CHARACTERISATION OF HERBICIDE BEHAVIOUR IN SOME INNOVATIVE GROWING MEDIA

A thesis presented in partial fulfilment of the
requirements for the degree of

Doctor of Philosophy
in Soil Science

at Massey University, Palmerston North

New Zealand.

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2008

ABSTRACT

An abundance of waste products from the forestry industry (sawdust and paper pulp) lead to the concept of using them as growing media for high value crops on a field scale. However, management of subsequent weed growth posed a problem as the impact of these novel media on the performance and fate of herbicides was unknown. Three aspects of sawdust and paper pulp waste were examined and compared to two cropping soils, viz. their effect on herbicide behaviour with regard to crop selectivity, weed control efficacy and the environmental fate of selected chemicals.

Cropping species such as lettuce and onions were more susceptible to alachlor and chlorpropham in sawdust than in paper pulp. The two cropping soils evaluated (Horotiu sandy loam and Mangateretere silt loam) tended to be intermediate although the former was often close to the sawdust and the latter to the paper pulp in terms of herbicide phytotoxicity to the crop plants. For the less water soluble herbicide pendimethalin, the differences in crop selectivity in the different media were not significant.

The effect of the media on the efficacy of weed control was evaluated through plant species with a much lower tolerance to the herbicides evaluated in contrast to the above species. For these plants the efficacy of the herbicides was generally lower in both the sawdust and paper pulp than in the two soils. The effect was more pronounced with the more soluble alachlor, where efficacy was reduced by factors of 5 – 10, compared to pendimethalin where efficacy reduction was by factors of 0 – 3.

The two high organic media had contrasting effects on the various environmental behaviour indices evaluated. Herbicide adsorption as quantified by distribution coefficient (K_d) was higher in the two novel media compared to both the Horotiu and Mangateretere soils. However, when the K_d was normalised to organic carbon (K_{oc}), there was less variation amongst the media indicating that organic matter is an important factor in controlling sorption in these media. However, despite the high level of adsorption in the sawdust, herbicides were most prone to leaching in this medium. Conversely the paper pulp tended to be more retentive while the two soils were intermediate. The degradation as quantified by half-lives ($t_{½}$) of the herbicides was generally slower in the two novel media, probably reflecting the higher sorption in these two media but also due to the lower level of microbial activity in the sawdust and paper pulp.

The study shows that herbicide behaviour in these carbon based media differs significantly from that expected from soil organic matter, mainly due to the non-humified nature of the organic matter in the media and its poor biological activity.

ACKNOWLEDGMENTS

I am grateful for the assistance and encouragement of many colleagues during this study and wish to sincerely thank the following:

Dr Anis Rahman, Senior Scientist, AgResearch, Ruakura Research Centre, for support and guidance throughout the project and for ensuring that resources and finance were available for this research.

Professor Nanthi S Bolan, Chair of Environmental Science, Centre for Environment Risk Assessment and Remediation (CERAR), University of South Australia, for his guidance and encouragement through much of the experimental phase of this project and supervising me for five years as my Massey University Supervisor.

Dr Kerry C Harrington, Senior Lecturer in Weed Science, Institute of Natural Resources, Massey University, who at a late stage took over the role of lead supervisor and ably guided me through the preparation of this thesis.

Dr Patrick Holland, Senior Scientist, Cawthron Institute, for his excellent technical guidance in the project and for critically reading the manuscript.

Dr John Waller, Biometrician, AgResearch, for guidance and assistance with the statistics, in particular with fitting the Bayesian smoothed curves to the bioassay and degradation data.

Dr Sally Gaw, Scientist, Chemistry Department, University of Canterbury, for helpful suggestions on the final draft of the manuscript.

Mike Trolove, AgResearch, Ruakura Research Centre, for technical assistance with the bioassay studies, the herbicide extractions and the rainfall and leaching studies.

Nancy James, my wife and friend for life, for wonderful support and understanding, particularly in the final stages of thesis writing.

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LIST OF ABBREVIATIONS

a.i.	Active ingredient
ANOVA	Analysis Of Variance
CAS	A division of the American Chemical Society
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon (see also OC)
DOM	Dissolved Organic Matter
DT_{50}	Time required for dissipation of the first 50% of the original pesticide concentration
EC	Emulsifiable Concentrate
ED_{10} (ED_{50}; ED_{90})	Effective Dose to reduce plant production to 10% (50%; 90%) of untreated
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
IUPAC	International Union of Pure and Applied Chemistry
K_d	Distribution (partition) coefficient (the ratio of pesticide adsorbed to that in solution)
K_{oc}	Soil organic carbon affinity coefficient (i.e. K_d normalised to OC content)
LD_{50} (LD_{90})	Lethal Dose required to kill 50% (90%) of the population
LOD	Limit Of Detection
$LSD_{0.05}$	Least Significant Difference with 95% confidence interval
MWHC	Maximum Water Holding Capacity
NOEL	No Observable Effect Level
NTU	Nephelometric Turbidity Unit
OC	Organic Carbon (often calculated from OM by dividing by 1.73)
ODTMA	Octadecyltrimethylammonium chloride (a surfactant)
OM	Organic Matter
PTFE	Polytetrafluoroethylene or Teflon®
pKa	Acid dissociation constant
rpm	Revolutions per minute
SD	Standard Deviation
SED	Standard Error of Difference
SEM	Standard Error of the Mean
SOM	Soluble Organic Matter
SPE	Solid Phase Extraction
$t_{½}$	First-order kinetic half-life
TDS	Total Dissolved Solids
WSSOM	Water Soluble Soil Organic Matter

CHAPTER 1

INTRODUCTION

CHAPTER 1: INTRODUCTION

1.1 Preservation of our Soil

The lifeblood of New Zealand’s agricultural economy is the soil, yet many of our farming practices are unsustainable and result in degradation of this precious resource. Degradation of the soil can be measured in many ways but the two most common indicators used are soil structure and soil organic matter (Haynes & Francis 1990). These two properties are related as soil organic matter is the “glue” which gives the soil its structure (Haynes & Swift 1990; Shepherd et al. 2000; Bruland & Richardson 2004; Krull et al. 2004). Therefore practices that result in a reduction of soil organic matter will ultimately lead to a loss of soil structure. Some cropping practices are among the most detrimental in this regard (Haynes et al. 1991).

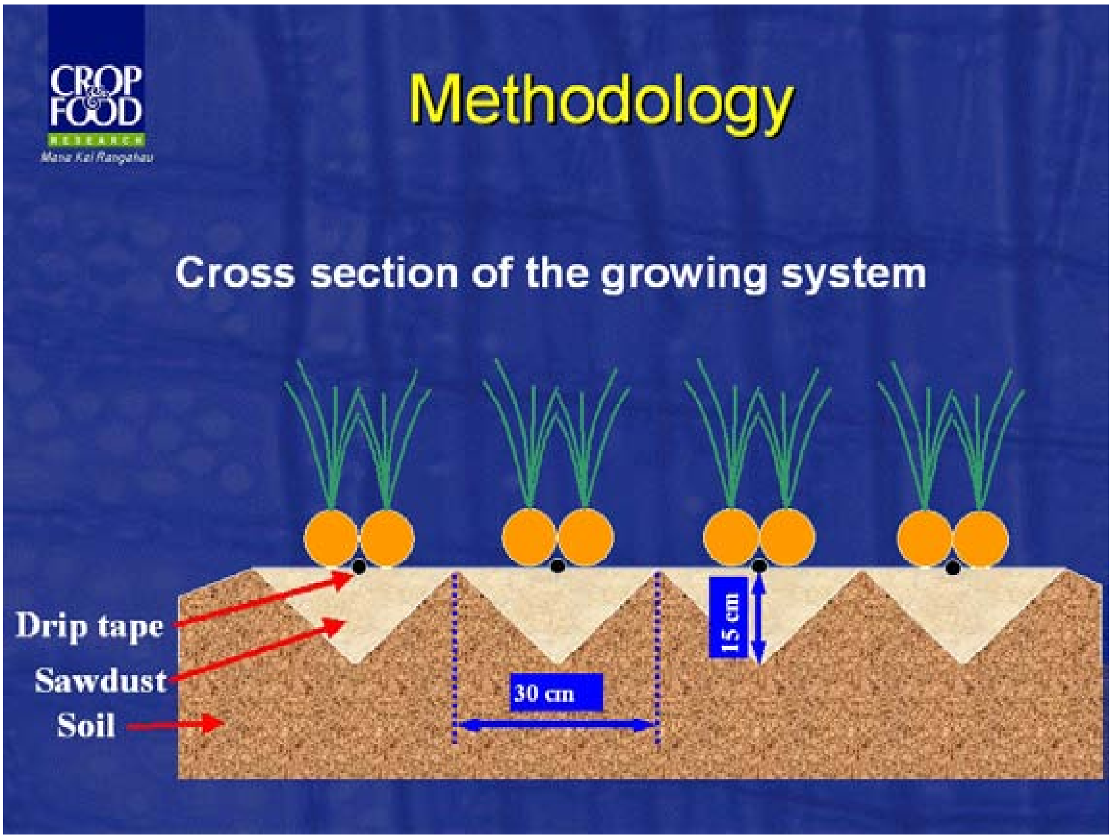
There are several remedial practices which can be used to reverse the loss of soil organic matter. Two of the most common are a rotation with a permanent crop (usually pasture) and the use of a cover crop which is incorporated back into the soil (Francis et al. 2002). Other ideas that have been proposed are to use other sources of carbon, particularly high carbon content waste material. This includes such diverse material as liquid and solid waste from sewage treatment plants, dairy (and other farming) effluent and waste products from the forestry industry (Aggelides & Londra 2000; Cooperband 2002; Huddleston & Young 2005). However the cost of transporting, spreading and incorporating these materials is often prohibitive and problems, as well as benefits, are not well documented.

With this in mind scientists at Crop & Food Research developed a growing system referred to as the “Rich Ditch” to overcome some of these constraints (Trolove & Reid 2003). As the “Rich Ditch” system offers practical solutions to some of the inherent problems associated with the application of solid waste soil amendments, some fundamental aspects of the media have been studied in detail within this thesis. However, the results and conclusions of this work will be equally applicable to any situation where solid waste of this nature is added to the soil by whatever means and for whatever reason.

1.2 The “Rich Ditch” Growing System

The Rich Ditch system (Fig. 1.1, Plate 1.1) uses a furrow filled with forestry waste (sawdust or paper pulp) as a medium to support the crop while nutrients are supplied hydroponically. The concept was to use the system to grow one or two high value crops hydroponically and afterwards the partly decomposed waste material used in the ditch would be incorporated into the soil and a traditional crop grown (Trolove & Reid 2003). With this system, fields with reduced soil organic matter would be selected and the waste filled furrows created. A crop of high value would then be grown to offset the cost of constructing the system.

Initially it was suggested to grow onions for export. A particular problem with onions grown traditionally in New Zealand is the excessive pungency which comes from the high sulphur content of our soils and additions from the common fertilisers (Trolove & Reid 2003). Onions grown in the Rich Ditch would be fed a low sulphur nutrient solution and thus have a reduced pungency and fetch premium prices in some of our export markets. The Rich Ditch can support two crops before the waste and the structure are degraded to the point where proper management is difficult. At this time the waste material is incorporated into the soil, amending the natural soil organic matter. The Rich Ditch system also appeared to offer other benefits, in particular the reduced use of herbicides for weed control (Trolove & Reid 2003).



Methodology

Cross section of the growing system

Fig. 1.1: **Diagram of the Crop & Food Research ‘Rich Ditch’ growing system (source, Crop & Food Research).**

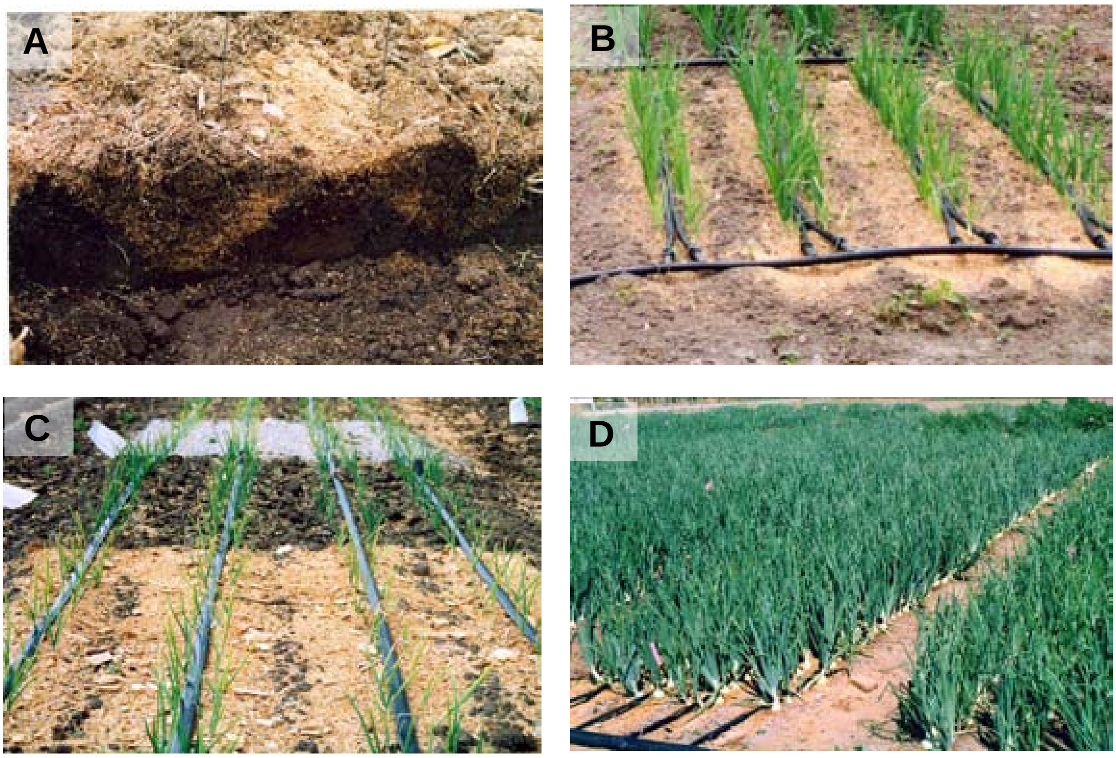


Plate 1.1: Onions being grown using the Rich Ditch growing system; A, newly formed beds showing furrows filled with sawdust, B, onions growing in sawdust, C, sawdust beds in foreground with paper pulp beds immediately behind, D, onion crop approaching maturity. Photographs courtesy of Stephen Trolove, Crop & Food Research.

1.3 Herbicide Use

High organic matter soil amendments are likely required the most in intensive cropping situations and, due to the high economic returns, most likely to be used there. Among the high value crops grown in intensive cropping systems are onions, tomato, lettuce and vegetable brassicas. All these crops have a high use of pesticides (Holland & Rahman 1999; Manktelow et al. 2005). For example, onion crops, due to their slow growth and uncompetitive nature, have a very high need for herbicides to maintain the crop weed free for the entire season (Manktelow et al. 2005). They are particularly sensitive to competition from weeds (Wilson 1977). Also, weeds present at harvest interfere with the drying and harvesting of the crop. Onions are quite sensitive to most of the herbicides available for weed control and generally those with long residual activity cannot be used (Cox 1968). This necessitates up to eight herbicide applications per season (Holland & Rahman 1999).

The Rich Ditch system has the potential to reduce herbicide input as the waste material used in the ditch contains no weed seeds so fewer herbicides would be required in the vicinity of the sensitive onion (or other crop) plants. However, as can be seen in Plate 1.1, the area between the rows remains partially exposed or thinly covered soil and thus is the source of weed seeds and subsequently weed growth. These weeds could be controlled mechanically with cultivation but it would be more cost effective to control them with a banded herbicide application. Unfortunately, the impact of waste material present on the soil surface on the behaviour of herbicides is largely unknown as is the behaviour of any herbicide that might move into the Rich Ditch itself. This is especially pertinent as the herbicides used for controlling weeds in the strips between the waste are likely to be persistent and more toxic to the crop.

1.4 Influence of Waste on Herbicide Behaviour

The performance of herbicides that act via the soil (often referred to as residual herbicides) and are taken up through plant roots or emerging shoots is strongly influenced by the soil (Rahman & James 1995). Several soil parameters are known to affect herbicide performance including the pH of the soil solution, soil structure, sand content and type of clay. However the single most influential soil property is the soil organic carbon (Rahman et al. 1977; Rahman & Matthews 1979; del Pino & Díaz 1998; Rae et al. 1998). The two main influences of soil organic carbon are its ability to adsorb the active pesticide molecules, thus rendering them biologically inactive (Weber & Peter 1982; Nègre et al. 2006), and as a host for soil microbes which generally are the principal route for herbicide degradation (Anderson 1984; Soulas & Lagacherie 2001).

Thus, it is reasonable to assume that the introduction of extra organic matter into the soil is likely to have a profound effect on the behaviour of any herbicides applied subsequently. The Rich Ditch system introduces large quantities of organic carbon into the immediate environment of herbicides used in the inter-row areas, and therefore it is highly likely to have a significant impact on the behaviour of these herbicides. There are four areas of herbicide behaviour that are most likely to be noticeably affected by the introduction of foreign growing media in the Rich Ditch system: sorption, plant uptake, persistence and degradation, and mobility and leaching. Fig. 1.2. illustrates the concept of the Rich Ditch system and diagrammatically conveys how herbicide behaviour may be influenced. This illustration also briefly describes how these behaviours might be studied and thus served as a concept plan for the research reported here.

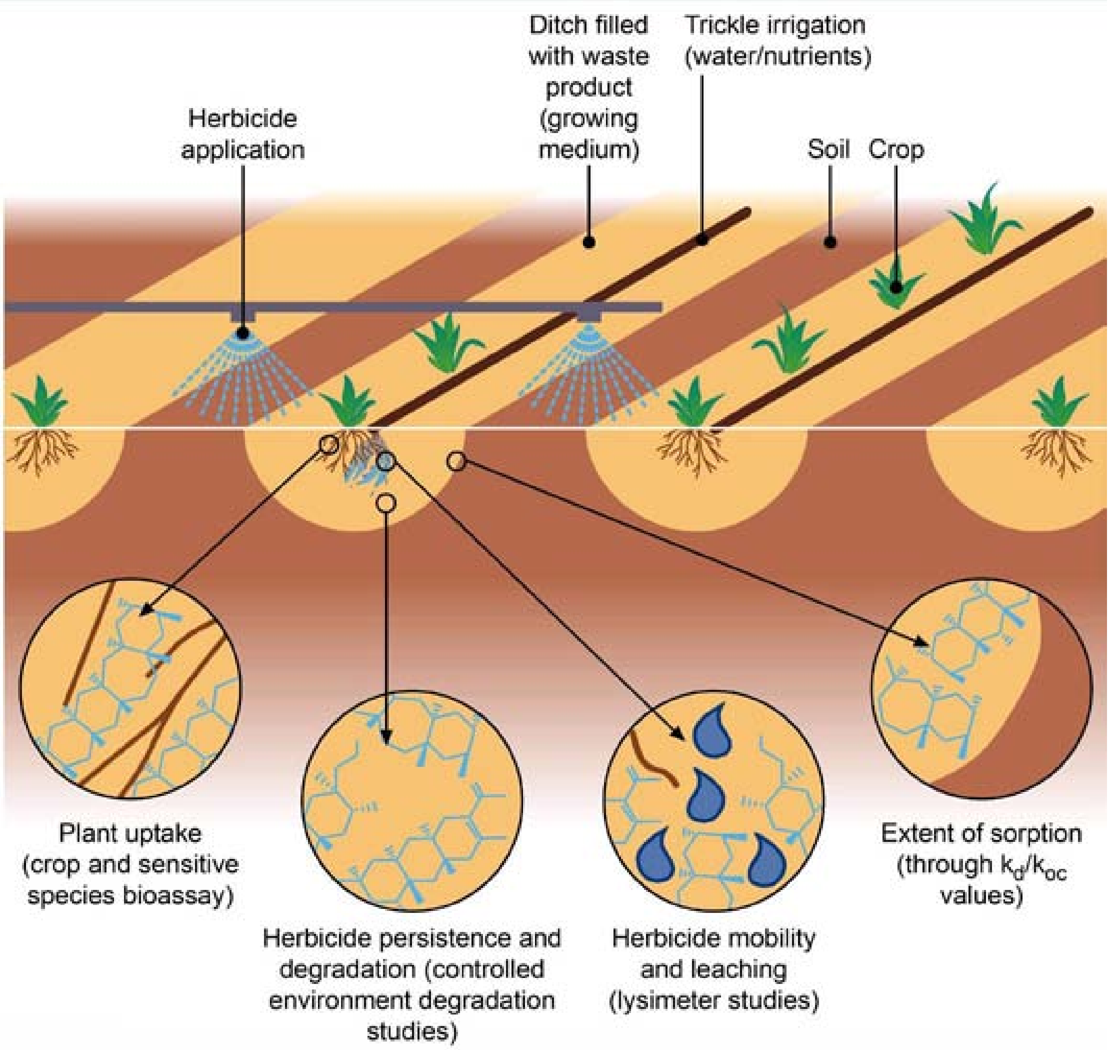


Fig. 1.2 Concept diagram of the soil/herbicide interactions that could be influenced by the introduced material of the Rich Ditch system. Artwork by Pauline Hunt, AgResearch.

1.5 Aims of this Research

The aim of this work was to investigate and characterise the behaviour of certain herbicides in some novel growing media with potential for use as soil amendments, specifically sawdust and paper pulp, and how this compares with their behaviour in two common cropping soils (Horotiu silt loam and Mangateretere silt loam).

In Chapter 3, the availability of three common herbicides (alachlor, chlorpropham and pendimethalin) for absorption by roots and coleoptile of both tolerant and susceptible plants (i.e. their bioavailability) has been investigated for the two high organic matter waste products, paper pulp and sawdust, as compared with their bioavailability in the two cropping soils. The hypothesis tested was that herbicides become less available to plants from these high organic matter media compared to soil.

In Chapter 4, the adsorption of five common herbicides (alachlor, atrazine, bromacil chlorpropham and pendimethalin) in the paper pulp and sawdust has been evaluated and compared to that of two soils. The degree of herbicide adsorption was established by determining the soil/solution distribution coefficient (K_d), i.e. the ratio of herbicide adsorbed to the soil compared to the herbicide in the solution. The hypothesis tested was that the herbicide soil/solution distribution coefficient is larger in high organic matter media compared to soil.

In Chapter 5 the persistence and degradation of two common herbicides (atrazine and bromacil) in paper pulp, sawdust and two soils was determined. The degradation half-life ($t_{½}$) was determined under a variety of conditions and compared to degradation in soil. The hypothesis tested was that herbicide degradation will be faster in high organic matter media compared to soil.

In Chapter 6 the mobility and leaching behaviour of two herbicides (atrazine and bromacil) was measured in paper pulp, sawdust and two soils, when subjected to either simulated rainfall or surface irrigation for several hours. Herbicide concentrations in the media profile and in the leachate were measured by both chemical means and bioassay. The hypothesis tested was that leaching of herbicides and their movement through the profile will be reduced in high organic matter media compared to soil.

In Chapter 7 the concluding discussion combines the findings and conclusions and creates a holistic view of the behaviour and fate of herbicides in various media and the implications of these findings in terms of herbicide use. This includes a discussion of the potential for pesticide fate simulation models to accurately depict the behaviour of herbicides in high organic matter media such as sawdust and paper pulp.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2: LITERATURE REVIEW

2.1 Use of High Organic Matter Waste Materials in Agriculture

The practice of incorporating organic matter in the form of crop residue to maintain soil health has been a feature of arable cropping for centuries and has been well researched (e.g. Allmaras et al. 1988; Wilhelm et al. 2004). Therefore, it was a natural progression to use high organic matter material sourced from other industries on farmland to improve soil health and add depleted nutrients (Korentajer 1991). There is also a need to sustainably dispose of large amounts of municipal and sewage waste (Aggelides & Londra 2000) and concentrated on-farm waste from animal housing and milking complexes (Longhurst et al. 2000). In many countries municipal waste is applied to cropping soils while in New Zealand, municipal waste (where disposed of in this manner) and animal effluent are both mostly applied to pasture (Korentajer 1991). These waste products are generally applied as solid suspensions in water and their impact on agricultural systems has undergone close scrutiny (e.g. Doyle et al. 1978; Korentajer 1991).

Taking the maintenance of soil health one step further is the desire to restore industrial or mining sites as well as severely degraded arable soils (Borgegård & Rydin 1989; Schuman & Beldon 1991; Huddleston & Young 2005). Restoration of these soils and sites usually involves greater input of organic matter and frequently involves the use of forestry waste including sawdust and paper mill sludge (White et al. 2003; Averett et al. 2004). However these sites tend to be restored to their native state which is often forest or rangeland and are generally not used for intensive agriculture (Averett et al. 2004; Huddleston & Young 2005).

On a smaller scale, another use of high organic matter waste material in agriculture is sawdust and other mulches for weed control purposes to avoid the use of herbicides (Hartley et al. 1996) and to control unwanted soil organisms (Akhtar & Alam 1993; Akhtar & Malik 2000). High organic matter waste materials have also been widely studied as a means of enhancing the degradation of organic pollutants (phytoremediation), including herbicides (Yassir et al. 1998; Moorman et al. 2001; Forouzangohar et al. 2005).

Irrespective of the reasons for the waste material being applied to the soil, the outcome is an increase in the soil organic matter (SOM). Sopper (1992) stated that recovery of native organic matter levels without amendments may require over 30 years but that can be shortened to as little as 6 years with sludge amendments. Seaker & Sopper (1988) reported that after 5 years of sludge amendment organic carbon increased from 3.1% to 7.6%. The addition of sawdust can have an even more dramatic effect, with Averett et al. (2004) reporting a 67% increase in carbon content, 6 months after the addition of 6 kg/m^2 of sawdust. Bendfeldt et al. (2001) found that the organic carbon increase was similar to the amount of carbon added after 5 years but was reduced to about 60% of the added carbon after 16 years. Conversely, using a modelling approach, Hyvönen et al. (1996) predicted that the carbon content in soil derived from added sawdust would halve in 2.5 years and be reduced to only 10% of the original amount after 20 years.

With the increase in SOM derived from the added organic substrate there is also likely to be; a) an increase in pesticide sorption (Section 2.2.1) and b) an increase in dissolved organic carbon (DOC) (Section 2.3). However, the extent of increase of either of these parameters is dependant on the age, condition and nature of the amended carbon (Hyvönen et al. 1996; Iglesias-Jiménez 1997; Kalbitz et al. 2000; Nilsson et al. 2005).

2.2 Processes Affecting Herbicide Behaviour in Soil

2.2.1 *Herbicide Adsorption*

One of the main governing influences of herbicide behaviour and fate in soils is adsorption within the soil (Weber et al. 1991). In adsorption, solute accumulation is generally restricted to a surface or interface between the solution and adsorbent (Weber et al. 1991). In contrast, absorption is a process in which the solute interpenetrates the sorbent phase by at least several nanometres (Kookana et al. 1998).

Classically, adsorption is the process that occurs when a gas or liquid solute accumulates on the surface of a solid. This process is dynamic and can be modelled by relating the amount of solute adsorbed to the sorbent phase to the amount of solute retained in the solvent phase (Weber et al. 1991). An expression of this type evaluated at a fixed system temperature constitutes what is called the adsorption isotherm. The simplest is a linear model where, when at equilibrium, the accumulation of solute by the sorbent is directly proportional to the solution phase concentration (Weber et al. 1991).

However, in classical experiments conditions favouring a linear isotherm were rare and as a consequence, first the Freundlich equation (1894) and then the Langmuir equation (1916) were developed to describe non-linear isotherms. These isotherms can also be used to describe herbicide adsorption in soil (where the herbicide is the solute and soil is the sorbent) (Bailey & White 1970). In this case the equilibrium is dependent on the concentration and nature of the herbicide, and the properties of the soil (adsorbent).

Organic matter is the principal adsorbent for most herbicides (Bailey & White 1964; Bailey & White 1970; Wang et al. 1999) followed by clay colloids (Bailey & White 1970; Weber et al. 2000; Taylor et al. 2004). The adsorption phenomenon is due to the attraction between a solid surface and a solution and is determined by the inherent properties of both (Rae et al. 1998; Gramatica & Guardo 2002). The intensity of adsorption varies according to the chemical characteristics of the pesticide and also to the nature and surface charge density of the adsorbent (Lambert 1967; Chiou et al. 1986; del Pino & Díaz 1998).

One of the more critical pesticide properties associated with determination of adsorption is its water solubility. When measures of adsorption (distribution coefficients) are unknown, pesticide solubility is frequently used as a predictor of leaching potential (Cohen 1990; Close 1993a). Also, several equations have been derived to estimate distribution coefficients from the water solubility of a pesticide (del Pino & Díaz 1998). However, solubility is a function of more fundamental chemical and physical properties of the pesticide molecule and these also define its distribution coefficients and other behavioural characteristics of the pesticide (Livingstone et al. 2001; Klamt et al. 2002; Hilal & Karickhoff 2004). Using a variety of approaches, these researchers have predicted both water solubility and distribution coefficients from two dimensional representations of molecular structure and a knowledge of their active substituents.

There are two general types of adsorption, physical and chemical (Bailey & White 1964; Bollag et al. 1992). Physical adsorption or van der Waals adsorption is due to dipole-dipole interactions, polarisation or induced dipole interactions and ion-dipole interactions. Chemical adsorption is due to coulombic forces between ionically charged particles or from bond formation between the adsorbent and adsorbate. A hydrogen bond may be classified under either physical or chemical adsorption depending on whether the parameter of heat of adsorption or that of bond formation is taken as the major criterion for classification (Bailey & White 1964).

The Freundlich adsorption equation (Eq. 2.1) remains the most frequently described for herbicide adsorption (Kinniburgh 1986; Weber et al. 1991; Weber et al. 2000)

$$x/m = \mathrm{K}C^{1/n} \qquad \text{Eq. 2.1}$$

where x is the weight of adsorbate taken up by weight m of the sorbent (in this case the soil), C is the concentration of the solution at equilibrium and K and n are constants. The constant K is also known as the distribution coefficient K_f for the non-linear Freundlich isotherm (Kinniburgh 1986; Weber et al. 1991). However, at the low concentrations that most herbicides are used at, the adsorption isotherm approaches linearity (i.e. $n = 1$) and this linear isotherm model has largely replaced the Freundlich model for practical purposes (Weber et al. 1991; Ma et al. 1993; Sluszny et al. 1999; Weber et al. 2000). It is usually presented as

$$K_d = (x/m)/C \qquad \text{Eq. 2.2}$$

or $$K_d = (\text{herbicide sorbed } (\mu g/g))/(\text{herbicide in solution } (\mu g/mL)) \qquad \text{Eq. 2.3}$$

The distribution coefficient (sometimes referred to as the partition coefficient) is unique for each herbicide/soil combination and as such is very useful when comparing either a single herbicide in multiple soils or multiple herbicides in a single soil. However, as previously discussed, the most influential factor in herbicide adsorption is soil organic matter and to make the distribution coefficient more versatile it is commonly normalised to organic carbon content (Weber et al. 1991; Sluszny et al. 1999; Weber et al. 2000; Bhandari & Lesan 2003), i.e.

$$K_{oc} = \frac{100\ K_d}{\%OC} \qquad \text{Eq. 2.4}$$

This soil organic carbon affinity coefficient (K_{oc}) has been found to show little variation (within experimental error) for a given pesticide over a wide range of soil types and organic carbon contents (Weber et al. 2000; Wauchope et al. 2002). This has proved very useful for New Zealand researchers as our agricultural soils typically have a much higher organic matter content than much of the rest of the world (Tate et al. 1997) but through K_{oc} we can apply international data on herbicide distribution coefficients to determine pesticide behaviour in local soils (Green et al. 1999; McNaughton et al. 1999).

2.2.2 *Herbicide Desorption*

Herbicide adsorption is a dynamic equilibrium in which the reverse chemical reaction is known as desorption. As with other imperfect reactions, the desorption isotherm does not exactly mirror the adsorption isotherm. Several factors come into play which result in an hysteresis effect (Mamy & Barriuso 2007). With time, the hysteresis effect is broadened as the molecules become more strongly adsorbed and with some herbicides there is also an element of non-reversibility to the adsorption process particularly where chemical bond formation or diffusion into nanometre soil interstices has taken place. This time-dependant or ageing effect can have significant implications for many herbicide-soil interactions such as herbicide leaching, degradation and bioavailability (Kookana et al. 1993; Fortin et al. 1997; Mamy & Barriuso 2007). For the fast-equilibrium adsorption sites located on the external surfaces of soil particles, desorption readily occurs and hysteretic behaviour is minimal. This equilibrium is reached within minutes (Boesten et al. 1989). For the slow-equilibrium sites located on the internal surfaces of the soil particles, desorption is slower and significant hysteresis occurs (Kookana et al. 1998). This equilibrium is only reached after several hours or days (Cox & Walker 1999; Renaud et al. 2004a; Mamy & Barriuso 2007). In addition to this there is increasing acknowledgement of a very slow equilibrium which occurs deep within the porous solid matrix and may involve chemical rearrangements of the sorbate molecules (Mamy & Barriuso 2007). The time-scale for this reaction is hundreds of days and it may comprise a large non-reversible component, meaning that desorption essentially does not take place.

2.2.3 *Herbicide Bioavailability*

For a herbicide to be available for uptake by plant roots and emerging shoots it must first be in solution and although root uptake is not simply a function of herbicide concentration, it has proved to be an adequate measure in many cases (Günther et al. 1989; Schroll et al. 1994; Trapp et al. 1994). As the amount of herbicide in solution is regulated by the adsorption phenomenon, the main determinants of bioavailability are sorption by soil organic matter and rates of diffusion from the sorbed state (Shelton & Doherty 1997). Herbicide bioavailability has traditionally been evaluated using bioassays with either root extension or the whole plant (Streibig 1988; Vasilakoglou et al. 2001; Pannacci et al. 2006). Such bioassays directly determine the biological activity of a soil active herbicide and this is intrinsically related to bioavailability (Günther et al. 1989). Further, bioassay can determine the ‘no observable effect level’ (NOEL) of a herbicide. The NOEL is the threshold defined as the soil concentration giving the maximum acceptable damage level, usually 5 or 10%, (Jensen & Streibig 1994). The NOEL is also a critical parameter when relating herbicide carryover to the potential for subsequent crop damage (Jensen & Kudsk 1988; Pannacci et al. 2006).

2.2.4 *Herbicide Degradation and Persistence*

The degradation rates of herbicides in soils can be thought of in terms of the molecules intrinsic stability to microbial and chemical decay, which is modified by soil factors such as organic matter, pH and climate (Briggs 1990). In soils with a high organic matter content (generally >10%), the primary factor controlling herbicide degradation in soil is microbial transformation (Greer & Shelton 1992; Aislabie & Lloyd-Jones 1995; Soulas & Lagacherie 2001). This degradation often follows simple exponential decay (Richter et al. 1992) and is thus assumed to follow first-order kinetics (Eq. 2.5) (Beulke & Brown 2001):

$$\mathrm{d}C/\mathrm{d}t = -kC \qquad \text{Eq. 2.5}$$

where C is concentration in the soil (mg/kg soil), t is the time (days) and k is the degradation rate (days^{-1}). Integration of Eq. 2.5 produces Eq. 2.6

$$C_t = C_0 \exp(-kt) \qquad \text{Eq. 2.6}$$

where C_t and C_0 are concentrations (mg/kg soil) at times t and 0 respectively. The logarithmic form of Eq. 2.6 gives a linear relationship for C and t (Eq. 2.7)

$$\ln(C_t) = \ln(C_0) - kt \qquad \text{Eq. 2.7}$$

The time taken for the concentration to be reduced to half the initial concentration is referred to as the half-life ($t_{½}$ (days)). Substitution into Eq. 2.7 gives:

$$t_{½} = \ln(2)/k \qquad \text{Eq. 2.8}$$

where k (the degradation rate) is the slope of the linear (logarithmic) plot. The common descriptor of degradation processes that fits first-order kinetics then is the half-life (Walker 1974; Walker 1987; Beulke & Brown 2001). However, as this method forces the degradation curve to fit first-order kinetics it is not always appropriate and can lead to erroneous conclusions concerning degradation and persistence. Therefore, for data that digress from first-order kinetics, the DT_{50} value (time required for 50% dissipation of the initial concentration) is used (Bottoni & Funari 1992). Unless a descriptive model that fits the data can be found the DT_{50} value is frequently determined manually from the plotted degradation data.

Degradation in soils with high organic matter and adequate rainfall tends to be much faster than in soils with low organic matter or where moisture is a limiting factor, due to the higher levels of microbial activity in the high organic matter soils (Bolan & Baskaran 1996; James et al. 1999). First-order kinetics is usually followed, albeit with a larger rate constant (*k*) (Kookana et al. 1995; James et al. 1999; Ma et al. 2004a). However, there are many reported cases of degradation that did not follow first-order kinetics because degradation is at times faster or slower than expected. A common cause of variation is enhanced mineralisation due to microbial adaptation (Aislabie & Lloyd-Jones 1995; Cox et al. 1996; Karpouzas et al. 1999; Aislabie et al. 2004). Other instances of variation are where desorption processes are reduced due to slower diffusion or stronger adsorption (Gustafson & Holden 1990; Shelton & Doherty 1997; Renaud et al. 2004b).

2.2.5 *Herbicide Transport*

The movement of herbicides through the soil is best studied in lysimeters using undisturbed soil (Kördel et al. 1992). The K_{oc} value of a herbicide is frequently used to describe its mobility and this, along with the herbicide's persistence (DT_{50} and $t_{½}$) are key parameters that determine leachability (Bottoni & Funari 1992). Due to the expense and time required to carry out lysimeter evaluations, considerable effort has gone into modelling pesticide fate and behaviour. One of the earliest proponents was Walker (1974) who proposed a simple model for herbicide persistence using soil temperature, soil moisture and a first order rate equation based on the experimentally determined herbicide half life ($t_{½}$).

Additions were soon made and the models became more complex with the introduction of computers and the ability to process large amounts of data. Early developments from the persistence model were to add a rainfall factor and to simulate the soil hydrology and thus obtain an estimation of pesticide transport (Addiscott 1977; Šimunek et al. 2003). However, measures of persistence (DT_{50} and $t_{½}$) and adsorption (K_{oc}) remain the key input parameters in these models (Bottoni & Funari 1992; Boivin et al. 2006). These parameters are frequently determined and the models optimised for mature soils with relatively low levels of organic matter. Some models have been tested in New Zealand for their fitness to the higher organic matter soils found here (Ma et al. 2000; Ma et al. 2004d; Müller et al. 2004). The introduction of large amounts of exogenous carbon to the equation by way of soil amendments is likely to test these models to the extreme. Linearity of important herbicide functions such as phytotoxicity has been demonstrated in mineral soils with a wide range of organic matter levels (Rahman 1976; Rahman et al. 1978a), but these results do not always extrapolate to high organic matter peat soils (Rahman et al. 1976).

Transport through the soil is dependant on the frequency and intensity of natural rainfall. However, rain frequently does not coincide with the programmes of researchers studying the effects of rainfall on the transport of herbicides (Shelton et al. 1985). Mechanical devices to simulate rainfall have been devised and used for many years to overcome the inconveniences of natural rainfall (Meyer & Harmon 1979). However, the resultant simulated rainfall often has some shortcomings and fails to match the physical characteristics of natural rain (Miller 1987). Moore et al. (1983) listed a number of desirable features for a rainfall simulator including: (a) accurate reproduction of natural rainfall, (b) nearly continuous, uniform application over the plot area, and (c) the ability to apply rainfall at varying durations and intensities of interest. Assouline et al. (1997) added to this the requirement for the simulated droplets to impact the soil surface with the same terminal velocity as natural rainfall of similar droplet size, and that this required a falling distance of 5.5 m. A rainfall simulator also needs to produce rainfall in the range of 5 to 30 mm/h to cover the range of normal rainfall (Assouline et al. 1997). Two types of rainfall simulator are frequently used, the ‘spray type’ using a pressurised nozzle, and the ‘drip type’ using hypodermic syringe needles (Bowyer-Bower & Burt 1989). A common difficulty with the ‘spray type’ rainfall simulators is that they produce a too-high rainfall rate for the desired drop size, tend to produce uneven distribution and are difficult to calibrate. The ‘drip type’ rainfall simulators overcome these restrictions but do produce droplets of a limited size range. However this can be overcome by placing a wire mesh below the droppers to randomly break up and scatter the drops from the drop formers (Bowyer-Bower & Burt 1989).

2.2.6 *Modelling Herbicide Transport*

With increasing pesticide use in agricultural production systems (Kishi & Ladou 2001) there is increasing concern regarding both their environmental and social costs (e.g. (Pretty et al. 2000; Reynolds et al. 2002; Firth et al. 2007). In New Zealand, the major use of herbicides is in primary production sectors (Holland & Rahman 1999; Manktelow et al. 2005) where the major mechanism for their dissipation is either absorption and detoxification within plants (Kreuz et al. 1996) or degradation in the soil (Anderson 1984). However, the agricultural system is not a closed system and leakages do occur, principally by way of leaching through the soil profile or through surface runoff (Kamrin 1997). Contamination of the environment by herbicides is normally monitored by chemical extraction and analysis of soil and water samples collected from the field (Close 1993b; Close 1993a; Close & Flintoft 2004). However, this is both time consuming and expensive, and more efficient approaches are continually being sought, including simulation modelling (Dubus et al. 2003).

Successful modelling of pesticide transport through the vadose zone and reliable prediction of residual activity in the soil are two goals that are pursued with vigour by many researchers (Coquet 2003; Šimunek et al. 2003). Accurate modelling of pesticide fate will enhance the ability to reduce offsite contamination by identifying high risk scenarios and locations (Huber et al. 2000; Ma et al. 2004b). In these situations the options could be to reduce pesticide rates, use alternative chemicals with different risk profiles or to simply avoid pesticide use altogether (Müller et al. 2004). The accurate prediction of herbicide persistence in the soil would have twofold benefit. Firstly, there is the relationship between persistence (as measured by distribution coefficient and half-life) and leaching in that herbicides that are more persistent also tend to be those that are detected offsite (Beulke et al. 2000). Secondly, some herbicides are required to persist in the soil for a length of time in order to achieve their purpose for use, i.e. to control unwanted plants. If the application rate could be accurately matched to the duration of weed control required (James et al. 2000) then the potential for excess herbicide to be leached from the root zone would also be reduced (Rahman & James 2002; Ma et al. 2004b).

Among the first proponents of modelling herbicide persistence was Walker (1974) who devised a model based on the first-order kinetics for degradation and components to determine the effects of temperature, soil moisture and herbicide concentration on degradation. These models became highly developed and could accommodate changing organic carbon content (hence changing adsorption) and changing microbial activity (hence changing degradation) with depth (Kookana & Aylmore 1994). Degradation models have been improved to incorporate non-first-order kinetics and with the development of more reliable modelling, pesticide dissipation models were developed which incorporated both degradation and leaching processes (Boesten 2000). The complexity of these models has increased simultaneously with the readily available increases in computational power of personal computers. Today, the average model is multivariate and capable of using real time data (Wauchope et al. 2003; Scorza & Boesten 2005).

2.2.7 *Modelling Herbicide Transport Under New Zealand Conditions*

In New Zealand several models have been used to predict herbicide persistence and movement with varying degrees of success. Some early evaluations of the German, knowledge-based system HERBASYS, showed that in our higher organic matter and/or allophanic soils the model generally overestimated persistence of simazine, bromacil, atrazine and ethofumesate compared to the results from 13 field trials (Günther et al.

1992). The reason for the overestimation was attributed to pesticide degradation data (used as input to the scenarios) being obtained under German climate conditions which did not relate well to New Zealand conditions.

Three different models, viz. GLEAMS (Groundwater Loading Effects of Agricultural Management Systems), LEACHM (Leaching Estimation and Chemistry Model) and HYDRUS-2D, were used by Close et al. (1998; Close et al. 1999) and Pang et al. (2000) to inversely calculate mobility (K_{oc}) and degradation ($t_{½}$) parameters for picloram, atrazine and simazine by comparing measured and simulated field data using the non-linear parameter optimisation package PEST (Doherty 1994). The pesticide attenuation parameters were then compared with the best available literature values. For picloram both GLEAMS and LEACHM produced K_{oc} values higher than the literature values indicating that its was less mobile, and $t_{½}$ values that were higher, indicating that it was more persistent. HYDRUS-2D predicted picloram K_{oc} and $t_{½}$ to be both lower than the literature values. For atrazine and simazine, all three models produced data that were more in keeping with literature values. Additionally, LEACHM, HYDRUS-1D (Šimunek et al. 2003) and GLEAMS were compared with Soil Plant Atmosphere System Model (SPASMO (Green et al. 2000)) for simulation of the dissipation of five pesticides, also using inversely calculated parameters (Sarmah et al. 2005; Sarmah et al. 2006). In this study all four models predicted the outcomes with a reasonable degree of accuracy but GLEAMS produced the best fit.

The inability of the laboratory derived herbicide properties to accurately predict environmental fate when used in various models is of concern. A basic premise of the environmental fate models was that they would be able to use the cheaper, more easily obtained laboratory produced data to predict the fate of herbicides under field use conditions, thus reducing the cost of expensive routine sampling (Wauchope et al. 2003). More accurate outputs from the models can be obtained using inverse modelling. Such outputs are very useful in comparisons with the laboratory-based data for experimental purposes, but they are not a suitable replacement because they are expensive to obtain and very site specific (Roulier & Jarvis 2003). For example Close et al. (1999) used six different methods to estimate Campbell's *a* and *b* parameters to calculate water retention for LEACHM and finally concluded that there were indications of preferential flow at the site and they could not obtain the parameters to accurately model preferential flow. Pang et al. (2000) came to a similar conclusion when using HYDRUS-2D, finding that non-ideal hydraulic processes due to anomalies such as cracks and perching in the soil could not be accurately modelled. Sarmah et al (2005; 2006) concluded that due to their complexity and difficulty in fitting the large number of parameters required, models such as LEACHM and HYDRUS-2D were of little improvement over the more simple, deterministic models such as GLEAMS and SPASMO.

In a study with acetochlor and terbuthylazine and using K_d and $t_{½}$ values independently derived in a laboratory incubation study, Ma et al. (2000) found that PRZM-3 (Carsel et al. 1998) significantly underestimated dissipation of both herbicides in the field. When these parameters were derived from the field trials through inverse modelling, the predicted dissipation was a better fit when using the two-rate dissipation sub-model, but not when using a simpler, single-rate sub-model. Also, PRZM-3 failed to predict the early appearance of herbicide in the subsoil layers, which was postulated to be the result of non-equilibrium sorption and transport (e.g. preferential flow) that cannot be simulated by this model. Using the same data set, Ma et al. (2004d) found the Root Zone Water Quality Model (RZWQM (Ma et al. 2004c)) resulted in poor prediction when a linear partitioning model was used but predictions were improved when a two-site sorption model was used. In a separate study involving acetochlor dissipation in two soils, Ma et al. (2004a) found that a simple model based on first-order kinetics did not adequately explain the dissipation of this herbicide but that more complex models based on quadratic, first-order double exponential, first-order biphasic or two-compartment functions were more appropriate.

Obtaining satisfactory fits from these models was not an easy task. To model the fate of acetochlor and terbuthylazine using RZWQM required the fitting of a complex time-dependent pesticide sorption model (Ma et al. 2004d) by someone sufficiently familiar with the model to be able to manipulate the source code and required more than 6 months of full-time effort. PRZM-3 proved to be less capable of modelling dissipation of these two herbicides, even when utilising a two-compartment degradation model. PRZM-3 did not predict the rapid appearance of residues in the 5 – 10 cm layer (Ma et al. 2000), presumably due to its inability to model preferential flow.

Müller et al. (2004) used Opus2 to model the dissipation of atrazine and found degradation to be the most important determinant in the fate of this herbicide but that the Arrhenius equation incorporated in Opus2 did not correctly describe the effect of temperature on degradation rates determined in the laboratory. As was the case with previous research mentioned above, modelling dissipation assuming first-order kinetics and laboratory derived half-lives did not accurately represent field dissipation but when the modelling function was changed to a biphasic, sigmoidal degradation equation, the results from Opus2 were significantly improved.

The models LEACHM, HYDRUS-2D, Opus2, PRZM and RZWQM, mentioned above, all use the Richards equation to model unsaturated water flow through the vadose zone, and all except OPUS2 use the convection/dispersion equation for solute transport to model the movement of pesticides, nutrients or pollutants (Ma et al. 2000; Ma et al. 2004b; Sarmah et al. 2005). An assumption of the Richards equation is that the profile is homogenous and undisturbed (Jacques et al. 2002). However, this is often not the case in practice, with a significant fraction of herbicides applied to cultivated ground, and most uncultivated soils are highly susceptible to preferential flow through biopores, fractures and other anomalies, which significantly alter the flow of water and solutes (Flury et al. 1994). The movement of water through fractures, macropores and flow processes such as interflow, fingering, funnelling, etc, are all grouped and called preferential flow. Of these models only HYDRUS-2D can accommodate preferential flow (Logsdon 2002).

SPASMO has been developed in New Zealand to describe the leaching of both organic and inorganic pollutants. It is a mechanistic model that predicts the transport of water through the root zone using a water capacity approach and considers the soil to have both mobile and immobile pathways for water and solute transport. The immobile domain represents the soil matrix while the mobile domain represents the pore space (Green et al. 2002). In a study of seven pesticides, mobility and degradation parameters were fitted to field persistence data using inverse modelling with GLEAMS, LEACHM and HYDRUS-2D. These parameters were then used to evaluate the performance of SPASMO which predicted accurately for soil water concentrations of the pesticides but tended to over-estimate the observed soil concentrations of the pesticides (Close et al. 2003). In a similar study where the pesticide attenuation parameters (K_{oc} and $t_{½}$) were optimised to fit the observed data with PEST and then used in model simulations, GLEAMS performed best and the SPASMO simulations were rated as reasonable (Sarmah et al. 2005).

SPASMO has also been used to predict the duration and extent of leaching of nitrate from a closed sheep feedlot (Rosen et al. 2004) and of arsenic from CCA-treated posts in a vineyard (Clothier et al. 2006). Additionally, SPASMO was used to create the decision-support tool ‘The GROWSAFE® Calculator’, to help growers and Regional Councils choose herbicides that are less likely to leach and/or build up in the soil (Green et al. 2004; Snow et al. 2004). The GROWSAFE® Calculator was developed for New Zealand conditions by running hundreds of iterations of SPASMO using soil data from the New Zealand Soils Database (Landcare Research), weather data from the National Weather Database (NIWA) and pesticide data from the international literature. The SPASMO outputs are stored within the calculator which then uses a probability approach to output selected results upon the input of selected criteria such as soil type and rainfall.

2.3 Soil Organic Carbon and Pesticide Fate

It is clear that the role of organic matter is paramount in determining the behaviour and fate of herbicides in soil. However, it is insufficient to simply quantify the amount of organic matter in the soil, it must also be qualified (Beyer et al. 1996; Ahmad et al. 2001). Ahmad et al. (2001) found significant correlations between aromaticity of the SOM and K_{oc} values and could thus explain the variations in K_{oc} values quoted in the literature. All the herbicide phenomena discussed in Section 2.2 occur at the interface of the soil particulates and the soil solution (Pignatello & Xing 1996). A very important component of soil organic material that has been implicated as critical to several of these phenomena is the component that is sufficiently small to be deemed as in solution (McDowell 2003). In particular the ratio of aromatic to linear carbon molecules is important as this has a strong impact on the adsorption of pesticides (Ahmad et al. 2001; Weishaar et al. 2003). However, the nature of this organic matter shows great variation in its structure depending on its parent material, soil type and agricultural use.

2.3.1 *Dissolved Organic Carbon*

Dissolved organic carbon (DOC) is generally described as complex organic matter present in the soil solution that passes through a 0.45 µm filter (Bolan et al. 1996; Chantigny 2003; Zsolnay 2003). This is the most bioavailable fraction of the SOM since all biological uptake mechanisms require an aqueous environment (Marschner & Kalbitz 2003) as do all sorption and diffusion mechanisms (Shelton & Doherty 1997). As this fraction of the SOM has by its nature a high surface area and is highly mobile, it has been implicated in the degradation and transport of pesticides since the 1970's (Ballard 1971). Initial emphasis was only on DOC that was sourced from naturally occurring organic matter, but more recently, with the increase of organic waste disposal on land, both endogenous and exogenous DOC have been demonstrated to play a role in these processes. Because of the environmental importance of exogenous DOC, the two types of DOC will be treated separately here.

2.3.2 *Endogenous DOC – Sorption and Transport*

Ballard (1971) implicated the role of DOC in the transport of DDT when he achieved greater movement of DDT after it was mixed with a soluble combination of organic matter and urea, and applied to the top of leaching columns. By the early 1980s Means & Wijayrathne (1982) had clearly identified the increased adsorptive capability of small organic particles. They found that organic particles which passed through a 0.45 µm filter were 10 to 35 times better as sorptive substrates for the herbicides atrazine and linuron than larger organic particles. Working with water soluble organic materials extracted with distilled water from a high organic carbon (27%) peat soil, Madhun et al. (1986) demonstrated for the first time the binding of pesticides to DOC. The DOC involved was quantified as having a mass range of 700 to 5000 Daltons and closely resembled fulvic acids. For the herbicides bromacil, diuron, simazine and chlorotoluron, they reported sorption about 70 times higher in the DOC solution compared to the soil from which it was extracted. They concluded, DOC would likely play an important role in the mobility and transport of pesticides. Conversely, Pennington et al. (1991) found that with water soluble soil organic matter (WSSOM) derived from soils containing relatively low organic matter contents, there was no measurable binding of the herbicides bromacil, metribuzin or alachlor.

In a further development of the sorption discussion, Barriuso et al. (1992b) studied the adsorption-desorption isotherms of atrazine, dimefuron and carbetamide on soil in the presence of both endogenous and exogenous DOC. They found the added dissolved organic matter (DOM) either increased or decreased adsorption of a given herbicide depending on the preceding conditioning of the soil or the DOM. In lysimeter studies with isoproturon and simazine, Worrall et al. (1999) found that leaching of these herbicides occurred largely in the first few samples following rainfall and this coincided with the movement of large amounts of DOC. A similar result was achieved by Williams et al. (2000) for napropamide using packed soil columns. The variation in the effects of DOC reported make it difficult to anticipate the effect of DOC on the sorption and transport of herbicides in any particular situation although, if large quantities of DOC are present, herbicide transport may be promoted.

2.3.3 *Endogenous DOC – Degradation*

In terms of degradation and abiotic hydrolysis in particular, Noblet et al. (1996) found only one of five pesticides studied was affected by the presence of DOM. Chlorpyifos exhibited a 32% decrease in hydrolysis rate in the presence of 34.5 mg/L DOM while atrazine, simazine, diazinon and methylparathion were unaffected. In a study on the effect of DOC on photodegradation, de Bertrand and Barceló (1991) concluded that in real environmental situations, the presence of DOC enhanced the photodegradation of carbaryl and carbofuran. Similarly, Gerecke et al. (2001) demonstrated DOC-mediated phototransformation of isoproturon and diuron in sunlit surface waters while Sakkas et al. (2002) observed a similar result for chlorothalonil. Conversely, Bachman & Peterson (1999) found increasing concentrations of DOC reduced photolysis reaction of carbofuran and attributed this to the binding of the pesticides to DOC. Navarro et al. (2004) investigated the effects of DOC in sea, river and ground waters on the degradation of terbuthylazine, simazine, atrazine and prometryn. They found light had little effect on the removal of the herbicides from river water but had a marked effect on their removal from sea and ground water, with pesticide removal inversely proportional to DOC concentration. The greatest persistence of all four herbicides was in the ground water. Considering these diverse results in the light of our high OM soils I would conclude that the OM would have a significant impact but, depending on the nature of the pesticide it could either enhance or retard degradation depending on the properties of the pesticide molecule. For instance, if the ionic strength of the OM resulted in an increase in the ionisation of the pesticide then degradation is highly likely to be enhanced.

2.3.4 *Exogenous DOC – Sorption and Transport*

The addition of organic amendments to the soil introduces another level of complexity and usually significantly alters normal herbicide behaviour. In studies with napropamide, Nelson et al. (1998) found that in soils amended with sewage sludge two years previously, the presence of higher levels of DOC doubled the amount of the herbicide in the breakthrough leachate (although < 1.5% of applied herbicide) but the overall higher levels of OC halved the depth at which the centre of mass of herbicide was found. In subsequent studies Nelson et al. (2000a) and Nelson et al. (2000b) demonstrated that for dry soils, the breakthrough peaks for both napropamide and DOM were concurrent while for wet soils the breakthrough for napropamide was significantly delayed compared to that of DOM. In experiments with atrazine, Celis et al. (1998) demonstrated that DOM derived from sewage sludge varied in its sorption ability depending on the way the sludge was treated. DOM from these sources generally reduced atrazine sorption on soil although composted sewage sludge had the opposite effect. In studies involving effluent from different sources, Seol & Lee (2000) concluded that for atrazine and prometryn the association with effluent DOM was small to negligible but noted even very small changes can be significant if taken over several years of effluent disposal. In a later study however, Seol & Lee (2001) found that alkaline effluent increased the pH of the leachate, enhanced dissolution of organic carbon and decreased average flow rates which allowed for increased desorption time. The coupled effect of these processes in some cases enhanced the movement of atrazine and prometryn. From the literature it would appear difficult to predict the effect of DOC on the sorption and transport of herbicides as there are several factors involved including: quantity of immobile OC added to the system, age and treatment of effluent and sludge and the chemical properties of the effluent.

However, the source of all the DOC considered has mainly been sewage and effluent and likely to differ in nature and quantity from DOC sourced from solid waste.

2.3.5 *Exogenous DOC – Degradation*

When comparing the effect of solid and liquid exogenous carbon on the degradation of 2,4-D and simazine, Cox et al. (2001) found that DOC from the liquid waste formed associations with 2,4-D but not with simazine. They also found solid waste generally had less effect on the soil half-life of the herbicide than when the exogenous carbon was in liquid form. However, the effects of the liquid amendment were radically different, increasing the half-life of 2,4-D and decreasing the half-life of simazine. The increased half-life of 2,4-D was attributed to the strong association of the more polar 2,4-D with the increased levels of DOC in the liquid waste.

2.4 Herbicides Used in this Study

The herbicides evaluated for bioavailability (Chapter 3) are those which are used for weed control in onion crops, viz; alachlor, chlorpropham and pendimethalin (O'Connor 2003). They are also used on other vegetable crops such as vegetable brassicas and lettuce. The two herbicides used for the degradation and leaching studies (Chapters 5 and 6) were atrazine and bromacil. These two herbicides were selected as both have been reported to have leached out of the root zone in New Zealand soils (Close 1993b; James et al. 1994; Close 1996; James et al. 2003; Müller et al. 2007).

2.4.1 *Selected Herbicide Properties*

Of the herbicides chosen for this study (Figs 2.1 – 2.5), atrazine is probably the most researched herbicide in the world. A Google Scholar search on atrazine resulted in more than 77,000 articles and papers referring to this herbicide. For the other herbicides in this study, a search on alachlor produced about 8,600 articles while pendimethalin, bromacil and chlorpropham produced only 4,400, 2,430 and 1,600 respectively. Within the large number of publications on these herbicides there is a diversity of results and conclusions. This particularly applies to some important properties such as soil sorption coefficients and herbicide half-lives in soil. These have previously been summarised in the review literature (Vogue et al. 1994; Wauchope 2006). The chemical family, mode of action, water solubility, and the range of values published in the literature for soil sorption, herbicide half-life in the soil and dissociation constant of these chemicals are presented in Table 2.1.

Table 2.1: Chemical family, mode of action, water solubility, soil organic carbon partition coefficient, half-life in soil and dissociation constant for the five herbicides used in these studies.

Herbicide	Chemical family[1]	Mode of action[2]	Solubility[3] (mg/L)	Partition coefficient[4] (K_{oc})	Half-life[4] (d)	pKa[5]
Alachlor	Chloroacetamide	Inhibition of cell division	242	120-209	14-70	0.62
Atrazine	Triazine	Photosystem II inhibitors	33	38-288	18-402	1.70
Bromacil	Uracil	Photosystem II inhibitors	700[6]	2.3-33	61-350	9.27
Chlorpropham	Carbamate	Inhibition of mitosis	89	245-816	30	4.68[7]
Pendimethalin	Dinitroaniline	Microtubule assembly inhibition	0.3	5000-29000	8-480	2.80

[1] (Tomlin 2003)

[2] (Heap et al. 2007)

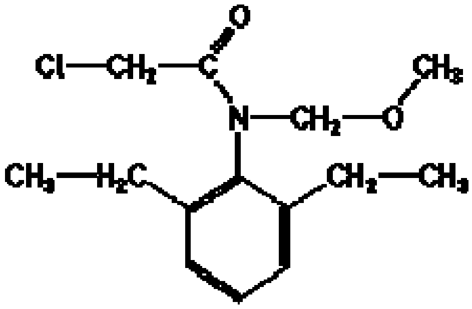
[3] Solubility in water at 25°C (Vogue et al. 1994; Wauchope 2006).

[4] Range of several published values (Vogue et al. 1994; Wauchope 2006).

[5] Dissociation constant (pKa) at 25°C (Tomlin 2003).

[6] Solubility at pH 7, at pH 5 = 807 and pH 9 = 1280 (Wauchope 2006).

[7] pKa at 20°C (Tomlin 2003).



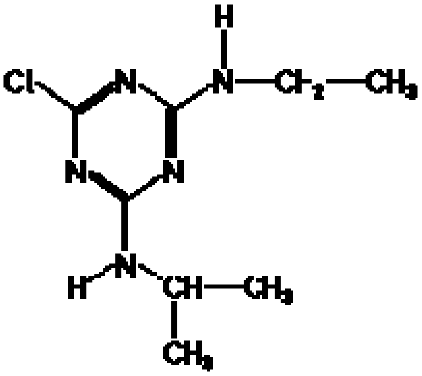
IUPAC[1]: 2-chloro-2′,6′-diethyl-*N*-methoxymethylacetanilide
CAS[2]: 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide

Fig. 2.1: Structure[3] and chemical names for alachlor.

[1] IUPAC, the International Union of Pure and Applied Chemistry.

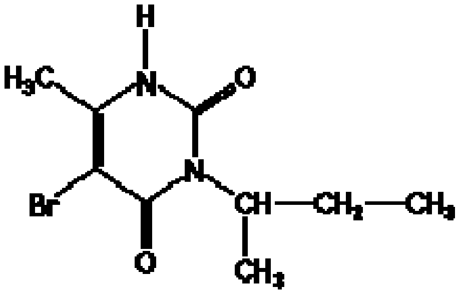
[2] CAS is a division of the American Chemical Society.

[3] Structure diagrams from (Wood 2006).



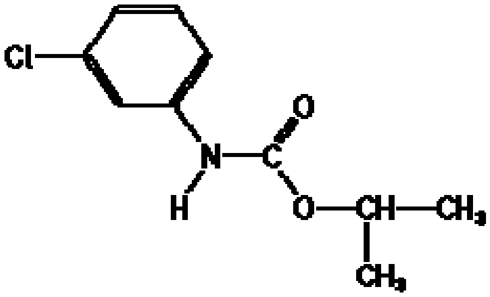
IUPAC:	6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine
CAS:	6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine

Fig. 2.2: Structure and chemical names for atrazine.



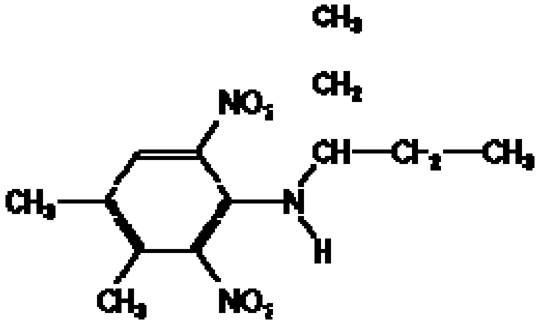
IUPAC:	(*RS*)-5-bromo-3-*sec*-butyl-6-methyluracil
CAS:	5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1*H*,3*H*)-pyrimidinedione

Fig. 2.3: Structure and chemical names for bromacil.



