Sorption and Release of Pesticides in Soils: The Role of Chemical Nature of Soil Organic Matter

Riaz Ahmad
B.Sc. (Hons) Agric., M.Sc. (Hons) Soil Science
The University of Agriculture, Faisalabad (Pakistan)

Thesis Submitted in the Department of Soil and Water, Faculty of Agriculture and Natural Resource Sciences, The University of Adelaide, Adelaide, South Australia, for the Degree of Doctor of Philosophy

October, 1999

Table of Contents

Abstract

Pesticides have become an indispensable component of modern agriculture. Their use has increased greatly during the last two decades and their occurrence in soil and underground water has become an important environmental concern. As the retention and release behaviour of pesticides remains poorly understood, particularly in the soils of Australia and Pakistan, the pesticide registration authorities in both countries rely considerably on overseas data, particularly from Europe and North America. However, the imported data may not always be applicable due to distinctive variations in the soils and climatic conditions. Hence the aims of this study were: (1) to examine the sorption behaviour of selected nonionic pesticides (carbaryl, phosalone, bifenthrin, dichlorvos and monocrotophos) and ionic pesticides (ametryn and imazethapyr) in a range of soils; (2) to characterise the nature of soil organic matter (SOM) in a diverse group of soils and relate the structural and molecular variations of organic matter to sorption of nonionic pesticides; and (3) to study the release behaviour of carbaryl and ethion from two historically contaminated soils and to elucidate the mechanism(s) of their aging/sequestration.

Firstly, methods of analysis for 13 commonly used pesticides (ametryn, imazethapyr, carbaryl, phosalone, bifenthrin, dichlorvos, monocrotophos, ethion, atrazine, trifluralin, dicrotophos, thiodicarb and methomyl) were developed using a reversed phase high performance liquid chromatograph with a UV/Visible detector using a C18 column. The contaminated soils were then screened for the pesticides reported to be contained therein, and retention and release studies were performed following the methods developed.

The sorption studies of the ionic and nonionic pesticides involved 48 soils collected from Australia, Pakistan and the UK. The studies were performed using the standard batch equilibration technique. Of the ionic pesticides, ametryn was found to be sorbed more strongly than imazethapyr in all soils studied. Sorption of ametryn was correlated significantly with both soil pH and organic carbon, whereas imazethapyr sorption was correlated significantly with pH. No correlation was found between the sorption coefficient (K_d) values of the pesticides and the clay contents of the soils.

Generally, sorption of nonionic pesticides increased with an increase in the octanol-water partition coefficient (K_{ow}) of the pesticide. The sorption coefficients per unit organic C (K_{oc}) of bifenthrin, phosalone and carbaryl varied by an order of magnitude among the soils and increased in the order listed. The sorption of carbaryl and phosalone in soils of the three countries were generally in the order of Pakistan>Australia>UK, with a wide variation in their K_{oc} values. The relationship between K_d and different particle size fractions of SOM showed that there was a slightly better correlation of K_d with 53 µm-2 mm than with <2 mm fraction of the particulate soil organic C, but a wide scatter in the data was evident. This indicated that not only the quantity but also the quality of the organic matter might be important in determining the sorption of nonionic pesticides.

The structural and chemical composition of the SOM in 27 soils was probed using the solid-state CP/MAS ^{13}C NMR technique. The SOM was characterised using C types derived from the NMR spectra and molecular components were inferred from NMR spectra using a simple molecular mixing model, known as Model Components and Simultaneous Equations (MCSE). The relationships were determined between K_{oc} of carbaryl and phosalone and the nature of the SOM in the soils. Substantial variations were revealed in the structural and chemical composition of organic matter in the soils studied. The existence of variations was supported by micromorphological examination, under a scanning electron microscope, of two soils contrasting in their sorption affinities. Among the structural components of SOM, the aromatic component was best correlated with the K_{oc} values of carbaryl and phosalone. Among the molecular components, lignin and charcoal were the best correlated. The study highlighted the importance of the chemical nature of SOM in determining sorption of nonionic pesticides and suggested that the nature of SOM from different environments is likely to be dissimilar. Consequently, variations in the sorption affinities are expected to be substantial.

The batch method was found to be unsuitable for determining the sorption of dichlorvos and monocrotophos due to degradation losses during the procedure. Therefore, an unsaturated flow method was adapted for these pesticides. Pesticide-free solution was fed at a constant flow rate through a sectionable horizontal infiltration column filled with pesticide-spiked soil at a known water content and bulk density. The approach was based on displacement of antecedent solution by invading water, and the amount of pesticide sorbed by the soil and the equilibrium solution concentration prior to the water imbibition were obtained from the plot of the pesticide content against the water content in the region beyond the plane of separation. The K_d values of dichlorvos and monocrotophos for a sandy loam soil obtained from the batch experiments were 17-fold and two-fold greater than the respective values obtained with the unsaturated flow method. The study has shown that the unsaturated flow technique is a better means of measuring the sorption of relatively fast degrading and more water soluble pesticides. As the sorption using this technique is calculated from the concentrations of pesticides extracted from both solid and solution phases, the data are free from errors resulting from degradation losses during the experiment.

Pesticides retained in soil may show progressively declining bioavailability with time. Therefore, release kinetics and bioavailability studies were carried out and the mechanisms of sequestration/aging were explored in historically contaminated soils collected from an old storage site in Pakistan containing carbaryl (having no further contamination since 1984) and soil from a cattle tick dipsite in Australia containing ethion (where its use was halted in 1973). The release of carbaryl followed a biphasic pattern. About 49% of carbaryl resisted desorption with water. Pulverisation of the soil for 8 min enhanced the release of the pesticide by up to 19% compared with unpulverised soil. This indicated that a fraction of carbaryl was entrapped in inaccessible micropore sites which were exposed by crushing the soil particles. However, 33%, possibly closely associated with the SOM, still remained resistant to release. A considerable fraction (~14%) of ethion was also unavailable for release into the binary solution (methanol:water, 60:40). Pulverisation had no significant effect on the release of ethion, which showed that the non-released fraction was tightly complexed in the soil matrix.

To assess the true bioavailability of aged carbaryl, degradation studies were carried out with a bacterial culture capable of utilising carbaryl as a sole carbon source. The addition of bacterial culture did not significantly improve the degradation of carbaryl beyond the water extractable fraction. However, there was complete degradation of the water-extracted carbaryl in the solution during the incubation period, with or without added nutrients. This showed that only the readily extractable fraction of carbaryl was accessible to the carbaryl degrading bacteria. The studies on microbial degradation of pulverised soils showed that an additional 12% of the total carbaryl was exposed to bacterial degradation after pulverisation. The rest (36% of the total) remained unavailable for microbial degradation. Entrapment of carbaryl within the soil micropores and partitioning deeply in the SOM matrix seem likely mechanisms of its sequestration.

Five nonionic surfactants (Triton X-100, Brij35, Ethylan GE08, Ethylan CD127 and Ethylan CPG660) at various concentrations, below and above their critical micelle concentrations (CMC), were used to mobilise carbaryl and ethion from the contaminated soils. Ethylan surfactants released more of the pesticides than Triton X-100 and Brij35. However, there was still a significant portion of carbaryl (>11%) and ethion (>17%) left in the soil. Some enhancement in the release of ethion below the CMC of the surfactants was evident, but there was no such impact of surfactants on the release of carbaryl below their CMC. The surfactants did not further increase the release of carbaryl and ethion at concentrations above 10 g L^{-1}. Use of surfactants to enhance release of carbaryl and ethion from contaminated soils appears to be a viable remediation technique.

Studies on alkaline hydrolysis of ethion and carbaryl using aqueous solutions with or without Ethylan CPG660 (pH 11) showed that incorporation of the surfactant at a concentration above the CMC inhibited the alkaline hydrolysis of both pesticides. Hence alkaline hydrolysis may not be an appropriate technique for decontamination following surfactant-enhanced release of highly hydrophobic compounds like ethion from the contaminated soils.

The key findings from the study are as follows:

- Soils from the three countries varied substantially in their sorption capacities for the pesticides due to their distinctive characteristics.
- The variations in sorption of nonionic pesticides were found to be related to differences in the structural and chemical composition of the SOM. There was a good correlation of K_{oc} of carbaryl and phosalone with aromaticity of SOM. Among the molecular components of SOM as predicted from MCSE, lignin and charcoal were the important contributors to the sorption capacities of the soils.

- Predictions based on data collected in one country or region may not be reliable when extrapolated to other regions. The study emphasised the need for local data.
- An unsaturated flow method was adapted and is proposed for determination of the sorption of readily degradable and water soluble pesticides.
- Inoculation with specific carbaryl degraders showed that an unreleasable fraction was not bioavailable to the organisms.
- Sequestration of carbaryl and ethion was found to be responsible for long term persistence of the compounds in soils.
- Surfactants showed a potential to mobilise the pesticides from long-contaminated soils. However, the surfactants could inhibit alkaline hydrolysis of some pesticides.

Statement

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

(Riaz Ahmad)

Acknowledgments

I am eternally indebted to my supervisors Dr Rai S Kookana (CSIRO, Land and Water) and Dr Angus M Alston (Department of Soil and Water) for their constant guidance, unqualified support, infinite patience, and encouragement during the period of this study. Rai's advice with many aspects of the project and his encouragement were invaluable. A Ph.D. supervisor must be much more than a capable scientist and I thank Rai for his generous help both as a supervisor and as a friend. Angus's advice and assistance were of immense value also, and his influence on the project was very significant. Angus has also retired during the significant portion of my candidature, yet has continued his input with warmth and conviction. Thank you Angus for your generous help and meticulous criticism.

Technical assistance of Mr Andrew Kerekes in HPLC use during the early days of my project, Mr Colin Rivers for his all round help, Mr John Terlet for demonstrating the use of scanning electron microscope, and Mr Maurice Amato for determination of C & N in soils is greatly acknowledged.

A special mention also for Dr Lukas Zwieten and Mr Matthew Ayres of Wollongbar Agricultural Institute, NSW, for their assistance in survey and collection of ethion-contaminated soil samples from old cattle tick dip sites.

Endless gratitude is due to Prof. Steve McGrath, Dr Richard Bromilow and Peter Nicholls of IACR, Rothamsted, UK for their esoteric attention, advice and encouraging attitude during the part of work at Rothamsted. Thanks to Miss Julia Knights for her help in locating and sampling the classical soils of Rothamsted and Ms Sarah Dunham for her help in Laboratory.

I am indebted to Mr Jan Skjemstad for his valuable suggestions on the characterisation of soil organic matter and for providing some NMR characterised classical soil samples. I sincerely thank Dr Ron Smernik for NMR characterisation of soils, valuable discussion, and critical comments on Chapter 6 of my thesis. Special thanks to Dr Paul Nelson for giving me the impetus to delve into interpretation of NMR data using his model. His generous help in modelling the NMR data and comments on work presented in Chapter 6 are invaluable. I would like to extend my thanks to Dr Bronwyn Harch (CSIRO Biometrics) for statistical analysis of the NMR data which allowed full interpretation of the NMR data.

My sincere thanks to Dr Megharaj Mallavarapu for providing carbaryl-degrading bacterial culture and for his technical advice in microbial degradation studies on carbaryl-contaminated soil.

Thanks also to all staff and students in Department of Soil and Water who made my life as a post-grad a rewarding experience. Special thanks to Sari for her calm encouragement during the write-up. To the night workers on the 4th floor, many thanks for.......well, thanks anyway, you know what I mean! It's nice to know I was never alone. Also thank you Sara for your help during final preparation of the dissertation.

Thanks Irene for your kind and generous love. We will never forget the moments we spent in your company. How was that wall painting? - the memory I will cherish! Let's hope, human body parts will be available in supermarket (a dream!). Also thanks Bimla jee for your love and support during our stay in Adelaide.

Thank you *Shabana* and *Shangraf* for your continuous support, understanding, encouragement and patience with late nights and lost week ends.

Finally and most sincerely, a huge and special tribute to my parents. Without their love, support and encouragement, I would have never gone this far.

Financial support provided by the World Bank through the Project ARP-II to the Government of the Punjab, Pakistan is greatly acknowledged.

List of Figures

Figure Page

List of Figures (Continued)

Figure Page

List of Figures (Continued)

List of Tables

List of Plates

Publications/conference papers arising from the Thesis

1. Ahmad, R., R. S. Kookana, and A. M. Alston. 1998. Sorption of carbaryl in twenty-one soils from Pakistan and Australia. ASSI National Soils Conference, Environmental benefits of soil management, Brisbane, Australia, 27-29 April, 1998.

2. Ahmad, R., R. S. Kookana, and A. M. Alston. 1998. The nature of organic matter affects sorption of carbaryl. The 9th International Congress on Pesticide Chemistry, London, UK, 2-7 August, 1998.

3. Ahmad, R., R. S. Kookana, and A. M. Alston. 1998. Sorption of ametryn, carbaryl and phosalone in selected soils of Pakistan. The 16th World Congress of Soil Science, Montpellier, France, 19-26 August, 1998.

