human health.

(iv) The result from this study also suggest that batch equilibrium method is not suitable to study the effects of formulation on pesticide sorption in soil. The formulation effects on sorption could be more effectively characterised by using a centrifugation technique under realistic soil moisture conditions.

(v) The knowledge from the current research may also affect pesticide regulations in the UK as the agrochemical products are widely applied to agricultural crops in this country. The research presented in this thesis provides some interesting results but are only based on relatively few chemical products. It is important to carry out field experiments in the future for a range of arable soils using different commercial products to investigate the effects of formulation on pesticide fate and behaviour under natural conditions. If results from the field experiments suggest that formulation really makes a difference in the field and cause enhanced leaching of pesticides; then it may affect pesticide regulations in the UK. At present the use of the co-formulants is not tightly regulated as they are not considered toxic to life. However, based on the current and future research, it may be possible that in addition to the active substances, the use of co-formulants in commercial pesticide products may also be firmly regulated by law that will set strict conditions on the ways these products are formulated and can be used. The regulatory authorities may bind the agrochemical companies to design safer formulations by using co-formulants that also minimise the leaching losses of the active substances, hence to ensure that these co-formulants do not harm life either directly or indirectly by affecting the behaviour of the active substance. In Particular, the types and concentrations of co-formulants that are currently being used in commercial pesticide formulations may subject to strict regulatory control.

7.3. Future research

(i) The key research requirement from these findings is that the formulation effects should be considered when designing the commercial plant protection products. In order to develop better formulations that are safe for the environment, it is not only important to test the formulation but it is also necessary to test the individual co-formulants. This can be achieved with more specific experiments by splitting the formulation into individual ingredients and then testing their effects in isolation as well as in combination with other co-formulants. This would provide key information to design and develop better formulations which may minimise the leaching losses of active substances through soil.

(ii) The leaching and sorption behaviour of pesticides was much more variable in sandy silt loam soil compared to the sandy loam soil. It would be valuable to carry out more detailed experiments in a wide range of arable soils varying in texture and organic matter content. This will help generate important data for comparisons. This research reports that the leaching losses of the fungicide azoxystrobin were greater from an EC formulation compared to those from the SC formulation. Although, these findings cannot be generalised to other test systems, it would be useful to test different formulation types for a wider range of chemicals in arable soils.

(iii) The current study in this thesis is based on the laboratory experiments under controlled experimental conditions. It is important to carry out field experiments in future to test whether formulation makes any difference in the real world under natural conditions. This could be achieved by doing some controlled leaching experiments with technical grade material and formulated products in the field by using small plots or lysimeters.

(iv) The desorption behaviour of propyzamide characterised by the centrifugation method could not be adequately linked to its leaching behaviour from soil columns, nor was it explained by modelling. The method employed has not been used previously and the unexpected desorption behaviour may be due to an experimental artefact. More detailed experiments are needed to improve this method so that it is applicable in future research to investigate the desorption behaviour of pesticides at natural soil water contents. It is recommended that longer desorption steps should be used in order to generate more robust desorption data. It would be useful if the sorption models in their extended form could be applied to leaching data. Additional processes in the model that also define formulation as a control would help generate more detailed information on the formulation effects. This would allow to do better extrapolation to the natural conditions in the field.

