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SORPTION AND MOVEMENT OF IONIC AND NON-IONIC PESTICIDES IN
SELECTED SOILS OF NEW ZEALAND

SUNDARAM BASKARAN

1994

**SORPTION AND MOVEMENT OF IONIC AND NON-IONIC PESTICIDES IN
SELECTED SOILS OF NEW ZEALAND**

A thesis presented in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy in Soil Science
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SUNDARAM BASKARAN

1994

Dedication

**This thesis is
dedicated
to my late beloved *Grand-mother***

ABSTRACT

There is a growing concern about the persistence of pesticide residues in soils and their subsequent movement to groundwater and surface water. Sorption of pesticide by soil particles is one of the key processes affecting the fate of pesticides in soil. The overall objective of this research was to examine the sorption and movement of ionic (2,4-D, atrazine and metsulfuron methyl) and non-ionic (phorate and terbufos) pesticides in a range of allophanic and non-allophanic soil materials of New Zealand.

Firstly, the methods of measuring pesticide in the soil solution were evaluated. The results suggested that radiotracer techniques can be used to measure low concentrations of pesticide in the soil solution during sorption studies. Based on this, the sorption and movement of pesticides was examined using ^{14}C -labelled compounds. Complete recovery of ^{14}C pesticide residues in soils was achieved by direct extraction of soils with a scintillation cocktail, which contained an organic solvent.

The effect of drying soils on the sorption and leaching of an inorganic anion (phosphate; P) and organic pesticides (2,4-D and phorate) was examined using field-moist, freeze-dried, air-dried and oven-dried soil samples. Compared to field-moist and freeze-dried, both air-drying and oven-drying of soil increased the sorption of P, but decreased the sorption of pesticides. Solubilization of organic carbon during air-drying and oven-drying may have increased the accessibility of P to sorption sites on the mineral surfaces and thereby increased the sorption. In contrast, the addition of water soluble organic carbon bound onto pesticides in solution and decreased the apparent sorption onto the soil; thereby increasing leaching.

Pesticide sorption was measured in a range of allophanic and non-allophanic topsoil and subsoil samples using a batch equilibrium technique. In general, pesticide sorption, as measured by the distribution coefficient (K_d), increased with an increase in octanol-water partition coefficient (K_{ow}) of the pesticide and followed the order: terbufos > phorate > 2,4-D > atrazine > metsulfuron methyl. The K_d values increased with increasing organic carbon content of the soils and when the sorption was normalised to organic carbon (K_{oc}) there was less variation in K_{oc} values between the soils. Removal of organic carbon decreased the sorption of pesticides and the

effect was more pronounced with non-ionic than with the ionic pesticides. The results suggest that organic carbon is the principal sorbent for non-ionic pesticides, whereas clay is also contributing to the sorption of ionic pesticides. Multiple regression models were developed to predict pesticide sorption based on soil properties. The existing empirical equations based on K_{ow} values gave unsatisfactory predictions of pesticide sorption in the soils examined.

The contribution of different particle size fractions of soils to sorption and desorption of pesticides was examined using two soils with contrasting characteristics. The K_d values decreased in the order: clay > silt > sand. Organic carbon accounted for most of the variation in K_d values between the particle size fractions, and the removal of organic carbon decreased the K_d values of the pesticides. Following four successive extractions with 0.01 M $CaCl_2$, 65-90% and 22-75% of the initially sorbed ionic and non-ionic pesticides, respectively were released from the particle size fractions. Greater amounts of pesticides were released from the soil fractions from which organic carbon had been removed than from natural soil fractions and the difference was greater for the non-ionic than the ionic pesticides.

Experiments were conducted to examine the effects of different sources of added carbon (peat, sludge, mushroom compost, pig manure and poultry manure), and dissolved organic carbon (DOC) on the sorption and movement of pesticides in soils. Added carbon sources increased the sorption of pesticides and followed the order: peat > sludge > pig manure > mushroom compost > poultry manure. The differences in the effect of carbon addition on the sorption of pesticides may be related to the differences in their effect on DOC and pH of the soil. Premixing DOC with the pesticide solutions decreased the pesticide sorption whereas premixing DOC with soil increased the pesticide sorption. Column studies showed that pesticide mobility was enhanced by the presence of DOC.

Column leaching experiments were conducted to examine the movement of pesticides through repacked soil cores (step-function and pulse inputs) and intact cores (step-function input) using two soils with different pesticide sorption

capacities. In repacked soil columns, the step-function experiments showed a symmetrical breakthrough curve (BTC) for a non-sorbed solute ($^3\text{H}_2\text{O}$) with a sigmoidal shape, whereas there was an asymmetrical BTC with extensive tailing for a sorbed solute (2,4-D). In the pulse experiments the leaching of pesticides decreased with an increase in the K_d values and leaching decreased in the order: terbufos > phorate > 2,4-D > atrazine. The results from the intact core experiments suggested that both the sorbed (2,4-D) and non-sorbed ($^3\text{H}_2\text{O}$) solutes move preferentially through macropores such as worm holes and root channels.

The convection-dispersion equation (CDE) either with an equilibrium or a bicontinuum non-equilibrium sorption process was used to simulate the measured effluent BTCs obtained by simultaneous displacement of $^3\text{H}_2\text{O}$ and 2,4-D. The CDE with an equilibrium sorption process failed to simulate the BTC for 2,4-D in repacked and intact soil columns; whereas the CDE with a bicontinuum non-equilibrium sorption process provided a good description of the experimental data. Both chemical (intraorganic matter diffusion) and physical (preferential flow) processes are involved in the non-equilibrium sorption during the movement of pesticides in soil.

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LIST OF SYMBOLS

A	=amount of pesticide added (kg ha^{-1})
a	=Langmuir sorption coefficient (binding constant)
C	=equilibrium solution concentration ($\mu\text{mol L}^{-1}$)
C_e	=leachate concentration ($\mu\text{mol L}^{-1}$)
C_o	=input concentration ($\mu\text{mol L}^{-1}$)
C_{DOC}	=concentration of dissolved organic carbon (mg L^{-1})
D	=dispersion coefficient ($\text{mm}^2 \text{hr}^{-1}$)
Er_i	=enrichment ratio of the (i) th particle size fraction
F	=fraction of equilibrium site
$f(i)$	=fraction of the total mass represented by (i) th particle size fraction
i	=(i) th particle size fraction
K	=Freundlich sorption coefficient (sorption at unit concentration)
K_d	=distribution coefficient (L kg^{-1})
K_s	=sorption rate coefficient (hr^{-1}) (non-equilibrium first-order model)
K_1	=Freundlich sorption coefficient in equilibrium site
K_2	=Freundlich sorption coefficient in kinetic site
K_{de}	=desorption rate coefficient (hr^{-1}) (non-equilibrium first-order model)
K_{ds}	=distribution coefficient of the pesticide in the sediment
K_{oc}	=distribution coefficient based on organic carbon (L kg^{-1})
K_{om}	=distribution coefficient based on organic matter (L kg^{-1})
K_{ow}	=Octanol-water partition coefficient
K_{DOC}	=distribution coefficient of pesticide in dissolved organic carbon (DOC)
$K_d(i)$	= K_d of pesticides in (i) th particle size fraction
L	=column length (mm)
N	=Freundlich sorption coefficient
n_1	=rate constant (Freundlich kinetic sorption)
P	=Peclet number
p	=liquid-filled pore volume
Q_1	=Freundlich kinetic sorption coefficient (sorption at unit time)
Q_2	=rate constant (bicontinuum non-equilibrium model)
R	=retardation factor
S	=sorbed concentration ($\mu\text{mol kg}^{-1}$)

S_m	=Langmuir sorption coefficient (sorption maximum)
S_s	=amount of pesticide sorbed onto the sediment
S_1	=sorbed phase concentration in equilibrium site
S_2	=sorbed phase concentration in kinetic site
t	=time (hr)
v	=average pore water velocity (mm hr^{-1})
W_s	=water solubility of pesticide
x	=distance in the direction of flow (mm)
Y	=relative contribution of K_d from sand, silt or clay on the whole soil basis
ρ	=soil bulk density (g cm^{-3})
θ	=volumetric water content ($\text{mm}^3 \text{ mm}^{-3}$)
β	=fraction of instantaneous retardation (bicontinuum non-equilibrium model)
ω	=Damkohler number

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Pesticide use has been credited as one of the major contributors to modern agricultural production. The discovery of pesticides that could control insects, plant diseases and weeds in crops and pastures dramatically changed plant production systems throughout the world. The use of pesticides has been emphasized by the growing worldwide demand for food and fibre. Economic returns to producers from the use of pesticides varied between \$ 3 and 4 for every \$ 1 spent (Pimentel *et al.*, 1981).

In New Zealand, pesticides are the main means of insect, disease and weed control in crops and pastures. During 1993, New Zealand spent approximately \$ 150 million on pesticides. Herbicides account for 60% of this total in overcoming an annual loss of \$ 339 million through weed infestation.

Increased use of pesticides in agriculture/horticulture is causing great concern with regards to surface and groundwater contamination. Evidence of pollution of surface water and groundwater with pesticide residues has been obtained in many overseas countries (Cohen *et al.*, 1986). Based on this evidence a range of pesticide compounds have been banned. Recently, groundwater contamination of triazine pesticides has been reported in the South Canterbury region of New Zealand (Close, 1991). This has received considerable public and scientific interest, primarily due to concern about the potential effects of these pesticides on human health.

Since most concern is associated with the presence of pesticides in the soil environment, it is essential that the processes affecting the transport of pesticides in the soil be understood. The main processes affecting the efficiency, and ultimate fate of pesticides in the soil are retention (sorption-desorption), transformation (biological and chemical degradation) by the soil and transport into the soil, the atmosphere and surface waters.

The movement of pesticide to groundwater is largely controlled by the extent of sorption onto soil particles and the rate of degradation. While the second process (pesticide degradation) is considered to be as important as the first process (sorption) in the transformation of pesticides in soil, a detailed study of this process would constitute a major work, which is beyond the scope of this study. In this study the sorption of a range of pesticides is examined in relation to its effect on movement to groundwater.

Methodologies to examine these transformation processes in soil have been developed overseas. Investigation of soil-pesticide relationships in New Zealand soils was initiated in 1972. In these studies the phytotoxicity of various pesticides was examined using bioassay techniques (Rahman, 1976; Rahman *et al.*, 1978; Rahman and Holland, 1985; Rahman, 1989). However, little progress has been made subsequently in quantifying the transformation of pesticides in New Zealand soils.

New Zealand soils in general contain fairly high levels of organic matter when compared to other soils (Burney *et al.*, 1975). A number of soils are derived from volcanic material and contain a high proportion of allophane. Further, most soils are acidic and have a pH range of 5.5-6.5. These three factors are known to have a marked influence on pesticide behaviour and make the New Zealand soils different from those used by other researchers in relation to pesticide interaction. For example it has been observed that the prediction equation developed overseas based on the organic matter content of a soil overestimates the effectiveness of herbicides in the pumice soils of New Zealand (A. Rahman, pers.comm.). This suggests that it may not always be appropriate to extrapolate the results of studies on soil-pesticide interactions carried out in overseas countries to New Zealand conditions.

The purpose of this study is to gain a better understanding of the sorption and movement of pesticides in New Zealand soils with the following overall objectives:

1.2 OBJECTIVES

1. To examine the sorption of ionic and non-ionic pesticides in a range of allophanic and non-allophanic soils and to investigate the soil properties

affecting sorption of pesticides.

2. To examine the contribution of organo-mineral fractions of soils to sorption-desorption of ionic and non-ionic pesticides.
3. To investigate the effect of organic carbon on the sorption and movement of pesticides in soils.
4. To examine the transport of pesticides and to develop models to predict their movement in soils.

The specific objectives of the various experiments are presented in the relevant chapters.

1.3 STRUCTURE OF THE STUDY

The thesis comprises 9 chapters.

Following the introduction (Chapter 1), a general review of literature (chapter 2) examines the processes governing the fate of pesticides in soil. A description of the pesticides with details of the analytical methods used for the measurement of pesticides in the soil solution is presented (chapter 3). The drying of soils in the laboratory and field has been shown to alter some of the soil properties that might affect the fate of pesticides in soils. To test this, an experiment was conducted to examine the effect of the drying of soils on the sorption and leaching of inorganic nutrient ions and organic pesticides and the results are presented in Chapter 4. Equilibrium sorption of pesticides in a range of allophanic and non-allophanic soils, and an assessment of the soil factors affecting sorption are presented in Chapter 5. Based on these results equations to predict the sorption of pesticides were developed and evaluated. The importance of the organo-mineral fractions and organic carbon on pesticide sorption are described in chapters 6 and 7, respectively. The effect of sorption on the transport of pesticides in the soil column is presented along with the modelling of data using a bicontinuum model (Chapter 8). A general summary of the research and suggestions for future work are presented in Chapter 9.

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

Since pesticides will continue to be used in the production of food and fibre, more should be learned about their fate in the soil environment (Freed and Haque, 1975). Therefore, a thorough knowledge and understanding of the soil processes affecting pesticides is imperative, if methods of controlling pesticide persistence and minimizing their undesirable effects are to be devised (Kaufman, 1974). If pesticides are applied under appropriate soil and environmental conditions, they can be proven to be effective in agriculture.

As concerns are mostly associated with the presence of pesticide residues in the soil, firstly it is essential that the processes affecting the fate of pesticides in soil be understood. It is not the intention of this review to cover all the information about pesticides, rather it attempts to provide a perspective on the processes governing the fate of pesticides in soil and the factors affecting these processes.

2.2 PESTICIDE USAGE IN NEW ZEALAND

Pesticides are the main means of pest and weed control in a number of sectors of the New Zealand economy. Among these sectors, the agriculture/horticulture industry accounts for the largest amount of pesticide use. There are over 900 pesticide products registered for use in New Zealand and these are based on at least 270 different active ingredients (MacIntyre *et al.*, 1989). On average, approximately 4000 tonnes of pesticide active ingredient are applied annually in New Zealand. Over 75% of this pesticide use occurs in North Island and is concentrated in regions with major horticultural industries.

The average total sales of pesticides in New Zealand from 1987-93 are shown in Figure 2.1. There has been a gradual increase in the total sales of pesticides from \$ 111 M (1987) to \$ 151 M (1993) and during this period alone, the sales of

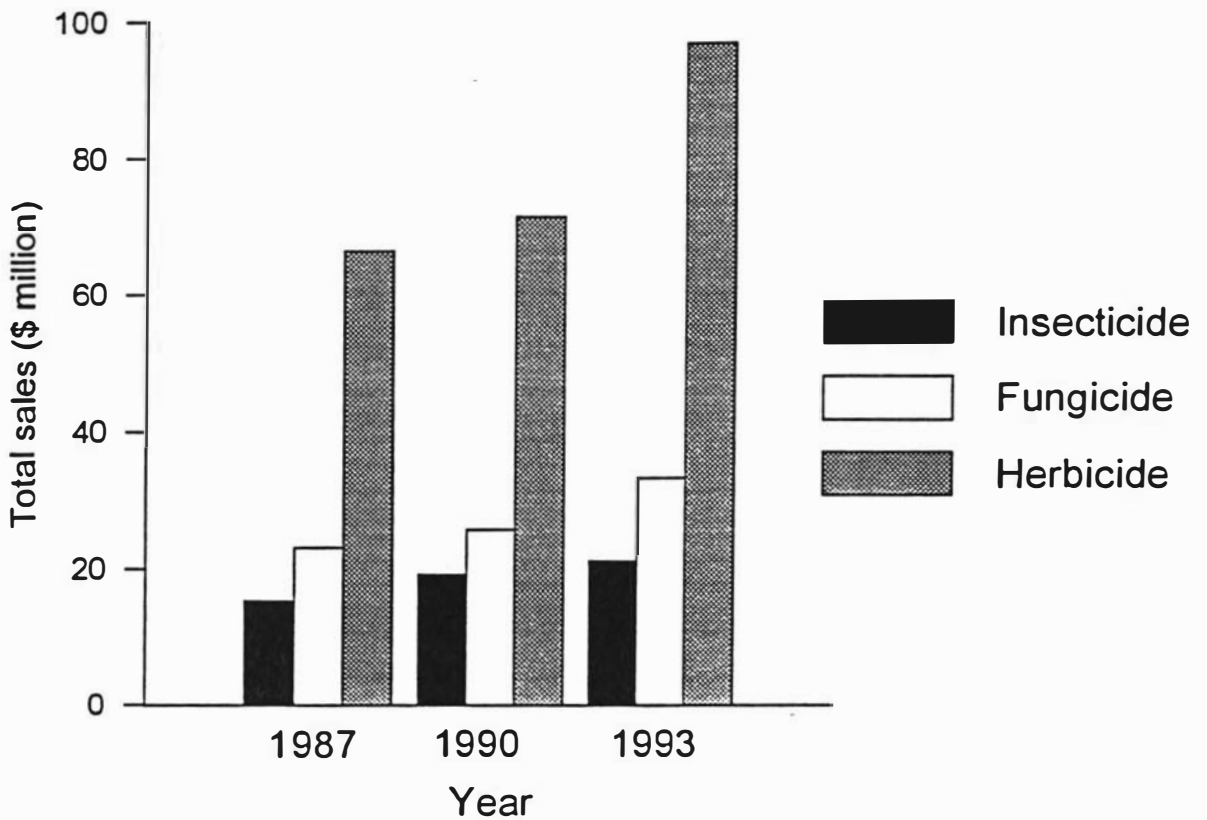


Fig 2.1 Trends in pesticide sales in New Zealand

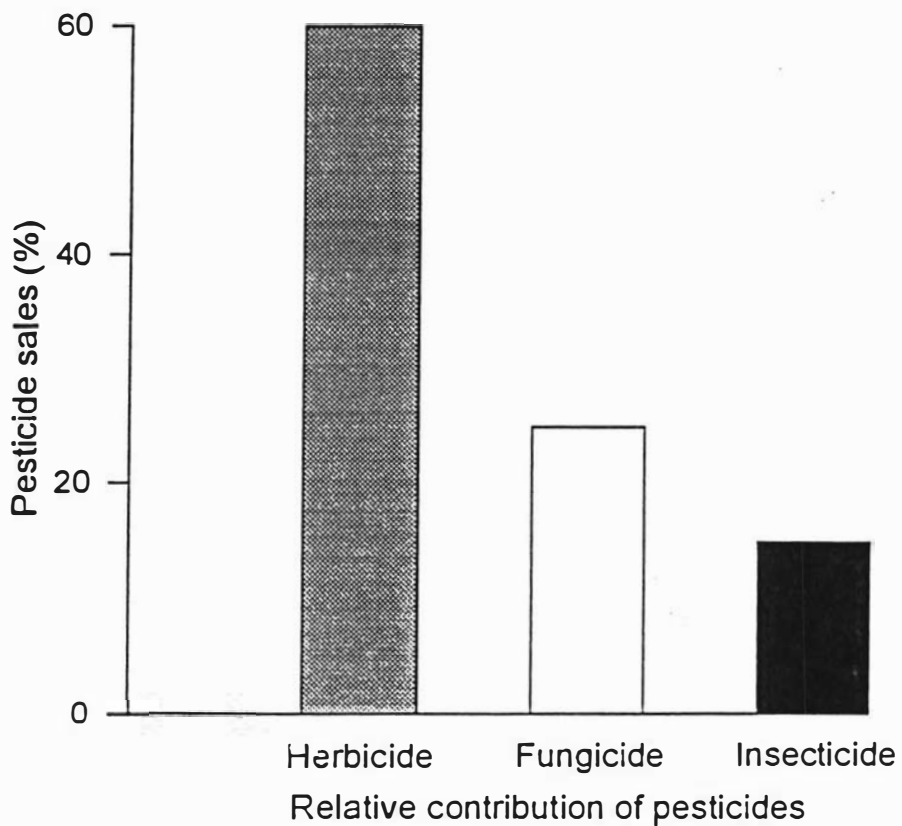


Fig 2.2 Relative contribution of herbicide, fungicide and insecticide to pesticide sales in New Zealand

pesticides increased by 35% (\$ 40 M) (AGCARM, 1993). Herbicides account for at least 60% of sales, with fungicides and insecticides accounting for a further 25 and 15%, respectively (Fig 2.2). This has been the trend for the past decade. This high percentage use of herbicides reflects the dominance of pastoral agriculture in New Zealand, in which disease and insect problems are generally minimal.

2.3 PESTICIDE CONTAMINATION OF SURFACE AND GROUNDWATER

Some pesticides are now recognised as posing a threat to groundwater quality. The U.S. Environment Protection Agency (EPA) indicated that 12 pesticides had been detected in drinking water wells in 18 States (Cohen *et al.*, 1984). In the last few years, several pesticides have been detected in groundwater under conditions where agricultural use could be identified as the source of contamination (Cohen *et al.*, 1986). Similarly pesticide residues have been detected in groundwater from the UK, Germany, The Netherlands and Australia.

Data on pesticides in surface and groundwaters in New Zealand are sparse. Close (1991) undertook a survey in 17 New Zealand regions (82 wells) to assess the pesticide contamination in groundwater. Detectable concentrations of pesticides were found in groundwater from six wells in Poverty Bay, Te Puke, Motueka, Pukekohe and Oamaru (Close, 1991). Pesticide concentration of less than 0.1 mg m^{-3} was found in four of the above mentioned wells. Among the pesticides, atrazine and simazine were detected in most of the wells.

2.4 PROCESSES AFFECTING THE FATE OF PESTICIDES IN SOIL

The fate of pesticides in the soil environment is governed by several processes. The fate of pesticides in soil is diagrammatically illustrated in Figure 2.3 and the processes identified as being the major determinants of pesticide fate in soils include:

- (i) Sorption-desorption
- (ii) Chemical and biological degradation
- (iii) Leaching
- (iv) Surface runoff

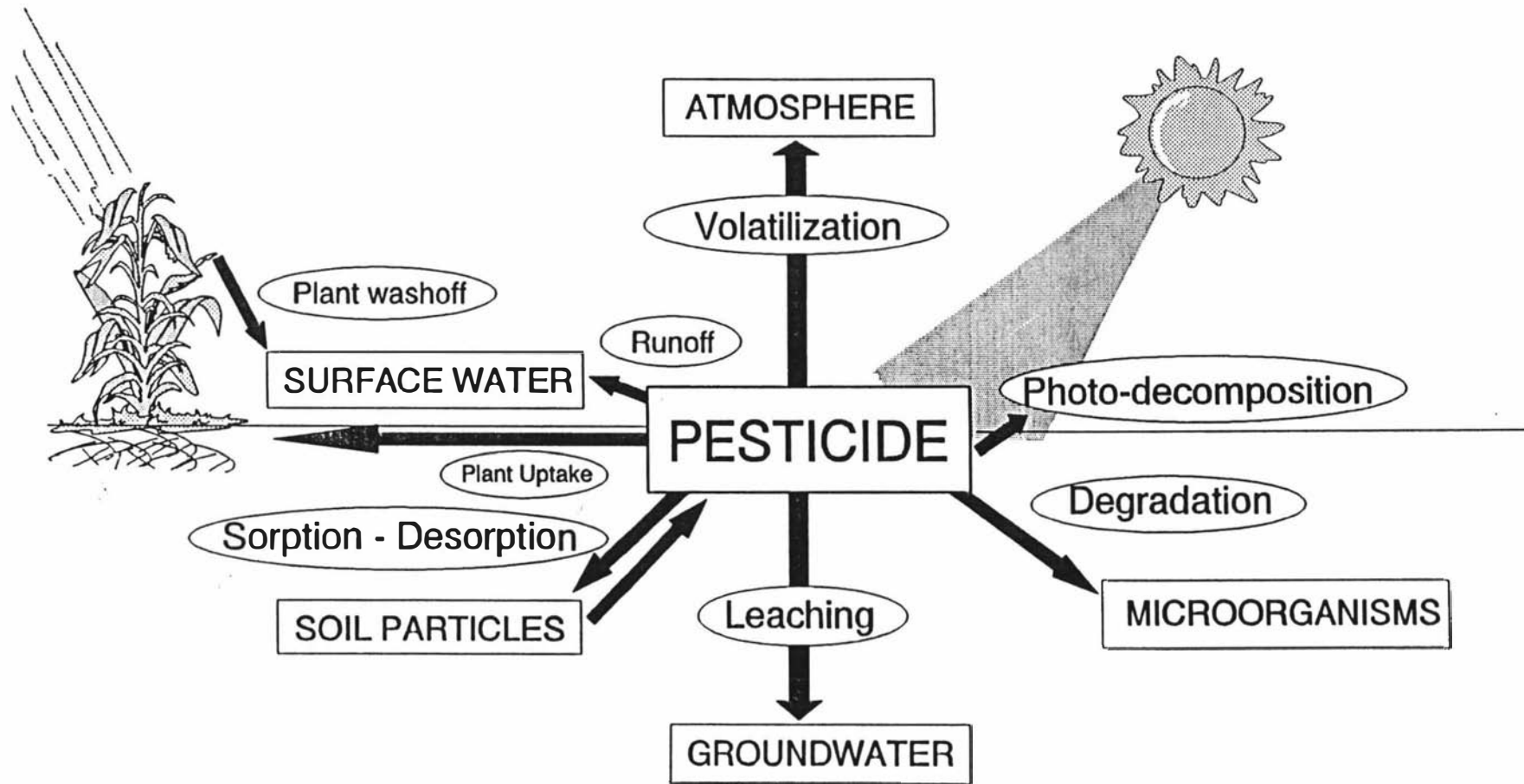


FIG 2.3 PROCESSES INVOLVED IN THE FATE OF PESTICIDES IN SOIL

(v) Volatilization

(vi) Plant uptake.

In this review firstly the reactions involved in these processes are discussed briefly.

2.4.1 Sorption-desorption processes

2.4.1.1 *Sorption*

In most publications dealing with pesticides in soils, one of the terms sorption, adsorption or partition is used, and these terms are applied broadly to include all sorption phenomena. In this chapter, the term sorption is used and refers to the uptake of a solute by the soil (or by a constituent of the soil) by physical or chemical bonding forces.

Sorption is one of the key processes affecting the fate of pesticides in the soil-water environment. It strongly influences chemical and biological transformations and transport to the atmosphere, groundwater and surface waters (Koskinen and Harper, 1990). The literature is replete with references on the sorption of pesticides in soils (e.g., Bailey and White, 1970; Hamaker and Thompson, 1972; Calvet 1980; Rao and Davidson 1980; Koskinen and Harper, 1990).

The extent to which a pesticide is sorbed by a soil is determined by both the nature of the soil and the pesticide. The effect of various soil and pesticide properties on sorption is discussed in detail in section 2.5.3. The solid phase of the soil is the primary site for sorption of pesticides. Both organic and inorganic solids in soils can serve as sorption surfaces.

The chemical characteristics of pesticides are largely responsible for their sorption in soil. Ionizable compounds, such as the weakly basic compounds (triazine) can be easily protonated at low soil pH values, whereas depending on the pH of the soil system weakly acidic pesticides (carboxylic acids and phenols) exist either as the undissociated molecules or the corresponding anion. The polarity of non-ionic pesticides is also of significance for their sorption to the organic and inorganic solid phases of a soil.

2.4.1.2 *Desorption*

Desorption studies provide information on the release of sorbed molecules. In many cases the desorption isotherm is more or less identical to the sorption isotherm. However, numerous studies have shown that the amount of a pesticide sorbed onto a soil and its subsequent desorption is not always a single-value relationship and, therefore, a portion of sorbed pesticide is resistant to desorption. This is termed a "hysteresis" process, and has been observed for a range of pesticides (Hornsby and Davidson, 1973a; Felsot and Dahm, 1979; Koskinen and Cheng, 1983; Kookana and Aylmore, 1993). Several factors have been proposed as contributing to hysteresis. One of the most obvious factors that could lead to a hysteretic effect would be non-attainment of equilibrium during the sorption/desorption process.

2.4.2 *Degradation*

Degradation is defined as the breakdown of the pesticide into various compounds. This is grouped into (i) abiotic or chemical degradation and (ii) biological degradation. These two processes are briefly discussed below.

2.4.2.1 *Chemical degradation*

The importance of abiotic transformations to the fate of pesticides has become widely recognised even in a medium in which intense biological activity takes place, such as soil (Wolfe *et al.*, 1990). Numerous investigators studied the abiotic transformation of pesticides (reviewed by Wolfe *et al.*, 1990; Crosby, 1970; Armstrong and Konrad, 1974) and observed that during the transformation of many pesticides, biological and chemical degradation takes place simultaneously (Wolfe *et al.*, 1980).

Among the numerous chemical degradation reactions occurring in water, sediment and soil, hydrolysis and redox reactions are the most prevalent. Although the presence of abiotic transformations has been demonstrated, it has often been shown that biological degradation mostly controls the degradation of pesticides in the soil environment.

2.4.2.2 *Biological degradation*

It has been established that microbes are more important in the transformation of pesticides than physical or chemical mechanisms (Munnecke *et al.*, 1982). Microorganisms are the key agents in the degradation of a vast array of pesticides in terrestrial and aquatic ecosystems. Excellent reviews on biological degradation of pesticides have been published (Kaufman, 1974; Bollag and Liu, 1990).

Microbial degradation of pesticides can be direct, a primary metabolic reaction, or indirect, the effect of microbial action resulting in a secondary transformation reaction. Based on the direct and indirect effect of microbes the processes involved in the microbial transformation of pesticides are grouped into five processes: (i) biodegradation; (ii) co-metabolism; (iii) polymerization; (iv) accumulation; and (v) the secondary effects of microbial activity. These transformation processes may involve more than one mechanism. Depending on the environmental conditions various products can be derived from the same parent compound.

The chemical structure of a pesticide determines its susceptibility to microbial degradation. For example 2,4-D and MCPA are susceptible to microbes whereas, atrazine, picloram and trifluralin are relatively resistant to microbes.

2.4.3 *Volatilization*

Volatilization is one of the principal pathways by which pesticides are lost from target areas after application. Two distinct processes are involved in the loss of pesticide into the atmosphere: (i) evaporation of pesticides into the air from the area of application. (ii) dispersion of the resulting vapour into the atmosphere by diffusion and turbulent mixing.

The major factors controlling the rate of volatilization are (i) the vapour pressure of the pesticide; (ii) the distribution of residues; and (iii) the moisture status of the soil or plant surface. In the case of pesticides with vapour pressure greater than 20 mPa the loss can exceed 90% of the application within 48 h or less when residues of volatile pesticides are exposed on moist soil or plant surfaces (Taylor and Spencer,

1990). The loss can be reduced by the incorporation of pesticides into the soil.

2.4.4 Leaching

One of the recent issues facing the fate of pesticides in soils is the assessment of the potential for pesticides to leach through the soil and appear in groundwater. Pesticide mobility in soils has been examined in several ways, including field studies, packed soil columns, various thin layer chromatography techniques and undisturbed soil cores (Banks and Merkle, 1979; Van Genuchten and Cleary, 1979; Helling, 1971; White *et al.*, 1986). It is assumed that this pesticide movement is the result of three processes: (i) pesticide diffusion in the aqueous phase; (ii) diffusion in the gas-phase, if the pesticide is volatile; and (iii) convection (mass flow) of pesticide due to the movement of the bulk fluid phase in which the pesticide is dissolved.

2.4.5 Surface runoff

Pesticide applied to the cropland, forest and other areas for pest control may enter surface waters by rainfall or irrigation runoff. Pesticide runoff includes dissolved, suspended particulate, and sediment-sorbed pesticide that is transported by water from a treated land surface. Processes and factors that determine the distribution of pesticides in surface waters have been published (Leonard, 1990), and detailed reviews on this subject are also available (Wauchope, 1978).

Annual runoff losses for soil-applied pesticides average about 1-2% of the application (Wauchope, 1978), however, more than 10% losses have been reported under simulated rainfall (Baker *et al.*, 1978). Computer models have been developed to simulate pesticide runoff losses for a wide range of pesticides, management, soil and climatic conditions (Bruce *et al.*, 1975; Haith, 1986).

The data on pesticide losses from runoff in New Zealand are sparse. Fox and Wilcock (1988) reported a loss of about 0.6% of the applied 2,4,5-T to gorse in the Waikato region of New Zealand. A similar study by Wilcock *et al.* (1991) showed a detectable concentration (0.26-0.55 ppb) of triclopyr in stream water.

Most of the pesticide runoff occurs through the movement of pesticide enriched sediments in the runoff. The contribution of various particle size fractions of soils to the sorption of pesticides is discussed in section 2.6.

2.4.6 Plant uptake

Herbicides are taken up by the plants through foliage or soil. Depending on the type of application different sites of uptake are possible and are discussed briefly below.

2.4.6.1 *Uptake of foliage-applied herbicides*

The activity of a foliage-applied herbicide depends on the amount of active ingredient reaching the site of action. Thus the efficiency of cuticle retention and penetration, absorption from the symplast, short and long-distance transport, metabolism and the degree of immobilization at metabolically non-active sites may determine pesticide activity (Fletcher and Kirkwood, 1982).

2.4.6.2 *Uptake of soil-applied herbicides*

Unlike the foliage-applied herbicides, soil-applied herbicides are not applied directly to the plant and the amount of active ingredient which reaches the absorbing surface of the roots depends on several processes. When a pesticide is applied to the soil it is subjected to several physical, chemical and biological processes as identified in section 2.4. Comparative studies have shown that plant roots absorb and translocate certain compounds more rapidly when they are applied to the soil than when they are applied to plant foliage.

2.5 SORPTION OF PESTICIDES IN SOILS

Among the various processes discussed in section 2.4, not surprisingly, sorption is the primary factor influencing the fate of pesticides in soils. Hence, sorption of pesticides and the soil factors affecting that sorption are discussed below.

When a pesticide is applied to a soil, a major part of it comes in contact with the soil

colloids. Sorption from solution is the most significant process in a soil-pesticide system. Sorption is one of the major factors affecting the pesticide persistence, biological activity and mobility in soils (Bailey *et al.*, 1968; Osgerby, 1973; Haque and Freed, 1974).

2.5.1 Methods for measuring pesticide sorption

The sorption capacity of a soil is usually measured by one of two methods: (i) batch sorption and (ii) column sorption. In the batch sorption the soil is equilibrated with a solution containing the ionic species at a constant soil:solution ratio. The amount of sorption is then calculated from the change in the concentration of the ion in solution. In the column sorption, a solution containing the ion is percolated through a column of soil at a constant flow rate until the concentration of the ion in the effluent solution reaches that of the influent solution. The amount of sorption is then calculated from the amount of the ion retained in the column, after accounting for the concentration of the ion in the soil solution. The important difference between these two methods is that, whereas the former method is a 'closed' system, the latter method is an 'open' system in which the solutes, other than the one in the influent solution, are removed by the percolating solution.

Although batch experiments are suited to the construction of sorption isotherms, and for describing the mechanisms involved, column experiments are more useful for studying the effect of sorption on solute leaching. The basic objective of both methods has been to measure the equilibrium relationship between the pesticide in solution and sorbed phase concentration.

2.5.2 Sorption isotherm models

Various mathematical relationships have been used to describe equilibrium pesticide sorption-desorption in a soil-water system. Among the most successful are the Freundlich and the Langmuir equations. The Freundlich equation is empirical, whereas the Langmuir equation has been developed to describe sorption of gases on homogenous surfaces.

2.5.2.1 *Freundlich equation*

The sorption isotherm is represented by a power function known as the Freundlich equation,

$$S = KC^N \quad (2.1)$$

Where S is the sorbed concentration ($\mu\text{mol kg}^{-1}$); C is the equilibrium solution concentration ($\mu\text{mol L}^{-1}$), and K and N are Freundlich sorption coefficients. The linear form of the Freundlich equation is

$$\log S = \log K + N \log C \quad (2.2)$$

The coefficients K and N may be obtained, respectively, as the intercept and slope of log-log plots of S versus C . The Freundlich equation has satisfactorily described the experimental results of pesticide sorption in many cases. Compilation of the coefficients for many compounds (Hamaker and Thompson, 1972; Rao and Davidson, 1980) suggested that values of the coefficient N in Equation 2.1 commonly range between 0.75-0.95.

2.5.2.2 *Linear equation*

If the value of N in Equation 2.1 is close to unity, a linear isotherm (Eq 2.3) is obtained.

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

Where K_d is the distribution coefficient (L kg^{-1}). The linear equation is a desirable simplification for complex environmental models, as it allows simpler mathematical solutions (Green and Karickhoff, 1990).

2.5.2.3 *Langmuir equation*

Another method of describing the sorption data is by the Langmuir equation. The Langmuir equation may be written:

$$S = a S_m C / (1 + aC) \quad (2.4)$$

Where S is the sorbed concentration, C is the equilibrium solution concentration, a is a Langmuir sorption coefficient, which reflects the relative rates of sorption-desorption at equilibrium and is thus an affinity term, and S_m is the sorption maximum.

The three versions of the linearizing transformations of this equation are:

$$S = S_m - S / (aC) \quad (2.5)$$

$$C/S = 1/(S_m a) + C/S_m \quad (2.6)$$

$$1/S = 1/S_m + 1/(CS_m a) \quad (2.7)$$

According to these equations, the plots between S and S/C , C and C/S and $1/C$ and $1/S$ should give a straight line. The Langmuir equation was originally developed for the sorption of neutral molecules on a neutral surface (Posner and Bowden, 1980). The three important assumptions of the Langmuir equation are: (i) the energy of sorption is the same for all sites and is independent of the degree of surface coverage, (ii) sorption occurs only on localized sites with no interaction between adjoining sorbed molecules, and (iii) sorption maximum represents a monolayer coverage. Given these fairly restrictive assumptions, it is not surprising that the Langmuir equation generally fails to describe pesticide sorption in a fairly heterogeneous medium such as soil.

2.5.2.4 *Linear vs nonlinear equations*

The deviation introduced by assuming the sorption isotherm to be linear instead of curvilinear (Freundlich) depends upon the values of C and N in the Freundlich equation. This can be represented by the ratio of sorption obtained by a nonlinear (Freundlich) equation (Eq 2.1) to that obtained by a linear equation (Eq 2.3) and is

equal to C^{N-1} (Rao and Davidson, 1980). A value of $C^{N-1} = 1$ indicates similar sorption by linear and nonlinear equations. A value > 1 means the amount sorbed is under-predicted, while a value < 1 means the amount sorbed is over-predicted by assuming a linear equation.

A plot of C^{N-1} versus C in the range of 0.1 to 10 $\mu\text{g ml}^{-1}$ and for N values ranging from 0.5 to 1.0 is shown in Figure 2.4. Rao and Davidson (1980) obtained a C^{N-1} value of 3 for $0.1 < C < 10.0$ and $0.5 < N < 1.0$, and suggested that for many modelling purposes a linear isotherm can be used in lieu of the Freundlich equation.

2.5.3 Factors influencing sorption

The extent to which a pesticide is sorbed by a soil is determined by several physical and chemical properties of both the soil and the pesticide compound. Bailey and White (1970) and Adams (1973) have reviewed the properties of pesticides and soils that influence pesticide sorption and the bioactivity of pesticides. Nicholls (1988) reported that sorption of pesticides in soil is influenced by: (i) physico-chemical properties of pesticides; (ii) soil properties; and (iii) climate.

2.5.3.1 *Pesticide properties*

Among the properties of pesticides, organic-aqueous (e.g., octanol-water) partition coefficient, water solubility and ionization are the most important properties which influence the sorption. Each property is briefly discussed below.

(i) Octanol-water partition coefficient

Lambert (1968) suggested that the role of soil organic matter was similar to that of an organic solvent and that partitioning of a neutral organic compound between soil organics and water should correlate well with its partitioning between water and organic solvents. Briggs (1973) has successfully derived a relationship between sorption of organic chemicals by soils and the octanol-water partition coefficient (K_{ow}) of the pesticides. The concentration of pesticide in water decreases as K_{ow} increases and consequently sorption increases. Pesticides with high K_{ow} are strongly sorbed and

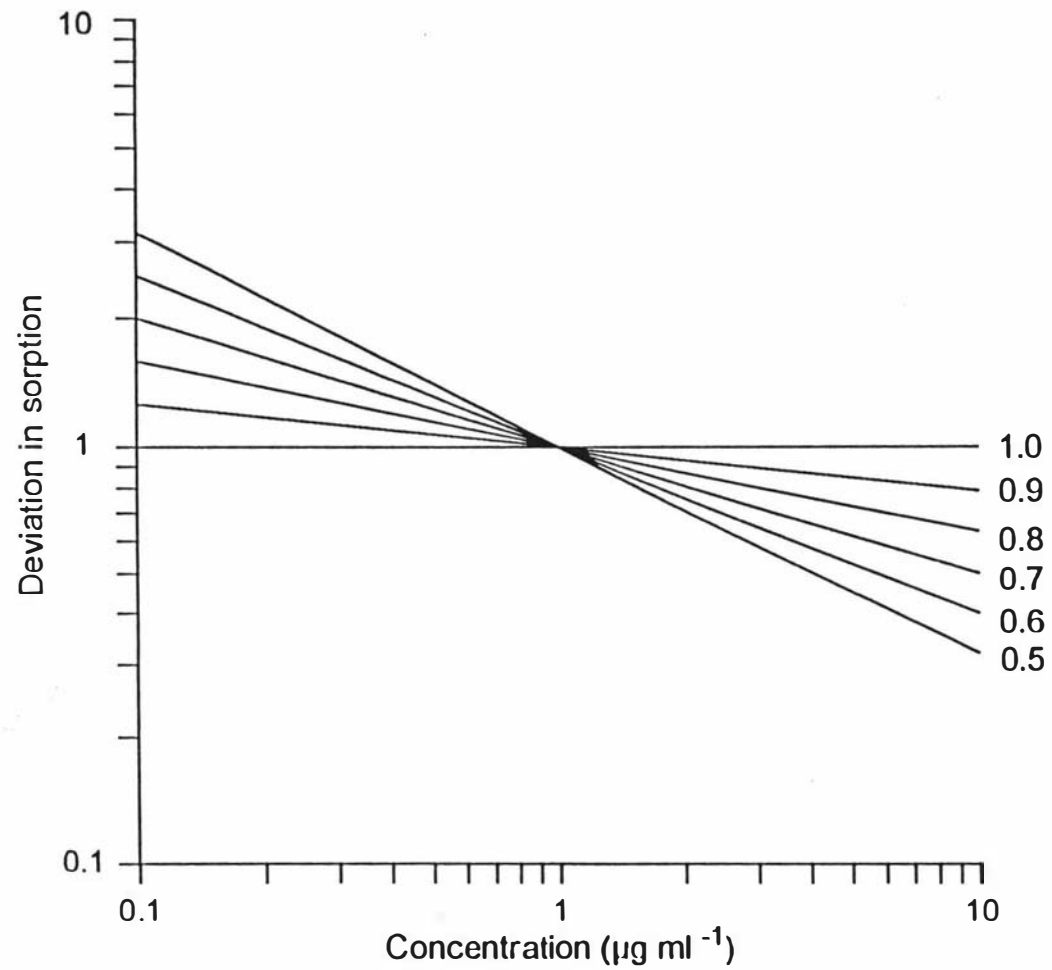


Fig 2.4 Deviation from nonlinear isotherm introduced by the linear sorption isotherm.
(The numbers near the lines are the values of the Freundlich coefficient, N)

provide little risk of leaching down to the groundwater.

(ii) Water solubility

Water solubility (W_s) of the organic chemicals can be regarded as partition of the chemical between itself and water (Briggs, 1981a). Chiou *et al.* (1979) showed a linear inverse relationship between $\log K_{ow}$ and $\log W_s$ for a wide range of chemical classes. Later Chiou *et al.* (1979) reported a similar relationship between sorption of many organic chemicals and W_s of the sorbate.

(iii) Ionization

Ionizability, as expressed by the ionization constant, has been described as one of the key properties of the ionizable pesticides that affect the sorption in soil (Weber, 1972; Weed and Weber, 1974). Weakly acidic pesticides ionize to anionic species as pH increases; they tend to be more mobile as pH increases and less mobile as pH decreases, because the molecular (non-ionized) species are more strongly sorbed by soil than are the anionic species. Weakly basic pesticides are strongly sorbed when the pH is close to the pH at which maximum dissociation occurs (i.e., pK_a of the pesticides).

2.5.3.2 Soil properties

A number of soil properties have been shown to influence the sorption of pesticides in soil, including organic matter, clay, pH, amorphous minerals and soil depth. Excellent reviews on soil-pesticide relationships have been published (Bailey and White, 1970; Adams, 1973; Osgerby, 1973; Weber and Weed, 1974). The following section will deal with each soil property separately.

(i) Organic matter

Soil organic matter is a complex polymeric mixture arising from microbial and chemical degradation processes, the exact structure of which has not yet been fully elucidated (Khan, 1978). The influence of soil organic matter on pesticide sorption

has been reviewed by Bailey and White (1970), Hayes (1970) and Adams (1973). Hayes (1970) described in some detail the chemistry of soil organic matter and the mechanisms involved in the sorption of pesticides. The soil organic matter is intimately bound to the surface of soil particles (Walker and Crawford, 1968; Lambert, 1968), even to the extent that in some circumstances most of the surface of clay particles may not be accessible to pesticide molecules (Hance, 1969).

Most researchers have judged organic matter to be the most significant soil property affecting pesticide sorption in soil (Hamaker and Thompson, 1972; Weed and Weber, 1974; Karickhoff *et al.*, 1979; Rao and Davidson, 1980). Hamaker and Thompson (1972) reported that soil organic matter is the principal sorbent for many non-ionic pesticides.

It has been suggested that the sorption mechanism of non-ionic organic chemicals in soil is a partitioning of the chemical between the aqueous phase and the hydrophobic organic matter (Chiou *et al.*, 1979). Partitioning is the uptake of solute in which the sorbed organic chemical permeates into the network of an organic medium. It is analogous to the extraction of an organic compound from water into an organic phase. When the organic phase is a solid (e.g., soil organic matter), partition is distinguished from sorption by the homogeneous distribution of the sorbed material through the entire volume of the solid phase. Non-polar organics are partitioned out of the polar aqueous phase and introduced onto the hydrophobic surface (organic matter) in the soil.

Several workers (Calvet, 1980; Peter and Weber, 1985; Singh, 1989; Johnson and Sims, 1993) have correlated pesticide sorption with soil properties, such as organic matter, clay, and soil pH, and concluded that soil organic matter was best correlated with the ionic and non-ionic pesticide sorption in soil. Based on these results it has been assumed that soil organic matter is the principal component of pesticide sorption and that pesticide sorption is normalised to the organic matter content of soil. When pesticide sorption is expressed per unit organic carbon (K_{oc}) the values were found to be less varied between soils. The K_{oc} concept and the assumption involved are discussed in section 2.5.5.

While the solid organic matter content of the soil acts as the principle component of pesticide sorption, the dissolved organic carbon (DOC) in solution can act as a vehicle for the movement of pesticides in soil. Recently there has been an increasing interest in elucidating the mechanisms involved in the interaction between DOC and pesticides (Logan *et al.*, 1992; Liu and Amy, 1993). The effect of DOC on the sorption and movement of pesticides is discussed in section 2.7.

In New Zealand, the effect of organic matter on the phytotoxicity of several pesticides has been examined using a bioassay technique (Rahman 1976; Rahman *et al.*, 1978; Nishimoto and Rahman, 1985). The results revealed a strong relationship between soil organic matter and the phytotoxicity of soil-applied pesticides.

(ii) Clay

The high surface area associated with clay particles is one reason why clays provide a sorbing surface in soils. The other factors are the electrical charge characteristics of clay surfaces and the nature of exchange cations. Sorption of pesticides by clay minerals has been reviewed by Bailey and White (1970), Weber (1972), Adams (1973) and Green (1974).

Clay minerals have a negative charge that is balanced by exchangeable cations and thus are important in sorption of cationic pesticides, such as paraquat and diquat (Weed and Weber, 1969) and those which can become cations on protonation, such as s-triazines (Weber, 1970). Hydrogen bonding to the oxygen atoms on clay surfaces or edge hydroxyls has been suggested to be the mechanism for sorption of pesticides (Bailey *et al.*, 1968). The contribution of different particle size fractions to sorption is discussed in section 2.6.

(iii) Amorphous minerals

The amorphous materials in soil include: oxides and hydroxides of iron (Fe) and aluminium (Al), and allophane. These amorphous oxides and hydroxides are efficient sorbents for some of the pesticides. Hilton and Yuen (1963) reported that the amorphous materials in Hawaiian soils greatly influenced the sorption of pre-

emergence herbicides. Hamaker *et al.* (1966) found that Fe and Al oxides sorbed picloram more strongly than clays. Similarly O'Connor and Anderson (1974) found a strong relationship between the Fe oxide content of soils and the sorption of 2,4,5-T. Increase in sorption of dicamba (Murray and Hall, 1989) and 2,4-D (Watson *et al.*, 1973) with increasing Fe oxide has been reported.

(iv) pH

Soil pH effects are of great importance with weakly basic (triazine) and acidic (phenoxy acid) pesticides because the relative quantities of weakly basic and acidic pesticide in ionic form is dependent on the pH of the soil system. Weakly basic pesticides become cations at low pH and this results in increased sorption (Weber *et al.*, 1969); whereas the acidic pesticides ionize to anionic form as pH increases (one or more pH units above the pK_a of acid) (Weber, 1993).

The pH dependent nature of surface charge on amorphous alumino-silicates and on hydrous oxides is noteworthy, from the practical point of view, in that soil pH is one property which is commonly altered by soil management. Sorption depends on the unique combination of available sites on clay surfaces and the extent of dissociation of the acidic or basic pesticide at each pH. Recently, Barriuso *et al.* (1992a) observed an increase in 2,4-D sorption with decreasing pH. They attributed the increase in sorption to the decrease of negative charge of the organic matter and the increase of positive charge on Fe and Al oxides as the pH decreased.

(v) Soil depth

Pesticide sorption in soils has been investigated more intensively in topsoil than subsoil horizons. However, given the concerns about pesticide movement to groundwaters, it is also important to understand the influence of subsoil horizons on pesticide mobility. Green and Obien (1969) noted a decrease in atrazine sorption with increasing depth. The partition coefficients (K_d) were 2.72, 1.06 and 0.35 for the A, B and C horizons, respectively. Huang and Frink (1989) reported that herbicide distribution in two Connecticut soil profiles was closely associated with organic matter and clay distribution. Barnes *et al.* (1992) reported a decrease in metolachlor

sorption with increasing depth in a Taloka silt loam. It has been shown that certain subsoil horizons of coastal plain soils had equal or similar sorption capacities for the ionic herbicides such as, atrazine, 2,4-D, cyanazine and dicamba (Johnson and Sims, 1993).

It has generally been shown that pesticide sorption decreases with increasing depth and this is attributed to a decrease in soil organic matter. However, it is not uncommon to find large increases in clay, Fe and Al oxide content as well as a lower organic matter content in many subsoil horizons. It is, likely therefore, that soil properties other than organic matter may have a greater influence on pesticide sorption in subsoils.

2.5.4 Techniques used to relate soil constituents to pesticide sorption

Two techniques have been widely used to relate various soil constituents to pesticide sorption by soils. These are: (i) correlation/regression and (ii) subtraction. These are briefly discussed below.

2.5.4.1 *Correlation/regression*

This technique involves measuring the pesticide sorption characteristics as well as other properties for a wide range of soils and then calculating correlation coefficients between them. The aim is to develop an empirical equation relating soil properties to pesticide sorption, which can be used to predict the sorption of pesticides under different soil conditions.

This technique has been widely used to measure the relationship between pesticide sorption coefficient and other soil properties, such as organic matter, pH, CEC, clay content and exchangeable cations (Table 2.1). In most studies the pesticide sorption coefficient was highly correlated with organic matter followed by clay content and pH (Talbert and Fletchall, 1965; Felsot and Dahm, 1979; Obrigawitch *et al.*, 1981; Singh, 1989; Johnson and Sims, 1993). One of the problems with this method is that the soil properties may be intercorrelated, hence it may be difficult to isolate the effect of an individual soil property to pesticide sorption. The problem of intercorrelation can

Table 2.1 Correlation and subtraction techniques used to relate soil properties to pesticide sorption

Soil	Pesticide	Correlated with	Reference
CORRELATION			
25 soils - Missouri	Atrazine, Simazine, Propazine, Prometone, Prometryne.	OM, pH, CEC, Ca, Mg, Sand, Silt, Clay	Talbert and Fletchall (1965)
11 soils - Denmark and Tanzania	Atrazine	OM, Fe, Al, Clay	Borggaard and Streibig (1988)
26 soils - Atlantic coastal plain	Atrazine, 2,4-D, Cyanazine, Dicamba Metolachlor	OM, pH, Clay, ECEC, Exchangeable acid, Fe, Al	Johnson and Sims (1993)
5 soils - Iowa	Aldicarb, Phorate Parathion, Terbufos Chlorpyrifos	OM, CEC, pH, clay, log solubility, log partition coefficient	Felsot and Dahm (1979)
42 soils - Belgium	2,4-D	OM, pH, CEC, Al	Moreale and Bladel (1980)
6 soils - North Carolina	Alachlor, Metolachlor	OM, clay, pH, CEC, surface area	Peter and Weber (1985)
32 soils - USA	Diuron, Simazine CIPC	pH, OM, clay, CEC	Harris and Sheets (1964)
65 soils - California	Simazine	pH, OM, clay, sand, silt, CEC, K.	Day <i>et al.</i> (1968)
6 soils - Virginia	Chlorsulfuron	OM, clay, pH, Ca, Mg, Al, CEC, Base saturation	Mersie and Foy (1985)
34 soils - Puerto Rico	Diuron, Ametryne	OM, pH, CEC, Ca, K, Mg, P ₂ O ₅ , sand, silt, clay	Liu <i>et al.</i> (1970)
SUBTRACTION			
Material removed	Pesticide	Observation	Reference
Organic matter	Aldicarb, Phorate, Parathion, Terbufos, Chlorpyrifos	Sorption decreased and desorption was more reversible in organic matter removed soils	Felsot and Dahm (1979)
Organic matter, Fe and Al oxide	2,4,5-T	Reduced sorption due to organic matter removal	O'Connor and Anderson (1974)
Organic matter	Fenamiphos, Simazine, Linuron, Diquat.	Diquat, linuron sorption decreased, whereas simazine sorption increased with organic matter removal	Singh (1989)
Organic matter	Parathion	Sorption decreased but good correlation with clay and Fe oxides	Wahid and Sethunathan (1978)
Humins & humic matter	Prometryn Metolachlor	Reduced sorption	Kozak <i>et al.</i> (1983)
Organic matter, Fe and Al oxides	Atrazine	Decreased sorption due to organic matter and Fe and Al oxide removal	Huang <i>et al.</i> (1984)

be overcome to some extent by the use of stepwise multiple regression analysis. Some researchers have used this technique in relating pesticide sorption to soil properties (Moreale and Blade, 1980; Johnson and Sims, 1993).

2.5.4.2 Subtraction

This technique is based on the assumption that various soil constituents contribute to pesticide sorption and the effect can be assessed by selectively removing them. This technique has been generally used to study the effect of the removal of organic matter, as well as the sequential extraction of organic matter and Fe and Al oxide on pesticide sorption by soils (Table 2.1). In most studies removal of organic carbon decreased the sorption of pesticides and the desorption was more reversible than in natural soils.

2.5.5 Distribution coefficient based on organic carbon

The importance of organic matter in pesticide sorption was discussed in section 2.5.3.1. Using correlation and subtraction techniques it has been claimed that organic matter is one of the main components of pesticide sorption in soils (Hamaker and Thompson, 1972; Chiou *et al.*, 1979; Rao and Davidson, 1980). Based on this the distribution coefficient (K_d) of pesticides can be expressed per unit organic matter (K_{om}) or organic carbon (K_{oc}) (Hamaker and Thompson, 1972).

$$K_{om} = \frac{(K_d) (100)}{\% OM} \quad (2.8)$$

$$K_{oc} = \frac{(K_d) (100)}{\% OC} \quad (2.9)$$

K_{om} or K_{oc} have been found to be a characteristic of a pesticide and varied less between soils. The principle assumptions involved in the calculation of K_{om} or K_{oc} are:

(i) sorption is limited to the organic carbon content of the soil and (ii) organic carbon has the same sorption capacity at different locations of a given soil or in different soils.

Regression equations have been developed to predict the K_{oc} of a pesticide using water solubility (W_s), or the octanol-water partition coefficient (K_{ow}) of the compound. The empirical equations for estimating K_{oc} of pesticides are tabulated (Table 2.2) along with some basic information on the data set used to derive each equation. A number of workers (Chiou *et al.*, 1979; Felsot and Dahm, 1979; Karickhoff *et al.*, 1979; Rao and Davidson, 1980; Briggs, 1981a; Brown and Flagg, 1981) reported a highly correlated empirical equation associating sorption of many pesticides to the K_{ow} of pesticides.

The equations were found to vary slightly between the groups of soils. Two reasons could be attributed for the variation in the prediction equation between the various groups of soils. Firstly that the nature of organic matter is likely to vary between the soil groups (Singh, 1989). Secondly in some soils clay minerals also contribute to the sorption of pesticides (Hassett *et al.*, 1981; Campbell *et al.*, 1991). For example Hassett *et al.* (1981) has observed that as the ratio of organic matter:clay decreases the K_{oc} value increases sharply, which illustrates that at low levels of organic matter, the contribution of clay to sorption is substantial. It is unlikely that the equation developed for a group of soils can be used to predict the K_{oc} value of a pesticide for a soil from a different region. One of the aims of the present work is to develop a predictive equation for a group of New Zealand soils.

2.6 EFFECT OF ORGANO-MINERAL FRACTIONS OF SOILS ON PESTICIDE SORPTION-DESORPTION

As discussed in section 2.4.1.1, sorption is one of the principal processes determining the environmental fate and transport of pesticides in soil-water systems. Thus pesticide-whole soil interactions have been extensively studied, and several reviews on this subject have been published (Bailey and White, 1970; Hamaker and Thompson, 1972; Hance, 1980; Rao and Davidson, 1980; Cheng, 1990). However, pesticide sorption by the organo-mineral fractions of soils has been given little consideration. Because of the larger surface areas and high organic matter, the finer fractions are expected to sorb larger quantities of pesticides than the coarser fractions. The effect of particle size fractions on pesticide sorption also depends on the method used to obtain those fractions.

Table 2.2 Prediction equations for estimating distribution coefficient based on organic carbon (K_{oc}) of pesticides from the octanol-water partition coefficient (K_{ow}) values

No	Equation	Adsorbent	Organic carbon (%)	Chemicals	r^2	Reference
1.	$\log K_{oc}^* = 0.904 \log K_{ow} - 0.539$	1 soil-USA	1.10	12 aromatic compounds	0.989	Chiou (1989)
2.	$\log K_{oc}^* = 0.52 \log K_{ow} + 0.87$	7 soils-UK	1.1-5.90	30 Pesticides	0.84	Briggs (1981a)
3.	$\log K_{oc}^* = 0.52 \log K_{ow} + 0.92$	17 soils-Australia	0.19-6.62	24 Pesticides	0.97	Briggs (1981b)
4.	$\log K_{oc}^* = 0.52 \log K_{ow} + 1.01$	5 soils-USA	0.51-3.81	5 Insecticides	0.96	Felsot and Dahm (1979)
5.	$\log K_{oc}^* = 0.87 \log K_{ow} + 0.05$	6 soils-Israel	0.10-2.40	2 Herbicides	0.73	Mingelgrin and Gerstl (1983)
6.	$\log K_{oc} = 1.00 \log K_{ow} - 0.317$	2 eroded soils and 14 sediments-USA	0.11-2.38	1 phenolic compound and 1 Herbicide	0.98	Hassett <i>et al.</i> , (1981)
7.	$\log K_{oc} = 1.23 \log K_{ow} - 0.40$	1 peat and 1 sandy soil-USA	0.4-27.8	3 Herbicides	0.989	Madhun <i>et al.</i> , (1986a)
8.	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	14 sediments-USA	0.086-3.29	10 polycyclic hydrocarbons	1.00	Karikchoff <i>et al.</i> , (1979)
9.	$\log K_{oc} = 0.973 \log K_{ow} - 0.006$	sediments-USA		8 Herbicides	0.94	Brown and Flagg (1981)
10.	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	soils		13 pesticides	0.91	Rao and Davidson (1980)

* Original equation expressed as K_{om} ; the factor 1.724 was used to convert K_{om} to K_{oc} ; $K_{oc} = 1.724 K_{om}$

2.6.1 Soil particle size fractionation

The effectiveness of soil dispersion procedures is crucial for a successful soil particle size fractionation. In standard methods of analysis of particle size, samples may be exposed to chemical pretreatment to remove organic matter, sesquioxide and other cementing agents before being dispersed by a combination of chemical and physical means (Gee and Bauder, 1986). Chemical dispersion treatments are not considered feasible for isolation of intact organo-mineral fractions.

Most studies of particle size fractionation have relied on ultrasonic dispersion of soil. Several researchers have compared the conventional chemical method with ultrasonic dispersion and concluded that ultrasonic dispersion was as effective as the chemical method (Healy and Claridge, 1974; Anderson *et al.*, 1981; Curtin *et al.*, 1987).

2.6.2 Chemical characteristics of particle size fractions

Some of the reported chemical characteristics of particle size fractions are summarized in Table 2.3. It has been shown that the clay fraction often accounts for 50% of the whole soil carbon (Anderson *et al.*, 1981; Christensen, 1985; Curtin *et al.*, 1987; Balesdent *et al.*, 1988; Bonde *et al.*, 1992). To compare the amount of soil organic matter in a particle size fraction from different soils, the carbon enrichment ratio (mg carbon/g separate to mg carbon/g whole soil) was calculated for each fraction. Some of the reported values in the literature are summarized in Table 2.3. Among the size separates, clay and silt had substantial amounts of amorphous and crystalline Fe and Al oxides (Table 2.3). The substantial amount of organic matter and sizable portion of Fe and Al oxides present in the clay and silt fractions showed the importance of these fractions in relation to other aspects of soil chemistry, such as the retention and cycling of nutrients, pollutants and pesticides.

2.6.3 Contribution of organo-mineral fractions of soils to sorption of pesticides

Contamination of groundwater and surfacewater by soil-applied pesticide residues is largely controlled by the extent of their sorption onto soil particles. While the sorption of a pesticide onto soil particles decreases the leaching of pesticide residues

Table 2.3 **Summary of literature on the chemical characteristics of particle size fractions**

Materials	Particle Size Fractions*	Chemical Characteristics (or) comments	Reference
4 Soils - Saskatchewan, Canada	fine clay coarse clay fine silt medium silt coarse silt sand	Soil carbon associated with $< 2 \mu\text{m}$, $2-50 \mu\text{m}$ and $> 50 \mu\text{m}$ fractions averaged 53.5, 43.4 and 3.3 %, respectively. Significant amounts of pyrophosphate and citrate dithionite - bicarbonate Fe and Al were present in clay and silt fractions. Carbon enrichment ratio was 1.6-2.9 and 1.4-2.4 in fine and coarse clay, respectively.	Curtin <i>et al.</i> (1987)
10 soils- New Zealand	clay silt sand	Clay and silt fraction has substantial amount of carbon and CEC.	Healy and Claridge (1974)
1 soil- Turkey	fine clay coarse clay fine silt medium silt coarse silt	Citrate dithionate and oxalate extractable Fe and Al decreased with increasing particle size.	Sayin <i>et al.</i> (1990)
1 soil - USA	fine clay coarse clay medium silt coarse silt sand	The organic carbon content increased with decreasing particle size.	Nkedi-Kizza <i>et al.</i> (1983)
7 soils - New Zealand	clay silt sand	Clay and silt fractions contained the largest proportion of whole soil carbon.	Tate and Churchman (1978)
2 soils - Saskatchewan - Canada	fine clay coarse clay fine silt coarse silt sand	55 to 58 % of organic carbon was in the clay fractions, with the greatest amount in the coarse clay ($2-0.2 \mu\text{m}$) fractions. The carbon enrichment ratio for fine silt, coarse clay and fine clay samples was 3.8, 2.25 and 1.8 respectively.	Anderson <i>et al.</i> (1981)
2 soils - Saskatchewan - Canada	fine clay coarse clay fine silt medium silt coarse silt sand	Clay, fine and coarse silt contained substantial amount of citrate dithionate bicarbonate extractable Fe and Al.	Huang <i>et al.</i> (1984)
4 soils - Canada	fine clay coarse clay fine silt medium silt coarse silt	Significant amount of carbon was present in coarse clay, fine silt and medium silt. However fine silt, fine clay contained substantial amount of amorphous Fe and Al.	Schnitzer and Kodama (1992)

Table 2.3 continued

Materials	Particle Size Fractions*	Chemical Characteristics (or) comments	Reference
1 soil - Canada	clay silt sand	Highest organic matter was present in clay (10.61 %) followed by silt (2.51%) fraction.	Kay and Elrich (1967)
4 soils - Denmark	clay silt fine sand 1 coarse sand fine sand 2	Sand size fraction contained less than 10 % of the soil carbon, whereas the clay contained 49-69 % and silt from 22-38 %. The carbon enrichment factor ranged from 3.3 to 16.4 for clay and from 1.8-9.9 for silt fraction.	Christensen (1985)
6 soils - Australia	clay silt sand	The clay (<2 μm) contained about 50 % of the soil organic matter, whereas silt and sand had about 25 % each.	Dalal and Mayer (1986)

* Fine clay: < 0.2 μm ; coarse clay: 0.2-2 μm ; fine silt: 2-5 μm ; medium silt: 5-20 μm ; coarse silt: 20-50 μm ; sand: > 50 μm

to groundwater, the erosion of pesticide enriched finer soil particles by runoff leads to surface water contamination.

It has been well documented that eroded sediments are enriched with clay size fractions and organic matter (Leonard, 1990). As discussed in section 2.4.1.1, a large volume of work has been carried out on the sorption of pesticides by whole soils, a limited amount of work has been reported on the effect of particle size on pesticide sorption (Table 2.4). Most of these studies have concentrated on the sorption of pesticides and desorption has not been reported in the organo-mineral fractions.

In New Zealand, sheet erosion is considered to be the dominant erosion type affecting approximately 217400 and 8318400 ha of land in the North and South Islands, respectively. Pesticide runoff includes dissolved, suspended particulate and sediment sorbed pesticide that is transported by water from a treated land surface (Leonard, 1990). Grant (1992) reported that one hectare could produce 6.4-10.3 tonnes of sediment from allophanic and non-allophanic soils of New Zealand at a rainfall event of 65mm. Some of the reported losses of pesticide during natural and simulated rainfall events are summarized in Table 2.5.

Approximately 1-2% of applied pesticide was lost through natural rainfall events, whereas losses of 5-10% were reported during simulated rainfall. Pesticide contamination in water bodies was much less than that measured in sediments.

The major source of pesticide contamination of groundwater and surface water is through the movement of pesticide residues in dissolved organic carbon (DOC) in soil. The importance of DOC in the sorption and movement of pesticide residue is discussed below.

2.7 EFFECT OF DISSOLVED ORGANIC CARBON (DOC) ON SORPTION AND MOVEMENT OF PESTICIDES

As discussed in section 2.5.3.1, soil organic matter is the principal sorbent of the majority of pesticides. In recent years, DOC has been the subject of considerable interest, because it has been reported to interact with pesticides, and thus affect the

Table 2.4 Summary of literature on particle size contributions to pesticide sorption-desorption by soils and sediments

Material and size fractions*	Pesticides	Observation	Reference
Soil: sand coarse silt medium silt fine silt coarse clay medium clay fine clay	Diuron and 2,4,5-T	Adsorption increased with decreasing particle size in proportion to OC content. Freundlich K values vary within a factor of 7, whereas the K_{oc} values vary only within a factor of 1.5. The K_{oc} values for non-ionic (Diuron) on whole soil and particle size are essentially the same. For ionic (2,4,5-T) the clay, silt and whole soil are the same and it is three times lower for the sand fraction.	Nkedi-Kizza <i>et al.</i> (1983)
Soil: sand silt clay	Lindane	Increased adsorption of lindane has been observed for clay followed by silt and sand fraction which corresponds to an increase in OC content.	Kay and Elrich (1967)
Soil sand silt coarse clay medium clay fine clay clay	DDT, Methoxychlor Endosulfon	Retention of pesticides was highest in the natural and organic matter removed fine and very fine clay fractions. Removal of OM with H_2O_2 reduced the retention of pesticides in the fine clay fractions.	Richardson and Epstein (1971)
Soil: sand coarse silt medium silt fine silt coarse clay fine clay	Atrazine	Besides organic matter, noncrystalline Al and Fe provide sites for atrazine adsorption, particularly in the $< 20 \mu m$ fractions.	Huang <i>et al.</i> (1984)
Soil: sand coarse silt fine silt clay	Tribunil	Adsorption increased with decreasing particle size. The Freundlich K value varied by a factor of 3 or 4 but K_{oc} values were quite similar among the fractions.	Raman (1987)

Table 2.4 continued

Material and size fractions*	Pesticides	Observation	Reference
Sediment: sand coarse silt medium silt fine silt clay	Aromatic and chlorinated hydrocarbon	The partition coefficient (K_d) were independent of sediment concentration and directly related to OM content. The K_p increases with increasing sorbent OC content. Highest K_{oc} of compounds for medium and fine silt followed by clay fraction and the lowest in sand fraction.	Karickhoff <i>et al.</i> (1979)
Sediment: clay and silt sand	Polycyclic aromatic hydrocarbons (PAH)	Positive relationship observed between % OC and PAH held by the sediment.	Evans <i>et al.</i> (1990)
Sediment: sand coarse silt medium silt fine silt coarse clay medium clay fine clay	Paraquat	Paraquat concentration is 20-50 fold higher in clay or fine silt compared to medium and coarse silt and as much as 1000 fold higher than sand. Isotherm coefficient determined on individual particle size fractions can be used to compute the paraquat distribution as a function of particle size in the whole sediment.	Karickhoff and Brown (1978)

* Fine clay: < 0.08 μm ; medium clay: 0.08-0.2 μm ; coarse clay: 0.2-2 μm ; clay: < 2 μm ; fine silt: 2-5 μm ; medium silt: 5-20 μm ; coarse silt: 20-50 μm ; sand: 50-2000 μm .