IUPAC:	isopropyl 3-chlorocarbanilate
CAS:	1-methylethyl (3-chlorophenyl)carbamate

Fig. 2.4: Structure and chemical names for chlorpropham.



IUPAC: *N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine
CAS: *N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine

Fig. 2.5: Structure and chemical names for pendimethalin.

The herbicides used in the bioavailability experiments were chosen to match typical farming uses for the crops evaluated. However, more persistent and mobile herbicides were used in the degradation and mobility experiments. The two herbicides selected have been widely used for this purpose and therefore there is a good understanding of their behaviour in the soil. All herbicides were used as supplied for commercial use (i.e. the formulated product as opposed to technical material) as the adjuvants present in the formulated products can have a significant effect on the soil interactions of the herbicide. For example, Reddy & Singh (1993) found that acrylic polymers reduced the leaching of bromacil in soil columns while Tan & Singh (1995) found a similar result with cationic surfactants. Rodríguez-Cruz et al. (2007) demonstrated the partial immobilisation of atrazine with the cationic surfactant ODTMA and Swarcewicz et al. (1998) found that a vegetable methylated rapeseed oil based surfactant significantly reduced the dissipation of trifluralin.

2.5 Summary of Literature Review

The soil/herbicide relationship is very complex and the influence that individual soils have on the behaviour and fate of herbicides varies considerably. There are also numerous factors which need to be taken into account when trying to understand and elucidate herbicide performance and environmental fate including soil structure, pH, soil moisture, microbial activity and external factors such as temperature and rainfall. It is evident from the literature however, that the predominant determinant which has the most influence on the herbicide is the organic matter of the soil. This factor mainly determines the biological activity, the propensity to leach and also the ultimate fate or degradation of the herbicide. However, even within the soil organic matter component there is variation due to its age, state, particle size, chemistry, molecular structure and solubility. One important fraction of the soil organic matter is the dissolved fraction. It has undergone intense scrutiny in recent years and has been implicated in many pesticide fate scenarios although diverse results have been reported. Attempts to describe herbicide fate have lead to numerous models which have tended to increase in complexity as understanding of various soil functions increases. However, it appears that the role of the researcher is not yet redundant and only by experimentation can the herbicide behaviour in a particular situation be determined, especially when unusual factors such as soil amendments are introduced.

CHAPTER 3

BIOAVAILABILITY AND PLANT UPTAKE

CHAPTER 3: BIOAVAILABILITY AND PLANT UPTAKE

3.1 Objective

To compare the bioavailability of three common herbicides (alachlor, chlorpropham and pendimethalin) in high organic matter paper pulp and sawdust to their bioavailability in Horotiu and Mangateretere soils using bioassays with tolerant and susceptible plant species. The hypothesis being tested is that high organic matter soil amendments lower the plant availability of herbicides due to overall greater adsorption to the OM.

3.2 Introduction

The experiments described in this chapter address the concern that the susceptibility of plants to herbicides used for weed control will differ when high organic matter amendments are added to the soil or used as growing media. Given that organic matter content is very important in determining the behaviour of herbicides in the soil (Section 2.3), presumably the addition of significant quantities of high organic matter amendments should reduce the amount of herbicide available to plants (bioactive) in the soil. This would be exhibited as the herbicide having reduced phytotoxicity in high organic matter amendments compared to soil.

However, this reasoning is based on the typical variation of naturally occurring organic matter in soils and may not necessarily hold true for organic matter of different types or in quantities well outside the norm. Also, any effect due to increased soil OM should not be dependant on whether it requires only small doses of herbicide to produce a response (sensitive species) or whether it requires greater doses (tolerant species). Thus, experiments were carried out to determine the phytotoxicity of herbicides applied to different media on tolerant and susceptible crop species grown in that media. Herbicide concentrations in the growing media can be determined by chemical extraction and quantification but the results may be difficult to interpret as there is no accurate data relating herbicide concentration to biological activity over time. Therefore, the impact of known concentrations of herbicides on test plants of selected crop and sensitive species were measured directly by comparing their growth with that of untreated plants (bioassay).

The tolerant species selected are all high value crops commonly grown in intensive agricultural systems where loss of soil organic matter is likely to occur and thus the use of soil amendments to improve soil health is a realistic option. The tolerant species used were onions (*Allium cepa* L.), lettuce (*Lactuca sativa* L.) and vegetable brassicas (*Brassica oleracea* L.). The herbicides selected, alachlor, chlorpropham and pendimethalin, are commonly used in field vegetable crops and the particular crop/herbicide combinations evaluated were determined by the registered uses for the individual herbicides (O'Connor 2003).

The sensitive plant species were selected based on the literature and they also had to be readily available in New Zealand. For alachlor, annual ryegrass (*Lolium multiflorum* Lam.) and foxtail millet (*Setaria italica* (L.) Beauv.) were used (Rahman & James 1994), for pendimethalin garden cress (*Lepidium sativum* L.), oats (*Avena sativa* L.) and sorghum (*Sorghum bicolor* (L.) Moench) (Pestemer & Zwerger 1999; Hatzinikolaou et al. 2004) and for chlorpropham annual ryegrass and garden cress (Pestemer & Zwerger 1999).

Both tolerant and sensitive plant species were evaluated as bioavailability is not necessarily a linear function and testing on species of differing susceptibilities will offer a better understanding of bioavailability over a range of concentrations.

3.3 Materials and Methods

3.3.1 *Media Preparation*

Four experiments were conducted in the glasshouse to test the biological activity of three herbicides on selected tolerant and sensitive species grown in four different growing media viz.: paper pulp, sawdust, Horotiu silt loam soil and Mangateretere silt loam soil. The Mangateretere soil was used as this was the soil in which the original Rich Ditch field trials were conducted in. The Horotiu silt loam soil was selected as this soil is one of the most researched soils in terms of pesticide behaviour in New Zealand. This soil is of volcanic origin in which all the clay is allophane while the Mangateretere soil is a recent alluvial soil. The paper pulp, sawdust and Mangateretere soil were collected from the Lawn Road Research Station of the New Zealand Institute for Crop and Food Research Limited, Hastings, on 19 April 2002. The sawdust and paper pulp had been recently delivered for their field trials and were still fresh, while the soil was collected to a depth of 10 cm from a fallow area. The Horotiu soil was collected from the Rukuhia Research Orchard in a manner similar to that for the Mangateretere soil. Immediately prior to use in experiments the media were passed through a 4-mm sieve, thoroughly mixed and four subsamples taken for moisture content determination. Moisture content was determined gravimetrically by drying the soil for 24 h at 105°C. No attempt was made to alter the water content by either wetting or drying prior to use in the experiments. Some physico-chemical properties of the growing media are presented in Table 3.1.

Table 3.1: Some physico-chemical properties of the four growing media.

Growing media	Organic C (%)	pH[1]	Density[2] (kg/L)	Sand[3] (%)	Silt[3] (%)	Clay[3] (%)
Paper pulp[4]	22	7.9	0.23	-	-	-
Sawdust[4]	46	5.8	0.13	-	-	-
Horotiu silt loam[5]	5.1	5.9	0.57	19	58	23
Mangateretere silt loam[4]	4.3	5.3	0.87	2	66	32

Growing media	CEC[6] (me/100 g)	Exchangeable bases (me/100 g)			
		Ca	Mg	K	Na
Paper pulp	93	95	1.9	0.6	2.3
Sawdust	9	4	1.3	1.8	1.1
Horotiu silt loam	14	4	0.6	0.4	0.1
Mangateretere silt loam	18	5	0.8	0.4	0.1

[1] pH determined in water.

[2] Bulk density of 4-mm sieved material packed with a constant pressure of 3.5 kg/cm^2.

[3] Texture analyses of both soils by AgResearch, Soil Fertility Service, Hamilton.

[4] Average of 5 samples by Analytical Research Laboratories Ltd, Napier.

[5] Analysis of samples by e-lab.limited, Hamilton.

[6] CEC – cation exchange capacity.

3.3.2 *Herbicides*

The herbicides were used as the formulated product viz.: alachlor (Corral, EC (emulsifiable concentrate), 48% active ingredient (a.i.)), pendimethalin (Stomp, EC, 33% a.i.) and chlorpropham (Chloro-IPC (Yates), EC, 40% a.i.). They have widely varying biological and chemical properties (Table 2.1), including solubility and mode of action. For Experiments 1 and 2 on tolerant species, most were applied at ¼, ½, 1 and 2 times the recommended label rate. Exceptions were made and the rates lowered for alachlor where the label claim is for use on transplanted crops, as these experiments used seedling plants. Much lower rates were used in Experiments 3 and 4 on sensitive species. A summary of the herbicide label claims and experimental doses are presented in Table 3.2.

Table 3.2: Summary of some of the registered uses for the three test herbicides in New Zealand (O'Connor 2003).

		Label rates	1x rate used in experiments	Calculated dose/pot (mg a.i.)			
Herbicide	Crop	(g a.i./ha)	(g a.i./ha)	¼x	½x	1x	2x
Alachlor	onion	1440 – 2400	2000	0.475	0.95	1.90	3.80
Alachlor	broccoli	2880	2000	0.475	0.95	1.90	3.80
Chlorpropham	onion	400 – 800	800	0.19	0.38	0.76	1.52
Chlorpropham	lettuce	1200 – 3200	3200	0.76	1.52	3.04	6.08
Pendimethalin	onion	341 – 500	500	0.119	0.238	0.475	0.95

3.3.3 *Laying Down of Pot Experiments*

At the commencement of each experiment 500 mL plastic punnets were filled with a pre-determined amount of the growing media, taking into account its water content. The wet weights were: sawdust – 173 g, paper pulp – 286 g, Horotiu soil – 409 g and Mangateretere soil – 585 g for Experiment 1 and 170 g, 200 g, 460 g and 600 g respectively for Experiments 2, 3 and 4. The pots were seeded with 10 seeds (except onions 20 seeds) and thinned to 6 plants (except onions 12 plants) soon after emergence. For Experiments 1 and 2 the tolerant species (onion var. Kiwi Gold, lettuce var. Cossack and broccoli var. Marathon) were used, while in Experiments 3 and 4 the susceptible species (foxtail millet, annual ryegrass, oats, sorghum and garden cress) were used. Table 3.3 lists the crop/herbicide combinations that were used in Experiments 1 and 2. Each combination was used on all four media types. Most of the crop/herbicide combinations involved pre-emergence application of the herbicide, the exception being alachlor which was applied post-emergence to the onions. Experiments 3 and 4 evaluated a greater range of rates and these were the same for each herbicide/species combination (Table 3.4). Experiments 2 and 4 were repeats of Experiments 1 and 3 respectively to examine the consistency of results at different times of the year. All experiments were carried out in a glasshouse. In each experiment there were three replications of each herbicide/species/media combination and six replications of the untreated controls and the pots were laid out in a randomised block layout.

All herbicide treatments were applied with a CO_2 powered, moving belt type precision sprayer in 200 L/ha water using a single, even spray, TeeJet 8001e flat fan nozzle at 200 kPa. The herbicides were pre-mixed in 1-L volumetric flasks and applied to the pots the day after they were seeded (except for the post-emergence alachlor treatment). Immediately after application of the herbicides the pots were placed under overhead irrigation and approximately 5 mm of water applied to activate the herbicide. A diary of key dates for the experiments is provided in Table 3.5. The average maximum daily temperature and total solar radiation (Ruakura Metrologic Station records) for the growth periods of species used is presented in Table 3.6.

For the duration of the experiments the pots were sub-irrigated as required to maintain moisture content of 80-100% of field capacity without leaching. The plants grown in paper pulp and sawdust were given weekly supplements of a commercial nutrient mix (Yates Thrive) with a neutral pH. After about 4 – 6 weeks (Table 3.5) the plants in each pot were harvested by cutting them at soil level. The top growth was placed in a labelled paper bag and dried at 80°C for 24 h prior to weighing. Dry matter weights were recorded and the results presented as treatment averages expressed as percent of the untreated controls. In the graphical presentations of the results the error bars represent ±1 standard error of the mean (SEM).

Further analysis of the data from Experiments 1 and 2 was carried out using the ANOVA directive of Genstat (9th Edition), where the analysis took into account the replicate blocks and allowed for the interaction between media and rates. To investigate the possible influence of organic carbon on the response the organic carbon content of the media was used as levels, and the linear and quadratic components of the media factor extracted in the analysis of variance. The linear and quadratic components of the rates were also extracted to help in investigating the interaction. The data from Experiments 3 and 4 were analysed using a Bayesian smoothing technique (Upsdell 1994) to determine definitive ED_{50} and NOEL (ED_{90}) values for each herbicide/species/media combination (Pestemer & Günther 1993).

Table 3.3: **List of treatments and the crop (tolerant) species they were used on for Experiments 1 and 2.**

Herbicide	Rate (g a.i./ha)	Time	Crop species
-	-	-	Onions, Broccoli, Lettuce
Alachlor	500	post-em	onions
Alachlor	1000	post-em	onions
Alachlor	2000	post-em	onions
Alachlor	4000	post-em	onions
Alachlor	500	pre-em	broccoli
Alachlor	1000	pre-em	broccoli
Alachlor	2000	pre-em	broccoli
Alachlor	4000	pre-em	broccoli
Chlorpropham	800	pre-em	lettuce
Chlorpropham	1600	pre-em	lettuce
Chlorpropham	3200	pre-em	lettuce
Chlorpropham	6400	pre-em	lettuce
Chlorpropham	200	pre-em	onions
Chlorpropham	400	pre-em	onions
Chlorpropham	800	pre-em	onions
Chlorpropham	1600	pre-em	onions
Pendimethalin	125	pre-em	onions
Pendimethalin	250	pre-em	onions
Pendimethalin	500	pre-em	onions
Pendimethalin	1000	pre-em	onions

Table 3.4: **List of treatments used on the sensitive species bioassays Experiments 3 and 4.**

Herbicide	Rate (g a.i./ha)
Untreated	-
alachlor, chlorpropham, pendimethalin	6
alachlor, chlorpropham, pendimethalin	28
alachlor, chlorpropham, pendimethalin	57
alachlor, chlorpropham, pendimethalin	283
alachlor, chlorpropham, pendimethalin	566
alachlor, chlorpropham, pendimethalin	1132
alachlor, chlorpropham, pendimethalin	2830

Table 3.5: Summary of key dates for Experiments 1 - 4.

	Date for:			
Experiment	Potting up	Pre-emergence application	Post-emergence application	Harvest
1	17.2.03	18.2.03	13.3.03	lettuce 13.3.03 broccoli 13.3.03 onions 28.3.03
2	13 - 14.5.03	15.5.03	16.6.03	lettuce 6.6.03 broccoli 10.6.03 onions 9.7.03
3	26.2.03	28.2.03	-	28.3.03 – 3.4.03
4	8 – 9.4.03	10.4.03	-	6 – 20.5.03

Table 3.6: Average daily maximum temperature and total solar radiation for the growth period (Table 3.5) of species used in Experiments 1 - 4.

	Lettuce		Broccoli		Onions	
Experiment	Temperature (°C)	Radiation (MJ/m^2)	Temperature (°C)	Radiation (MJ/m^2)	Temperature (°C)	Radiation (MJ/m^2)
1	22.7	382	22.7	382	22.8	611
2	17.4	184	17.5	213	16.0	405
	Alachlor[1]		Chlorpropham[2]		Pendimethalin[3]	
3	23.0	456	22.8	331	23.8	347
4	19.5	394	19.2	351	19.2	358

[1] Foxtail millet and annual ryegrass

[2] Annual ryegrass and garden cress

[3] Garden cress and oats (Exp. 3) or sorghum (Exp. 4)

3.4 Results

3.4.1 *Overview*

For Experiments 1 and 2, broccoli plants grew well in all untreated growing media while the onions and lettuce grew better in the sawdust and paper pulp than in either of the two soils. None of the herbicides resulted in chlorotic symptoms in the tolerant species, however, both alachlor and chlorpropham suppressed growth when used at higher rates. For some of the combinations there was actually a promotion of plant growth when the herbicide was applied at a quarter of the normal field use rate. Similar responses have been observed with low rates of many chemicals including the triazine herbicide simazine (Appleby 1998; Van Der Schalie & Gentile 2000).

The dry matter yield results for each of the tolerant species are presented in Figs 3.1 – 3.10 as percent of the untreated controls with the error bars representing ±1 standard error of the mean (SEM). The growth of the sensitive species generally followed typical logistic dose-response curves (Pestemer & Zwerger 1999) and these are presented in Figs 3.11 – 3.22 as dry matter yield as percent of the untreated controls with the error bars representing ±1 SEM. Oats proved quite tolerant of pendimethalin (Experiment 3) and these were replaced with the more susceptible sorghum in Experiment 4.

3.4.2 *Herbicide/Tolerant Species Interactions in Four Growing Media*

3.4.2.1 <u>Alachlor on Onions</u>

When applied at twice the label rate, alachlor resulted in significant growth reduction of the onions in sawdust in both experiments (Figs 3.1 and 3.2; Table 3.7) and of the onions grown in the Horotiu soil in Experiment 1 only (Fig. 3.1; Table 3.7). The onions grown in either the paper pulp or Mangateretere soil were not affected by alachlor at any of the rates used in either experiment.

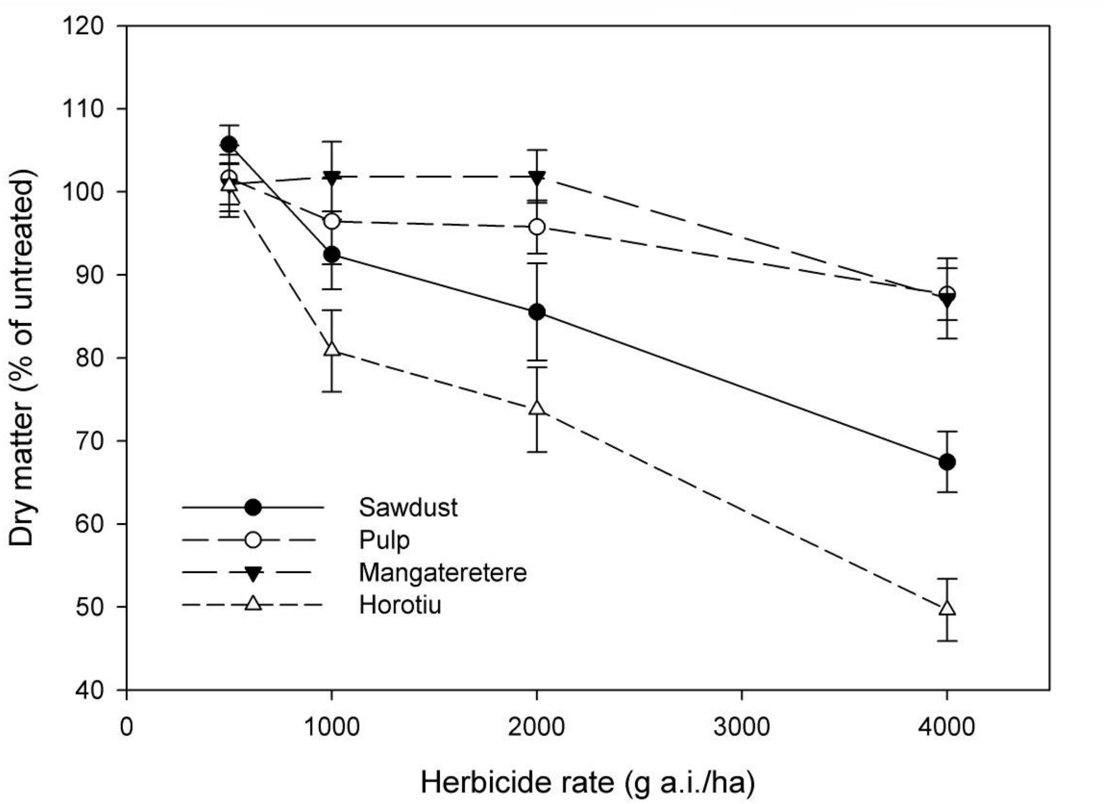


Fig. 3.1: **Effect of different rates of alachlor on onions in four growing media in Experiment 1.**

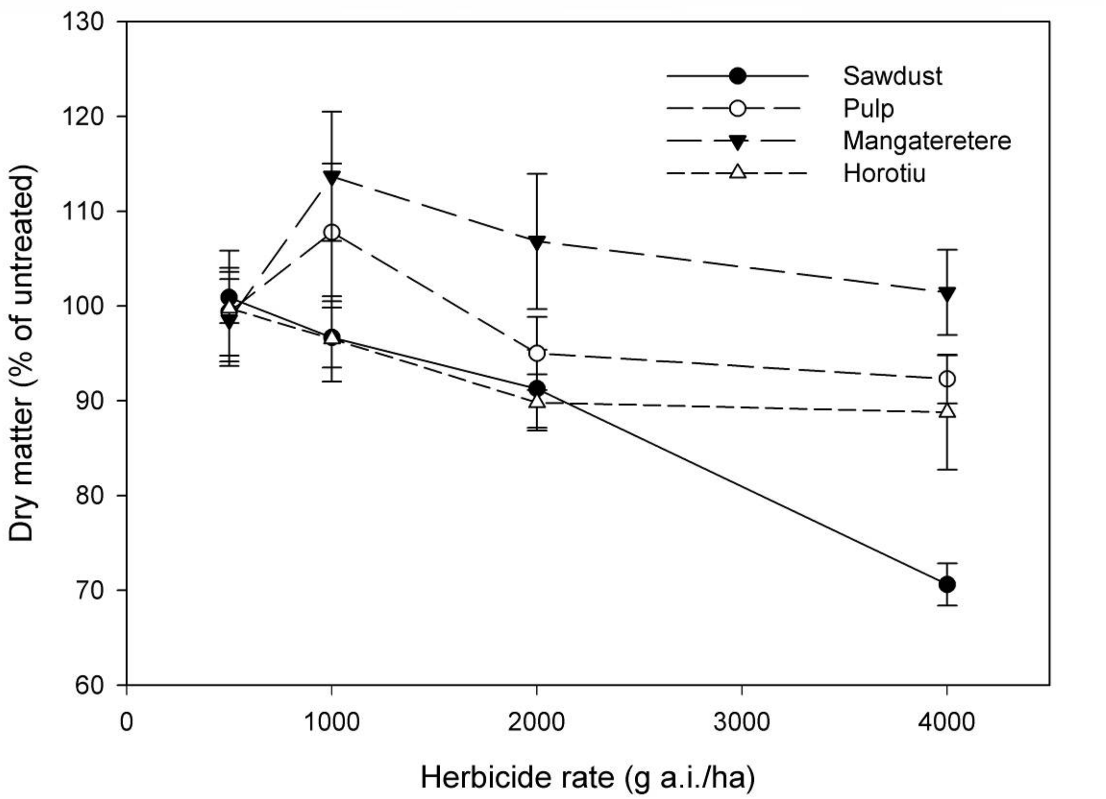


Fig. 3.2: **Effect of different rates of alachlor on onions in four growing media in Experiment 2.**

Table 3.7: Mean dry matter production and standard error for the crop species grown in Experiments 1 and 2.

		Mean dry matter[1] (% of untreated)				
	Bioassay	Growing media				
Herbicide	species	Pulp	Sawdust	Mangateretere soil	Horotiu soil	SED[2]
Experiment 1						
Alachlor	onions	97.7	88.6	98.1	76.3	4.24
	broccoli	99.5	81.6	95.6	86.7	3.15
Chlorpropham	onions	93.3	86.6	89.9	90.2	3.68
	lettuce	80.5	70.6	72.6	59.4	4.66
Pendimethalin	onions	98.0	105.0	98.3	99.0	3.99
Experiment 2						
Alachlor	onions	98.7	89.9	105.0	94.0	3.36
	broccoli	95.4	86.0	101.4	87.0	3.10
Chlorpropham	onions	73.9	59.3	97.0	82.6	4.10
	lettuce	54.8	58.2	60.4	62.9	3.65
Pendimethalin	onions	97.5	102.8	105.5	107.5	4.31

[1] Mean of the four herbicide application rates.

[2] Standard error of differences of means.

3.4.2.2 Alachlor on Broccoli

The alachlor label states to apply the herbicide after the broccoli are transplanted in the field. In this experiment the alachlor was applied pre-emergence after seeding. However, the rate was reduced to compensate for the reduced tolerance of seedling plants to the herbicide. Despite this, the high rate of alachlor resulted in severe crop suppression, especially in Experiment 1 (Fig. 3.3) where the growth of broccoli was reduced in all growing media but significantly more so in the sawdust and the Horotiu soil (Table 3.7). In Experiment 2 also, the growth was significantly reduced in these two media (Fig. 3.4; Table 3.7). Plate 3.1 presents a photographic illustration of these results. The reduction in plant growth can be seen in the sawdust and Horotiu soils as the rate of applied alachlor increases from left to right.

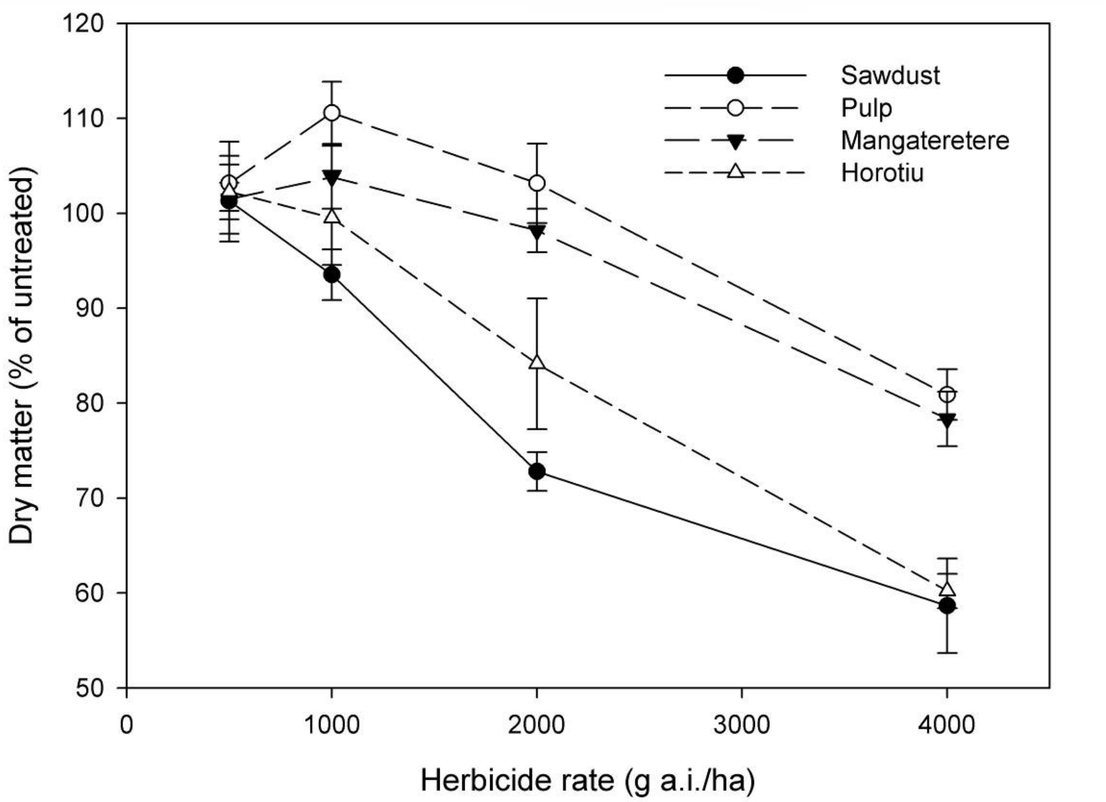


Fig. 3.3: **Effect of different rates of alachlor on broccoli in four growing media in Experiment 1.**

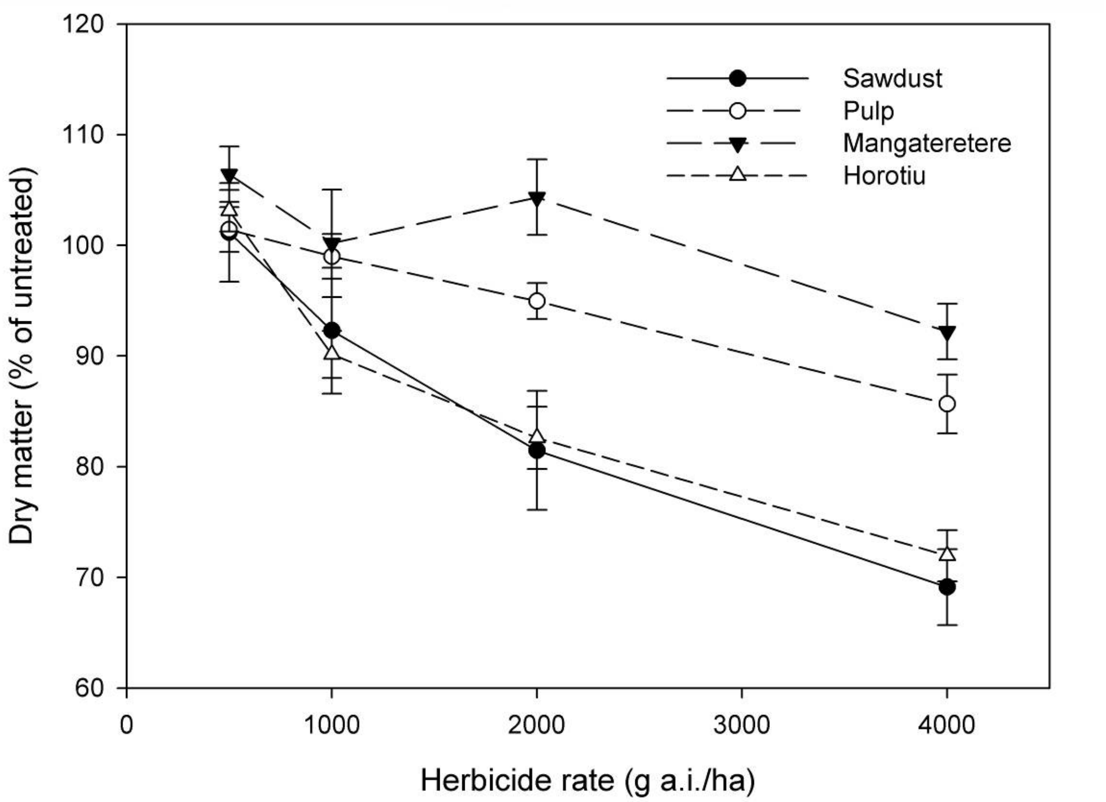


Fig. 3.4: **Effect of different rates of alachlor on broccoli in four growing media in Experiment 2.**

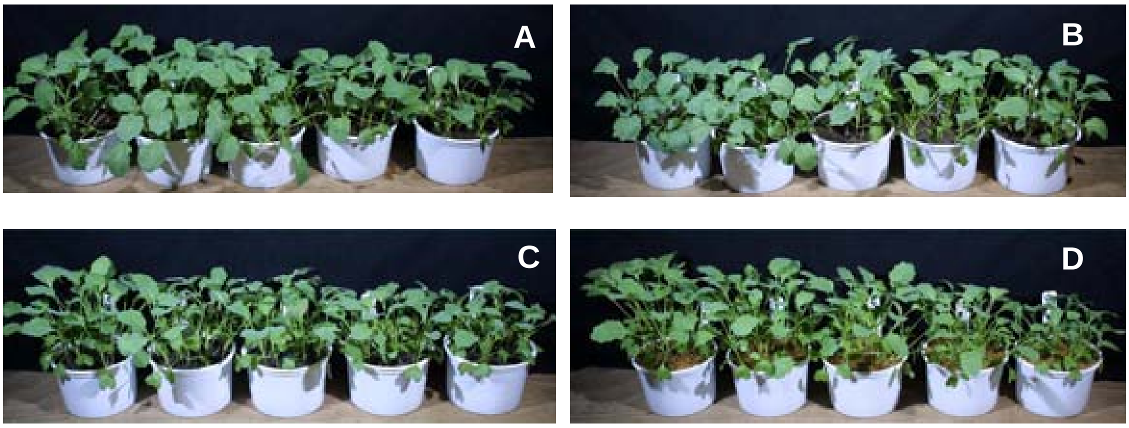


Plate 3.1: Effect of different rates of alachlor on broccoli (from L→R, untreated, 500, 1000, 2000 and 4000 g a.i./ha) in four growing media (A – Horotiu, B – Mangateretere, C – paper pulp, D – sawdust), a single replicate of Experiment 1.

3.4.2.3 Chlorpropham on Onions

Chlorpropham proved damaging to onions when used at twice the recommended rate. In Experiment 1, the onions grown in sawdust suffered greater damage than those in the other three media, although the results were not significantly different (Fig. 3.5; Table 3.7). The within treatment variability of the chlorpropham treatments was noticeably higher than for many of the other treatments and probably reflected variations within the media itself. These variations may have become critical as the concentrations of herbicide in the soil approached toxic levels. In Experiment 2 (Fig. 3.6), the effect on the growth of onions was greater than in Experiment 1. This is likely due to the cooler conditions under which the second experiment was conducted (Table 3.6). Much of the onion growth takes place in the field under summer conditions and the cooler conditions of the second experiment appear to have rendered them more susceptible to herbicide damage. Additionally, in Experiment 2, the onions grown in sawdust suffered significantly more herbicide damage than those in the other three media (Table 3.7). It is likely the kind of damage observed here is why three of the four proprietors of this herbicide recommend application only when the onion plants become more mature (i.e. after the flag stage).

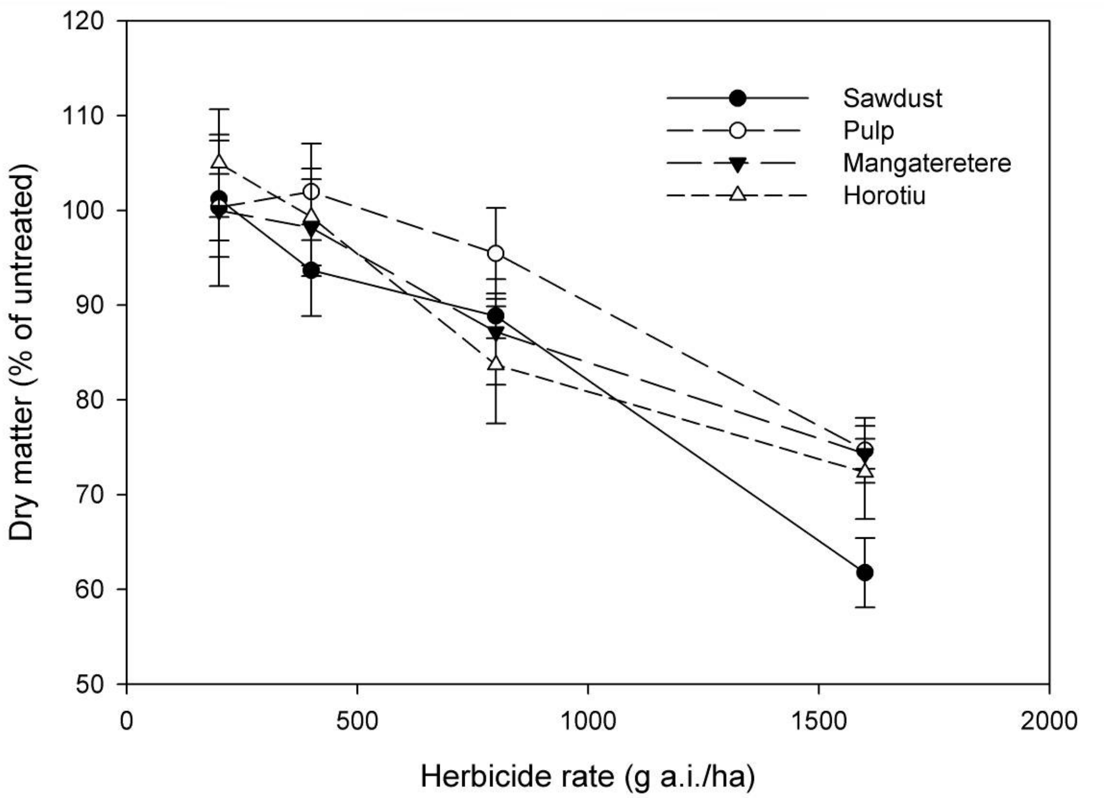


Fig. 3.5: **Effect of different rates of chlorpropham on onions in four growing media in Experiment 1.**

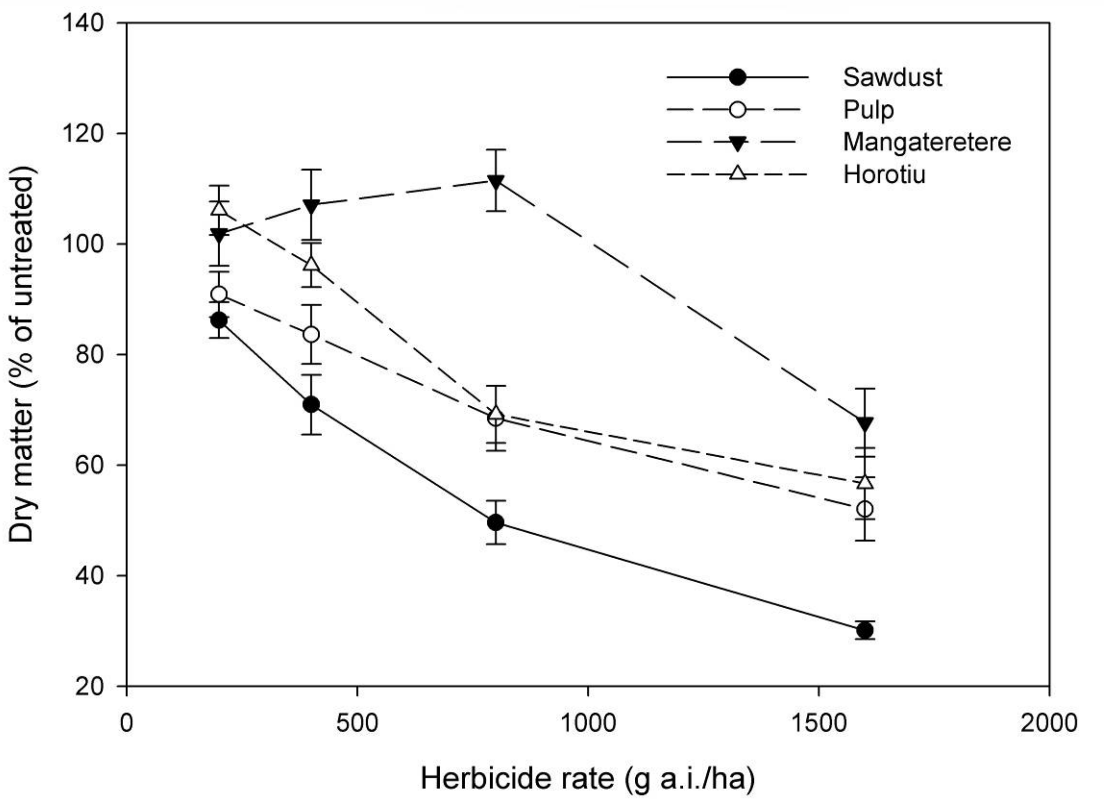


Fig. 3.6: **Effect of different rates of chlorpropham on onions in four growing media in Experiment 2.**

3.4.2.4 Chlorpropham on Lettuce

Chlorpropham proved even more damaging to lettuce than it was to onions despite being applied exactly according to label recommendations. In Experiment 1 the performance of chlorpropham was similar in three of the media but caused significantly ($P<0.05$) more damage in the Horotiu soil (Figs 3.7 and 3.8; Table 3.7). In Experiment 2 the growth suppression was nearly identical in all four media (Fig. 3.8). The photographic record presented in Plate 3.2 shows the severe phytotoxicity of chlorpropham to lettuce, particularly when applied at twice the normal use rate.

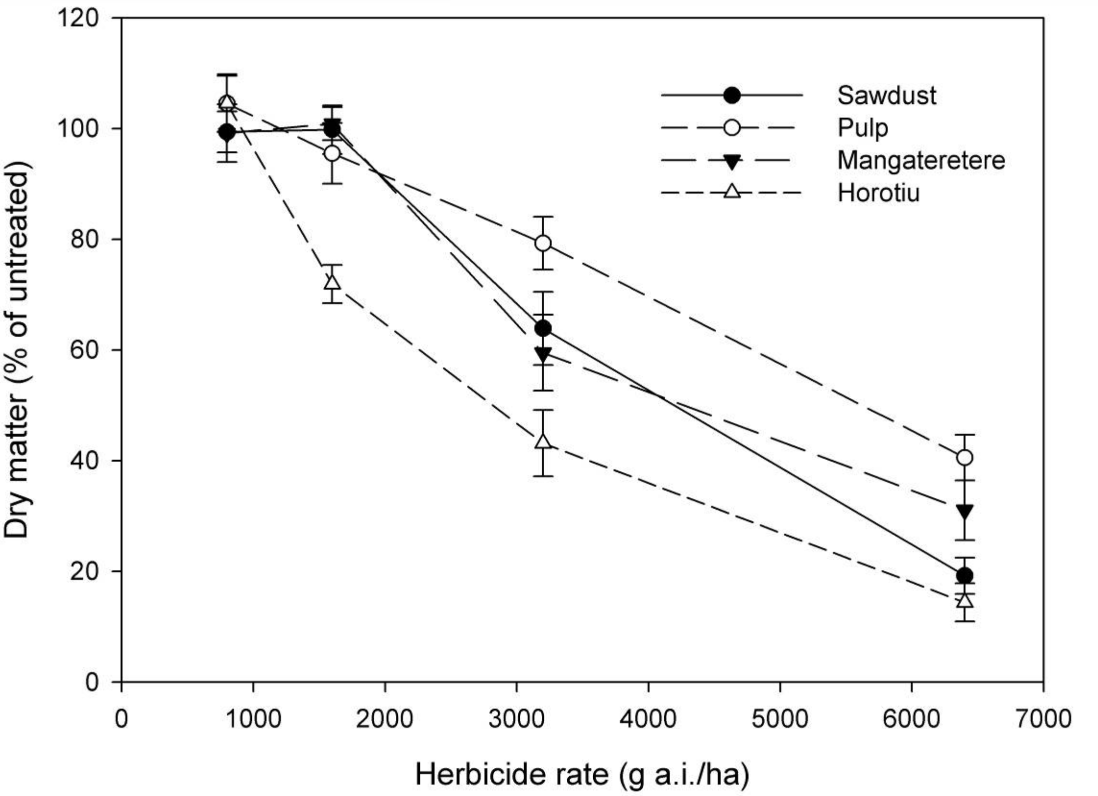


Fig. 3.7: **Effect of different rates of chlorpropham on lettuce in four growing media in Experiment 1.**

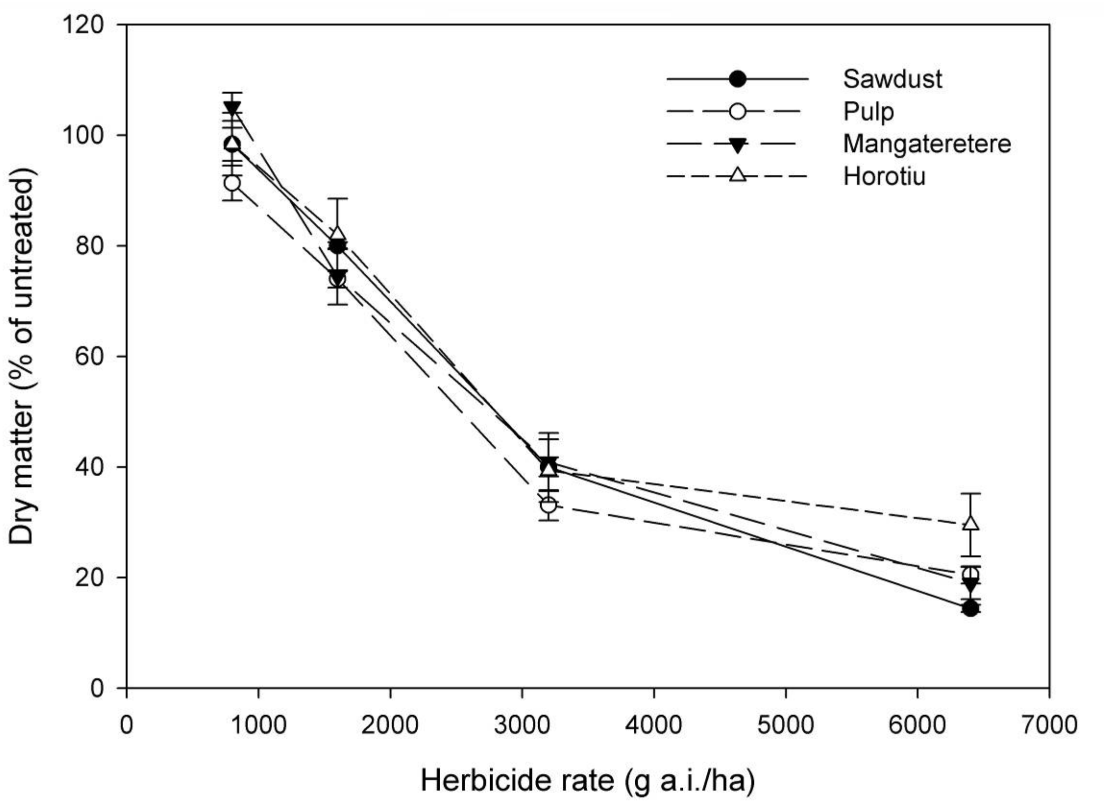


Fig. 3.8: **Effect of different rates of chlorpropham on lettuce in four growing media in Experiment 2.**

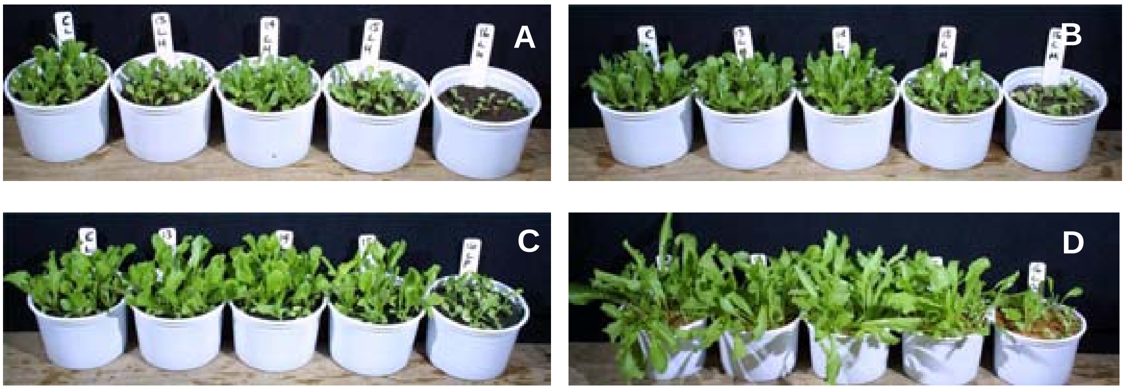


Plate 3.2: **Effect of different rates of chlorpropham on lettuce (from L→R, untreated, 200, 400, 800 and 1600 g a.i./ha) in four growing media (A – Horotiu, B – Mangateretere, C – paper pulp, D – sawdust), a single replicate of Experiment 1.**

3.4.2.5 Pendimethalin on Onions

Of the three herbicides evaluated here, pendimethalin was the only one not causing phytotoxic damage to onions when applied at rates above those recommended (Figs 3.9 and 3.10). In both experiments there was no effect from increasing the rate of herbicide and neither were there any differences due to the media in which the onions were grown (Table 3.7).

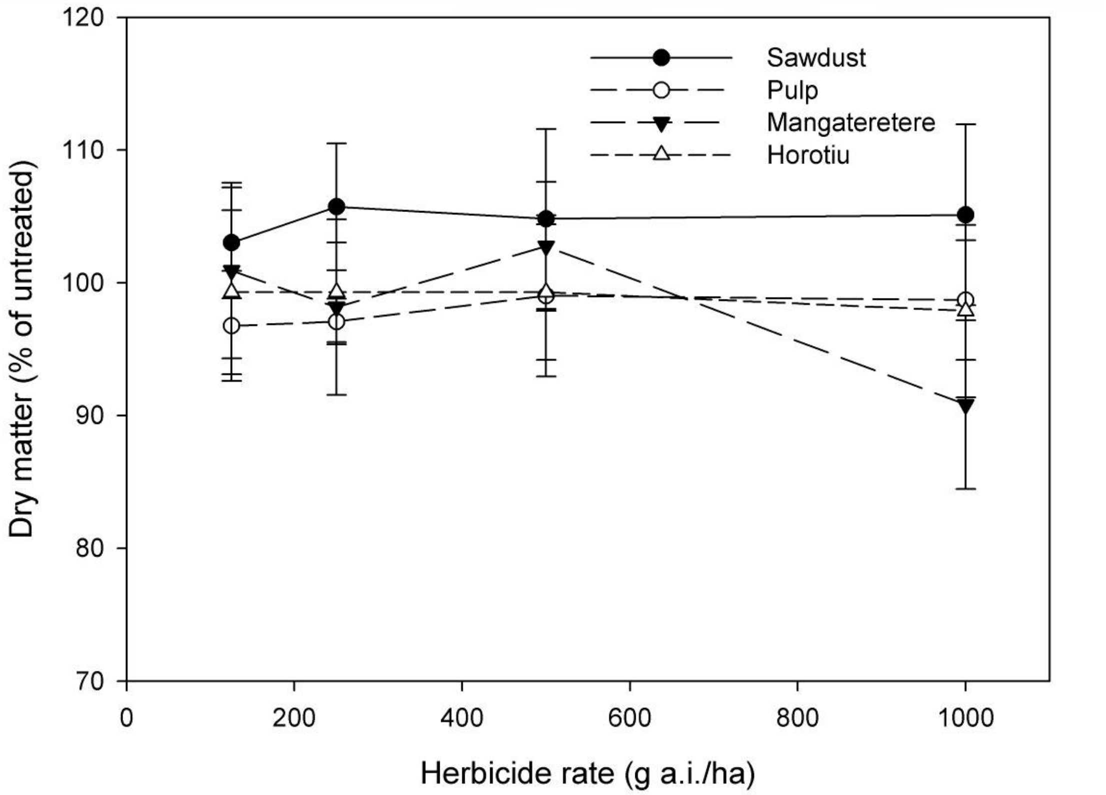


Fig. 3.9: **Effect of different rates of pendimethalin on onions in four growing media in Experiment 1.**

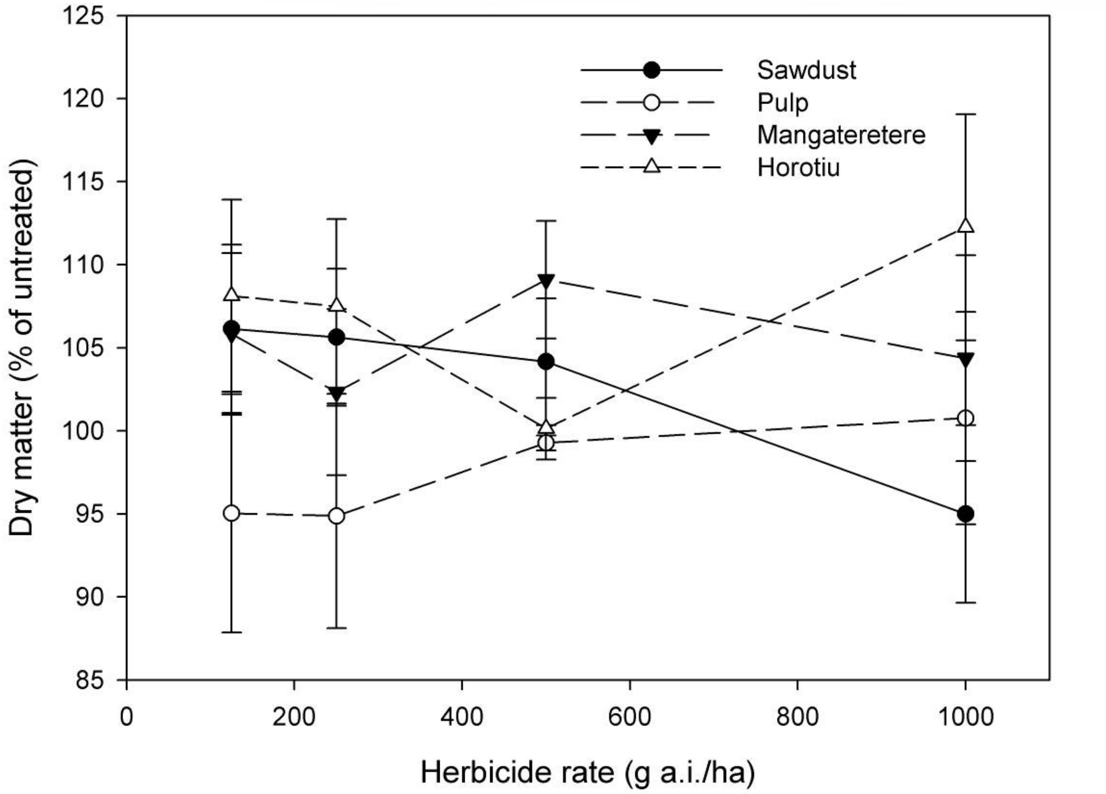


Fig. 3.10: **Effect of different rates of pendimethalin on onions in four growing media in Experiment 2.**

3.4.2.6 Effect of Organic Carbon on Bioavailability for the Tolerant Species

The analyses of variance of the interaction of dry matter production and organic carbon content of the media for the 10 different combinations of herbicide and tolerant crop species failed to yield a single significant interaction. In both Experiments 1 and 2 the different media frequently resulted in significantly different levels of bioavailability of the herbicides evaluated, but the differences in plant growth do not appear to be related to organic carbon content. In Experiment 1, both alachlor and chlorpropham resulted in less damage to the tolerant species when applied to paper pulp compared to the other three media. However, in Experiment 2, it was the Mangateretere soil which exhibited the least damage from alachlor and chlorpropham. Additionally, when these herbicides were used in sawdust, the media with the highest organic carbon content, they often caused the highest level of damage to the test plants. Thus, it must be concluded that differences in the bioavailability of various herbicides in the different media cannot be explained by their organic carbon content. The interpretation of this experimental data is covered in Section 7.3.1.

3.4.3 *Dose-response Curves for Sensitive Species in Four Growing Media*

3.4.3.1 Alachlor on Foxtail Millet

Foxtail millet was significantly more susceptible to alachlor when grown in either of the two soils compared to either paper pulp or sawdust (Figs 3.11 and 3.12). Also the shape of the dose response curves differed between the media types. The dose response curves for paper pulp and sawdust media were much steeper than that of either of the two soils.

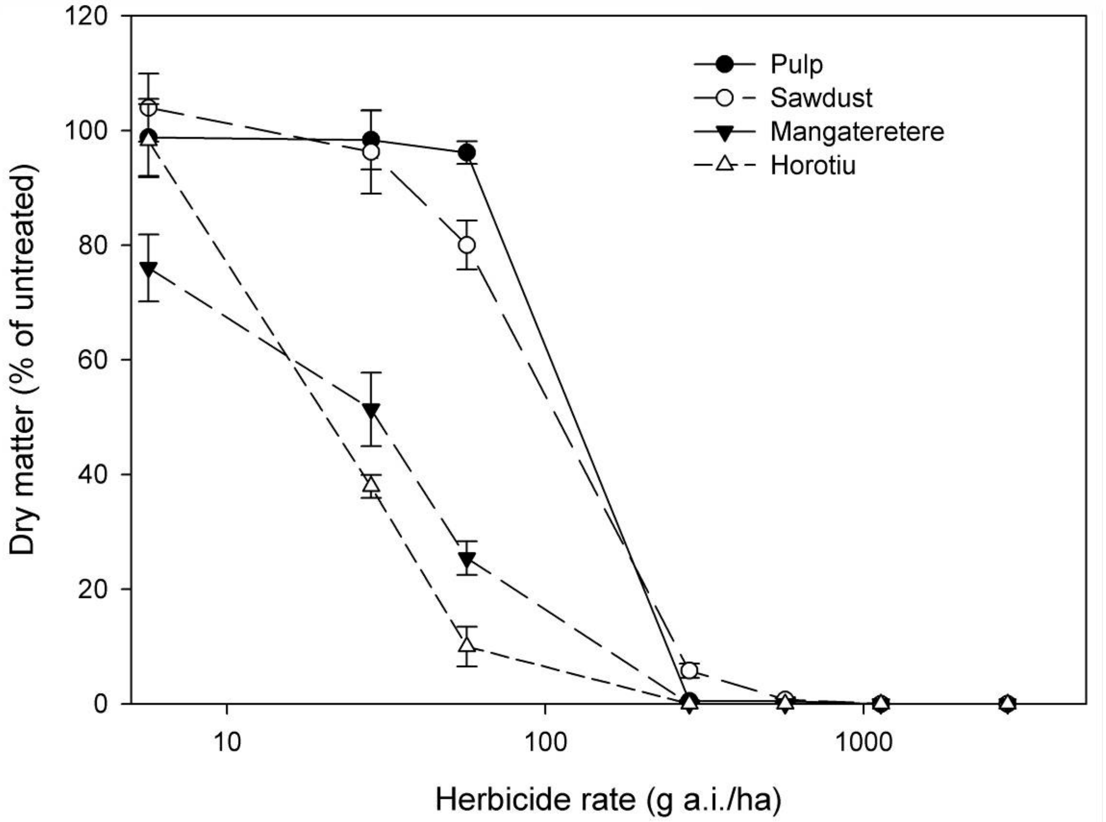


Fig. 3.11: **Comparison of dose-response curves for foxtail millet and alachlor in Experiment 3.**

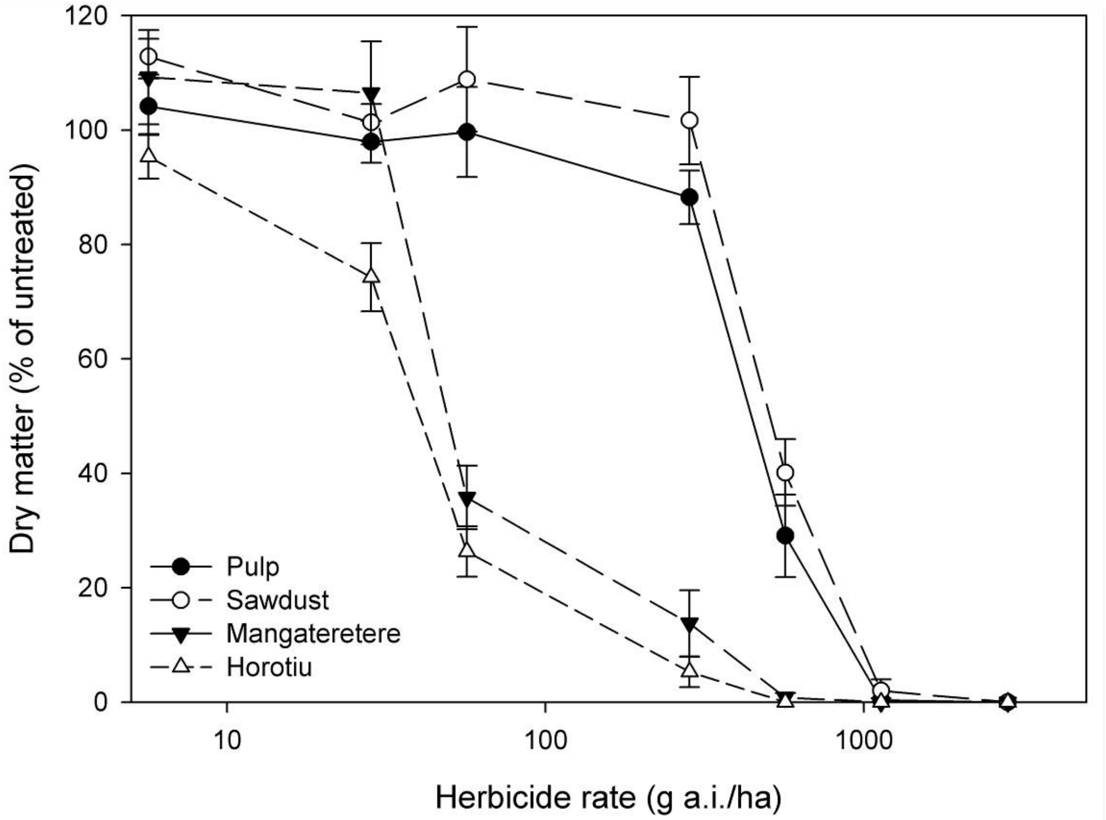


Fig. 3.12: **Comparison of dose-response curves for foxtail millet and alachlor in Experiment 4.**

3.4.3.2 Alachlor on Annual Ryegrass

The results for annual ryegrass and alachlor are similar to those for foxtail millet, particularly for Experiment 4 (Figs 3.13 and 3.14). In Experiment 3, although there was still the large difference in biological activity between the soils and the paper pulp and sawdust, the shape of the dose response curves remained similar (Fig. 3.13).

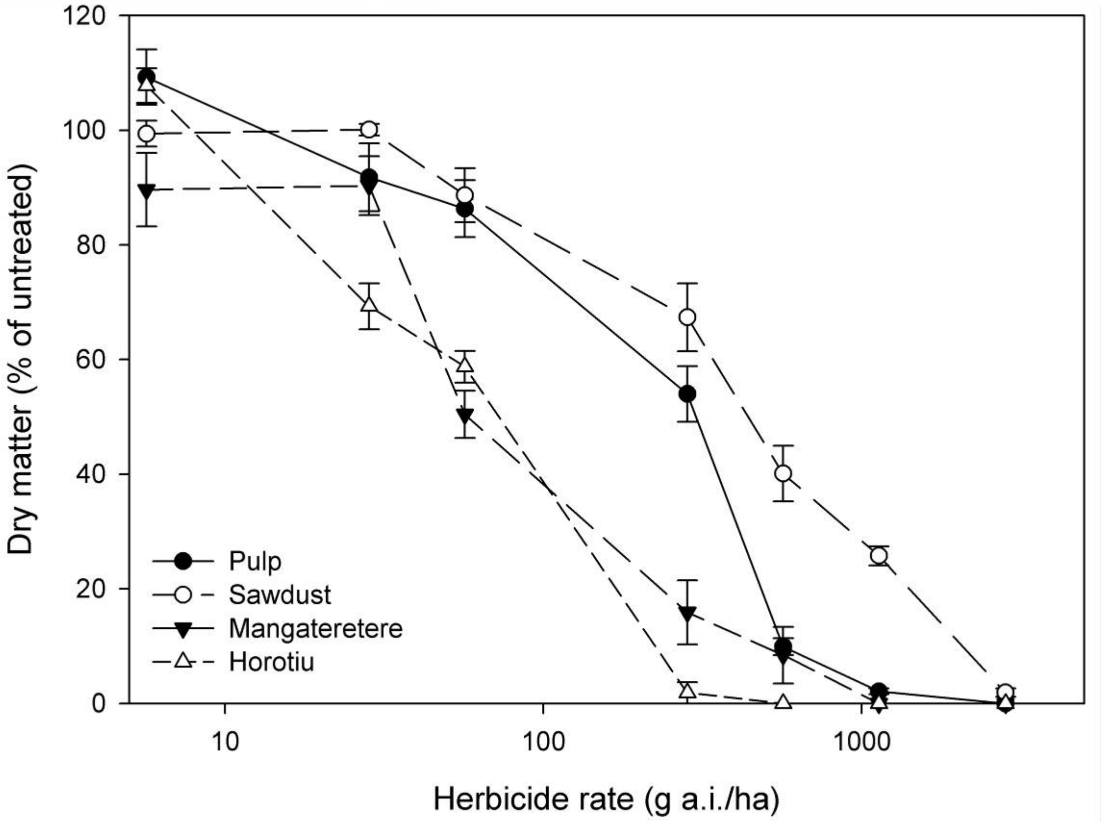


Fig. 3.13: Comparison of dose-response curves for annual ryegrass and alachlor in Experiment 3.