7.4. Conclusion

The work carried out in this thesis has demonstrated that the co-formulants in commercial plant protection products can have a significant influence on the environmental fate and behaviour of pesticides. This research explicitly focused on the effects of formulation on the sorption and leaching of four pesticides in sandy loam and sandy silt loam soils. This was achieved by comparing the behaviour of technical grade and formulated products of pesticides under controlled experimental conditions. The effects of formulation on the leaching behaviour of pesticides were investigated by carrying out a series of column leaching experiments. Sorption behaviour was characterised by batch-equilibrium method as well as an *in-situ* centrifugation technique under realistic soil moisture conditions close to those in the field. The results report that the leaching of pesticides from the formulated products was always greater than that from their technical grade materials and this was highly statistically significant (p<0.001). The effects of residence time and soil type on the leaching behaviour of pesticides were also found to be highly statistically significant. Both solubility of the active substance and the type of formulation also influenced the effect of formulation on leaching behaviour of pesticides. The effects of formulation on the sorption and desorption behaviour of propyzamide could not be isolated by a standard batch-equilibration method. However, the availability of propyzamide in pore water from the formulated product was greater than that from the technical grade material in sandy loam soil and this was highly significant (p<0.001). Desorption of propyzamide investigated by the centrifugation method showed an unexpected behaviour which could not be explained readily. Results suggested that any effect of formulation on pesticide sorption was not sufficient to explain fully the effect of formulation on leaching behaviour. Two-site and three-site models applied and fitted the sorption phase of experiments well. However, the models failed to describe the observed desorption behaviour of propyzamide. The research presented in this thesis carries important implications and highlights gaps in the existing knowledge about the formulation effects on pesticide behaviour in soil and suggest that impact of co-formulants on pesticide behaviour should be considered during the risk assessments.

Appendix A

Table A.1: *Volumes of water (cm^3) leached from sandy loam soil treated with technical grade material and commercial formulation of propyzamide during various irrigation events.*

	Technical grade material					**Commercial product (Kerb Flo)**				
Time intervals	1	7	14	21	28	1	7	14	21	28
Replicates										
1	54.33	54.13	54.30	53.96	53.16	53.95	53.76	52.88	52.74	52.84
2	54.05	55.76	54.82	54.14	53.55	54.08	54.37	53.89	53.13	52.08
3	53.61	54.30	54.80	53.84	54.08	54.03	54.09	52.92	54.65	52.68
4	54.88	54.39	54.44	53.21	52.57	53.54	54.27	52.77	53.26	53.18

Table A.2: *Volumes of water (cm^3) leached from sandy silt loam soil treated with technical grade material and commercial formulation of propyzamide during various irrigation events.*

	Technical grade material					**Commercial product (Kerb Flo)**				
Time intervals	1	7	14	21	28	1	7	14	21	28
Replicates										
1	53.41	53.80	53.67	52.35	52.76	53.96	54.79	52.88	53.34	53.37
2	53.41	53.22	53.29	51.87	52.87	53.48	55.03	54.21	53.74	53.76
3	52.72	54.91	53.04	52.60	53.33	53.74	53.78	53.53	53.08	53.26
4	53.77	53.65	53.81	52.37	53.27	53.53	55.38	53.78	53.56	53.38

Table A.3: *Masses of propyzamide (µg) in water leached from sandy loam soil treated with technical grade and commercial product on different time intervals after treatment.*

Treatment	**Technical grade propyzamide (µg)**					**Commercial Product (Kerb Flo) (µg)**				
Time interval	1	7	14	21	28	1	7	14	21	28
Replicates										
1	7.10	6.00	6.00	2.20	0.50	9.71	11.30	11.10	2.60	2.60
2	7.00	6.70	6.60	3.20	1.10	16.80	9.20	5.40	8.50	3.10
3	7.00	5.40	5.50	2.20	1.60	15.70	11.40	10.60	7.70	7.90
4	7.70	7.60	4.40	3.20	1.10	15.50	13.60	6.30	7.50	7.40

***Table A.4:** Masses of propyzamide (µg) in water leached from sandy silt loam soil treated with technical grade and commercial product on different time intervals after treatment.*

Treatment	**Technical grade propyzamide (µg)**					**Formulated propyzamide (µg)**				
Time intervals	1	7	14	21	28	1	7	14	21	28
Replicates										
1	4.81	3.77	2.15	2.10	3.20	7.55	2.74	2.11	10.70	5.90
2	2.14	1.60	2.13	1.04	3.20	6.42	2.75	2.71	9.70	7.53
3	4.75	1.65	2.12	1.60	3.73	8.60	5.40	3.21	8.50	7.50
4	5.40	3.75	1.61	2.10	3.20	5.35	2.21	2.70	9.64	5.34