Table 2.5 **Summary of literature on the runoff losses of pesticides from natural and simulated rainfall**

Chemical	Location	Crop/cover	Total seasonal losses, % of application	Reference
Natural rainfall				
Atrazine Alachlor	Maryland Maryland	Corn Corn	0.1 0.16	Wu (1980)
Picloram	Arizona	Pinyon-Juniper	1.1	Johnsen (1980)
Glyphosate	Ohio	No-till corn	< 1	Edwards <i>et al.</i> (1980)
2,4-D Picloram	Oregon Oregon	Rangeland Rangeland	0.014 0.35	Norris <i>et al.</i> (1982)
2,4-D	Saskatchewan, Canada	Wheat stubble, fallow	4.1 (6-year average) 0.3	Nicholaichuk and Grover (1983)
Cyanazine	Pennsylvania	Fallow	0.73-5.7 conventional 0.01-0.75 (no-till)	Hall <i>et al.</i> (1984)
Atrazine Simazine	Maryland	Corn (conventional & no-till)	1.6 (Conventional) 1.1 (no-till)	Glenn and Angle (1987)
Simulated rainfall				
Atrazine Propachlor Alachlor	Iowa Iowa Iowa	Corn	0.76-6.1 0.97-5.7 1.0-8.6	Baker <i>et al.</i> (1982)
Atrazine Carbofuron	California	Fallow and corn residue	0.7-6.3 0.8-11.4	Haith (1986)
Atrazine	Stoneville, USA	Corn	4-8 (emulsion liquid) 9-12 (granule and wettable powder)	Wauchope (1987)
Atrazine Alachlor Chlorpyrifos	Wisconsin	Grass	5.8 4.0 0.2	Sauer and Daniel (1987)
Alachlor Carbofuron Terbufos	Illinois	Corn	1-2 1-11 1-6	Felsot <i>et al.</i> (1990)

fate of these pesticides in the soil or aquatic system (Ballard, 1971; Carter and Suffet, 1982; Landrum *et al.*, 1984; Madhun *et al.*, 1986b; Lee and Farmer, 1989). Several investigators have reported that the apparent solubilities of pesticide solutes increase in the presence of DOC (Wershaw *et al.*, 1969; Chiou *et al.*, 1986), and this can sometimes increase the movement of pesticides in soils (Kan and Tomson, 1990; Logan *et al.*, 1992; Liu and Amy, 1993).

In order to understand the mechanisms involved in the interaction between DOC and pesticides, it is necessary to know the sources and characteristics of the DOC.

2.7.1 Sources of DOC

The sources of DOC are grouped into endogenous and exogenous DOC and are briefly discussed below.

2.7.1.1 *Endogenous DOC*

This consists of naturally-occurring dissolved material namely humic acid, fulvic acid and water soluble soil organic matter. These are macromolecules with complex three-dimensional molecular structures comprised of hydrophobic and hydrophilic sites (Wershaw, 1986). It has been shown that the composition of water soluble soil organic matter is similar to that of humic and fulvic acid (Linehan, 1977).

2.7.1.2 *Exogenous DOC*

A number of organic manures, which act as a source of organic matter are applied to soil through agricultural practices. These include: sewage sludge, pig manure, mushroom compost, poultry, cattle and sheep manure. It has been shown that application of manure greatly increases the amount of soluble carbon in the soil solution (Meek *et al.*, 1974). Studies examining addition of exogenous DOC on the fate of pesticides are scanty (Barriuso *et al.*, 1992b).

2.7.2 Measurement of DOC

Various methods have been used to measure the DOC in soils. These include: (i) a dry combustion method, which involves combustion of the sample at a high temperature ($> 300^{\circ}\text{C}$) with subsequent measurement of the evolved CO_2 (Bremner and Tabatabai, 1971); (ii) A wet oxidation method in which the amount of oxidising agent used in the process is measured (Tate *et al.*, 1988); and (iii) The absorbance of light at different wavelengths (250-300 nm) for measuring DOC concentration in water samples (e.g., Dobbs *et al.*, 1972; De Haun *et al.*, 1982; Moore, 1985; Timperley, 1985).

2.7.3 Effect of DOC on sorption of pesticides

Several studies have suggested that sorption of pesticides by soil colloids or sediments is affected by the presence of DOC in the soil solution (Carter and Suffet, 1982; Lee and Farmer, 1989). Hassett and Anderson (1982) observed that the addition of DOC derived from natural water and sewage decreases the sorption of hydrophobic organic compounds. O'Connor and Connolly (1980) proposed that the observed decrease in the partition coefficient of hydrophobic compounds with increasing sediment concentration can be explained by the release of DOC from the sediment to the aqueous phase. Similarly Lee *et al.*, (1990) observed a reduction in sorption of napropamide on clay when peat humic acid was present in the slurry.

Caron *et al.* (1985) found that the addition of DOC to the aqueous phase reduces the sorption of DDT by sediments. Recently, it has been shown that DOC from exogenous and endogenous sources influenced the sorption of pesticides in soil (Barriuso *et al.*, 1992b). They reported that preincubation of soil with DOC generally increased sorption, whereas pesticide sorption decreased when DOC was preincubated with pesticide.

Several reasons have been attributed to the decrease in sorption of pesticides in the presence of DOC. These include: (i) interaction between DOC and pesticide in solution (Carter and Suffet, 1982; Madhun *et al.*, 1986b; Lee and Farmer, 1989), and (ii) competition on sorption sites between DOC and the pesticide (Lee *et al.*, 1990).

Infrared (IR) spectroscopy has been shown to be a good technique to reveal the binding mechanisms of pesticides with DOC (Burns *et al.*, 1973; Khan, 1974; Senesi and Testini, 1980; Madhun, 1984). The binding mechanisms include ion exchange process in diquat, paraquat, chlordimeform and triazines (Madhun, 1984; Burns *et al.*, 1973; Khan, 1973, 1974; Maqueda *et al.*, 1983; Senesi and Testini, 1980), hydrogen bonding in triazines and substituted ureas (Senesi and Testini, 1980, 1983; Madhun, 1984), and charge transfer complexes in triazines, substituted ureas, and bipyridilium herbicides (Khan, 1973, 1974; Mueller-Wegener, 1977; Senesi and Testini, 1980, 1982, 1983; Madhun, 1984). Recently, Hermosin and Cornejo (1993) studied the binding mechanism of 2,4-D by organo-clays using IR spectroscopy and reported a hydrogen bonding between carbonyl group of 2,4-D and ammonium group of the interlayer organic cations.

2.7.4 Effect of DOC on movement of pesticides

In recent years, the effect of DOC on the transport of pesticides has attracted much attention because of (i) the interaction between the contaminant and DOC and (ii) mobility of DOC in the aquifer. The literature pertaining to the effect of DOC on the transport of pesticides is briefly discussed below.

Abdul *et al.* (1990) reported that humic acid is more effective than water in removing the more hydrophobic nonpolar organic contaminants from aquifer material. Similarly Logan *et al.* (1992) showed the enhanced movement of chlordane in the presence of humic acid. Kan and Tomson (1990) and Liu and Amy (1993) also demonstrated the facilitated transport of organic contaminants in the presence of DOC.

Recently, it has been shown that in soil column studies aqueous phase DOC enhances the transport of polynuclear aromatic hydrocarbons, whereas solid phase DOC retards transport (Liu and Amy, 1993). Enfield *et al.* (1989) demonstrated the facilitated or enhanced transport of the hydrophobic compounds pyrene and hexachlorobenzene in the presence of DOC.

It has been observed that an increase in the solution pH increases the DOC

concentration in soil solution thereby decreasing pesticide sorption (Lee *et al.*, 1990). Addition of liming materials, ammonia or other basic fertilizers is very effective in increasing soil pH. The increase in soil pH may enhance pesticide concentrations in the solution phase, thereby contributing to greater mobility in the soil. Smith and Willis (1985) demonstrated enhanced movement of several pesticides in soil columns with the application of anhydrous ammonia.

2.8 MOVEMENT OF PESTICIDES IN SOIL

The movement of pesticides through soils following landfill disposal or agricultural application is of great concern whenever there is potential threat to groundwater contamination. The miscible displacement technique is commonly employed in the laboratory using columns of repacked soil to examine the physical and chemical processes involved in the movement of solutes.

Two types of experiments are commonly conducted to examine the mechanisms involved in the leaching of pesticides. The first and most common type involves a step-function change in influent concentration (C_i) from 0 to C_o for the chemical species of interest during the transport of solute through a soil column. The leachate concentration (C_e) is monitored following this change, and a breakthrough curve (BTC) is obtained relating C_e/C_o to the number of liquid-filled pore volumes (p) of solute. Often C_i is then changed back to 0 and the falling limb (or desorption) of the BTC measured.

In the second type of experiment, a pulse of solute is applied to the soil surface or mixed with the surface soil. Water is then usually percolated through the column for a period and the distribution of applied solute within the soil measured by destructive sampling.

2.8.1 Modelling solute leaching

Models are a simplified description of reality. The development of simulation models for forecasting pesticide behaviour is an attractive way of evaluating solutions to some agricultural and environmental problems. Models are being increasingly used as

management tools to predict the fate of pesticides in soil (Wagenet and Rao, 1990).

2.8.1.1 *Uses of simulation models*

Development of simulation models, which predict the leaching of pesticides in soils have the following benefits: (i) help to assess the time required for the soil-applied pesticide to be dissipated to some acceptable, regulated level before entering groundwater. (ii) provide information on the likely environmental impact of a new pesticide before its actual use. (iii) assist farmers and growers in designing effective crop, soil and chemical management strategies. (iv) achieve a minimum environmental impact and maximum crop-yield response from the minimum amount of pesticide application.

2.8.1.2 *Type of simulation models*

Many models for the transport of non-reactive and reactive (pesticide) solutes have been developed over the years, some simple and some complicated. The simplicity or complexity of a model often depends on whether it is constructed from a research, management or screening perspective. Several reviews have been written recently on solute transport models (Addiscott and Wagenet, 1985; Brusseau and Rao, 1990; Jury and Flühler, 1992; Selim, 1992) and also the various pesticide fate models have been discussed in detail (Wagenet and Rao, 1990). The importance of sorption in the movement of pesticides can be examined by using the Convection-Dispersion equation (CDE). This model has been used extensively to simulate the movement of pesticides (e.g., Davidson *et al.*, 1968). The CDE model involves both equilibrium and non-equilibrium sorption processes. Each model is briefly discussed below.

2.8.2 **Convection-Dispersion equation**

The convection-dispersion equation (CDE) is the classic deterministic and mechanistic approach, based on miscible displacement theory (Nielsen and Biggar, 1962), to modelling the transport of solute through the soil by water. This model assumes that physical convection (i.e., mass flow) and molecular diffusion combine to displace a solute in a porous media.

2.8.2.1 Non-sorbing solutes

For steady-state water flow conditions, the non-reactive solute movement can be described by the CDE as (Nielsen and Biggar, 1962; Kirkham and Powers, 1972; Wagenet, 1983; Cameron and Scotter, 1986)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.10)$$

Where t is time (hr), D is the dispersion coefficient ($\text{mm}^2 \text{hr}^{-1}$), x is distance in the direction of flow (mm) and v is average pore water velocity (mm hr^{-1}).

The solution of Equation 2.10 for the case of a continuous solute input is,

$$C/C_0 = 1/2 \left[\text{erfc} \left[\frac{1-p}{2(Dp/vL)^{1/2}} \right] + e^{vL/D} \text{erfc} \left[\frac{1+p}{2(Dp/vL)^{1/2}} \right] \right] \quad (2.11)$$

Where p is liquid-filled pore volume, L is column length (mm). The relation between C/C_0 for various values of p obtained from Eq 2.11 a gives breakthrough curve for the solute concerned when diffusion and mass flow are the processes of displacement.

2.8.2.2 Sorbing solutes

Some solutes are sorbed during transport. Additional terms can be included in the CDE to account for the sorption of the solutes and the equation may be rewritten as (Lapidus and Amundson, 1952)

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.12)$$

where ρ is soil bulk density (g cm^{-3}) and θ is volumetric water content ($\text{mm}^3 \text{mm}^{-3}$).

The CDE can be solved analytically for certain initial and boundary conditions (reviewed by Van Genuchten and Alves, 1982) and also numerically (De Smedt and Wierenga, 1978; Van Genuchten and Alves, 1982). One of the most important steps in model formulation is the description of the sorption term.

2.8.3 Equilibrium sorption model

In most of the studies involving the CDE model it has been assumed that sorption of solutes (pesticides) follows a linear isotherm. The linear sorption equation has been given in section 2.5.2.2. Differentiating Eq 2.3 with respect to time yields

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t} \quad (2.13)$$

Substituting dS/dt in Equation 2.12 by $K_d dC/dt$, Equation 2.12 can be written as,

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} K_d \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.14)$$

Equation 2.14 can be written as,

$$\frac{\partial C}{\partial t} (1 + \frac{\rho}{\theta} K_d) = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.15)$$

Under conditions of assumed local equilibrium, isotherm singularity and isotherm linearity the transport equation yields

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.16)$$

Where

$$R = 1 + (\frac{\rho}{\theta}) K_d \quad (2.17)$$

In Eq 2.16, R is referred to as the retardation factor (dimensionless) (Davidson and Chang, 1972).

Nonlinear sorption isotherms for pesticides can be represented by the Freundlich equation, which has been described in section 2.5.2.1. The time differentiated Freundlich equation (Eq 2.1) is

$$\frac{\partial S}{\partial t} = KNC^{N-1} \frac{\partial C}{\partial t} \quad (2.18)$$

The transport equation is then equivalent to equation 2.16 except for the definition of R , which is given by

$$R = 1 + \left(\frac{\rho}{\theta}\right) KNC^{N-1} \quad (2.19)$$

It has been appreciated that the assumption of describing sorption as a linear, equilibrium, reversible process is not always a valid representation. Most early studies that used such a representation (Kay and Elrick, 1967; Davidson *et al.*, 1968; Davidson and McDougal, 1973) showed a substantial deviation between calculated and measured effluent curves in laboratory column studies. This led to the development of a non-linear, equilibrium model (Van Genuchten *et al.*, 1974) and non-equilibrium sorption models (Hornsby and Davidson, 1973b; Selim *et al.*, 1976; Cameron and Klute, 1977; Rao *et al.*, 1979).

Brusseau and Rao (1989a) have critically reviewed the literature dealing with non-linear sorption isotherms, non-singular isotherms (hysteresis), and non-equilibrium sorption isotherms during transport of solute under steady state water flow conditions.

2.8.4 Non-equilibrium sorption models

The local equilibrium assumption is a major component of the conventional solute transport equation. Detailed laboratory and field transport studies, however, have revealed that, in many cases, this assumption is invalid. This suggests that non-equilibrium conditions exist during the transport of organic chemicals. Hence various non-equilibrium kinetic models have been developed and are reviewed in the literature (Brusseau and Rao, 1989a; Brusseau and Rao, 1990). The non-equilibrium sorption models available in the literature include a one-site first-order model and a bicontinuum model. These are briefly discussed below:

2.8.4.1 *One-site first-order model*

Early attempts to model sorption kinetics involved a first-order simple reversible kinetic reaction (Davidson and McDougal, 1973; Hornsby and Davidson, 1973b) in

which the sorption rate is taken as a function of the concentration difference between the sorbed and solution phases. The equation for the sorbed component S may be written as

$$\frac{\partial S}{\partial t} = K_s \frac{\theta}{\rho} C - K_{ds} S \quad (2.20)$$

Where K_s and K_{ds} are the sorption and desorption rate coefficients (hr^{-1}). It has been shown that this model has failed to predict pesticide movement in soil (Rao and Jessup, 1983). Organic chemicals have been found to exhibit a two-stage approach to equilibrium, a short fast uptake followed by an extended period of slower uptake (Hamaker and Thompson, 1972; Karickhoff, 1980; Wu and Gschwend, 1986). This type of behaviour is approximated using a bicontinuum approach. This bicontinuum approach has been relatively more successful for organic chemicals (Brusseau and Rao, 1989a) and for inorganic ions (Selim, 1992).

2.8.4.2 Bicontinuum model

Transport models employing the bicontinuum-sorption formulation, often referred to as two-site models, assume that sorption is instantaneous for a fraction of the sorbent and rate limited for the remainder (Selim *et al.*, 1976; Cameron and Klute, 1977). The bicontinuum models presented by Selim *et al.* (1976) and Cameron and Klute (1977) are mathematically equivalent in non-dimensional form, to the transport-related non-equilibrium model (two region) developed by Van Genuchten and Wierenga (1976).

With the bicontinuum model, sorption is conceptualized to occur in two domains:

$$C \sim S_1 = S_2 \quad (2.21)$$

Where S_1 and S_2 are the sorbed phase concentration ($\mu\text{mol kg}^{-1}$) for the equilibrium and kinetic sites, respectively.

At equilibrium, sorption on both types of sites is described by the Freundlich equation,

$$S = S_1 + S_2 = K_1 C^N + K_2 C^N = KC^N \quad (2.22)$$

Where K_1 and K_2 are the Freundlich sorption coefficient for the equilibrium and kinetic sites, respectively.

Assuming that equilibrium sites represent some fraction F of the total available sorption sites, the following relationship may be stated:

$$S_1 = FKC^N \quad (2.23)$$

$$S_2 = (1-F) KC^N \quad (2.24)$$

The bicontinuum sorption model coupled to the CDE may be written in the dimensionless form (Nkedi-Kizza *et al.*, 1989),

$$\frac{\partial C^*}{\partial p} + (\beta R - 1) NC^{*(N-1)} \frac{\partial C^*}{\partial p} + (1 - \beta) R \frac{\partial S^*}{\partial p} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (2.25)$$

$$(1 - \beta) R \frac{\partial S^*}{\partial p} = \omega (C^{*N} - S^*) \quad (2.26)$$

by defining the following nondimensionless parameters:

$$C^* = C/C_0 \quad (2.27a)$$

$$P = \nu L/D \quad (2.27b)$$

$$S^* = [S_2 / (1-F) KC_0^{N-1}] \quad (2.27c)$$

$$R = [1 + (\rho / \theta) KC_0^{N-1}] \quad (2.27d)$$

Note that in using the empirical relationship, the linearized sorption coefficient, $K_d = KC_0^{N-1}$ (Nkedi-Kizza *et al.*, 1989) was used.

$$p = vt/L \quad (2.27e)$$

$$\beta = [1 + F (\frac{P}{\theta}) KC_0^{N-1} / R] \quad (2.27f)$$

$$\omega = Q_2(1-\beta)RL/v \quad (2.27g)$$

$$X = (x/L) \quad (2.27h)$$

Where P is the Peclet number, which represents the dispersive-flux contribution to transport, x is distance in the direction of flow (mm), L is column length (mm), β is the fraction of instantaneous retardation, ω is the Damkohler number, which is a ratio of hydrodynamic residence time to characteristic time for sorption and Q_2 is rate constant. These last two terms specify the degree of non-equilibrium existing in the system.

2.9 SUMMARY

The fate of pesticides in the soil environment is governed by various transformation processes that include: sorption, degradation (chemical and biological), volatilization, movement to groundwater and runoff in surface water. Among the various processes, sorption by the organic and inorganic constituents of the soil matrix is one of the key processes affecting the fate of pesticides in soil. Though the sorption of pesticides

by soils is well documented overseas, little work has been done with New Zealand soils.

Though the soil organic matter has been shown to be the principal sorbent for many pesticides, recent studies have shown the importance of DOC (endogenous) in enhancing the movement of pesticides in soil. Therefore, further evaluation of the origin and the effect of exogenous carbon on the sorption and movement of pesticides is required.

The sorption of pesticides onto the soil particles reduces the movement of pesticides to groundwater, but the erosion of finer particles enriched with pesticides by surface runoff leads to surface water contamination. Sorption of pesticides by the whole soil has been examined extensively, but only a limited amount of work has been reported on the effect of particle size on pesticide sorption-desorption.

Sorption of pesticides onto the soil particles influences the pesticide movement to groundwater. Several mathematical models involving equilibrium and non-equilibrium processes have been developed to predict the movement of solutes to groundwater. However, it has been shown that sorption non-equilibrium is affecting the movement of pesticides in soil. Therefore it is necessary to examine the effect of sorption on the movement of pesticides in soil.

The overall objectives of this thesis are; (a) to examine the sorption of ionic and non-ionic pesticides in a range of allophanic and non-allophanic soils and to identify the soil properties affecting the sorption of pesticides, and (b) to examine the effect of sorption on the movement of pesticides in soil.

CHAPTER 3

AN EVALUATION OF METHODS OF MEASUREMENT OF PESTICIDES IN SORPTION STUDIES

3.1 INTRODUCTION

In sorption experiments the concentration of pesticides in the soil solution is measured using UV spectrophotometry or Gas Liquid Chromatography (GLC) or High Performance Liquid Chromatography (HPLC) or radiotracer techniques. Among the various methods listed above, UV spectrophotometric methods have been used widely in pesticide sorption studies because of the low cost and ease of use (Cyr *et al.*, 1977). However, the presence of soluble carbon in soil interferes with the measurement of pesticides in soil solution using UV spectrophotometry (Singh 1989; Martin and Camazano, 1991).

Alternatively, GLC and HPLC are the most useful techniques available for determining pesticides in the soil solution (Eagle *et al.*, 1991). Chromatography generally involves the separation of a mixture of compounds as a result of the differences in the equilibrium distribution of individual compounds between the mobile and the stationary phases. In GLC, the vapour pressure of a compound is a key factor influencing resolution. HPLC separations are based primarily on solubility, and the mobile phase is important. However, these methods require extraction and cleaning procedures to remove unwanted constituents from the extract that may interfere with the subsequent analyses (Eagle *et al.*, 1991).

Tracer techniques can be used to investigate certain properties of large populations of atoms or molecules by making observations of the behaviour of small numbers of tracer atoms. The characteristics of the tracer atoms need to be similar to those of the atoms in the compounds of interest. Isotopes can act as tracers and both radioactive and non-radioactive isotopes have been used as tracers. Among the various radioactive materials, ^{14}C is the most commonly used radionuclide in pesticide research (Anon, 1991) and the pesticide compounds are labelled with ^{14}C .

In pesticide sorption studies, sorption is often estimated from the amount of ^{14}C remaining in solution. The concentration of ^{14}C in solution can be easily measured using a liquid scintillation counter (LSC). Measurement of ^{14}C remaining in the soil solution and that sorbed onto soil particles provides information on the mass balance of pesticides in soils. It has been shown that the residual ^{14}C pesticides in soil can be measured directly by extracting with a scintillation cocktail (Lavy *et al.*, 1972) or the dry combustion method (Cheng and Farrow, 1976).

A range of centrifuge tubes have been used to examine the sorption of pesticides in soil under laboratory conditions. Unless the materials are tested for their ability to sorb these chemicals, the validity of the experimental results may be in question. It has been shown that silicone rubber, nalgene tubing and tygon R-3603 rapidly sorb pesticides (Topp and Smith, 1992).

3.2 OBJECTIVES

The objectives of this experiment were:

- (i) to compare various methods of measurement of pesticide in the soil solution during sorption studies.
- (ii) to develop a suitable method for the extraction of ^{14}C pesticides in soils.
- (iii) to examine the sorption of pesticides by a range of centrifuge tubes used in the batch and column studies.

3.3 METHODS AND MATERIALS

3.3.1 Pesticides

Three ionic herbicides namely, metsulfuron methyl, atrazine and 2,4-D and two non-ionic organophosphorus insecticides, phorate and terbufos were used in this study. These pesticides represent the important classes of organic chemicals frequently used in cereal cropping and pastoral agriculture in New Zealand.

Analytical grade and ^{14}C -labelled metsulfuron methyl (96.5% radiochemical purity; specific activity 2.31 MBq mg^{-1}) was supplied gratis by Du Pont New Zealand Ltd.

Analytical grade and ^{14}C -labelled atrazine (97% radiochemical purity; specific activity 1.98 MBq mg^{-1}) was obtained gratis from Ciba-Geigy Corporation. Analytical grade and ^{14}C uniformly labelled 2,4-D (98% radiochemical purity; specific activity 1.85 MBq mg^{-1}) was provided gratis by Dow Chemical Company, U.S.A. Analytical grade phorate, terbufos and methylene ^{14}C -labelled compounds were obtained gratis from the American Cyanamid Company. The labelled phorate and terbufos compounds were more than 98% radiochemically pure and their specific activities were 1.51 and 2.22 MBq mg^{-1} , respectively. The important properties of the pesticide compounds are summarised in Table 3.1.

3.3.1.1 *Metsulfuron methyl*

Metsulfuron methyl (2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) amino]- carbonyl] amino] sulfonyl] benzoic acid belongs to the sulfonylurea group, recently developed as a major new class of herbicide. It is highly active against a wide spectrum of broadleaf and grass weeds. It is an ionic herbicide, which is highly soluble in water (1100 mg L^{-1} at pH 5 and 9500 mg L^{-1} at pH 7). The structural formula is given in Figure 3.1.

3.3.1.2 *Atrazine*

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) herbicide belongs to the s-triazine group and is in the form of a water dispersible granule. Simazine and metribuzin are other important herbicides in this group. The structural formula is given in Figure 3.1. It has a low solubility in water (33 mg L^{-1}). In New Zealand it is used for control of certain broad leaf weeds in cropping. These herbicides can become cations on protonation, which depends on the soil pH and pK_a of the herbicide.

3.3.1.3 *2,4-D*

2,4-D (2,4-dichlorophenoxy acetic acid) belongs to the phenoxy acetic group of herbicides, which constitute 17% of the total herbicide used in New Zealand (Maber and Pinnell, 1992). It is widely used for control of many broad leaf weeds in pasture.

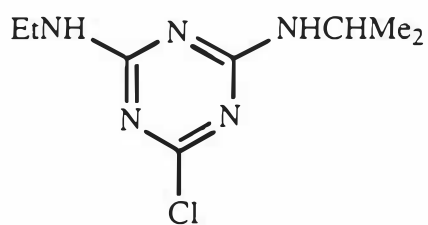
Table 3.1 Some important properties of the pesticides^a

Properties	Metsulfuron methyl [*]	Atrazine	2,4-D	Phorate	Terbufos
Chemical class	sulfonylurea herbicide	triazine herbicide	phenoxyacetic acid herbicide	organophosphorus insecticide	organophosphorus insecticide
Molecular formula	C ₁₄ H ₁₅ N ₅ O ₆ S	C ₈ H ₁₄ ClN ₅	C ₈ H ₆ Cl ₂ O ₃	C ₇ H ₁₇ O ₂ PS ₃	C ₉ H ₁₂ O ₂ PS ₃
Molecular weight	381	215	221	260	288
Aqueous solubility (mg L ⁻¹)	1100 (pH 5) 9500 (pH 7)	33	750	22	5
Vapour pressure (mm Hg)	2.5 * 10 ⁻¹²	8 * 10 ⁻⁶	2.89 * 10 ⁻⁷	6.4 * 10 ⁻⁴	3.2 * 10 ⁻⁴
Ionizability (pK _a)	3.3	1.7	2.8	non-ionic	non-ionic
log K _{ow} ^b	0	2.50	2.81	3.33	3.68

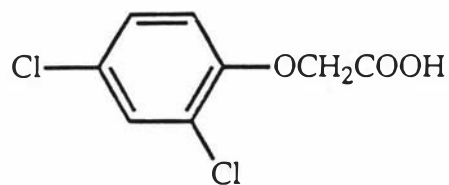
^a Source Wauchope *et al.* (1992)

^b The values of log K_{ow} for atrazine (Briggs 1981b); 2,4-D (Chiou *et al.*, 1977); and phorate and terbufos (Felsot and Dahm, 1979)

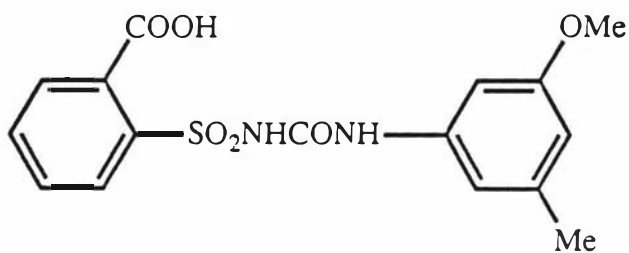
^{*} Metsulfuron methyl was later used in the sorption experiment (Chapter 5)



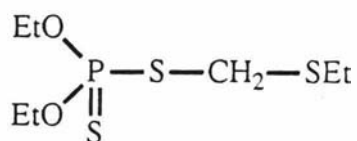
Atrazine



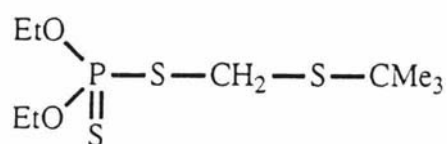
2,4-D



Metsulfuron methyl



Phorate



Terbufos

Figure 3.1 Structural formulae of the pesticides

The herbicides in this group are ionizable and are non-volatile. The solubility of 2,4-D in water is 700 mg L^{-1} . The structural formula is given in Figure 3.1. The pK_a of 2,4-D is 2.8.

3.3.1.4 *Phorate*

Phorate (O,O - diethyl S-ethylthiomethylphosphorodithioate) is a soil applied granular insecticide and belongs to the organo-phosphate group. The structural formula is given in Figure 3.1. This insecticide is applied as a furrow or band treatment at sowing or planting. It controls stem weevil, flies and mites in carrot, stem weevil in new sown pasture and aphids in cereal crops. It is a non-ionic pesticide, which has a low solubility in water (22 mg L^{-1}). It is non-volatile in nature.

3.3.1.5 *Terbufos*

Terbufos (S (1,1-dimethylethyl) thio)methyl O,O-diethylphosphorodithioate) is a soil applied systemic insecticide for protection from grass grub, stem weevil and aphids in newly sown pasture and cereal crops. The structural formula is given in Figure 3.1. It is a non-ionic pesticide and non-volatile in nature.

3.3.2 Methods for pesticide analysis

Only atrazine, 2,4-D, phorate and terbufos were used in the experiments evaluating the methods of measurement.

3.3.2.1 *UV spectrophotometer*

The most important consideration in the quantitative determination of pesticides using a UV spectrophotometer is to identify the wavelength (λ) that corresponds to the absorption maximum. The four pesticides were scanned between 200-400 λ using an SP8-300 UV spectrophotometer to obtain the optimum λ for measurement. Scanning was conducted for all the four chemicals (atrazine, 2,4-D, phorate and terbufos) in aqueous solutions (H_2O , 0.01 M CaCl_2) and in the presence of soil extracts. The interference of soluble organic matter on the scanning was examined

using increasing amounts of soil extracts.

3.3.2.2 *Gas liquid chromatography (GLC) and High performance liquid chromatography (HPLC)*

(i) **Atrazine**

Atrazine concentration in the soil solution was measured using a Hewlett 5890 GLC equipped with an nitrogen phosphorus detector. A GLC method as described by Singh *et al.* (1990) was used in this study. The glass column (0.91 m by 2 mm i.d.) was packed with 100-120 mesh ultrabond 20M on carbowax 0.125-0.149 mm. The carrier gas was nitrogen at a flow rate of 20 ml min⁻¹. Flow rates of H₂ and air through the detector were 18 and 20 ml min⁻¹, respectively. The detector temperature was 300°C and the column temperature was 150°C, the retention time was 1.5 min.

(ii) **2,4-D**

The concentration of 2,4-D in equilibrium solution after sorption was measured using HPLC as described by Hoke *et al.* (1986). The HPLC conditions were as follows: mobile phase, methanol-H₂O (80:20); flow rate, 1 ml min⁻¹; detector wavelength, 280 nm (0.01 attenuation); injection volume 20 µl. The HPLC was equipped with a variable-wavelength UV detector and an integrator-recorder. The column used was a 10 cm C18 column (ODS) and was preceded with a 3 cm guard column.

(iii) **Phorate and Terbufos**

Phorate and terbufos concentrations in the soil solution were measured using GLC on a glass column (180 cm by 2 mm i.d.) packed with 5% DC-200 on 100-200 mesh Carbowax 20 M maintained at 160°C (Ahmad *et al.*, 1979). The GLC was equipped with N-P-FID detector maintained at 230°C and the injector at 200°C. The carrier gas was helium at a flow rate of 60 ml min⁻¹. Hydrogen and air flow rates were 30 and 25 ml min⁻¹, respectively.

3.3.2.3 Radiotracer technique

(i) Principles of radiotracer technique

The relative ease with which radionuclides may be detected, and quantitatively measured, has led to their widespread use as tracers in biological studies. The behaviour of tracer isotopes is similar to that of the more abundant unlabelled compound and detection can be made by simple radioassay procedures. Quantitative analyses can be made by determining specific activity (SA) of the compound. Specific activity (SA) is defined as the activity of particular radioactive atoms per unit mass of its element of compound. The units of SA are the becquerel (or curie) per gm or mole of substance.

$$SA = \frac{{}^{14}\text{C labelled pesticide (Bq)}}{\text{unlabelled pesticide (mmol)}} \quad (3.1)$$

From the specific activity measurements the concentration of the unlabelled compound during sorption experiments can be estimated. One of the problems with the use of the tracer technique in soils is that isotopic exchange of the added tracer with other compounds present in the soil may complicate the interpretation of the results. In the case of pesticides, however, exchange of ${}^{14}\text{C}$ with native carbon compounds present in the soil is unlikely to occur during the sorption period and hence the SA remains the same before and after sorption.

$$SA_{\text{initial}} = SA_{\text{final}} \quad (3.2)$$

$$\frac{{}^{14}\text{C labelled pesticide initial}}{\text{unlabelled pesticide initial}} = \frac{{}^{14}\text{C labelled pesticide final}}{\text{unlabelled pesticide final}} \quad (3.3)$$

After the sorption period the ${}^{14}\text{C}$ activity in the equilibrium solution is then radioassayed. The concentration of unlabelled pesticide in the equilibrium solution after sorption can be calculated from the SA of added solution and the activity of ${}^{14}\text{C}$ pesticide in the equilibrium solution.

$$\begin{aligned} &\text{Final concentration of unlabelled pesticide} \\ &= \frac{1}{SA_{\text{initial}}} * {}^{14}\text{C labelled final} \end{aligned} \quad (3.4)$$

This equation assumes that the pesticide compound has not been degraded and that all the ^{14}C remains associated with the compound. The amount of pesticide sorbed was calculated as the difference between the initial and the final concentration of pesticide in solution.

(ii) Liquid Scintillation Counting

Liquid scintillation counting is the most popular method of counting the low energy beta radiation emitted by the nucleides such as, ^3H and ^{14}C that are used extensively in biological studies (Patterson and Green, 1965). In general terms the liquid scintillation source is a sample consisting of radioactive material, one or two organic fluors, a detergent and a solvent, contained in a vial. The most common solution used for counting ^{14}C compounds is a mixture of two volumes of toluene (containing 0.4% 2,5-Diphenyloxazole (PPO) and 0.01% Dimethyl POPOP) and one volume of Triton X-100 (Patterson and Green, 1965) known as scintillation cocktail, which was used in this experiment.

(iii) Quenching

The liquid scintillation technique is based on the linear relationship between the amount of light being emitted from the vial and the number of beta particles emitted by the samples. In practice a number of factors will influence the amount of light emitted per beta emission and these affect the counting efficiency. This phenomenon is referred to as quenching.

Quenching is defined as any process that reduces the quantum efficiency of the energy transfer between the β^- particles and light output and hence reduces the pulse height and counting efficiency. The important factors, which affect the counting efficiency are the absorption of light by the chemicals (chemical quenching) present in the samples or by the colour (colour quenching) of the extracts. The number of counts recorded must be corrected for quenching (quench correction), to reflect the actual number of beta particles emitted from the samples. Two approaches are found to be effective for quench correction. One is to build a quench curve using an internal standard and another is to use an internal standard. In this experiment the

effect of colour quenching on the recovery of ^{14}C pesticides was examined using an internal standard. Known amounts of ^{14}C pesticides in solvent (methanol) were taken in a set of scintillation vials and the solvent was allowed to evaporate. Increasing amounts (0-1 ml) of Tokomaru and Patua soil extracts in 0.01 M CaCl_2 from two soils (the Tokomaru silt loam and the Patua silt loam), which varied in soil organic carbon were added followed by 10 ml of scintillation cocktail and the activities were measured.

3.3.3 Measurement of ^{14}C labelled pesticides in soil

To calculate the mass balance of pesticides during sorption and movement experiments, it is necessary to measure the amount of ^{14}C labelled pesticides that remain in the soil. The amount of residual ^{14}C labelled pesticides in the soil is measured by two methods.

3.3.3.1 *Direct extraction with scintillation cocktail*

The direct extraction technique refers to assaying the sample for ^{14}C using an organic solvent (dioxane or toluene) based scintillation cocktail. 10 ml of the dioxane or toluene based scintillation cocktail was added to the soil containing ^{14}C labelled pesticide and shaken for various time intervals. The cocktail containing the organic solvent was directly assayed using the liquid scintillation counter.

3.3.3.2 *Dry combustion*

Recovery of ^{14}C pesticide was examined by combusting a soil sample spiked with ^{14}C pesticide using a Leco combustion apparatus (Cheng and Farrow, 1976). A known amount of ^{14}C labelled pesticide was added to 0.5 g of the Egmont soil and placed in a ceramic combustion cup. The $^{14}\text{CO}_2$ evolved by sample oxidation was trapped in NaOH solution. One ml of NaOH was subsequently mixed with 10 ml of PCS scintillation cocktail (PCS is a liquid scintillation cocktail manufactured by Amersham / Searle corporation) and the ^{14}C activity was measured using the liquid scintillation counter.

3.3.4 Sorption of the pesticides by centrifuge tubes

To examine the sorption of pesticides by soil, it is important to measure the extent of sorption of pesticides onto the centrifuge tubes used for sorption measurement. Sorption studies were conducted with ^{14}C atrazine, 2,4-D, phorate and terbufos using a range of centrifuge tubes. The tubes included: polycarbonate, polypropylene, glass tubes with silicone rubber caps and glass tubes with teflon caps. The pesticide solutions were shaken without soil for 30, 60, 120 and 240 minutes and the samples were removed after their respective times. The ^{14}C activity was measured and the concentration of the pesticides was calculated according to Equation 3.4. The assumptions involved in this equation are discussed in detail in section 3.3.2.3. The amount of pesticide sorbed is calculated as the difference between the initial and the final concentration of pesticides in solution.

3.4 RESULTS AND DISCUSSION

3.4.1 UV spectrophotometer

3.4.1.1 *Scanning*

The results of the scanning showed that the wavelength (λ) at which maximum absorption occurred varied between the pesticides. For example, spectrophotometric scans of atrazine and 2,4-D are shown in Figure 3.2a. Atrazine gave peaks at λ 220 and 265 nm, and 2,4-D at λ 232 and 280 nm. Phorate and terbufos gave peaks at 227 and 225 nm, respectively. These optimum λ were subsequently used for measuring pesticide concentration in soil solution. However interference from soil organic matter at these λ was observed, when the pesticide solution was prepared in the CaCl_2 extract of soil. For 2,4-D in aqueous solution a larger absorption peak is obtained at 230 than at 280 nm. However a large absorption peak was observed for soil extract alone at a wavelength near 230 nm (Fig 3.2b). This masked the absorption peaks for 2,4-D prepared in soil extract and it was not possible to use the absorption peaks at 230 nm to measure the concentration of 2,4-D in soil solution. Therefore absorption at 280 nm which gave some separation was used. Similarly two peaks are obtained for atrazine at 265 nm and 220 nm. Since the peak at 220 is very

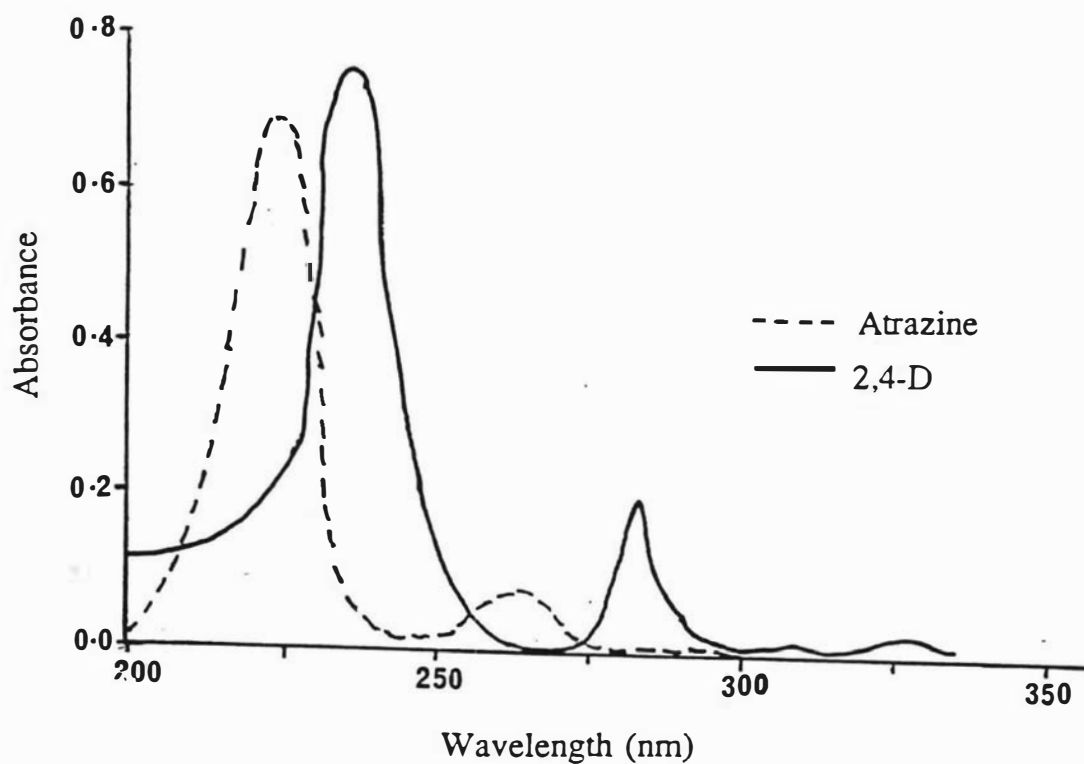


Fig 3.2a Spectrophotometric scan of atrazine and 2,4-D

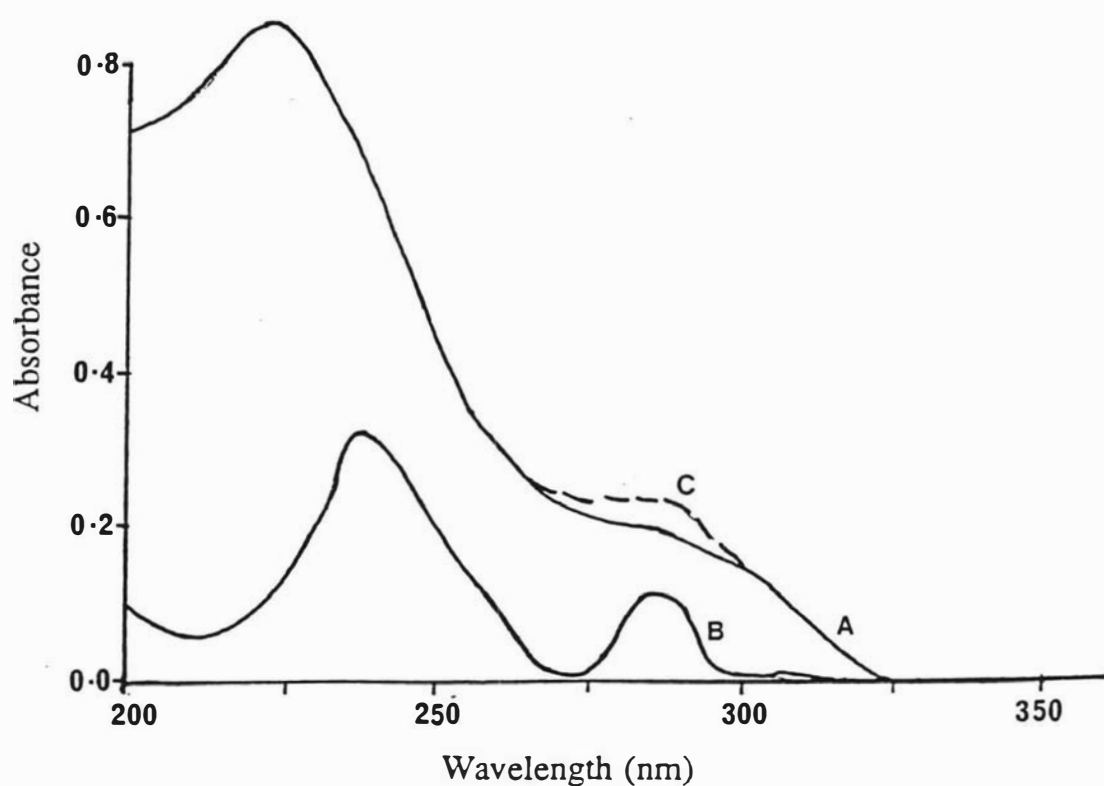


Fig 3.2b Spectrophotometric scan of (B) 2,4-D in aqueous (0.01 M CaCl₂), (A) 0.01 M CaCl₂ soil extract and (C) 2,4-D in 0.01 M CaCl₂ extract

close to the peak for water soluble organic matter it was decided to measure atrazine concentration at 265 nm. In the case of phorate and terbufos, the absorption peaks were close to the peak for soil hence it was not possible to overcome the interference from the organic matter.

3.4.1.2 *Standard preparation*

The pesticide standard was prepared in aqueous 0.01 M CaCl_2 and a 0.01 M CaCl_2 extract of a soil. The linear range of concentration for the UV spectrophotometric analysis varied between the pesticides. The linear range of concentration obtained in aqueous solution was 9.30-74.4 $\mu\text{mol L}^{-1}$ for atrazine, 9.05-72.4 $\mu\text{mol L}^{-1}$ for 2,4-D, 7.69-38.5 $\mu\text{mol L}^{-1}$ for phorate and 6.94-13.9 $\mu\text{mol L}^{-1}$ for terbufos. However, when pesticide standards were prepared in a 0.01 M CaCl_2 extract of soil, soluble carbon in the extract interfered with the measurement. In all instances the absorbance of the blank (soil extract) sample was higher than the pesticides at low concentration ($< 9.05 \mu\text{mol L}^{-1}$). UV spectrophotometry methods have been found to be useful in sorption and degradation studies involving pure clay minerals, which contain negligible amounts of organic matter. Because of the problems associated with organic carbon interference in the measurement of pesticides using UV in this study, Gas Liquid Chromatography (GLC) and High Performance Liquid Chromatography (HPLC) were used to measure pesticide concentrations in the soil solution.

3.4.2 Gas liquid and High performance liquid chromatography

For atrazine, phorate and terbufos, Gas Liquid Chromatography (GLC) was used, whereas High Performance Chromatography (HPLC) was used to measure 2,4-D.

For atrazine a standard curve was obtained using GLC and the linear range of concentration in the measurement of atrazine was 0-74.4 $\mu\text{mol L}^{-1}$. Similarly for 2,4-D, a standard curve was obtained using a range of solution concentrations (0-72.4 $\mu\text{mol L}^{-1}$). The peak for 2,4-D was obtained after a retention period of 5.21 min. The linear range of concentrations for phorate and terbufos were found to be 0-38.5 $\mu\text{mol L}^{-1}$ and 0-13.9 $\mu\text{mol L}^{-1}$, respectively.

The concentration of pesticide in the equilibrium solution after sorption was measured using GLC and HPLC methods and compared with the equilibrium concentration estimated from liquid scintillation counting and UV spectrophotometry (Table 3.3).

3.4.3 Radiotracer technique

The ^{14}C activities obtained in the presence of different amounts of soil extract, obtained from the two soils (Patua and Tokomaru), which varied in their organic carbon content are reported in Table 3.2 along with the colour intensity of the extract as measured by the absorption at a wavelength of 210 nm. The absorption measurements at 210 nm indicated that with increasing levels of soil extract increasing amounts of soluble carbon were added. The recovery of ^{14}C pesticides was between 96.5 and 99.5% and the recovery was not affected by the amounts of 0.01 M CaCl_2 extract added. This suggests that there had been no colour quenching and quench correction was not required.

3.4.4 Comparison of UV, GLC/HPLC and radiotracer techniques

The linear range, the minimum concentration measured and the concentration of pesticides after sorption, as measured by different methods, are compared and presented in Table 3.3. The results suggest that the linear range of concentration obtained varied between the methods. Generally the linear range was lower for GLC/HPLC than for UV. The presence of organic matter in soil extracts interferes with the measurement using the UV spectrophotometer. Interference from organic matter in the measurement of pesticide concentration can be overcome by removing organic matter using activated carbon. However use of activated carbon in pesticide analysis is likely to affect the measurement because of the sorption of pesticide by activated carbon. Interference in HPLC using a UV detector for the analysis of 2,4-D was overcome by using a guard column. Because of the interference of organic matter, the minimum concentration obtained using a UV spectrophotometer was much higher than GLC/HPLC.

Table 3.2 Effect of increasing amount of soil extract on the recovery of ^{14}C pesticides (33 Bq of ^{14}C was added)

(a) Tokomaru

Pesticides	% Recovery*					
	Volume of soil extract					
	0 (0) ^a	0.2 (0.086)	0.4 (0.102)	0.6 (0.124)	0.8 (0.158)	1.0 (0.197)
Atrazine	100 ± 3.5	98.5 ± 4.3	99.0 ± 4.8	97.8 ± 2.8	98.6 ± 6.1	97.2 ± 2.8
2,4-D	99.8 ± 4.6	97.8 ± 2.7	98.6 ± 3.5	99.0 ± 1.5	98.0 ± 2.8	96.9 ± 4.5
Phorate	100 ± 2.8	98.9 ± 3.9	97.6 ± 2.5	96.5 ± 4.8	97.6 ± 2.0	99.2 ± 3.5
Terbufos	99.6 ± 1.6	99.5 ± 4.1	98.5 ± 3.0	98.3 ± 5.4	99.1 ± 4.8	98.5 ± 2.8

(b) Patua

Pesticides	% Recovery					
	Volume of soil extract					
	0 (0)	0.2 (0.180)	0.4 (0.212)	0.6 (0.260)	0.8 (0.287)	1.0 (0.317)
Atrazine	98.9 ± 3.5	96.5 ± 4.3	98.6 ± 4.8	98.8 ± 2.8	99.0 ± 6.1	97.9 ± 2.8
2,4-D	100 ± 5.2	98.8 ± 3.8	98.0 ± 4.6	97.3 ± 2.5	98.6 ± 6.5	97.9 ± 3.6
Phorate	99.5 ± 2.3	98.9 ± 3.6	97.9 ± 4.0	98.5 ± 5.3	97.1 ± 1.8	98.2 ± 3.6
Terbufos	99.8 ± 3.6	97.5 ± 4.3	99.5 ± 5.4	98.0 ± 3.5	99.5 ± 2.6	99.0 ± 4.0

^a The values within bracket indicate the intensity of colour as measured by the optical density at a wavelength of 210.

* Standard error of mean

Table 3.3 Linear range, minimum concentration and soil solution concentration of pesticides as measured by different methods

	Pesticides	UV	HPLC	GLC	LSC
Linear range ($\mu\text{mol L}^{-1}$)	atrazine	9.30-74.4		0-74.4	
	2,4-D	9.05-72.4	0-72.4		
	phorate	7.69-38.5		0-38.5	
	terbufos	6.94-13.9		0-13.9	
Minimum concentration ($\mu\text{mol L}^{-1}$)	atrazine	9.30		2.32	0.46
	2,4-D	9.05	2.26		0.45
	phorate	7.69		1.92	0.38
	terbufos	6.94		1.74	0.35
Soil solution concentration ($\mu\text{mol L}^{-1}$) [*]	atrazine	13.95		2.32	2.13
	2,4-D	13.57	2.26		2.46
	phorate	11.53		1.85	1.96
	terbufos	10.41		1.60	1.54

^{*} Concentration of pesticide in solution after sorption measurement

The UV spectrophotometer, GLC/HPLC and tracer techniques were used to measure the concentration of pesticides in an equilibrium solution after sorption by soils (Table 3.3). The results indicate that the method involving UV spectrophotometry overestimated the equilibrium concentration and so results in an underestimation of sorption. There was a good agreement between GLC/HPLC and tracer techniques in the measurement of equilibrium concentrations. Since, the use of ^{14}C labelled compounds makes the sorption measurement easier and less laborious, the radiotracer method was used in all subsequent experiments.

3.4.5 Recovery of ^{14}C labelled pesticides in soil

Recovery of ^{14}C pesticide sorbed onto the soil particles was examined by two methods: (i) direct extraction with scintillation cocktail and (ii) dry combustion. These methods are discussed below.

3.4.5.1 *Direct extraction with scintillation cocktail*

The recovery of ^{14}C pesticides sorbed by the Egmont soil was examined using dioxane and toluene based scintillation cocktails and the results are presented in Table 3.4.

Table 3.4 Recovery of ^{14}C labelled pesticides by a direct extraction technique

Cocktail	Pesticide	Shaking time (min) ^a			
		15	30	60	120
Dioxane	atrazine	79 ± 2.5	94 ± 4.0	93 ± 3.5	94 ± 5.0
	2,4-D	82 ± 3.2	90 ± 1.6	97 ± 2.3	95 ± 4.3
	phorate	80 ± 4.0	93 ± 2.3	94 ± 3.4	93 ± 1.3
	terbufos	78 ± 3.5	92 ± 4.6	96 ± 2.1	98 ± 3.6
Toluene	atrazine	96 ± 3.9	98 ± 5.2	98 ± 4.4	95 ± 2.9
	2,4-D	90 ± 4.3	99 ± 5.9	97 ± 4.0	101 ± 5.6
	phorate	92 ± 2.5	97 ± 4.3	96 ± 3.5	99 ± 4.6
	terbufos	93 ± 1.9	94 ± 3.6	97 ± 2.5	97 ± 3.8

^a standard error of mean

The recovery increased with increasing time of extraction. However, almost complete recovery (> 93%) of the sorbed ^{14}C pesticides was achieved after 60 minutes of shaking. Initially there was a slight increase in the recovery with the dioxane based cocktail. However the difference in recovery between the cocktails became narrow after 60 minutes of shaking. The results show that toluene or dioxane present in the scintillation cocktail can act as a good partition solvent and thereby can achieve almost complete recovery of the ^{14}C pesticides remaining in soil.

3.4.5.2 Dry combustion

The recovery of ^{14}C from spiked soil samples was nearly complete for all the pesticides (Table 3.5). The recovery ranged from 93.8-96.4 percent. Similarly Cheng and Farrow (1976) reported ^{14}C recoveries of between 93 and 103 percent for 2,4-D, picloram and methabenzthiazuron.

Table 3.5 Percent recovery of ^{14}C labelled pesticide using a combustion technique

Soil	Percent recovery of ^{14}C in labelled pesticide ^a			
	atrazine	2,4-D	phorate	terbufos
Egmont	93.8 ± 1.2	96.4 ± 0.7	94.8 ± 1.6	95.6 ± 4.0

^a Standard error of mean

Although both the methods are reliable, the direct extraction method described is simple to use. Hence the direct extraction method is followed for mass balance studies in the subsequent experiments.

3.4.6 Sorption of the pesticides by centrifuge tubes

A range of centrifuge tubes, which included polycarbonate, polypropylene and glass tubes, have been used for sorption measurements. The sorption of pesticides onto

these materials was examined by shaking the pesticides for different time intervals. The results indicate that there was a decrease in the solution concentration of atrazine, 2,4-D, phorate and terbufos when the pesticide solution was shaken in polypropylene, polycarbonate or glass tubes fitted with silicon rubber caps. However, complete recovery of the pesticides was obtained following the extraction of the tubes with a scintillation cocktail suggesting negligible amounts of degradation or volatilization had occurred. The results indicate that the decrease in the concentration of pesticide in solution after shaking for different periods was due to sorption onto the tubes. Negligible amounts of atrazine and 2,4-D were sorbed onto polypropylene and glass tubes fitted with a teflon caps, whereas 10-20% was sorbed onto polycarbonate and glass tubes fitted with silicone rubber caps (Table 3.6).

Table 3.6 Pesticide sorption to centrifuge tubes

Material	Pesticide	% recovered in solution ^a			
		30 min	60 min	120 min	240 min
Polycarbonate	atrazine	94.0 ± 3.6	90.9 ± 2.4	86.2 ± 4.5	80.5 ± 1.3
	2,4-D	92.7 ± 0.5	90.5 ± 1.5	85.3 ± 2.0	82.0 ± 3.2
	phorate	77.0 ± 2.2	70.3 ± 0.4	56.8 ± 1.5	37.3 ± 2.0
	terbufos	70.9 ± 1.4	63.2 ± 2.0	50.0 ± 0.6	31.9 ± 4.8
Polypropylene	atrazine	98.9 ± 0.8	100.2 ± 1.6	97.8 ± 0.5	99.4 ± 1.2
	2,4-D	99.6 ± 1.5	101.4 ± 2.8	98.9 ± 1.8	99.0 ± 4.6
	phorate	68.8 ± 2.1	52.3 ± 3.4	35.3 ± 2.2	28.2 ± 1.4
	terbufos	72.0 ± 3.5	48.5 ± 2.4	32.6 ± 0.6	27.5 ± 1.5
Glass tubes with silicone rubber	atrazine	90.6 ± 1.5	86.4 ± 2.3	88.0 ± 1.1	83.8 ± 0.8
	2,4-D	88.5 ± 1.8	80.2 ± 3.5	83.3 ± 2.6	86.6 ± 1.3
	phorate	66.3 ± 2.4	42.6 ± 1.0	30.7 ± 3.6	26.5 ± 0.4
	terbufos	74.6 ± 1.5	50.3 ± 2.6	26.2 ± 2.0	22.6 ± 4.1
Glass tubes with teflon cap	atrazine	101.3 ± 2.0	98.0 ± 3.6	97.9 ± 2.3	98.6 ± 0.6
	2,4-D	100.8 ± 1.7	97.5 ± 4.1	99.0 ± 0.5	99.8 ± 3.5
	phorate	99.8 ± 2.5	96.7 ± 0.7	98.6 ± 3.2	97.4 ± 1.6
	terbufos	99.0 ± 1.2	97.2 ± 2.6	98.1 ± 0.7	98.5 ± 1.9

^a standard error of mean

A significant amount of phorate and terbufos was sorbed onto polycarbonate, polypropylene and glass tubes fitted with silicone rubber caps whereas a negligible amounts were sorbed onto glass tubes fitted with teflon caps. Topp and Smith (1992) reported that atrazine and metolachlor sorbed rapidly to silicone rubber, tygon and nalgene materials. Chlordane sorption onto polypropylene centrifuge tube has been reported by Logan *et al.* (1992). Based on these results sorption of pesticides was measured using glass tubes with teflon caps in all the subsequent experiments.

3.5 CONCLUSIONS

The important conclusions drawn from this experiment are:

1. In soils the presence of water soluble organic matter interferes with the measurement of pesticide in soil solution using UV spectrophotometry.
2. Pesticides in soil solution during sorption studies can be measured quantitatively by GLC/HPLC or radiotracer techniques. Sometimes HPLC requires a guard column to remove the soluble soil carbon.
3. The pesticides in soil solution can be measured quantitatively by the radiotracer technique. Measurement of quenching indicated that there was no interference from soil organic matter on the measurement of radioactivity.
4. For mass balance studies of pesticides during sorption and movement, the pesticide remaining in a soil can be estimated by direct extraction of that soil with a scintillation cocktail containing an organic solvent.
5. Glass tubes fitted with teflon caps are most suitable for pesticide sorption studies under laboratory conditions.

CHAPTER 4

EFFECTS OF THE DRYING OF SOILS ON SORPTION AND LEACHING OF AN INORGANIC PHOSPHATE ION AND ORGANIC PESTICIDES

4.1 INTRODUCTION

One of the important properties of a soil, that determines the extent of leaching and redistribution of nutrient ions and pesticides, is its sorption capacity for the solutes concerned (Bailey and White, 1970; Wann and Uehara, 1978). Sorption of these solutes by soils is affected by the properties of the soil and the solute and by experimental variables (Barrow, 1978; Pignatello, 1989).

Drying, freezing and refrigeration are some of the processes commonly employed to facilitate the handling and storage of soil samples for any chemical, biological and physical analysis in the laboratory. Further, in many situations, topsoils are subjected to drying during summer months. Drying soils has been shown to alter both the physical and the chemical properties of the soils and some of the reported changes due to drying are presented in Table 4.1.

Briefly, some of the changes due to drying soils include: an increase in the solubility of the organic matter (Raveh and Avimelech, 1978; Bartlett and James, 1980; Haynes and Swift, 1985a), an increase in the aggregate size (Kubota, 1972), a decrease in the amorphous and crystalline iron and aluminium (Comfort *et al.*, 1991), an enhancement of the crystallization of iron and aluminium hydrous oxides (Sims and Ellis, 1981), and an increase in the negative charge on the soil surfaces (Balasubramanian and Kanehiro, 1978). These changes in soil properties resulting from drying are likely to influence the retention and leaching of nutrient ions and pesticides by soils.

It has been shown that air-drying of soils increased the sorption of phosphate (Haynes and Swift, 1985a) and sulphate (Comfort *et al.*, 1991), whereas it decreased the sorption of nitrate (Balasubramanian and Kanehiro, 1978). However, there has

Table 4.1 Summary of literature on the effects of drying on soil properties

Soils	Drying treatments	Observation	Reference
1 soil - USA	moist, air-dry	Drying of soils increased the soluble organic carbon and surface acidity. The effect of drying on soil pH has been found to be variable.	Bartlett and James (1980)
1 soil - Israel	moist oven-dry (105°C) oven-dry (40°C)	Drying increased the amount of soluble organic carbon and acidity whereas it decreased the soil pH.	Raveh and Avimelech (1978)
11 soils - New Zealand	moist, air-dry	Drying caused an increase in the soluble carbon, EDTA Fe and Al and a decrease in soil pH of approximately 0.1 pH units. Drying had no effect on oxalate or pyrophosphate extractable Fe and Al.	Haynes and Swift (1985a)
6 soils - USA	Field-moist, air-dry, cool and frozen	Air-drying of soils caused a decrease in the EDTA and oxalate extractable Fe and Al, whereas it decreased the soil pH.	Comfort <i>et al.</i> (1991)
9 soils - New Zealand	moist, air-dry	Drying of soils caused an increase in the soluble organic matter, EDTA Al and Fe, but had no significant effect on pH, amorphous Al and Fe and CEC.	Haynes and Swift (1985b)
11 soils - Japan	moist, air-dry, oven-dry	Poor dispersibility and the irreversible aggregate formation due to drying has been observed.	Kubota (1972)
2 soils - Hawaii	field-moist, air-dry, oven-dry	Drying of soils increased the negative charge on the soil surface and decreased the pH.	Balasubramanian and Kanehiro (1978)

been only limited study of the effect of drying on the sorption of organic pesticides (Rutherford and Chiou, 1992).

Solubilization of organic matter due to drying soils can have a profound effect on the sorption of organic pesticides. For example, movement of pesticides in soil was found to be accelerated by the movement of soluble organic matter (Ballard, 1971). It has also been shown that the removal of water during drying is likely to reduce the competition of water molecules for sorption sites (Rutherford and Chiou, 1992).

In New Zealand large amounts of phosphatic fertilizers (1.2 m.t) and pesticides (4000 tonnes active ingredients) are used annually to overcome P deficiency and to control pests and weeds on pasture soils (White, 1992; AGCARM, 1993). The fate of these solutes in soils depends to some extent on the drying conditions of the soils.

4.2 OBJECTIVES

The main objective of the work reported in this thesis was to examine the sorption of pesticides. Therefore, it was considered important to examine the effect of soil drying on the sorption of pesticides. The important objectives of this experiment were:

- (i) to examine the effects of drying soils on the sorption and leaching of an inorganic nutrient ion (phosphate) and the organic pesticides 2,4-D and phorate.
- (ii) the effects of drying on other soil properties in relation to sorption.

4.3 MATERIALS AND METHODS

4.3.1 Soils

Top-soil samples (0-15 cm) representing two soil series (Patua and Tokomaru) were used in this study. The Patua silt loam (Typic Hapludand) is an allophanic soil originating from andesitic ash, the Tokomaru silt loam (Typic Fragiaqualf) is a non-allophanic soil originating from siliceous loess. The soils have varying clay mineralogy, clay content (Jackson, 1956), organic carbon (Bremner and Tabatabai,

1971), oxalate-extractable Fe and Al (McKeague and Day, 1966) and cation-exchange capacity (Blakemore *et al.*, 1987), but are predominantly of low pH (Table 4.2).

Table 4.2 **Some characteristics of the soils used**

Parameter	Patua silt loam	Tokomaru silt loam
Parent material	Andesitic tephra	Siliceous loess
Classification	Typic Hapludand	Typic Fragiaqualf
Clay content (%)	18.0	24.7
Dominant clay mineral	Allophane (23%) Volcanic glass (67%)	Mica/Illite (54%) Halloysite (36%), Vermiculite (3%)
pH (H ₂ O)	5.56	5.80
Organic Carbon (%)	8.2	3.2
CEC (meq 100g ⁻¹)	36	20

Fresh soil samples were collected in field-moist condition, passed through a 2 mm sieve and stored at < 4°C. The soil samples were dried by three different methods. These included: freezing overnight followed by freeze drying for 3 days; air-drying at room temperature (20-25 °C) for one week; oven-drying at 60°C for 24 h. The latter treatment was used to simulate the removal of water from soil under field condition during summer months. Although drying at 60°C is considered to be more likely at the upper end of simulated drying under field conditions, we chose this temperature because the soil was dried only for a short period. We assumed the effect on soil properties (e.g., P sorption) of drying at higher temperature for a shorter period is the same as that of drying in the field at lower temperatures for longer period (Barrow and Shaw, 1975).

Sorption of phosphate and pesticides was measured in all soil samples. Also the effect of drying on soluble organic carbon (Tate *et al.*, 1988) and 0.05 M EDTA and

oxalate extractable Fe and Al (Farmer *et al.*, 1980) was measured (Table 4.3).

4.3.2 Pesticides

Two pesticides (2,4-D and phorate) of contrasting chemical properties were used in this experiment. 2,4-D is a weak acid widely used to control broadleaf weeds in pasture. Phorate is a non-ionic pesticide used to control stem weevil in newly sown pasture and crops. The other important properties of the pesticides are discussed in Chapter 3.

4.3.3 Phosphate sorption

Subsamples (1g) of soil were shaken with 10 ml solutions of 0.01 M CaCl_2 containing varying amounts of phosphate ($0\text{--}15.6 \text{ mmol L}^{-1}$) added as KH_2PO_4 in an end-over-end shaker for 40 h at 25°C . At the end of the shaking period the pH was measured and the solution separated by centrifugation (110 Hz) and filtration. Phosphate concentration in the solution was measured by the method of Murphy and Riley (1962). The amount of the sorbed ion was determined from the difference between the amount added and that remaining in the solution.

4.3.4 Pesticide sorption

Soil samples (1g) were shaken with 10 ml solutions of 0.01 M CaCl_2 containing a range of concentrations of ^{14}C labelled (ring) 2,4-D ($0\text{--}72.4 \mu\text{mol L}^{-1}$) and methylene ^{14}C phorate ($0\text{--}61.5 \mu\text{mol L}^{-1}$) for 4 h at 25°C in an end-over-end shaker. At the end of the equilibration period the solution was separated by centrifugation (110 Hz) and filtration. The ^{14}C activity of the filtrate was measured using a liquid scintillation counter and the final concentration of the pesticides in the solution was determined using the following equation.

$$\text{Final concentration} = \frac{\text{initial concentration}}{^{14}\text{C initial}} * ^{14}\text{C final} \quad (4.1)$$

16 mg/L 32 mg/L

This equation is valid only if it is assumed that the pesticides have not been degraded and that all the ^{14}C remains associated with the parent compounds. Measurement of ^{14}C pesticides remaining in the soil after sorption and subsequent mass balance calculations indicated that there was no evidence for degradation of pesticides within the 4 h equilibration period. The amount of pesticides sorbed was calculated as the difference between the initial and the final concentration of pesticides in solution.

4.3.5 Kinetics of phosphate and pesticide sorption

The effect of drying on the rate of sorption of phosphate and pesticides was investigated using the field-moist and oven-dried Patua soils. These two samples were used because they differed widely in the extent of phosphate and pesticide sorption. Soil samples were shaken with 0.01 M CaCl_2 solutions containing a range of concentrations of phosphate or pesticides on an end-over end shaker at a soil : solution ratio of 1:10 for various periods ranging from 5 min to 96 h. The amount of sorbed phosphate or pesticide was measured as before. The amount of ^{14}C pesticides remaining in the solution and retained by the soil were measured after the sorption measurements. The mass balance calculations indicated that most (99 to 101%) of the added pesticides was accounted for and there was no evidence for degradation of 2,4-D or phorate within the periods used for the kinetic study.

The amount of P and pesticides sorbed at a constant equilibrium concentration (4 mM P and 4 μM 2,4-D or phorate) for different equilibration periods was interpolated from the sorption isotherm. The relationship between time and sorption at a constant equilibrium concentration was fitted to the Freundlich kinetic equation (Barrow, 1983).

4.3.6 Leaching experiments

Leaching experiments were conducted using soil columns in glass tubes (100 mm long and 15 mm internal diameter). The columns were packed to different depth at a bulk density of 0.81 g cm^{-3} with field-moist, freeze-dried, air-dried and oven-dried Tokomaru and Patua soils. The columns were preleached with three pore volumes of 0.01 M CaCl_2 . Preleaching was carried out to attain a saturated condition prior

to the addition of a pulse of 2,4-D, phorate or phosphate. Although the concentration of soluble carbon in the leachate was not measured, it was anticipated that preleaching would have removed some of the organic carbon solubilized during the initial drying of the soils. The removal of the soluble carbon is likely to have an effect on the subsequent leaching of pesticides.

A pulse of 10 mmol of P as KH_2PO_4 or 20 μmol of 2,4-D or phorate as ^{14}C labelled compound was added to the soil surface. The columns were then leached with three pore volumes of 0.01 M CaCl_2 solution. At the end of the leaching period, the soil in the column was mixed thoroughly and the sorbed P was extracted with 0.1 M NaOH (McLaughlin *et al.*, 1977) and the 2,4-D and phorate with scintillation solution (Lavy *et al.*, 1972). The concentration of P and the activity of ^{14}C 2,4-D and phorate in the soil extracts and in the leachate were determined as described in section 4.3.3 and 4.3.4.

4.3.7 Statistical analysis

Differences between treatment means were tested for significance using analysis of variance (SAS, 1985).

4.4 RESULTS AND DISCUSSION

4.4.1 Effect of drying on soil properties

The effect of drying on some of the soil properties is presented in Table 4.3. Moisture content, measured by oven-drying (105°C), of the field-moist soils was 42.3 and 60.9% for Tokomaru and Patua soils, respectively which was close to the field capacity of the soils. The moisture content decreased to 2.40 and 1.86% during freeze-drying, 7.4 and 11.2% during air-drying and 1.62 and 3.95% during oven-drying (60°C) for the Tokomaru and Patua soils, respectively. In the field the moisture content of the surface soil (10 cm depth) of Tokomaru silt loam varies from approximately 47% during winter (July) to approximately 9% during summer (March) (Scotter *et al.*, 1979).