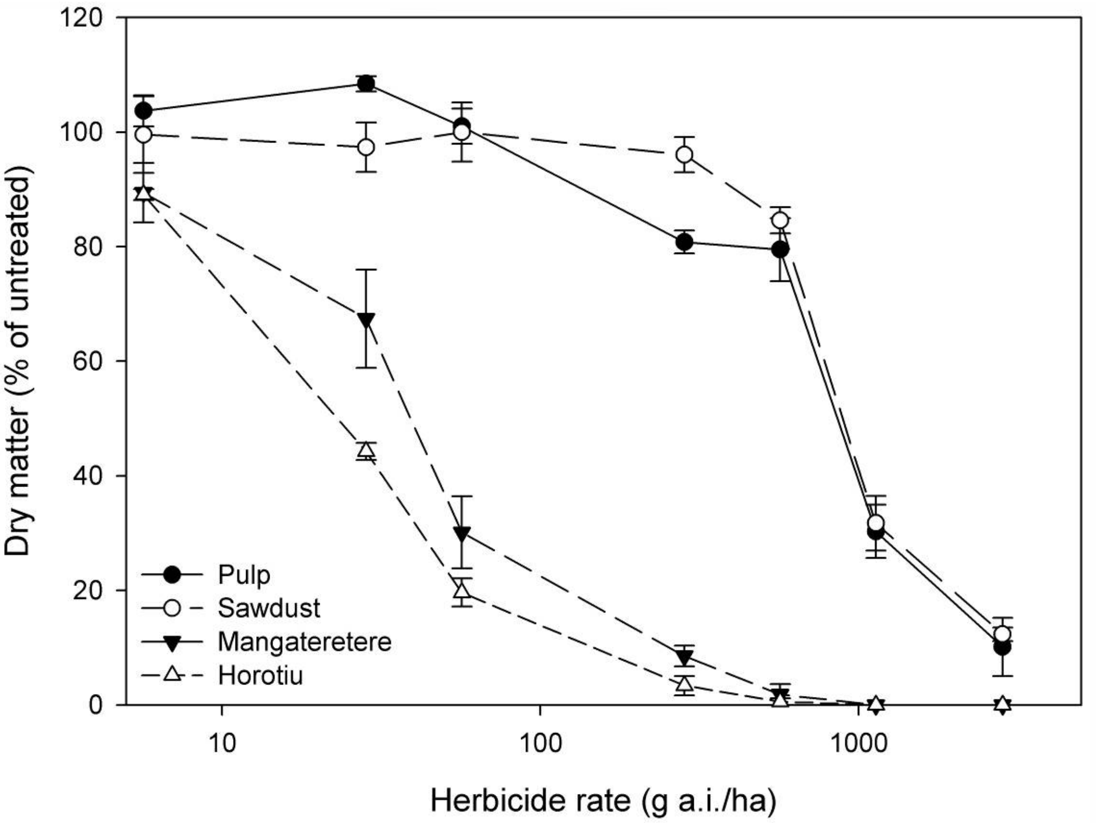


Fig. 3.14: Comparison of dose-response curves for annual ryegrass and alachlor in Experiment 4.

3.4.3.3 Chlorpropham on Annual Ryegrass

For annual ryegrass and chlorpropham there were also differences in biological activity between the four growing media but, in this case, the phytotoxicity of chlorpropham was generally similar in paper pulp, sawdust and the Horotiu soil and significantly greater in the Mangateretere soil (Figs 3.15 and 3.16).

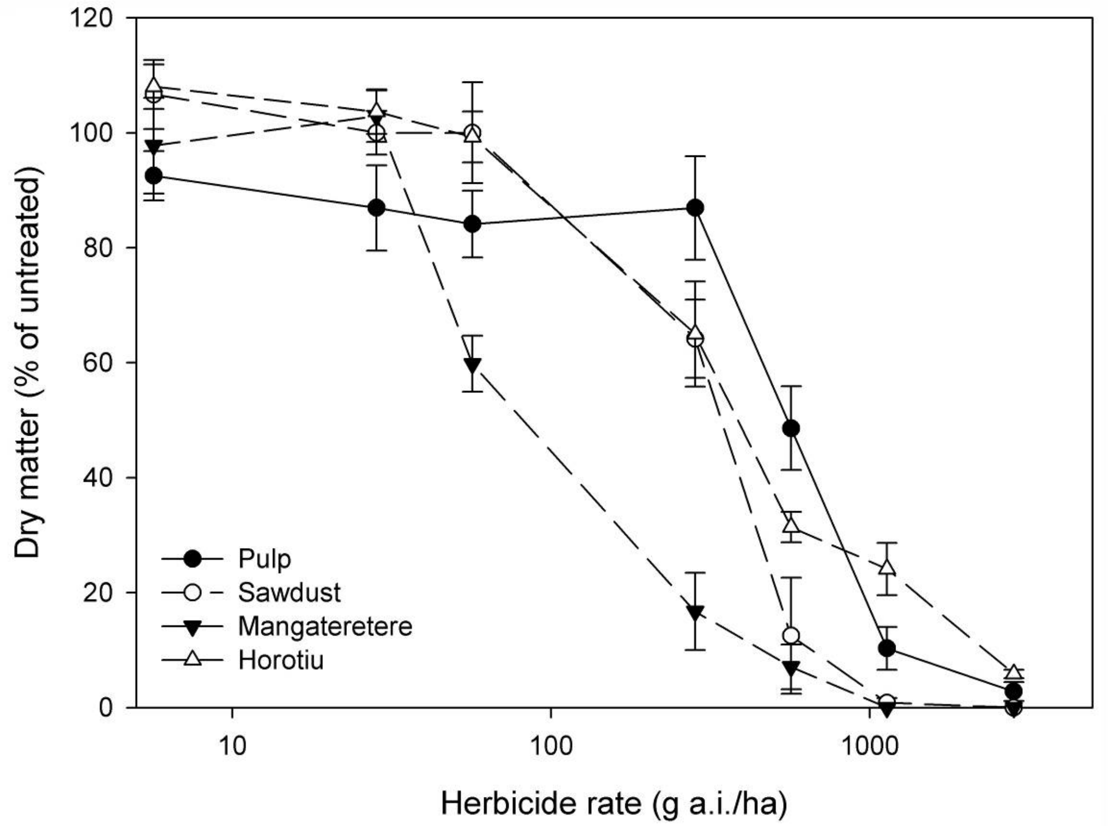


Fig. 3.15: **Comparison of dose-response curves for annual ryegrass and chlorpropham in Experiment 3.**

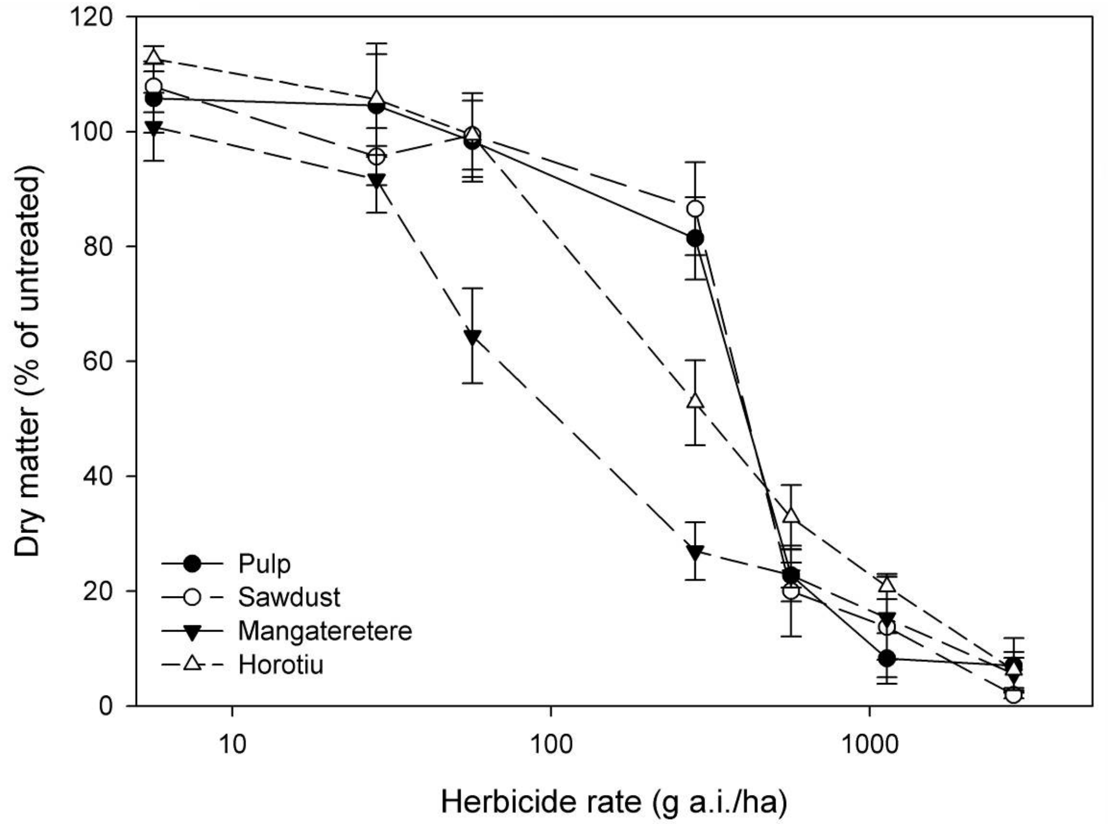


Fig. 3.16: **Comparison of dose-response curves for annual ryegrass and chlorpropham in Experiment 4.**

3.4.3.4 Chlorpropham on Garden Cress

Garden cress proved to be much less sensitive to chlorpropham than annual ryegrass was and only in one experiment and on a single medium were all the plants killed by the herbicide. Generally, in this herbicide/species combination there was little difference in the phytotoxicity of chlorpropham in the different media although in Experiment 3 the herbicide was less bioactive in paper pulp (Fig. 3.17) while in Experiment 4 it was more bioactive in sawdust (Fig. 3.18) than in the other three media.

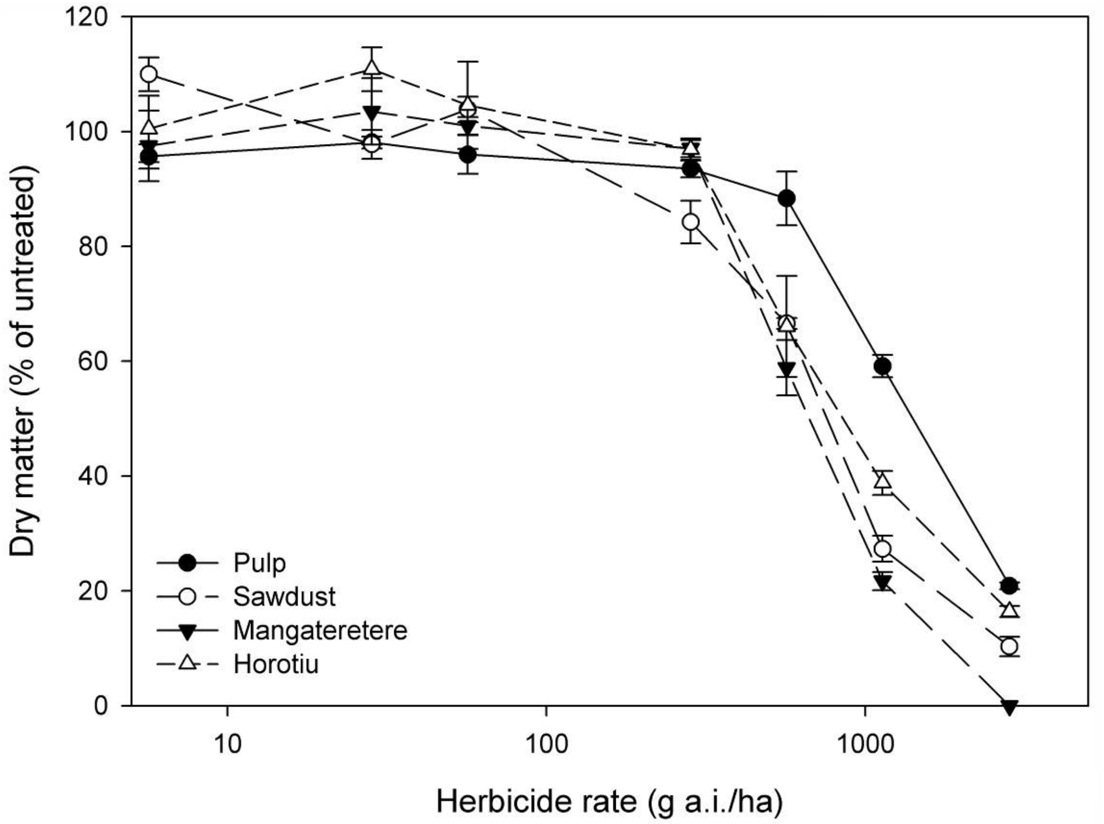


Fig. 3.17: Comparison of dose-response curves for garden cress and chlorpropham in Experiment 3.

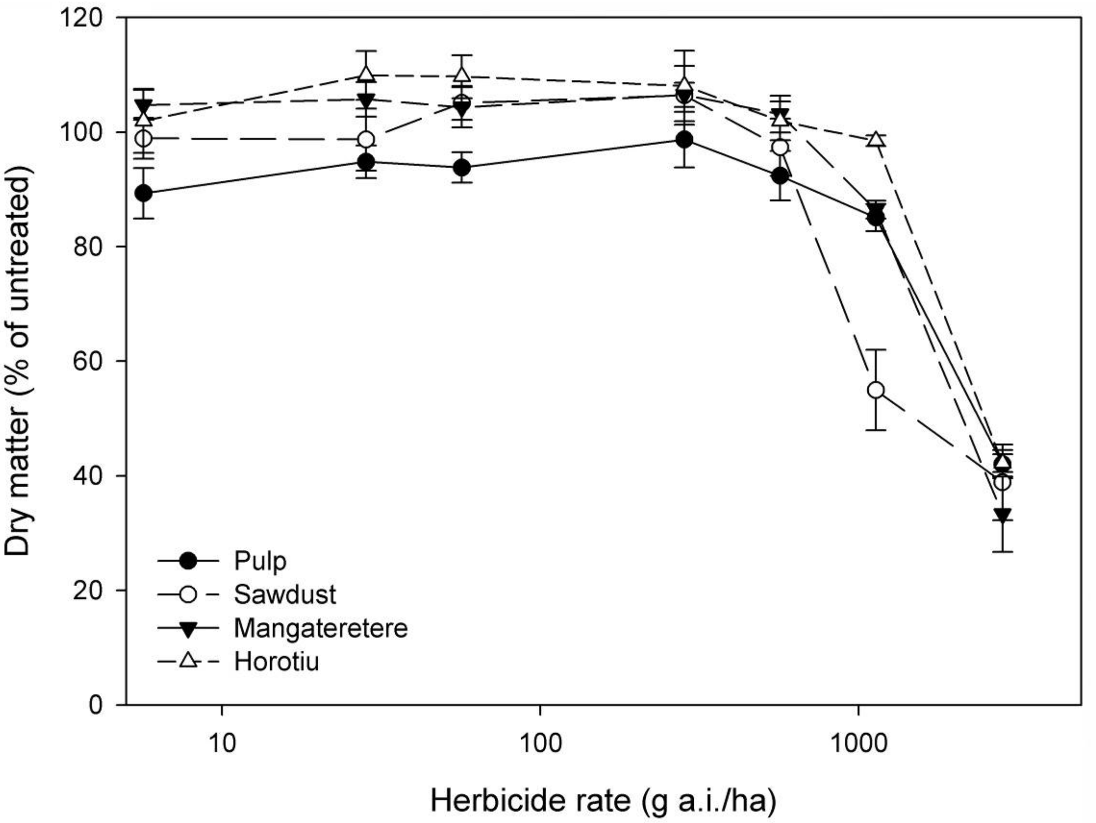


Fig. 3.18: Comparison of dose-response curves for garden cress and chlorpropham in Experiment 4.

3.4.3.5 Pendimethalin on Garden Cress

Pendimethalin showed less activity against garden cress in paper pulp in Experiment 3 (Fig. 3.19) and exhibited more activity in sawdust in Experiment 4 (Fig. 3.20) than in the other three media. These results are very similar to those of garden cress and chlorpropham.

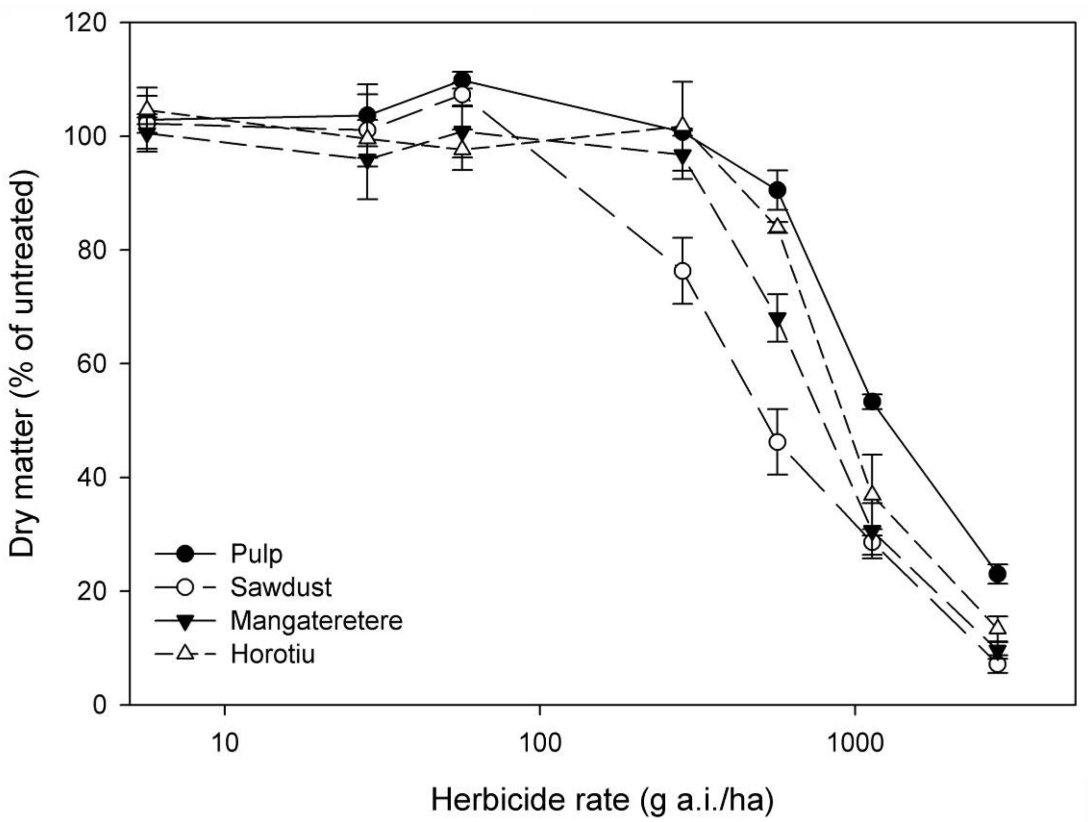


Fig. 3.19: **Comparison of dose-response curves for garden cress and pendimethalin in Experiment 3.**

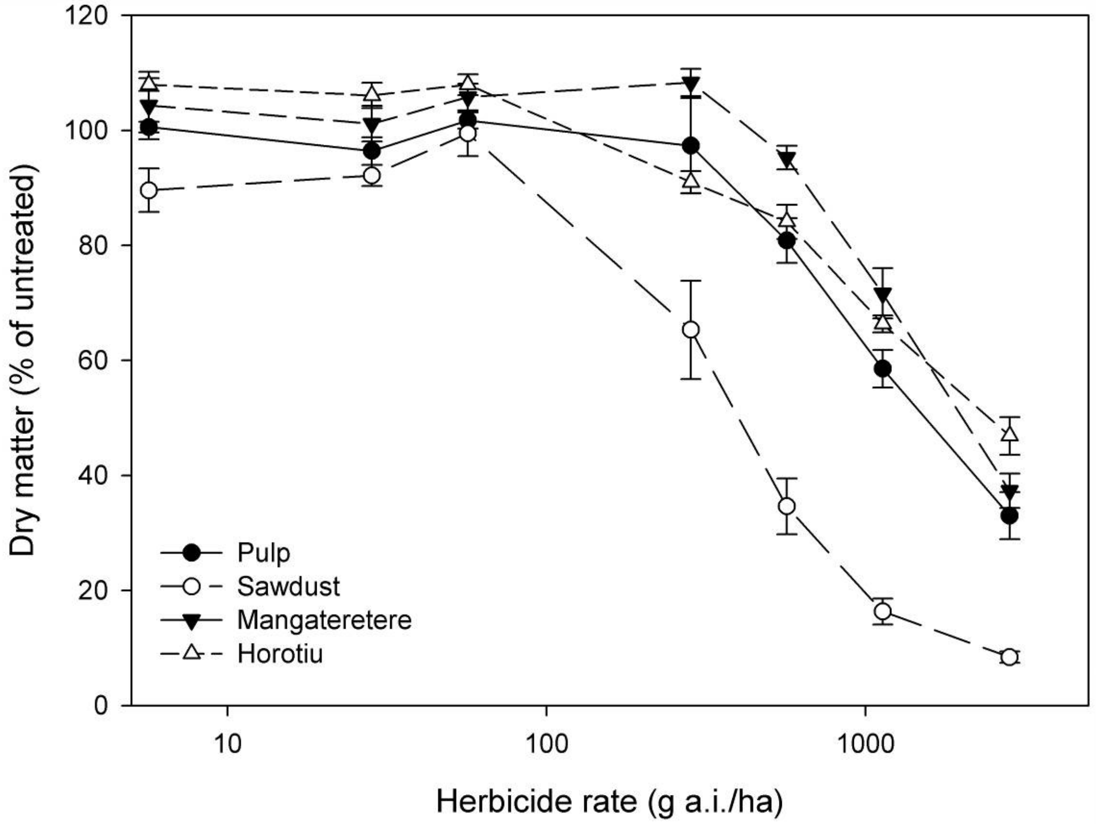


Fig. 3.20: **Comparison of dose-response curves for garden cress and pendimethalin in Experiment 4.**

3.4.3.6 Pendimethalin on Oats and Sorghum

In Experiment 3 oats showed good tolerance to pendimethalin (Fig. 3.21) and appear unsuitable as a sensitive bioassay species despite being used extensively elsewhere for root extension assays (Pestemer & Zwerger 1999; Hatzinikolaou et al. 2004; Chauhan et al. 2006). There was however, an indication that the phytotoxicity of pendimethalin in sawdust was lower than in the other three media. Sorghum was more susceptible than oats to pendimethalin but it showed significantly less damage when grown in the Mangateretere soil compared to the other three media (Fig. 3.22).

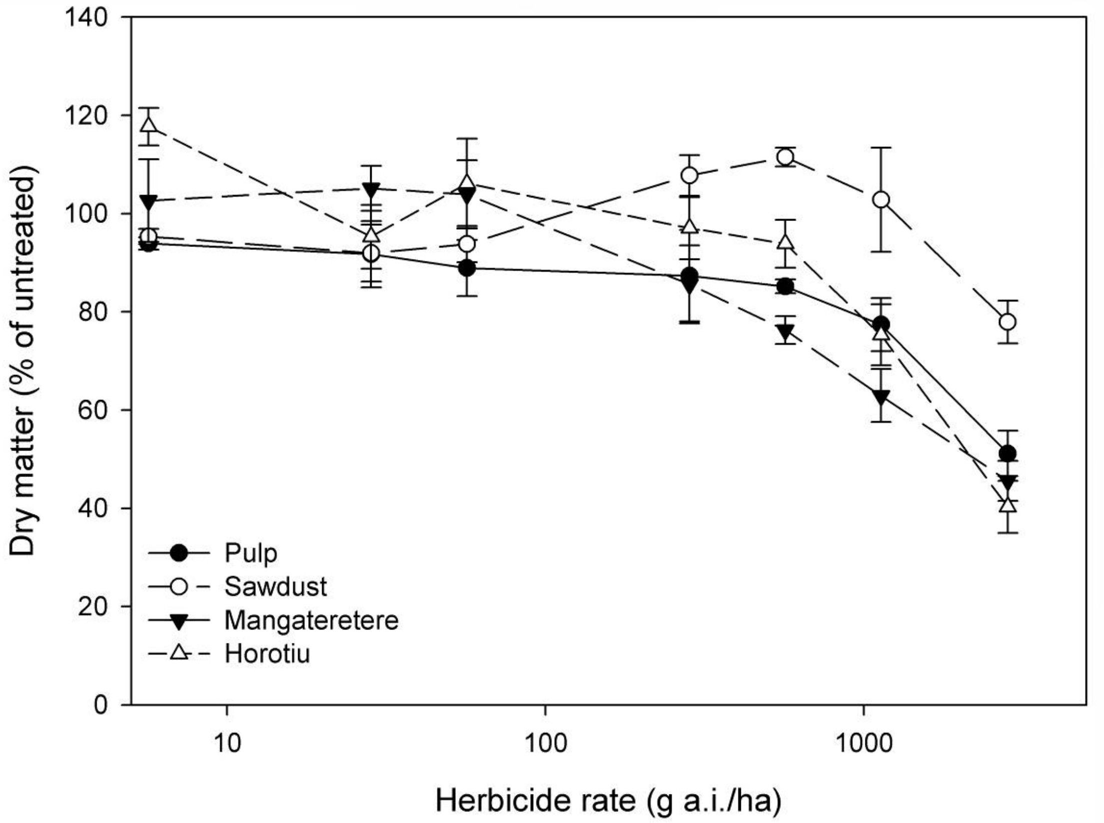


Fig. 3.21: Comparison of dose-response curves for oats and pendimethalin in Experiment 3.

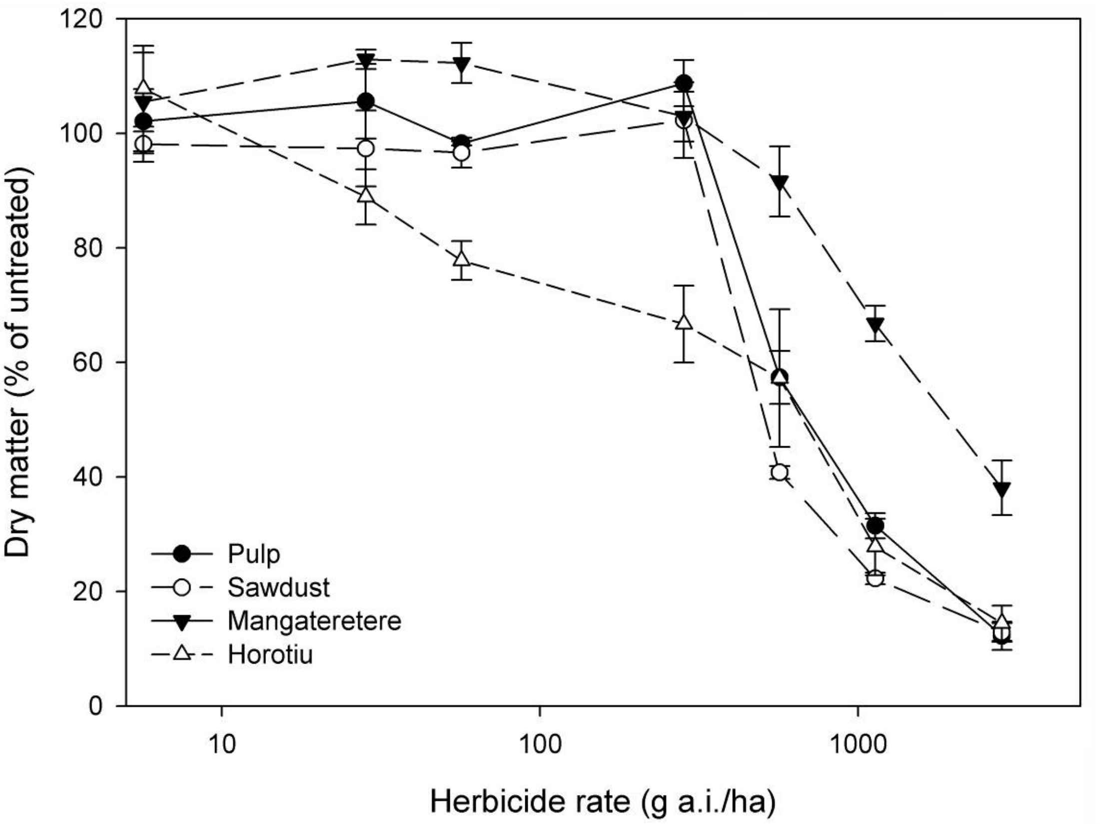


Fig. 3.22: Comparison of dose-response curves for sorghum and pendimethalin in Experiment 4.

3.4.4 *Parameters of the Dose-response Curves*

Due to variation in plant response to herbicide doses in the various media it was difficult to draw firm conclusions from the dose response curves as they are presented in Figs 3.11 – 3.22. The conventional treatment of dose response curves is to fit the data to a logit model as in Fig. 3.23 (Streibig 1988; Streibig & Kudsk 1993). This model is a symmetrical, sigmoid curve where the upper limit of the curve (*D*) represents the untreated control and the lower limit (*C*) is frequently zero at large doses but not necessarily so. This bioassay dose response curve is usually summarised by the estimate of herbicide potency, ED_{50} (effective dose to reduce plant production to 50% of untreated) and its confidence interval or standard deviation (Streibig 1988; Rahman 1989). Another useful value which can be determined from the dose response curve is the ED_{90} (effective dose to reduce plant production to 90% of untreated). This statistic is traditionally used as the limit of detection of herbicide residues by bioassay (Pestemer & Günther 1993). To avoid confusion the ED_{90} statistic is frequently referred to as the NOEL (No Observable Effect Level) as some refer to the same statistic as the ED_{10} (effective dose to reduce plant production by 10%) (Pestemer & Zwerger 1999).

The traditional logit model for representing dose response curves has three limitations: it is symmetrical, plant production from the untreated (zero rate) are not actually used in fitting the model and the model can not handle stimulated, excess plant growth which sometimes results from subtoxic doses of a herbicide (Jensen & Kudsk 1988; Streibig 1988; Jensen & Streibig 1994). Therefore it was decided to apply a new approach that would overcome the deficiencies of previous models. Thus a Bayesian smoothing technique (Upsdell 1994) was used to estimate the curve and its 95% confidence interval for each chemical and replicate (examples in Figs 3.24 – 3.29). This approach has the advantage of not requiring the data to behave according to a particular model, and can also use the control (zero rate) data as points on the line. The LD_{50} and NOEL points for the sensitive plant species, along with their relative standard errors, could then be extracted with greater accuracy (Tables 3.8 and 3.9).

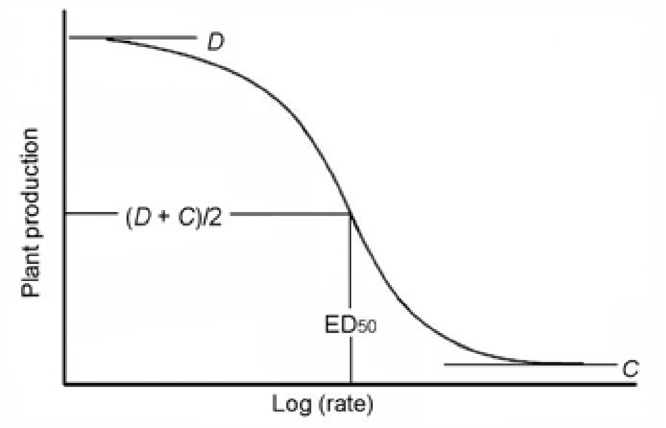


Fig. 3.23 Logistic model of a dose response curve and the determination of the ED_{50} value.

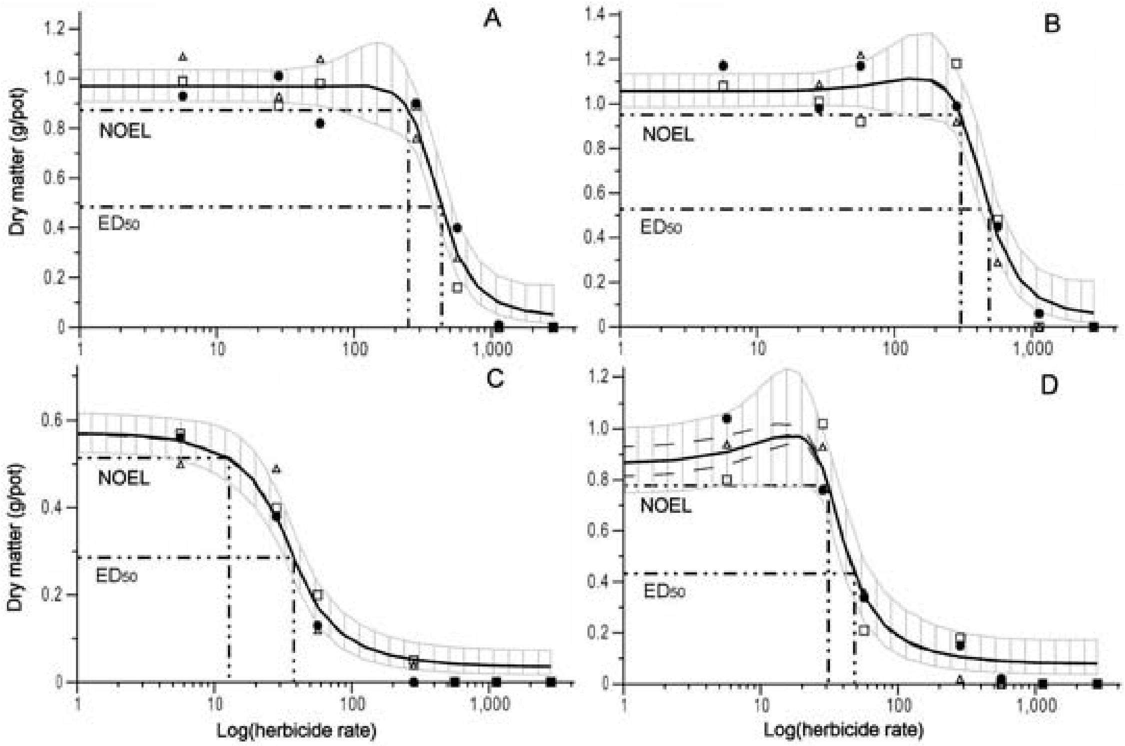


Fig. 3.24: Foxtail millet with alachlor in four media, fitted dose-response curves with 95% confidence limits (hatched shading) and graphic representation of NOEL and ED_{50} values: A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

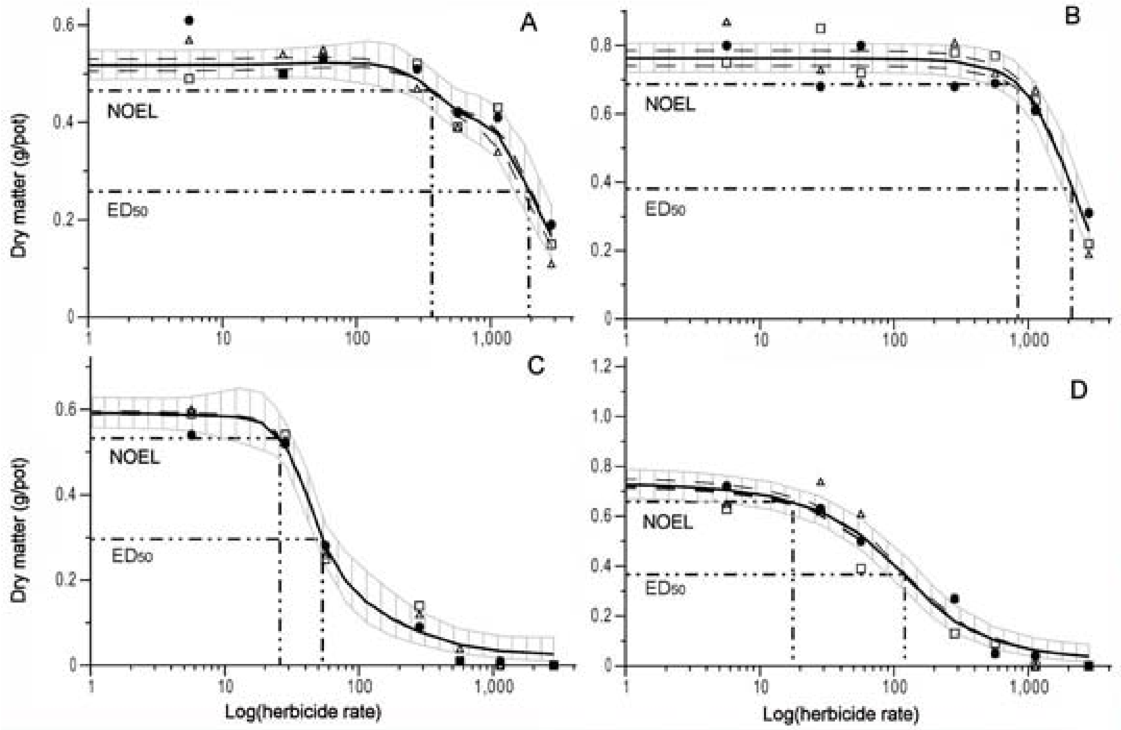


Fig. 3.25: Annual ryegrass with alachlor in four media, fitted dose-response curves with 95% confidence limits (hatched shading) and graphic representation of NOEL and ED_{50} values: A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

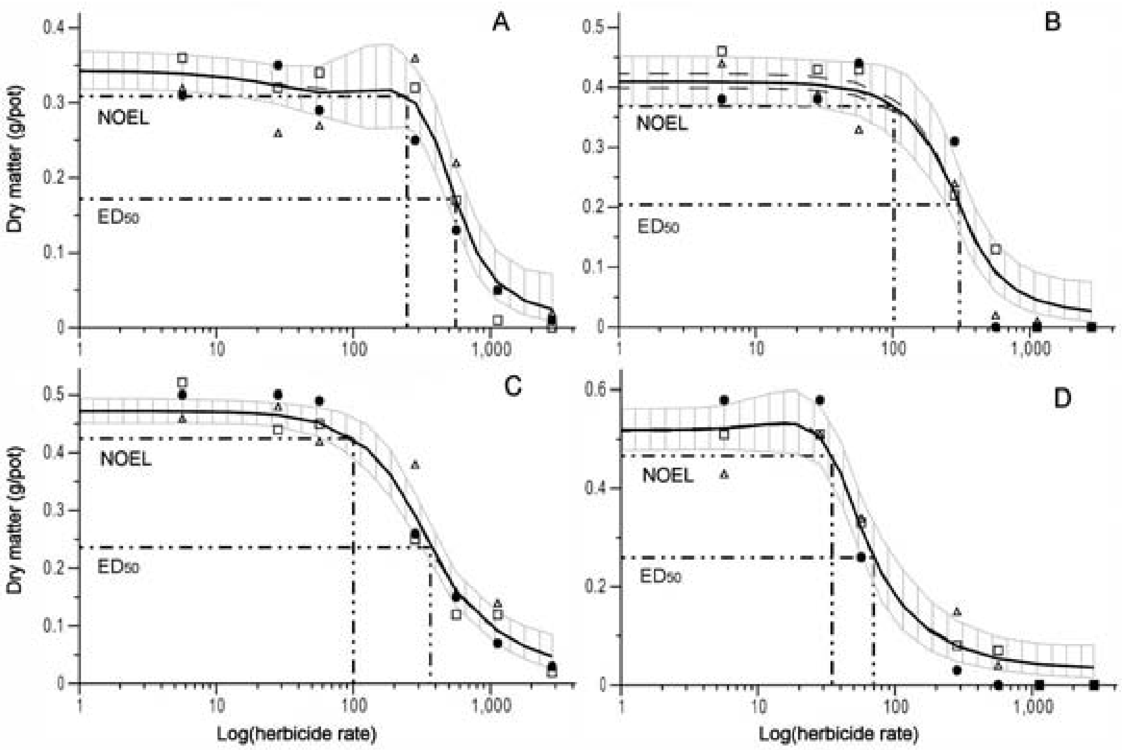


Fig. 3.26: Annual ryegrass with chlorpropham in four media, fitted dose-response curves with 95% confidence limits (hatched shading) and graphic representation of NOEL and ED_{50} values: A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

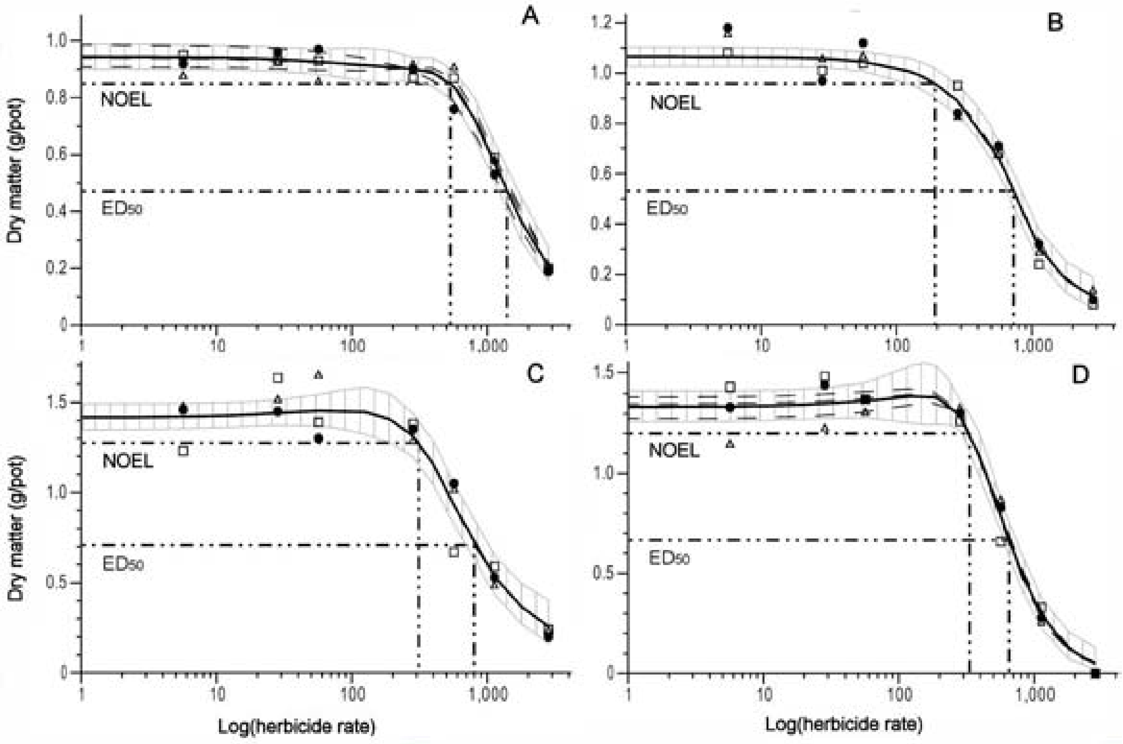


Fig. 3.27: Garden cress with chlorpropham in four media, fitted dose-response curves with 95% confidence limits (hatched shading) and graphic representation of NOEL and ED_{50} values: A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

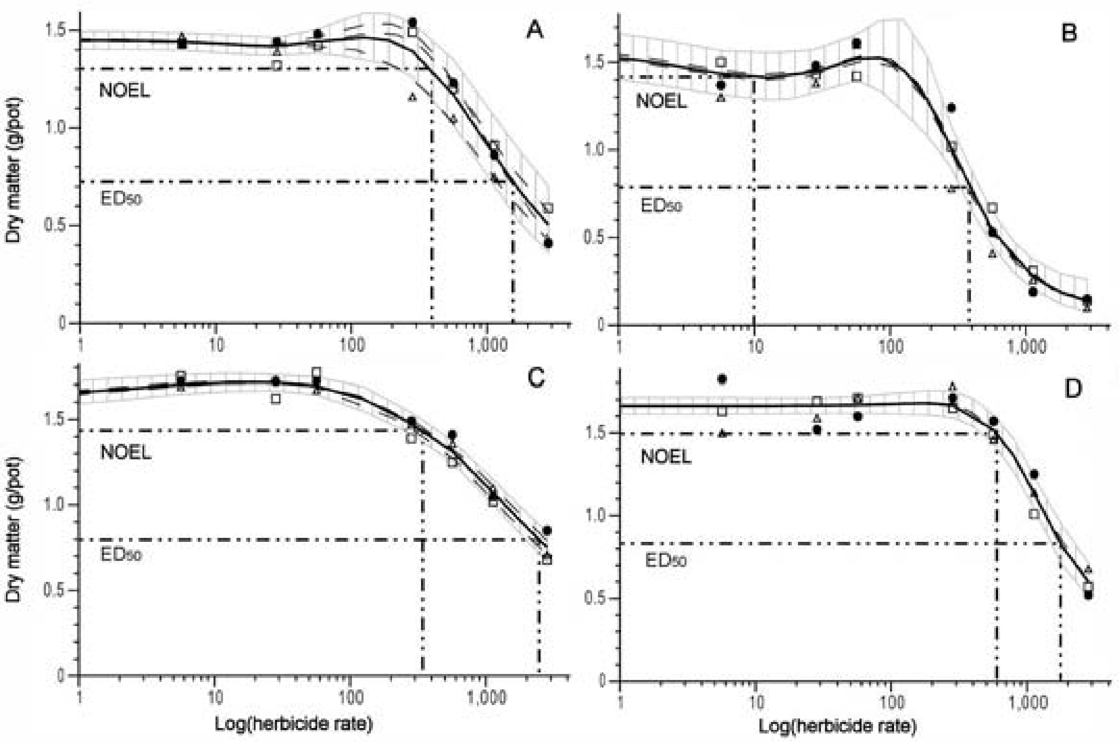


Fig. 3.28: Garden cress with pendimethalin in four media, fitted dose-response curves with 95% confidence limits (hatched shading) and graphic representation of NOEL and ED_{50} values: A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

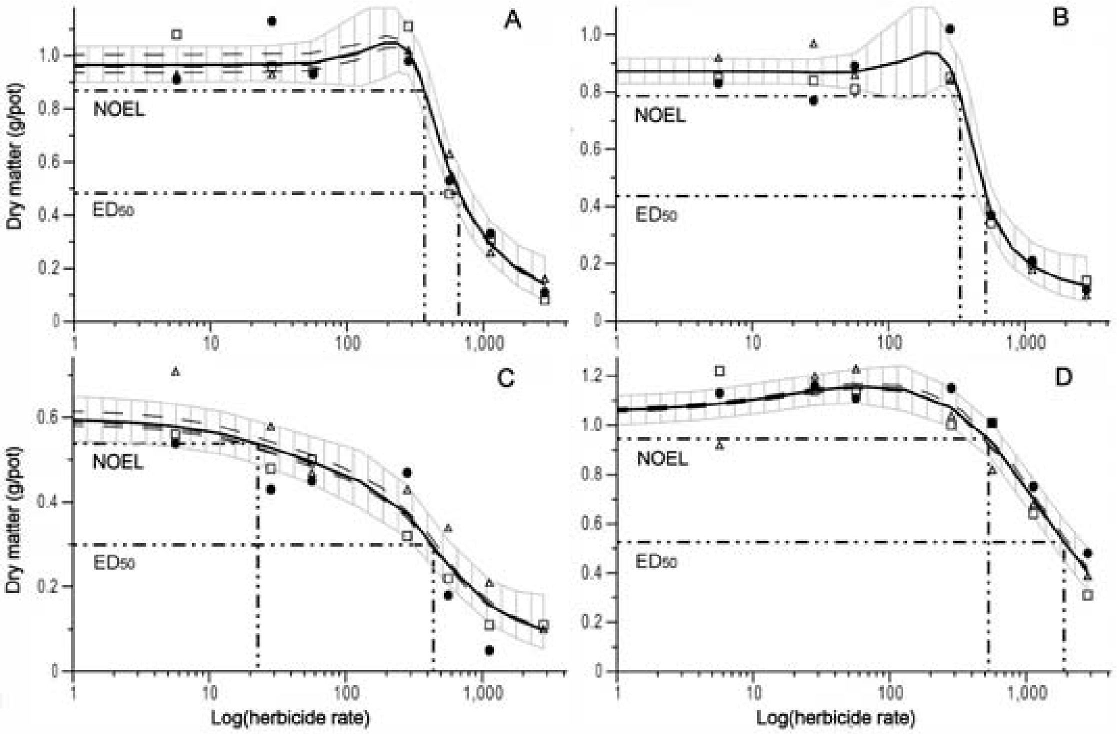


Fig. 3.29: Sorghum with pendimethalin in four media, fitted dose-response curves with 95% confidence limits (hatched shading) and graphic representation of NOEL and ED_{50} values: A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

Table 3.8: NOEL (ED_{90}) values for all combinations of herbicides, sensitive bioassay species, and growing media for Experiments 3 - 4.

			Exp. 3		Exp. 4	
Herbicide	Bioassay species	Growing media	NOEL (g a.i./ha)	sd[1]	NOEL (g a.i./ha)	sd[1]
Alachlor	millet	Horotiu soil	4.7	1.00	13	0.44
		Mangateretere soil	1.7	1.30	31	0.10
		paper pulp	61	0.22	294	0.18
		sawdust	36	0.18	305	0.15
	ryegrass	Horotiu soil	12	0.37	26	0.22
		Mangateretere soil	27	0.40	18	0.60
		paper pulp	44	0.40	366	0.24
		sawdust	75	0.36	837	0.24
Chlorpropham	ryegrass	Horotiu soil	101	0.31	77	0.40
		Mangateretere soil	35	0.17	24	0.29
		paper pulp	248	0.50	209	0.37
		sawdust	103	0.60	185	0.50
	cress	Horotiu soil	312	0.18	1305	0.14
		Mangateretere soil	333	0.08	952	0.14
		paper pulp	535	0.12	992	0.20
		sawdust	193	0.24	592	0.20
Pendimethalin	cress	Horotiu soil	642	0.12	342	0.15
		Mangateretere soil	393	0.12	598	0.13
		paper pulp	533	0.10	393	0.28
		sawdust	190	0.20	10	0.40
	oats	Horotiu soil	491	0.40	-[2]	-
		Mangateretere soil	202	0.40	-	-
		paper pulp	473	0.60	-	-
		sawdust	2084	0.22	-	-
	sorghum	Horotiu soil	-	-	23	0.90
		Mangateretere soil	-	-	533	0.15
		paper pulp	-	-	371	0.08
		sawdust	-	-	355	0.09

[1] Standard deviation for the mean of the three replicates.

[2] Not evaluated.

Table 3.9: **ED_{50} values for all combinations of herbicides, sensitive bioassay species, and growing media for Experiments 3 - 4.**

Herbicide	Bioassay species	Growing media	Exp. 3 ED_{50} (g a.i./ha)	Exp. 3 sd[1]	Exp. 4 ED_{50} (g a.i./ha)	Exp. 4 sd[1]
Alachlor	millet	Horotiu soil	20	0.25	38	0.09
		Mangateretere soil	22	0.22	48	0.12
		paper pulp	108	0.12	434	0.08
		sawdust	91	0.11	489	0.10
	ryegrass	Horotiu soil	55	0.12	54	0.07
		Mangateretere soil	59	0.08	120	0.16
		paper pulp	257	0.13	1927	0.14
		sawdust	452	0.08	2112	0.08
Chlorpropham	ryegrass	Horotiu soil	367	0.08	291	0.16
		Mangateretere soil	70	0.14	94	0.18
		paper pulp	560	0.10	396	0.08
		sawdust	307	0.12	412	0.14
	cress	Horotiu soil	801	0.10	2526	0.07
		Mangateretere soil	654	0.05	2129	0.09
		paper pulp	1398	0.09	2583	0.09
		sawdust	732	0.06	1579	0.28
Pendimethalin	cress	Horotiu soil	936	0.07	2460	0.13
		Mangateretere soil	800	0.06	1760	0.10
		paper pulp	1230	0.06	1552	0.24
		sawdust	521	0.09	381	0.09
	oats	Horotiu soil	2120	0.16	-[3]	-
		Mangateretere soil	2240	0.34	-	-
		paper pulp	*[2]	*	-	-
		sawdust	*	*	-	-
	sorghum	Horotiu soil	-	-	440	0.17
		Mangateretere soil	-	-	1903	0.14
		paper pulp	-	-	661	0.11
		sawdust	-	-	518	0.08

[1] Standard deviation for the mean of the three replicates.

[2] Insufficient data to calculate.

[3] Not evaluated.

3.5 Discussion

3.5.1 *Herbicide-Tolerant Species Interactions in Four Growing Media*

In Experiments 1 and 2 significant differences were often recorded in responses of the tolerant species to the different herbicides evaluated as well as between the growing media. Alachlor is mostly absorbed through the emerging coleoptile of a plant and its foliar uptake is extremely limited (Jaworski 1969). Thus, when applied post-emergence to onions it should have been well tolerated by the crop (Scherp 1971; Tsiropoulos & Miliadis 1998). The damage to onion plants observed in these experiments indicates that there was significant root uptake. The differing responses between the growing media (Table 3.7) confirm that the damage was from root uptake. If the damage had been due to foliar uptake, the level of damage should have been similar in all the growing media. Generally, the onions were more tolerant of alachlor when grown in either the Mangateretere soil or the paper pulp and were more susceptible when grown in either the Horotiu silt loam soil or the sawdust.

When comparing these results with the physico-chemical properties of soils (Table 3.1) commonly known to influence herbicide behaviour (Bailey & White 1970), it appears that the well subscribed rules do not apply to the novel growing media used in this study. For example, the sawdust has twice the organic carbon content of the paper pulp and ten times that of the Mangateretere soil, yet onion plants grown in sawdust were generally more susceptible to alachlor compared to the other media. Also the pH values of the sawdust and Horotiu silt loam soils are intermediate to those of the paper pulp and the Mangateretere soil while for bulk density the converse is true. Thus it is difficult to correlate any of these properties to the herbicide response of onions.

Alachlor is primarily active on monocotyledonous plants especially Poaceae with less activity towards dicotyledonous species (Scherp 1971; El-Nahhal et al. 1998). This herbicide has also been used for pre-emergence weed control in broccoli (Scherp 1971). However, in these experiments, alachlor was safe only in the Mangateretere soil and the paper pulp when used at the recommended rate. It caused significant damage to broccoli plants in all media when used at twice the recommended rate. Similar to the situation for onions, the damage was more severe to broccoli in both the Horotiu soil and the sawdust.

Chlorpropham has both foliar and soil activity indicating that it is absorbed into the plant by a variety of mechanisms (Stenersen 2004). In these experiments it was applied pre-emergence so all uptake would have been by either the roots, emerging shoots or a combination of both. Similarly pendimethalin is also absorbed by both the emerging shoot and by plant roots (Copping & Hewitt 1998). The differentiation of herbicide phytotoxicity in the different growing media was not as marked for chlorpropham and pendimethalin as observed for alachlor. However, for chlorpropham the onion grown in the sawdust were more susceptible to damage than when grown in the other three media and, although not always significant, there were differences between the media similar to that for alachlor.

3.5.2 *Dose-Response Curves for Sensitive Species in Four Growing Media*

Many of the dose response curves produced from Experiments 3 and 4 appear to have little symmetry e.g. foxtail millet and alachlor (Figs 3.11 and 3.12) and annual ryegrass and chlorpropham (Figs 3.15 and 3.16). For some combinations the lowest herbicide rate used resulted in some plant damage (e.g. Figs 3.11 and 3.14) while the highest herbicide rate used did not stop the plants from growing (e.g. Figs 3.18 – 3.22). Also, the herbicide pendimethalin frequently caused stimulation of plant growth when applied at subtoxic rates (Figs 3.19 and 3.20). These situations would all lead to difficulty in fitting the traditional logit model. A reasonably accurate ED_{50} value could be determined using the equation (Fig. 3.23)

$$(D + C)/2 \qquad \text{Eq.3.1}$$

where D is the weight of the untreated control and C is estimated to be zero. However, the ability to produce a realistic NOEL value would be severely tested. Similar problems associated with calculating the NOEL have been previously identified and discussed but no solutions offered (Rahman 1989). Using the Bayesian smoothing technique overcame these reported difficulties. For the results reported in this thesis, this technique enabled the determination of accurate NOEL values for most of the experimental combinations of herbicide, plant species and growing media. The only exceptions were where the highest herbicide rate evaluated resulted in less than 50% reduction in plant production and the method unable to produce credible NOEL and ED_{50} values (Figs 3.24 – 3.28).

The NOEL and ED_{50} values mostly relate well to each other (Tables 3.8 and 3.9). There is only one herbicide/species combination where having the lowest ED_{50} value does not equate to also having the lowest NOEL value (viz. chlorpropham and cress in Experiment 3). The two experiments also relate well in this regard although there is some variation in the numeric value of the two parameters. This variation is realistic as the experiments were carried out about 6 weeks apart and although in a glasshouse, some climatic conditions such as temperature and solar radiation differed between the two (Table 3.6). Such differences have previously been reported with bioassays and are overcome by using both treated (with known rates) and untreated controls when using this technique to measure phytotoxic herbicide residues (Rahman 1989; Sandral et al. 1997; Nègre et al. 2006).

In Experiments 3 and 4 the herbicides evaluated were generally more phytotoxic in the soils than in the two high organic media (Tables 3.8 and 3.9). ED_{50} values were often in the range of 5 to 10 times higher in the high organic media than in the two soils. Notable exceptions to this were for garden cress and pendimethalin and to a lesser extent garden cress and chlorpropham, where the herbicide was more toxic in sawdust.

3.5.3 *Bioavailability*

For an herbicide to be absorbed by the emerging shoot or by the roots of a plant it must be in solution (Stalder & Pestemer 1980). The two main factors which determine the quantity of the herbicide in solution are its water solubility and its adsorption onto soil particles (mostly organic matter and clay). However, for the herbicide to be solubilised it must be in the vicinity of the soil water. This usually requires movement of the herbicide from the dry soil surface where it usually is applied into the region of the soil where there is free soil water. Normally this is achieved by incorporating the herbicide mechanically with a light cultivation, or through applying irrigation or by waiting for rainfall (Crafts & Yamaguchi 1960) and is referred to as “activation” of the herbicide. In the present experiments the herbicide was “activated” by applying overhead irrigation which ensured the herbicides were in solution and available for plant uptake. Both alachlor and chlorpropham are considerably more soluble than pendimethalin (Table 2.1) and are thus more likely to have been moved deeper into the soil profile by the applied irrigation than pendimethalin was. This could be the reason why these two herbicides were more damaging to the onions in some growing media. However, it could equally be argued that for various reasons onions have a better tolerance of pendimethalin. The probability of alachlor being leached into the root zone of the crop is acknowledged on this product’s label where it states that in cucurbits, crop injury may result from heavy rainfall immediately after application (O'Connor 2003) or by shallow seeding, incorporation, or high rates on lightly textured soil (O'Connor 2006).

The second most influential parameter affecting the quantity of herbicide in solution is the sorption capacity of the soil (or growing media). Herbicides are adsorbed by clay colloids in the soil (Pantani et al. 1994) and by the soil organic matter (Lueking et al. 2000), with the latter being far more important in soils with moderate to high levels of organic matter (Rahman 1976; Rahman et al. 1978a). It was expected that the four growing media used in these experiments would differ in their herbicide adsorbance capacity leading to large variations in the bioavailability of applied herbicides. With organic carbon contents ranging from 4.3 to 46%, the growing media used here were extremely diverse (Table 3.1). However, organic carbon content alone is an insufficient indicator and the nature of that organic matter is also very important (Baskaran et al. 1996b; Ahmad et al. 2001). For instance in this case the sawdust was in a raw, undecomposed state and comprised mostly of relatively large particles of cellulose with a very low surface area to mass ratio. On the other hand, the paper pulp, while only having half the organic carbon content (22%) of sawdust, was much more degraded as the cellulose had been broken down in the chemical process of paper making. The two soils, with considerably less organic carbon than either the sawdust or paper pulp, could be expected to behave very differently from the other two media because of this.

There is little literature available on the behaviour of herbicides in non-decomposed organic amendments. The literature generally reports on either composted, high organic matter amendments (Barriuso et al. 1992b; Baskaran et al. 1996b; Nelson et al. 1998; Sluszny et al. 1999; Cox et al. 2000; Cox et al. 2001) or on their interactions after they have been in the soil for certain periods of time (Iglesias-Jiménez 1997). Without exception all these authors report on enhanced adsorption of herbicides with the addition of high organic matter amendments. Although soil amendment/soil mixtures were not evaluated in this study, the similar bioactivity of the herbicides in both the soil and the high organic matter growing media indicates that sorption in them was fairly similar and thus soil/organic amendment mixtures would also be similar. As the major difference between the substrates used in literature studies and this study is the composting and decomposition of the amendment, then this must be viewed as a significant and a critical difference.

Results from these experiments therefore illustrate that the nature of the organic matter is also critical in terms of herbicide performance as has been suggested by some researchers in recent years (Iglesias-Jiménez 1997; Cox et al. 2000; Ahmad et al. 2001). When considering the 24 herbicide/plant combinations investigated in the four experiments it is clear that herbicides were more active in the Horotiu soil and least active in the paper pulp, with the Mangateretere soil and sawdust somewhat intermediate and exhibiting varied results. Thus the original hypothesis that high organic matter soil amendments lower plant availability, was supported by the results for the high organic matter paper pulp amendment, but generally not supported by results for the high organic matter sawdust amendment, which exhibited some inconsistencies. The reasons for this were clarified by the sorption studies to be discussed in Chapter 4.

3.6 Conclusions

The bioavailability of three herbicides was compared in four diverse growing media through glasshouse experiments. Plant species which normally show tolerance to these herbicides as well as species that are susceptible, were grown in media augmented with known amounts of the herbicide. Most of the herbicide/media combinations were characterised by a negative response in plant dry matter to increasing herbicide rate. An improved method for fitting dose response curves to bioassay data was developed and this contributed to understanding plant responses to low doses of the herbicides evaluated. Differences in plant response resulting from the media were greatest with alachlor and least with pendimethalin and appeared to be related to herbicide solubility with the more soluble herbicides moving more freely into the root zone of the plants. Overall there was a strong trend for plants grown in the Horotiu silt loam soil to exhibit more herbicide phytotoxicity than plants grown in the paper pulp with the Mangateretere soil and sawdust intermediate and exhibiting greater variation on phytotoxic behaviour of the herbicides. These differences could not be correlated to any single physico-chemical property of the media from those normally used to explain differences in herbicide phytotoxicity and behaviour. The raw, undecomposed sawdust, although comprising nearly 50% organic carbon, often behaved more like the lightly textured silt loam soil in terms of the higher degree of herbicide bioavailability. Conversely the paper pulp, although containing only half the organic carbon of the sawdust, proved to have the greater influence on herbicide phytotoxicity through lowering herbicide bioavailability. It is clear from these results that organic carbon alone is not a good indicator of potential herbicide bioavailability to plants. The nature of the organic matter also plays a critical role, with undecomposed cellulose (sawdust) offering little in terms of reducing herbicide bioavailability. The original hypothesis that high organic matter soil amendments lower plant availability, was well supported by the results of the high organic matter paper pulp amendment, but the results were less supportive for the high organic matter sawdust amendment which exhibited inconsistent results.

CHAPTER 4

ADSORPTION

CHAPTER 4: ADSORPTION

4.1 Objective

To determine the soil/solution distribution coefficient (K_d) of five commonly used cropping herbicides (alachlor, atrazine, bromacil chlorpropham and pendimethalin) in Horotiu and Mangateretere soils, paper pulp and sawdust. The hypothesis being tested here was that high organic matter soil amendments increase the soil/solution distribution coefficient of herbicides.

4.2 Introduction

The importance of herbicide adsorption as the main governing influence of herbicide behaviour and fate in soils has previously been discussed (Section 2.1.1). The results obtained from the sorption studies described here will be used in the qualitative and quantitative descriptions of the experimental herbicide behaviour patterns in relation to degradation and transport described in this thesis.