***Table A.5:** Mean mass (g) of propyzamide leached from sandy loam and sandy silt loam soils treated with technical grade and formulated propyzamide on different leaching occasions. The value in parentheses is the standard deviation for four replicates.*

Soil type	**Formulation**	**1**	**7**	**14**	**21**	**28**
Sandy loam	Technical grade	7.21 (0.33)	6.42 (0.95)	5.61 (0.95)	2.70 (0.61)	1.08 (0.45)
Sandy loam	Commercial product (Kerb Flo)	14.42 (3.19)	11.38 (1.78)	8.36 (2.91)	6.56 (2.65)	5.28 (2.78)
Sandy silt loam	Technical grade	4.28 (1.45)	2.69 (1.23)	2.00 (0.26)	1.71 (0.51)	3.33 (0.27)
Sandy silt loam	Commercial product (Kerb Flo)	6.98 (1.40)	3.28 (1.44)	2.68 (0.45)	9.64 (0.90)	6.57 (1.12)

***Table A.6:** Multi-way ANOVA for the tests of between-subject effects for formulation, residence time and soil type on the leaching behaviour of propyzamide through soil.*

Source	**Type III Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Corrected Model	869.063[a]	19	45.740	15.434	.000
Intercept	2486.785	1	2486.785	839.129	.000
Days	153.436	4	38.359	12.944	.000
Formulation	280.463	1	280.463	94.638	.000
SoilType	127.033	1	127.033	42.866	.000
Days * Formulation	41.939	4	10.485	3.538	.012
Days * SoilType	210.542	4	52.636	17.761	.000
Formulation * SoilType	10.346	1	10.346	3.491	.047
Days * Formulation * SoilType	45.302	4	11.325	3.822	.008
Error	177.812	60	2.964		
Total	3533.659	80			
Corrected Total	1046.874	79			

a. R Squared = .830 (Adjusted R Squared = .776)

Table A.7: *Volumes of water (cm^3) from individual replicates leached from sandy loam soil treated with technical grade material of studied pesticides on day 1 and day 7 after treatment.*

Treatment	**Technical grade material of pesticides**							
Chemicals	**Azoxystrobin**		**Propyzamide**		**Triadimenol**		**Cyproconazole**	
Time intervals	**1**	**7**	**1**	**7**	**1**	**7**	**1**	**7**
Replicate								
1	54.08	53.78	54.33	54.13	53.95	53.91	54.06	53.79
2	53.99	53.76	54.05	55.76	53.94	54.01	54.04	53.28
3	54.11	53.99	53.61	54.30	53.92	54.00	53.98	53.89
4	54.06	53.98	54.88	54.39	53.92	53.99	54.18	53.55

Table A.8: *Volumes of water (cm^3) from individual replicates leached from sandy loam soil treated with commercial products of studied pesticides on day 1 and day 7 after treatment.*

Treatment	**Commercial products of pesticides**							
Chemicals	**Azoxystrobin**		**Propyzamide**		**Triadimenol**		**Cyproconazole**	
Time intervals	**1**	**7**	**1**	**7**	**1**	**7**	**1**	**7**
Replicate								
1	54.00	54.00	53.95	53.76	53.78	53.79	54.13	53.96
2	54.25	54.14	54.08	54.37	53.96	53.97	54.25	54.00
3	54.07	53.95	54.03	54.09	54.11	53.94	53.90	53.48
4	54.12	54.20	53.54	54.27	53.87	53.93	54.20	53.52

Table A.9: *Masses of pesticides (µg) leached in water from individual replicates of sandy loam soil treated with technical grade materials of different pesticides on day 1 and day 7 after treatment.*