Table 4.3 Effect of drying on some of the soil properties (freeze-dry basis)

Property	Patua silt loam				Tokomaru silt loam			
	Moist	Freeze-dry	Air-dry	Oven-dry	Moist	Freeze-dry	Air-dry	Oven-dry
Moisture (%)	60.94	2.40	11.16	3.95	42.31	1.86	7.44	1.62
pH (H ₂ O)	5.30	5.40	5.56	5.04	5.53	5.37	5.80	5.04
Soluble organic carbon (mg L ⁻¹)	224	233	306	476	96	100	115	1844
Oxalate	Fe(%)	1.21	1.23	1.30	1.51	0.36	0.34	0.38
	Al(%)	4.22	4.20	4.40	4.74	0.08	0.09	0.09
EDTA	Fe(%)	0.027	0.026	0.035	0.039	0.20	0.20	0.26
	Al(%)	0.27	0.28	0.48	0.56	0.11	0.10	0.20
CEC (me 100g ⁻¹)	30.27	29.55	31.18	30.05	19.11	20.10	21.28	20.86

The pH of the soil increased with air-drying but decreased with oven-drying. However, freeze-drying had no consistent effect on pH. The effect of air-drying on soil pH has often been found to be variable (Bartlett and James, 1980) and has been attributed to the transformation of the various ions in soils. The increase in pH with air-drying in this experiment may be due to the mineralization of organic nitrogen to ammoniacal nitrogen (ammonification), which results in the release of hydroxyl ions. It has been found that oven-drying often decreases the pH, and this has been attributed to the increasing hydrolysis of the water molecules causing an increase in their proton donating ability, or the breaking of hydrogen bonds within the soil organic matter resulting in the exposure of new acidic groups (Raveh and Avimelech, 1978). There was no effect of drying on the CEC and total organic carbon. However there was a substantial increase in the amount of soluble organic carbon with air-drying and oven-drying (Table 4.3).

Both EDTA and oxalate extractable iron (Fe) and aluminium (Al) increased with air-drying and oven-drying. These increases were higher in the Patua than in the Tokomaru soil. However, there was no difference between freeze-dried and moist soils on EDTA and oxalate extractable Fe and Al. The EDTA extractable Fe and Al include mostly organically bound metal ions (McBride *et al.*, 1983), indicating that drying increased the extractability of organic matter to which these metal ions were complexed. Oxalate extractable Fe and Al originate mainly from the short range order hydrous oxides (Parfitt and Childs, 1988). It has generally been observed that drying increases the crystallization of Fe and Al oxides (Sims and Ellis, 1981) and thereby decreases the amount of oxalate extractable Fe and Al. The reason for the increases in oxalate extractable Fe and Al with drying is not clear.

4.4.2 Phosphate sorption

The phosphate sorption isotherms are presented in Figure 4.1. The Patua silt loam sorbed almost 7 times more phosphate than did the Tokomaru silt loam. This can be related to the very different clay mineralogy of these soils. The former soil contains significant amounts of short range order clays, such as allophane and Fe and Al hydrous oxides, whereas the latter soil is dominated by layer silicates, such as illite and vermiculite (Table 4.2). It has been shown that phosphate sorption is higher in

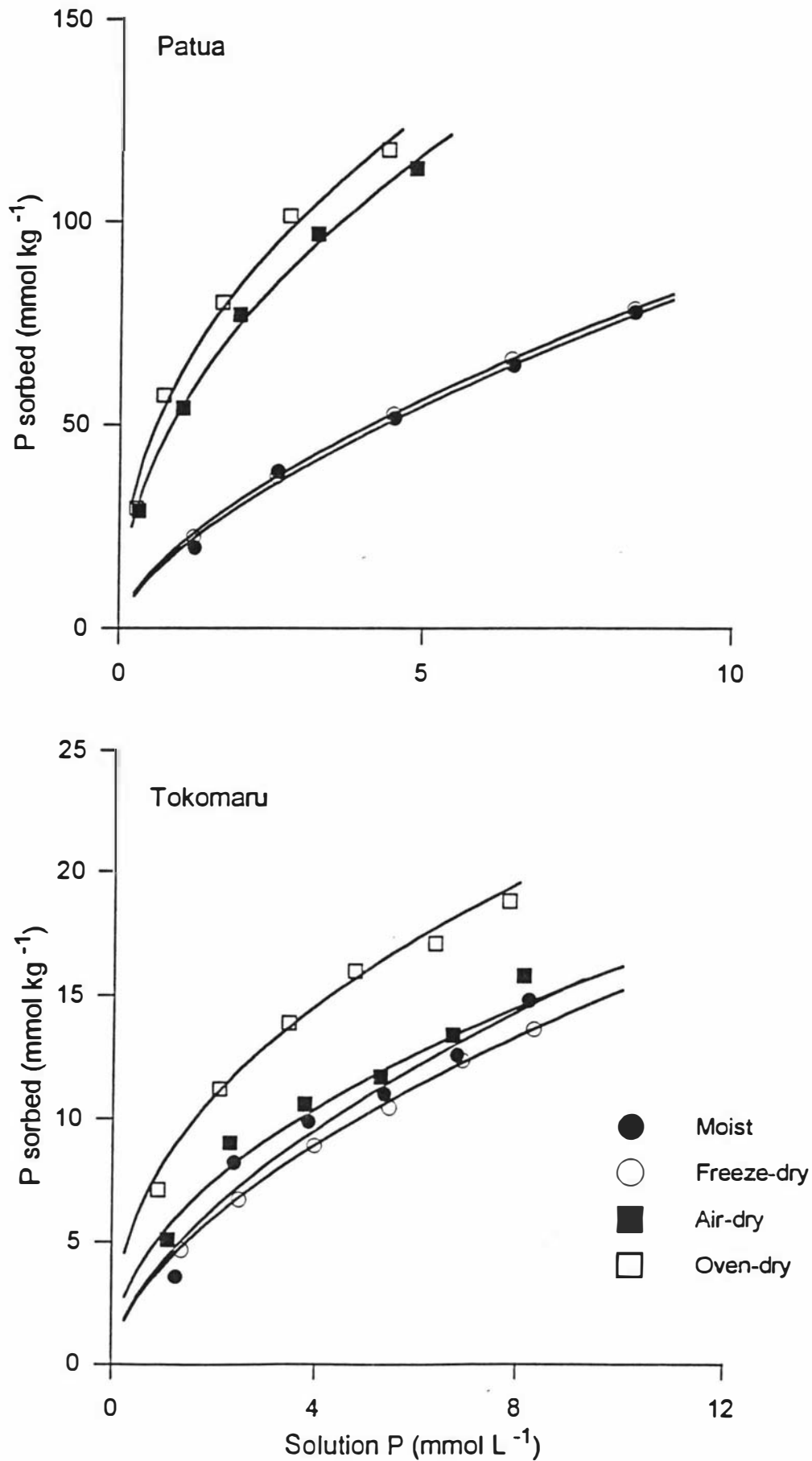


Fig 4.1 Effect of drying on phosphate sorption

soils dominated by allophane and Fe and Al hydroxides than in soils dominated by layer silicates (Parfitt, 1978).

In both soils the sorption isotherms for phosphate were non-linear and were described adequately by the Freundlich equation (Eq 4.2).

$$S = KC^N \quad (4.2)$$

where S is the sorbed concentration (mmol kg^{-1}), C is the equilibrium solution concentration (mmol L^{-1}) and K and N are Freundlich sorption coefficients. Over a limited range of solution concentration the Freundlich equation has often been found to describe the sorption of anions better than other equations (Mead, 1981).

Both air-drying and oven-drying increased the sorption of phosphate in both soils and the effect was more pronounced in the Patua soil than in the Tokomaru soil. However, there was no difference in sorption between the moist and freeze-dried soils (Fig 4.1). Air-drying and oven-drying increased the linear coefficient (K) but decreased the exponential coefficient (N) of the Freundlich equation (Table 4.4). However, no significant difference existed between the freeze-dried and moist soils in K and N values. The increase in K values may be attributed to the formation of new sites for the sorption of phosphate. Barrow and Shaw (1975) have shown that the N values, in general are less affected by experimental variables, such as pH and temperature. Although the reasons for the decrease in N values with drying are not clear, it has been observed that N values decrease with increasing competition by other anions for sorption sites (Murali and Aylmore, 1983) thus increasing the release of native phosphate (Barrow, 1978).

4.4.3 Pesticide sorption

The sorption isotherms of 2,4-D and phorate for the two soils are presented in Figures 4.2 and 4.3. The Patua soil sorbed almost 4 times more 2,4-D and twice as much phorate than did the Tokomaru soil. This can be related to the higher amounts of organic carbon and short range order clay minerals in the former soil

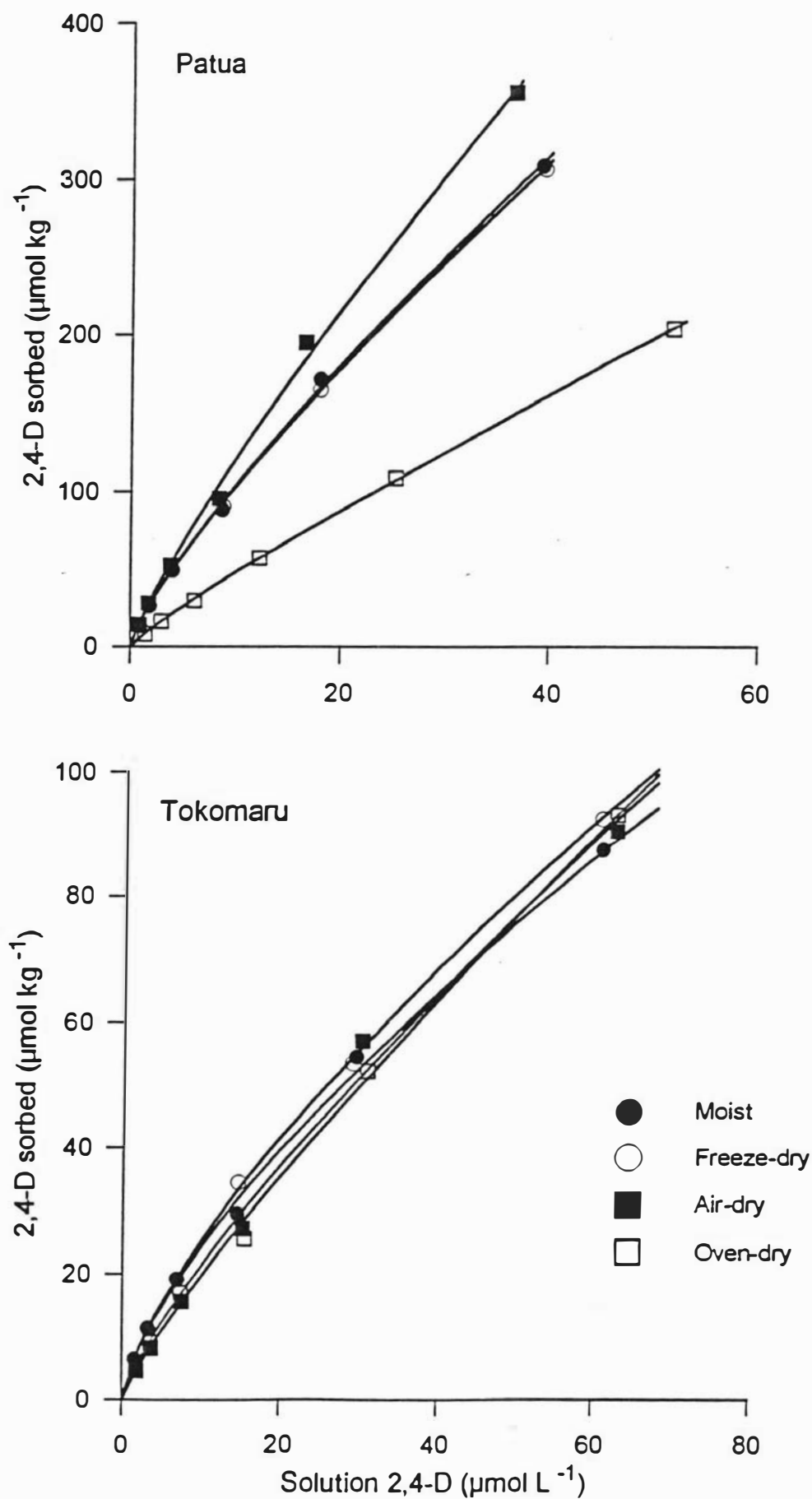


Fig 4.2 Effect of drying on 2,4-D sorption

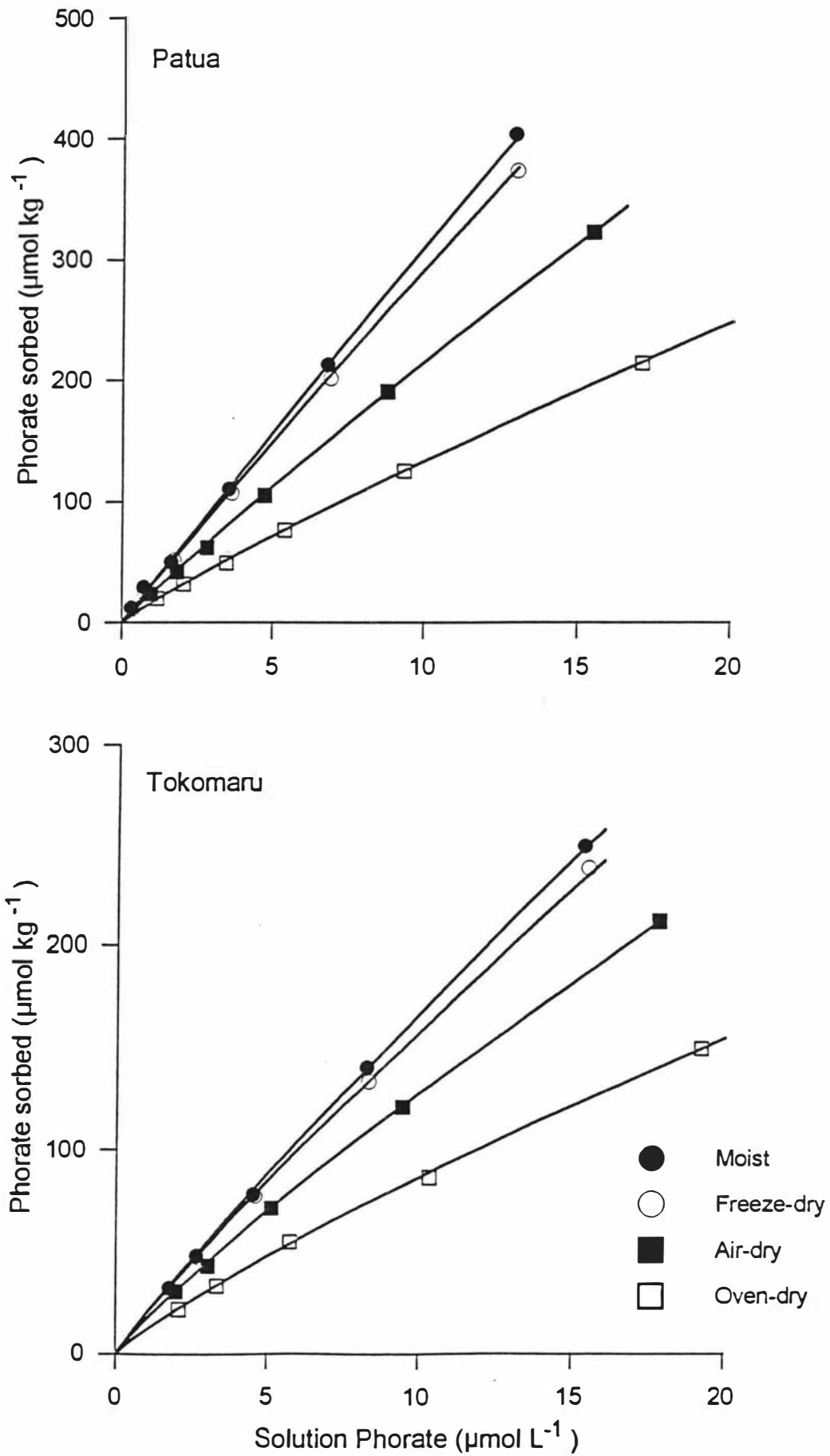


Fig 4.3 Effect of drying on phorate sorption

than in the latter soil. The importance of organic carbon in the sorption of pesticides is discussed in Chapter 5. As in the case of phosphate, the Freundlich equation adequately described pesticide sorption. The N coefficients were much higher than those of phosphate sorption and were close to one in all soils. This indicates that the isotherms were approaching a linear form.

In contrast to phosphate, air-drying slightly decreased the 2,4-D sorption by Tokomaru soil but increased the sorption by Patua soil (Table 4.4). In both soils oven-drying decreased the sorption of 2,4-D and the effect was more pronounced in the Patua than in the Tokomaru soil. Phorate sorption decreased significantly with air-drying and oven-drying in both soils. However, there was no difference between moist and freeze-dry soil for both 2,4-D and phorate sorption. Air-drying and oven-drying decreased both the linear (K) and the exponential (N) coefficients of the Freundlich equation (Table 4.4). The decrease in K values may be related to a decrease in the number of sites for pesticide retention. The N value for organic pesticide sorption is often found to be close to 1 and to varies less in experimental conditions (Kookana *et al.*, 1992). The decrease in N value may be attributed to competition for sorption sites by organic molecules released during drying (Murali and Aylmore, 1983).

The results indicated that in general air-drying and oven-drying increased the sorption of phosphate but decreased the sorption of 2,4-D and phorate by soils and the effect was more pronounced in the Patua than in the Tokomaru soil. Also the effect is greater for non-ionic than ionic pesticides. However the sorption of phosphate and pesticides was similar in both moist and freeze-dried soils. Haynes and Swift (1985a) suggested that the effect of drying on phosphate sorption was transient and tended to disappear after a long period of equilibration.

Recently Bramley *et al.* (1992) observed that the activation energy for the reaction of phosphate with a moist soil sample was similar to that of an air-dry sample. Based on this they suggested that the process involved in the continuous reaction of phosphate with soil is the same, whether the soil is moist or dry. This is consistent with the results of Olsen and Court (1982) who have found that the effect of wetting and drying treatments on phosphate sorption could not be reversed by a longer

Table 4.4 Effect of drying on the Freundlich sorption coefficients (K, N) and retardation factor (R) for Phosphate and pesticides

Soil	Drying treatments	Phosphate			Pesticides					
					2,4-D			Phorate		
		K	N	R	K	N	R	K	N	R
Patua	Moist	19.2	0.65	27.88	17.42	0.89	21.03	32.45	0.98	55.19
	Freeze-dry	20.3	0.63	29.23	17.30	0.90	20.15	31.92	0.96	53.67
	Air-dry	53.9	0.48	70.26	18.41	0.84	23.97	25.21	0.90	41.34
	Oven-dry	62.5	0.44	79.63	6.26	0.80	10.86	17.13	0.89	28.24
	LSD (0.05)	4.15	0.09	4.56	1.87	0.10	4.06	3.36	0.07	4.36
Tokomaru	Moist	4.2	0.59	8.52	3.42	0.79	4.89	20.01	0.92	49.60
	Freeze-dry	4.0	0.58	8.12	3.30	0.83	4.24	19.85	0.90	48.20
	Air-dry	5.3	0.50	9.69	3.14	0.85	3.45	17.23	0.87	40.70
	Oven-dry	8.2	0.42	13.46	2.90	0.71	3.03	12.16	0.85	28.12
	LSD (0.05)	1.45	0.08	2.68	1.16	0.07	1.32	2.10	0.08	4.35

equilibration time of the soil sample with phosphate solution.

4.4.4 Kinetics of phosphate and pesticide sorption

The data on the rate of phosphate, 2,4-D and phorate sorption were fitted to the following Freundlich type kinetic equation (Barrow, 1983):

$$S = Q_1 t^{n_1} \quad (4.3)$$

where S is the amount sorbed at a constant solution concentration (mmol kg^{-1}), t is the time (hr), Q_1 is the sorption at unit time and n_1 is the rate constant. A small value of n_1 indicates that the reaction is fast at first but becomes slower whereas a large value of n_1 indicates that the reaction is slow at first but continues for a long period (Barrow, 1983).

The Freundlich kinetic equation described the sorption data adequately (Fig 4.4). Barrow (1980) observed that at a constant solution concentration the rate of phosphate sorption by a range of soils followed the Freundlich kinetic equation. In the case of organic pesticides, however the rate of sorption has often been found to follow the Freundlich two-site kinetic equation (Kookana *et al.*, 1992). In most studies involving pesticides, the sorption has been measured at a single initial concentration. Under this condition both the sorption and the concentration in solution change with time. The relationship between sorption and time can only be treated as a two dimensional relationship if the concentration is kept constant (Barrow, 1983). It is important, however, to note that even if the equilibrium concentration is kept constant, the sorption kinetics are also affected by the experimental variables (Barrow, 1983), hence it may be difficult to compare the rate of solute sorption between different experiments.

The rate of sorption indicated that more than 90% sorption of both phosphate and pesticides had occurred within the experimental equilibration periods (4 and 40 h for pesticides and phosphate, respectively) used to examine the effect of drying on the extent of sorption. The n_1 values for phosphate (0.32 and 0.42) were higher than those for 2,4-D (0.10 and 0.11) and phorate (0.06 and 0.09). This suggests that

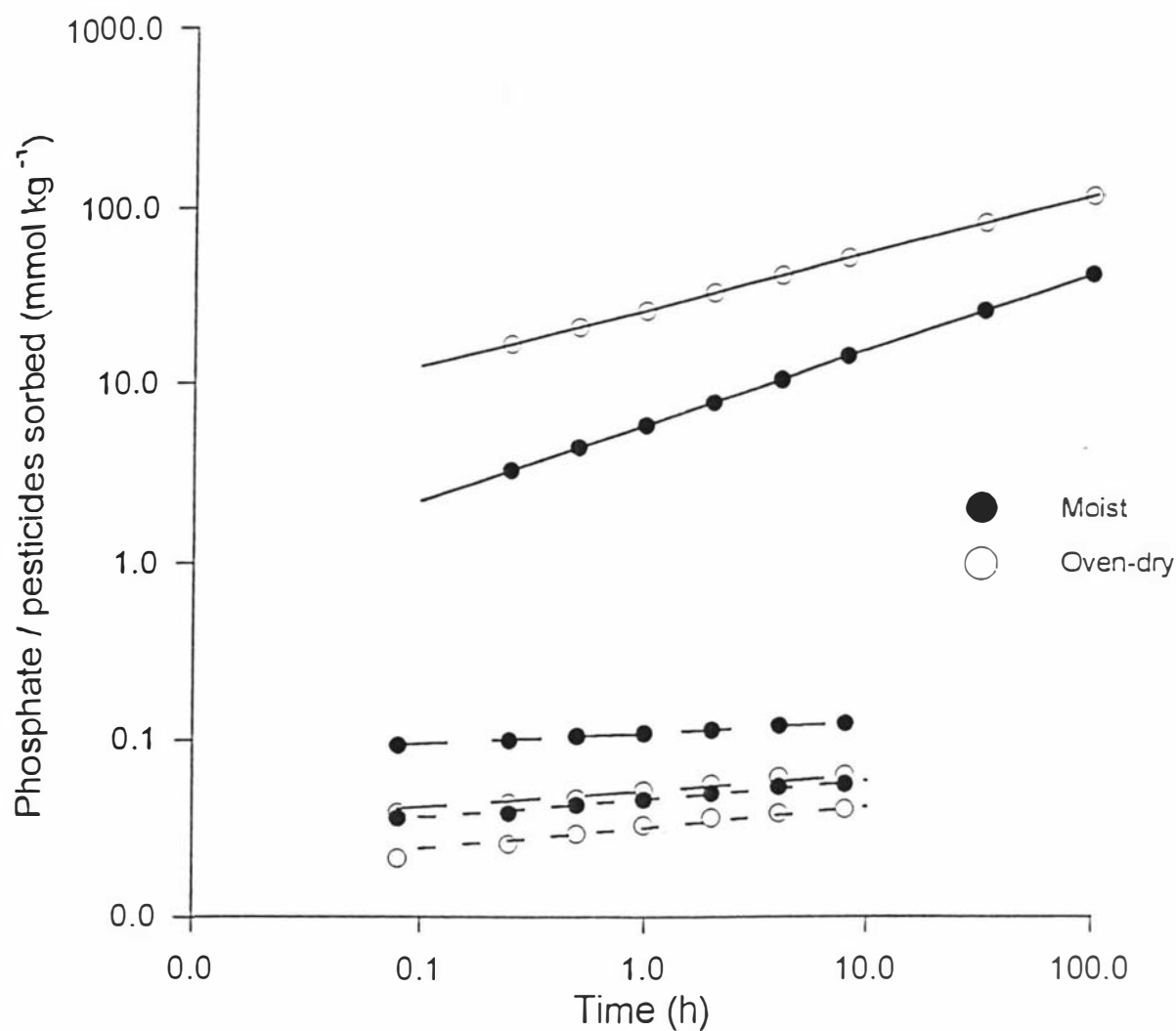


Fig 4.4 Effect of drying on sorption kinetics of phosphate (—), 2,4-D (---) and phorate (—) in Patua soil

Best fitted equation: $S = Q_1 t^{n1}$

	Moist		Oven-dry	
Phosphate :	$S = 5.88 t^{0.42}$	$(r^2 = 0.99)$	$S = 26.05 t^{0.32}$	$(r^2 = 0.99)$
2,4-D :	$S = 0.046 t^{0.10}$	$(r^2 = 0.99)$	$S = 0.032 t^{0.11}$	$(r^2 = 0.98)$
Phorate :	$S = 0.108 t^{0.07}$	$(r^2 = 0.98)$	$S = 0.051 t^{0.09}$	$(r^2 = 0.97)$

phosphate sorption is slow at first but tends to continue for a long period. Whereas 2,4-D and phorate sorption is rapid at first and then becomes slower. These results are consistent with the results of Barrow (1980) for phosphate and of Kookana *et al.* (1992) for pesticides. There was only a small difference in the n_1 values between the moist and oven-dry soils. This suggests that the rate of sorption was not greatly affected by the drying process.

4.4.5 Leaching of phosphate and pesticides

The results of the column experiments are shown in Table 4.5. As expected from the results in the batch sorption (Fig 4.1), the Patua soil retained all of the phosphate in the column, whereas the Tokomaru soil only retained 74-79% of the added phosphate in the column and the rest was lost in the leachate. However, in both soils there was no effect of drying on the leaching of phosphate. In the case of the Patua soil, as all of the added P was sorbed onto the moist soil, drying, which increased sorption in the batch studies would not be expected to have any effect on leaching. Whereas in the case of Tokomaru soil, since there was some leaching in the field-moist and freeze-dried soil, oven-drying, which increased sorption in the batch studies would be expected to decrease the leaching. The reason for the absence of any drying effect on leaching of P in the Tokomaru soil was not clear, and this illustrates the limitation of extrapolating batch experiments to column leaching. There may be, however some differences in the distribution of phosphate within the soil column between the drying treatments.

In the Patua soil, field-moist, freeze-dried and air-dried soils retained most of the 2,4-D and phorate in the column; whereas the oven-dried soil retained only 80% (2,4-D) and 96% (phorate) of the added pesticide in the column. In the Tokomaru soil, however, between 45-78% of the added 2,4-D and 90-96% of the added phorate was retained in the column and the rest was lost in the leachate. Both air-drying and oven-drying increased the extent of leaching of pesticides.

The mobility of phosphate, 2,4-D and phorate in soils can also be estimated in terms of the retardation factor (R) calculated according to the following relationship (Rao and Jessup, 1983).

Table 4.5 Effect of drying on the percent distribution of added P or pesticides in the soil column and leachate

Soil	Drying	Phosphate (%)		Pesticides (%)			
		soil column	leachate	2,4-D		Phorate	
				soil column	leachate	soil column	leachate
Patua	Moist	100	- [†]	100	-	100	-
	Freeze-dry	100	-	100	-	100	-
	Air-dry	100	-	100	-	100	-
	Oven-dry	100	-	80	20	96	4
Tokomaru	Moist	76	24	78	22	95	5
	Freeze-dry	75	25	75	25	96	4
	Air-dry	79	21	65	35	94	6
	Oven-dry	74	26	45	55	90	10
LSD (0.05)		10.6	6.4	8.3	9.1	3.2	4.3

[†] Negligible amount of P or pesticides was found in the leachate.

$$R = 1 + \left(\frac{\rho}{\theta}\right) NKC^{N-1} \quad (4.4)$$

Where R is the retardation factor, which is an index of mobility; ρ is the soil bulk density (g cm^{-3}); θ is the volumetric water content ($\text{mm}^3 \text{ mm}^{-3}$), K and N are Freundlich sorption coefficients and C is the equilibrium solution concentration. It should be noted that the higher the R value, the greater the retention of ions by soil and the lesser the mobility.

The calculated R values for phosphate and pesticides for the soils are reported in Table 4.4. The R values for phosphate and pesticides were higher for the Patua soil than the Tokomaru soil. There was a marked increase in R value for phosphate after drying in both the soils. In the case of 2,4-D and phorate a reduction in R value was observed for both soils when oven-dried.

In summary, the results suggest that the effect of air-drying and oven-drying on sorption was not transient (as evident from the kinetic study) and resulted from changes in other soil properties. Drying altered the soil pH and increased the solubility of organic carbon. The effect of these changes on the sorption of phosphate and pesticides is discussed below.

4.4.6 Drying effects on soil properties in relation to phosphate and pesticide sorption

A decrease in soil pH has generally been shown to increase the sorption of both inorganic and organic anions (Barrow, 1989; Barriuso *et al.*, 1992a). In the present study however the changes in soil pH were not large enough to cause the large increase in phosphate sorption observed due to drying. It also failed to explain the decrease in 2,4-D and phorate sorption with a decrease in pH during drying. However it has been reported that non-ionic pesticides (e.g., phorate) are less affected by changes in pH. The effect of pH on the sorption of pesticides was examined in detail and is discussed in Chapter 7.

There was a substantial increase in the amounts of soluble organic carbon with air-

drying and oven-drying. An increase in water soluble organic matter during drying has been attributed to the breaking of hydrogen bonds in the organic matter (Raveh and Avimelech, 1978) or to the lysis of the microbial cells killed during drying (Bartlett and James, 1980). Removal of water from soil through drying will result in the macromolecules in soil organic matter changing into a highly condensed state. Such shrinkage of organic matter may result in the disruption of organo-mineral associations and the subsequent release of some low molecular weight humic components. The effect of drying was therefore likely to result in greater accessibility of phosphate to sorption sites on mineral colloids that were previously obstructed by the presence of organic matter (Haynes and Swift, 1989).

The sorption of organic compounds such as pesticides in soil is considered to result mainly from partitioning of the compound between the soil solution and the organic phase in the soil (Chiou, 1989). The release of soluble organic carbon during the drying of soils causes the pesticide compound to remain in the soil solution and thereby decreases the apparent sorption onto the soil particles. The soluble organic carbon in particular has been implicated as an agent in the accelerated mobility of pesticides in soils (Pennington *et al.*, 1991). Using both the infra red spectrum and gel-filtration techniques, Madhun *et al.* (1986b) have shown that the soluble organic carbon binds large amounts of herbicides.

In the present experiment, drying had no effect on the leaching of phosphate, whereas it increased the leaching of pesticides. The sorption of pesticides was substantially decreased on oven-drying in both the soils hence the increased leaching. The increased leaching of pesticide may be attributed to the increases in soluble organic carbon during drying. The concentration of soluble organic carbon in soils varies seasonally. During the summer months the soils are subjected to drying in the field and the longer the dry period, the greater the concentration of soluble organic carbon in the soil solution (Chittleborough *et al.*, 1992). In the present study there was a substantial increase in the amounts of soluble organic carbon in the air-dry and oven-dry soils. Preliminary desorption studies have shown that the extraction of soil with soluble organic carbon increases the desorption of the sorbed pesticides. A detailed study on the importance of soluble organic carbon on the sorption and movement of pesticides is reported in Chapter 7.

4.5 CONCLUSIONS

The important conclusions of the experiments reported in this chapter are:

1. Air-drying and oven-drying increased the sorption of phosphate but decreased the sorption of pesticides by soils and the effect was more pronounced in allophanic (Patua) than in non-allophanic (Tokomaru) soil.
2. In column experiments, there was less leaching of phosphate and 2,4-D from the Patua than from the Tokomaru soil. In both the soils, there was no effect of drying on the leaching of phosphate; whereas oven-drying increased the leaching of 2,4-D and phorate.
3. Drying of soils increased the soluble organic carbon. Solubilization of organic matter increases the accessibility of phosphate ions to sorption sites on the mineral surfaces and thereby increases sorption.
4. Soluble organic carbon, however, binds organic pesticides and thereby decreases the apparent sorption of pesticides onto soil particles.
5. Based on the results from this experiment, in all the subsequent experiments field-moist soil was used to examine the sorption of pesticides.

CHAPTER 5

PESTICIDE SORPTION BY ALLOPHANIC AND NON-ALLOPHANIC SOILS

5.1 INTRODUCTION

Increased pesticide use in agriculture has led to a general concern regarding their potential threat as contaminants in the soil and aquatic environment. Sorption and degradation are considered to be the two important processes affecting the fate of pesticides in soils. Pesticide sorption processes are undoubtedly one of the major determinants affecting the persistence, biological activity and movement in soil (Bailey *et al.*, 1968; Haque and Freed 1974). Soil-pesticide interactions have been examined extensively overseas (Bailey and White 1970; Weed and Weber 1974; Rao and Davidson 1980; Yaron *et al.*, 1985). The majority of studies have been limited to pesticide sorption in surface soils. However, given the concern about pesticide movement to groundwaters, it is desirable to understand the influence of surface as well as subsoil horizons on sorption.

A number of soil properties have been shown to influence the sorption of pesticides in soil, including organic carbon content, soil texture, pH, Fe and Al oxide content and clay mineralogy. However, in numerous studies the sorption of pesticides has been found to depend primarily on the organic carbon content of the soil (Hamaker and Thompson 1972; Chiou *et al.*, 1979; Karickhoff *et al.*, 1979; Rao and Davidson 1980; Singh *et al.*, 1989; Johnson and Sims, 1993). Based on this, Hamaker and Thompson (1972) recommended that soil organic carbon content be used to normalize the distribution coefficient (K_d) of soils and the normalized parameter be designated as K_{oc} . The parameter, K_{oc} , of a pesticide is found to be constant for a group of soils and the K_{oc} values for a range of non-ionic pesticides has been found to be correlated with the octanol - water partition coefficient (K_{ow}) of those pesticides. Based on this, several empirical relationships have been developed to predict the K_{oc} of pesticides from their K_{ow} values (Chiou *et al.*, 1979; Felsot and Dahm, 1979; Karickhoff *et al.*, 1979; Briggs 1981a) (Table 2.2).

Table 5.1 Soil descriptions

Series	Depth (cm)	Horizon	USDA Taxonomy*	Parent Material
Patua	0-20	Ah	Typic Hapludand	Andesitic tephra
	20-30	Bw1		
	30-50	Bw2		
	50-68	Bw3		
Egmont	0-20	Ah	Typic Hapludand	Moderately weathered Andesitic tephra
	20-30	Bw1		
	30-46	Bw2		
	46-60	Bw3		
Warea	0-20	Ah1	Typic Hapludand	Andesitic tephra
	20-30	Bw1		
	30-50	Bw2		
	50-60	Bw3		
Hangatahua	0-19	Ah1	Typic Udivitrant	Andesitic sands and gravels
	19-31	Bw1		
	31-65	Bw2		
Papakauri	0-15	Ah	Typic Hapludand	Weathered basalt scoria
	40-60	Bw2		
Kerikeri	0-15	Ah	Typic Haplohumult	Weathered basalt scoria
	25-40	Bw2		
Horotiu	0-20	Ap	Vitric Hapludand	Rhyolitic sands and gravels
	20-35	Bw1		
	35-55	Bw2		
	55-70	Bw3		
Hamilton	0-20	Ah/Ad	Typic Haplohumult	Weathered distinct tephra of Hamilton ash formation
	20-30	Btg1		
	30-60	Btg2		
Tokomaru	0-15	Ah1	Typic Fragiaqualf	Siliceous loess
	15-22	ABg		
	27-45	ABg/Btg		
	45-60	Btg		
Himatangi	0-20	Ah	Typic Udipsamment	Aeolian sand
	20-45	Bw1		

* Keys to Soil Taxonomy by soil survey staff.
 SMSS Technical Monograph No.19.Fourth edition 1990.
 Virginia Polytechnic Institute and State University.

agriculture where high amounts of pesticides are used to control pest and weeds. The parent materials include andesitic tephra, weathered basalt, rhyolitic tephra and siliceous loess. The clay minerals include allophane, vermiculite, kaolinite, halloysite and micaceous minerals. The soil samples were passed through a 2 mm sieve and stored in field moist condition at 4°C.

5.3.2 Soil characteristics

The soil samples were analysed for various physical and chemical properties that are considered important in the sorption and mobility of pesticides. These include, particle size analysis, pH, organic carbon, cation exchange capacity (CEC) and oxalate extractable Fe and Al. The particle size analysis was carried out following the international pipette method (Black, 1965) to estimate the percent clay, silt and sand. The pH of the soils was determined on a 1:2.5 soil-water suspension and organic carbon by dry combustion using a Leco furnace (Bremner and Tabatabai, 1971). The CEC was determined by the ammonium acetate method (Blakemore *et al.*, 1987) and the oxalate-extractable Fe and Al was determined by the method outlined by McKeague and Day (1966). The concentration of Fe and Al were determined by atomic absorption - spectrophotometry.

5.3.3 Pesticides

The five pesticides selected for this experiment (metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos) are used extensively in pastoral agriculture and cereal cropping in New Zealand. To have a wide range of K_{ow} values, metsulfuron methyl was included in this experiment. It is to be noted that metsulfuron methyl was not used in the methods of measurement (Chapter 3). These pesticides include both ionic (2,4-D, atrazine and metsulfuron methyl) and non-ionic (phorate and terbufos) forms. All the pesticides used in this experiment were ^{14}C labelled with a radiochemical purity of > 98% (Chapter 3).

5.3.4 Pesticide sorption

Sorption isotherms were determined by a standard batch equilibrium method. Sorption was measured at various concentrations of radioactively ^{14}C labelled atrazine (0, 4.6, 9.3, 18.6, 37.2 and $74.4 \mu\text{mol L}^{-1}$), metsulfuron methyl (0, 2.6, 5.2, 10.5, 21.0 and $42.0 \mu\text{mol L}^{-1}$), 2,4-D (0, 4.5, 9.0, 18.1, 36.2 and $72.4 \mu\text{mol L}^{-1}$), phorate (0, 3.9, 7.7, 15.4, 30.8 and $61.5 \mu\text{mol L}^{-1}$) and terbufos (0, 0.9, 1.8, 3.5 and $6.9 \mu\text{mol L}^{-1}$) using 0.01 M CaCl_2 as a background electrolyte. Three replicates of 1 g soil samples were equilibrated with 10 ml of pesticide solutions by shaking on an end-over-end shaker for 4 h at $25^\circ\text{C} \pm 1$ in glass culture tubes fitted with teflon caps (section 3.4.6). Preliminary experiments showed that more than 90% of the sorption occurs within 1 h (Chapter 4). At the end of the equilibrium period, the suspension was centrifuged at 8000 rpm for 15 min and a one ml aliquot was taken for analysis. The final concentration of pesticides in the solution was calculated using the equation:

$$\text{Final concentration} = \frac{{}^{14}\text{C}_{\text{final}}}{{}^{14}\text{C}_{\text{initial}}} * \text{initial concentration} \quad (5.1)$$

This equation assumes that the pesticide compound has not been degraded and that all the ^{14}C remains associated with the compound. The amount of pesticide sorbed was calculated as the difference between the initial and the final concentration of pesticide in solution. Measurement of the pesticide remaining in the soil after the sorption experiment provided another check that there was no loss of pesticide through degradation within the 4 h equilibration period (Chapter 3).

Preliminary experiments indicated that considerable sorption of phorate and terbufos occurred on the walls of the polypropylene centrifuge tubes (Chapter 3, section 3.4.6). There was no sorption of atrazine, 2,4-D and metsulfuron methyl by the polypropylene tubes. Hence glass culture tubes fitted with teflon caps were used for pesticide sorption studies. Sorption isotherms were determined for all pesticides using surface soil samples from soils developed from four contrasting parent materials (Egmont - andesitic tephra; Papakauri - basaltic scoria; Horotiu - rhyolitic alluvium; Tokomaru - quartz-feldspathic loess). The soils are discussed in section 5.4.1. The results indicated that the isotherms had an approximately linear form (section 5.4.2),

hence the sorption by other soil samples was measured at a single solution concentration of metsulfuron methyl ($10.5 \mu\text{mol L}^{-1}$); atrazine ($18.6 \mu\text{mol L}^{-1}$); 2,4-D ($18.1 \mu\text{mol L}^{-1}$); phorate ($15.4 \mu\text{mol L}^{-1}$) and terbufos ($6.9 \mu\text{mol L}^{-1}$).

5.3.5 Effect of organic carbon removal on pesticide sorption

In a separate experiment the effect of the removal of organic carbon on the sorption of pesticides in soils was examined. The removal of organic carbon was achieved by hydrogen peroxide treatment according to the method of Black (1965). The residual organic carbon content of the soil was also measured.

5.3.6 Statistical analysis

The distribution coefficient (K_d) of each pesticide for each soil was calculated from the following equation:

$$\text{Distribution coefficient } (K_d) = \frac{\text{Sorbed } (\mu\text{mol kg}^{-1})}{\text{Equilibrium concentration } (\mu\text{mol L}^{-1})} \quad (5.2)$$

Multiple regression analysis was carried out between the K_d of pesticides and the various soil properties. The soil properties which describe the variation in pesticide sorption were selected using a stepwise multiple regression analysis. There are two methods of stepwise multiple regression - the step up and step down methods. The step down method was used to select the best combination of soil properties which describe sorption. In this method, the regression of the dependent variable, Y (K_d), on all independent variables, X (soil properties) is calculated. The variable which gives the least contribution, as measured by the significance test, is omitted first. The regression of Y on the remaining X variables is computed and the same rule is applied. The process continues until all the remaining X variables are significant. All statistical analyses were accomplished by use of the Statistical Analysis System (SAS, 1985).

5.4 RESULTS AND DISCUSSION

5.4.1 Soil Characteristics

The ten soil series used in this experiment provide a broad spectrum of soil properties. Based on the clay mineralogy, the soils were broadly grouped into allophanic (Egmont, Patua, Warea, Hangatahua, Horotiu, Papakauri and Kerikeri) and non-allophanic (Tokomaru, Hamilton and Himatangi) soils. These soils are further grouped into four categories, based on their parent materials. These were: andesitic, basaltic, rhyolitic and non-allophanic soils.

The important characteristics of the soils are presented in Table 5.2. The soil pH is slightly acid to near neutral (4.9 to 6.8) and in general increased with depth. The organic carbon varied from 0.2 to 16.7 percent and decreased with depth. The organic carbon in Ah horizons of allophanic soils was higher than in Ah horizons of non-allophanic soils. The important characteristics of the four groups of soils are discussed below.

5.4.1.1 *Allophanic*

(i) **Andesitic**

Four soil series, (Egmont, Patua, Warea and Hangatahua) are derived from andesitic ash erupted from Mt Egmont. The Ah horizons of these soil series had very high sand content (>60%), organic carbon (>6%), CEC (>21 meq 100g⁻¹) and low clay content. The subsoil horizons (BW1 to BW3) contained appreciable amounts of Fe, Al and Si (Table 5.2). These soils contained varying quantities of allophane along with halloysite and the allophane content increased with depth (Palmer *et al.*, 1981).

(ii) **Basaltic**

The Papakauri and Kerikeri soil series are derived from a weathered basalt and contain high organic carbon (>8%) and CEC (>25 meq 100 g⁻¹) in the Ah horizon. Unlike andesitic pumice soils, these soils have low sand and high clay (>40%)

Table 5.2 Some important characteristics of the soil samples

Soil	Horizon	pH (H ₂ O) (1:2.5)	Organic Carbon (%)	CEC (me/100g)	Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)
1. Patua	Ah	5.56	8.2	36.0	57.0	25.1	18.0	1.21	4.22
	Bw1	5.52	8.7	22.6	47.0	26.0	26.2	1.79	5.40
	Bw2	5.37	5.9	20.6	52.2	24.1	23.7	1.79	5.93
	Bw3	5.37	5.2	19.4	55.6	23.0	21.0	1.20	7.10
2. Egmont	Ah	6.07	8.7	39.4	47.0	27.4	25.6	1.02	3.20
	Bw1	6.47	5.3	15.8	54.4	27.0	18.3	1.36	4.74
	Bw2	6.75	2.9	12.1	55.0	21.8	22.7	1.40	4.90
	Bw3	6.78	1.9	13.0	51.8	23.0	25.1	1.77	5.00
3. Warea	Ah1	5.37	11.7	33.3	29.4	44.4	26.2	1.40	4.62
	Bw1	5.55	8.7	22.3	37.0	40.4	22.4	1.50	5.30
	Bw2	5.85	6.6	18.5	48.8	33.6	17.5	1.82	5.81
	Bw3	6.27	4.2	10.6	60.0	27.3	12.7	1.71	5.24
4. Hangatahua	Ah1	5.96	6.9	21.9	65.4	13.2	21.4	1.30	1.40
	Bw1	6.37	1.5	6.7	68.6	16.3	15.0	0.97	1.60
	Bw2	6.53	0.8	4.5	74.4	18.6	7.2	0.94	1.12
5. Papakauri	Ah	5.96	16.7	46.1	9.8	45.0	45.1	3.73	3.63
	Bw2	6.34	7.8	22.6	8.0	43.4	48.0	3.20	5.23
6. Kerikeri	Ah	5.73	8.7	28.5	4.2	38.0	57.7	0.30	0.50
	Bw2	5.16	3.3	8.0	6.0	26.0	68.0	0.25	0.45
7. Horotiu	Ap	5.53	5.8	22.1	34.9	42.0	23.4	0.78	3.30
	Bw1	5.88	4.1	17.0	34.0	46.0	20.0	0.81	3.72
	Bw2	6.30	1.1	12.4	48.2	32.8	19.0	0.82	3.50
	Bw3	5.70	0.2	11.6	86.3	8.5	5.1	0.78	3.41
8. Hamilton	Ah/Ap	5.29	3.4	14.7	27.3	27.0	45.7	0.67	0.32
	Btg1	4.82	1.4	9.9	24.6	34.4	40.2	0.63	0.24
	Btg2	4.98	1.1	11.6	14.7	24.3	60.0	0.66	0.32
9. Tokomaru	Ah1	5.80	3.2	20.0	12.2	62.2	25.6	0.36	0.08
	ABg	5.64	2.3	18.0	8.7	67.3	24.0	0.25	0.12
	ABg/Btg	6.37	1.0	13.8	9.6	66.6	23.8	0.31	0.10
	Btg	6.60	0.6	16.0	7.2	62.6	30.2	0.40	0.09
10. Himatangi	Ah	5.85	2.2	8.9	90.1	7.4	2.5	0.15	0.08
	Bw1	6.48	0.2	4.8	92.4	6.0	1.5	0.11	0.05

contents. The dominant clay minerals are kaolinite, vermiculite, allophane and gibbsite (Orbell and Hewitt, 1981). Both Ah and Bw2 horizon of the Papakauri soil contain higher amounts of Fe and Al than the Kerikeri soil.

(iii) **Rhyolitic**

Two soil series (Horotiu and Hamilton) are derived from Rhyolitic tephra and varied in their physical and chemical characteristics. The Horotiu soil series had high organic carbon (>6%), sand content and CEC (22 meq 100g⁻¹) in the Ah horizon. The Bw1 and Bw2 horizons contained high amounts of Fe and Al and a high sand content. This soil series contained allophane along with volcanic glass (Bruce, 1979). In contrast, the Hamilton soil series had low pH (4.85 to 5.25), a low organic carbon content (3%) and a high clay content in the Aw1 horizon. The clay content increased whereas pH decreased with depth. The clay mineralogy indicated that it contained vermiculite, halloysite and volcanic glass (Bruce, 1979). The Btg1 and Btg2 horizon contained low amounts of Fe and Al.

5.4.1.2 *Non-allophanic*

The other two soil series (Tokomaru and Himatangi) contained lower organic carbon and CEC in all horizons than the other soil series (Table 5.2). The Tokomaru soil series contained higher amounts of hydrous mica, kaolinite and illite (Pollok, 1975). The ABg and Btg horizon of the Tokomaru soil had a high silt content (>50%). The Himatangi soil series had a very high sand content (>90%) and low organic carbon (2.3%) and clay (2.5%) contents.

5.4.2 Pesticide Sorption Isotherms

5.4.2.1 *Sorption isotherms*

Equilibrium sorption isotherms were determined for the pesticides at various concentrations using one top soil from each group (Egmont - allophanic andesitic; Papakauri - allophanic basaltic; Horotiu - allophanic rhyolitic; Tokomaru - non-allophanic). The sorption isotherms obtained are shown in Figure 5.1. All sorption

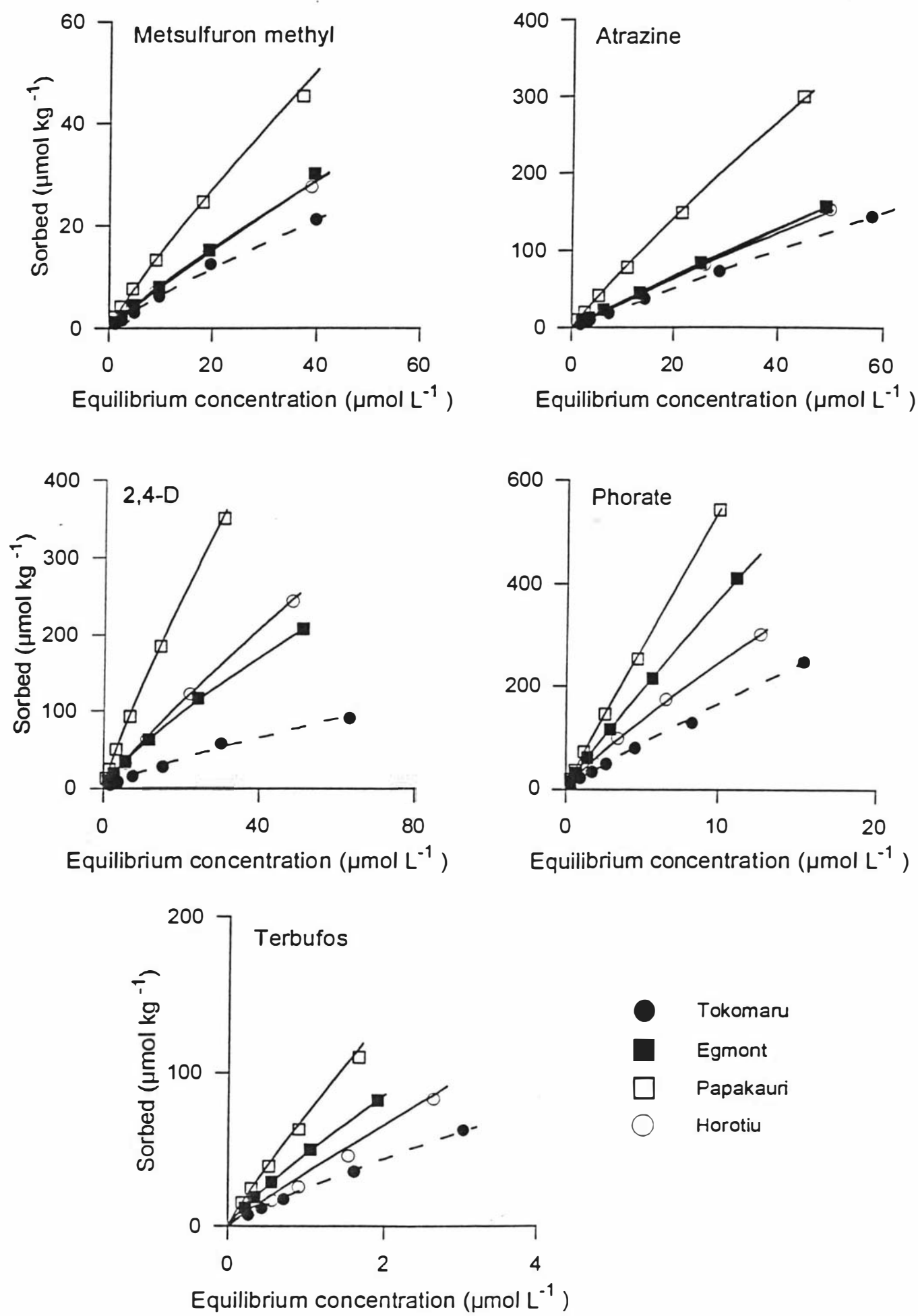


Fig 5.1 Pesticide sorption isotherms in allophanic (—) and non-allophanic (---) soils

isotherms were adequately described by the Freundlich equation with an R^2 value > 0.97 (Eq 5.3).

$$S = KC^N \quad (5.3)$$

where S is sorbed concentration ($\mu\text{mol kg}^{-1}$), C is the equilibrium solution concentration ($\mu\text{mol L}^{-1}$) and K and N are Freundlich sorption coefficients. When $N=1$, Eq 5.3 becomes the linear equation,

$$S = K_d C \quad (5.4)$$

in which K_d is the distribution coefficient (L kg^{-1}).

The parameters of the Freundlich sorption isotherms for the different soils are given in Table 5.3. In the present experiment the N values ranged from 0.86 to 0.93 for metsulfuron methyl, 0.92 to 0.98 for atrazine, 0.79 to 0.89 for 2,4-D, 0.88 to 0.96 for phorate and 0.84 to 0.94 for terbufos in the various soils (Table 5.3). Similar N values that are close to 1 have been reported for pesticide sorption in many studies (Singh *et al.* 1990; Mallawatantri and Mulla, 1992). Compilations of sorption data for many organic compounds (Hamaker and Thompson, 1972) indicated that the N values commonly range between 0.75 and 0.95. Rao and Davidson (1980) also compiled measured N values for a range of ionic and non-ionic pesticides and they found the mean value to be 0.87 with a coefficient of variation of $\pm 15\%$. Because of these findings, the Freundlich sorption coefficient (N) has, for convenience, frequently been assumed in pesticide transport studies, to be equal to one (giving a linear isotherm). The implications of assuming a linear isotherm (i.e., $N=1$) are discussed below.

5.4.2.2 *Linear vs non-linear sorption isotherms*

The error introduced in the estimation of sorption of pesticides by assuming the sorption isotherm to be linear depends upon the values of C and N . This error can be represented by the ratio of sorption obtained by the non-linear (Freundlich) equation (Eq 5.3) to that obtained by the linear equation (Eq 5.4) and is equal to

Table 5.3 Freundlich sorption coefficients (K, N) of pesticides in soils

Sorption coefficients	Soils*			
	Tokomaru	Egmont	Papakauri	Horotiu
Metsulfuron methyl				
K	0.89 ± 0.12	1.13 ± 0.06	1.90 ± 0.15	0.94 ± 0.08
N	0.86 ± 0.02	0.88 ± 0.06	0.89 ± 0.04	0.93 ± 0.16
Atrazine				
K	2.69 ± 0.35	3.95 ± 0.19	9.06 ± 0.68	3.68 ± 0.22
N	0.98 ± 0.05	0.95 ± 0.03	0.92 ± 0.04	0.95 ± 0.03
2,4-D				
K	3.43 ± 0.36	8.95 ± 0.88	18.84 ± 2.0	7.82 ± 0.65
N	0.79 ± 0.02	0.80 ± 0.01	0.86 ± 0.04	0.89 ± 0.05
Phorate				
K	20.01 ± 1.5	43.08 ± 3.2	59.67 ± 4.3	32.56 ± 2.8
N	0.92 ± 0.03	0.94 ± 0.04	0.96 ± 0.02	0.88 ± 0.02
Terbufos				
K	24.42 ± 2.1	47.15 ± 3.8	73.29 ± 4.6	34.60 ± 3.5
N	0.84 ± 0.03	0.87 ± 0.05	0.91 ± 0.03	0.94 ± 0.04

* Standard error of mean

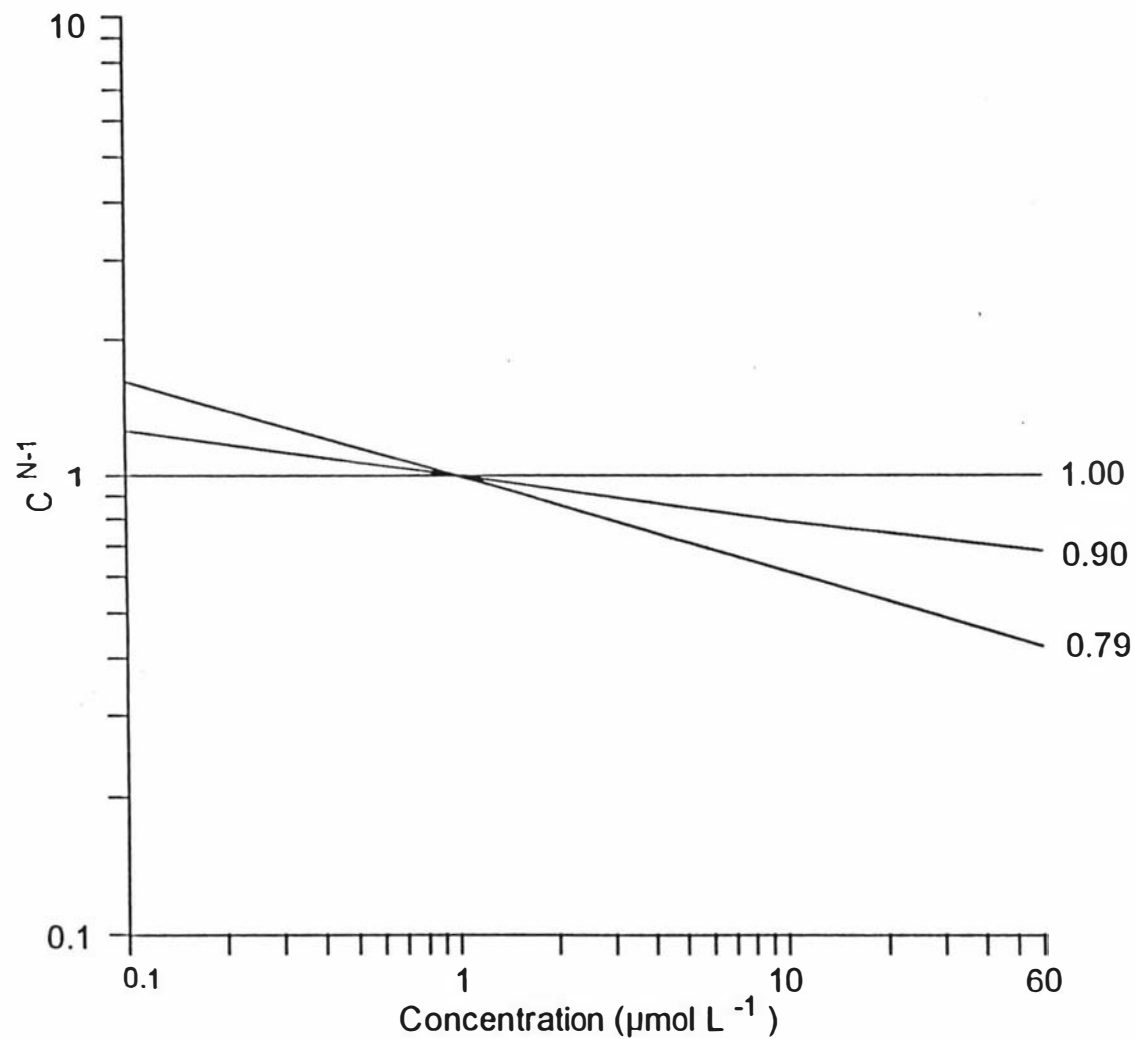
C^{N-1} (Rao and Davidson, 1980). A value of $C^{N-1} = 1$ indicates similar prediction of sorption by linear and non-linear equations. A value < 1 means the amount sorbed is over-predicted, while values > 1 means the amount sorbed is under-predicted by assuming a linear equation (section 2.5.2.4).

A plot of C^{N-1} versus C in the range of 0.1 to 60 $\mu\text{mol L}^{-1}$ (concentrations used for the sorption isotherm) and for N values ranging from 0.79 to 1.0 is shown in Figure 5.2. In the present experiment, for the concentrations used ($C=0.1$ to 60 $\mu\text{mol L}^{-1}$) and the lowest N value observed ($N=0.79$), the C^{N-1} values indicated that by assuming a linear equation ($N=1$) the sorption was under-predicted by a factor of 1.62 at the lowest concentration of 0.1 $\mu\text{mol L}^{-1}$ and over-predicted by a factor of 0.42 at the highest concentration of 60 $\mu\text{mol L}^{-1}$. Rao and Davidson (1980) reported that for $0.1 < C < 10.0$ and $0.5 < N < 1.0$, a C^{N-1} value of 3, and suggested that for many modelling purposes a linear isotherm can be used in lieu of the Freundlich isotherm. Thus, based on the low values of C^{N-1} obtained in our study (0.42-1.62) we felt justified in assuming that the sorption could be described by a linear isotherm in which the K_d values were estimated from sorption measured at a single solution concentration. In several other studies the distribution coefficient (K_d) has also been obtained by measuring the sorption using a single solution concentration (Mallawatantri and Mulla, 1992; Barriuso *et al.*, 1992a).

5.4.2.3 *Distribution coefficient (K_d) of pesticides*

The extent of pesticide sorption by the soils was obtained from the K_d values (Eq 5.2) (Table 5.4). The K_d values of pesticides obtained in this experiment were slightly higher than those previously reported for these compounds. In general, pesticide sorption followed the order: terbufos $>$ phorate $>$ 2,4-D $>$ atrazine $>$ metsulfuron methyl. The order of pesticide sorption is consistent with the octanol-water partition coefficient (K_{ow}) of pesticides. Sorption of all pesticides was higher in allophanic soils than non-allophanic soils. This can be explained by the presence of high amounts of organic carbon in the former soils.

The K_d values averaged over all soils and horizons were 20.7, 18.1, 4.88, 3.24 and 0.54 L kg^{-1} for terbufos, phorate, 2,4-D, atrazine and metsulfuron methyl, respectively



5.2 Deviation from nonlinear isotherm introduced by the linear sorption isotherm. (The numbers near the lines are the values of Freundlich coefficient, N obtained in this experiment)

Table 5.4 Distribution coefficients (K_d , K_{oc}) of pesticides for the soils

Soil	Horizon	Metsulfuron methyl		Atrazine		2,4-D		Phorate		Terbufos	
		K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
		(L kg ⁻¹)									
Patua	Ah	0.61	7	2.00	25	9.60	117	30.28	369	33.45	408
	Bw1	0.82	9	3.34	39	14.86	171	34.74	399	37.57	432
	Bw2	0.47	8	1.11	19	9.84	167	16.38	278	18.20	308
	Bw3	0.45	9	1.16	22	9.36	180	12.46	240	13.58	261
Egnont	Ah	0.67	8	3.60	42	4.81	55	39.58	455	42.03	483
	Bw1	0.90	17	2.78	53	7.49	141	26.23	495	29.97	566
	Bw2	0.34	12	1.38	47	2.15	74	12.95	446	15.07	519
	Bw3	0.23	12	1.06	49	2.04	103	6.42	338	7.50	395
Warea	Ah1	1.53	13	6.19	53	13.28	114	45.21	386	48.50	415
	Bw1	1.05	12	3.73	43	10.76	124	28.74	330	32.21	371
	Bw2	0.81	12	2.02	30	7.24	110	17.47	265	20.93	317
	Bw3	0.56	13	1.23	30	4.64	110	10.14	241	14.79	352
Hangatahua	Ah1	0.53	8	3.32	48	4.38	63	33.80	490	29.86	433
	Bw1	0.22	15	1.02	67	1.21	81	4.40	293	5.39	359
	Bw2	0.10	12	0.62	76	0.85	104	1.86	233	2.29	286
Papakauri	Ah	1.11	7	7.70	46	11.50	69	55.59	333	65.70	381
	Bw2	0.58	7	4.66	60	6.60	84	24.10	309	32.96	423
Kerikeri	Ah	0.89	10	3.97	46	5.45	63	38.20	382	44.26	509
	Bw2	0.47	14	1.59	49	4.22	129	9.08	275	13.90	421
Horotiu	Ap	0.79	14	3.19	55	5.65	97	26.75	461	28.60	493
	Bw1	0.53	13	1.67	41	5.07	123	12.49	305	13.76	336
	Bw2	0.20	18	0.69	64	1.73	162	2.65	241	2.78	252
	Bw3	0.06	29	0.13	65	0.39	195	0.57	285	0.68	340
Hamilton	Ah/AP	0.73	21	2.69	79	3.78	111	18.97	558	20.72	610
	Btg1	0.27	19	0.88	63	2.46	176	5.29	378	6.27	448
	Btg2	0.13	12	0.63	56	2.21	197	3.93	357	4.15	376
Tokomaru	Ah1	0.46	15	2.50	78	1.52	45	17.42	553	18.50	584
	ABg	0.35	15	2.24	97	1.18	51	10.83	471	11.71	509
	ABg/Btg	0.20	20	1.27	125	0.54	53	4.65	456	5.03	493
	Btg	0.10	16	0.86	139	0.40	64	2.84	458	2.98	477
Himatangi	Ah	0.26	12	2.33	107	0.94	43	8.22	379	10.42	436
	Bw1	0.05	25	0.34	148	0.08	35	0.64	322	1.23	615
LSD (0.05)		0.13	4	0.32	16	0.41	24	10.6	46	13.5	62

(Table 5.4). Rao and Davidson (1980) compiled data on pesticides and reported K_d values of 3.20 for atrazine (56 soils), 0.78 for 2,4-D (9 soils) and 8.8 for phorate (4 soils). Recently, Johnson and Sims (1993) examined atrazine and 2,4-D sorption by 26 Atlantic coastal plain soils with organic matter contents of 0.1 to 2.8% and reported an average K_d of 0.81 and 0.65, respectively. Walker *et al.* (1989) investigated metsulfuron methyl sorption on 24 soils with organic matter contents of 1.64 to 59.0% and obtained estimated K_d values of 0.040 to >10.

5.4.2.4 *Influence of soil depth on the distribution coefficient (K_d)*

Pesticide sorption was greater in surface horizons than in subsoils. For example, the average K_d of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos for the surface horizons of the soils were 0.80, 5.71, 6.09, 32.22 and 36.45 L kg⁻¹ respectively, which decreased to 0.42, 1.56, 4.33, 11.71 and 13.63 L kg⁻¹ respectively, for the subsoils. The average decrease in pesticide sorption with depth was greater (65%) for non-ionic pesticides (phorate and terbufos) than ionic pesticides (45%) (metsulfuron methyl, atrazine and 2,4-D). The difference in the percentage decrease in K_d with depth between the ionic and non-ionic pesticides indicated that the soil components involved in the sorption varied between the ionic and non-ionic pesticides. Many researchers have reported the preponderant role of organic carbon in pesticide sorption (Felsot and Dahm, 1979; Walker *et al.* 1989; Mallawatantri and Mulla, 1992; Barriuso *et al.* 1992a; Johnson and Sims 1993). In the present experiment the K_d of pesticides generally did follow the order of the organic carbon contents in the soils (Table 5.2) but there were some exceptions, particularly for ionic pesticides.

For example the allophanic subsoils sorbed significant amounts of 2,4-D and the non-allophanic Hamilton and Tokomaru subsoils sorbed significant amounts of 2,4-D and atrazine, respectively. The sorption of these ionic pesticides by the subsoils may be related to the content of clay minerals (see below). Increases in the K_d of 2,4-D at depth in Brazilian (Barriuso *et al.* 1992a) and Atlantic coastal plain soils (Johnson and Sims, 1993) have also been reported. Johnson and Sims (1993) attributed the increased K_d values to the presence of greater levels of Fe and Al oxides, organic matter and clay in the Kalmia subsoils.

In summary, the surface horizons of these ten soil series had greater ability to sorb pesticides than subsoils. The decrease in sorption with depth was lower for ionic pesticides than for non-ionic pesticides. Identification of soil properties throughout the entire soil profile could be of considerable importance in the development of management strategies to avoid groundwater contamination by pesticides. The effect of soil properties on sorption of pesticides is discussed in the following section.

5.4.3 Relationship between pesticide sorption and soil properties

5.4.3.1 Simple correlation studies

Simple correlations between the K_d values of pesticides and various soil properties are presented in Table 5.5. When all the soil horizons (surface and subsurface) were considered together, organic carbon content was best correlated with the K_d values of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos ($r=0.85^{***}$, 0.90^{***} , 0.84^{***} , 0.94^{***} and 0.96^{***} respectively). The other soil properties which gave significant correlations were CEC and oxalate-extractable Fe. Oxalate-extractable Al was also significantly correlated with the K_d values of 2,4-D and metsulfuron methyl ($r=0.64^{***}$ and 0.36^* , respectively). The K_d of metsulfuron methyl, atrazine and 2,4-D increased with decreasing pH.

The significant correlations observed between the K_d values of pesticides and the soil properties are consistent with those reported in the literature. Significant positive correlations between atrazine K_d values and organic matter and CEC ($r=0.61^{**}$ and 0.61^{**}) were reported by Johnson and Sims (1993). Similar results were also reported by Felsot and Dahm (1979) who found a strong correlation between sorption of organophosphorus insecticides and organic matter. Walker *et al.* (1989) reported a strong positive correlation between metsulfuron methyl K_d values and organic matter ($r=0.939^{***}$) and a negative correlation with pH. Recently Mallawatantri and Mulla (1992) reported a significant positive correlation between 2,4-D sorption and organic matter ($r=0.83^{**}$). Highly significant correlations between 2,4-D sorption and organic matter ($r=0.83^{**}$), exchangeable Al ($r=0.82^{**}$) and soil pH ($r=-0.79^{**}$) were reported for 42 Belgian soils (Moreale and Bladel, 1980).