4. Kookana, R. S., S. Baskaran, R. Ahmad, H. Katou, and W. J. Bond. 1998. Measuring sorption of organic compounds in soil by an unsaturated flow method. The 16th World Congress of Soil Science, Montpellier, France, 19-26 August, 1998.

5. Ahmad, R. and R. S. Kookana. 1998. How important is the nature of organic matter in determining the sorption of pesticides? The 9th International meeting of the International Humic Substances Society, Adelaide, Australia. 21-25 September, 1998.

6. Ahmad, R. and Kookana, R. S. 1999. Extrapolation of pesticide sorption data between regions. Second International Conference on Contaminants in the Soil Environment in the Australasia-Pacific Region, New Delhi, India. 12-17 December, 1999 (Invited Speaker).

Further manuscripts are in preparation for journal publication.

To Allah Almighty, the Creator of earth

CHAPTER 1

General Introduction

Pesticides have become an integral component of modern agriculture and have brought undeniable benefits in the form of efficient production of food and fibre globally. In recent decades, there has been a steady increase in their usage in many countries throughout the world, including Pakistan and Australia. During 1997, the total sale of pesticides in Australia was $1107 million (Australian Commodity Statistics, 1998) and in Pakistan it was Rs9904 million (Federal Department of Plant Protection Pakistan Report, 1998). The rapidly expanding use of pesticides has made a large contribution to increased agricultural productivity in both Australia and Pakistan.

However, due to widespread use of these chemicals, their occurrence in soil, air and water has become an important environmental concern in many areas of the world. There is a large body of evidence on contamination of surface and ground water with pesticides throughout the world (e.g. Triegel and Gue, 1994; Funari et al., 1995; Eke et al., 1996). In addition to the diffuse source contamination of soil and water in Australia and Pakistan, point source contamination has also been a cause of concern. In Australia, there are over 1600 contaminated cattle tick dip sites in New South Wales and Queensland, whereas in Pakistan, around 1900 old pesticide stores have been located in the residential areas of the Punjab province since 1980. At these contaminated sites, very high concentrations of pesticide residues exist in both countries.

The majority of research on pesticide behaviour has been carried out in Europe and North America. Despite an increasing amount of research being conducted, the behaviour of pesticides in Australian soils remains poorly understood (Kookana et al., 1998) and such knowledge in Pakistani soils lags even further behind. Therefore, Pakistan, in particular, has to depend heavily on overseas data for legislative purposes, due to lack of monitoring programs and inadequate data on soil and groundwater contamination. However, much of the European and North American data may not be applicable to Australian and Pakistani soils due to their different properties.

Sorption on soil is central to the fate and bioavailability of organic pesticides, and remediation of contaminated soils. The release and movement of pesticides through the root zone, vadose zone and into ground water is greatly dependent on the extent to which they interact with soil constituents. Sorption and release behaviour of pesticides may be determined by the soil organic matter (SOM), in addition to the other soil properties like pH, clay and sesquioxide content. It is widely recognised that sorption of nonionic pesticides onto the soil is highly dependent on the quantity of SOM (e.g. Hamaker and Thompson, 1972; Means et al., 1982; Xing et al., 1994). However, current understanding of the underlying fundamental reactions that occur between pesticides and natural sorbents is not well developed (Luthy et al., 1997). Accordingly, it is assumed that all SOM behaves in the same fashion for sorption, and generally a constant value of sorption of a nonionic pesticide per unit organic matter (K_{oc}) has been reported. However, the properties of the soil organic materials with respect to sorption are likely to vary as a result of SOM source, soil chemical and biological processes. Therefore, it is difficult to establish a general rule to predict sorption behaviour simply from the total quantity of SOM. Questions remain as to whether the soils of different countries or different regions of a country differ in their organic matter composition, and how appropriate is the extrapolation of sorption data from overseas to the soils of Australia and Pakistan.

Simple commercially available organic materials such as humic acid salts and cellulose are sometimes employed as sorbents in studies of pesticide-sorbent interactions (e.g. Garbarini and Lion, 1986) even though they are not representative of natural humic substances. Humic materials (humic and fulvic acids) extracted from soils have also been used (e.g. Garbarini and Lion, 1986; Chiou et al., 1987). However, traditional methods of extraction of organic matter constituents from soil prior to their chemical characterisation do not permit us to be sure that the observed properties are always those which exist in the soil. Therefore, there is a compelling incentive to understand, in quantitative terms, the structural and chemical composition of organic matter in whole soil and the role of its constituents in the sorption of nonionic pesticides. Solid-state ^{13}C NMR spectroscopy can provide information on the composition and structure of complex SOM without prior extraction (Kinchesh et al., 1995) although, it provides little information about the molecular nature of its components. However, by using quantitative solid-state NMR spectroscopy and a simple mixing model, C types in SOM can be explained by a mixture of common biomolecules such as saccharides, amino acids, lignin, cutin, and possibly chitin and charcoal (Nelson and Baldock, 1999).

Since sorption occurs relatively rapidly, most of the processes governing pesticide fate in soil (e.g. leaching and degradation) are influenced by desorption or release of pesticide back into solution. Following sorption of a pesticide to soil, its availability may change with the residence time of the compound in soil, a phenomenon known as "aging". The slow release of pesticide residues from the long-contaminated soil can pose a threat to the aquifer, particularly in Pakistan where relatively shallow underground water is used for drinking purposes. There is a lack of information on the rate of release of pesticides from contaminated soils and consequent potential contamination of groundwater. Sorption is reported to have a large influence on biodegradation: much of the sorbed chemical may not be available or accessible to microorganisms (e.g. Ogram et al., 1985). This highlights the need for better understanding of the sorption and release behaviour of pesticides in these historically contaminated soils.

The management of contaminated sites presents a challenge. After a long contact time of pesticide with soil, there are questions about the extent and magnitude of bioavailability of the aged pesticide and about the feasibility of the remediation of these soils. Even low concentrations of aged residues of persistent pesticides in soil may be potentially hazardous, because remobilisation could eventually lead to leaching to groundwater. Therefore, information on the release behaviour of such pesticides is essential for a better understanding of their potential adverse impact on environment and for development of remediation strategies.

Considering the reasons described above, this study was designed:

- to evaluate the sorption characteristics of ionic and nonionic pesticides in soils from Australia, Pakistan and the UK.

- to characterise the SOM and establish relationships of structural and compositional variations of SOM with the sorption of nonionic pesticides.

- to understand the release behaviour of selected pesticides from historically contaminated soils and strategies to enhance the release.

Studies were carried out to understand the sorption behaviour of 5 nonionic (carbaryl, phosalone, bifenthrin, monocrotophos and dichlorvos) and 2 ionic (ametryn, and imazethapyr) pesticides in soil. The sorption behaviour of these commonly used pesticides in Australian and Pakistani soils is not clear and has rarely been studied, except for limited information on the sorption of carbaryl on Western Australian soils. This required the development/optimisation of methods of analysis of the pesticides (Chapter 3). During the studies on sorption described in Chapter 4, it became evident that for the rapidly degradable pesticides such as monocrotophos and dichlorvos, the classical batch method is not applicable. Therefore, a new method of sorption determination based on unsaturated flow was adapted (Chapter 5). To understand how the chemical nature of SOM influences the binding of two hydrophobic nonionic pesticides (carbaryl and phosalone), characterisation of SOM was carried out on ^{13}C NMR and interpretations were made from NMR data to infer various molecular components of SOM using a simple molecular mixing model. Relationships were sought between sorption affinities and SOM components, which is considered in Chapter 6.

The release behaviour of two nonionic pesticides, carbaryl and ethion, was studied in soils collected from historically contaminated sites in Australia and Pakistan (Chapter 7). As constrained release of sequestered pesticides have been reported, the main questions asked were these. How much of the aged pesticide (carbaryl and ethion) is easily released in aqueous solutions or in the presence of a cosolvent? What fraction of pesticide residue is bioavailable? What are the possible reasons for the long persistence of carbaryl (an easily biodegradable pesticide) in the long-contaminated soil from Pakistan? Can these aged pesticides be mobilised using surfactants to enhance their release and potential of remediation?

The final chapter (Chapter 8) contains a brief general discussion, suggestions for future research and general conclusions. X-ray diffraction spectra of the soils, absorbance spectra of the pesticides, and sorption data by the unsaturated flow method have been included in appendices.

CHAPTER 2

Review of Literature

2.1 Introduction

Pesticides have become an indispensable component of modern agricultural systems and are being increasingly used to ensure the production of adequate supplies of food and enhance the quality of produce. Due to the widespread use of these toxic chemicals, their occurrence in soil, surface and groundwaters has become an important environmental concern. In recognition that soil is a sink for most widely used pesticides, the past two decades have seen much progress in our understanding of fate and behaviour of pesticides in soil. In this chapter, current knowledge on the retention and release behaviour of pesticides in soil is reviewed and the gaps in our knowledge, which form the basis of aims of the thesis, are identified.

2.2 Pesticide Usage in Agriculture

Pesticides are not new. The use of inorganic compounds, such as copper compounds, for combating insect pests and diseases is mentioned in the Bible (Eke et al., 1996). Until early 1940s, chemicals classified as pesticides were mainly inorganic compounds containing heavy metals, sulphur, arsenic, fluorine, borate, and chlorate (Kuhnt, 1995). After 1945, a new generation of organic chemicals emerged which enabled farmers to become efficient producers of high quality food and fibre. These included organochlorine, organophosphate, and carbamate insecticides, phenoxyacetic acid, triazine and bipyridylium herbicides, dithiocarbamate and dicarboximide fungicides and allethrin. This marked the starting point of intensive use of pesticides in agriculture (Egler, 1964). These organic compounds became a ubiquitous component of the Green Revolution in agriculture worldwide as they were relatively inexpensive, more effective, broad spectrum, and less toxic to non-target species than the inorganic compounds previously used.

Over the past three decades, there has been a large increase in the use of chemicals in the global agriculture. Figure 2.1 shows that there has been a steady increase in the world use of pesticides with a noticeable relative increase in use of herbicides and decrease in use of fungicides. Pesticide use in the United States of America has grown 33-fold since 1945 (Pimental et al., 1991). It increased from approximately 1.9×10^5 tons to 3.9×10^5 tons during the period between 1965 and 1985 (Postel, 1988). In 1990, the total consumption of pesticides in China touched the mark of 2×10^6 tons of a.i., 70% of which were insecticides and 14% fungicides (Carvalho, et al., 1997). The use of pesticides is also increasing rapidly in countries like Australia and Pakistan.

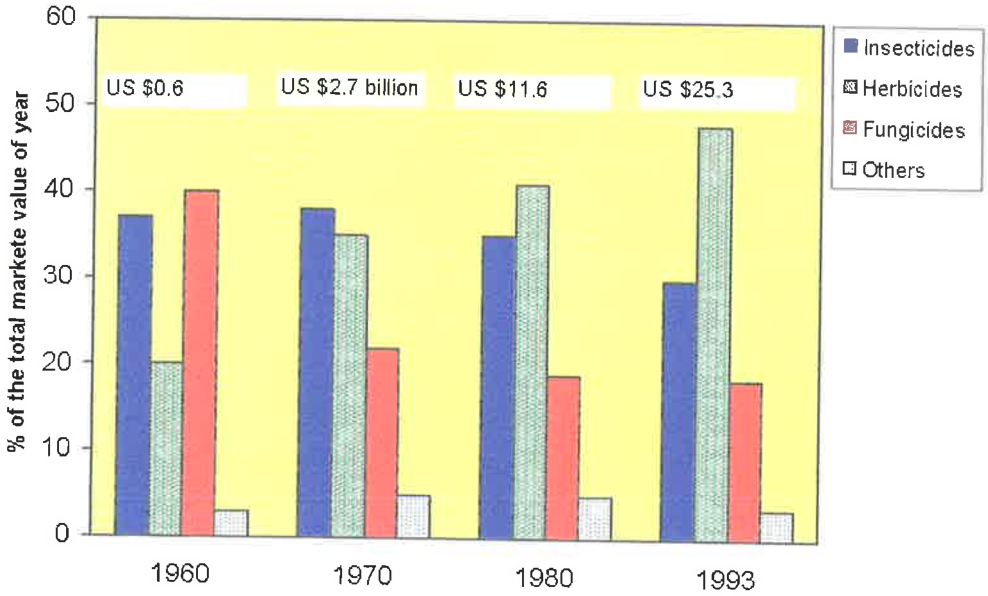


Figure 2.1 Trends in the world use of pesticides (after Carvalho et al., 1997)

2.2.1 Pesticide Use in Australia

There are about 400 active ingredients with several thousand formulations used in agricultural and veterinary chemicals in Australia (PESKEM PC, 1995). In 1989, the cost of agricultural chemicals to farmers represented approximately 4.6% of the total farm costs (AAVCC, 1990). During the period between 1991 and 1992, 14.9 million hectares of land were treated with herbicides, 3.1 million hectares with insecticides and 0.8 million hectares with fungicides (McLennan, 1996). In addition, farmers treated 159.4 million animals with tickicides in cattle/sheep dips. The Agricultural and Veterinary Chemicals

Association of Australia Limited has estimated net productivity gains to Australian agriculture from using these agrochemicals, at $2500 million annually (Cribb, 1989), whereas Kookana et al. (1998b) reported the benefits as high as A$5000 million each year.