Treatment	**Technical grade materials of pesticides (µg)**									
Chemicals	**Azoxystrobin**		**Propyzamide**		**Triadimenol**		**Cyproconazole A**		**Cyproconazole B**	
Leaching days	**1**	**7**	**1**	**7**	**1**	**7**	**1**	**7**	**1**	**7**
Replicate										
1	5.90	5.84	7.10	6.00	27.77	23.74	5.72	4.63	1.77	1.73
2	5.94	6.87	7.00	6.70	28.78	23.83	5.54	5.93	1.87	2.51
3	5.94	5.42	7.00	5.40	27.90	24.80	5.90	5.008	2.18	1.73
4	6.08	5.82	7.70	7.60	27.64	25.78	6.01	4.97	2.29	1.89

Table A.10: *Mass of pesticides (µg) leached from individual replicates of sandy loam soil treated with formulated products pesticides on day 1 and day 7 after treatment.*

Treatment	**Commercial products of pesticides (µg)**									
Chemicals	**Azoxystrobin**		**Propyzamide**		**Triadimenol**		**Cyproconazole A**		**Cyproconazole B**	
Leaching days	**1**	**7**	**1**	**7**	**1**	**7**	**1**	**7**	**1**	**7**
Replicate 1	7.80	8.35	9.71	11.30	89.18	94.25	24.78	21.49	11.48	9.56
2	9.90	8.72	16.80	9.20	104.19	104.69	23.98	20.05	10.51	9.10
3	7.70	10.29	15.70	11.40	99.90	106.29	22.92	20.09	10.16	9.81
4	8.62	9.10	15.50	13.60	121.10	103.80	22.06	21.60	10.04	9.33

Table A.11: *Average mass (g) of pesticides leached from the two treatments through sandy loam soil on different leaching intervals. The values in the parenthesis are the standard deviation for four replicates.*

Pesticides	Technical Day 1	Formulated Day 1	Technical Day 7	Formulated Day 7
Azoxystrobin	5.965 (0.08)	8.504 (1.014)	5.991 (0.619)	9.114 (0.840)
Propyzamide	7.21 (0.33)	14.42 (3.19)	6.42 (0.95)	11.38 (1.78)
Cyproconazole A	5.793 (0.207)	23.437 (1.195)	5.134 (0.556)	20.805 (0.851)
Cyproconazole B	2.031 (0.247)	10.547 (0.656)	1.966 (0.370)	9.447 (0.305)
Triadimenol	28.020 (0.515)	103.593 (13.269)	24.538 (0.954)	102.256 (5.437)

Table A.12: *Multi-way ANOVA for the tests of between-subject effects for formulation, time and pesticide on the leaching behaviour of studied pesticides through sandy loam soil.*

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	60393.304^{a}	15	4026.220	200.086	.000
Intercept	46032.968	1	46032.968	2287.643	.000
Formulation	14026.312	1	14026.312	697.048	.000
Days	57.726	1	57.726	2.869	.096
Pesticide	34209.086	3	11403.029	566.682	.000
Formulation * Days	6.098	1	6.098	.303	.584
Formulation * Pesticide	13689.992	3	4563.331	226.778	.000
Days * Pesticide	4.779	3	1.593	.079	.971
Formulation * Days * Pesticide	16.247	3	5.416	.269	.847
Error	1126.857	56	20.122		
Total	105065.511	72			
Corrected Total	61520.161	71			

R Squared = .982 (Adjusted R Squared = .977)

Table A.13: *Two-way ANOVA to test between-subject effects of solubility and residence time on the leaching behaviour of studied pesticides through sandy loam soil.*

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	34280.946[a]	7	4897.278	10.223	.000
Intercept	41190.935	1	41190.935	85.988	.000
Days	34.893	1	34.893	.073	.788
Solubility	34227.382	3	11409.127	23.817	.000
Days * Solubility	18.671	3	6.224	.013	.998
Error	26825.616	56	479.029		
Total	102297.497	64			
Corrected Total	61106.562	63			

a. R Squared = .561 (Adjusted R Squared = .506)