Table 5.5 Simple correlation coefficients (r) between K_d of pesticides and soil properties

Soil Property	Metsulfuron methyl	Atrazine	2,4-D	Phorate	Terbufos
Surface and subsoil horizons					
pH	-0.29 ^{NS}	-0.14 ^{NS}	-0.37 [*]	-0.20 ^{NS}	-0.17 ^{NS}
OC	0.88 ^{***}	0.90 ^{***}	0.84 ^{***}	0.94 ^{***}	0.96 ^{***}
Clay	0.23 ^{NS}	0.34 ^{NS}	0.18 ^{NS}	0.26 ^{NS}	0.31 ^{NS}
CEC	0.72 ^{***}	0.80 ^{***}	0.68 ^{***}	0.90 ^{***}	0.90 ^{***}
Fe	0.41 [*]	0.56 ^{***}	0.61 ^{***}	0.49 ^{**}	0.57 ^{***}
Al	0.36 [*]	0.21 ^{NS}	0.64 ^{***}	0.26 ^{NS}	0.28 ^{NS}
Surface horizon					
pH	-0.38 ^{NS}	0.12 ^{NS}	-0.26 ^{NS}	0.25 ^{NS}	0.27 ^{NS}
OC	0.91 ^{***}	0.89 ^{***}	0.85 ^{**}	0.97 ^{***}	0.97 ^{***}
Clay	0.41 ^{NS}	0.46 ^{NS}	0.22 ^{NS}	0.46 ^{NS}	0.49 ^{NS}
CEC	0.51 ^{NS}	0.66 [*]	0.77 ^{**}	0.91 ^{***}	0.89 ^{***}
Fe	0.47 ^{NS}	0.80 ^{**}	0.71 [*]	0.78 ^{**}	0.84 ^{**}
Al	0.69 ^{NS}	0.66 [*]	0.82 ^{**}	0.73 [*]	0.65 [*]
Subsoil horizons					
pH	-0.19 ^{NS}	0.04 ^{NS}	-0.37 ^{NS}	-0.16 ^{NS}	-0.13 ^{NS}
OC	0.85 ^{***}	0.84 ^{***}	0.80 ^{***}	0.92 ^{***}	0.94 ^{***}
Clay	0.10 ^{NS}	0.27 ^{NS}	0.13 ^{NS}	0.13 ^{NS}	0.18 ^{NS}
CEC	0.72 ^{***}	0.72 ^{***}	0.75 ^{***}	0.79 ^{***}	0.77 ^{***}
Fe	0.50 [*]	0.63 ^{**}	0.59 ^{**}	0.59 ^{***}	0.66 ^{***}
Al	0.58 ^{**}	0.42 ^{NS}	0.72 ^{***}	0.58 ^{**}	0.60 ^{**}

NS, *, **, *** = Not Significant, or significant at 0.05, 0.01 or 0.001 levels of probability, respectively

When the topsoils were considered alone, only organic carbon was highly correlated with the K_d of metsulfuron methyl ($r=0.91^{***}$), atrazine ($r=0.89^{***}$), 2,4-D ($r=0.85^{***}$), phorate ($r=0.97^{***}$) and terbufos ($r=0.97^{***}$). Whereas when the subsoils were considered alone, organic carbon, Fe and Al were highly correlated with the K_d of the pesticides.

The soil properties which gave significant correlation coefficients with pesticide K_d values were organic carbon, CEC, oxalate extractable Fe and Al (Table 5.5). However, these soil properties were inter-correlated in the simple correlation analysis. Hence it is possible that there is no direct cause and effect relationship between pesticide sorption and a given soil property, but that they are related through their common correlation with some other property. In order to overcome the problems involved in the simple correlation, multiple regression analyses were carried out (see below).

5.4.3.2 *Multiple regression equations*

Stepwise multiple regression analyses were carried out between the K_d values of pesticides and soil properties to select the best combination of properties, that describes pesticide sorption. Multiple regression equations were obtained for topsoil and subsoil together and also separately to predict the pesticide sorption (Table 5.6).

When topsoil plus subsoil horizons were considered together the multiple regression equation developed using all the soil properties (pH, organic carbon, CEC, Clay, Fe and Al) explained 83, 88, 89, 94 and 96% variation in the sorption of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos, respectively. However, the stepdown multiple regression analysis indicated that the significant soil properties, which describe the sorption of metsulfuron methyl ($R^2=0.81^{***}$), atrazine ($R^2=0.86^{***}$), and 2,4-D ($R^2=0.87^{***}$) were organic carbon, CEC and Fe; organic carbon and Al; and organic carbon, pH and Al, respectively. The two soil properties, organic carbon and Fe gave a predictive equation for the sorption of phorate ($R^2=0.93^{***}$) and terbufos ($R^2=0.95^{***}$).

Table 5.6 Multiple regression equation between K_d of pesticides and soil properties.

Pesticide	Multiple regression equation ^a	R ²	Measured K _d	Predicted K _d
			(L kg ⁻¹)	
Surface and Subsoil horizons				
Metsulfuron methyl	Y=0.35+(0.13 OC)-(0.01 CEC)-(0.16 Fe)	0.81 ^{***}	0.05-1.53	0.60
Atrazine	Y=0.63+(0.45 OC)-(0.18 Al)	0.86 ^{***}	0.13-7.70	2.24
2,4-D	Y=12.80-(2.21 pH)+(0.66 OC)+(0.73 Al)	0.87 ^{***}	0.08-14.86	4.93
Phorate	Y=3.29+(3.88 OC)-(1.23 Al)	0.93 ^{***}	0.57-55.6	18.11
Terbufos	Y=2.83+(4.65 OC)-(1.41 Al)	0.95 ^{***}	0.68-75.7	20.77
Surface soil horizon				
Metsulfuron methyl	Y=3.99-(0.64 pH)-(0.05 OC)	0.75 ^{***}	0.26-1.53	0.72
Atrazine	Y=1.99+(0.65 OC)-(0.12 CEC)	0.90 ^{***}	2.00-7.70	3.63
2,4-D	Y=45.83-(7.93 pH)+(1.00 OC)-(0.07 clay)	0.98 ^{***}	0.94-13.28	6.11
Phorate	Y=10.27+(2.91 OC)	0.93 ^{***}	8.22-55.60	32.21
Terbufos	Y=7.03+(3.90 OC)	0.95 ^{***}	10.40-75.7	36.44
Subsoil horizons				
Metsulfuron methyl	Y=0.16+(0.12 OC)-(0.13 Al)	0.86 ^{***}	0.05-1.05	0.17
Atrazine	Y=-2.74+(0.55 pH)+(0.55 OC)-(0.27 Al)	0.86 ^{***}	0.13-4.66	1.55
2,4-D	Y=6.49-(1.09 pH)+(1.27 OC)-(1.32 Fe)+(0.47 Al)	0.92 ^{***}	0.08-14.86	4.34
Phorate	Y=1.48+(3.77 OC)-(0.84 Al)	0.91 ^{***}	0.57-34.70	11.69
Terbufos	Y=1.61+(4.36 OC)-(0.91 Al)	0.87 ^{***}	0.68-37.7	13.61

^a Predicted K_d = intercept + (bi*soil property)+....

^{***} = Significant at 0.001 level of probability

When the topsoils were considered alone, organic carbon had a greater influence on pesticide sorption. This is evident from the higher correlation coefficient for organic carbon in surface soils than in subsoil and also surface plus subsoils (section 5.4.3.1). The multiple regression analysis indicated that in subsoils, in addition to organic carbon, Fe and Al are also contributing significantly to the variation in K_d values. Together with organic carbon they accounted for 86, 86, 92, 87 and 92% of the variation in K_d values of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos, respectively. This suggests that in subsoils both organic matter and the clay minerals are involved in the sorption of ionic pesticides. Recently Johnson and Sims (1993) observed that the soil properties, pH, organic matter, ECEC, exchangeable acidity and amorphous Fe and Al, explained 87, 69, 55, 74 and 82% variation in the sorption of atrazine, cyanazine, dicamba, 2,4-D and metolachlor, respectively.

The K_d values predicted from the multiple regression equations are compared with the range of measured K_d values for the different pesticides (Table 5.6). The range in measured K_d values was wider when the surface and subsoils were considered together than when they were considered separately.

5.4.4 Sorption dependence on soil organic carbon

Inspection of the simple correlation (Table 5.5) shows that the organic carbon content of the soil alone accounted for more than 80% of the variation in K_d values. High positive correlations between the K_d of pesticides and the soil organic carbon has been reported by many investigators (Felsot and Dahm 1979; Karickhoff *et al.*, 1979; Barriuso *et al.*, 1992a; Mallawatantri and Mulla 1992; Johnson and Sims 1993). Since in most studies soil organic carbon content has correlated well with pesticide sorption, the use of a K_d value based on organic carbon content (K_{oc}) was proposed by Hamaker and Thompson (1972). This relationship is obtained by dividing the K_d values of soils, by their respective soil organic carbon contents (section 2.5.5):

$$K_{oc} = \frac{(K_d) (100)}{\%OC} \quad (5.5)$$

The K_{oc} values were calculated for each pesticide and are reported in Table 5.4. It is obvious that the K_{oc} values for a given pesticide vary much less than do the K_d values. The variation in K_{oc} is also much less for non-ionic pesticides (phorate, terbufos) than ionic pesticides (atrazine, metsulfuron methyl and 2,4-D).

The K_{oc} values of phorate and terbufos varied by a factor of 2.5 between soils. However, the K_{oc} values of 2,4-D were greater in most of the allophanic subsoil horizons as well as in the Hamilton soil whereas the K_{oc} of atrazine was higher in the Tokomaru subsoil horizons than in the surface horizon. It has been shown that allophanic clay has high sorption capacity for phenoxy herbicides (2,4,5-T) (O'Connor and Anderson, 1974) which may be one of the reasons for the high K_{oc} values in these soils. In the Hamilton soil, low pH in the subsoil horizons increased the 2,4-D sorption. The pH of the Hamilton subsoil horizons was 1-2 units lower than the other soils used in this experiment (Table 5.2). There was less variation in the K_{oc} values of metsulfuron methyl, which may be attributed to the low sorption of this compound.

Briggs (1981b) reported that if the soil organic matter in different soils behaves similarly then the K_{oc} value of a pesticide for different soils should be similar. Based on this he developed an empirical relationship between K_{oc} and K_{ow} of pesticides to predict the K_{oc} values (Table 2.2). Singh *et al.* (1989) observed that the K_{oc} values of 2 pesticides varied between four Western Australian soils. The empirical equation that Briggs (1981b) developed for other Australian soils failed to predict the measured K_{oc} values of Singh *et al.* (1989). Unless the sorptive strength of organic carbon in subsurface horizons is higher than in surface soils, which is unlikely, an appreciable amount of sorption in the subsurface horizons must be by soil minerals. Involvement of clay in organic compound sorption has been indicated in many studies (Campbell *et al.*, 1991; Hassett *et al.*, 1981). To examine further the effect of organic carbon, the topsoil and subsoil samples were treated with H_2O_2 to remove organic carbon and sorption was then measured.

5.4.5 Effect of removal of organic carbon on pesticide sorption

The K_d and K_{oc} of pesticides from which organic carbon had been removed (oxidised

soils) are presented in Table 5.7. As expected, the removal of organic carbon greatly reduced the sorption of all pesticides. The decrease in sorption was greater for non-ionic (phorate and terbufos) than for ionic (atrazine, metsulfuron methyl and 2,4-D) pesticides. For example, the decrease in K_d of non-ionic pesticides ranged from 56 to 94 percent whereas it varied from 2 to 90, from 3 to 89 and from -46 to 80 percent for atrazine, 2,4-D and metsulfuron methyl respectively. This is consistent with the results reported by Felsot and Dahm (1979) for phorate and terbufos and other ionic and non-ionic pesticides (Singh *et al.*, 1989). The difference in percent decrease in sorption with organic carbon removal between ionic and non-ionic pesticides indicates that organic carbon is the most important sorbent for non-ionic pesticides. Whereas for ionic pesticides in addition to organic carbon, the clay mineral fraction in the soil also contributes to sorption.

The K_{oc} values were also calculated for oxidised soils (Table 5.7). The K_{oc} values of non-ionic pesticides (phorate and terbufos) were identical to the values observed in natural soils, but they differed for ionic pesticides (metsulfuron methyl, atrazine and 2,4-D). For example, the K_{oc} values of 2,4-D in the oxidised Egmont and Horotiu subsoil horizons were very much higher than those for their natural counterparts. Whereas the K_{oc} values for atrazine were higher in the oxidised Tokomaru subsoil than their natural counterparts. Similarly the K_{oc} values of ionic pesticides (metsulfuron methyl, atrazine and 2,4-D) were higher in the Hamilton oxidised soil than in the natural soil.

A possible explanation was sought for the increased K_{oc} values of 2,4-D and atrazine in the oxidised soils. The peroxide treatment could have modified the soil properties, which are considered to be important in the sorption of ionic pesticide. One such effect often noted is the increased availability of sorption sites on mineral surfaces, which otherwise remain largely masked by organic matter (Hance, 1969). Mineral surfaces are expected to readily sorb ionic pesticides (Green, 1974). Egmont and Horotiu soils contain appreciable amounts of allophane and it appears that allophane with a net positive charge could be an effective adsorber for 2,4-D in these soils.

The increase in K_{oc} values of 2,4-D, atrazine and metsulfuron methyl in the Hamilton soil may be attributed to the decrease in pH with peroxide treatment. The pH of the

Table 5.7 Distribution coefficients (K_d , K_{oc}) of pesticides in H_2O_2 treated soils

Soil	Horizon	Metsulfuron methyl		Atrazine		2,4-D		Phorate		Terbufos	
		K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
		(L kg ⁻¹)									
Patua	Ah	0.23	13	1.06	58	2.72	151	8.16	461	9.04	384
	Bw3	0.20	14	0.56	40	2.00	143	5.24	374	5.45	389
Egmont	Ah	0.17	19	0.55	65	1.82	214	4.07	538	4.30	582
	Bw3	0.08	21	0.22	55	1.89	472	1.10	275	1.22	305
Warea	Ah	0.22	15	1.34	89	3.36	217	5.85	390	5.45	363
	Bw3	0.18	14	0.60	46	1.77	136	4.60	358	5.20	400
Hangatahu a	Ah1	0.13	17	0.45	56	1.28	168	4.01	527	3.65	456
	Bw2	0.03	28	0.05	62	0.24	304	0.21	262	0.29	362
Papakauri	Ah	0.38	11	3.42	96	5.17	146	13.40	378	19.34	552
	Bw2	0.26	10	1.86	70	3.52	133	10.16	260	12.45	478
Kerikeri	Ah	0.15	14	0.55	50	1.49	134	4.96	446	6.04	549
	Bw2	0.11	16	0.42	58	1.58	219	3.05	424	3.62	517
Horotiu	Ap	0.13	12	1.06	95	2.16	196	4.83	439	5.90	537
	Bw3	0.01	25	0.01	25	0.09	259	0.12	333	0.15	375
Hamilton	Ah/Ap	0.24	38	1.81	282	1.02	160	3.76	588	4.29	670
	Btg2	0.19	56	1.35	397	0.75	221	1.27	374	1.49	438
Tokomaru	Ah1	0.08	20	1.32	314	0.28	67	2.21	526	2.58	614
	Btg	0.04	27	0.84	560	0.11	73	0.61	407	0.68	453
Himatangi	Ah	0.03	23	0.15	115	0.10	77	0.54	415	0.60	461
	Bw1	0.01	20	0.04	80	0.03	60	0.16	348	0.22	440
LSD (0.05)		0.08	7	0.56	48	0.45	73	2.9	97	3.5	84

Hamilton soil after the peroxide treatment was found to be 4.1 as compared to 4.9 of the untreated soil. The increased K_{oc} value of atrazine in the oxidised Tokomaru soil can be explained by the presence of 2:1 clays (such as micaceous minerals and vermiculite) with a permanent negative charge, which might have provided sites for atrazine sorption. If mineral surfaces sorb ionic pesticides then this will increase the apparent K_{oc} . This effect will be greater if the organic carbon content is reduced.

5.4.6 Prediction of pesticide sorption

Pesticide characteristics such as, solubility in water (W_s) and octanol-water partition coefficient (K_{ow}) have frequently been used to predict the K_{oc} values of pesticides in soils or sediments. Briggs (1973) introduced the application of this approach to pesticide sorption in soils. Subsequently, several researchers have proposed empirical relationships between the K_{oc} values and the K_{ow} values of different pesticides (Karickhoff *et al.*, 1979; Rao and Davidson, 1980; Briggs 1981a; Chiou *et al.*, 1983) or S values (Chiou *et al.*, 1983). It has been shown however, that the K_{oc} values can be better predicted using K_{ow} values than by using W_s values (Gerstl and Yaron, 1983; Madhun *et al.*, 1986a). Hence in this study it was decided to predict the K_{oc} values of pesticides based on their K_{ow} values.

Numerous empirical equations have been developed for a variety of pesticides to predict K_{oc} values using K_{ow} values and these are tabulated in Table 2.2. The measured mean K_{oc} values for each pesticide along with the values obtained in the literature and the values calculated using different regression equations are summarized in Table 5.8. The results show that in general the measured K_{oc} values are in good agreement with the literature values. However, among the ten prediction equations compared (Table 5.8), only four equations adequately predicted the sorption of pesticides.

The first four empirical equations (Table 2.2) developed for cropping soils (Felsot and Dahm, 1979; Briggs 1981a; Briggs, 1981b; Chiou *et al.*, 1983) provided the closest estimate of the K_{oc} values for some of the pesticides used in this experiment. For example, Eq 1 predicted the K_{oc} of atrazine, 2,4-D, phorate and terbufos reasonably well, whereas it under-predicted the K_{oc} values of metsulfuron methyl. However, Eq

Table 5.8 Comparison of experimental K_{oc} values of five pesticides with literature values and values estimated using prediction equations from Table 2.2

Pesticides	K_{oc} based on this study	Literature values ¹	Estimated from equation ²									
			1	2	3	4	5	6	7	8	9	10
Metsulfuron methyl	7-29	5.42 (1)	0.3	7.41	8.31	10.23	1.12	0.5	0.4	0.6	0.9	0.7
Atrazine	19-148	54 (2), 23 (3), 102 (4), 169 (5)	52	147	165	204	170	152	473	194	266	247
2,4-D	35-197	64 (6), 24-685 (2)	100	214	240	295	312	311	1138	398	423	514
Phorate	232-558	431 (7)	296	399	448	551	885	1030	4964	1318	1300	1764
Terbufos	252-615	577 (7)	613	607	681	838	1784	2306	13378	2951	2768	4043

¹Sources: 1. Walker *et al.* (1989); 2. Barriuso *et al.* (1992a); 3. Singh *et al.* (1990); 4. Huang *et al.* (1984); 5. Clay and Koskinen, 1990; 6. Mallawatantri and Mulla, 1992; 7. Felsot and Dahm 1979.

²The numbers relate to equation no. given in Table 2.2.

2 and 3 reasonably predicted the K_{oc} values of all the pesticides used in this experiment. Equation 4 predicted the K_{oc} values of metsulfuron methyl and phorate well, but over-predicted the K_{oc} values of atrazine, 2,4-D and terbufos. The other six equations predicted higher sorption of all pesticides except metsulfuron methyl (Table 5.8). The K_{ow} value for metsulfuron methyl (1) is far below the range of K_{ow} values (10-316227) used to develop the prediction equations (Table 2.2) in the literature, which may be one of the reasons for the under-prediction of this compound.

Unlike the soils used for the development of the prediction equations (Table 2.2), the pasture soils of New Zealand are rich in organic carbon with different clay minerals, that include allophane, kaolinite, vermiculite, halloysite and micaceous minerals and therefore sorb large amount of pesticides. Hence it was decided to develop an empirical equation using K_{ow} values to predict the K_{oc} values of pesticides in these soils.

The K_{ow} values of the five pesticides were used to derive an equation for estimating the K_{oc} of pesticides. Linear least square fitting of the $\log K_{ow}$ and $\log K_{oc}$ yielded the relationship:

$$\log K_{oc} = 0.414 \log K_{ow} + 0.995 \quad r^2 = 0.82 \quad (5.6)$$

The relationship between $\log K_{oc}$ and $\log K_{ow}$ along with the range in the measured K_{oc} values are shown in Figure 5.3. Overall, the agreement between the measured K_{oc} values and the K_{oc} values predicted using the above equation (Eq 5.6) were reasonably good, generally agreeing within a factor of 2.5. Also included in the figure (Fig 5.3) the prediction lines based on Eq 1 and 2 (Table 2.2). These two equations provided the closest estimates of K_{oc} values.

The prediction equations reported in Table 2.2 have different values of slopes and intercepts. The equations with lower values of slope (0.52) gave reasonable predictions whereas the equations with higher slope values (>0.87) over-predicted sorption in these soils. Since the relationship involves log transformation, a small change in the value of slope is likely to cause a large change in the predicted values. A sensitivity analysis was carried out to examine the importance of slope in the prediction equations.

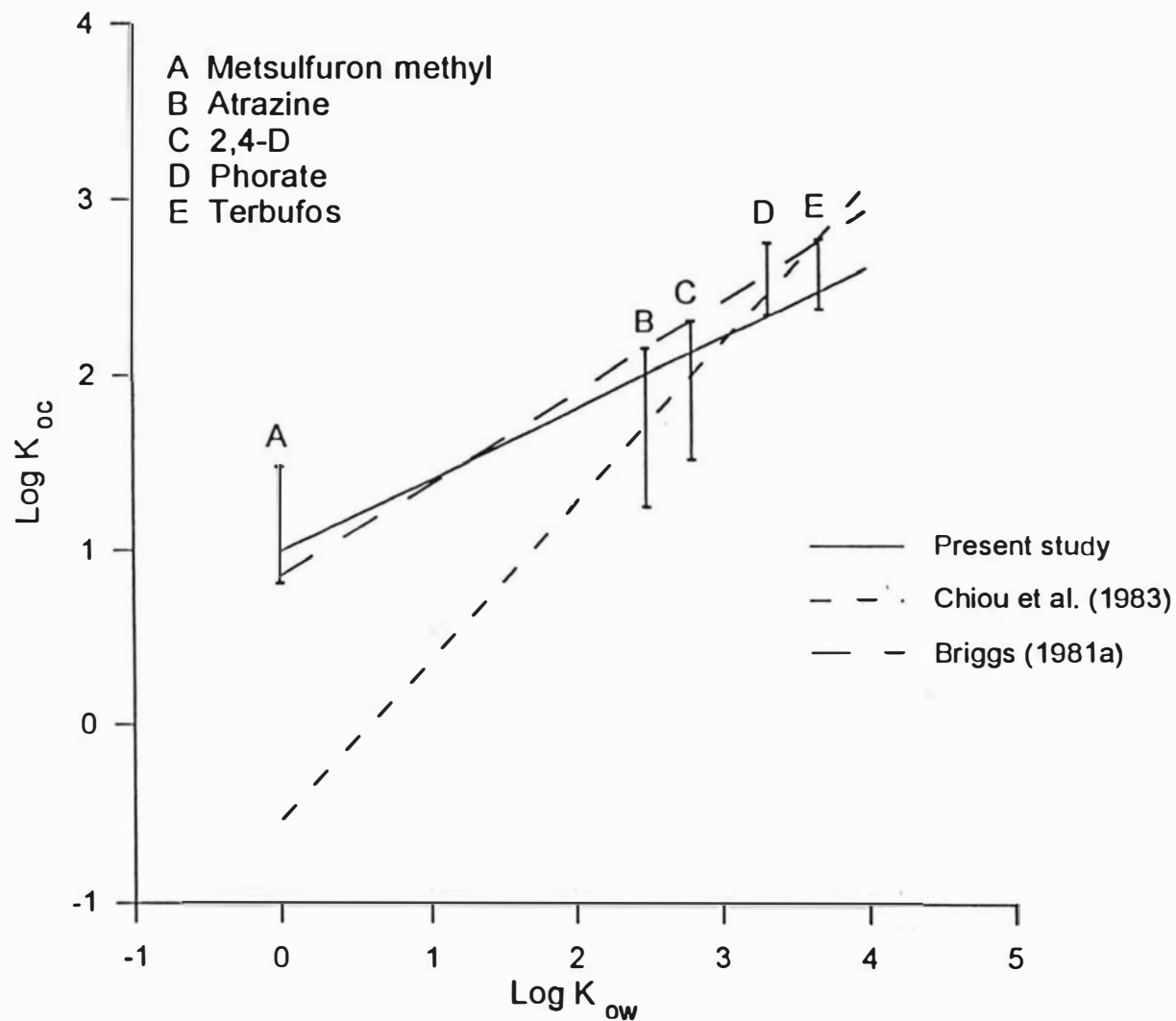


Fig 5.3 Relationship between the distribution coefficient of pesticides based on organic carbon (K_{oc}) and octanol-water partition coefficient (K_{ow}). The range of K_{oc} values for the various pesticides used in this study is also presented

5.4.7 Sensitivity analysis of the prediction equations

In order to test the sensitivity of the prediction equations, the slope in equation 2 (0.52) (Table 2.2) was varied and the effect of change in the value of the slope of the equation on the prediction of K_{oc} values of pesticides was investigated.

Table 5.9 shows the effect of changing the initial slope on the prediction of K_{oc} values.

Table 5.9 Effect of change in slope of the prediction equation on K_{oc} of pesticides

Slope	K_{oc} of pesticides ^a				
	Atrazine	Metsulfuron methyl	2,4-D	Phorate	Terbufos
0.520	147	7.41	214	399	607
0.546	171 (16) ^b	7.41	253 (18)	487 (22)	757 (24)
0.572	191 (30)	7.41	300 (40)	595 (49)	943 (55)

^a Equation 2 (Table 2.2): $\log K_{oc} = 0.52 \log K_{ow} + 0.87$

^b Values in parentheses indicate the percent K_{oc} increase over the original slope (0.520)

Equation 2 with a slope of 0.52 predicted adequately the K_{oc} values of all pesticides. Increasing the initial slope in equation 2 (0.52) (Table 2.2) by 5 and 10% increased the K_{oc} by 16-24 and 35-55% respectively. The effect is greater for the pesticides with higher K_{ow} (phorate and terbufos) than with lower K_{ow} (atrazine, metsulfuron methyl and 2,4-D) values.

In general the equations with higher slopes (>0.52) over-predicted the K_{oc} values. The higher slope obtained in these equations may be due to the narrow range of

K_{ow} values of pesticides used to develop the prediction equation. For example, the highest slope of 1.23 was reported in prediction equation 7 (Table 2.2) and this equation over-predicted the K_{oc} values of pesticides in the present experiment (Table 5.8). The narrow range of K_{ow} values (1.86-2.65) of pesticides used to develop the prediction equation 7 may be the possible reason for this higher slope, which resulted in the over-prediction of the K_{oc} values. These results illustrate the importance of slope in prediction equations. Care therefore must be taken in using K_{oc} values of pesticides derived from the prediction equations.

5.5 CONCLUSIONS

The soils used in this experiment were predominantly under pastoral agriculture or cereal cropping in New Zealand in which pesticides are commonly used. The results of this study indicate that:

1. Allophanic soils sorbed higher amounts of pesticides than did non-allophanic soils.
2. In general, the sorption of pesticides followed the order: terbufos > phorate > 2,4-D > atrazine > metsulfuron methyl and it decreased with depth.
3. The K_d values of pesticides were highly correlated with organic carbon, suggesting that organic carbon is the most important single factor involved in sorption.
4. Soil organic carbon is the most important sorbent for non-ionic pesticides, whereas for ionic pesticides, in addition to organic carbon the clay mineral fraction also contributes to sorption. A detailed study on the importance of clay and organic carbon content of the soils on pesticide sorption is discussed in chapters 6 and 7 respectively.
5. The K_{ow} values of pesticides were used to derive an equation for estimating K_{oc} of pesticides in these soils. Estimates of K_{oc} based on the prediction equation were within a factor of 2.5 of the measured values.

CHAPTER 6

CONTRIBUTION OF ORGANO-MINERAL FRACTIONS OF SOILS TO SORPTION AND DESORPTION OF IONIC AND NON-IONIC PESTICIDES

6.1 INTRODUCTION

The results in Chapter 5 indicate that organic carbon and the clay minerals are the dominant factors contributing to the sorption of pesticides in New Zealand soils under study. While the sorption of pesticides onto the soil particles decreases the leaching of pesticide residues to groundwater, the erosion of pesticide-enriched finer soil particles by surface runoff may lead to surface water contamination. The fine fractions (clay and silt) of the soils are selectively carried off the field during runoff events. It has been well documented that eroded sediments in general are enriched with clay size particles and organic matter (Leonard, 1990).

It is likely that fractions which are subject to erosion tend to sorb more pesticides than do non-eroded sediments. Studies examining the importance of particle size in the sorption of pesticides have been reviewed in section 2.6.3 (see Table 2.4). Most of the studies have concentrated mainly on the sorption of pesticides and desorption from different particle size fractions has not been reported. Studies by Nkedi-Kizza *et al.* (1983) on the sorption of herbicides by soil separates from a mollisol demonstrated that both clay and silt (2- 20 μm) make a significant contribution to whole-soil sorption capacity. The difference in the extent of sorption between the particle size fractions has been related to the difference in the amount of organic carbon and amorphous oxides associated with each fraction (Huang *et al.*, 1984). Recently, it has been shown that organic matter associated with the coarse clay fraction has a high affinity for atrazine (Laird *et al.*, 1994).

6.2 OBJECTIVES

The objectives of this experiment were:

- (i) to investigate the sorption and desorption of ionic and non-ionic pesticides by different particle size fractions of the soil.

- (ii) to examine the role of organic carbon in sorption and desorption of pesticides by particle size fractions.
- (iii) to predict the sorption of pesticides by the whole soil using the sorption values for the individual particle size fractions.
- (iv) to estimate the possible extent of pesticide losses through surface runoff.

6.3 MATERIALS AND METHODS

6.3.1 Soils

Topsoil and sub-soil samples from two contrasting pasture soils (Egmont and Tokomaru), that varied widely in their clay mineralogy and organic carbon content were used in this study. The field-moist soils were collected and passed through a 2 mm sieve and stored in a moist condition at 4°C in sealed polythene bags. The chemical characteristics of the soil samples and their USDA classification are presented in Table 6.1.

6.3.2 Pesticides

Two ionic and two non-ionic pesticides were used in this study. The ionic herbicides, 2,4-D and atrazine and the non-ionic organophosphorus insecticides, phorate and terbufos were ^{14}C labelled with a radiochemical purity of >98%. These pesticides are widely used in pastoral and cropping situations in New Zealand. The chemical properties of the pesticides are discussed in section 3.3.1.

6.3.3 Particle size fractionation

Particle size fractionation was performed by both ultrasonic dispersion of the soil samples (Genrich and Bremner 1974) and the conventional (hydrogen peroxide/calgon) pipette method (Jackson 1974). In the former method it is possible to achieve the fractionation of a soil sample into different particle sizes without having to remove the organic matter. For ultrasonic dispersion, the field moist samples were subjected to ultrasonic vibration at 20kHz for 3 min using an ultrasonicator. Small amounts of NaOH were used to achieve maximum dispersion.

Table 6.1 Classification and chemical characteristics of soils

Soil	Depth (cm)	Horizon	USDA Classification	pH	organic carbon (%)	Oxalate extractable		
						Fe	Al	Si
						(%)		
Egmont	0-20	Ah	Typic Hapludand	6.07	8.7	1.02	3.20	1.35
	46-60	Bw3		6.78	1.9	1.77	5.00	2.02
Tokomaru	0-15	Ah1	Typic Fragiaqualf	5.80	3.2	0.36	0.08	0.02
	45-60	Btg		6.60	0.6	0.40	0.09	0.10

It has been reported that drying of allophanic soils causes irreversible aggregation and poor dispersibility (Kubota, 1972). Hence field moist soil samples were used for fractionation, which generally facilitates better dispersion (R. Parfitt, pers. comm.). In the case of the method involving H_2O_2 , the soil samples were treated with sufficient amounts of 30% H_2O_2 to remove most of the organic carbon and to achieve a complete dispersion. The dispersed sample was then separated by the sedimentation and centrifugation procedures of Jackson (1974). The soil samples were separated into three particle size fractions, which included sand (2000-63 μm), silt (63-2 μm) and clay (< 2 μm). All the particle size fractions were washed with 0.01 M CaCl_2 solution until Na free, and then the fractions were freeze-dried before use.

6.3.4 Characterisation of particle size fractions

6.3.4.1 *Chemical analysis*

The pH of the various particle size fractions was measured at a 1:2.5 solid to solution ratio. Organic carbon was determined by the Leco combustion method (Bremner and Tabatabai, 1971). Oxalate extractable Fe, Al and Si were measured using an atomic absorption spectrophotometry (Blakemore *et al.*, 1987).

6.3.4.2 *Clay mineralogy*

(i) X-ray diffraction

X-ray diffraction (XRD) analysis of the clay samples was carried out by smearing the clay samples on a glass slide and allowing to dry to a moist paste prior to X-radiation. The clay samples were irradiated with X-rays from 4° to 16° 2θ using a Phillips PW 1840 X-ray diffractometer.

(ii) Transmission Electron Microscopy

The clay samples were also examined by transmission electron microscopy (TEM) using a Phillips EM400T electron microscope.

(iii) Infrared spectroscopy

For infrared (IR) spectrum analysis, the clay samples were made into discs using 1.0 mg clay (Egmont) and 170 mg potassium bromide. IR spectra were recorded between 4000-200 CM^{-1} on a Pye Unicam SP 200 Spectrophotometer.

6.3.5 Pesticide sorption

Pesticide sorption by the whole soil and particle size fractions was measured using a standard batch method. Preliminary experiments had shown that the sorption isotherm approached a linear form (Chapter 5). Hence the distribution coefficient (K_d) values were estimated from the sorption measured at a single solution concentration of atrazine ($18.6 \mu\text{mol L}^{-1}$), 2,4-D ($18.1 \mu\text{mol L}^{-1}$), phorate ($15.4 \mu\text{mol L}^{-1}$) and for terbufos ($6.9 \mu\text{mol L}^{-1}$) at a 1:10 soil:solution ratio using 0.01 M CaCl_2 as background electrolyte solution. Three replicates of 0.5 g soil and particle size fractions were equilibrated with 5 ml pesticide solution in glass culture tubes fitted with teflon-lined caps for 4 h at 25°C in an end-over-end shaker. At the end of the equilibration period the tubes were centrifuged at 2500 rpm for 15 min and a one-ml aliquots taken for analysis. The ^{14}C activity of the aliquots was measured using a liquid scintillation counter. The amount of pesticide sorbed was calculated as the difference between the initial and final concentration in solution.

6.3.6 Prediction of K_d values of whole soil

The K_d values for the whole soil samples were calculated from the K_d values obtained for the particle size fractions, using the following equation (Karickhoff *et al.*, 1979). The calculated K_d values were then compared with the measured K_d values.

$$K_d = \sum_i K_d(i) f(i) \quad (6.1)$$

Where,

$K_d(i)$ = K_d of pesticides in (i) th size fraction

$f(i)$ = Fraction of the total mass represented by component i

K_d = Kd of whole soil
 i = (i) th size fraction

The relative contribution of particle size fractions to the K_d of the whole soil was calculated from the following equation:

$$Y = \frac{K_d(i) f(i)}{K_d} \quad (6.2)$$

where

Y = relative contribution of K_d from sand, silt or clay on the whole soil basis

6.3.7 Pesticide desorption

Desorption was carried out in pesticide-free 0.01 M CaCl_2 solutions. After the sorption measurement, the contents of each tube was weighed to account for the amount of pesticide present in the solution prior to the desorption measurements. A quantity of pesticide-free 0.01 M CaCl_2 solution was added to obtain a soil solution ratio of 1:10. The tubes were then vibrated to disperse the soil pellet and the samples were shaken for 4 h and recentrifuged. The desorption process with 0.01 M CaCl_2 was repeated four times. The concentration of pesticide present in the aqueous solution after each desorption step was determined.

At the end of four desorption steps, the amount of residual pesticide remaining in the soil was measured by extracting the soil samples with the scintillation cocktail as discussed in section 3.3.3.1. Concentrations of ^{14}C in the solutions were determined using a liquid scintillation counter and the amount of pesticide calculated. The mass balance of the initially-added pesticide was calculated.

6.3.8 Effect of organic carbon on sorption and desorption of pesticides

In a separate experiment, the effects of organic carbon on sorption and desorption by particle size fractions and the whole soil were examined. The organic carbon in

the fractions was removed by treatment with H_2O_2 using the method described by Black (1965). Sorption and desorption of pesticides in the oxidised particle size fractions and the whole soil were measured. The concentration of pesticides present in the aqueous solution was measured using the method described in section 6.3.5.

6.3.9 Prediction of pesticides in surface runoff

Movement of pesticide-enriched sediments during surface runoff and the subsequent release of the sorbed pesticide is likely to contribute to the contamination of the aquatic system (Leonard, 1990). It has been reported that the concentration of pesticide in the soil material in the runoff zone is enriched through the selective deposition of clay and organic matter (Leonard, 1985). The selective deposition of clay and organic matter in the eroded sediments is expressed as the 'enrichment ratio'. The amount of pesticide attached to the sediment and lost through surface runoff is the product of pesticide concentration in the sediment (S_i), sediment yield and the enrichment ratio (Er_i) (Leonard, 1985). An attempt was made to predict the loss of pesticide through sediments during surface runoff. Sediment yield and enrichment ratio can be obtained from the erosion studies.

6.3.9.1 *Pesticide concentration in the sediment*

The pesticide concentration in the sediment can be calculated from the pesticide concentration in soil solution (C) and the distribution coefficient for the sediment (K_{ds}) as described below.

Pesticide added to the soil is partitioned into solid and solution phases according to the following equation:

$$A = S + C \theta \rho \quad (6.3)$$

where A is the amount of pesticide added (kg ha^{-1}), S is the sorbed concentration ($\mu\text{mol kg}^{-1}$), C is the concentration of pesticide in the soil solution ($\mu\text{mol L}^{-1}$) and θ is the volumetric water content ($\text{mm}^3 \text{mm}^{-3}$), and ρ is the soil bulk density (g cm^{-3}). The sorbed amount (S) and the concentration in solution (C) is related by the

following linear sorption equation:

$$S = K_d C \quad (6.4)$$

where K_d is the distribution coefficient ($L\ kg^{-1}$) of the pesticide in the whole soil. Substitution of Equation 6.4 in Equation 6.3 and further rearrangement gives

$$C = \frac{A}{(K_d + \theta \rho)} \quad (6.5)$$

From the concentration in solution (C) and the K_d values for the sediments (K_{ds}) the amount of pesticide sorbed onto the sediment (S_s) can be calculated using the following equation:

$$S_s = K_{ds} C \quad (6.6)$$

where K_{ds} is the distribution coefficient of the pesticide in the sediment. The value of K_{ds} can be calculated from the K_d values of the individual fractions of the soil and the enrichment ratio of the fractions in the sediments.

$$K_{ds} = \sum K_d(i) f_i Er_i \quad (6.7)$$

where $K_d(i)$ is the distribution coefficient of the pesticide in the (i)th size fraction and Er_i is the enrichment ratio of the (i)th size fraction. The potential amount of pesticide lost through surface runoff is the product of pesticide sorbed concentration in the sediments (S_s) and sediment yield.

6.3.9.2 Sediment loss

In New Zealand, sheet and rill erosion are the two most common erosion types by which sediments are carried off in the runoff. A recent study by Grant (1992) reported that 6.4 and 10.3 tonnes of sediment would be eroded per ha from allophanic and non-allophanic soils, respectively, after 65 mm rainfall event. Although these values are used for the estimation of runoff losses of pesticides, it is important to point out that sediment loss depends on a number of factors which

include slope, intensity of rainfall, cover crops and land management.

Soil, pesticide and sediment data used for the prediction of pesticide losses in surface runoff for allophanic and non-allophanic soils are given Table 6.2. The predicted pesticide losses were calculated for the recommended rate of atrazine (2 kg ha⁻¹), 2,4-D disodium salt (2 kg ha⁻¹), phorate (5 kg ha⁻¹) and terbufos (3 kg ha⁻¹) (New Zealand agrichemical & plant protection manual, 1993) for pasture and cereal crops. The main objective of this exercise is to illustrate how the runoff losses of pesticides could be estimated using the parameters given in Table 6.2 rather than to calculate the actual amount of pesticide losses for the soils used in this experiment.

Table 6.2 Soil, pesticide and sediment data for prediction of pesticide losses in runoff

Soil, sediment and pesticide data	Egmont (allophanic)	Tokomaru (non-allophanic)
Bulk density (g cm ⁻³)	0.85	1.05
Volumetric water content (cm ³ cm ⁻³)	0.48	0.50
Sediment loss (t ha ⁻¹) [*]	6.4	10.3
Enrichment ratio [*]	1.115	1.114
Pesticide distribution coefficient (L kg ⁻¹)		
Atrazine	3.60	2.50
2,4-D	4.81	1.52
Phorate	39.58	17.42
Terbufos	42.03	18.50

^{*} Grant (1992)

6.4 RESULTS AND DISCUSSION

6.4.1 Distribution of particle size fraction

The particle size fractions obtained by ultrasonic dispersion and the conventional pipette method are presented in Table 6.3.

Table 6.3 Comparison of the particle size distribution of the soils by
(A) the conventional pipette and (B) the ultrasonic dispersion method

Soil	horizon	Sand		Silt		Clay		Organic carbon	
		A	B	A	B	A	B	A	B
		(%)							
Egmont	Ah	47.0	49.5	27.4	26.0	25.6	24.2	1.1	8.7
	Bw3	51.8	53.3	23.0	22.6	25.1	23.0	0.5	1.9
Tokomaru	Ah1	12.2	12.4	62.2	60.9	25.6	24.7	0.7	3.2
	Btg	7.2	9.4	62.6	64.0	30.2	26.3	0.1	0.6

The particle size distribution obtained by ultrasonic dispersion compared favourably with the conventional pipette method used in defining soil texture. Although slightly lower clay and silt fractions were obtained by ultrasonic dispersion, in general this was compensated by a slightly higher sand content. Similar results were reported for New Zealand soils by Healy and Claridge (1974). The decrease in clay and silt fractions in ultrasonic dispersion has been attributed to the presence of clay as stable aggregates of sand or silt size, or as coatings on the larger mineral particles (Anderson *et al.*, 1981). The organic carbon in the whole soil after ultrasonic dispersion was very close to that of the original soil. However, treatment of soils with H_2O_2 to facilitate dispersion has resulted in the loss of considerable amounts of organic carbon. Since pesticide sorption is very much dependent upon the organic

matter content, only the size fractions obtained by ultrasonic dispersion were used in the subsequent sorption and desorption experiments.

6.4.2 Characteristics of particle size fractions

The pH of the silt and clay fractions obtained by ultrasonic dispersion were 0.1-0.2 pH units lower than that of the whole soil and the sand fractions (Table 6.4). Curtin *et al.* (1987) also observed that the pH of the 0.2 to 20 μm fraction was 0.3-0.4 units less than that of a whole soil, and also the fine clay ($<0.2 \mu\text{m}$), and the larger ($>20 \mu\text{m}$) fractions. They attributed this partly to the differences in the amount of titrable acidity. A plot of organic carbon vs the log mean particle diameter of the particle size fractions is presented in Figure 6.1. Organic carbon content increased with decreasing particle size. Several researchers have observed a similar pattern for the distribution of organic carbon in particle size fractions (Nkedi-Kizza *et al.*, 1983; Raman 1987). The relative proportions of soil organic carbon associated with the clay ($<2 \mu\text{m}$), silt (2-63 μm) and sand ($>63 \mu\text{m}$) fractions of the present soils averaged 37.3, 45.5 and 16.3%, respectively. This study shows that significant amounts of organic matter accumulated in the finer fractions (clay and silt).

The poorly ordered inorganic materials, as measured by the amount of Fe, Al and Si extracted by the acid-oxalate reagent, decreased with increasing particle size. The clay and silt fractions contained substantial amounts of Fe, Al and Si (Table 6.4). Similar observations have been reported in many studies (Huang *et al.*, 1984; Curtin *et al.*, 1987 and Sayin *et al.*, 1990). Among the soil fractions, the Egmont topsoil and sub-soil horizon fractions contained the largest amounts of Fe, Al and Si. The higher amounts of Fe, Al and Si in the Egmont soil can be explained by the presence of allophanic clays, whereas the lower extractable Fe, Al and Si in the Tokomaru soil may be due to the presence of the micaceous minerals, illite and vermiculite.

6.4.3 Clay mineralogy

6.4.3.1 X-ray diffraction

The clay mineralogy of the soils examined is summarized in Table 6.5. The X-ray

Table 6.4 **Some important characteristics of particle size fractions**

Particle size fraction	pH	Organic Carbon (%)	Oxalate extractable		
			Fe	Al	Si
			(%)		
Egmont - Ah					
Sand	6.27	4.5	0.58	2.12	0.77
Silt	5.97	9.6	1.04	3.15	1.49
Clay	5.85	12.8	1.24	3.98	1.80
Egmont -Bw3					
Sand	6.88	0.94	0.30	1.32	0.64
Silt	6.56	2.36	1.52	6.30	2.95
Clay	6.48	3.22	2.16	10.40	5.15
Tokomaru - Ah1					
Sand	5.70	1.50	0.14	0.09	0.03
Silt	5.60	3.20	0.27	0.23	0.04
Clay	5.72	4.75	0.56	0.35	0.05
Tokomaru - Btg					
Sand	6.80	0.19	0.07	0.05	0.04
Silt	6.41	0.48	0.12	0.19	0.06
Clay	6.33	0.94	0.37	0.32	0.04

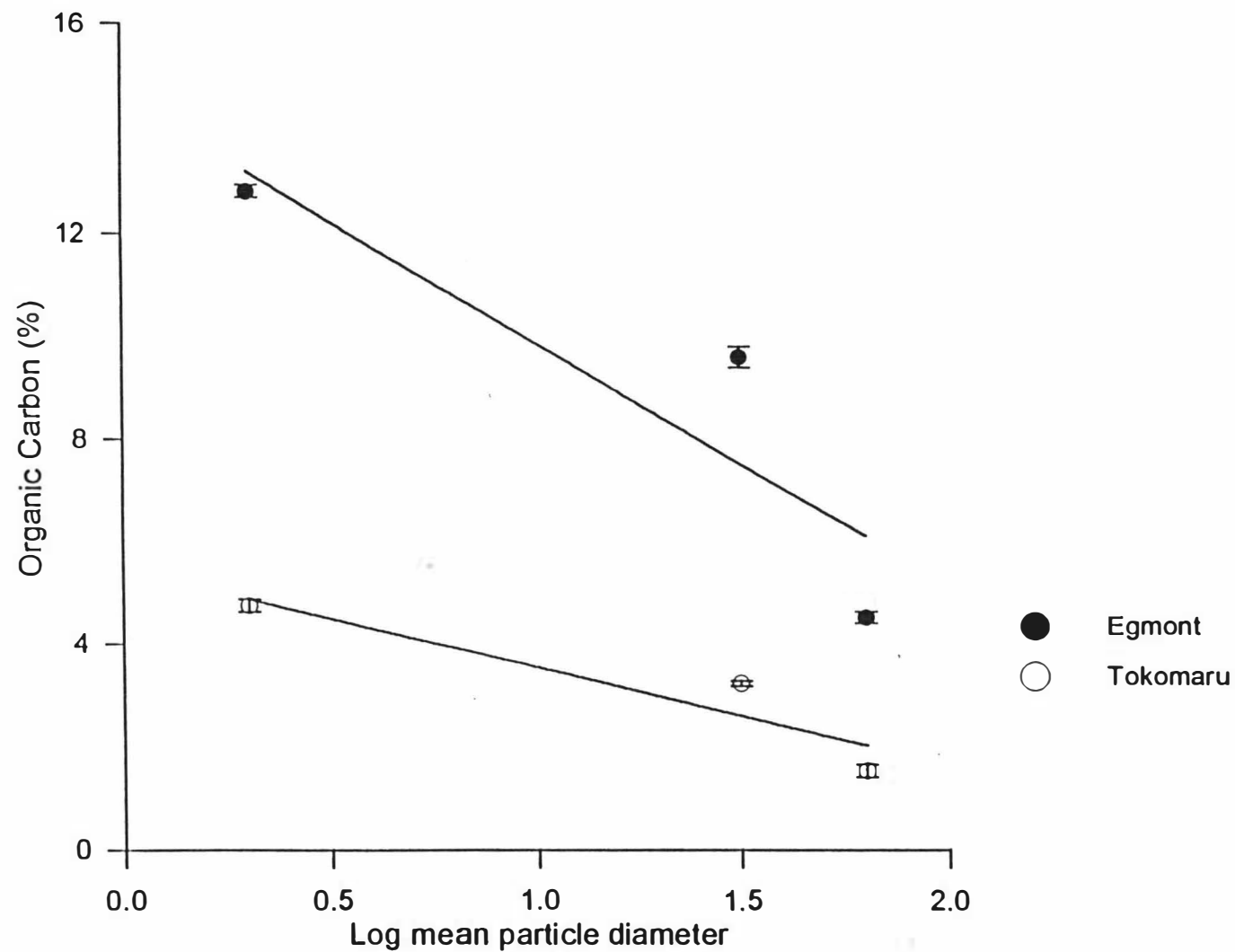


Fig 6.1 Relationship between organic carbon and particle size in the Egmont and the Tokomaru soil. (Vertical bars represent standard error of mean)

pattern of the clay fraction of the Tokomaru soil indicates that mica/illite are the dominant clay mineral species present in the Ah1 and Btg horizon.

Table 6.5 **Distribution of minerals in clay fractions of the Egmont and the Tokomaru soils as indicated by X-ray diffraction analysis**

Soil	Horizon	mica/ illite	Vermiculite	Allophane
Egmont	Ah	-	-	+ + +
	Bw3	-	-	+ + + +
Tokomaru	Ah1	+ + +	+ +	-
	Btg	+ + +	+	-

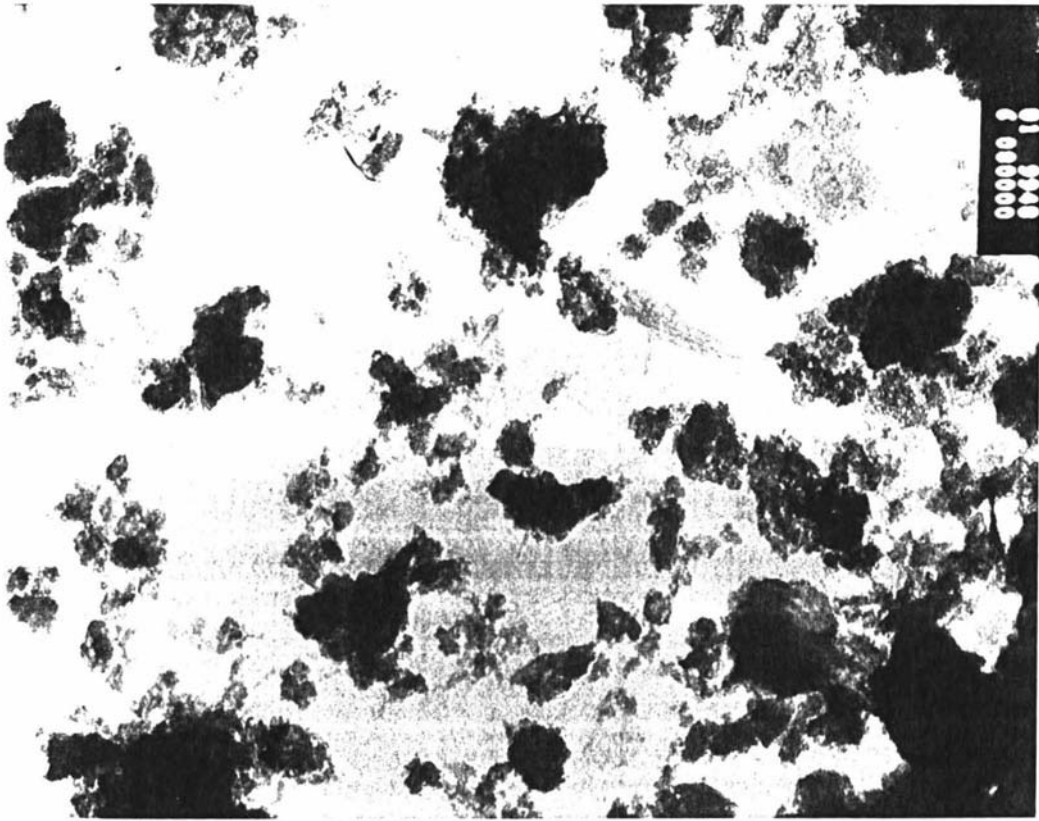
+ + + +	=	large amount
+ + +	=	considerable amount
+ +	=	moderate amount
+	=	small amount
-	=	not identified

Vermiculite clay is also present in small amounts in the Ah1 horizon. The X-ray diffraction pattern for the Egmont clay sample showed a significant plateau between 4 and 16° 2 θ indicating the presence of short-range order materials (Naidu *et al.*, 1987).

6.4.3.2 *Transmission electron microscopy*

The < 2 μm fractions of the Tokomaru and the Egmont soils were examined with the Transmission Electron Microscope (TEM) and the results are presented in Figure 6.2. The Tokomaru clay fraction showed the presence of large flakes of illite along with clusters of crystalline iron oxide and hydroxides. The TEM examination of the Egmont clay fraction showed the presence of poorly-ordered materials (Fig 6.2). A

(A)



(B)



few particles of halloysite in the form of long tubes were also identified in the sample.

6.4.3.3 *Infrared spectroscopy*

The IR spectra of the Egmont clay (Ah and Bw3 horizons) show the presence of proto-imogolite allophane (Russell *et al.*, 1981; Parfitt and Henmi 1980; Naidu *et al.*, 1987) with bands near 3500, 1000, 690, 580 and 440 cm^{-1} (Fig 6.3). The spectrum had additional bands near 1100, 1040, 480 cm^{-1} characteristic of the spectrum of halloysite separated from volcanic ash soils. However the bands were broad, suggesting a poorly ordered halloysite structure (Russell *et al.*, 1981).

6.4.4 Sorption of pesticides by whole soil and particle size fractions

The extent of pesticide sorption was expressed as a distribution coefficient (K_d), which is the ratio of pesticide concentration in the soil to that in the soil solution. The K_d values of ionic and non-ionic pesticides for the topsoil and sub-soil particle size fractions are presented in Figure 6.4.

The K_d values range by a factors of 4.5 and 2.5 for ionic and non-ionic pesticides, respectively, among the particle size fractions. Similarly Nkedi-Kizza *et al.* (1983) have observed that the Freundlich K values range within factors of 16 and 7 for ionic and non-ionic herbicides, respectively among particle size fractions. Pesticide sorption was greater in surface horizon particle size fractions than subsoils and the difference is greater for non-ionic than ionic pesticides.

In general, sorption of pesticides in both soils followed the order: clay > silt > sand. The difference in K_d values between clay and sand fractions was higher for ionic than non-ionic pesticides. Kay and Elrick (1967), Karickhoff *et al.* (1979), Nkedi-Kizza *et al.* (1983) and Huang *et al.* (1984) also found a similar pattern of sorption of pesticides by particle size fractions, and reported that the sorption increases in proportion to the organic carbon content of the particle size fraction.

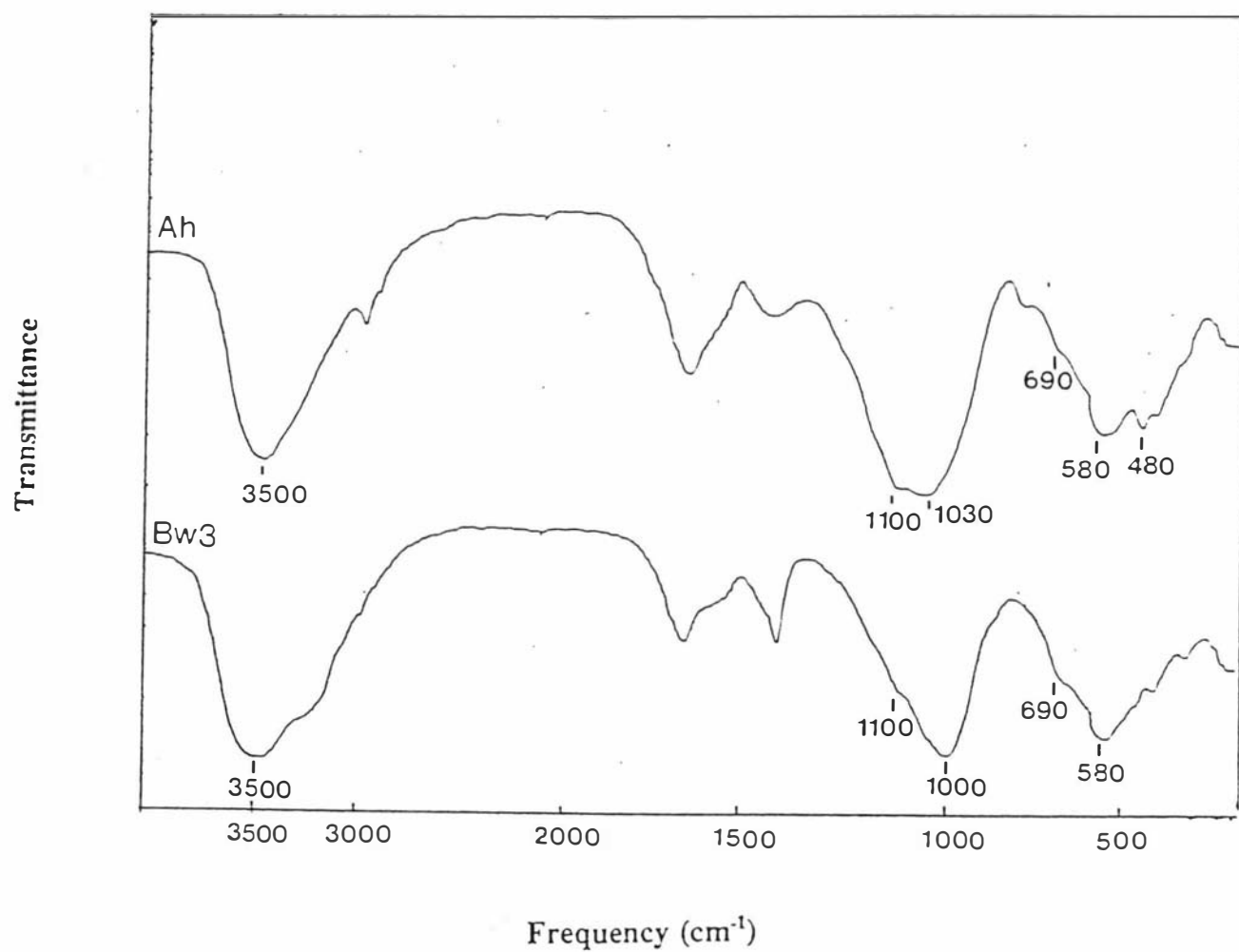


Fig 6.3 Infrared spectra of Egmont Ah and Bw3 horizon clay

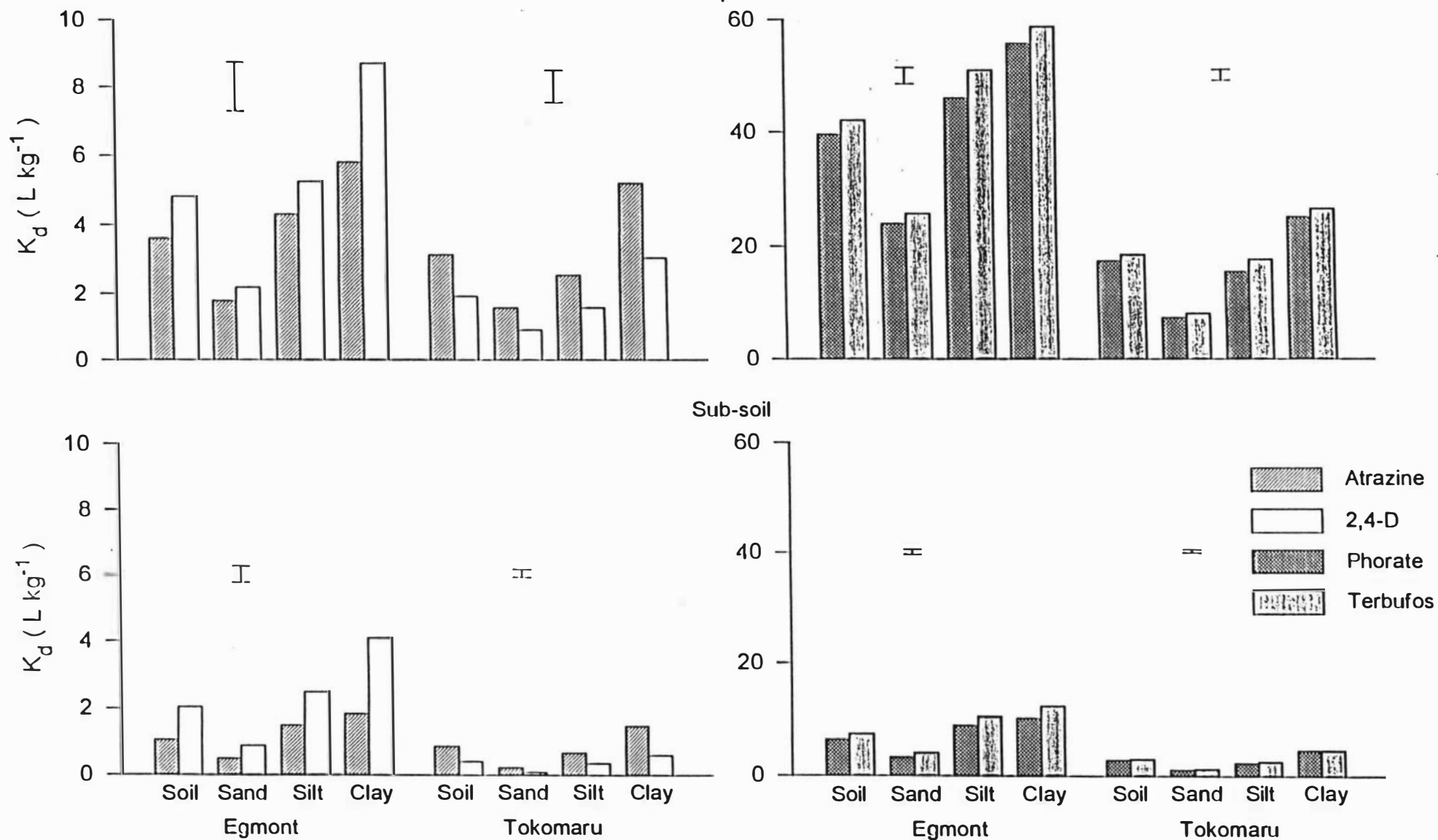


Fig 6.4 Distribution coefficient (K_d) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in whole soil and particle size fractions. (Vertical bars represent LSD (0.05))

Clay fractions from the Egmont soil always sorbed more pesticides than did the clay fractions from the Tokomaru soil. The difference in the sorption of pesticides can be attributed mainly to the difference in the amount of organic carbon and Fe and Al oxides in the size fractions. However, the order of sorption of ionic pesticides by clay fractions varied between the soil samples. The Egmont clay sorbed higher amounts of 2,4-D than atrazine, whereas the Tokomaru clay sorbed higher amounts of atrazine than 2,4-D (Fig 6.4). The Egmont clay sample was composed of mainly amorphous aluminium silicate and oxides of Fe and Al, which are likely to have a high point of zero net charge (pH=8). This results in a net positive charge at the pH at which the pesticide retention was measured (pH 6.3) and 2,4-D anions are likely to be retained on these positive sites. The higher K_d value of atrazine in the Tokomaru clay can be explained by the presence of 2:1 clays (such as the micaceous minerals, illite and vermiculite) with permanent negative charge (Bolan et al., 1986). The cationic species of atrazine is retained onto these negative sites.

6.4.5 Relative contribution of particle size fractions to the distribution coefficient (K_d) of the whole soil

The relative contributions of the particle size fractions to the whole-soil K_d of pesticides is presented in Figure 6.5. The relative contribution is determined by both the K_d values of the particle size fractions and the proportions of these fractions in the whole soil (Eq 6.2). As expected, the relative contribution of K_d in the Egmont soil increased with decreasing particle size and the effect was more pronounced for the ionic pesticides. For example, the relative contributions of the clay, silt and sand fractions to the K_d value of 2,4-D for the Egmont whole soil was 43.6%, 30% and 22.2%, respectively. Whereas, the clay, silt and sand fractions contributed 35%, 32%, 30%, respectively to the K_d values of the non-ionic pesticides.

Although in general the K_d values for the silt fraction were less than that for the clay fraction, in the Tokomaru soil, the relative contribution of the silt fraction to the whole soil K_d was higher for both ionic and non-ionic (except atrazine) pesticides. This is expected because in the Tokomaru soil the silt fraction alone constitutes more than 60% of the textural composition (Table 6.3). In the case of atrazine both the clay and silt fractions contributed equally to the sorption. This again highlights the

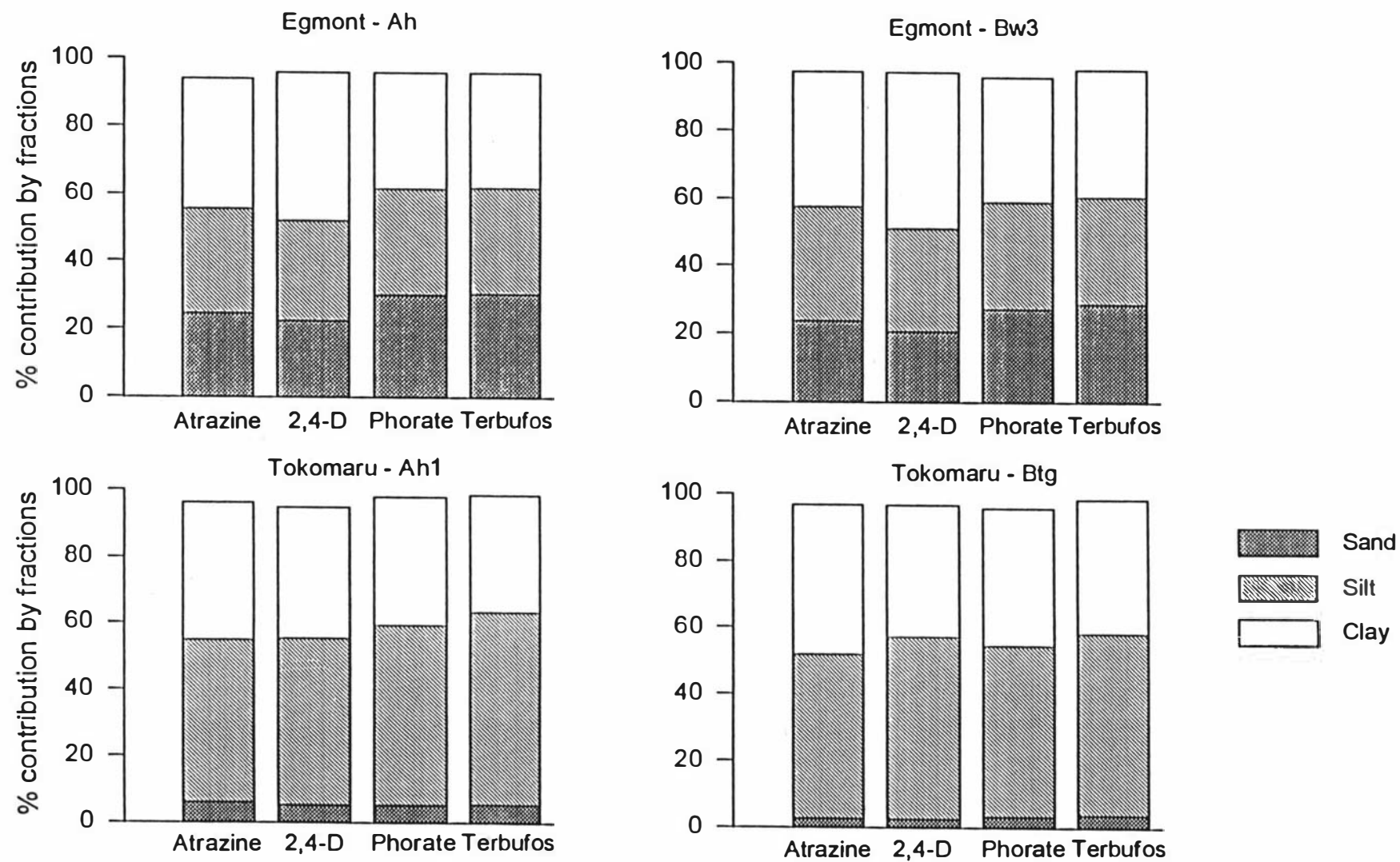


Fig 6.5 Relative contribution of particle size fractions to the distribution coefficient (K_d) of pesticides

importance of negative charge in the Tokomaru clay to the sorption of atrazine cations.

The relationship between the measured K_d values of the pesticides of the whole soil and the K_d values estimated using Eq 6.1 is presented in Figure 6.6. The results indicated that the predicted K_d values are in close agreement with the measured K_d values. The maximum deviation between the predicted and the measured K_d values was only 4.3%. The reason for the slight difference between the measured and predicted K_d values is due to the lower recovery of the particle size fractions obtained by ultrasonification. From Table 6.3, the summation of particle sizes separated by ultrasonification yielded 98-99.7 percent of the original weight indicating a slight loss of mineral or organic matter that may have floated off during separation.

In all the earlier studies (Table 2.1) no attempt has been made to match the measured K_d value for the whole soil with that estimated from the particle size fractions on a whole soil basis. The results of this study indicated that a reasonable estimate of whole soil K_d can be calculated from the K_d values for the particle size fractions. Similarly Karickhoff and Brown (1978) reported that the K_d values of the individual fractions can be used to compute the K_d value of the whole soil. On this basis an attempt was made in the present study to estimate the K_d value of the soil from the K_d values measured for the individual particle size fractions. This enabled us to predict the amount of pesticide likely to be lost through erosion of sediment during surface runoff (see below).