Use of pesticides has grown steadily in Australia since the 1950s. Data for the sale at factory gate indicates that sale of pesticides increased greatly from A$166 million to A$1107 million per annum over the period of 1981 to 1997 (Figure 2.2) with herbicides making up to 65% ($714 million) followed by insecticides accounting for 24% ($268 million) of the total sale in 1997 (Australian Commodity Statistics, 1998) (Figure 2.3). The remaining 11% consists of fungicides, growth regulators and miscellaneous products. However, figures for the weight of active ingredients or individual chemical product sold for use in agriculture are not routinely available on either a nationwide or a statewide basis.

2.2.2 Pesticide Use in Pakistan

Pakistan, predominantly an agricultural country, embarked upon using pesticides in 1954 with a meagre use of 254 tons of active ingredient (a.i.). Data compilation from the Pakistan Agricultural Pesticides Association (PAPA) bulletins (1991, 1994, 1995) show that since 1981, pesticide consumption has increased steadily from 905 metric tons of a.i. (import value being Rs 204 million) to 4919 metric tons a.i. in 1993 costing Pakistan Rs 5339 million (Figures 2.2 & 2.3). This is indeed a large rise both in terms of quantum (544% increase) and value (2617% increase). Insecticides make up 85% of the total pesticides and herbicides only 6%. This division between categories of pesticides partly reflects the relative use in developed and developing countries: herbicides dominate in the developed countries like Australia, where their potential for labour-saving is advantageous and in contrast, insecticides are generally the most important class of pesticides used in the developing countries. In Pakistan, about 91% of the total amount is applied directly to soil or plantations. Up to 75% of the insecticides are used for pest control on cotton, which is most susceptible to pest attack. The rest are used on crops like rice, maize, sugarcane, and vegetables.

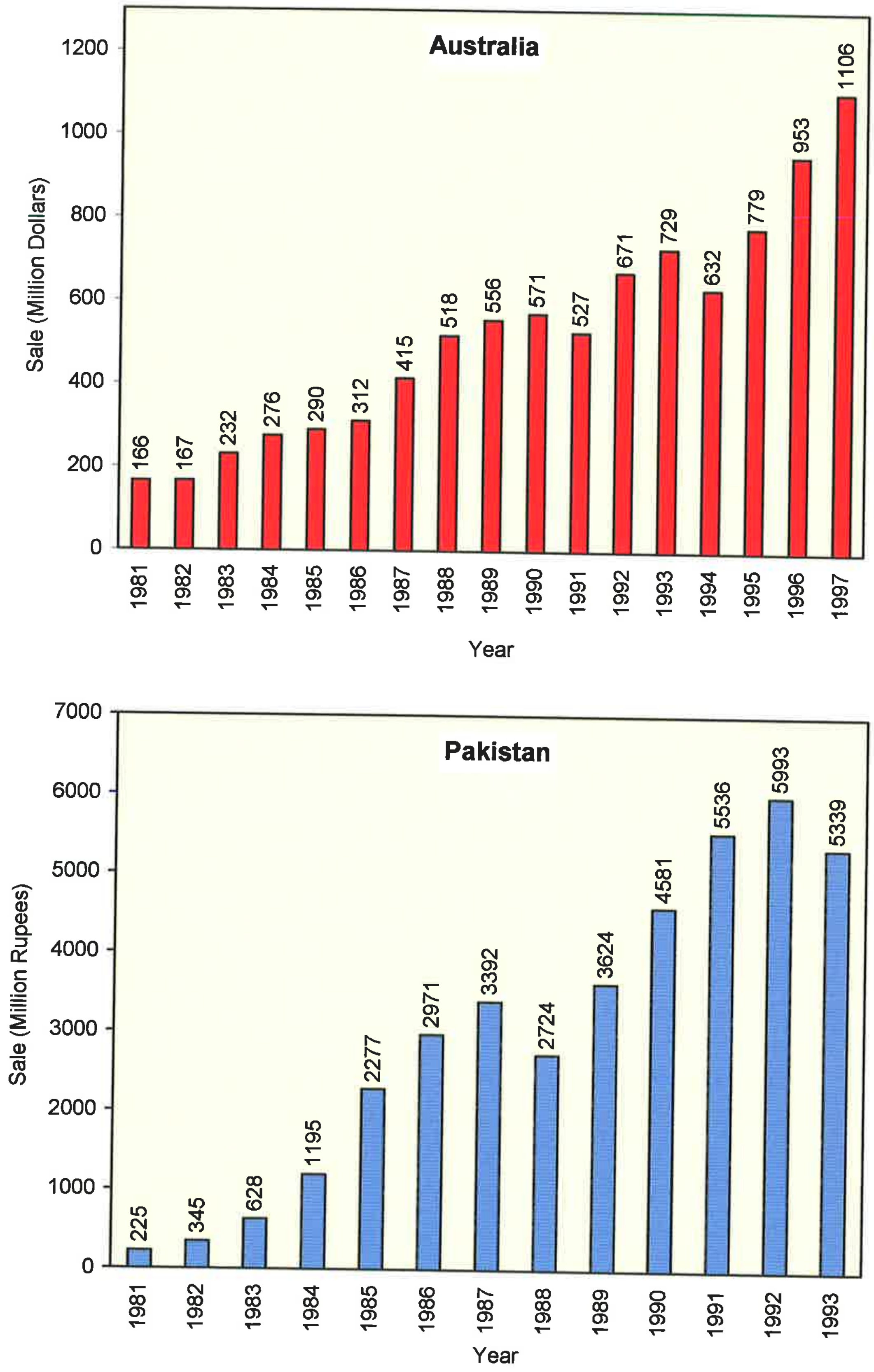
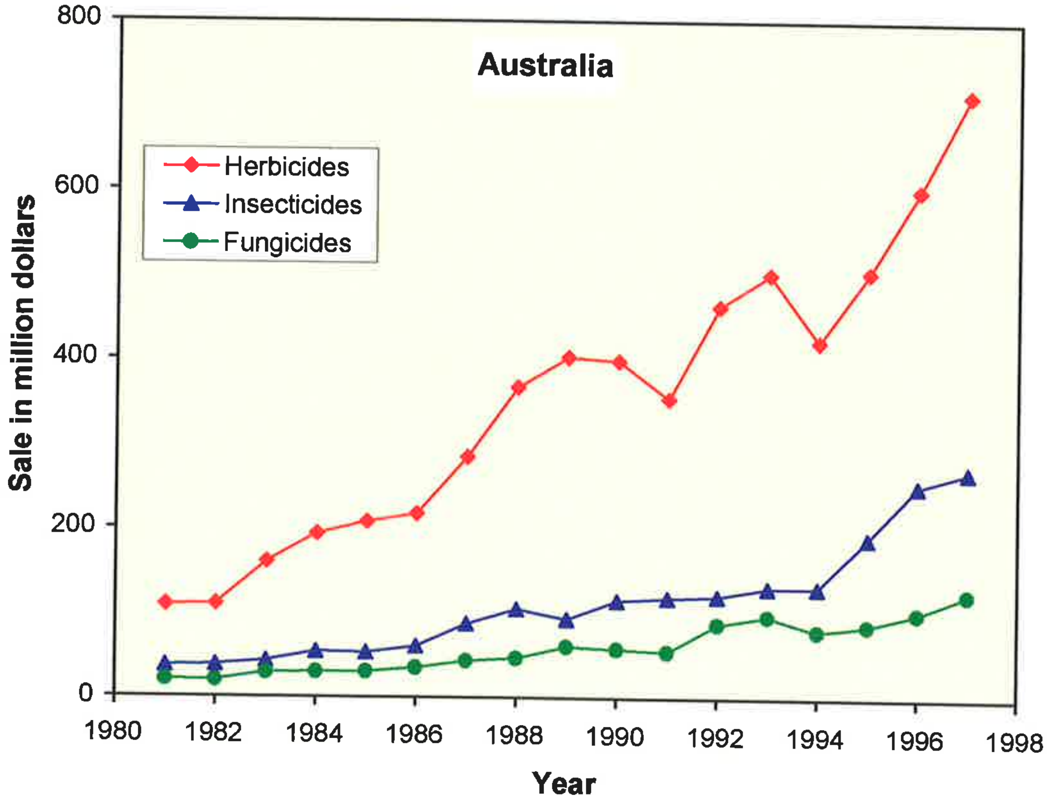


Figure 2.2 Sale of pesticides in Australia and Pakistan (Rs1.0 = A$0.03)



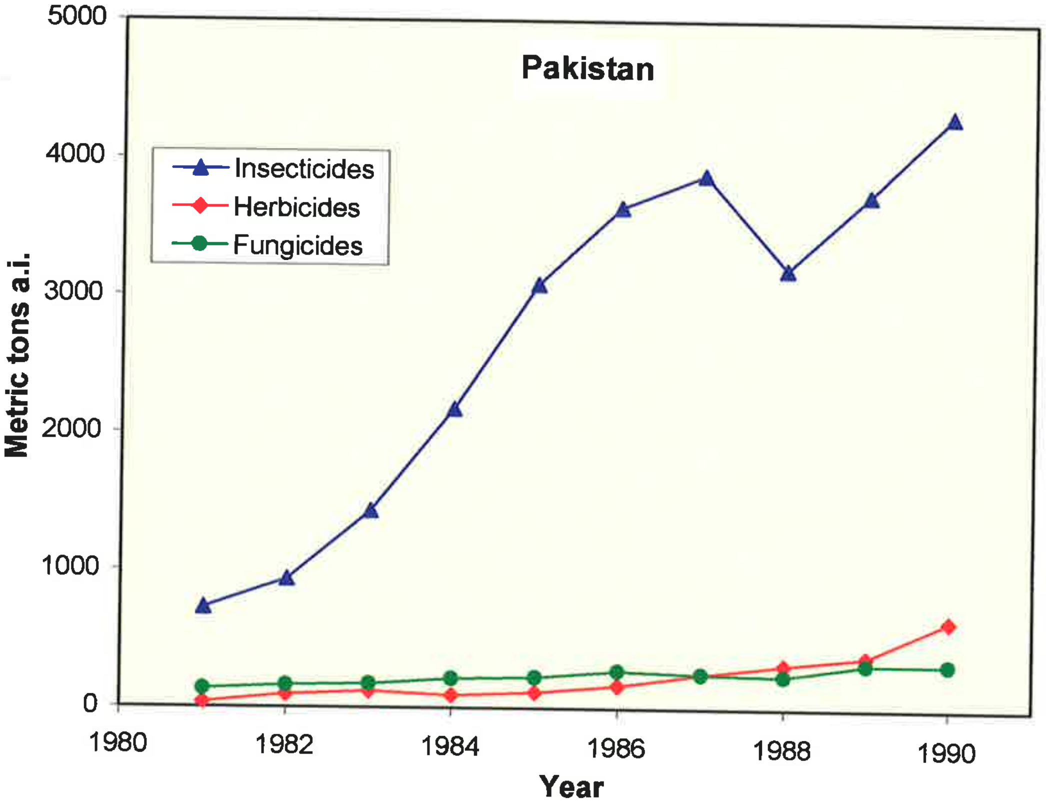


Figure 2.3 Trend in use of major groups of pesticides in Australia and Pakistan

There are over 310 chemical formulations, based on 150 active ingredients sold under 220 brands in Pakistan (Parvez, 1993). The organophosphates and synthetic pyrethroids are the most important groups of pesticides in terms of both value and quantity. The use of herbicides, although small, is increasing. There has been more or less a steady use of fungicides over the last decade.

2.3 Pesticide Contamination of Surface and Groundwater

Of all the environmental contaminants, pesticides have probably been the most widely criticised due to their potential threat to the surface and underground water. Only 0.1% of the pesticides used in agriculture reaches target pests and the rest is distributed into the ecosystem (Pimental and Levitan, 1986). The latter may cause serious air and water contamination (Pimental et al., 1991).

Many reports on pesticide contamination of groundwater, under conditions where agricultural use could be identified as a source of contamination, have been documented throughout the world. For example, at least 74 pesticides have been found in the groundwaters of 38 States of the USA since 1979: forty six of the pesticides were used in normal agriculture (Triegel and Gue, 1994). In 1990, one of the detailed surveys of pesticide contaminations in groundwaters conducted by the US Environmental Protection Agency (USEPA) estimated that about 10% (10,000 nationwide) of community water system wells and 4% (450,000 nationwide) of rural domestic wells contained detectable amounts of one or more pesticides (USEPA, 1990). More recently, the results from the National Water-Quality Assessment (NAWQA) program of the United States completed during 1993-1995 indicated that 54% of the 1034 site samples collected from shallow groundwater in agricultural and urban areas across the United States were contaminated with one or more pesticides (Kolpin et al., 1998). Similarly, reports on contamination of surface as well as groundwater are also available from other countries of the world e.g. U.K. (Croll, 1991; Eke et al., 1996) and Germany (Friesel et al., 1986).

