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PERSISTENCE AND MOVEMENT OF ATRAZINE AND ISOPROTURON IN AGRICULTURAL SOIL

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Persistence and Movement of Atrazine and Isoproturon in Agricultural Soil

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ABSTRACT

Physically based distributed models to predict persistence and movement of organic chemicals in soils have achieved only limited success because our understanding of many of the processes which govern chemical behaviour in soils is incomplete. The objectives of this study were to provide a better quantitative understanding of (1) sorption phenomena, (2) effect of soil physical properties on solute movement, (3) influence of soil solution chemistry on chemical behaviour and (4) importance of spatial and temporal heterogeneity of soil physico-chemical properties and agricultural practices on the persistence and movement of organic chemicals. The objectives were achieved using (i) laboratory batch equilibrium studies with atrazine and isoproturon on clay soil, (ii) studies on leaching of atrazine and isoproturon in a large (1.1 m x 0.8 m id.), undisturbed and heavily cracked clay soil core under controlled hydrological conditions and (iii) studies on the persistence and leaching of isoproturon in the field where a heavy textured clay soil was subject to different agricultural practices over the growing season of a winter barley crop. Sorption K_d's derived from batch 'equilibrium' studies for both atrazine and isoproturon by < 2 mm clay soil were approximately 3.5 litres / kg which was consistent with those determined for field studies. The similarity of K_{oc}'s for the < 2 mm clay soil and < 2 mm clay soil oxidised with hydrogen peroxide suggested that the sorption of isoproturon was strongly influenced by soil organic matter. By contrast, K_{oc}'s for atrazine sorption by oxidised soil were three times greater than those for < 2 mm soil indicating that the soil mineral components might have affected sorption of this herbicide. No significant differences between the sorption of either herbicide by < 2 mm clay soil and (i) < 250 µm clay soil, (ii) clay soil mixed with wheat straw or ash at ratios similar to those observed on plots 6 and 10 at the field site or (iii) < 2 mm clay soil in the presence of dissolved organic matter as opposed to organic free water, were observed. Field studies show that isoproturon was more persistent in the cultivated horizon of land where straw and stubble had been burnt than in soil where straw was incorporated. In the field experiment different mole drainage systems were found to affect the efficiency with which water was removed from the upper horizons but this had no effect on the total amount of isoproturon lost by leaching. This suggests that other processes including biodegradation, volatilisation or immobilisation of leaching chemicals in subsoils must be responsible for the difference in the isoproturon concentrations observed in the cultivated horizons where straw had been burnt or incorporated. Temporal variation of sorbed isoproturon residues, and associated sorption/desorption coefficients, were controlled by rainfall whilst spatial variation was found to be more strongly dependent on natural heterogeneity of soil physico-chemical properties than on agricultural practices. However, variation was both irregular and complex and could not be predicted in a simple way. This, taken with the complexity of the sorption/desorption mechanisms and the variability of water and solute flow pathways at the local scale suggests that the development of succesful physically based distributed models for the field scale remains unlikely. Whilst such models are unquestionably beneficial in contributing to our understanding of the behaviour of organic chemicals at the local scale, field scale management models can probably be more successful where relatively simpler conceptual approaches are adopted.

CONTENTS

CHAPTER 1

INTRODUCTION

A. GROUNDWATER CONTAMINATION

During the last decade many reports have been published which suggest that contamination of potable water supplies with pesticides and other organic chemicals is widespread and, in many areas, may exceed water quality standards (eg. see Miller, 1987). The evidence for pesticides has been comprehensively reviewed for both western Europe (Leistra and Boesten, 1989) and the United States (Hallberg, 1989), and other organic chemicals have been considered by Kenrick *et al* (1988). The most surprising aspect of such surveys has been the consistent and widespread identification of a number of chemicals which had previously been thought to present no risk to groundwater. These include chemicals which have been shown to be rapidly degradable, such as atrazine, and those which are extremely water insoluble, such as DDT and its derivatives. Failure to recognise that such problems might arise has been largely attributed to the use of inadequate models and methodologies to screen and assess both existing and new synthetic organic chemicals to determine their likely environmental fate and behaviour. For example, sorption/desorption equilibria and kinetics studies have largely relied on the use of batch techniques which are subject to a number of artifacts (Rao and Davidson, 1980; Sparks, 1989). Furthermore, contaminant mobility has been investigated in repacked homogenous soil cores under laboratory conditions whilst natural soils contain structural features such as voids and earthworm burrows which can accelerate the movement of organic solutes to subsoils and groundwater (Beven and Germann, 1982; Jury 1992).

B. CONTAMINANT TRANSPORT AND FATE MODELLING

The rapid increase in the number of publications detailing the occurrence of ever increasing numbers of contaminants in groundwater has provoked increasing public concern to which there has to be a responsible scientific reply. As a result environmental legislation is becoming ever more stringent and consequently the pressure on modellers to produce more successful management tools is mounting. If those responsible for the development of contaminant transport models to determine the fate of pollutants are to rise to this challenge, a change of emphasis is needed in favour of physically based and spatially distributed models, rather than the current preoccupation with simple empirical approaches. Only when this change takes place will it become possible to adequately identify the source of pollution problems and make objective decisions as to how they can best be alleviated. However, there are a number of reasons why contemporary attempts to develop physically based distributed models have achieved only limited success.

1) Sorption of contaminants is generally assumed to be both instantaneous and completely reversible, whereas equilibration has been found to take place on timescales ranging from a few seconds to many years (Pignatello,1989 and references therein). Furthermore, hysteresis has often been observed, and in many cases a proportion of the contaminant is completely resistant to desorption under natural field conditions (Brusseau and Rao, 1989a).

2) Many modellers have failed to recognise the importance of soil structural features. Consequently parameters accounting for preferential flow of water and bypass of sorption sites by solutes have rarely been incorporated in model structures (Beven and Germann, 1982; White, 1985; Van Genuchten *et al*,1990).

3) The importance of mobile colloids with regard to contaminant mobility has yet to be widely acknowledged and incorporated in model structures. Suspended particulate matter such as clay or ash, and dissolved macromolecular substances including water soluble organic matter and bacteria, are now known to influence contaminant mobility (Bengtsson *et al*, 1987; McCarthy and Zachara, 1989).

4) Models have rarely incorporated parameters to account for spatial and temporal variation

arising from intrinsic factors such as natural soil heterogeneity (Donigian Jr and Rao, 1987a; Weber *et al*, 1991; Weber *et al*, 1992) or extrinsic factors such as agronomic operations (Donigian and Rao, 1987a; Weber and Miller, 1989).

C. OBJECTIVES OF THIS STUDY

The objectives of this study, set within the context of the four limitations to modelling discussed above, are to provide a better quantitative understanding of these sorption and transport phenomena. By doing so, it is hoped that this will provide the necessary impetus for modellers to represent these phenomena in future model structures. To do this, laboratory experiments were designed to investigate the influence of solid-solution ratios, crop residues, soil organic fractions, particle size fractions and dissolved organic carbon on the sorption of atrazine and isoproturon to clay soil (Part 1). A large undisturbed heavily cracked clay soil core was used to investigate the effect of preferential flow pathways on atrazine and isoproturon leaching and dispersion under controlled laboratory conditions (Part 2). The extent to which the distribution of isoproturon residues in space and time was controlled by intrinsic factors such as natural heterogeneity of soils and extrinsic factors such as cultivation and drainage was determined in a field experiment (Part 3).

The herbicide isoproturon (see Chapter 3, section C for physico-chemical properties) was chosen as the principal compound for study because it has been widely detected in groundwater in cereal growing areas of the United Kingdom (Ends Report, 1992) and it was possible to investigate its persistence and mobility in a heavy textured clay soil under realistic agricultural practices. Atrazine (see Chapter 3, section C for physicochemical properties) was chosen because it is one of the most frequently detected herbicides in groundwater (Gamble and Khan,1992). Although it has similar physicochemical properties to isoproturon, it has a markedly different chemical configuration, making it possible to investigate the influence of chemical composition on persistence and mobility.

D. LAYOUT OF THESIS

The literature is reviewed in Chapter 2 with a discussion of recent advances and unresolved problems in our understanding of the persistence and movement of organic chemicals in structured soils. The development of a high performance liquid chromatography technique for the analysis of atrazine and isoproturon in soil and water is presented in Chapter 3 and the effect of commonly used laboratory apparatus on pesticide recovery is considered in Chapter 4. The experimental results are presented in three parts. Part 1 (Chapters 5 & 6) is devoted to sorption phenomena, Part 2 (Chapters 7 & 8) gives data from the soil core study and Part 3 (Chapters 9-11) those from field experiments. For simplicity the materials and methods used for each experiment are described in a single chapter on methodology in each part of the study. Preceding each part, introductory comments outline the objectives of the experiments to be discussed and sets them within the overall context of the study; finally each part has concluding remarks summarising the main findings. The major factors and processes controlling the behaviour of isoproturon in the field, and organic chemicals in soils in general, which have been determined in this study are presented with implications for modelling in the final chapter.

CHAPTER 2

PERSISTENCE AND MOVEMENT OF ORGANIC CHEMICALS IN AGRICULTURAL SOILS: A REVIEW

A. INTRODUCTION

Pesticides play a major role in agriculture helping to ensure adequate yields of food crops. However, their use has to be efficient, to ensure economic viability, and environmentally benign. If these two objectives are to be met, then we need to know much about the interaction between the pesticides with both the mineral and organic fractions in soils, and the factors which govern their transport throughout the soil profile with the risk of being moved into streams, rivers and lakes or to deep aquifers. Therefore, this review has been divided into three main sections. Section B - Sorption / Desorption Phenomena - discusses the mechanisms of interaction between organic chemicals and soils. Section C - Transport Phenomena - discusses water flow in soils and its impact on the transport of solutes. Section D - The Influence of Intrinsic and Extrinsic Factors on the Persistence and Movement of Organic Chemicals in Soils - evaluates the importance of spatial and temporal heterogeneity of soil physico-chemical properties and weather, and the effect of agricultural operations on chemical behaviour. Whilst the emphasis of the review will focus on pesticides, other organic chemicals will also be considered because agricultural practices such as sewage sludge application and wastewater irrigation represent major sources of toxic organic chemical inputs to agricultural land. Because there is so much concern about the safety of pesticide use, there is now a rapidly expanding literature on all aspects of their usage, and of their transport and fate in soils. Consequently, it was necessary to be selective in the literature presented here but, nevertheless, the intention was to present the information impartially.

B. SORPTION / DESORPTION PHENOMENA

B.1 Significance of Sorption / Desorption

The success of physically based management and research models to describe the movement and fate of organic chemicals in the soil system is largely dependent on our understanding of very diverse processes that include leaching, volatilisation, biodegradation, chemical degradation, and sorption / desorption on soil organic matter and mineral components. The importance of sorption / desorption should not be underestimated. Regardless of the physico-chemical properties of most organic contaminants, their behaviour in soils is most likely to be determined by their relative partitioning between the solid and solution phase. This has been demonstrated by Hamaker and Thompson (1972) who found that in soils with 20% moisture content the percentage of contaminant sorbed ranged from 80% for compounds with distribution coefficients of 1.0, up to 99.5% for those with distribution coefficients of 50.0. A similar argument was presented by Hartley and Graham-Bryce (1980) who also stressed both that partition into the vapour phase is generally less than 1%, even for the most volatile compounds including fumigants, and that the importance of sorption to solids is no less significant when the difference in volume occupied by each phase in soils is taken into consideration. Pignatello (1989) noted that, even in extremely dry conditions, soil colloids are normally coated with a very thin film of water as further evidence of the importance of solid-solution partition processes ie. an element of film diffusion is normally involved so direct solid-gaseous phase exchanges are extremely rare. The significance of sorptive processes is also manifest in the influence they have on the other processes discussed above. Biodegradation, for example, has been reported to be more pronounced for molecules in the solution phase as opposed to the sorbed phase (Ogram *et al*, 1985; Schrapp, 1992), and the literature abounds with reports demonstrating the influence of phase partitioning on chemical processes such as hydrolysis, oxidation, reduction and photolysis.

B.2 Mechanisms of Sorption/Desorption

Whilst there is almost universal agreement on the importance of sorption / desorption, considerable controversy surrounds the theories that are currently being invoked to explain the behaviour of nonionic organic compounds in soils. Chiou *et al* (1979) have suggested a mechanism analogous to the partitioning of a nonionic organic substance between a hydrophilic aqueous phase (e.g. water) and a hydrophobic organic phase (e.g. octanol). Consequently they have proposed that the water solubility and the octanol/water partition coefficient of a given compound are useful parameters for the prediction of that compound's behaviour in soils. Although substantial evidence is available which lends support to Chiou's theory, Mingelgrin and Gerstl (1983) have concluded that the evidence is insufficient to demonstrate the theory's universal applicability and therefore the use of a chemical's octanol-water partition coefficient or water solubility as predictors of sorptive behaviour is largely unjustified. Whilst Mingelgrin and Gerstl (1983) favour the more traditional concepts of specific site surface interactions, they nevertheless acknowledge that, under field conditions, sorption / desorption is most likely characterised by a continuum of phenomena ranging from three dimensional partition to fixed site adsorption. Recent evidence in favour of these two major theories is summarised and evaluated below. More complete details (and earlier evidence) can be obtained by referring to Chiou *et al* (1979) and Mingelgrin and Gerstl (1983). In contrast, the interaction of ionic compounds are more clearly understood. More extensive discussions of contaminant interactions with minerals can be obtained by referring to Mingelgrin and Prost (1989) or Mortland and Zielke (1989), and with organic matter by referring to Hamaker and Thompson (1972) or Senesi and Chen (1989).

Strong linear correlations between sorption of nonionic organic chemicals and soil organic matter content (eg. Chiou *et al*, 1981, 1983, 1985 and references therein), and reports that normalisation of sorption coefficents on an organic matter or organic carbon basis reduces the variability in sorption characteristics of different soils for a given chemical (eg. Kenaga and Goring, 1980), lend support to partition theory. However, examination of the experimental procedures and results for many studies usually shows that an alternative explanation of the sorptive mechanisms is often equally, or even more, plausible. L type and S type isotherms have frequently been reported for nonionic compounds on organic matter / soils (Weber and

Miller, 1989) suggesting that cooperative sorption and / or finite sorption capacities often exist. Thus a simple partition theory would be inappropriate to explain sorption. Further difficulties exist in trying to reconcile partition theory with sorption in low organic matter soils where the correlation between uptake of nonionic organic compounds and organic matter content is relatively weak (Schwartzenbach and Westall, 1981). However, Rutherford *et al* (1992) claim that this is only due to analytical difficulties associated with the reliable detection of extremely low contaminant concentrations on low organic matter soils but it is difficult appreciate why this should be so. Many reports also exist which demonstrate a strong correlation between sorption of organic compounds and relatively hydrophilic soil mineral components (eg. see Mingelgrin and Prost, 1989; Mortland and Zielke, 1989 and references therein). Furthermore, the intimate association between organic matter and clay sized particles, especially in low organic matter soils and subsoils, renders the importance of the sorption coefficient-organic matter content correlations in many studies somewhat suspect. The assertion that normalisation of sorption coefficients on an organic matter basis reduces the variability in sorption of a given compound by different soils is also questionable. Hamaker and Thompson (1972) have demonstrated that normalised sorption coefficients vary considerably for many compounds in different soils, and in an extensive field study of the spatial distribution of napropamide sorption coefficients, Elabd *et al* (1986) have found that normalisation on an organic matter basis actually increased variation in the same field. Nevertheless, Chiou *et al* (1986, 1987) and Rutherford *et al* (1992) have investigated the influence of compositional variations in organic matter and their effect on the solubility of nonionic compounds, and have concluded that such variability is to be expected and is thus not inconsistent with partition theory.

Low activation energies associated with the sorption of nonionic organic chemicals by soils have been considered to support a partition mechanism (Chiou *et al*, 1979; Madhun *et al*, 1986; Pignatello, 1989). This evidence has been refuted by Mingelgrin and Gerstl (1983) who claim that the interaction of nonionics with organic matter is dependent on the degree of competition that exists with other solute molecules or the solvent and, consequently, activation energies may be high. Furthermore, physical interactions can often occur on specific surface sites with extremely low activation energies (Adamson, 1976) creating an illusion of partition processes. If a partition-like process was primarily responsible for sorption, then desorption might also be expected to be an inactivated process. However, desorption has been shown to be an activated process requiring activation energies of equal, or greater, magnitude to those required for sorption (Pignatello, 1989). Another difficulty lies in the frequent use of completely mixed batch reactor systems to study sorption. In such systems, diffusive retardation is considerably reduced relative to field conditions and consequently reactions will proceed at faster rates with low activation energies so creating an illusion of an inactivated partition process.

Chiou *et al* (1983) have invoked the lack of competition between binary mixtures of nonionic organic solutes for organic surfaces in support of their partition theory. Although Adamson (1976) has presented evidence to suggest that competition does occur, most of it is indirect. The lack of studies designed to specifically address this problem leaves the issue unresolved and it is clearly an area where more research is required.

Solubility enhancement of nonionic organic chemicals by water soluble organic matter (eg. Caron *et al*, 1985; Chiou *et al*, 1986; Traina *et al*, 1989; Lee and Farmer, 1989) may lend support to partition theory. It has been postulated that this might occur by a surfactant-like micellation process (Rochus and Sipos, 1978) which has since been supported by studies by Guetzloff and Rice (in press). However, the interaction with water soluble organic matter becomes more complex in the presence of a second sorbing surface such as soils or aquifer solids (Enfield *et al*, 1989; Dunnivant *et al*, 1992; Larsen *et al*, 1992) and the mechanisms of interaction remain poorly understood. It is not unreasonable to assume that they will be subject to all the same arguments as with solid phase organics, and therefore they will not be discussed further here (the influence of water soluble organic substances on the behaviour of contaminants in soils is discussed further in section D.1).

More recently Chiou *et al* (1990) have implicated the small surface area of organic matter, determined by the BET (N_2) method, as evidence for a partition mechanism. They have suggested that partition occurs on the external surface of a polymer-like material. Pennell and Rao (1992) refute this theory and in support of their argument, have demonstrated that the surface area of organic matter is dependent on the means used to measure it. They have shown that a large discrepancy occurs between quantitation of surface area using N_2 and that using ethylene glycol (EG) as the surface saturating compound and that the difference is due to their mode of surface interaction. Pennell and Rao (1992) propose that a much more complex 3-dimensional matrix, with many reactive moieties and functional groups on both internal and external surfaces such as those reported by Hayes *et al* (1989), is a more plausible model for the sorptive surface. These authors do not dispute that a partition type process occurs on the external surface of organic matter. They only stress that specific site interactions are also possible and that the importance of the internal surfaces cannot be ignored, especially with regard to the more polar contaminants. Chiou *et al* (1992) claim that the model proposed by Pennell and Rao (1992) is unnecessarily complex and arises from the use of techniques (eg. EG) where the solid itself is penetrated by the sorbate resulting in an overestimate of surface area based on 'inner surfaces'. These 'inner surfaces', in the absence of more direct experimental evidence, Chiou *et al* (1992) believe to be of little importance.

Although many reports lend support to partition theory, contemporary research has resulted in a large body of evidence which refutes or diminishes the significance of it. Despite this, it would be unwise to discount partition as a sorptive mechanism, and in some cases it may well even be the most prominent mechanism, but it can rarely, if ever, be considered to be either the sole mechanism involved or universally applicable. Specific site interactions appear more likely regardless of the nature of the sorbent or the sorbate. Consequently, the conclusion of Mingelgrin and Gerstl (1983) that "sorption is a continuum of possible interactions starting with fixed site adsorption and ending with true partition between three-dimensional phases" remains the most appropriate interpretation of sorption ten years on.

B.3 Sorption/Desorption Behaviour

Despite the controversy surrounding the mechanism of sorption/desorption, it is now apparent that the approach to equilibrium is not instantaneous in either the sorptive or desorptive directions. Both are biphasic processes, with a rapid initial phase of sorption or desorption followed by a considerably slower rate of contaminant uptake or release. It is unfortunate that most studies have approached this problem from the sorptive step alone; studies incorporating an investigation of desorption, including those of Weber (1982), Di Toro *et al* (1982), Bowman and Sans (1983, 1985b), Pignatello (1990a) and Uchrin *et al* (1986), remain the exception rather than the rule. Where investigations of the corresponding desorptive behaviour have been undertaken, hysteresis effects (sometimes described as nonsingularity, nonequilibrium, slowly reversible or resistant sorption) have often (Bowman and Sans, 1977; Di Toro and Horzempa, 1982; Koskinen and Cheng, 1983), but not always (Bowman and Sans, 1985a; Wauchope and Meyers, 1985), been observed. Rao and Davidson (1980) have suggested that these effects are possibly more apparent than real, attributing them to methodological artifacts, biological and chemical degradation, failure to establish equilibrium and competitive adsorption. However evidence is now available suggesting that nonsingularity may be both real and significant (Rao and Davidson, 1980). Contemporary work in this field of research has recently been subject to extensive critical reviews by Brusseau and Rao (1989a) and Pignatello (1989), and the implications of these phenomena for transport, bioavailability, long-term persistence and remediation of contaminated land are discussed by Pignatello (1993). Since these reviews were published, many advances in our understanding of the mechanisms of slowly reversible sorption, and their importance at the field scale, have been made. It is these advances which are considered in detail here.

Pignatello and Huang (1991) have investigated the nonequilibrium sorption behaviour of atrazine and metolachlor in Typic Dystrochept soils in Connecticut for a period of 15 months following their application. Desorption coefficients (K_{app}) were determined by suspension of field soils in water for 24 hr and sorption coefficients (K_d) were determined by supplementing the same samples with herbicide solutions. The nonequilibrium index (K_{app} / K_d) increased with time, following herbicide application, ranging from 2.3 to 22 for atrazine and from 13 to 42 for metolachlor. Thus, the labile fraction decreased with time from 0.60 to 0.09 and from 0.10 to 0.056 for atrazine and metolachlor respectively. The existence of slowly reversible fractions of trichloroethylene (TCE) in silty clay soil from a long term (18 yr) waste disposal site was investigated by Pavlostathis and Jaglal (1991). Miscible displacement experiments required approximately 24000 pore volumes to remove 72% of the sorbed TCE residues. A further two displacement events (24 hr), interspersed with two 24 hr equilibration periods, removed only 1% of the initial soil TCE. The authors stressed that the rate of TCE removal decreased with time and was eventually lower than the advective transport rate but they were unable to conclude whether diffusion or chemisorption was the predominant limiting factor. Nevertheless, this study demonstrates the considerable time periods that may be required to clean up contaminated soil, not only for the resistant fraction but also the relatively labile fraction. Scribner *et al* (1992) found that where simazine had been applied to maize for twenty years, the K_{app} values for 'aged' simazine residues were approximately 15 times greater than the corresponding K_d values for freshly added ^{14}C-simazine. Simultaneous measurements of simazine concentrations in drainflow (C) were made and divided by the equilibrium simazine concentration from ^{14}C-simazine batch studies (C_e). These authors also found that the fractional equilibrium (C / C_e) fell from 1.0 at simazine application to 0.05 two to three months later. These data suggest that a resistant fraction may be formed very rapidly in soils and they demonstrate that considerable errors will be incurred in model predictions of persistence and leaching if equilibrium has been assumed where nonequilibrium parameters are more appropriate.

The mechanisms currently postulated as being responsible for nonequilibrium sorption are shown in Fig 2.1. They can be divided into two classes - (1) transport-related nonequilibrium and (2) sorption-related nonequilibrium.

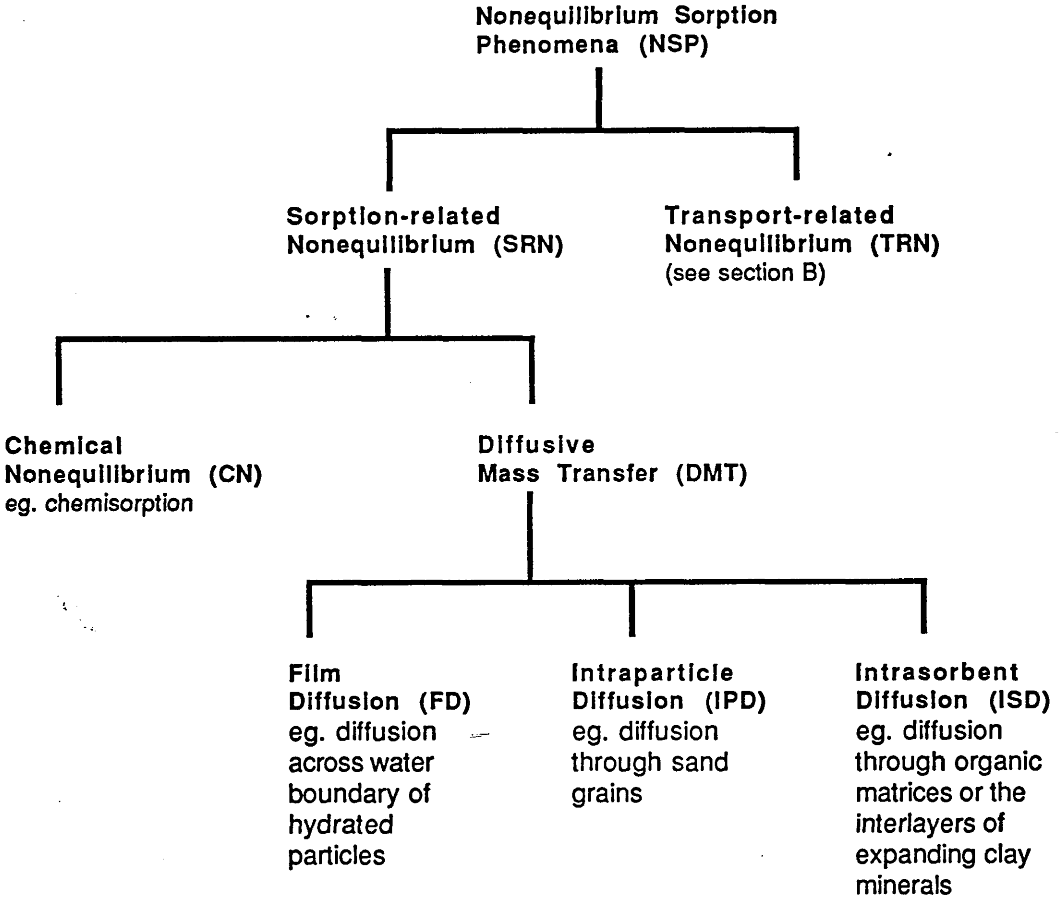


Fig 2.1 **Classification of Nonequilibrium Sorption Phenomena**
(after Brusseau and Rao 1991b)

(1) transport or flow-related nonequilibrium arises from the influence of soil structural heterogeneity on pore water velocities and solute retention times, which may limit the mobilisation of sorbed contaminants and / or the immobilisation of soluble contaminants. These factors are discussed in section C - Transport Phenomena.

(2) sorption-related nonequilibrium can be attributed to either chemical processes or diffusive

mass transfer. Chemical processes should be more correctly defined as chemical kinetics. This process is distinct from the others in that it postulates nonequilibrium to be subject to result from the chemical interaction of the sorbate with the sorbent, e.g. by covalent bonds. Assessing the importance of chemical kinetics remains one of the most challenging problems in elucidating the mechanisms of slowly reversible sorption phenomena. The difficulties arise in developing methodologies that enable the chemical processes to be investigated in the absence of physical constraints. Sparks and co-workers (eg. see Sparks 1987, Sparks 1989) have developed experimental methods and pioneered the application of chemical kinetics theory to heterogenous natural solids but the research remains in its infancy. The importance of chemical kinetics with regard to the sorption of nonionic organic chemicals is debatable (see section B.2) but is likely to contribute to the sorption of more complex molecules such as pesticides which frequently contain a number of polar groups (Brusseau and Rao, 1991; Brusseau *et al*, 1991). Pignatello (1993) argues that "Although a contribution of adsorption to the kinetic component is conceivable ..." (citing a study by Szecody and Bales, 1989) he concludes that "it is difficult to believe that adsorptive forces alone could account for the long-term behaviour that is routinely observed". Whilst this conclusion is appropriate at the present time, it may need to be reassessed in the future as chemical kinetics research expands.

Intraparticle diffusion and intrasorbent diffusion are the sorption-related processes most frequently cited as being responsible for nonequilibrium phenomena. Retarded intraparticle diffusion arises from the resistance molecules face when diffusing through permeable porous media that are composed of smaller pores than the diffusing chemical. Intrasorbent diffusion is similar in that it involves diffusive resistance in, for example, three dimensional organic matrices or expanding clay minerals. Intrasorbent diffusion differs from intraparticle diffusion in that the latter applies to noninteractive colloids such as sand grains whereas the former applies to 'solids' with the potential for sorption / desorption to take place. Brusseau *et al* (1991) have reviewed the evidence in support of these mechanisms and have designed an experiment to specifically assess their importance. They concluded that intrasorbent diffusion, more specifically intraorganic matter diffusion, was primarily responsible for the sorption of a large number of hydrophobic organic chemicals including benzene, toluene, anthracene, naphthalene, chlorobenzene, tetrachloroethene and quinoline in a fine sandy soil.

B.4 Classification and Numerical Characterisation of Sorption/Desorption

Given the enormous amount of work that has been done in the sorption / desorption field, some system of classification and numerical characterisation of the various phenomena observed was essential to facilitate comparisons and verification of each set of findings. Such a system appears to have evolved through a process of 'natural selection' and is largely the outcome of the classification proposed by Giles *et al* (1960, 1974) and the Langmuir and Freundlich equations. This system of classification is described and explained, and its benefits and limitations evaluated below.

The classification of Giles *et al* (1960, 1974) is shown in Fig 2.2 along with the conditions which favour the occurence of each isotherm and examples of different groups of compounds that have been known to exhibit such behaviour. Isotherms are most frequently characterised by the Freundlich equation which can be fitted to isotherms of the S, L and C type (Weber and Miller, 1989). The Freundlich isotherm is a simple empirical relationship relating the solid concentration (S) to the equilibrium solution concentration (C), a sorption strength index (K_f, frequently referred to as the Freundlich coefficient) and an index of linearity (1 / n)

$$S = K_f C^{1/n} \qquad (2.1)$$

where S = x / m = mass sorbate / mass sorbent.

For simplicity, the logarithmic transformation (2.2) of equation 2.1 is frequently used such that 1 / n and K_f can be derived by linear regression of log S against log C

$$\log S = \log K_f + 1 / n \log C \qquad (2.2)$$

Where isotherms are S shaped or L shaped, 1 / n values will be >1 or <1 respectively. For C type isotherms, 1 / n is unity and consequently the characterisation of the isotherm can be reduced to a simple proportionality relationship (2.3) where S is related to C by a single distribution coefficient (K_d)

$$S = K_d C \qquad (2.3)$$

which is frequently expressed on an organic carbon (2.4) or an organic matter (2.5) basis to compare sorption of contaminants by different soils.

$$K_{oc} = (K_d / \%\ \text{organic carbon})^*100 \qquad (2.4)$$

Assuming a conversion factor of 1.724 (i.e. % organic matter = 1.724 x % organic carbon) then

$$K_{om} = K_{oc} / 1.724 \qquad (2.5)$$

Equations 2.1 and 2.3 are both empirical ie. there are no mechanistic constraints on the value that the sorption coefficients can have. Although the sorbent has a finite reactive surface, no limit for S is ever reached regardless of the magnitude of C (Hamaker and Thompson, 1972). Despite this problem, the relationships have proved to be very useful for characterising soil sorption over restricted concentration ranges observed in the field or simulated in the laboratory. However, the use of these relationships to extrapolate to concentrations which are less or greater than the range of concentrations for which they were developed should be avoided (Hamaker and Thompson, 1972; Hartley and Graham-Bryce, 1980). Difficulties such as these can be overcome by using much more rigorous equations with a sound theoretical basis. Of these the Langmuir equation (2.6) is the most widely known

$$S = QbC / (1 + bC) \qquad (2.6)$$

where Q is the maximum sorption capacity and b is the surface sorption affinity

However, this equation was developed for the sorption of gases on solid sufaces and is rarely found to give a good fit to sorption from solution onto soil surfaces. This is because the relationship assumes constant sorption energies over the sorbing surface; this assumption will never be satisfied for heterogenous soil colloids (Hamaker and Thompson, 1972). Future directions in the numerical characterisation of sorption data have been discussed by Kinniburgh (1986) who argues in favour of using nonlinear modelling techniques as being a more direct and rigorous approach to data interpretation.

Giles *et al* (1974) attribute the benefits of classification and numerical interpretation of sorption isotherms to the fact that they can be used to aid:

(1) identification of the sorption mechanism

(2) diagnosis of the orientation of solute molecules at colloidal surfaces, and changes in their orientation

(3) differentiation between the sorption of monodisperse and associated species

(4) detection of impurities in the carrier solvent and the sorbing medium

(5) measurement of specific surface of the sorbing medium

In short, isotherm shapes can be used to investigate sorption mechanisms and their numerical characterisation can be used to compare results. Despite these advantages, considerable care should be exercised in the use of isotherms. For example, where $1 / n$ is close to unity the same raw data set could be fitted equally well, in a statistical sense, by either the Freundlich equation or the simple proportionality relationship (Nicholls, 1988). Hamaker

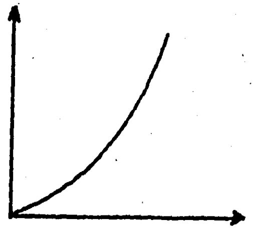
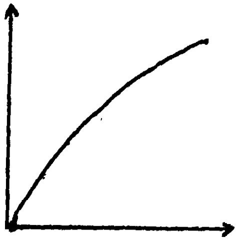
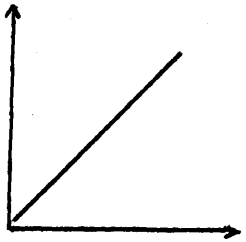
CLASS	SHAPE	CONDITIONS	EXAMPLES
S		(1) fixed point interaction between solute and sorbent (2) moderate intermolecular atraction (3) competition occurs between the solute, the solvent and sorbed species for sorbent reaction sites	(1) lipophilic solutes on hydrophilic surfaces (2) hydrophobic solutes on lipophilic surfaces (3) hydrophilic solutes on hydrophilic surfaces
L		(1) multiple interactions between solute and sorbate (2) high intermolecular attraction of solute molecules giving rise to large clusters (3) little to no competition between solute and solvent for sorption sites	(1) lipophilic solutes on lipophilic surfaces (2) ionisable solutes on oppositely charged surfaces (3) low to moderately hydrophilic solutes on hydrophilic surfaces
C		(1) sorbent is porous (2) sorbent is relatively pure (3) solute is more strongly attracted by the sorbent than the solvent	(1) nonionic compounds on organic surfaces (assuming a partition process is responsible for sorption) (2) most groups of organic chemicals over narrow concentration ranges

Fig 2.2 **Classification of Solute Sorption Isotherms: Shape, Conditions and Examples** (based on Weber and Miller, 1989)

and Thompson (1972) have demonstrated that assuming linearity where the Freundlich equation was more appropriate could give rise to errors of 30 - 40% in the predicted equilibrium concentration. It should be apparent that numerical interpretation of isotherms is largely subjective and, consequently, subject to abuse. For many datasets, the isotherm fitting is at the mercy of individual researchers, and their choice of isotherm most frequently reflects their own theories. The literature abounds with reports in which the authors state that their data were best fitted by a particular isotherm. Raw data and information on the appropriateness of alternative isotherms are rarely presented but are clearly required in the interest of rigorous scientific enquiry.