Herbicide soil/solution distribution coefficients are normally determined using the slurry method (Weber et al. 2004). This comprises measuring the amount of herbicide adsorbed from a specific solution concentration by a specified amount of soil. Assuming linear adsorption isotherms for the herbicides evaluated here (Weber et al. 2000), the ratio of herbicide adsorbed (µg/g) to herbicide remaining in the solution (µg/mL) is the distribution coefficient (K_d, Eq. 2.2, Section 2.2.1). Distribution coefficients are generally determined at herbicide concentrations approximating those in soils following use at recommended rates with sufficient rainfall to bring the soil to field capacity and distribute the chemical throughout the top 10-cm of soil (Weber et al. 2000). Three herbicides (alachlor, chlorpropham and pendimethalin) were selected as they are commonly used in vegetable production and are likely to be used within a Rich Ditch system. For comparison two herbicides (atrazine and bromacil) with longer residual activity and greater leaching potential, were also included in this study. Typical crop use and associated recommended rates for the five herbicides included in this study are presented in Table 4.1. The actual herbicide rate used in the experiments (Table 4.1) was approximately twice the field use rate which is the situation if double overlap occurs during field application (Konomi et al. 2005).

The slurry method for determination of the soil/solution distribution coefficient is not standardised although both the OECD and USEPA have published guidelines (OECD 2000; USEPA 2002). Unfortunately, these guidelines are not universally applied with researchers using a variety of methods, however, some aspects are reasonably consistent. The most common slurry method is usually referred to as the batch equilibrium method and is carried out at either ambient temperature or 25°C, for 24 h with a soil to water ratio of between 1:1 and 1:5. Most methods use a weak electrolyte solution (0.01M $CaCl_2$) that maintains a background electrolytic strength similar to natural soil solution, to extract the water soluble fraction. The largest variation in technique between methods used by researchers is in the amount of soil used, which ranges from 0.5 to 100g (Clay & Koskinen 1990; Barriuso et al. 1992a; Francioso et al. 1992; Ma et al. 1993; Liu et al. 1995; Baskaran et al. 1996a; Gerritse et al. 1996; Wang et al. 1999; Guo et al. 2000; Vasilakoglou et al. 2001; Dorado et al. 2003; Oliver et al. 2003; Taylor et al. 2004; Mamy & Barriuso 2007).

Table 4.1: Registered use rates for the five herbicides in various crops in New Zealand (O'Connor 2003).

Herbicide	Crop	Label rates	Rate used in experiment
Alachlor	onions	1440 – 2400 g a.i./ha	4000 g a.i./ha
Atrazine	maize	750 - 1500 g a.i./ha	3000 g a.i./ha
Bromacil	asparagus[1]	1600 – 2400 g a.i./ha	6400 g a.i./ha
Chlorpropham	lettuce	1200 – 1600 g a.i./ha	3200 g a.i./ha
Pendimethalin	peas	1650 – 1980 g a.i./ha	3960 g a.i./ha

[1] Frequently for asparagus 2 applications per year are made, at the commencement of the harvesting season and again at the end using the lower rate (Rahman et al. 1986). The rate used in the experiment was calculated as twice the sum of the two applications.

4.3 Materials and Methods

4.3.1 *Batch Equilibrium Method*

The method used for this study followed the suggestions of Weber et al. (2000) and Barriuso et al. (1992a) and used soil (media), herbicide and water ratios that related to field use. The moisture content of the media was determined gravimetrically by oven drying quadruplicate samples (10 g) at 105°C for 24 h. The media was used in field moist state, with 50 g dry weight equivalent for the two soils and 10 and 20 g dry weight equivalent for the paper pulp and sawdust respectively, weighed into either 250 mL conical flasks or 250 mL polypropylene centrifuge bottles. These were adjusted to contain 28 g of water by the addition of purified water as required, and the herbicide (formulated product) fortification was added in a 2 mL water aliquot. The media and added herbicide was thoroughly mixed by hand shaking, ensuring that material adhering to the sides was shaken off and incorporated with the bulk of the soil, and allowed to stand at ambient temperature (≈20°C) for 24 h. The herbicide fortification was calculated assuming the herbicide (Table 4.1) was applied evenly at twice the highest application rate and incorporated to a depth of 100 mm. The bulk density of the media determined previously (Table 3.1) was used to obtain the required fortification in mg/kg dry soil. There were two replications of each media/herbicide combination and two extra 2 mL aliquots were collected in glass vials for chemical quantification of the fortification amount.

4.3.2 *Determination of Herbicide Fortification*

Since technical grade herbicide samples were not used for the adsorption studies, herbicide fortification was obtained using commercial formulations. With the exception of alachlor, the retained herbicide fortification aliquots (2 mL) were prepared for quantification by diluting with 8 mL of 50:50 methanol:water and this solution used for HPLC determination. The alachlor fortification was passed through a C-18 solid phase extraction column (Phenomenex Strata C18E) and the herbicide was eluted from the C-18 column with 2 mL ethyl-acetate. The eluant was diluted 1:100 (in two steps of 1:10 dilution each) in preparation for quantification by Gas Chromatography (GC).

4.3.3 *Determination of Herbicide in Extracted Soil Solution*

After standing for 24 h to equilibrate at low moisture content, 70 mL of 0.01M $CaCl_2$ solution was added to the media and the mixture shaken for 1 h in order to obtain sufficient soil solution for herbicide quantification (Wang et al. 1999; Weber et al. 2000; Vasilakoglou et al. 2001). The slurry was then either centrifuged or allowed to stand for a short time before supernatant liquid was recovered. The supernatant was vacuum filtered (Whatman GF/C glass fibre filters), volume determined and passed through a C-18 solid phase extraction column (Phenomenex Strata C18E) to retain the herbicide. The herbicide was eluted from the C-18 column with 2 mL methanol (except for alachlor which was eluted with ethyl-acetate). The methanol solution was reduced under a gentle stream of nitrogen at 35°C before being made up to 0.5 mL with methanol and then to 1.0 mL with purified water. Atrazine, bromacil, chlorpropham and pendimethalin concentrations were determined by HPLC. After drying the alachlor residue was redissolved in ethyl acetate for determination by GC.

4.3.4 *Determination of Total Herbicide in the Media*

To estimate the percentage recovery of herbicides from the sorption media, after standing for 24 h, a further two flasks of each media/herbicide combination were extracted with 70 mL solvent (dichloromethane for alachlor, chlorpropham and pendimethalin; methanol for atrazine; 1.5% NaOH solution for bromacil). The flasks were shaken for 1 h and allowed to stand for a short time before 10 mL of the dichloromethane was recovered. Except for atrazine and bromacil, the supernatant was reduced under a gentle stream of nitrogen at 35°C to dryness before being made up to 0.5 mL with methanol and then to 1.0 mL with purified water (or with 1 mL ethyl acetate for alachlor). For atrazine the supernatant (10 mL) was diluted with 90 mL pure water and passed through a C-18 solid phase extraction column (Phenomenex Strata C18E) to retain the herbicide. The herbicide was eluted from the C-18 column with 2 mL methanol and reduced under a gentle stream of nitrogen at 35°C to dryness before being made up to 0.5 mL with methanol and then to 1.0 mL with purified water. For bromacil the supernatant (10 mL) was extracted once with 5 mL dichloromethane. After vortex mixing and centrifugation the volume of dichloromethane recovered was measured and the solvent reduced under a gentle stream of nitrogen at 35°C to dryness before being made up to 0.5 mL with methanol and then to 1.0 mL with purified water. Atrazine, bromacil, chlorpropham and pendimethalin concentrations were determined by HPLC. Alachlor was determined by GC.

4.3.5 *Quantification by High Performance Liquid Chromatography (HPLC)*

All analyses were run on a Shimadzu™ HPLC system comprising: an SCL-10AVP System Controller, LC-10ATVP Pump, FCV-10ALVP Low Pressure Gradient Control Valve, DCU-14A Degasser, SIL-10AVP Auto Injector, CTO-10ASVP Column Oven, SPD-M10AVP Diode Array UV Detector and Shimadzu Class VP (ver. 6.14) Chromatography Data System. The analyses were run isocratically using a C-18, reverse-phase, 5 µm, 100 Å, 150 x 4.6 mm, ODS3 column (Prodigy, Phenomenex®), a mobile phase flow rate of 1 mL/min and a column temperature of 35°C. The conditions for individual herbicides are presented in Table 4.2. Sample injection volume was 20 µL. Quantification was by integration of peak areas. Calibration curves were made using a dilution series (0.05 to 50 ppm) of each herbicide prepared in methanol/water (50/50, v/v). Confirmation was by visual inspection of peak selection and base line and using external standards (1.0 and 10.0 mg/L) that were run after every 6 - 8 samples.

Table 4.2: Parameters for individual herbicides quantified by HPLC.

Herbicide	Mobile phase (methanol:water, v/v)	Retention time (min)	Detection wavelength (nm)
Atrazine	52:48	10.6	222
Bromacil	44:56	11.5	278
Chlorpropham	64:36	9.3	240
Pendimethalin	80:20	10.0	230

4.3.6 *Quantification of Alachlor by Gas Chromatography (GC)*

Samples were analysed by gas chromatography using an Agilent 6890N gas chromatogram fitted with dual micro electron capture (ECD) and nitrogen-phosphorous (NPD) detectors, programmed temperature vapourisation (PTV) inlet, and 7683B auto injector. Subsamples of 2 µL each of sample extracts and calibration standards were injected into the PTV inlet which was held at 70°C for 0.1 min and ramped at 150°C/min to 280°C where it was held for the duration of the analysis. The PTV injector was operated in pulsed splitless mode with electronic pressure control at an initial head pressure of 45 psi for 1.9 min followed by a constant pressure of 30 psi and a split flow of 100mL/min at 2 minutes.

Helium was used as the carrier gas and chromatographic separation was achieved using an Agilent Ultra-2 glass capillary column (25m x 0.2mm x 0.33mm). The GC column was held at 70°C for 2 min then increased to 150°C at 50°C/min, followed by 3.5°C/min to

200°C and a final increase to 280^oC at 40°C/min with a hold of 5 min. The ECD and NPD were held at temperatures of 300 and 325°C respectively, and nitrogen was used as the make-up gas.

The concentration of alachlor in the extracts was determined using external standard quantitation. Calibration curves were made using a dilution series of alachlor prepared in ethyl acetate (0.05 to 10 ppm). Data analysis was completed using Agilent Environmental Chemstation software and the identification and quantitative reporting of alachlor was confirmed by comparison of the results from the dual detectors.

4.4 Results

4.4.1 *Determination of Herbicide Concentrations*

The herbicide fortification solutions related well to the theoretical calculations (Table 4.3) and the small differences could be attributed to errors in the factory formulated product (Anonymous 2007) and errors in measuring very small quantities of the product when making the original stock solution. It is due to these difficulties that most researchers use technical material. However, the use of technical material in sorption experiments could produce results that differ from those of the formulated product as the adjuvants in the latter could affect adsorption (Weber et al. 1993; Swarcewicz et al. 1998). In these experiments, inaccuracies in the stock solutions were negated by accurately determining the amount of herbicide in the fortification solutions by analysis.

Table 4.3: Comparison of theoretical and actual fortification.

	Fortification (µg active)									
	Alachlor		Atrazine		Bromacil		Chlorpropham		Pendimethalin	
Media	Fort.[1]	%[2]	Fort.[1]	%[2]	Fort.[1]	%[2]	Fort.[1]	%[2]	Fort.[1]	%[2]
Horotiu	282	90	204	97	401	89	225	119	279	115
Mangateretere	250	101	152	91	332	93	200	103	248	113
Paper pulp	333	105	204	98	401	91	267	116	330	120
Sawdust	267	95	251	125	383	90	213	104	264	114

[1] Theoretical fortification based on field use rate (x2) and bulk density of media.

[2] Actual spike as determined by chromatographic analysis and expressed as a % of the theoretical value.

Extraction of atrazine from the media using methanol was efficient while the sodium hydroxide extraction of bromacil was slightly less effective, particularly in the two soils (Table 4.4). Due to the very low recovery of alachlor, chlorpropham and pendimethalin from the media with dichloromethane this extraction method could only be described as unreliable (Table 4.4). Generally, dichloromethane extraction from the two organic media was better than from the two soils, although recovery of pendimethalin was poor from both.

Table 4.4: Percent recovery of five herbicides from four media.

	Recovery (% of measured fortification)[1]				
Media	Alachlor	Atrazine	Bromacil	Chlorpropham	Pendimethalin
Horotiu	24-28	114-120	77-81	43-44	12-13
Mangateretere	46-56	115-120	73-76	45-50	18-24
Paper pulp	57-64	105-107	77-87	71-74	20-23
Sawdust	70-82	108-113	89-96	90-98	24-24

[1] Range of duplicate samples.

4.4.2 *Calculation of Distribution Coefficients*

Due to the difficulties in achieving high recoveries of some herbicides from the different media, the distribution coefficient (Table 4.5) was calculated with the assumption that herbicide adsorbed to the media equalled herbicide fortification, as measured, minus herbicide in solution (Briggs 1981; Reddy et al. 1992).

Table 4.5: Distribution coefficients (K_d) range of duplicate samples, for five herbicides in four media .

	Distribution coefficient (K_d)[1]				
Media	Alachlor	Atrazine	Bromacil	Chlorpropham	Pendimethalin
Horotiu	5.21-5.81	5.33-5.95	1.18-1.26	20.6-22.8	459-544
Mangateretere	4.37-5.26	4.11-4.17	1.06-1.14	16.0-17.1	223-319
Paper pulp	22.7-26.8	19.1-19.5	5.51-5.89	41.5-48.4	679-768
Sawdust	35.0-35.1	29.1-30.1	9.8-10.8	175-195	3379-3732

[1] K_d was determined at a concentration in the soil solution equivalent to 2x normal use rates distributed throughout the top 10-cm of soil.

The distribution coefficients for the four media show great variation (Table 4.5). Solubility in water (Table 2.1) was a strong influence e.g. bromacil, the most soluble, and pendimethalin, the least soluble, had the lowest and highest K_d values respectively. However, this was not the only factor as the other three herbicides with intermediate water solubilities did not follow the same ranking. Media organic carbon contents also had a profound influence on adsorption with distribution coefficients for the two soils being significantly lower than those for the two organic media. As previously discussed (Section 2.2.1), the soil/solution distribution coefficient is a property of each individual soil, but, as the most influential property of soil is adsorption to its organic carbon, it is frequently normalised to the organic carbon content according to Eq. 2.4 to give the soil organic carbon affinity coefficient (K_{oc}).

$$K_{oc} = \frac{100\ K_d}{\%OC} \qquad \text{Eq. 2.4}$$

The soil K_{oc} coefficients for the four media are presented in Table 4.6 calculated from the organic carbon contents in Table 3.1. Normalisation was generally successful in equalising the distribution coefficient for each herbicide, with relatively less variation in the K_{oc} values amongst the media. The K_{oc} values for the highly soluble bromacil are essentially equal, which is the ideal outcome of normalisation and is consistent with the adsorption of this herbicide being mainly to the organic carbon content of the media. Alachlor and atrazine were quite similar to each other and all their K_{oc} values were within a factor of 2 of each other. Both these herbicides had their lowest K_{oc} in sawdust. The K_{oc} values for chlorpropham and pendimethalin showed slightly greater variation between the media. These two herbicides also differed in that their K_{oc} values were lowest in the paper pulp and approximately half the values for the other three media (Table 4.6).

Table 4.6: Soil organic carbon affinity coefficients (K_{oc}) for five herbicides in four media.

	Soil organic carbon affinity coefficient (K_{oc})				
Media	Alachlor	Atrazine	Bromacil	Chlorpropham	Pendimethalin
Horotiu soil	108	111	24	425	9834
Mangateretere soil	112	96	26	384	6304
Paper pulp	112	88	26	204	3288
Sawdust	76	64	22	403	7730

To further evaluate the relationships between distribution coefficient and organic carbon content, the two were plotted against each other and these are presented in Figures 4.1 and 4.2. Regression lines were also fitted and the descriptive parameters for the fits are presented in Table 4.7. These show a very good fit for bromacil (Fig. 4.1) and the fit becomes progressively worse for those herbicides which exhibit greater adsorption (Figs 4.1 and 4.2). Examination of Fig. 4.1 reveals that the plots for alachlor and atrazine could be better explained with an asymptotic curve with K_d becoming constant at very high levels of organic carbon. However, while this is a plausible explanation, the same reasoning would have to be applied to the plots of chlorpropham and pendimethalin (Fig. 4.2) with the conclusion that a better fit for these plots would be an exponential curve that described K_d values approaching infinity at high organic carbon levels. These models are extreme interpretations of a curve which is essentially represented by three points and factors other than organic carbon content (e.g. pH) could have influenced the partitioning.

Therefore it must be concluded that there is insufficient proof from these data that the correlation of the distribution coefficient with organic carbon should be represented by anything other than a straight line.

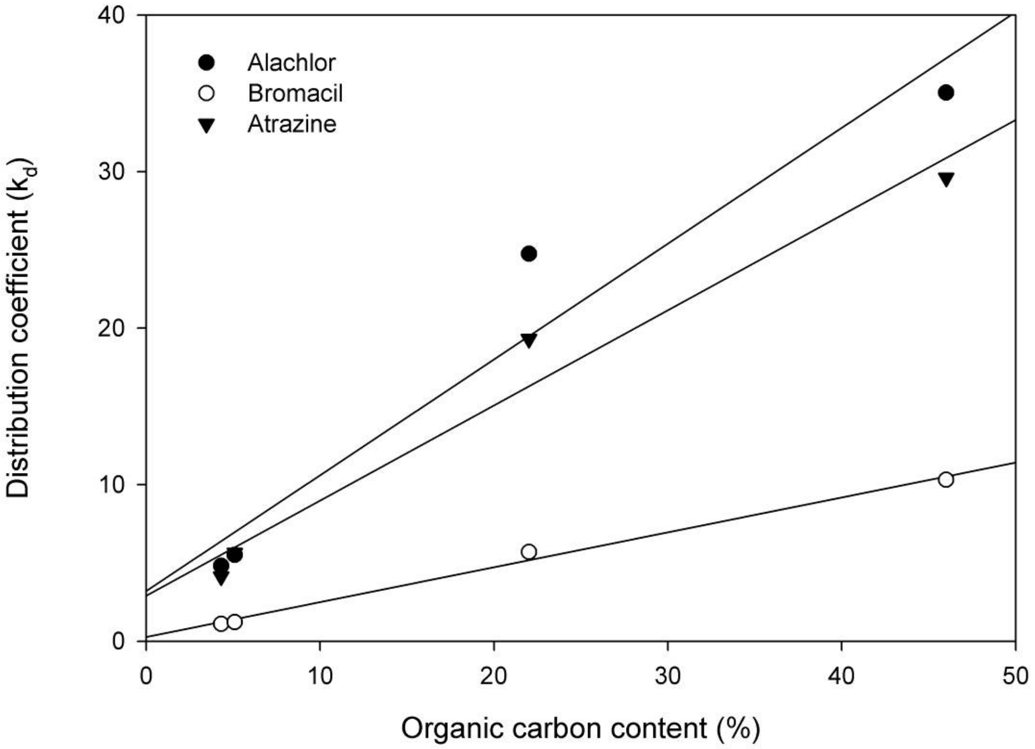


Fig. 4.1: The relationship between the distribution coefficients (K_d) of alachlor, atrazine and bromacil and the organic carbon content of the four media.

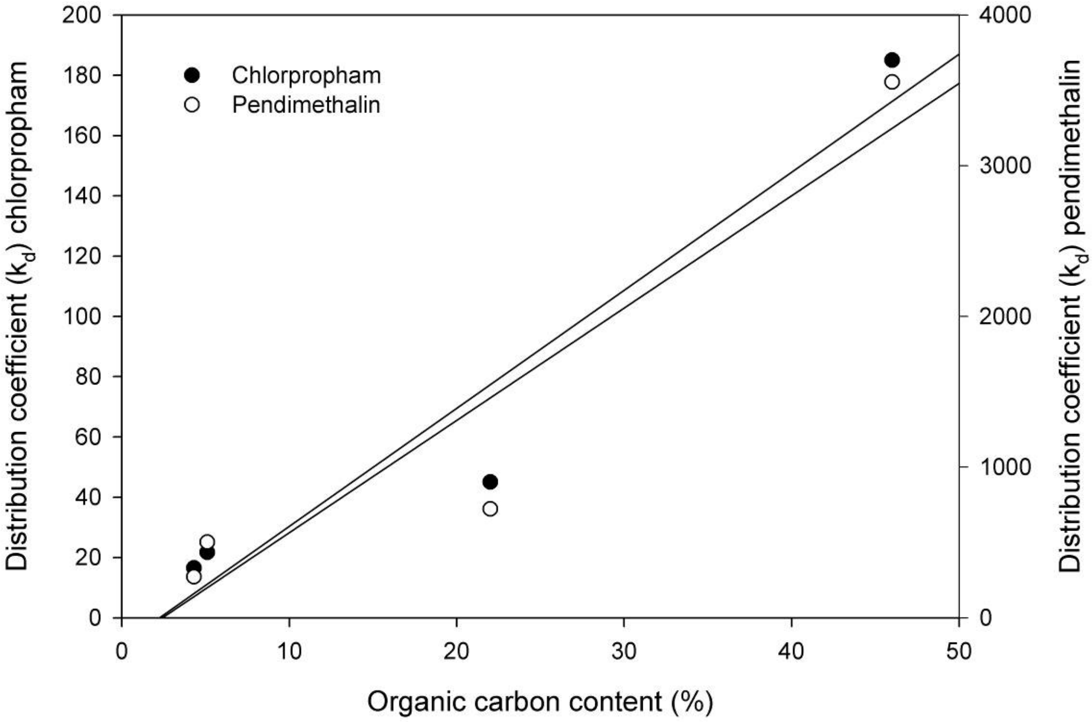


Fig. 4.2: **The relationship between the distribution coefficients (K_d) of chlorpropham and pendimethalin and the organic carbon content of the four media.**

Table 4.7: **Slope, standard error of the slope (SE) and R^2 value for fitted linear regressions of distribution coefficients (K_d) and organic carbon content of the four media (Figs 4.1 and 4.2).**

Media	Alachlor	Atrazine	Bromacil	Chlorpropham	Pendimethalin
Slope	0.74	0.61	0.22	3.92	74.5
SE	0.127	0.075	0.013	0.786	18.01
R^2 (%)	94.4	97.1	99.3	92.6	89.5

4.5 Discussion

The hypothesis being tested through these experiments was that high organic matter soil amendments increase the soil/solution distribution coefficient of herbicides. This hypothesis was very well supported by the results for the five herbicides presented here (Table 4.7). In addition, it was also demonstrated that the increases in the soil/solution distribution coefficients were strongly correlated to the organic carbon content (Figs 4.1 and 4.2) and that the soil organic carbon affinity coefficient (K_{oc}) was a good descriptor for herbicide adsorption that was independent of organic carbon content (Table 4.6). The slight variation in K_{oc} values amongst various media can probably be attributed to the differences in the nature of the organic carbon along with other environmental parameters such as pH.

With the exception of those for alachlor, most of the K_{oc} values presented in Table 4.6 fall within the range reported in the international literature (Table 2.1). In some respects this is not surprising as the range of values for atrazine, bromacil, chlorpropham and pendimethalin vary by factors of 7.6 (38 – 288), 14.3 (2.3 – 33), 3.3 (245 – 816) and 5.8 (5000 – 29000) respectively while the range for alachlor varies only by a factor of 1.7 (120 – 209). The K_{oc} values for alachlor determined from the two soils and from paper pulp (108 – 112) are a little lower than the lowest literature value of 120 while that for sawdust (76) is much lower. The two other values to fall outside the published range were for chlorpropham (204) and pendimethalin (3288), which are both in paper pulp. The most likely reason for this is the high pH of the paper pulp has resulted in increased ionisation of the chlorpropham and pendimethalin molecules making them more water soluble. With these strongly adsorbed herbicides a small increase of the quantity in solution leads to a large decrease in the distribution coefficient (Eq. 1.3).

The K_{oc} values that fall well outside the published range are all determined in organic media and as there appears to be no published data for these types of media, direct comparisons are difficult to make. However, Wauchope et al. (1992) after an extensive review of the literature published “best estimates” of a single K_{oc} and this value has been used to inversely determine a theoretical soil/solution distribution coefficient for each of the herbicide media combinations used in this study (Table 4.8). Most of the experimental values for atrazine and bromacil in the two soils (Table 4.5) closely align with these estimated distribution coefficients (Figs 4.3 - 4.5 and Table 4.9). Although the fourteen of the twenty experimental values are lower than the theoretical ones most are quite close in value with only one experimental K_d differing by more and a factor of 2 from the estimated value. Thus, these results generally endorse the value of an accurately determined soil organic carbon affinity coefficient as a means of estimating individual distribution coefficients, even in high organic matter media (Weber et al. 2000).

Table 4.8: Theoretical distribution coefficients (K_d) calculated from a "best estimate" single value K_{oc} as determined by Wauchope et al. (1992).

	Theoretical distribution coefficient (K_d)				
Media	Alachlor[1]	Atrazine[1]	Bromacil[1]	Chlorpropham[1]	Pendimethalin[1]
Horotiu	9	5.1	1.6	20	255
Mangateretere	7	4.3	1.4	17	215
Paper pulp	37	22	7.0	88	1100
Sawdust	78	46	15	184	2300

[1] "best estimate" K_{oc} values are:170, 100, 32, 400 and 5000 for alachlor, atrazine, bromacil, chlorpropham and pendimethalin respectively.

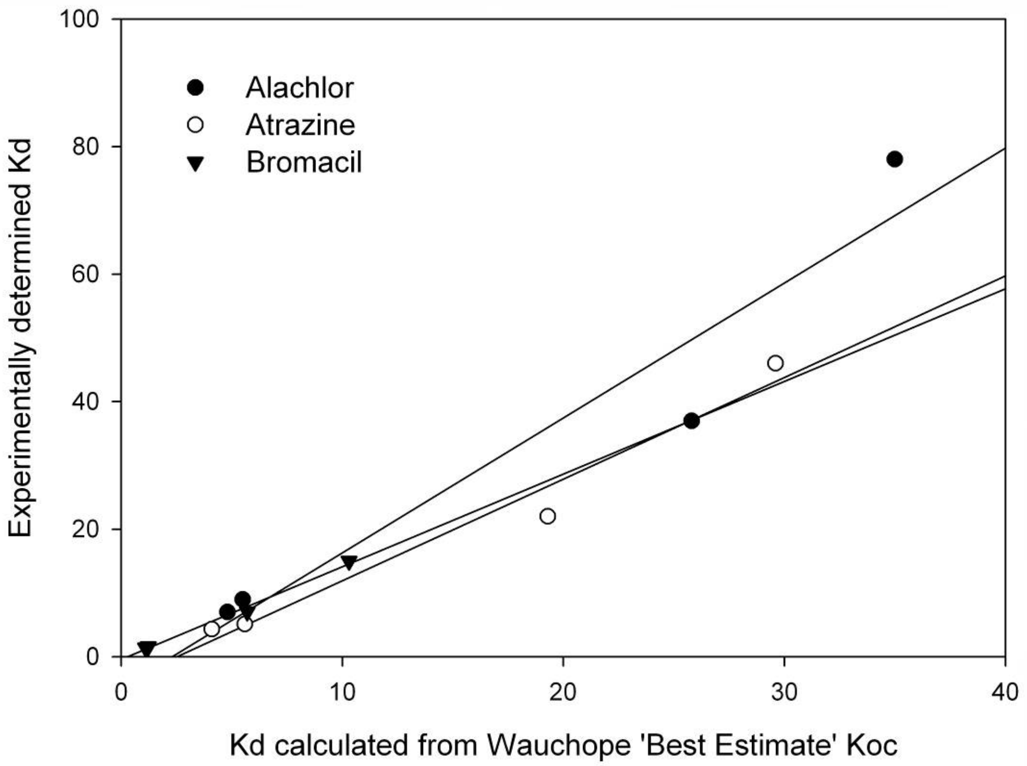


Fig. 4.3: The relationship between the experimentally determined distribution coefficients and those calculated from the 'Best Estimate' K_{oc} of Wauchope et al. (1992) for alachlor, atrazine and bromacil in the four media.

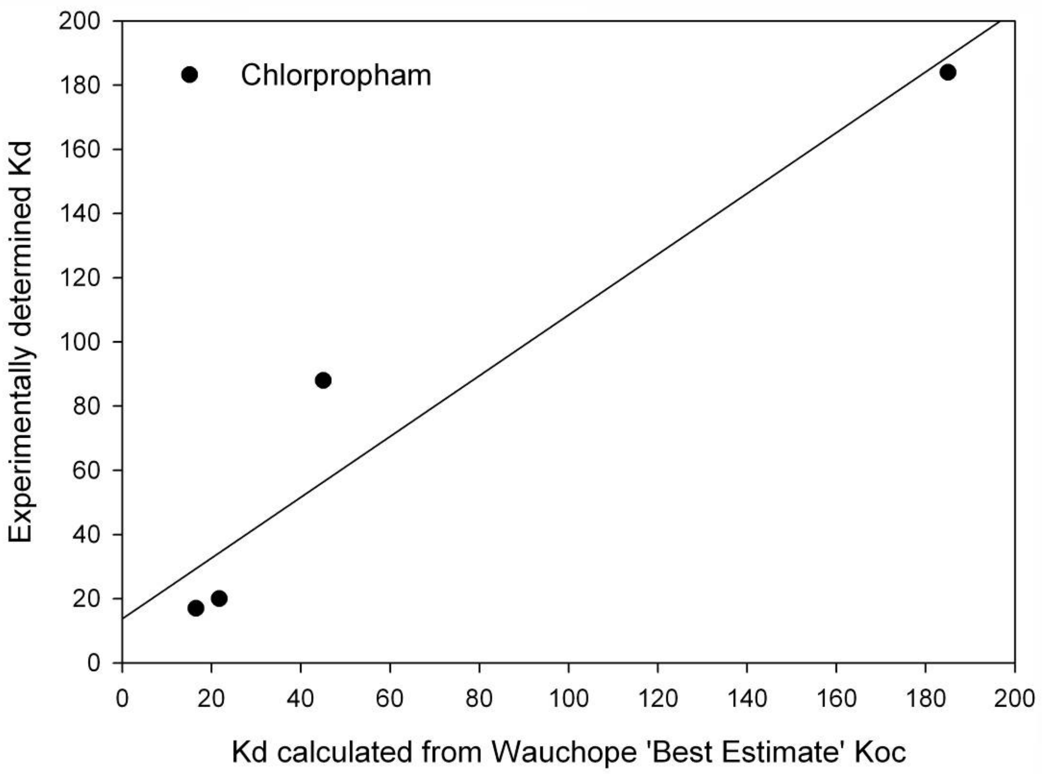


Fig. 4.4: **The relationship between the experimentally determined distribution coefficients and those calculated from the 'Best Estimate' K_{oc} of Wauchope et al. (1992) for chlorpropham in the four media.**

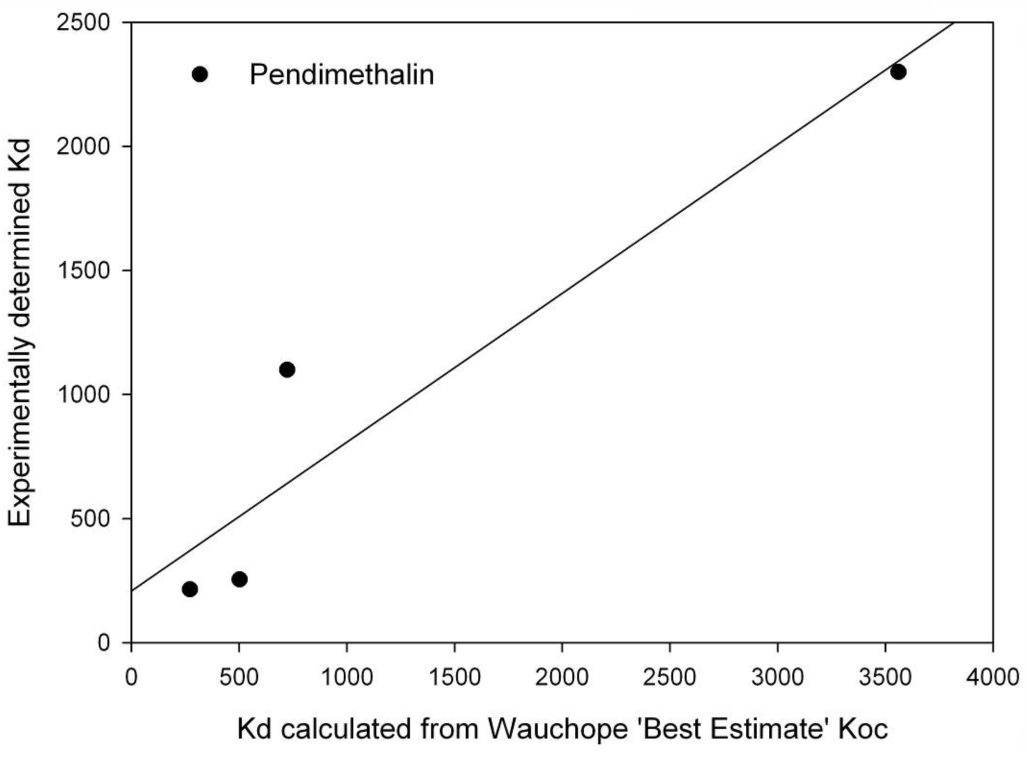


Fig. 4.5: **The relationship between the experimentally determined distribution coefficients and those calculated from the 'Best Estimate' K_{oc} of Wauchope et al. (1992) for pendimethalin in the four media.**

Table 4.9: Slope, standard error of the slope (SE) and R^2 value for fitted linear regressions of experimental and calculated distribution coefficients (K_d) in the four media (Figs 4.3 – 4.5).

Media	Alachlor	Atrazine	Bromacil	Chlorpropham	Pendimethalin
Slope	0.437	0.609	0.682	0.977	1.492
SE	0.088	0.075	0.045	0.197	0.361
R^2 (%)	92.5	97.1	99.1	92.5	89.5

Recently, both atrazine and bromacil have been studied in New Zealand soils with respect to their degradation and dissipation behaviour (Close et al. 1998; Close et al. 1999; Pang et al. 2000; Close et al. 2003; Sarmah et al. 2005; Close et al. 2006; Sarmah et al. 2006). In the course of these studies, adsorption of atrazine and bromacil was determined under a range of conditions in the laboratory and also inversely calculated from field dissipation data. Using a very high soil:water ratio of 1:10, Aislabie et al. (2004) determined atrazine adsorption isotherms in two soils. They found that the isotherms were not linear in either soil. In a Himatangi sand K_d values ranged from 3.08 to 3.43 (K_{oc}; 94 – 104) with decreasing atrazine concentration. Corresponding data for the higher organic carbon Kiripaki soil were 2.6 – 2.9 (K_{oc}; 37 – 42).

While data from the Himatangi sand were similar to those of experiments reported here, the figures from the Kiripaki soil were much lower. In a typical soil at 60% MWHC, a normal field application rate of 1500 g a.i./ha would equate to about 4 – 8 mg/L atrazine in the soil solution (assuming even distribution to 5 cm depth). Although this is in the mid-range of concentrations used to produce their adsorption isotherms, Aislabie et al. (2004) used a large soil:water ratio which actually exposed the soil to approximately 10 times the recommended amount of atrazine for normal use. It is possible that these high quantities of atrazine and large volumes of water used in the slurry process resulted in overloading of sorption sites in the Kiripaki soil and thus an unrealistically low K_{oc} and non-linear adsorption isotherms were produced.

In a leaching study of atrazine in a Bruntwood soil (which has A horizon characteristics similar to the Horotiu soil) using the pesticide dissipation model Opus2, Müller et al. (2004) found that experimentally derived degradation parameters for the soil provided reasonable predictions of atrazine dissipation in the field but also noted that the model was particularly sensitive to small changes in K_{oc}. They used a K_{oc} value of 46.5 and also tested the model with the K_d value of 3.68 determined by Baskaran et al. (1996a) in the Horotiu soil. However, both these values are lower than determined in the present studies. The K_d determined by Baskaran et al. (1996a) was based on a batch equilibrium of only 4 h duration and although they claim 80% adsorption within 1 h, this period is well short of the more frequently used 24 h period and probably the reason for the low K_d value found (Cox & Walker 1999; Mamy & Barriuso 2007). The origin of the K_{oc} value of 46.5 was a personal communication and although undocumented it is very close to the theoretical K_{oc} derived from the K_d of Baskaran et al. (1996c) and the soil organic carbon content of the Bruntwood soil (Müller et al. 2004).

Close et al. (2006) using the slurry method with a 1:2 soil:water ratio determined atrazine and bromacil to have K_d values of 4.47 and 4.88 respectively in a Motupiko soil (2.38% OC) and 2.92 and 0.73 respectively in a Waikiwi soil (3.89% OC). The corresponding K_{oc} values were 188 and 205 for the Motupiko soil and 75 and 19 for the Waikiwi soil. The two K_{oc} values for the higher organic carbon Waikiwi soil are very similar to those determined in the present experiments, but the two values from the lower organic carbon Motupiko soil were much higher, especially for bromacil which at 205 is approximately 6 times the highest value in the international literature (Wauchope 2006). The authors recognised that their values were higher than literature values but offered no reason for this. Weber et al. (2000) in a study of hundreds of published K_d and K_{oc} values found instances of large errors in the K_{oc} values due to inaccurate calculation of organic carbon content from the measured soil organic matter content. The derivation of the organic carbon contents used by Close et al. (2006) are not described. The presence of other sorbates, such as clay material, in large quantities may also contribute (Lee et al. 1990; Pantani et al. 1994; Senseman et al. 1995).

When Sarmah et al. (2006) modelled the leaching of bromacil through the same two soils, they found that the laboratory determined K_{oc} values produced a poor fit of the modelled leaching patterns compared to those from the field experiments. To produce a better fit the authors inversely determined the best K_{oc} value to use and these values varied depending on the leaching model used to produce them. In the higher organic carbon Waikiwi soil the inversely modelled K_{oc} values were 20, 32, 52 and 38 for the pesticide dissipation models LEACHM, HYDRUS-1D, GLEAMS and SPASMO respectively, while the corresponding values for the Motupiko soil were 22, 4, 44 and 22 respectively. These K_{oc} values obtained by inverse modelling were a closer match to the experimental results presented in this chapter than the data reported by Close et al. (2006). The main difference in experimental methods between the two was that Close et al. (2006) used a soil:water ratio of 1:2 while for the experiments reported here, the lower 5:3 ratio for soil was used for the equilibrium (24 h) period with more water being added only for the final extraction (1 h). Thus it appears that the recommendation of Weber et al. (2000) is correct, that procedures to determine soil adsorption should reflect field conditions as much as possible.

4.6 Conclusion

The hypothesis tested through these experiments was that high organic matter soil amendments increase the soil/solution distribution coefficient of herbicides. This hypothesis was clearly well supported by the results for the five herbicides evaluated here. It was also demonstrated that the increases in the soil/solution distribution coefficients were strongly correlated to the organic carbon content and that the normalised soil organic carbon affinity coefficient was a good descriptor of adsorption that was independent of organic carbon content. However, these coefficients need to be determined under conditions that closely replicate field conditions i.e with a low water:soil ratio. The effect of adsorption as measured by the distribution coefficient on degradation and transport will be examined in subsequent chapters.

CHAPTER 5

PERSISTENCE AND DEGRADATION

CHAPTER 5: PERSISTENCE AND DEGRADATION

5.1 Objective

To determine the degradation parameters of two commonly used herbicides (atrazine and bromacil) under a variety of environmental conditions in four diverse growing media, viz. Horotiu and Mangateretere soils, paper pulp and sawdust. The hypothesis being tested was that herbicides degrade more rapidly in the presence of high organic matter soil amendments.

5.2 Introduction

The persistence of herbicides in soil is critical to developing their environmental profile and eventual fate (James et al. 1999; Ma et al. 2000). Carrying out degradation and persistence studies in the field will produce an environmental profile that cannot be refuted as it arguably fits a real scenario (Lavy et al. 1996). However, it is difficult to quantify and parameterise the various environmental conditions that influence degradation in such field situations as they are constantly changing. Without an adequate understanding of the interactions with key environmental conditions it then becomes very difficult to extrapolate and predict herbicide degradation under diverse conditions (Di et al. 1998). It is easier and more economical to determine the effect of environmental parameters, such as temperature and microbial activity, on degradation rates under controlled conditions and then extrapolate to field conditions (Oppong & Sagar 1992).

The studies reported in this chapter were carried out at three different temperatures which span the range of soil temperatures experienced in the field during the spring/summer growing season. A sterilised control was included to evaluate the importance of microbial activity on degradation. In addition, the influence of a fluctuating soil temperature regime on degradation (Ahmad et al. 2001) was investigated because this has been found to enhance biological activity (Visser et al. 1984). All studies were carried out at a constant water content of 60% maximum water holding capacity (MWHC). Several previous studies have showed little effect of soil moisture contents between 40 and 80% MWHC on degradation rates (James et al. 1995; James et al. 1998; James et al. 1999).

5.3 Materials and Methods

5.3.1 Media Preparation

The four media used in this study; sawdust, paper pulp and Mangateretere and Horotiu soils, were taken from the samples prepared for the bioavailability study (Section 3.3.1).

5.3.2 *Determination of Maximum Water Holding Capacity (MWHC)*

The MWHC was determined by the 24-hour water saturation method using Hilgard cups (Grandmaison & Laflamme 1986; Mabuhay et al. 2003). The cups were lightly packed with field moist media and placed on a bed of wet sand containing sufficient water to wet the base of the cup and allowed to stand for 24 h. If the sand became too dry, more water was added. A moist filter paper prevented the surface of the media from drying. The cups were allowed to stand for a further 24 h on moist sand for the media to equilibrate to its MWHC. After weighing, the cups were dried at 105°C for 24 h and reweighed. MWHC was determined after correcting for tare weight as follows:

$$\text{MWHC (\%)} = \frac{(\text{wet wt} - \text{dry wt}) \times 100}{\text{dry wt}} \qquad \text{Eq. 5.1}$$

MWHC was determined on six replicates for each of the two soils and on 12 replicates for the paper pulp and the sawdust. Table 5.1 presents the averaged results of the MWHC determinations along with the standard deviation of the mean. The MWHC values for the two soils are similar to those reported earlier (Günther et al. 1993; Ahmad et al. 2003). There is little literature on the water holding capacity of sawdust and paper pulp as used in this study, although sawdust-derived soil conditioners are known to improve the water holding capacity of different soils (Rajor et al. 1996), suggesting that sawdust must have a greater water holding capacity than soil. The results presented here show that paper pulp has about 3 – 5 times and sawdust has about 4 – 8 times the water holding capacity of these soils.

Table 5.1: Maximum water holding capacity values for the four media.

	Media			
	Horotiu soil	Mangateretere soil	Sawdust	Paper pulp
MWHC (%)	106	54	452	281
sd	3.9	2.6	19.6	16.4

5.3.3 *Determination of Media pH*

The pH values of the four media were determined at the commencement of the degradation study using the slurry method (Schofield & Taylor 1955). For the two soils the standard soil:water ratio of 1:2 was used, but for the paper pulp and sawdust the quantity of water had to be increased to obtain a suitable slurry. The ratios used were 1:6 (paper pulp:water) and 1:5 (sawdust:water). The measurements were made on material that passed through a 2-mm sieve and the slurry was made up with de-ionised water and allowed to stand at an ambient temperature (≈20°C) for 16 h to equilibrate. The results (average of 24 measurements) are presented in Table 5.2. These differ slightly from the values reported by a commercial laboratory (Table 3.1, but also included in this table). The differences are most likely due to sampling variability, i.e. taking the samples for analysis from slightly different locations (soils) or from different sacks of paper pulp and sawdust.

Table 5.2: pH values and the standard error of the mean (SEM) for the four media measured prior to commencement of the degradation experiments and compared to that determined in the commercial laboratories.

	Media			
	Horotiu soil	Mangateretere soil	Sawdust	Paper pulp
pH, this study	5.51	5.44	5.59	7.71
SEM	0.003	0.006	0.025	0.018
pH commercial lab[1]	5.9	5.3	5.8	7.9

[1] From Table 3.1

5.3.4 *Degradation Studies*

Degradation studies were carried out in all four media for the herbicides atrazine and bromacil. These two herbicides were selected as they are known to persist in the environment (James et al. 1994; James et al. 2003) and would thus provide a good comparison between the media. The degradation was determined at a herbicide concentration in soil equivalent to a field application of twice the label use rate (O'Connor 2003) incorporated to a depth of 100 mm. The twice label rate was used as this is the worst case scenario that arises when spray overlap occurs during application in the field. The studies were carried out at 10°C, 20°C, 30°C and 20±5°C (as a diurnal sine curve) in the dark at 60% MWHC. Additionally, the 20°C study was also carried out using autoclave-sterilised media (Yutai et al. 1999). Autoclave sterilisation was carried out twice on 1 kg soil samples prior to the soil being mixed and weighed into the flasks.

The moisture contents of the media were determined gravimetrically by drying quadruplicate samples (10 g) at 105°C for 24 h. The media were then weighed into 250 mL Erlenmeyer flasks (10, 20 and 50 g dry wt equivalents for sawdust, paper pulp and the two soils, respectively; see also Section 4.3.1) and brought to 2 g below the 60% MWHC weight by adding deionised water. The flasks were fortified by adding the required amount of herbicide in 2 mL of water and shaken by hand to mix the herbicide and media. Four additional aliquots of 2 mL were placed directly into small glass vials, sealed and frozen, to be used as controls. The herbicide fortification solution was made up from the formulated products Atradex (900 g/kg atrazine) and Hyvar X (800 g/L bromacil) to better match the field situation. The flasks were loosely sealed with aluminium foil and placed in the respective temperature regimes. They were weighed at weekly intervals and water added as required to maintain the moisture content. Eight flasks were frozen immediately after shaking (Day 0) and two were removed from each temperature regime and frozen after 3, 7, 14, 21, 28, 42, 56 and 84 days had elapsed. All flasks remained frozen at -20°C until required for analysis.

5.3.5 *Herbicide Extraction*

5.3.5.1 Procedure for Atrazine Extraction from Media

The extraction method was a slight modification of James et al. (1994). After the flasks containing atrazine were defrosted, deionised water was added to bring the weight of water in the flask (including soil water) to 30 g and 70 ml of methanol was added. The flasks were sealed and shaken on an orbital shaker at 50°C for 3 hr and then allowed to settle overnight at ambient laboratory temperature (20°C). If there was more than 30 g water present in the flask on completion of the study then sufficient methanol was added to maintain a 70:30 methanol to soil water ratio. After settling, either a 10 ml aliquot of supernatant liquid was drawn off or, where more than 70 mL of methanol was added, then an aliquot equal to 10% of the total solution was drawn off. The aliquot was placed in a Schott bottle and 90 mL deionised water added. This was aspirated under vacuum through Extract-Clean™ solid phase extraction columns containing 0.5 g of C18 silica based sorbent material. The sorbed material was eluted twice with 2 mL of methanol and the combined eluent evaporated to dryness under a gentle stream of nitrogen at 30°C. The residue was re-dissolved in 0.5 ml of methanol and 0.5 ml of water added. The resolubilised extract was filtered through an Anatop 10™, 0.2 µm PTFE syringe filter in preparation for quantification by HPLC.

5.3.5.2 Procedure for Bromacil Extraction from Media

The bromacil extraction method was modified from James & Lauren (1995). After the flasks containing bromacil were defrosted, deionised water was added to bring the weight of water in the flask (including soil water) to 30 g and 70 ml of 1.5% w/v aqueous sodium hydroxide was added. The flasks were sealed and shaken on an orbital shaker for 1 h at 20°C and then allowed to settle overnight at ambient laboratory temperature (20°C). If there was more than 30 g water present in the flask on completion of the study then sufficient sodium hydroxide solution was added to maintain a 70:30 sodium hydroxide solution to soil water ratio. After settling, either a 10 ml aliquot of supernatant liquid was drawn off or, where more than 70 mL of sodium hydroxide solution was added, then an aliquot equal to 10% of the total solution was drawn off. The aliquot was placed in a test tube and acidified to a pH of about 2-3 with 1 ml of 5 N hydrochloric acid. This was extracted with 10 mL of dichloromethane. After the dichloromethane was added it was vortex-mixed for 1 min and centrifuged at 3600 rpm for 10 min before the dichloromethane was drawn off. The volume of recovered dichloromethane was measured and then evaporated to dryness under a gentle stream of nitrogen at 30°C. The residue was re-dissolved in 0.25 ml of methanol and 0.75 ml of water added. The resolubilised extract was centrifuged at 2000 *g* for 20 min and filtered through an Anatop 10™, 0.2 µm syringe filter in preparation for quantification by HPLC. Were the recovered dichloromethane was less than that added, a numerical correction was made to the final quantity of bromacil to account for this.

5.3.5.3 Treatment of the Control Fortification Samples

The control fortification samples were diluted in the scintillation vial with either 14 or 18 mL of purified water to give either an 8 fold or a 10 fold dilution before quantification by HPLC. Additionally, samples of the diluted fortification controls were drawn off and passed through the Anatop 10™ 0.2 µm PTFE syringe filters used above, to check whether there was any sorption of the herbicide by the filters used in the extraction from media procedures 5.3.5.1 and 5.3.5.2 above.

5.3.5.4 Quantification by HPLC

All analyses were carried out as previously described in Chapter 4 (Section 4.3.5).

5.4 Results

5.4.1 *Herbicide Fortification Control Samples*

As the herbicide fortification solutions were made from the formulated products, some discrepancy from the calculated amount was expected due to allowable variation during manufacture of the formulated product (Anonymous 2007). The actual amounts of the fortifications are presented in Table 5.3 along with the calculated values and showed the actual amount ranged from 90 – 122% of the of calculated. The actual fortification amounts were used to normalise all the degradation results, with all results being presented as percentages of the original fortification after correction for recovery (see Section 5.4.2). There was no detectable sorption of either atrazine or bromacil onto the Anatop 10^{TM} 0.2 µm PTFE syringe filters used during the cleanup of the extracted samples.

Table 5.3: Fortification of herbicide added to each flask for the degradation studies.

	Fortification (µg)					
	Atrazine			Bromacil		
Media	Theoretical	Actual	%	Theoretical	Actual	%
Horotiu	214	207	97	457	457	100
Mangateretere	183	219	120	391	387	99
Paper pulp	261	307	118	557	503	90
Sawdust	231	281	122	405	492	121

5.4.2 *Herbicide Extraction*

The extraction method for atrazine collected 10% of the total extractant and concentrated this into in 1 mL prior to quantification, thus it is assumed this resulted in 10% of the original fortification being concentrated into 1 mL. Clay and other colloidal particles rapidly settled in the methanol/water supernatant solution and the SPE extraction proceeded without difficulty. However, the supernatant solution of the sawdust (and to a small degree the paper pulp) was highly discoloured with soluble extractives which persisted through the SPE cleanup and discoloured the analyte solution.

The extraction of bromacil was more complicated than for atrazine and several modifications to the published method (James & Lauren 1995) were required for the high organic matter paper pulp. For consistency extractions for all four media were then carried out using the modified procedure. The sodium hydroxide extraction of the paper pulp was problematic with sodium hydroxide partially breaking down the paper pulp and producing copious fine material which remained suspended even after centrifugation. After a sample of the supernatant was recovered this suspended material then mixed with the added dichloromethane (DCM) and prevented the latter from being separated by centrifugation. The published method required three separate partitions into DCM to remove all the dissolved bromacil from the supernatant sample. To solve the problem, a single, larger aliquot of DCM was added to the supernatant sample and after mixing and centrifugation, the recoverable DCM was removed with a Pasteur pipette and its volume measured. After quantification all results were corrected for the fraction of DCM recovered (x DCM added/DCM recovered) but no other corrections (e.g. for recovery) were made.

The efficiency of the extraction methods was evaluated on eight of the Day-0 samples for each herbicide/media combination. The percent recovery and SEM for each combination are presented in Table 5.4. These data show that recovery from the high organic matter paper pulp and sawdust was both efficient (% recovery > 90%) and consistent (SEM < 2). Recovery from the two soils was generally not as good, with recovery of atrazine efficient but not consistent (SEM > 2) while recovery of bromacil was consistently less efficient (74 – 86%, Table 5.4). However, these results for bromacil are consistent with those of Jolliffe (1967) who, using a similar method, recovered between 39% and 75% of added bromacil after 3 days in six different soils and 87% from a quartz sand. Zimdahl et al. (1970), also using the method of Jolliffe (1967), averaged 87% recovery of bromacil. Furtula & Kuo (2004) obtained 80-88% recovery from soil following a shaking with methanol extraction of fortified samples. Strongly alkaline conditions are known to degrade substituted uracils (Brown 1962), but there is no reason to suspect that alkaline conditions would only do this in soil and not in either the paper pulp or sawdust so it was concluded that this was not a factor. Jolliffe (1967) also found no evidence of alkaline degradation in the extraction procedure for up to 2 h.

Although the extraction of atrazine from the Horotiu and Mangateretere soils was more variable than from either the paper pulp or sawdust (Table 5.4), it was still in keeping with published values using a variety of extraction methods. For example, in a comparison of atrazine extraction by shaking with methanol or by accelerated solvent extraction (where methanol is pumped through the soil at elevated pressure and temperature) the SEMs for four soils (six replicates) ranged from 1.10 to 3.17% for the shaking method and from 0.35 to 3.5% for the accelerated solvent extraction (Gan et al. 1999). The SEM for duplicate samples and using methanol:water (9:1) for extraction of atrazine from soil in a column leaching experiment ranged from 14 to 64% (Kruger et al. 1993). Using a similar method but with three replicates, Khan & Marriage (1977) recovered between 92.5 and

96.5% of atrazine from fortified soil samples with SEM values of 2.4 and 1.5 respectively. In a method using microwave assisted extraction (extracting directly into water at elevated temperature and pressure), Xiong et al. (1998) produced recovery data with SEMs ranging from 1.6 to 2.0% from three replicates.

Table 5.4: Recovery of atrazine and bromacil from the eight Day-0 samples compared to the original fortification.

	Atrazine			Bromacil		
	Fortification	Recovery		Fortification	Recovery	
Media	(µg)	%	SEM	(µg)	%	SEM
Horotiu soil	207	96.4	3.01	457	85.7	0.85
Mangateretere soil	219	94.8	2.72	387	73.9	1.52
Paper pulp	307	96.2	0.96	503	94.9	1.66
Sawdust	281	93.1	1.98	492	99.3	1.90

The extraction and cleanup procedures proved effective for quantification by HPLC with no co-extractants adjacent to or interfering with the peak of the analyte (Figs 5.1 – 5.8). Sawdust contains many water soluble extractives (mostly polyphenols) (Karagöz et al. 2005) and the methanol extraction of atrazine from sawdust concentrated highly coloured tannins (Scalbert et al. 1989). However, these pigments eluted early from the HPLC column and resulted in little, if any, interference with the atrazine peak (Fig. 5.4). The sodium hydroxide extraction of bromacil from the paper pulp and sawdust also contained a significantly higher level of co-extractants than for either of the two soils, but they eluted rapidly through the HPLC column and did not result in any interference with the bromacil peak (Figs 5.5 – 5.8).

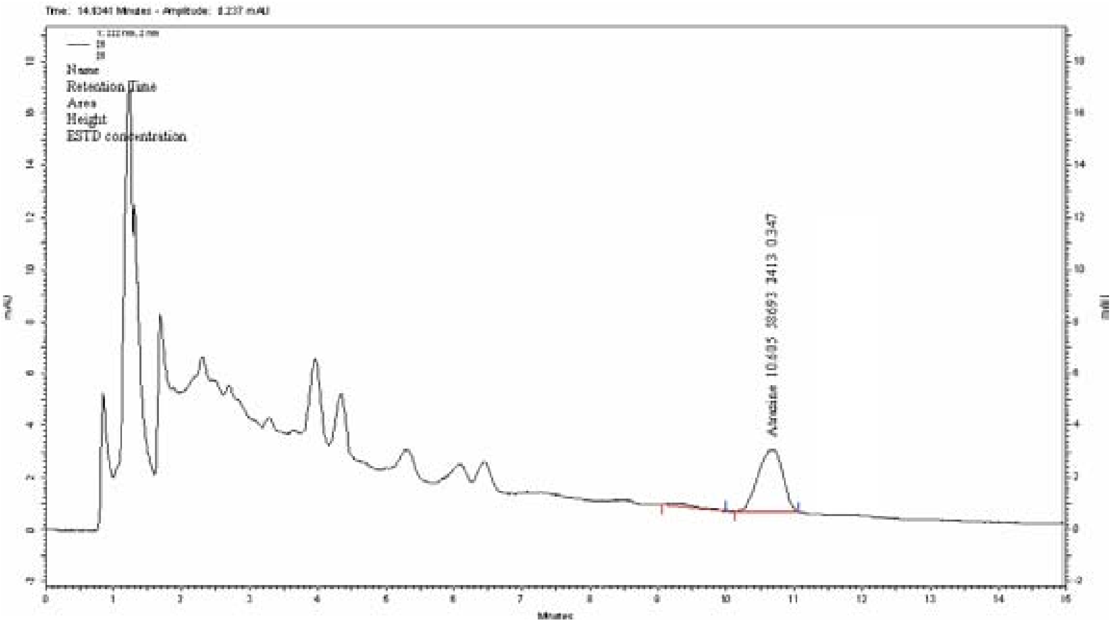


Fig. 5.1: **HPLC chromatograms for atrazine (0.35 µg/g) extracted from Horotiu soil with methanol and SPE cleanup.**

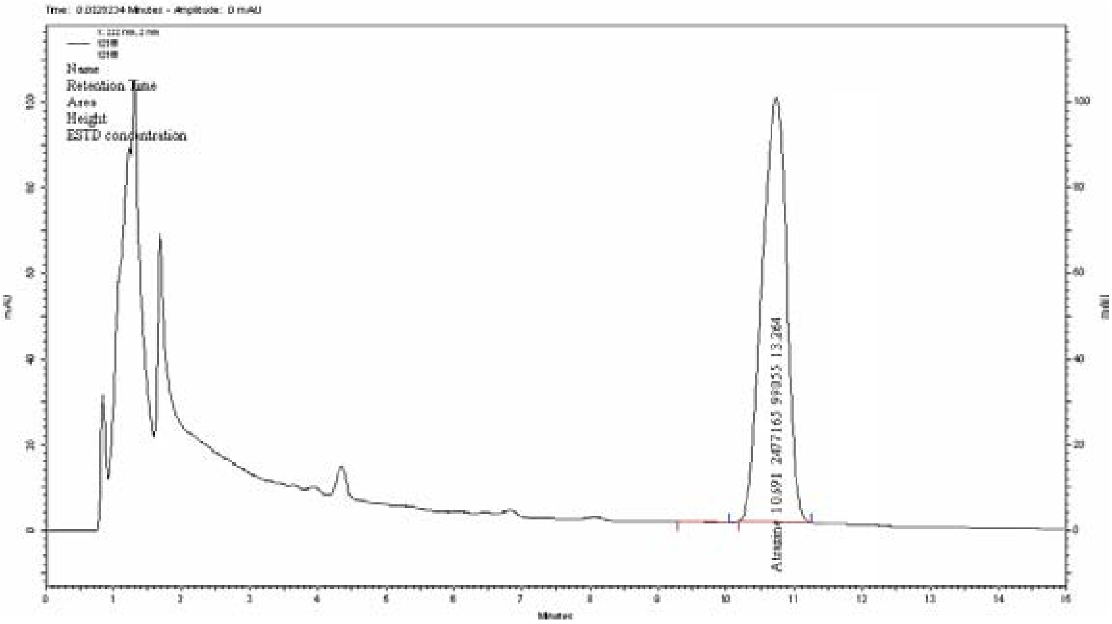


Fig. 5.2: **HPLC chromatograms for atrazine (13.3 µg/g) extracted from Mangateretere soil with methanol and SPE cleanup.**

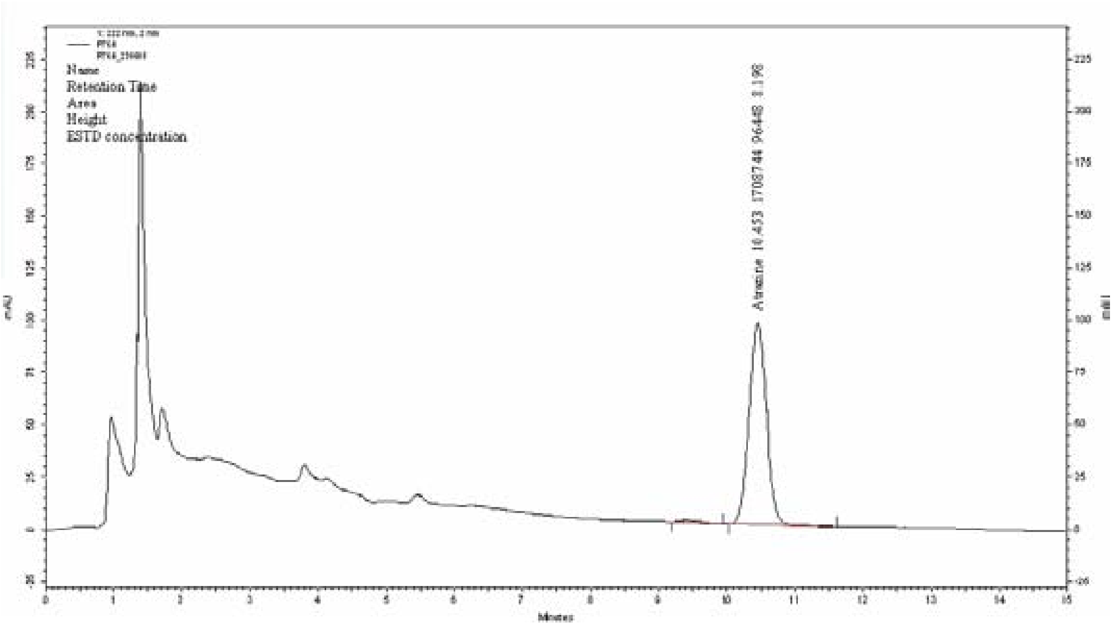


Fig. 5.3: HPLC chromatograms for atrazine (8.2 µg/g) extracted from paper pulp with methanol and SPE cleanup.

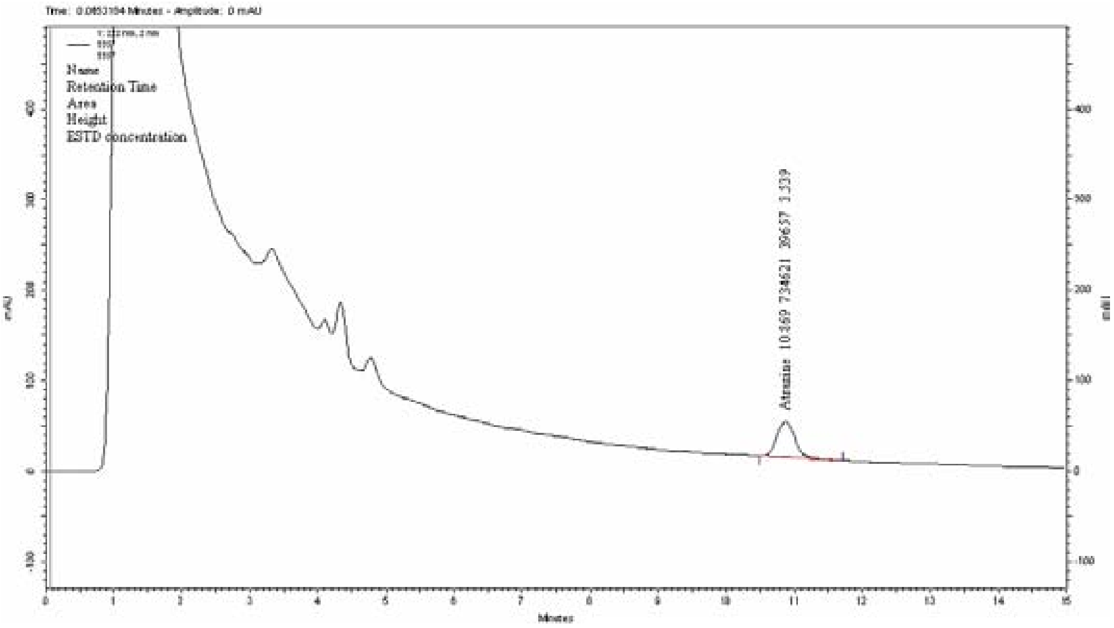


Fig. 5.4: HPLC chromatograms for atrazine (3.5 µg/g) extracted from sawdust with methanol and SPE cleanup showing the large initial peak from the coloured, soluble matter co-extracted.