6.4.6 Relationship between pesticide sorption and organic carbon content

Pesticide sorption in general increased with decreasing particle size. These results are reasonable in view of the higher organic carbon content of the fine fraction than of the coarse fraction. A significant correlation was obtained between organic carbon content of the fractions and the K_d values of ionic and non-ionic pesticides (Fig 6.7). The corresponding linear regressions are:

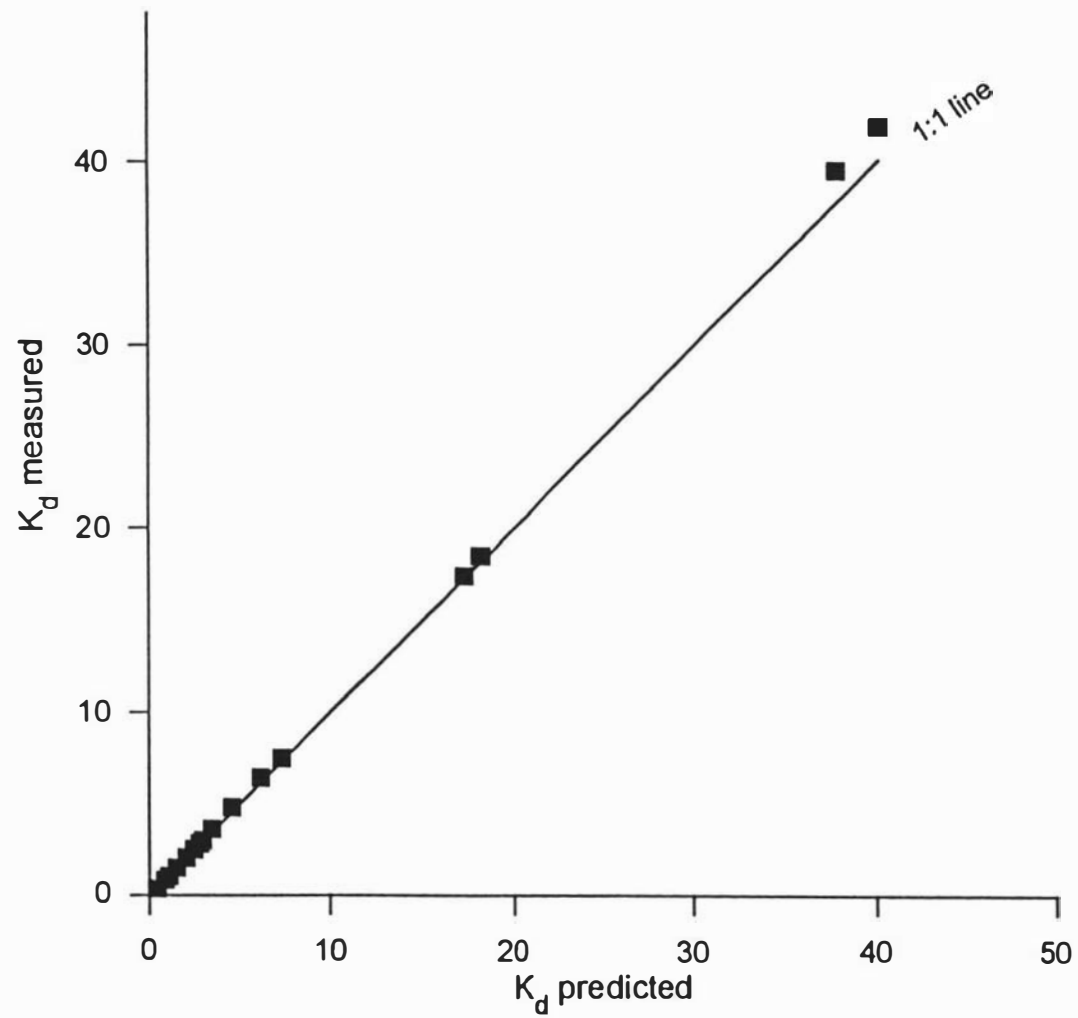


Fig 6.6 Relationship between measured and predicted distribution coefficient (K_d) of pesticides on a whole soil basis

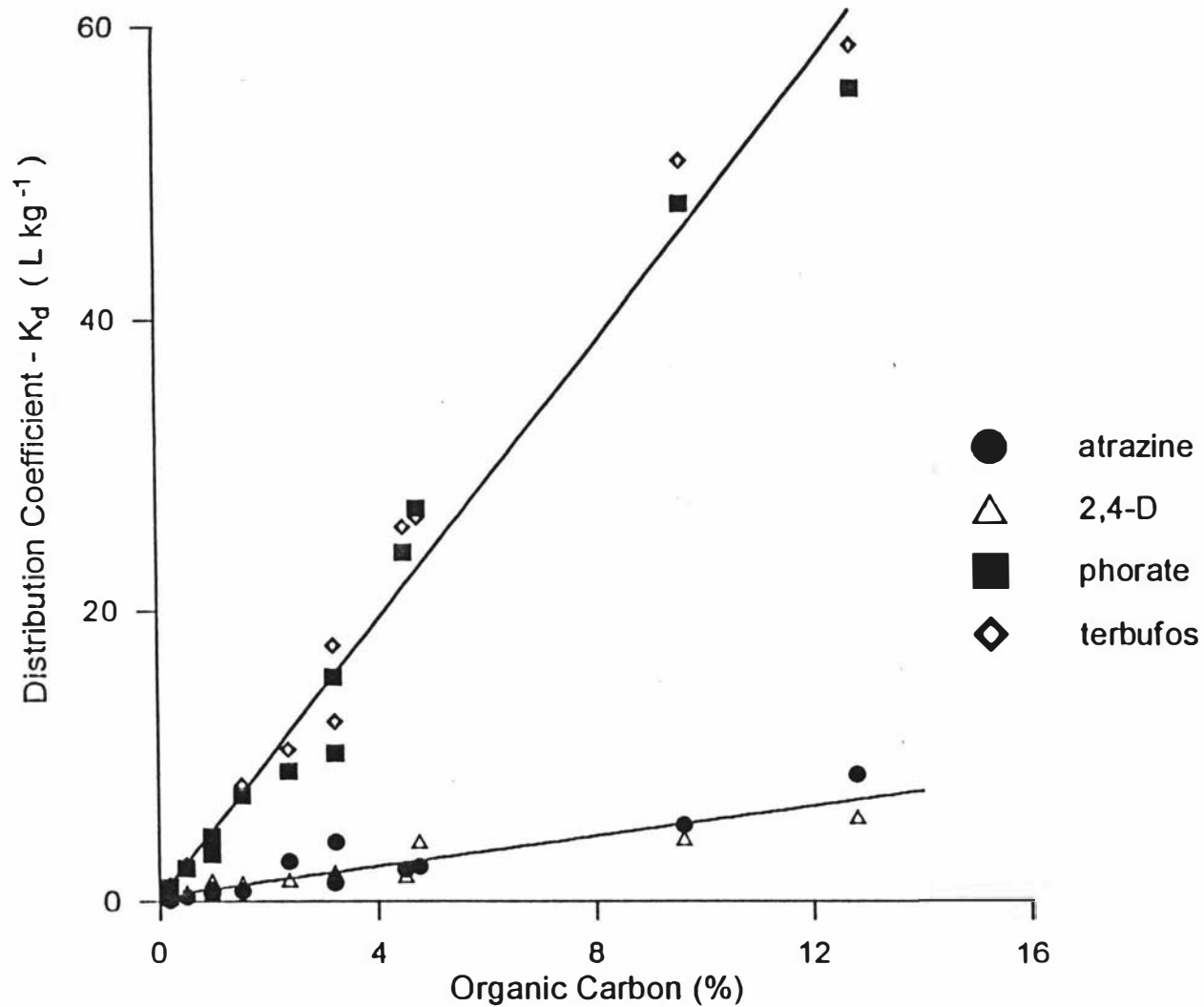


Fig 6.7 Relationship between organic carbon and distribution coefficient (K_d) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in particle size fractions

$$K_d = 0.36 + 0.51 (\%OC) \quad (R^2=0.84) \quad (\text{Ionic pesticides}) \quad (6.8)$$

$$K_d = 0.32 + 4.74 (\%OC) \quad (R^2=0.97) \quad (\text{Non-ionic pesticides}) \quad (6.9)$$

Linear correlations between organic carbon and sorption of ionic and non-ionic pesticides have often been reported in the literature (Felsot and Dahm, 1979; Peter and Weber 1985; Johnson and Sims, 1993).

The R^2 value indicated that organic carbon accounted for greater variation in the K_d value for the non-ionic (97%) than for the ionic (84%) pesticides. Johnson and Sims (1993) also observed a lower coefficient of determination for the ionic pesticides (dicamba, 2,4-D and atrazine) than the non-ionic pesticide (metolachlor). In the present study, the slope of the regression equations indicated that the increase in K_d value per unit increase in organic carbon was 8 times greater for the non-ionic than for the ionic pesticides.

The positive correlation between organic carbon and K_d has justified the use of a sorption coefficient based on organic carbon (K_{oc}). While the K_d values of pesticides for different particle size fractions ranged by a factor of 4.5, the K_{oc} values varied only by a factor of 1.5 (Table 6.6). The K_{oc} values of non-ionic pesticides were essentially the same for the whole soil as for the different particle size fractions, in both topsoil and subsoil horizons (Table 6.6). This indicates that organic carbon is primarily responsible for sorption of non-ionic pesticides by any particle size fraction.

However, the K_{oc} values of 2,4-D in the Egmont subsoil particle size fractions were consistently higher than the topsoil fractions. Similarly the K_{oc} value of atrazine was higher in the Tokomaru subsoil particle size fractions. The increase in K_{oc} values of ionic pesticides in subsoils indicates that either the organic carbon varied in the sorption capacity for the pesticides between the soils, or that in addition to organic matter, clay minerals are also contributing to the sorption of ionic pesticides. The high organic carbon content in the surface horizon particle size fractions probably masks the effect of clay minerals on sorption, so that the K_d values are controlled mainly by the organic carbon content.

Table 6.6 **Distribution coefficients (K_d and K_{oc}) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in whole soil and particle size fractions**

Fractions	K_d (L kg ⁻¹)				K_{oc} (L kg ⁻¹)			
	Atrazine	2,4-D	Phorate	Terbufos	Atrazine	2,4-D	Phorate	Terbufos
Egmont - Ah								
Whole soil	3.60	4.81	39.58	42.03	41	55	455	483
Sand	1.77	2.17	24.01	25.73	39	48	533	572
Silt	4.30	5.23	47.92	50.91	46	54	498	529
Clay	5.79	8.70	55.78	58.78	45	68	436	459
Egmont - Bw3								
Whole soil	1.06	2.04	6.42	7.48	55	107	336	392
Sand	0.49	0.80	3.27	4.04	52	85	348	430
Silt	1.48	2.74	9.02	10.5	62	116	382	445
Clay	1.82	4.08	10.24	12.40	57	127	318	385
Tokomaru - Ah1								
Whole soil	2.50	1.52	17.40	18.50	79	48	553	587
Sand	1.25	0.72	7.30	8.04	83	48	486	536
Silt	2.01	1.25	15.46	17.59	63	39	483	550
Clay	4.15	2.42	25.01	25.35	88	51	526	534
Tokomaru - Btg								
Whole soil	0.85	0.40	2.84	2.98	137	65	458	481
Sand	0.24	0.08	1.02	1.15	126	42	537	605
Silt	0.66	0.34	2.27	2.54	138	71	473	529
Clay	1.45	0.60	4.46	4.52	155	64	474	481

6.4.7 Sorption of ionic and non-ionic pesticides in the oxidised soil and particle size fractions

To examine the effect of organic carbon on the sorption of pesticides by the size fractions, the topsoil and subsoil particle size fractions were treated with H_2O_2 to remove organic carbon and the sorption was measured (Table 6.7). Removal of organic carbon in general decreased the sorption of pesticides by all particle size fractions. The effect of organic carbon removal on pesticide sorption is greater for non-ionic than ionic pesticides and greater for topsoil particle size fractions than subsoil fractions. The decrease in K_d values (with organic carbon removal) of non-ionic pesticides ranged from 84 to 90% in particle size fractions in surface and subsoil horizons. The average reduction in K_d of ionic pesticides ranged from 60 to 80%, in topsoil particle size fractions but the reduction in K_d values for ionic pesticides was lower in the sub-soil fractions. In the Egmont soil, the reduction in K_d of 2,4-D and atrazine was 7-60 and 79-85%, respectively, whereas in the Tokomaru soil the reduction in K_d values of atrazine and 2,4-D was 0-38% and 66-80%, respectively.

The K_{oc} values of non-ionic and ionic pesticides for the natural and oxidised fractions in the Egmont and the Tokomaru soils are presented in Figure 6.8. The results indicated that removal of organic carbon has no significant effect on the K_{oc} values of non-ionic pesticides whereas it increased the K_{oc} values of ionic pesticides. Removal of about 85% organic carbon in the Egmont particle size fractions resulted in a 2 fold increase in the K_{oc} of 2,4-D in the surface and a 4-fold increase in the subsoil horizons compared to the natural soil particle size fractions (Fig 6.8). Similarly in the Tokomaru sub soil horizon, the K_{oc} of atrazine in the oxidised particle fractions was 4-5 times higher than in the natural soil particle size fraction (Fig 6.8).

The presence of Fe and Al oxides offers a key to the reason why the oxidised Egmont subsoil horizon particle size fractions sorbed much greater amounts of 2,4-D than the surface horizon fractions. Given that the oxidised Egmont subsoil horizon particle size fractions have less organic carbon (Table 6.8) than the surface soil, greater exposure of Fe and Al oxides is expected in the subsoil particle size fractions than in the surface horizon fractions. In the topsoil fractions organic carbon coats the surfaces of the clays leaving less exposure of Fe and Al oxides. Appelt *et al.*

Table 6.7 Distribution coefficients (K_d and K_{oc}) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in oxidised soil and particle size fractions

Fractions	K_d (L kg ⁻¹)				K_{oc} (L kg ⁻¹)			
	Atrazine	2,4-D	Phorate	Terbufos	Atrazine	2,4-D	Phorate	Terbufos
Egmont - Ah								
Whole soil	0.55	1.82	4.07	4.30	65	214	538	582
Sand	0.37	0.45	2.51	2.43	71	86	483	467
Silt	0.80	1.87	4.88	5.44	70	163	424	473
Clay	1.27	2.04	7.08	7.85	87	141	488	541
Egmont - Bw3								
Whole soil	0.22	1.89	1.1	1.22	55	472	275	305
Sand	0.07	0.30	0.29	0.38	64	273	264	345
Silt	0.15	1.54	1.06	1.16	43	440	303	331
Clay	0.42	2.23	1.72	1.80	84	446	344	360
Tokomaru - Ah1								
Whole soil	1.32	0.28	2.21	2.58	315	67	526	614
Sand	0.77	0.12	1.21	1.42	275	43	432	507
Silt	1.90	0.39	2.48	2.64	380	78	496	528
Clay	2.64	0.56	3.52	3.85	357	76	476	520
Tokomaru - Btg								
Whole soil	0.84	0.11	0.61	0.68	560	73	407	453
Sand	0.16	0.02	0.21	0.28	320	40	420	560
Silt	1.08	0.12	1.02	1.05	514	57	486	500
Clay	1.47	0.20	1.35	1.73	459	62	422	541

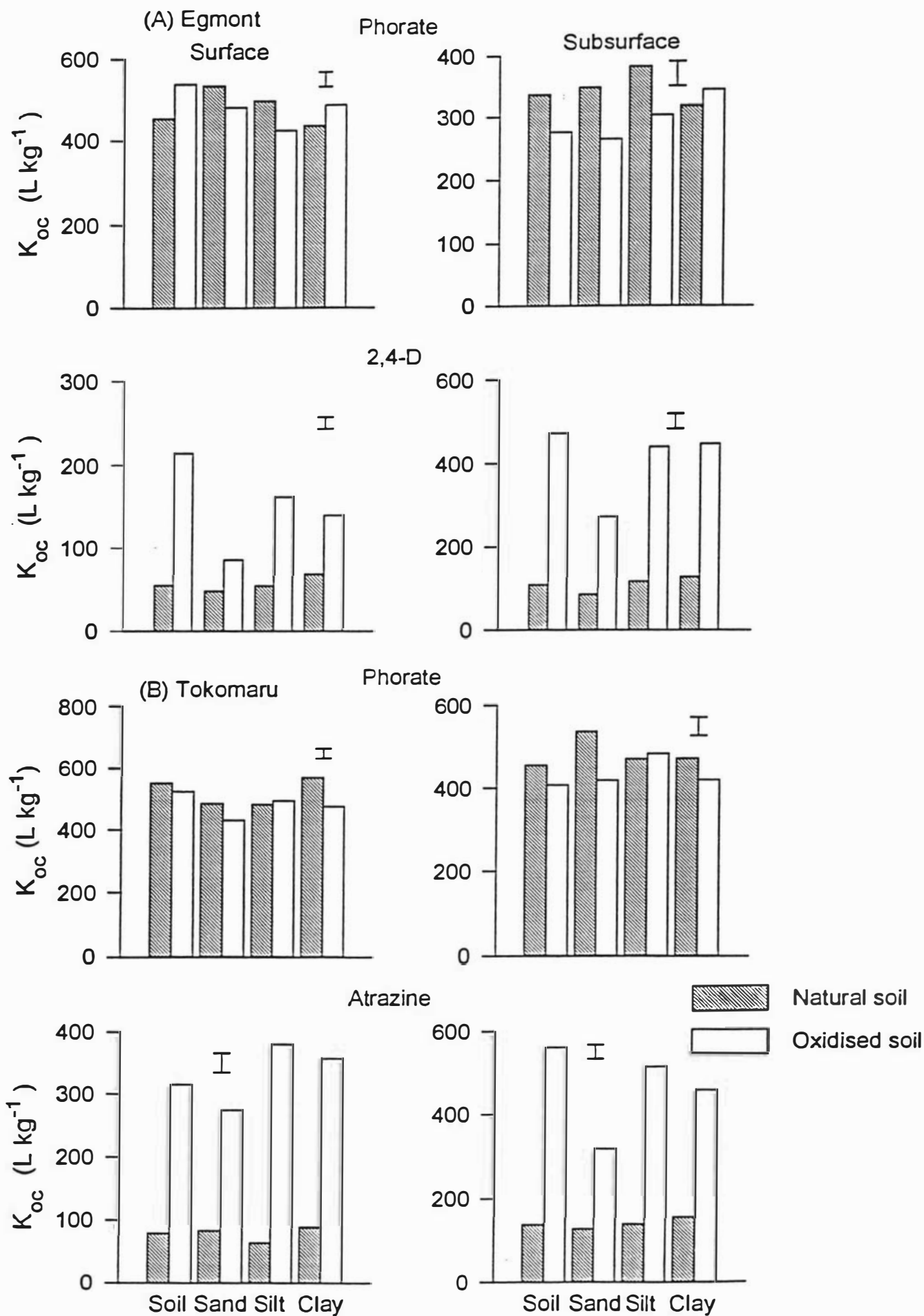


Fig 6.8 Comparison of K_{oc} of ionic (atrazine and 2,4-D) and non-ionic (phorate) pesticides in (A) Egmont and (B) Tokomaru natural and oxidised soil and particle size fractions. (Vertical bars represent LSD (0.05))

Table 6.8 **Some important characteristics of oxidised particle size fractions**

Particle size fraction	Organic Carbon (%)	Oxalate extractable		
		Fe	Al	Si
		(%)		
Egmont - Ah				
Sand	0.52	0.53	2.02	0.75
Silt	1.15	1.07	3.10	1.52
Clay	1.45	1.26	3.90	1.84
Egmont - Bw3				
Sand	0.11	0.24	1.18	0.56
Silt	0.35	1.50	6.19	2.90
Clay	0.50	2.12	10.18	5.02
Tokomaru - Ah1				
Sand	0.28	0.13	0.08	0.02
Silt	0.50	0.28	0.21	0.05
Clay	0.74	0.59	0.33	0.12
Tokomaru - Btg				
Sand	0.05	0.08	0.04	0.03
Silt	0.21	0.10	0.17	0.05
Clay	0.32	0.35	0.31	0.03

(1975) and Murray and Hall (1989) also found a high sorption of salicylic acid on subsoils containing high amounts of Fe and Al oxides. The increase in K_{oc} of 2,4-D in the Egmont sub-soil fraction indicates that in addition to organic carbon, clay minerals carrying positive charges are also contributing to the sorption of ionic pesticides. The higher K_{oc} values of atrazine in the Tokomaru soil particle size fractions can be attributed to the presence of 2:1 clays (micaceous illite and vermiculite) resulting in a greater permanent negative charge (Bolan *et al.*, 1985).

6.4.8 Desorption

The percentage of sorbed ^{14}C pesticide desorbed during each sequential desorption step and the amount of residual pesticide remaining in the soil from the Tokomaru soil are presented in Table 6.9. The results show that 92-98% of the ^{14}C pesticides were recovered from the soil by either desorption or subsequent extraction indicates that there was no evidence for degradation of pesticide during the desorption period.

Desorption of pesticides was less from the Egmont topsoil particle size fractions, which have a high organic carbon content (8.7%), than from the particle size fractions from the Tokomaru soil. Desorption of pesticides from particle size fractions followed the order: sand > silt > clay. The lower the organic carbon in the fractions, the greater the desorption. Following four successive extractions with 0.01 M CaCl_2 , 65-90 and 22-75% of the initially sorbed ionic and non-ionic pesticides, respectively were released from surface horizon particle size fractions (Fig 6.9). In the sub-soil horizon, 75-90 and 55-90% of ionic and non-ionic pesticides, respectively were released. It shows that desorption is greater with ionic than non-ionic pesticides in natural soil particle size fractions particularly in the top soil. These results reflect the strong binding capacity of non-ionic pesticides to organic carbon (Felsot and Dahm, 1979; Kookana and Aylmore, 1993). It shows that for non-ionic pesticides the desorption was considerably enhanced in subsoil horizon particle size fractions, whereas the release of ionic pesticides was essentially the same between the surface and subsoil horizon particle size fractions.

Sorption from the oxidised soil fractions was generally more reversible than from natural soil fractions. Following four successive extractions with 0.01 M CaCl_2 , 85-

Table 6.9 Recovery of ¹⁴C pesticides during desorption from the Tokomaru soil

Pesticides	Added (μmol L ⁻¹)	Sorbed (μmol kg ⁻¹)	¹⁴ C pesticide recovery during desorption steps* (%)				¹⁴ C pesticide in soil (%)	Total recovery (%)
			1	2	3	4		
Atrazine	18.6	41.95	58 ± 4.6	16 ± 2.0	5 ± 0.5	5 ± 0.4	10 ± 1.0	94 ± 3.5
2,4-D	18.1	23.89	59 ± 5.5	13 ± 1.7	9 ± 1.0	6 ± 0.2	11 ± 0.6	98 ± 4.0
Phorate	15.4	78.05	23 ± 2.4	15 ± 3.0	11 ± 0.3	8 ± 0.5	35 ± 2.6	92 ± 2.8
Terbufos	6.9	39.42	20 ± 1.7	14 ± 0.8	10 ± 0.6	8 ± 0.6	44 ± 2.1	96 ± 3.1

* Standard error of mean

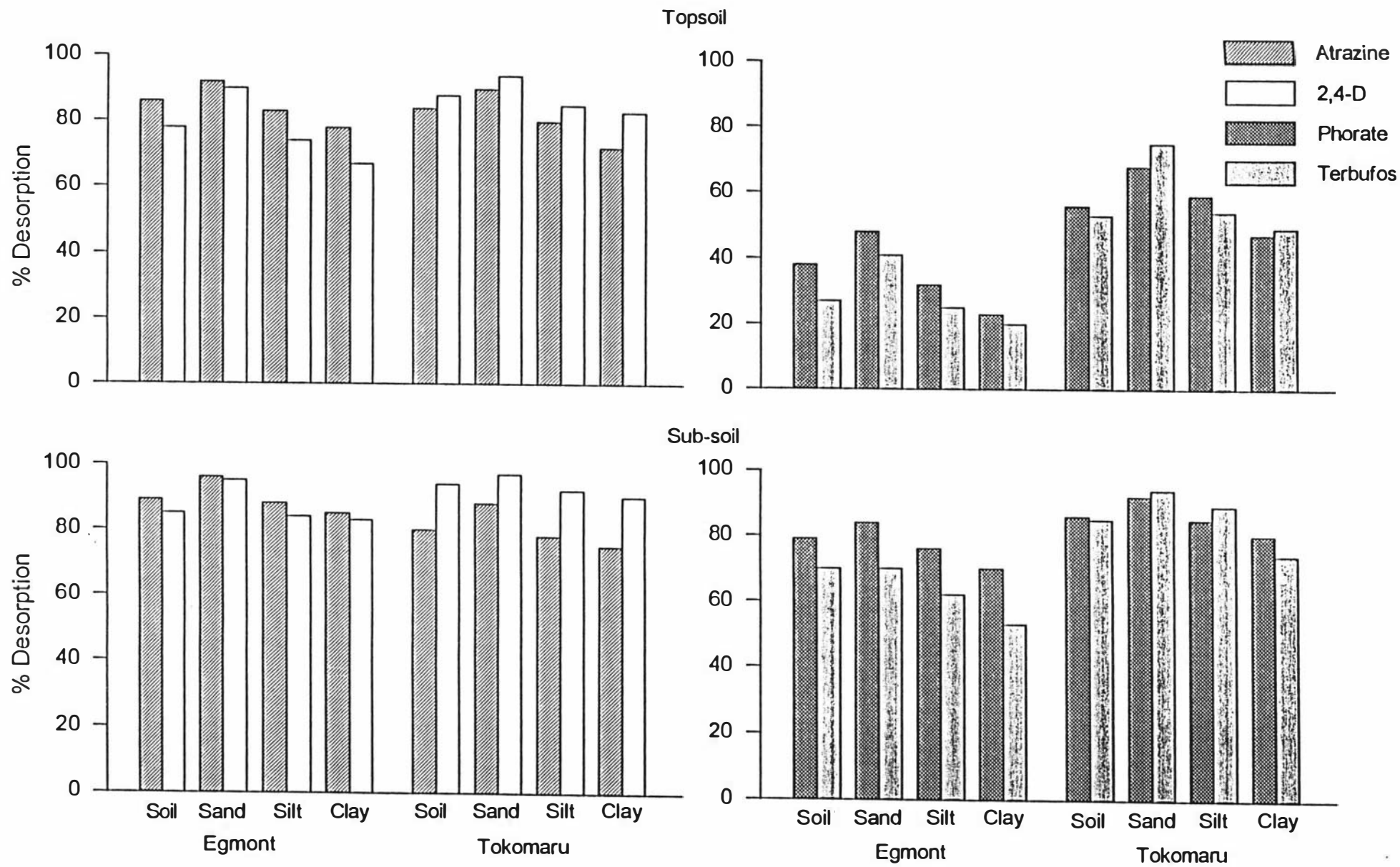


Fig 6.9 Desorption of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides from whole soil and particle size fractions

97% of the initially sorbed non-ionic pesticides were released from the oxidised soil particle size fractions (Fig 6.10). It is interesting to note that the oxidised Egmont Bw3 and Tokomaru Btg horizon particle size fractions exhibited the greatest sorption of 2,4-D and atrazine but the desorption of the pesticides was lowest in these soils. These results would tend to indicate that 2,4-D and atrazine are strongly bonded in the Egmont Bw3 and the Tokomaru Btg horizon particle size fractions, respectively.

The K_d values for the desorption steps were calculated and compared with that for the sorption process (Table 6.10). The K_d values of pesticides during the desorption steps was higher than that during the sorption steps. An increase in K_d value of pesticide during desorption over sorption generally indicates the sorption-desorption hysteresis (Laird *et al.*, 1994). The results show that the increase in K_d of pesticides was higher for non-ionic (phorate) than ionic pesticides (2,4-D and atrazine) for natural soil and particle size fractions in the Egmont and the Tokomaru soils. This suggests that the hysteresis effect is greater for non-ionic than ionic pesticides. The increase in K_d values of pesticides for the desorption steps followed the order: clay > silt > soil > sand (Table 6.10). This suggests that the sorption-desorption hysteresis for non-ionic pesticides is associated with the organic carbon in the fine fraction (clay and silt).

The K_d values of the ionic and non-ionic pesticides during desorption from the whole soil and the particle size fractions decreased by 83-90 and 60-85%, respectively, after the H_2O_2 treatment (Table 6.10). In other words the K_d values calculated for the desorption step of the oxidised soil fractions approaches the K_d values calculated for the sorption step (Table 6.10). The closer agreement between the K_d values calculated for the desorption and the sorption steps for the non-ionic pesticides for the oxidised soil fractions indicated that relatively less sorption-desorption hysteresis occurred in these fractions. This suggests that non-ionic pesticides are bound more tightly to the organic surfaces (natural) than to inorganic (mineral) surfaces.

6.4.9 Predicted pesticide losses in surface runoff

Table 6.11 shows the predicted pesticide losses with sediment resulting from a rainfall event of 65 mm. Total pesticide losses predicted for allophanic soil samples were 3.5,

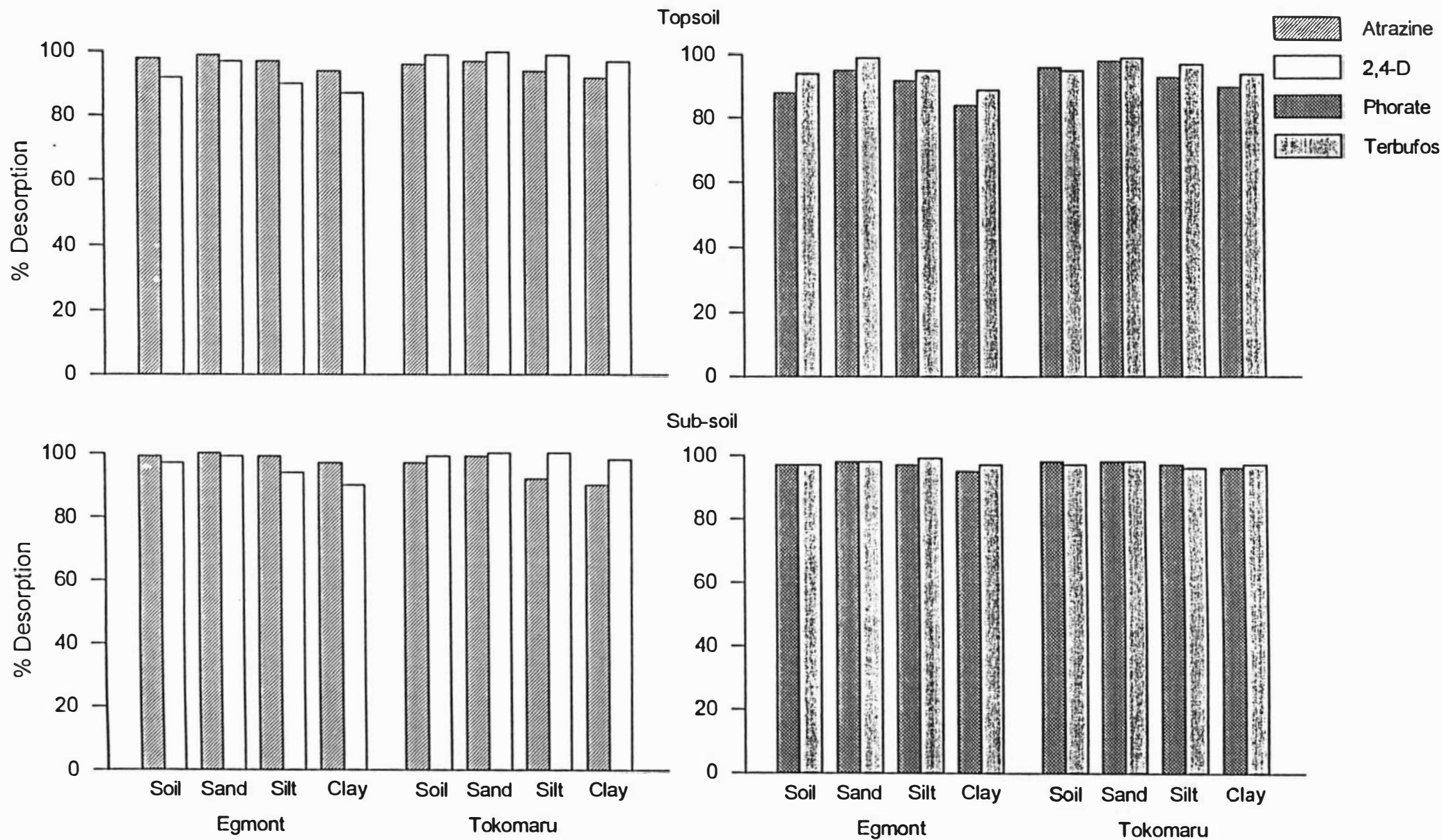


Fig 6.10 Desorption of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides from oxidised whole soil and particle size fractions

Table 6.10 Distribution coefficient (K_d) values of ionic (atrazine and 2,4-D) and non-ionic (phorate) pesticides during sorption and desorption in the Egmont and the Tokomaru natural and oxidised soil and particle size fractions

Pesticides	Treatment	Distribution Coefficient (K_d) (L kg ⁻¹) [*]							
		Whole soil		Sand		Silt		Clay	
		sorption	desorption	sorption	desorption	sorption	desorption	sorption	desorption
Egmont									
2,4-D	Natural	4.81 ± 0.5	7.47 ± 1.2	2.17 ± 0.3	3.60 ± 0.6	5.23 ± 0.8	10.06 ± 1.6	8.70 ± 0.9	17.24 ± 2.1
	Oxidised	1.81 ± 0.3	3.08 ± 0.6	0.45 ± 0.1	0.76 ± 0.2	1.87 ± 0.3	3.42 ± 0.5	2.09 ± 0.6	4.73 ± 0.3
Phorate	Natural	39.58 ± 3.8	66.20 ± 5.9	24.01 ± 2.5	36.26 ± 2.1	47.92 ± 4.6	84.04 ± 6.8	55.78 ± 3.5	90.48 ± 4.3
	Oxidised	4.56 ± 1.0	6.02 ± 1.3	2.51 ± 0.5	3.01 ± 0.4	4.88 ± 0.7	6.00 ± 0.2	7.08 ± 1.2	10.02 ± 0.3
Tokomaru									
Atrazine	Natural	2.91 ± 0.2	5.46 ± 1.0	0.24 ± 0.1	0.36 ± 0.1	2.01 ± 0.3	6.20 ± 1.3	5.43 ± 0.6	9.02 ± 0.9
	Oxidised	1.31 ± 0.3	3.23 ± 0.6	0.16 ± 0.05	0.19 ± 0.03	1.52 ± 0.5	2.62 ± 0.1	2.64 ± 0.3	4.25 ± 0.1
Phorate	Natural	17.40 ± 2.5	29.26 ± 2.6	7.30 ± 2.3	11.23 ± 1.6	15.46 ± 1.3	26.35 ± 3.6	25.01 ± 3.6	40.62 ± 3.8
	Oxidised	2.21 ± 0.3	3.15 ± 0.9	1.21 ± 0.2	1.71 ± 0.4	2.48 ± 0.4	3.30 ± 0.5	3.52 ± 0.9	4.81 ± 0.6

^{*} Standard error of mean

3.4, 3.8 and 3.9 percent for atrazine, 2,4-D, phorate and terbufos, respectively. Corresponding losses of pesticides for non-allophanic soils were 4.4% for atrazine, 2.6% for 2,4-D, 5.2% for phorate and 5.3% for terbufos.

Table 6.11 Predicted pesticide losses with sediment runoff resulting from a 65 mm rainfall event

Soil	Sediment loss (t ha ⁻¹)	Pesticides	Pesticide losses (g ha ⁻¹)	Pesticide losses (% of application)
Egmont	6.4	Atrazine	68	3.55
		2,4-D	71	3.41
		Phorate	187	3.78
		Terbufos	112	3.85
Tokomaru	10.3	Atrazine	88	4.42
		2,4-D	79	2.57
		Phorate	257	5.13
		Terbufos	154	5.18

Although the sorbed pesticide concentration in the size fractions was higher in the allophanic soil (Egmont) than in the non-allophanic soil (Tokomaru) the total runoff losses of all pesticides were slightly higher in the non-allophanic than the allophanic soils. This is due to higher sediment losses from the former than the latter soil. It has been reported that the seasonal runoff losses of pesticides from agricultural lands due to natural rainfall were 1-2% for most pesticides (Wauchope 1978). Similarly using a rainfall simulator it has been estimated that 1.8-11% of fonofos, alachlor and cyanazine (Baker *et al.*, 1978), 0.8-22.1 of propachlor, atrazine and alachlor (Baker and Laflen, 1979), and 0.75-8.6 percent of propachlor, atrazine and alachlor (Baker *et al.*, 1982) is lost through runoff.

6.5 CONCLUSIONS

The important conclusions from this experiment are:

1. The particle size fractions obtained by ultrasonic dispersion compared favourably with the conventional pipette method.
2. Organic carbon and oxalate-extractable Fe and Al increased with decreasing particle size. The clay, silt and sand fractions contributed 37.3, 45.5 and 16.3% of the organic carbon, respectively.
3. Sorption of ionic and non-ionic pesticides by the particle size fractions followed the order: clay > silt > sand.
4. The relative contribution of K_d increased with decreasing particle size in Egmont soil. The predicted K_d values obtained from the individual particle size fractions are in close agreement with the measured K_d values.
5. The organic carbon content of the particle size fractions are significantly correlated with the K_d value of pesticides. The K_{oc} values of non-ionic pesticides are essentially the same for the whole soil as for the particle size separates.
6. In addition to organic carbon, the Fe and Al present in the finer fractions (clay and silt) also provides sites for ionic pesticide sorption.
7. The percent desorption was greater with ionic pesticides than non-ionic pesticides in the natural soil fractions. Among the size fractions, the percentage desorption was greatest in the sand fraction, which retained lesser amounts of pesticide and the least desorption occurred in the clay fraction.
8. The percentage desorption was greater with non-ionic pesticides than ionic in the oxidised soil fractions.
9. The loss of pesticide through surface runoff can be estimated from the concentration of pesticide in sediments, the sediment yield and the enrichment ratio.

CHAPTER 7

IMPORTANCE OF CARBON ADDITION ON SORPTION AND MOVEMENT OF PESTICIDES IN SOIL

7.1 INTRODUCTION

Results in Chapters 5 and 6 indicate that while the sorption of non-ionic pesticides by soils greatly depends on the organic carbon content, the sorption of ionic pesticides is related to both the soil clay minerals and the organic carbon content. Increased sorption of organic pesticides with an increasing organic carbon content in the solid phase has been well documented (Hamaker and Thompson, 1972; Karickhoff *et al.*, 1979; Means *et al.*, 1982). Several techniques have been used to examine the importance of organic carbon in the sorption of pesticides. These techniques have been discussed in Chapter 2, and include: correlation, additive (addition of carbon), subtractive (removal of carbon by H_2O_2) and the use of model compounds (e.g., humic acid).

The movement of organic chemicals in soils and sediments is influenced by the distribution of the organic chemicals between the aqueous and the solid phases. The distribution is modified by the presence of dissolved organic carbon (DOC) in the aqueous phase. In recent years DOC has been the subject of great interest because of its ability to interact with organic chemicals and thus affect the fate of these chemicals in the soil or aquatic systems. A number of investigators (Carter and Suffet, 1982; Landrum *et al.*, 1984; Madhun *et al.*, 1986b; Lee and Farmer, 1989) have found that the interaction of pesticides with DOC increases the apparent solubility of these chemicals (Chiou *et al.*, 1986), and thereby results in an increase in the mobility of the chemicals in soils (Kan and Tomson, 1990; Logan *et al.*, 1992; Liu and Amy, 1993).

Large quantities of organic manures have been used in agriculture as sources of plant nutrients. It has often been shown that the application of manures increases the soil carbon content (Sommerfeldt *et al.*, 1988; Guo *et al.*, 1993) resulting in increased

pesticide sorption (Bellin *et al.*, 1990; Guo *et al.*, 1993) and decreased pesticide leaching. It has also been shown that manure application greatly increases the amount of DOC in solution (Meek *et al.*, 1974; McGill *et al.*, 1986) and alters the pH of the soil (Stewart *et al.*, 1992). These two changes due to manure addition have implications on the sorption and leaching of pesticides.

The effect of DOC on the sorption of pesticides has mostly been examined using endogenous DOC either directly extracted from soil or commercial humic materials (e.g., Aldrich humic acid). Recently Barriuso *et al.* (1992b) showed the importance of exogenous as well as endogenous DOC on the sorption of herbicides by soils. Therefore in this experiment the importance of carbon additions on pesticide sorption is discussed in relation to its effect on increasing the carbon content of soil, increasing DOC and changing the pH of the soils.

7.2 OBJECTIVES

The objectives of the experiment described in this chapter were:

- (i) to examine the effect of addition of a range of carbon sources on the sorption of pesticides.
- (ii) to examine the relationship between indigenous carbon and pesticide sorption induced by exogenous carbon
- (iii) to study the effect of DOC on the sorption and mobility of pesticides.
- (iv) to examine the effect of pH on the sorption of pesticides
- (v) to elucidate the origin of the effect of exogenous carbon on the sorption and movement of pesticides in soils

7.3 MATERIALS AND METHODS

7.3.1 Soils

Three surface soil materials, Egmont, Tokomaru and Tui mine tailings, were used in this experiment. The Tokomaru and the Egmont were two contrasting pasture soils which varied widely in their carbon content and clay mineralogy (Table 7.1), whereas the tailings are the finely ground waste material from the Tui gold mine and had a

negligible amount of carbon. Rehabilitation of the mine tailings requires application of large amounts of organic carbon.

Table 7.1 Important characteristics of the soil materials

Soil materials	pH	Organic carbon	Sand	Silt	Clay	DOC (mg kg ⁻¹)
		(%)				
Tailings	4.07	0.06	96.5	1.2	0.8	14
Tokomaru	5.80	3.15	12.4	60.9	24.7	96
Egmont	6.07	8.70	48.0	27.4	25.6	230

7.3.2 Sources of carbon material

The different materials used to supply carbon include: peat, sludge, pig manure, mushroom compost and poultry manure. Some important characteristics of the carbon sources are presented in Table 7.2

Table 7.2 Some important characteristics of carbon materials

Carbon materials	Moisture (%)	pH ¹	Carbon ² (%)	DOC (mg L ⁻¹)
1. Peat	68.0	3.85	43.8	765
2. Sludge	60.5	6.42	26.6	488
3. Pig manure	57.6	6.65	34.6	995
4. Mushroom compost	63.4	6.80	32.3	1388
5. Poultry manure	68.5	6.58	38.8	1965

¹ pH in water (1:2.5 manure : water)

² Carbon by Leco Combustion (Bremner and Tabatabai, 1971)

7.3.3 Pesticides

Two ionic (atrazine and 2,4-D) and two non-ionic (phorate and terbufos)

radioactively labelled (^{14}C) pesticides with a radio chemical purity of $>95\%$ were used in this experiment. The important characteristics of the pesticides were described in Chapter 3.

7.3.4 Incubation

Varying amounts of carbon materials were mixed with the soil to supply 1, 2 and 4% carbon (equivalent to 10, 20 and 40 t carbon ha^{-1}). The samples were mixed thoroughly and water was added to bring the moisture content up to field capacity. The soil samples were incubated for one week at this moisture level in polythene bags and then freeze dried.

7.3.5 Preparation of dissolved organic carbon

The DOC was obtained from the different carbon materials by water extraction (Barriuso *et al.*, 1992b). The extraction was carried out by equilibrating the different carbon materials with water (1:3 solid : solution ratio) for 24 h in an end-over-end shaker. The samples were centrifuged at 12000 rpm for 15 min before filtration. The extracts were filtered through 0.45 μm Millipore filter membranes before use.

7.3.6 Pesticide sorption

Pesticide sorption in natural and carbon-amended soil materials was examined in the laboratory using the batch equilibration method. Preliminary experiments have shown that the sorption isotherm had an approximately linear form (Chapter 5). Hence the distribution coefficient values (K_d) were estimated from the sorption measured at a single solution concentration. A 10 ml aliquot of ^{14}C labelled pesticide solution of atrazine ($18.6 \mu\text{mol L}^{-1}$), 2,4-D ($18.1 \mu\text{mol L}^{-1}$), phorate ($15.4 \mu\text{mol L}^{-1}$) and terbufos ($6.9 \mu\text{mol L}^{-1}$) in 0.01 M CaCl_2 was equilibrated with 1 g soil in a glass culture tube fitted with a teflon cap. The contents of the tubes were shaken in an end-over-end shaker for 4 h at 25°C . After equilibration the tubes were centrifuged at 2500 rpm for 15 min and a one-ml aliquots were taken for analysis. The ^{14}C activity of the pesticide was measured using a liquid scintillation counter. The amount of pesticide sorbed was calculated as the difference between the initial and

final concentrations in solution. Sorption was measured using duplicate soil samples.

7.3.7 Effect of DOC on pesticide sorption

Two approaches have been used to examine the effect of DOC on pesticide sorption by the tailings (Barriuso *et al.*, 1992b). One involves mixing DOC with the pesticides prior to sorption and the other involves mixing DOC with the tailings prior to sorption measurement. The tailings were used because they contain negligible amounts of DOC when compared to the other two soils (Table 7.1).

7.3.7.1 *Preincubating DOC with pesticide*

The DOC (10 ml) extracted from the carbon materials was mixed with 10 ml aliquot of each pesticide solution (at $18.6 \mu\text{mol L}^{-1}$ for atrazine, $18.1 \mu\text{mol L}^{-1}$ for 2,4-D, $15.4 \mu\text{mol L}^{-1}$ for phorate and $6.9 \mu\text{mol L}^{-1}$ for terbufos) and were shaken for 24 h at 25°C . The pesticide solutions were also mixed with 0.01 M CaCl_2 and used as a reference. Then, 10 ml of each mixture was equilibrated with 1.0 g tailings for 4 h, in an end-over-end shaker at 25°C . After equilibration the amount of pesticide sorbed was determined by the method described in Section 7.3.5.

7.3.7.2 *Preincubating DOC with soil*

The DOC (10 ml) from each carbon source was added to 1.0 g tailings and shaken in an end-over-end shaker for 24 h at 25°C . The tailings were also shaken with 0.01 M CaCl_2 and used as a reference. The centrifuged supernatant was then replaced by 10 ml of each pesticide solution ($18.6 \mu\text{mol L}^{-1}$ for atrazine, $18.1 \mu\text{mol L}^{-1}$ for 2,4-D, $15.4 \mu\text{mol L}^{-1}$ for phorate and $6.9 \mu\text{mol L}^{-1}$ for terbufos) and the tubes were vibrated to disperse the tailings pellet. The supernatant solution was retained for the analysis of DOC. The suspensions were equilibrated for 4 h at 25°C , centrifuged, and the pesticide sorbed was determined. The amount of DOC sorbed by the tailings prior to the addition of pesticide solution was also calculated.

7.3.8 Effect of pH on sorption

Addition of different carbon sources to soils has been found to have a varying effect on soil pH and thereby likely to have affected the sorption of pesticides. It was therefore decided to examine, in a separate experiment, the effect of soil pH on pesticide sorption using the Egmont and the Tokomaru soils. Soil samples were incubated with varying amounts of $\text{Ca}(\text{OH})_2$, HCl or NaOH. Although both $\text{Ca}(\text{OH})_2$ and NaOH increase the pH of the soil, NaOH has been shown to solubilize the native soil organic carbon (Lee *et al.*, 1990). Comparison of pesticide sorption between the $\text{Ca}(\text{OH})_2$ - and NaOH-amended soils may help to isolate the effect of pH *per se* and DOC on sorption. The $\text{Ca}(\text{OH})_2$ was added as a fine powder to the soil samples and water was added to bring the moisture content up to field capacity. The HCl and NaOH were added as a dilute solution to give the same moisture content. The amounts of $\text{Ca}(\text{OH})_2$ and HCl added varied between the two soils (Fig 7.6). The soil samples were incubated at this moisture level in polythene bags at 20°C for 4 weeks. The moisture level and pH was monitored at regular intervals. There were 13 treatments (four levels each of acid, NaOH and $\text{Ca}(\text{OH})_2$ + one control) for the Egmont soil and 12 treatments for the Tokomaru soil (four levels each of NaOH and $\text{Ca}(\text{OH})_2$ + three levels of HCl + one control). The sorption of pesticides by the pH amended soil samples was measured as described in section 7.3.5. The amount of DOC in the pH amended soil samples was also measured.

7.3.9 Effect of DOC on the movement of pesticides

7.3.9.1 Soil column studies

The effect of DOC on pesticide movement was examined by leaching soil columns with solutions of either 0.01 M CaCl_2 or DOC of known concentration. Borosilicate glass columns (2.72 cm i.d.) were uniformly packed with either the tailings or the Egmont soil in 1-2 cm increments to a depth of 14 cm to minimize particle size aggregation. These two soil materials were used because they varied widely in carbon content, sorption of pesticides and DOC. The columns were packed to a bulk density of 1.3 and 0.85 g cm⁻³ for the tailings and the Egmont soil, respectively. The total volume of water held in the soil column was determined from the difference between

the mass of the soil in the column after the flow of excess water effectively ceased and the oven-dry mass of soil at this point.

The column was preleached with one pore volume of 0.01 M CaCl₂, then a 5 ml pulse of ¹⁴C-labelled pesticide (18.6 μmol L⁻¹ for atrazine, 18.1 μmol L⁻¹ for 2,4-D, 15.4 μmol L⁻¹ for phorate and 6.9 μmol L⁻¹ for terbufos) was added on top of the soil column. The columns were immediately leached with either 0.01 M CaCl₂ or a DOC solution at a constant flux (0.12 ml min⁻¹) using a peristaltic pump. A total of 15 pore volumes was leached through the tailings and 18 pore volumes through the Egmont soil. The DOC solution (210 mg L⁻¹) used in this experiment was collected from a surface stream near a peat deposit at Paraparaumu, North Island, New Zealand. The leachates draining from the columns were collected in 7 ml aliquots. At the end of the experiment the leachate samples were analysed for ¹⁴C activity using a liquid scintillation counter and for DOC concentration. At the end of the experiment the soil column was sectioned into 1 cm sections and each section was analysed for organic carbon content and ¹⁴C activity. The mass balance of the added pesticides was calculated to determine any loss during the experimental period.

7.3.9.2 *Movement of organic chemicals in the presence of DOC and the retardation factor*

The movement of organic chemicals in soil columns has been described by the following advective-dispersive one-dimensional equation (Lapidus and Amundson, 1952):

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (7.1)$$

Where C is the equilibrium solution concentration (μmol L⁻¹), t is time (hr), D is the dispersion coefficient (mm² hr⁻¹), x is the distance in the direction of flow (mm), v is the average pore-water velocity (mm hr⁻¹), S is the sorbed concentration (μmol kg⁻¹) and R is referred to as the retardation factor (Davidson and Chang, 1972).

The retardation factor accounts for the effect of sorption on the movement of solutes. For a linear sorption isotherm ($S = K_d C$), the retardation factor R is given

by

$$R = 1 + \left(\frac{\rho}{\theta}\right) K_d \quad (7.2)$$

Where ρ is the soil bulk density (g cm^{-3}), θ is the volumetric water content ($\text{mm}^3 \text{ mm}^{-3}$) and K_d is the distribution coefficient (L kg^{-1}).

Many researchers have obtained evidence for the interaction of organic chemicals with aqueous DOC, which facilitates the movement of organic chemicals in soils (Kan and Tomson, 1990; Logan *et al.*, 1992; Liu and Amy, 1993). In the presence of DOC in solution, the retardation factor is modified to (Kan and Tomson, 1990)

$$R = 1 + \left(\frac{\rho}{\theta}\right) K_d / (1 + K_{\text{DOC}} C_{\text{DOC}}) \quad (7.3)$$

Where K_{DOC} and C_{DOC} are the pesticide/DOC distribution coefficient and concentration of dissolved organic carbon (mg L^{-1}), respectively.

The K_{DOC} values of the pesticides were calculated from the K_{ow} of the compound using the following equation (Kan and Tomson, 1990):

$$K_{\text{DOC}} = 0.63 K_{\text{ow}} \quad (7.4)$$

Using Eq 7.3 the R values of the pesticides leached with CaCl_2 and DOC were calculated.

7.3.10 Interaction of pesticides with DOC

The interactions between pesticides and DOC extracted from various carbon sources were examined using infrared (IR) spectroscopy. The DOC from the different sources of carbon was obtained by water extraction (Barriuso *et al.*, 1992b) as described in section 7.3.5. The DOC sample was freeze dried before use. A known amount of the freeze-dried DOC (10 mg) was added to solutions (50 ml) containing a known concentration of atrazine ($18.6 \mu\text{mol L}^{-1}$), 2,4-D ($18.1 \mu\text{mol L}^{-1}$), phorate ($15.4 \mu\text{mol L}^{-1}$) or terbufos ($6.9 \mu\text{mol L}^{-1}$) and allowed to equilibrate for 4 h. The DOC-pesticide complexes were then freeze dried. The freeze dried samples were

made into KBr discs using 170 mg KBr and 1.0 mg either the freeze dried DOC, the DOC-pesticide complex or the pure pesticide. The IR spectrum for pure pesticides, DOC and DOC-pesticide complexes were obtained for wavelengths of 4000 cm^{-1} to 200 cm^{-1} using a Pye Unicam model SP3-300 infrared spectrophotometer.

7.3.11 Chemical analysis

The initial moisture content of the different carbon materials was determined by drying the samples in an oven at 105°C overnight. The DOC concentration of the aqueous extracts of the carbon materials and the soil samples was measured by digesting the extracts with $\text{K}_2\text{Cr}_2\text{O}_7$ (Tate *et al.*, 1988). The pH, organic carbon and textural composition of the soils were measured as outlined in Chapter 5.

7.3.12 Statistical analysis

Differences between the treatment means were tested for significance using an analysis of variance test (SAS, 1985).

7.4 RESULTS AND DISCUSSION

7.4.1 Characteristics of the soils

The important characteristics of the three soil materials used in this experiment are presented in Table 7.1. The pH of the tailings was less than that of the soils. The soil materials varied widely in organic carbon content (0.06 to 8.7%). The particle size distribution showed that tailings had a very high sand content.

7.4.2 Characteristics of carbon materials

The different sources of carbon had a high moisture content (57.6 to 68.5%). The pH was slightly acid in peat (3.85) and nearly neutral (6.42 to 6.80) in the other carbon materials. The carbon content ranged from 26.6 to 43.8 % (Table 7.2) and followed the order: peat > poultry manure > pig manure > mushroom compost > sludge. These were comparable with values reported earlier (Mahimairaja, 1993;

Stewart *et al.*, 1992). The DOC concentrations in the different carbon materials ranged from 488 to 1965 mg L⁻¹ (Table 7.2).

7.4.3 Sorption of pesticides by soils

Pesticide sorption, as measured by the distribution coefficient (K_d), was greatest in the Egmont soil followed by the Tokomaru soil and the tailings (Table 7.3). Generally the K_d values followed the order of the organic carbon content of the soils. Many other studies have also shown the importance of organic carbon on the extent of pesticide sorption in soils (Chapter 5). In general, pesticide sorption followed the order: terbufos > phorate > 2,4-D > atrazine. This order of pesticide sorption by the soil materials is related to the partition coefficient of the pesticides in octanol (K_{ow}). The relationship between the K_d or K_{oc} and K_{ow} values of pesticides is discussed in detail in Chapter 5.

Table 7.3 Distribution coefficient (K_d) of pesticides for each soil

Soil	Atrazine	2,4-D	Phorate	Terbufos
Tailings	0.62	0.71	0.95	1.27
Tokomaru	2.50	1.52	17.42	18.50
Egmont	3.60	4.81	39.58	42.03

7.4.4 Effect of carbon additions on the distribution coefficients (K_d) of pesticides

The effect of carbon addition on K_d values of pesticides for the three soil materials is presented in Figures 7.1 to 7.3. Addition of peat, sludge and pig manure increased the K_d values of all pesticides. Mushroom compost and poultry manure addition increased the K_d values of atrazine, phorate and terbufos, whereas they slightly decreased the sorption of 2,4 D. The increase in sorption of pesticide per unit of carbon addition was highest for the tailings followed by the Tokomaru and the Egmont soils. For example, addition of 1% carbon from peat increased the K_d values

by 86, 40 and 20%, respectively in the tailings, the Tokomaru and the Egmont soils. The increase in k_d values (Fig 7.1-7.3) with carbon addition decreases with an increase in the indigenous organic carbon content of the soil.

Although the K_d values increased with an increase in added carbon, the increase was not in proportion to the carbon addition. The results indicated that, the increase in sorption per unit of carbon addition, decreased with increasing rates of carbon. This is evident when the K_d values were normalised to the carbon content (K_{oc}). For example, the effect of the addition of peat and poultry manure on the K_{oc} of pesticides in the Tokomaru soil is shown in Figure 7.4. Although the K_d values increased with increasing carbon (Fig 7.1), the K_{oc} values decreased with the addition of carbon and the decrease in K_{oc} was greater for poultry manure than peat. The decrease in K_{oc} with carbon additions was greater for non-ionic than for ionic pesticides.

The addition of carbon sources to soil materials not only increased in total carbon content, but also caused changes in the DOC and pH, which have implications to the sorption of pesticides. Irrespective of the source of carbon materials, the addition of carbon has increased the DOC in the aqueous phase (Table 7.4).

Table 7.4 Effect of additions of Carbon materials on the pH and DOC in the tailings and the Tokomaru and the Egmont soils

Carbon source	pH			DOC (mg L ⁻¹)		
	Tailings	Tokomaru	Egmont	Tailings	Tokomaru	Egmont
Control	4.05	5.35	5.90	10	88	218
Peat	3.60	4.80	5.15	52	121	310
Sludge	5.40	5.40	5.95	38	103	282
Pig manure	5.90	5.80	6.10	68	130	328
Mushroom compost	6.70	6.80	6.60	77	143	363
Poultry manure	6.85	6.95	6.95	86	162	382

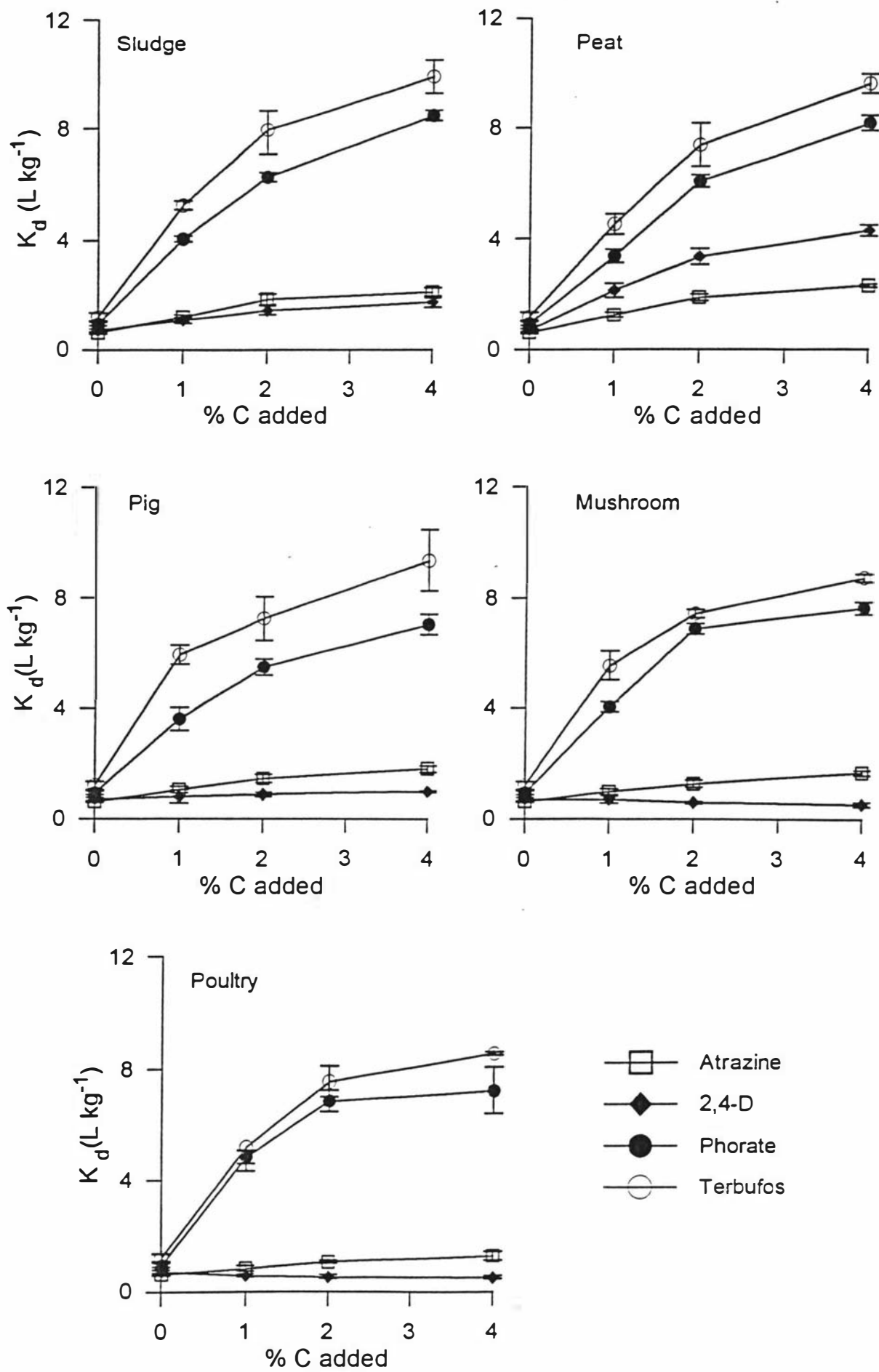


Fig 7.1 Effect of addition of carbon on the distribution coefficient (K_d) of pesticides in the tailings. (Vertical bars represent standard error of mean)

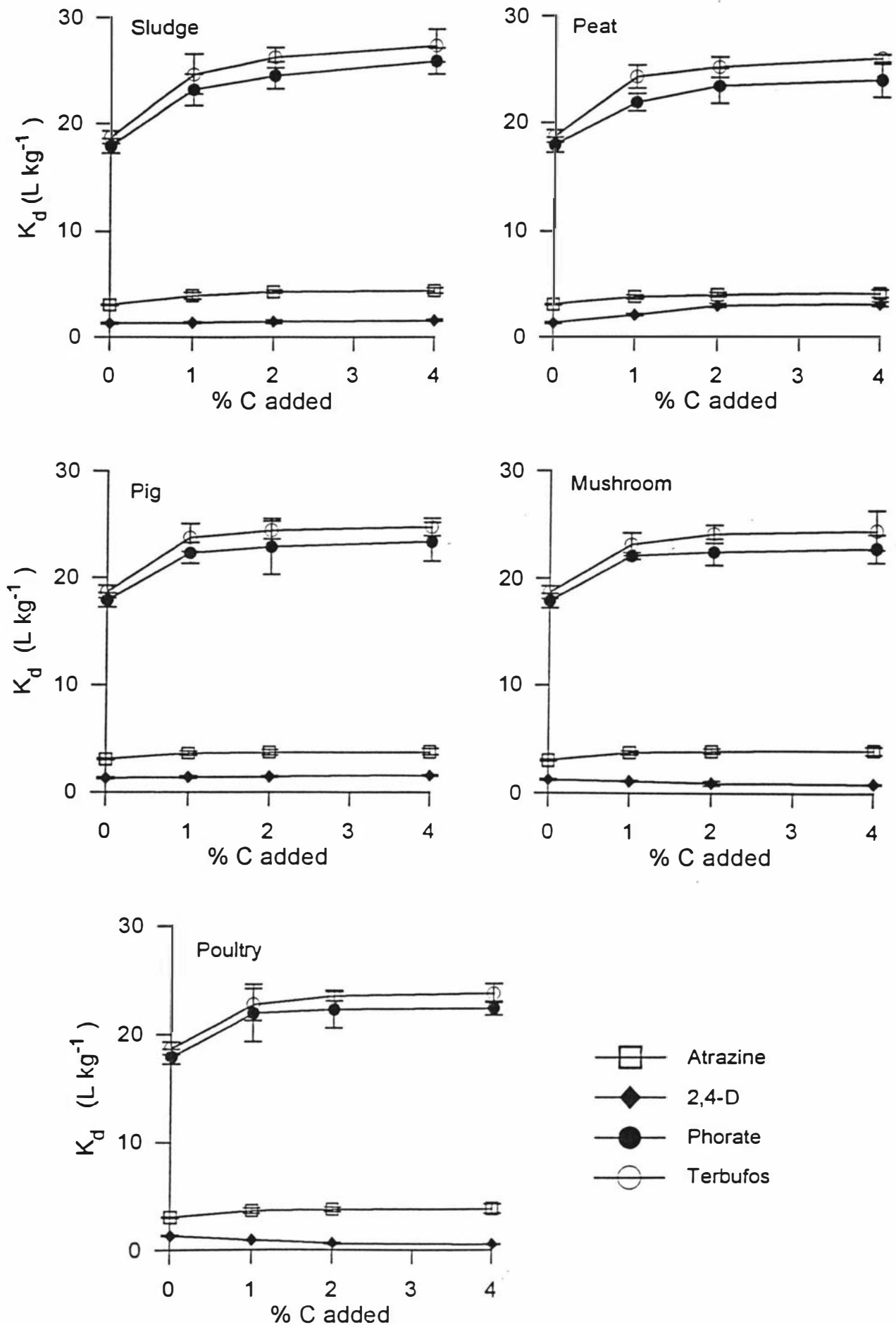


Fig 7.2 Effect of addition of carbon on the distribution coefficient (K_d) of pesticides in the Tokomaru soil. (Vertical bars represent standard error of mean)

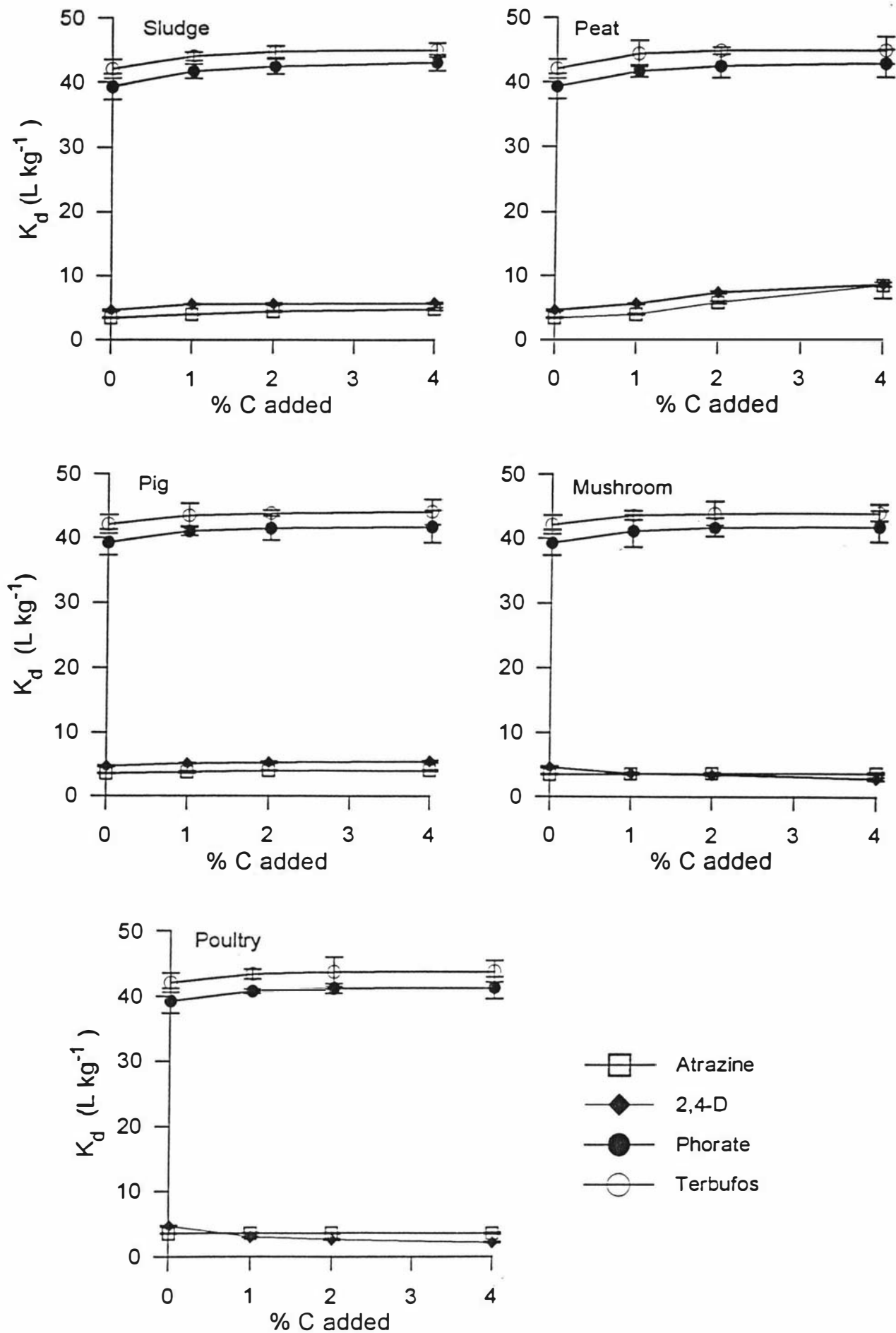


Fig 7.3 Effect of addition of carbon on the distribution coefficient (K_d) of pesticides in the Egmont soil. (Vertical bars represent standard error of mean)

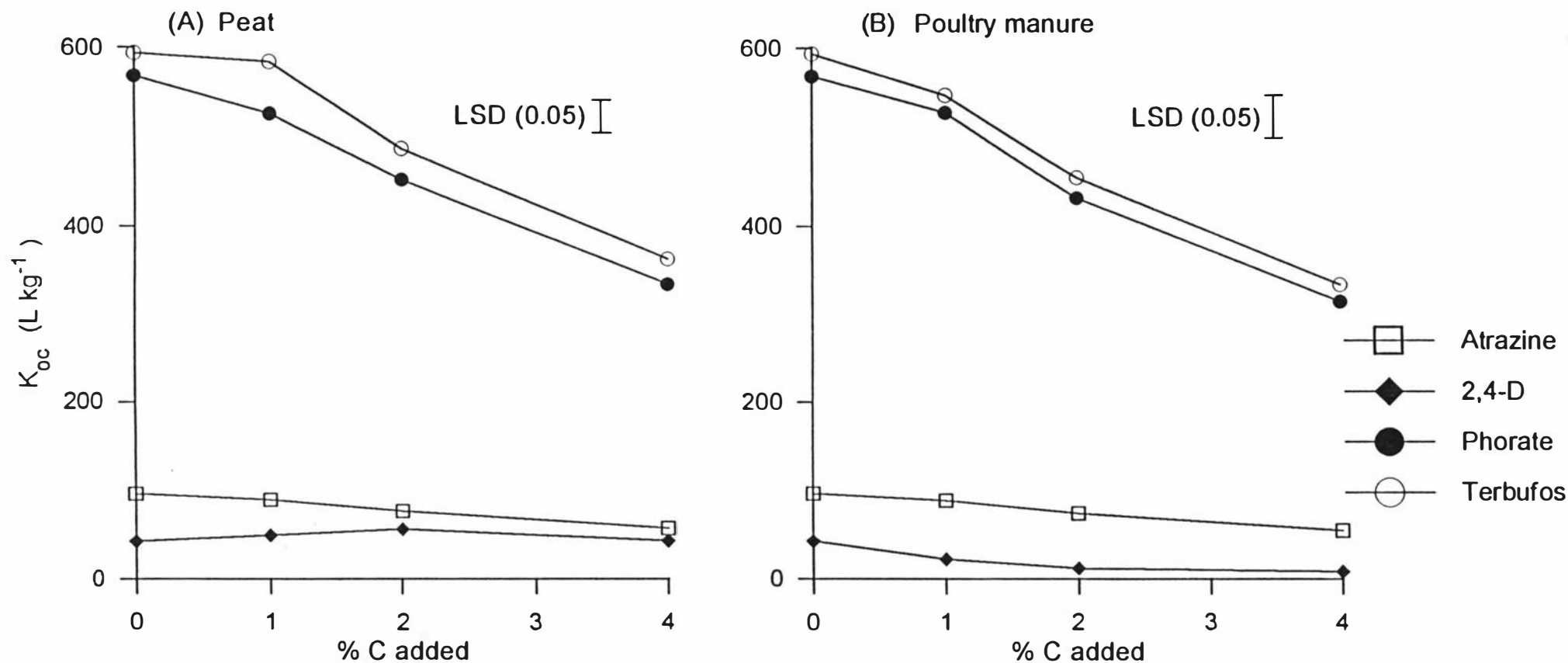


Fig 7.4 Effect of additions of (A) peat and (B) poultry manure on the distribution coefficient based on organic carbon (K_{oc}) in the Tokomaru soil

Studies by Meek *et al.* (1974) and McGill *et al.* (1986) have also shown that carbon addition through different manures greatly increased the concentration of DOC in the soil solution. The DOC in solution varied between the soils as well as between the added carbon materials. The increase in DOC concentration with carbon additions was in the order: poultry manure > mushroom compost > pig manure > peat > sludge and the effect was most pronounced in the Egmont soil followed by the Tokomaru soil and the tailings (Table 7.4). While the difference in DOC concentration in soils amended with various carbon sources may be attributed to the difference in the DOC concentration of the original sources, the difference in DOC between the soils may be attributed to the difference in the sorption of DOC by the soil materials.