C. TRANSPORT PHENOMENA

C.1 Significance of Water Flow for the Transport and Fate of Organic Chemicals

Like sorption / desorption, the flow of water is critical to the redistribution and ultimate fate of organic chemicals in soils. Water behaves as a solvent mobilising sorbed chemicals and transporting them past other sorption sites, on which they may or may not be immobilised, and ultimately to groundwater and / or surface water outside the soil itself. Solubilisation of organic chemicals in water has been shown to enhance their bioavailability to microbes for degradation (Ogram *et al*, 1985), and to higher animals and plants for translocation into food chains (Schrapp, 1992). The ability of flowing water to entrain and transport microparticulates, such as clay particles, ash and sewage sludge colloids, has been identified as a possible loss pathway for hydrophobic organic chemicals (Vinten *et al*, 1983; Jones *et al*, 1989; McCarthy and Zachara, 1989). The chemical versatility of 'water' (ie. its potential to take on an great diversity of chemical compositions ranging from a relatively pure neutral aqueous solution to complex acidic or basic solvents), and the transient nature of this versatility, confers upon it the ability to catalyse a wide range of chemical processes (eg. hydrolysis, oxidation and reduction) which influence the fate of organic chemicals. Thus, it should be apparent that a thorough understanding of the mechanisms by which water moves through soil is a prerequisite to understanding the transport and fate of chemicals in soils.

C.2 Water Movement in Soil

Lawes (1862, cited in Beven and Germann, 1982 and Nicholls, 1988) demonstrated that structural features in soils such as root channels and earthworm burrows exerted a strong influence on water flow and nutrient leaching in soils at Rothamsted Experimental Station. Despite this, most research has focussed on fluid flow in hypothetical media or repacked homogeneous soil columns (Brusseau and Rao, 1988). It was not until the 1980s following the publication of a review entitled "Macropores and Water Flow" by Beven and Germann (1982) that the emphasis changed to favour research on undisturbed soil monoliths, and well developed structured soils at the field scale. In the subsequent decade, numerous reviews have been published detailing the fundamental aspects of fluid flow in heterogeneous porous media (White, 1986; Bouma, 1990), the effect of fluid flow on chemical transport (Rao and Jessup, 1983; Brusseau and Rao, 1990; Jury, 1992) and modelling (van Genuchten and Jury, 1987; Jury and Ghodrati, 1989). Only the fundamental aspects of water flow and its impact on the transport and fate of organic chemicals will be outlined here. Evidence from the aforementioned reviews will not be reiterated but the reviews themselves will be cited where appropriate to assist the reader in identifying further information. The emphasis of the discussion will focus on more recent evidence pertaining to the effect of intrinsic and extrinsic factors on water flow and the consequences for the transport and fate of organic chemicals (see section C).

Soils consist of a number of structural features including animal burrows, root channels, cracks and fissures formed both by weathering, swelling and shrinkage or freezing and thawing, and soil pipes formed by the erosive action of flowing water (Beven and Germann, 1982). Morphological techniques for the investigation of soil structure are now well developed at both the microscale and the field scale (eg. see Bouma, 1990). Consequently, rapid improvements in our understanding of the structural heterogeneity of soils and its effect on water flow have now been realised (Neilsen *et al*, 1983). Although an infinite diversity of flow pathways occur, a number of distinctive phenomena have been widely observed. These include fingering and short circuiting, which are discussed below by reference to the hypothetical breakthrough curves for conservative water tracers shown in Fig 2.3.

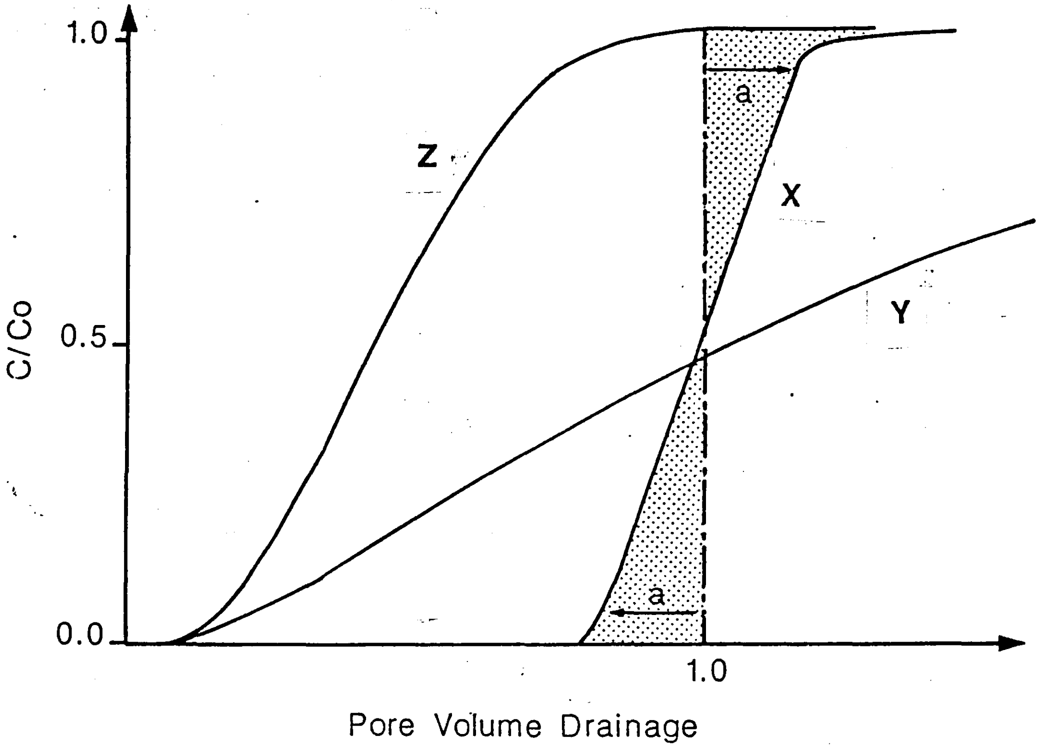


Figure 2.3 Hypothetical Breakthrough Curves in Soils Containing a Homogeneous Pore Structure (X), a Heterogeneous Pore Structure and a Macropore Dominated Pore Structure (Z)

The use of conservative water tracers has revolutionised the study of soil hydrology. They comprise a wide range of chemicals that are highly soluble, non-volatile, non-toxic, recalcitrant and non-interactive and that remain stable in the solution phase over long time periods. Thus, different chemicals can be used to label multiple water inputs to a study field or soil core, and the resulting hydrographs can be separated into component parts associated with each tracer input by measuring the concentration of the tracer chemicals in outflows. The most frequently used tracers are tritiated water (Nkedi-Kizza *et al*, 1983), ionic anions such as bromide and chloride (Tyler and Thomas, 1981) and ionised organic compounds such as fluorobenzoic acids (Bowman, 1984). Other compounds such as fluorescent dyes (Smart and Laidlaw, 1977; Smettem and Trudgill, 1983) can also be used but they require much more care as they may interact with soil solids, or be degraded or volatilised. These tracers are said to be non-conservative and should only be used where more conservative chemicals are inappropriate.

Water flow through homogeneous porous media exhibit breakthrough curves like that depicted by curve X in Fig 2.3 and, hence, the application of Darcy's first law (Darcy, 1856) is appropriate. Although the Darcy equation has given a good approximation of saturated flow in small homogeneous repacked soil columns, its relevance to undisturbed soil cores and field soils is debatable. Biggar and Neilsen (1962) have demonstrated the occurence of breakthrough curve asymmetry in a slightly aggregated homogeneous repacked soil column. Even in the most homogeneous field soils some degree of aggregation occurs which may give rise to 'lines of weakness' (least resistance) along which flow will take place more readily. Furthermore, preferential flow, or 'fingering' as the phenomenon has become known, has been widely observed in homogeneous sands (Glass *et al*, 1987; Hillel and Baker, 1988). This phenomenon arises from the instability of a moving water front as it meets some resistance such as a distinctive textural discontinuity in the soil profile (Glass *et al*, 1989). For these reasons, breakthrough curve X in Fig 2.3 has been depicted as deviating further from the vertical at one pore volume drainage than is usually the case (White, 1986; Bouma, 1991).

Under field conditions, most soils contain some degree of structural development. This may range from being very weak in light textured or frequently disturbed soils to being very strong in heavy textured, undisturbed land. These soils are characterised by breakthrough curves similar to Y (heterogeneous pore systems) and Z (macropore dominated pore systems) depicted in Fig 2.3. For the former case, ie. curve Y, the Darcy equation may still provide an acceptable approximation of flow depending on the degree to which asymmetry occurs. However, the more pronounced the macropore network, the more likely will be short-circuiting (bypass flow, preferential flow, channelling flow) culminating in earlier breakthrough, whilst movement through the bulk soil matrix will control the degree of tailing that occurs. In such soils, with breakthrough analogous to that depicted by curve Z, Darcian principles do not adequately describe the infiltration and redistribution of water (Beven and Germann, 1982) so other methods have to be found. The most popular amongst these have been two domain concepts (also defined as mobile-immobile and bi-continuum concepts), in which flow occurs in (and between) a macropore domain and a matrix (or micropore) domain. The literature abounds with evidence in support of two domain concepts (eg. see van Genuchten *et al* , 1990) and models developed to predict such behaviour (reviewed by van Genuchten and Jury, 1987).

It could be argued that a major drawback of the two domain concept is that it has promoted research geared towards increasingly mechanistic interpretations of water flow in preference to phenomenological studies. It may prove more beneficial if water flow is described by a dynamic flow velocity continuum. Such a concept recognises that water movement:-

(1) can occur through all the pore structures simultaneously or at different times, depending on rainfall patterns and antecedent soil moisture conditions
(2) will be characterised by spatially and temporally controlled pore water velocities
(3) can take place between the different structural features
(4) can have a net upwards or downwards direction

By adopting such a concept, water movement can be modelled using average pore water velocities or transfer functions (see Jury, 1982). This avoids the need for disputed definitions of soil structural features and water flow in them (identified by Beven and Germann, 1982 as being a major problem that still has to be resolved). Spatial variation of flow pathways can be integrated and model input parameters can be derived from hydrographs and conservative tracer concentrations in streams, field drainage systems and soil core effluents. Consequently, disruptive sampling of study sites can also be avoided, giving researchers greater confidence in the outcome of their work. However, Davidson *et al* (1983) argue that such an approach is inadequate because it fails to provide "the insight required in many instances to explain observations that depend on the properties of the pores and the behaviour of water and solutes at a molecular scale". Which approach individuals favour will obviously depend on their individual research goals but, clearly, nothing can be gained from pursuing complex and disruptive mechanistic research strategies where a phenomenological approach is all that is required.

C.3 Solute Movement In Soil

Many solutes, in contrast to water, behave like nonconservative tracers. Breakthrough curves for mobile chemicals may be retarded relative to water movement, and may exhibit flatter peaks or longer and higher tails. The specific form of the breakthrough curve is dependent on the physico-chemical properties of the chemical and soil solids, the chemical composition of the soil solution and the structure of the soil through which the chemical moves. Some generalised hypothetical examples are presented by way of explanation followed by more specific studies from the literature.

In homogeneous granular porous media where structural development is relatively weak, spatial variation of soil physical features and transport related nonequilibrium have little effect on solute movement. Movement is controlled by the properties of the solute itself and the heterogeneity of soil physico-chemical characteristics. The more reactive the solute and / or the sorbing surface, then the greater the solute retention times will be and the broader the breakthrough curves will become (Fig 2.4a). By contrast, where flow occurs in two domains, the effect of structural heterogeneity and transport-related nonequilibrium becomes more apparent. Such soils are characterised by rapid solute breakthrough and sharp well defined peaks with long tails (Fig 2.4c). Retention times are strongly dependent on the frequency, size and continuity of the macropores whilst the length and height of the tails are controlled by diffusive mass transfer and sorption / desorption of the solute. The more interactive the solute, the more rapidly it will be removed from solution, suppressing the height and length

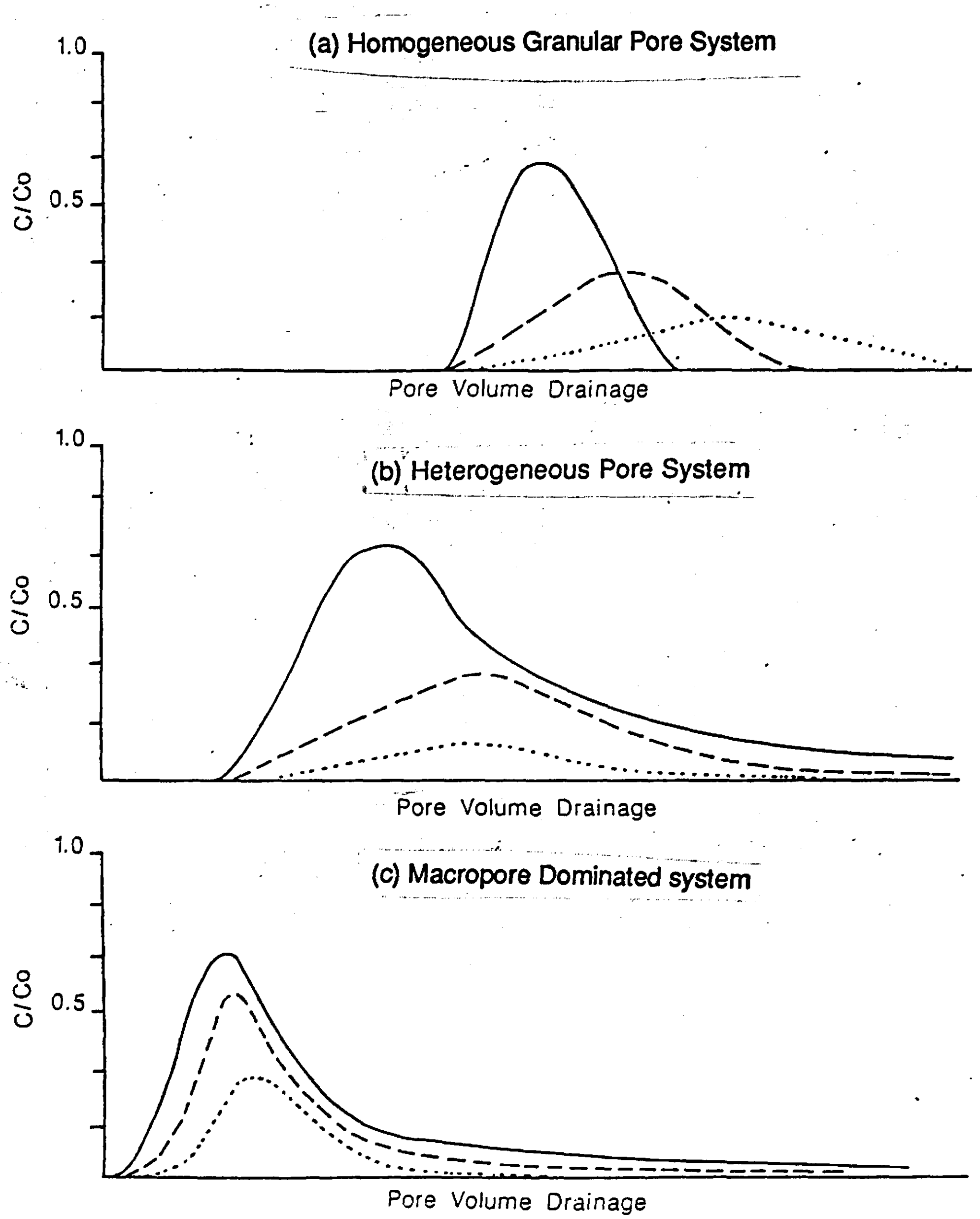


Fig. 2.4 **Hypothetical Breakthrough Curves for Solutes In Structured Soils** (the three different curves in each soil can be conceptualised as being noninteractive [—], moderately interactive [- -] or strongly interactive [•••] compounds in soils with identical physico-chemical properties. Alternatively, they may be considered to represent the behaviour of a given chemical in soils containing low [—], medium [- -] or high [•••] organic matter contents)

of the breakthrough curve tail. However, slow sorption phenomena may give rise to extremely long tails, albeit of low concentrations. A feature of such pore systems that is of great environmental significance is their ability to transmit a relatively large proportion of strongly interactive solutes. There are two main reasons for this. Firstly, where macropores have large diameters and are very long, a fraction of the solute may be transported over a long distance without coming into contact with potential sorption sites. Secondly, flow velocities in these pore structures may be such that 'mass transfers do not proceed to completion before "new" fluids have displaced incompletely equilibriated "old" fluids' (Wu and Gschwend, 1986). These are the most likely mechanisms whereby extremely interactive compounds have been able to reach groundwaters (Miller, 1987). The breakthrough curves depicted in Fig 2.4 b are the most frequently observed under natural field conditions. They are characteristic of heterogeneous porous systems which exhibit a dynamic continuum of flow phenomena (see section C.2) and comprise an infinite diversity in form, intermediate between the two extremes depicted in Fig 2.4 a and c.

To investigate the effect of the physico-chemical properties of the chemicals themselves on their transport, it is useful to use repacked homogeneous soil columns. Wilson *et al* (1981) investigated the transport of a range of organic compounds through a 140 cm long repacked sandy soil column. Retardation factors (velocity of tritiated water / apparent velocity of organic solute) ranged from <2.5 for chloroform, 1,2-dibromo-3-chloropropane, dichlorobromomethane, 1,2-dichloroethane, tetrachloroethene, 1,1,2-trichloroethane, trichloroethene and chlorobenzene to 3.4 for 1,4-dichlorobenzene and 9.4 for 1,2,4-trichlorobenzene. Seip *et al* (1986) studied the leaching of chlorinated hydrocarbons (1,1,2-trichloroethane, trichloroethene, tetrachloroethene and 1,3,5-trichlorobenzene), light aromatic compounds (benzene, toluene, *m* -xylene, nitrobenzene and dimethylphthalate) and chlorophenols from two forest soils (0.2% and 3.7% organic matter content) and an agricultural soil (2.2% organic matter). Chlorophenols were more strongly retarded than any of the chlorinated hydrocarbons (excepting 1,3,5-trichlorobenzene) or the light aromatics which both moved at similar rates. In the high organic matter forest soil, the chlorophenols were never detected in leachates, and in the low organic matter forest soil the chlorinated hydrocarbons moved almost as fast as water.

More realism is obtained if investigations of solute movement are carried out on undisturbed soil cores or under field conditions. White *et al* (1986) investigated leaching of pesticides in a well structured undisturbed clay soil core. Following one pore volume of drainage, almost 100% of a preceding bromacil pulse and 85% of a napropamide pulse were recovered in the column effluent. The authors attributed this loss to preferential flow along cracks. By contrast, in a field study of napropamide movement through a relatively unstructured loamy sand soil (Jury *et al* , 1986), 73% of the applied napropamide was localised within the surface 10 cm of soil with only trace concentrations being detected at depths of 180 cm. This behaviour is more consistent with the physico-chemical properties of the compound and, taken into consideration with the study of White *et al* (1986), demonstrated the importance of soil structure on leaching.

C.4 Transport of Organic Chemicals Sorbed on Suspended Particulate Matter

The kinetic energy of flowing water confers upon it the ability to dislodge, entrain and transport solid particles (Morgan, 1986). Pilgrim *et al* (1978) suggested that rainsplash could dislodge surface particles which could then be carried down through the soil profile by flowing water. The chemical composition of the interstitial soil water might also promote mobilisation of microparticulates. M^c^Dowell-Boyer (1992) reports that, even though flow velocity was held constant, decreasing the ionic strength of water flowing through sand mobilised colloids sorbed on the surface of the sandgrains. Guenzi and Beard (1967) suggested that sorption of organic chemicals such as DDT on these mobile colloids might enhance their transport, but the theory was not explicitly tested for many years.

Vinten *et al* (1983) found that transport of the strongly sorbed pesticides DDT and paraquat could be enhanced by sorption to mobile microparticulates. When sorbed on sewage sludge derived solids, 18% of DDT applied to a loamy sand reached a depth of 9 cm, and sorption of paraquat on a Li-montmorillonite suspension resulted in 50% of the pesticide reaching a depth of 12 cm. Jones *et al* (1989) have observed a substantial long term downwards migration of extremely persistent polycyclic aromatic hydrocarbons in soils at Rothamsted Experimental Station. The authors suggested that transport of the compounds in association with mobile colloids was partially responsible.

D. THE INFLUENCE OF INTRINSIC AND EXTRINSIC FACTORS ON THE PERSISTENCE AND MOVEMENT OF ORGANIC CHEMICALS IN SOILS

A wide range of different factors affect the transport and fate of organic chemicals in soils. These include the method by which the chemical is applied to the soil, contemporary land management practices, prevailing weather and climate, physical and chemical properties of the soil and the physico-chemical properties of the applied chemicals themselves. Donigian Jr and Rao (1987a) have classified them as intrinsic factors, comprising spatial and temporal variability of inherent natural factors such as rainfall and soil structural features, and extrinsic factors, such as cultivation and drainage, resulting from man's activities. The effects of the major intrinsic and extrinsic factors on the persistence and leaching of organic chemicals under field conditions are discussed below.

D.1 Intrinsic Factors

The major intrinsic factors controlling the persistence of organic chemicals, and the movement of water and solutes, in soils are the natural heterogeneity of the soil physical and chemical properties, and the spatial and temporal variation of rainfall.

Natural heterogeneity of soil physico-chemical properties is one of the most important factors controlling persistence. Unfortunately a complete review is not possible here because there are many thousands of relevant publications. As previously discussed, the major sorption sites in soils comprise organic matter and clay minerals. It is important to distinguish between the spatial and temporal variation of the bulk organic matter and minerals, and the physico-chemical heterogeneity of organic matter and mineral matrices themselves. If it is assumed that nonionic organic chemicals undergo only partition processes, then their persistence is most likely dominated by the spatial distribution of organic matter. For most other organic chemicals, the inherent physico-chemical heterogeneity of the organic matter and clay minerals will also have to be taken into consideration. Senesi (1993) discusses the physico-chemical heterogeneity of humic substances and the means by which they might interact with a wide range of organic chemicals including pesticides, PAHs and phenols. In subsoils where organic material is generally less abundant, the structure of clay minerals and the presence of mottles such as iron and aluminium oxides may dominate sorption / desorption (Mingelgrin and Prost, 1989). In addition to the soil solids, the heterogeneity of the soil solution must also be taken into consideration when investigating sorption / desorption phenomena. The chemical composition of the soil solution may either promote or suppress the interaction of contaminants with the solid phase. Solution chemistry is primarily a function of the organic substances that are solubilised in water as it moves through the soil profile. These include low molecular weight humic and fulvic acids which comprise hydrophillic, hydrophobic-acid and hydrophobic-neutral components. The heterogeneity of soil interstitial waters has been reviewed by Malcolm (1993). The mobilisation and transport of sorbed organic chemicals, and the immobilisation of solutes, will depend on the mixture of these components present in the soil at any point in space and time. The interaction of a wide range of organic chemicals, including pesticides (Madhun *et al*, 1986; Lafrance *et al*, 1988; Lee *et al*, 1990; Barriuso *et al* , 1992), PAHs (Larsen *et al* , 1992), PCBs (Hassett and Millicic, 1985; Chiou *et al* , 1986; Dunnivant *et al*, 1992) , chlorobenzenes (Chiou *et al*, 1986; Larsen *et al*, 1992) and solvents (Larsen *et al* , 1992), with dissolved organic matter have now been investigated. Many of these studies, particularly those with hydrophobic chemicals, demonstrate that the chemicals interact strongly with dissolved organic matter resulting in greater leaching (Enfield *et al* , 1989; Dunnivant *et al* , 1992). However, a number of studies have shown that even though interactions between organic chemicals and dissolved organic matter take place, chemical leaching was not significantly enhanced (eg. see Lafrance *et al* , 1988; Larsen *et al* , 1992).

These observations might be explained by the immobilisation of dissolved organic matter, and its associated chemicals, on clay minerals in subsoils. Strong affinity of clay minerals for dissolved organic matter has been demonstrated by Jardine *et al* (1989). The complex interactions between dissolved organic matter (and its subcomponents), organic chemicals and soil solids, their effect on subsurface migration of dissolved organic matter and their implications for chemical transport have been discussed by M^c Carthy (1993).

The implications of the soil solids versus solutions in controlling sorption / desorption can be conveniently conceptualised by the sorbent motivated-solvent motivated continuum of Weber *et al* (1991). Sorbent motivated sorption occurs where the sorbing surface has an overwhelming affinity for the sorbate (eg. the cationic pesticide paraquat on cation exchange sites of expanding clay minerals). In contrast, solvent motivated sorption takes place when a chemical is strongly repelled by water (eg. water immiscible petroleum hydrocarbons) causing them to accumulate at the solid/solution interface or on internal sorption sites of three dimensional matrices. In an effort to overcome the difficulties of characterising the multitude of different sorption / desorption interactions associated with the intrinsic natural heterogeneity of soil colloids and solutions, Weber *et al* (1992) have developed a distributed reactivity concept. The basis of the concept being that all the reactions occurring simultaneously at local sorption sites can be integrated in the form of a composite isotherm (linear or nonlinear) developed from a mass balance on the sorbed solute.

Jury *et al* (1986) demonstrated the importance of variation of soil structure by leaching 36 undisturbed soil cores, taken from a 1.44 ha loamy sand field with 23 cm of water for two weeks following a pulse of chloride and the nonionic herbicide napropamide. Four distinct types of breakthrough curve were found. Of the 36 cores, 32% exhibited breakthrough at or near one pore volume drainage, 56% exhibited retarded flow, 6% exhibited maximum napropamide concentration at one pore volume drainage and 6% exhibited bimodal breakthrough. All the breakthrough curves had long tails demonstrating that a portion of the water and the herbicide moved much more slowly through the soil. Such preferential flow pathways might be expected to predominate in surface horizons where their development will be promoted by cultivation, plant roots and earthworm activity. By contrast, subsoils are usually more dense with relatively few cracks and voids and consequently, a lower potential for preferential flow to take place. However, Kung (1990a) has found that most water (labelled with rhodamine) moving through a sandy subsoil was transmitted through <50% of the matrix between 1.5 and 2.0 m, <10% between 3.0 and 3.5 m and <1% between 5.6 and 6.6 m. Kung (1990b) defines this behaviour as 'funnelling'. This is a process, distinct from fingering or short-circuiting, whereby flow is concentrated into a series of irregular columns by water flow in regions of textural discontinuity eg. inclined bedding planes with interbedded sands.

Earthworm burrows constitute a major source of the structural heterogeneity in soils. In conventionally ploughed soils, these burrows may be disrupted at the interface with the subsoil and exert little influence on water flow to deeper horizons, whereas under zero-cultivation earthworm populations have been found to increase, creating a network of long continuous pores capable of rapidly transmitting water to subsoils (Ehlers *et al*, 1975; Germann *et al*, 1984). Edwards *et al* (1990) monitored water movement through individually instrumented earthworm burrows and found that those >5 mm in diameter removed between 1 and 10% of rainfall during twelve stormflow events.

The second major intrinsic factor controlling persistence and leaching is rainfall, and more specifically its seasonality, timing, intensity and duration. Leaching of any chemical is clearly controlled by seasonality of rainfall which varies throughout the world. Nicholls (1988) has discussed the impact of rainfall on leaching of pesticides in maritime climates such as the United Kingdom. He stresses that long term rainfall is constant throughout the year and that other meteorological factors, principally temperature, are also important in controlling leaching. In winter, rainfall normally exceeds evapotranspiration and consequently leaching predominates, whereas there is a net upwards movement of water in summer when evapotranspiration exceeds rainfall. Consequently the greatest risk to groundwater normally occurs with autumn applied chemicals whilst those applied in spring are more likely to remain in the surface horizon where their degradation will be favoured by high summer temperatures. Within any climatic zone, the day to day leaching of water and solutes will be influenced by the intensity and duration of rainfall. Germann *et al* (1984), Priebe and Blackmer (1989), Jardine *et al* (1990) and Wilson *et al* (1990) have demonstrated the sensitivity of macropore flow responses to rainfall, and the importance of timing in relation to pesticide application has been demonstrated by Isensee *et al* (1990). The latter authors reported that a low intensity, 4.8 mm, rainstorm event beginning twelve hours after application resulted in atrazine and cyanazine concentrations of up to 200 µg / litre in groundwater. High concentrations (up 600 µg / litre) of the herbicide isoproturon have also been reported in drainage waters from a mole drained heavy clay soil where rainfall occurred soon after spring application (Harris, 1991) but this author stressed that the impact on surface and groundwaters would be reduced when dilution was taken into account.

D.2 Extrinsic Factors

Extrinsic factors control persistence and leaching through their impact on the intrinsic factors discussed in section D.1. They include cultivation, artificial drainage, wastewater irrigation, crop residue disposal, agrochemical application and application of sewage sludge. The first three factors all have a profound effect on the movement of water in soils, and consequently chemical leaching, whilst the latter three factors are principally associated with the soil chemical characteristics and persistence.

Much research has focussed on comparing the persistence and leaching of agrochemicals under conventional mouldboard ploughing and reduced or no-tillage practices. Many studies (eg. see Pidgeon and Soane, 1977 and references therein) have found that more pronounced macropore networks develop under reduced cultivation due the lack of disturbance and greater earthworm populations (Ehlers, 1975). Consequently they should have a greater potential to transmit water and promote chemical leaching. These assertions have been substantiated by a number of studies. Andreini and Steenhuis (1990) have studied water movement through undisturbed grided soil monoliths from conventionally cultivated and no-till plots. Short circuiting occurred throughout the no-till monolith but only below the cultivated horizon (where water moved more slowly) in the conventionally cultivated monolith. Surprisingly, the overall water velocity was similar in both monoliths at 6.14 and 6.36 cm / day under conventional cultivation and no-till respectively. However, the authors attribute these findings to the re-establishment of earthworm burrows in the conventionally cultivated monolith. Isensee *et al* (1990) have found atrazine and alachlor residues in groundwater under no-till plots to be two to fifty times greater than under conventionally cultivated plots. In contrast Fermanich and Daniel (1991) found that more than two times as much (19.7% of applied) of the insecticide carbofuran leached from undisturbed conventionally cultivated columns than from no-till columns. The effect of cultivation becomes even more confusing with Shirmohammadi *et al* (1977) reporting that no difference in the leaching behaviour of a wide range of pesticides could be found under these two cultivation techniques. Although the effect of cultivation on soil structure, and to a lesser extent water movement, is now well understood the consequences for the transport and fate of chemicals require further investigation. For example, the conflicting evidence presented here might be due to other differences between conventionally cultivated and reduced tillage land such as organic matter content and microbial activity. If further advances are to be made, then further multidisiplinary experiments at the field scale are desirable.

The agricultural productivity of heavy clay soils and soils with textural discontinuities in maritime areas is frequently dependent on the installation of an artificial drainage system to control the water table. By their very nature, drainage systems are likely to enhance leaching of chemicals within the soil matrix and their removal from the system altogether. The installation and efficiency of different drainage systems for water management in agricultural soils has been discussed by Castle *et al* (1984). Mole drainage systems are amongst those most frequently employed. Their use in water table management and their impact on pesticide leaching has been investigated by Harris (1991). He has found that isoproturon loadings in drainflow from a clay soil over the 1989-90 growing season were twice as great in close spaced pipes (21.9 g / ha) than in conventional mole drains (12.2 g / ha) or expanded mole drains (12.3 g / ha). Plastic pipe drainage systems have also been extensively used. Harris (1991) found that such pipes enhanced the leaching of pesticides relative to conventional mole drains, and Kladivko *et al* (1991) reported that leaching of atrazine, cyanazine, alachlor, carbofuran, terbufos and chlorpyrifos increased as the spacing between such pipes was decreased. Both authors attribute these results to the greater water removal and a reduction in the soil-solute contact time in land managed by closely spaced drainage systems.

The timing, frequency and method of pesticide application to soils exerts a significant impact on the subsequent behaviour of the chemicals. Weber and Miller (1989) briefly discussed the effect of pre-emergent, post-emergent and pre-plant incorporation of pesticides on their sorption / desorption, runoff, vapour phase diffusion, and hydrodynamic transport in soils, and absorption, exudation and retention by crops and crop residues. The importance of ensuring that pesticide application is undertaken during a dry spell is apparent from the foregoing discussion on the impact of rainfall on leaching soon after application. Wyman *et al* (1985) found that aldicarb residues were restricted to the top 0.3 m and the top 0.6 m of potato fields in which the insecticide was applied at crop emergence and planting respectively. However, one year later the aldicarb residues were found throughout the surface 1.5 m regardless of the time of herbicide application (Jones *et al*,1986). Frequency of application should be restricted to the minimum necessary for adequate weed control, otherwise the concentrations of the more persistent chemicals may become so great that they might be carried over into the subsequent growing season and restrict the range of crops that can be grown (Boyd *et al* , 1990). The rate of application must also be carefully controlled; Scribner *et al* (1992) demonstrated that sugarbeet crops can be damaged if simazine application is too great. Furthermore, increasing the frequency and / or rate of pesticide application could enhance leaching. Racke and Lichtenstein (1987) found that the amount of bound residues of parathion in a silt loam soil decreased with an increase in the application rate. Thus, the proportion of the insecticide present in an extractable form, and consequently its potential to be mobilised and transported, increased. Furthermore, the formation of bound residues was greater for a mixed soil (analogous to pre-plant incorporation) than in soils where the insecticide was applied to the surface. Although pre-plant incorporation is desirable from an environmental perspective, economics dictate that surface application will remain the preferred option for farmers. Pesticide spraying usually involves the application of approximately 200-500 litres water / ha but it is unlikely that this will be a sufficient volume of water to promote pesticide leaching except under exceptional circumstance such as soils close to field capacity or extremely dry, heavily cracked clays. In dry areas where farmers have to supplement rainfall with irrigation, careful judgement must be exercised to avoid excessive leaching of agrochemicals. Wyman *et al* (1985) found that irrigation at a level equivalent to evapotranspirational losses + 60% resulted in greater aldicarb leaching, diminished foliar residues, reduced insect control and reduced crop yields when compared to irrigation at levels equivalent to transpirational losses alone. Clearly, there are dangers when excess irrigation is used in agriculture.

In addition to pesticide application, agricultural land is frequently subject to chemical inputs by way of wastewater irrigation and sewage sludge disposal. These materials comprise a complex cocktail of organic substances ranging from volatile solvents through to very persistent aromatic hydrocarbons and chlorinated insecticides. The risks of chemicals leaching to groundwater during wastewater irrigation are particularly high because applications usually range up to 250 000 litres water / ha (2.5 cm) every other day during the growing season (Weber and Miller, 1989). Even where leaching is minimal, a considerable amount of organic chemicals present in wastewater itself may be immobilised somewhere within the soil matrix with the potential to be taken up into food chains or leached to groundwater at a later date. By contrast, the application of sludges favours more rapid sorption which is enhanced by the simultaneous supplementation of the soil organic matter with the organic substances in the sludge itself. However, depending on the source of the sludge, it may contain a large proportion of organic solvents and / or surfactants which might enhance the solubility of some contaminants and promote leaching. The environmental fate and behaviour of sludge derived organic contaminants have been reviewed by Jacobs *et al* (1987) and Wild and Jones (1992).

The means by which a farmer disposes of crop residues following harvest will also affect the behaviour of organic chemicals present in, or applied to, farmland. Incorporation of either intact straw or ash will have little impact on the abundance of organic matter in the cultivated horizon. The amount of carbon added is only a small proportion of that orcanic carbon already present in the soil (Johnny Johnston, personal communication). Dao (1991) reported that the greatest sorptive capacity of intact wheat straw for metribuzin and its S-ethyl derivative was associated with the lignin fraction of the straw, whilst the cellulose fraction was of little significance. Decomposition of wheat straw was found to increase the proportion of the lignin fraction relative to cellulose, and consequently the sorptive capacity of the residue increased. The carbon rich cuticular tissue of plants has also been demonstrated to have high sorptive capacities for pesticides and other organic chemicals (Kerler and Schonherr, 1988; Schonherr and Reiderer, 1989; Boyd *et al*, 1990). Boyd *et al* (1990) have invoked partition theory to explain the sorption of benzene, ethylbenzene, and 1,2,3-trichlorobenzene by corn residues when they found that normalisation of residue partition coefficients on an organic matter basis resulted in coefficients similar to those previously reported for soils. Consequently they concluded that it may not be necessary to distinguish between the effects of soil carbon and residue carbon when predicting the behaviour of nonionic organic chemicals in soils.