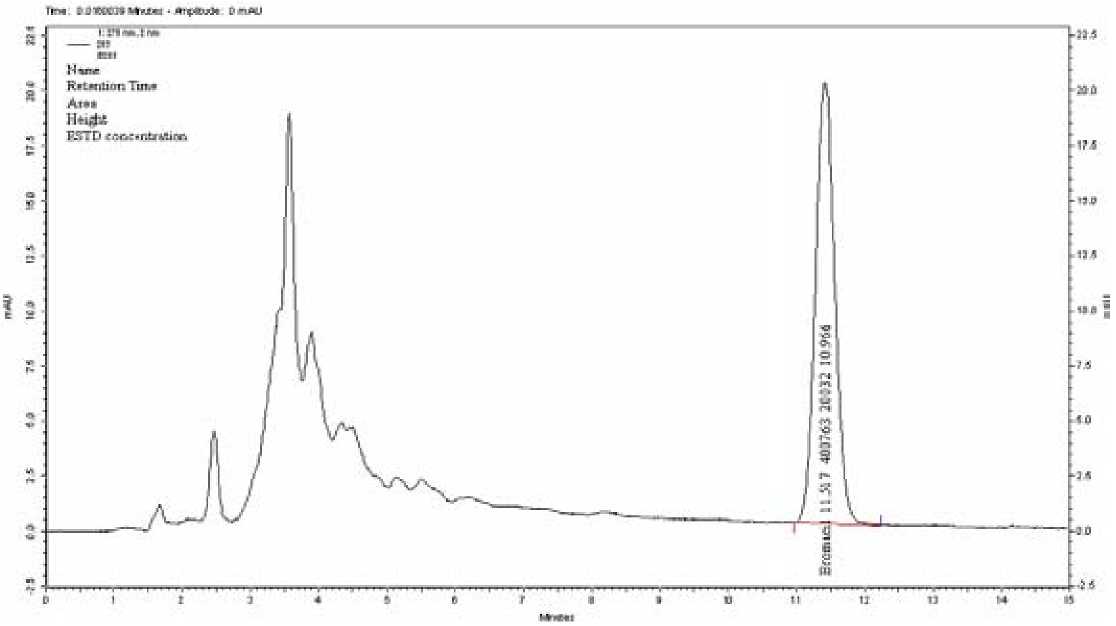


Fig. 5.5: **HPLC chromatograms for bromacil (11.0 µg/g) extracted from Horotiu soil with NaOH soln and DCM partitioning.**

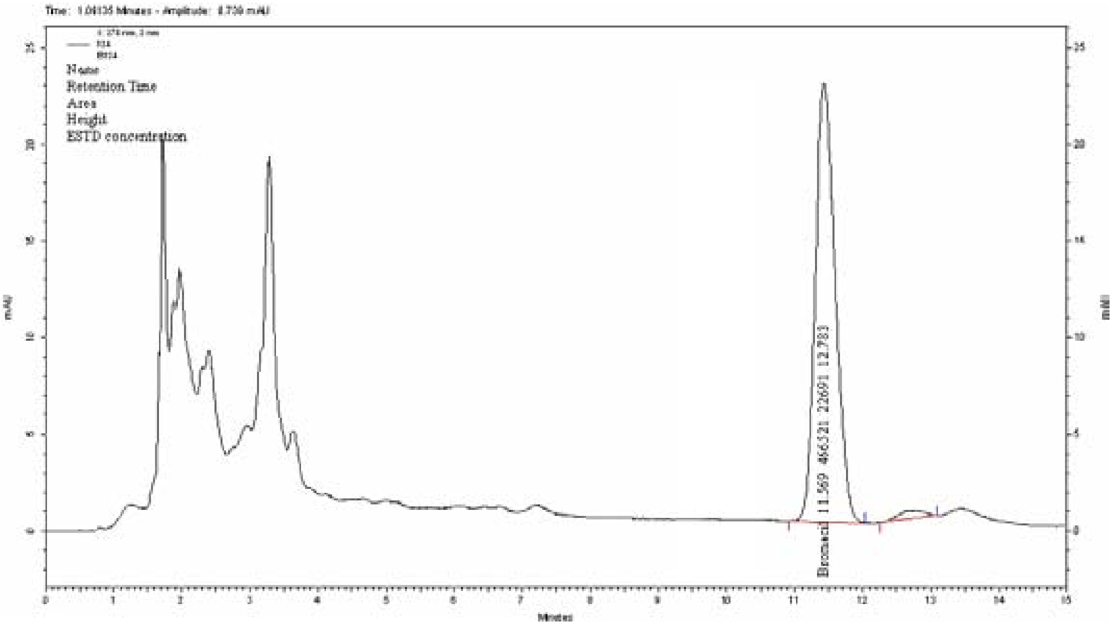


Fig. 5.6: **HPLC chromatograms for bromacil (12.8 µg/g) extracted from Mangateretere soil with NaOH soln and DCM partitioning.**

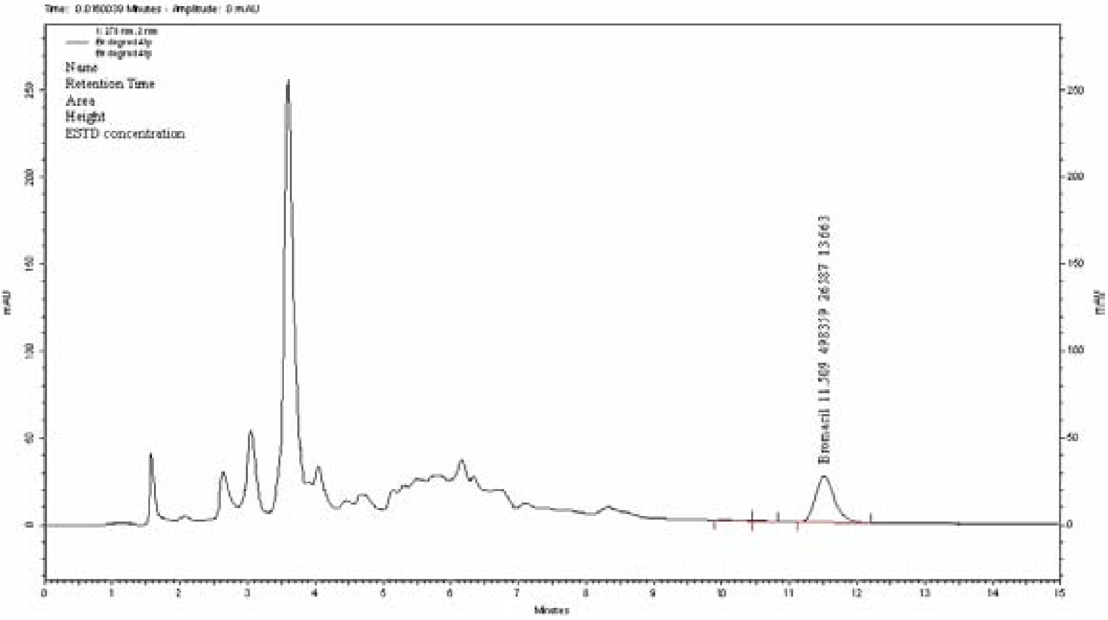


Fig. 5.7: **HPLC chromatograms for bromacil (13.7 µg/g) extracted from paper pulp with NaOH soln and DCM partitioning.**

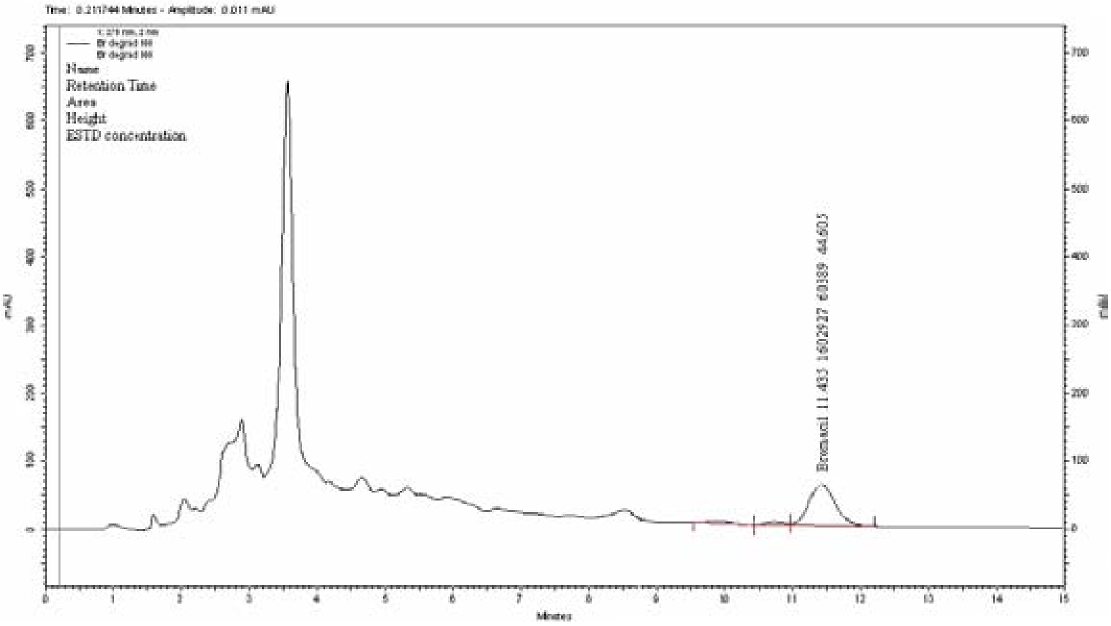


Fig. 5.8: **HPLC chromatograms for bromacil (44.6 µg/g) extracted from sawdust with NaOH soln and DCM partitioning.**

5.4.3 *Degradation Profiles*

As explained previously, the principal cause of herbicide degradation is microbial degradation and in its general form follows first-order kinetics with an exponential decay curve (Section 2.2.4). Thus, in examining herbicide degradation the first hypothesis to test is that herbicide degradation is exponential in nature and follows first-order kinetics (Heiermann et al. 1995). The test for this is to replot each decay curve on a semi-log scale (on the *y* or herbicide concentration axis) and test for a straight line (linear regression analysis) (Beulke & Brown 2001; Beulke et al. 2005). The degradation plots are thus presented in Figs 5.9 – 5.18 with the normal plot at the top of each figure and the semi-log plot at the bottom. The degradation half-life ($t_{½}$, assuming 1st order kinetics) and the R^2 linear regression statistic for each combination of media and degradation regime are presented in Table 5.5. Half-life is calculated from the slope of the regression line according to the previously derived Eq. 1.8 (Section 2.2.4) (del Pino & Díaz 1998; Beulke & Brown 2001):

$$t_{½} = \ln(2)/\text{slope} \qquad \text{Eq. 1.8}$$

and the standard error (SE) of the half-life is estimated by back prediction according to the equation:

$$\text{SE}\,(t_{½}) = \frac{\ln(2).\text{SE(slope)}}{(\text{slope})^2} \qquad \text{Eq. 5.2}$$

5.4.3.1 Degradation of Atrazine in Four Media under Five Different Regimes

The degradation of atrazine in the four media (paper pulp, sawdust, Horotiu soil and Mangateretere soil) at 10°C, 20°C, 30°C, 20±5°C and at 20°C in sterilised media are presented in Figs 5.9 – 5.13 respectively.

At 10°C the degradation of atrazine was slow in paper pulp, sawdust and Mangateretere soil ($t_{½}$ of 125, 75 and 89 d respectively) with >40% of the original fortification remaining after 84 d. Degradation of atrazine in the Horotiu soil was considerably faster ($t_{½}$ = 17 d) with >90% of the original fortification degrading in just over 40 d. Semi-log plots of these reveal that for the paper pulp, sawdust and Mangateretere soil, degradation appears to closely follow first-order kinetics and linear regression shows that between 93.5 and 95.5% of the variation of the data is accounted for by the regression line (Table 5.5). For the Horotiu soil, linear regression can still explain 91.3% of the variation in the data yet a visual examination of the plot (Fig. 5.9b) reveals what appears to be a Logit (bi-sigmoidal) curve with faster initial degradation followed by a slower second phase.

Degradation of atrazine at 20°C follows the same trend, however the half-lives are significantly shorter at this temperature ($t_{½}$ of 70, 39 and 21 d for paper pulp, sawdust and Mangateretere soil respectively), and the differences in the degradation rates between the different media are more pronounced (Fig. 5.10). The linear fit for first-order kinetics is very good for these three media with R^2 values >96% for each of them. However, degradation in the Horotiu soil is poorly described by first-order kinetics (R^2 = 76.7%).

The plots of atrazine degradation at 30°C (Fig. 5.11) reveal a high degree of similarity to degradation at 20°C, the only significant difference being the increased slope of the regression lines indicating more rapid degradation at 30°C. Half-lives for paper pulp, sawdust and the Mangateretere soil were 39, 23 and 17 d respectively at this temperature. Again, degradation of atrazine in these three media is well described by first-order kinetics while the Horotiu soil shows greater deviation (R^2; 71.9%).

Degradation of atrazine in the fluctuating temperature regime (Fig. 5.12) is very similar to its degradation at 20°C (Fig. 5.10) which is the mean temperature of the fluctuating regime.

Figure 5.13 clearly shows that degradation of atrazine in the sterilised media is significantly reduced in all cases, although for paper pulp and sawdust the reduction is smaller (Table 5.4). This demonstrates the role of microbial activity on the degradation of this chemical. The most dramatic effect was on the Horotiu soil where the half-life of atrazine at 20°C was increased from 13 d to 55 d by sterilisation. Also of note with this soil was that with sterilisation the degradation curve was now well described by first-order kinetics (Fig. 5.13 lower) with an R^2 of 95.9%.

Atrazine consistently underwent more rapid degradation in the Horotiu soil with the decay curve having the appearance of a logistic curve (except when sterilised) rather than an exponential curve. The implications of this are discussed in Section 5.5.5. Degradation was always slowest in paper pulp.

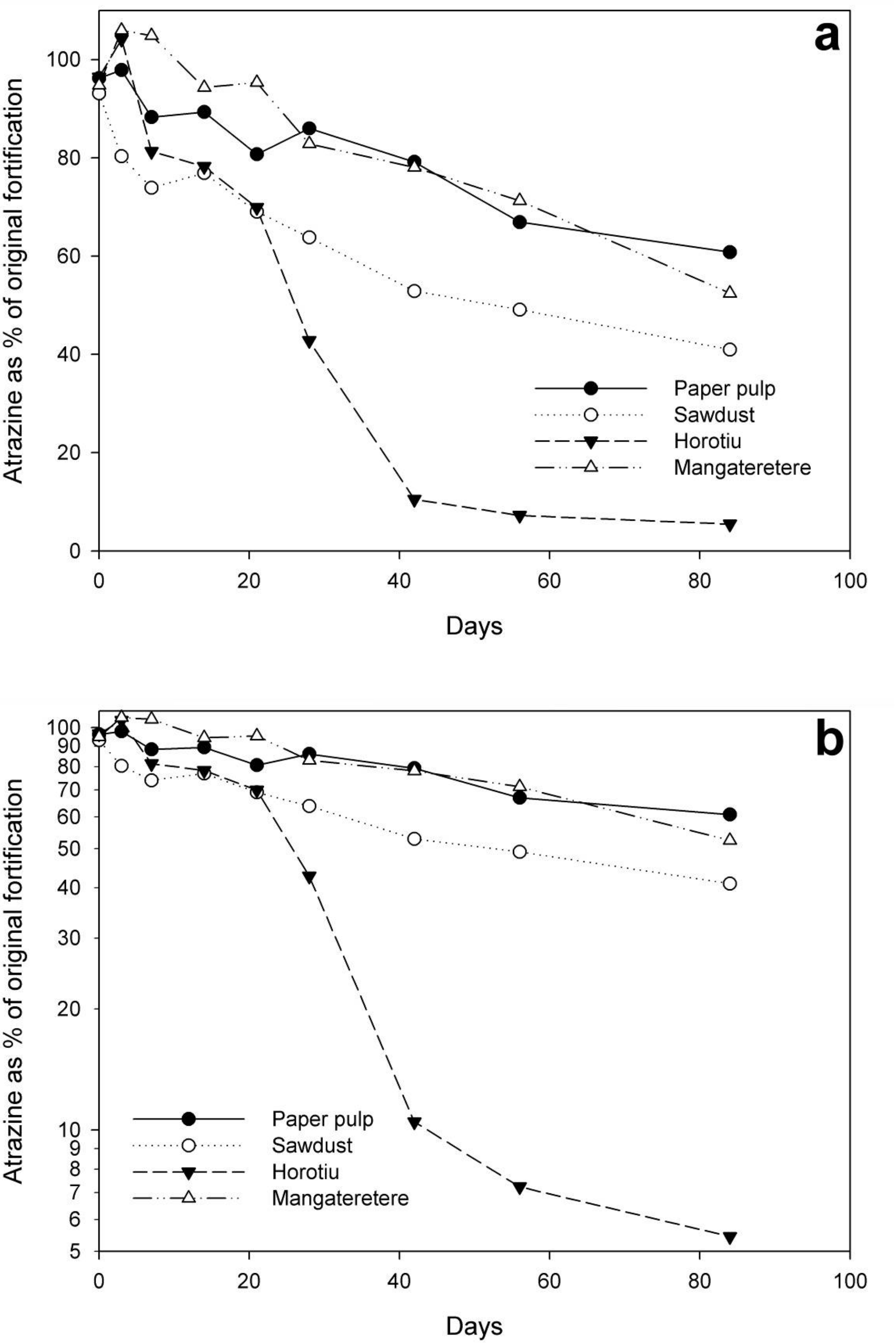


Fig. 5.9: **Atrazine degradation at 10°C with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.**

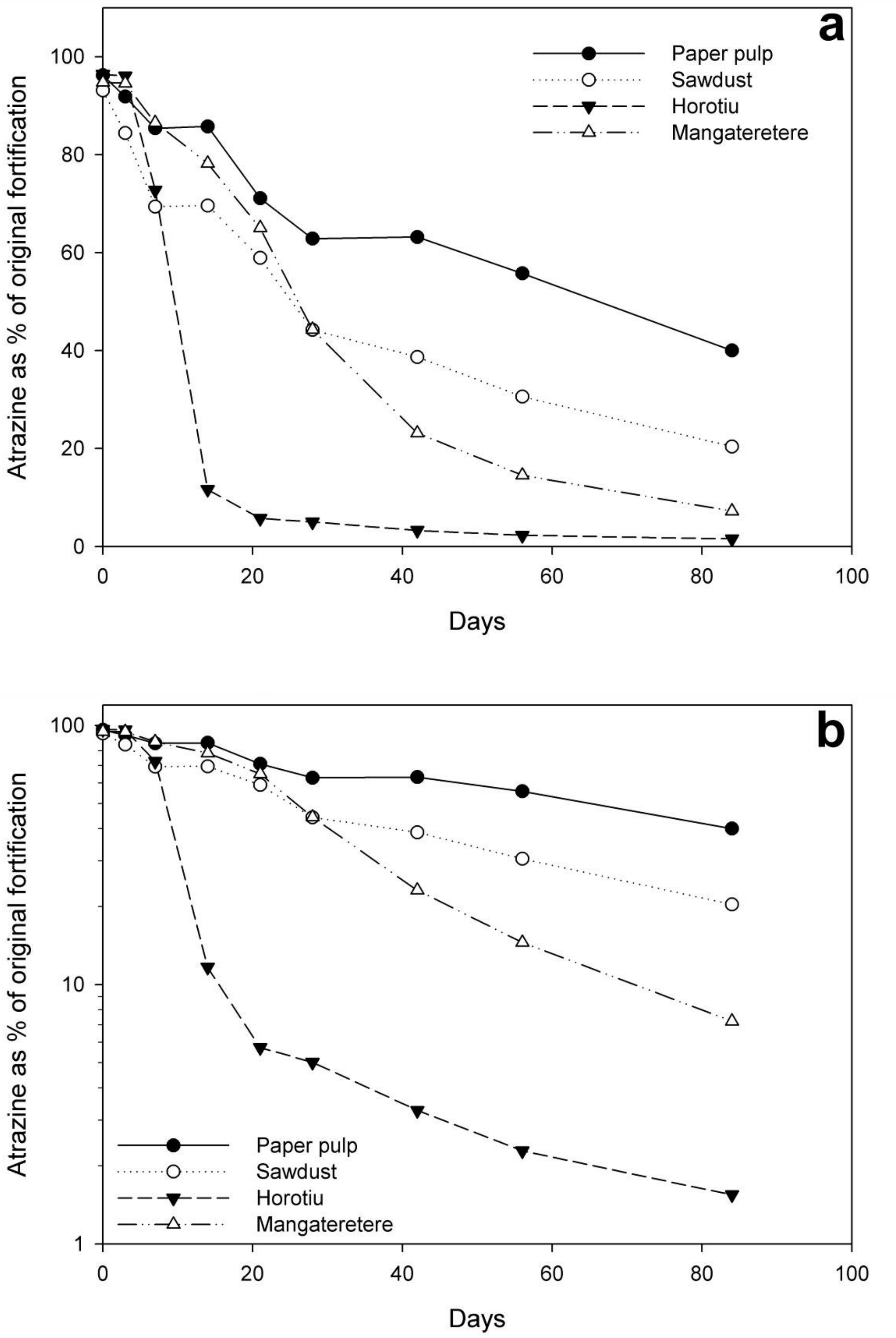


Fig. 5.10: Atrazine degradation at 20°C with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

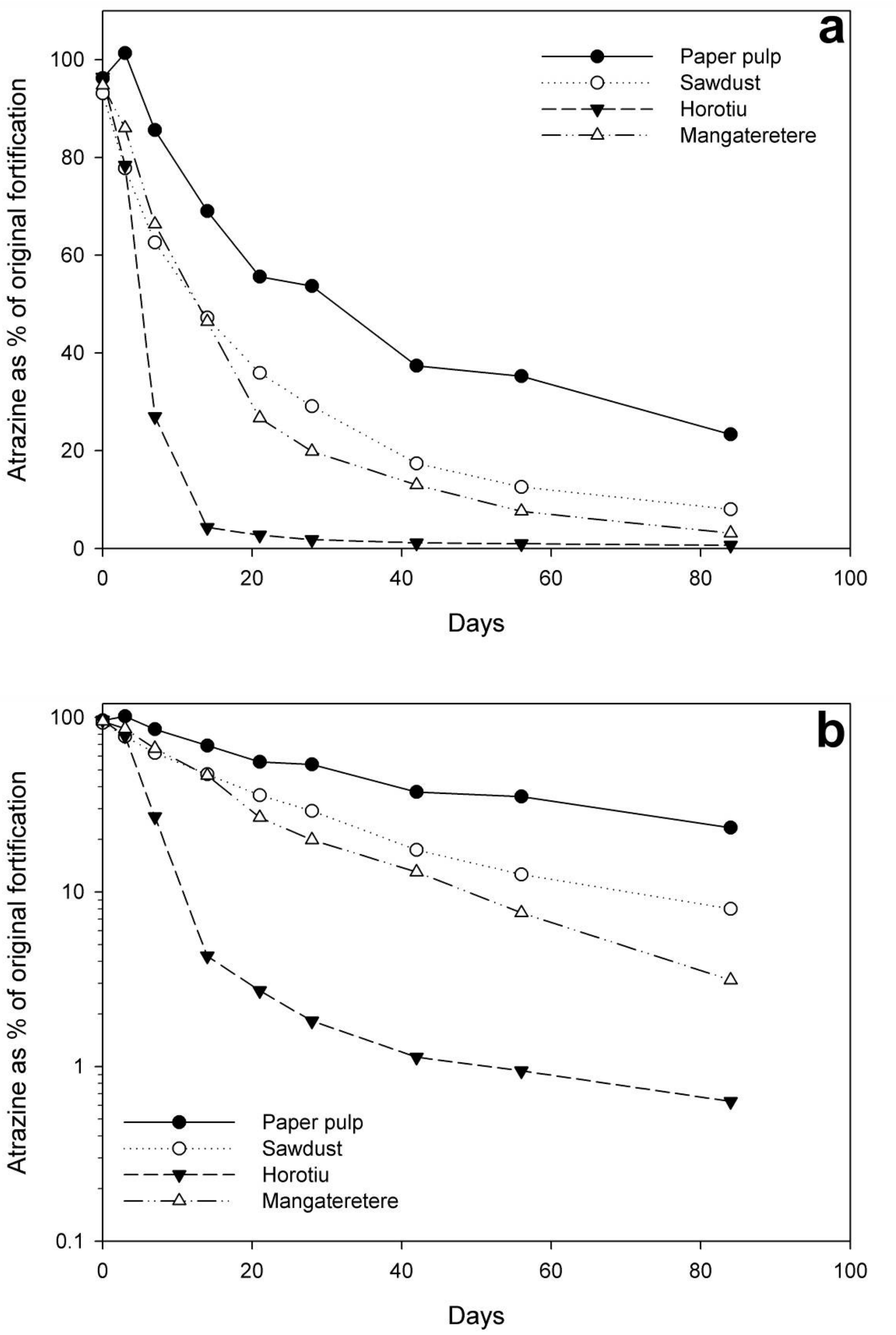


Fig. 5.11: Atrazine degradation at 30°C with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

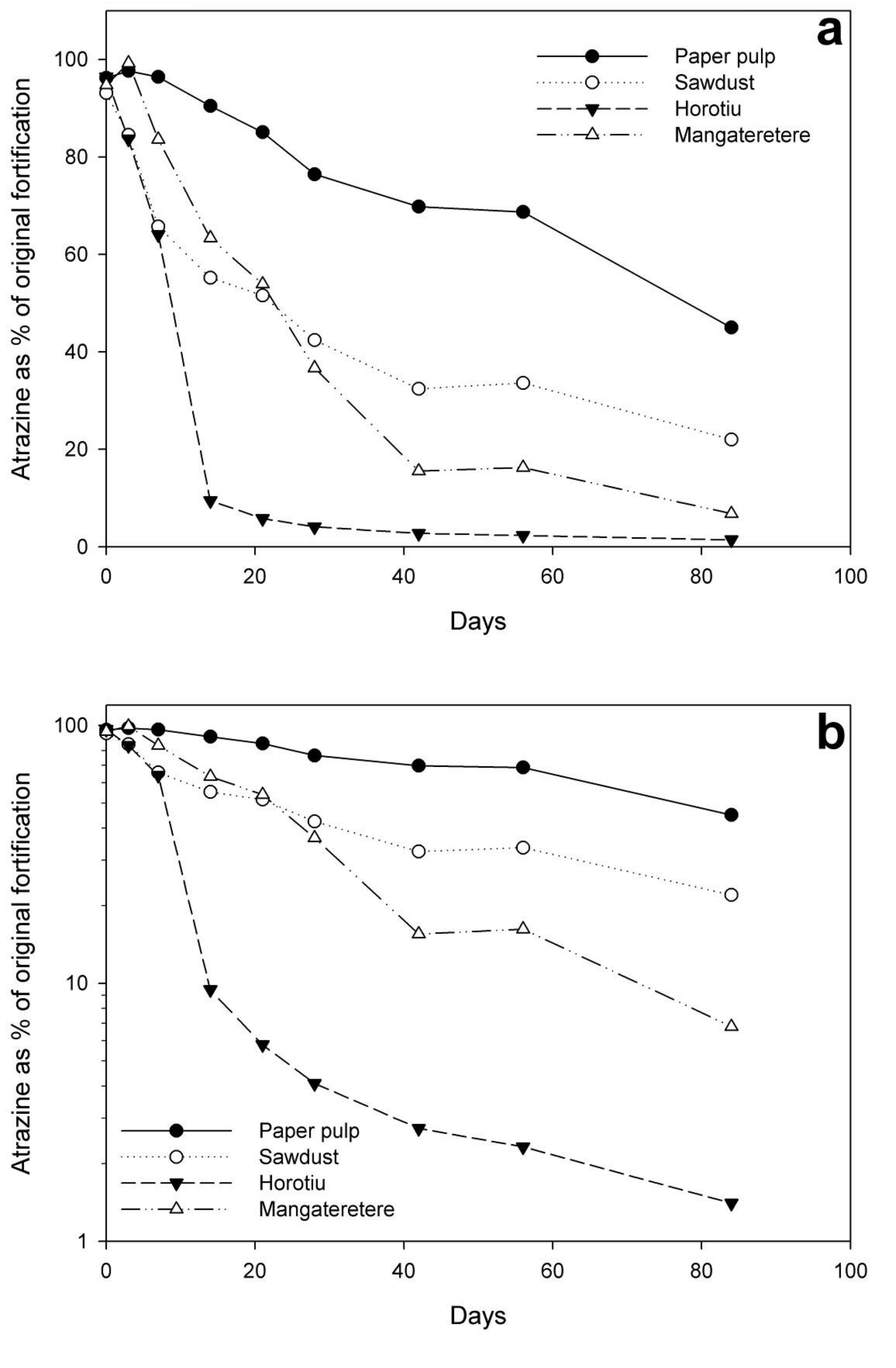


Fig. 5.12: **Atrazine degradation under a fluctuating temperature regime (20±5°C) with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.**

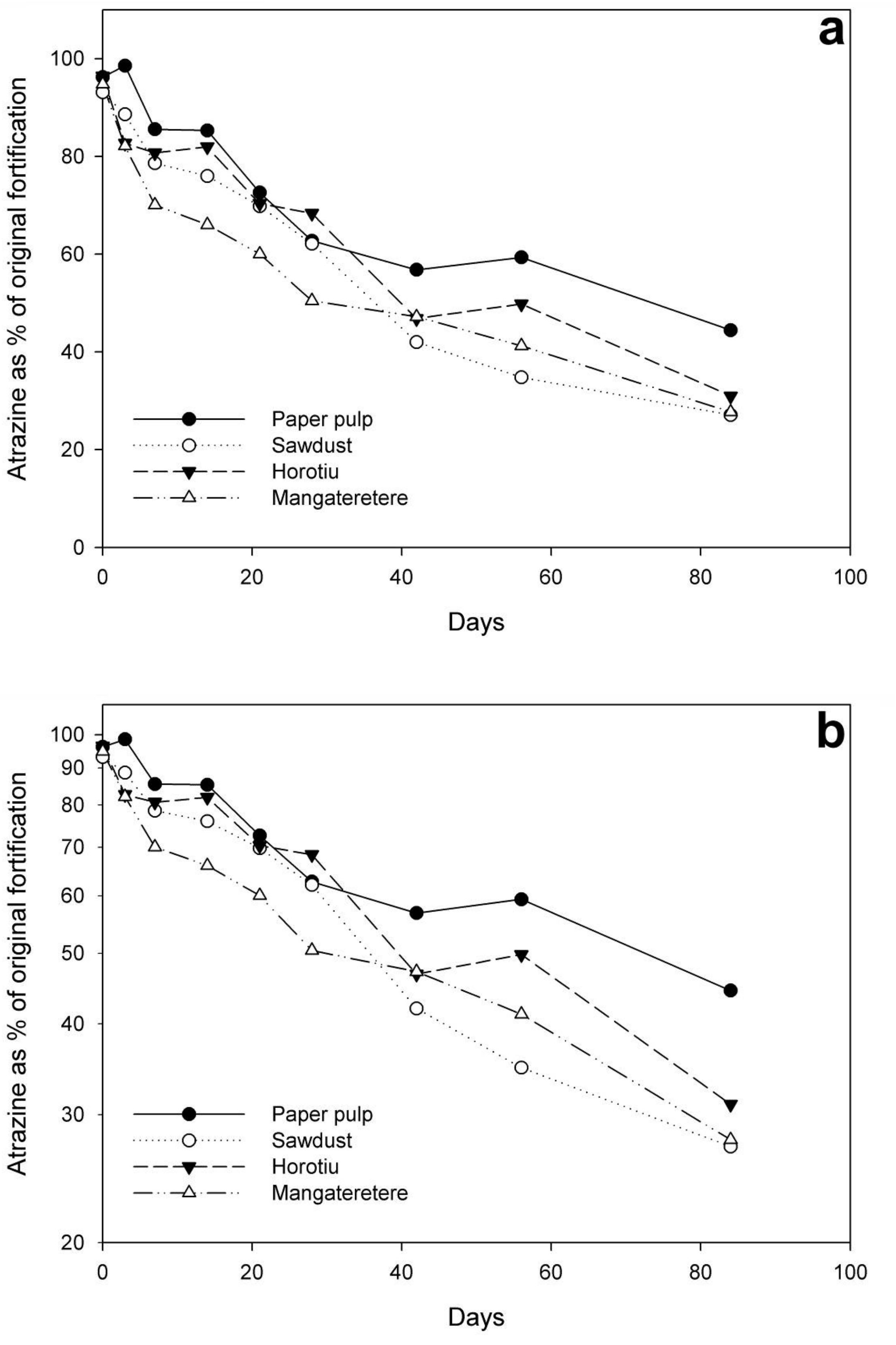


Fig. 5.13: Atrazine degradation at 20°C sterilised with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

5.4.3.2 Degradation of Bromacil in Four Media under Five Different Regimes

The degradation of bromacil in the four media (paper pulp, sawdust, Horotiu soil and Mangateretere soil) at 10°C, 20°C, 30°C, 20±5°C and at 20°C in sterilised media are presented in Figs 5.14 – 5.18 respectively. In these experiments the degradation of bromacil was considerably slower than that of atrazine except in paper pulp (Table 5.5).

At 10°C the degradation of bromacil was slow in all four media with >60% of the original fortification remaining after 84 d (Fig. 5.14). The considerable degree of extrapolation required resulted in large errors in the half-life estimates ($t_{½}$ ranging from 170 to 724 d, Table 5.5). This is reinforced by the low R^2 values which reveal poor fits of the linear regression equation (Table 5.5).

At 20°C the degradation rate increased sufficiently in paper pulp (Fig. 5.15), so that a realistic half-life (64 d) can be obtained with an R^2 of 98.6% (Table 5.5). However for sawdust, the Horotiu soil and particularly for the Mangateretere soil, the fit remains poor and the half-lives are well outside the duration of the experiments.

Figure 5.16 shows that degradation of bromacil at 30°C was significantly faster in paper pulp, sawdust and the Horotiu soil ($t_{½}$ of 33, 68 and 85 d respectively) but remained largely untransformed in the Mangateretere soil ($t_{½}$ = 300 d, Table 5.5).

As degradation was very slow in sawdust and the two soils, no valid comparisons can be made concerning enhanced degradation under the fluctuating temperature regime (Fig. 5.17). However, degradation of bromacil in paper pulp was enhanced under the 20±5°C regime compared to that in the 20°C regime ($t_{½}$ of 52 and 64 d respectively). Also due to slow degradation, comparisons can not be made for three of the sterile media (Fig. 5.18). However, for paper pulp, sterilisation greatly slowed degradation ($t_{½}$ of 64 and 288 d for the unsterilised and sterilised respectively).

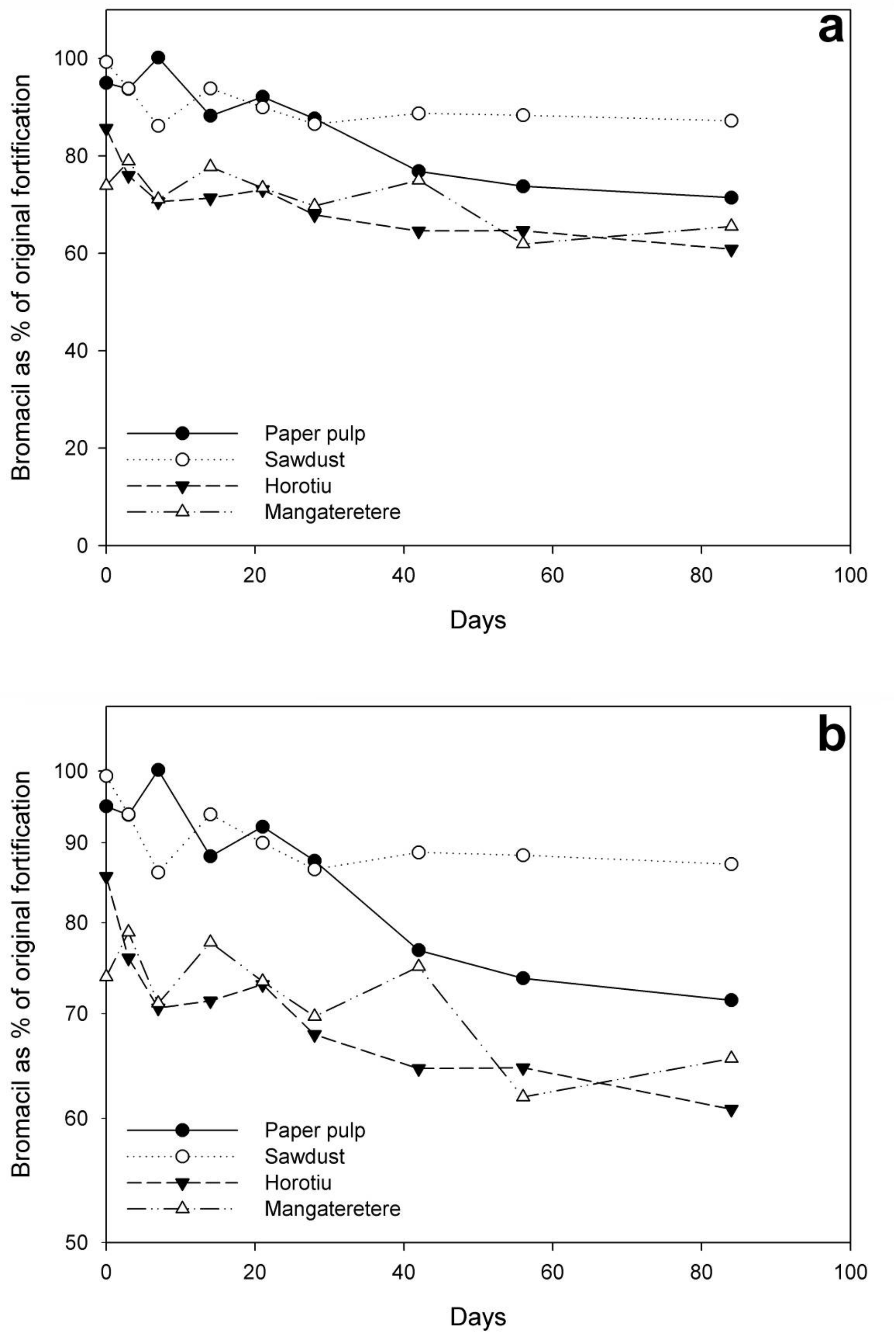


Fig. 5.14: Bromacil degradation at 10°C with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

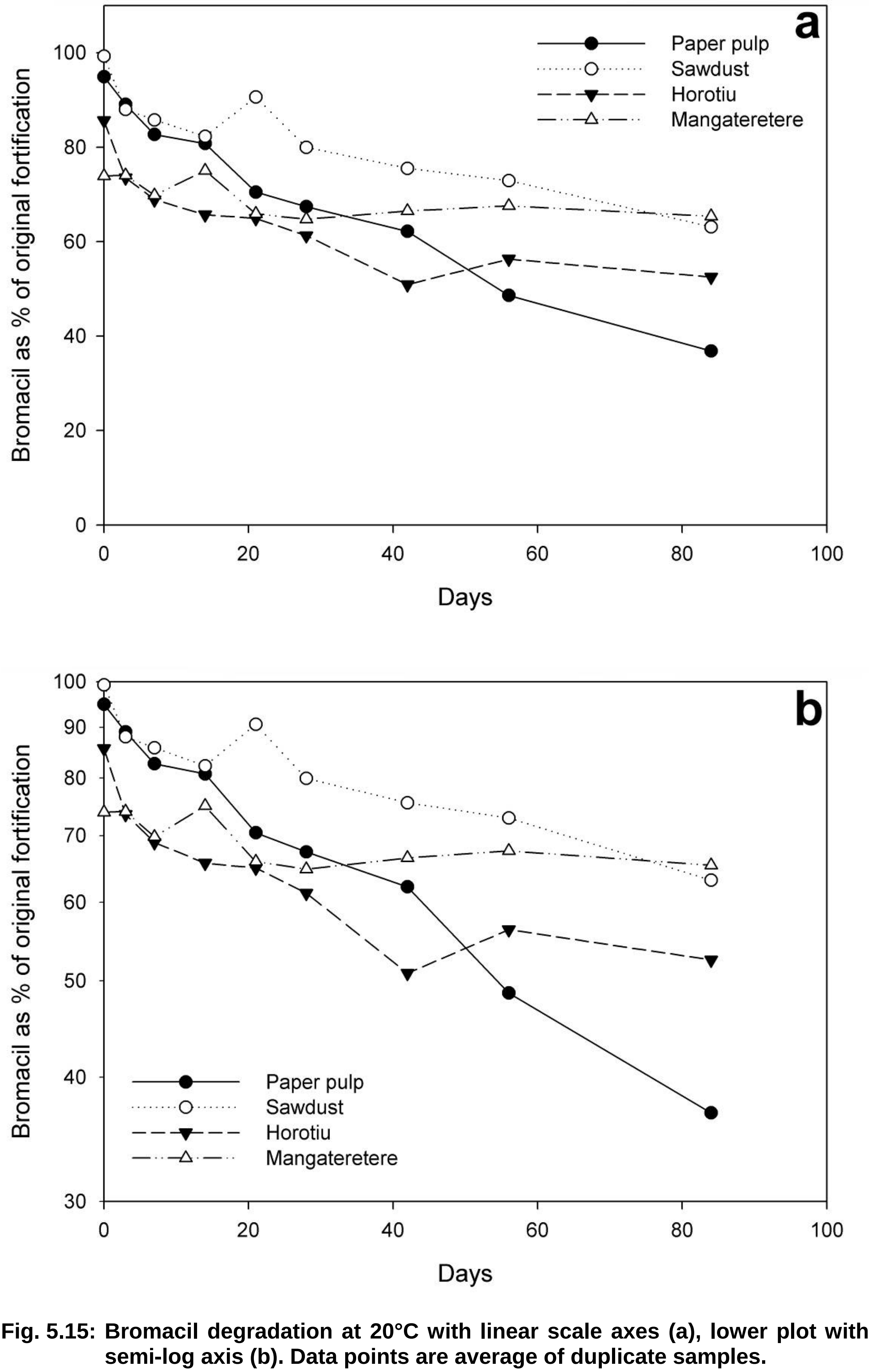


Fig. 5.15: Bromacil degradation at 20°C with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

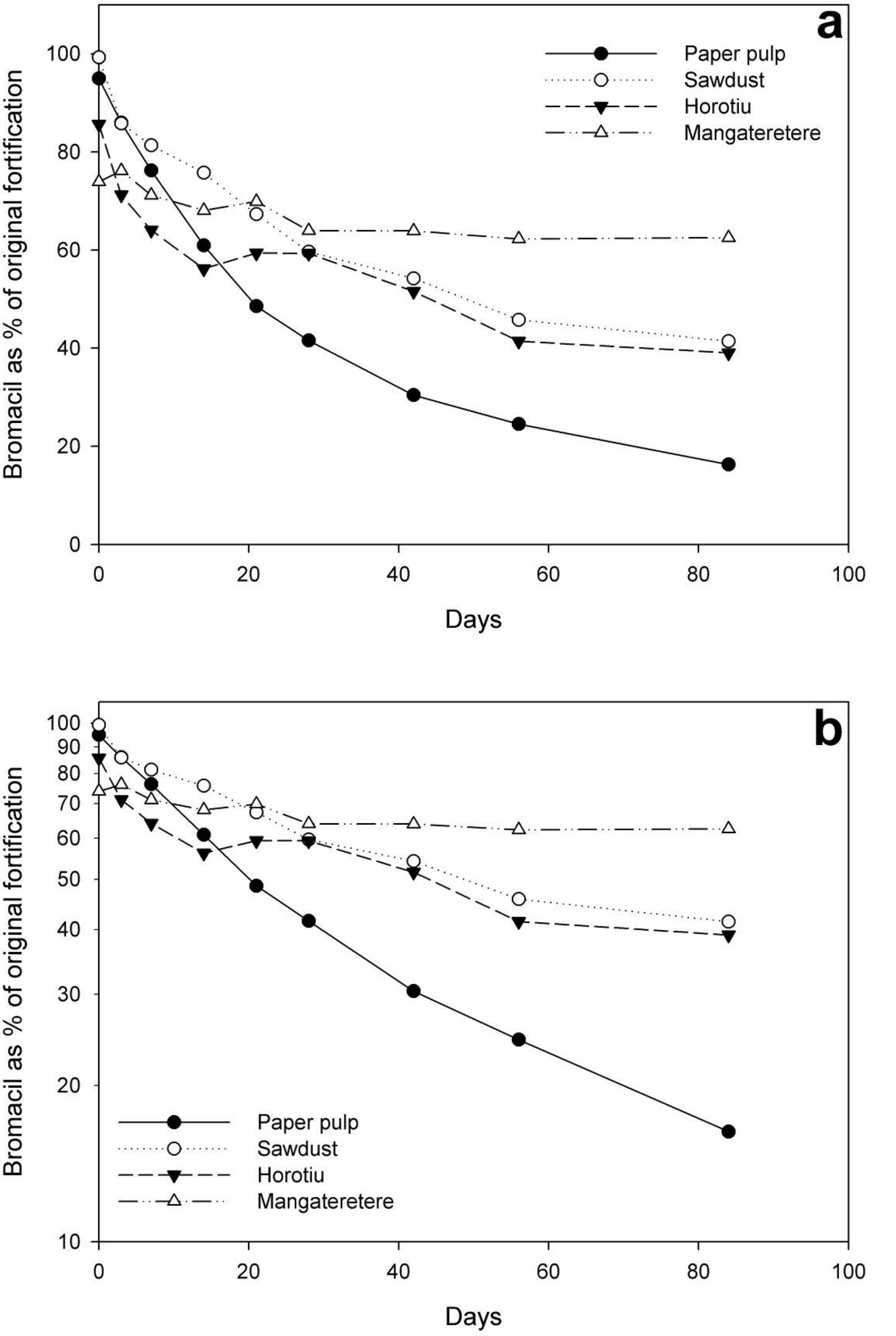


Fig. 5.16: Bromacil degradation at 30°C with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

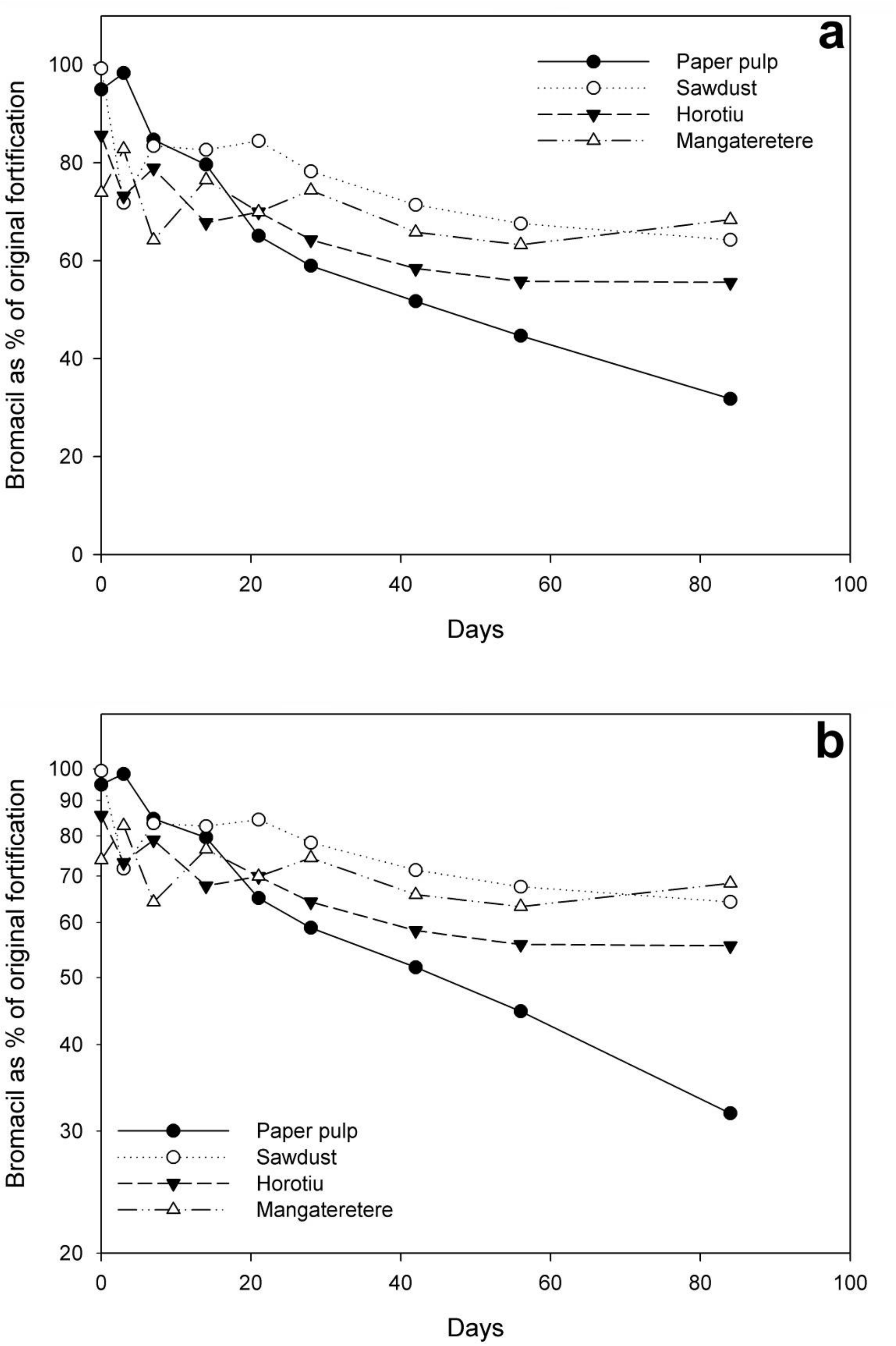
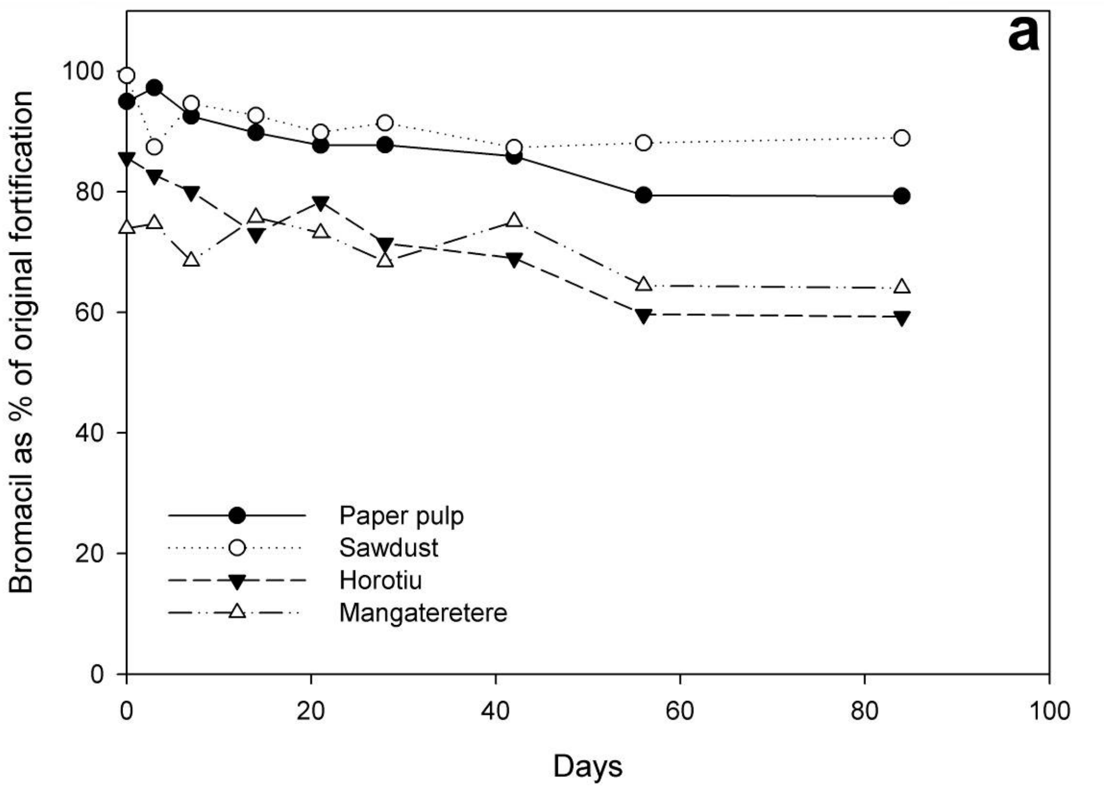


Fig. 5.17: Bromacil degradation under a fluctuating temperature regime (20±5°C) with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.



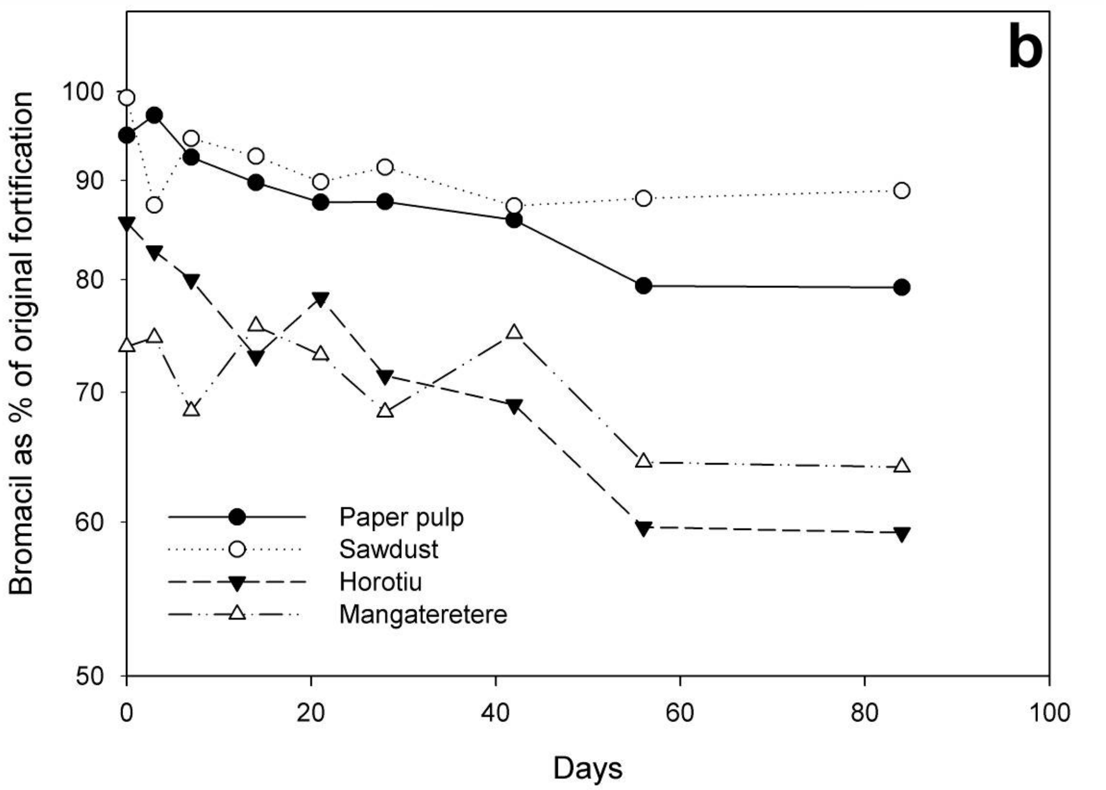


Fig. 5.18: Bromacil degradation at 20°C sterilised with linear scale axes (a), lower plot with semi-log axis (b). Data points are average of duplicate samples.

Table 5.5: **Degradation half-life ($t_{½}$** (d) ±SE**, assuming 1st order kinetics) and R^2 linear regression statistic for degradation of atrazine and bromacil in four media under five different degradation regimes.**

	Degradation temperature					
	10°C		20°C		30°C	
Media	$t_{½}$ (d)	R^2 %	$t_{½}$ (d)	R^2 %	$t_{½}$ (d)	R^2 %
	atrazine					
Horotiu	17±2	91.3	13±3	76.7	12±3	71.9
Mangateretere	89±9	94.0	21±1	98.3	17±1	97.8
Paper pulp	125±13	93.5	70±5	96.0	39±3	96.0
Sawdust	75±6	95.5	39±2	97.6	23±2	96.4
	bromacil					
Horotiu	219±47	75.2	136±31	73.3	85±13	86.0
Mangateretere	338±121	53.0	485±197	46.5	300±67	74.1
Paper pulp	170±24	88.1	64±3	98.6	33±2	97.2
Sawdust	724±401	31.8	155±11	87.9	68±7	93.2

	Degradation temperature			
	20±5°C		20°C sterile	
Media	$t_{½}$ (d)	R^2 %	$t_{½}$ (d)	R^2 %
	atrazine			
Horotiu	13±3	75.6	55±4	95.9
Mangateretere	21±1	96.9	53±4	95.9
Paper pulp	79±6	95.9	75±8	92.0
Sawdust	43±5	92.2	45±3	97.5
	bromacil			
Horotiu	141±26	81.0	153±20	89.5
Mangateretere	423±267	26.5	418±160	49.4
Paper pulp	52±3	97.7	288±38	88.9
Sawdust	183±54	61.8	827±475	30.2

5.5 Discussion

5.5.1 *Hypothesis Testing*

The hypothesis to test with regard to herbicide degradation was that there was exponential decay which followed first-order kinetics. The test for this was a linear graph on a semi-log plot of the degradation data. Clearly, for many of the 40 degradation scenarios presented in Table 5.5 this hypothesis was well supported. Degradation of atrazine in either paper pulp, sawdust or the Mangateretere soil, at all temperature regimes, followed first-order kinetics. Degradation of atrazine in the Horotiu soil did not follow first-order kinetics at any temperature in field fresh soil. However, after the soil was sterilised, degradation of this herbicide did follow first-order kinetics.

5.5.2 *Degradation of Atrazine and Bromacil*

In the case of bromacil, degradation rates were so slow that for many of the media/temperature combinations, neither degradation kinetics nor half-life could be accurately determined from the results of these 84 d experiments. The five cases where an accurate half-life could be determined (i.e. $t_{½}$ < the duration of the experiment) all exhibited first-order kinetics. Thus bromacil in paper pulp at 20, 30 and 20±5°C and in sawdust and Horotiu soil at 30°C underwent exponential decay. Unfortunately, for herbicides that exhibit very slow degradation, laboratory determination of half-lives and other degradation parameters is not a viable proposition as soil microbial activity in the reaction flasks tends to diminish rapidly after ca. 3 months (Sparling et al. 1998).

In terms of relative rates of degradation in the four media, atrazine and bromacil exhibited nearly opposite trends. Using data from the 30°C experiment, the relative rates of degradation of atrazine were Horotiu>Mangateretere>sawdust>paper pulp while for bromacil the ranking was paper pulp>sawdust>Horotiu>Mangateretere (Table 5.5). The most significant variation was for paper pulp where atrazine degraded more slowly compared to the other media while bromacil degraded more rapidly. The most likely reason for this is the pH of the paper pulp, which at 7.9 was the only basic medium (Table 3.1). Bromacil being a very weak acid (pKa 9.27, Table 2.1) would be more soluble in the alkaline paper pulp and less soluble in the three acid media (Table 3.1) while atrazine being a weak base (pKa 1.70, Table 2.1) would be less soluble in the paper pulp and more soluble in the other media (Weber et al. 2007). As the herbicide molecules must be in solution (bioaccessible) in order to be mineralised the pH mediated equilibria between solution and solid phase explains the relative rates of degradation for the two herbicides in the different media.

Mangateretere soil was the most acidic of the four media (Table 3.1). Therefore, atrazine would be more soluble in this soil (although this could be partially offset by cationic adsorption of the protonated atrazine molecule) than bromacil and their relative degradation rates in the four media will be the reverse of that for paper pulp. This is reflected in the results except for the Horotiu soil which initially exhibited faster degradation of atrazine. This was most probably due to enhanced microbial activity and not solubility effects. The Horotiu soil and sawdust had similar pH levels, intermediate between the paper pulp and Mangateretere soil, so with the noted exception of atrazine in Horotiu soil, their degradation rates were also intermediate.

Since the degradation of both atrazine and bromacil follow first-order kinetics in these situations, the prediction and modelling of their environmental fate is easier as the degradation follows expected and well understood pathways (Beulke & Brown 2001; Green et al. 2004; Müller et al. 2004; Beulke et al. 2005). Deviation from first-order kinetics may introduce considerable uncertainty in the estimated half-lives and degradation parameters, which in turn may result in discrepancies between predicted and observed dissipation patterns in the field (Beulke et al. 2000).

Two of the regimes under which degradation was evaluated were included specifically to investigate the role of the soil biota in degradation of the herbicides atrazine and bromacil. The fluctuating temperature regime (20±5°C) was included to test whether the fluctuating temperature conditions that are normally found in the field are likely to impact on the degradation rate through the fluctuating temperature stimulating microbial activity (Visser et al. 1984). Fluctuating temperature was postulated as the cause of enhanced degradation of clopyralid under similar regimes (Ahmad et al. 2003). Conversely, the increase in degradation during the high temperature part of the cycle is thought unlikely to be completely offset by the reduced degradation during the cooler part of the cycle (Heiermann et al. 1995). Determining degradation rate in the laboratory at a set temperature and assuming this will match degradation in the field when the average temperature is the same could lead to erroneous predictions (Beulke et al. 2005).

For the experiments reported here, the degradation half-lives for atrazine in Horotiu and Mangateretere soils (13 and 21 d, respectively) were identical in the 20°C and the 20±5°C regimes while in the paper pulp and sawdust the half-lives for atrazine were slightly longer in the 20±5°C regime compared to the set temperature of 20°C (Table 5.5). In the case of bromacil, due to its slow degradation, only a single comparison was possible, i.e. in paper pulp its degradation was significantly faster in the 20±5°C regime than at a constant 20°C (52 and 64 d respectively). Thus it would appear that the degradation of atrazine in fluctuating temperature conditions is less likely to deviate from predictions based on laboratory derived data than that of bromacil.

5.5.3 *Microbial Degradation*

The ultimate test for microbial degradation is to sterilise the soil and thus eliminate microbial activity from the equation (Wolf & Martin 1974; Accinelli et al. 2001). In these experiments, sterilisation of the media produced mixed results. As the experiment was not maintained under strict sterile conditions, microbes could have been reintroduced when the flasks were opened to add water. However, it is highly unlikely that the introduced microbes would be in sufficient quantities or even be the required species to have any significant impact on the results. For atrazine, degradation half-lives remained nearly the same in both paper pulp and sawdust when the media was sterilised (Table 5.5) while the same process more than doubled its half-life in the two soils. For bromacil the only viable comparison that could be made was for paper pulp where sterilisation extended the half-life by a factor of five. Although the data are of dubious significance, it is interesting to note that in sawdust, bromacil experienced a similar extension of half-life (from 155 to 827 d) while the half-lives of this herbicide in the non-sterilised and sterilised regimes were similar for the two soils (Table 5.5).

It is evident from these results that microbial activity does play an important role in the degradation of atrazine as has previously been reported by many authors (Aislabie & Lloyd-Jones 1995; Accinelli et al. 2001). For bromacil this evidence is less convincing but there is a common theme in the literature for microbial degradation of this herbicide, albeit very slow in some cases. Bromacil is variously recognised as less biodegradable (Rhodes et al. 1970; Madhun & Freed 1987), while Gardiner et al. (1969), Wolf & Martin (1974) and Zimdahl et al. (1970) make a strong case for its microbial degradation. Bingeman et al. (1962) and Jordan et al. (1965) eliminated the chemical processes of oxidation and photodecomposition respectively as pathways for degradation. More recently, organisms that use this chemical as their sole source of C and N have been isolated (Chaudhry & Cortez 1988). The results from the experiments reported here support the importance of microbial activity in the degradation of bromacil in both the paper pulp and sawdust, where half-lives were significantly longer in the sterilised media. However, half-lives in the sterilised soils were the same as for the non-sterilised soils indicating that other degradation processes such as chemical hydrolysis were predominant.