The pH of the soil amended with different sources of carbon also varied depending on the carbon source. Irrespective of the soil material, peat addition had the lowest pH (3.8 to 5.2), and poultry manure addition had the highest pH (6.5 to 6.8). The change in pH due to the addition of carbon sources is caused by the release of protons and/or hydroxyl ions from the transformation of various elements in the carbon sources (e.g., N transformations in poultry manure).

The results indicate that the addition of different carbon materials causes changes in the DOC and pH of the soil material and thereby affects the sorption of pesticides. Release of DOC in the aqueous phase is likely to result in the retention of pesticides in solution, which causes a decrease in K_d . Many studies have shown that the sorption of organic chemicals by soils or sediments is affected by the presence of DOC (Hassett and Anderson, 1979; O'Connor and Connolly, 1980; Koskinen and Cheng, 1983; Gschwend and Wu, 1985; Lee *et al.*, 1990). Means and Wijayaratne (1982) showed that estuarine colloidal material, which contains DOC is more effective than bulk organic matter in associating with the polar pesticides, atrazine and linuron. Similarly it has been shown that the sorption of weakly acidic and basic chemicals is a pH dependent phenomenon (Watson *et al.*, 1973; Barriuso *et al.*, 1992a; Weber, 1993). In order to explain the results, the effect of DOC and pH on pesticide sorption was examined in separate experiments.

7.4.5 Effect of DOC on pesticide sorption

7.4.5.1 *Preincubating DOC with pesticide*

Irrespective of the source of DOC examined, pesticide sorption by the tailings tended to decrease when the DOC was mixed with the pesticides prior to the sorption measurements (Fig 7.5A). The decrease in sorption was more for non-ionic than ionic pesticides and followed the order: terbufos > phorate > atrazine > 2,4-D. This suggests that DOC is more effective in associating with non-ionic than ionic pesticides. The decrease in sorption is greater with DOC from poultry manure and mushroom compost than from pig manure, peat and sludge which may be attributed to the difference in the DOC concentration between the different DOC sources. Similarly, Barriuso *et al.* (1992b) observed a decrease in herbicide sorption when the herbicide was mixed with DOC before adding to the soil.

The general decrease of pesticide sorption after DOC-pesticide incubation could be explained by formation of DOC-pesticide complexes (Carter and Suffet, 1982; Madhun *et al.*, 1986b; Lee and Farmer, 1989; Barriuso *et al.*, 1992b). The decrease in sorption may also be attributed to the apparent enhancement of water solubility of the pesticides when interacted with DOC (Chiou *et al.*, 1986).

7.4.5.2 *Preincubating DOC with soil*

Pesticide sorption increased when DOC was mixed with the tailing prior to the sorption measurements (Fig 7.5B). Pre-mixing of soil with 0.01 M CaCl₂ however did not affect the sorption of pesticides. The increase in sorption due to DOC addition is greater with non-ionic than ionic pesticides and followed the order (the range in increase due to the addition of various sources of DOC is given in brackets): terbufos (26-32%) > phorate (23-29%) > atrazine (9.7-17.2%) > 2,4-D (3.95- 26.9%). These results are consistent with those reported by Barriuso *et al.* (1992b), who observed an increased sorption of herbicide by incubating DOC with soil.

Measurement of DOC in the soil solution after incubation with DOC indicated that approximately 30.6, 33.7, 36.2, 42.1 and 45.5 percent of the carbon added from

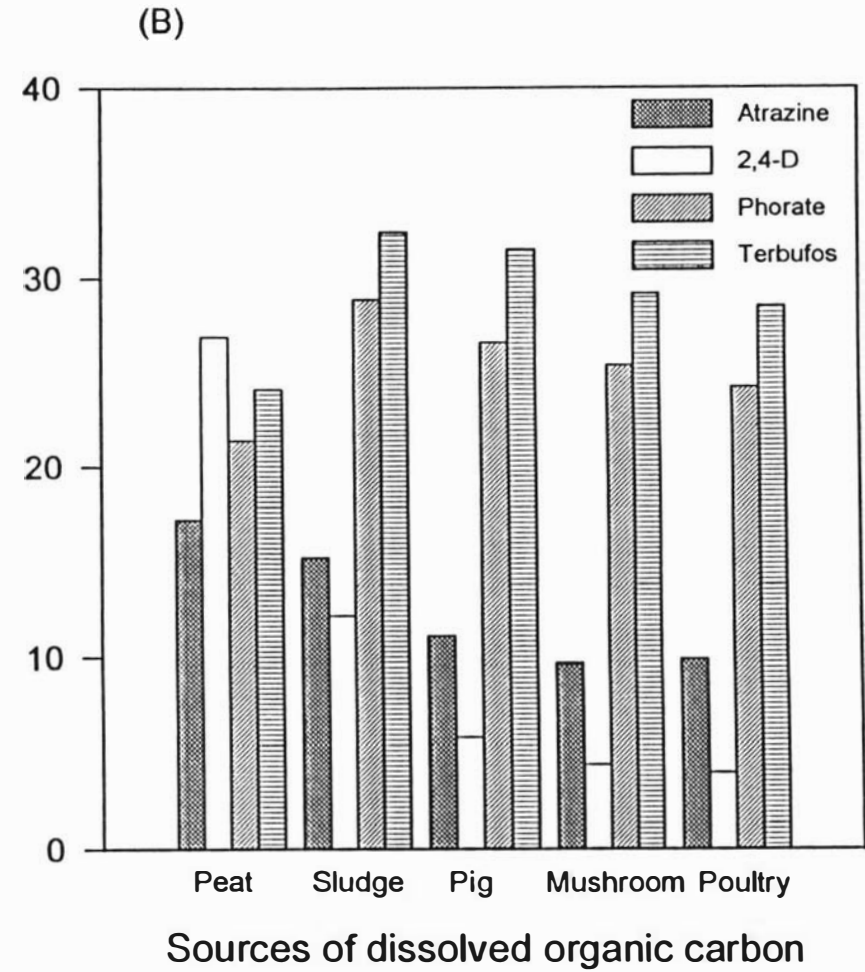
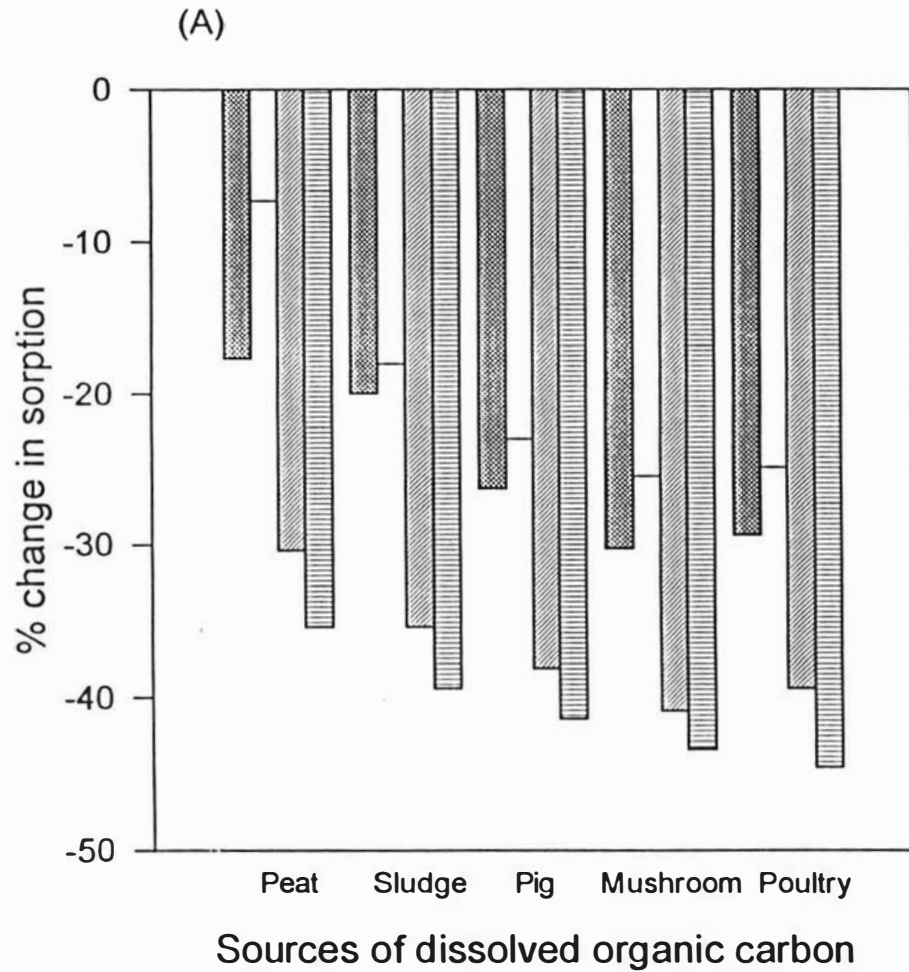


Fig 7.5 Effect of DOC on the sorption of pesticides by the tailings due to (A) preincubation of DOC with pesticides and (B) preincubation of DOC with soil. (The results are expressed as percent increase or decrease in sorption)

poultry manure, peat, mushroom compost, pig manure and sludge, respectively was retained by the tailings. Many researchers have reported the sorption of DOC by soils (Moore, 1989; Jardine *et al.*, 1989; Barriuso *et al.*, 1992b; Gu *et al.*, 1994). Increased sorption of pesticides in DOC incubated tailings could be explained by the increase in carbon content due to sorption of DOC from solution. Sorption of DOC from different carbon materials during soil incubation could modify the hydrophobic - hydrophilic characteristics of the soil surfaces, thereby increasing the number of sorption sites for less water soluble pesticides (Barriuso *et al.*, 1992b).

7.4.6 Effect of pH on pesticide sorption

The results of soil pH modification with HCl or with Ca(OH)_2 for the two soils are presented in Figure 7.6. They show that the two soils differed appreciably in their buffering characteristics. The buffer curve for the Egmont soil had a lower slope than that for the Tokomaru soil. The higher buffering capacity of the Egmont soil reflects the presence of allophanic clay and the higher organic carbon content of this soil. This is consistent with the result reported by Bolan *et al.* (1986).

For both the Egmont and the Tokomaru soils, the K_d values of 2,4-D and atrazine increased with decreasing pH (Fig 7.7). The effect of pH on sorption was more pronounced for 2,4-D than for atrazine and was greater for the Egmont than for the Tokomaru soil. The increase in K_d value for atrazine was significant when the pH was below 4. Sorption of phorate and terbufos was less affected by the change in pH. The decrease in K_d values (L kg^{-1}) from the highest pH to the lowest pH followed the order: 2,4-D (49.5) > atrazine (6.7) > terbufos (3.0) > phorate (2.1).

Three reasons could be given for the effect of pH on sorption of pesticides by soils: (i) ionization of the pesticide compounds. (ii) modification of soil surface charge. (iii) solubilization of organic carbon in soil.

Firstly, the increased sorption of 2,4-D with a decrease in pH was due to an increase in the percentage of the undissociated (non-ionic) form of 2,4-D. At higher pH, while the proportion of 2,4-D present in the anionic form increases, the positive sites onto which the anionic species are sorbed decrease resulting in less sorption. It has

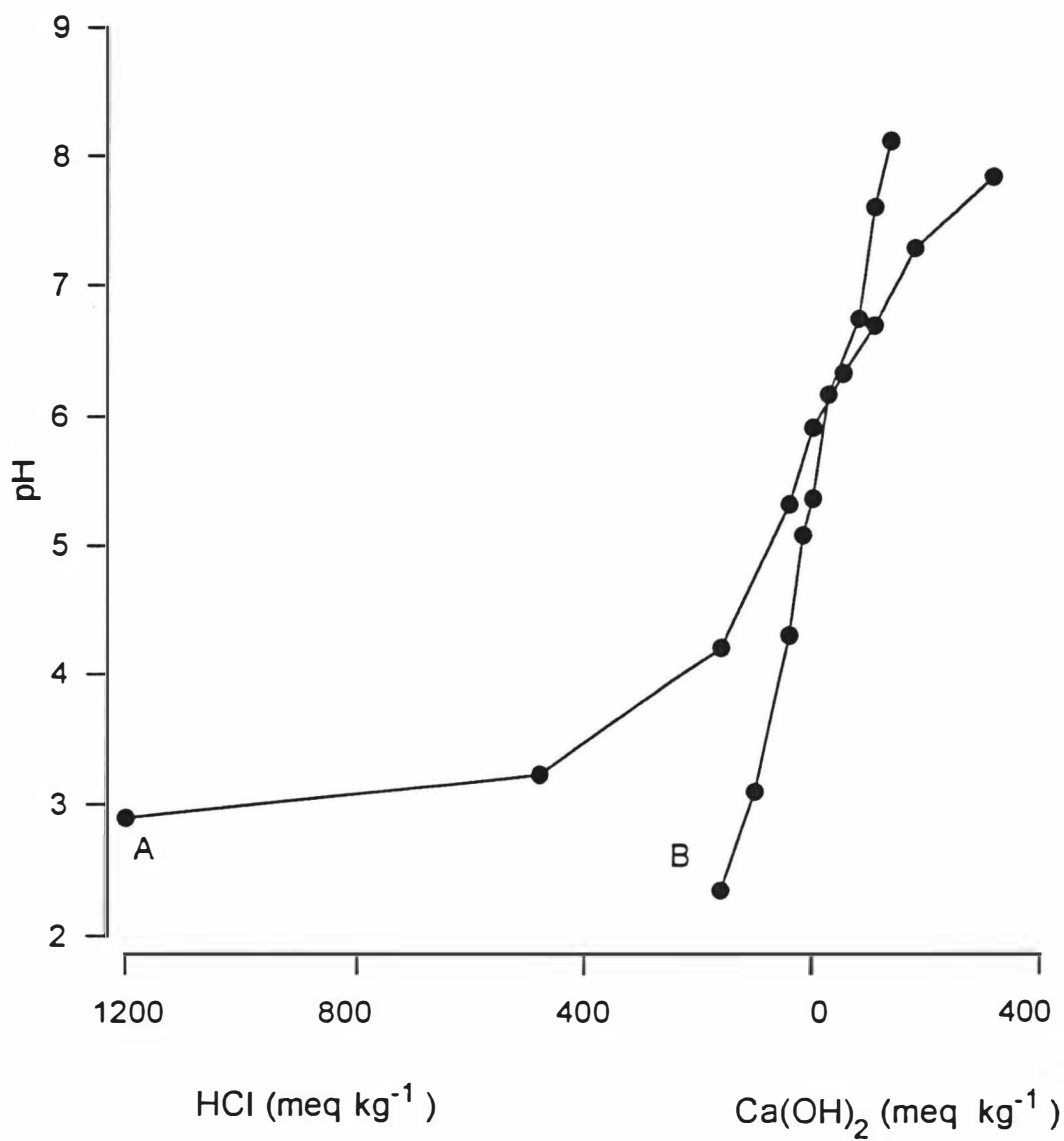


Fig 7.6 Soil pH modification with HCl or Ca(OH)₂ for the Egmont (A) and the Tokomaru (B) soils

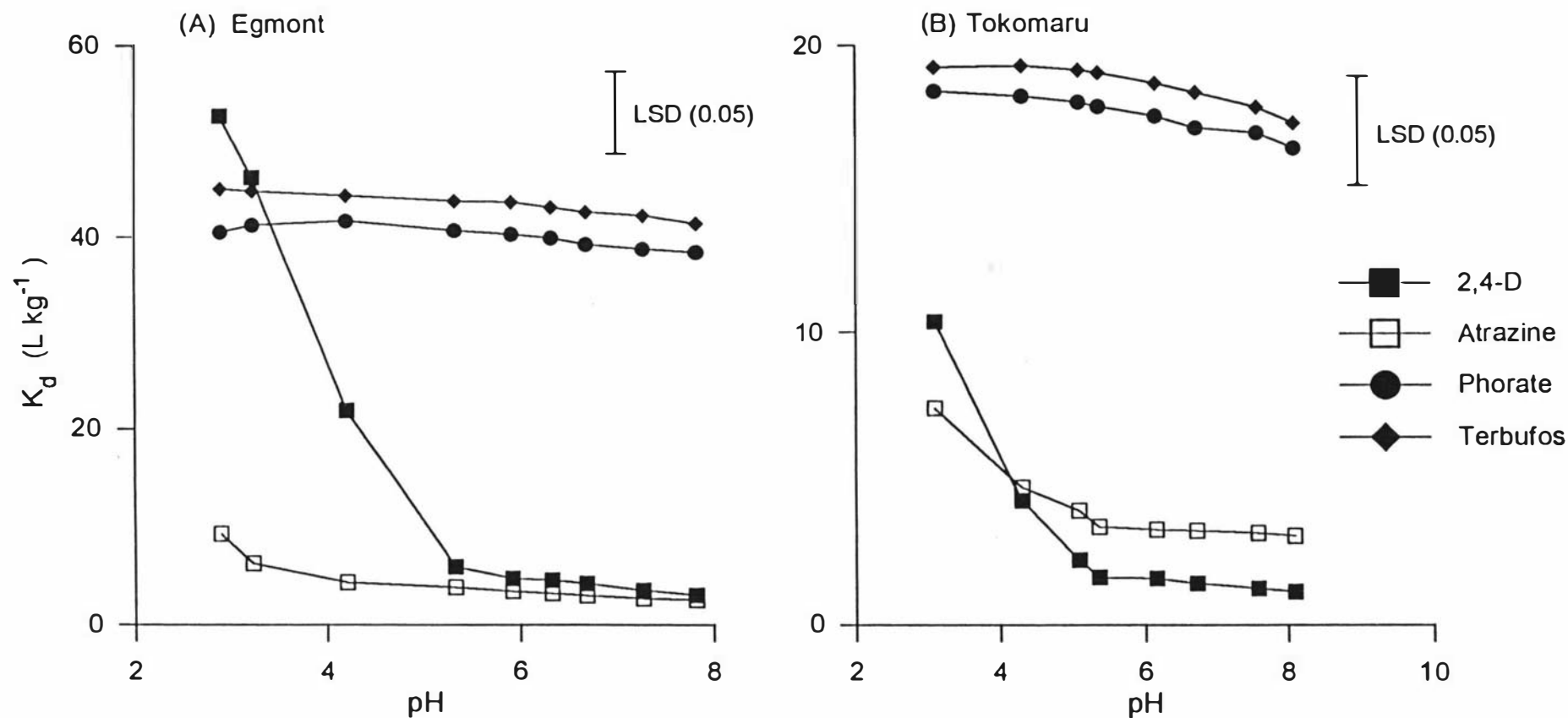


Fig 7.7 Effect of pH on the distribution coefficient (K_d) of pesticides in the Egmont (A) and the Tokomaru (B) soils incubated with HCl or $\text{Ca}(\text{OH})_2$

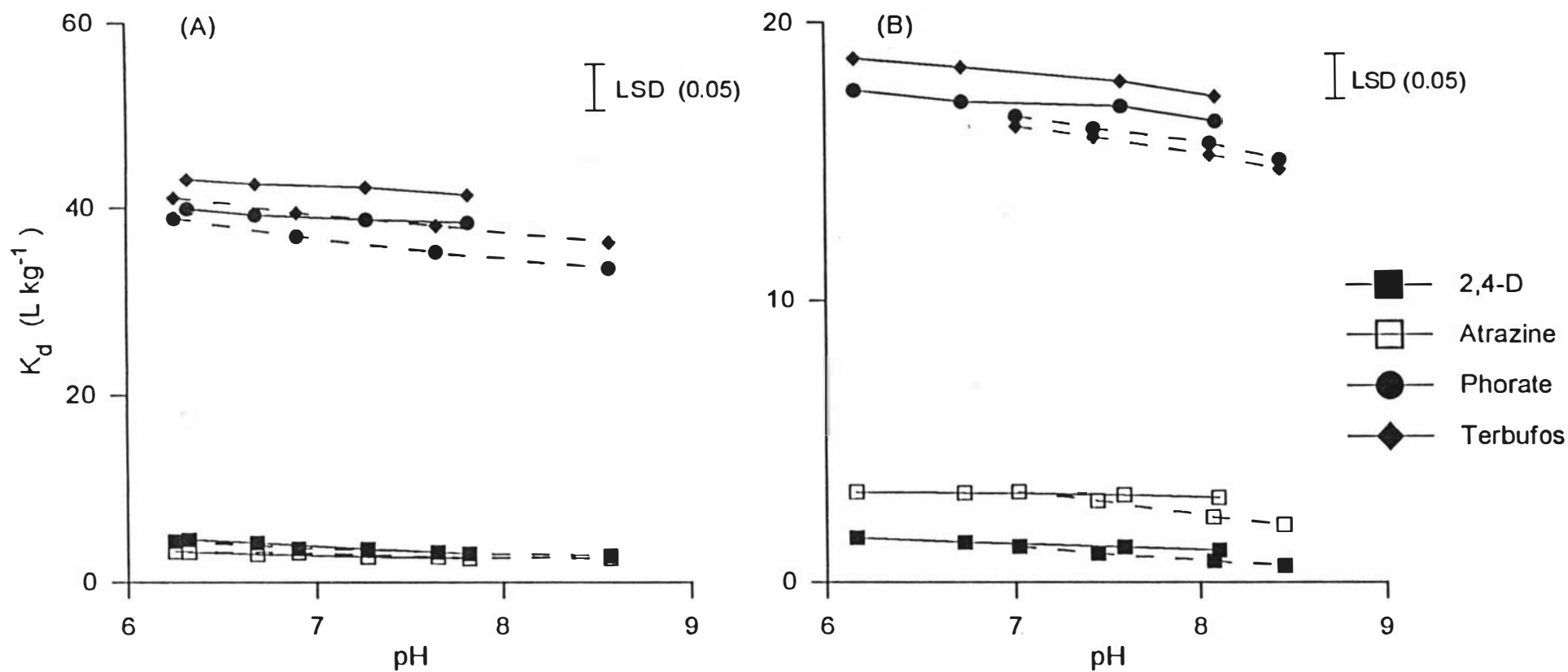


Fig 7.8 Effect of pH on the distribution coefficient (K_d) of pesticides in the Egmont (A) and the Tokomaru (B) soils incubated with Ca(OH)_2 (—) or NaOH (- - -)

been shown by Weber (1970) and Watson *et al.* (1973) that weakly acidic (2,4-D) and basic chemicals (s-triazine) are highly sorbed at pH values close to the molecules' pK_a (pK_a of 2,4-D and atrazine is 2.8 and 1.7, respectively).

Secondly, in variable charge soils, a decrease in soil pH increases the net positive charge on the surface (Haynes, 1982). The negatively charged 2,4-D ions are sorbed onto the positive sites through electrostatic attraction. This may be one of the reasons for the increase in 2,4-D sorption with a decrease in pH. However the increase in positive charge is unlikely to explain the increase in the sorption of the positively charged atrazine ions.

Thirdly, the pH of the soil affects the DOC concentration in solution. There was a difference in the effect of pH on the K_d values between the NaOH - and the $\text{Ca}(\text{OH})_2$ -amended soils (Figure 7.8). The decrease in pesticide sorption with increasing pH was greater when the soil was incubated with NaOH than $\text{Ca}(\text{OH})_2$. The difference in K_d values between the NaOH and $\text{Ca}(\text{OH})_2$ amended soils was greater for the Egmont than for the Tokomaru soil. Similarly, it has been shown that the sorption of napropamide decreased when the pH was raised with NaOH (Lee *et al.*, 1990). This was attributed to the interaction of napropamide with the soluble carbon released into solution by the NaOH treatment.

The amount of soluble carbon in the soil incubated with $\text{Ca}(\text{OH})_2$ or NaOH was measured. There was a substantial increase in the amount of DOC when the soil was incubated with NaOH (Fig 7.9). In the present experiment, the decrease in K_d values of pesticides in the soils incubated with NaOH can be explained by the interaction of pesticides with DOC in the aqueous phase. Figure 7.10 gives the relationship between the difference in DOC and K_d values between the NaOH- and the $\text{Ca}(\text{OH})_2$ -amended Egmont soil. It is evident that the decrease in sorption of pesticides in the NaOH - amended soil is related to the increase in DOC concentration. Smith and Willis (1985) suggested that the enhanced transport of pesticides through the soil column with the application of anhydrous ammonia is mainly due to the release of soluble carbon.

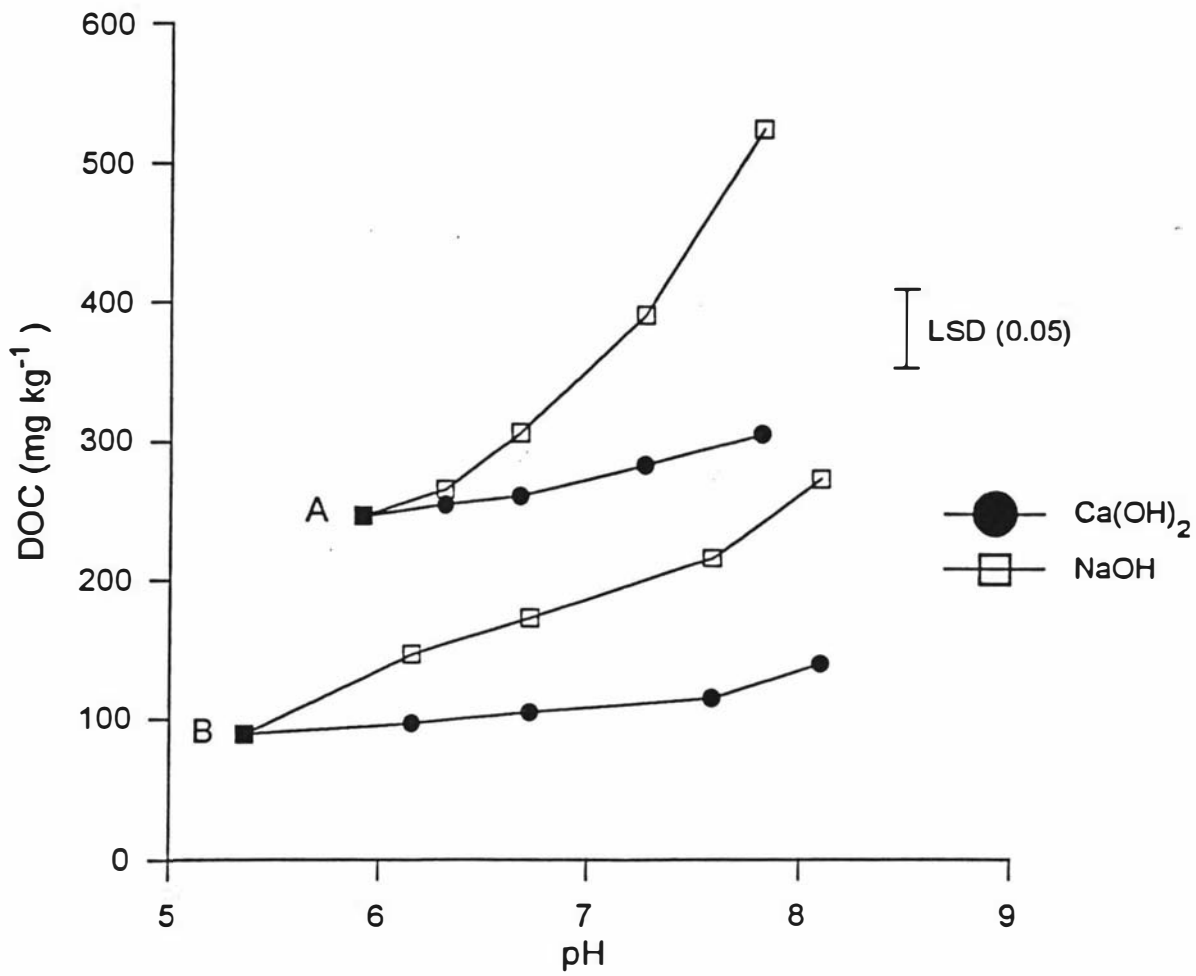


Fig 7.9 Effect of pH on dissolved organic carbon (DOC) of the Egmont (A) and the Tokomaru (B) soil incubated with Ca(OH)₂ or NaOH

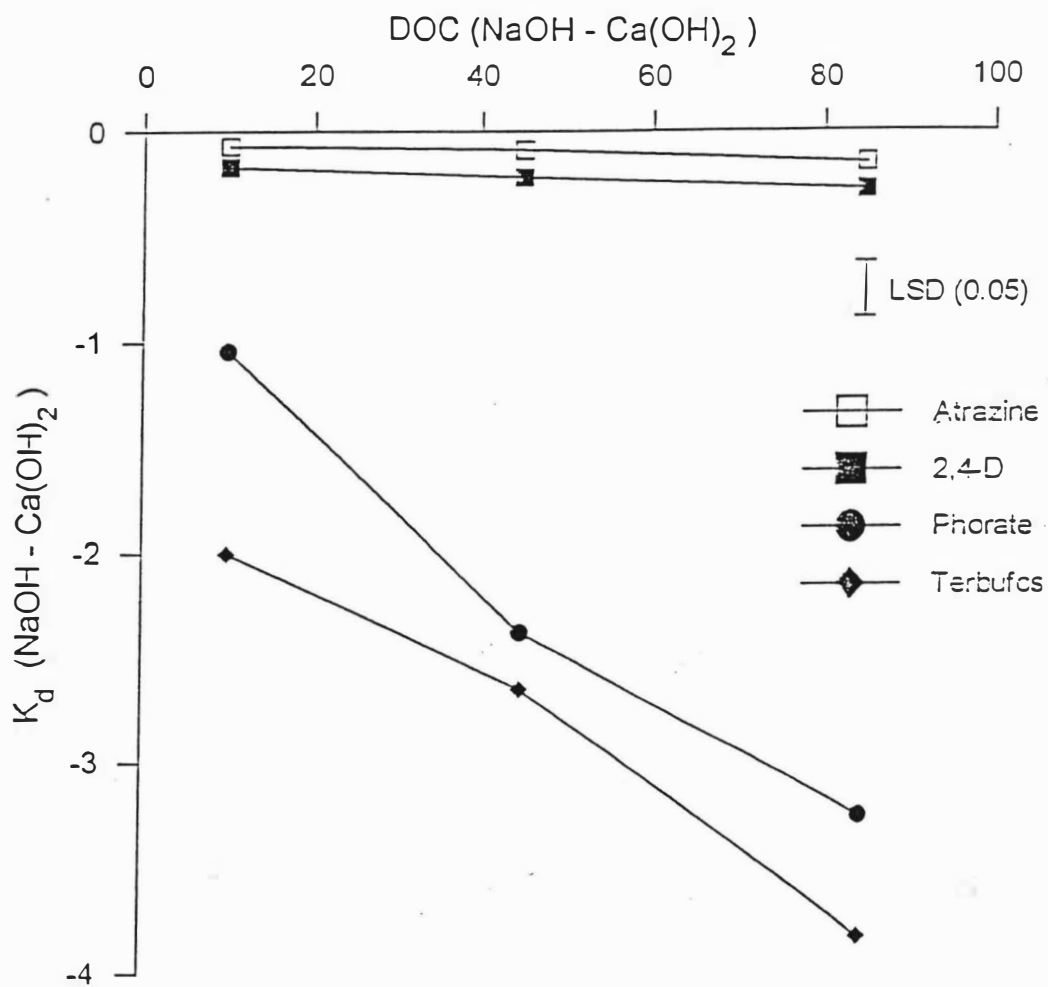


Fig 7.10 Relationship between difference in dissolved organic carbon (DOC) and the distribution coefficient (K_d) between the NaOH and Ca(OH)₂ Egmont soil

7.4.7 Effect of DOC on the movement of pesticides

7.4.7.1 Column breakthrough experiments

Breakthrough curves (BTC's) for the pesticides eluted with CaCl_2 or DOC in the tailings and the Egmont soil are presented in Figures 7.11 and 7.12. The mass balance calculation indicated that 95 to 98% of the ^{14}C pesticide was recovered from the aqueous and solid phases and shows no evidence for degradation of pesticides within the experimental period.

As would be expected from the batch-sorption data (Section 7.4.3), all the four pesticides appeared later in the leachate from the Egmont column than from the tailings column. A greater shift of the BTC of pesticides to the right indicates increased sorption, thus a decreased mobility in the Egmont soil. The Egmont soil contains high amounts of organic carbon whereas the tailings contain negligible amounts of organic carbon. It has been observed that the soils containing high amounts of organic carbon sorb more pesticides than soils that are low in organic carbon (Chapter 5).

Among the pesticides examined 2,4-D and atrazine appeared earlier in the leachate than did phorate and terbufos. The relative mobility of pesticides followed the order: atrazine > 2,4-D > phorate $\geq$ terbufos. In general the non-ionic pesticides (phorate, terbufos) were relatively less mobile than the ionic pesticides (atrazine, 2,4-D). These results indicate that phorate and terbufos having low water solubility are more resistant to leaching with either CaCl_2 or DOC in both the soils. This is consistent with the results reported by Abdul *et al.* (1990) indicating that the low water soluble chemicals are more strongly held by the soil particles.

From Figures 7.11 and 7.12, the percentage of the added pesticides found in the leachate at 0 to 2, 2 to 4, 4 to 6 and 6 to 10 pore volumes is summarised in Table 7.5. In the tailings, CaCl_2 is more effective than DOC in removing phorate and terbufos from the soil at the early stages of the leaching. However as the leaching continues, the DOC becomes more effective in removing phorate and terbufos between 2 to 4 and 4 to 6 pore volumes (Table 7.5). In contrast, 2,4-D and atrazine were more

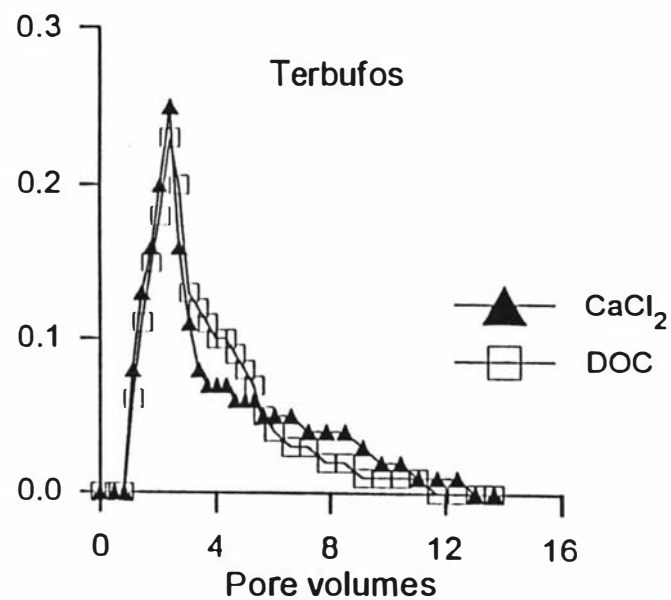
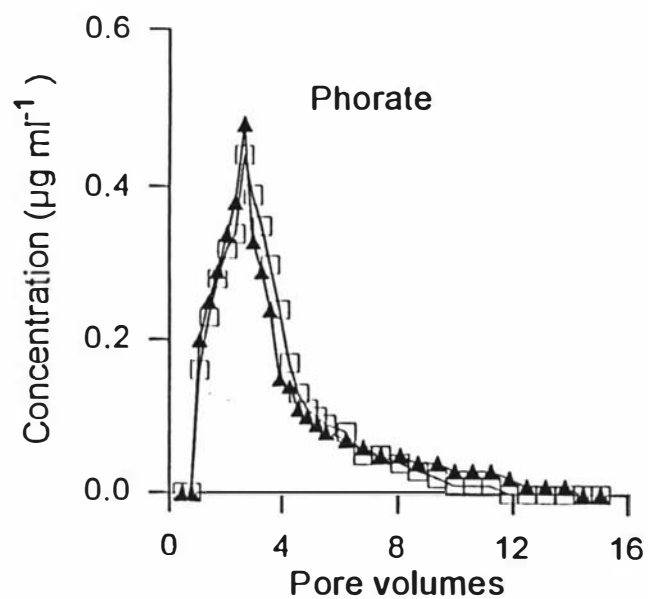
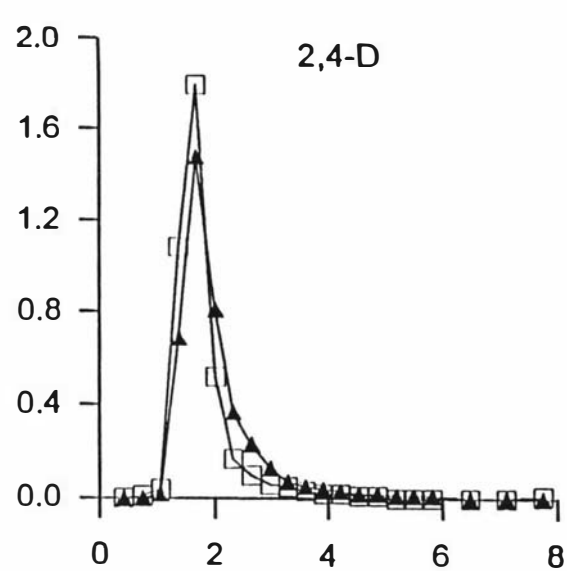
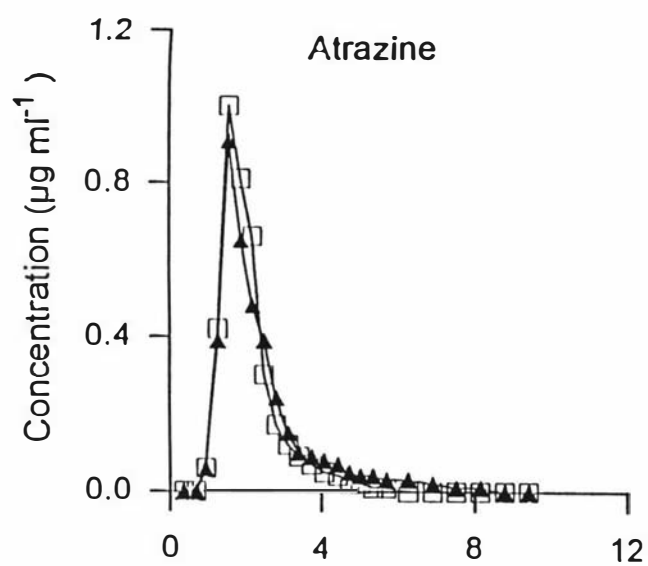


Fig 7.11 Breakthrough curves for pesticides leached with either CaCl_2 or dissolved organic carbon (DOC) in the tailings

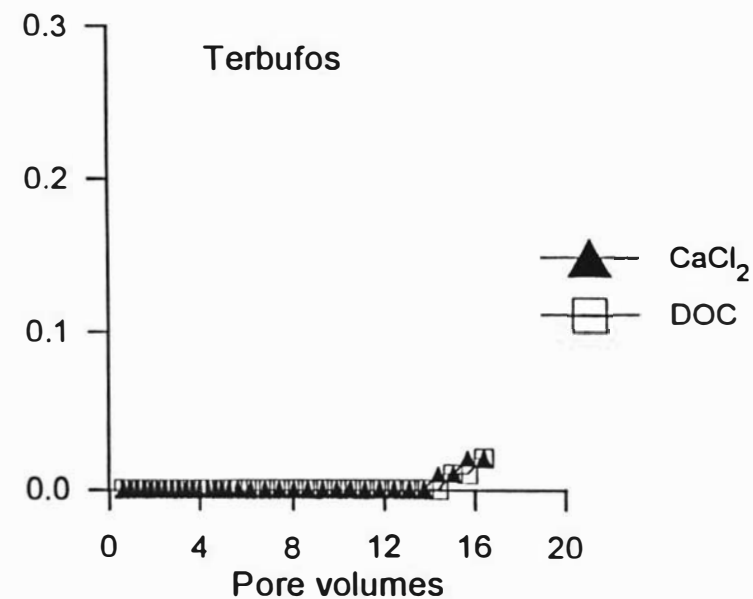
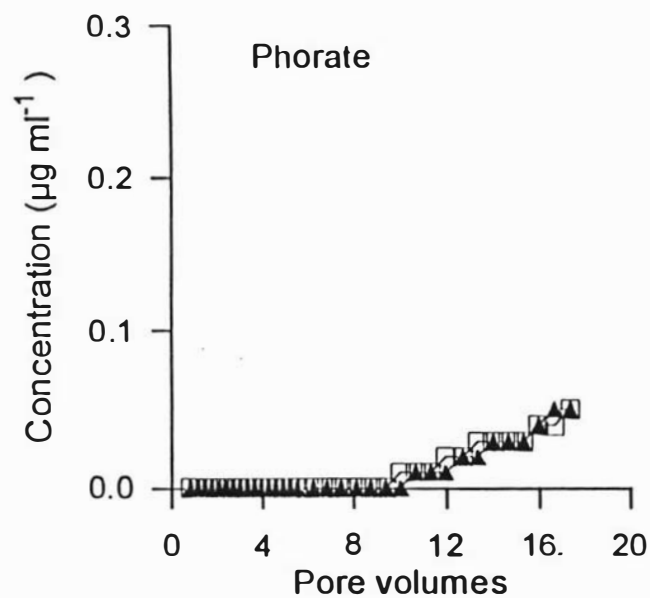
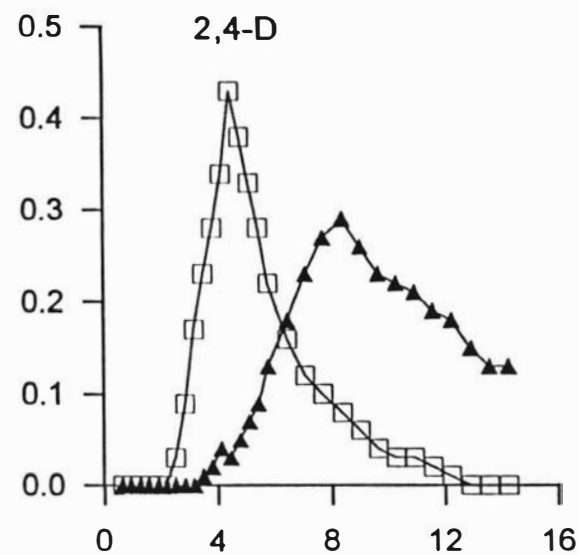
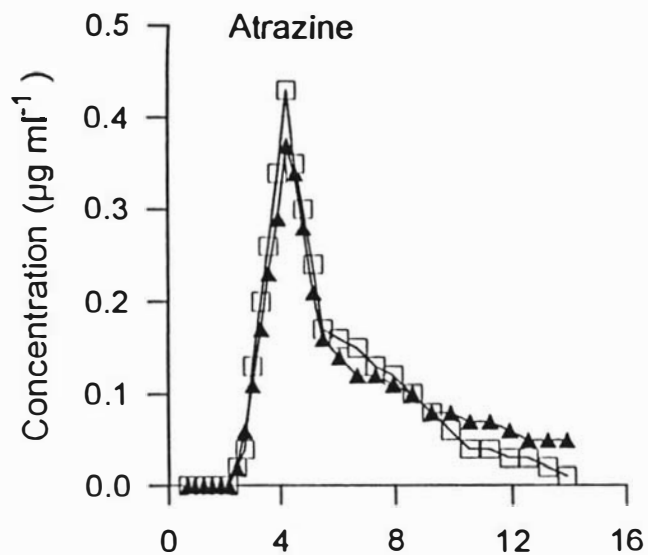


Fig 7.12 Breakthrough curves for pesticides leached with either CaCl_2 or dissolved organic carbon (DOC) in the Egmont soil

Table 7.5 Distribution of pesticides in the leachate at different pore volumes during leaching with either CaCl₂ or DOC

Soil	Compound	0 to 2PV		2 to 4PV		4 to 6PV		6 to 10PV	
		CaCl ₂	DOC	CaCl ₂	DOC	CaCl ₂	DOC	CaCl ₂	DOC
Tailings	Atrazine	50.25	57.25	36.25	35.25	7.75	5.6	1.75	-
	2,4-D	75.00	86.00	22.14	10.75	2.5	1.55	-	-
	Phorate	27.00	24.75	46.8	51.5	14.75	17.25	7.5	5.25
	Terbufos	28.75	25.00	37.00	44.5	17.5	21.5	12.0	6.5
Egmont	Atrazine	ND	ND	14.75	16.25	37.5	41.25	15.25	16.00
	2,4-D	ND	ND	1.75	28.5	13.75	45.00	37.5	10.75
	Phorate	ND	ND	ND	ND	ND	ND	ND	ND
	Terbufos	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not detected

effectively removed by DOC throughout the leaching. In the Egmont soil, negligible amounts of phorate and terbufos were detected in the leachate, whereas considerable amounts of atrazine and 2,4-D were removed by DOC throughout the leaching (Table 7.5).

7.4.7.2 *Effect of DOC in column leaching*

In the tailings the leaching with DOC increased the organic carbon content of the solid phase (Fig 7.13). Similarly, Logan *et al.* (1992) showed an increase in the organic carbon content of the solid phase by the addition of humic acid as DOC. However, sorption of added DOC is impeded in soils containing appreciable quantities of indigenous organic carbon (Jardine *et al.*, 1989). This might have been the reason for a lesser increase in carbon with DOC leaching in the Egmont soil than in the tailings. The increase in the solid phase organic carbon might have retarded the movement of phorate and terbufos at the early stages of leaching. Recently, Liu and Amy (1993) showed that the sorption of DOC on soil can retard the movement of polycyclic aromatic hydrocarbons. The effect of DOC in facilitating the movement of phorate and terbufos through the tailings at later stages of leaching can be explained by the increase in soluble carbon in the aqueous phase after the addition of 2 pore volumes (Fig 7.14).

In the Egmont soil, the mobility of 2,4-D was significantly enhanced when the column was leached with DOC. It has often been shown that 2,4-D sorption is pH dependent (Watson *et al.*, 1973; Barriuso *et al.*, 1992a). At higher pH, the sorption of 2,4-D is lower, and so mobility increases (Nicholls, 1988). In this experiment the pH of the leachate was also measured after the introduction of either DOC or CaCl₂. The column leached with CaCl₂ was 0.1 to 0.2 pH units higher than that leached with DOC. However, the difference in pH between the CaCl₂ and DOC leached columns is not large enough to cause such an early breakthrough of 2,4-D when the column was leached with DOC. This indicates that, the DOC facilitates the transport of 2,4-D in the soil column through the interaction of 2,4-D with DOC. Since the Egmont soil had higher indigenous organic carbon, phorate and terbufos would not be expected in the leachate. However, the results of phorate concentration in the soil section (Fig 7.15) showed the presence of a higher concentration of pesticide in the

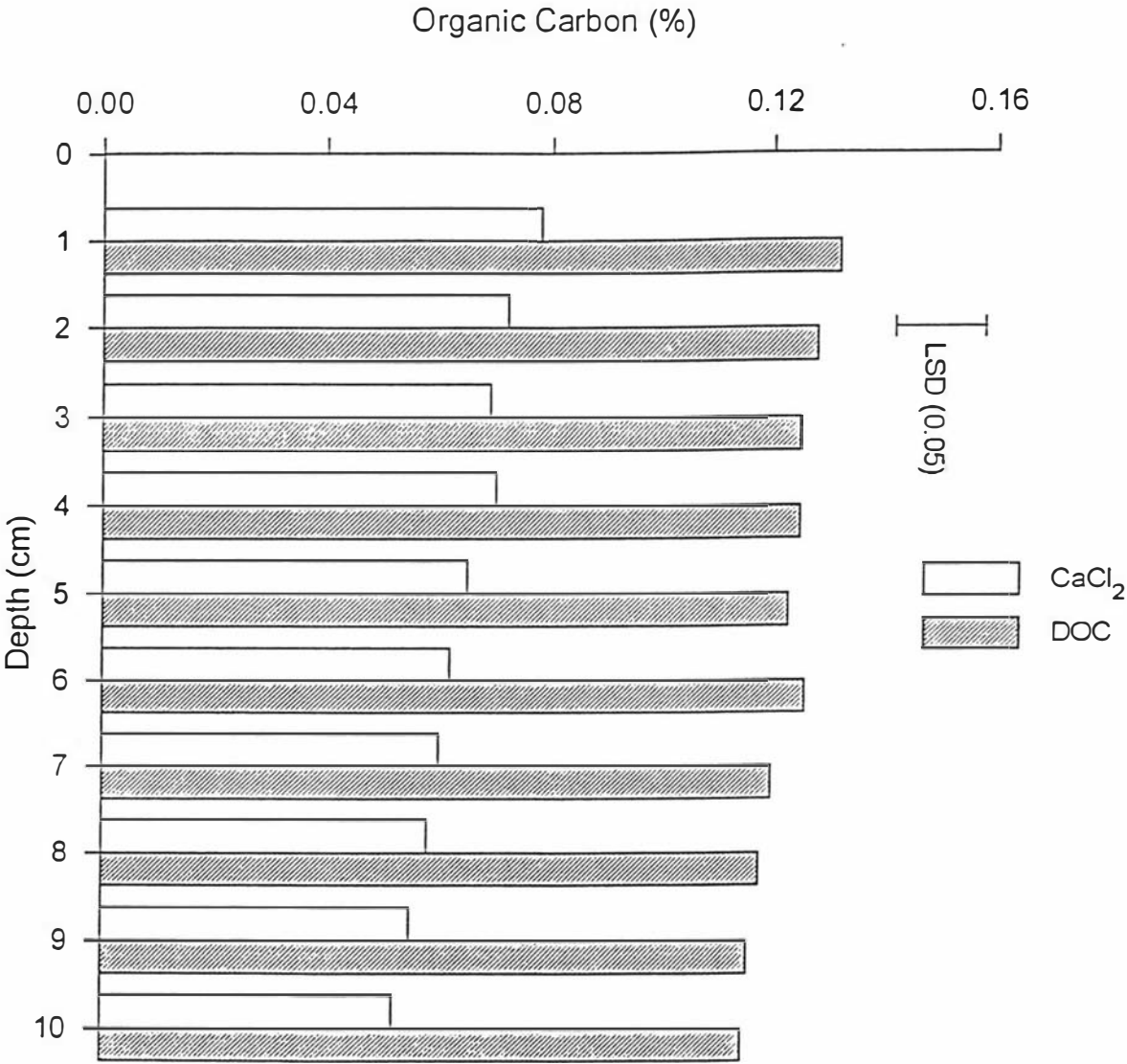


Fig 7.13 Percent organic carbon of the solid phase following leaching with either CaCl₂ or dissolved organic carbon (DOC) in the tailings

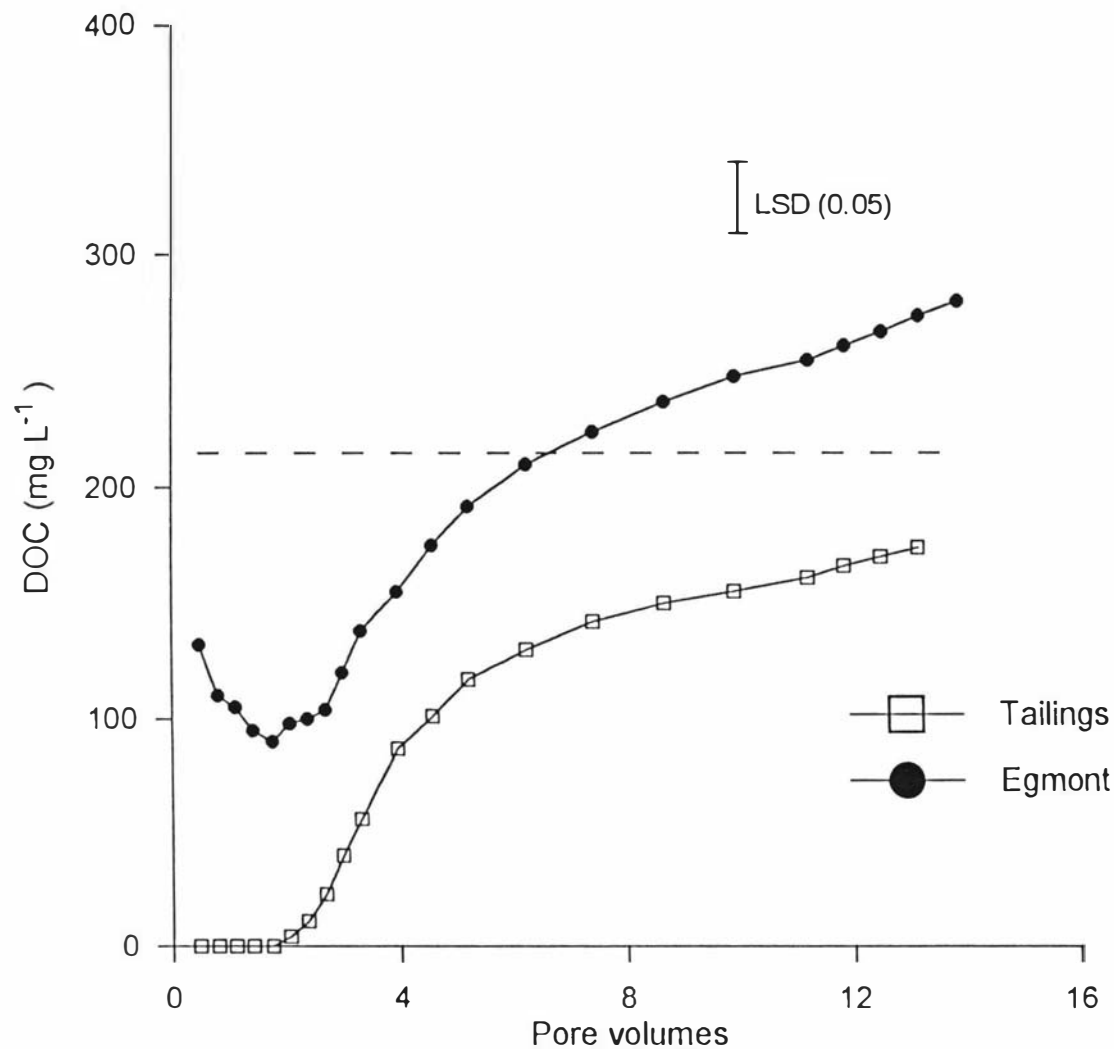


Fig 7. 14 Dissolved organic carbon (DOC) concentration in the column leachate in the tailings and the Egmont soil (Dashed line indicates the concentration of DOC used to leach the pesticides in the soil column)

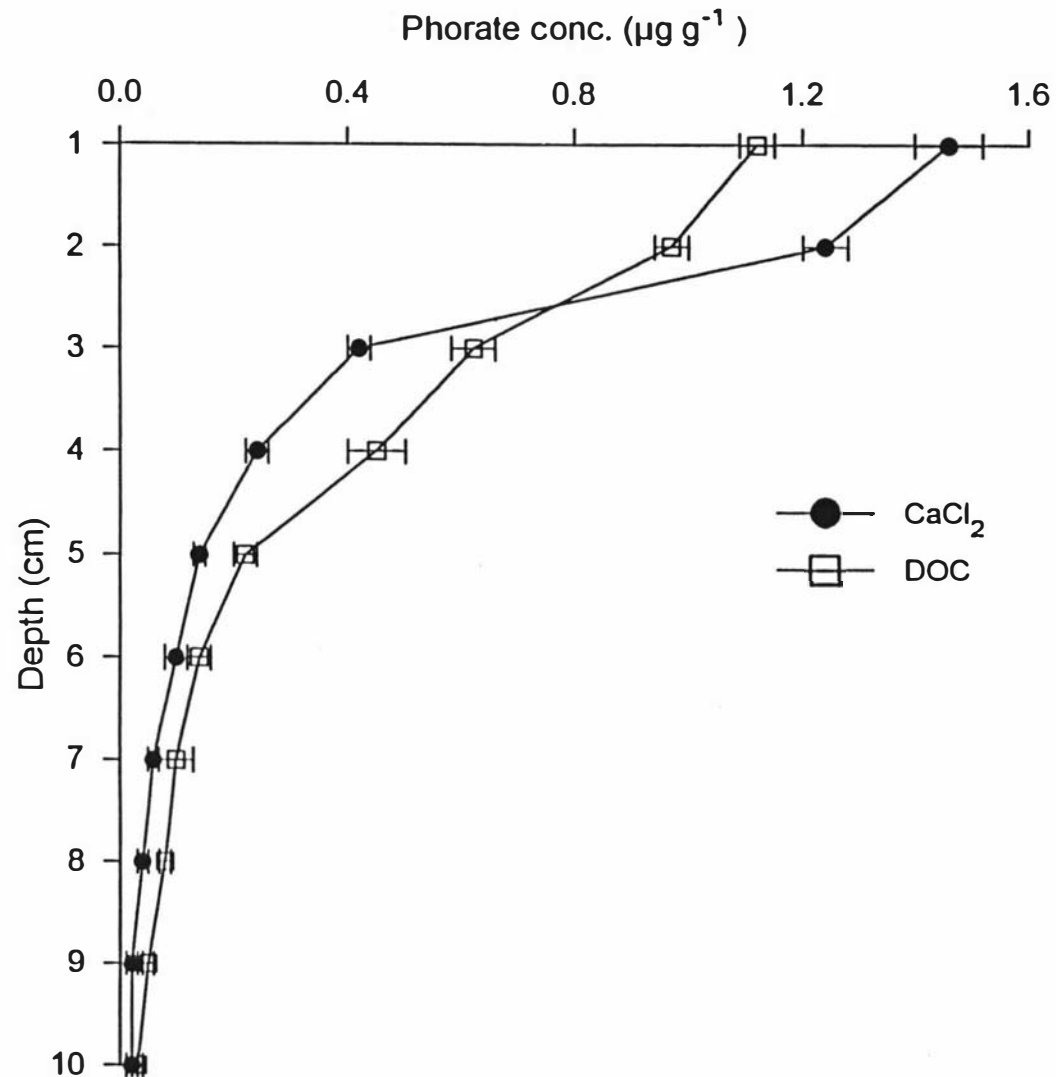


Fig 7.15 Phorate concentration of the soil column following leaching with either CaCl_2 or dissolved organic carbon (DOC) in the Egmont soil. (Horizontal bars represent standard error of mean)

deeper layers when the column was leached with DOC than when leached with CaCl_2 .

7.4.7.3 *Soil column characteristics and the retardation factor*

The soil column breakthrough data for the four pesticides examined are presented in Table 7.6 along with the retardation factor (R). In the pulse experiments the R value is measured from the pore volume at which the peak concentration of the pesticides appears in the leachate (Logan *et al.*, 1992). The predicted R value was calculated using equation 7.3 (Kan and Tomson, 1990).

The R values for pesticides were higher for the Egmont soil than for the tailings reflecting the greater retardation and lesser mobility of pesticides occurs in the Egmont soil. In general the R values were less for pesticides leached with DOC than CaCl_2 . This reflected the enhanced mobility of pesticides in the presence of DOC. For example it is seen from the Table 7.6, that the transport of 2,4-D in the Egmont soil was twice as fast in the presence of DOC than with CaCl_2 . The relationship between the measured and the predicted R values is shown in Figure 7.16. The results show that the measured R values were slightly lower than the predicted values (Table 7.6). In contrast, Logan *et al.* (1992) have shown that the measured R was higher than the predicted R values and reported that the increase in organic carbon content of a soil by the addition of humic acid retarded the movement of Chlordane in the soil column.

In this experiment, leaching the soil materials with DOC increased the organic carbon both in the solid and aqueous phases. While the increase in organic carbon in the solid phase increased the partitioning of the pesticides from the aqueous phase onto the solid phase, the increase in the aqueous phase carbon, on the other hand, is likely to cause the pesticide to remain in solution and so enhance the transport of pesticide. Similarly Enfield *et al.* (1989) showed the facilitated movement of pyrene and hexachlorobenzene in the presence of the macromolecules dextran and DOC whereas the retention of humic acid on the soil column reduced the movement. Recently Liu and Amy (1993) demonstrated that the increase in aqueous phase DOC can enhance the movement, whereas the solid phase DOC can retard the movement of organic

Table 7.6 Column breakthrough data and retardation factors

Soil	Compound	K_d (L kg ⁻¹)	ρ_b (g cm ⁻³)	θ (cm ³ cm ⁻³)	DOC (mg L ⁻¹)	Retardation factor	
						Observed	Predicted*
Tailings	Atrazine	0.62	1.3	0.42	0	1.60	2.92
		0.62	1.3	0.42	210	1.57	2.85
	2,4-D	0.71	1.3	0.42	0	1.68	3.20
		0.71	1.3	0.42	210	1.52	3.02
	Phorate	0.95	1.3	0.42	0	2.67	3.95
		0.95	1.3	0.42	210	2.60	3.29
	Terbufos	1.27	1.3	0.42	0	2.76	4.93
		1.27	1.3	0.48	210	2.73	3.40
Egmont	Atrazine	3.50	0.85	0.48	0	4.54	7.20
		3.50	0.85	0.48	210	4.23	6.94
	2,4-D	4.64	0.85	0.48	0	8.37	9.21
		4.64	0.85	0.48	210	4.50	8.56
	Phorate	39.30	0.85	0.48	0	-	70.52
		39.30	0.85	0.48	210	-	55.20
	Terbufos	42.03	0.85	0.48	0	-	75.51
		42.03	0.85	0.48	210	-	46.72

* The predicted retardation factor was calculated from equation 7.3. The K_{Doc} of the pesticides were calculated using Equation 7.4. The values of K_{ow} for the pesticides are given in Table 3.1. The K_{Doc} values as calculated from Equation 7.4 are: 199 for atrazine, 406 for 2,4-D, 1353 for phorate, and 3021 for terbufos.

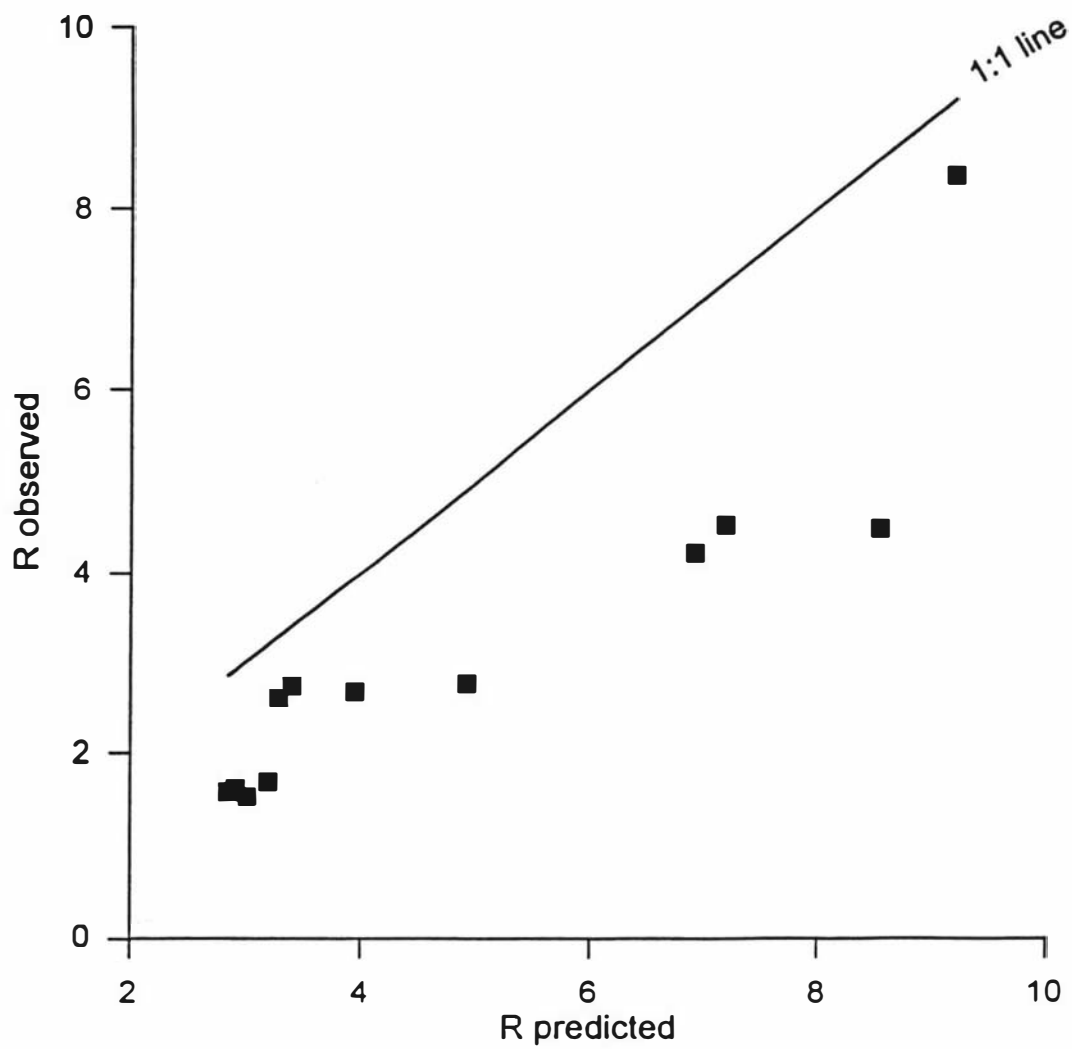


Fig 7.16 Relationship between the predicted and the observed retardation factor (R) in soil column leaching

contaminants.

7.4.8 Infrared Spectroscopy

7.4.8.1 Spectra of DOC (Figure 7.17)

The infrared spectra of DOC extracted from various carbon sources, pure pesticides and DOC - pesticide complexes are shown in Fig 7.17 to 7.23. The IR spectra presented for different DOC closely resemble the IR pattern published for water soluble organic matter (Madhun *et al.*, 1986b), humic acid (Senesi and Testini, 1980) and water soluble extracts from sewage sludge (Baham and Sposito, 1983).

The IR spectrum of the DOC samples shows broad and poorly resolved absorption bands indicating the presence of many functional groups (Madhun *et al.*, 1986b). Further, the spectrum bands for different sources of DOC closely resemble each other. The important absorption bands are in the region of wave lengths 3700-3000 cm^{-1} (H-bonded OH groups and N-H and C-H stretching vibrations), near 2980 cm^{-1} (aliphatic C-H stretching), 1800-1500 cm^{-1} (C=O stretching, aromatic C=C stretching, COO^- symmetric stretching, N-H bending vibration), 1430-1400 cm^{-1} (C-H and O-H bending, phenolic C-O stretching), and 1200-1000 cm^{-1} (O-H deformation and C-O stretching of COOH). In addition, small bands are evident at 1500 cm^{-1} (aromatic C=C), in the region 1400-1300 cm^{-1} (O-H deformation, CH_3 bending or C-O stretching) in DOC extracted from poultry manure.