The widely reported contamination has enhanced public pressure to regulate pesticide application due to its potential adverse effects on the environment and human health. Based on the evidence of serious threat to the environment, a range of pesticides e.g.

hexachlorobenzene (BHC), 1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane (DDT), 1R,4S, 4aS,5R,6R,7S,8S,8aR)-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4:5,8-dimethanonapthalene (dieldrin), 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (heptachlor) and 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methaniondene (chlordane) have now been banned or severely restricted in most of the countries in the world.

2.3.1 Pesticide Contamination in Pakistan

In Pakistan, groundwater is precious, as much of the drinking water used for human beings and domestic animals is drawn from shallow groundwater, and this is the primary reason for the growing concern about the influence of agriculture on its quality. As the water table in more than 10% of the area of cultivated land is within 1.5 m of the ground surface, increased usage of both insecticides and herbicides, together with their potential for downward leaching and surface flushing has become a major threat to the aquifer (Hussain et al., 1996). Heavy use of pesticides in some areas, especially for cotton and rice, has raised concerns about the possible contamination of water supplies and dangers to human and animal health. Indeed, an increasing number of water samples from hand pumps in the cotton growing areas of the Punjab has been shown to contain pesticide residues.

A preliminary study of shallow groundwater contamination by pesticides was initiated by Ali and Jabbar (1991). They collected drinking water samples from hand pumps in the cotton growing area, drawing water from the 9-13 metre depths, and the chemical (pesticide) industrial area of Kala Shah Kaku (Sheikhupura). About 70% of the water samples were contaminated with one or more of the pesticides monocrotophos, cyhalothrin and endrin. The contamination of groundwater samples is, therefore, a real concern and monitoring studies are urgently required in other areas of the country. Unfortunately, the only other report on drinking water contamination in Pakistan focuses on cattle drinking water in Karachi (Parveen and Masud, 1988). The study revealed contamination of 13% samples with chlorinated pesticides or their metabolites, and some samples were found to contain γ BHC in the range of 1.0 to 16.4 mg L^{-1}.

Another source of groundwater contamination is pesticide stores. There are some 1900 stores in the Punjab alone, and most of these are located in residential areas. Before the transfer of pesticide business from the government to the private sector (in 1980), the yearly procurement of pesticides exceeded the sale and as a result, there had been an accumulation of stock. This old stock is still lying in the stores under poor storage conditions, and groundwater quality has been adversely affected due to leakage from the containers. The concentrations of a range of pesticides in the groundwater beneath the subsoils may be high enough to pose a health threat to the nearby residents who use hand pumps to draw supplies of potable water. The problem is exacerbated where water tables are shallow. Unfortunately, no investigation has been made to establish the level of groundwater contamination in the vulnerable areas surrounding these sites.

2.3.2 Pesticide Contamination in Australia

In Australia, data on surface and groundwater contamination from pesticides are limited because of the lack of systematic monitoring programs. However, pesticides have been detected in Australian ground waters (Stadter et al., 1992; Knight, 1993), and in recent years several monitoring programs have been initiated. Groundwater contamination of a Western Australian shallow sand aquifer by two herbicides, 2,4-D and 2,4,5-T, originating from disposal of effluent from a pesticide manufacturing plant has been reported by Appleyard (1993). There is also evidence of atrazine and fenamiphos in groundwater in a residential area of Perth, Western Australia as a result of the storage and handling of these chemicals in a residential property (Appleyard, 1995). In the Shepparton East area of New South Wales (NSW), the overall proportion of pesticide-positive samples has been reported to be 49%, containing pesticides such as chlorpyrifos, endosulfan, DDE, and heptachlor epoxide: atrazine and simazine were the most frequently detected pesticides (Bauld, 1996). A report on the pesticide monitoring of surface waters undertaken by the Central and North Western Regional Water Quality Program by the New South Wales Department of Water Resources in the Macquarie, Namoi, Gwydir and Border Rivers basins in the Central and North-Western part of NSW showed the presence of various pesticides such as profenofos, chlorpyrifos, atrazine, diuron, prometryn, metolachlor, and very frequent and increased levels of endosulfan (Cooper, 1996). Atrazine and its metabolite DEA has been detected in ground waters of Queensland (Bauld, 1996). In

Victoria, Bauld et al. (1992) reported, after analysing 10 water samples from wells for more than 30 pesticides, that half of the samples contained atrazine and simazine. The same products have also been found in South Australia (Stadter et al., 1992). In Piccadilly Valley, a horticultural catchment in South Australia, about 83% of the surface water and all of the sediment samples tested were found to contain pesticide residues (Thoma, 1990). Studies on pesticides like atrazine, chlorsulfuron, dichlobenil, glyphosate, paraquat, simazine, picloram, and trifluralin have also been reviewed by Ferris and Haigh (1993). These reports of surface and groundwater contamination from various sources in Australia suggest that monitoring of ground and surface water systems needs to be done on a larger scale.

Soils at cattle and sheep dip sites are massively contaminated with organochlorines (OCs) and other pesticides. There are some 1607 cattle tick dip sites in north-eastern NSW and along the Queensland border, as documented by the Cattle Tick Dip Management Committee (DIPMAC, 1992). Substantial contamination in the soils around concrete dipping baths and associated draining pens has been reported by NSW Agriculture. Of the many chemicals used as tickicides at these sites (Table 2.1), DDT has been detected at concentrations as high as 6 percent of the soil by weight, and ethion, an organophosphate, has been detected at 0.23 percent of the soil by weight (Zwieten and Grieve, 1995). Each of these chemicals can present a potential hazard to human health and/or the environment. However, to the best of my knowledge, no study regarding contamination of underground water around these sites has been reported in literature.

Table 2.1 History of chemicals employed as tickicides in New South Wales cattle dips

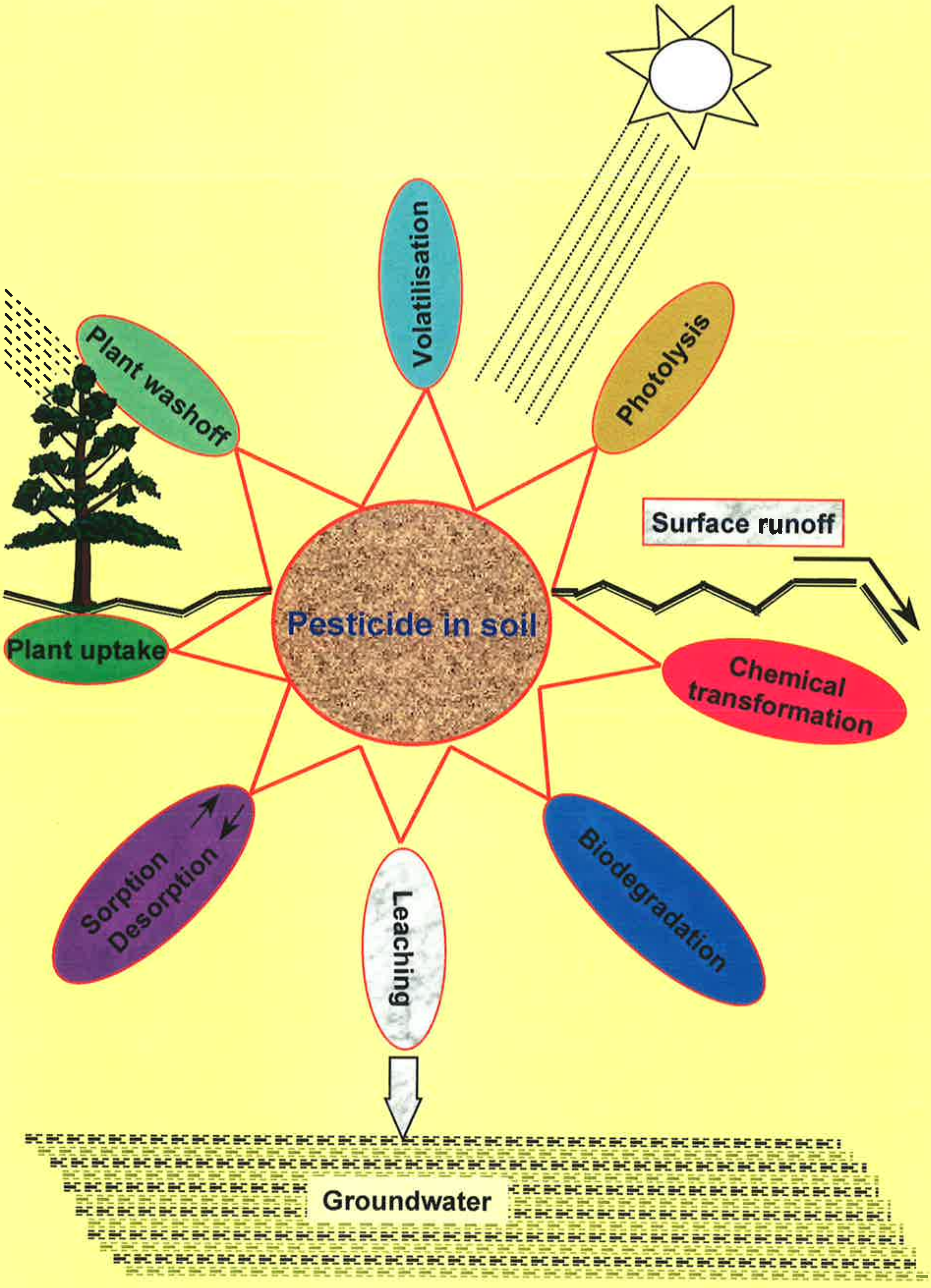
Tickicide	Period of use
Arsenic (trioxide)	?-1955
DDT	1955-1962
BHC	1955-1962
Carbaryl	1963-1970
Coumaphos	1962-1965
Carbophenothion	1962-?
Chlorpyrifos	1969-1974
Bromophos ethyl	1969?
Dioxothion	1962-1976
Ethion	1962-1976
Chlordimeform	1973-1976
Cymyazole	1977-1986
Chloromethiuron	1977-?
Amitraz	1976-present
Promacyl	1977-present
Cypermethrin	1979-present
Chlorofenvinphos	1979-present
Flumethrin	1986-present

Source: DIPMAC (1992)

2.4 Processes Governing Fate and Behaviour of Pesticides in Soils

The fate and behaviour of pesticides in soil is governed by several processes including sorption-desorption, degradation, leaching and volatilisation. The schematic diagram in Figure 2.4 illustrates these processes.

Figure 2.4 Processes governing the fate and behaviour of pesticides in soil environment


Volatilisation
Photolysis
Plant washoff
Surface runoff
Pesticide in soil
Plant uptake
Chemical transformation
Biodegradation
Sorption
Desorption
Leaching
Groundwater

2.4.1 Sorption

The term "sorption" is defined generally as the transfer of a solute between a fluid and a solid phase. Sorption of organic solutes by soil can occur as the result of either an adsorption process or a 'partition process'. It is used to denote the uptake of a solute by soil or its constituents without reference to a specific mechanism. Adsorption is an interaction between solute and a site on the surface of the soil particle. The interaction is caused by van der Waals forces (physical adsorption) or the formation of a chemical bond (chemisorption). A partition process is distribution of an organic solute between water and organic matter fraction of the soil by molecular forces common to solution, and is similar to the distribution of an organic solute between water and an organic solvent such as n-octanol (Chiou et al., 1979; Chiou and Schmedding, 1982; Smith et al., 1988).

Sorption is one of the major processes affecting the interactions between pesticides and solid phase in the soil environment. It plays an important role in regulating the rates and magnitudes of other processes that govern the fate and transport of organic contaminants in soils and sediments. It may cause a decrease in the biological activity of a pesticide and its rate of biological degradation, or enhance nonbiological degradation due to catalyzing hydrolysis (Stevenson, 1994). The transport of an organic chemical is also significantly affected by chemical sorption onto soil. The interactions involved between pesticides and soil have been reviewed by Hamaker and Thompson (1972), White (1976), Calvet (1980), Hartley and Graham-Bryce (1980), Khan (1980), Hance (1988), Koskinen and Harper (1990) and Stevenson (1994).

Although information on the sorption of various pesticides on Australian soils is increasing slowly with the time, information is still lacking on the sorption of common pesticides on a range of soil types (Kookana et al. 1998a). There is no significant study on sorption behaviour of pesticides in Pakistani soils reported in literature.

2.4.2 Factors Controlling Sorption

The behaviour of a pesticide in the soil and its distribution in the environment are strictly dependent on its sorption, which in turn depends on two main interacting factors viz., pesticide properties and soil properties (Nicholls, 1988; Koskinen and Harper, 1990).

2.4.2.1 Properties of the Pesticide

The molecular properties of the pesticide of particular importance in solute-surface interactions are: water solubility, ionisability, and the nature of formulation.