5.5.4 *Degradation Half-life*

For atrazine the range of field half-lives reported in the United States Agricultural Research Service (ARS-USDA) pesticide properties database range from 18 to 148 d with an average of 60 d (Wauchope et al. 1992). The low half-life of 18 d is from the GLEAMS user manual (Davies et al. 1990) and its origins are uncertain. The next lowest half-lives are several in the range of 45 - 50 d. In New Zealand Rahman & Brown (1977), using bioassay methods to determine atrazine residues in samples collected from field trials, found half-lives of 56-112 d and 210-300 d for a Hamilton silt loam and a Matawhero heavy silt loam respectively, while Rahman et al. (1978b) determined a half-life of about 90 days for both a Horotiu sandy loam soil and a Hamilton clay loam soil using similar methods. In a laboratory experiment Ghani et al. (1996) determined a dissipation time (DT_{50}) of 45 - 55 d for a Horotiu sandy loam soil at 22.5°C.

The half-lives found in the experiments reported here generally relate well to both the international and local findings. Degradation of atrazine in the Horotiu soil was much faster than that reported internationally and it did not conform to the simple first-order kinetics model. This will be addressed later in the discussion. Degradation in the Mangateretere soil was also relatively fast but did follow first-order kinetics and can be compared to field data for other New Zealand soils (Rahman et al. 1978b). Considering the field degradation in the Hamilton soil would have occurred while soil temperatures ranged between 10 and 20°C, then degradation in Mangateretere soil is not dissimilar to that in the Hamilton soil (Rahman et al. 1978b). However, degradation in the Matawhero soil was considerably slower than any of the laboratory determined rates (Rahman et al. 1978b). Degradation of atrazine in the paper pulp and sawdust, although slower than in the two New Zealand soils were quite comparable to some of the rates reported by Wauchope et al. (1992).

There are few data reported for half-life of bromacil in New Zealand where it is used mostly for weed control in asparagus (Sanders et al. 1996). Sanders et al. (1996) reported detectable residues have generally dissipated within 3 – 6 months. This could indicate a half life of less then 60 days or dissipation could be accounted for by the herbicide leaching rather than degrading. As they also report high concentrations of bromacil at greater depths it is probably the latter which is a better description of the reason for dissipation of bromacil from the surface soil layer. Sarmah et al. (2006) used inverse modelling to estimate the half-life of bromacil in two soils from results of a leaching experiment. In a silt loam soil from Nelson with 2.38% organic carbon, the estimates ranged from 54 d (HYDRUS-1) to >1000 d (LEACHM) with GLEAMS and

SPASMO estimates intermediate with 156 and 176 d respectively. In the second soil (silt loam, Southland), which had a higher organic carbon content (3.29%), the estimated half-life ranged from 60 d (HYDRUS-1) to 474 d (GLEAMS) with SPASMO and LEACHM estimates intermediate at 103 d for both.

The great majority of the data for bromacil comes from USA where it is used extensively for weed control in citrus orchards in Florida and California and in pineapples in Hawaii (Reddy et al. 1992; Zhu & Li 2002). In a field study on a silt loam soil Gardiner et al. (1969) determined a half-life of 5 – 6 months for bromacil when applied at 4.48 kg a.i./ha. Using an undescribed loam soil Zimdahl et al. (1970) showed that degradation of bromacil followed first-order kinetics with half-lives of 214 and 158 d at 13.2 and 31.2°C respectively. In a 125 day experiment using a flooded sandy soil (pH 7.1 and OC 1.1%), Wolf & Martin (1974) found bromacil to have a half-life of 146 d and that degradation essentially ceased when the soil was sterilised. They also postulated that degradation of bromacil in their experiments followed a hyperbolic type of rate law, with degradation over the first 10 days much greater than for the following 105 days. However, this was based solely on the first two bromacil quantifications carried out on Days 0 and 10 of the study and more likely reflects the difficulty in extraction of residues aged for even a short time (Cox & Walker 1999) especially as they were using only a weak extractant (ethanol).

In a study using $^{14}CO_2$ evolution as the means of determining bromacil degradation in a sandy soil (pH 7.3, OC 0.7%) and a mucky peat (pH 5.4, OC 48%) at three temperatures, Madhun & Freed (1987) claimed there was little difference in degradation rates due to soil type but that temperature had a major effect, with half-lives ranging from 46,200±38,707 d at 25°C to 5,856±3,957 d at 35°C. But as these results were extrapolated from a 27 d and a 36 d experiment for the sandy soil and mucky peat respectively they appear to be unreliable and contrary to field observations. The half-lives reported in the SCS/ARS/CES pesticide properties database (Wauchope et al. 1992) derived from a variety of sources including the manufacturer (E.I. du Pont de Nemours and Co.) range from 61 – 349 d with an average of 207 d.

The half-lives for bromacil determined in the experiments reported here are comparable to those reported in the literature. The average half-life in paper pulp of 64 d at 20°C corresponds well with the shortest half-life of 61 d reported in the literature. The half-lives of 136 d and 155 d for Horotiu soil and sawdust respectively are shorter than the average of 207 d in the ARS-USDA database but still well within the range of results. It is likely the fast dissipation in our sandy soils has allowed growers to use bromacil in asparagus crops.

5.5.5 *Models for Enhanced Degradation*

Degradation of atrazine in the Horotiu soil differed from that in the other three media. Not only were calculated half-lives significantly shorter (12 – 17 d) in the Horotiu soil, but the temperature dependence was less and significant deviation from first-order kinetics was observed (Figs 5.9 – 5.11). Commonly, this behaviour has been referred to as enhanced degradation. This deviation of soil degradation from first-order kinetics has often been observed for sulfonylurea herbicides and is explained through a decreased availability of the molecule to soil microbes as, after a period of time, the molecules shift to a “protected compartment” after adsorption (Joshi et al. 1985; Lehr et al. 1996; Strek 1998; James et al. 1999). This is similar to the ‘aging effect’ which enhances the retention of sorbed organic chemicals by facilitating the formation of bound residues via chemical and/or physical non-equilibrium sorption processes, thus causing the chemical to become less susceptible to desorption and degradation (Pignatello 1998). In this compartment the slower degradation is probably due mainly to chemical hydrolysis, the rate of which is generally slower than that of the microbial degradation (Joshi et al. 1985). It can be described by a biphasic, protected-compartment or bi-exponential, second-order rate equations (Gustafson & Holden 1990; Yutai et al. 1999; Beulke & Brown 2001; Morrica et al. 2002; Sánchez et al. 2003; Charney et al. 2005).

The biphasic model is based on the Hoerl equation (Eq. 5.3):

$$C_t = a\,\exp(bt).t^x \qquad \text{Eq. 5.3}$$

where C_t is the fraction of the original concentration present at time t and a, b and x are constants derived from the fitted plot between C_t and t (Cumming et al. 2002; Sánchez et al. 2003). However this model is not frequently used. A more commonly used model is the bi-exponential (Beulke & Brown 2001; Morrica et al. 2001; Sánchez et al. 2003). This is a second-order rate equation and is a derivation of the first-order rate equation Eq. 2.6 to include two rate constants k_1 (fast) and k_2 (slow) both having units of days^{-1} (Eq. 5.4) (Swarcewicz et al. 1998; Yutai et al. 1999):

$$C_t = C_0\,((1\text{-}a)\exp(-k_1t) + a.\exp(-k_2t)) \qquad \text{Eq. 5.4}$$

where a (mg/kg soil) is a constant representing the fraction of the degradation that occurs at rate k_2. This model is used where degradation initially proceeds at a constant fast rate and then continues at a constant slower rate (Morrica et al. 2002).

Results of the present study on degradation of atrazine demonstrate the importance of microbial activity (cf. non-sterile vs sterile soil, Figs 5.10 and 5.13). However, the degradation process appears to be more complex than explained by the bi-exponential model. The present results show a rapid degradation phase followed by a slower degradation phase, as described in the model, but in the present case the rapid degradation phase is proceeded by a lag-phase as the microbial population either multiplies or adapts in the presence of a new food source. For the degradation at 10°C the lag-phase is 21 days (Fig. 5.9) while at 20 and 30°C it is 7 and 3 days respectively (figs 5.10 & 5.11). Microbial degradation with a lag-phase is better modelled by fitting a logistic curve represented by Eq. 5.5 (Strek 1998; Di et al. 2001; Aislabie et al. 2004):

$$C_t = C_0/(1 + a.\exp(-kt)) \qquad \text{Eq. 5.5}$$

where a is a regression coefficient and k the rate constant.

This model was fitted to the atrazine data using the “Fitcurve” directive in GENSTAT (Version 9) and selecting a logistic curve. The fitted curve and original data are presented in Figs 5.19 – 5.21 and show a very close fit to the data. Dissipation times (DT_{50}) calculated from the logistic curve are presented in Table 5.6 along with their R^2 values. These show significant difference from the half-lives ($t_{½}$) if first-order degradation kinetics were assumed. Using a method similar to the test for first-order kinetics, the accuracy of the logistic fit can often be viewed and tested more readily after logit transformation (linearization) of the data:

$$\text{logit}(C_t) = \ln(C_t/(1 - C_t)) \qquad \text{Eq. 5.6}$$

where C_t is the fraction of the original concentration present at time t. However, plots of the linearised data show significant deviation from straight lines (Fig. 5.22). Therefore, accurate, freeform curves were fitted to the data using the Bayesian smoothing technique (see Section 3.4.3.7) (Upsdell 1994) and DT_{50} times established from these fits (Figs 5.23 – 5.25, Table 5.6).

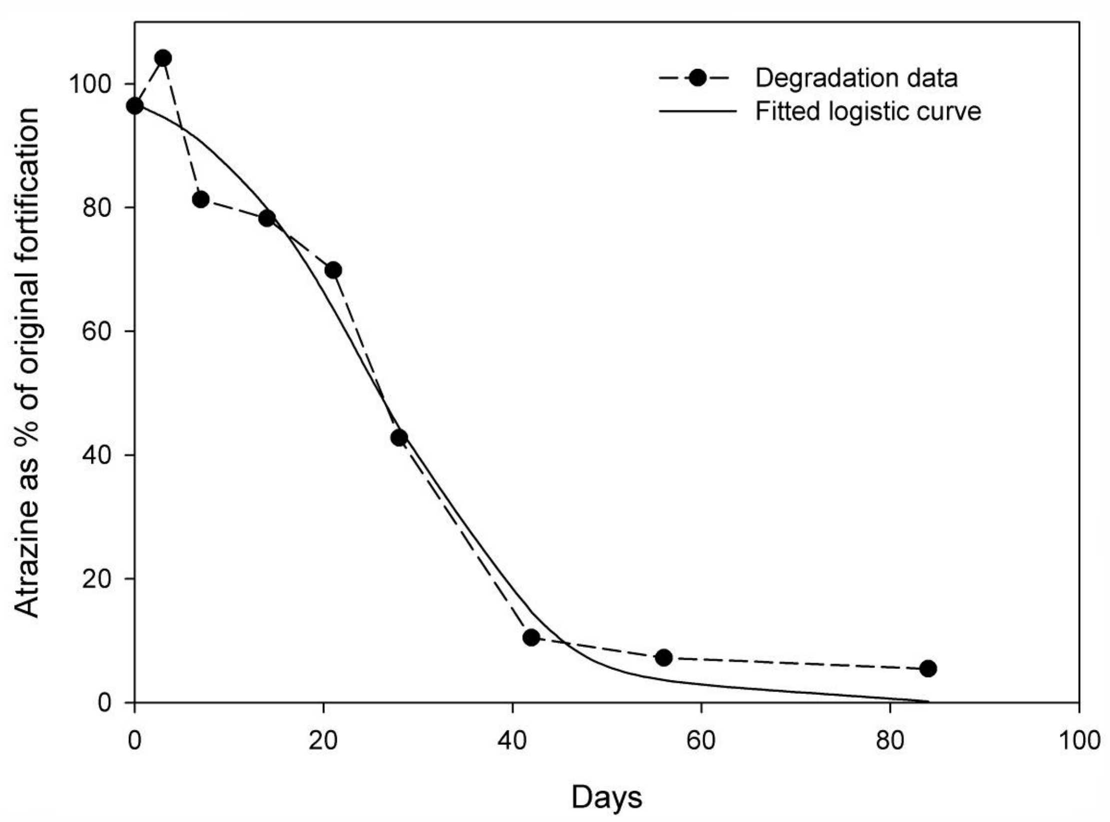


Fig. 5.19: Atrazine degradation at 10°C in Horotiu soil and a fitted logistic curve.

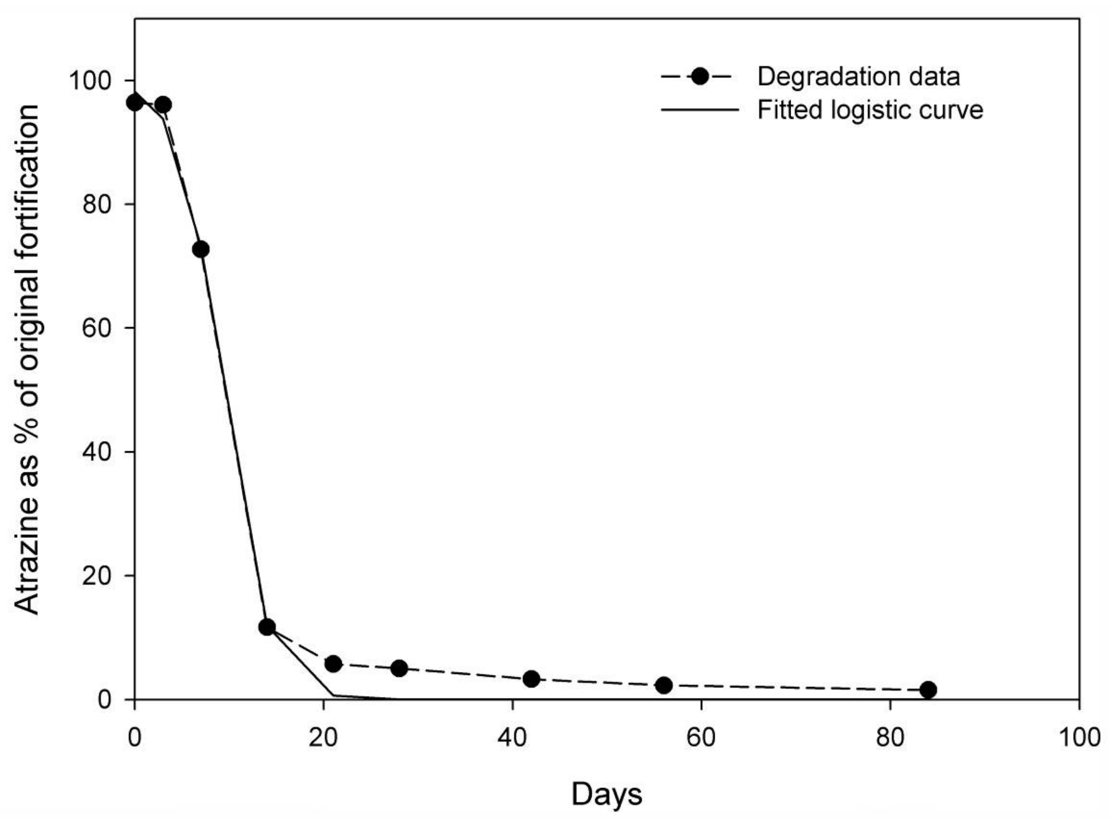


Fig. 5.20: Atrazine degradation at 20°C in Horotiu soil and a fitted logistic curve.

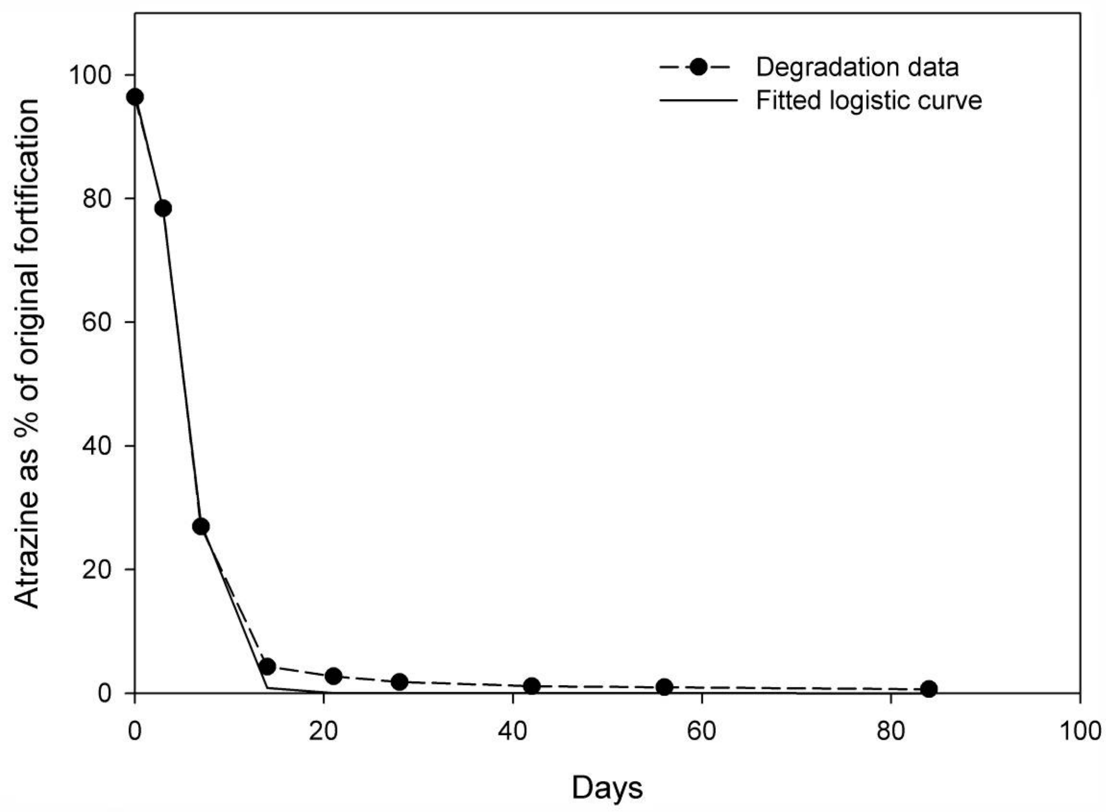


Fig. 5.21: Atrazine degradation at 30°C in Horotiu soil and a fitted logistic curve.

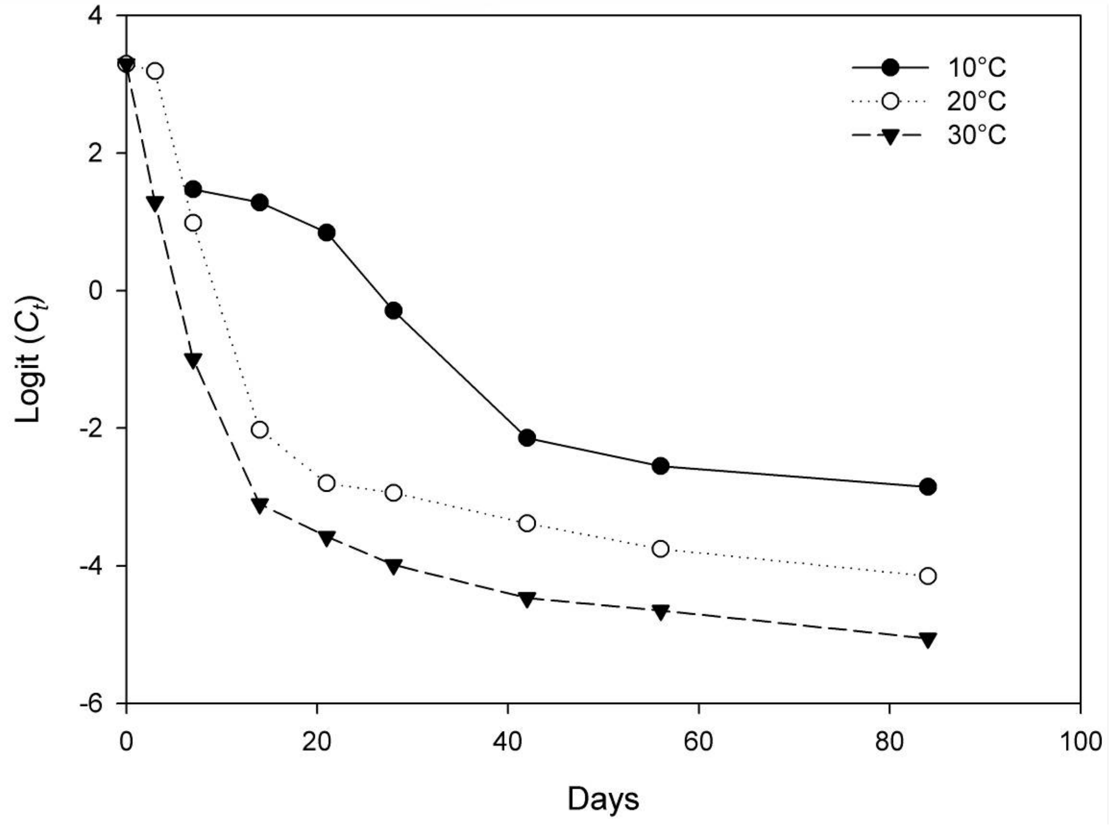


Fig. 5.22: Linearisation of the fitted logistic curves for degradation of atrazine

degradation at 10, 20 and 30°C in Horotiu soil.

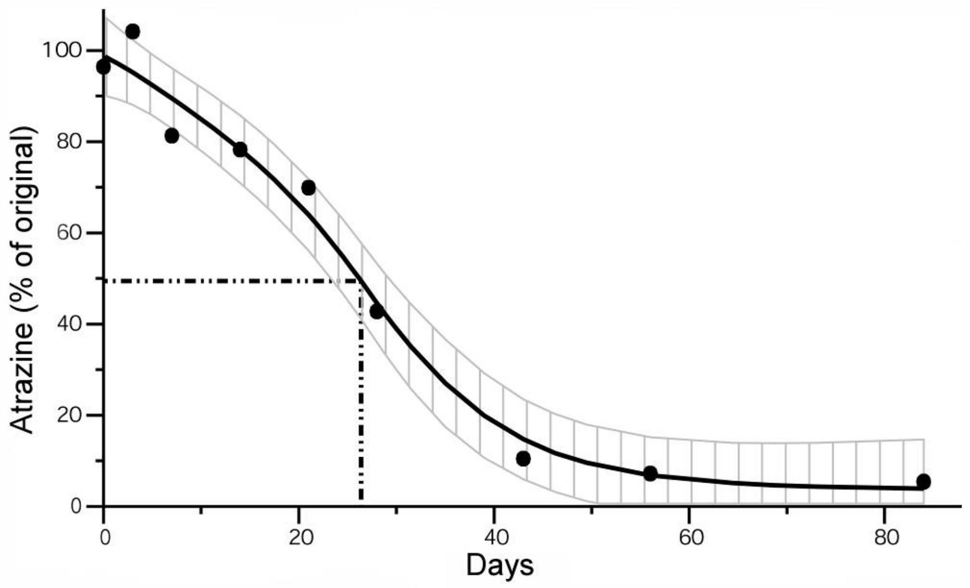


Fig. 5.23: **Atrazine degradation at 10°C in Horotiu soil and a fitted Bayesian smoothed curve with 95% confidence intervals (grey hatched area).**

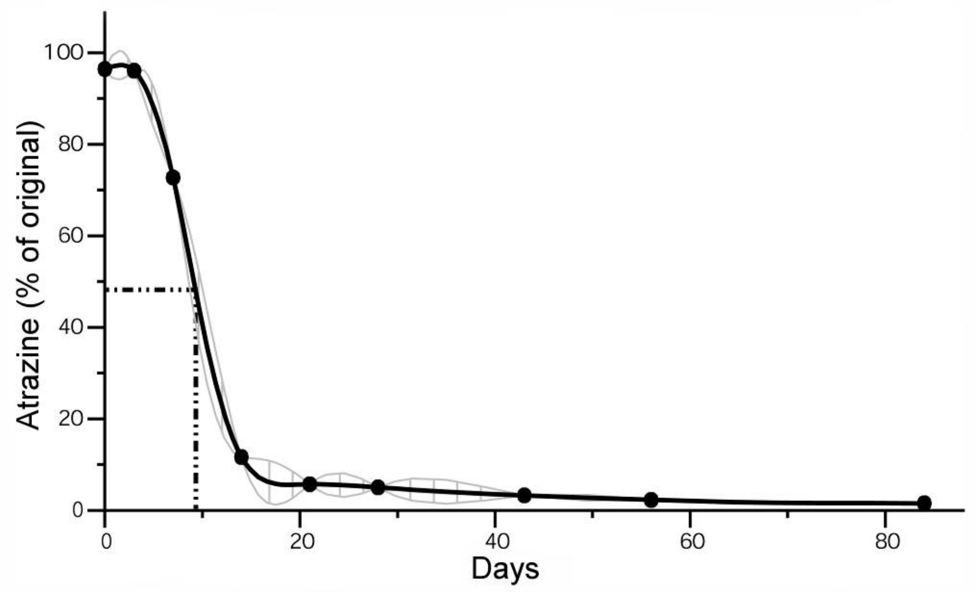


Fig. 5.24: **Atrazine degradation at 20°C in Horotiu soil and a fitted Bayesian smoothed curve with 95% confidence intervals (grey hatched area).**

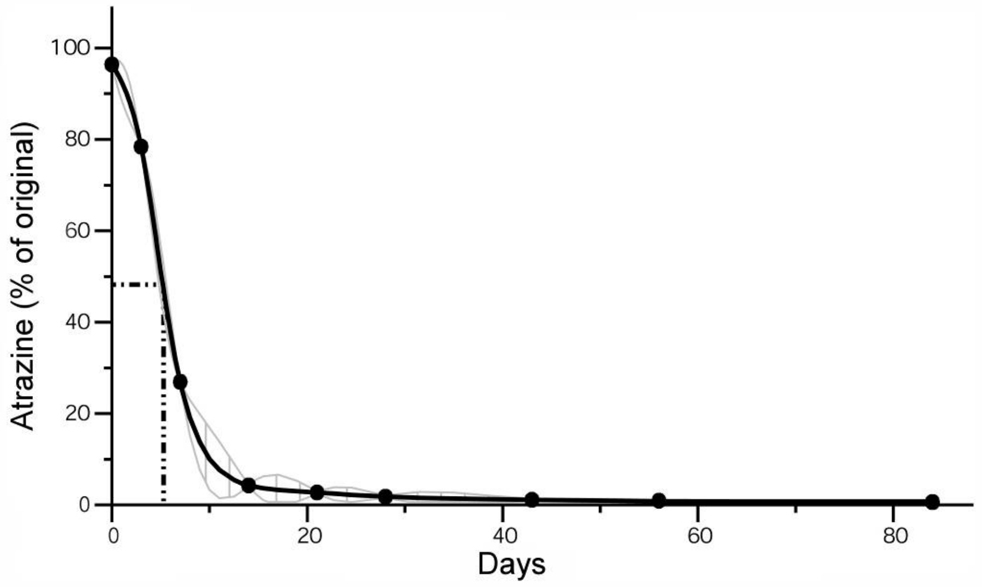


Fig. 5.25: **Atrazine degradation at 30°C in Horotiu soil and a fitted Bayesian smoothed curve with 95% confidence intervals (grey hatched area).**

Table 5.6: **Determination of dissipations time (DT_{50}) for atrazine in the Horotiu soil at three temperatures using two curve fitting methods.**

Degradation	Logistic curve			Bayesian smoothed curve	
temperature	DT_{50} (d)	SE	R^2	DT_{50} (d)	SE
10°C	25.4	2.59	97.1	26.4	1.50
20°C	9.4	0.47	99.3	9.3	0.32
30°C	5.1	0.26	99.7	5.3	0.14

5.5.6 *Descriptors for Enhanced Degradation*

For this soil showing enhanced degradation and second-order kinetics, the dissipation time (DT_{50}) is a more accurate descriptor of the degradation process than the half-life ($t_{½}$). Derivation of an accurate dissipation time requires the fitting of an appropriate curve which fully describes the data. The logistic curves fitted to the data (Figs 5.19 – 5.21) appeared not to be of good fit (were not straight lines) when linearised (Fig. 5.22), despite having very high R^2 values (Table 5.6). A better fit was achieved with the Bayesian smoothing technique (Figs 5.23 – 5.25). However, the dissipation times derived from both curve fitting methods were statistically equal (Table 5.6). The dissipation time is derived from the centre of the fitted curve, and due to the nature of the fitting mechanism this is the most robust portion of the fit. Close inspection of the logistic curves reveals that most of the deviation occurs in the tail area and that in general the fit is very good. Therefore, either of these methods should give accurate dissipation times for a given set of data. Using degradation data for atrazine in the similar Bruntwood silt loam soil, Müller et al.

(2004) concluded that a sigmoidal curve (similar to the logistic curve used here) closely fitted the field dissipation pattern for this herbicide and, when used with the OPUS2 model, produced a predicted dissipation pattern that matched the field data.

5.5.7 *Causes of Enhanced Degradation*

It has been demonstrated that enhanced degradation involves the adaptation of certain soil microbes to degrade the particular herbicide concerned (Aislabie et al. 2004). The Mangateretere soil used in the present study had no history of exposure to atrazine (and neither did the paper pulp or sawdust) and did not exhibit any symptoms of enhanced degradation whereas the Horotiu soil has a long history of repeat annual applications of atrazine. It appears that in this soil the microbial population has adapted and is now able to more quickly degrade this herbicide. This phenomenon has been previously reported and in a few instances the microbes responsible have been isolated. Cox et al. (1996) found evidence of accelerated degradation of the herbicide isoproturon and demonstrated the involvement of soil microbes by sterilising the soil. They were also able to isolate a mixed bacterial culture which quickly degraded isoproturon in culture.

In New Zealand enhanced degradation of a herbicide was first reported for EPTC in 1979 (Rahman et al. 1979; Rahman & James 1983) and an *Anthrobacter* sp. bacteria was later identified as being responsible (Tam et al. 1987). Rahman et al. (1996) in a study on the degradation of flumetsulam reported the rate of degradation over the first 2 weeks as being considerably faster than in subsequent weeks, while James et al. (1999) reported rapid initial dissipation of chlorsulfuron and triasulfuron which resulted in dissipation times (DT_{50}) considerably shorter than the calculated half-lives ($t_{½}$) when first-order kinetics were assumed. In these experiments the period of rapid degradation was about 3 days and the half-lives were greater than the dissipation times by factors of 3 - 7 in the laboratory and 1.5 – 2 for field determined rates. Bolan & Baskaran (1996) found enhanced degradation of the herbicide 2,4-D by soil microbial activity particularly in soils containing greater than 12% organic carbon. More recently, satisfactory modelling of the field dissipation of acetochlor and terbuthylazine using a range of predictive simulation models could only be achieved when biphasic, two-rate or two-compartment sub-models were invoked (Ma et al. 2000; Ma et al. 2004a; Ma et al. 2004d). Similarly for predictions of field persistence of atrazine in a Bruntwood silt loam soil (very similar to the Horotiu soil we used) using the model Opus2, Müller et al. (2004) required the implementation of a sigmoidal degradation equation to explain the accelerated degradation observed in the field.

For both atrazine and bromacil a gram-negative rod bacterium (*Pseudomonas* sp.) has been isolated from atrazine and bromacil-contaminated soil and used to demonstrate its ability to degrade these chemicals at faster than normal rates (Chaudhry & Cortez 1988; Clausen et al. 2002). In fortified soil inoculated with the active strains of this species, results showed that 50% of the atrazine fortification was mineralised in 14 days (Clausen et al. 2002) while bromacil was completely degraded within 7 days and a molar equivalent amount of bromide was recovered (Chaudhry & Cortez 1988). In New Zealand Aislabie et al. (2004) isolated the bacterium *Anthrobacter nicotinovorans* from a Himatangi soil exhibiting enhanced rates of atrazine mineralisation.

5.6 Conclusions

The hypothesis being tested in this part of the investigation was that herbicides degrade more rapidly in the presence of high organic matter soil amendments. The reasoning behind this was that herbicides tend to degrade more rapidly in high organic matter soils due to these supporting greater microbial biomass, and therefore high organic matter waste material would simply be an extension of this. However, it was found that the pH of the media had a more profound effect on the degradation rate than the organic carbon content. Microbial degradation also proved to be an important factor in the mineralisation of these herbicides and was the cause of enhanced degradation in the Horotiu soil which had a long history of application of atrazine. Removal of the microbial component by sterilisation slowed the degradation of atrazine in the two soils more than it did in the two organic media. For bromacil the converse was true where sterilisation of the organic media had a significant impact in slowing degradation while it had no effect on degradation in the two soils. Therefore it can be concluded that the hypothesis is not correct because organic matter content *per se* did not directly relate to degradation rates which were mainly governed by pH and microbial activity. The volume and nature of organic matter may indirectly affect degradation through their influence on microbial activity and pH.

CHAPTER 6

MOBILITY AND LEACHING

CHAPTER 6: MOBILITY AND LEACHING

6.1 Objective

To compare the leaching behaviour of two herbicides (atrazine and bromacil) in two cropping soils and two high organic matter soil amendments. The hypothesis being tested was that high organic matter soil amendments reduce movement and leaching of herbicides through the soil profile.

6.2 Introduction

In New Zealand's arable and vegetable cropping systems most weeds emerge from depths of 0 – 5 cm, with few emerging from depths greater than 7.5 cm (James et al. 2002; Rahman et al. 2004). The depth of 30 cm is frequently considered as the depth of the weed root zone and herbicides which move below this depth are no longer available for weed control (Vasilakoglou et al. 2001). For control of seedling weeds, herbicides need to be in the top 10 cm layer of soil and once leached below this depth their functionality as herbicides is eroded. Also if herbicides are leached to greater depths, especially to the level of the groundwater, they become a major environmental issue. For larger weeds with roots that penetrate deeper into the soil, herbicides retain their primary role until either degraded or leached below the root zone. Also, most of the herbicides used in arable and vegetable cropping in New Zealand are applied to cultivated soil (Rahman et al. 2001; D'Emden & Llewellyn 2004). In view of this, the leaching studies reported here were carried out on disturbed soil to depths of 10 – 30 cm using either packed columns or lysimeters (Heppell et al. 2004).

In laboratory leaching studies two methods are commonly used to apply water to the column or lysimeter, either by irrigation close to the top of the column, which usually does not disturb the soil surface and thus has little effect on infiltration rate (Johnson 1995), or by simulated rainfall, which disturbs the soil surface and can severely influence infiltration and solute transport (Wang et al. 2002; Heppell et al. 2004). In the latter case, factors such as raindrop kinetic energy, rain intensity and duration, soil structure and texture and chemical properties of solutes in the soil can all influence solute transport, but raindrop kinetic energy is the dominating factor (Wang et al. 2002). Rainfall drops reach terminal velocity, and hence maximum kinetic energy, after falling about 5.5 m (Assouline et al. 1997).

Rainfall generation in leaching studies is commonly achieved by either a sprinkler system or an array of hypodermic needles (Bowyer-Bower & Burt 1989). Desirable features of a rainfall simulator include: accurate reproduction of natural rainfall drop sizes and energies, uniform application over the plot area and the ability to apply rainfall of varying duration and intensity (Miller 1987). Benefits of the sprinkler system are random droplet application and the range of droplet sizes (Bowyer-Bower & Burt 1989). However, control of rainfall intensity, droplet size and uniformity of rainfall distribution are often problems associated with sprinkler type rainfall simulators (Chevone et al. 1984; Bowyer-Bower & Burt 1989). Hypodermic needle arrays are better at producing droplets of a smaller size range and more precise and regular application (Chaudhary et al. 1978). Major problems with hypodermic drip-type rainfall simulators are the uniformity of droplet size and the drop falling repeatedly in the same spot (Chaudhary et al. 1978). However, these can be successfully overcome by suspending a wire mesh 20 cm below the droppers. This breaks up and randomly scatters water drops into a distribution of drop sizes closer to that of natural rainfall (Bowyer-Bower & Burt 1989).

Natural rainfall intensity and raindrop size show considerable variation from gentle misting precipitation to intense tropical storms. However, the majority of rainfall events comprise raindrops of a limited size distribution, with rainfall intensities of 10 – 200 mm/h, all having raindrops in the range of 1.6 – 2.7 mm diameter (Park et al. 1983). Rainfall simulators commonly have outputs of 50 to 150 mm/h with droplets from 1.8 to 2.8 mm (3 – 12 µL) diameter (Meyer & Harmon 1979; Shelton et al. 1985; Miller 1987).

The present studies on the movement and leaching of herbicides in four media fell into two categories. Firstly, surface irrigated packed soil columns were used with the leaching results determined by bioassay. Secondly, simulated rainfall onto a packed lysimeter target was used with the leaching results determined by chemical analyses.

6.3 Materials and Methods

6.3.1 *Column Bioassay Studies*

Two bioassay leaching experiments were carried out using the herbicides atrazine and bromacil in the four media: paper pulp, sawdust, Horotiu silt loam soil and Mangateretere silt loam soil. The 30 cm long polyvinyl chloride columns of 10 cm diameter (Fleming et al. 1992; Futch & Singh 1999) were set up as in Plate 6.1 with a clear, acetate sheet on one side to facilitate observation of the movement of water down the column. The four media, as prepared earlier (Section 3.3.1), were packed into the columns to attain the required bulk density (Table 3.1) with four replicates for each herbicide. After placing two string markers on top of the packed media a 10 mm layer of media fortified with herbicide was added to the top of the column. The fortified media contained herbicide equivalent to twice the field use rate (Table 4.1) based on the cross sectional area of the column. This equated to 2.36 mg a.i. of atrazine and 5.03 mg a.i. of bromacil per column. Extra columns were set-up without the treated layer to act as untreated controls. The columns were covered with a sheet of filter paper and 10 mm of sand to ensure even distribution of the water added to the top of the column (Zandvoort et al. 1980; Fleming et al. 1992). De-ionised water was added to the column in 10 – 15 mL aliquots per event (with a total volume of 375 – 750 mL depending on the media) over 42 h and 97 h for Experiments 1 and 2 respectively, until excess water flowed from the bottom of the column (Table 6.1). An aliquot (≈100 mL) of the breakthrough water (the first water to seep from the bottom of the column) was collected and herbicide content determined by HPLC after SPE cleanup (Section 4.3).

For Experiment 2 the breakthrough leachate was also analysed for turbidity (Haach Model 2100N Turbidimeter), total dissolved solids (Haach Sension 378 with a TDS probe), pH (Haach Sension 378 with a pH probe) and dissolved oxygen (Haach Sension 378 with a DO probe). All these properties of the leachate have been associated with leaching of herbicides and groundwater contamination (Pitt 1996; Petersen et al. 2003).

On completion of the water additions the columns were left to equilibrate for 24 h before the void at the top of the column was filled with untreated media and the column capped. The columns were laid on their sides, opened longitudinally by removing the acetate sheet and the soil levelled with the side walls in preparation for bioassay using oats (*Avena sativa*) as in Plates 6.4 – 6.7 (Rahman & Brown 1977; Reddy & Singh 1993; Futch & Singh 1999). Three seeds of oats were planted in each 20-mm soil increment. The columns were surface irrigated daily and maintained in a glasshouse with day temperatures of 22 - 26°C and night temperatures down to 16°C. After about 3 weeks of growth in the glasshouse, plants were scored for herbicide damage on a 0 – 10 scale and then harvested for dry matter determination (Section 3.3.3).

The plant dry matter data were plotted vs column depth and used to assess the depth to which the chemical had moved down the column. A 20-mm soil increment was considered to be free of herbicide if the shoot dry weight was within 90% (NOEL) of that recorded in the untreated soil of the control columns. The distance from the string marker to the soil increment determined to be free of herbicide was then recorded as the depth to which phototoxic residues had leached.

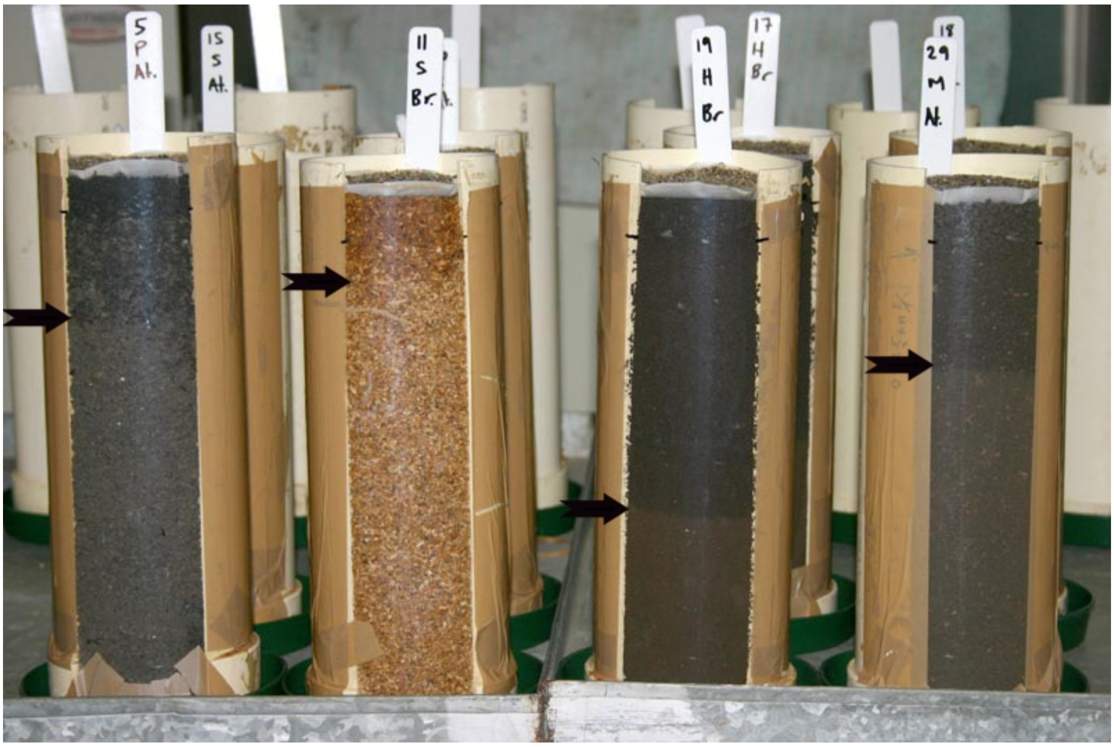


Plate 6.1: Examples of the leaching columns containing the four media and illustrating water moving down the column (arrows). Left → Right; paper pulp, sawdust, Horotiu soil, Mangateretere soil.

Table 6.1: Quantity of water added to the top of column for the bioassay leaching experiments and the theoretical total water content of the media in the columns on completion.

	Media in	Initial	Water added[1]		Total water[2]		Rainfall equivalent[3]	
	column	moisture	Exp 1	Exp 2	Exp 1	Exp 2	Exp 1	Exp 2
Media	(g)	(%)	(mL)	(mL)	(% of MWHC[4])	(% of MWHC[4])	(mm)	(mm)
Horotiu	1340	39.2	550	540	76	75	70	69
Mangateretere	2050	19.3	400	415	72	73	51	53
Paper pulp	540	54.3	670	750	39	43	85	96
Sawdust	300	106.4	400	375	84	81	51	48

[1] For Experiment 1 the water was added over 42 h while for Experiment 2 the water was added over 97 h.

[2] Total water is the combination of the water added during the experiment and the water present in the media at commencement.

[3] Rainfall equivalent = water added/cross-sectional area of column.

[4] MWHC (maximum water holding capacity) of paper pulp = 281%, sawdust = 452% Horotiu soil = 106% and Mangateretere soil = 54% (Table 5.1).

6.3.2 *Rainfall Studies*

6.3.2.1 Rainfall Simulator

The rainfall simulator comprised a Perspex reservoir (1.0 m x 0.5 m x 10 mm deep) with a square array of 20 gauge hypodermic needles 30 mm apart (Plate 6.2). The 20 gauge (0.58 mm bore) hypodermic needles were restricted by placing a filament of 5-amp fuse wire through the needle. A 4-mm stainless steel mesh was placed 20 cm below the droppers to fracture the uniform droplets generated by the hypodermic needles and randomise droplet distribution. Constant rainfall was produced with a peristaltic pump but intensity could be altered via the pump controller changing the speed of the peristaltic pump. The simulator had a 20 L header tank for rapid filling and was mounted 5.6 m above the target lysimeter.

Plate 6.2: The rainfall generator mounted 6 m above the floor.

The rainfall simulator was able to replicate rainfall intensities from 4.3 to 127 mm/h (Fig. 6.1) and produced droplets which ranged in size from 1.2 to 3.1 mm diameter at all intensities. The size distribution of the simulated raindrops are presented in Fig. 6.2 along with a sample of natural raindrops collected during a light shower of rain. Raindrop size was measured using the flour pellet method where drops are captured on a bed of flour, individually picked off and weighed wet and again after drying (Park et al. 1983).

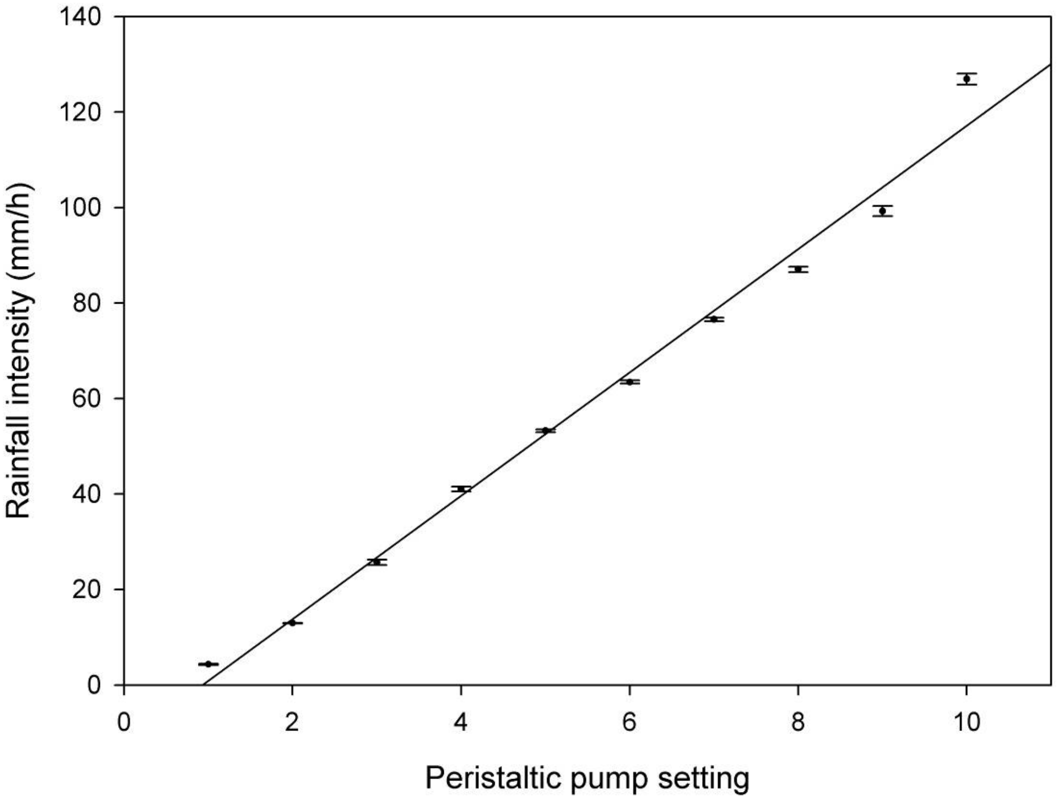


Fig. 6.1: Rainfall intensities (error bars ± SEM) as determined by the variable controller for the peristaltic pump. R^2 = 0.988.

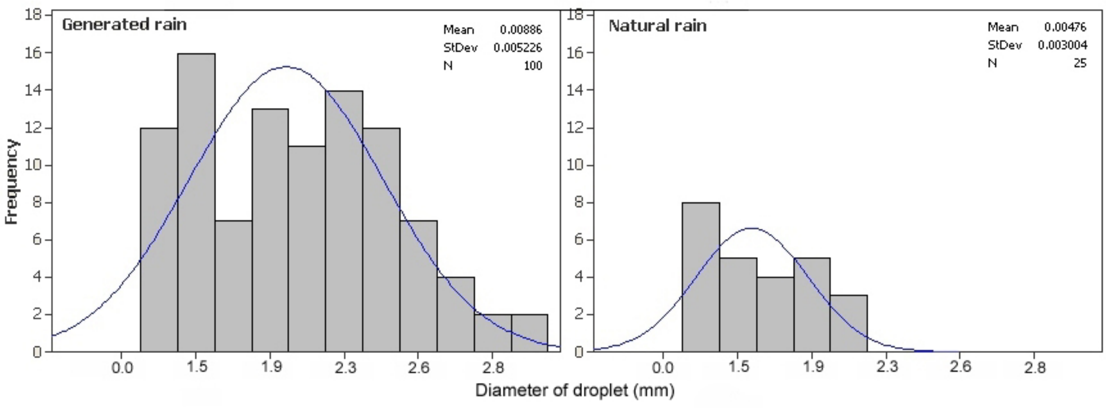


Fig. 6.2: **Distribution of generated raindrop sizes (mm) at intensity of 26 mm/h (pump setting 3) compared to a sample of natural raindrops collected during a light rainfall event.**

6.3.2.2 Lysimeter

The lysimeter was a rectangular stainless steel container (1.1 m x 0.5 m x 0.3 m deep) with drainage holes at 83 mm apart in the base. Each drainage hole was in a square rimmed with 3 mm walls to prevent lateral flow along the base of the lysimeter (Plate 6.3). Leachate could be collected separately from each drainage hole or several holes combined (Plate 6.3). For the experiments reported here the lysimeter was divided into four quarters with a stainless steel partition so that four treatments could be carried out under similar conditions. The lysimeter was packed with the media to obtain a predetermined bulk density to 10 cm depth. All media were equilibrated to a moisture content of 50% MWHC prior to packing in the lysimeter. A plumb-bob was used to align the lysimeter directly under the rainfall simulator.

Prior to the running of the experiments described here, the lysimeter was tested with sand to ensure that water did not preferentially flow down the sidewalls or partitions. The outputs from the drain holes in the base were individually measured and showed that although some channelling of water did occur in the sand, the volume of water collected from the centre drain holes was nearly the same as from the drain holes on the perimeter.

Plate 6.3: The lysimeter showing drainage holes in the base and in operation with sawdust and paper pulp.

6.3.2.3 Leaching Experiments

Three unreplicated leaching experiments were carried out. Experiment 3 investigated the movement of both atrazine and bromacil through paper pulp and sawdust, while Experiment 4 investigated the movement of the same two herbicides through the Horotiu silt loam soil and the Mangateretere silt loam soil. Experiment 5 investigated the movement of atrazine and bromacil through 10 cm of Horotiu silt loam soil topped with 5 cm of either paper pulp or sawdust in order to evaluate the effect a thin layer of organic media overlying soil would have on herbicide leaching through the soil.

The time for the breakthrough leachate to first appear was recorded in each experiment as well as the time for each of the 1-L collection bottles to be filled. In Experiments 3 and 4 the rainfall was carried out continuously for 7 h and then stopped overnight, before being continued for a further 1 or 2 hours the next morning. In Experiment 5 the rainfall was for a single 8 h period. After allowing the contents of the lysimeter to stabilise for 1 or 2 days the media were carefully removed in 10-mm layers, with each layer (from each quarter) individually bagged.

The leachate samples were vacuum filtered (0.45 µm glass fibre filters (Konomi et al. 2005)) prior to 100 mL subsamples being passed through C-18 SPE cartridges to extract the herbicide. Elution, cleanup and quantification by HPLC were as previously described (Sections 4.3.4 and 4.3.5). The filters were separately eluted with methanol, then the eluent concentrated and herbicide residues determined. Moisture content of the various media layers were determined gravimetrically prior to extraction, cleanup and quantification of herbicide as previously described (Sections 4.3.4 and 4.3.5).

For Experiments 3 and 4 the leachate was also measured to determine turbidity, total dissolved solids, pH and dissolved organic carbon (Shimadzu TOC Analyser 5000 (Ghani et al. 2007)).

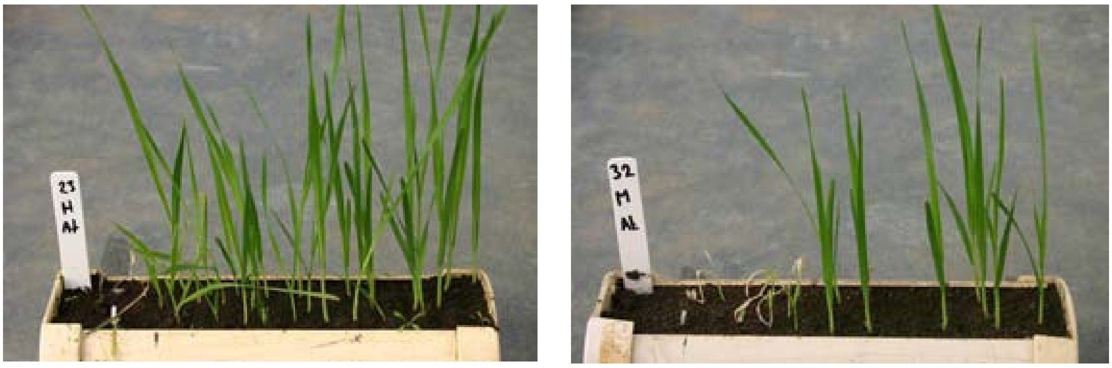
6.4 Results

6.4.1 *Bioassay Studies*

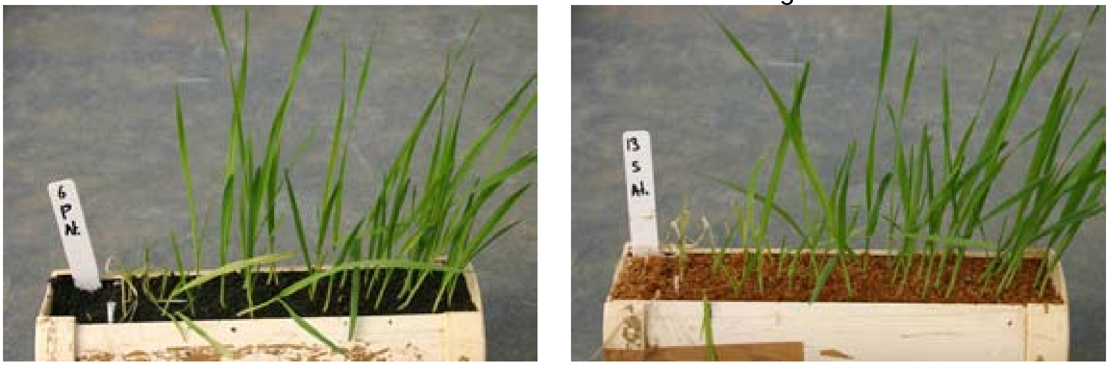
Examples of the response of oats to the herbicides leached through the packed columns are presented in Plates 6.4 – 6.7. These show differing results for leaching in each of the media as well as differences between the two herbicides, atrazine and bromacil. The averaged results for each experiment are presented in Figs 6.3 – 6.6 with error bars equal to ±1 SEM for the averages containing at least three none-zero values. However, the data presented here was not easy to interpret due to large variation at some points and to the saw tooth nature of some plots. Therefore, freeform curves were also fitted to these data using the Bayesian smoothing technique (Upsdell 1994). The intercept of these curves with the ED_{90} (NOEL) value was used to determine the actual distance leached (Figs 6.7 - 6.10).

In most instances use of the Bayesian smoothing technique enabled more precise determination of the ED_{90} value with a small SEM (Table 6.2). The three exceptions all occurred in Experiment 1, two with atrazine (Horotiu soil and sawdust) and one with bromacil (sawdust). For the two cases in sawdust the problem was that the herbicide leached right through the column and there was no upper asymptote to the curve, and the only conclusion that can be made is that in sawdust in Experiment 1, both atrazine and bromacil leached more than the depth of the column, possibly due to preferential flow as discussed below. This was confirmed by atrazine and bromacil both being detected in the breakthrough leachate from the respective columns (Table 6.3). For the third instance, that of atrazine in the Horotiu soil, it appears that the problem was large variation in the results from the four replicate columns. Examination of the results from individual columns reveals that three of them produced results indicating a leaching depth of about 20 cm while the fourth had increasing damage to the oats at greater depths. This may indicate some preferential flow in the fourth column due to imperfect packing. Despite this variation, the plot of the averaged dry matter for oats in the Horotiu soil (Fig. 6.3) indicates that the leaching depth of atrazine in this soil was about 20 cm. However, variation in the data for depths on either side of this depth (i.e. 18 and 22 cm depths) resulted in the Bayesian smoothed curve missing this point (Fig. 6.7 C).

Generally, in both experiments bromacil was shown to be more mobile than atrazine (Table 6.2). Also, both herbicides leached less in paper pulp than in the other media and both herbicides leached less in the Mangateretere soil than in the Horotiu soil. In Experiment 1, both herbicides leached more in the sawdust than in the other media while in Experiment 2 the leaching in sawdust was very similar to that in the Mangateretere soil. The reduced leaching of the herbicides in sawdust in Experiment 2 could be the result of less water added to the column (Table 6.1) although it is difficult to envisage that the approximately 6% less water applied in Experiment 2 resulted in a 40% and 25% reduction of the distance leached for atrazine and bromacil respectively. It is more likely that the greater period of time over which the water was added in Experiment 2 (Table 6.1) resulted in the reduced leaching of the herbicides in sawdust. Beltran et al. (1998) found the K_d values for atrazine decreased with increasing flow rate, resulting in increased mobility in four Australian soils with 0.1 – 3.0% organic carbon and pH of 3.32 – 6.65).

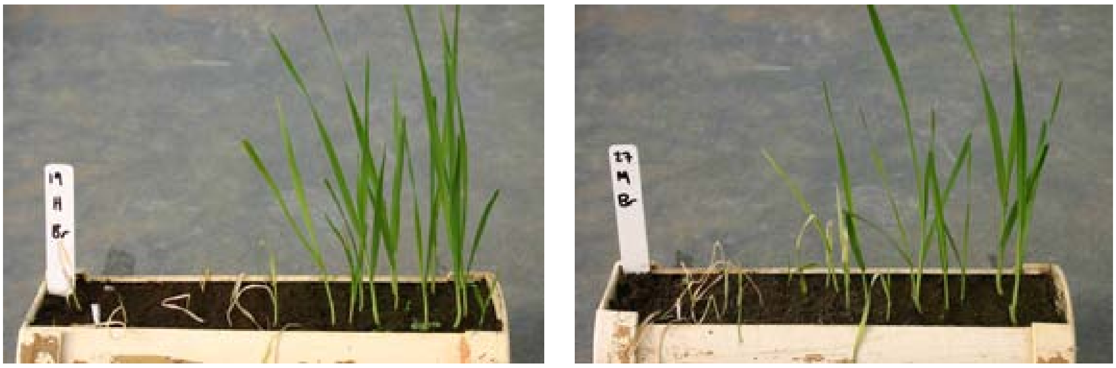


Horotiu soil Mangateretere soil

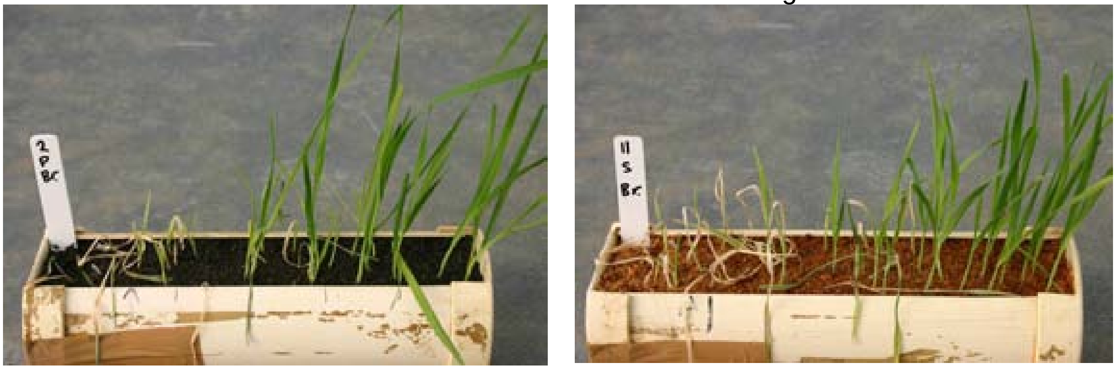


Paper pulp Sawdust

Plate 6.4: **Bioassay of leaching columns to detect movement of atrazine using oats, Experiment 1. String markers indicating the top of the untreated media are visible at the left end of the column.**



Horotiu soil Mangateretere soil



Paper pulp Sawdust

Plate 6.5: **Bioassay of leaching columns to detect movement of bromacil using oats, Experiment 1.**

Horotiu soil Mangateretere soil

Paper pulp Sawdust

Plate 6.6: Bioassay of leaching columns to detect movement of atrazine using oats, Experiment 2.

Horotiu soil Mangateretere soil

Paper pulp Sawdust

Plate 6.7: Bioassay of leaching columns to detect movement of bromacil using oats, Experiment 2.