CHAPTER 3

DEVELOPMENT OF A HIGH PERFORMANCE LIQUID CHROMATOGRAPHY METHOD FOR THE ANALYSIS OF ATRAZINE AND ISOPROTURON RESIDUES IN SOILS AND WATER

A. INTRODUCTION

A high performance liquid chromatography (HPLC) analytical method had to be developed for the determination of atrazine and isoproturon in environmental samples. It was desirable to have an adequate separation of the compounds (baseline resolution) with run times of less than ten minutes to facilitate routine analysis of a large number of water and soil samples. It was also necessary to minimise the need for sample preparation prior to analysis. Target detection limits were set at 1.0 µg / litre and 10 µg / kg for both herbicides in water and soil respectively.

B. HPLC SYSTEM CONFIGURATION

The analytical system consisted of a Merck Hitachi LC organiser, L-6200 intelligent pump and an L-3000 photo-diode array detector. They were controlled using Merck Hitachi D-6000 DAD Manager and HPLC Manager software packages on an IBM model AT computer. The LC organiser consisted of a Rheodyne injection port fitted with a 20 µl loop (the system did not contain a thermostat). The chromatography column used throughout the study was a Hibar Merck LiChroSpher C18 reversed phase column; 250 x 4 mm id with 5µm beads. No on-line helium degassing facilities were available. Solvents were degassed in a fume cupboard and used directly from the bottles in which they were supplied.

C. CHEMICALS

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), 99% purity, was obtained from Supelco Ltd, and isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea), 99.9% purity, from Ehrenstorfer Laboratories. Organic free water was prepared using Millipore Milli-RO 4 and Milli-Q purification systems. BDH HiPerSolv UV grade acetonitrile and HiPerSolv methanol were used throughout. Selected physico-chemical properties of atrazine and isoproturon are listed in Table 3.1.

Table 3.1 Selected Physico-chemical Properties of Atrazine and Isoproturon

	Atrazine	Isoproturon
Molecular Formula	$C_8H_{14}ClN_5$	$C_{12}H_{18}N_2O$
Molecular Weight	215.69	206.29
Melting Point (^0C)	176	155
Vapour Pressure (mbar)	3.15×10^{-5}	3.14×10^{-4}
Solubility (mg / L water, 20 ^0C)	33	70

D. PREPARATION OF ATRAZINE AND ISOPROTURON STANDARD SOLUTIONS

Stock solutions containing atrazine, isoproturon and a mixture of both herbicides (1.0 mg / ml) were prepared in 100% methanol. All three stock solutions were diluted with Milli-Q water to provide standards (100 ml) corresponding to 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 5.0, 10.0 and 20.0 mg / litre atrazine, isoproturon and a mixture of both compounds. Standard solutions were placed in a water bath at 25^{0}C for 3 hr and stirred vigorously on a magnetic stirrer for 5 min prior to their use.

E. OPTIMISING THE SEPARATION OF ATRAZINE AND ISOPROTURON

Analytical conditions were initially set at 60% acetonitrile (ACN) : 40% water at a flow rate of 1.0 ml / min which had previously been found to optimise the separation of atrazine in environmental samples. Using a 50 µl 'Hamilton' glass syringe, 20 µl aliquots of 1.0 mg / litre atrazine and isoproturon standard solutions were injected (separate analyses for each herbicide) and scanned over the 200-360 nm range to determine their respective ultra violet (UV) absorption spectra. The spectrum for atrazine consists of one well defined peak with maximum absorbance at 225 nm (Fig 3.1). By contrast, isoproturon has two peaks - one at 210 nm and another at 245 nm (Fig 3.1). Although greater absorbance occurred at 210 nm, the 245 nm wavelength was adopted for isoproturon to avoid any problems with baseline interferences that might have arisen at the lower wavelength.

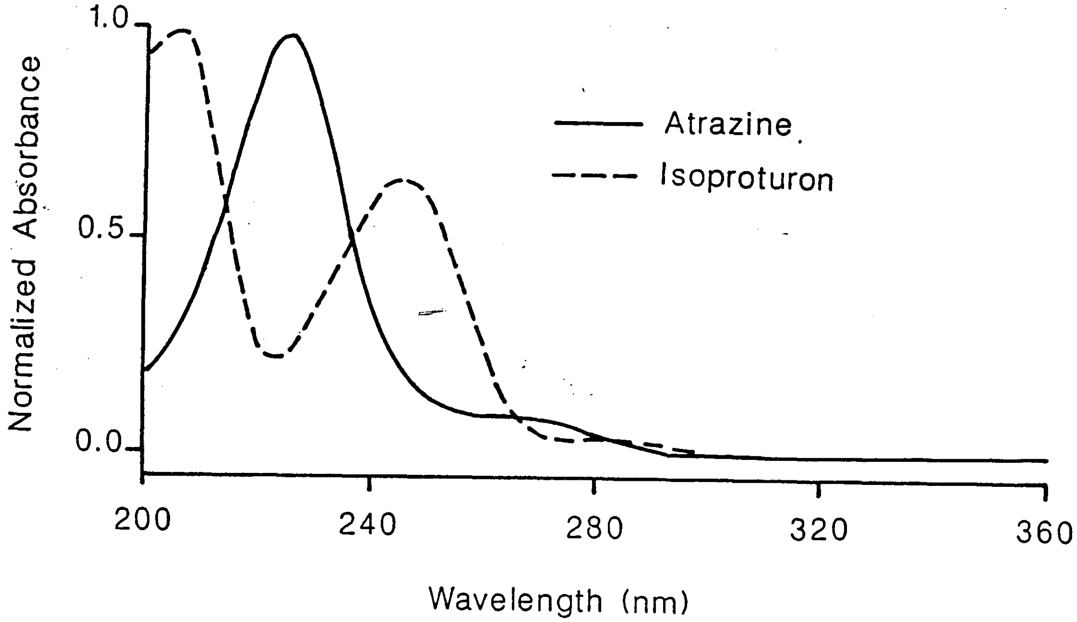


Fig. 3.1 Ultra Violet Absorption Spectra of Atrazine and Isoproturon

Using a standard solution containing a mixture of 1.0 mg / litre atrazine and 1.0 mg / litre isoproturon, the mobile phase composition and flow rate were systematically varied until the optimum separation of the herbicides was achieved. Optimum separation occurred with a mobile phase comprising 60% ACN / 40% water at a flow rate of 0.8 ml / min. Resolution of atrazine and isoproturon was estimated to be >1.0 at 1.0 mg / litre (estimate from chromatography resolution charts) but fell rapidly at concentrations above 5.0 mg / litre.

F. CALIBRATION

Using the optimum separation conditions, i.e. 60% ACN, 0.8 ml / min, calibration equations were developed for (a) atrazine only, (b) isoproturon only and (c) a mixture of both atrazine and isoproturon. The mean peak area for atrazine (225 nm) and isoproturon (245 nm) and their respective coefficients of variation at each standard concentration are shown in Table 3.2. Atrazine equation 2 and isoproturon equation 2 were determined at a later date for the calibration of a replacement HPLC column. The relevant parameters for each calibration equation, i.e. the general linear model $y = a + bx$, are listed in Table 3.3.

G. METHOD VERIFICATION

The optimum separation conditions were verified for their use in sorption / desorption studies with Brimstone clay soil taken from a site which had not previously been treated with isoproturon (see Chapter 5, section A for discussion of soil physico-chemical properties). Triplicate 25 g subsamples of <2 mm air dry clay soil was extracted by shaking with 50 ml organic free water on a rotary shaker for 24 hr. The extracts were centrifuged at 4000 xg for 10 min and filtered through a 0.22 µm cellulose acetate filter prior to HPLC analysis. No peaks were identified within the time windows of either atrazine or isoproturon elution (retention times for atrazine and isoproturon are not reported here because they varied considerably throughout the day as temperature was not controlled). Subsequently atrazine or isoproturon were added to subsamples of the extracts which were re-analysed to confirm that the chemicals were not present in the initial samples. Resolution of both compounds was >1.0 with no coelution being observed. Consequently, the separation conditions and the models in Tables 3.2 and 3.3 respectively were considered suitable for the analysis of atrazine and isoproturon in the sorption studies in Part 1 and the sorption / desorption studies in Part 3.

To assess the suitability of the method for the analysis of isoproturon residues in soils obtained from the experimental plots at Brimstone Farm, triplicate 25 g subsamples of clay soil

Table 3.2 HPLC Calibration Data for Analyses with Mobile Phase Composition 60% Acetonitrile:40% Water and a Flow Rate of 0.8 ml/min

Concentration (mg / litre)	No of Samples	Mean Peak Area (area %)	C.V.
Individual Standard Solutions*			
Atrazine equation 1			
0.05	5	8280	0.195
0.10	5	17427	0.086
0.25	5	34419	0.079
0.50	5	67774	0.053
1.00	5	127919	0.049
5.00	5	543604	0.030
10.0	5	1087670	0.005
20.0	5	2123463	0.008
Isoproturon equation 1			
0.025	5	5052	0.315
0.050	5	7256	0.280
0.100	5	9534	0.073
0.250	5	19968	0.059
0.500	5	38589	0.056
1.000	5	67297	0.050
5.000	5	328914	0.024
10.00	5	676921	0.022
20.00	5	1297314	0.007
Atrazine equation 2			
0.50	5	66006	0.016
1.00	5	139896	0.023
2.50	5	330880	0.018
5.00	5	682906	0.028
10.0	5	1393318	0.012
Isoproturon equation 2			
0.50	5	39770	0.071
1.00	5	70240	0.024
2.50	5	170870	0.018
5.00	5	337156	0.011
10.0	5	682984	0.011
Mixed Standard Solutions**			
Atrazine			
0.25	3	29331	0.073
0.50	3	61435	0.052
1.00	3	120796	0.004
2.50	3	292567	0.018
5.00	3	580191	0.003
Isoproturon			
0.25	3	18007	0.069
0.50	3	28629	0.052
1.00	3	56671	0.015
2.50	3	133573	0.015
5.00	3	267784	0.006

* Calibration data for individual atrazine and isoproturon standard solutions used in Part 1 sorption studies. ** Calibration data for standard solutions containing a mixture of atrazine and isoproturon used in Part 2 lysimeter studies.

(obtained from an isoproturon treated area) were extracted with 80% methanol / 20% water (this solvent mixture has previously been demonstrated to be an efficient extraction medium for pesticides in soils by Cotterill, 1980) for 24 hr on a rotary shaker. The extracts were prepared for HPLC analysis as described above. In the time window of isoproturon elution (5.45-5.48 min on this occasion) it was found that the resulting chromatograms were congested by peaks, none of which could be identified unequivocally as being isoproturon. Consequently, it was necessary to reoptimise the separation for the analysis of isoproturon residues in soils taken from the field experiment (see Part 3). Extensive manipulation of mobile phase composition (acetonitrile / water mixtures) and flow rate failed to resolve the compounds extracted from the soil. In an attempt to overcome this problem, acetonitrile was substituted by methanol in the mobile phase. All the peaks were clearly resolved (baseline resolution) during the first run with 60% methanol / 20% water at 0.8 ml / min. Spectral analysis of eluting compounds identified isoproturon as a clearly resolved peak with a retention time of 11.99 min. This was verified by reanalysing a subsample of the extract to which isoproturon had been added. Extensive manipulation of the mobile phase composition and flow rate failed to decrease run time and improve the sharpness of the isoproturon peak without reducing the resolution. Although the run time (15 min) with 60% methanol / 20% water at 0.8 ml / min was greater than the target run time desired for routine analysis, the method was calibrated to permit isoproturon residues (Table 3.4) to be measured in soils taken from the field experiment (parameters for the general linear model based on this data are given in Table 3.5). It should be noted that this run time was double that adopted for the laboratory sorption / desorption studies where atrazine and isoproturon were added to soils before extraction.

Analysis of 0.22 µm filtrates of drainage water from the experimental plots at Brimstone Farm with 60% ACN at a flow rate of 0.8 ml / min demonstrated that these conditions were likely to be suitable for analysis of atrazine and isoproturon residues in water samples collected during the lysimeter experiments (see Part 2). This was confirmed by analysing water samples subsequently spiked with a mixture (in the lysimeter studies both herbicides were analysed in water samples simultaneously) of both atrazine and isoproturon. Thus the method calibration

(Table 3.2) and model parameters in Table 3.3 were considered appropriate for the lysimeter studies.

Table 3.3 **Model Parameters for Analyses with Mobile Phase Composition - 60% Acetonitrile : 40% Water and a Flow Rate of 0.8 ml/min**

	Model Parameters*		
	a	b	r^2
Individual Standard Solutions			
Atrazine equation 1	-113.90	0.0094332	1.000
Isoproturon equation 1	-82.048	0.0153590	0.999
Atrazine equation 2	0.0592	0.0000072	0.999
Isoproturon equation 2	-0.0356	0.0000147	1.000
Mixed Standard Solution			
Atrazine	-0.023125	0.0000086	1.000
Isoproturon	-0.060543	0.0000189	1.000

* the general linear model: $y = a + bx$

Table 3.4 **Field Studies Calibration Data for Analyses with Mobile Phase Composition 60% Methanol:40% Water and a Flow Rate of 0.8 ml/min***

Isoproturon Concentration (mg/litre)	No of Samples	Mean Peak Area (area %)	CV
0.25	5	23065	0.063
0.50	5	40096	0.056
1.00	5	70656	0.039
5.00	5	329135	0.010
10.0	5	662659	0.013
20.0	5	1274004	0.014

* Only quantifications of residual isoproturon were based on these data. Sorption / desorption coefficients were quantified using the acetonitrile based separations (see Chapter 12).

Table 3.5 Summary of HPLC Mobile Phase Composition and Model Parameters for the Analysis and Quantitation of Atrazine and Isoproturon Concentration in Each Part of the Study

Experiment	Mobile Phase Composition	Flow Rate (ml / min)	Run Time (min)	Model Parameters a	Model Parameters b	Detection Limit (mg / litre)
Part 1 Sorption/desorption Studies*						
Atrazine equation 1	60% ACN:40% H_2O	0.8	7.5	-113.90	0.0094332	0.10
Isoproturon equation 1	60% ACN:40% H_2O	0.8	7.5	-82.048	0.0153590	0.10
Atrazine equation 2	60% ACN:40% H_2O	0.8	7.5	0.0592	0.0000072	0.10
Isoproturon equation 2	60% ACN:40% H_2O	0.8	7.5	-0.0356	0.0000147	0.10
Part 2 Lysimeter Studies						
Atrazine	60% ACN:40% H_2O	0.8	7.5	-0.02313	0.0000086	0.25
Isoproturon	60% ACN:40% H_2O	0.8	7.5	-0.06054	0.0000189	0.25
Part 3 Field Studies**						
Isoproturon	60% CH_3OH:40% H_2O	0.8	15.0	-0.16402	0.0000157	0..25

* these conditions were also used for the determination of sorption/desorption coefficients in Part 3 Field Studies (see Chapter 12).

** these conditions were only used for the quantitation of residual isoproturon (see Chapter 12).

H. ROUTINE APPLICATION OF METHOD

Fresh Milli-Q water was used each day. Water and acetonitrile were degassed for 10 min prior to their use. Before analysis, the HPLC pumps were purged with water, acetonitrile and finally a mixture of 40% water / 60% acetonitrile for approximately 1.0 min each. The flow rate was then switched down to 0.8 ml / min and the instrument left until the pressure stabilised. Then a noise test was carried out to assess the suitability of the baseline response for analysis. In the event that the baseline was unsatisfactory, the pumps were again purged and solvents were further degassed if necessary. When satisfactory baselines were achieved, a blank run was undertaken to assess whether any impurities were present in the solvents or if they were eluting from the chromatography column. Where impurities were observed, the column was cleaned up by eluting with various solvents (water, acetonitrile and methanol as appropriate) before proceeding further. In the absence of any impurities, a 1.0 mg / litre mixed atrazine and isoproturon standard was injected to determine the retention time of the compounds under the prevailing conditions. Experimental samples were then analysed in batches of up to fifty per day. Approximately 3.0 min column regeneration time was allowed between each analysis. Problems were rarely experienced while operating the instrument in this way. Spectral analysis was usually adequate for unequivocal identification of atrazine and isoproturon. On the few occasions when it was not, subsamples of the original sample were spiked with an atrazine or isoproturon standard solution and re-analysed. The calibrations were verified approximately every 250 samples. New standard solutions (0.5, 5.0 and 20.0 mg / litre) were prepared on each occasion to avoid problems with systematic errors and each solution was analysed in duplicate. The calibration equations listed were adequate throughout the lifetime of the HPLC column with one exception. This occurred when there were difficulties with the operating pressure of the HPLC, which tended to fluctuate rapidly and increase to unacceptably high levels. Consequently run times were significantly reduced and coelution problems were experienced. These results were discarded. On replacement of the HPLC column, the original calibration equations were found to be inadequate so a recalibration of the instrument was carried out. Data pertaining to this recalibration is presented as atrazine equation 2 and isoproturon equation 2 in Tables 3.2, 3.3 and 3.5. All the results in chapter 6 and also selected results in chapters 4 and 11 (see individual chapters for further details) were calculated using these equations.

I. SUMMARY AND CONCLUSIONS

The HPLC mobile phase composition and the model parameters used in each part of the study are summarised in Table 3.5. Run times of less than seven minutes were possible for the sorption phenomena experiments, lysimeter studies and sorption/desorption experiments in Part 3 with no need for sample cleanup other than mandatory centrifugation and/or filtration. Although the run time for the analysis of isoproturon residues in field experiment soils was twice as long as had been hoped, the method was considered appropriate because no special cleanup was required. Target detection limits were not attainable directly by HPLC analysis. However, they were easily reached following sample concentration by solid phase extraction and evaporation (see Chapters 4, 7 and 9).

CHAPTER 4

HERBICIDE EXTRACTION EFFICIENCY, RECOVERY FROM LABORATORY APPARATUS AND REFINEMENT OF BATCH METHOD

A. INTRODUCTION

Before undertaking any analysis of field or laboratory derived samples it was desirable to obtain some indication of the efficiency of the extraction procedure to be used and the possible effect of frequently used laboratory apparatus on the recovery of the pesticides. Cotterill (1980) has demonstrated that methanol was a more efficient extraction medium for a wide range of herbicides in nine different soils than either acetonitrile or chloroform. The literature abounds with reports that suggest that sorption to plastics such as polythene and polypropylene constitutes a major source of error in many studies and that the use of borosilicate glass or Teflon apparatus should be used in preference wherever possible. The use of microfilters in chromatographic applications has also been identified as a possible loss pathway for organic chemicals and consequently their performance should always be assessed prior to their use in experiments.

Prior to undertaking the experiments in this study, an investigation was carried out to determine the most efficient extraction medium for isoproturon residues in clay soil from Brimstone farm. Mixtures of methanol and water, and acetonitrile and water, were both investigated. The effect of extraction time was also studied. Only an end over end shaker was used; other techniques such as Soxhlet extraction were considered inappropriate for the routine extraction of large numbers of samples. Sorption of both atrazine and isoproturon to polypropylene centrifuge tubes, glass vials and Nalgene 0.22 µm cellulose acetate microfilters was investigated and the use of Waters' C18 Sep-Pak® cartridges for concentration of aqueous samples was also studied.

B. MATERIALS AND METHODS

B.1 Sorption to Laboratory Apparatus

Ten 50 ml polypropylene centrifuge tubes were prewashed as described in Chapter 5, to remove impurities before use. Twenty millilitres of aqueous atrazine or isoproturon solution (approximately 5 mg / litre with respect to each herbicide) was added to each tube which was then capped and placed on an end over end shaker for 24 hr. At the end of this period, pesticide concentrations in the solution were determined directly using HPLC. A similar procedure was used to test the glass vials with the exception that they were only prewashed with organic free water. Nalgene® 0.22 µm cellulose acetate filters were tested by filtering 20 ml of the pesticide stock solutions and analysing the filtrate by HPLC. The stock solution was analysed in triplicate to determine initial herbicide concentrations.

B.2 Concentration by Solid Phase Extraction

Waters C18 Sep-Pak® cartridges were preconditioned by eluting them with 5 ml methanol followed by 5 ml organic free water. The cartridges were then eluted with 5, 10, 20 or 50 ml of the herbicide stock solutions previously used in the 'sorption to laboratory apparatus' study. The eluants were retained and a 5 ml subsample of each was concentrated 50-fold by using a rotary evaporator (65 ^{0}C) followed by evaporation on a dri-block under a stream of nitrogen (30 ^{0}C). Subsamples of the concentrate were analysed by HPLC to assess atrazine and isoproturon breakthrough. The Sep-Pak cartridges were eluted with 1.0 ml methanol to recover the sorbed herbicides and the concentration in the elutant determined by HPLC.

B.3 Extraction Efficiency

Extraction efficiency was determined for freshly fortified clay soil prepared by mixing 500 g <2 mm untreated oven dried soil with 250 ml 10 mg / litre aqueous isoproturon solution. The mixture was dried at 30 ^{0}C for several days and homogenised by regrinding to pass a 2 mm sieve. Triplicate 10 g subsamples of fortified soil were mixed with 20 ml of extractant, which varied from 100% organic free water to 100% methanol or 100% acetonitrile, in a polypropylene centrifuge tube and shaken for 24 hr. The tubes were then centrifuged at 4000 xg for 15 min and the supernatant solutions were filtered through cellulose acetate microfilters prior to HPLC analysis. Extraction efficiency was expressed as a percentage recovery of initially applied herbicide.

C. RESULTS AND DISCUSSION

C.1 Sorption to Laboratory Apparatus

Results have been expressed as a percentage recovery of the initial herbicide input. Mean recoveries ± the standard deviation for all ten replicates, are given in Table 4.1. Recovery of atrazine from the glass vials and polypropylene centrifuge tubes was 104% and 98%, respectively, and the mean recovery of isoproturon was 102% and 103%, respectively. Thus it was concluded that sorption to the experimental apparatus was unlikely to constitute a significant source of loss during the study. However, the Nalgene 0.22 μm cellulose acetate filters did represent a significant source of loss with 15% of the applied atrazine and 17% of the applied isoproturon failing to be recovered in the filtrate.

In an earlier experiment, K_d's for both atrazine and isoproturon were found to exhibit an inverse relationship with the solid:solution ratio over the range 0.1-20 g soil : 20 ml solution. The calculated K_d's were found to range from 0.07 to 402 litres / kg for sorption of isoproturon by 5.0 and 1.0 g clay soil / 20 ml solution respectively (the worst case). Although such behaviour has been reported previously (e.g. see O' Connor and Connolly, 1980; Di Toro and Horzempa, 1982; Koskinen and Cheng, 1983; Horzempa and Di Toro, 1983; Voice *et al*, 1983), the range of differences in sorption coefficients reported by others has been small and the effect has only been observed for extremely hydrophobic compounds. Concentration dependent filtration losses have now been identified as the most probable cause of the anomalous results in the earlier experiments. Stock solutions of approximately 0.5, 1.0, 2.5 and 5 mg / litre atrazine or isoproturon were prepared in 100 % organic free water or a mixture of 80 % methanol / 20 % water (ie. the adopted extraction solvent, see section C.3). Each of these stock solutions were analysed in duplicate to determine the initial herbicide concentrations prior to filtration. Replicate 10 ml subsamples of each stock solution were then passed through 0.22 µm Nalgene cellulose acetate filters and the filtrate was reanalysed. The herbicide recoveries in the filtrates are shown in Table 4.2. Regression of mean herbicide input concentrations for atrazine (Atr) and isoproturon (Ip) against herbicide concentations in filtrates gave equations 4.1 - 4.4.

100 % water

Atr (mg / litre) = 1.086 * Atr concentration in filtrate, $r^2 = 1.000$ (4.1)

Ip (mg / litre) = 1.222 * (Ip concentration in filtrate^0.941), $r^2 = 1.000$ (4.2)

80 % methanol / 20 % water

Atr (mg / litre) = 1.0 * Atr concentration in filtrate, $r^2 = 1.000$ (4.3)

Ip (mg / litre) = 1.0 * Ip concentration in filtrate, $r^2 = 1.000$ (4.4)

Table 4.1 Sorption of Atrazine and Isoproturon to Laboratory Apparatus

Sample	% Applied Herbicide Recovered					
	Glass Vials		Polypropylene Tubes		Nalgene Filters	
	Atrazine	Isoproturon	Atrazine	Isoproturon	Atrazine	Isoproturon
1	99	98	95	102	81	81
2	102	102	97	100	88	88
3	109	99	99	104	82	81
4	104	105	100	106	83	81
5	103	105	96	105	83	81
6	104	101	98	96	82	79
7	105	103	99	103	87	86
8	100	100	98	102	89	88
9	102	104	100	106	86	82
10	108	99	101	107	89	85
Mean	104	102	98	103	85	83
St. Dev.	3.3	2.3	1.9	3.4	3.1	3.3

Table 4.2 Effects of Filtration on Atrazine and Isoproturon Material Balance Losses

Mean Input Concentration (mg / litre)*	Replicates	Concentration Recovered in Filtrate Mean	Concentration Recovered in Filtrate St. Dev.
Atrazine in 100 % water			
0.55	3	0.53	0.01
1.05	3	0.96	0.01
2.40	3	2.18	0.002
4.94	3	4.56	0.05
Isoproturon in 100 % water			
0.57	3	0.45	0.03
1.08	3	0.88	0.01
2.55	3	2.19	0.06
5.04	3	4.51	0.01
Atrazine in 80 % methanol / 20 % water			
0.58	2	0.57	0.01
1.10	2	1.09	0.01
2.32	2	2.27	0.003
4.84	2	4.82	0.03
Isoproturon in 80 % methanol / 20 % water			
0.66	2	0.62	0.002
1.12	2	1.10	0.03
2.81	2	2.68	0.06
5.10	2	5.06	0.02

* based on duplicate analysis of stock solutions

FOOTNOTE: All results presented in this thesis for atrazine and isoproturon in water have been corrected in accordance with equations 4.1 and 4.2 where filters were used. The 95 % confidence interval for the one parameter model fits to the mixed solvents data spanned 1.0 therefore none of the data relating to extraction of soil with 80 % methanol / 20 % water has been corrected for filtration losses. In Part 1 ultracentrifugation was used in preference to filters.

Repeating the solid:solution ratio experiment for isoproturon sorption by clay soil and correcting herbicide concentrations in solution on the basis of equations 4.1 and 4.2 showed that K_d's ranged from 2-5 over the range 1.0-20 g soil:20 ml solution. Results at a solid:solution ratio of 0.1 g soil:20 ml solution were not reliable because the amount of herbicide removed from solution fell within the margin of error for HPLC analysis. To verify the appropriateness of the correction factors for filtration losses eight replicate batch experiments were carried out at a ratio of 1 g soil:20 ml solution using ultracentrifugation (10000 xg) in place of microfiltration. The K_d's for isoproturon sorption by clay soil ranged from 2-5 with a mean value of 2.8 litres/kg.

C.2 Concentration by Solid Phase Extraction

Retention and breakthrough of atrazine and isoproturon from Waters Sep-Pak C18 cartridges are given in Table 4.3. No atrazine breakthrough was observed, even when the cartridge was eluted with 50 ml of 5 mg / litre stock solution. Breakthrough of isoproturon was observed on every occasion, but only amounted to 0.01% on elution of 5 ml of stock solution and never exceeded 0.5%, regardless of the volume of stock solution used to elute the cartridge. Furthermore, analysis of the concentrate has shown that retention on the cartridge was complete with the exception of the cartridge eluted with 50 ml of stock solution, for which the retention was only 93%. On the basis of these results, it was concluded that no corrections were required when C18 cartridges were used for pre-concentration of samples prior to HPLC analysis.

Table 4.3 **Retention and Breakthrough of Atrazine and Isoproturon on Waters C18 Sep-Pak Cartridges**

Volume of Stock Applied (ml)	% Applied Atrazine		% Applied Isoproturon	
	Breakthrough	Retention	Breakthrough	Retention
5	0	101	0.01	102
10	0	105	0.17	109
20	0	109	0.46	100
50	0	92	0.29	93

C.3 Extraction Efficiency

The extraction efficiency of methanol and acetonitrile was comparable over the range of aqueous mixtures investigated with the exception of the 1:1 and 3:1 organic solvent : water mixtures where the methanol based extractant was more efficient (Fig 4.1). This was consistent with the findings of Cotterill (1980) and consequently a mixture of 80% methanol and 20% water was adopted as the extraction medium for this study. The drop in extraction efficiency with 100% methanol or 100% acetonitrile was also consistent with the findings of Cotterill (1980) and is most likely explained by an inability of the organic solvent to adequately contact hydrophilic surfaces of the soil in the absence of an aqueous phase.

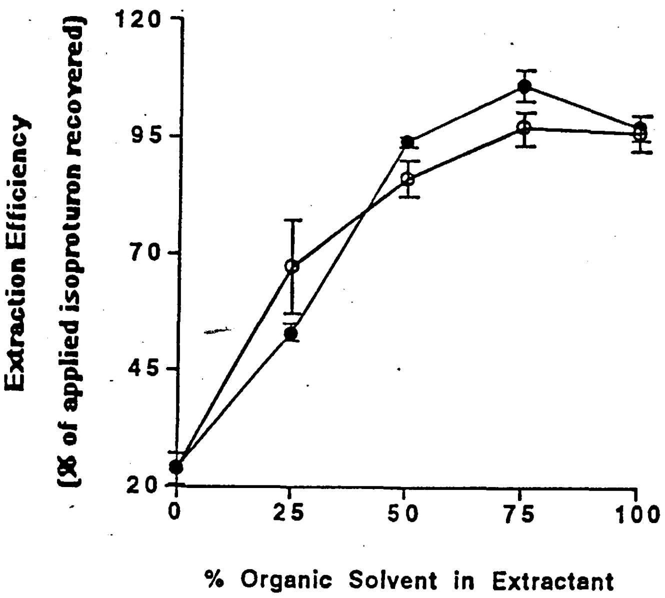


Figure 4.1 The Efficiency of Isoproturon Extraction From Clay Soil Using Methanol (●) and Acetonitrile (O) Based Extractants

All sorption mass balance experimental data in Part 1 have been corrected on the assumption that extraction efficiency was 95 %. However, field results were not corrected for extraction efficiency because these studies have been based on extraction of freshly fortified soil, whereas field experiments were based on the extraction of isoproturon residues from soil at intervals of up to twelve months following application. It has been demonstrated that extraction efficiency of a given solvent decreases with an increase in the age of pesticide residues (Pignatello and Huang, 1991). Furthermore, under natural field conditions residual carryover from previous chemical applications contribute to the mass balance at any given time. Thus, any attempt to quantify the extraction efficiency would be extremely complicated and might give rise to an estimate of residual pesticide concentration that deviates further and further from the true concentration with increasing residence time in the field.

D. CONCLUSION

It was not necessary to correct results for sorption on glass vials or polypropylene centrifuge tubes; however, a correction for material balance losses on cellulose acetate filters was made. Although correction of results to account for material balance losses due to the use of 80% methanol / 20% water as an extractant was desirable, no adjustment was made because it was impossible to determine extraction efficiency at any instant in time for field studies and consequently the corrected value might have deviated further and further from the true concentration with increasing residence time in the field.

PART 1

SORPTION PHENOMENA

PART 1: INTRODUCTORY COMMENTS

The importance of soil organic matter versus mineral components of soil in contributing to the sorption of organic chemicals by soils is discussed in Chapter 2, section B. In this study (Chapter 6), the sorption of atrazine and isoproturon by a clay soil from which the organic matter was removed by oxidation with hydrogen peroxide was investigated to provide insight into the importance of partitioning versus specific site interactions as a plausible mechanism of sorption. Specific site interactions may be expected to increase with increasing surface area of the sorbent (Stumm and Morgan, 1970). Therefore, the sorption characteristics of both herbicides on the <250 µm size fraction of the clay soil were investigated and compared to those of the <2 mm size fraction as a further test of the importance of specific site interactions.

An aspect of contemporary agricultural practice that is likely to exert some influence on the transport and fate of organic chemicals is the method of disposal of crop residues. Following the harvest of cereal crops and, to a lesser extent, of oil seed rape, peas and beans, farmers are faced with a major residue disposal problem. Typically, combine harvesting yields in excess of 5 tonnes / ha wheat straw and 3 tonnes / ha barley straw (U.K. National Farmers Union briefing notes). How a farmer disposes of straw depends on whether there is an on farm use or it can be sold; in either case the straw is removed and this organic matter is not returned to the soil. If neither of these practices is adopted then the next option has depended on his cultivation practice. Under minimum tillage practices, characterised by minimal soil disturbance, the residue has usually been burnt to aid subsequent drilling with a requirement for incorporating the ash which, if the temperature of the burn has been low, will contain much carbon. By contrast, conventional cultivation systems like ploughing provide the farmer with the option of incorporating the straw back into the soil and, with the ban on straw burning after the 1992 harvest, straw incorporation has become more widely practised in the United Kingdom. Depending on which residue disposal option is chosen, there could be different implications for the mobilisation of existing chemicals and the immobilisation of those subsequently applied. This could lead to considerable differences in their potential to leach to groundwater (see Chapter 2, section D.2 and Part 3 - Field Studies). In this study (Chapter 6) the sorption of atrazine and isoproturon by soil / residue mixtures at typical ratios observed under field conditions has been investigated. The assertion of Boyd *et al* (1990) that it may be unnecessary to distinguish between crop residue (corn straw) carbon and soil humus carbon when using the amount of soil organic matter in predicting the fate of organic compounds will be addressed and the implications of crop residues for the mobilisation / immobilisation and susceptibility of pesticides to leach to groundwater will also be discussed.

As discussed in Chapter 2 section D.1, the persistence and movement of organic chemicals in soils may be strongly dependent on the chemical composition of the soil interstitial solution. In Chapter 6 the effects of soil solutions containing organic matter, at concentrations similar to the maximum observed in the field study (see Chapter 11), on sorption of atrazine and isoproturon by clay soil are investigated and compared with sorption from solutions which were free of organic matter. Different theories for the interactions of pesticides in three phase systems, ie. solid-dissolved colloid-solution, are discussed. The effects of dissolved organic matter on isoproturon transport were investigated in the field study and are discussed later in Chapter 11, section C.

CHAPTER 5

METHODS USED TO INVESTIGATE SORPTION KINETICS OF ATRAZINE AND ISOPROTURON ON WHEAT RESIDUES AND CLAY SOIL

A. SORBENTS

Samples of wheat straw, ash and clay soil were obtained from Brimstone Farm. The soil, taken from the Ap horizon, is a pelo-stagnogley of the Denchworth series (Typic haplaquept). Wheat straw was collected from a 1 m x 1 m quadrat randomly placed on plot 6 and wheat ash from two 1 m x 1 m quadrats randomly placed on plot 10 prior to residue incorporation in the cultivated horizon after harvest 1991. The soil was air dried and gently ground to <2 mm prior to the experiments. Wheat straw was washed in organic free, deionised water to remove soil particles and other debris before being air dried and cut into lengths of 1.0-1.5 cm. Wheat ash was used directly. Selected physico-chemical properties of the clay soil are given in Table 5.1 (methods of analysis are described in Chapter 9). HPLC analyses showed that all the sorbents were free of atrazine and isoproturon at concentrations greater than 10 µg / kg.