7.4.8.2 Spectra of pure pesticides (Figure 7.18)

The important spectrum bands for atrazine show aromatic C=C, strongly H-bonded C=O of ketones (1600-1500 cm^{-1}), OH deformation and phenolic OH, C-H deformation of CH_2 and CH_3 , COO^- asymmetric stretching (1360 cm^{-1}), C-O stretching and OH deformation (1150-1020 cm^{-1}). The important spectrum bands corresponding to 2,4-D appeared at 1745 cm^{-1} (carboxylic C=O), 1490 cm^{-1} (aromatic ring C=C), and 1250 cm^{-1} (carboxylic O-H and out of plane and C-H deformation). The important spectra of phorate and terbufos bands are in the region of 1390 cm^{-1} (OH-deformation and C-O stretching of phenolic OH, C-H deformation of CH_2 and

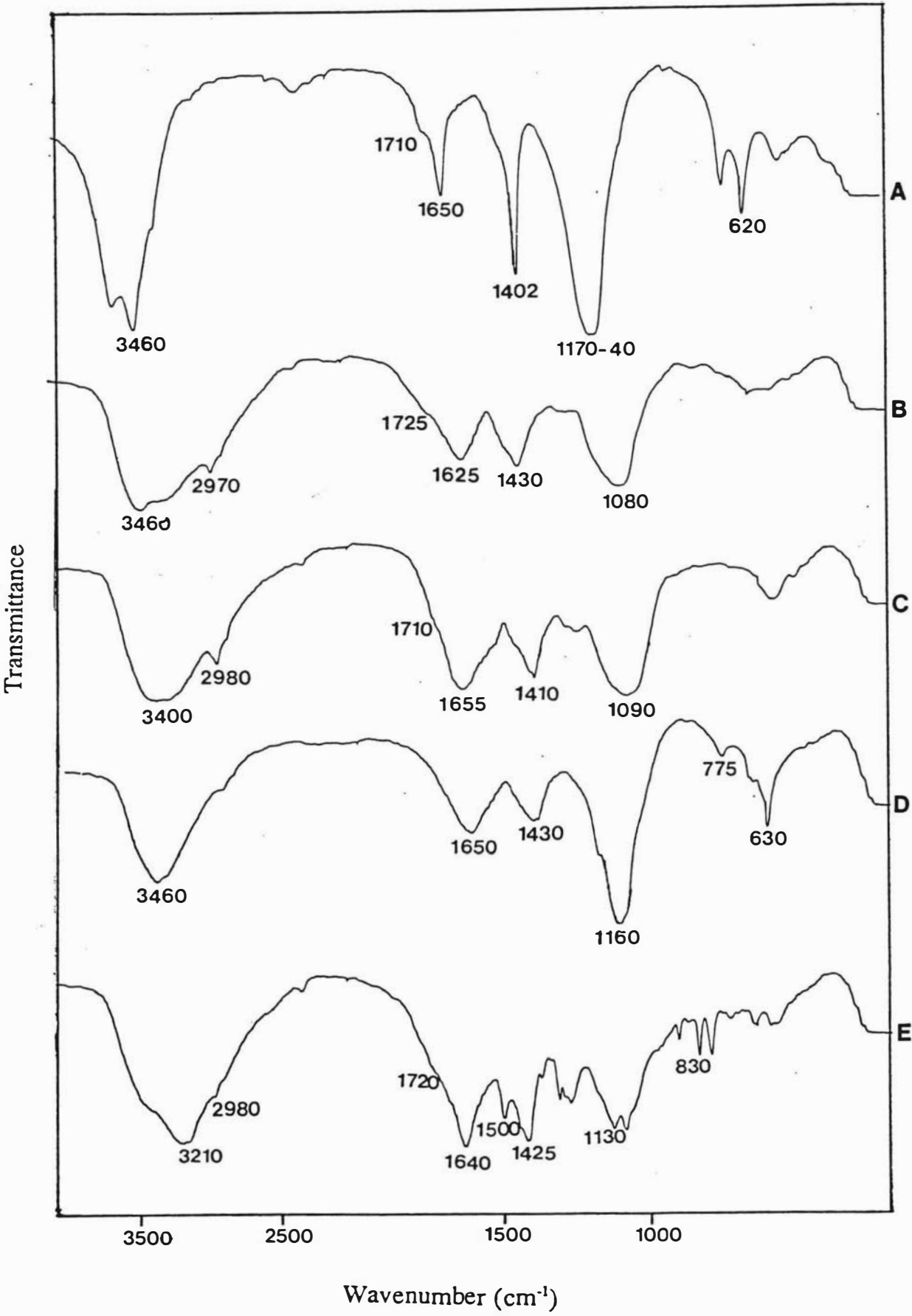


Fig 7.17 Infrared spectra of DOC extracted from (A) sludge, (B) peat, (C) pig manure, (D) mushroom compost and (E) poultry manure

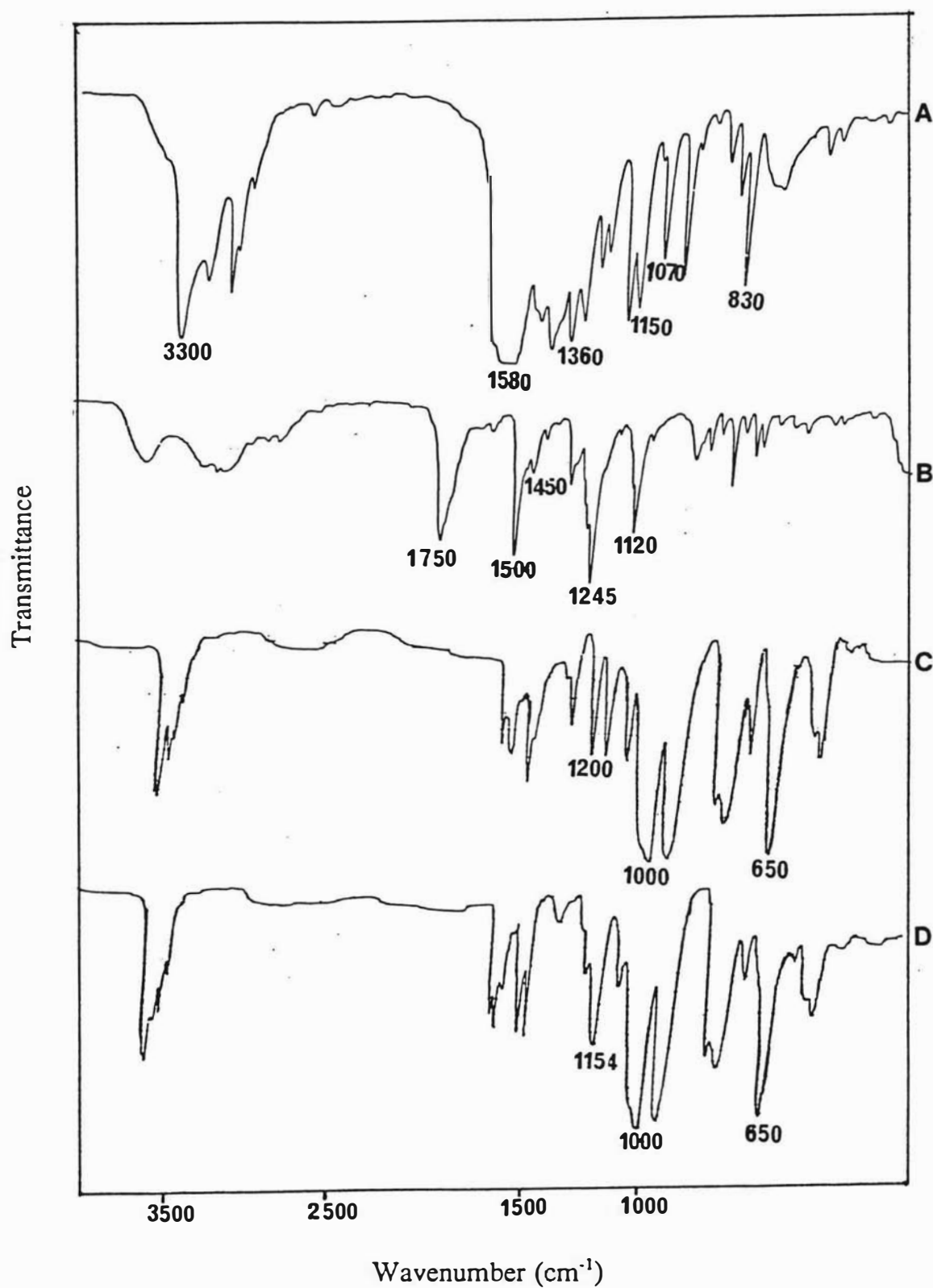


Fig 7.18 Infrared spectra of pesticides (A) Atrazine, (B) 2,4-D, (C) Phorate and (D) Terbufos

CH₃ groups), and 1150 cm⁻¹ (C-O stretching and O-H deformation).

7.4.8.3 *Spectra of DOC-pesticide complexes (Figures 7.19 - 7.23).*

The IR spectra for DOC-atrazine complexes show changes in absorption bands when compared with spectra of the pure compound and DOC alone. The absorption bands in the range 1725-1710 cm⁻¹ show a poor shoulder, whereas intensity increases in the region 1650 to 1600 cm⁻¹ observed in the complexes. Similar results were reported for atrazine-humic acid complexes (Sullivan and Felbeck, 1968) and other triazine herbicides (Senesi and Testini, 1980) using infrared spectra. Triazine herbicides are weakly basic chemicals that can be protonated at low pH values. Hence, the interaction between the deprotonated COOH group of DOC and the protonated N-H groups in atrazine may result in ionic bond formation (Senesi and Testini, 1980). The pH of the DOC-atrazine complexes were 2 pH units above the pK_a of atrazine (1.7), at which most of the atrazine is present as non-ionic molecules. Therefore, the changes in the spectrum bands cannot be explained using an ionic bond mechanism. The effects are due to the secondary (deprotonated) amino group of s-triazine and OH or C=O groups of the DOC when involved in H-bonding with the herbicides (Hayes, 1970; Senesi and Testini, 1980; Stevenson, 1982).

The IR spectra for DOC-2,4-D complexes also show some changes in absorption bands when compared with the spectra of DOC. The intensity reduced at 1725 to 1710 cm⁻¹ whereas it increased at 1650 to 1610 cm⁻¹ and 1430 to 1405 cm⁻¹. Recently Hermosin and Cornejo, (1993) also observed an increase in peak intensity at 1634 cm⁻¹ for 2,4-D-clay complexes. Acidic pesticides such as 2,4-D contain COOH, which may ionize depending on the pH. At high pH, repulsion by negatively charged organic matter may occur, so sorption by anion exchange is unlikely. The mechanism thus appears to include H-bonding or charge transfer between the COOH group of the herbicide and the C=O or NH groups of DOC. Charge transfer through ion exchange has been considered to be one of the mechanisms for the retention of organic anions in soils (Zielke *et al.*, 1989). Similarly charge transfer and H-bonding were postulated as the adsorption mechanism for other acidic pesticides such as, chlorsulfuron (Shea, 1986).

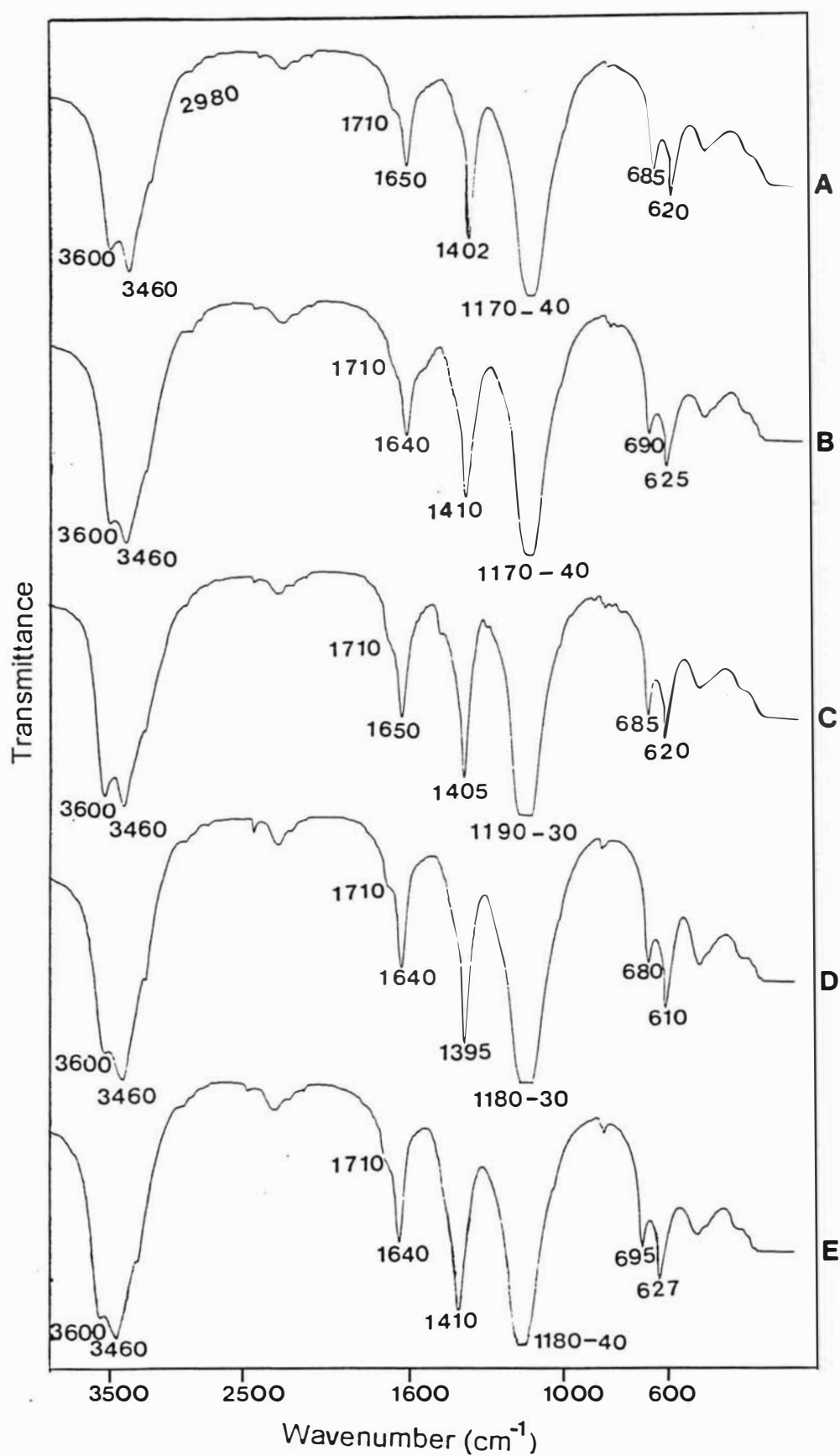


Fig 7.19 Infrared spectra of (A) sludge DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos

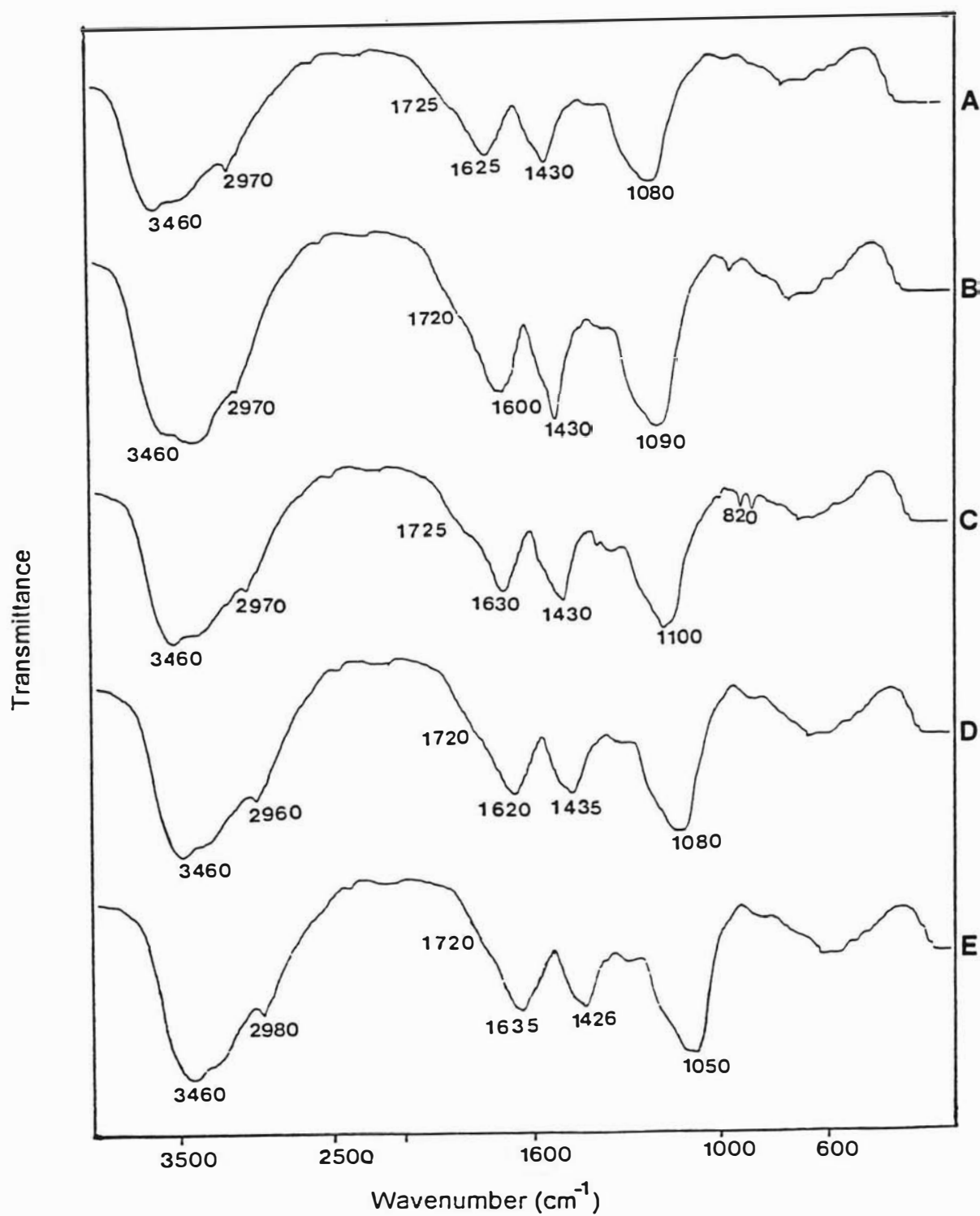


Fig 7.20 Infrared spectra of (A) peat DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos

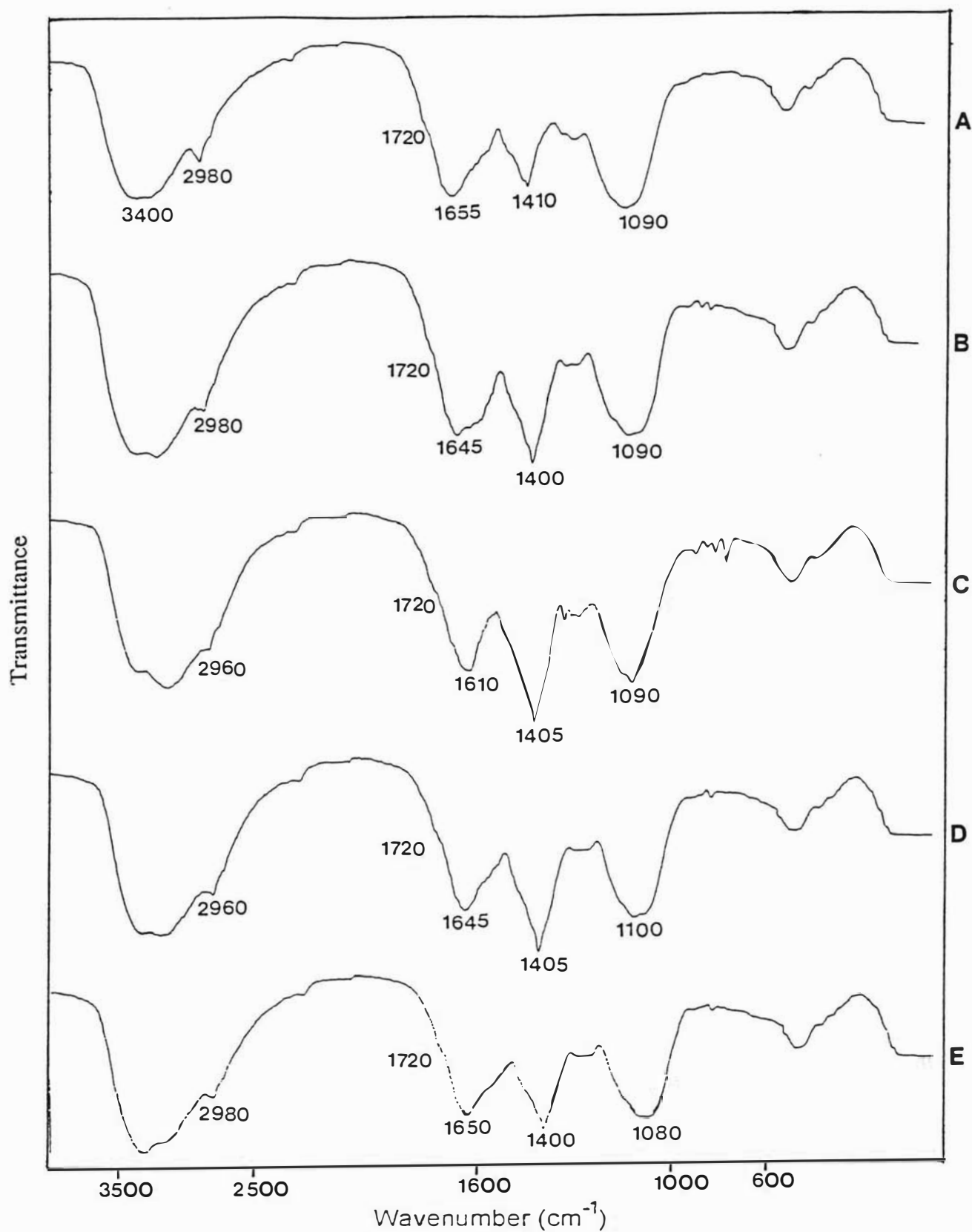


Fig 7.21 Infrared spectra of (A) pig manure DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos

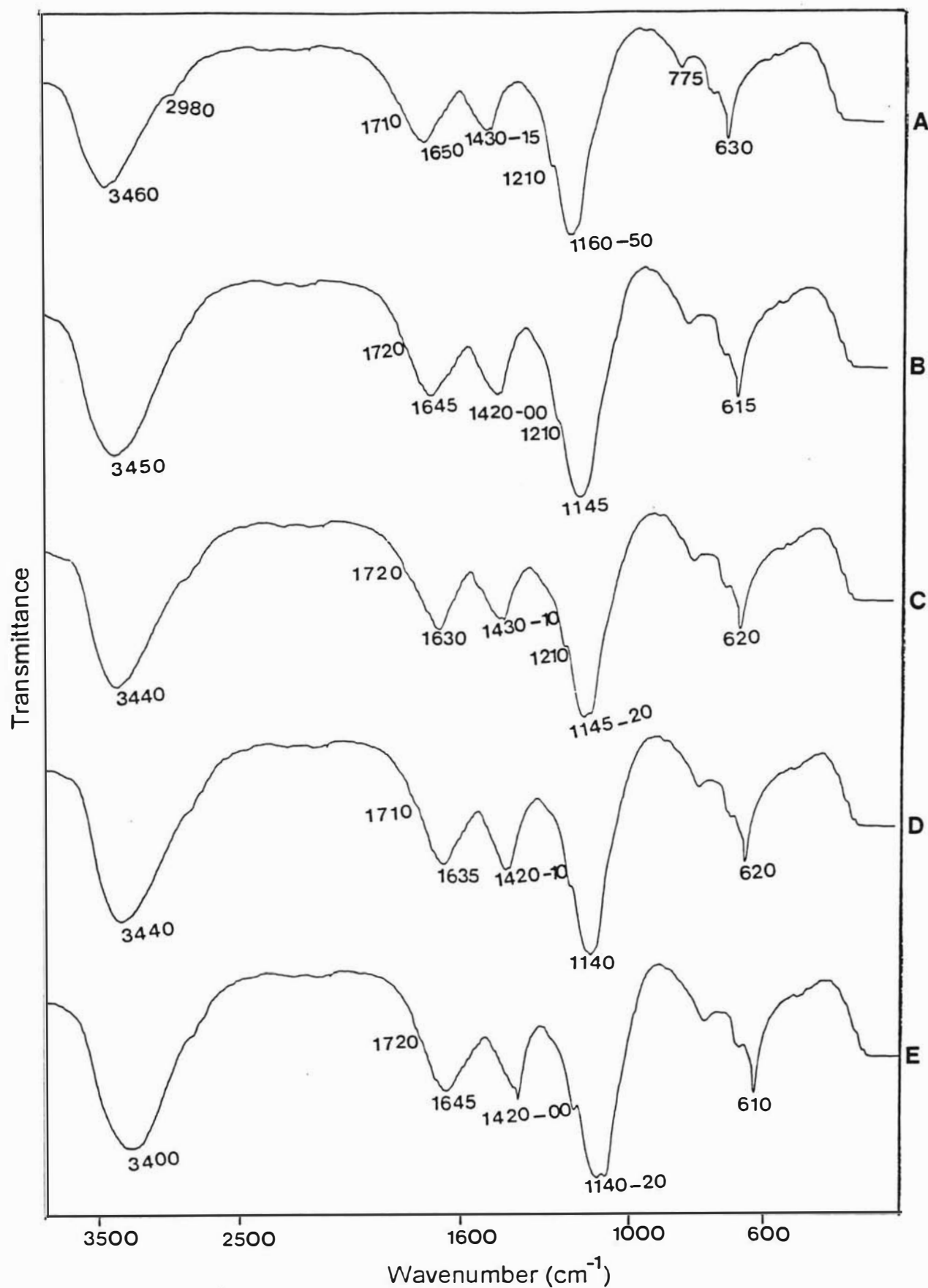


Fig 7.22 Infrared spectra of (A) mushroom compost DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos

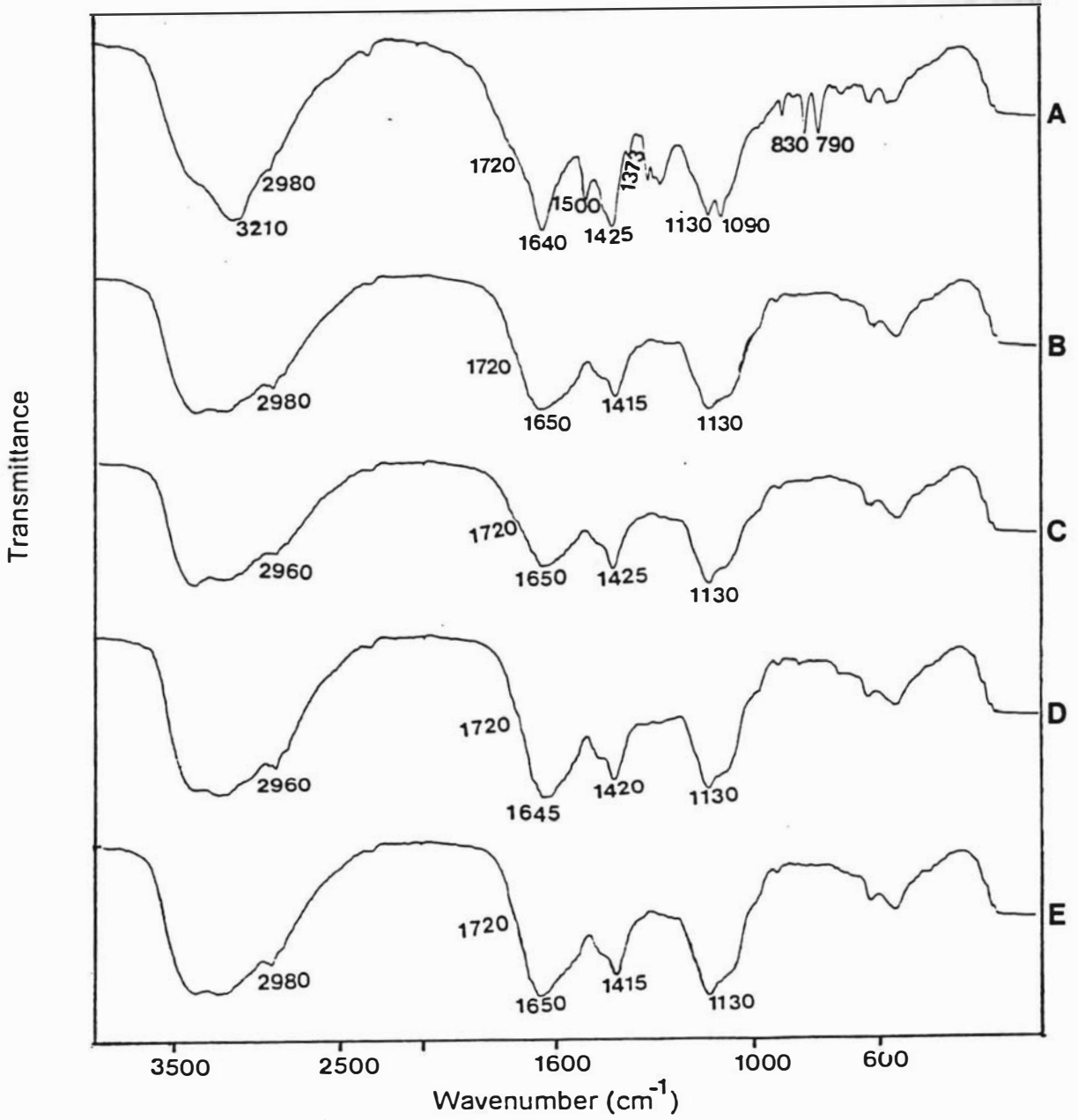


Fig 7.23 Infrared spectra of (A) poultry manure DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos

The IR spectra for the DOC-non-ionic pesticides show slight changes from the spectra of the pure pesticide and DOC alone. There is a slight shifting of spectrum bands observed at 1400 and 650 cm^{-1} in DOC-non-ionic pesticide. For example, the spectrum band at 1390 cm^{-1} observed in phorate and terbufos has been shifted to a new position at 1400-1430 cm^{-1} . Similarly the spectrum band at 650 cm^{-1} in phorate and terbufos has either disappeared or shifted to 627-610 cm^{-1} in some of the DOC-pesticide complex. These shifts may be due to changes in the out-of-plane C-H vibration frequencies, suggesting the formation of charge transfer complexes between the pesticide and DOC. Experimental evidence for the formation of charge transfer complexes between non-ionic chemicals, water soluble organic matter (Madhun, 1984) and sludge humic acid (Senesi *et al.*, 1994) has been reported. Apart from the charge transfer mechanism, it has been suggested that hydrophobic bonding is one of the predominant mechanisms for the sorption of non-ionic pesticides onto organic matter (Senesi *et al.*, 1994).

Although it was not possible to elucidate the exact mechanism for the interaction of pesticides with DOC, the IR spectra demonstrate the formation of DOC-pesticide complexes. When these complexes are formed in solution it enhances the movement of pesticides in soils; but when the DOC is sorbed onto the soil surface the formation of DOC-pesticide complexes impede the movement of pesticide in solution. It is likely that the release of these complexes from the soil surface may enhance the movement of pesticide to ground water.

7.5 CONCLUSIONS

The important conclusions from these experiment are:

1. Addition of carbon to soil through different carbon materials increased the pesticide sorption and the rate of increase depends on the indigenous carbon content of the soil.
2. The increase in pesticide sorption per unit of carbon addition is reduced at higher rates of carbon addition.
3. Irrespective of the source of carbon materials, the addition of carbon increases the aqueous phase DOC and alters the pH.
4. In general, preincubating DOC with soil increased pesticide sorption due to

sorption of DOC onto soil.

5. Preincubation of DOC with pesticide decreased pesticide sorption due to the formation of DOC-pesticide complexes in solution.
6. The K_d values of 2,4-D and atrazine decreased with increasing pH, whereas that of phorate and terbufos was unaffected by the change in pH.
7. Sorption of pesticides decreased more with an increase in pH when the soil pH was amended with NaOH than with $\text{Ca}(\text{OH})_2$. Increasing soil pH with NaOH releases more DOC into soil solution and this decreases pesticide sorption.
8. The results of the soil column study indicate that DOC is effective in enhancing the movement of pesticides. Increase in solid phase carbon retards the movement of pesticides. On the other hand increase in aqueous phase DOC facilitates the movement of pesticides.
9. The results from IR spectra indicate the formation of DOC-pesticide complexes. However using IR spectra it was not possible to identify the exact mechanisms for the interaction of pesticides with DOC.

CHAPTER 8

EFFECT OF SORPTION ON THE MOVEMENT OF PESTICIDES IN SOILS

8.1 INTRODUCTION

An important problem in modern agriculture and horticulture is the loss of pesticides and soil nutrients from the root zone by leaching. Leached pesticides may ultimately contaminate groundwater. Pesticide leaching has been reported to be substantial in some soils and significant amounts have been detected in groundwater in U.S (Cohen *et al.*, 1986).

The miscible displacement technique has been widely used to examine the redistribution and leaching of pesticides in soils (Davidson *et al.*, 1968; Rao and Davidson, 1979). Laboratory studies using repacked soil columns can help clarify the complex interactions between the physical and chemical processes involved in the movement of pesticides (Davidson *et al.*, 1968). Of the various processes, sorption is one of the most important affecting the pesticide movement in soils (Brusseau and Rao, 1989a).

Several mathematical models have been developed to predict the movement of pesticides in soils. These models have been discussed in detail in Chapter 2. Among these models, the convection dispersion equation (CDE) has been used widely to simulate the movement of solutes in soils and to identify the various mechanisms involved in their movement (Murali and Alymore, 1981). The CDE model can incorporate both equilibrium sorption and non-equilibrium sorption processes during the movement of solutes in soils. In models involving equilibrium sorption, the sorption process is often simplified by making the following assumptions.

- (i) sorption attains instantaneous equilibrium (i.e. the kinetics of sorption are ignored).
- (ii) the sorption isotherm is linear.
- (iii) the sorption-desorption isotherm is singular (i.e. there is no hysteresis).

However, it has been reported that sorption non-equilibrium affects the leaching of pesticide and the effects of non-equilibrium sorption on solute movement were reviewed by Brusseau and Rao (1989a). Physical non-equilibrium and chemical non-equilibrium are reported to be the predominant rate-limiting mechanisms for the sorption of many pesticides during their movement in soils (Brusseau and Rao, 1989a). The physical non-equilibrium, which is attributed mainly to the variation in the distribution of flow paths in soils, has been studied extensively (Van Genuchten and Wierenga, 1976; Van Genuchten *et al.*, 1977; Rao *et al.*, 1979; Nkedi-Kizza *et al.*, 1984). In contrast chemical non-equilibrium, which involves sorbate diffusion within the matrix of sorbent organic matter (intraorganic matter diffusion) or mineral particles (intramineral diffusion), has received attention only in recent years (Nkedi-Kizza *et al.*, 1989; Brusseau and Rao, 1989b; Brusseau and Rao, 1991).

Selim *et al.* (1976) and Cameron and Klute (1977) have developed a bicontinuum non-equilibrium CDE model to simulate the movement of pesticides in soils. This model has been subsequently used (Rao *et al.*, 1979; Nkedi-Kizza *et al.*, 1989; Brusseau and Rao, 1991; Brusseau *et al.*, 1991) to describe the processes involved in the non-equilibrium sorption of pesticides during transport. This model is discussed in detail in Chapter 2 and in the experiments outlined in this Chapter an attempt was made to simulate the movement of pesticides using both the equilibrium sorption CDE and the non-equilibrium sorption CDE models.

The results of the experiments in Chapter 5 indicate that the pasture soils of New Zealand varied greatly in the sorption of pesticides. In this experiment the effect of sorption on the movement of pesticide was examined using both step-function and pulse inputs on soils with low and high sorption capacities.

8.2 OBJECTIVES

The objectives of the experiment described in this chapter were:

- (i) to investigate the difference in the movement of 2,4-D between two soils, which varied in their capacity to sorb pesticides.
- (ii) to examine the difference in the movement of four pesticides (2,4-D, atrazine, phorate and terbufos) which varied in their sorption onto soils.

- (iii) to compare the movement of 2,4-D in repacked and intact soil cores.
- (iv) to examine the suitability of CDE models with either equilibrium sorption or non-equilibrium sorption to predict the movement of 2,4-D.

8.3 MATERIALS AND METHODS

8.3.1 Soils

Soil samples taken from the Ah horizon of Patua loam, a Typic Hapludand (medial, mesic) and Tokomaru silt loam (Ah1), a Typic Fragiaqualf (fine silty, mixed, mesic) were used to examine the movement of pesticides. The important properties of these soils were described in Chapter 5. These two soils differed in their capacity to sorb pesticides, as measured by the distribution coefficient (K_d) values (Table 5.4).

8.3.2 Column experiments

Two types of column experiment were conducted to examine the movement of pesticides in soils (Table 8.1).

Table 8.1 Types of column leaching experiments conducted

Column set up	Leaching procedure	Solutes	Soils
Repacked	Step input	$^3\text{H}_2\text{O}$, 2,4-D	Tokomaru (Ah1) and Patua (Ah)
	Pulse input	atrazine, 2,4-D, phorate and terbufos	Tokomaru (Ah1) and Patua (Ah)
Intact core	Step input	$^3\text{H}_2\text{O}$, 2,4-D	Tokomaru (Ah1)

One involved a step-function experiment in which a known volume of pesticide solution at a constant concentration was introduced into the soil. The applied pesticide solution was subsequently displaced through the soil column with 0.01 M CaCl_2 at the same flux. The number of liquid-filled pore volumes (p) of solution passed through the column was calculated by dividing the cumulative outflow volume

by the total volume of water in the soil column. Leachate pesticide concentrations were expressed as relative concentrations (C_e/C_0), where C_e and C_0 were, respectively, leachate and input concentrations. Plots of C_e/C_0 vs p are referred to as breakthrough curves (BTC).

In the second type of column experiment a pulse of pesticide added to the soil column was leached with a known amount of pesticide free solution (0.01 M CaCl_2) and the concentration of pesticide in both the leachate and the soil column was measured.

The type of column experiment, soil and the solute used are summarised in Table 8.1. The step function experiments were carried out using both repacked (disturbed) and intact (undisturbed) soil columns. Whereas the pulse experiments were carried out using only the repacked soil columns.

8.3.2.1 *Repacked soil column experiments*

Plate 8.1 shows the experimental set up used to examine the movement of pesticides through the repacked soil columns in the laboratory. For these experiments, PVC tubes (200 mm long and 51.2 mm internal diameter) were used. The base of the columns was sealed with a nylon mesh with an effective pore diameter of $60\ \mu\text{m}$ to retain the soil in the column. Both step function input and pulse input experiments were carried out using the repacked soil columns.

(i) Step-function experiment

For the step-function experiment, both the Patua (Ah) and the Tokomaru (Ah1) soils were used to examine the movement of ^{14}C 2,4-D. The columns were packed to a bulk density of 0.88 and $1.05\ \text{g cm}^{-3}$ for the Patua and the Tokomaru soils respectively, with a 140 mm soil depth. The columns were covered with a plastic cap to prevent evaporation. Each cap had three pinholes through which hypodermic needles were inserted to drip the solution onto the centre of the column. Acid washed sand was used to cover the soil surface, so that the flow from the hypodermic needles would be spread evenly over the core area.

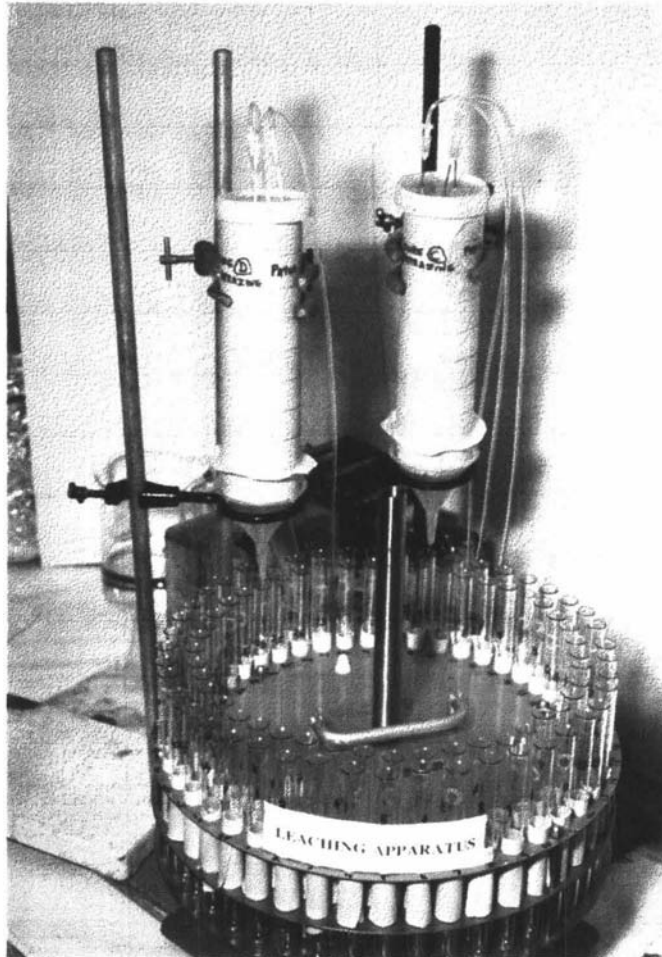


Plate 8.1 Experimental setup - Repacked soil column experiment

Initially the columns were saturated with 2 pore volumes of 0.01 M CaCl_2 . Then a known concentration of ^{14}C labelled 2,4-D ($22 \mu\text{mol L}^{-1}$) along with tritiated water ($^3\text{H}_2\text{O}$) (67 Bq ml^{-1}) was added to the soil columns as a step-change input at a constant flux (0.25 ml min^{-1}) using a peristaltic pump. The $^3\text{H}_2\text{O}$ was used as a conservative tracer to study the movement of non-sorbed solute in the soil column. Details pertinent to the experimental conditions are presented in Table 8.2. After passing 7 and 35 pore volumes of input solution through the Tokomaru and the Patua soils respectively, the applied 2,4-D and $^3\text{H}_2\text{O}$ was subsequently displaced from the soil column with 0.01 M CaCl_2 (9 and 35 pore volumes for the Tokomaru and the Patua soils, respectively) to initiate desorption at the same flux. The leachate from the soil columns was collected using an automatic fraction collector.

The liquid-filled pore volume was determined as the difference between the mass of the soil in the column - after excess water flow had effectively ceased at the end of the experiment - and the oven-dry mass of soil. The activity of $^3\text{H}_2\text{O}$ and ^{14}C in the leachate was measured using a liquid scintillation counter for dual labelling (Nkedi-Kizza *et al.*, 1985). At the end of the experiment the soil samples were analysed for ^{14}C 2,4-D (Lavy *et al.*, 1972).

(ii) Pulse experiment

Preliminary experiments using a step-function input have indicated that a long duration is required to achieve the complete breakthrough of atrazine, phorate and terbufos. This may result in the degradation of the pesticides and thereby complicate the interpretation of the results. Hence it was decided to examine the movement of these pesticides using a pulse input. For the pulse experiments, movement of ^{14}C atrazine, 2,4-D, phorate and terbufos was examined in the Patua (Ah) and the Tokomaru (Ah1) soils. Borosilicate glass columns (200 mm long and 27.2 mm inner diameter) were used in these experiments. It has been shown that a considerable amount of phorate and terbufos is sorbed onto the walls of polythene materials, whereas negligible amounts are sorbed onto glass (Chapter 3, section 3.4.6). Hence the leaching of these pesticides was carried out using the borosilicate glass columns. Soil was added in small increments to the columns to minimize particle size segregation. The columns were packed to a bulk density of 1.05 and 0.88 g cm^{-3} for

Table 8.2 Experimental parameters for the repacked and intact soil column studies

Parameters	Repacked soil columns				Intact core
	Step-input		Pulse input		
	Tokomaru (Ah1)	Patua (Ah)	Tokomaru (Ah1)	Patua (Ah)	Tokomaru (Ah1)
Column length (mm)	140	140	140	140	140
Inner diameter (mm)	51.2	51.2	27.2	27.2	74.3
Bulk density (g cm ⁻³)	1.05	0.88	1.05	0.88	1.16 [*]
Pore water velocity (mm hr ⁻¹)	13.73	17.04	7.06	8.1	7.06
Soil water content (mm ³ mm ⁻³)	0.53	0.47	0.50	0.46	0.49
Dispersion coefficient (mm ² hr ⁻¹)	80.8	155.0	-	-	101.5
Input concentration (μmol L ⁻¹)	22.6	22.6	22.6 ^a	22.6	22.6

^{*} Source (Bramley, 1989).

^a The input concentration is expressed as mg L⁻¹; when expressed as molar concentration it varied between the pesticides in the pulse experiment: 2,4-D (22.6 μmol L⁻¹); atrazine (23.2 μmol L⁻¹); phorate (19.2 μmol L⁻¹) and terbufos (17.2 μmol L⁻¹).

the Tokomaru and the Patua soils respectively, to a depth of 140 mm.

The columns were preleached with two pore volumes of 0.01 M CaCl_2 , then a 5 ml pulse of ^{14}C labelled pesticide of known concentration ($5\ \mu\text{g ml}^{-1}$) of 2,4-D ($22.6\ \mu\text{mol L}^{-1}$); atrazine ($23.2\ \mu\text{mol L}^{-1}$); phorate ($19.2\ \mu\text{mol L}^{-1}$) and terbufos ($17.2\ \mu\text{mol L}^{-1}$) was applied onto the top of each soil column. The columns were immediately leached with 0.01 M CaCl_2 at a constant flux ($0.2\ \text{ml min}^{-1}$) using a peristaltic pump. The leachate fractions were analysed for ^{14}C pesticide concentration using a liquid scintillation counter. After the completion of leaching, the soil columns were sectioned into 2 cm sections and analysed for the ^{14}C pesticides (Lavy *et al.*, 1972) and the mass balance calculated (section 3.4.5.1).

8.3.2.2 *Intact (undisturbed) soil core experiment*

The majority of the leaching studies were performed in the laboratory with repacked soil columns (Kay and Elrick, 1967; Davidson and Chang, 1972; Rao and Davidson, 1979). However, it has been reported that repacked soil columns are not representative of field conditions (i.e. the natural flow paths observed under field condition are disturbed in the repacked soil column). It was therefore decided to examine the leaching of the pesticide 2,4-D, using an undisturbed cores of the Tokomaru soil with step-function inputs.

(i) Core collection

The undisturbed soil core samples (Tokomaru silt loam) were collected from the Massey University No.4 Dairy farm. The soil cores were taken by driving steel corers into a depth of about 140 mm. After driving a corer into the desired depth, soil was removed from around the corer in such a way that the core could be lifted out easily with little disturbance. The length of the soil corer was 140 mm with an inner diameter of 74.3 mm.

Before starting the leaching experiment, the base of the soil core was covered with a nylon mesh with an effective pore diameter of $60\ \mu\text{m}$ to retain the soil in the column. The vegetation was cut as short as possible and the soil core was weighed.

The total volume of water held in the soil column was determined by the method described in section 8.3.2.1.

(ii) Step-function experiment

Initially the soil column was saturated with 2 pore volumes of 0.01 M CaCl_2 . Then 6.4 pore volumes of a known concentration of ^{14}C 2,4-D ($22 \mu\text{mol L}^{-1}$) along with $^3\text{H}_2\text{O}$ (67 Bq ml^{-1}) was applied as a step-change input into the soil at a constant flux (0.1 ml min^{-1}) using a peristaltic pump. The applied 2,4-D and $^3\text{H}_2\text{O}$ were subsequently displaced from the soil column with 0.01 M CaCl_2 to initiate desorption at the same flux. The number of pore volumes of 0.01 M CaCl_2 passed to desorb the sorbed solute was the same as that of the sorption step. The leachate was collected as an aliquot gradually increasing in volume from 25 ml to 30 ml as leaching progressed (i.e. the first 20 samples were 25 ml, the next samples were 30 ml). The experimental parameters are reported in Table 8.2. The activity of $^3\text{H}_2\text{O}$ and ^{14}C in the leachate was counted using the liquid scintillation counter for dual labelling.

At the end of the experiment, Nile blue dye (0.05%) was applied on the soil surface. Dyes have been frequently used to investigate the flow paths through the soil (Omoti and Wild, 1979). The basic assumption made in interpreting dye patterns is that the more solution that passes a given point, the more darkly stained are those regions. Thus, stained regions are interpreted as being regions of relatively fast flow and the unstained regions to be of relatively slow flow. The purpose of applying dye was to:

1. Determine whether there was any edge-flow between the cylinder wall and soil.
2. Detect any preferential flow through macropores.

Finally the soil core was weighed, oven-dried at 105°C for 4 days, and reweighed to calculate the pore volume during leaching.

8.3.3 Dual label counting

In column experiments a non-sorbed solute ($^3\text{H}_2\text{O}$) along with a sorbed pesticide solute labelled with ^{14}C were used to examine the movement of sorbed solutes. Since both the isotopes (^3H and ^{14}C) are low energy beta emitters, the overlapping of

energy spectra of those isotopes is possible (Appendix 1). Hence it is necessary to correct for interference between the two isotopes.

The channel settings for maximum separation of $^3\text{H}_2\text{O}$ and ^{14}C are shown in Appendix 1. The channel settings are:

Channel one (Ch 1) : 0 - 400

Channel two (Ch 2) : 400 - 670

The counts in channel one are largely due to ^3H (97.69%) with some spillover of ^{14}C (20%). The spillover was calculated from the activity of ^{14}C in channel two. The counts in channel two are due to ^{14}C (80%) with negligible spillover of ^3H (2.31%) into this channel.

$$\begin{array}{rclcl} 97.69\%^3\text{H} & + & 20\% ^{14}\text{C} & = & \text{Ch1 (CPM)} \\ 2.31\%^3\text{H} & + & 80\% ^{14}\text{C} & = & \text{Ch2 (CPM)} \\ 100\%^3\text{H} & + & 100\%^{14}\text{C} & = & \text{Ch1 (CPM) + Ch2 (CPM)} \end{array}$$

In order to account for the interference of one isotope with the other, the following simultaneous equations were derived and solved to ascertain the true counts of each isotope. The background counts were subtracted from the total counts before interference factors were calculated.

$$0.9769x + 0.2y = \text{Ch1(CPM)} \quad (8.1)$$

$$0.0231x + 0.8y = \text{Ch2(CPM)} \quad (8.2)$$

Where x and y indicates the true count rates of $^3\text{H}_2\text{O}$ and ^{14}C , respectively. Multiplying Equation 8.1 by 4 and subtracting it from Equation 8.2 gives,

$$3.8845x = 4 \text{ Ch1(CPM)} - \text{Ch2(CPM)} \quad (8.3)$$

The true count rate of $^3\text{H}_2\text{O}$ (x) is obtained by:

$$x = \frac{4 \text{ CH1(CPM)} - \text{CH2(CPM)}}{3.8845} \quad (8.4)$$

The true count rate of ^{14}C (y) is calculated by substituting the true count rate of $^3\text{H}_2\text{O}$ (x) in Equation 8.1:

$$y = \frac{\text{CH1(CPM)} - 0.9769x}{0.2} \quad (8.5)$$

Equations 8.4 and 8.5 provide the true count rates of $^3\text{H}_2\text{O}$ and ^{14}C , respectively.

8.3.4 Modelling the non-sorbing and sorbing solutes in soil column studies

8.3.4.1 *Theoretical considerations and numerical methods*

Sorbed solute movement in a packed soil column can be described by the CDE model (Lapidus and Amundson, 1952):

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (8.6)$$

where C is solution concentration ($\mu\text{mol L}^{-1}$), S is sorbed concentration ($\mu\text{mol kg}^{-1}$), t is time (hr), D is the dispersion coefficient ($\text{mm}^2 \text{ hr}^{-1}$), x is distance in the direction of flow (mm), v is average pore water velocity (mm hr^{-1}), ρ is soil bulk density (g cm^{-3}) and θ is volumetric water content ($\text{mm}^3 \text{ mm}^{-3}$).

However, various physical, chemical and biological processes affect the movement of pesticides in soils. Among the processes, sorption is the most important. Additional terms can be included in the CDE to account for the sorption of solutes. The following CDE model (Eq 8.7) with an equilibrium sorption process was tested for the BTCs of $^3\text{H}_2\text{O}$ and 2,4-D in the Tokomaru and the Patua soils.

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (8.7)$$

where R is retardation factor. It has been shown that a non-equilibrium sorption condition exists during the movement of pesticides in soils (Rao *et al.*, 1979; Brusseau and Rao, 1989a). Several mathematical models have been proposed for equilibrium and non-equilibrium sorption. The details of the various models have been described in Chapter 2, section 2.8.3 and 2.8.4. The occurrence, cause, and effect of non-equilibrium sorption during leaching was reviewed by Brusseau and Rao (1989a). The non-equilibrium sorption models are based on a bicontinuum conceptualization. Bicontinuum sorption models, often referred to as "two-site" models, have been used to represent chemical non-equilibrium. This model is conceptually similar to the "two region" model used to represent physical non-equilibrium. In the "two region" model the soil water is partitioned into mobile and immobile phases (Nkedi-Kizza *et al.*, 1984). In this study, a bicontinuum sorption model (two sites) was used to fit the experimental BTC for 2,4-D in the Tokomaru (Ah1) and the Patua (Ah) soils in repacked soil columns and for 2,4-D in the intact soil core experiment.

The bicontinuum sorption model encompasses either a chemical or physical process as the hypothesized mechanism causing sorption non-equilibrium. According to the bicontinuum model the sorption is assumed to occur onto two sets of sites. Sorption is in instantaneous equilibrium at one set of sites and at other set of sites sorption is in non-equilibrium, and is rate limited by sorption kinetics. The following equations (Eq 8.8- 8.10) describe the sorption of a solute on the two types of sites assumed in this model (Selim *et al.*, 1976; Cameron and Klute, 1977):

$$S_1 = FKC^N \quad (8.8)$$

$$S_2 = (1-F) KC^N \quad (8.9)$$

$$\frac{\partial S_2}{\partial t} = K_1 S_1 - K_2 S_2 \quad (8.10)$$

Where S_1 and S_2 are the sorbed phase concentration ($\mu\text{mol kg}^{-1}$) for the equilibrium and kinetic sites, respectively and K_1 and K_2 are the Freundlich sorption coefficient for the equilibrium and kinetic sites, respectively.

Substitution of Equations 8.8-8.10 in Equation 8.6 gives the following bicontinuum sorption model coupled to the CDE in the dimensionless form (Nkedi-Kizza *et al.*, 1989),

$$\frac{\partial C^*}{\partial p} + (\beta R - 1) N C^{*(N-1)} \frac{\partial C^*}{\partial p} + (1 - \beta) R \frac{\partial S^*}{\partial p} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (8.11)$$

$$(1 - \beta) R \frac{\partial S^*}{\partial p} = \omega (C^{*N} - S^*) \quad (8.12)$$

by defining the following nondimensionless parameters:

$$C^* = C/C_0 \quad (8.13a)$$

$$P = \nu L/D \quad (8.13b)$$

$$S^* = [S_2 / (1 - F) KC_0^{N-1}] \quad (8.13c)$$

$$R = [1 + (\rho/\theta) KC_0^{N-1}] \quad (8.13d)$$

Note that in using the empirical relationship, the linearized sorption coefficient, $K_d = KC_0^{N-1}$ (Nkedi-Kizza *et al.*, 1989) was used.

$$p = \nu t/L \quad (8.13e)$$

$$\beta = [1 + F (\frac{\rho}{\theta}) KC_0^{N-1} / R] \quad (8.13f)$$

$$\omega = Q_2(1-\beta)RL/v \quad (8.13g)$$

$$X = (x/L) \quad (8.13h)$$

Where P is the Peclet number, which represents the dispersive-flux contribution to transport, x is distance in the direction of flow (mm), L is column length (mm), β is the fraction of instantaneous retardation, ω is the Damkohler number, which is a ratio of hydrodynamic residence time to characteristic time for sorption and Q_2 is rate constant. These last two terms specify the degree of non-equilibrium existing in the system.

8.3.4.2 *Model parameter estimation*

A number of model parameter needs to be estimated to run the program. These parameters include: Peclet number (P), retardation factor (R), fraction of instantaneous retardation (β) and Damkohler number (ω). Model parameters were determined using the nonlinear least-squares optimization program (Van Genuchten, 1981).

The bicontinuum model employs Peclet number in place of the hydrodynamic dispersion coefficient in the equilibrium sorption CDE model. Peclet number incorporates any dispersion resulting from non-equilibrium sorption as well as that from hydrodynamic dispersion (Rao *et al.*, 1980; Brusseau and Rao, 1989a). Peclet number describes the shape of the BTC, i.e. (magnitude of dispersion) and retardation factor (R) describes its position (relative to the mean velocity of water) (Brusseau and Rao, 1989a).

The Peclet number was determined by fitting the nonlinear least-squares optimization program to the BTC of tritiated water, with the R set at unity. The value for R was calculated (Eq 2.27d) by using the measured sorption isotherm parameters (K and N) and bulk density (ρ) and volumetric soil-water content (θ) values from the soil

column experiments. With the values of P and R fixed, the non-equilibrium sorption parameters (ω and β) for the sorbing solutes were optimized to obtain the best fit to the experimental BTC. The solute transport equations (Eq 8.11 and 8.12) were solved under constant solute flux boundary conditions by the finite-difference method. Model parameter values are presented in Table 8.3.

8.4 RESULTS AND DISCUSSION

8.4.1 Repacked soil column experiment

8.4.1.1 *Step-function experiment*

Breakthrough curves (BTC) for the step-function experiments (repacked soil columns) are presented in Figure 8.1. Tritiated water ($^3\text{H}_2\text{O}$) has been widely used as a tracer to study the movement of non-sorbed solute in laboratory experiments (Rao and Davidson, 1979; Nkedi-Kizza *et al.*, 1989; Riise *et al.*, 1994), and serves as a reference for the sorbed solute. A shift of the BTC for the test solute (2,4-D) to the right of the $^3\text{H}_2\text{O}$ BTC indicates increased sorption and a decreased mobility. As would be expected from the batch-sorption data (Chapter 5), 2,4-D appeared later in the leachate from the Patua loam (Ah) column than from the Tokomaru silt loam (Ah1) column. A greater shift of the BTC of 2,4-D to the right indicates increased sorption, thus a decreased mobility in the Patua soil. The Patua soil contains high amounts of organic carbon and significant amounts of short-range order clays (allophane) whereas low levels of organic carbon and vermiculite dominate the Tokomaru soil (Chapter 5). It has been observed that soils containing high amounts of organic carbon and short-range order clays, such as allophane sorb more 2,4-D than soils containing low levels of organic carbon and crystalline clays (Chapter 5). The K_d values (Table 5.4) indicated that the sorption of 2,4-D was six times greater in the Patua soil than in the Tokomaru soil.

It has been reported that the position of the BTC for a sorbed solute is governed by the extent of sorption, whereas the shape of the BTC is defined by the kinetics of the sorption-desorption process (Brusseau and Rao, 1989a). The $^3\text{H}_2\text{O}$ BTCs were symmetrical and sigmoidal in shape, which suggests the absence of physical non-

Table 8.3 Model parameter values for the step-function experiment

Column set up	Soil	Solute	parameter						
			P	R	K	N	Q_2 (hr ⁻¹)	β	ω
Repacked column	Tokomaru	³ H ₂ O	23.9	1.00					
		2,4-D	23.9	4.52	3.42	0.79	0.016	0.600	0.30
	Patua	³ H ₂ O	16.0	1.00					
		2,4-D	16.0	20.81	17.42	0.84	0.0080	0.520	0.66
Intact core	Tokomaru	³ H ₂ O	10.2	1.00					
		2,4-D	10.2	4.52	3.42	0.79	0.007	0.40	0.50

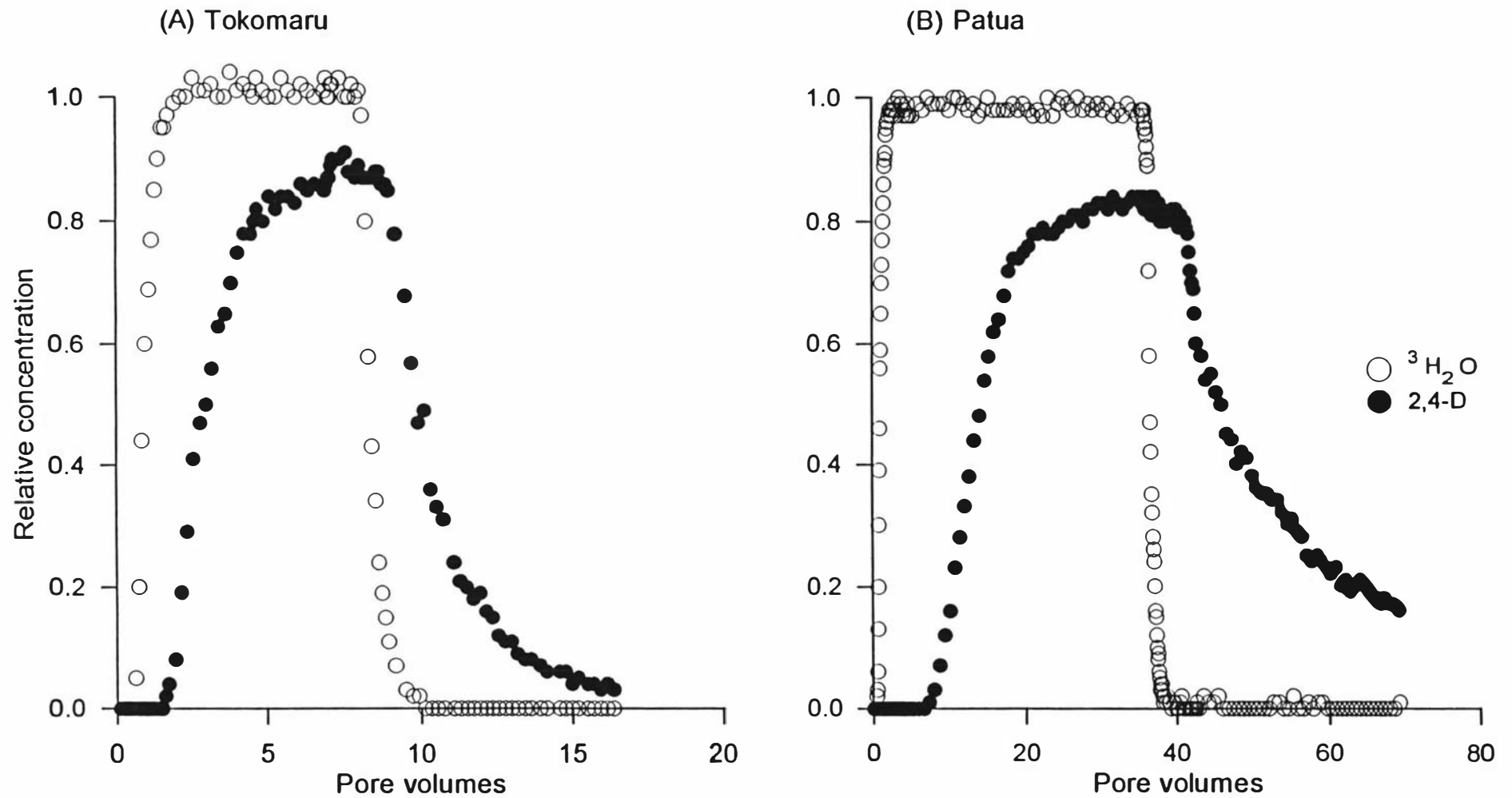


Fig 8.1 Breakthrough curve (BTC) for $^3\text{H}_2\text{O}$ and 2,4-D in the Tokomaru (A) and the Patua (B) soils
- Step-function experiment

equilibrium processes in the porous medium (Nkedi-Kizza *et al.*, 1987; Brusseau and Rao, 1989a). The experimental BTC for 2,4-D is asymmetrical in shape with extensive tailing when C_e/C_0 approached 1.0 or $C_e/C_0 = 0$.

Tailing is a common feature of BTC, and has been attributed to a wide range of physical and chemical processes (Van Genuchten *et al.*, 1974). The possible explanation for the observed tailing of BTC include: (i) non-equilibrium sorption during flow due to either kinetics-controlled or diffusion-controlled rate limiting processes (Rao and Davidson, 1979; Rao *et al.*, 1979); and (ii) non-singular sorption-desorption isotherms (i.e. an hysteresis effect) (Hornsby and Davidson, 1973a; Van Genuchten *et al.*, 1974). It has been shown that sorption non-singularity or hysteresis is greater for non-ionic than ionic (2,4-D) pesticides (Chapter 6). Since the sorption and desorption isotherm for 2,4-D is near linear and near singular (Chapter 5 and 6), the tailing of the 2,4-D BTC is assumed to be mainly due to non-equilibrium sorption.

8.4.1.2 Pulse experiment

The results of the pulse experiment (repacked soil columns) are shown in Figure 8.2. In this experiment effectively all the applied ^{14}C pesticides were recovered in either the leachate or the extractions from the segmented soil column (92-98%) (Table 8.4). In the Tokomaru soil, 28% of atrazine and 43% of 2,4-D were found in the leachate, whereas only small amounts of phorate and terbufos (< 6%) were leached through the soil. In the Patua soil, low amounts of atrazine (22%) and 2,4-D (12%) were found in the leachate, and phorate and terbufos were not detected at all in the leachate. Measurement of the residual pesticides in the soil indicated that most of the added phorate and terbufos remained in the soil column. The relative order of mobility in the Patua soil was atrazine > 2,4-D > phorate $\geq$ terbufos, whereas in the Tokomaru soil the order was 2,4-D > atrazine > phorate > terbufos. The increasing order of mobility follows the decreasing order of K_{ow} values (Table 3.1). In general the non-ionic pesticides (phorate and terbufos) were relatively less mobile than the ionic pesticides (atrazine and 2,4-D). The behaviour of ionic pesticides varied between the soils, which is attributed to the difference in the charge distribution between the soils (Section 6.4.7).

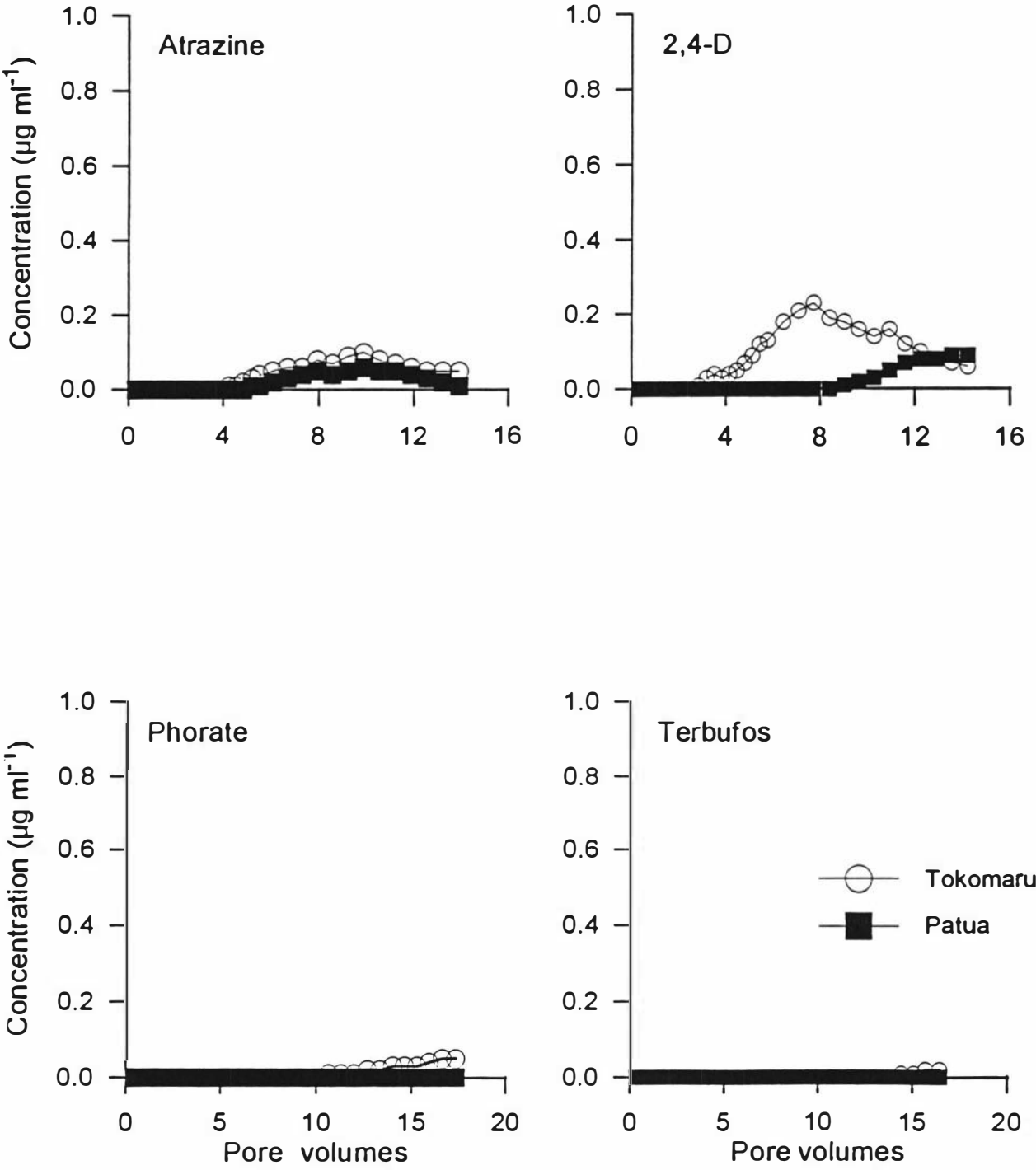


Fig 8.2 Leaching of ¹⁴C pesticides through the Tokomaru and the Patua soil columns - Pulse experiment

Table 8.4 Mass balance of ^{14}C pesticides in the column experiment and the distribution coefficient (K_d) values obtained in the batch experiment

Pesticides	Pulse experiment			Batch experiment
	¹⁴ C leachate	¹⁴ C recovery from soil	Total recovery	K _d (L kg ⁻¹)
	(%)			
Tokomaru				
atrazine	28 ± 4	65 ± 8	93 ± 4	3.46
2,4-D	43 ± 2	55 ± 10	98 ± 7	2.43
phorate	6 ± 1	90 ± 12	96 ± 10	17.42
terbufos	5 ± 2	87 ± 7	92 ± 6	18.40
Patua				
atrazine	22 ± 5	69 ± 6	91 ± 3	3.02
2,4-D	12 ± 3	82 ± 8	94 ± 11	9.60
phorate	ND ⁺	93 ± 2	93 ± 2	30.28
terbufos	ND	96 ± 4	96 ± 4	33.45

⁺ Not detectable

The distribution of ^{14}C pesticides in the soil column was examined and the results are shown in Figure 8.3, where the concentration of pesticides (mg kg^{-1} soil) is plotted against soil depth. The retention of pesticides was high at the soil surface and decreased with depth. This is consistent with the results reported for other pesticides (Logan *et al.*, 1992; Riise *et al.*, 1994; Stehouwer *et al.*, 1994). Most of the pesticide residues remaining in the soil column were retained in the top 2 cm depth and higher amounts of non-ionic (phorate and terbufos) than ionic (atrazine and 2,4-D) pesticide were retained in this section. These results suggested that the mobility of atrazine and 2,4-D was greater than that of phorate and terbufos. The retention of pesticides in the upper layer (2 cm) was greater in the Patua than the Tokomaru soil, which is consistent with the higher amounts of organic carbon in the Patua soil.

Results from the batch experiment confirmed that the sorption of phorate and terbufos was greater compared with that of 2,4-D and atrazine (Chapter 5). Sorption of pesticides was higher in the Patua than in the Tokomaru soil (Chapter 5, Table 5.4). The variation in K_d of pesticides between the soils can be explained by the difference in the organic carbon content of the soils, the K_d values increase with increasing levels of soil organic carbon. An attempt was made to relate the K_d values calculated from the batch experiment (Chapter 5, section 5.4.4) to the leaching of pesticides in the pulse experiment. An inverse relationship between K_d values and the percentage of ^{14}C pesticides recovered from the leachate (Fig 8.4) suggested that sorption was the key process controlling the movement of pesticides. Recently Riise *et al.*, (1994) reported an inverse relationship between the batch sorption coefficient and the percent atrazine and tribenuron methyl leached.