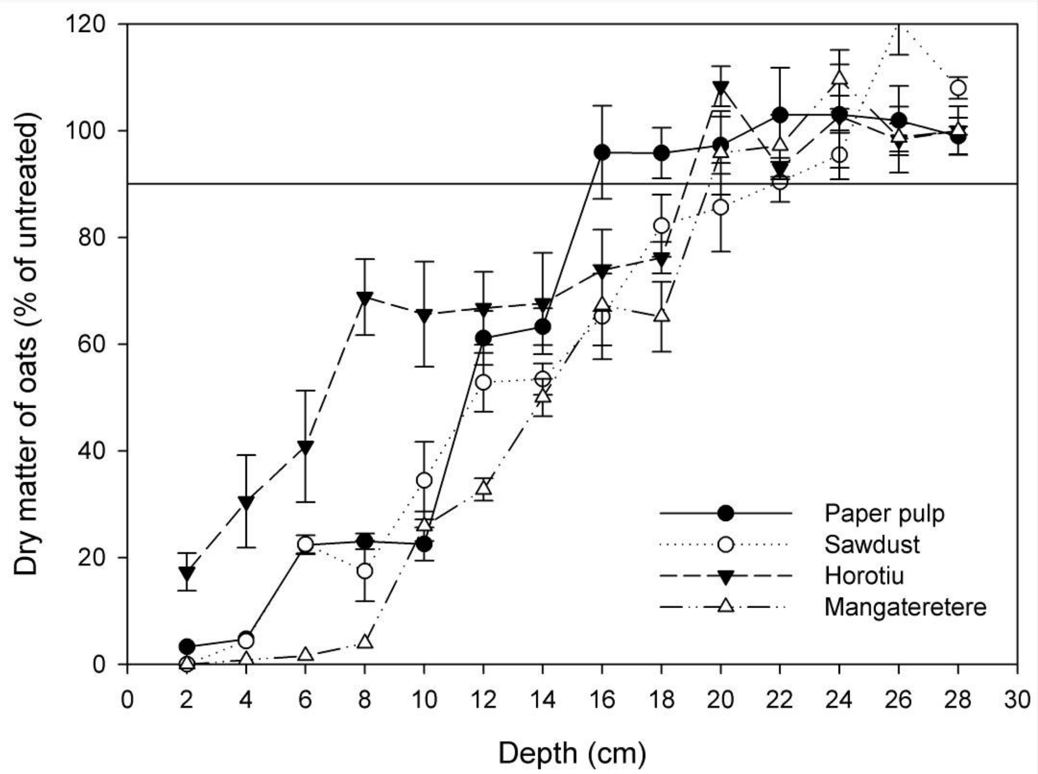


Fig. 6.3: **Dry matter of oats grown in leaching columns to detect movement of atrazine with detection limit of 90% of untreated, Experiment 1. Error bars ± 1 SEM.**

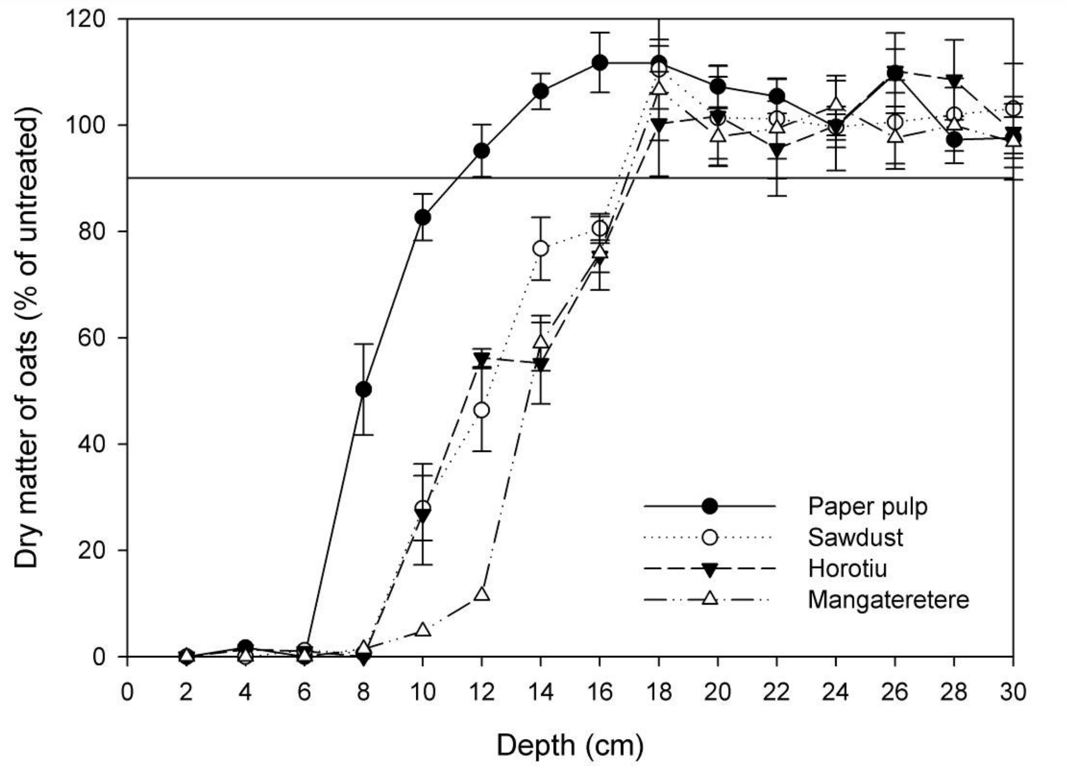


Fig. 6.4: **Dry matter of oats grown in leaching columns to detect movement of atrazine with detection limit of 90% of untreated, Experiment 2. Error bars ± 1 SEM.**

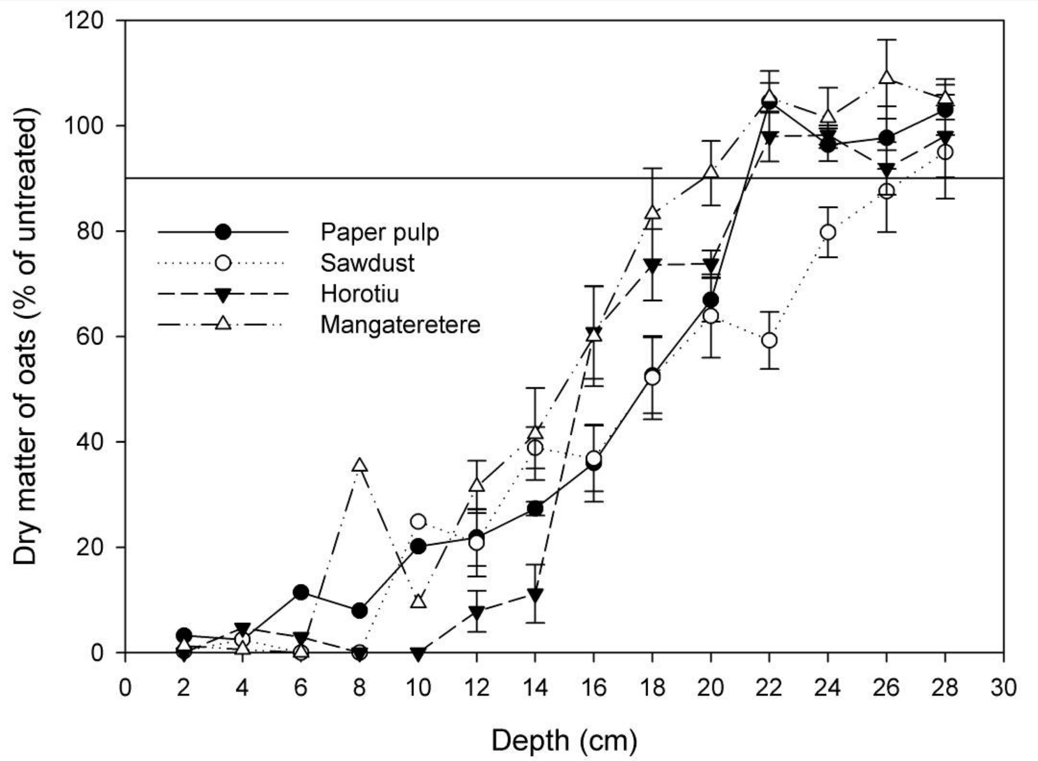


Fig. 6.5: Dry matter of oats grown in leaching columns to detect movement of bromacil with detection limit of 90% of untreated, Experiment 1. Error bars ± 1 SEM.

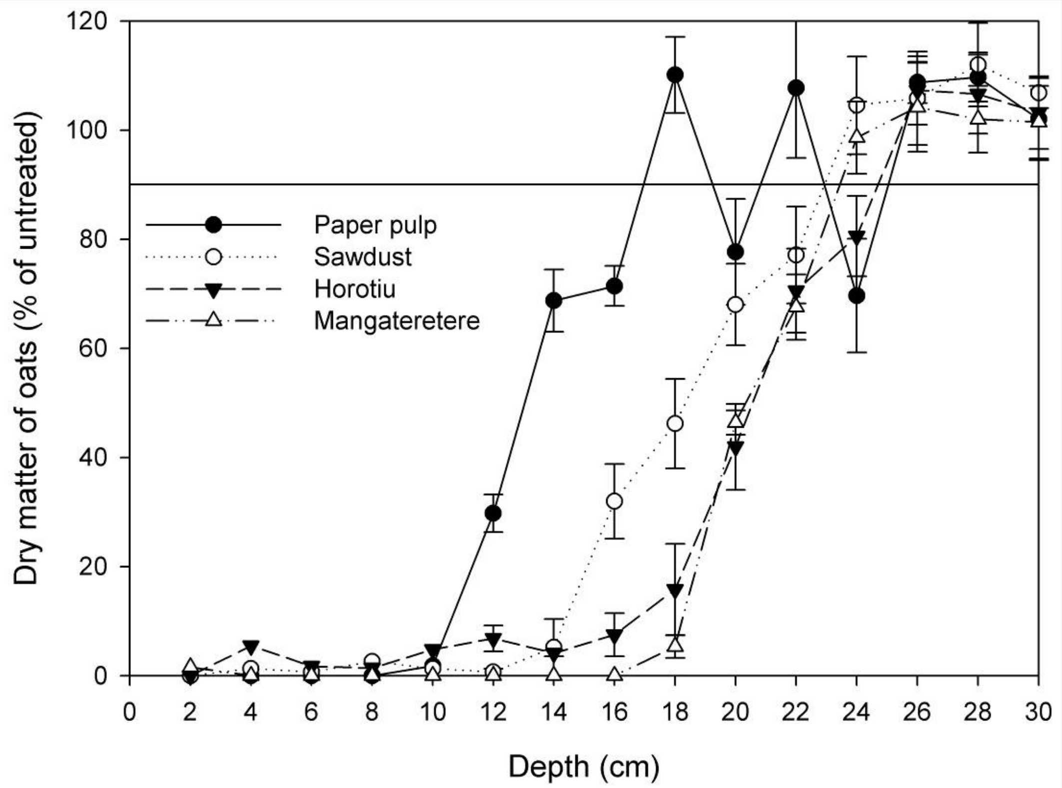


Fig. 6.6: Dry matter of oats grown in leaching columns to detect movement of bromacil with detection limit of 90% of untreated, Experiment 2. Error bars ± 1 SEM.

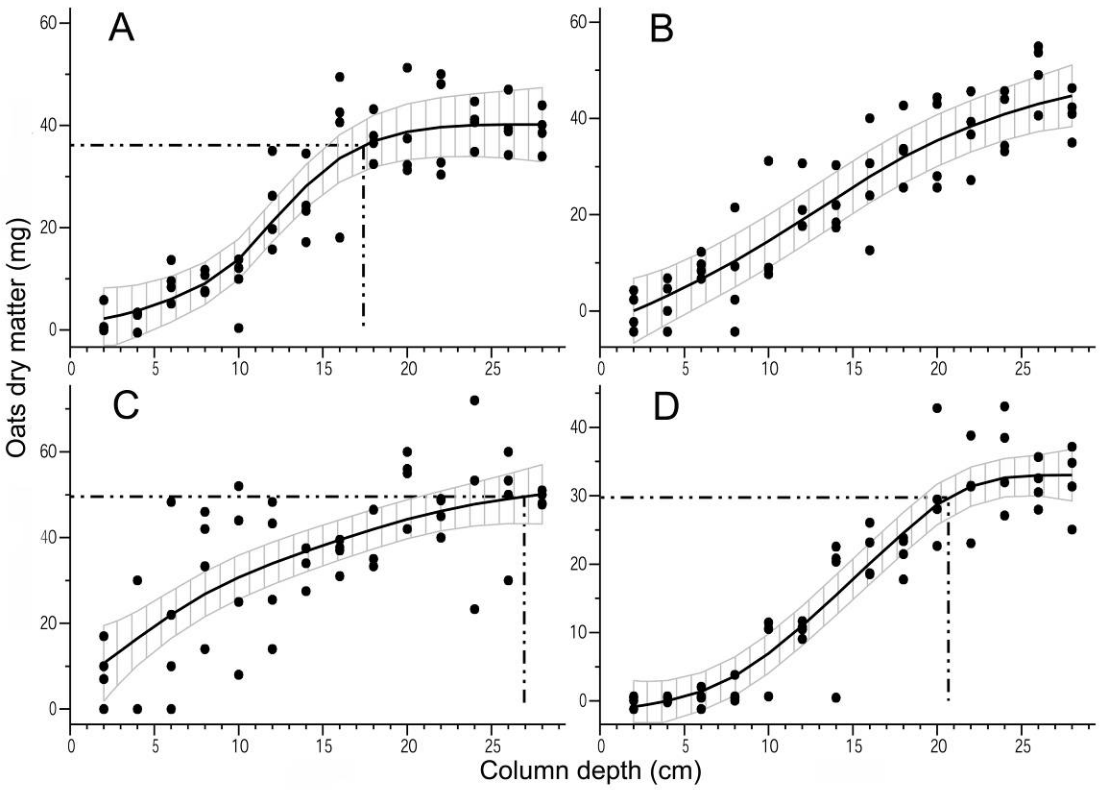


Fig. 6.7: Movement of atrazine in Experiment 1, Flexicurves of dry matter of oats grown in leaching columns with detection limit of 90% of untreated (broken line) and 95% confidence interval (hatched area): A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

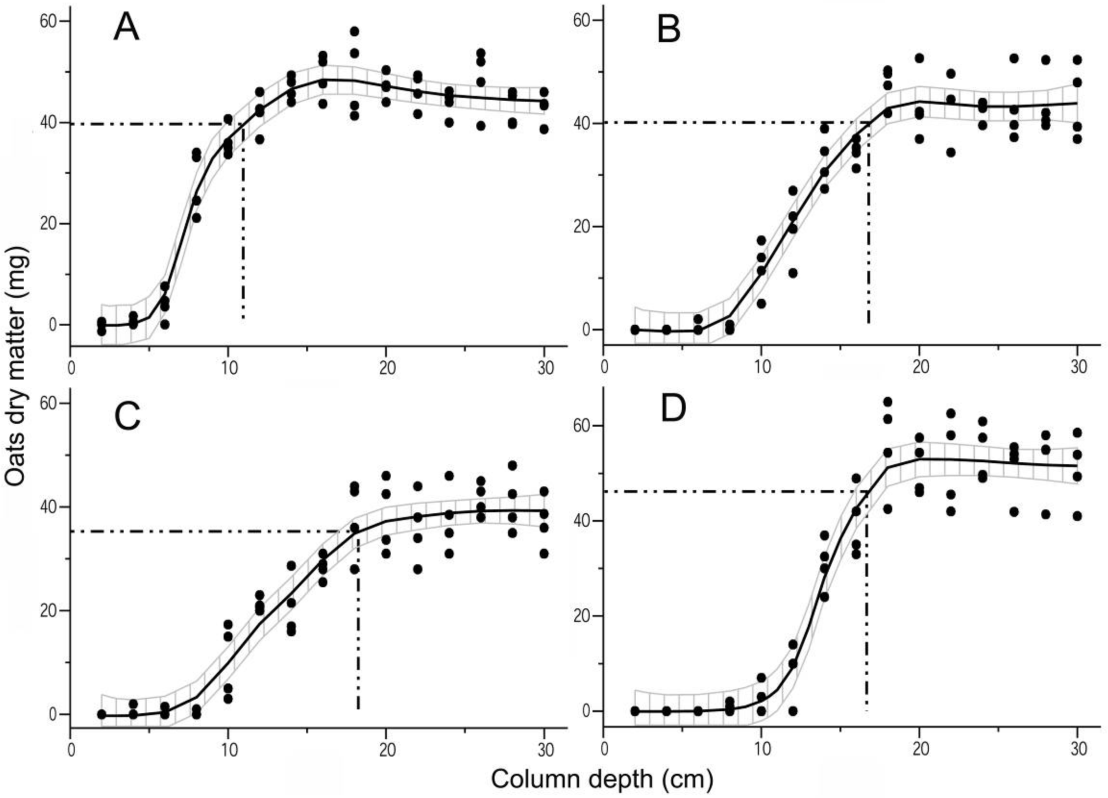


Fig. 6.8: Movement of atrazine in Experiment 2, Flexicurves of dry matter of oats grown in leaching columns with detection limit of 90% of untreated (broken line) and 95% confidence interval (hatched area): A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

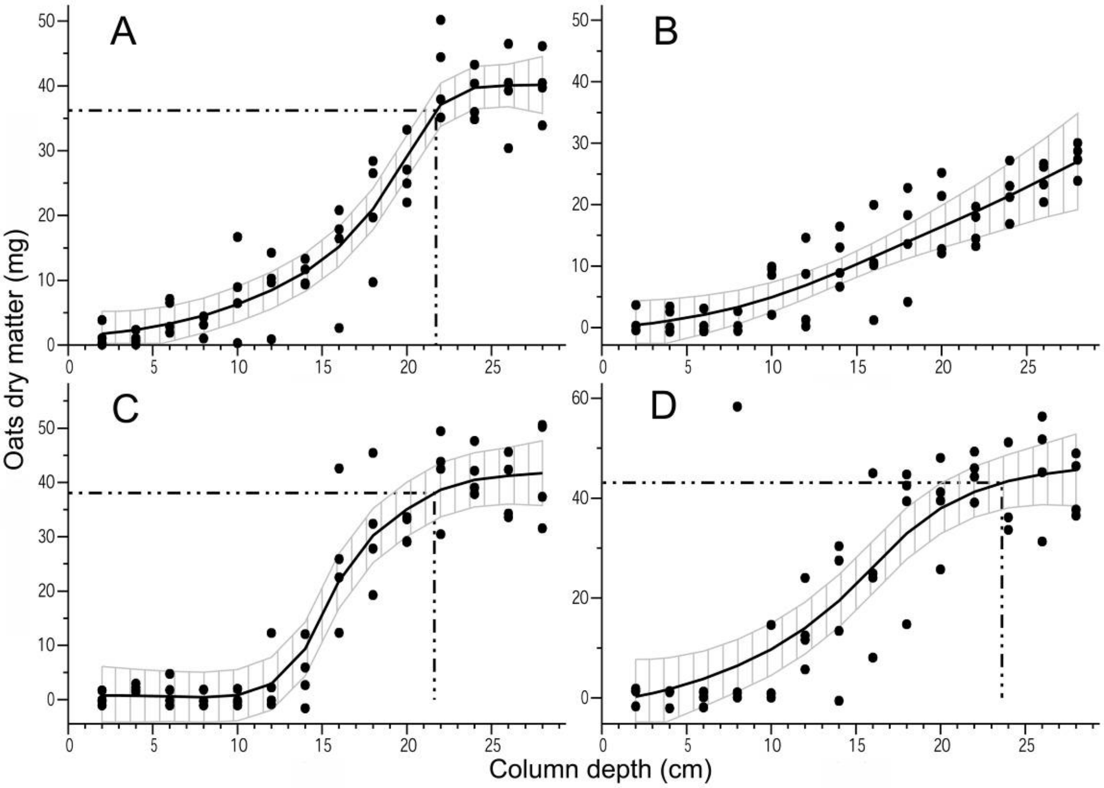


Fig. 6.9: Movement of bromacil in Experiment 1, Flexicurves of dry matter of oats grown in leaching columns with detection limit of 90% of untreated (broken line) and 95% confidence interval (hatched area): A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

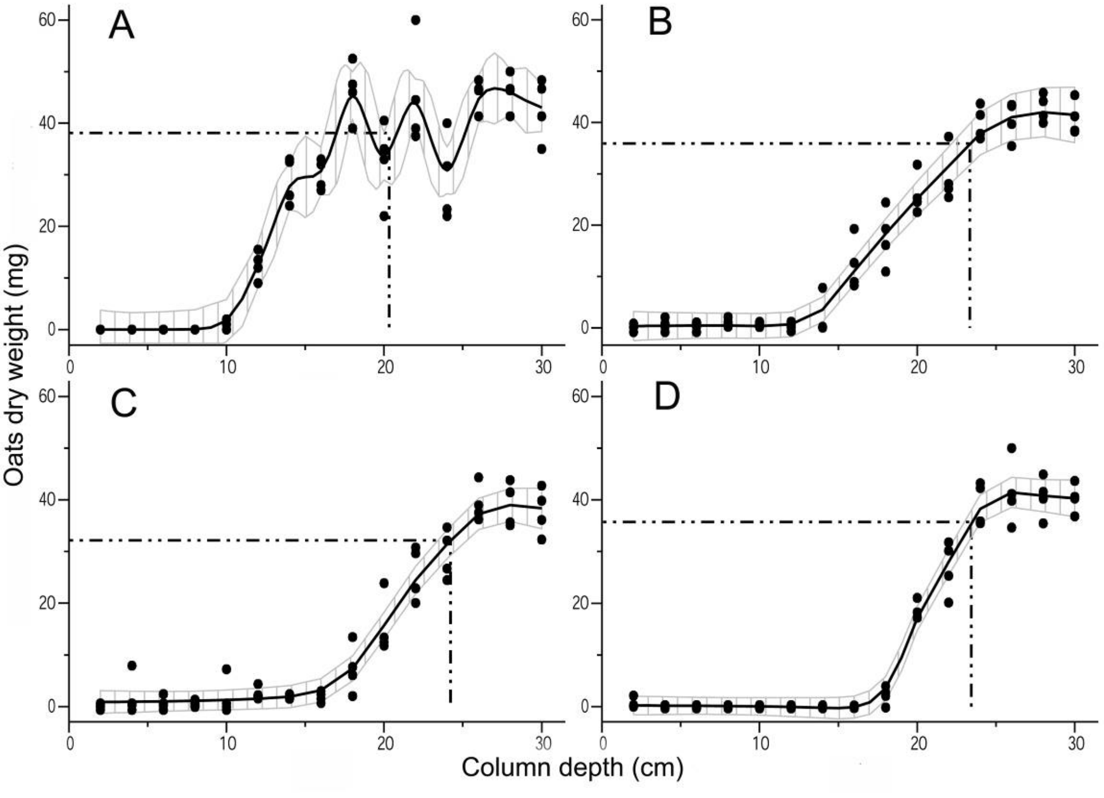


Fig. 6.10: Movement of bromacil in Experiment 2, Flexicurves of dry matter of oats grown in leaching columns with detection limit of 90% of untreated (broken line) and 95% confidence interval (hatched area): A paper pulp, B sawdust, C Horotiu silt loam and D Mangateretere silt loam.

Table 6.2: Distance leached, for atrazine and bromacil, through packed columns and determined by bioassay.

	Distance leached							
	Atrazine				Bromacil			
	Experiment 1		Experiment 2		Experiment 1		Experiment 2	
Media	(cm)	SEM	(cm)	SEM	(cm)	SEM	(cm)	SEM
Horotiu	27.0	-[1]	18.2	0.50	21.6	0.85	24.2	0.20
Mangateretere	20.7	0.55	16.7	0.20	23.6	1.50	23.4	0.20
Paper pulp	17.4	0.85	11.0	0.30	21.7	0.25	20.3	1.00
Sawdust	>30	-	16.8	0.25	>30	-	23.3	0.35

[1] SEM unable to be determined due to insufficient data points on both sides of the estimated leaching depth.

The quantities of herbicide in the breakthrough leachate (Table 6.3) are in contrast to the distance the herbicide leached determined by bioassay (Table 6.2). For example, although both herbicides appeared to leach less in the Mangateretere soil compared to the Horotiu soil there were generally much greater quantities of the herbicide in the breakthrough leachate of the Mangateretere soil. Similarly with the paper pulp and sawdust the amount of herbicide in the breakthrough leachate did not necessarily reflect the distance the herbicide leached in the column. These results are probably due to preferential flow of water through imperfectly packed columns and also to the difference in the bioavailability of herbicides amongst the media. This is easy to visualise in the columns with the very granular paper pulp and sawdust but less so with the Mangateretere soil. Preferential flow is also supported by the quantities of water added (Table 6.1). For paper pulp in particular, the water flowed through the column without completely saturating the media, and by the time water was draining freely from the bottom of the column, the paper pulp had only reached about 40% of its MWHC. This contrasts to the two soils reaching 72 – 76% of MWHC and sawdust 81 – 86% of MWHC. However, despite these results indicating that some preferential flow occurred, the impact was minimal on overall transport of the herbicides. The highest concentration of herbicide in the breakthrough leachate only equated to 0.006% and 0.009% of that applied for atrazine and bromacil respectively.

Table 6.3: Concentration of atrazine and bromacil in the breakthrough leachate (≈100 mL) of the two column leaching experiments.

	Herbicide concentration in leachate (ng/mL)[1]							
	Atrazine				Bromacil			
Media	Exp. 1	SEM	Exp. 2	SEM	Exp. 1	SEM	Exp. 2	SEM
Horotiu	0	0	64	45	0	0	4	2
Mangateretere	132	32	61	32	293	75	438	104
Paper pulp	0	0	43	19	400	266	10	5
Sawdust	17	11	10	5	96	55	113	42

[1] LOD = 1 ng/mL

The media in the columns had a significant impact on the quantity and quality of the water (Table 6.4). All the media lowered the pH of the water although the paper pulp had only a small effect. The breakthrough leachate from sawdust and the Mangateretere soil was quite acidic compared to the neutral water that was added. Understandably the leachate from all media was also more turbid and contained more dissolved solids. The Horotiu soil resulted in the lowest turbidity and the Mangateretere soil the highest of all the media while sawdust produced the lowest amount of dissolved solids and paper pulp produced the most. Both paper pulp and sawdust lowered the dissolved oxygen content of the water while the two soils had little effect. However, there was no relationship between any of the measured properties of the leachate and the concentration of herbicide in the leachate.

Table 6.4: Properties of the breakthrough leachate (≈100 mL) compared to the water used in the column Experiment 2.

Media	pH	Turbidity (NTU[1])	TDS[1] (mg/L)	DO[1] (mg/L)
Water	7.39	0.27	90	8.0
Horotiu	6.61	16	447	8.7
Mangateretere	5.81	85	558	7.7
Paper pulp	7.13	53	573	2.0
Sawdust	4.12	57	248	4.0
$LSD_{0.05}$	0.08	6.8	27.1	0.52

[1] NTU = Nephelometric turbidity unit, TDS = total dissolved solids, DO = dissolved oxygen

6.4.2 *Lysimeter studies*

6.4.2.1 Overview

The output of the rainfall generator showed minor variations between different quarters of the lysimeter with SEMs of 3 – 5% (Table 6.5). Overall, there was good consistency between experiments. In most cases the quantity of leachate collected was about 2.5 – 4 L less than applied to the surface and this water can be accounted for by increases in the moisture content of the media and some evoporation. For example the amount of water required to increase the media moisture content from the initial 50% MWHC to 90% MWHC was 3.0, 2.3, 3.2 and 2.9 L for the Horotiu soil, Mangateretere soil, paper pulp and sawdust respectively. Also, the lysimeter was allowed to drain overnight and although most of the leachate was collected and measured, some was lost when the collection bottles overfilled.

One of the anomalies is the paper pulp/bromacil combination in Experiment 3 where the quantity of leachate collected was slightly greater than the calculated input amount but this only amounted to 5% extra and this is within the SEM of the measured rainfall intensity. The other is for the Mangateretere soil/atrazine combination in Experiment 4 where only 4 L of leachate was collected despite 18 L of rainfall impacting that sector of the lysimeter. However, in this case the water simply ponded on the soil surface with very little infiltration. It would appear that in this instance the high kinetic energy of the raindrops resulted in significant splash erosion and breakdown of soil aggregates which sealed the soil surface (Plate 6.8) (Park et al. 1983).

Table 6.5: Measured rainfall output from the rainfall generator, calculated rainfall (water) intercepted by the target and quantity of the leachate collected for all three lysimeter experiments.

Experiment 3	Rainfall intensity		Water onto target	Water over 9 h	Leachate collected
Treatment	(mm/h)	SEM	(mL/h)	(L)	(L)
Paper pulp/atrazine	18.87	0.45	2830	25.5	21
Paper pulp/bromacil	21.34	1.01	2668	24.0	25
Sawdust/atrazine	20.17	1.15	2521	22.7	20
Sawdust/bromacil	18.67	0.51	2801	25.2	19

Experiment 4	Rainfall intensity		Water onto target	Water over 8 h	Leachate collected
Treatment	(mm/h)	SEM	(mL/h)	(L)	(L)
Horotiu/atrazine	23.28	0.75	2910	18.9	15
Horotiu/bromacil	23.40	0.82	3511	22.8	19
Mangateretere/atrazine	18.69	0.37	2804	18.2	4
Mangateretere/bromacil	19.57	0.36	2446	15.9	13

Experiment 5	Rainfall intensity		Water onto target	Water over 8 h	Leachate collected
Treatment	(mm/h)	SEM	(mL/h)	(L)	(L)
Paper pulp[1]/atrazine	20.74	0.15	2593	21.1	18
Paper pulp[1]/bromacil	20.02	0.89	2502	20.3	16
Sawdust[1]/atrazine	19.68	0.81	2460	20.0	16
Sawdust[1]/bromacil	22.74	0.33	2842	23.1	19

[1] A 5 cm layer of this media overlaid 10 cm of Horotiu soil.

Plate 6.8: The soil surface on completion of the rainfall Experiment 4 showing the Horotiu soil (left) which was still permeable and the Mangateretere soil (right) which was now largely impervious to water.

The time taken to collect the first litre of leachate varied (Table 6.6) and this was partly due to the slightly greater water holding capacity of the media (for instance paper pulp was generally slower than the other media) or occasionally due to the surface dynamics (especially in the case of the soils). However, after the initial breakthrough, the subsequent flow of leachate was quite consistent.

Table 6.6: Time taken (min) to collect the first four sequential litres of leachate from the lysimeter leaching Experiments 3, 4 and 5.

	Atrazine				Bromacil			
Media	1st L	2nd L	3rd L	4th L	1st L	2nd L	3rd L	4th L
Horotiu[1]	56	22	24	23	57	18	17	19
Mangateretere[1,2]	150	52	93	-[5]	85	17	27	35
Paper pulp[3]	95	26	29	23	73	25	17	23
Sawdust[3]	84	34	31	27	110	28	26	23
Paper pulp/Horotiu[4]	103	25	25	25	94	29	26	25
Sawdust/Horotiu[4]	92	33	31	31	86	25	23	21

[1] Experiment 4.
[2] Permeation of the Mangateretere soil was poor and water ponded on the surface.
[3] Experiment 3.
[4] Experiment 5.
[5] The 4th litre bottle from the Mangateretere soil filled overnight.

6.4.2.2 Leaching of Atrazine in Four Media

The results of atrazine leaching through the four media are presented in Fig. 6.11. The results for the two organic media and for the Horotiu soil generally show increasing concentrations of atrazine with successive samples of leachate. However results from the Mangateretere soil show reduced infiltration and high concentrations of atrazine in the early leachate samples. Thus the results from this soil should be separated but not disregarded as they probably reflect a common field phenomenon. For the Mangateretere soil, the impact erosion of the droplets and the increased exposure time of the ponded water on the soil surface resulted in herbicide enrichment, and when the leachate finally permeated the soil (either through conventional or preferential flow), it still contained a large amount of herbicide. The concentration of herbicide then rapidly decreased in subsequent aliquots.

By comparison the leachate from the other media initially contained little or no atrazine with concentrations increasing steadily with time (Fig. 6.11). When the rainfall was stopped, leachate continued to flow from the lysimeter albeit at a reduced rate. This leachate was allowed to accumulate overnight but analysis showed that it contained significantly less herbicide (Fig. 6.11). After the rainfall was started again the following morning the atrazine concentration in the leachate continued to rise as before. However, for paper pulp the rise commenced from the reduced overnight concentration whereas for the sawdust the rise in atrazine concentration immediately rose to the level it had attained the day before and continued to rise from that point. With the Horotiu soil the rain drops failed to infiltrate on start-up the following morning and only a single leachate sample could be collected.

The leachate from the sawdust contained detectable residues of atrazine commencing with the breakthrough sample while no or very little atrazine was found in the first leachate samples from the Horotiu soil or the paper pulp. However from the eighth sample onward concentrations of atrazine in the Horotiu soil leachate rose rapidly while atrazine concentrations in leachate from the paper pulp were much lower until about the 16th sample when concentration started to rise sharply. From the tenth sample onward, atrazine concentrations in the sawdust leachate were intermediate between the Horotiu soil and the paper pulp.

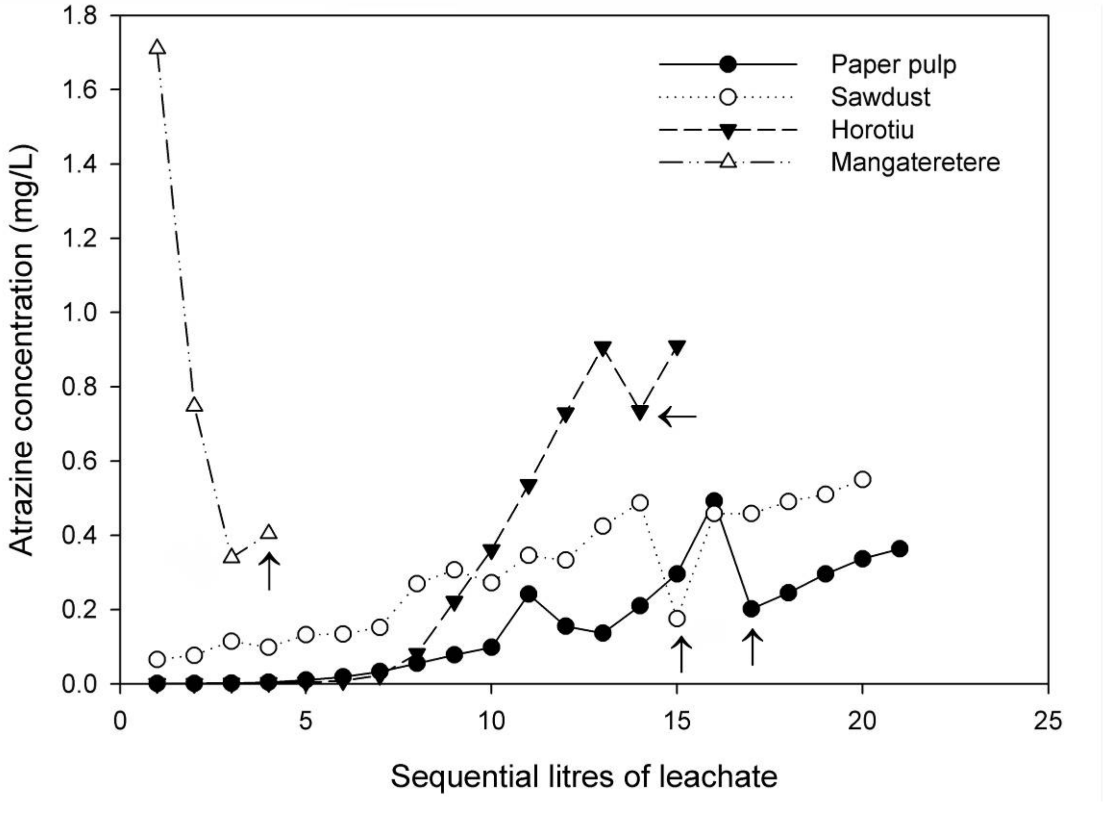


Fig. 6.11: **Atrazine concentration in each sequential litre of leachate collected. Note; for the Mangateretere soil, permeation of the water was poor and water ponded on top. Arrows indicate the first sample after the overnight break in rainfall.**

The movement of atrazine through the four media is illustrated in Fig. 6.12. Again, the Mangateretere soil was a special case. Here the highest concentrations of atrazine were found on the soil surface (reflecting the lack of infiltration) and at the bottom which demonstrates that there was some preferential flow which moved the atrazine directly to the bottom of the lysimeter where it accumulated. It is possible that with water ponding on the surface some preferential flow occurred down the sides of the lysimeter.

In the other media, the atrazine was moved down the profile with the water flow showing a classical sigmoidal distribution in the soil profile for a pulse input. Atrazine moved the greatest distance in sawdust and the Horotiu soil and least in paper pulp. The centre of the atrazine mass for these three media was at 3.6, 4.9 and 5.0 cm for paper pulp, sawdust and Horotiu soil respectively.

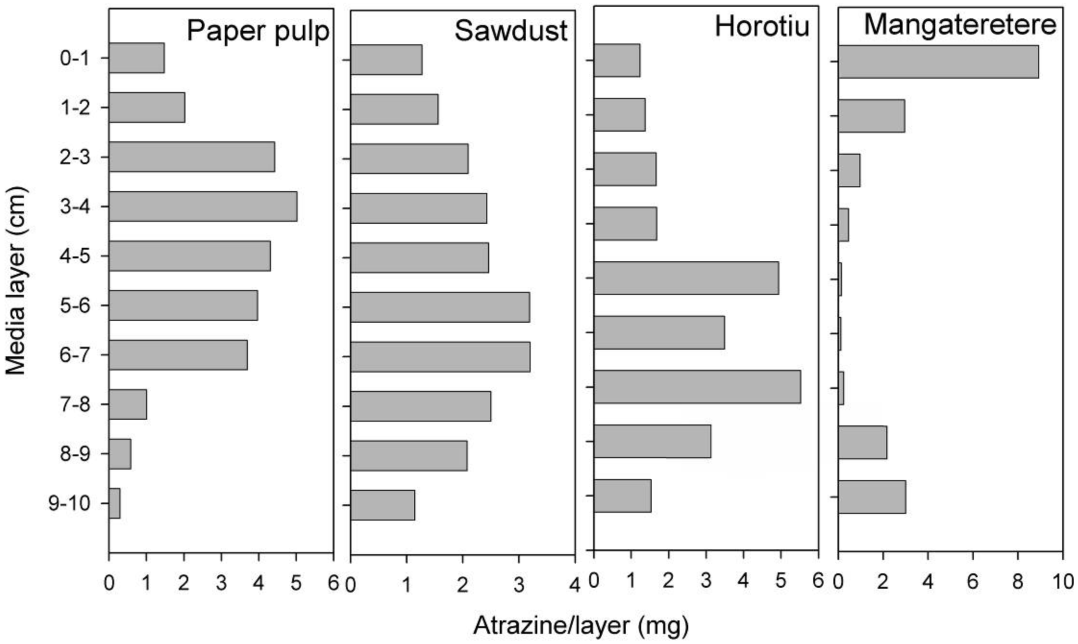


Fig. 6.12: Quantity of atrazine in each of the sequential 1-cm layers of media on completion of the leaching experiments.

The individual and combined mass of atrazine measured in the media and in the leachate are presented in Table 6.7. These data, expressed as percent of that applied to the media surface at commencement of the experiments, account for 54 – 81% of the applied atrazine, with the greatest amount in the Horotiu soil and its leachate and the least in the Mangateretere soil and its leachate.

In an essentially closed system such as the one in which these experiments were carried out, we should be able to account for most, if not all, of the herbicide in the system. In this experiment the herbicide that was applied to the surface of the media at commencement must be either still in the media or in the leachate or a combination of both. The only losses from the system would normally be through degradation but as atrazine has half-lives of between 13 and 70 days at 20°C, minimal loses would be expected through degradation due to the short duration of the experiments (Table 5.5). The only other losses from the system were loss of leachate during bottle changing and when the collection bottles overfilled during the night. However, considering that most of the rainfall water has previously been accounted for, the loses here could not be more than 1 or 2 L of leachate or less than 1% of the applied atrazine.

Table 6.7: Quantity of atrazine recovered from media and leachate on completion of the lysimeter leaching experiments, as a function of the amount applied (mass balance).

	Recovered atrazine as percent of applied		
Media	Media	Leachate	Total
Paper pulp	55.8	6.8	62.6
Sawdust	54.8	13.3	68.1
Horotiu soil	68.3	12.6	80.9
Mangateretere soil	46.0	7.8	53.8

It must be accepted that there have been inefficiencies in the recovery of atrazine. Recovery of atrazine from water using SPE techniques is now an industry standard and very little can go wrong with this method, therefore the unaccounted herbicide is most likely due to incomplete extraction of residues from the media. Atrazine has proven difficult to extract from organic media and few methods approach 100%, with many achieving only about 80% (Goh et al. 1990; Heatwole et al. 1997; Xiong et al. 1998; Gan et al. 1999). Others report difficulties with the extraction of atrazine e.g. Bouaid et al. (2001), using a solid phase micro extraction method following solvent extraction with methanol, reported 72-123% extraction for several pesticides but only 47% for atrazine. Similarly, Neurath et al. (2004) in a packed column experiment to determine atrazine leaching recovered only 37 – 41% of the applied atrazine using methanol extraction from the soil.

Although recovery of atrazine from the media in some instances was low it still provides valuable results on the movement of atrazine through the profile. There is no reason to suspect that atrazine would be preferentially extracted from certain layers and it may be assumed that the magnitude is the same for all layers. Therefore, the shape of the atrazine concentration through the profile is valid and it is only the relative concentrations that are proportionally low due to incomplete extraction.

6.4.2.3 Leaching of Bromacil in Four Media

The results of bromacil leaching through the four media are presented in Fig. 6.13. In a case similar to that for atrazine (Section 6.4.2.2) the results for the Mangateretere soil should be treated separately due to the rainfall ponding on the surface and poor infiltration (although not as low as for atrazine). In this case also the breakthrough leachate had a much higher concentration of bromacil than subsequent samples.

The results for the other three media were also remarkably similar to those for atrazine except the concentrations of bromacil in the leachate were higher and the rapid rise in the concentration of bromacil in the leachate from the Horotiu soil occurred earlier at the fifth sample (Fig. 6.13). As with atrazine the rainfall was stopped overnight and the leachate collected during this period showed reduced concentration of bromacil but also rose steadily on commencement of the rainfall the following morning. Similarly, the rise in bromacil concentration in the paper pulp leachate was gradual whereas that for the sawdust immediately rose to the level of the previous day and continued to rise from that point.

The most notable difference from the atrazine results however was that concentrations of bromacil in the Horotiu soil leachate peaked with the 11th sample and then declined at about the same rate as they had risen (Fig. 6.13). Bromacil concentrations in the sawdust and paper pulp leachate also appear to have peaked, but both these events occurred after the rainfall was restarted on the second day so they could also be influenced by other factors. All these observations are in keeping with the fact that bromacil has higher water solubility than atrazine and was highly mobile in these media.

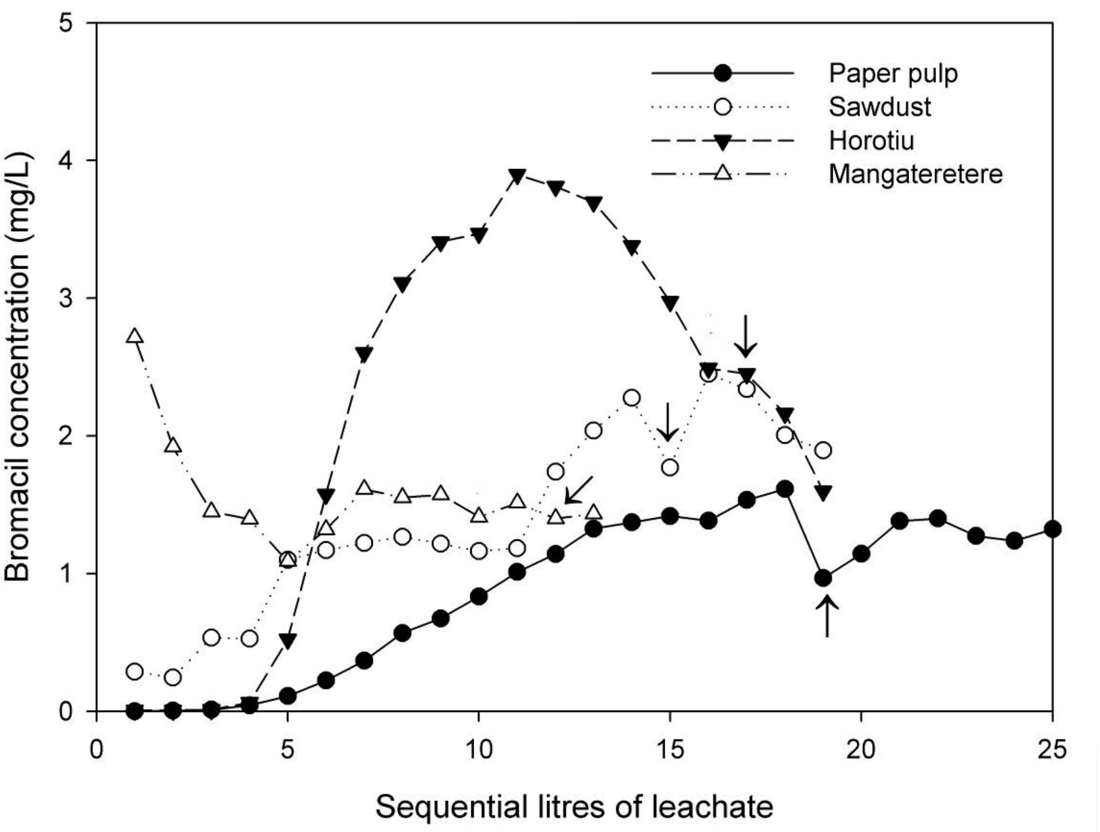


Fig. 6.13: **Bromacil concentration in each sequential litre of leachate collected. Note: for the Mangateretere soil, permeation of the water was poor and water ponded on top. Arrows indicate the first sample after the overnight break in rainfall.**

The movement of bromacil through the four media is illustrated in Fig. 6.14. Again, the Mangateretere soil is a special case where highest concentrations of bromacil were found on the soil surface (reflecting the lack of infiltration). With the other media, bromacil was moved down the profile with the water flow, with most movement in paper pulp and least in sawdust and the Horotiu soil (excluding the Mangateretere soil). The centre of the bromacil mass for these three media was at 7.0, 6.3 and 6.2 cm respectively for paper pulp, sawdust and Horotiu soil. As expected the distance that bromacil moved through the profile was greater than for the less water soluble atrazine. However, bromacil moved the most in the paper pulp, whereas atrazine moved the least in this media. This is because bromacil is more basic (higher pKa) than atrazine (Table 2.1) and in the slightly basic paper pulp (Table 3.1) it would have been more soluble than in the slightly acid soils and sawdust, thus leading to greater movement through the profile. However, the greater mobility through the profile did not lead to greater quantities in the leachate (Fig. 13), but rather concentrated the bromacil in the bottom layer of the paper pulp.

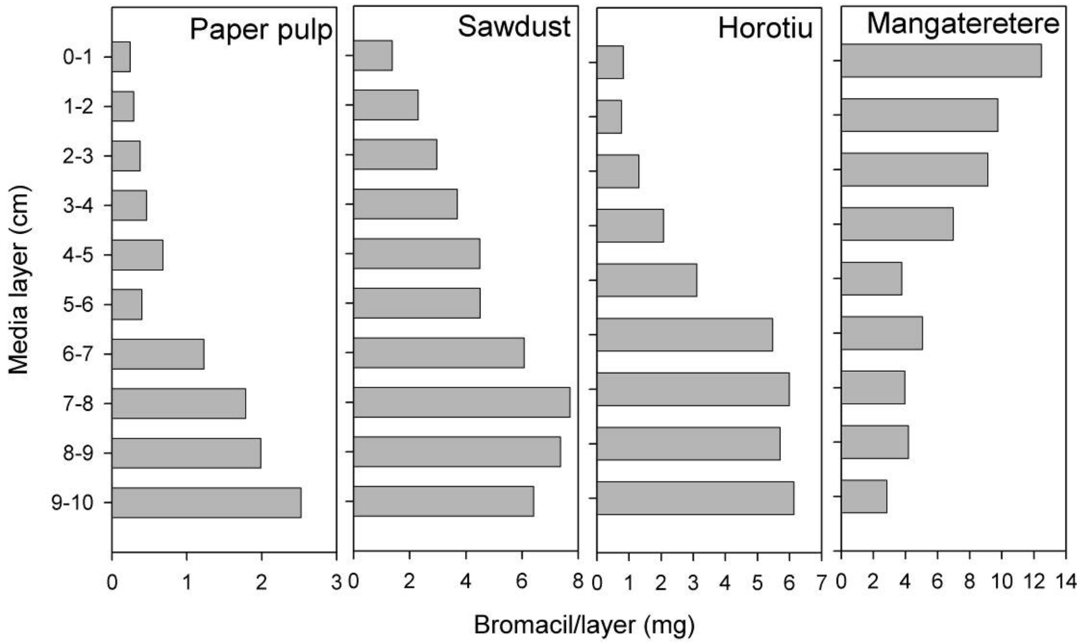


Fig. 6.14: **Quantity of bromacil in each of the sequential 1-cm layers of media on completion of the leaching experiments.**

The individual and combined mass of bromacil measured in the media and in the leachate are presented in Table 6.8. These data, expressed as percent of that applied to the media surface at commencement of the experiments, account for 46 – 92% of the applied bromacil, with the greatest amount in the sawdust and its leachate and the least in the paper pulp and its leachate. In general, greater percentage of bromacil than atrazine was found in the leachate indicating the higher mobility of the former. Again, these results differ from those for atrazine where the two extremes were in the two soils. That the Mangateretere soil had a high total recovery of bromacil and only poor total recovery of atrazine could be related to the impermeability of the soil in the atrazine experiment. The ponded water could have resulted in uneven distribution of atrazine, on the surface and along macroflow pathways, which was missed during sample collection from the various layers.

Table 6.8: **Quantity of bromacil recovered from media and leachate on completion of the lysimeter leaching experiments, as a function of the amount applied (mass balance).**

	Recovered herbicide as percent of applied		
Media	Media	Leachate	Total
Horotiu soil	32.3	42.4	74.7
Mangateretere soil	65.6	23.0	88.5
Paper pulp	14.1	31.6	45.7
Sawdust	59.0	33.2	92.2

6.4.2.4 Leaching of Atrazine and Bromacil through Horotiu Soil Overlaid with either Paper Pulp or Sawdust

The results of atrazine and bromacil leaching through Horotiu soil topped with a layer of paper pulp or sawdust are presented in Fig. 6.15. As expected, bromacil was more mobile than atrazine when in the same media but both herbicides were considerably more mobile in sawdust than in paper pulp. Residues of bromacil and atrazine were found in the first and second samples, respectively, of leachate collected from the sawdust/Horotiu soil profile, while for the paper pulp/Horotiu profile corresponding residues were found in the seventh and eleventh samples. The concentration of bromacil in the leachate from the sawdust/Horotiu soil profile peaked at the ninth sample in a manner similar to that of bromacil in the Horotiu soil (Fig. 6.13). However, the peak in the mixed layer profile was much lower, with peak concentration of bromacil about one third that of the Horotiu soil.

The shape of the leaching curve for bromacil in the paper pulp/Horotiu soil profile (Fig. 6.15) was intermediate between that of the Horotiu soil and paper pulp (Fig. 6.13) although the breakthrough was slightly delayed in the mixed profile.

The concentration of atrazine in the leachate from the paper pulp/Horotiu soil profile was both reduced and delayed (Fig.6.15) compared to paper pulp alone (Fig. 6.11). This appears to be the influence of the layer of Horotiu soil as by itself, the thinner layer of paper pulp in the mixed profile would not be expected to have this effect. However, the layer of Horotiu soil appears to have less impact in the sawdust/Horotiu soil profile (Fig. 6.15) as here the concentration of atrazine in the leachate exceeded that for sawdust alone and was also much greater than for the Horotiu soil alone for the corresponding samples (Fig. 6.11). Some, or all of these differences could be attributed to the layering as placing two media with different particle and bulk densities one over the other can result in an anomaly in the hydraulic conductivity at the interface which can affect the leaching of solutes (Snow et al. 1994; Vandervaere et al. 1997).

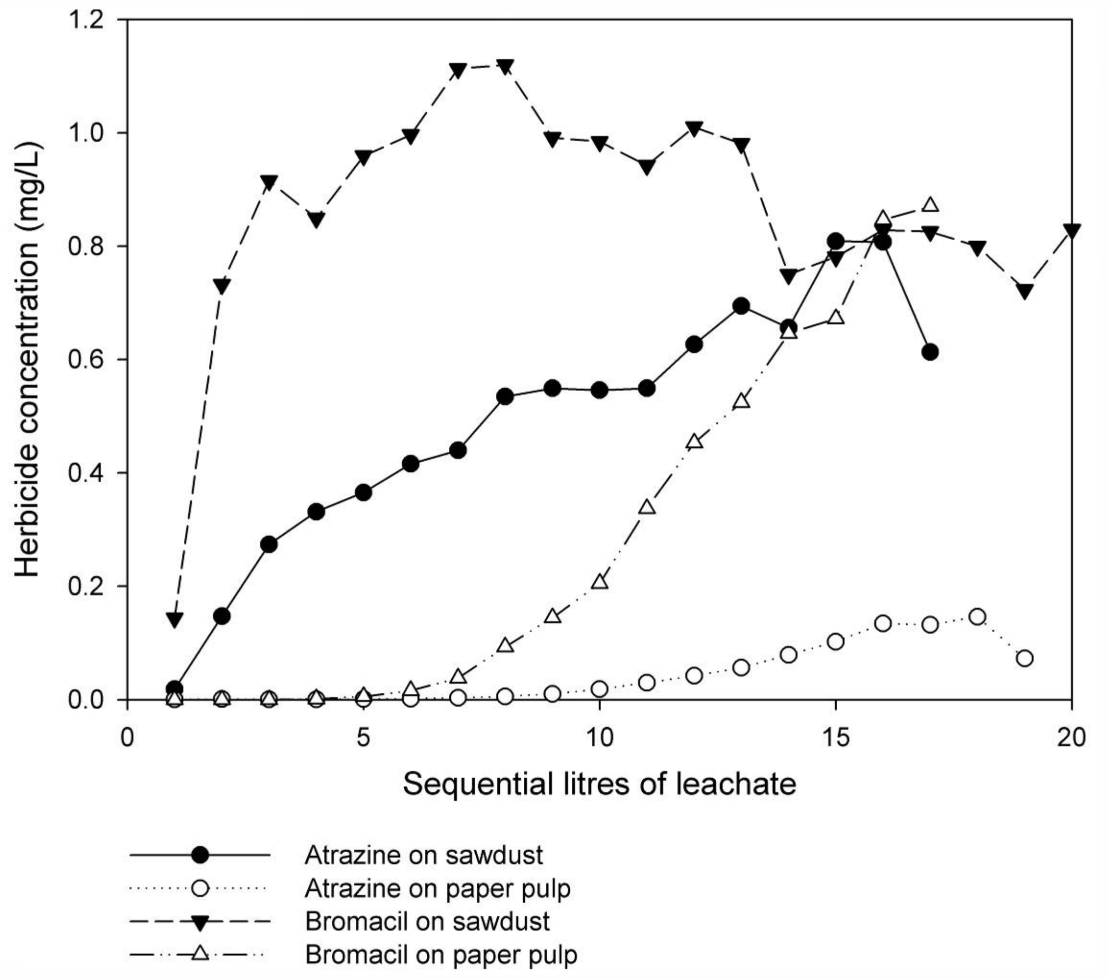


Fig. 6.15: **Herbicide concentration in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil overlaid with 5 cm of either paper pulp or sawdust after herbicide application to the surface of the media.**

The movement of atrazine and bromacil through the media combinations is illustrated in Fig. 6.16. The greatest quantities of the herbicides were retained in the layer of organic media on top of the Horotiu soil except for bromacil in the paper pulp layer. The concentration profiles for atrazine (Fig. 6.16 A and B) indicate that the bulk of atrazine was still moving down the profile and this is supported by the leachate data where concentrations of atrazine were increasing with consecutive samples (except for the final sample which was collected after the rainfall was stopped and here the atrazine concentration was lower as in the previous experiments). For the more water soluble bromacil however, the movement of the herbicide down the profile was more pronounced. In the sawdust/Horotiu soil combination it appears to have reached a steady state with greater quantities in the high organic matter sawdust and with lower, but very similar concentrations throughout the soil profile (Fig. 6.16 C). By this time the bromacil concentrations in the leachate were also fairly constant (Fig. 6.15). Bromacil residues in the paper pulp/Horotiu soil combination were also spread fairly evenly through the profile although here there are lower residues in the paper pulp and a slight peak in herbicide concentration towards the bottom of the soil profile. These leaching patterns can be compared to those in the single media (Figs 6.12 and 6.14). In the single media both atrazine and bromacil leached more from the sawdust than from the paper pulp. This result is also reflected in the layer experiment with both herbicides leaching more from the sawdust/Horotiu soil combination than from the paper pulp/Horotiu soil combination.

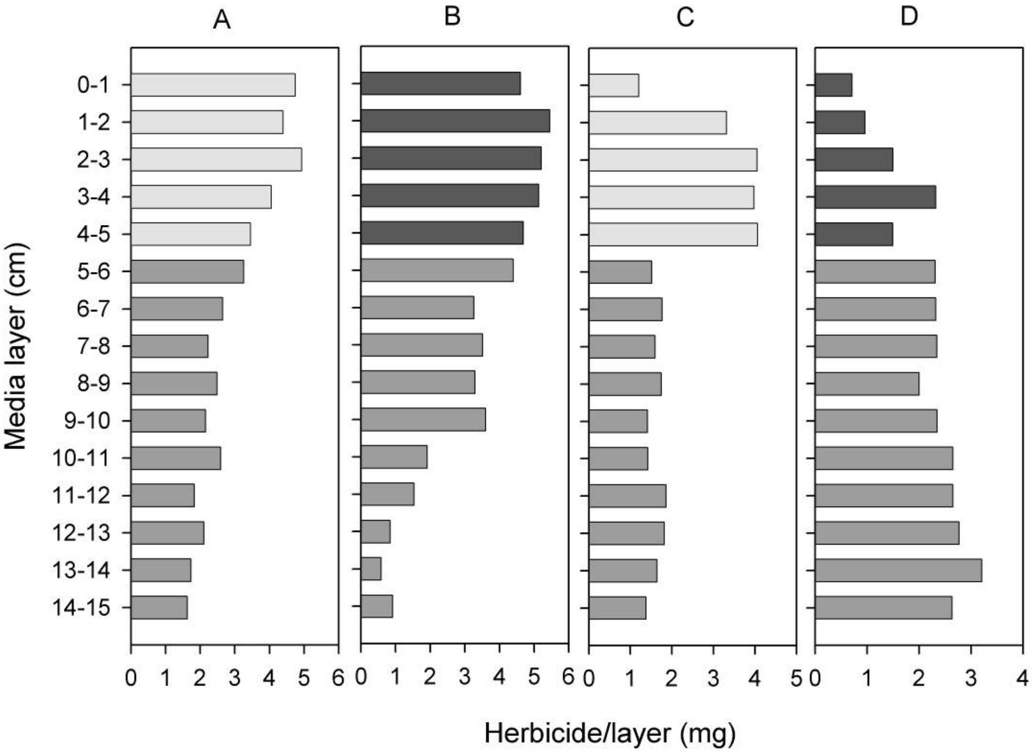


Fig. 6.16: **Quantity of herbicide in each of the sequential 1-cm layers of media on completion of the leaching experiment (0-5 cm organic amendment; 6-15 cm Horotiu soil);**
A, atrazine applied to sawdust over Horotiu soil.
B, atrazine applied to paper pulp over Horotiu soil.
C, bromacil applied to sawdust over Horotiu soil.
D, bromacil applied to paper pulp over Horotiu soil.

The individual and combined masses of atrazine and bromacil measured in the media and in the leachate are presented in Table 6.9. These data, expressed as percent of that applied to the media surface at commencement of the experiments, account for 73 – 99% of the applied herbicide. Bromacil shows the greatest variation with 73.2% mass recovery from the paper pulp/Horotiu soil combination and 98.7% mass recovery from the sawdust/Horotiu soil combination. These results are in keeping with previous results where it was also more difficult to extract bromacil from paper pulp than from sawdust (Table 6.8).

Table 6.9: Quantity of herbicide recovered from media and leachate on completion of the lysimeter leaching Experiment 5, as a function of the amount applied (mass balance).

	Recovered herbicide as percent of applied					
	Atrazine			Bromacil		
Media[1]	Media	Leachate	Total	Media	Leachate	Total
Paper pulp	41.6	1.4	82.5	13.8	9.6	73.2
Horotiu soil	39.5			49.8		
Sawdust	35.8	13.9	87.2	32.7	34.1	98.7
Horotiu soil	37.6			31.8		

[1] 5 cm of either paper pulp or sawdust overlaying 10 cm of Horotiu soil.

6.4.2.5 Properties of the Leachate Collected from the Leaching Experiments

Some chemical and physical properties of the leachate collected from the lysimeter during Experiments 3 and 4 are presented in Table 6.10. These show that pH was highest in leachate from paper pulp and lowest from sawdust although that of the Mangateretere soil was similar to the sawdust. The leachate from the Mangateretere soil was the most turbid with levels about four times greater than the other three media. This high level of turbidity was due to the high level of clay particles in this soil (Table 3.1) and is probably the main cause of the reduced infiltration.

Dissolved solids were also highest in the leachate of the Mangateretere soil but were also high in the paper pulp and the Horotiu soil. DOC was about 10 times higher in the two organic media compared to the two soils. DOC levels in the leachate of the sawdust were twice that of the paper pulp. This could be because the sawdust had twice the organic carbon content of the paper pulp or simply an artefact of the milling and pulping processes. Although the Mangateretere soil has a lower organic carbon content than the Horotiu soil, the initial concentrations of DOC were significantly higher but quickly dropped off compared to those from the Horotiu soil. It is possible that in the Mangateretere soil much of the leached organic carbon was associated with the finer clay colloids that quickly moved down the soil profile (Oades 1988; Hassink & Whitmore 1997).

Table 6.10: Properties of the first five 1-litre aliquots of leachate from samples of the four media for Experiments 3 and 4.

Media	Sequential litre	pH	Turbidity (NTU[1])	TDS[1] (mg/L)	DOC[1] (mg/L)
Horotiu	1	6.02	278	1119	25
Horotiu	2	6.26	251	1380	21
Horotiu	3	6.30	303	1186	19
Horotiu	4	6.05	318	1060	18
Horotiu	5	6.35	415	928	14
Mangateretere	1	5.85	1984	1455	73
Mangateretere	2	5.64	1185	1441	57
Mangateretere	3	6.24	1381	1015	37
Mangateretere	4	6.45	1211	720	34
Mangateretere	5	6.16	1244	462	11
Paper pulp	1	7.65	251	1044	345
Paper pulp	2	7.80	185	961	286
Paper pulp	3	7.66	202	780	254
Paper pulp	4	8.08	403	560	211
Paper pulp	5	7.98	324	471	169
Sawdust	1	5.13	123	275	700
Sawdust	2	5.17	214	260	543
Sawdust	3	5.91	303	386	465
Sawdust	4	6.05	318	460	417
Sawdust	5	6.72	415	528	362

[1] NTU = Nephelometric turbidity unit, TDS = total dissolved solids, DOC = dissolved organic carbon

For Experiment 5 the various chemical and physical properties of the leachate have been plotted along side the herbicide concentration in the leachate to evaluate possible relationships between leachate properties and herbicide concentration. These plots are presented in Figs 6.17 – 6.24 and their regression coefficients along with the nature of the relationship (positive or negative) are presented in Table 6.11.

The relationship between atrazine and dissolved organic carbon concentrations in the leachate are examined in Fig. 6.17 by plotting changes in their concentrations with time. Considerably more dissolved organic carbon originated from the sawdust layer than from the paper pulp layer. However this appears to have had little influence on the concentration of atrazine. The concentration of DOC rose sharply with the second leachate sample but then decreased steadily with each subsequent sample. Conversely, the concentration of atrazine rose steadily with each consecutive leachate sample. For the paper pulp, the DOC and atrazine were released more slowly but DOC still peaked well before the leached atrazine.

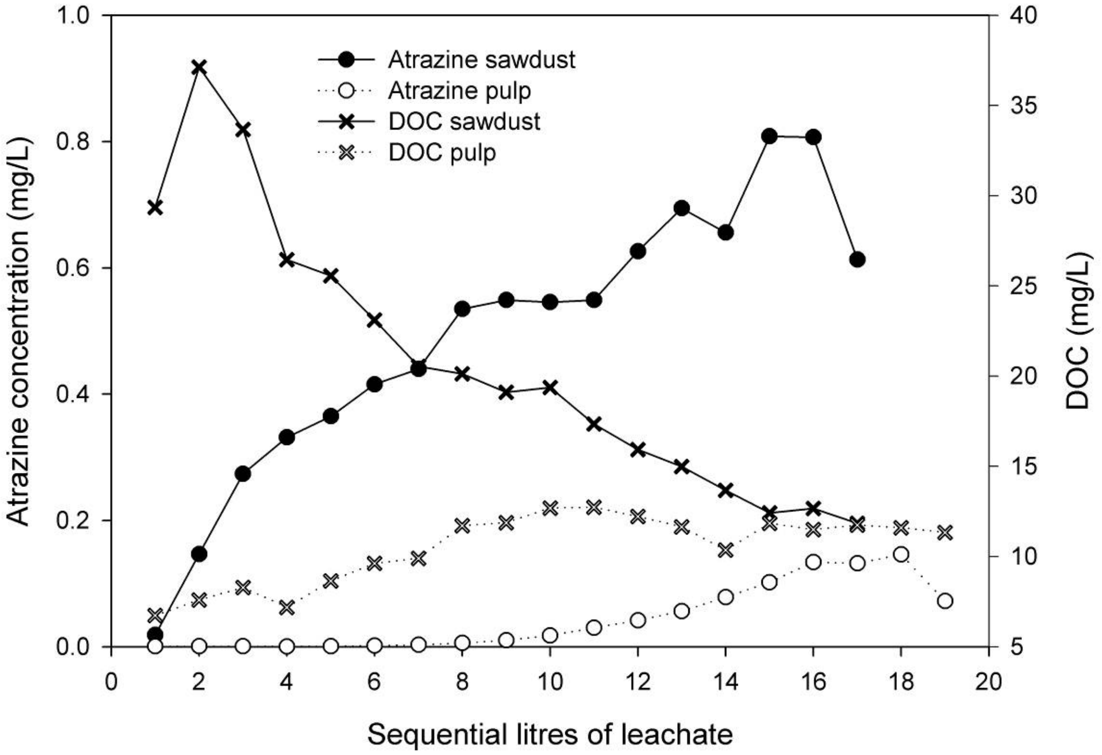


Fig. 6.17: **Atrazine concentration and DOC in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

The dissolved solids originating from the sawdust/Horotiu soil and paper pulp/Horotiu soil combinations are of similar magnitude and profile (Fig. 6.18). When compared to the data for the individual media (Table 6.10) it appears that the effect of the two layers is additive with the paper pulp/Horotiu soil combination producing more dissolved solids than the sawdust/Horotiu soil combination. From this initial high concentration the quantity of dissolved solids fell steadily and is highly unlikely to have any relationship with the amount of atrazine leached from the profiles.