B. CHEMICALS

The chemicals used were those described in Chapter 3, section C.

Table 5.1 **Selected Physico-chemical Properties of Brimstone Clay** *

% Sand		**% Clay**		**pH**	
mean	12.31	mean	56.3	mean	7.3
St. Dev.	0.66	St. Dev.	3.34	St. Dev.	0.09
% Silt		**% Organic Carbon**		**Texture Class**	
mean	31.39	mean	4.74	Clay	
St. Dev.	3.74	St. Dev.	0.04		

*Statistics derived from triplicate analysis

C. EFFECT OF SOIL SOLID AND SOLUTION PHASE ORGANIC MATTER CONTENT, SOIL PARTICLE SIZE AND CROP RESIDUES ON THE SORPTION OF ATRAZINE AND ISOPROTURON BY CLAY SOIL

C.1 Particle Size Fractionation

A <250 µm size fraction was separated from a portion of the bulk < 2 mm air dry clay soil by shaking for 3 hr on a sieve bank. The <250 µm size fraction was washed with a liberal volume of organic free water, air dried, gently ground and passed through the 250 µm sieve a second time to ensure homogenisation.

C.2 Oxidation of Organic Matter of the <2 mm Whole Soil

Approximately 200 g <2 mm clay soil was mixed with approximately 300 ml 30% hydrogen peroxide solution in a 1.5 litre Pyrex beaker and left to stand for 1 hr. The beaker was then placed on a sand bath at 400 ^{0}C to rapidly evaporate the hydrogen peroxide solution. When cool, the remaining residue was removed from the beaker and reground to pass through a 2 mm sieve.

C.3 Preparation of Wheat Residue and Soil Mixtures

Uniform residue incorporation, of ash or straw, at the end of the 1991 harvest at Brimstone Farm would have resulted in residue : soil ratios of 3 g wheat ash : kg soil and 17 g wheat straw : kg soil in the cultivated horizon. Assuming uniform incorporation, 3 g wheat ash can be considered to be equivalent to 17 g wheat straw. Crop residues / soil mixtures were prepared by combining 8.5 g wheat straw or 1.5 g wheat ash with 0.5 kg soil, mixing thoroughly and dividing into 5 g portions. Mixtures prepared in this way appeared to more closely resemble soils collected from the field than mixtures which were prepared in individual sample proportions (eg. by combining 4.915 g soil with 0.085 g straw).

C.4 Preparation of Dissolved Organic Matter (DOC) Solutions

DOC was prepared by shaking 500 g leaf litter, collected from a small copse at Lancaster

University, with 1.0 litre organic free water on a reciprocating box shaker for 72 hr. The mixture was filtered through a Whatman GF/A filter paper and then passed through a 0.45 µm cellulose acetate membrane filter. The resulting filtrate was referred to as DOC solution. The DOC concentration of the resulting solution was determined using a DOC analyser and diluted to approximately 28 mg DOC / litre (the maximum concentration observed in drainage water from the Brimstone Farm experimental plots). A portion of the DOC stock solution was mixed with atrazine and isoproturon standards to produce solutions of approximately 5 mg herbicide / litre DOC solution.

C.5 Organic Matter Content and pH

The organic matter content of each treatment was determined by 'loss on ignition' at 375 °C for 16 hr after drying the treated soils at 110 °C overnight (see also Chapter 9, section B.2.b.IV) . The pH for three replicates of each treatment was measured after shaking the soil, or mixtures of soil and crop residues, for 1.0 hr.

C.6 Preparation of Centrifuge Tubes

Fifty millilitre polypropylene centrifuge tubes were washed in 5% Decon 90 solution, rinsed with deionised water shaken on a rotary shaker with 20 ml of 80% methanol / 20% water overnight, and finally rinsed with organic free water and dried in a drying cupboard. Analysis of 'conventional' sorption blanks showed sorption of the herbicides to the tubes was not a problem when they were prepared this way (see Table 4.1, Chapter 4). Nevertheless, a set of sorption blanks were run during this study.

C.7 Sorption Kinetic Studies

For each treatment listed in Table 5.2, fifteen replicate 50 ml polypropylene centrifuge tubes (prewashed as described in section C.6) were prepared with 5 g of the appropriate adsorbent (with the exception of the crop residue/soil mixtures where a solid:solution ratio of 2 g solid:20 ml solution was used in anticipation of greater herbicide sorption and the 'sorption blank' treatment where no sorbent was present - see section C.9) and 20 ml of approximately 5 mg / litre atrazine or isoproturon solution (absolute herbicide concentration at t = 0 was determined by HPLC analysis). Sorbent masses were accurate to ±0.001 g and solution volumes to ±0.02 ml. The pH of the solution was measured but not standardised. Neither the background electrolyte concentration nor temperature were controlled. All operations were conducted at room temperature and the samples were then stored in a refrigerator at 4 °C until HPLC analysis was possible. The tubes were wrapped in metal foil and placed on a rotary shaker for 24 hr to monitor sorption kinetics. Three tubes corresponding to each treatment were withdrawn for analysis after 1.0, 3.0, 6.0, 12.0 and 24.0 hr periods. The soil was separated from solution by centrifugation at 4000 xg for 10 min. A 1.0 ml aliquot of each supernatant solution was removed and recentrifuged at 10000 xg for a further 10 min prior to HPLC analysis.

Table 5.2 Summary of Treatment Effects Investigated in Kinetics and Mass Balance Studies

Treatment	Solid	Solution
1) Whole soil	5 g < 2 mm clay soil	20 ml organic free water
2) Abiotic control	5 g < 2 mm autoclaved clay soil	20 ml organic free water
3) Sorption blank	no soil	20 ml organic free water
4) Particle size fraction	5 g < 250 µm clay soil	20 ml organic free water
5) Oxidised Soil	5 g < 2 mm 30 % H_2O_2 oxidised soil	20 ml organic free water
6) Wheat ash	0.006 g wheat ash / 1.994 g < 2 mm clay soil	20 ml organic free water
7) Wheat straw	0.034 g wheat straw / 1.966 g < 2 mm clay soil	20 ml organic free water
8) DOC solution	5 g < 2 mm clay soil	20 ml DOC solution

C.8 Mass Balance Studies to Determine 24 hr Sorption Coefficients

Following the measurement of atrazine and isopoturon concentration in the solutions of the three replicates of each treatment after 24 hr equilibration time during the kinetics experiments, the remainder of each supernatant solution was discarded. Sorbed atrazine and isoproturon residues were then extracted by shaking the soil with 20 ml of a mixture of 80% methanol and 20% water on a rotary shaker for 16 hr. The soil was separated from solution by centrifugation at 4000 xg for 10 min. A 1.0 ml aliquot of each supernatant solution was removed and recentrifuged at 10000 xg for a further 10 min prior to HPLC analysis. Solid phase concentrations were calculated and actual (measured) distribution coefficients were derived from this data in conjunction with the solution concentrations determined during the kinetics experiment.

C.9 Assessment of Potential Material Balance Losses During Kinetics Experiments Resulting from Microbial Decomposition and/or Sorption to Centrifuge Tubes

Results of sorption studies have frequently been subject to considerable uncertainty. Often, no account has been taken of possible material balance losses arising from such processes as photolysis, volatilisation, hydrolysis and biodegradation (Rao and Davidson, 1978) and experimental artifacts such as sorption to reaction vessels (see Chapter 4). Throughout this study, sorption experiments were carried out in the dark, by covering the centrifuge tubes with black polythene or metal foil, and by storing samples in a refrigerator to minimise photolysis. Although volatilisation was possible, the loss was considered to be minimal for the compounds of interest. Potential losses by hydrolysis were continuously assessed by monitoring HPLC chromatograms for the occurrence of hydroxy-atrazine, 4-methoxyaniline or 4-chloromethoxyaniline. By doing so it was also possible to assess potential losses by biodegradation because hydroxy-atrazine has been reported to be the preliminary breakdown product of biotic degradation of atrazine (Gamble and Khan,1992). Biodegradation was also assessed by the inclusion of a sterilised abiotic control soil in the kinetics studies described above. The soil used was sterilised by autoclaving. Sorption of herbicides to centrifuge tubes was investigated by preparing 'conventional' sorption blanks where centrifuge tubes were shaken with herbicide stock solutions, but no soil (see Table 5.2). Analysis of standard solutions stored in a refrigerator showed little evidence of breakdown of either herbicide over a three month period. Only a slight shoulder was observed on the trailing edge of the parent compounds after about two months.

C.10 HPLC Analysis

HPLC analysis was undertaken using the mobile phase composition and flow rates described in Chapter 3, section I (ie. individual atrazine and isoproturon equation 2 listed in Table 3.5).

CHAPTER 6

SORPTION OF ATRAZINE AND ISOPROTURON BY CLAY SOIL OF DIFFERENT SIZE FRACTIONS AND ORGANIC MATTER CONTENTS, CLAY SOIL MIXED WITH CROP RESIDUES AND CLAY SOIL IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

A. SORPTION KINETICS AND 'EQUILIBRIUM' DISTRIBUTION COEFFICIENTS

The kinetics of atrazine and isoproturon uptake from solution, and their 24 hr 'equilibrium' distribution coefficients for sorption by clay soil as affected by those treatments listed in Table 5.1 (see Chapter 5) are given in Figure 6.1 and Table 6.1 respectively. The organic carbon contents and pH of the soil used in each treatment are shown in Table 6.2. Over the seven different treatments, pH ranged from 6.0-6.5 ± 0.1 and from 6.0-6.3 ± 0.1 for atrazine and isoproturon respectively (Table 6.2). It was considered unlikely that differences in pH of this magnitude would significantly affect the sorption of either atrazine or isoproturon. Although the sorption of atrazine has been reported to be pH dependent (e.g. see Perdue and Wolfe, 1982, 1983), effects are usually observed at pH < 5 where increased atrazine sorption has been postulated to result from interactions with protonated carboxyl groups (Wang *et al*, 1992).

Sorption of organic compounds to laboratory apparatus during the course of batch experiments has frequently been reported to be a problem (e.g. see Rao and Davidson, 1980). However, the sorption blanks (Figure 6.1) indicate that this was not a problem for atrazine or isoproturon in this study. Given the high water solubility of these herbicides, this was perhaps not surprising.

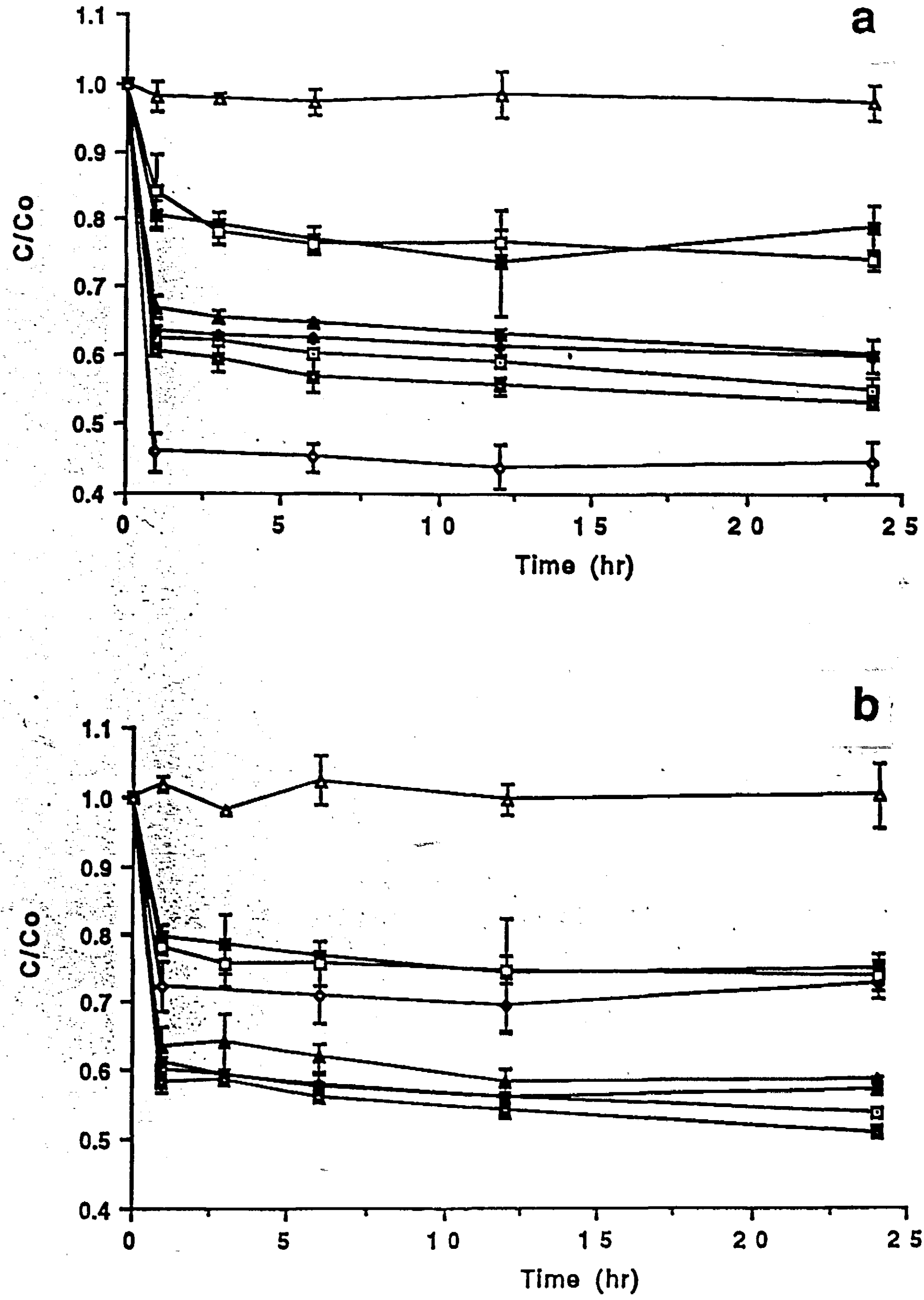


Figure 6.1 Sorption of atrazine (a) and isoproturon (b) by < 2 mm clay soil (—▫—), < 2 mm sterilised clay soil (—◆—), < 250 µm clay soil (—⊠—), < 2 mm clay soil oxidised with hydrogen peroxide (—◇—), < 2 mm clay soil mixed with straw (—■—), < 2 mm clay soil mixed with ash (—□—.), < 2 mm clay soil in the presence of DOC (—▲—) and sorption blanks containing no soil (—△—)

Table 6.1 Atrazine and Isoproturon Sorption Coefficients and Recoveries for the 24 hr Mass Balance Studies*

Sorption Treatment	% Recovery Solution		Solid		Total		Kd (Litres / kg)		Koc (Litres / kg)	
	mean	St.D.	mean	St.D.	mean	St.D.	mean	St.D.	mean	St.D.*
Atrazine										
Whole soil	55	2	46	4	101	3	3.4	0.4	84	10
Abiotic control	60	0.5	46	0.5	105	0.1	3	0.1	76	1
< 250μm fraction	53	0.4	45	2	98	2	3.4	0.2	85	5
Oxidised soil	44	3	58	2	102	4	5.2	0.3	261	17
Soil/straw	79	3	31	1	109	4	3.9	0.1	97	2
Soil/ash	74	1	31	2	105	3	4.3	0.3	85	7
DOC	57	2	48	1	105	3	3.3	0.1	83	2
Isoproturon										
Whole soil	54	1	53	1	107	2	4	0.03	99	1
Abiotic control	57	1	44	3	101	3	3.1	0.2	78	6
< 250μm fraction	51	1	53	3	104	2	4.1	0.2	104	5
Oxidised soil	73	2	29	3	102	4	1.6	0.1	81	7
Soil/straw	75	2	34	3	109	4	4.6	0.4	115	10
Soil/ash	74	2	40	4	114	4	5.5	0.6	109	11
DOC	58	0.4	53	2	112	2	3.7	0.1	91	3

*S.D. is the standard deviation, N = 3.

Table 6.2 Organic Carbon Content and pH of the Sorption Treatments

Sorption Treatment	% Organic Carbon		pH (mean ± 0.1)	
	mean	St.Dev.	Atrazine	Isoproturon
Whole soil	4.3	1.2	6.1	6.0
Abiotic control	4.1	0.1	6.0	6.1
<250μm fraction	4.2	0.1	6.1	6.2
Oxidised soil	1.9	0.02	6.1	6.1
Soil/straw	3.9	0.1	6.3	6.3
Soil/ash	5.2	0.2	6.5	6.2
DOC	4.3	1.3	6.3	6.3

Sorption of atrazine and isoproturon by clay soil sterilised in an autoclave was investigated to assess the importance of biodegradation. The Koc for atrazine sorption by sterilised soil (76 ± 1.0) and < 2 mm whole soil (84 ± 10) were not significantly different. Thus, it was concluded that biodegradation of atrazine was not a problem over the 24 hr time period of this experiment. This is consistent with other published reports (e.g. see Gamble and Khan, 1990). Whilst K_{OC}'s for isoproturon sorption by sterilised and whole soil suggest that sorption by the latter may be slightly greater than the former, total recoveries of over 100 % of the initially applied isoproturon at the end of the experiments suggest biodegradation did not occur (Table 6.1). The differences observed for sorption coefficients were most likely due to small differences in the extraction efficiency of the soil after 24 hr, e.g. note that the standard deviations on recoveries from the solid phase were generally a little greater than those for recoveries from the solution phase (Table 6.1). Recoveries of both atrazine and isoproturon from the solid phase in these experiments were corrected assuming a herbicide extraction efficienciency of 95% (see Chapter 4). In some cases the extraction efficiency may have been a little greater, e.g. note the total recoveries of 114 ± 4 % and 112 ±2 % calculated for isoproturon sorption by soil/ash mixtures and sorption in the presence of DOC (Table 6.1). This assertion can be supported by Nicholls *et al* (1993) who used a correction factor of 97.1 % for isoproturon recovery for experiments with clay soil from the same site although they used a different extraction procedure. Therefore, it must be concluded that there was unlikely to be any significant differences in isoproturon sorption by sterilised and whole soil.

Sorption coefficients for the < 2 mm whole soil in this study are consistent with those reported elsewhere. The mean K_{OC} for atrazine, 84 ± 10 litres / kg, was similar to that of 102 ± 6 litres / kg reported by Hamaker and Thompson (1972) to be the mean of eight different studies with soils containing organic carbon contents ranging from 0.1 to 44%. Furthermore, all the K_{OC}'s given in Table 6.1 for atrazine sorption in this study fall within the overall range of 52 to 412 litres / kg for the eight studies considered by Hamaker and Thompson (1972). The Kd for isoproturon sorption by < 2 mm whole soil, 4 litres / kg, was slightly greater than that of 3 litres / kg reported by Nicholls *et al* (1993) or that of 2.2 - 3.3 litres / kg reported by Bromilow and associates (personal communication) for clay soil from the same site. However, this difference probably arose from using the mass balance approach (subject to the variation in extraction efficiency discussed above) to derive distribution coefficients. Where K_d was estimated using isoproturon recovery from the solution phase alone, a value of 3.3 litres / kg was obtained for the < 2 mm whole soil, which is in much closer agreement with the aforementioned studies.

The debate surrounding the importance of soil organic matter content for sorption of organic compounds was discussed in Chapter 2. In this study a subsample of the < 2 mm whole soil was oxidised with hydrogen peroxide until approximately half the organic matter content was removed from the soil (Table 6.2). The mean single point distribution coefficient (K_d) for isoproturon sorption by < 2 mm whole soil (4.3 ± 1.2 % organic carbon) was 4.0 ± 0.03 litres / kg, approximately double that of 1.6 ± 0.1 litres / kg for the oxidised soil which contained 1.9 ± 0.02 % organic carbon. Normalisation of the K_d's on an organic carbon basis gave similar K_{oc}'s of 99 ± 1.0 litres / kg and 81 ± 7 litres / kg for sorption by < 2 mm whole soil and oxidised soil respectively. Furthermore, the K_{oc}'s for all seven treatments investigated ranged from only 78 ± 6 to 115 ± 10 litres / kg. This indicates that organic matter exerted a strong influence on the sorption of isoproturon by this clay soil, indeed it was likely to be the most important factor. This can be supported by the linearity of isoproturon sorption isotherms discussed in Chapter 4 and previously reported by Nicholls *et al* (1993). This, taken in conjunction with the extremely rapid sorption rates (Figure 6.1, see also section B), suggests that isoproturon sorption is likely to be dominated by partitioning into the soil organic matter and is free from competition with water molecules. By contrast, sorption of atrazine was more complex. Removal of organic matter from the soil resulted in an increase in sorption with the K_{oc} of the oxidised soil (261 ± 17 litres / kg) being approximately three times greater than that of the < 2 mm whole soil (Table 6.1). Assuming that the hydrogen peroxide oxidation itself had no effect on sorption, then this result suggests that atrazine may have been sorbed by sites on the clay minerals previously occupied by organic matter. Gamble and associates have reported similar effects from their investigations of atrazine sorption/desorption kinetics. For example, Wang *et al* (1992) report stoichiometric binding capacities of 0.1-0.4 µM atrazine / g soil containing approximately 13 % organic carbon depending on pH whilst Gamble and Ismaily (in press) found that in a mineral soil containing 8 % organic carbon the mean binding capacity (in neutral aqueous solutions) was 0.7 µM atrazine / g soil. Wang *et al* (1992) postulated that the sorption of atrazine by organic matter was strongly pH dependent, i.e. sorption increased with an increase in the protonation of carboxyl groups at pH < 5, whilst sorption by mineral components was only weakly affected by pH. They offered no explanation as to the mode of interaction between atrazine and soil mineral components.

Another important dimension to the partition versus adsorption debate has been the importance of soil particle size. Stumm and Morgan (1970) have asserted that specific site interactions may be expected to increase with an increase in the surface area of the sorbent. Nkedi-Kizza *et al* (1983) investigated the sorption of diuron and 2,4,5-T to five different size fractions, ranging from 0.2-2000 µm, of a sandy clay loam. They reported that Freundlich sorption coefficients for diuron varied by a factor of 7 over this particle size range, but only by a factor of 1.5 when the sorption coefficients were normalised on an organic carbon basis. By contrast, a different K_{OC} value could be assigned to sorption of 2,4,5-T by size fractions ≤ 50 µm (fines) and those between 50 and 2000 µm (coarse). The cationic herbicide paraquat exhibited a much more complex relationship with particle size for five natural sediments (Karickhoff and Brown, 1978). For individual sediments, sorption coefficients varied over two orders of magnitude within the particle size range < 0.08 to > 64 µm and was correlated with the cation exchange capacity of the size fractions. Sorption by pure clay suspensions (hectorite and montmorillonite) showed that sorption was favoured by the mid-size range i.e. 0.065-0.44 µm. In this study, no significant differences were observed for the sorption of atrazine and isoproturon between < 2 mm whole soil and < 250 µm whole soil Table 6.1) which both contained the same amount of organic matter (Table 6.2). However, this may have been partly due to slaking of the < 2 mm size fraction into a mixture of smaller sized particles.

Sorption of atrazine and isoproturon by a mixture of < 2 mm clay soil and wheat straw in proportions similar to those estimated for cultivated horizons in the field, i.e. 17 g wheat straw / kg soil, was only slightly greater than that by soil alone - 97 ± 2 compared to 84 ± 10 litres / kg for atrazine and 115 ± 10 compared to 99 ± 1 litres / kg for isoproturon (Table 6.1). However, it should be noted that fresh, intact wheat straw was used in this study. Dao (1990) has reported that the sorptive capacity of wheat straw for metribuzin increased as the straw decayed and the proportion of lignin relative to cellulose in the residue increased. Boyd *et al* (1992) investigated the sorption of nonionic organic chemicals by corn residues and plant cuticles and concluded that it was unnecessary to distinguish between crop residue carbon and soil humus carbon when predicting the fate of such compounds because both functioned as a partition phase. Thus, it might be possible that sorption of these herbicides, particularly isoproturon, may have been enhanced if partially decomposed straw had been used. Indeed, it should be noted that there was a slight tendency towards increasing sorption coefficients with time in the field plot managed by straw incorporation (see Chapter 11). However, it is difficult to attribute this effect solely to the decomposition of crop residues given the complexity of field behaviour. In any case, the same effect was observed on the plot where the crop residues were burnt. Furthermore, the contribution of wheat straw carbon to the mixture was minute in comparison to that of the soil humus carbon. A similar tendency towards slightly increased sorption of isoproturon, but not atrazine, was observed for the soil / wheat ash mixtures (Table 6.1). The K_d's reported for sorption of both herbicides by mixtures of both soil and straw, and soil and ash (Table 6.1) are consistent with the K_d's reported for the field study (see Chapter 11).

The presence of dissolved organic carbon in soil solutions has been reported to enhance the solubility of a wide range of organic compounds (e.g see Madhun *et al*, 1986; Larsen *et al*, 1992; Chiou *et al*, 1986) including atrazine (La France *et al*, 1988). Given the influence of organic matter on isoproturon sorption (see above) then it might be expected that the presence of DOC in solution would enhance the solubility of this herbicide by creating an additional 'partition/adsorption medium'. However, K_{oc}'s for atrazine (83 ± 2 litres / kg) and isoproturon (91 ± 3 litres / kg) sorption by < 2 mm whole soil in the presence of 28 mg DOC / litre were virtually identical to those for sorption in the presence of organic-free water. The concentration of DOC, 28 mg / litre used corresponds to the maximum concentration detected in drainflow from the Brimstone site during a two year monitoring programme, which was approximately 4-5 times greater than typical background concentrations of 6 mg DOC / litre (see Chapter 10). A number of explanations can be offered to explain the lack of any solubility enhancement effects in this experiment. Firstly, sorption may have been strongly sorbent-motivated whereby the physico-chemical composition of the solid phase exerted a much stronger influence on the herbicides in solution than the chemical composition of the solution (Weber *et al*, 1991). Secondly, the organic matter in solution may have been dominated by dissolved humic as opposed to fulvic acids which have been reported to interact more readily with atrazine (Wang *et al*, 1992). Thirdly, the chemical composition of dissolved organic matter has been reported to vary greatly within and between soils (Malcolm, 1993) so it is possible that the DOC used in this study would not have the same effect on sorption as that DOC present in soil interstitial solutions from the field site. However, it should be noted that there was no evidence to support a solubility enhancement effect under field conditions either (see chapter 11). Finally, as discussed above the interaction of atrazine with organic matter is strongly pH dependent, particularly at $pH < 5$. The pH of the DOC solutions used in this study were 6.3 ± 0.1 for both herbicides (see Table 6.2) so the protonation of carboxyl groups on DOC, reported to be a requirement of atrazine sorption (e.g. see Perdue and Wolfe, 1982, 1983; Wang *et al*, 1992), was unlikely to be significant.

B. EMPIRICAL KINETICS MODELS

The uptake of chemicals from solution is usually fitted with a first order negative exponential function:

$$- dC/dt = kC_o \qquad (6.1)$$

where C is the contaminant concentration at time t, C_o is the contaminant concentration at $t = 0$ and k is the first order sorption constant.

Integrating (1) gives:

$$C = C_o e^{-kt} \qquad (6.2)$$

Assuming such conditions, the 'half-equilibrium' time, similar to the half life concept for contaminant loss in the field, can be calculated to facilitate the comparison of data:

$$C/C_o = e^{-kt} \qquad (6.3)$$

and where $C/C_o = 0.5$:

$$0.5 = e^{-kt_{0.5}} \qquad (6.4)$$

where $t_{0.5}$ is the 'half-equilibrium' time.

The first order exponential relationship is probably the most frequently used model to fit sorption results. However, a number of other empirical models have sometimes been used. These include the straightforward power law where the contaminant concentration is directly proportional to some power (n) of time:

$$C = t^n \qquad (6.5)$$

the fractional power or modified Freundlich equation:

$$C = kt^n \qquad (6.6)$$

where k and n are constants such that $n \neq 1$,

the Elovich equation:

$$C = A + (1 / b) \ln(t + t_o) \qquad (6.7)$$

where A, b and t_o are constants although the last is usually sufficiently small to be disregarded (Aharoni and Sparks, 1991),

the pseudo-first-order equation:

$$C/C_\infty = 1 - b\exp(-at) \qquad (6.8)$$

where C_∞, b and a are all constants such that C_∞ is the contaminant concentration remaining in the soil when $t \rightarrow \infty$ (Aharoni and Sparks, 1991), and:

$$C = a + (b / \mathrm{sqrt}(t)) \qquad (6.9)$$

where C is concentration, sqrt(t) is the square root of time and a and b are constants (e.g. see Crank, 1975).

Finally, in some instances, e.g. rapid sorption of solvents or extremely slow sorption of recalcitrant contaminants such as highly chlorinated species, the linear model:

$$C = a + bt \qquad (6.10)$$

may prove most useful.

Of these, equation 6.9 provided the best fit to the kinetics data presented in Figure 6.1 (see Table 6.3). This was not surprising given the dinstinctive biphasic behaviour observed and the very rapid uptake during the initial phase of sorption. This model is usually interpreted in two-site terms, i.e. chemical sorption is assumed to be rate-limited by diffusion through micropores or organic matrices (e.g. see Chapter 2). Long term persistence of atrazine in soils has been reported. For example, Capriel *et al* (1985) report that 7, 17 and 22 % of ^{14}C-labelled atrazine applied to a mineral soil in1973 was still present in the humic acid, fulvic acid and humin fractions of the soil respectively, nine years later. They attributed this persistence to the formation of bound residues. Pignatello and Huang (1991) reported the presence of atrazine in soil 15 months after its last application and in a later paper Pignatello *et al* (1993) attributed this long term persistence to radial diffusion kinetics in microparticles. Although the limited time scale of the sorption experiments undertaken in this project precludes definitive conclusions on slow sorptive phenomena, the observation that atrazine sorption increased (on an organic carbon basis) when organic matter was partially removed from the soil (see section A) may offer support for radial diffusion kinetics. By contrast, long term persistence of isoproturon is more likely to be caused by intraorganic matter diffusion (Chapter 2). However, it has been suggested that an understanding of these microscale phenomena at the field scale may not be necessary (Brusseau *et al*, 1991). At the field scale, the behaviour of interest may be adequately represented by the 24 hr 'equilibrium' constant and some knowledge of the fraction of the the chemical persisting in the soil over the long term e.g. the chemical half life.

Table 6.3 Parameters and Goodness of Fit for the Model y = a + (b / sqrt(x)) when Applied to the Sorption Kinetics Data shown in Figure 6.1

Sorption Treatment	Parameter a estimate	Parameter a 95% CI	Parameter b estimate	Parameter b 95% CI	r^2
Atrazine					
Whole soil	0.589	0.556-0.622	0.013	0.010-0.016	0.999
Abiotic control	0.612	0.599-0.626	0.012	0.011-0.013	1.000
< 250μm fraction	0.562	0.531-0.594	0.014	0.011-0.016	0.999
Oxidised soil	0.462	0.386-0.539	0.017	0.012-0.022	0.996
Soil/straw	0.378	0.364-0.392	0.020	0.019-0.021	1.000
Soil/ash	0.378	0.360-0.395	0.020	0.018-0.021	1.000
DOC	0.633	0.604-0.662	0.012	0.009-0.014	0.999
Isoproturon					
Whole soil	0.566	0.538-0.594	0.014	0.012-0.016	0.999
Abiotic control	0.576	0.556-0.596	0.013	0.012-0.015	1.000
< 250μm fraction	0.547	0.512-0.582	0.014	0.012-0.017	0.999
Oxidised soil	0.708	0.685-0.732	0.009	0.008-0.011	1.000
Soil/straw	0.374	0.366-0.383	0.020	0.019-0.020	1.000
Soil/ash	0.368	0.364-0.372	0.020	0.020-0.020	1.000
DOC	0.611	0.571-0.651	0.012	0.009-0.015	0.999

The use of empirical models such as those described here is advantageous insofar as it is possible to predict sorption from the change in one variable, usually contaminant concentration, with time. Consequently, these models have been widely used as a means of obtaining forecasts which provide a useful *approximation* of contaminant behaviour under the same conditions as those under which the experiment was done i.e. without having to resort to the time and expense of measuring or deriving the more numerous and complex input parameters required for mechanistic models. However, there are major limitations to the use of empirical models. Although specifically discussing their use to fit chemical kinetics data, the limitations in the use of empirical models generally have been eloquently summarised by Aharoni and Sparks (1991):

> '... no consistent theoretical derivation can be found for these equations ... there is no correlation between the applicability of any of these equations and the nature of the process, dissimilar processes are fitted by the same equation and similar processes are fitted by different equations.'

Thus, where it is necessary to obtain more rigorous predictions of contaminant behaviour or where the model is to be used for research purposes such as parameter sensitivity analysis, mechanistic models may be more appropriate. The scientific literature on mechanistic models is vast. Those pertaining to sorption kinetics have been reviewed by Pignatello (1989) and Brusseau and Rao (1990).

PART 1: CONCLUDING REMARKS

Sorption of atrazine and isoproturon was extremely rapid with most of the herbicide being removed from solution within the first hour of the 24 hr sorption experiments. Whilst, a second phase of slow sorption appeared to occur over the remaining 23 hr of the experiment, the duration of the experiment precludes any definite conclusions on long term sorption phenomena. If long-term behaviour was found to be consistent with the model fits presented in Chapter 6 then the proportion of the herbicide participating in this long term behaviour would be 50-60% compared to that of 40-50% participating in the preliminary phase of rapid sorption. For example, approximately 38% of the atrazine initially present in solution was removed by < 2 mm whole soil within 1.0 hr, but if sorption continued in accordance with the fitted model then up to 60% more atrazine would be removed from the solution if time was not a limiting factor. This suggests that the 24 hr 'equilibrium' distribution coeficients may be inadequate to characterise the sorption of these chemicals in the field. However, it should be stressed that the overall behaviour of interest for any chemical is dependent on a diverse range of factors (e.g. mass transfer considerations, sorptive reversibility and agricultural management practices) so sorption coefficients, derived using batch techniques alone are unlikely to adequately describe chemical transport and fate (see Part 3).

The batch technique used here gave reproducible results unaffected by losses arising from either sorption to experimental apparatus or biodegradation. With K_d's of approximately 3 and 4 for atrazine and isoproturon respectively, these herbicides can both be classified as moderately persistent. Despite the similarity of their overall K_d's, a higher K_{oc} for atrazine on oxidised clay soil suggests that the sorption of this herbicide was partially influenced by the soil mineral components whilst the similarity of the K_{oc}'s for isoproturon sorption by oxidised and whole soil suggests organic matter dominated its sorption. This indicates that whilst partitioning into organic matter may be an important sorption mechanism for both herbicides, specific site interaction or radial diffusion in mineral grains might contribute to the sorption of atrazine. However, the lack of any significant difference between sorption of atrazine by < 250 µm and < 2 mm size fractions of the clay soil fail to support this assertion. The presence of straw or ash in the solid phase, or DOC in the solution phase, had no marked affect on the sorption of either herbicide. These results were consistent with the results of the field experiments which have been presented in Part 3.

PART 2

SOIL CORE STUDIES

PART 2: INTRODUCTORY COMMENTS

The importance of water movement through soils and its implications for the redistribution of organic chemicals within soil profiles and their transport into surface water and groundwater was discussed in Chapter 2. Whilst most realism is obtained by conducting investigations of chemical leaching under field conditions, laboratory studies are advantageous insofar as it is possible to exert some control over hydrological conditions, namely simulated rainfall intensity and duration. Most early work used small, repacked soil columns (eg. Wilson *et al*, 1980; Seip *et al*, 1985). Lately, the results obtained from such studies have been questioned because the columns do not represent the natural physical and chemical heterogeneity of soils at the field scale (White *et al*, 1986).