Table A.14: *Mass of azoxystrobin (µg) leached in water through sandy loam soil from individual replicates on day 1 and day 7 after treatment with technical grade material and commercial products*

Treatment	Technical grade (µg)		Priori Xtra (µg)		Headway (µg)	
Leaching days	**1**	**7**	**1**	**7**	**1**	**7**
Replicate 1	5.904	5.842	7.800	8.352	22.248	16.616
2	5.938	6.872	9.896	8.720	19.328	13.440
3	5.936	5.424	7.704	10.288	20.992	16.984
4	6.080	5.824	8.616	9.096	21.320	16.096
Mean	**5.965**	**5.991**	**8.504**	**9.114**	**20.972**	**15.784**
STDEV	0.079	0.619	1.014	0.840	1.218	1.605

Table A.15: *Two-way ANOVA to test between-subjects effects of formulation type and residence time on the leaching behaviour of azoxystrobin through sandy loam soil.*

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	730.191[a]	5	146.038	141.763	.000
Intercept	2933.024	1	2933.024	2847.154	.000
Days	13.814	1	13.814	13.409	.002
Formulation type	675.615	2	337.807	327.917	.000
Days * Formulation type	40.762	2	20.381	19.785	.000
Error	18.543	18	1.030		
Total	3681.758	24			
Corrected Total	748.734	23			

a. R Squared = .975 (Adjusted R Squared = .968)

Table A.16: *Two-way ANOVA to test between-subjects effects of formulation and residence time on the leaching behaviour of diastereomer A of cyproconazole through sandy loam soil.*

Source	**Type III Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Corrected Model	1124.607[a]	3	374.869	598.932	.000
Intercept	3043.674	1	3043.674	4862.908	.000
Days	10.831	1	10.831	17.304	.001
Formulation	1109.889	1	1109.889	1773.281	.000
Days * Formulation	3.887	1	3.887	6.210	.028
Error	7.511	12	.626		
Total	4175.791	16			
Corrected Total	1132.117	15			

a. R Squared = .993 (Adjusted R Squared = .992)

Table A.17: *Two-way ANOVA to test between-subject effects of formulation and residence time on the leaching behaviour of diastereomer B of cyproconazole through sandy loam soil.*

Source	**Type III Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Corrected Model	258.291[a]	3	86.097	477.378	.000
Intercept	575.604	1	575.604	3191.523	.000
Days	1.357	1	1.357	7.522	.018
Formulation	255.864	1	255.864	1418.676	.000
Days * Formulation	1.071	1	1.071	5.937	.031
Error	2.164	12	.180		
Total	836.060	16			
Corrected Total	260.456	15			

a. R Squared = .992 (Adjusted R Squared = .990)

Appendix B

Table B.1: *Masses of propyzamide (µg) in pore water from all replicates on various time intervals for sandy loam soil*

Treatment	**Technical grade propyzamide (µg)**					**Commercial Product (Kerb Flo) (µg)**				
Leaching Days	1	7	14	21	28	1	7	14	21	28
Replicates										
1	1.023	0.389	0.207	0.233	0.158	1.307	0.660	0.352	0.273	0.172
2	0.937	0.482	0.304	0.220	0.180	1.082	0.601	0.356	0.299	0.268
3	1.056	0.422	0.167	0.211	0.106	1.505	0.871	0.559	0.277	0.211
4	1.109	0.330	0.238	0.150	0.134	1.498	0.792	0.295	0.370	0.264

Table B.2: *Masses of propyzamide (µg) in pore water from all replicates on various time intervals for sandy silt loam soil*

Treatment	**Technical grade propyzamide (µg)**					**Formulated propyzamide (µg)**				
Leaching Days	1	7	14	21	28	1	7	14	21	28
Replicates										
1	1.670	0.974	0.412	0.273	0.232	1.349	0.879	0.505	0.412	0.306
2	1.279	0.705	0.505	0.302	0.200	1.392	0.931	0.447	0.458	0.269
3	1.218	0.800	0.394	0.325	0.255	1.453	0.670	0.539	0.325	0.200
4	1.505	0.827	0.406	0.348	0.232	1.157	0.792	0.435	0.574	0.274