8.4.2 Intact soil core experiment

The BTC for the intact soil core experiments are presented in Figure 8.5. The results show that there was an early breakthrough for both the non-sorbed ($^3\text{H}_2\text{O}$) and the sorbed (2,4-D) solutes in the intact cores, when compared with the repacked columns. The leaching curves of $^3\text{H}_2\text{O}$ and 2,4-D are rather close in the initial stages of the experiment, indicating the rapid movement of both the sorbed and the non-sorbed solute in intact soil cores. Significant amounts of $^3\text{H}_2\text{O}$ were detected in the first sample of leachate. Unlike those reported for the repacked soil column experiments

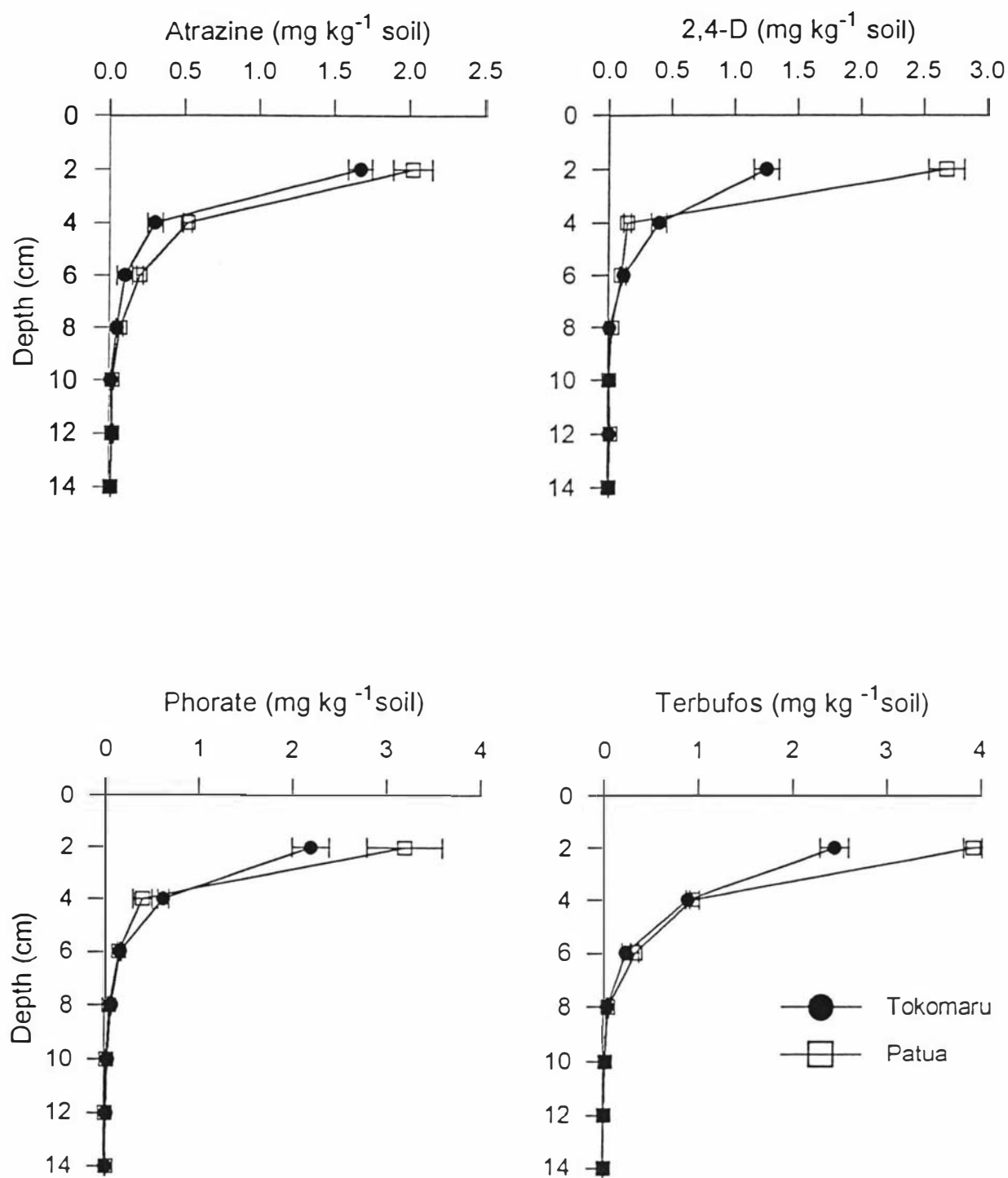


Fig 8.3 Distribution of pesticides in the Patua and the Tokomaru soil column. (Horizontal bars represent standard error of mean)

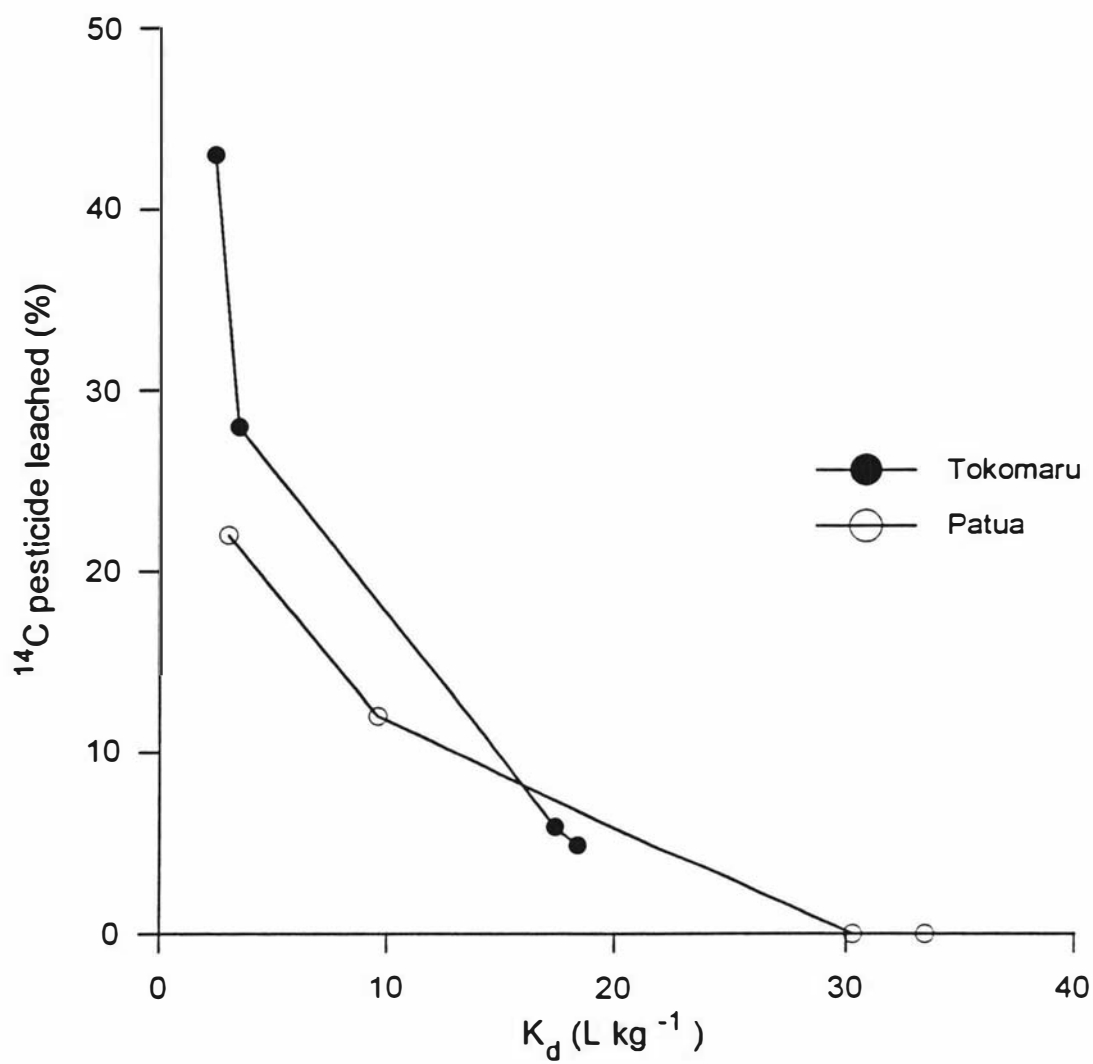


Fig 8.4 Relationship between the distribution coefficient (K_d) and the percent of pesticide leached

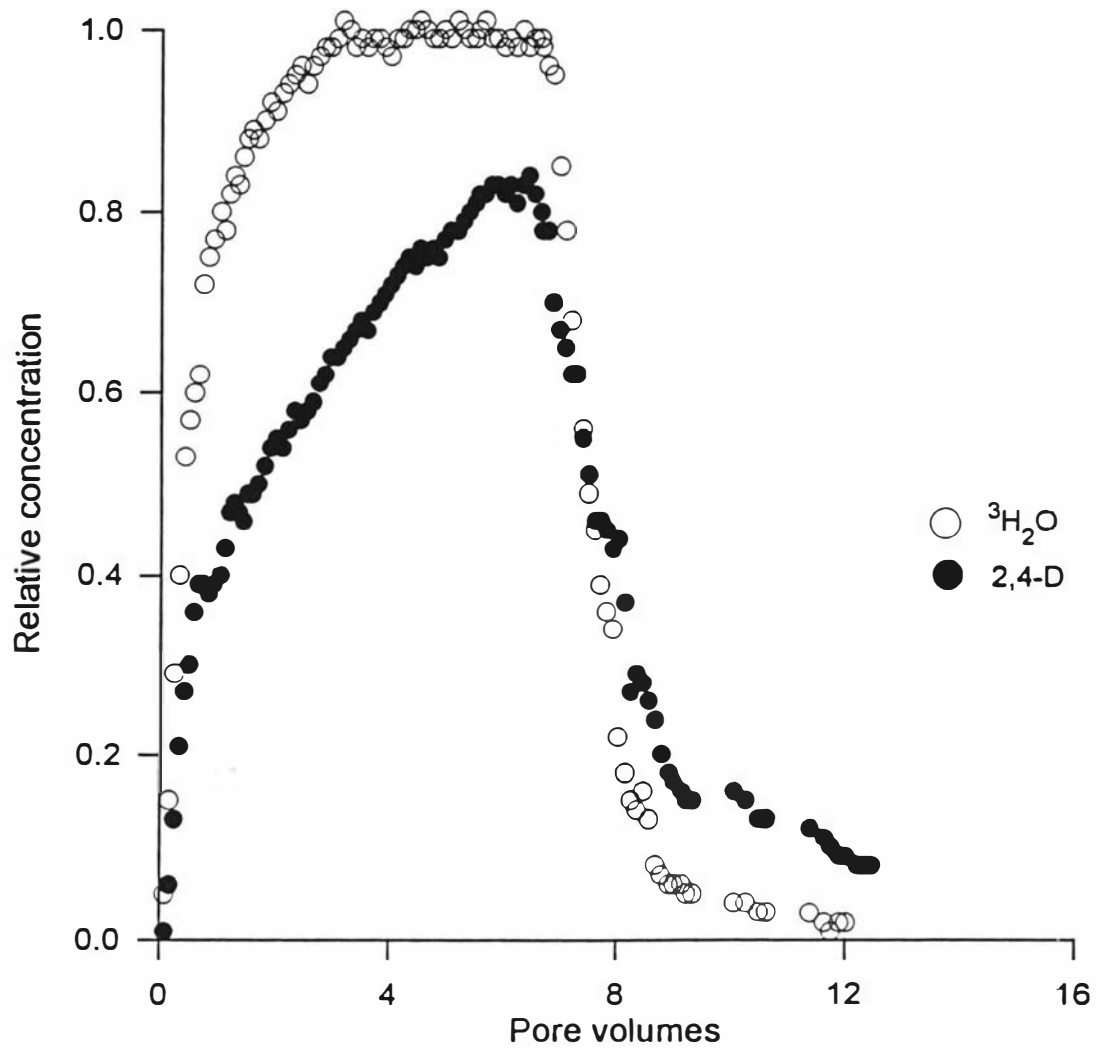


Fig 8.5 Breakthrough curve (BTC) for $^3\text{H}_2\text{O}$ and 2,4-D in the Tokomaru soil - Undisturbed soil core experiment

figure 8.1), the breakthrough curve for $^3\text{H}_2\text{O}$ was markedly asymmetric. Similarly the BTC for 2,4-D was asymmetric with a breakthrough at an early stage of the experiment, whereas extensive tailing was observed when C_e/C_0 approached 1 and again when C_e/C_0 approached 0. While the early breakthrough of 2,4-D in the intact core is attributed to preferential flow, the tailing of the BTC at the latter part of the experiment can be attributed to the physical and/or chemical non-equilibrium conditions existing in the soil column during flow.

3 Repacked versus intact soil core experiments

The BTC for $^3\text{H}_2\text{O}$ and 2,4-D in repacked and undisturbed soil cores were compared and are presented in Figure 8.6. In the undisturbed soil core a general shift in the BTC for $^3\text{H}_2\text{O}$ and 2,4-D to the left was observed, when compared to the repacked soil column. Higher leaching losses of $^3\text{H}_2\text{O}$ and 2,4-D were recorded, up to one pore volume, from the intact soil core compared with the repacked soil column, but lower losses were recorded over most of the remainder of the BTC.

In an ideal case of miscible displacement of a solute it has been shown that for a non-sorbed solute the relative concentration (C_e/C_0) of 0.5 would be obtained at one pore volume (Biggar and Nielsen, 1962). Experiments with undisturbed soils usually show earlier BTC, with a different shape to that observed in repacked soil column experiments (Bouma *et al.*, 1983; White *et al.*, 1984). The early breakthrough for both sorbed and non-sorbed solutes indicated preferential flow through worm holes and root channels, which allowed very little mixing between the input solution and the soil.

The results of the dye studies showed that the preferred pathways for water flow was through large pores, worm holes and root channels (Plate 8.2). Overall, the results are remarkable in showing that both sorbed and non-sorbed solutes can leach through the soil within one pore volume. Using intact soil cores it has been shown that even strongly sorbed chemicals are vulnerable to leaching, as observed for phosphate (Anchanasaut *et al.*, 1978), napropamide and bromacil (White *et al.*, 1986), napropamide (Jury *et al.*, 1986) and for alachlor, cyanazine and atrazine (Czapar *et al.*, 1992).

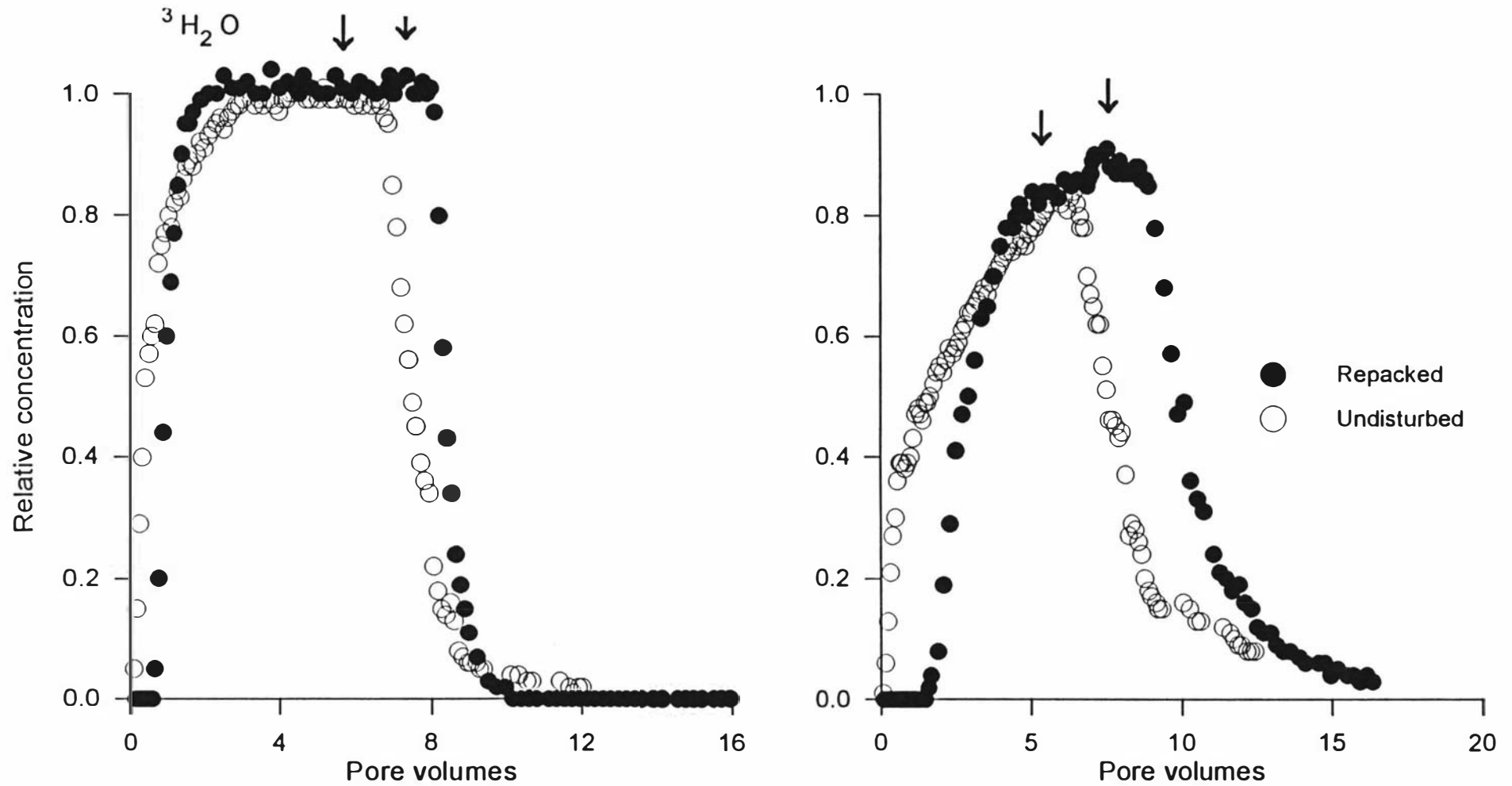


Fig 8.6 Breakthrough curve (BTC) for $^3\text{H}_2\text{O}$ and 2,4-D in repacked and undisturbed soil core experiments. (The arrows indicate a change in input from $^3\text{H}_2\text{O}$ and 2,4-D to CaCl_2).

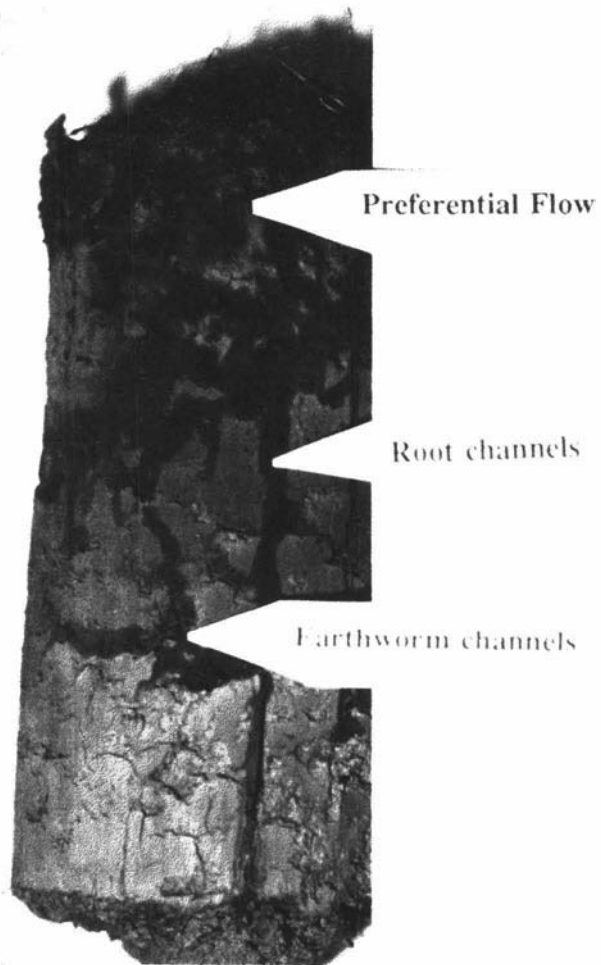


Plate 8.2 Preferential flow of dye through root channels and earthworm channels

8.4.4 Model simulation

An attempt was made to simulate the BTC for non-sorbed ($^3\text{H}_2\text{O}$) and sorbed (2,4-D) solutes in repacked (step function inputs) and intact soil columns using the equilibrium sorption and the non-equilibrium sorption (bicontinuum model) CDE model.

8.4.4.1 *Equilibrium CDE model*

(i) Repacked soil column

Comparison of the experimental BTC and that simulated assuming equilibrium sorption (Eq 8.6) for $^3\text{H}_2\text{O}$ and 2,4-D is shown in Figure 8.7A and B. In repacked soil columns, close agreement was obtained between simulated and experimental BTCs for the non-sorbed solute ($^3\text{H}_2\text{O}$), whereas large deviations were observed for the sorbed solute (2,4-D) (Fig 8.7A and B). The sorbed solute (2,4-D) appeared much earlier in the leachate than predicted by the model. In the present study a symmetrical BTC was observed for $^3\text{H}_2\text{O}$, whereas an asymmetrical BTC was observed for 2,4-D. According to Rao and Davidson (1979) if the sorption is linear and singular, symmetrical BTCs are obtained where sorption is in an instantaneous equilibrium condition. Asymmetrical BTCs are obtained where sorption is in a non-equilibrium condition. It has been reported that the simple CDE model with equilibrium sorption, predicts symmetrical BTCs, but it fails to predict asymmetrical BTCs (Davidson *et al.*, 1968). Many workers have observed deviations between the measured BTC and simulated BTC using the simple CDE model for sorbed solutes such as pesticides (e.g., Davidson *et al.*, 1968).

The failure of the CDE model with equilibrium sorption process (Eq 8.6) to describe the experimental BTCs for the sorbed solute (2,4-D) shows that non-equilibrium sorption occurs during the movement of pesticides in the present experiment. It has been reported that under steady-state flow conditions the equilibrium condition for sorption is unlikely to occur (reviewed by Brusseau and Rao, 1989a) and a rate limited process is responsible for tailing when C_e/C_0 approaches 1 or C_e/C_0 approaches 0.

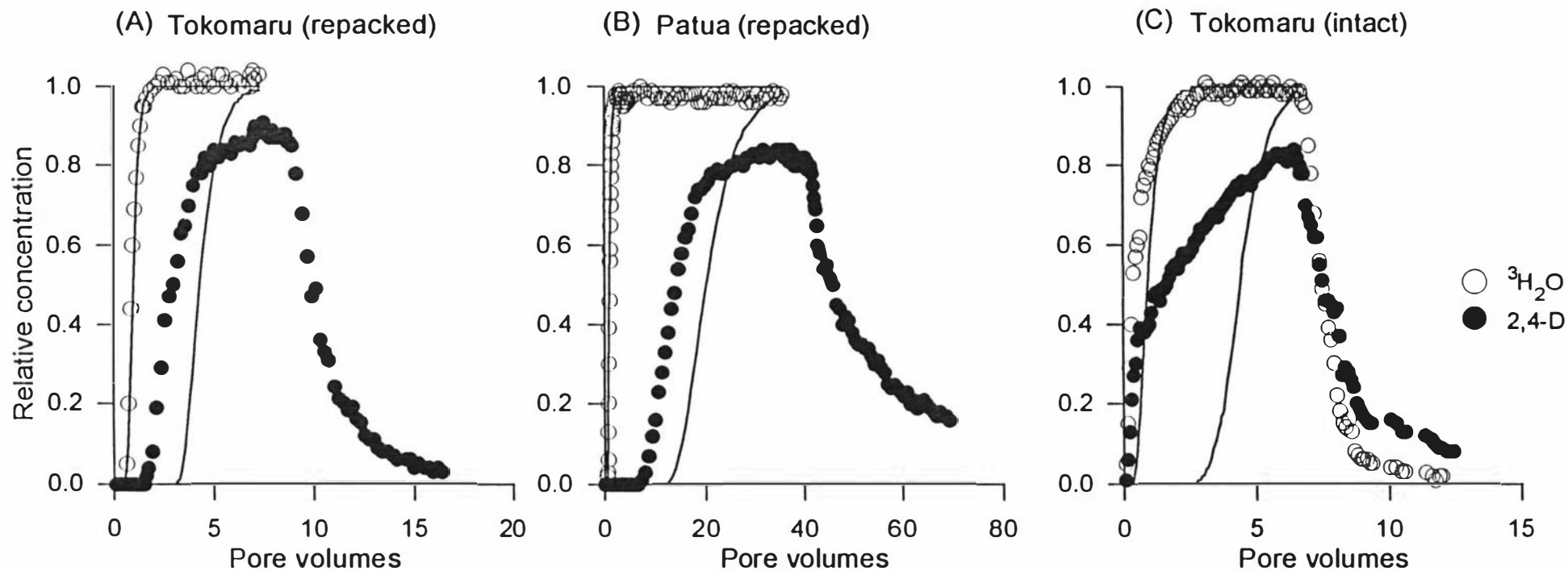


Fig 8.7 Measured (○ $^3\text{H}_2\text{O}$; ● 2,4-D) and simulated (line) breakthrough curve (BTC) using equilibrium CDE model for $^3\text{H}_2\text{O}$ and 2,4-D in soil columns of (A) repacked Tokomaru, (B) repacked Patua, and (C) intact Tokomaru soil column

(ii) Intact soil core experiment

In the intact core experiments, the equilibrium CDE model adequately described most parts of the $^3\text{H}_2\text{O}$ BTC but there was a slight deviation between the simulated and the measured BTC in the early stages of the experiment (Fig 8.7C). However most deviation was observed between the simulated and the measured BTC for the sorbed solute (2,4-D). The failure of the equilibrium sorption CDE model (Eq 8.6) for the non-sorbed solute ($^3\text{H}_2\text{O}$) at the early stages of the experiment precluded us from concluding that non-equilibrium condition do occur at an early stage. However the good description of the equilibrium model for the non-sorbed ($^3\text{H}_2\text{O}$) solute at the later stages of the experiment suggest that at the early stages solute moved preferentially through root channels and worm holes, but within a short time the solute moved uniformly in the core. However the failure of the equilibrium CDE model for the sorbed solute (2,4-D) may be due a combination of an early breakthrough through root channels and worm holes in the early stages of the experiment and sorption non-equilibrium when C_e/C_0 approached 1.

In view of the asymmetrical (skewed) and non-sigmoidal BTCs observed for the sorbed solute (2,4-D) in both the repacked (Fig 8.1) and the intact soil cores (Fig 8.5), the validity of the local equilibrium assumptions in the CDE model have been questioned. In this study an attempt was made to analyse the experimental BTC for 2,4-D in repacked soil columns and intact cores using the bicontinuum non-equilibrium sorption model and the results are discussed in the following section.

8.4.4.2 *Bicontinuum sorption model*

A bicontinuum non-equilibrium sorption model (Eq 8.11 and 8.12) was used to simulate the experimental BTC for 2,4-D in repacked and intact soil cores and the results are depicted in Figure 8.8. In the case of non-sorbed solute ($^3\text{H}_2\text{O}$) there was no difference between the BTC simulated using equilibrium CDE (Fig 8.7) and that simulated using the non-equilibrium CDE (Fig 8.8) both in the repacked and intact cores. Hence the bicontinuum model is discussed only for the sorbed solute (2,4-D).

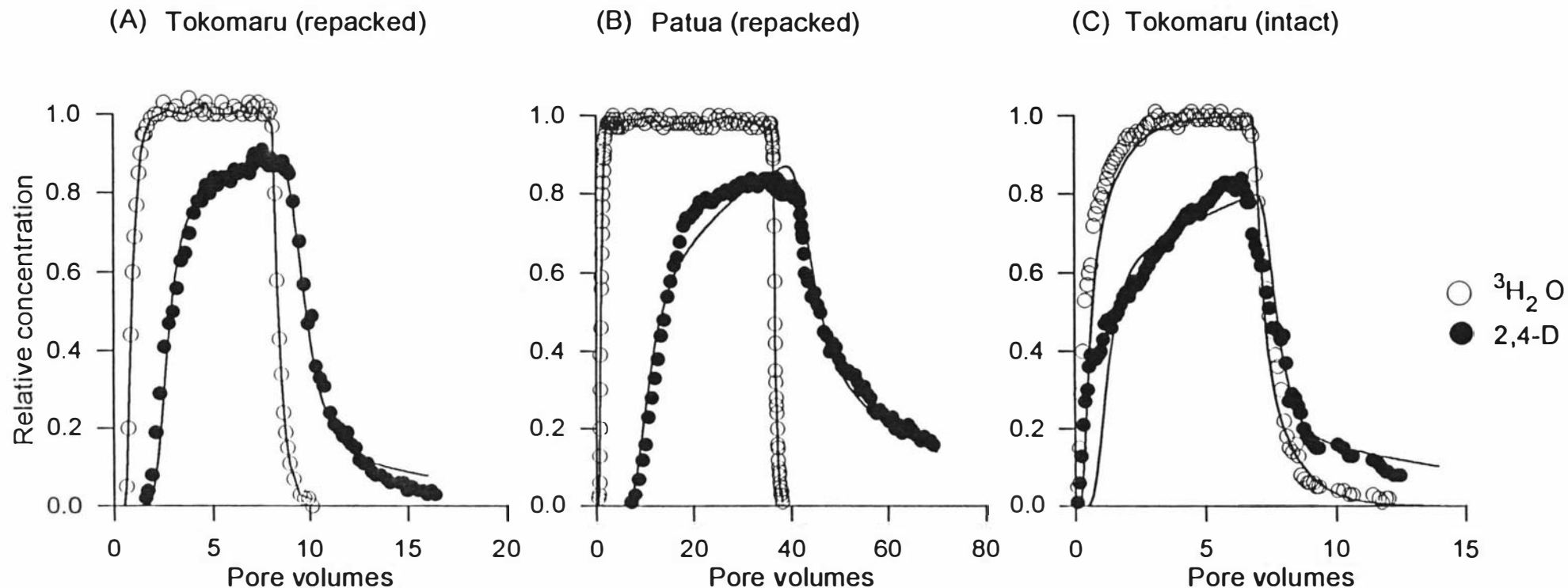


Fig 8.8 Measured ($\circ$ $^3\text{H}_2\text{O}$; $\bullet$ 2,4-D) and simulated (line) breakthrough curve (BTC) using non-equilibrium bicontinuum model for $^3\text{H}_2\text{O}$ and 2,4-D in soil columns of (A) repacked Tokomaru, (B) repacked Patua, and (C) intact Tokomaru soil column

(i) Repacked soil column

Comparison of the simulated and the experimental BTC for 2,4-D in the Tokomaru and the Patua soils reveals that the bicontinuum model provided a good description of the data (Fig 8.8A and B). The simulations were made using a nonlinear sorption isotherm, with N values of 0.79 in the Tokomaru and 0.84 in the Patua soils (Fig 8.8). The N values were obtained from batch sorption isotherm (Chapter 5). To investigate the impact of nonlinearity on prediction, simulation of 2,4-D BTC for the Tokomaru and the Patua soils was obtained by assuming $N=1$. The results of these simulations were compared with previous simulations using the N values from the isotherm (Figure 8.9). It is apparent that there is little difference whether the N value was taken as 0.79/0.84 (N values from the isotherm) or 1 (the value for a linear isotherm). This relative insignificance of nonlinearity in comparison to non-equilibrium sorption in relation to movement of pesticides has been observed by others (Van Genuchten *et al.*, 1977; Hutzler *et al.*, 1986; Nkedi-kizza *et al.*, 1989).

(ii) Intact soil core experiment

The bicontinuum model described the experimental BTCs for 2,4-D in the intact core better (Fig 8.8C) than did the equilibrium sorption model (Fig 8.7C); there was still a slight deviation between the simulated and the observed BTC for 2,4-D in the early stages of the experiment. The value of dispersion obtained from the optimization program for the intact soil core ($101.5 \text{ mm}^2 \text{ hr}^{-1}$) was higher than that obtained for the repacked soil column ($80.5 \text{ mm}^2 \text{ hr}^{-1}$). The higher value of dispersion obtained for intact soil cores indicates the influence of soil structure (i.e. there is wide range of pore sizes contributing to flow), hence faster rates of leaching of solute are expected to occur in intact cores. McLay *et al.* (1992) reported a higher dispersivity value for undisturbed soil cores than repacked soils for sulphate leaching. This provides further evidence for the relatively faster movement of both sorbed and non-sorbed solute through root channels and worm holes particularly at the early stages of the experiment. However the non-equilibrium behaviour of the sorbed solute in the latter stages may represent contributions from chemical (sorption) non-equilibrium.

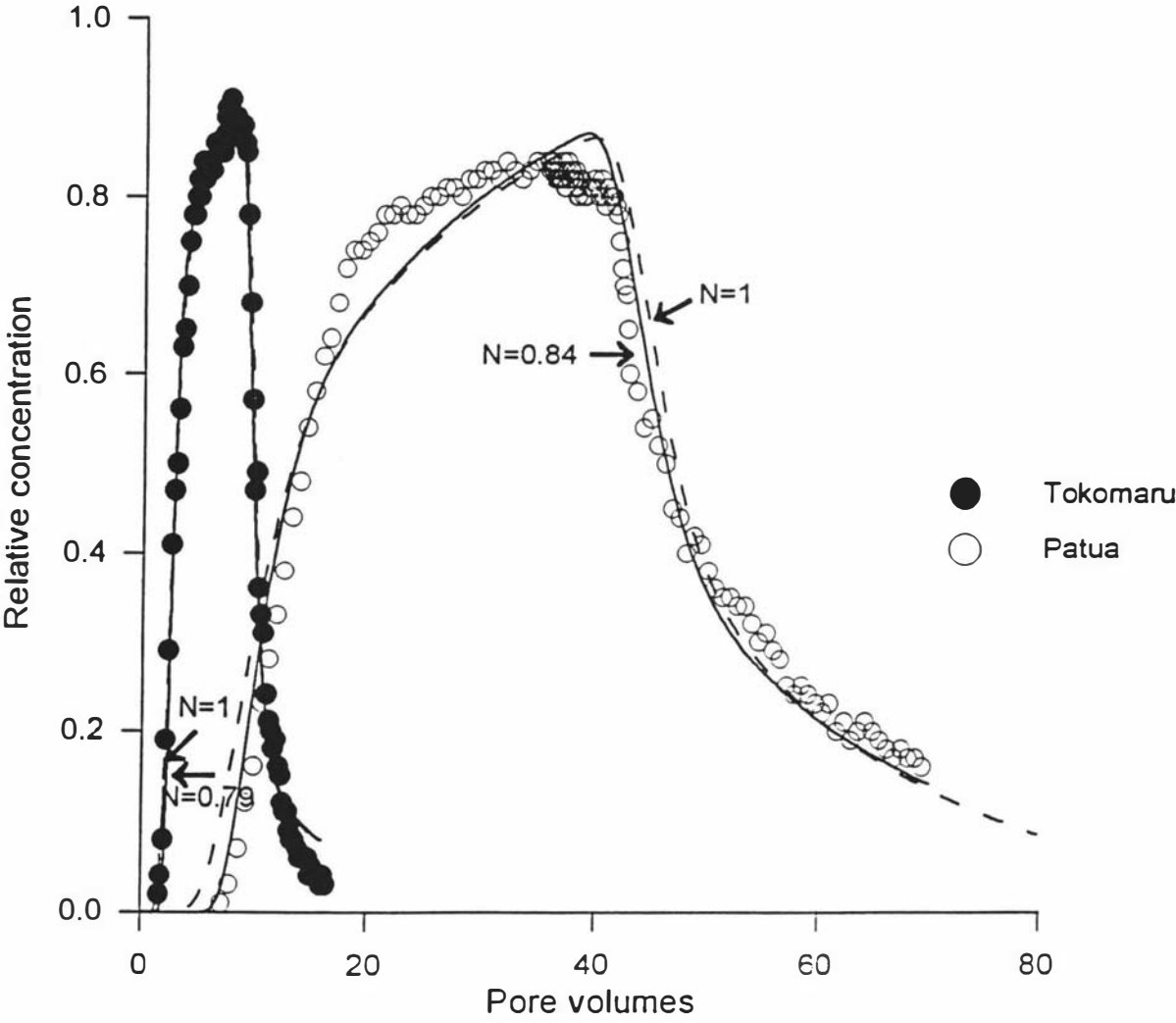


Fig 8.9 Measured and simulated (line) breakthrough curve (BTC) for 2,4-D in the Tokomaru and the Patua soil. Comparison of a linear (---) and nonlinear (—) isotherm are shown.

8.4.5 Significance of model parameters

The values of the four dimensionless parameters, P , R , β and ω obtained either independently or by fitting the bicontinuum model to the experimental BTC of 2,4-D and $^3\text{H}_2\text{O}$ are presented in Table 8.3.

(i) Peclet number (P)

Peclet number (P) represents the contribution of hydrodynamic dispersion to solute transport. The P value determined from the BTC of a non-sorbed solute ($^3\text{H}_2\text{O}$) was used to simulate the BTC of the sorbed solute (2,4-D). The estimated P value was 23.9 in the Tokomaru and 16 in the Patua soil for the repacked soil columns, whereas it was 10.2 in the intact soil core experiment. As P increases, the BTC approaches a symmetrical and sigmoidal shape. For P values less than 10, the BTC is often found to be noticeably asymmetrical (Brusseau and Rao, 1989a).

(ii) Retardation factor (R)

The retardation factor represents the effect of sorption on transport. The R values used when modelling the column experiments were calculated using the K and N values determined from the batch sorption experiment. The calculated R values for 2,4-D were 4.52 and 20.81 in the Tokomaru and the Patua soils, respectively. The higher the R value, the greater the retardation of solute by the soil and the lesser the mobility.

(iii) β and ω

The other two unknown parameters (β and ω) are the most difficult to determine independently. A nonlinear least-squares optimization program (Van Genuchten, 1981) was used to determine the values for these two parameters. The term β represents the fraction of the sorption sites with instantaneous sorption, whereas ω (Damkohler number) represents the ratio of hydrodynamic residence time to characteristic time for sorption (i.e. mass transfer coefficient) (Nkedi-Kizza *et al.*, 1989; Brusseau and Rao, 1991).

The β values determined for 2,4-D were 0.6 and 0.52, and the ω values were 0.30 and 0.66 in the Tokomaru and Patua soils respectively in the repacked soil column experiment. In the intact core experiment the β and ω values obtained for 2,4-D were 0.4 and 0.50, respectively.

The β values indicated that instantaneous sorption occurs in 60% and 52% of the sorption sites, respectively in the Tokomaru and the Patua soils in the repacked soil column experiment. The β values obtained in this experiment are in general less than that obtained for other pesticides (Brusseau and Rao, 1991; Veeh *et al.*, 1994) and for inorganic solutes (Kookana *et al.*, 1994). The value of β depends not only on the solute and sorbent characteristics, but also on the column length, input concentration and flow conditions (Jardine *et al.*, 1985; Seyfried and Rao, 1987). The fraction of sites in instantaneous equilibrium (β value) in the Tokomaru soil was higher in the repacked soil columns (60%) than in the intact cores (40%). Seyfried and Rao (1987) observed a lower β value in intact soil cores which they attributed to higher sorption sites in kinetic (immobile) than equilibrium (mobile) regions, because of the smaller pores in the kinetic (immobile) region.

It has been reported that as non-equilibrium increases (i.e. as ω decreases), the BTC shifts toward the left and both early breakthrough and tailing increase (Brusseau and Rao, 1989a). When the ω values are greater than 1 sorption is near equilibrium, whereas non-equilibrium prevails when ω value is lesser than 1 (Brusseau *et al.*, 1989). The ω values obtained in this experiment were < 1 which indicates the importance of non-equilibrium processes for 2,4-D movement in the Tokomaru and the Patua soils. Similarly ω values < 1 have been reported for many organic pesticides, such as atrazine, simazine and alachlor (Brusseau and Rao, 1991), chlorsulfuron (Veeh *et al.*, 1994) and inorganic solutes, such as cadmium (Kookana *et al.*, 1994).

(iv) Rate constant (Q_2)

The β and ω values obtained from the optimization program were used to calculate the rate constant (Q_2) using the following equation:

$$\omega = Q_2 (1-\beta) RL / v \quad (8.14)$$

The calculated Q_2 values of 2,4-D are: 0.016 hr^{-1} for the Tokomaru soil and 0.0080 hr^{-1} for the Patua soil in repacked soil columns. It is to be noted that the higher the Q_2 value the lower the rate of sorption. The Q_2 value calculated for 2,4-D in an intact soil core (0.007 hr^{-1}) was lower than that calculated for the repacked soil column experiment (0.016 hr^{-1}). It has been observed that Q_2 values for polar compounds are less than those for nonpolar compounds (Brusseau and Rao, 1989b). The Q_2 value for 2,4-D (a polar compound) observed in this experiment was also considerably less than that for non-polar organic chemicals reported in the literature (Brusseau and Rao, 1989b). The rate constant (Q_2) for 2,4-D was much larger for the Tokomaru soil with low organic carbon (3.2%) than the Patua soil with high organic carbon (8.7%). This inverse relationship between Q_2 and organic carbon content has been observed by other researchers (Nkedi-Kizza *et al.*, 1989; Brusseau and Rao, 1989a; Brusseau and Rao, 1989b). The inverse relationship between the Q_2 and organic carbon suggest that organic matter is likely to be a principal component for the non-equilibrium sorption of organic pesticides in soil. It has been suggested that sorption non-equilibrium is the result of rate limited mass transfer of sorbate from the exterior surface of the organic matter into interior matrix (i.e., intraorganic matter diffusion) (Brusseau and Rao, 1989b; Nkedi-Kizza *et al.*, 1989; Brusseau *et al.*, 1991).

8.5 CONCLUSIONS

The important conclusions drawn from these experiments are:

1. Pesticides are less mobile in soils with high sorption (K_d value) than in soils with low sorption.
2. Non-ionic pesticides were relatively less mobile than ionic pesticides.

3. In repacked soil columns symmetrical BTCs are obtained for the non-sorbed solute ($^3\text{H}_2\text{O}$), but asymmetrical BTCs are obtained for the sorbed solute (2,4-D).
4. Asymmetry and early BTCs for both non-sorbed and sorbed solutes in undisturbed soil cores revealed the importance of the preferential flow of solutes through worm holes and root channels.
5. The CDE model with an equilibrium sorption process adequately described the BTCs for non-sorbed solute ($^3\text{H}_2\text{O}$) in repacked and intact core experiments. However a slight deviation was observed between the measured and the simulated BTC at the early stages of the experiments with intact cores. The CDE model failed to simulate the BTCs for the sorbed solute (2,4-D) in repacked and intact core experiments.
6. The CDE model with a bicontinuum non-equilibrium sorption process simulated the BTCs for 2,4-D in repacked and intact soil core experiment.
7. The inverse relationship between the rate constant (Q_2) and the organic carbon content of the soil suggests that mass transfer of solute from the exterior surface of the organic matter into interior matrix (i.e., intra-organic matter diffusion) is likely to be the reason for non-equilibrium sorption during the movement of pesticides in soils.

CHAPTER 9

SUMMARY AND CONCLUSION

The work presented in this thesis may be summarised as follows:

9.1 Review of literature

Pesticides are the major means of weed and pest control in modern agriculture. Approximately 4000 tonnes of active ingredients are applied annually in New Zealand to overcome the loss due to pests and weeds. Continued application of pesticides is reported to contaminate surface water and groundwater. The extent of groundwater pollution by pesticides has been investigated in several countries. However in New Zealand, information on pesticide contamination of groundwater is scarce although detectable concentrations of pesticides have been found recently in the waters of six wells.

The present extensive use of pesticides has resulted in a great deal of interest in their fate and behaviour in soil. The fate of pesticides in soil is governed by several processes. These include:

- (i) Sorption-desorption
- (ii) Chemical and biological degradation
- (iii) Leaching
- (iv) Surface runoff
- (v) Volatilization
- (vi) Plant uptake

Among these various processes, sorption is the key process affecting directly or indirectly all the other processes of pesticide transformation in soils (Fig 9.1). Although a number of studies have been conducted to examine the phytotoxicity of pesticides in New Zealand soils, only little progress has been made in quantifying the transformation of pesticides in soils.

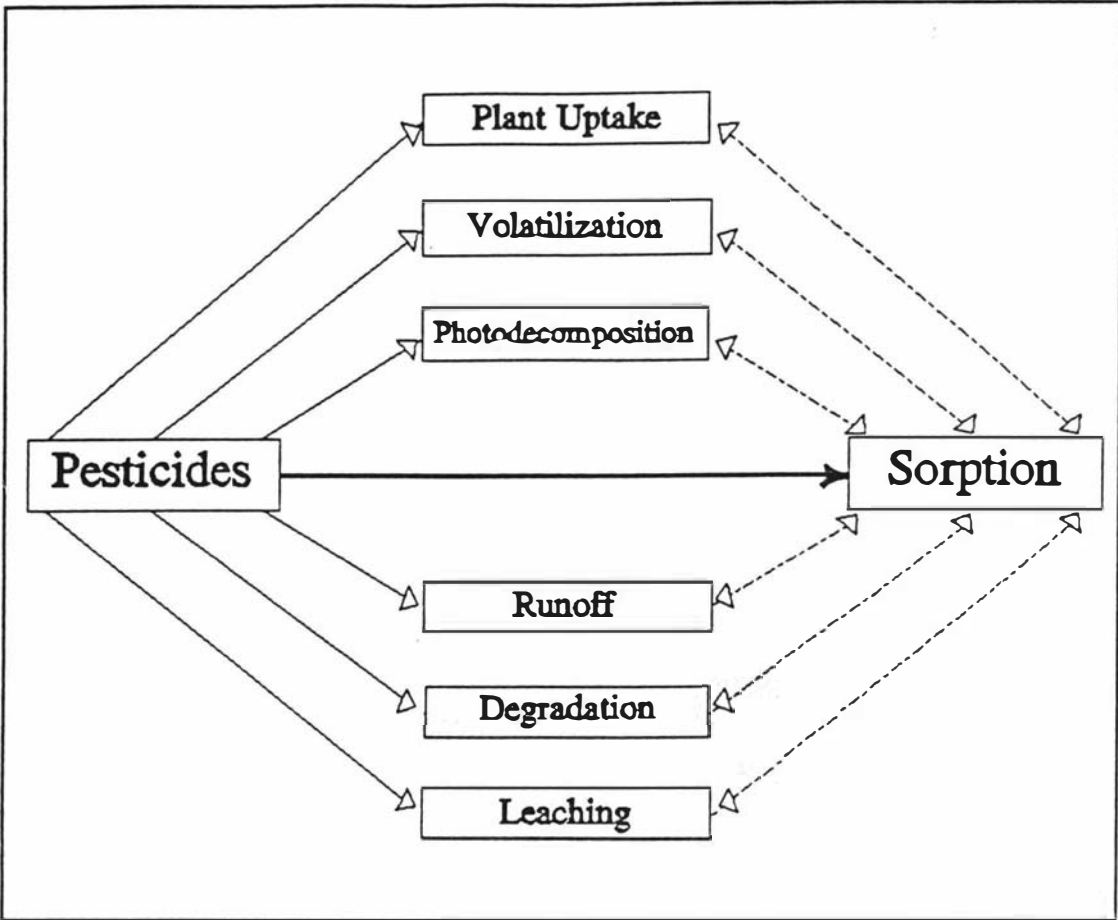


Fig 9.1 Effect of sorption on the fate of pesticides in soils

Sorption as the key process affecting the fate of pesticides in soils. Sorption of pesticides to soil particles has the following implications:

1. decreases the leaching losses
2. inhibits the degradation
3. enhances the loss through surface runoff
4. reduces the uptake by plants
5. reduces the volatilization losses
6. reduces the photodecomposition

Sorption of pesticides by soils is determined by both soil and pesticide properties. Though several studies have been conducted overseas to examine the sorption of pesticides in surface soils, it appears that only a few studies have reported on sorption by subsoil horizons. Sorption of pesticides by subsoil horizons is important, particularly in relation to the leaching of pesticide residues to groundwater. Therefore, in this study sorption of a range of pesticides, which included both insecticides and herbicides, was examined in different soil horizons.

Though the sorption of pesticides by various soil groups has been examined in detail, only a little attention has been given to the contribution of different soil particle size fractions to pesticide sorption. While the sorption of pesticides onto soil particles decreases the leaching of pesticide residues to groundwater, the erosion of pesticide-enriched finer soil particles by runoff leads to surface water contamination. Therefore the contribution of soil particle size fractions to the sorption-desorption of pesticides was examined, and also the potential loss of pesticides from eroded sediment was estimated.

The movement of pesticide to groundwater is largely controlled by the extent of sorption onto soil particles. The higher the sorption, the lower the mobility of pesticides in soil. Dissolved organic carbon (DOC) in the aqueous phase can act as a carrier of pesticides to deeper layers and thereby enhances the movement of pesticide residues to groundwater. Therefore, in this study the effect of carbon addition on the sorption and movement of pesticides was examined.

In most studies involving modelling the movement of pesticides in soils, the sorption of pesticides is considered to be instantaneous. However, recent studies have shown that non-equilibrium sorption occurs during the movement of pesticides in soils. The effect of sorption on the movement of pesticides was examined in the laboratory using both disturbed and undisturbed soil column experiments. The overall objective of this study was to examine the sorption and leaching of pesticides in allophanic and non-allophanic soils of New Zealand.

9.2 Measurement of pesticides in sorption studies

Different methods were evaluated in order to identify a suitable method for measuring pesticides in the soil solution during sorption studies. The methods included: ultra violet (UV) spectrophotometry, gas liquid chromatography (GLC), high performance liquid chromatography (HPLC), and a radio tracer technique. UV spectrophotometry has been used successfully in the measurement of pesticide concentrations during sorption in pure clay materials; whereas in soils the presence of water soluble organic matter has been found to interfere with the measurement of pesticides in soil solution. Use of GLC and HPLC were found to be successful in measuring low concentrations of pesticides in soil solution. However, these methods are laborious and sometimes require pre-extraction with organic solvents. Radioactive labelled pesticides can be used to measure the concentration of unlabelled pesticides in soil solution. A method for direct measurement of the residual ^{14}C pesticides in soil has been developed. This involved the extraction of soil with a scintillation cocktail containing an organic solvent, such as toluene.

In batch studies, pesticide sorption is often measured using centrifuge tubes. It is important that the tubes used for sorption measurements sorb negligible amounts of pesticides. A range of centrifuge tubes were examined for their ability to sorb pesticides. Sorption of pesticides in glass tubes fitted with teflon caps was found to be negligible and these tubes were used subsequently for the sorption measurements.

9.3 The effect of drying of soils on pesticide sorption

Drying, freezing and refrigeration are some of the pretreatments used to facilitate the analysis of soils in the laboratory. These treatments can be expected to affect the reactions of many solutes in soils. Since the main aim of this thesis was to examine the sorption and movement of pesticides in soils, any pretreatment of soils may have resulted in large errors. Therefore, a laboratory experiment was conducted to examine the effect of drying of soils on the sorption of an inorganic solute (phosphate) and two organic pesticides (2,4-D and phorate). Two soils (Tokomaru silt loam and Patua silt loam) with contrasting mineralogy and varying organic carbon contents were used in this experiment.

Compared to field-moist and freeze-dried soil, both air-drying and oven-drying of soil increased the sorption of phosphate, whereas they decreased the sorption of pesticides. The sorption kinetics indicated that there was no effect of drying on the rate of sorption of either phosphate or pesticides. In column experiments there was less leaching of phosphate and pesticides from the Patua soil than from the Tokomaru soil. In both soils, there was no effect of drying on the leaching of phosphate, whereas air-drying and oven-drying increased the leaching of pesticides.

Compared to field-moist and freeze-dried soils, both air-drying and oven-drying increased the water soluble organic carbon in soil. Solubilization of organic matter during air-drying and oven-drying increased the accessibility of P to sorption sites on mineral surfaces and thereby increased the sorption. At the same time the water soluble organic matter bound the pesticides and thereby decreased the apparent sorption onto soil surfaces and increased leaching. Based on these results the sorption and movement of pesticides was examined using either field-moist or freeze-dried soils.

9.4 Equilibrium sorption of pesticides in soils

Using a standard batch method, sorption of three ionic (metsulfuron methyl, atrazine and 2,4-D) and two non-ionic (phorate and terbufos) pesticides was examined in a range of allophanic and non-allophanic soils from various depths collected in the North Island, New Zealand. The effect of soil properties on the sorption of pesticides was investigated using both the correlation technique and the subtractive technique. In the latter technique the sorption of pesticides by soils was examined before and after the removal of a specific component (e.g., organic carbon). Prediction of pesticide sorption from the octanol water partition coefficient (K_{ow}) was examined.

The distribution coefficient (K_d) was used as an index of pesticide sorption in soils. Allophanic soils sorbed higher amounts of pesticides than did non-allophanic soils, which is attributed to the higher amounts of organic matter and the presence of amorphous allophane clay in the former soils. Pesticide sorption followed the order: terbufos > phorate > 2,4-D > atrazine > metsulfuron methyl. Sorption was greater

in surface soils than subsoils. For example, the average K_d values of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos for the surface soils were 0.8, 5.71, 6.09, 32.22 and 36.45 L kg⁻¹, respectively, which decreased to 0.42, 1.56, 4.33, 11.71 and 13.63 L kg⁻¹, respectively for the subsoils.

Among the soil properties, organic carbon content was best correlated with the K_d of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos ($r=0.85^{***}$, 0.90^{***} , 0.84^{***} , 0.94^{***} and 0.96^{***} , respectively). Multiple regression models were developed to predict the pesticide sorption from soil properties. The multiple regression equation developed using all the soil properties (pH, organic carbon, CEC, clay, Fe and Al) explained 83%, 88%, 89%, 94% and 96% of the variation in the sorption of metsulfuron methyl, atrazine, 2,4-D, phorate and terbufos, respectively. Organic carbon and oxalate extractable Al were the most important variables in the models, and together they described more than 80% of the variability in sorption.

When pesticide sorption was normalised to the organic carbon content of soils (K_{oc}) the values varied much less than did the K_d values. The variation in K_{oc} is much less for non-ionic pesticides than for ionic pesticides.

Sorption of 2,4-D, atrazine and metsulfuron methyl increased with decreasing pH, whereas sorption of phorate and terbufos was unaffected.

As expected, removal of organic carbon greatly reduced the sorption of all pesticides. However, the decrease in sorption due to the removal of organic carbon was greater for non-ionic than for ionic pesticides. Most of the empirical equations, based on K_{ow} values, developed for other soils in overseas countries gave unsatisfactory predictions of pesticide sorption in the soils examined. A separate empirical equation was developed to predict the sorption of pesticides in the soils examined, based on the K_{ow} values of the pesticides.

9.5 Organo-mineral contribution to pesticide sorption-desorption

A standard batch technique was used to examine the contribution of organo-mineral fractions of soils to the sorption-desorption of ionic and non-ionic pesticides. An

attempt was made to predict pesticide sorption by whole soils using the sorption values obtained for the organo-mineral fractions.

The relative proportions of soil organic carbon associated with the clay ($< 2 \mu\text{m}$), silt ($2\text{-}63 \mu\text{m}$) and sand ($> 63 \mu\text{m}$) fractions of the soils averaged 37.3, 45.5 and 16.3%, respectively. Organic carbon content and Fe, Al and Si extracted by an acid-oxalate reagent decreased with increasing particle size. Sorption of pesticides followed the order: clay $>$ silt $>$ sand. The correlation between organic carbon content of the fractions and the K_d values was higher for the non-ionic ($r^2=0.98$) than for ionic ($r^2=0.84$) pesticides. Removal of organic carbon decreased the sorption of pesticides by the particle size fractions and the effect was greater for non-ionic than ionic pesticides. The K_{oc} values of non-ionic pesticides in the natural and the fractions from which organic carbon had been removed were essentially the same but the K_{oc} values of the ionic pesticides increased with the removal of organic carbon. The sorption of non-ionic pesticides was mainly dependent upon the organic carbon content of the size fractions, whereas the clay minerals also contributed to the higher K_d values of ionic pesticides in the clay fractions.

The relative contribution of particle size fractions to the K_d value of the whole soil depends on the K_d value and the mass of the individual size fractions. In general the relative contribution increased with decreasing particle size and the effect was more pronounced for the ionic pesticides. The measured K_d of pesticides for the whole soil closely agree with the K_d values estimated from the particle size fractions.

Pesticide desorption was in the order: sand $>$ silt $>$ clay. Following four successive extractions with 0.01 M CaCl_2 , 65-90% and 22-75% of the initially-sorbed ionic and non-ionic pesticides, respectively, were released from the particle size fractions. Sorption from the oxidised fractions was generally more reversible than from the natural soil fractions.

The eroded sediment contains clay-sized material, which is enriched with organic carbon. The loss of pesticide through runoff can be estimated from the concentration of pesticide in sediments, the sediment yield and the enrichment ratio. Subsequent release of these pesticide residues from the eroded sediment is likely to contaminate

surface water and groundwater.

9.6 Effect of carbon addition on pesticide sorption and movement in soils

The importance of exogenous organic carbon and dissolved organic carbon (DOC) additions to the sorption of pesticide was examined using a standard batch technique. The exogenous carbon sources included: peat, poultry manure, pig manure, mushroom compost and sewage sludge. The effect of DOC on pesticide sorption was examined by either preincubating DOC with the pesticide or preincubating DOC with the soil prior to sorption measurements.

Additions of carbon from different sources to soils increased the K_d of all pesticides and followed the order: terbufos > phorate > 2,4-D > atrazine. However the increase in K_d values with carbon additions decreased with an increase in the amount of native carbon (endogenous) in the soil materials. The DOC in the aqueous phase increased irrespective of the source of carbon added. The increase in DOC concentration with carbon addition was in the order: poultry > mushroom > pig > peat > sludge. The addition of the different carbon sources also caused changes in the pH and the difference in the effect of the carbon sources on K_d values could be explained by the changes in DOC and the pH.

Premixing DOC with the pesticide formed stable complexes with DOC and thereby decreased the sorption of pesticides in soil. However, pesticide sorption increased when DOC was premixed with soil, which is attributed to the sorption of DOC onto the soil materials. Column studies showed the enhanced movement of pesticides in the presence of DOC. Retention of DOC by the soil could retard the movement of pesticides in the soil column, whereas an increase in DOC in the aqueous phase could enhance the movement of pesticides. Infra red spectra showed evidence of the interaction between pesticides and DOC by various mechanisms, which include H-bonding and charge transfer mechanisms.

The effect of pH on pesticide sorption was examined using soil samples amended with HCl, $\text{Ca}(\text{OH})_2$ or NaOH. Sorption of 2,4-D and atrazine decreased with increasing pH, whereas phorate and terbufos sorption was unaffected by the change

in pH. However, the decrease in sorption of pesticides was greater when the soil pH was increased with NaOH. A substantial increase in DOC was observed when the soil was incubated with NaOH. The difference in sorption between NaOH and $\text{Ca}(\text{OH})_2$ amended soil samples was attributed to the increase in DOC in the aqueous phase when the soil was incubated with NaOH.

9.7 Effect of sorption on movement of pesticides in soils

Miscible displacement experiments were conducted to examine the effect of sorption on the movement of pesticides in repacked and intact soil cores using step-function and pulse experiments. Breakthrough curves (BTCs) from the miscible displacement of pesticides were measured in two soils. These BTC data were used to model the leaching of pesticides using a convection-dispersion equation (CDE) with equilibrium or non-equilibrium sorption processes.

In step-function experiments using repacked soil columns, 2,4-D appeared later in the leachate from the soil with a high K_d value (Patua soil) than in the soil with a low K_d value (Tokomaru soil). The BTC for the non-sorbed solute ($^3\text{H}_2\text{O}$) showed a symmetrical and sigmoidal shape, which suggested the absence of physical non-equilibrium processes. However, the BTC for the sorbed solute (2,4-D) shows asymmetrical and extensive tailing when C_e/C_0 approached 1 or C_e/C_0 approached 0 indicating non-equilibrium. As this tailing behaviour was not observed for $^3\text{H}_2\text{O}$ it suggested that the non-equilibrium was related more to chemical than to physical processes in the repacked columns. In intact soil cores an early BTC for both the non-sorbed ($^3\text{H}_2\text{O}$) and the sorbed (2,4-D) solute was observed. The BTC's for $^3\text{H}_2\text{O}$ and 2,4-D were asymmetrical in shape. However, there was an extensive tailing observed for 2,4-D when C_e/C_0 approached 1 or C_e/C_0 approached 0. These results suggest that both the highly sorbed (2,4-D) and non-sorbed ($^3\text{H}_2\text{O}$) solute flows preferentially through macropores such as worm holes and root channels.

In pulse experiments, significant amounts of ionic pesticides (atrazine and 2,4-D) appeared in the leachate from the Tokomaru and the Patua soil. Only very low amounts of non-ionic pesticides (phorate and terbufos) were detected in the leachate from the Tokomaru soil and neither of these pesticides was detected in the leachate

from the Patua soil. The amount of pesticide leached decreased with an increase in the K_d values of the pesticides.

The CDE with equilibrium sorption simulated the BTC for $^3\text{H}_2\text{O}$ in repacked soil columns, whereas the same model failed to simulate the BTC for 2,4-D in the repacked and intact soil cores. However, good agreement was obtained between the measured BTC for 2,4-D both in repacked and in intact core and the simulated BTC using the bicontinuum non-equilibrium sorption model. The rate of sorption decreased with an increase in the organic matter content of the soil, which suggests that mass transfer of sorbate from the exterior surface of the organic matter into interior matrix (intraorganic matter diffusion) is likely to be responsible for non-equilibrium sorption.

9.8 Suggestions for future research

Organic pesticides in general have low solubility in water and hence pesticide solutions are prepared using organic solvents such as methanol. The effect of a cosolvent on the sorption and movement of pesticides in soils needs to be examined in detail. This will have some practical implications, because organic solvents occur in soil solutions at waste disposal sites, at land treatment sites and in cases of accidental spills.

Clay size fractions are enriched with organic carbon and are effective in the retention of pesticides. The practical implications of this observation needs to be evaluated by examining the sorption of pesticides in eroded sediments and earthworm casts, which are also enriched with clay fractions and organic carbon. While the solid phase organic carbon enhances the sorption of pesticides in soils, the aqueous phase DOC enhances the movement of pesticides. Further research is needed to examine the mechanisms involved in the interaction of different pesticides with DOC from different sources.

Non-equilibrium sorption during the movement of pesticides in soils is attributed mainly to the intra organic matter diffusion of pesticides. Experimental methods that allow direct assessment of this mechanism need to be developed. An extension of

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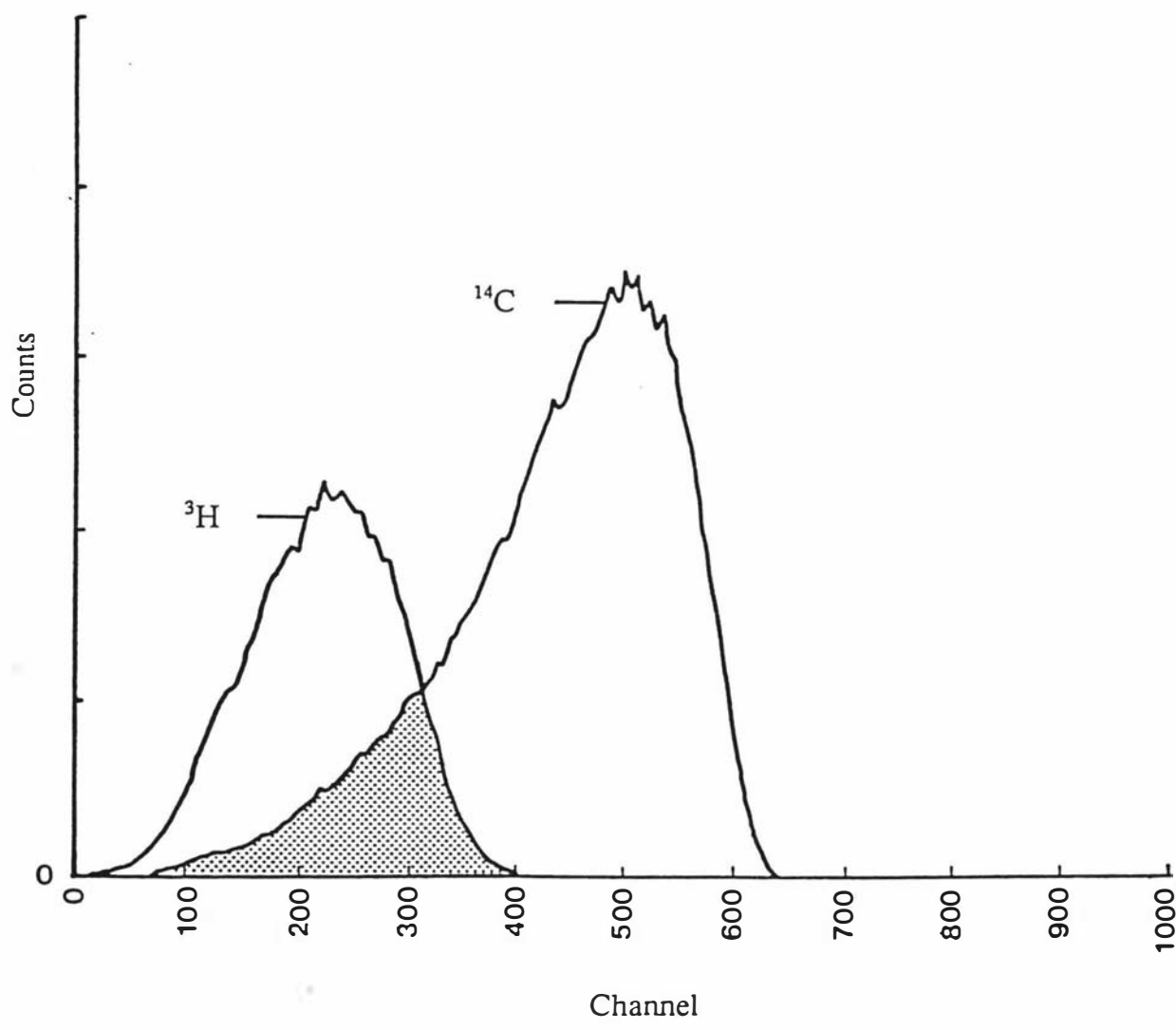
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Non-equilibrium sorption during the movement of pesticides in soils is attributed mainly to the intra organic matter diffusion of pesticides. Experimental methods that allow direct assessment of this mechanism need to be developed. An extension of

this work to test the validity of the non-equilibrium sorption model under field conditions is required. The undisturbed soil core showed the preferential flow of pesticides through macropores. Further research is needed to examine the preferential flow of pesticides through macropores such as worm holes and root channels under field conditions.



Appendix 1 Channel settings for dual label counting

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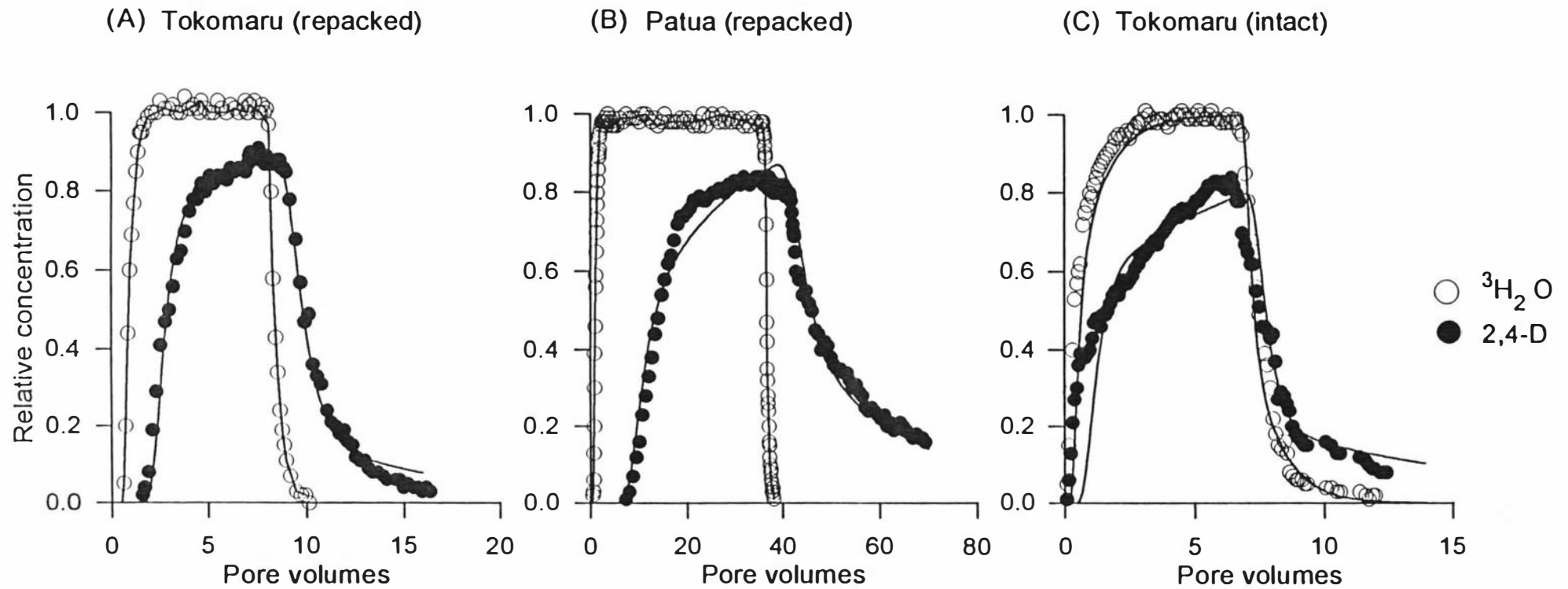


Fig 8.8 Measured ($\circ$ $^3\text{H}_2\text{O}$; $\bullet$ 2,4-D) and simulated (line) breakthrough curve (BTC) using non-equilibrium bicontinuum model for $^3\text{H}_2\text{O}$ and 2,4-D in soil columns of (A) repacked Tokomaru, (B) repacked Patua, and (C) intact Tokomaru soil column

(i) Repacked soil column

Comparison of the simulated and the experimental BTC for 2,4-D in the Tokomaru and the Patua soils reveals that the bicontinuum model provided a good description of the data (Fig 8.8A and B). The simulations were made using a nonlinear sorption isotherm, with N values of 0.79 in the Tokomaru and 0.84 in the Patua soils (Fig 8.8). The N values were obtained from batch sorption isotherm (Chapter 5). To investigate the impact of nonlinearity on prediction, simulation of 2,4-D BTC for the Tokomaru and the Patua soils was obtained by assuming $N=1$. The results of these simulations were compared with previous simulations using the N values from the isotherm (Figure 8.9). It is apparent that there is little difference whether the N value was taken as 0.79/0.84 (N values from the isotherm) or 1 (the value for a linear isotherm). This relative insignificance of nonlinearity in comparison to non-equilibrium sorption in relation to movement of pesticides has been observed by others (Van Genuchten *et al.*, 1977; Hutzler *et al.*, 1986; Nkedi-kizza *et al.*, 1989).

(ii) Intact soil core experiment

The bicontinuum model described the experimental BTCs for 2,4-D in the intact core better (Fig 8.8C) than did the equilibrium sorption model (Fig 8.7C); there was still a slight deviation between the simulated and the observed BTC for 2,4-D in the early stages of the experiment. The value of dispersion obtained from the optimization program for the intact soil core ($101.5 \text{ mm}^2 \text{ hr}^{-1}$) was higher than that obtained for the repacked soil column ($80.5 \text{ mm}^2 \text{ hr}^{-1}$). The higher value of dispersion obtained for intact soil cores indicates the influence of soil structure (i.e. there is wide range of pore sizes contributing to flow), hence faster rates of leaching of solute are expected to occur in intact cores. McLay *et al.* (1992) reported a higher dispersivity value for undisturbed soil cores than repacked soils for sulphate leaching. This provides further evidence for the relatively faster movement of both sorbed and non-sorbed solute through root channels and worm holes particularly at the early stages of the experiment. However the non-equilibrium behaviour of the sorbed solute in the latter stages may represent contributions from chemical (sorption) non-equilibrium.