2.4.2.1.1 Solubility in Water

The solubility of a nonionic pesticide in water is sometimes considered as an indicator of sorption. Since sorption in soils takes place in aqueous medium, interactions between water and pesticide are of particular importance. However, complexity of various sorption mechanisms leads to a situation which is confusing to find a general rule (Calvet, 1980). A decrease in solubility indicates an increase in the hydrophobic characteristics of pesticides and hence is related to increased sorption by soil. Several investigators have tried to establish a relationship between sorption and water solubility. For example, a linear inverse relationship between sorption (partition) coefficient and water solubility has been widely recognised for nonionic pesticides (e.g. Kenega and Goring, 1980; Karickhoff, 1981). However, there are contradictory reports on the relationship between sorption coefficient and water solubility (e.g. Ellgehausen et al., 1981; Mingelgrin and Gerstl, 1983). The molecular structure of the pesticide is an example of a property which may affect sorption and hinder the expected relationship between sorption coefficient and water solubility of the compound (Mingelgrin and Gerstl, 1983).

2.4.2.1.2 Ionisability

Ionisability refers to the strength of ionisable functional groups present. Generally, sorption increases with functional groups such as R_3N^+-, -$CONH_2$,-OH, -NHCOR, -NH_2, -OCOR and -NHR (Khan 1980). The ionisation of pesticides depends on the pH of the soil system. Pesticides with acidic properties are proton donors and at high pH become anions due to dissociation, basic pesticides become cations at low pH, resulting in increased sorption whereas non-ionic pesticides may be subjected to temporary polarisation, contributing to sorption on a charged surface (Weber et al., 1993). The possibility for a molecule to become ionised or remain neutral explains the dependence of pesticides-soil interactions on the soil pH (Calvet, 1980; Koskinen and Harper, 1990). Therefore, it would be expected that the ionic pesticides would be less bioactive in acid soils where they would be sorbed as molecular or protonated species than in alkaline soils where they would be present in the anionic form.

2.4.2.1.3 Nature of Formulation

Pesticide formulations are usually designed to improve the solubility and distribution of the active ingredient. Formulations include solids (wettable powders, granules, dusts) and liquids (water soluble, oil soluble, emulsifiable concentrate) containing different percentages of active ingredient. The influences of formulation on predicting the pesticide behaviour including sorption of the active ingredient onto soil have been largely neglected (Augustijn-Beckers et al., 1994), even though it is clear that the initial behaviour of a pesticide in the soil will be affected greatly by the physical nature of the formulation and the presence of additives such as wetting agents, emulsifiers, surfactants and dispersing agents (Hartley and Graham-Bryce, 1980). It is difficult to draw any definite conclusion about the effects of sorption of additives included in the formulated products due to the contradictory nature of the results of the studies so far undertaken (Bayer, 1967; Huggenberger et al., 1973; Yamane and Green, 1972; Morita, 1976; Fleming et al., 1992).

2.4.2.2 Properties of the Soil

A number of soil properties have been reported to influence sorption of pesticides in soil. These include organic matter and clay contents, soil pH, soil water contents, soil temperature and organic cosolvents in the soil solution.

2.4.2.2.1 Soil Organic Constituents

Soil organic matter (SOM) plays an important role in the sorption of pesticides. Higher sorption in soil is often associated with higher organic matter (Roberts et al., 1996), but the mechanism of the interaction is complex and not fully understood (Carringer et al., 1975; Shea, 1986).

Organic matter can be broadly classified into humic and non-humic substances, both of which can play a role in pesticide sorption (Morrill et al., 1982). Humified material is often stronger sorbent due to the presence of oxygen containing functional groups such as –COOH, phenolic, aliphatic, enolic, –OH, and C=O. Sorption of nonionic pesticides is well correlated with the SOM content (Karickhoff et al., 1979; McCall et al., 1980; Schwarzenbach and Westall, 1981), but this is not so for ionic pesticides due to a range of possible sorption mechanisms (Hance, 1988). However, for triazines, organic matter has been correlated to the sorption in SOM studies (e.g. Johnson and Sims, 1993, Kookana et al., 1998a). From the stand point of interactions of nonionic pesticides with SOM, certain differences are expected to occur in the sorption affinity of a given compound to SOMs of soils from different geographical regions due to compositional variations. A review on sorption of nonionic pesticides with particular reference to the nature of SOM is presented in Section 2.5.

2.4.2.2.2 Soil Clays

Clay minerals can make a significant contribution to pesticide sorption. However, the importance of clay minerals decreases with increase in organic matter content of the soil. The 1:1 type of clay minerals like kaolinite possess low surface area and low negative charge and they have a lower capacity for sorption than the 2:1 type clay minerals like montmorillonite and vermiculite (Bailey and White, 1970). Weber (1970b) reported that s-triazine herbicides were readily sorbed onto various clay minerals including illite, montmorillonite and kaolinite. Apart from clay minerals, the clay size fraction of soils generally contains variable proportions of noncrystalline to poorly crystalline inorganic components such as Al and Fe oxides which have been shown to offer sites capable of sorbing atrazine (Huang et al., 1984). However, crystalized oxides and hydroxides are generally reported to be poor sorbents of pesticides (Calvet, 1980). The degree of sorption of pesticides to minerals also depends on the structure of the organic chemicals. For example, some pesticides possess hydroxyl or carboxyl functional groups that may or may not possess a negative charge, depending on the pH of the soil-water system. If the pH is sufficiently high, these functional groups will dissociate and acquire a negative charge. The negatively charged molecules may be sorbed by oxide surfaces and by the edges of aluminosilicate clay minerals (Dragun, 1998).

Pesticide sorption in surface soils has been studied extensively, but there are few reports on studies of sorption in subsoil horizons. The clay, Al, and Fe oxide content may increase in subsoil horizons which may influence pesticide sorption in the subsoil horizon. Dipyridylium herbicides are more strongly sorbed on soils having a significant clay content than on soils having low clay contents (Kookana and Aylmore, 1993). Barners et al. (1992) reported a decrease in metolchlor sorption with increase in depth. However, Johnson and Sims (1993) reported equal capacities of ionic herbicides in subsoil horizons of coastal plain. These results clearly indicate that for assessment of pesticide movement to ground waters, it is necessary to understand the influence of subsoil horizons in the vadose zone on sorption.

2.4.2.2.3 Soil pH

The acidity or basicity of the soil is another factor that may have a great influence on the process of sorption, in particular, for ionisable pesticides (Nicholls, 1988). The effect of soil pH on the sorption of a pesticide depends on soil constituents and the chemical nature of the pesticide. The soil pH regulates the electrostatic charge of soil colloids (organic matter and oxides) and the chemical dissociation or protonation of pesticide molecules. Charge modification of either the sorbent or the chemical influences sorption involving electrostatic interactions (Hingston et al., 1972).

Studies conducted by Colbert et al. (1975) and Ladlie et al. (1977) indicated that sorption of s-triazines increased with decrease in pH. Basic pesticide molecules become protonated at lower pH and therefore, more strongly sorbed to the soil colloids. Conversely, the acidic pesticides ionise and become anions as pH increases (one or more pH units above the pK_a)

and sorption is less (Weber, 1993). Sorption goes through a maximum for pH values around the pK_a of the pesticide but this maximum also depends on other soil properties (Barriuso et al., 1992). However, this is a general rule for weakly basic and acidic pesticides (Hingston et al., 1972). Sorption modifications with soil pH are moderate for the nonionic pesticides.

In some Australian soils, sorption studies on pesticides like simazine, chlorsulfuron, triasulfuron and strychnine showed that sorption of these pesticides decreased with increasing soil pH (Blacklow and Pheloung, 1992, Kookana et al., 1997). The soils of Australia and Pakistan are mostly alkaline in nature. Therefore, the behaviour of pesticides in these soils, particularly, for ionic pesticides is expected to be quite different from the soils of Europe and North America where soils are mostly acidic in nature. Soil pH is related to the cultivation practices. Therefore, the management practices e.g. fertilising, cropping and liming of alkaline soils of Australia and Pakistani soils can easily modify the soil pH and eventually affect the behaviour of the pesticides applied to the soils (Kookana et al., 1998).

2.4.2.2.4 Soil Water Contents

Soil water contents or degree of water saturation in the soil has been shown to have an effect on pesticide sorption. The competition between water and pesticide molecules for sites varies for different pesticides depending on their structure and the nature of the site. Some pesticides are poor competitors with water for sorption sites. In general, sorption increases with a decrease in water content (Calvet, 1980) probably due to new sites becoming available for sorption as the soil dries.

2.4.2.2.5 Soil Temperature

Soil temperature is considered to be an important environmental factor affecting sorption. It not only influences directly the sorption of pesticides but also interacts with other environmental factors. As sorption is an exothermic process, an increase in temperature generally leads to decreased sorption (Harris and Warren, 1964). However, the results obtained from the literature indicate that the effect of temperature on sorption of pesticides onto the soil is highly variable. A study conducted by Valverde-Garcia et al. (1988) shows that the elevation of temperature favoured sorption of thiram and dimethoate on organic soils. They attributed this enhanced sorption to the increased number of active sites on humus. A similar interpretation for sorption of lindane was presented by Khan et al. (1996). In contrast, studies on sorption of cyanazine on different homoionic peats by Dios-Cancela et al. (1990) showed a decreased sorption with increase in temperature, which was attributed to either a decrease in the attractive forces between the pesticide and the peat or a change in the solubility of the pesticide. In a study on sorption of atrazine on kaolinite and montmorillonite clays, Fruhstorfer et al. (1993) postulated that since the rise in the temperature causes an increase in the kinetic energy of the molecules with constant electrostatic attraction, this leads to a decrease in sorption of atrazine. Morrill et al. (1982) reviewed several studies which also showed a decrease in sorption of organic compounds with increasing temperature. In a review of studies on the effect of temperature on the sorption to soil, organic material and minerals, Calvet (1980) concluded that temperature may increase, decrease or have no overall effect on sorption of pesticides.

2.4.2.2.6 Presence of Organic Cosolvents in Soil Solution

Waste disposal sites and industrial wastewater treatment systems may contain solvents that enhance movement of sparingly soluble organic compounds. Rao et al. (1985) presented the solvophobic theory for sorption of hydrophobic organic compounds (HOCs) by soil from aqueous organic binary solvent mixtures. The theory predicts that the sorption coefficient of HOCs from such mixtures decreases exponentially as the fraction of organic cosolvent increases, because of the increased HOC solubility in the binary solvent. This theory has been applied to several hydrophobic organic compounds (e.g. Nkedi-Kizza et al., 1985; Lee et al., 1990b). However, several other hypotheses have been proposed to explain this phenomenon, such as direct competition between the pesticide and solvent for sorption sites, pesticide-cosolvent interaction via hydrohobic bonds (Arienzo et al., 1993), and interactions of the solvent with SOM which result in swelling of the SOM.

Sorption from mixed organic-water solutions can provide interesting observations. e.g. for sparingly soluble pesticides, the prediction of the sorption for aqueous solution can be made from the data obtained with the mixtures of water and cosolvent by the use of Rao's solvophobic theory (Rao et al., 1985). The studies conducted by Kookana et al. (1990) showed that sorption coefficients of two herbicides, linuron and simazine, from aqueous solutions extrapolated from sorption data for methanol/water mixtures were practically the same as those obtained experimentally. They suggested that sorption in aqueous solutions for pesticides of low water solubilities can accurately be predicted by the use of organic cosolvents.

2.4.3 Desorption/Reversibility of Sorption

A pesticide can be released from soil sorption sites when its concentration in the solution phase decreases due to dilution, volatilisation, or translocation. Desorption plays an important role in determining the fate and behaviour of pesticides in soil. It determines whether the solid phase offers a permanent sink or only temporary reservoir, regulating the release of the pesticide molecule back into the solution in response to a decrease in soil solution concentration. The amount of pesticide desorbed in soil solution depends upon the type of soil constituents and the strength of bonding.

The quantity of a pesticide sorbed to a soil and its desorption is not always a single-value relationship. Consequently, less pesticide is desorbed from soils than predicted by the sorption isotherm which is often referred as to "hysteresis" (Ma et al., 1993). Hysteresis has been observed for many pesticides (Koskinen and Cheng, 1983; Kookana and Aylmore, 1993). Laird et al. (1994) by comparing the hysteresis phenomenon in various clays found that extensive hysteresis resulted from atrazine adsorption on organic components, while little or no hysteresis was observed for clay minerals. Hysteresis is more common under low soil pH, high organic matter content, long reaction time, high degradation rates, and frequent drying and wetting (Clay and Koskinen, 1990; Pignatello and Huang, 1991). Although there is no universal explanation for the differences between sorption and desorption isotherms, several causes may be responsible for the observed hysteresis such as kinetic adsorption (Pignatello and Huang, 1991), degradation (Ma et al., 1993) and irreversible conjugation with soil organic components (Stevenson, 1976). Experimental art~~e~~ifacts may also contribute to the observed hysteresis phenomenon due to changes in soil structure, ionic strength, and dissolved organic carbon content of the solution phase during desorption processes (Bowman and Sans, 1985; Gschwend and Wu, 1985; Brusseau and Rao, 1989; Wang et al., 1992).