The primary objective of this part of the project was to establish a large undisturbed soil core which would more adequately represent field scale variability, albeit under laboratory conditions. The core was instrumented with suction samplers, gravity drainage samplers, pressure transducer tensiometers (PTT) and time domain reflectometry probes (TDR) to facilitate the collection of data which could be used for the verification and validation of existing bicontinuum chemical transport models and also the development of new models. By excavating the core from the Brimstone site, it was also possible to compare leaching behaviour under controlled laboratory conditions with that observed in the field and thus to assess the potential use of such cores as substitutes for expensive large scale field experiments.

The excavation of the undisturbed soil core and its subsequent set-up in the laboratory is discussed in Chapter 7. Experimental schedules for a preliminary series of experiments, carried out to assess the performance of the core instrumentation and data logging facilities, are also described. Some useful data were obtained during these early experiments and consequently, Chapter 8 has been devoted to a discussion on the nature and variability of atrazine and isoproturon solute breakthrough curves under unsaturated conditions. PTTs have to be recalibrated after all the experiments on the core are completed and TDR switching mechanisms were found to be faulty so none of this data is discussed here.

CHAPTER 7

ESTABLISHMENT AND PERFORMANCE EVALUATION OF A LARGE, INSTRUMENTED, UNDISTURBED SOIL CORE FOR THE INVESTIGATION OF WATER FLOW AND CHEMICAL LEACHING

A. CORE EXCAVATION AND LABORATORY SET-UP

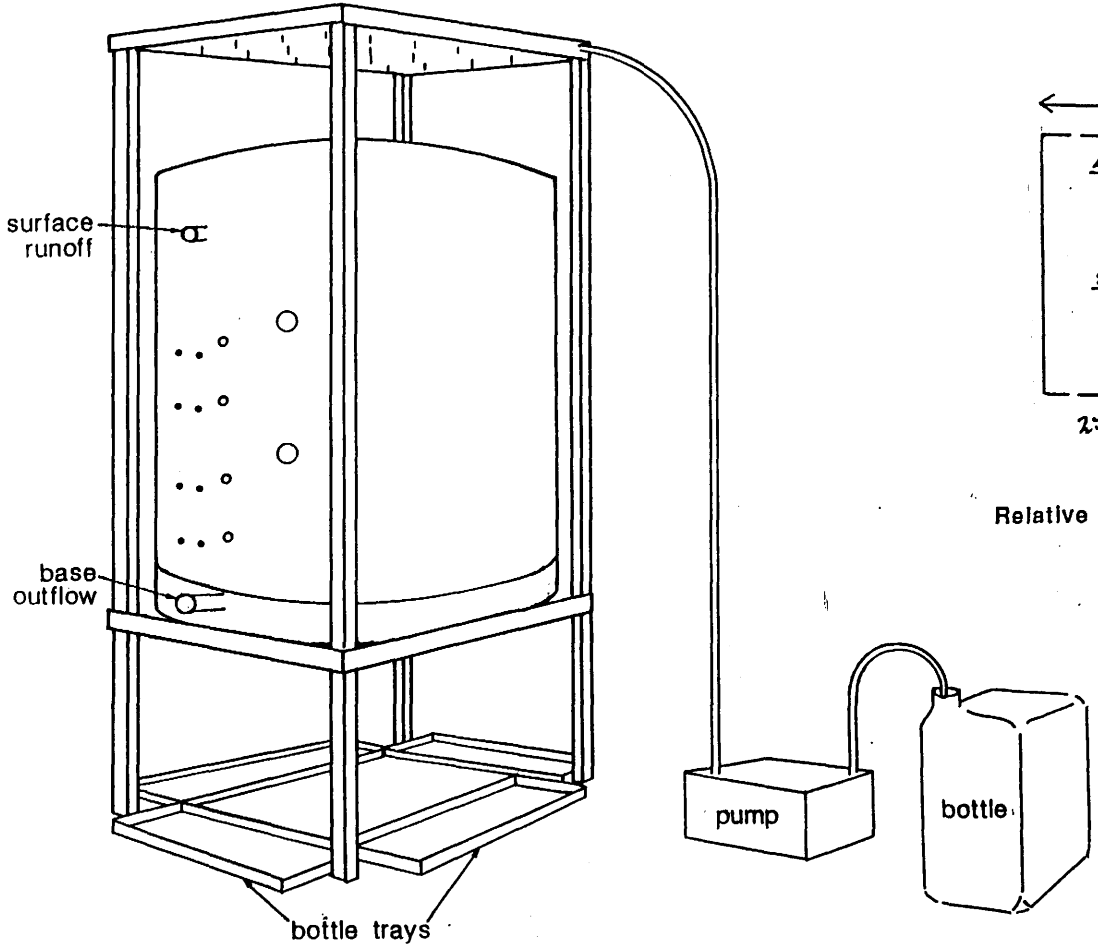
A.1 Core Excavation

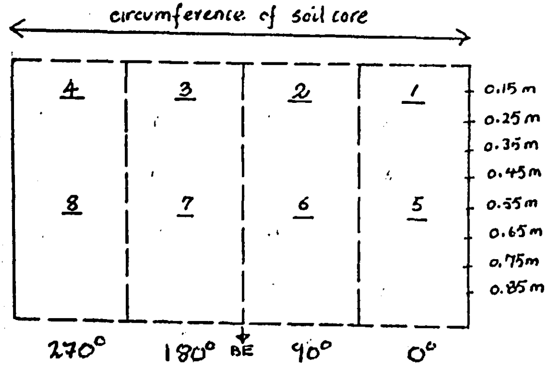
The soil core is contained in a glass fibre reinforced polyester cylinder (0.8 m od., 0.788 m id., 1.35 m long) with a steel base plate coated with Araldite, containing an integral drainage sampling point (Howse and Goss, 1982). Using this cylinder, an undisturbed soil core was excavated from the southern discard area of the Brimstone Farm site using a procedure previously described in detail by Belford (1979).

A.2 Laboratory Set-up

The undisturbed soil core was set up in the laboratory as shown in Fig 7.1. Specialist contractors were employed to lift the soil core onto a reinforced stainless steel framework mounted on wheels (A) so that the soil core could be moved if required. A second frame (B) was bolted onto the base framework to support the rainfall sprinkler (C). The rainfall sprinkler was constructed using 12 precision bored, square edged brass tubes into which '20 gauge' hypodermic syringe needles were inserted at 5 cm intervals such that rainfall could be uniformly applied to the soil surface. Each rod was connected to a single feeder rod using brass valves so that each rod could be turned off independently if problems were encountered or if a lower rainfall application density was required. The feeder rod was connected to a Watson Marlow computer driven peristaltic pump (D) and a 25 litre polypropylene bottle (E) containing the input solution.

Eight water samplers were installed in the soil core such that four of them were equidistant





Relative positions of the core water samplers

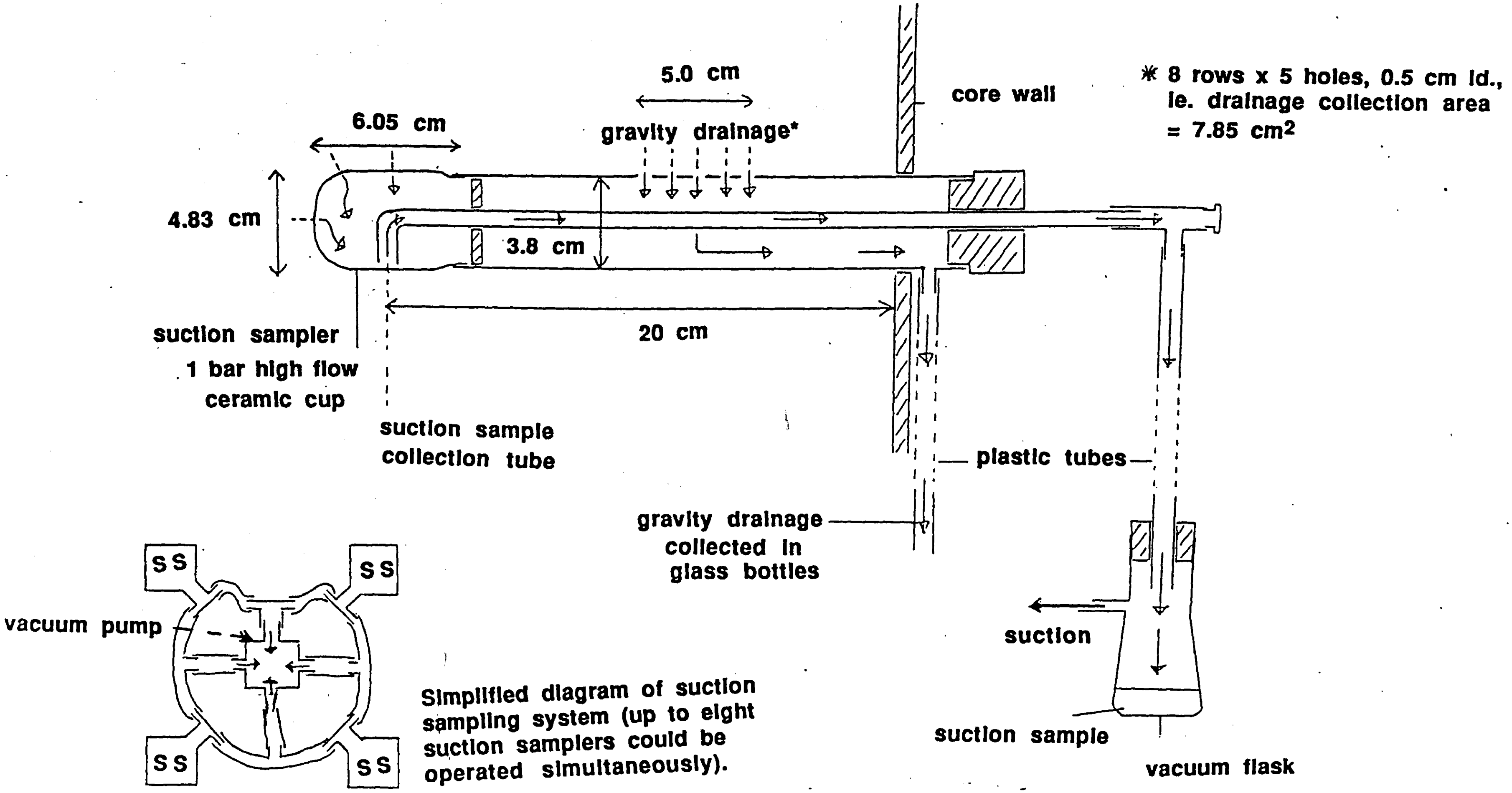
Figure 7.1 **Laboratory Set-up of the Undisturbed Soil Core** (not to scale) from each other in a horizontal plane at the bottom of the cultivated horizon and the remaining four were installed directly below in a horizontal plane at 0.55 m, equivalent to the depth of mole drains in the field, (F). The precise location of each sampler is described in relation to the position of sampler 1 in the inset to Figure 7.1. Each water sampler incorporated a suction sampler (SS) and a zero suction, or gravity drainage (GD), sampler as shown in Fig 7.2. The samplers were installed in the core such that the tip of the suction sampler was 0.2 m from the core side. Suction samples were collected in 500 ml vacuum flasks connected by a manifold to a high vacuum pump and zero suction samplers drained freely into 500 ml amber glass bottles. All collection bottles were secured in a rack at the bottom of the cylinder (G). Sampling points were also installed to facilitate the collection of surface runoff (H) and water reaching the base of the soil core (I).

Sixteen tensiometers were inserted in the core, arranged in four banks of four such that the instruments in each horizontal plane were equidistant and the vertical separation of each plane was 0.2 m (J). All tensiometers were inserted so that the tip of their ceramic cups was 0.2 m from the core side. The design and construction of the pressure transducer tensiometers has been described by Henderson (CRES/QA/WIN/TEN/1.0/9105). Sixteen pairs of time domain reflectometry probes were constructed from 0.25 m x 0.003 m id. stainless steel rods, wired and completely embedded within the soil in four banks of four in a similar arrangement to the tensiometers (K). The construction, theoretical background and operation of the time domain reflectometry system has been described by Henderson (*in preparation*). All core instrumentation was arranged to maximise the distance between each instrument so that interference was minimised. Data logging, with the exception of solute sampling, was completely automated and has been described by Blakely (*in preparation*).

B. CALIBRATION OF CORE INSTRUMENTATION

B.1 Calibration of Rainfall Simulator

The rainfall simulator was calibrated by running the peristaltic pump at speeds of 5, 10, 15, 20 and 25 rpm (revolutions per minute) for 30 min periods. The water was collected in a bucket / -



Simplified diagram of suction sampling system (up to eight suction samplers could be operated simultaneously).

Figure 7.2 Combination Suction/Zero-suction Water Sampling Apparatus (after Lam, 1992) using a funnel, made from polythene, suspended under the sprinkler. The calibration was given by equation 7.1.

$$\text{Pump speed (rpm)} = 0.99 + (9.6\times10^{-3} * \text{rainfall application rate, mm / hr}) \quad r^2 = 0.999 \qquad (7.1)$$

The uniformity of rainfall application was investigated by suspending four plastic trays below the hypodermic syringe needles so that water from 44 of the needles was collected in each tray. The rainfall simulator was run at pump speeds of 5, 15 and 25 rpm for 30 min periods. The volume of water collected in each of the four trays was measured and the uniformity of water application was calculated using equation 7.2.

$$C_u = 100 * \{1.0 - (x / mn)\} \qquad (7.2)$$

where C_u is the uniformity coefficient, n is the number of observations, m is the mean value of the observations and x is the deviation of the individual observation from the mean value (Christiansen, 1942; *cited in* Andreini and Steenhuis, 1990).

Uniformity coefficients of 89%, 93% and 94% were obtained at pump speeds of 5, 15 and 25 rpm respectively; thus the uniformity of rainfall application was acceptable. The total water inputs for experiments 2 and 3 were less than the expected 5 mm / hr; actual application rates were approximately 3.9 and 3.4 mm / hr for experiments 2 and 3 respectively (see Table 7.1). This temporal distribution suggests that rainfall application was variable within any time span.

B.2 Calibration of Pressure Transducer Tensiometers and Time Domain Reflectometry Probes

Calibration of the pressure transducer tensiometers has been discussed in detail by Henderson (CRES/QA/WIN/TEN/1.0/9105). Time domain reflectometry probes will be calibrated on completion of the soil core studies when soil from the core itself can be used in the calibration procedure. These are not discussed further here because tensiometer and reflectometry data are not considered in the results (Chapter 8).

Table 7.1 Simulated Rainfall Events

	Rainfall Application Rate (mm / hr)		Rainfall Duration (hr)	
	Intended	Actual	Intended	Actual
Pre-wetting Experiment* unlabelled	2.0	1.4	10	10
Experiment 1 86.9±0.7 mg bromide/litre	variable**		240	144
Experiment 2 40.6±0.21 mg PFBA/litre	5.0	3.9	10	11
Experiment 3 31.56±0.07 mg 2,6-DFBA/litre	5.0	3.4	10	12

* Duration between pre-wetting experiment and experiment 1 = 34 hr, duration between experiment 1 and experiment 2 = 35 hr, duration between experiment 2 and experiment 3 = 245.5 hr.

** variable rainfall over 0.5 hr intervals such that intended daily totals were 4.2, 9.8, 23.8, 1.4, 14.4, 3.6, 16.6, 3.8, 18.0, 1.2, and 3.6 mm / day which was equivalent to 100.4 mm over 240 hr duration of experiment. Actual application was only 19.67 mm when the experiment was terminated after 144 hr. The temporal variability of this application is uncertain.

C. VERIFICATION OF THE SUITABILITY OF POTASSIUM BROMIDE, PENTAFLUOROBENZOIC ACID AND 2,6-DIFLUOROBENZOIC ACID AS WATER TRACERS

C.1 Calibration and Analysis of Tracers in Core Effluent

The tracers used in this study were analysed by high perfomance liquid chromatography using the method described by Bowman (1984). Calibration equations used for bromide, pentafluorobenzoic acid and 2,6-difluorobenzoic acid quantitation in this study are shown below.

Bromide Concentration (mg / litre) = -0.024122 + (1.9439x10^{-5} x abs 205 nm)

$r^2 = 1.000$ (7.3)

PFBA Concentration (mg / litre) = -0.10312 + (4.8833x10^{-5} x abs 205 nm)

$r^2 = 0.999$ (7.4)

2,6-DFBA Concentration (mg / litre) = 0.026995 + (2.7647x10^{-5} x abs 205 nm)

$r^2 = 1.000$ (7.5)

It should be noted that difficulties were frequently encountered in the use of Bowman's method. Whilst the tracers were all clearly resolved with no overlap between them, elution times were erratic on a day to day basis. Standard injections had to be made frequently to provide confidence in the results obtained. These difficulties were even experienced with a new chromatography column and the reason for them was not apparent. It is possible that the method may be very sensitive to small fluctuations in mobile phase pH and / or temperature but further work will be required to resolve these difficulties.

C.2 Batch Sorption Studies of Tracer Conservativity

Conservativity of the tracers was evaluated by carrying out batch sorption studies on clay soil taken from the undisturbed soil core when the solution samplers were installed. Triplicate 20 g samples of soil (1 sample from 15 cm depth and 2 from 55 cm depth) were mixed with 20 ml tracer solutions at their experimental input concentrations and shaken on a rotary shaker for the duration of the leaching experiments on the undisturbed soil core. They were then centrifuged at 4000 xg for 30 min and the supernatant solutions filtered through Nalgene 0.22 μm filters prior to HPLC analysis.

Recoveries (mean of three replicates) were 113%, 117% and 105% for bromide, PFBA and 2,6-DFBA respectively. Thus, it was assumed that all three tracers were conservative over the duration of the leaching experiments.

D. MATERIALS AND METHODS FOR PRELIMINARY PERFORMANCE ASSESSMENT EXPERIMENTS

D.1 Herbicide Application

Applying the herbicides in a similar manner to that in the field proved to be a major problem. It involved uniformly applying 125 mg active ingredient (isoproturon in Arelon WDG and atrazine in Boots brand footpath weed killer) in just 20 ml solution to a surface area of 0.5024 m^2 (equivalent to 2.475 kg herbicide / ha). To do this, a small perfume bottle with an aspirator was used. Earlier assessments with water and laboratory paper towels suggested that a uniform application of pesticide was achieved.

D.2 Simulated Rainfall Events

The series of rainfall events simulated during this study is listed in Table 7.1. Before applying the herbicides, a prewetting experiment was carried out because the soil was dryer than under normal field conditions and this might have influenced the sorption of the chemicals (eg. see chapter 11). This experiment also provided an opportunity to monitor the response of a very dry soil to rapid wetting, and consequently, data was logged at short intervals (see below). Fourteen millimetres of rain were applied over a 10 hr period and the herbicides were applied immediately after the rainfall was stopped. During the next 34 hr, no further rainfall was applied to allow the herbicides to equilibriate with the soil before proceeding with the leaching experiments.

The objective of experiment 1 (labelled with 86.9±0.7 mg bromide / litre) was to recreate a 10 day series of rainfall events which had been recorded at the Brimstone site in November 1989. By doing so it was hoped to improve on the isoproturon sampling resolution obtained in the field at that time. However, during the course of the experiment it became apparent that the rainfall simulator was not functioning properly and the event was terminated after 6 days. It was obvious that rainfall application rates were substantially lower than they should have been. Furthermore, during periods when rainfall application rates should have been extremely low (ie. pump speeds <5 rpm), no water was being applied. Air bubbles had formed in the the tubing and the resistance associated with them was too great to be overcome at low pumping speeds. This result indicates that further performance assessment studies will have to be carried out on the rainfall simulator before any further leaching experiments can be undertaken.

In experiment 2 (labelled with 40.6±0.21 mg PFBA / litre), rainfall was applied at 5 mm / hr for 10 hr to try and induce macropore flow and produce some drainage samples for herbicide and tracer analysis. This was successful and consequently another identical rainfall event, experiment 3 (labelled with 31.56±0.07 mg 2,6-DFBA / litre), was applied to investigate solute mixing behaviour within the core.

D.3 Protocol for Data Logging, Solute Sample Collection and Analysis

During the prewetting of the soil core, tensiometer measurements were recorded every 5 min and TDR responses once every 15 min to monitor rapid changes in the response of a dry soil to wetting. In experiments 1-3, tensiometer measurements were recorded every 15 min and TDR responses once every 30 min. Data were backed up on floppy disks and a remote hard disk on a daily basis.

The protocol for solute sample collection was flexible to facilitate sampling that was reactive to the dominant flow responses at any time. When gravity drainage occurred, priority was given to maximising the resolution of this drainage (ie. sampling as frequently as possible). During periods when there was no gravity flow, vacuum (0.5 bar) was applied to each suction sampler in turn to obtain solute samples. Whenever possible, sample volumes greater than 10 ml were collected so that there would be no difficulty in detecting atrazine and isoproturon at concentrations down to 1 µg / litre. However, it was frequently impossible to obtain 10 ml solution from suction samplers in under 10 min, so some sample volumes were less than 10 ml. When gravity drainage occurred, solute samples were also obtained, where possible, from the closest suction sampler to the gravity drainage, so that the chemical composition of the two samples could be compared for differences which might be attributable to mobile and immobile phase water. Suction was rarely applied to more than two suction samplers at the same time to avoid disrupting the natural water flow pathways in the soil unnecessarily; it also prevented the pump overheating.

Suction sample volumes and gravity drainage sample volumes were measured in measuring cylinders immediately after collection and the collection time noted. Samples were placed in Bakelite screw capped glass vials and stored in a refrigerator until analysis. All pesticide analyses were completed within two weeks and tracer samples within one month of sample collection. Wherever possible, samples were analysed for both herbicides and tracers, but in the event that there was insufficient sample volume to concentrate for herbicide analysis, only the tracer concentrations were measured. Analysis of atrazine and isoproturon concentration was carried out as described in Chapters 3. Where samples required concentration, the method using Sep-Pak cartridges (see chapter 4) was used to reduce a known volume of the sample to 1.0 ml. Where required this concentrate was reduced further (to a minimum volume of 100 µl) under a stream of air free nitogen at ambient temperatures.

CHAPTER 8

WATER FLOW AND HERBICIDE TRANSPORT IN UNSATURATED CLAY SOIL: INFERENCES FROM SUCTION SAMPLERS AND BREAKTHROUGH CURVES

A. WATER FLOW PHENOMENA

A.1 Macropore Flow

Breakthrough curves for PFBA (experiment 2) and DFBA (experiment 3) would suggest that the movement of water in this clay soil was dominated by bypass flow. This is illustrated most clearly by the displacement of bromide by PFBA in gravity drainage sample 5 (0°, 0.55 m) during experiment 2 (Fig 8.1 a) and the displacement of bromide and PFBA by DFBA in gravity drainage sample 8 (270°, 0.55 m) during experiment 3 (Fig 8.1 c). This is supported by the dominant contributions PFBA and DFBA make to the hydrograph separations for gravity drainage samplers 5 (Fig 8.2 a), in experiment 2, and 8 (Fig 8.2 c), in experiment 3, respectively.

The installation of suction samplers in the core was intended to provide data that might indicate the chemical composition of the soil solution in the matrix so that it could be compared to that in marcroporous areas (which was presumably sampled by gravity drainage). However, in experiment 3 the similarity of the chemical composition of suction samplers 2, (90°, 0.15 m) (Fig 8.3 d), and 3, (180°, 0.15 m) (Fig 8.3 e), to that of gravity drainage sample 8 (Fig 8.1 c) and the similarity of suction sample 7 (180°, 0.55 m) (Fig 8.3 g) to gravity drainage sample 5 (Fig 8.1 b) would suggest that both the suction samplers and the zero suction samplers were (largely) monitoring the same flow phenomena - in this case bypass flow. This should not be overly surprising given that it would be necessary for the matrix to approach /-

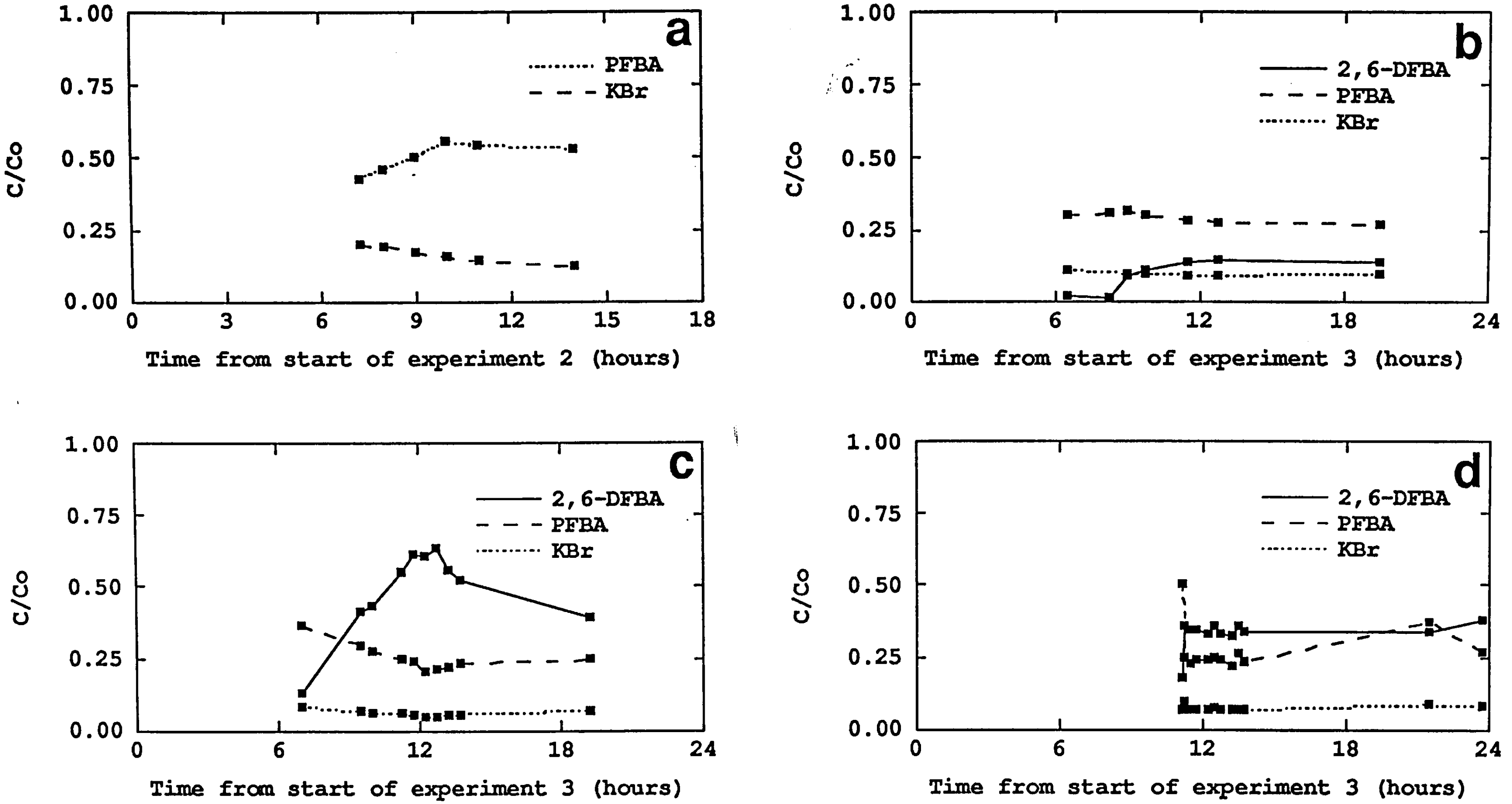


Figure 8.1 Concentration of KBr, PFBA and 2,6-DFBA in water collected from gravity drainage samplers 5 (a) during experiment 2 and 5 (b), 8 (c) and the core base (d) during experiment 3 (Positions of all samplers are given in Figure 7.1)

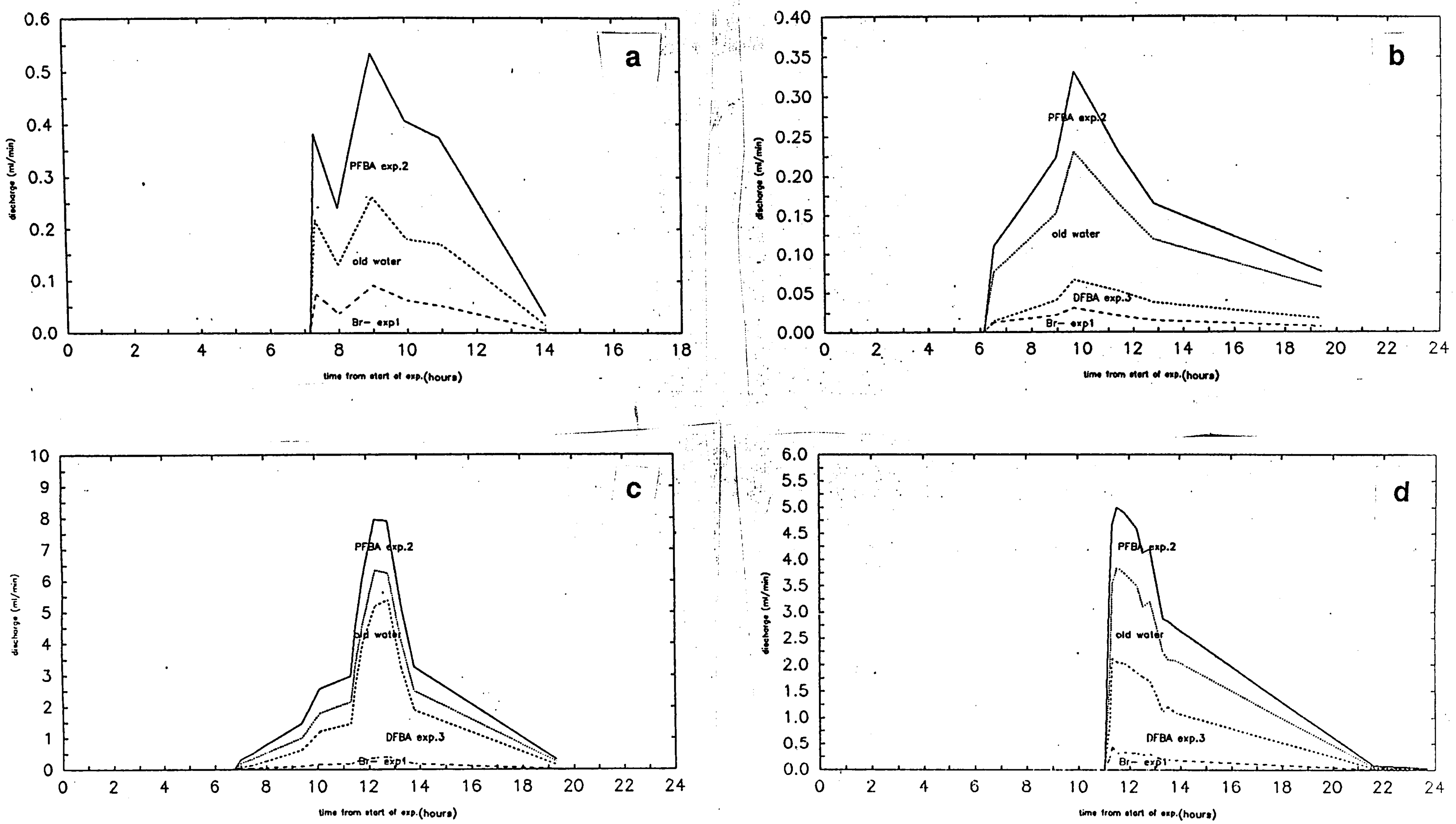


Figure 8.2 **Hydrograph separations for gravity drainage sampler 5 (a) during experiment 2 and samplers 5 (b), 8 (c) and the core base (d) during experiment 3** (Positions of all samplers are given in Figure 7.1)

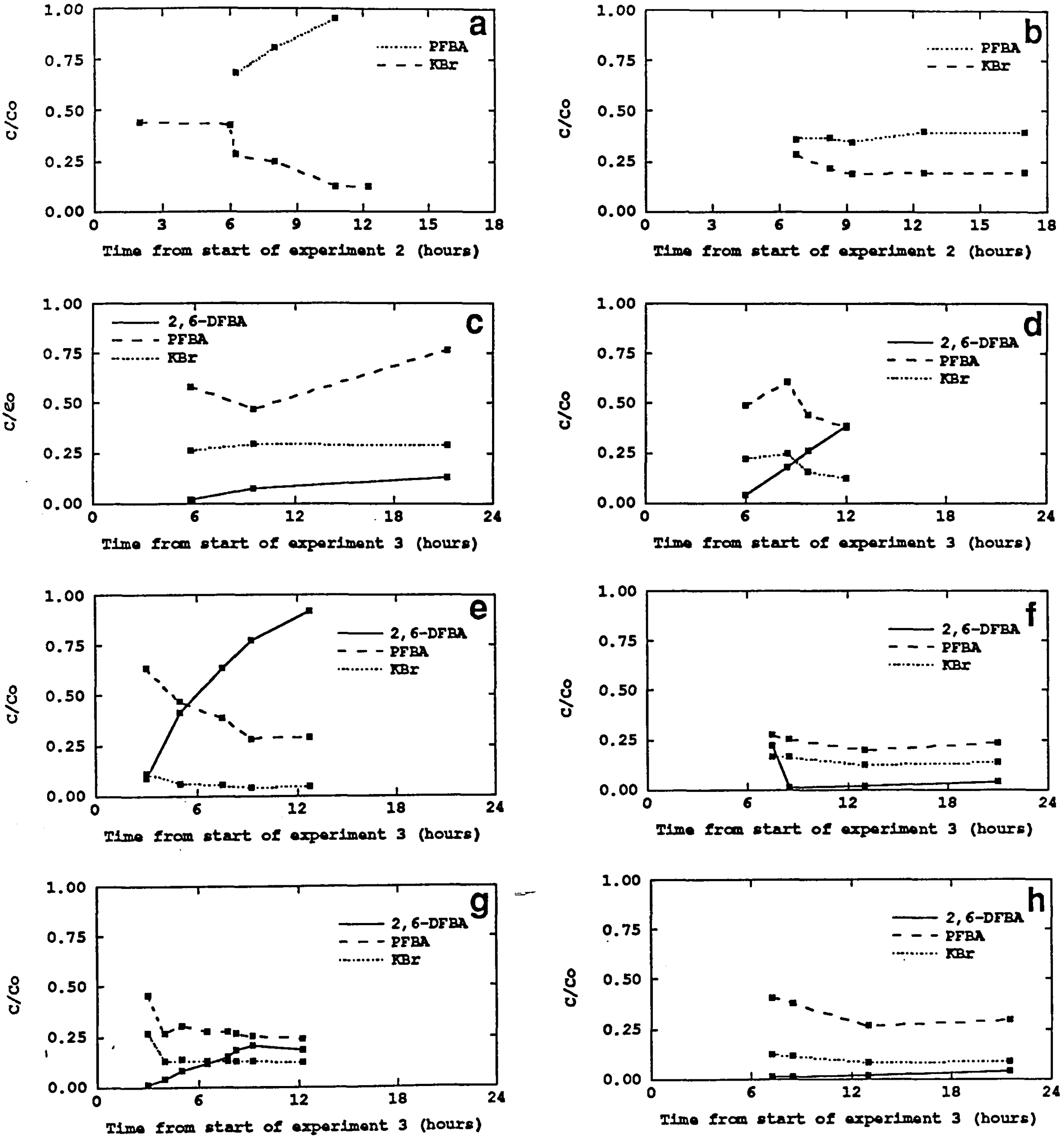


Figure 8.3 Concentration of KBr, PFBA and 2,6-DFBA in water collected from suction samplers 3 (a) and 7 (b) during experiments 2 and 1 (c), 2 (d), 3 (e), 5 (f), 7 (g) and 8 (h) during experiment 3 (Positions of all samplers are given in Figure 7.1)

saturation before water samples could be withdrawn from it by suction.