Table B.3: *Mean mass (µg) of propyzamide measured in pore water for sandy loam and sandy silt loam soils treated with technical grade and formulated propyzamide on different leaching occasions. The value in parentheses is the standard deviation for four replicates.*

Soil type	Formulation	**1**	**7**	**14**	**21**	**28**
Sandy loam	Technical grade	1.031 (0.07)	0.406 (0.06)	0.229 (0.06)	0.204 (0.04)	0.144 (0.03)
Sandy loam	Commercial product (Kerb Flo)	1.348 (0.20)	0.731 (0.12)	0.391 (0.12)	0.305 (0.04)	0.229 (0.05)
Sandy silt loam	Technical grade	1.418 (0.21)	0.827 (0.11)	0.429 (0.05)	0.300 (0.03)	0.230 (0.02)
Sandy silt loam	Commercial product (Kerb Flo)	1.338 (0.13)	0.818 (0.11)	0.497 (0.05)	0.398 (0.07)	0.258 (0.05)

Table B.4: *Results from the test to select best soil to solution ratio to be used in sorption and desorption experiments on propyzamide in sandy loam soil (a), and in sandy silt loam soil (b).*

(a) Sandy loam						
Sample ID	Soil to solution ratio	Ci (μg mL^{-1})	Ce (μg mL^{-1})	Cs (μg g^{-1})	Total sorption (μg)	% sorption
S1.1	1: 5	0.542	0.170	1.860	3.72	68.63
S1.2	1: 5	0.542	0.156	1.930	3.86	71.22
Mean		*0.542*	*0.163*	*1.895*	*3.79*	*69.93*
S1.1	1 : 2	0.542	0.088	0.908	1.816	83.76
S1.2	1 : 2	0.542	0.082	0.920	1.84	84.87
Mean		*0.542*	*0.085*	*0.914*	*1.828*	*84.32*

(b) Sandy silt loam						
Sample ID	Soil to solution ratio	Ci (μg mL^{-1})	Ce (μg mL^{-1})	Cs (μg g^{-1})	Total sorption (μg)	%sorption
S2.1	1 to 5	0.542	0.202	1.700	3.4	62.73
S2.2	1 to 5	0.542	0.166	1.880	3.76	69.37
Mean		*0.542*	*0.184*	*1.790*	*3.58*	*66.05*
S2.1	1 to 2	0.542	0.098	0.888	1.776	81.92
S2.2	1 to 2	0.542	0.104	0.876	1.752	80.81
Mean		*0.542*	*0.101*	*0.882*	*1.764*	*81.37*

Table B.5: *Results from the test to determine the equilibration time of propyzamide using a soil to solution ration of 1:5 in sandy loam and sandy silt loam soils.*

Sandy loam					
Time intervals (hours)	Ci (μg mL^{-1})	Ce (μg mL^{-1})	Cs (μg mL^{-1})	Total sorption (μg)	% sorption
1	1.13	0.460	3.905	6.700	59.40
6	1.13	0.364	4.115	7.660	67.91
12	1.13	0.342	4.210	7.880	69.86
24	1.13	0.319	4.515	8.110	71.90
48	1.13	0.320	4.610	8.100	71.81
Sandy silt loam					
1	1.13	0.349	3.350	7.810	69.24
6	1.13	0.307	3.830	8.230	72.96
12	1.13	0.288	3.940	8.420	74.65
24	1.13	0.227	4.055	9.030	80.05
48	1.13	0.208	4.050	9.220	81.74