A complete understanding of desorption is critical to predicting the fate and transport of pesticides. Pignatello and Huang (1991) observed that the soil samples contaminated with atrazine and metolachlor contained a large fraction of the pesticide in slowly reversible sorbed state which increases with time. They hypothesised that after initial contact of a pesticide with soil, the slowly reversible (resistant) fraction will become increasingly prevalent compared with more rapidly reversible fractions. It has been indicated that diffusion of pesticide molecules into microsites in the soil matrix can continue with the time of contact (Pignatello, 1990). Much of the research on desorption has been carried out in conjunction with batch sorption studies where the pesticide contact time is short. Data are sparse and our level of understanding is insufficient to make predictions for the release of pesticides from historically contaminated soils, where contact times may have been months or years.

2.4.4 Degradation

Degradation of pesticides in soil occurs via a number of processes especially chemical, microbial and photochemical (Guth, 1981). The molecular characteristics of pesticides determine the relative contribution of each of these processes. However, chemical and microbial processes are the most significant.

Chemical degradation of pesticides occurs as solutes in the aqueous phase or in the adsorbed forms on the solid phase surfaces. Chemical transformations include hydrolysis, redox reactions and photolysis (transformation due to radiation particularly ultraviolet). Of these transformation reactions, hydrolysis often dominates (Smith, 1988). The hydrolysis reactions are strongly pH-dependent and can be significant transformation pathways in soil and water. It has been observed that during the transformation of many pesticides, chemical and biological degradation take place simultaneously (Wolfe et al., 1990). Pesticide transformations in soil have been extensively reviewed by Kau~~f~~fman and Kearney (1976), Cros~~s~~by (1976) and Smith (1988).

Microorganisms are the major agents involved in the degradation of pesticides in the soil environment. Microbial degradation in soil is of two types. In the first type, little or no degradation occurs on exposure to the pesticides, but some microbes later adapt to use the added chemical as a source of carbon and energy. In the second type of degradation, decomposition starts as soon as the pesticides reach the soil due to catalysis by enzymes already present in the microbial population. This type of degradation occurs by co-metabolism. Sorption by clays and organic matter can protect a pesticide from biodegradation by retarding their release into solution (Scow, 1993).

In Australian soils, degradation has been usually reported to follow first order kinetics for atrazine (Haigh and Ferris, 1991), trifluralin (Jolly and Johnstone, 1994) and sufonylureas (Blacklow and Pheloung, 1992). Kookana et al. (1995) reported that degradation of metalaxyl, linuron, metribuzin, and prometryn (under laboratory conditions) followed first order kinetics with half-lives in the same order of magnitude as those of European and American soils. However, the data on pesticide behaviour in soils of one country may not always be applicable to the soils of other countries due to possible differences in soil and climatic conditions. For example sulfonylurea herbicides (e.g. chlorsulfuron, metsulfuron methyl, triasulfuron) have the potential to persist for years in alkaline soils of Australia (Taylor et al., 1996; Sarmah et al., 1998) compared with their low (weeks) persistence in acidic to neutral soils common to many parts of the America and Europe. Also, 13-20 times longer persistence of atrazine (half life more than 100 weeks) has also been reported in Australian soils compared with those observed in soils of Romania and America (Bowmer, 1991). Long term persistence of trifluralin has also been observed by Jolly and Johnstone (1994).

Several organic compounds including pesticides such as parathion, 1,2-dibromoethane (EDB) and dibromochloropropane (DBCP), have been reported to persist in soils for periods of years despite being biodegradable (Buxton and Green, 1987; Steinberg et al., 1987). It indicates that the organic compounds in the soil are in bound state and unavailable to degrading bacteria. This suggests that desorption of bound pesticides into the aqueous phase is a pre-requisite for the biodegradation. The reports on long-term persistence of some pesticides are listed in Table 2.2.

Table 2.2 Persistence of organic compounds in soil

Compound	Persistence (years)*	Reference
Atrazine	9	Capriel and Haisch (1983)
BHC	16	Nash and Harris (1973)
Chlordane	16	Nash and Harris (1973)
Chlorfenvenphos	4	Chisholm (1975)
Dicamba	4	Burnside et al. (1971)
EDB	19	Steinberg et al. (1987)
Endrin	16	Nash and Harris (1973)
Heptachlore	16	Nash and Harris (1973)
Isodrin	16	Nash and Harris (1973)
Oryzalin	3	Golab et al. (1975)
Paraquat	6	Fryer et al. (1975)
Picloram	8	Burnside et al. (1971)
Simazine	20	Scribner et al. (1992)
Tordon	5	Burnside et al. (1971)
Toxaphene	16	Nash and Harris (1973)
Trifluralin	3	Golab et al. (1975)

*Compounds still present in soil at the time indicated

Figure 2.5 exhibits half-lives of various groups of pesticides based on data compiled from the literature (Carvalho et al., 1997). The potential impact of pesticides on the soil environment and groundwater can be inferred from information on pesticide half-lives in soils. The pesticides which have longer half-lives may likely to be transported to the groundwater.

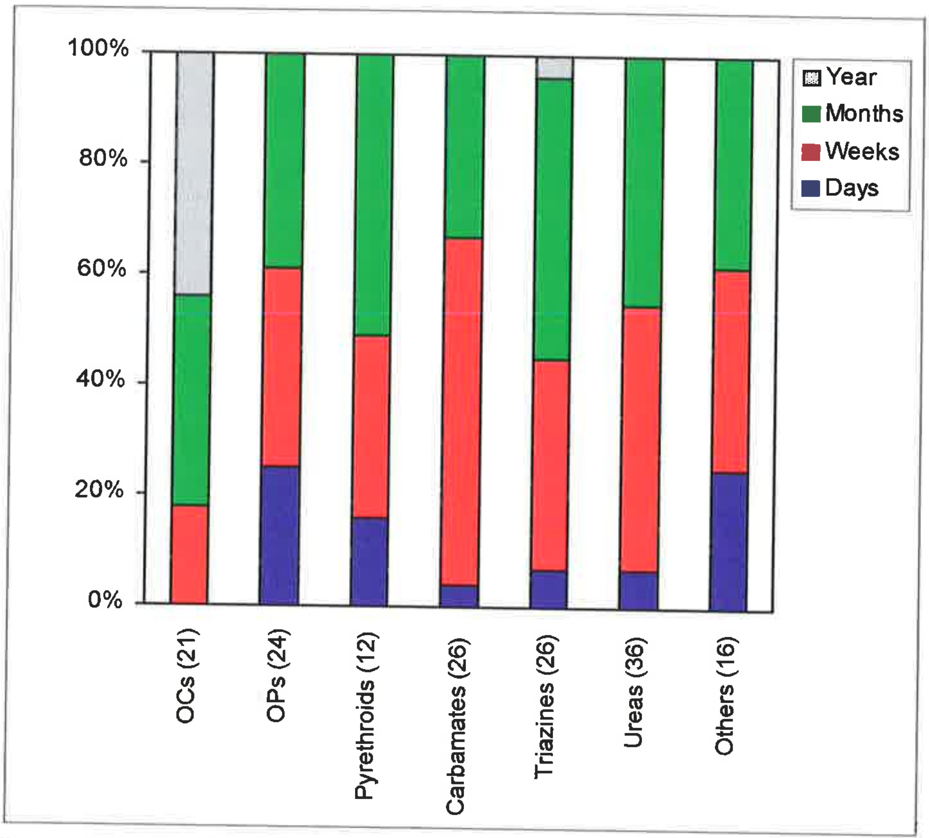


Figure 2.5 Pesticide half-lives in soils, based on data compiled from the literature (after Carvalho et al., 1997). [Numerals indicate the numbers of compounds used to obtain the data]

2.4.5 Leaching

Leaching of dissolved pesticides occurs simultaneously through mass transfer and molecular diffusion. Pesticide movement in soil is governed by two processes: mass flow and dispersion. Leaching is the physical transport of pesticide by net downward movement in the soil water. It depends on the physical and chemical characteristics of pesticides like formulation, method and time of application and environmental conditions. The degree of leaching in soil depends on the rate at which other removal processes occur (Boesten and van der Linden, 1991). If pesticide is substantially lost through other removal processes, there may be little availability for removal by leaching.

Leaching of pesticides in soil is also dependent on its sorption on the soil constituents. In general, the more a pesticide is sorbed, the less is available for leaching (Chesters et al., 1989). Less leaching is expected for soils high in organic matter (Chesters et al., 1989). For most of the pesticides, with exception of diquat and paraquat (Helling, 1970), SOM is more closely related to leaching than is clay obviously due to being the principal sorbent. Other factors may also affect leaching e.g. soil pH greatly influence the leaching indirectly by influencing sorption of triazines and sulfonylurea herbicides. Even the strongly sorbed pesticides such as chlorpyrifos have been reported to be found in ground waters of Australia (Bauld, 1996). Frequency and amount of irrigation greatly influence the leaching. More frequent irrigations are reported to cause less leaching than same volume of water applied less frequently (Troiano et al., 1993). The movement of pesticides in soil has been reviewed by Helling (1970), Leistra (1980) and Hance (1987).

2.4.6 Volatilisation

Volatilisation of pesticides from soil is dependent on the inherent vapour pressure of the pesticide, soil water content and temperature (Taylor and Spencer, 1990). Greater losses of pesticides by volatilisation from soil occur with higher vapour pressure. As reported by Taylor and Spencer (1990), pesticides with vapour pressure greater than 20 mPa can have a loss exceeding 90% of the application within 48 hours or less. In such cases volatilisation contributes considerably to residue dissipation in soil and, therefore, is often misinterpreted as degradation. However, degradation especially mineralisation is a mechanism for real elimination of the pesticide residues, volatilisation only transfers the residues into another medium. For relatively nonvolatile pesticides, volatilisation losses are small. For example, volatilisation losses of surface applied atrazine (v.p. 4×10^{-2} mPa at 20°C) and simazine (v.p. 8×10^{-4} mPa at 20°C) are reported to be only 2.4 and 1.3%, respectively over 23 days (Glotfelty et al., 1989).

Volatilisation of pesticides increases with soil water content (Walker and Bond, 1977). This is because the vapour pressure of pesticides increases as water displaces the chemical from adsorption sites. In contrast, volatilisation losses are low from dry soil due to the greater likelihood of stronger pesticide sorption to the soil (Glotfelty et al., 1989) e.g. for surface application of trifluralin (v.p. 13.7 mPa at 20°C), the loss through volatilisation ranged from 25% in 50 hours from a dry soil to 90% over 7 days from a moist soil (Glotfelty et al., 1984). Water is also involved in the movement of pesticides to the soil surface for volatilisation. As water evaporates from the soil surface, soil water moves towards the surface by capillary action carrying with it pesticide residue in the soil solution. However, the water layer above the soil surface in flooded soil such as in rice puddled soils can inhibit volatilisation losses (Parr and Smith, 1973). Volatilisation of pesticides also increases with temperature due to increase in vapour density of the pesticide (Wienhold et al., 1993). The formulation of pesticide may also influence its volatilisation e.g. encapsulated formulation for the controlled release of pesticide may reduce its volatilisation losses (Taylor and Glotfelty, 1988).

The factors which control pesticide volatilisation include, properties of the compound (vapour pressure, solubility, air-partition coefficient, soil-water coefficient and degradation rate), soil environment, climatic factors and management and usage factors. A detailed discussion on volatilisation of pesticides and the factors influencing it is presented by Spencer et al. (1995).

2.5 Soil Organic Matter and Sorption of Nonionic Pesticides

As discussed earlier, SOM is one of the most important components of the soil matrix. It consists of humic substances and partially decomposed biomass. When present above trace levels in soil particles, SOM is the predominant sorbent of nonionic organic compounds. However, due to difficulty in isolating unaltered SOM and characterising its chemical and physical properties (Schnitzer, 1991), the mechanisms involved in the sorption of these organic compounds have not been clearly understood and deserve further investigation (Shea, 1986; Stevenson, 1994; Almendros, 1995). It is also important to note that methods of extraction of organic materials from soil may alter its nature, and the observed properties may differ from those of organic matter *in situ*.

Until the late 1970s, the literature widely reported sorption of nonionic organic compounds from water by soil as an adsorption phenomenon. Later, Lambert (1968) and Swoboda and Thomas (1968) speculated that the role of organic matter was empirically analogous to a solvent medium. However, no evidence was reported to support this hypothesis. Chiou et al. (1979) was the first who, on the basis of repeated observations of linear isotherms, low heats of sorption, and significant correlations of sorption coefficients with both the SOM content and solute aqueous solubility, proposed that the sorption of nonionic organic compounds to soil and sediment in aqueous systems is due to partition of the compound between water and the organic matter. Therefore, in the following years the mechanism of sorption of these compounds became a subject of profound interest. During the last decade, the mechanism of sorption to SOM has attained a high level of attention and continuous discussion (Kyle, 1981; Mingelgrin and Gerstl, 1983; MacIntyre and Smith, 1984; Curl and Keoleian, 1984; McCarthy and Jimenez, 1985; Garbarini and Lion, 1986) because of its fundamental importance to the transport, bioavailability and toxicity of hydrophobic organic compounds (Xing and Pignatello, 1997).