Given the assertion that both types of water sampler monitored the same flow phenomena, then the appearance of PFBA and DFBA in samplers at 0.55 m shortly after their appearance in samplers at 0.15 m is also indicative of flow through cracks and voids with rapid bypass of much of the soil matrix. For example, DFBA was detected at 0.55 m in suction sample 7 three hours after the start of experiment 3 (Fig 8.3 g) and in the effluent draining from the base of the core (1.1 m) after 11 hours (Fig 8.1 d). However, because the drainage system at the bottom of the core would have to be saturated before any drainage could occur, then it is fair to assume that DFBA labelled water reached the bottom of the core more rapidly. This is supported by the hydraulic conductivity, 2.7×10^{-4} m / sec, calculated from a 3 hr period of continuous drainage from the bottom of the core during experiment 3 (see Fig 8.1 d).

A.2 Matrix Advection

Although the results suggest that water movement through cracks and voids was dominant in these experiments, the importance of micropore advection cannot be ignored. This is most apparent from the distribution of bromide in the soil core. Bromide was used as the tracer for experiment 1 which was terminated early because of difficulties in the operation of the rainfall simulator (see chapter 7). As a result of these difficulties, it was unlikely that substantial bypass flow was generated during this rainfall event. Thus, bromide was more likely to flow slowly throughout the cultivated horizon and perhaps even to greater depths. This assertion can be supported by the following observations. (1) For each individual suction sampling point, the bromide concentation remained relatively constant throughout the whole sampling period, and displacement by either PFBA in experiment 2 or DFBA in experiment 3 was limited (e.g. see Fig 8.3 c, f and h). (2) The contribution of bromide to the hydrograph separations for gravity drainage sampler 5 in experiment 2 (Fig 8.2 a) and 5 and 8 during experiment 3 (Fig 8.2 b and c) was minimal.

The relatively constant distribution of bromide, PFBA and DFBA in suction samples 1 (0°, 0.15 m) (Fig 8.3 c), 5 (0°, 0.55 m) (Fig 8.3 f) and 8 (270°, 0.55 m) (Fig 8.3 h) would suggest that the soil solutions in the locality of these samplers was not subject to mixing. Thus it is extremely likely that the soil solution was almost stagnant (relative to rapid exchanges in solution elsewhere as discussed below) and flow was dominated by micropore advection. The substantial contributions of 'old water' (that initially present in the core prior to the commencement of the experiments + that added during the prewetting experiment) to the hydrograph separations for gravity drainage samplers 5 during experiment 2 (Fig 8.2 a) and gravity drainage samplers 5 and 8, and the core base effluent (Fig 8.2 b, c and d respectively) during experiment 3 is also indicative of micropore advection. This is because the 'old water' had been present in the soil core for a considerable time before commencing the experiments and, consequently, was likely to have migrated from 'remote' sites within the soil matrix.

A.3 Mixing Behaviour

Whilst it is possible to identify evidence in support of bypass flow and micropore advection as distinct flow phenomena, as above, this approach may be unnecessarily restrictive, simplistic and consequently counterproductive. Although such a conceptualisation is very convenient insofar as these phenomena are of great importance in governing the potential for short term rapid transport of solutes through the soil (bypass flow) and longer term persistence within it (micropore advection), the evidence from these experiments would suggest that water flow is best considered to be a continuum of phenomena rather than a series of distinct individual processes. Mixing of water flowing down cracks with that in the soil matrix appeared to be common. The presence of old water in the hydrograph separations for both experiment 2 (Fig 8.2 a) and experiment 3 (Fig 8.2 b, c and d) suggests that water has moved out of the soil matrix and mixed with water flowing along cracks and voids. By contrast, the very slow displacement of bromide by PFBA in suction samples 3 (Fig 8.3 a) and 7 (Fig 8.3 b) during experiment 2 and the displacement of both bromide and PFBA by DFBA in suction sampler 7 (Fig 8.3 g) during experiment 3 might be indicative of water movement from cracks and voids into the soil matrix.

In some cases mixing was much less pronounced. Near suction sampler 5 during experiment 3 (Fig 8.3 f), little mixing occured at all. In the stagnant areas discussed above, ie. in the locality of suction samplers 1 and 8, in addition to the aforementioned sampler 5, it seems probable that any mixing that occured was predominantly by micropore advection. Even where bypass flow was predominant, the extent of mixing varied substantially. For example, contrast the displacement of bromide and PFBA by DFBA in gravity drainage samplers 5 (Fig 8.1 b) and 8 (Fig 8.1 c) during experiment 3. The pulsing behaviour exhibited by drainage from the base of the core (Fig 8.1 d) is also indicative of pronounced mixing.

A.4 Core Water Balance

The water balance for the soil core during the course of experiments 2 and 3 is shown in Table 8.1. By the end of experiment 2, 0.15 pv * (pore volumes) water had been applied to the core, ie. the sum of water applied during the prewetting experiment and experiment 1 and experiment 2. This was only sufficient to generate gravity drainage from sampler 5 which produced 4.7×10^{-4} pv drainage or 0.3 % of the total water applied to this time. Water was withdrawn by all the suction samplers, except numbers 1 and 4, but only samplers 3 and 7 gave a marked response. A further 0.08 pv rainfall was applied during experiment 3 resulting in a pronounced flow response. Gravity drainage samplers 5 and 8, and the core base sampler, began to respond 6, 7 and 11 hours after the start of DFBA application respectively

*FOOTNOTE: pv was estimated to be 0.2512 m^3 [i.e. pv = $\pi r^2 h p$ where r is the core radius (m), h is the core height (m) and p is the soil porosity (m^3/m^3), estimated at 0.5 m^3/m^3 from Harris *et al* (1984), such that pv = 3.14 x 0.16 x 1.0 x 0.5 = 0.2512 m^3]. It should be noted that this was the pv at the start of the experiments prior to rainfall application. During the experiments, the total volume increased from 0.5024 m^3 to 0.5529 m^3, i.e. an increase in h of 0.002 m, due to swelling.

(Fig 8.1 b, c and d). Gravity drainage samplers 5 and 8 and the core base sampler produced 4.9×10^{-4}, 0.006 and 0.004 pv drainage respectively (equivalent to 0.2%, 2.8% and 1.7% of the water applied to that time). Gravity drainage samplers 6 and 7 also responded during experiment 3 but the amounts of drainage were minimal. The total water lost by gravity drainage at the end of experiment 3 was 0.012 pv (2907.7 ml) or 5% of that applied as rainfall over the series of experiments. It is interesting to note that only the gravity drainage samplers installed at a depth of 0.55 m responded during the experiment and that suction samplers 3 and 7, in the same vertical stack, gave much more marked responses than any other suction samplers. This may indicate that flow was more pronounced in this region than any other area of the core.

Table 8.1 **Soil Core Water Balance for Experiments 1-3**

	Water Recovery					
Solution Sampler	Experiment 2		Experiment 3		Total	
	(ml)	(% of applied)	(ml)	(% of appied)	(ml)	(% of applied)
SS1	0.0	0.000	2.3	0.004	2.3	0.004
SS2	0.5	0.001	6.0	0.010	6.5	0.011
SS3	68.2	0.180	45.3	0.078	113.5	0.195
SS4	0.0	0.000	3.7	0.006	3.7	0.006
SS5	2.7	0.007	7.5	0.013	10.2	0.018
SS6	0.5	0.001	2.8	0.005	3.3	0.006
SS7	92.7	0.244	398.8	0.685	491.5	0.845
SS8	4.9	0.013	8.1	0.014	13.0	0.022
GD5	119.0	0.314	122.5	0.211	241.5	0.415
GD6	0.0	0.000	4.4	0.008	4.4	0.008
GD7	0.0	0.000	28.0	0.048	28.0	0.048
GD8	0.0	0.000	1630.9	2.803	1630.9	2.803
BE	0.0	0.000	1002.9	1.723	1002.9	1.723
Total	288.5	0.760	3263.2	5.608	3551.7	6.104

B. SPATIAL AND TEMPORAL VARIABILITY OF SOIL SOLUTION CHEMICAL COMPOSITION AND MECHANISMS OF SOLUTE TRANSPORT

B.1 Spatial and Temporal Variability

Suction samplers 3 and 7 have proven to be very useful for assessing the spatial variability of soil solution chemistry. This is because they consistently gave a good response and it was possible to obtain samples from them simultaneously. The chemical compostion of these samples was directly comparable at every point in time. During experiment 2 it can be seen that both atrazine and isoproturon concentrations, at 0.5-1.2 mg / litre, were up to twenty times greater in suction sampler 3 (0.15 m) than in suction sampler 7 (0.55 m), (Fig 8.4 a). At a depth of 0.15 m, isoproturon concentration was consistently higher than atrazine concentration whilst at 0.55 m depth they were similar. In gravity drainage sample 5, 0.55 m, (Fig 8.4 b) isoproturon concentrations (0.15-0.55 mg / litre) were also consistently higher than those of atrazine, which ranged from 0.1-0.25 mg / litre. By contrast, during experiment 3, atrazine was detected in all samplers (Fig 8.5 a-d) at greater concentrations than isoproturon. It should also be noted that although suction sampler 7 and gravity drainage sampler 5 were both located at a depth of 0.55 m, herbicide concentrations in water from the latter during experiment 2 were up to 10 times greater. Of the 125 mg of atrazine and the 125 mg of isoproturon initially applied to the core, 0.02% and 0.04% respectivley were lost from gravity drainage sampler 5 during experiment 2 (Table 8.2).

During experiment 3, the magnitude of the difference between the herbicide concentrations in suction samplers 3 and 7 had changed (Fig 8.5 a). Atrazine concentration was only up to ten times greater at 0.15 m than at 0.55 m, whilst isoproturon was no longer detected above 1.0 µg / litre at 0.55 m (suction sampler 7). In gravity drainage sampler 5 (Fig 8.5 b), only atrazine was detected at similar concentrations to suction sampler 7, ranging from 0.015 to 0.04 mg / litre. By contrast, in gravity drainage sampler 8, atrazine concentration was up to twenty times greater at 0.1-0.3 mg / litre (Fig 8.5 c). Furthermore, isoproturon was also detected at concentrations of up to 0.08 mg / litre. Atrazine and isoproturon were both detected in water draining from the base of the core (Fig 8.5 d) at concentrations ranging from 0.05-0.25 mg / litre and 0.025-0.30 mg / litre respectively. No data are shown for the 0.15 m samplers, other than suction sampler 3, because insufficient sample volume (Table 8.1) was usually obtained for analysis.

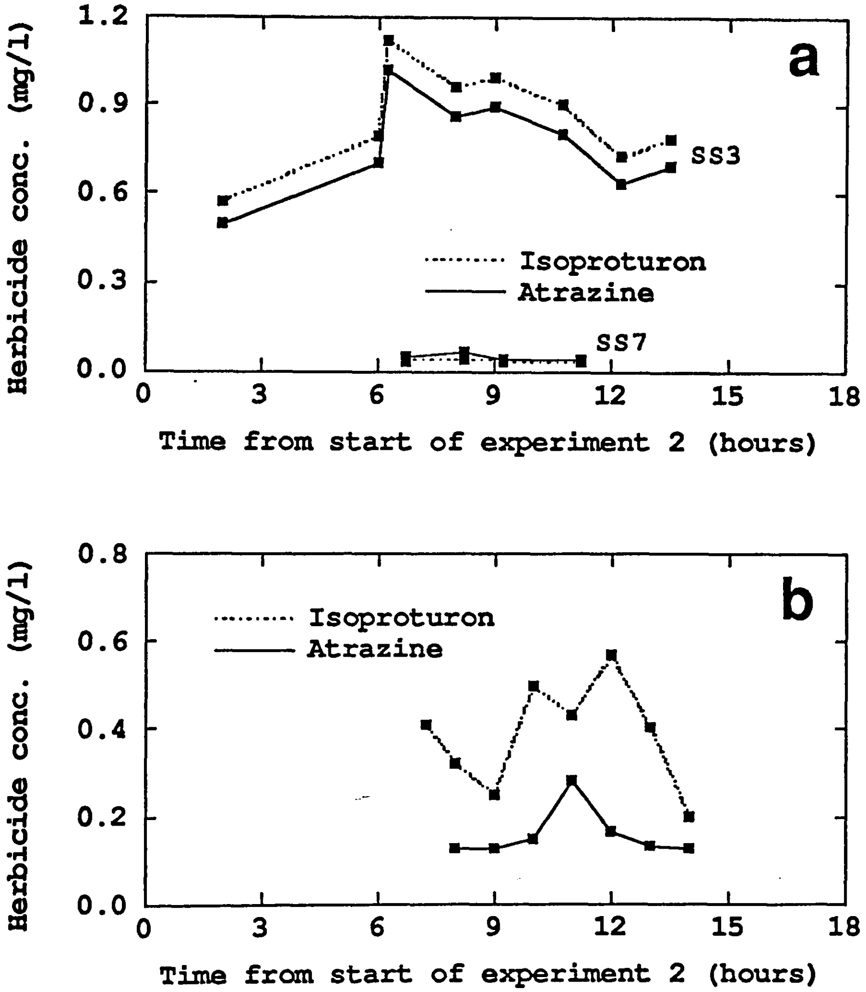


Figure 8.4 Concentration of atrazine and isoproturon in water collected from suction samplers 3 and 7 (a) and gravity drainage sampler 5 (b) during experiment 2 (Positions of all samplers are given in Figure 7.1)

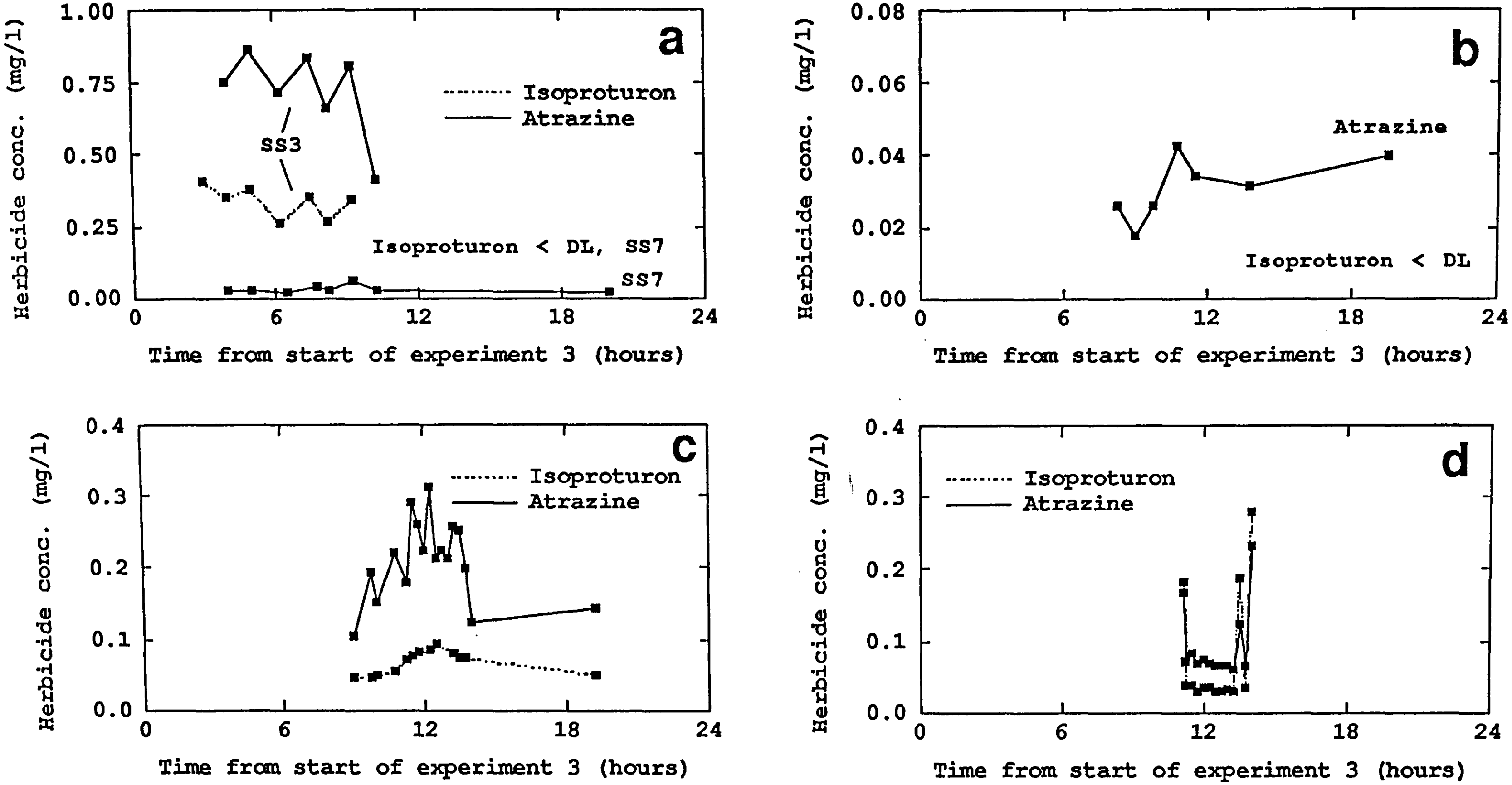


Figure 8.5 Concentration of atrazine and isoproturon in water collected from suction samplers 3 and 7 (a), gravity drainages samplers 5 (b) and 8 (c), and the core base (d) during experiment 3 (Positions of all samplers are given in Figure 7.1)

Table 8.2 Mass Balance for Atrazine and Isoproturon for Experiments 1-3

Solution	Atrazine Recovery						Isoproturon Recovery					
	Experiment 2		Experiment 3		Total		Experiment 2		Experiment 3		Total	
Sampler	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)
SS1	-		0.0005	0.0002	0.0005	0.0002	-		0.0030	0.0012	0.0030	0.0012
SS2	0.0003	0.0002	0.0009	0.0004	0.0012	0.0005	0.0002	0.0002	0.0020	0.0008	0.0024	0.0010
SS3	0.0531	0.0425	0.0611	0.0244	0.1142	0.0457	0.0595	0.0476	0.0298	0.0120	0.1488	0.0596
SS4	-		0.0001	0.00004	0.0001	0.00004	-		0.0058	0.0028	0.0068	0.0028
SS5	0.0001	0.0001	0.0007	0.0003	0.0008	0.0003	0.0007	0.0006	0.0014	0.0006	0.0028	0.0012
SS6	@		@				@		@			
SS7	0.0037	0.0030	0.0103	0.0041	0.0140	0.0056	0.0030	0.0024	0.0020	0.0008	0.0080	0.0032
SS8	0.0005	0.0004	*		0.0005	0.0002	0.0003	0.0002	0.0014	0.0004	0.0014	0.0006
GD5	0.0190	0.0152	0.0034	0.0014	0.0224	0.0090	0.0463	0.0370	0.0018	0.0008	0.0944	0.0378
GD6	-		*				-		*			
GD7	-		0.0007	0.0003	0.0007	0.0003	-		*			
GD8	-		0.3197	0.1279	0.3197	0.1279	-		0.1564	0.0626	0.1744	0.0626
BE	-		0.0585	0.0234	0.0585	0.0234	-		0.0888	0.0356	0.0888	0.0356
Total	0.0763	0.0614	0.4554	0.1824	0.5326	0.2130	0.1100	0.0880	0.2928	0.1172	0.4856	0.2052

- no samples collected; @ insufficient sample volume for analysis; * concentration < 1.0 µg / L

Over the course of experiments 2 and 3 (approximately 270 hr and 0.37 pv applied rainfall), the concentration of both atrazine and isoproturon at 0.15 m (suction sampler 3) decreased by up to approximately 50%, whilst at 0.55 m (suction sampler 7) the atrazine concentration stayed the same but isoproturon could not be detected above 1.0 µg / litre (contrast Fig 8.4 a 8.5 a). In gravity drainage sampler 5, the temporal decline was even more marked with atrazine showing a ten-fold decrease in experiment 3 over that observed in experiment 2 (contrast Fig 8.4 b with 8.5 b). Like suction sampler 7, isoproturon was not detected. Temporal variation for individual samplers, within each experiment, was also substantial, the most extreme examples being the variation of atrazine concentration in gravity drainage sampler 8 (Fig 8.5 c) and both atrazine and isoproturon in the core base drainage (Fig 8.5 d) during experiment 3.

B.2 Mechanisms of Solute Transport

The significantly higher concentration of atrazine and isoproturon in gravity drainage sampler 5 at 0.55 m depth than in suction sampler 7 at the same depth during experiment 2, and the similar trend for atrazine in the same samplers during experiment 3, suggests that bypass flow may enhance solute transport. This is consistent with results presented elsewhere for atrazine (Isensee *et al* ,1990) and isoproturon (Harris,1991) leaching under field conditions. Such behaviour is feasible because flow in cracks and voids reduces the solid to solution contact time and consequently the potential for solutes to be immobilised on stationary surfaces is reduced (see eg. Wu and Gschwend, 1986; chapter 2, section C). It should also be noted that breakthrough of water tracers and herbicides were virtually simultaneous for the gravity drainage samplers which suggests that a fraction of the herbicides moved through the soil extremely rapidly with only limited contact occurring between the stationary phase and the moving solute as postulated by Bouma (1991). The practical significance of such processes is apparent from the relatively high concentrations detected in water draining from the bottom of the core - 1.1 m below the point of application! Although the concentrations exceed the European Union directive for drinking water (0.1 µg / litre for a single compound and 0.5 µg / litre for the sum of all those compounds detected), the public health implications should be kept in perspective. The experiments conducted here are analogous to field flush phases soon after pesticide application and concentration of any herbicide in a sample flush is likely to be substantially decreased as the water moves through a catchment system into ever greater volumes of water (Harris, 1991).

As with water flow, attempts to generalise solute transport into rigid bypass flows and micropore advection is counterproductive. For example, the atrazine concentration of gravity drainage samplers 5 and 8 varied by 8 fold. However, this can possibly be explained by the difference in mixing in the vicinity of these two samplers. The dominant contribution of 'old water' and, hence, micropore advection to gravity drainage sampler 5 gives rise to low herbicide concentrations. By contrast, gravity drainage sampler 8 was characterised by rapid breakthrough of DFBA from the surface horizon containing recently added herbicide. Further difficulties arise in the assertion made above that the suction samplers and gravity drainage samplers were, in some cases, monitoring identical flow phenomena. Markedly lower herbicide concentrations in suction samples than in gravity drainage samples suggests that the suction samplers are indeed monitoring micropore advection by sampling matrix solutions. Thus it should be apparent that solute transport, like water flow, is very complex and may be best conceptualised as a continuum phenomena, where transport may occur primarily by bypass flow or molecular diffusion, but is more likely comprised of dynamically mixing fluids.

PART 2: CONCLUDING REMARKS

The performance of the undisturbed soil core exceeded all expectations. Apart from the preliminary difficulties experienced with the calibration of the rainfall simulator and a manufacturing fault in the TDR switching mechanisms there were no instrument failures or data logging problems. No leakage occured where instruments were inserted in the core and there was no evidence to suggest that water was running down the core wall. Consequently, it will be possible to undertake further experiments on the core with only limited work required to improve the performance of the rainfall simulator calibration and to replace the TDR switches. The success of the combination of suction and zero suction water samplers was particularly encouraging and it is likely that further samplers will be installed in the core at 0.35 m and 0.75 m to give better depth resolution of solution samples in future experiments. However, the sorption characteristics of the porous ceramic cups will have to be verified if the compounds of interest are more hydrophobic than the compounds studied here. The development of such a facility under laboratory conditions for the collection of data which can be used for the development, verification and validation of bi-continuum models for water and solute transport is unparalleled.

Despite the failure of experiment 1 some very useful data was obtained in experiments 2 and 3. Evidence was obtained in support of a number of hydrological phenomena. These include macropore flow along cracks, stagnant zones characterised by micropore advection and molecular diffusion and also mixing of matrix flows with macropore flows. The transport of atrazine and isoproturon was found to be closely related to these flow phenomena. Herbicide transport appeared to be favoured by macropore flows which bypassed much of the bulk soil matrix resulting in rapid movement of atrazine and isoproturon to the base of the core. Decreases in the soil-solution contact time are believed to be principally responsible for this behaviour. Marked spatial and temporal variations in solution chemistry were observed. Herbicide concentrations at 0.15 m were up to sixty times greater than those at 0.55 m early in the experiment but around 245 hr later the difference had declined to a factor of ten. The concentrations of both herbicides at 0.55 m were substantially lower in experiment 3 than they were in experiment 2. At 0.55 m, the concentration of atrazine in gravity drainage samples during experiment 3 varied by a factor of eight, which could be attributed to differences in the solute mixing behaviour at the two localities from which drainage was obtained. Given the variability of breakthrough curve form and the chemical composition of the suction samples for both the water tracers and the herbicides, it is suggested that water flow and solute transport are best conceptualised as a continuum of flow phenomena rather than rigidly defined macropore flows and matrix flows.

PART 3

FIELD STUDIES

PART 3: INTRODUCTORY COMMENTS

Contemporary attempts to model the persistence and movement of organic chemicals in soils have achieved only limited success. This has been partly due to the generally accepted assumption that sorption of contaminants by soils is instantaneous and completely reversible (Jury and Ghodrati, 1989). However, evidence is now available which would suggest that equilibration takes place on timescales ranging from a few seconds to many years (Pignatello, 1989). Furthermore desorption hysteresis is often observed (Brusseau and Rao, 1991a) and in many cases a fraction of the contaminant will be completely resistant to desorption under natural field conditions (Kaufman *et al*, 1976), (see also Chapters 1 & 2).

The problem has been further confounded by the failure to represent these processes by model parameters which accurately reflect their spatial and temporal variability at the field scale. Field averaged estimates of parameters such as sorption coefficients and pore water velocities have frequently been used in models, but result in poor predictive ability (Elabd *et al*, 1986). Soil physicists and hydrologists have recognised the significance of this problem with regard to the movement of water through structured soils. Consequently, methods for characterising the variability of soil physical properties are now well established (Biggar and Nielson, 1976; Jury *et al*, 1976; Van der Pol *et al*, 1977; Jury *et al*, 1982). By contrast, the variability of soil chemical characteristics is less well understood. The most comprehensive studies, including those of Jones *et al* (1983) and Cooper *et al* (1985), have been undertaken with the purpose of producing extensive data sets for the verification and validation of pesticide transport and fate models such as PRZM, SESOIL and PESTAN. Whilst a number of studies have yielded extensive data on the spatial and temporal variability of pesticide residues (Jones *et al*, 1983; Cooper *et al*, 1985; Elabd *et al*, 1986), relatively little information on their respective sorption coefficients are available. Furthermore, where data on sorption coefficients have been presented, they have often been indirectly derived from soil organic matter content (Jones *et al*, 1983).

The primary objective of this study was to investigate the nature and significance of the spatial and temporal variability of isoproturon residues and their associated sorption/desorption coefficients at the field scale under realistic agricultural practices. The relationship between sorption/desorption coefficients and residual isoproturon concentration was examined to ascertain the potential usefulness of such coefficients as parameters in pesticide transport and fate models. Organic matter content was also determined for each soil sample to facilitate the derivation of normalised sorption coefficients. Thus it was possible to assess the feasibility of indirect estimation of sorption coefficients from the more widely available data on soil organic matter content (Chapter 11).

The investigation was carried out on part of the Brimstone Experiment (Catt, 1991). The primary objective of the Brimstone Experiment (Phase 2) was to investigate the effects of contemporary agricultural practices on the environmental fate and behaviour of agrochemicals, such as nitrates and pesticides, whilst maintaining economically viable food crop production on this heavy textured soil which requires under drainage to achieve good yields (Harris, 1991). Emphasis has been placed on the development of drainage techniques, cropping regimes and soil management practices which will reduce the migration of pesticides to groundwaters and minimise runoff to surface water resources. Extensive data sets have been produced which are being used for the verification and validation of agrochemical transport and fate models (Muir, 1991). This research programme is jointly managed by the ADAS Soil and Water Research Centre at Cambridge (formerly the Field Drainage Experimental Unit) and the Agriculture and Food Research Council Institute of Arable Crops Research at Rothamsted Experimental Station. The core research programme is funded by the Ministry of Agriculture Fisheries and Food.

In addition to quantifying the spatial and temporal variation of isoproturon residues and associated sorption/desorption coefficients, a number of other objectives have been designed in this study to complement the primary objectives of the Brimstone Experiment. The variability of soil physicochemical properties was measured to determine if it was possible to use them in the development of simple models for the prediction of residual isoproturon concentration in cultivated horizons (Chapter 10). The relative importance of intrinsic factors such as soil physicochemical properties and rainfall as opposed to extrinsic factors such as cultivation and drainage (extrinsic because it is artificially induced) in controlling the persistence and leaching of isoproturon was investigated (Chapter 11) in an effort to identify the most environmentally benign combination of agricultural practices on heavy textured soil.

CHAPTER 9

SITE DESCRIPTION, SAMPLING PROCEDURES AND EXPERIMENTAL ANALYSIS

A. THE BRIMSTONE FARM EXPERIMENTAL SITE

A.1 Description of Experimental Site

The site covers an area of approximately 5 ha overlying a heavy clay soil of the Denchworth series (Table 9.1) near Faringdon, Oxfordshire (OS grid ref 248947). The mean annual precipitation is 680 mm with a mean annual temperature of 10 °C. The site lies 100 m A.O.D. on a gently undulating plateau on a 2% slope with a south-easterly aspect (Smith and Trafford, 1976, cited in Cannell *et al*, 1984).

A.2 Design of Experimental Plots

The site consists of 20 experimental plots, 14 of which are currently in use, as shown in Fig 9.1. A detailed schematic diagram of the plot design is shown in Fig 9.2. Each plot has been hydrologically isolated to a depth of 1.1 m by installing a continous sheet of polythene down the slope at the eastern and western boundaries of the plots (A). At the northern boundary of each plot, a 1 m deep x 0.1 m wide interceptor trench containing a 0.075 m id. clay pipe has been backfilled with freely permeable material to intercept any water moving downslope (B). To ensure that no surface movement of water occurs between plots, the polythene barrier has been covered with an inverted 0.1 m id. PVC gutter (C). A 3.0 m wide grass verge/access

FOOTNOTE: Sections A.1 through A.3 are a summary of Cannell *et al* (1984), Castle (1991) and Harris (1991). More complete details of the Brimstone Experirment can be obtained by referring to these papers.

Table 9.1 **Representative Profile Description of Clay Soil at Brimstone Farm***

Subgroup	Denchworth series
Series	Pelo-stagnogley soil
Lithology	Swelling clay
Relief	Valley side in Oxford Clay vale
Slope / elevation	2o / 100m
Land use	Arable (previous), experimental site (present)
Horizons	
Ap (0-20cm)	Colour: 10YR4/2, non-calcareous clay, medium subangular blocky structure, medium packing density, many fibrous roots, smooth clear boundary.
Bg1 (20-35cm)	Colour: 5Y5/1, non-calcareous clay, coarse subangular blocky structure, high packing density, many fibrous roots, abrupt clear boundary.
Bg2 (35-62cm)	Colour: 10YR4/2, non-calcareous clay, strong medium prismatic structure, high packing density, many fibrous roots, smooth clear boundary.
Bgk (62-89cm)	Colour: N5/O, very calcareous clay, strong medium prismatic structure, high packing density, common fibrous roots, smooth clear boundary.
BCgk (89-112cm)	Colour: N5/O, very calcareous clay, moderate to very coarse prismatic structure, high packing density, a few fibrous roots.

* after Cannell *et al* (1984).

roadway (D) has been maintained upslope of the interceptor trench to ensure that its efficiency in removing surface water is not restricted by clods falling on the surface of the backfill material during cultivation. The overall dimensions of the plots are 59.0 m x 41.0 m. Hydrological measurements were conducted over the full width of the plot but only for 46.0 m downslope of the interceptor trench at the top of the plot (hydrological area). Soil physico-chemical studies were restricted to the central 40.0 m x 28.0 m (agronomic area) of the plots where it was possible to undertake agricultural operations in the normal way. Plot drains were installed 46.0 m downslope of the interceptor trench at a depth of 0.9 m and backfilled with permeable material to collect water draining from the mole channels at 0.55 - 0.6 m depth (E). Above the mole channels, this trench was backfilled with soil to the surface. A further 3.0 m downslope of the plot drain, an interceptor drain was installed at a depth of 0.35 m to collect a combination of surface flow and cultivated horizon throughflow (F).