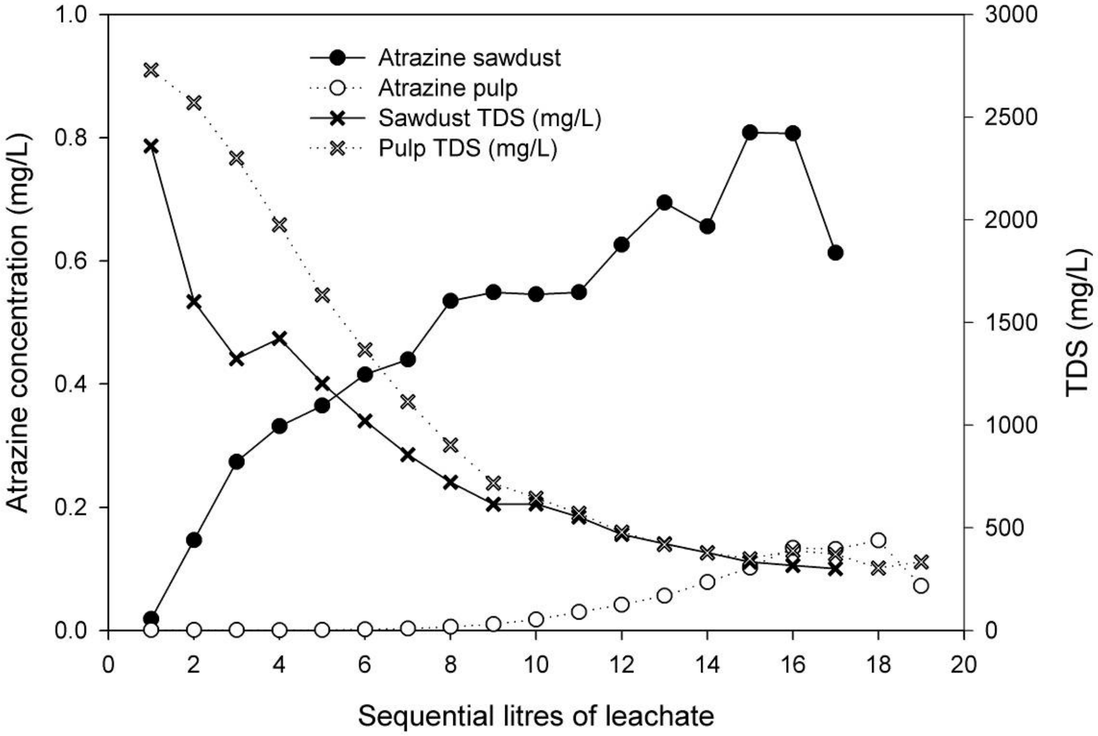


Fig. 6.18: **Atrazine concentration and TDS in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

Unlike the case with dissolved solids, turbidity was considerably reduced in the media combinations (Fig. 6.19) where it appears that the organic layer had protected the Horotiu soil from degradation by the raindrops and the soil in turn effectively filtered the leachate from the organic layer resulting in leachate of much lower turbidity than that from any of the individual media (Table 6.10). Again, there was no indication of relationship between leachate turbidity and atrazine concentration.

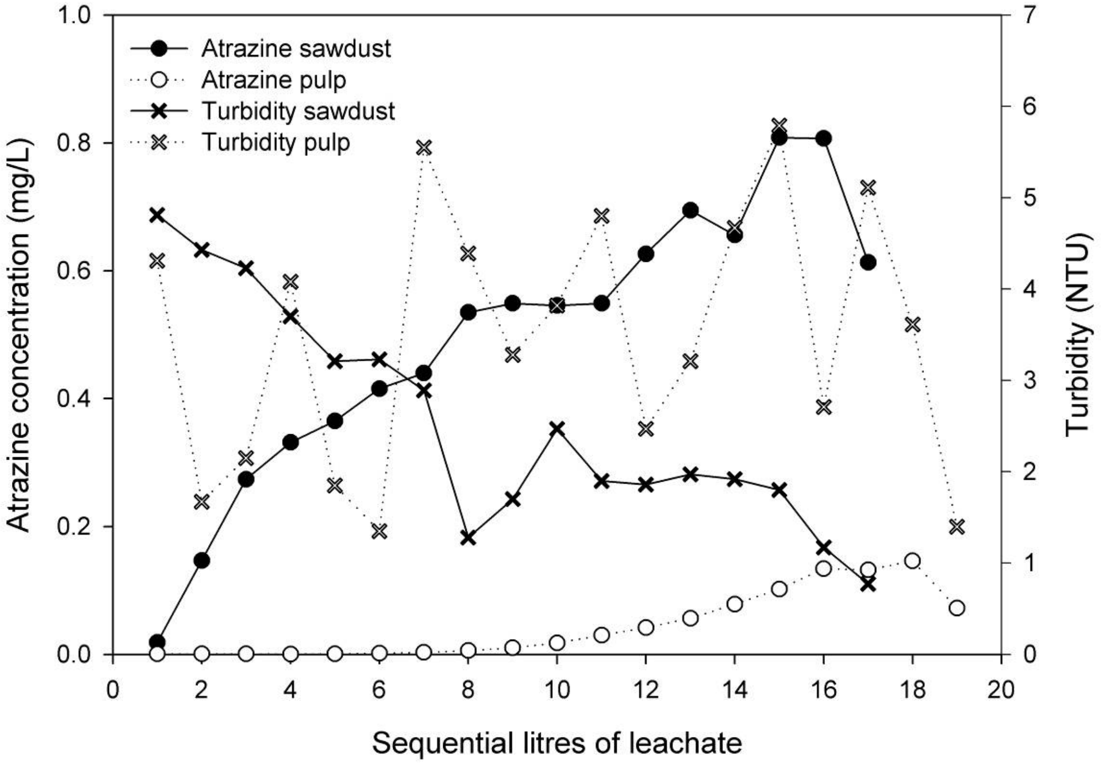


Fig. 6.19: **Atrazine concentration and turbidity in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

The pH of the leachate from both organic media/Horotiu soil combinations rose steadily but still remained slightly acid for the duration of the experiment (Fig.6.20). Although the rise in pH of the leachate was accompanied by an increase in atrazine concentration and regression analysis indicates a relationship (Table 6.11), it is probably not a causal relationship as there is no supporting evidence in the literature to suggest that movement of atrazine is dependant on pH. Although there was a high level of atrazine leaching from the sawdust/Horotiu soil combination, there was much less leaching from the paper pulp/Horotiu soil combination, even though the pH was similar for both.

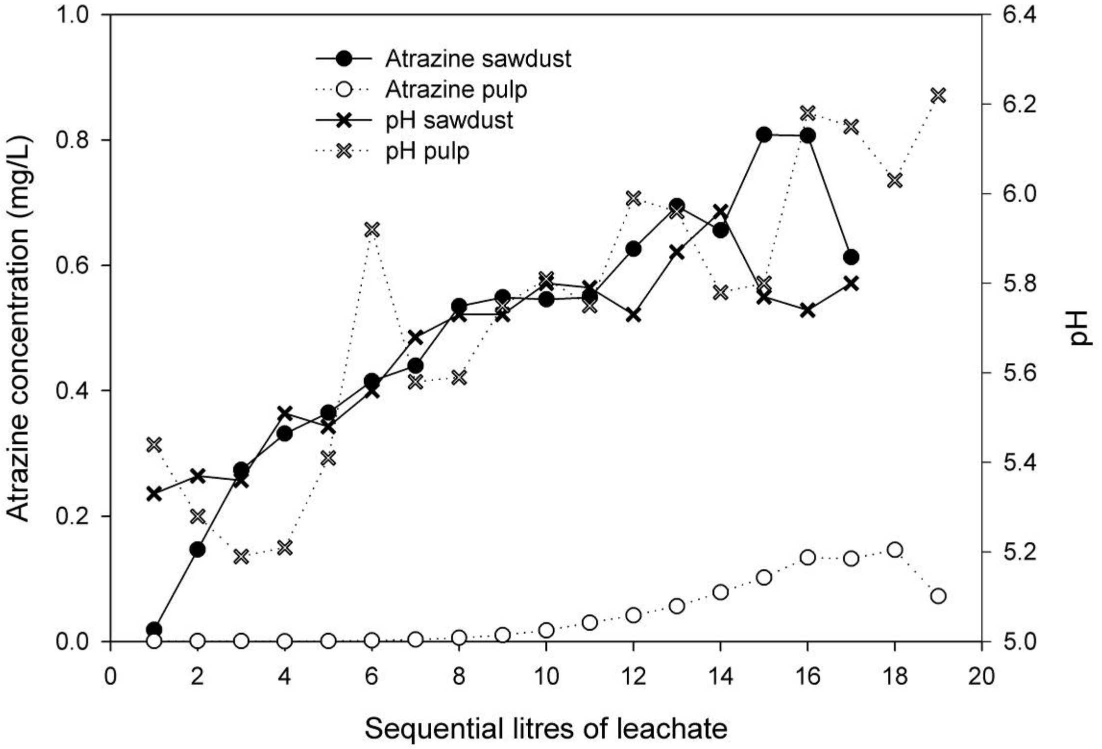


Fig. 6.20: **Atrazine concentration and pH in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

The results for bromacil are presented in Figs 6.21 – 6.24 and although bromacil was more water soluble than atrazine there is still no evidence that any of the measured leachate properties had any impact on the leaching of this herbicide (Table 6.11). Of the two herbicides evaluated here, bromacil has the highest pKa and consequently most likely to be influenced by the pH of the leachate. In this experiment the pH of the leachate from the paper pulp/Horotiu combination showed great variation but overall it was higher than for the sawdust/Horotiu soil combination (Fig. 6.24). However, bromacil was more mobile in sawdust than in the paper pulp (Table 6.9).

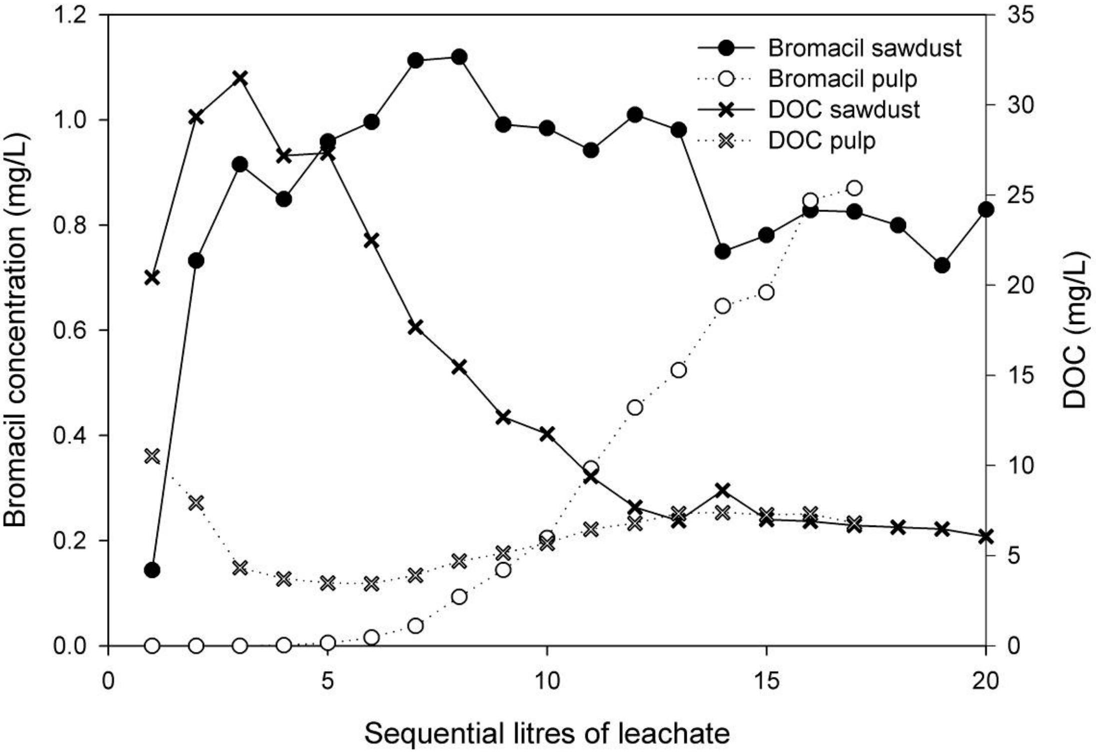


Fig. 6.21: **Bromacil concentration and DOC in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

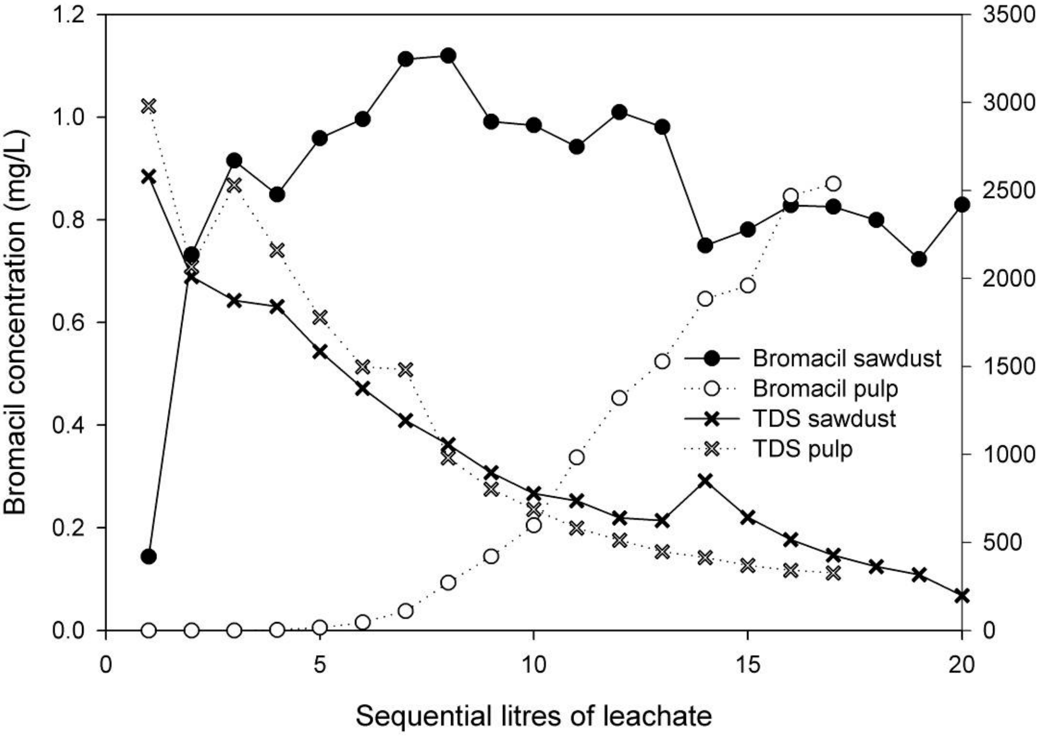


Fig. 6.22: **Bromacil concentration and TDS in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

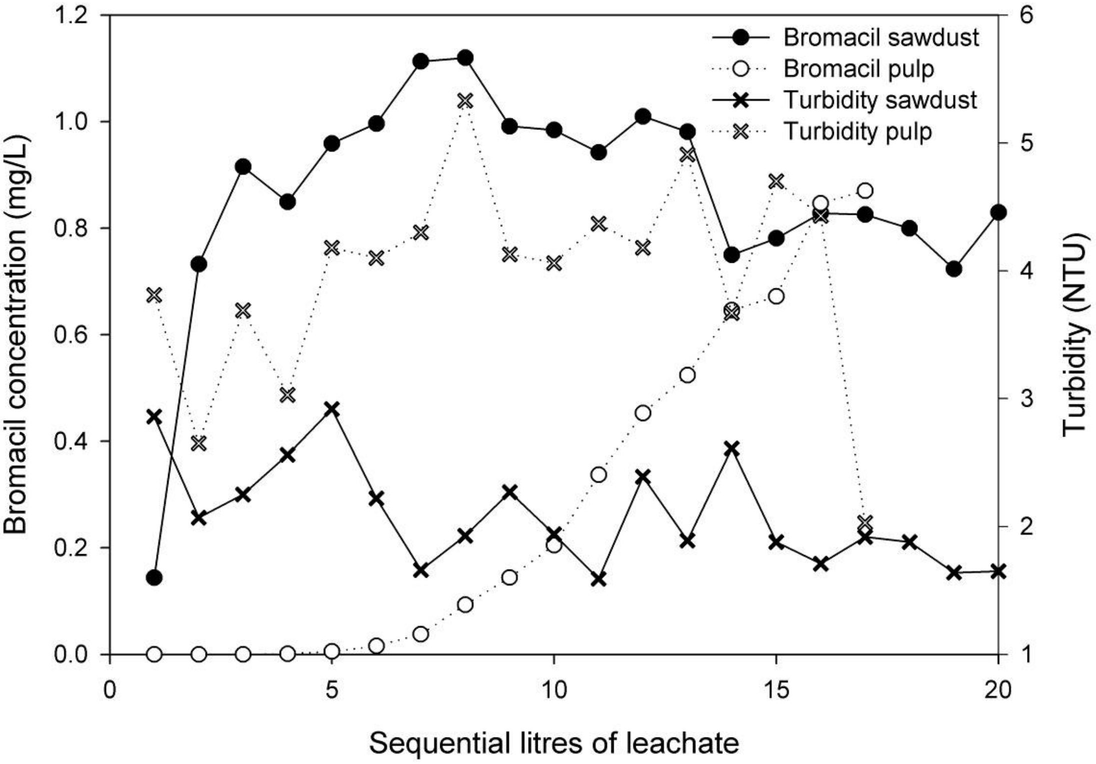


Fig. 6.23: Bromacil concentration and turbidity in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.

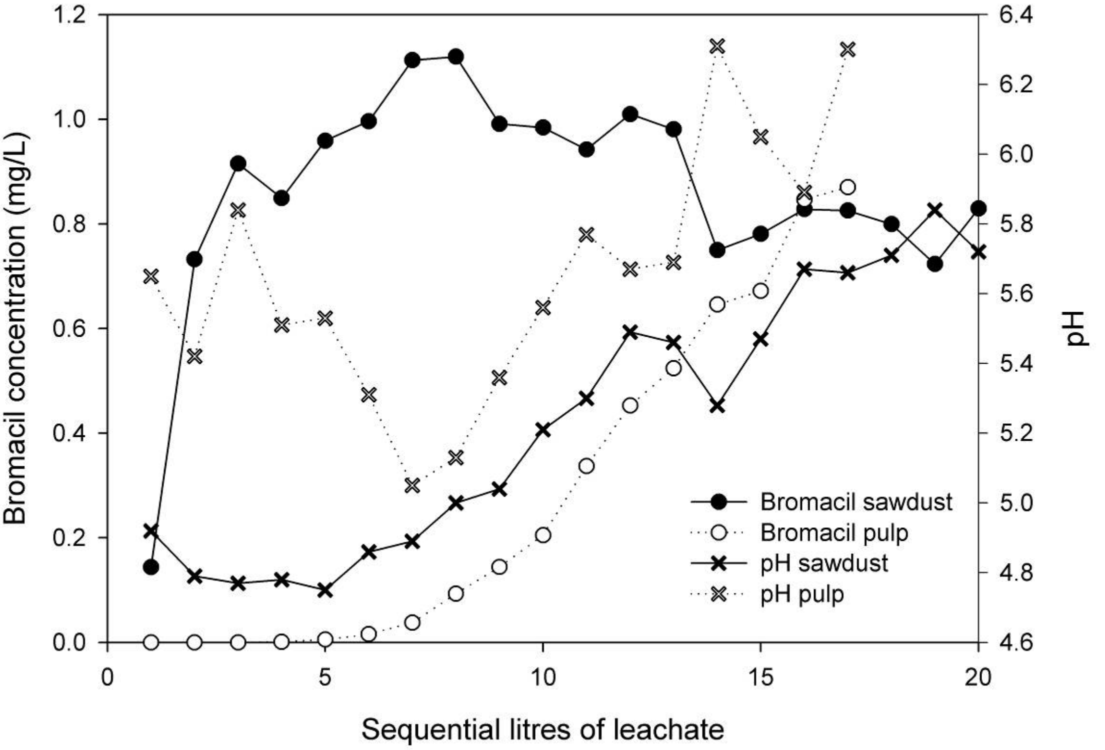


Fig. 6.24: **Bromacil concentration and pH in each sequential litre of leachate collected from a profile comprising 10 cm of Horotiu soil topped with 5 cm of either paper pulp or sawdust.**

Table 6.11: Pearson's correlation coefficients (r) for sequentially measured herbicide concentration and leachate properties for Experiment 5.

	Pearson's correlation coefficient (r)			
Media	pH	Turbidity (NTU)	TDS (mg/L)	DOC (mg/L)
	Atrazine			
Paper pulp/Horotiu soil	0.74	0.226	-0.688	0.506
Sawdust/Horotiu soil	0.877	-0.898	-0.958	-0.913
	Bromacil			
Paper pulp/Horotiu soil	0.766	-0.029	-0.800	0.430
Sawdust/Horotiu soil	-0.019	-0.343	-0.380	-0.037

6.5 Discussion

6.5.1 *Column Bioassay Studies*

That atrazine and bromacil are highly mobile in the soil environment has been widely reported previously (Briggs 1990; Close 1993b; Close 1993a; James et al. 1994; Close et al. 1998; Close et al. 1999; Green et al. 1999; Zhu & Li 2002; Close et al. 2003; James et al. 2003; Ma et al. 2004b). However, their movement through organic media is largely unknown and this led to the hypothesis being tested here, that high organic matter soil amendments reduce the leaching of herbicides through the soil profile. The direction of the hypothesis is based on the knowledge that herbicide adsorption is a key determinant of herbicide leaching and that herbicide adsorption is highly influenced by soil organic matter content (Section 2.2.1). Therefore, it was assumed that the very high organic carbon content of paper pulp and sawdust would restrict the movement of atrazine and bromacil through the profile when compared to two common cropping soils (Horotiu and Mangateretere).

In a study using columns packed with a sandy soil, Zandvort et al. (1980) found that bromacil moved rapidly through a sandy profile with 200 mm of water moving it more than 32 cm down a 6-cm diameter column. Futch & Singh (1999) found that 32 mm of water added to the top of the column was sufficient to move bromacil 34.7 cm down the column. Using a sandy soil (97% sand, 1.1% organic matter and pH 6.4) in 130-cm columns and bioassay to determine leaching depth, Reddy & Singh (1993) found that 50 mm of rainfall moved bromacil to 110 cm down the column. Also, using 8-cm long columns, they found 30% of the applied bromacil in the first pore volume (the volume of water required to fill the pore space in the soil, in this case ≈ 30 mm rainfall) leached from a saturated soil, with 43% in the second pore volume and the first five pore volumes contained 100% of the applied bromacil.

In all these experiments with sandy soils in packed columns, bromacil proved more mobile than in Experiments 1 and 2 where 48 – 96 mm of water moved bromacil only between 20 and 30 cm with little found in the first 100 mL of leachate, depending on the media. This is consistent with the theory that higher levels of organic carbon in the soil will restrict the leaching of herbicides through the profile as the sandy soils all contained considerably less organic carbon than the Mangateretere and Horotiu soils used in the present experiments.

For atrazine, Fleming et al. (1992), also using a sandy soil (98% sand and 0.7% organic matter), found that 76 mm of water applied over 2 h moved 14% the herbicide to the 30 –

35 cm depth while 152 mm of water over 4 h moved 25 % of the applied atrazine to the 35 – 40 cm depth. However, when 152 mm of water was applied over a 12-day period there was significantly less movement of the herbicide with only 11% of the atrazine found in the 30 – 35 cm layer. Rodríguez-Cruz et al. (2007) demonstrated in a sandy soil with very low organic matter (0.58% OM and 82% sand) that atrazine leached more rapidly (peak concentration of 30% of applied at about 1 pore volume of leachate and 95% leached with 5 pore volumes) than in a soil containing more organic matter and less sand (1.76% OM and 56% sand) where peak elution (15% of applied atrazine) occurred after 2 pore volumes and about 7 pore volumes were required to elute 95% of the atrazine.

Similar to the case for bromacil discussed above, here atrazine was demonstrated to be more mobile in sandy soils with low organic matter content than in either the Mangateretere or Horotiu soils which have higher organic carbon content. However, in the present experiments, atrazine was leached to significantly greater depths of the columns in Experiment 1 compared to Experiment 2 while the leaching of bromacil was similar in both experiments. These differences for atrazine can be accounted for by the length of the leaching event. In Experiment 1 the water was added over a 42 h period while in Experiment 2 it was added over a 97 h period. This result is similar to that of Fleming et al. (1992) even though the leaching period in the two experiments reported here only differed by a factor of 2 while that of Fleming et al. (1992) differed by a factor of 72. It has long been recognised that the distribution coefficients (K_d) of many herbicides increase with exposure time (Walker 1987; Connaughton et al. 1993; Walker et al. 1999; Renaud et al. 2004a). Renaud et al. (2004a) demonstrate this to be due to rates of diffusion, as the slowing diffusion of the herbicide molecule over time from within the adsorbing substrate to the soil pore space becomes the rate limiting step in desorption kinetics. Thus K_d, although a very indicator of potential herbicide mobility, it is not a perfect one.

The two experiments reported here that used packed columns and bioassays to determine the distance the herbicide leached produced mixed results. Overall, the movement of both atrazine and bromacil was restricted in the paper pulp but they often moved further in the sawdust than in the Horotiu soil, and always moved further in the sawdust than they did in the Mangateretere soil (Table 6.2). Comparing these results with the distribution coefficients determined earlier (Table 4.5) there is a good match for two of the four media. Paper pulp has the second largest distribution coefficient for both herbicides (K_d = 19.3 and 5.7 for atrazine and bromacil respectively) and this medium was found to be most restrictive to the movement of these herbicides. Distribution coefficients were the lowest for the Mangateretere soil (4.14 and 1.1 for atrazine and bromacil respectively) but those for the Horotiu soil were only slightly higher (K_d = 5.64 and 1.22 for atrazine and bromacil respectively) and both herbicides frequently leached the more in the Horotiu soil, presumably due to its much higher sand content (Table 3.1). The anomalous medium was the sawdust. The distribution coefficients for the two herbicides in sawdust are higher than for paper pulp (K_d = 29.6 and 10.3 for atrazine and bromacil respectively) yet the herbicides in sawdust always leached further than in the paper pulp, Mangateretere soil and sometimes more than the Horotiu soil.

Results from the column bioassay studies are consistent with other studies for the soils in that there is increasing retardation of herbicide movement with increasing organic carbon content. However, results with the high organic media were not entirely consistent with this theory as although the paper pulp restricted the downward movement of atrazine and bromacil more than the two soils did, the sawdust did not. Thus based on these studies the original hypothesis that high organic matter soil amendments reduce the leaching of herbicides was supported by the results from the paper pulp but not by those from the sawdust.

Sawdust has two obvious properties that could contribute to this result. The first is the physical nature of the medium which is a coarse, granular product with few small particles and a large macropore volume. Macropore volume is one of the parameters used in modelling the rapid movement (preferential flow) of pesticides through the soil profile (Jacobsen et al. 1997; Roulier & Jarvis 2003). Rapid water flow precludes sufficient contact time for adsorption to occur especially if the adsorption sites are internal to the large sawdust particles. In the present experiments this characteristic of the sawdust is a probable cause of the greater movement of the herbicides through this medium. The second property is the surface area and nature of the surface for adsorption. The sawdust used in the present experiments was fresh with no obvious signs of decay. The particles retained their cellulose structure which is largely impervious to water. This leads to a very low surface area to mass ratio and reduced sites at which internal adsorption can occur (Kookana et al. 1998; Bendfeldt 1999; Bendfeldt et al. 2001). Sawdust is frequently used as a sorbent for removal of pollutants such as dyes and heavy metals from aqueous solution (Malik 2003; Özacar & Sengil 2005), but it is frequently further processed, usually composted and/or heat treated, to promote its sorptive ability (Malik 2003).

The present experiments demonstrated that sawdust was highly sorptive, producing the highest K_d values of the four media tested (Table 4.5). However, it appears that in undecayed sawdust the sorption is weak due to few internal adsorption sites being present. The high level of surface adsorbed herbicide is readily desorbed in a fast equilibrium (Mamy & Barriuso 2007) and thus fails to prevent the rapid movement of the herbicides through the profile as demonstrated in the present study. The case for weak adsorption (Section 2.2.1) is supported by the relative ease of recovery of herbicides from the sawdust compared to the other three media (Tables 4.4 and 5.4).

In experiments such as those reported here, meaningful comparisons between treatments can only be made when accurate and reproducible data on leaching can be obtained. Bioassays, although able to demonstrate good sensitivity to herbicides can provide variable results, particularly when the concentration of the herbicide is within the ED_{50} – ED_{90} range (Streibig & Kudsk 1993). This is also clearly demonstrated in Figs. 6.3 – 6.6 where the errors of the individual data points are on occasion quite large. However, treatment of these data with the Bayesian smoothing technique (Figs 6.7 – 6.10) produced an ED_{90} value (deemed to be the leaching depth of the herbicide) with greater certainty and a smaller error than could be interpreted from the simple plots (Figs 6.3 – 6.6).

6.5.2 *Rainfall Studies*

The results for the rainfall leaching experiments with the Mangateretere soil are not very useful due to lack of infiltration. However, the other three media generally performed as expected from their distribution coefficients. Atrazine leached less from the paper pulp while sawdust and the Horotiu soil were similar to each other. Bromacil leached most from the Horotiu soil while paper pulp and sawdust were similar to each other. Although the overall results generally as predicted by the distribution coefficients, the detailed leaching pattern for the sawdust was not. Whereas for both herbicides in paper pulp and Horotiu soil there were no residues detected in the early leachate samples, the two herbicides were detected in all leachate samples collected from the sawdust lysimeter.

With atrazine these results are also reflected in the distance the herbicide is moved through the media profile, i.e. the greatest movement in the Horotiu soil and sawdust and least in the paper pulp. Bromacil however, moved more in the paper pulp than in the Horotiu soil and sawdust. This was attributed to the effect of the high pH paper pulp on the solubility of the weak acidic bromacil molecule (Eisenberg et al. 1987). However, greater movement of bromacil through the paper pulp did not relate to greater quantities in the leachate but rather lead to high concentrations in the bottom layer of the paper pulp (Fig. 6.14). Whether this would have leached out in high concentrations if further rainfall had been applied is unfortunately unknown but indications are that it would as the concentration of bromacil in the leachate from the paper pulp was still increasing while concentrations of bromacil in the leachate from both the Horotiu soil and sawdust had already peaked (Fig. 6.13).

Having demonstrated that most of the results obtained in these experiments are readily explained by the distribution coefficients of the herbicides or their solubility in an alkaline media, can the properties of the leachate derived from these media explain the exceptions and/or cast light on the processes involved in herbicide transport? The most obvious anomalous results were for sawdust. In the packed column leaching experiment both atrazine and bromacil leached further than was expected according to the previously determined distribution coefficient and in the rainfall trial residues of both herbicides were detected in the leachate earlier than expected. The same phenomenon is most likely responsible for both these results, which is that small quantities of the herbicides were very mobile in the sawdust and very quickly leached through and out of the profile. In the packed column experiments this phenomenon was responsible for plant dieback at depths greater than expected and in the rainfall experiments in the premature expression of residues from the profile. Although the sawdust produced a large quantity of dissolved organic carbon which was quickly eluted from the profile, the correlation of herbicide concentration to this was either poor or the relationship was a negative one (Table 6.11).

Using an experimental setup similar to that used for these experiments, Konomi et al. (2005) found in a calcareous soil (3.1% organic matter, 60% sand, 12% clay and pH 7.3) that about 1.5% of the applied atrazine was present in the first leachate sample collected. Atrazine concentration in the leachate peaked at about 3.3% just prior to the equivalent of one pore volume passing through the lysimeter and then dropped rapidly with very little atrazine in the leachate between 4 and 6 pore volumes after commencement. However, when organic compost was added to the soil at the equivalent of 134 kg/ha, no (or very little) atrazine was detected in the first leachate sample. Also for two types of compost with 26 and 28% organic carbon peak elution of atrazine was both reduced and delayed while a third compost with 16% organic carbon delayed elution but did not reduce the peak concentration.

Although in the experiments of Konomi et al. (2005) the organic material was mixed into the soil, the results were similar to ours for paper pulp (where the organic material was in a layer atop the soil) in that the addition of high organic carbon significantly reduced and delayed the leaching of atrazine from the soil profile. However, this differed for sawdust as in the present experiments the addition of sawdust to the top of the soil profile increased the quantity of atrazine in the leachate.

Results from the rainfall studies are also inconsistent with the simple theory that soil media with higher levels of organic carbon will retard the movement of herbicides down the profile. The downward movement and leaching of atrazine was retarded by the paper pulp but results for sawdust and the Horotiu soil were very similar despite the very large difference in their organic carbon contents. Conversely, bromacil was more mobile in the paper pulp and less mobile in the sawdust compared to the Horotiu soil. Thus based on these studies the original hypothesis that high organic matter soil amendments reduce the leaching of herbicides has to be considered false. However, the behaviour of the various growing media can be rationalised in terms of their very different physico-chemical characteristics in relation to herbicide sorption and movement of water (Kookana et al. 1998).

6.5.3 *Influence of Media Leachate Properties in the Transport of Atrazine and Bromacil*

The conclusion drawn earlier from the results of the leaching experiments was that none of the measured properties of the leachate appeared to have any influence on the amount or rate of herbicide leached with the exception of bromacil being more mobile in the high pH paper pulp. Shelton & Miller (2002) were also unable to find a relationship between atrazine flux in surface runoff and either total dissolved solids, dissolved oxygen or turbidity of the runoff water.

As discussed previously (Section 2.3.1) DOC has been both implicated in the transport of pesticides as well as absolved of any involvement. In both rainfall and leaching studies reported here sawdust produced the largest quantities of DOC but the highest concentration was found in either the second or third aliquot (L) of the leachate samples and then declined rapidly after that. Compared to this the concentration of atrazine rose steadily and gave a very good negative relationship to DOC (R^2 = 83.4, Table 6.11). Conversely there was no relationship between sawdust DOC and bromacil concentrations as although the concentration of both initially rose sharply, that of the DOC also declined rapidly while that of bromacil held steady. DOC, as a property of the media, should be evenly distributed throughout and therefore it would be expected to appear in the leachate immediately and then remain a steady concentration as the DOC from higher levels was percolated through the profile. However, this was not the case as the concentration of DOC from the sawdust steadily declined from an initial high concentration. This indicates that the sawdust DOC was highly mobile and that DOC from throughout the profile, including the surface where the herbicide was located, was very quickly eluted. However, there is no spike in the herbicide concentration and therefore there was no evidence herbicide was moved preferentially through the profile in association with the DOC.

The elution of DOC from the paper pulp followed a different pattern to that of the sawdust. Overall the paper pulp produced significantly less DOC and except for a small flush at the beginning its concentration slowly increased with successive samples for the first 10 – 12 samples. Because the leaching patterns for the two herbicides also showed the same gradual increase in concentration, the regression analyses showed a weak relationship (R^2 of 25.6 and 18.4 for atrazine and bromacil respectively). However, examination of the leachate concentration patterns (Figs 6.17 and 6.21) reveals that there is not much commonality to base a real relationship on.

These conclusions are supported by the recent findings of other researchers. Smith Jr et al. (2006) found that herbicides with high solubility and low organic partitioning coefficients (K_d) tended to be transported in the solute phase as opposed to being attached to particles. This is supported by Petersen et al. (2003) who found that the turbidity of surface drainage water was positively and strongly correlated to the movement of pendimethalin (low solubility, large K_d, Table 2.1) whereas it was not correlated to the concentration of ioxynil, which has a solubility (42 mg/L) and K_{oc} value (210) similar to atrazine (Petersen et al. 2003; Malouki et al. 2004). Spark & Swift (2002) also found the naturally occurring DOC in five soils of medium to high OC content had little or no effect on the sorption/transport characteristics of four diverse pesticides including atrazine.

Central to these two extremes is the herbicide napropamide, with moderate solubility (70 mg/L) and intermediate K_{oc} value (462) (Wauchope 2006), which showed modified behaviour in the presence of DOC with just under 6% of the applied napropamide moving as DOC complexes (Williams et al. 2000). Working with the same soil Williams et al. (2002) found 7% of the applied napropamide underwent DOC-facilitated transport in a soil amended with sewage sludge compared to only 2.4% in the unamended soil.

One of the aims of the experimental setup used here was to replicate natural rainfall in both intensity and kinetic energy. It is anticipated that natural rainfall would have a similar effect on cultivated soil in the field to the results reported here. In the case of the Mangateretere soil (and to a lesser extent in the Horotiu soil) rainfall of sufficient intensity could result in reduced infiltration and build-up of herbicide enriched surface water which is then likely to result in significant runoff and movement of herbicide off-site. In a packed lysimeter experiment similar to those reported here Heppell et al. (2004) found that losses of the herbicide isoproturon increased from 0.25% to 0.5% of that applied when the soil surface was partly sealed and infiltration reduced.

6.6 Conclusions

The hypothesis being tested in this part of the investigation was that high organic matter soil amendments reduce the leaching of herbicides through the soil profile. The reasoning behind this was the knowledge that herbicide adsorption is a key determinant of herbicide leaching and that herbicide adsorption is highly influenced by soil organic matter content. Therefore, it was assumed that the very high organic carbon content of paper pulp and sawdust would restrict the movement of atrazine and bromacil through the profile when compared to two common cropping soils (Horotiu and Mangateretere soil). This hypothesis was tested using two different experimental setups. In the column leaching experiments, both atrazine and bromacil leached less distance in the paper pulp, followed by the Mangateretere soil, the Horotiu soil and sawdust where the highest levels of movement occurred.

Results from simulated rainfall and lysimeter followed a similar pattern. Thus the hypothesis held true for the behaviour of both atrazine and bromacil in paper pulp which proved retentive to leaching compared to the two cropping soils. However, for the sawdust organic matter content had less bearing on the leaching of the herbicides than other factors. These included its large particle size and related pore volume which allowed preferential flow, and the low particle surface area to weight ratio of the undecayed nature of the cellulose offering fewer internal binding sites for the herbicides. Also, leaching was generally greater in the sandier Horotiu soil compared to the Mangateretere soil even though the Horotiu soil contains slightly more organic carbon.

The herbicides applied to the media/Horotiu soil combinations exhibited behaviour that could be predicted from the study of their behaviour in the single media experiments. Both atrazine and bromacil leached more from the soil topped with a layer of sawdust than from that topped with paper pulp.

CHAPTER 7

CONCLUDING DISCUSSION AND IMPLICATIONS OF RESULTS

CHAPTER 7: CONCLUDING DISCUSSION AND IMPLICATIONS OF RESULTS

7.1 Reason for this Research

The recycling of waste products in a sustainable manner is important in modern society. Forestry waste products have not been well utilised with the consequent build-up of large dumps of sawdust and paper-pulp waste. Using these products in the broad-acre, arable agriculture industry is one method of utilising significant quantities of the stockpiled waste. Although many over-tilled soils would likely benefit from the additional organic carbon that soil amendments would provide, simply spreading sawdust onto the soil surface would be uneconomical. Thus, the “Rich Ditch” cropping system could be a novel way to overcome this constraint, but within this cropping system herbicides would still be required for control of weeds. This led to questions regarding how herbicides would perform and be influenced by the presence of these high organic carbon amendments. From such questions came the experimental hypotheses which have been addressed in Chapters 3 to 6 of this thesis.

7.2 Summary of Conclusions

7.2.1 *Chapter 3: Bioavailability and Plant Uptake*

The bioavailability of three cropping herbicides was compared in two arable soils and two forestry waste products through glasshouse bioassay experiments. Herbicide bioavailability in each case was reduced in the paper pulp compared to the two soils but herbicide bioavailability in sawdust differed for the different herbicides. The hypothesis that high organic matter soil amendments decrease bioavailability of herbicides to plants was well supported by the results for the high organic matter paper pulp amendment, but the results were less supportive for the high organic matter sawdust amendment which exhibited inconsistent behaviour.

7.2.2 *Chapter 4: Adsorption*

The batch equilibrium method was used to determine adsorption of five herbicides in the four media investigated in Chapter 3. For these media, increases in the soil/solution distribution coefficients (K_d) were strongly correlated to the organic carbon content. Additionally, the distribution coefficient based on organic matter (K_{oc}) was a good descriptor of adsorption which was independent of organic carbon content. The hypothesis being tested through these experiments was that high organic matter soil amendments increase the soil/solution distribution coefficient of herbicides. This hypothesis was very well supported by results for all the five herbicides evaluated here.

7.2.3 *Chapter 5: Persistence and Degradation*

Degradation of two herbicides was carried out in four different temperature regimes and in sterilised media. Although microbial degradation was an important factor in the mineralisation of these herbicides, overall, the pH of the media had a more profound effect on the desorption and subsequent degradation rate than the organic carbon content. The hypothesis being tested in this part of the investigation was that herbicides degrade more rapidly in the presence of high organic matter soil amendments. It was concluded the hypothesis was only partially correct as organic matter content *per se* did not strongly relate to degradation rates which were mainly governed by pH and microbial activity.

7.2.4 *Chapter 6: Mobility and Leaching*

Leaching studies were carried out with two herbicides in top-irrigated packed columns as well as in a packed lysimeter with simulated rainfall. Results from the two experimental setups varied due to the impact of the simulated rainfall on the surface structure of the media. Organic carbon content, pH and structure of the media were all factors which affected the movement of water and leaching of the two herbicides. The hypothesis being tested in this part of the investigation was that high organic matter soil amendments reduce the leaching of herbicides through the soil profile. The hypothesis was true for paper pulp but for sawdust organic matter content had less bearing on the leaching of the herbicides than other over-riding factors, such as hydraulic conductivity, that were media specific. In sawdust, these also included its large particle size and related pore volume which allowed preferential flow, and the low particle surface area to weight ratio of the undecayed nature of the cellulose offering fewer internal binding sites for the herbicides.

7.2.5 *Overall*

In these studies the original hypotheses were generally shown to be not true with herbicide adsorption being the most noticeable exception. The reason for this was the hypotheses simply assumed the behaviour of herbicides would be more strongly influenced by the organic carbon content than other properties. However, in practice other characteristics of the two high organic matter amendments frequently had greater impact on the behaviour of herbicides than did their organic carbon content alone. This has important ramifications for the use of these waste products in agriculture.

7.3 Implications of these Findings

7.3.1 *Crop Susceptibility to Herbicide Phytotoxicity*

Foremost among a growers considerations when choosing a herbicide is that of crop safety. Under normal circumstances this information is clearly presented on the herbicide label, where crops in which the herbicide can be used and the rates of application are documented. However there are no guarantees that this information will hold true when the product is used in radically different growth media. If, for instance in the “Rich Ditch” growing system, the crop is grown in a trench filled with coarse structured, undecayed sawdust and herbicide is sprayed onto the surface of the sawdust, would the crop plants be more susceptible to phytotoxic damage? The original hypothesis, that increased adsorption in the high organic matter media would lead to lower bioavailability and reduced crop damage, did hold true for the paper pulp but not for sawdust.

In Chapter 4 the adsorption properties of the four media were compared and of the four hypotheses proposed throughout this thesis, the one postulating that herbicide adsorption is greater in high organic matter amendments is the only one which showed convincing supportive results. Relating this to the fact that a herbicide molecule must be in the soil solution before it is able to be absorbed by a plant root (Günther et al. 1989; Schroll et al. 1994; Trapp et al. 1994), it is logical to assume, that the soil solution distribution coefficient (K_d), which describes the amount of herbicide in solution, should partly or wholly describe the plant bioavailability of the herbicide. However, exposure time of the root surface to the herbicide is also important, as the herbicide in the soil solution is in equilibrium with the adsorbed material and the solution will be recharged from this source. But, there is always hysteresis and an element of non-reversibility in the adsorption/desorption equilibrium (Connaughton et al. 1993; Ma et al. 1993; Weber et al. 1998; Bhandari & Lesan 2003; Taylor et al. 2004; Mamy & Barriuso 2007) and this will affect the quantity of herbicide available for plant uptake, especially when exposure time is short. Also, desorption is inversely proportional to adsorption (Mamy & Barriuso 2007), so there will be less desorption from strongly adsorbed herbicides or from media which is a stronger sorbate.

Results presented in Chapter 3 on crop sensitivity show that bioavailability of the more water soluble herbicide alachlor exhibited the greatest variation between various media but this was not related to organic carbon content. For example, broccoli grown in sawdust was significantly more susceptible than when grown in paper pulp (Figs 3.3 and 3.4), although sawdust had twice the organic carbon content of paper pulp (Table 3.1). Nor is it related to K_d values, as those for paper pulp and sawdust are much higher than for the two soils (Table 4.5) yet there was greater phytotoxicity to plants grown in sawdust compared to the other media. This can best be explained by weak bonding/rapid desorption of the herbicide molecule from the surface of the sawdust allowing rapid recharge of the soil solution. This weak bonding/fast reaction overcomes the reduced herbicide in solution and results in greater phytotoxicity to plants grown in sawdust.

Thus, neither organic matter content nor K_d value are an adequate predictor of crop susceptibility to herbicide phytotoxicity in high organic soil amendments.

7.3.2 *Efficacy of Weed Control Programmes*

In this study, investigating the effect of the soil amendments on efficacy of weed control involved plant species with a much lower tolerance to the herbicides (Section 3.4.3). For these plants the efficacy of the herbicides was generally lower in both the sawdust and paper pulp compared to the two soils (Figs 3.11 – 3.22). The effect was more pronounced with the more soluble alachlor, where efficacy was reduced by factors of 5 – 10, compared to pendimethalin where efficacy was reduced only by factors of 0 – 3. Also, most of the sensitive species showed greater sensitivity to herbicides when grown in sawdust compared to paper pulp (Tables 3.8 and 3.9).

In the previous section it was concluded that K_d was not always a good indicator of crop susceptibility. However, this might not be true for highly sensitive plant species where the amount of herbicide required to cause phytotoxic damage is much lower. Thus for these species, to test if the K_d value is comparable to the plant bioavailability of the herbicide the relationship between the K_d and ED_{50} values was examined, i.e. to see if the ED_{50}/K_d ratio would be constant irrespective of the growing media. The average of the K_d and ED_{50} values determined in these experiments (Tables 3.9 and 4.5) are presented in Table 7.1 along with their ratios. Taking into consideration the experimental errors, which are cumulative, the results presented in Table 7.1 generally show strong relationships although there are a few anomalies e.g. chlorpropham and pendimethalin in the sawdust.

Table 7.1: **Relationship between ED_{50} values (Table 3.7) and the distribution coefficients (K_d, Table 4.5) for combinations of herbicides, bioassay species, and growing media.**

			Exp. 3		Exp. 4	
Bioassay species	Growing media	K_d (mL/g)	ED_{50} (g a.i./ha)	ED_{50}/K_d	ED_{50} (g a.i./ha)	ED_{50}/K_d
		Alachlor				
Millet	Horotiu	5.5	20	3.6	38	6.9
	Mangateretere	4.8	22	4.6	48	10.0
	paper pulp	26	108	4.2	434	16.7
	sawdust	35	91	2.6	489	14.0
Ryegrass	Horotiu	5.5	55	10.0	54	9.8
	Mangateretere	4.8	59	12.3	120	25.0
	paper pulp	26	257	9.9	1927	74.1
	sawdust	35	452	12.9	2112	60.3
		Chlorpropham				
Ryegrass	Horotiu	22	367	16.7	291	13.2
	Mangateretere	17	70	4.1	94	5.5
	paper pulp	45	560	12.4	396	8.8
	sawdust	185	307	1.7	412	2.2
Cress	Horotiu	22	801	36.4	2526	115
	Mangateretere	17	654	38.5	2129	125
	paper pulp	45	1398	31.1	2583	57.4
	sawdust	185	732	4.0	1579	8.5
		Pendimethalin				
Cress	Horotiu	502	936	1.9	2460	4.9
	Mangateretere	271	800	2.9	1760	6.5
	paper pulp	723	1230	1.7	1552	2.2
	sawdust	3556	521	0.2	381	0.1
Sorghum	Horotiu	502	-	-	440	0.9
	Mangateretere	271	-	-	1903	7.0
	paper pulp	723	-	-	661	0.9
	sawdust	3556	-	-	518	0.2

The ED_{50}/K_d relationship was strongest for alachlor where most of the ratios were within a factor of 2 of each other for each combination of bioassay species and experiment (Table 7.1). However, for both chlorpropham and pendimethalin the relationship was not as well demonstrated, because in sawdust their bioavailability was considerably greater (low ED_{50}) than would be estimated from the K_d value. One possible explanation for this may be that the adsorption bonding on the poorly decayed sawdust is relatively weak as there are few internal adsorption sites where the stronger bonding occurs (Iglesias-Jiménez

1997; Ahmad et al. 2001; Mamy & Barriuso 2007). These weakly bonded herbicide molecules are readily and quickly desorbed from the sawdust into the soil solution where they are able to be absorbed by the plant roots (Weber et al. 1993; Mamy & Barriuso 2007). Another exception is for alachlor in the Horotiu soil where although the data show a good match in Experiment 3, it is less so in Experiment 4. Alachlor was consistently more bioactive (lowest ED_{50}) in the Horotiu soil compared to the other media in both experiments but this sensitivity appeared to be accentuated in Experiment 4, resulting in lower ED_{50}/K_d ratios (Table 7.1). Thus it is concluded that the measure of adsorption, the distribution coefficient (K_d) was not always an good predictor of crop susceptibility to herbicide phytotoxicity.

Another characteristic of the various media not yet discussed is its bulk density. The bulk density of the media evaluated here varies by a factor of 6.6 from the heaviest (Mangateretere soil) to the lightest (sawdust). A consequence of this is that when a herbicide is applied on a per hectare basis, the mass of media under the hectare (assuming a constant depth) and thus the total adsorption sites are likely to be quite different between the substrates. If there are limited sites for herbicide adsorption, then the quantity of media under a given area (volume) becomes critical. To investigate this the K_d values (Table 4.5) were normalised (K_{dd}) by multiplying with the bulk density of the medium (Table 3.1) and these figures are presented in Table 7.2. Whereas the K_d value has units of volume/mass, the K_{dd} is unitless but should be considered the distribution coefficient per unit volume (K_d is distribution coefficient per unit mass). Normalising the K_d for bulk density of the medium has the effect of equalising the distribution coefficient in the same manner as normalisation to organic carbon content (K_{oc}, Table 4.6). However, as organic carbon content and bulk density are related (Adams 1973; Thomas et al. 1996), then this is not a surprising outcome.

Table 7.2: Distribution coefficients (K_d) for five herbicides in four media normalised for bulk density of the medium (K_{dd}).

	Normalised distribution coefficient (K_{dd})				
Media	Alachlor	Atrazine	Bromacil	Chlorpropham	Pendimethalin
Horotiu soil	3.14	3.21	0.70	12.4	286
Mangateretere soil	4.19	3.60	0.96	14.4	236
Paper pulp	5.69	4.44	1.31	10.4	166
Sawdust	4.56	3.85	1.34	24.1	462

To evaluate the relationship between the distribution coefficient normalised for bulk density (K_{dd}) and the bioavailability as represented by the ED_{50} value (Table 3.9), the K_{dd} value was substituted for the K_d value in Table 7.1 and the resulting figures presented in Table 7.3. Comparing the two tables reveals that the K_d value was a better descriptor of bioavailability (less variance in the ED_{50}/K_d ratio; Table 7.1) for the more water soluble herbicide alachlor while the K_{dd} value was a better descriptor for bioavailability of the less soluble herbicide pendimethalin (less variance in the ED_{50}/K_{dd} ratio; Table 7.3). For chlorpropham, which has a water solubility intermediate to alachlor and pendimethalin, the results were mixed - with the K_d value being a marginally better descriptor for the bioassay species annual ryegrass but the K_{dd} value being a significantly better descriptor for the bioassay species garden cress.

Table 7.3: Relationship between ED_{50} values (Table 3.7) and the distribution coefficients normalised for bulk density (K_{dd}, Table 7.1) for combinations of herbicides, bioassay species, and growing media.

Bioassay species	Growing media	K_{dd} (mL/g)	Exp. 3 ED_{50} (g a.i./ha)	Exp. 3 ED_{50}/K_{dd}	Exp. 4 ED_{50} (g a.i./ha)	Exp. 4 ED_{50}/K_{dd}
		Alachlor				
Millet	Horotiu	3.1	20	6.5	38	12.3
	Mangateretere	4.2	22	5.2	48	11.4
	paper pulp	5.7	108	18.9	434	76.1
	sawdust	4.6	91	19.8	489	106
Ryegrass	Horotiu	3.1	55	17.7	54	17.4
	Mangateretere	4.2	59	14.0	120	28.6
	paper pulp	5.7	257	45.1	1927	338
	sawdust	4.6	452	98.3	2112	459
		Chlorpropham				
Ryegrass	Horotiu	12.4	367	29.6	291	23.5
	Mangateretere	14.4	70	4.9	94	6.5
	paper pulp	10.4	560	53.8	396	38.1
	sawdust	24.1	307	12.7	412	17.1
Cress	Horotiu	12.4	801	64.6	2526	204
	Mangateretere	14.4	654	45.4	2129	148
	paper pulp	10.4	1398	134	2583	248
	sawdust	24.1	732	30.4	1579	65.5
		Pendimethalin				
Cress	Horotiu	286	936	3.3	2460	8.6
	Mangateretere	236	800	3.4	1760	7.5
	paper pulp	166	1230	7.4	1552	9.3
	sawdust	462	521	1.1	381	0.8
Sorghum	Horotiu	286	-	-	440	1.5
	Mangateretere	236	-	-	1903	8.1
	paper pulp	166	-	-	661	4.0
	sawdust	462	-	-	518	1.1

As the K_{dd} value partly corrects for the situation where there are limited adsorption sites, it follows that for the more water soluble herbicide alachlor, number of adsorption sites is not a limiting factor in plant bioavailability. This is presumably because high water solubility allows greater permeation of the soil profile with a consequent greater number of adsorption sites being available. For this herbicide the unmodified distribution coefficient was a good indicator of its relative bioavailability in the different media (Table 7.1).

Conversely, the bioavailability of the less water soluble herbicide pendimethalin was better described by a modified distribution coefficient (K_{dd}) where fewer adsorption sites were available. This is presumably because low water solubility restricts permeation of the soil profile leading to fewer adsorption sites being available and in the less dense media this becomes a limiting factor. Thus for this herbicide, the distribution coefficient normalised for bulk density (K_{dd}) was a good indicator of its relative bioavailability in the different media (Table 7.3).

In the case of chlorpropham, which has an intermediate water solubility, results from Tables 7.1 and 7.3 indicate that either the K_d or the K_{dd} value can be used to assess its bioavailability to annual ryegrass but that the K_{dd} value is much better for assessing its bioavailability to garden cress. This is possibly due to the relative sensitivities of bioassay species and their root structures. Annual ryegrass has a fibrous root system with more roots near the surface where the chlorpropham is concentrated and this could be why it is more sensitive (Table 3.9) compared to garden cress which has a taproot with fewer roots near the surface.

It appears that the physico-chemical properties of the growing media that most affect crop susceptibility to herbicides are different to those which affect herbicide efficacy on more sensitive species. Herbicide uptake by both the crop and weed species is dependent on the herbicide being in the soil solution and available for uptake. However, where higher herbicide adsorption in sawdust leads to reduced efficacy on sensitive plants, it does not relate to the susceptibility of less sensitive crop species which actually show greater susceptibility when grown in this medium. So, although the K_d value was not a good indicator of crop susceptibility it was much better indicator of herbicide efficacy on sensitive species. For highly adsorbed herbicides the K_d value as a predictor of efficacy was further improved by normalising to bulk density (K_{dd}).

7.3.3 *Improved parameter estimation*

The use of an advanced curve fitting method based on the Bayesian smoothing technique (Upsdell 1994) improved the estimation of several parameters associated with biological systems. This technique fitted a curve directly to the experimental data points in a manner which minimised error variation and thus the resulting curve closely matched the observations. Traditionally, curves have been fitted to experimental data by choosing a curve type that best fits the data (exponential, sigmoidal, logistic etc.) and by adjusting variables within the relevant equation to obtain the best fit. This method however has some well documented shortcomings which were able to be overcome with the Bayesian smoothing technique used in this thesis.

In Chapter 3 Bayesian smoothed flexicurves produced improved estimations of the NOEL for all 24 different herbicide/growing media/plant species combinations. In many instances the improvement made was associated with the stimulation of plant growth by sublethal doses of herbicide (Figs 3.24 – 3.29). The resultant upward trend in the curve can not be modelled with the traditional logistic curve and thus the NOEL determined from a fitted logistic curve is often lower than the actual value. The Fitting of a Bayesian smoothed curve successfully overcame this problem.

In Chapter 5 the Bayesian smoothing technique was successfully used to produce more accurate estimations of the degradation variable, DT_{50} value, in instances where herbicide degradation was accelerated due to enhanced microbial activity. Traditionally, degradation following first-order kinetics is well represented by an exponential decay curve. However, when enhanced microbial activity contributes to the degradation there is frequently a lag phase (Fig. 5.24) as microbial populations build-up through availability of the new food source. This lag phase cannot be characterised in the exponential model and in these instances both logistic and sigmoidal models have been used to more accurately represent the decay curve. But as both these curves are symmetrical, they can not accurately represent both the lag phase and the degradation tail. This is because at low herbicide concentrations and with time, the accelerated degradation due to enhanced microbial activity tends to decrease and the curve shape reverts to the more traditional exponential shape. The Bayesian smoothed flexicurves used to analyse the degradation data in this thesis produced non-symmetrical curves which better fitted the experimental data and thus more accurate (smaller error) DT_{50} values were able to be determined from the fitted curves (Table 5.6).

In Chapter 6 the fitting of Bayesian smoothed curves allowed an accurate determination of herbicide leaching when using plants as bio-indicators of the presence of herbicide in the profile. The leaching of herbicides through the heterogeneous media columns was, understandably, not even and therefore the development of the plants grown in the columns was also not even. However, the Bayesian smoothing technique was able to fit non-symmetrical or freeform curves which better matched the experimental data and minimised the standard error of the estimates of herbicide activity derived from the curve. Thus, more reliable estimates of the leaching depth of the herbicides were able to be made, based on the point where the herbicide no longer had a significant impact on plant growth (Figs 6.7 – 6.10).

7.3.4 *Environmental Fate Modelling and the Present Experiments*

The two most crucial parameters associated with environmental fate modelling are the K_d and $t_{½}$ values described in Chapters 4 and 5 respectively. However, it appears that laboratory derived parameters are often inadequate for accurate prediction of pesticide fate using the presently available models. It is well known that herbicide sorption is time dependant (Connaughton et al. 1993; Mamy & Barriuso 2007) and we required a time-dependent sorption model to accurately predict dissipation of acetochlor and terbuthylazine (Ma et al. 2004b). Whether time-dependent sorption models could be defined from laboratory experiments does not appear to have been evaluated and could well be a worthwhile project in the future.

As the present laboratory based degradation studies were conducted in what is essentially a closed system (i.e. no inputs other than purified water and air), they do not accurately mimic field conditions where there are often other inputs of nutrients and micro-organisms and the herbicide is also diluted by dissipation. Therefore, laboratory half-lives for herbicides, derived in closed-system incubators, would be expected to be longer than field half-lives (Di et al. 1998). However, these concerns with laboratory data do not limit their usefulness. In the absence of any field-based data, laboratory derived information can provide a good approximation of the expected field behaviour, especially when compared to similar chemicals of which more is known as their relativity in laboratory sourced data will usually hold true for field conditions (Beulke et al. 2000; Boesten 2000). Also, for the reasons discussed earlier, predictions of herbicide dissipation in the field is usually overestimated when using laboratory based parameters (Ma et al. 2000; Ahmad et al. 2003; Ma et al. 2004a) and thus they are useful, conservative estimates concerning herbicide fate.

All the experiments described in Chapter 6 were carried out in lysimeters packed with sieved soil/soil amendments and also used non-soil media with coarse structure, low bulk density and extensive macropore space. The models developed for water and solute movement through undisturbed and homogenous soils are less likely to perform well in such situations than those designed to accommodate preferential flow. However, even models such as HYDRUS-2D and MACRO (Jarvis 1994), that can accommodate preferential flow, still use parameters such as hydraulic conductivity which are measured in columns of undisturbed soil (Šimunek et al. 2003). These data are difficult to obtain for paper pulp and sawdust since a requirement for measuring hydraulic conductivity is that they must be packed at ‘field density’ (McLaren & Cameron 1996) which is not defined in the literature and is also likely to show considerable variation for batches of different ages and origin. However, sufficient experimentation with packing densities and subsequent simulation modelling should overcome this. Another aspect of most environmental fate models is that they are designed to simulate events over weeks and months (SR Green pers. com.) whereas the events of the present experimental set-ups were of a considerably shorter time-scale.

Results of experiments described here do however give a very good description of the behaviour of herbicides in the high organic carbon content, forestry waste-products, sawdust and paper pulp, relative to their behaviour in two common cropping soils. Thus, as herbicide behaviour in these two soils is well documented, then valid conclusions can be drawn concerning the relative behaviour and fate of herbicides in the organic media and by interpolation, in mixtures of the soil and organic media. In terms of influencing the environmental fate of herbicides, the two organic media had contrasting impacts. Paper pulp acted like a sponge and generally retarded the movement of herbicides, while sawdust acted more like a drain pipe where herbicides were moved more rapidly through the profile.

7.3.5 *Enhanced degradation of herbicides*

The identification of a case of enhanced degradation in a soil with a history of repeated use of that herbicide was serendipitous as it was not one of the aims of this research. However, the occurrence of enhanced degradation has major consequences for those primary industries which regularly use residual herbicides to control weeds, e.g. the arable and vegetable sectors. The failure of these herbicides to provide sufficient long term weed control could result in serious crop losses. In some instances alternative herbicides may be available but in many cases the weeds would need to be managed through additional herbicide applications. This would not only increase the cost of crop production but also lower the sustainability of the industry due to increased herbicide use.

7.4 Areas of Future Study

This thesis has highlighted several areas where productive research could be carried out in the future.

Time-dependent sorption appears to be an area critical to the accurate modelling of pesticide fate. This is particularly true for herbicides with a long residual life in the soil such as atrazine and bromacil.

The nature of the organic matter, especially DOC has also been demonstrated to have a marked effect on the sorption and mobility of pesticides (Thomsen et al. 2002), so complementary to this would be determining the role of various functional groups in the sorption process, identifying critical factors for modelling and quantifying these relationships and the possible role of exogenous DOC containing different functional groups.

There is also a need for a laboratory method for determination of herbicide degradation that includes both dissipation and micro-organism management components and for examining herbicide degradation and adsorption/desorption at different pH values.

The effect of organic amendments on the loss of pesticide through runoff, as when ponding occurs there could be greater loss through runoff.

Examining the fate of herbicides in organic amendments at various stages of decomposition; for example the organic amendments may hold onto herbicides, but when they start decaying the bound herbicides may be released – similar to the effect of biosolid application on heavy metal bioavailability – what is called the ‘time bomb’ effect.

Investigations into the nature of sorption to organic amendments, examining such criteria as; weak adsorption, low surface area, porosity etc.

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