A series of earlier studies showed that the extent of uptake of a given nonionic organic compound (e.g. pesticide) by soil is strongly dependent on the SOM content (e.g. Means et al., 1980; Xing et al., 1994). The degree of sorption from the solution onto the solid phase of the soil may be described by a soil-water partitioning coefficient (K_p). The sorption can also be expressed on the basis of organic C as:

$$K_{oc} = \frac{K_p}{f_{oc}} = \frac{S_{eq}}{C_{eq}\, f_{oc}} \qquad (1)$$

where K_p is the partition coefficient, C_{eq} is the equilibrium concentration of the sorbate in the aqueous phase, S_{eq} is the amount sorbed per unit mass of the soil at equilibrium, and f_{oc} is the fraction of soil organic C.

The value of K_{oc} of a nonionic organic compound has often been reported to be the same for different soils or size fractions of soil (Chiou, 1981; Karickhoff, 1981; Schwarzenbach and Westall, 1981) and it is often assumed that K_{oc} is approximately constant for a given nonionic compound (Gschwend and Wu, 1985; Chiou, 1989; Green and Karickhoff, 1990). Thus, once K_{oc} of the compound is measured, the sorption (K_p) of that compound in any soil or sediment can be obtained from the Equation (1).

Several linear equations have been developed to predict distribution coefficients for contaminants in soils. These equations are based on the contaminant's octanol-water partition coefficient, K_{ow} or its aqueous solubility, S_w (Means et al., 1980; Briggs et al., 1981b, Chiou, 1989) and they sometimes employ a single soil characteristic, the fraction of the soil organic C (f_{oc}). A list of empirical equations which utilise either S_w or K_{ow} to estimate K_{oc} is cited in Table 2.3.

Table 2.3 Prediction equations for estimating sorption coefficients based on per unit organic C (K_{oc}) of pesticides from water solubility (S_w) or octanol-water partition coefficient (K_{ow}) values

No	K_{oc} prediction equation	Soil percent OC range	Chemicals utilised	Reference
1	$\log K_{oc} = -0.557 \log S_w + 4.277$	1.6 (one soil)	14 pesticides	Chiou et al. (1979)
2	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	0.09 - 3.29	10 polycyclic hydrocarbons	Karickhoff et al. (1979)
3	$\log K_{oc} = -0.54 \log S_w + 0.44$	0.09 - 3.29	10 polycyclic hydrocarbons	Karickhoff et al. (1979)
4	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	0.033 (one sediment)	8 herbicides	Karickhoff et al. (1979)
5	$\log K_{oc} = 0.52 \log K_{ow} + 1.01$	0.51 - 3.81	5 insecticides	Felsot and Dahm (1979)
6	$\log K_{oc} = -0.55 \log S_w + 3.64$	not specified	118 pesticides	Kenega and Goring (1980)
7	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	not specified	118 pesticides	Kenega and Goring (1980)
8	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	not specified	13 pesticides	Rao and Davidson (1980)
9	$\log K_{oc} = -0.82 \log S_w + 4.07$	0.11 - 2.38	4 polycylic hydrocarbons	Means et al. (1980)
10	$\log K_{oc}^* = 0.90 \log K_{ow} + 0.69$	0.33 - 11.41	24 pesticides	Briggs (1981 a)
11	$\log K_{oc}^* = 0.90 \log K_{ow} + 0.62$	1.88 - 10.21	100 pesticides	Briggs (1981b)
12	$\log K_{oc} = 0.973 \log K_{ow} - 0.006$	0.033 (one sediment)	8 herbicides	Brown and Flagg (1981)
13	$\log K_{oc} = 1.00 \log K_{ow} - 0.317$	0.11 - 2.38	1 phenolic compound and 1 herbicide	Hassett et al (1981)
14	$\log K_{oc} = 0.72 \log K_{ow} + 0.49$	< 0.01 - 33.0	12 aromatic compounds	Schwarzenbach and Westall (1981)
15	$\log K_{oc} = -0.594 \log S_w - 0.197$	0.66 - 2.38	5 aromatic compounds	Karickhoff (1981)
16	$\log K_{oc} = 0.989 \log K_{ow} - 0.346$	0.66 - 2.38	5 aromatic compounds	Karickhoff (1981)
17	$\log K_{oc} = 0.87 \log K_{ow} + 0.05$	0.1 - 2.40	2 herbicides	Mingelgrin and Gerstl (1983)
18	$\log K_{oc} = 1.23 \log K_{ow} - 0.40$	0.4 - 27.8	3 herbicides	Madhun et al. (1986)
19	$\log K_{oc} = 0.904 \log K_{ow} + 0.539$	1.10 (one soil)	12 aromatic compounds	Chiou (1989)

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

In predicting sorption of pesticides in soils using these empirical equations, it is generally assumed that organic matter in various soils is homogeneous and interacts in the same manner with the nonionic pesticides. However, such uniform behaviour of organic matter among different types of soils is unlikely, given the structural and compositional variability that can exist. Therefore, such estimation may lead to misconceptions about the nature of the interaction, and wrong predictions about the fate of nonionic pesticides in the soil. Xing et al. (1994) reported a pronounced difference between K_{oc} values predicted from K_{ow}, and laboratory measured K_{oc} values. The major cause of variation in observed sorption coefficient may be due to the difference in polar or nonpolar character of organic matter and its structure and configuration, which can affect the sorption of organic compounds. Furthermore, the fats-waxes-resin fraction in soil, implicated by Hartley (1960) as responsible for sorption of organic contaminants by soil, may compose from 2 to >20% of the organic matter (Stevenson, 1982).

The assumption of constancy of K_{oc} is invalid in many instances. For example, Singh et al. (1990) reported variations in sorption of linuron and fenamiphos per unit mass of organic C (K_{oc}) when comparing the data obtained from Australia with that from the rest of the world. Some information on the variability in K_{oc} values for selected nonionic compounds in soils is presented in Table 2.4. The values of K_{oc} vary, even if the differences between measurement procedures used by various investigators are taken into consideration. There are ample reasons to believe that penetration of pesticide molecules into the organic phase takes place. Moreover, in moist soils and aqueous systems, water displaces organic compounds from the mineral sorption sites and the contribution of mineral sorption is overshadowed by organic matter partitioning (Chiou, 1990). This is reported to be true even for sorbents with organic C fraction of less than 0.1% (Schwarzenbach and Westall, 1981; Ball and Roberts, 1991; Piatt et al., 1996). However, below this critical value, the organic fraction may not be valid predictor of the partitioning of nonpolar organic compounds. Therefore, the variation in K_{oc} values in the given Table 2.4 most probably reflects the differences in the quality of the organic matter in those soils.

Depending on the soil type, not only the quantity but also the quality of the organic constituents vary considerably (Schnitzer, 1991; Kogel-Knabner,1993) as the organic

Table 2.4 Sorption coefficient (K_{oc}) values of nonionic compounds in various soils

Compound	K_{oc} (L kg^{-1})[#]	% Organic Carbon	Reference
EDB	36 - 160	0.9 - 37.4	Hamaker and Thompson (1972), Mingelgrin and Gerstl (1983)
Piperophos	124 - 13149	3.1 - 17.6	Hata and Isozaki (1980)
Carbaryl	86 - 221	0.3 - 11.4	Briggs (1981a)
Napropamide	190 - 2108	0.2 - 4.1	Mingelgrin and Gerstl (1983), Wu et al. (1975)
Parathion	314 - 15861	0.3 - 10.5	Biggar et al. (1978), King and McCarty (1968), Yaron and Saltzman (1972)
Phorate	364 - 6862	0.3 - 54.7	King and McCarty (1968), Felsot and Dahm (1979)
Lindane	736 - 2589	2.1 - 35.3	Kay and Elrick (1967), McCall et al. (1980), Mills and Biggar (1969)
Disulfoton	810 - 8723	0.3 - 7.9	King and McCarty (1968), Graham-Bryce (1968), Graham-Bryce (1969)
Chlorpyrifos	2164 - 35170	2.1 - 11.4	Felsot and Dahm (1979), McCall et al. (1980)
DDT	131541 - 443137	2.8 - 6.7	McCall et al. (1980), Chiou et al. (1979), Shin et al. (1970)
3-Methycholanthrene	363764 - 6396040	1.4 - 7.1*	Hassett et al. (1980a)*
Dibenzanthracene	566334 - 3066996	1.4 - 7.1*	Hassett et al. (1980a)*

[#] Original values expressed as K_{om}; the factor 1.724 was used to convert to K_{oc}; $K_{oc}=1.724\ K_{om}$

*Lowest organic carbon samples not included matter in soils differs widely in terms of the degree of humification as well as their composition e.g. humic materials of grassland soils are rich in humic acids, whereas fulvic acid dominate in forest soils (Stevenson, 1994). The SOM may vary from soil to soil in its polarity, elemental composition, aromaticity, condensation, and degree of diagenetic evolution from a loose polymer to condensed coal like structures (Grathwohl, 1990; Garbarini and Lion, 1986; Gauthier et al, 1987; Preston and Newman, 1992). Therefore, type and age of SOM may affect the sorption of nonionic pesticides (Grover, 1974). However, the sorption coefficient K_{oc} ignores these properties which are known to affect the sorption of nonionic organic compounds (Xing et al., 1994).

Studies that have been conducted on the influence of the nature of organic matter on sorption of organic pollutants have been restricted to commercial and pure humic materials as sorbents (Benoit et al., 1996; Chin et al., 1997), although they are not strictly representative of natural humic substances (Malcolm and MacCarthy, 1986; Maxin and Kögel-Knabner, 1995). It would be of desirable to investigate the differences in chemical nature of SOM from different regions and to relate the structure and composition of natural SOM to the binding capacity for hydrophobic organic compounds.

2.6 Techniques for Characterising the Chemical Structure of Soil Organic C

2.6.1 Wet Chemical Methods of Extraction and Characterisation

Chemical characterisation of soil organic C involves the use of water and organic solvents as extractants and various degradative procedures considered selective in their attack on specific molecular structures. This chemical fractionation of SOM yields three major fractions: humic acids, fulvic acids and humin (Hayes, 1985). In this classical technique humic substances are fractionated merely on the basis of their extractability in alkali solution at pH values ranging from 10-13, and subsequent solubility on acidification of the alkali extract to pH 2 (Figure 2.6A). The unextracted alkali insoluble fraction is referred to as humin. The material which remains soluble in the acidified alkaline extract is the fulvic acid fraction, while that which precipitates is humic acid fraction. However, all these humic acid fractions are not discrete compounds, since each fraction containing a multitude of different chemical structures which can be further fractionated and purified to reduce heterogeneity (Swift, 1985). Humic substances are also reported to differ in molecular weight, elemental composition, acidity and cation exchange capacity (Figure 2.6B).

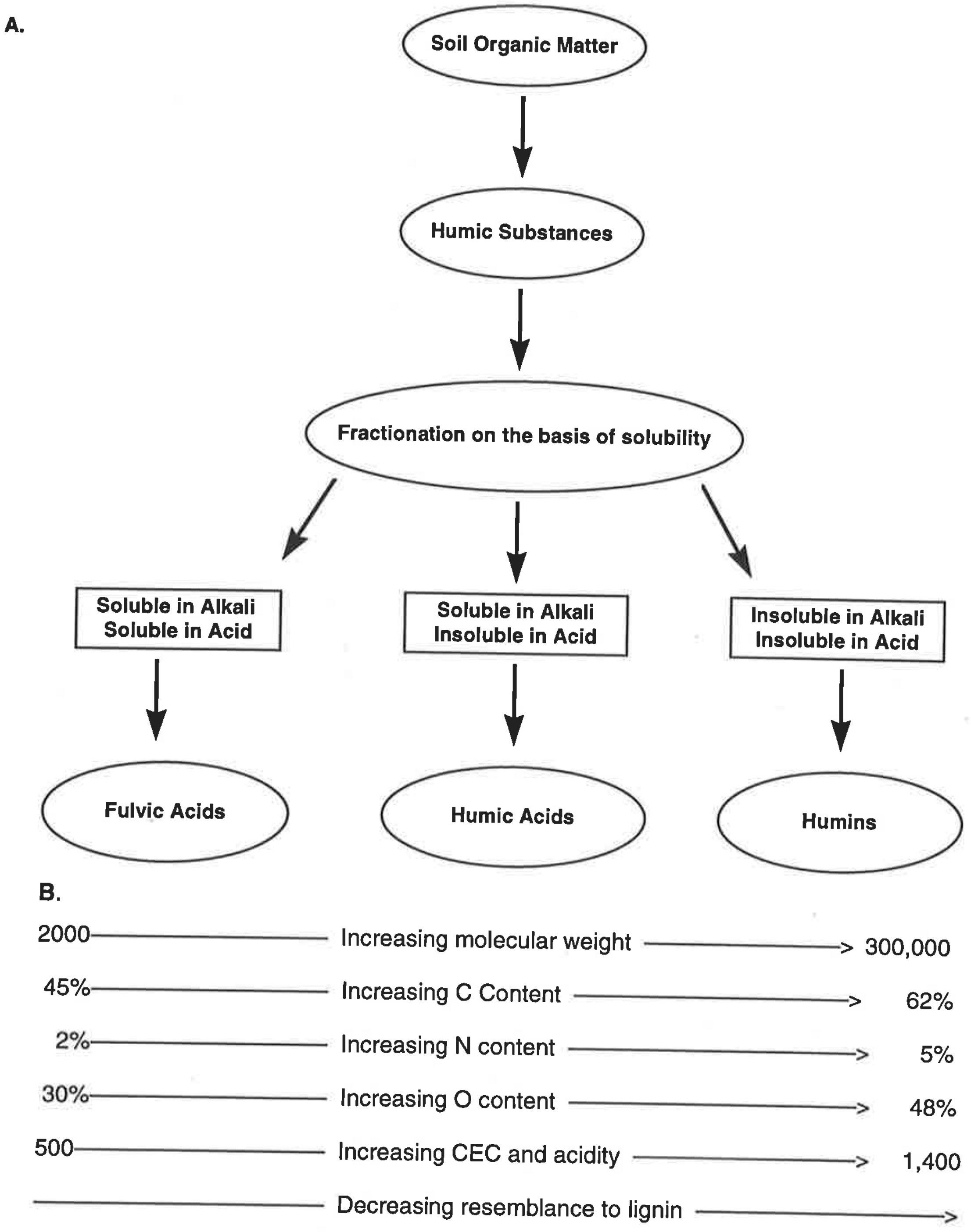


Figure 2.6 (A) Classical fractionation scheme of SOM and (B) Characteristic properties of humic substances (Adapted from the citation by Collins et al.,1997)