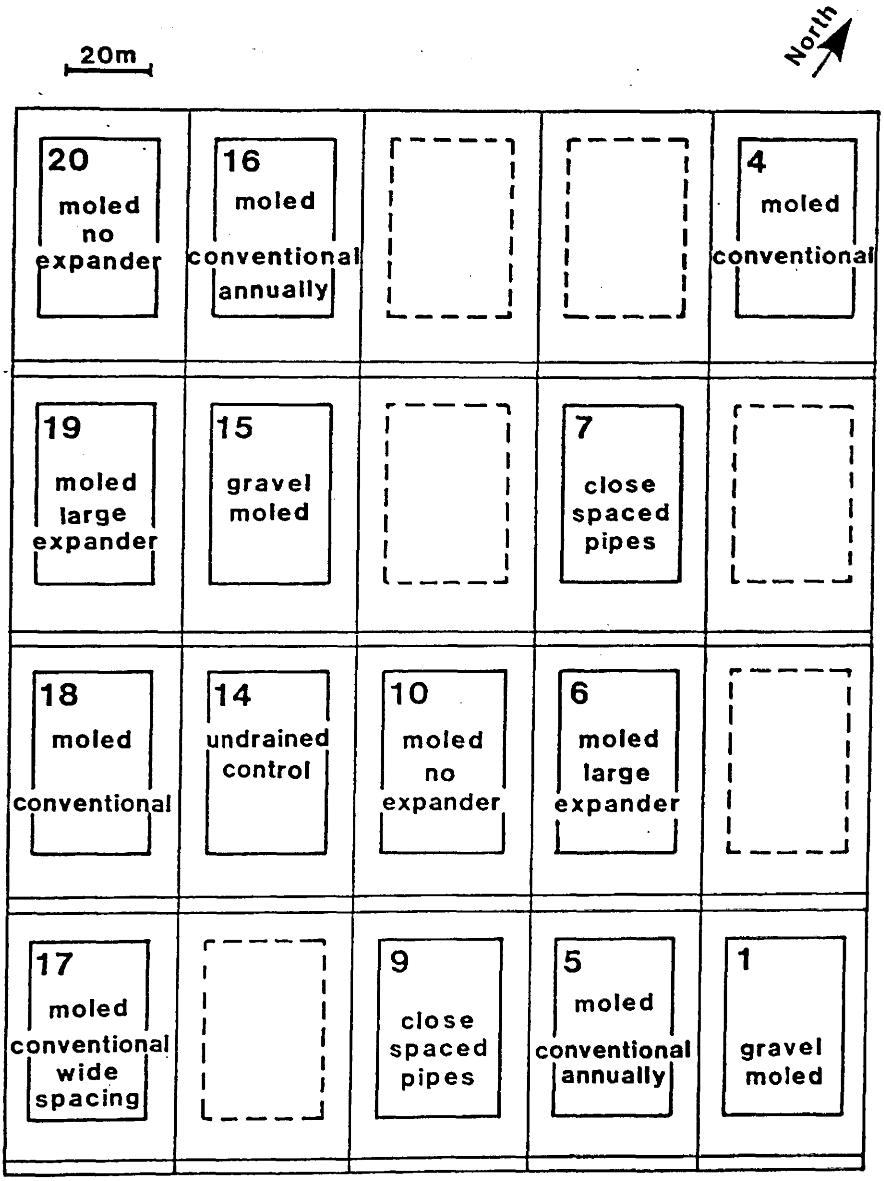


Figure 9.1 **Layout of Experimental Plots at Brimstone Farm**
(after Castle, 1991)

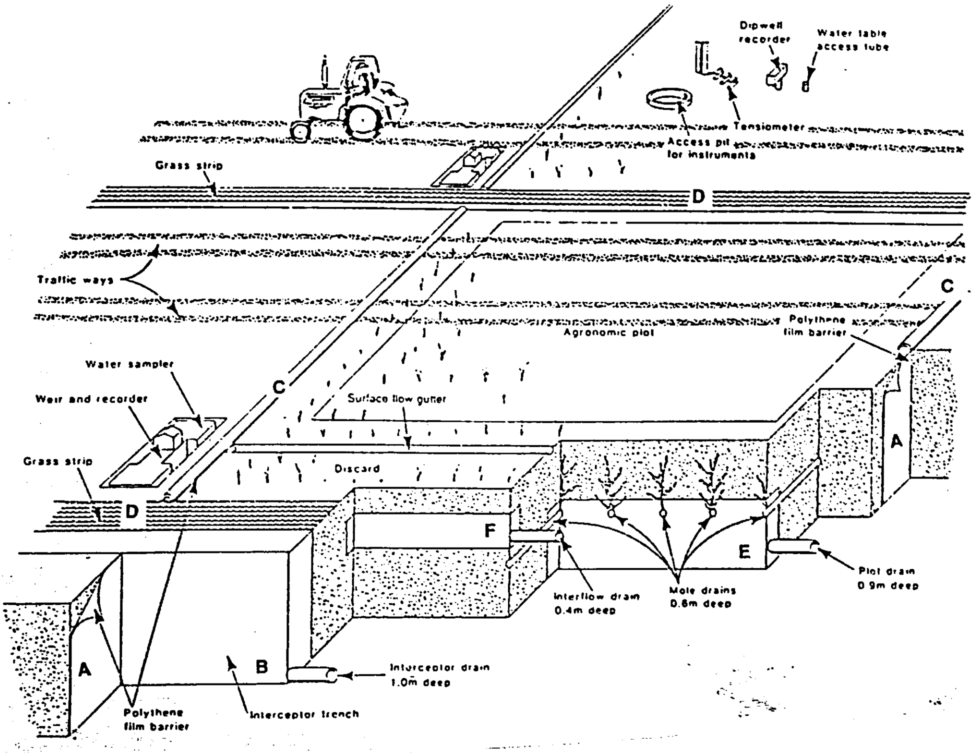


Figure 9.2 Isolation and Instrumentation of Experimental Plots at Brimstone Farm (A-E are discussed in the text; after Castle, 1991)

A.3 Data Collection

Discharge of both drainflow and combined surface flow / throughflow was monitored using a V-notch weir (Fig 9.3) fitted with a float and potentiometer device which activated an electronic data logger when flow occured. The system has been calibrated over the range 0 - 7.0 litre / sec (Talman, 1980, cited in Cannell *et al*, 1984). Water samples for pesticide residue analysis were collected at hourly intervals from the 'U' bend reservoir in the filter bin of the weir gauging system. Epic programmable samplers fitted with Teflon tubing and amber collection bottles were used for sample collection. A vacuum evacuation system, containing polythene and rubber fittings and with clear glass bottles, was operated as a backup. Isoproturon concentration in drainage water was determined by the MAFF CSL Pesticide Analysis Group using HPLC and GC-MS techniques as described elsewhere (Mason, 1991). Meteorological data was obtained using two fully automatic weather stations.

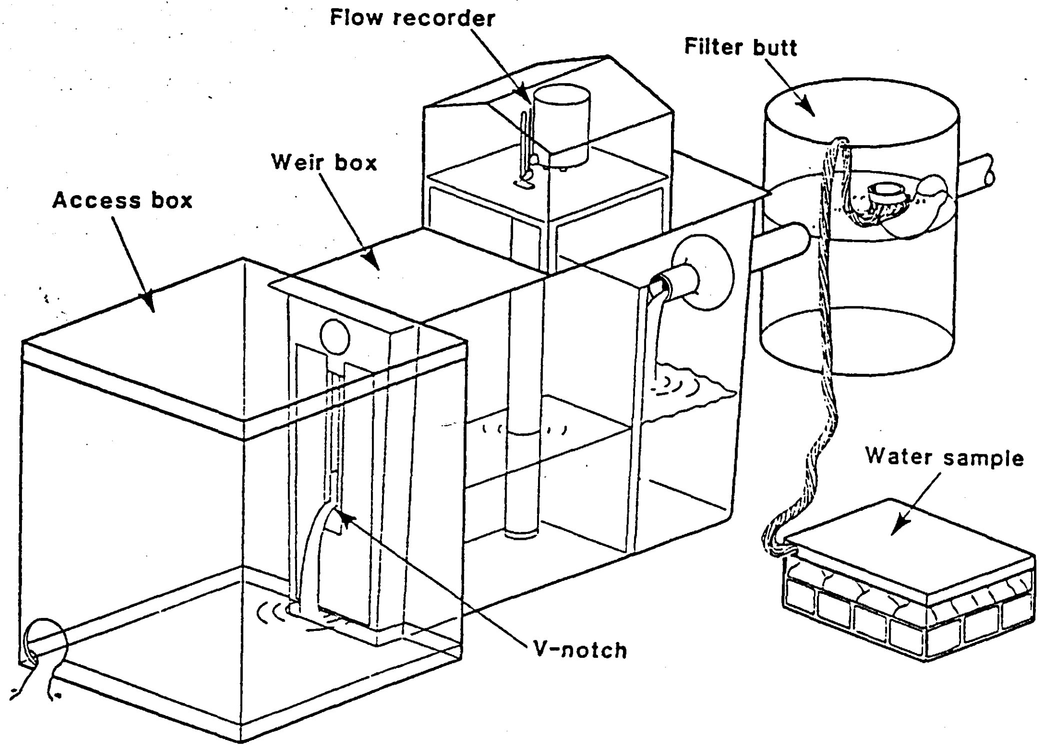


Figure 9.3 **Discharge Monitoring and Water Sampling System**
(after Castle, 1992)

Full details of the data collection responsibilities for the Brimstone Experiment core programme can be found in Catt (1991). In addition this volume provides a summary of the experiments being undertaken by each of the sub-collaborators. Full details of the Lancaster experiments are given in Section B.

B. LANCASTER EXPERIMENTS

B.1 Sampling Procedure 1990-91

B.1.a Introduction

Twenty five 0.075 m id. undisturbed soil cores were taken from quasi-random points on both plots 6 and 10. On each plot, twenty cores were taken to a depth of 0.4 m and a further five were taken to a depth of 1.0 m. The soil cores were sectioned in the field and stored in a refrigerator until taken to Lancaster.

B.1.b Determination of Sampling Points

The initial positions of the core sampling points were determined by the random generation of two sets of data derived from the intersections of an n m^2 cartesian grid superimposed on the 40.0 x 28.0 m agronomic area of the plots. A further five relief points were generated which could be used in preference to the initial positions if any difficulties were experienced with the designated sampling points on the day of core sampling. Adjustments were only necessary to minimise interferences to or from mole drains, instrumentation, tramlines and previous sampling points. The following specific criteria were used.

1) Move 0.5 m or 1.0 m east or west of initial point to the closest available area which is at least 0.3 m from the nearest mole channel.

2) Move 0.5 m or 1.0 m north or south to the closest available area which is at least 0.5 m from the nearest disturbance.

3) Allow for a position 0.5 m south of final selected point for future comparative cores.

B.1.c Measuring Out Sampling Points

The eastern inverted gutters of plots 6, 10 and 14 were marked at 0.5 m intervals to determine the position of the northern coordinate. At the relevant positions, a tape measure was stretched from the eastern to the western margin of the plots enabling the western coordinate to be identified with ease. By using this technique it is estimated that the sampling points were accurate to within 0.1 m^2 of their actual positions.

B.1.d Core Extraction

Undisturbed soil cores were obtained by driving a 1.0 x 0.075 m id. steel tube into the plots to the required depth (0.4 m or 1.0 m) using a petrol driven coring machine. The 0.4 m tubes were pulled out by hand and the 1.0 m tubes were removed using a winch. The aluminium liners containing the undisturbed soil cores were removed from the outer steel core using a horizontally mounted winch; the soil cores were then examined and sectioned as required.

B.1.e Core Sectioning

The undisturbed soil cores were sectioned such that each portion could be related to phenomena of hydrological and / or pedological significance. All the 0.4 m cores were divided into three sections. The uppermost section equated with the Ap horizon which is characterised by considerable soil disturbance and water movement. This horizon was commonly found to be 0.13 m - 0.18 m thick and could be easily distinguished from the underlying more consolidated material. The base of this horizon and the upper face of the more consolidated material below was frequently angled by the action of the plough. On plot 6, the incorporation of straw appeared to be uniform throughout the Ap horizon while on plot 10, ash also appeared well distributed. The middle section was taken as being that mass of consolidated material below the Ap horizon but above 0.25 m depth. This section includes soil that had, at some time previously, been subjected to some disturbance and it could be easily identified by its deep black colouring. In a number of cores, this black horizon extended below 0.25 m and in such cases the thickness of the middle section was increased to ensure that it included all the black material. The third section was taken as being that below 0.25 m or the black horizon, whichever was deeper.

The 1.0 m cores were divided into six sections. The upper three sections were similar to those taken for the 0.4 m cores. The remainder of the core was sectioned at 0.6 m and 0.8 m giving three sections, each of which was 0.2 m thick. The 0.4 - 0.6 m section can be equated with the zone of soil just above the mole channels while the 0.6 m+ and the 0.8 m+ sections can be related to previously reported changes in soil characteristics approximating to these depths (Cannell *et al* , 1984).

The consolidated material was commonly found to contain many large cracks and fissures down to a depth of 0.4 m or more, into which top soil from the Ap horizon had been transported.

B.1.f Plot Restoration

Considerable problems were experienced with top soil from the Ap horizon falling into the hole created by core extraction. This top soil was removed as far as possible and the hole was plugged with bentonite to the top of the consolidated soil, above which it was filled with topsoil.

B.2 Methods of Analysis 1990-91

B.2.a Isoproturon Residues

Sample Preparation - the edge of the soil cores were sliced off with a sharp knife to minimise the risk of cross contamination which may have arisen during the sampling process. This residue was discarded and the remainder of the core sections were cut into small pieces and set aside in metal foil trays to be air dried at room temperature. Air dry samples were ground < 2 mm and stored in polythene bags for analysis.

Isoproturon Residue Extraction - 4 x 15 g replicates of each sample were weighed into 50 ml polypropylene centrifuge tubes and set aside for extraction. One replicate of each sample was mixed with 30 ml of 80 % methanol / 20 % water solution, capped and placed on a rotary shaker for a 24 hr period to extract isoproturon residues. The tubes were centrifuged at 4000 x g for 20 min and then the supernatant solutions were carefully decanted, made up to 30 ml with 80 % methanol / 20 % water solution and mixed with another of the replicates. These tubes were returned to the shaker and the whole procedure was repeated for each of the four replicates in turn. Following the final extraction, the supernatant solution was diluted to 25 ml with 80 % methanol / 20 % water solution and filtered through a Nalgene 0.22 µm cellulose acetate filter prior to HPLC analysis. Isoproturon concentration was determined by HPLC analysis as described in Chapter 3.

B.2.b Soil Physicochemical Properties

I. Bulk Density - determined as the mass per unit volume of the undisturbed soil cores taken for soil analysis.

II. Particle Size Distribution - the pipette method of Bascombe (1974) was used following dispersion of a 10 g subsample of oven dried soil with 20 ml of 10 % sodium hexametaphosphate solution and oxidation with 25 ml of 6 % hydrogen peroxide solution.

III. Insoluble Carbonate Content - a 5 g subsample of < 2 mm oven dried soil was extracted by stirring briskly with 100 ml of 1.0 M hydrochloric acid and then allowing to stand for 3 hr. The % $CaCO_3$ equivalent was then determined by the rapid titration method of Piper (1942) :

$$\%\ CaCO_3\ \text{equivalent} = (\text{blank titre} - \text{actual titre}) * 5 \qquad (9.1)$$

IV. Organic Matter Content - the extracted soil residues from the $CaCO_3$ determinations were oven dried at 105 ^{0}C overnight and organic matter content was then determined by ' loss on ignition ' at 375 ^{0}C for 16 hr. Percentage loss on ignition was calculated as follows :

$$\% LOI = [(W2 - W3) / (W2 - W1)] * 100 \qquad (9.2)$$

where W1 was the weight of the crucible, W2 was the weight of the crucible plus oven dried soil and W3 was the weight of the crucible plus ignited soil (all in g).

V. Exchangeable Cations - 3.00 g air dry < 2mm soil was extracted by leaching with 100 ml of 1.0 M ammonium acetate at pH 7. A 25 ml portion of the extract was mixed with 1 mL strontium nitrate and analysed for calcium and magnesium using a Perkin Elmer Model 2380 Atomic Absorption Spectrophotometer. The instrument was calibrated with ammonium acetate standards, dosed with strontium nitrate, over the 0 - 5.0 mg / litre range for calcium and the 0 - 0.5 mg / litre range for magnesium. Analysis was undertaken with an air - acetylene flame and slit width of 0.7 nm at wavelengths of 422.7 nm and 285.2 nm for calcium and magnesium respectively. Potassium and sodium were determined by Flame Emission Spectrophotometry using a Corning Model 400 Flame Photometer calibrated over the 0 - 10.0 mg / litre range.

VI. Cation Exchange Capacity - 3.00 g air dry < 2 mm soil was saturated by leaching with 100 ml 1M sodium acetate solution. The sodium saturated soil was then leached with 100 ml of 1.0 M ammonium acetate and the sodium recovered was quantified by flame emission spectrophotometry as described above.

B.2.c Dissolved Organic Carbon in Leachate from the Plots

Sampling Procedure - one subsample (approximately 25 ml) was selected at random from the samples obtained from both plots 6 and 10 on each day that flow occurred. Where both interflow and deep drainflow occurred on the same day, a subsample of each was obtained. The samples were stored in 28 ml screw capped glass vials or 50 ml medical flat soda glass bottles and stored in a cold store until analysis was possible.

Analytical Methods (Edward Tipping, *personal communication*) - samples were filtered through Whatman GF/C glass fibre filter papers (ashed in a muffle furnace at 450 ^{0}C to remove trace organics) prior to analysis. The optical absorbance of all samples was determined in duplicate at 230, 240, 250 and 260 nm on a Phillips Pye Unicam PU 8610 UV/VIS single beam kinetics spectrophotometer fitted with an automatic flow cell. Using the observed absorbance as a guideline, a representative subset of samples was selected for DOC quantitation on a Phase Separations TOCSIN aqueous carbon analyser. DOC quantitation was based on duplicate analyses with an accuracy of ±0.05 mg / litre. The calibration was carried out against potassium hydrogen phthalate over the 0 - 10 mg / litre range. Linear least squares techniques were then used to identify the best relationship between optical absorbance and DOC concentration. This was found to occur at 330 nm using eqn 9.3 (r^2 = 0.99).

$$\text{DOC (mg / l)} = 3.35 + 47.4(\text{UV abs 330nm}) \qquad (9.3)$$

Thereafter DOC concentration was determined indirectly from optical absorbance. Where a sample was obtained which fell outside the calibration range, DOC concentration was determined directly and the least squares fit adjusted accordingly.

B.3 Soil Sampling Procedure 1991-92

Following the failure to detect isoproturon in the subsoil during the 1990-91 season and the resulting reappraisal of objectives for 1991-92, the sampling procedure was changed. Twenty five 1 m^2 sampling areas were designated on the agronomic area of each of the two experimental plots investigated using a quasi-random approach to avoid intereferences to/from tramlines and experimental instrumentation. On each sampling occasion (9 in total) during 1991-92, samples were taken from one of the intersections of a hypothetical 0.3 m^2 cartesian grid superimposed on the central 0.6 m^2 of the original 1 m^2 area. The sampling interval was flexible to facilitate the collection of data as soon as possible following any significant rainfall event or drainflow from the plots. In the event that a long period elapsed without significant rainfall and/or drainflow, sampling was undertaken at intervals of approximately one month. The first set of samples were collected two days before the pre-emergent herbicide application (2.475 kg IPU / ha) on 9/10/91. Samples were collected on five occasions (5/11/91, 21/11/91, 14/1/92, 19/2/92 and 31/3/92) during the winter months prior to a spring post-emergent isoproturon application of 1.625 kg / ha on 5/4/92. Samples were collected on a further three occasions (13/4/92, 13/5/92 and 17/6/92) during the spring and early summer of 1992.

Samples were obtained by using a specially made 25 cm x 3 cm id trowel. This was the only feasible method to obtain consistent samples during the winter months when the soil was too wet and sticky to allow the use of small bore coring devices. Although the use of coring devices would have been possible during 1992 when the soil was considerably drier the trowel was used throughout to minimise sampling discrepancies.Vertical variation within the cultivated horizon was ignored. Each individual sample was ground and homogenized to give an average for the whole cultivated horizon in each of the 25 sampling squares of the plot on each sampling date. To minimise disturbance to the plots access to sampling points was achieved via tramlines and duckboards; hollows created by sampling were backfilled with adjacent topsoil from outside designated sampling areas.

B.4 Methods of Analysis 1991-92

B.4.a Measurement of Isoproturon Residues (IPUr) and Associated Sorption (Kd) and Desorption (Kapp) Coefficients in the Cultivated Horizon

Soils were dried, ground and prepared for analysis as in the previous year. All samples were dried, ground, extracted and analysed within two weeks of the sampling date. IPUr was extracted from 20 ± 0.001 g replicates of each sample by shaking with 30 ± 0.02 ml of 80 % methanol / 20 % water solution in 50 ml polypropylene centrifuge tubes on a rotary shaker for 24 hr. The extraction efficiency of this procedure was quantified at 95% for freshly added IPU but, because the effect of residue aging on extraction efficiency was unknown, data presented herein has not been corrected for this loss. The tubes were centrifuged at 4000 x gravity for 30 min and then the supernatants were carefully decanted, made up to 30 ml with 80 % methanol / 20 % water solution and filtered through a Nalgene 0.22 µm filter unit prior to HPLC analysis. Kd and Kapp was measured by shaking 10 ± 0.001 g of each sample plus 20 ± 0.02 ml of approximately 5 mg / litre aqueous IPU solution or organic free water respectively in 50 ml polypropylene centrifuge tubes on a rotary shaker over a 24 hr equilibration period. The tubes were centrifuged at 4000 x g for 30 min and the supernatants were carefully decanted and passed through a Nalgene 0.22 µm filter prior to HPLC analysis. Where IPU concentration in the aqueous systems were too low to be measured in the filtrate directly (only Kapp measurements) the samples were concentrated by passing a 10 ml aliquot through a Water's C18 Sep-Pak solid phase extraction cartridge. IPU was then recovered by eluting the cartridge with 1.0 ml of methanol. Where concentrations of greater than 10 fold were necessary, the 1.0 ml methanol concentrate was reduced further on a Tecam Dri-Block under a stream of nitrogen. Maximum concentration factors employed in this study were 100 fold with an associated detection limit of 2.5 µg IPU / litre. No IPU losses were detected due to sorption on the centrifuge tubes, however, losses on Nalgene cellulose acetate filters was found to range from 11% in solutions of 5.0 mg IPU / litre to 22% in solutions of 0.5 mg IPU / litre. All data reported here have been corrected in accordance with this filter loss. Single point sorption and desorption distribution coefficients were calculated in accordance with the usual procedure (see equation 9.4).

Kd (or Kapp) = IPU on solid phase / IPU in solution (litres / kg) (9.4)

B.4.b Assessment of Variation Associated with Methods Employed to Measure IPU_r, K_d and K_{app}

The proportion of variation that arose from inherent methodological variation as opposed to variation arising from natural processes or anthropogenic influences occurring in the field was determined. The excess soil collected during the experiment was composited, passed through a 2 mm sieve and mixed thoroughly several times to create a homogenous sample. Using the techniques described above, eight replicates each of the IPU extractions, K_d's and K_{app}'s were measured using the homogenized soil. All the K_{app} measurements included sample concentration to ensure maximum variability of the method was characterized.

B.4.c Dissolved Organic Carbon

Dissolved organic carbon was determined using the method described for the previous phase of the programme (1990-91). Samples were analysed in duplicate at 330 nm with an integration period of 3.0 sec and time delay of 1.0 sec. Concentration was predicted from the mean absorbance using equation 9.3. In anticipation of a second successive 'dry' winter , the sampling interval was increased to one sample every hour of drainflow from both plots 6 and 10 during each flow event.

CHAPTER 10

SPATIAL VARIATION OF SOIL PHYSICO-CHEMICAL PROPERTIES AND THEIR RELATIONSHIP TO THE DISTRIBUTION OF ISOPROTURON RESIDUES IN CULTIVATION HORIZONS

A. NATURE OF THE VARIABILITY OF PHYSICOCHEMICAL PROPERTIES AND ISOPROTURON RESIDUES IN CULTIVATED SOIL

A.1 Physico-chemical Properties

Selected physicochemical properties in the Ap horizons of plots 6 and 10 are listed in Table 10.1. Generally distributions had normal to slight positive skews with the exception of calcium which was negatively skewed. This is consistent with most published reports suggesting that environmental data exhibit a tendency towards positive skews and frequently even log normal distributions due to the impossibility of observing negative values (Haynes *et al*, 1982). The negative skew of calcium is not surprising as the plots had been limed a few weeks prior to sampling. Coefficients of variation were generally of the order 10-30 % with the exception of exchangeable sodium (55 % plot 6, 68 % plot 10), insoluble carbonates (63 % plot 6, 35 % plot 10) and silt content (61 % plot 6, 41 % plot 10). The mean clay contents of 68 % and 61 % on plots 6 and 10 respectively are higher than the mean clay content of 55 % reported for the Ap horizon at the Brimstone site by Cannell *et al* (1984). Possibly this can be explained by an underestimate of the silt contents in this study as discussed in section A.3. Sand contents (9.6 % on plot 6 and 8.6 % on plot 10), organic matter content (8.6 % on plot 6 and 9.0 % on plot 10) and bulk density (860 kg / m^3 on plot 6 and 925 kg / m^3 on plot 10) were consistent with those reported by Cannell *et al* (1984) and Harris *et al* (1984). The mean thickness of the Ap horizon (0.16 m) was 0.06 m less than that reported by Cannell *et al*

Table 10.1 Descriptive Statistics for the Spatial Distribution of Physico-chemical Properties in the Ap horizon of Plots 6 and 10 at Brimstone Farm

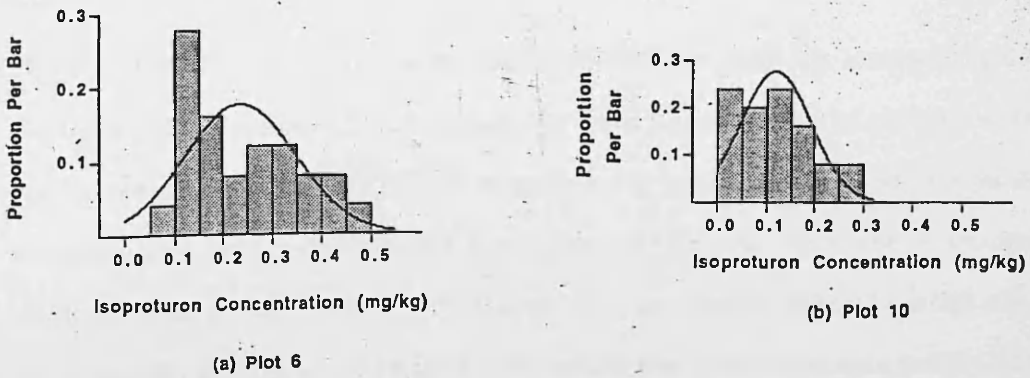
	Carbonates (equivalents)		Sodium (meq / kg)		Potassium (meq / kg)		Calcium (meq / kg)		Magnesium (meq / kg)		CEC (meq / kg)	
	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10
Cases	25	25	25	25	25	25	25	25	25	25	25	25
Minimum	0.50	1.00	0.65	0.51	3.75	3.71	44.7	190	3.89	3.89	1304	1304
Maximum	8.00	8.00	3.77	4.35	8.14	8.40	280	306	8.39	6.69	2942	2667
Range	8.50	7.00	3.12	3.84	4.39	4.69	235	115	4.50	2.80	1638	1362
Mean	3.46	5.46	1.33	1.06	6.08	6.03	204	256	5.92	5.76	1979	1717
Variance	4.73	3.73	0.53	0.52	1.80	1.46	3150	876	1.41	0.58	179521	176155
Std. Deviation	2.17	1.93	0.73	0.72	1.34	1.21	56.1	29.6	1.19	0.76	424	420
Std. Error	0.43	0.39	0.15	0.14	0.27	0.24	11.2	5.92	0.24	0.15	84.7	83.9
Skewness (G1)	0.64	-0.62	1.77	3.99	0.05	0.35	-1.33	-0.62	0.28	-0.80	0.70	1.12
Kurtosis (G2)	-0.23	-0.51	3.17	15.7	-1.16	-0.29	1.26	-0.41	-0.32	-0.03	0.17	-0.06
C.V.	0.63	0.35	0.55	0.68	0.22	0.20	0.28	0.12	0.20	0.13	0.21	0.25

	Organic Matter Contemt (%)		% Sand		% Silt		% Clay		Bulk Density (kg/m^3)		Ap Horizon Thickness (m)	
	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10
Cases	25	25	25	25	25	25	25	25	25	25	25	25
Minimum	5.48	2.07	5.33	6.23	6.13	4.03	29.7	42.1	570	346	0.13	0.12
Maximum	10.4	19.2	14.8	15.6	58.8	50.9	84.1	88.5	1267	1356	0.22	0.20
Range	4.94	17.5	9.49	9.40	52.6	46.9	54.4	46.4	697	1011	0.09	0.08
Mean	8.56	9.01	9.63	8.60	22.0	30.7	68.3	60.7	860	925	0.16	0.16
Variance	1.24	7.21	4.61	4.80	178	155	177	159	26797	43146	0.00	0.00
Std. Deviation	1.12	2.69	2.15	2.19	13.3	12.5	13.3	12.6	164	208	0.02	0.02
Std. Error	0.22	0.54	0.43	0.44	2.67	2.49	2.66	2.52	32.7	41.5	0.00	0.00
Skewness (G1)	-0.70	1.87	0.16	1.74	1.41	-0.62	-1.54	0.59	0.19	-0.76	1.13	0.33
Kurtosis (G2)	0.38	9.50	0.33	2.94	1.84	-0.62	2.22	-0.66	-0.18	1.18	0.91	0.05
C.V.	0.13	0.30	0.22	0.26	0.61	0.41	0.20	0.21	0.19	0.23	0.14	0.12

(1984) but can possibly be partially explained by surface compaction during soil coring.

A.2 Isoproturon Residues

The variability of isoproturon residues in the cultivated layers of plots 6 and 10 on October 14th 1990 are shown in Fig 10.1 a and b respectively. A curve has been superimposed on the frequency distributions to highlight the deviation of the results from the normal distribution. On both plots, slight positive skews of 0.54 and 0.41 were observed for plots 6 and 10 respectively. The mean isoproturon concentration of 0.23 mg / kg on plot 6 was almost double that of 0.12 mg / kg observed on plot 10 which had a greater frequency of lower concentrations. The range in concentration on plot 6 (0.39) was also substantially greater than that on plot 10 (0.23). These results are very different from those obtained for the more intensive field study conducted in 1991-92 (see Chapter 11 for results) where isoproturon concentration was significantly greater on plot 10 than on plot 6 on every sampling occasion. This is somewhat surprising because there was no reason to believe that the discrepancy was attributable to changes in field conditions. The only explanation that can be offered was that the sequential extraction procedure used in the 1990-91 study was not reliable. For example it is possible that previously extracted residues became readsorbed when the extractant was added to a fresh batch of soil.



(a) Plot 6

(b) Plot 10

Figure 10.1 Frequency Distribution of Atrazine and Isoproturon Residues in the Cultivated Horizon of plots 6 and 10

A.3 Similarities and Differences Between Plots 6 and 10*

Students t-tests* (Table10.2) indicated that only isoproturon concentration, insoluble carbonate content and exchangeable calcium were significantly different on plots 6 and 10 at the p 0.05 level. The t statistics for clay and silt content were also greater than the critical t value (2.000 with 48 DF at 0.05), but only just. The p values of 0.021 and 0.042 for silt and clay respectively demonstrate that there were only 2% and 4% chances of committing Type 1 errors. Furthermore, there was no reason to expect significant differences in soil texture for the two plots (Cannell *et al*, 1984) and the apparent differences in these results can possibly be explained by methodological errors arising from the overestimation of clay from settling velocities. Differences in carbonate and calcium concentration can be attributed to variation in spreading of lime added to the plots a few weeks prior to sampling. Isoproturon concentration exhibited the greatest difference between plots. Possible reasons for this are discussed fully in Chapter 11.

B. RELATIONSHIP BETWEEN THE SPATIAL VARIABILTY OF SOIL PHYSICO-CHEMICAL PROPERTIES AND THE DISTRIBUTION OF ISOPROTURON RESIDUES IN THE CULTIVATED LAYER

B.1 Pearson Correlation Coefficients

Pearson correlation coefficients (Table 10.3) demonstrate that no strong association existed

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***FOOTNOTE** The significance of the differences between plots was examined by using Student's t-tests. Physico-chemical properties on plots 6 and 10 were not related and there was no reason to suspect any specific direction in the results. Consequently independent two-tailed tests were performed - the null hypothesis being that there was no significant difference between plots. The 0.05 significance level was adopted (critical t = 2.000 with 60 DF). Probability distributions and F-tests demonstrated that the raw data were suitable for the test with the exception of isoproturon which was obviously significantly different in the absence of any testing.

Table 10.2 t-test on Differences Between Physico-chemical Properties and Isoproturon Residues in the Cultivated Horizon of Plots 6 & 10

Variable	t - Statistic	DF	Probability
Autumn 90 Ip Conc (mg / Kg)	4.297	48	0
Spring 91 Ip Conc (mg / Kg)	-5.451	48	0
Autumn 91 Ip Conc (mg / Kg)	1.371	48	0.177
Carbonates (equivalents)	-3.446	48	0.001
Sodium (meq / Kg)	1.313	48	0.195
Potassium (meq / Kg)	0.118	48	0.907
Calcium (meq / Kg)	-4.111	48	0
Magnesium (meq / Kg)	0.559	48	0.579
CEC (meq / Kg)	1.346	48	0.185
% SOM	-0.779	48	0.440
% Sand	1.666	48	0.102
% Silt	-2.38	48	0.021
% Clay	2.091	48	0.042
Bulk density (Kg / m3)	-1.218	48	0.229

Table 10.3 Pearson Correlation Coefficients Between Isoproturon Concentration and Soil Physico-chemical Properties

	Autumn 90 Ip Conc (mg / Kg)		
Physico-chemical Property	Plot 6	Plot 10	Combined Plots
Carbonates (equivalents)	-0.100	0.279	-0.207
Sodium (meq / Kg)	-0.163	-0.279	-0.071
Potassium (meq / Kg)	0.586	0.657	0.522
Calcium (meq / Kg)	-0.157	0.166	-0.324
Magnesium (meq / Kg)	0.221	-0.204	0.125
% SOM	0.017	-0.258	-0.163
% Sand	-0.168	-0.023	0.034
% Silt	0.143	-0.285	-0.185
% Clay	-0.117	0.266	0.181
Bulk density (Kg / m3)	-0.142	0.031	-0.142
CEC (meq / Kg)	0.313	-0.335	0.190
Spring 91 Ip Con (mg / Kg)	0.184	0.191	-0.203

between isoproturon concentration and soil physicochemical properties determined in the autumn of 1990. Generally correlation coefficients were significantly less than ±0.5. The highest coefficients observed were 0.586 and 0.657 for potassium on plots 6 and 10 respectively. This might indicate that the micas which dominate the mineralogy of the

Denchworth series clay soil posses important sorption sites for isoproturon; alternatively the correlation might have arisen purely by chance. Pooling results for both plots to create a larger population failed to result in any improvement.

B.2 Multivariate Interpretation of Data using Principal Components Analysis

Principal components analysis was used in an attempt to determine whether or not more subtle relationships existed which were obscured by the relatively simple structure of Pearson coefficients. All the variables listed in Table 10.3 were included in this analysis and the results are given in Table 10.4. Eigenvalues decreased gradually for both plots 6 and 10. Component 1 accounted for only 24.9 % and 23.5 % of the variation on plots 6 and 10 respectively and on both plots the sum of the first five components accounted for approximately 60 % of variation. These data are insufficient to demonstrate any strong association between isoproturon concentration and the physicochemical properties investigated. Despite these findings, the possibility that physicochemical properties are influencing the distribution of isoproturon cannot be ruled out. The results merely suggest that other factors, including the hydrological regime and biodegradation, might be more important.