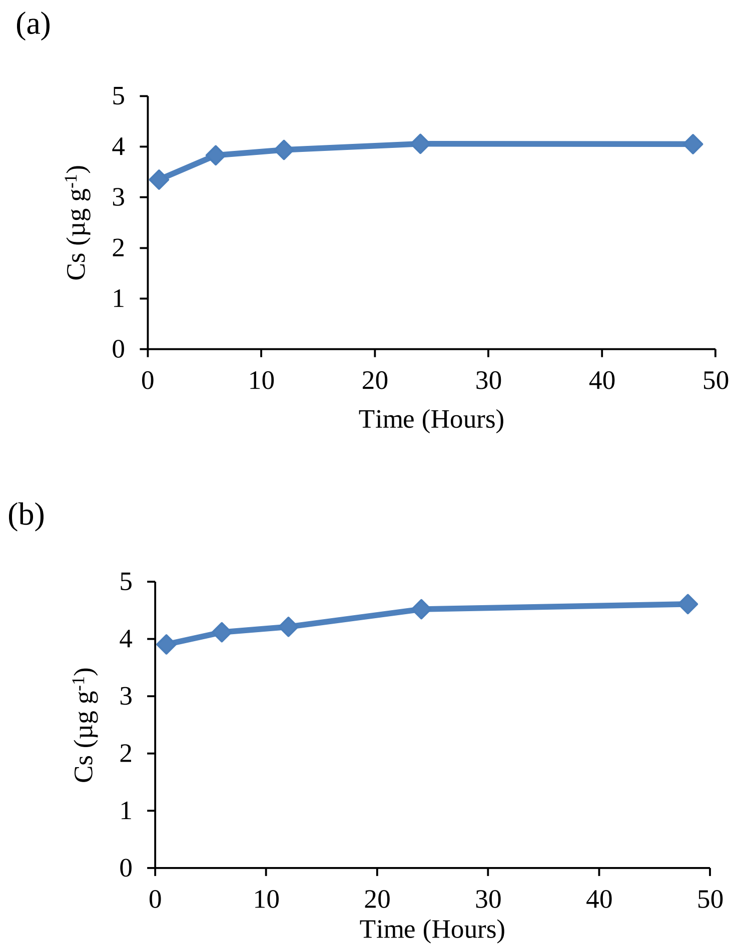
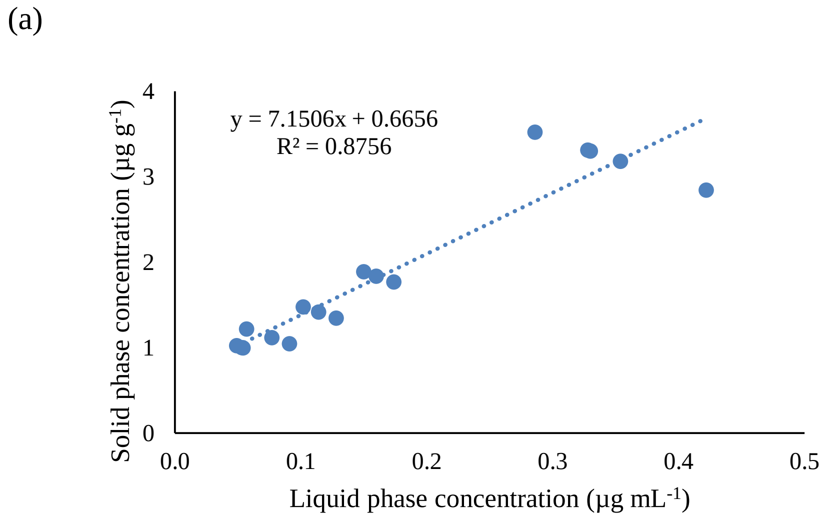


Figure B.1: *Results from test to select the equilibration time for propyzamide using soil to solution ratio of 1:5 in sandy loam (a) and sandy silt loam soil (b).*