Table 10.4 Eigenvalues, Variances and Component Loadings of Isoproturon and Soil Physico-chemical Properties

	Component 1		Component 2		Component 3		Component 4		Component 5	
	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10
Eigenvalue	2.988	2.818	2.144	1.967	2.144	1.536	1.422	1.278	1.047	1.178
Variance	24.90	23.49	17.87	16.40	13.69	12.80	11.85	10.65	8.729	9.818
Loadings										
% Silt	0.817	-0.781	0.493	-0.566	0.095	-0.002	0.096	0.009	0.048	-0.090
% Clay	-0.785	0.752	-0.502	0.583	-0.219	-0.009	-0.117	0.127	-0.114	0.017
Mg Concentration (meq / kg)	0.638	-0.728	-0.236	0.180	-0.269	0.192	-0.036	0.123	0.291	0.315
K Concentration (meq / kg)	0.554	-0.715	-0.594	0.398	0.302	-0.051	0.266	-0.099	-0.150	0.270
Bulk Density (kg / m^3)	-0.545	0.065	0.264	0.607	0.138	0.623	0.345	-0.134	0.025	0.198
Insoluble carbonates (equivalents)	0.363	-0.361	0.612	0.573	0.167	-0.225	0.286	-0.158	-0.451	-0.471
Cation Exchange Capacity (meq / kg)	0.393	0.009	-0.606	-0.360	-0.142	0.694	0.254	0.312	0.292	0.196
Isoproturon Concentration (mg / kg)	0.430	0.276	-0.555	-0.306	0.179	0.517	0.118	-0.292	-0.324	-0.188
Ca Concentration (meq / kg)	0.182	0.218	0.210	-0.060	-0.810	0.066	0.093	-0.771	-0.072	0.417
% Sand	-0.208	0.180	0.050	0.099	0.770	-0.252	0.131	0.539	0.407	0.548
Organic Matter content (%)	-0.367	0.361	-0.195	-0.110	-0.080	0.188	0.780	0.305	-0.324	-0.311
Na Concentration (meq / kg)	-0.100	0.425	0.191	-0.414	-0.262	-0.470	0.643	-0.186	0.504	0.304

CHAPTER 11

EFFECT OF CROP RESIDUE MANAGEMENT AND DRAINAGE ON THE PERSISTENCE AND MOVEMENT OF ISOPROTURON IN A STRUCTURED CLAY SOIL OVER THE GROWING SEASON OF A WINTER BARLEY CROP

A. PERSISTENCE OF ISOPROTURON RESIDUES IN THE CULTIVATED HORIZON

A.1 Chronology

The general trends of isoproturon dissipation, sorption K_d and desorption K_{app} from autumn 1991 to early summer 1992 are shown in Figure 11.1. Carryover of isoproturon residues from previous herbicide applications (see Table 11.1) was approximately 0.2 mg / kg. Following the pre-emergent herbicide application, isoproturon in the cultivated horizon declined rapidly on plot 6 (Fig 11.1 a), but more slowly on plot 10 (Fig 11.1 b). This suggests that biodegradation may be an important loss mechanism. For example, burning may have destroyed a large proportion of the soil microbial community on plot 10 whilst the incorporation of straw on plot 6 may represent an enhanced supply of carbon to the microbes, possibly stimulating faster and/or greater degradation of the herbicide. The corresponding half-lives for isoproturon in each of the twenty five sample squares on each plot for the period 5 November 1991 to 30 March 1992 are given in Table 11.2. The median half-life on plot 6 was 45 days and that on plot 10 was 89 days. Such results must be interpreted with care given the temporal and spatial variability of intrinsic factors, including moisture content and temperature, in the field. Nevertheless, the half-life reported here for plot 10 (ie. median of 89 days) is quite similar to that of 75 days reported by Nicholls *et al* (1993) for the same soil and herbicide under carefully

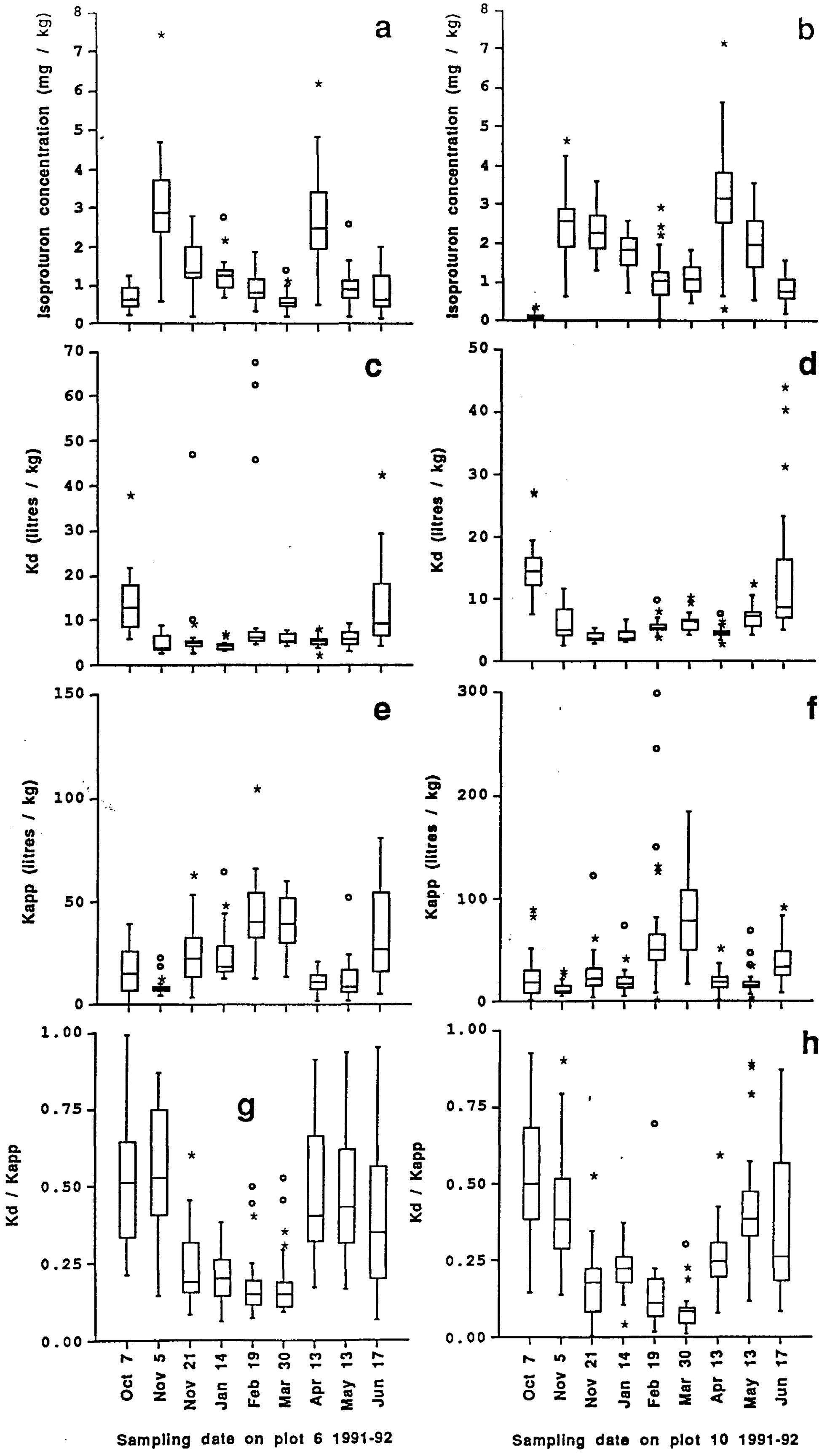

Figure 11.1 The spatial and temporal variation of IPUr (a - plot 6, b - plot 10), Kd (c- plot 6, d - plot 10), Kapp (e - plot 6, f - plot 10 and sorption/desorption nonideality indices (g - plot 6, h - plot 10) in the cultivated horizon

Table 11.1 Variability of Isoproturon Residues and Sorption / Desorption Coefficients in the Cultivated Horizon of Plot 6 and 10

	Sampling Date 1991-92																	
Isoproturon Concentration (mg / kg)	7/10/91		5/11/91		21/11/91		14/1/92		19/2/92		30/3/92		13/4/92		13/5/92		17/6/92	
	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10
minimum	0.01	0.02	0.58	0.64	0.17	1.28	0.65	0.73	0.32	0.04	0.16	0.44	0.47	0.32	0.20	0.53	0.11	0.25
maximum	0.44	0.36	7.47	4.68	2.78	3.59	2.75	2.56	1.85	2.91	1.36	1.82	6.21	7.18	2.58	3.55	1.98	1.57
mean	0.15	0.11	3.03	2.53	1.51	2.27	1.23	1.73	0.90	1.08	0.61	1.08	2.70	3.22	0.99	1.99	0.83	0.79
C.V.	0.72	0.80	0.43	0.40	0.40	0.25	0.38	0.29	0.39	0.65	0.43	0.38	0.46	0.44	0.50	0.41	0.58	0.53
Kd (litres / kg)																		
minimum	5.99	7.47	2.92	2.47	2.67	2.80	2.99	3.19	4.73	3.76	4.36	4.03	2.30	2.81	2.98	4.11	4.41	5.06
maximum	38.1	27.2	8.84	11.8	47.1	5.38	7.11	6.76	67.5	9.82	7.92	10.2	8.29	7.45	9.38	12.4	42.8	44.2
mean	13.9	15.0	5.09	6.06	6.84	3.92	4.28	4.10	12.4	5.65	5.90	6.18	5.38	4.55	6.03	6.97	13.3	13.9
C.V.	0.51	0.32	0.37	0.45	1.25	0.17	0.23	0.24	1.43	0.22	0.19	0.25	0.25	0.23	0.28	0.28	0.73	0.80
Kapp (litres / kg)																		
minimum	3.34	1.26	4.60	4.76	3.59	3.63	12.2	4.55	12.2	1.39	12.9	16.0	1.42	1.03	1.88	2.49	5.01	8.07
maximum	38.8	90.4	22.4	30.5	63.6	674	64.0	73.2	105	299	59.5	510	20.6	51.7	51.5	68.9	80.4	91.5
mean	17.2	23.6	8.50	12.0	24.7	70.3	24.4	20.8	42.9	71.7	38.4	124	19.2	19.1	11.8	20.3	32.6	39.1
C.V.	0.77	0.98	0.47	0.52	0.60	2.15	0.55	0.65	0.47	0.98	0.37	1.05	0.40	0.57	0.88	0.75	0.67	0.61
Kd / Kapp																		
minimum	0.21	0.15	0.15	0.14	0.09	0.01	0.06	0.05	0.07	0.02	0.10	0.01	0.18	0.08	0.16	0.12	0.07	0.08
maximum	287	15.8	1.45	1.23	4.07	1.15	0.38	1.49	1.70	3.68	0.53	0.30	5.43	4.45	3.39	2.72	3.74	1.27
mean	20.2	2.09	0.69	0.61	0.45	0.22	0.21	0.27	0.32	0.28	0.19	0.09	0.70	0.48	0.91	0.57	0.65	0.44
C.V.	3.25	1.63	0.50	0.60	1.78	1.04	0.39	0.97	1.25	2.58	0.62	0.74	1.44	1.83	0.92	1.01	1.15	0.75

controlled laboratory conditions with temperature of 10 °C and moisture content at 80% of field capacity. Although insufficient data was available to derive half lives for the summer months, more rapid preliminary dissipation following the pre-emergent herbicide application in April (Fig 11.1) and evidence of low herbicide carryover at the end of the previous summer (see above) suggests that higher temperatures may favour more rapid breakdown. The possible effects of the differences in mole drainage between the two plots is discussed later in section B.2.

Table 11.2 **Half life of IPUr over the period 5 November 1991 to 30 March 1992**

	Plot 6	Plot 10
N	22	25
minimum	15	31
maximum	97	483
mean	50	151
median	45	89
st.dev.	22	133
skewness	0.34	1.19
CV.	0.45	0.88

K_d was more consistent on plot 10 (Figure 11.1 d) with mean values ranging from 4-7 litres / kg throughout the sampling period with the exception of 7 October 1991 (mean K_d = 15) and 17 June 1992 (mean K_d = 14) when they were more variable and up to three times greater than on any other occasion. The differences observed on these dates were most likely related to changes in the moisture status of the soil and / or differences in ambient temperature. Similar behaviour was observed for plot 6 (Fig 11.1 c), with the exception that K_d was much more variable on this plot than on the burnt plot on 21 November 1991 ($K_d = 7 \pm 9$) and 19 February 1992 ($K_d = 12 \pm 18$) - sampling dates which were preceded by major rainstorm events. A possible explanation for this behaviour was that isoproturon residues sorbed to intact wheat straw on plot 6 were more labile than those sorbed to ash particulates in plot 10, making them more susceptible to changes in the soil moisture status. This assertion is supported by the results of Ghadiri *et al* (1984) who reported that atrazine intercepted by flat and standing straw was easily desorbed by rainfall. By contrast, carbon on oxidized ash particulates closely resembled activated carbon or charcoal and, consequently, their capacity for retention of sorbed residues was likely to be greater than that of intact straw. K_{app} was lowest on 5 November, 27 days after the pre-emergent herbicide application, and then increased rapidly as isoproturon concentration fell on both plots (Fig 11.1 e, f). This trend was repeated again following the post-emergent application in spring. K_{app} exhibited the same sensitivity to changes in soil moisture content as K_d, becoming much more variable on 21 November 1991 and 19 February 1992. It was also noticeable that extreme values were frequently observed, particularly for K_{app}, which were up to five times greater than respective mean values. This might be explained by distributed reactivity concepts (Weber *et al* , 1991). For example, the proportion of incorporated wheat straw or ash in each individual sample varied markedly.

Nonideality indices (K_d/K_{app}), ie. the fractional equilibrium, decreased with an increase in the age of isoproturon residues as reported elsewhere for atrazine and metolachlor (Pignatello and Huang, 1991) and simazine (Scribner *et al*, 1992). By 14 January 1992, 97 days following the pre-emergent application, the nonideality index on both plots had fallen to approximately 0.25 where it remained until the post-emergent application on 4 April 1992 (Fig 11.1 g, h). Mean K_{app}'s were typically two to four times greater than the corresponding K_d's over this period. Normalisation of K_d's on a soil organic matter basis had little effect on their variability. On 14 January 1992 normalisation resulted in a slight increase from 29 to 30%. Similar effects have been reported for napropamide sorption by a sandy soil (Elabd *et al*,1987). These results are in direct contrast to frequent reports that normalisation acts to suppress variability due to the dominant influence of organic matter on sorption (Chiou *et al*, 1979; Rutherford *et al*, 1992) and indicates that great care must be taken if K_d's, used in contaminant modelling, are to be derived indirectly from soil organic matter contents.

A.2 Effect of Intrinsic and Extrinsic Factors on the Persistence of Isoproturon

The significance of the differences observed for isoproturon concentration, Kd, Kapp and the nonideality indices between the two plots on each sampling date, tested using the Students t-test, are given in Table 11.3. Differences may have arisen because of intrinsic or extrinsic factors (see Donigian Jr and Rao, 1987; Beck *et al*, 1993), or more likely a combination of both. Only their effect on persistence is discussed here; the importance of agricultural practices for leaching is considered in section B.

Table 11.3 t-scores and p-values for T-tests to Assess the Significance of the Differences Between Plot 6 and 10*

Date	Isoproturon Concentration		Kd		K app		Kd / Kapp	
	t score	p value	t score	p value	t score	p value	t score	p value
7/10/91	**1.373**	**0.176**	-0.632	0.531	-1.246	0.219	1.378	0.175
5/11/91	1.530	0.133	-1.472	0.148	**-2.371**	**0.022**	0.790	0.434
21/11/91	**-4.524**	**0.000**	1.699	0.096	-1.503	0.139	1.426	0.160
14/1/92	**-3.677**	**0.001**	0.650	0.519	0.934	0.355	-1.143	0.259
19/2/92	-1.168	0.248	1.904	0.063	-1.976	0.054	0.244	0.808
30/3/92	**-4.813**	**0.000**	-0.734	0.467	**-3.260**	**0.002**	**3.770**	**0.000**
13/4/92	-1.401	0.168	**2.437**	**0.019**	**-3.223**	**0.002**	0.841	0.405
13/5/92	**-5.208**	**0.000**	-1.829	0.074	**-2.298**	**0.026**	1.701	0.096
17/6/92	0.061	0.952	-0.226	0.822	-0.946	0.349	1.207	0.234

*t scores and p values given in bold type indicate that the difference between plots 6 and 10 for the given parameter on the given date was significant at the 0.05 level.

The primary extrinsic factor contributing to the difference in persistence of isoproturon reported here was the method of crop residue management. This investigation would suggest persistence may be enhanced in the cultivated horizon of burnt land relative to that where crop residues were chopped and ploughed in. The burnt plot (plot 10) was found to have significantly (0.05 level) greater isoproturon concentrations (five occasions out of nine) and Kapp's (four occasions out of nine) than plot 6 where straw was incorporated (Table 11.3). By contrast, Kd's were relatively consistent over the season and were significantly different for the two plots only on 13 April 1992, nine days following the post-emergent herbicide application

(Table 11.3). The nonideality index was only significantly different (ie. lower on plot 10) for the two plots on 30 March 1992, just before the postemergent application of the herbicide. The sensitivity of the K_d's on the unburnt plot and the K_{app}'s on both plots to rainfall was indicative of the importance of intrinsic factors as a source of variation.

Isoproturon concentration sometimes increased within individual 1 m^2 sampling areas on successive sampling dates up to and including 30th March 1992. No further isoproturon application was made until the post-emergent application on 4 April 1992. It was unlikely that these changes could be attributed to atmospheric deposition of the herbicide. Consequently, this indicates the importance of variation at the local scale (ie. within each 1m^2 sampling area). To determine whether the variability reported in Figure 11.1 and Table 11.1 reflects extrinsic factors at the field scale or intrinsic variation arising from the heterogeneity of soil physicochemical characteristics at the local scale further studies were undertaken. On the 13 May an additional sampling square was designated on each plot, and nine separate samples were taken from each and the variability of isoproturon concentration, K_d and K_{app} within the individual square was compared with that for the whole plot (Table 11.4). Variation within the 1m^2 sampling areas was usually not much less than, or approximately equal to, that for the whole plot. This suggests that both extrinsic factors, such as cultivation, and natural intrinsic heterogeneity contributed to the variation in persistence of isoproturon. The variation associated with the experimental methods employed in this investigation are also given in Table 11.4. These data would suggest that, at most, approximately half (and frequently much less than this) the variability reported for IPU_r, K_d and K_{app} within the 1 m^2 subplots and the whole plots could be attributed to methodological variation. Thus, one can have confidence that the variability reported here was an accurate reflection of intrinsic and extrinsic factors operating at the field scale.

Table 11.4 Comparison of the Variability of Isoproturon Concentration, Kd and Kapp at the Field Scale and the Local Scale with that of the Experimental Methods Employed

	Method		Subplot		Whole Plot	
	Plot 6	Plot 10	Plot 6	Plot 10	Plot 6	Plot 10
N	8	8	9	9	25	25
Isoproturon Concentration (mg / kg)						
mean	1.17	1.30	2.27	1.92	1.23	1.99
minimum	1.09	1.15	1.33	1.42	0.65	0.53
maximum	1.23	1.58	3.54	2.59	2.76	3.55
C.V.	0.05	0.10	0.37	0.18	0.38	0.41
Kd (Litres / kg)						
mean	3.65	3.86	7.61	7.93	4.28	6.97
minimum	3.05	3.26	5.37	5.63	2.99	4.11
maximum	4.31	4.46	8.69	10.3	7.11	12.4
C.V.	0.13	0.10	0.18	0.21	0.23	0.28
Kapp (Litres / kg)						
mean	14.6	14.9	-	42.7	24.4	20.7
minimum	13.2	11.7	-	11.6	12.2	2.49
maximum	16.9	20.5	-	151	64.0	68.9
C.V.	0.08	0.20	-	1.01	0.55	0.75

B. LEACHING OF ISOPROTURON FROM MOLE DRAINAGE SYSTEMS

B.1 Water Balance of Experimental Plots

The water balances for both plots over the period October 1991 to June 1992 are given in Table 11.5. Total rainfall was 307 mm (45% of the long term annual average) and potential evapotranspiration of 398 mm, resulted in a negative water balance of -91 mm. However, the amount of water lost by drainflow in this period was four times greater from the unburnt plot (11.01 mm) than from plot 10 (3 mm). Approximately 50% of the total drainflow from plot 6 and 30% of that from plot 10 occurred during November 1991 and February 1992 when rainfall exceeded potential losses by evapotranspiration and cracks in the soil remained open. These results are consistent with those reported by Harris (1991) for the 1989-90 and 1990-91 winters, and suggest that drainage was dominated by macropore flow. The drainage response was faster on plot 6 because the expanded mole drainage system created a more pronounced macropore network, which was less susceptible to break down than that associated with the unexpanded mole drains plot 10 (Harris, 1991). Despite rainfall exceeding 30 mm in March and 40 mm in April, May and June 1992, there was only 1.4 mm and 0.6 mm of drainflow from plots 6 and 10 respectively. This can be attributed to the partial closure of cracks during March, increased water use by the barley crop and evaporation. During the 1991-92 growing season, no measurable water loss occured from either plot by combined cultivated horizon throughflow / surface runoff.

Table 11.5 Water Balance of Plots 6 and 10 1991-92

Month	**Rainfall**	**PEt**	**Rainfall - PEt**	**Total Drainflow (mm)**	
1991-92	**(mm)**	**(mm)**	**(mm)**	**Plot 6**	**Plot 10**
October	33.6	31.8	1.80	0.0	0.0
November	51.3	17.2	34.1	3.2	0.6
December	13.8	14.2	-0.40	0.8	0.3
January	27.1	7.20	19.9	2.4	0.2
February	20.4	22.1	-1.70	3.2	1.4
March	31.0	43.1	-12.1	0.0	0.0
April	42.0	59.6	-17.6	1.4	0.5
May	43.4	100.6	-57.2	0.0	0.0
June	44.8	102.6	-57.8	0.01	0.1
Total	307.4	398.4	-91	11.01	3.1

B.2 Isoproturon Residues in Drainflow

Leaching of isoproturon from plots 6 and 10 during 1991-92 is shown in Figure 11.2 a and b respectively. The chemographs provide only limited information because the water samples from low drainflows had to be bulked for analysis. Isoproturon concentrations peaked in November 1991 when rainfall led to through drainage after the pre-emergent herbicide application . Concentrations were 30 µg / litre and 120 µg / litre on plots 6 and 10 respectively and several factors may have contributed to this difference. Firstly, the total volume of drainflow from the plot 6 was greater than that from plot 10 (Table 11.5) so that the concentration may /-

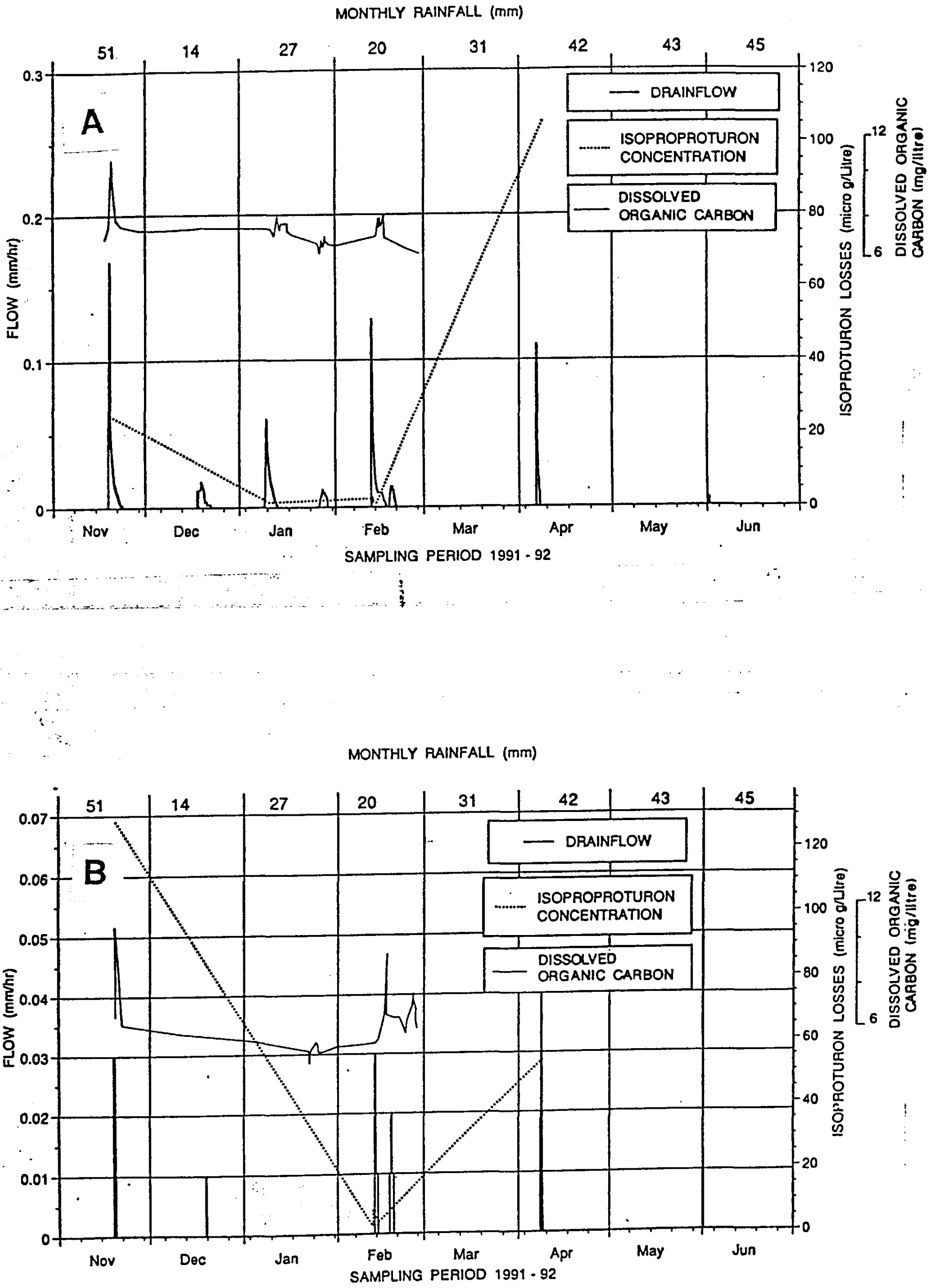

Figure 11.2 **Discharge and IPU and DOC concentrations in drainflow from plots 6 (A) and 10 (B)**

have been reduced due to dilution. Secondly, the rate at which the solute passed through plot 6 was greater than that through plot 10 (Fig 11.2) resulting in a decrease in soil-solute contact times. This may either enhance or suppress leaching depending on whether the compound of interest exists primarily in the solid or solution phase prior to leaching. Finally, it is possible that transport facilitated by the sorption to mobile particulate ash was partially responsible for the elevated isoproturon concentrations in the drainflow from plot 10. Graham *et al* (1992) reported that particle assisted (ie. surficial material) transport may have been partially responsible for the occurence of atrazine residues in vertisol cracks at depths of up to 1.25 m whilst they were absent from the adjacent soil matrix. On a previous sampling occasion ash particles were frequently observed in cracks to a depth of 0.4 m and sometimes even as deep as 1.0 m. The dilution effect appears to have been the major factor causing the difference in November 1991 given that the reversibly sorbed or labile fraction on plot 10 was significantly lower than that on plot 6 (see section A.2) and the isoproturon existed primarily on the solid phase. By contrast, during April 1992 following the post-emergent application, the peak isoproturon concentration on plot 6 (105 μg / litre) was more than double that on plot 10 (55 μg / litre). This extremely interesting observation suggests that a fundamental change had occurred in the mechanism controlling leaching losses. The volume of water lost in drainflow from plot 6 was three times greater than that from plot 10 (Table 11.5), so dilution was not responsible. Consequently, it appears that leaching was controlled by the soil-solution contact time. Prior to this event the 'equilibrium' isoproturon solution concentration of the interstitial soil water was likely to be greater than that in plot 10 because isoproturon residues in plot 6 were possibly more labile, ie. they had higher nonideality indices, than those in plot 10 at the end of March 1992 (eg. see section A.2). Consequently, when the interstitial solution was partially displaced by the April rainfall event, the drainflow concentrations were greater than those from plot 10. Furthermore, the faster drainage response of plot 6 relative to plot 10 would reduce the soil-solution contact time in the subsoil resulting in a lower potential for resorption of isoproturon lower down the profile than in plot 10. During the intervening months, December 1991 to March 1992, the pesticide concentrations had declined to <5 mg / litre - a background or residual level reported by Harris (1991) to be typical of drainflow derived from a range of different agricultural practices.

Regardless of the temporal variation in isoproturon concentration, the total amounts of isoproturon lost in drainflow from plots 6 and 10 over the period November 1991 to February 1992 were similar (Table 11.6), 178 mg and 164 mg respectively, equivalent to <0.001% of the pre-emergent application. Although less isoproturon was retained in the cultivated horizon of plot 6 than plot 10 the difference was not all lost in drainflow (Table 11.6) and its fate is of interest. Volatilization or biodegradation may have been partially responsible for the difference in isoproturon between the two plots. Despite the more pronounced macropore network in plot 6 it is difficult to envisage that volatilization alone would have been responsible for the lower persistence of isoproturon in the cultivated horizon of this plot. Microbial populations may be greater in soils with crop residues incorporated enhancing biodegradation relative to land on which the straw was burnt. Biodegradation might also have been enhanced in plot 6 because more of the isoproturon was present in the solution phase (eg. see Ogram *et al*, 1985).

Table 11.6 Isoproturon Loadings In Drainflow 1991-92 (mg)

Month 1991-92	Plot 6	Plot 10
November	152	146
December	2	3
January	6	2
February	18	13
Total	178	164

Another possible contributor to the imbalance of isoproturon between the two plots is resorption of soluble residues in the subsoil. However, during the 1991-92 winter, there was no cultivated horizon throughflow / surface runoff therefore it was impossible to assess the difference in the isoproturon concentration of water entering the subsoil from the surface horizon. It is reasonable to assume, however, that the isoproturon concentration of the interstitial water entering the subsoil in plot 6 may have been higher than that in plot 10 because the labile fraction was greater in the former plot (all else being equal). Assuming that there was no significant difference in the physicochemical composition of the subsoil in each plot and, given the significantly higher amount of isoproturon (Fig 11.2) in the drainflow from plot 6 than plot 10 in November 1991 and *vice versa* in February 1992, it was apparent that the herbicide had not reached an equilibrium distribution between the subsoil itself and the interstitial water (this in itself would suggest that flows were dominated by the soil macroporosity). However, this does not mean that resorption in the subsoil was unimportant, only that it is impossible to assess its significance in this study.

The imbalance between the plots might also be attributable to partitioning into a third phase, eg. dissolved organic matter or mobile colloidal material. Sorption experiments with wheat residues has shown that the solutions mixed with intact straw were more coloured than those mixed with ash. This suggests that greater solubilization of organic matter might be expected in the plot where intact straw was incorporated than in the burnt plot. The presence of organic matter in solution has frequently been reported to enhance the solubility of organic contaminants (Chiou *et al*, 1986, La France *et al*, 1988; Barriuso *et al*, 1992; Lee and Farmer, 1989) and facilitate their transport in soils (Enfield *et al*, 1989; McCarthy and Zachara, 1989; Dunnivant *et al* 1992). Neither of these assertions are supported by this field study. Dissolved organic carbon concentrations in the drainflow from the two plots investigated were not significantly different, suggesting that dissolved organic matter was in equilibrium with the solid phase (Fig 11.2): clay soils have a large capacity to sorb dissolved organic matter (Jardine et al, 1989). Given that total loss of organic carbon in drainflow from plot 6 was greater than from plot 10, the amount of isoproturon lost from the former plot should also be greater than that from the latter plot if DOC enhanced the solubility of the herbicide and facilitated transport. Table 11.6 shows that this was not so.

PART 3: CONCLUDING REMARKS

Sorbed isoproturon residues and soil physico-chemical properties in the cultivated horizon of plot 6 and 10 before the pre-emergent herbicide application in 1990 exhibited normal distributions. Isoproturon concentration was significantly different on the two plots and may have been related to calcium carbonate content which was the only soil physico-chemical property to exhibit a significant difference between the plots. However, relationships between individual physico-chemical properties and isoproturon concentration were weak with the exception of exchangeable potassium. This may indicate that interactions occurred between isoproturon and micas although earlier studies indicated that organic matter dominated isoproturon sorption (see Chapter 6). Multivariate statistical analysis failed to reduce the dimensionality of the data. Consequently, isoproturon concentration could not be predicted from soil physico-chemical properties in a simple way.

Over the growing season of a winter barley crop (1991-92), isoproturon sorption coefficients for the cultivated horizon were stable. However, there was some evidence to suggest that they increased during long dry spells. By contrast, desorption coefficients increased rapidly as isoproturon concentration fell following both the pre-emergent and post-emergent herbicide applications. Herbicide concentration was most variable before the pre-emergent application in October 1991 but remained relatively constant throughout the remainder of the sampling period (ie. to June 1992). On most sampling dates, isoproturon concentration was more variable on plot 6 than on plot 10. Desorption coefficients were generally more variable, and sorption coefficients were generally less variable than isoproturon concentration. Both sorption coefficients were dependent on the intrinsic heterogeneity of soil physico-chemical properties and rainfall. Sorption nonideality became more pronounced with time after herbicide application. Normalising sorption coefficients on a soil organic matter basis failed to reduce their variability unlike the results in Chapter 6. However, this does not mean that a partition mechanism was unlikely to be responsible for sorption, only that sorption was affected by a number of factors in a complex way.

Isoproturon concentration in the cultivated horizon of plot 10 was significantly higher than in plot 6 on four sampling dates out of nine. Despite this, there was no difference in the total isoproturon lost in drainflow between the two plots. This suggests that other processes such as biodegradation, volatilisation or subsoil immobilisation were important loss pathways. Further research in this area is necessary. The difference in crop residue disposal practices is believed to be principally responsible for the difference observed between plots 6 and 10. Differences between the plots could not be attributed to solubilisation effects of dissolved organic matter in the soil interstitial water. This is consistent with the sorption study presented in chapter 6. However, further studies are required in years with more typical rainfall giving rise to cultivated horizon throughflow to assess the differences between the chemical composition of interstitial water entering subsoils and that leaving via mole drains. By doing so it will be possible to speculate on subsoil immobilisation of dissolved organic carbon and pesticides.

CHAPTER 12

CONCLUSION

This study has shown that isoproturon was more persistent in the cultivated horizon of a heavy textured soil where ash was ploughed in rather than chopped wheat straw. However, over the growing season of a winter barley crop, there was no difference in the amount of isoproturon lost from mole drains underlying the experimental plots subject to these different crop residue disposal practices. This was despite the fact that the plot where straw was incorporated had expanded mole drains which were three times more efficient at removing water than the non-expanded mole drains in the burnt plot. This suggests that other processes such as volatilisation, biodegradation or immobilisation of leached chemicals in the subsoil were important loss pathways and that further research in these areas is required. This result, of great practical importance, was not suggested by sorption studies in the laboratory which demonstrated that neither the incorporation of ash or straw resulted in significant increseas in the sorption of isoproturon when compared tosorption by soil alone. Hence, there is a need to treat results from laboratory studies with caution. Experiments on the undisturbed soil core demonstrated that a continuum of flow phenomena were responsible for leaching losses but macropore flow was primarilly responsible for the rapid movement of chemicals to deeper depths.

This study was also significant in that it demonstrates the importance of taking into consideration spatial variation of physicochemical parameters and solute flow parameters in transport and fate models. The spatial variability of sorption/desorption coefficients, soil physicochemical properties and flow pathways are not likely in themselves to constitute an insurmountable obstacle to reliable prediction. What is more discouraging is their temporal uncertainty (eg. the sensitivity of variation of sorption/desorption coefficients to temporal changes in the weather) which will be a relatively difficult problem to overcome. The lack of any simple relationships between residual isoproturon concentration and sorption coefficients or soil physicochemical properties, and the difficulty of adequately characterising the spatial and temporal heterogeneity of solute flow pathways, will give rise to problems in the development of useful mechanistic models. The complexity of pesticide behaviour is so great that it might prove more productive to channel efforts into the development of conceptually simpler models.

Mechanistic models might be satisfactory at the local scale with appropriate definition of the temporal variability of sorption/desorption coefficients and solute flow pathways. However, the overall behaviour of interest at the field scale may be dependent on the extremes of the local parameter values describing flow rates and sorption reactions, since the most mobile fractions will control movement to groundwater, streams or drains, whilst the least mobile will determine long term retention in the cultivated horizon. Research on the effects of soil heterogeneity on water flows suggests that mechanistic models used with average "effective" parameter values cannot be expected to describe field scale responses adequately (Binley *et al*, 1990). This conclusion must extend to chemical variables that are dependent on flow pathways. Thus, the problem of characterising spatial and temporal variation of soil physicochemical properties and solute flow pathways cannot be ignored (Keith Beven, personal communication 1992).

Increasingly stringent environmental legislation will necessitate the development of robust predictive models which can be used by environmental scientists and decision makers to help identify problems and resolve those that have arisen. The results presented here suggest that such models must address the prediction of the distribution of residence times of any given chemical at the field scale, as affected by the dynamics of both flow pathways and chemical behaviour. Such a model may ultimately be more conceptual in nature (eg. Jury , 1982). Any simplified model, however, also implies uncertainty and it will be necessary to examine the role of the collection of appropriate data and the use of such data in constraining predictive uncertainty (see for example Beven and Binley, 1991).

One of the original objectives of this study was

"to provide a better quantitative understanding of these sorption and transport phenomena... it is hoped that this will provide the necessary impetus for modellers to represent these phenomena in future model structures"

Unfortunately this cannot be satisfied because the results of the study suggest that it is unlikely that mechanistic models can be successful at the field scale. Should this prove to be the case then it could be very important in saving others much effort and directing them to other, perhaps more profitable avenues of research. This is not to say that such models will not be useful in contributing to our understanding of chemical behaviour at the local scale. Nevertheless, future research needs are probably best satisfied by large, long term field scale behaviour assessment studies which can provide the necessary empirical inputs for conceptually simpler models.

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