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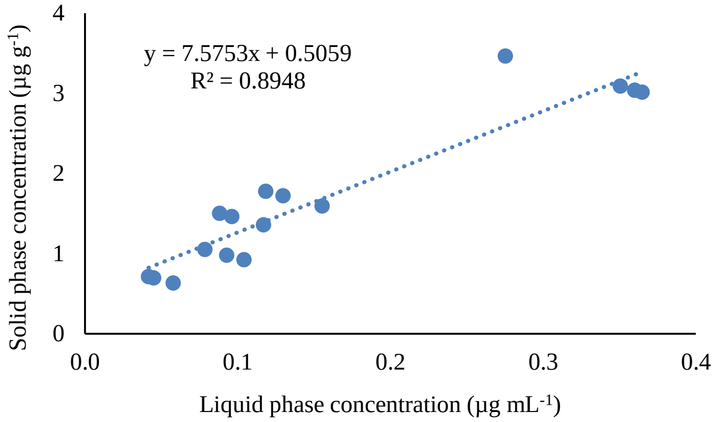
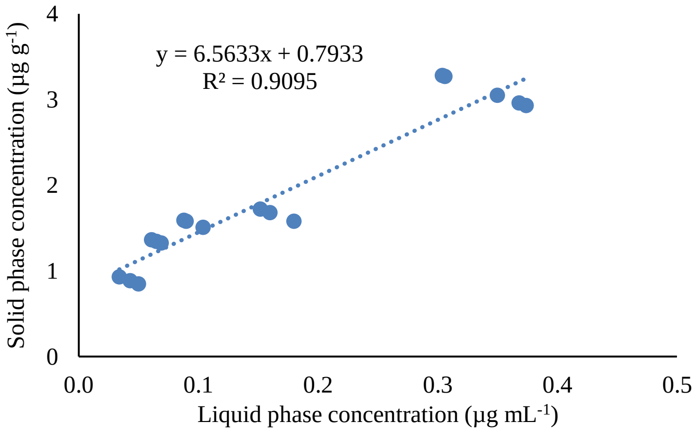


Figure B.2: *Linear fittings of the sorption isotherms of propyzamide from the batch experiments in sandy loam soil (a) technical grade material (b) formulated material*

(a)



(b)

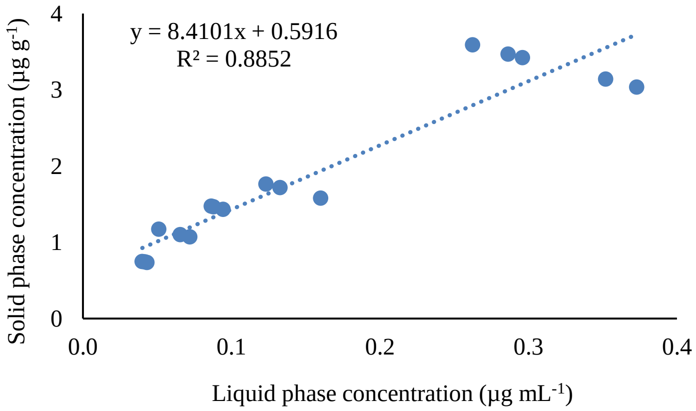


Figure B.3: *Linear fittings of the sorption isotherms of propyzamide from the batch experiments in sandy silt loam soil (a) technical grade material (b) formulated material*

Table B.6: *Multi-way ANOVA to test between-subject effects of formulation, residence time and soil type with mass of propyzamide in pore water in sandy loam and sandy silt loam soil as dependent variable*

Source	**Type III Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Corrected Model	13.108[a]	19	.690	71.881	.000
Intercept	26.793	1	26.793	2791.610	.000
Days	11.995	4	2.999	312.453	.000
Formulation	.249	1	.249	25.919	.000
SoilType	.474	1	.474	49.437	.000
Days * Formulation	.020	4	.005	.532	.713
Days * SoilType	.085	4	.021	2.202	.079
Formulation * SoilType	.149	1	.149	15.511	.000
Days * Formulation * SoilType	.136	4	.034	3.532	.012
Error	.576	60	.010		
Total	40.476	80			
Corrected Total	13.684	79			

a. R Squared = .958 (Adjusted R Squared = .945)

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