Until recently, the chemistry of SOM had been usually investigated using extraction procedures followed by purification of the extract and its analysis by traditional organic analytical techniques (Skjemstad et al., 1998). The use of alkaline reagents to extract soil organic fractions prior to the application of characterisation procedures has been criticised. This is due to several reasons including doubtful alkaline extractability of SOM, differences in the chemical characteristics such as cation binding capacity and hydrophobicity exhibited by the extracted organic material compared with that of the same material sorbed onto the soils and also due to artefacts formed during the process of alkaline extraction (Baldock and Nelson, 1999). The chemical extraction procedures have been used to isolate organic components selectively, but result in considerable modification of covalent bonding, which changes the chemical nature of the sample (Worobey and Barrie Webster, 1981). With the development of modern and sophisticated spectroscopic techniques of characterising soil organic C, it is now possible to avoid the use of wet chemical methods of extraction and characterising organic matter.

2.6.2 Spectroscopic Methods of Characterisation

Infrared spectroscopy, pyrolysis mass spectroscopy and solid state ^{13}C NMR spectroscopy are three modern spectroscopic techniques which can be applied to probe the composition of soil organic C. These techniques can be directly used on whole soils or soil fractions: without altering their chemistry. Recent developments in these methods and their application to the study of organic materials in soils and geological materials have been documented by Wilson (1987), Williams and Fleming (1989), Kinchesh et al. (1995), Preston (1996), and Skjemstad et al. (1997). A brief description of solid state ^{13}C NMR spectroscopy is given below, as it is one of the most powerful techniques that has demonstrated potential for reliable characterisation of SOM (Hatcher et al., 1981; Kinchesh et al., 1995; Preston, 1996). It can give the composition of SOM without altering the sample. However, there are some limitations in using this technique. To get a spectra with reasonable and acceptable signal:noise ratio in a reasonable time, the soil samples must contain organic C content of at least 0.5% (Skjemstad et al., 1997). Also the presence of paramagnetic ions such as Fe and Mn in the sample broadens the peaks and reduces the efficiency of signal acquisition. Therefore, more recently, NMR with the advent of cross-polarisation (CP) and magic angel spinning (MAS) techniques is preferably used to improve the resolution of the solid state NMR spectra. Treatment of soil samples with 2% HF has been recommended by Skjemstad et al. (1994) to get rid of these ferromagnetic and paramagnetic materials and to concentrate organic C through the dissolution of a portion of the inorganic matrix to improve the signal:noise ratio.

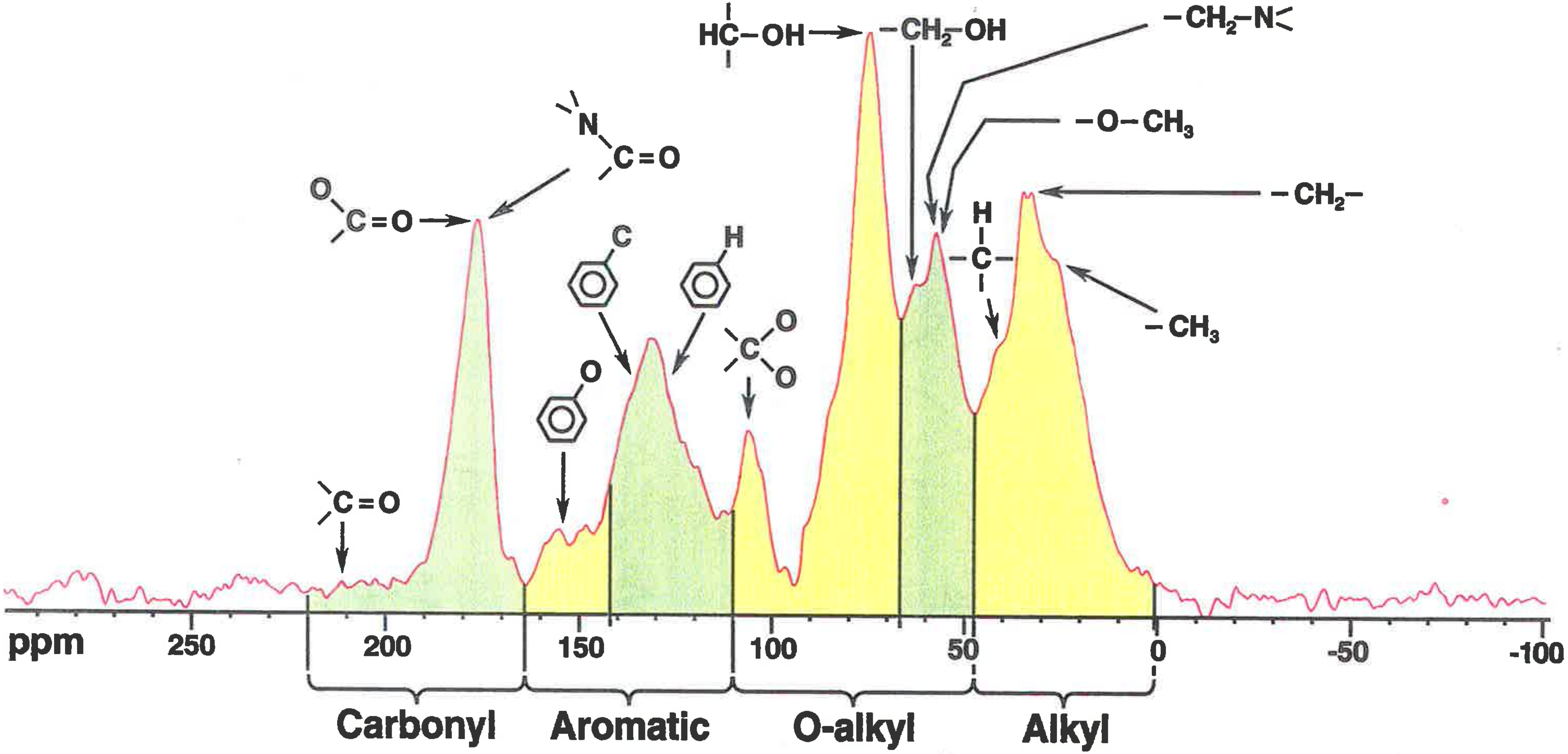
The position of peaks in the NMR spectrum gives the information on the chemistry of organic materials while the quantitative information can be obtained by integrating the areas under the peaks of NMR spectrum. A typical soil spectrum acquired by applying the conventional solid state cross polarisation magic angle spinning (CPMAS) ^{13}C NMR exhibiting 4 major regions and chemical shift assignments of peaks is presented in Figure 2.7. The alkyl region (0-45 ppm) contains all lipids but also alkyl side chains in other chemical structures such as proteins and carbohydrates. The O-alkyl region (45-110 ppm) represents alcohols and ethers with proteinaceous and methoxy C near 55 ppm. The aromatic region (110-165 ppm) represents all aromatic and unsaturated structures while the carbonyl region (165-220 ppm) includes carboxylic acids, esters and amides.

2.7 Experimental Approaches to Measurement of Sorption of Pesticides on Soil

The sorption equilibrium is usually characterised by the sorption isotherm. Measurements of isotherms are commonly obtained in laboratory by using standard batch techniques. Such techniques, in which the sorbate is added to the sorbent in an aqueous suspension and equilibrated, have been used in numerous studies (Hance, 1988; Burchill et al., 1981; Gschwend and Wu, 1985; Kögel-Knabner et al., 1991; Johnson and Farmer, 1993). Such experiments are routinely performed in many laboratories, and one can easily study sorption processes with time spans of hours to weeks depending on the nature of the compound.

Despite the importance of generating data on chemical sorption (Mills and Biggar, 1969; Bowman and Sans, 1977; Briggs, 1981a; Gerstl et al., 1981; Gerstl et al., 1983) and apparent ease of such experiments, there are some limitations. For weakly sorbed pesticides the common batch procedure which involves measurement of the concentration in the solution phase, may lead to large experimental errors. These are because the

Figure 2.7 The general chemical regions and typical chemical shift assignments for solid state^{13}C NMR



HC–OH
–CH2–OH
–CH2–N<
–O–CH3
–CH2–
–CH3
N C=O
O C=O
C=O
ppm
250
200
150
100
50
0
-50
-100
Carbonyl
Aromatic
O-alkyl
Alkyl

concentration change before and after equilibration can be relatively small compared with the error in pesticide measurements (Boesten, 1990; Brownawell et al., 1990; Johnson and Farmer, 1993). Another problem in using batch methods, in the case of hydrolysable and relatively fast-degrading pesticides, is that all loss of the compound from solution is usually attributed to the sorbed phase, thereby producing erroneously higher sorption values. Similar errors may occur with volatile pesticides.

The limitations of measuring sorption inherent in the classical batch technique have motivated the development of alternative methods such as those involving the use of flow reactors (Carski and Sparks, 1985; Celorie et al., 1989; Qualls and Haines, 1992). However, these techniques are very rarely used in environmental sciences. Column flow experiments provide another option which allows simple measurements of sorption. The flow system involves continuous flow of a pesticide solution of known concentration through a soil column. The amount of pesticide sorbed is usually determined by its disappearance from the liquid phase. Grice and Hayes (1972) suggested another flow method with suspensions, using dialysis cells. However, difficulties may arise with the microporous membrane, which may have sorptive properties and poor mechanical resistance (Calvet, 1980). Other methods of determining equilibrium sorption coefficients using the flow method are the breakthrough maxima method (Kookana et al., 1992a,b) and the retardation method (Johnson and Farmer, 1993).

These developments do not overcome the problem of degradation of the pesticides during the determination, and indeed the problem may be exacerbated as flow method takes longer than batch method. Moreover, results may be less accurate in case of more water soluble pesticides due to the relatively small changes in concentration that occur. There is clearly a need to develop new techniques for measuring sorption of pesticides with high water solubilities and low DT_{50}s (degradation time for 50% loss of the pesticide).

2.8 Analytical Techniques for Pesticides

The concentration of pesticides in solution is usually measured by UV/Visible spectrophotometry, gas chromatography (GC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC) or radiotracer techniques. Of these methods of determination, UV/Visible spectrophotometric methods have been used extensively because of their low cost and relative simplicity (Cys et al., 1977). However, using these methods, the presence of soluble carbon in soil interferes with the pesticide determination in the soil solution (Martin and Camazano, 1991).

Gas and liquid chromatography have now become the most popular analytical techniques used for pesticides determination in the soil solution (Eagle et al., 1991). Gas chromatography technique involves a variety of detectors such as coulometric array, electron capture, electrochemical, flame ionisation, flame photometric, mass selective, photoionisation and nitrogen/phosphorus-selective. In GC, the vapour pressure of an organic compound is important in its resolution (Skoog et al., 1988). GC systems, are not capable of determining thermally labile and nonvolatile pesticides.

High performance liquid chromatography in the fastest growing of all the analytical techniques. In HPLC, the mobile phase plays an important role in separation of the compound. It involves UV/Visible, fluorescence, refractive-index, electrochemical, mass spectrometric and photo-diode-array detectors. The increased use and popularity of HPLC is attributed to the sensitivity of the method, its ready adaptability to accurate quantitative determinations, and its suitability for determining thermally labile and polar pesticides (Sherma, 1995). In the light of the mildness of technique and plethora of high efficiency columns currently available, HPLC would seem to be eminently suitable for determination of those compounds for which GC is unsuitable. A further advantage of HPLC may lie in the need for a less extensive cleanup step than is required with GC methods or indeed no clean up at all.

More recently, capillary electrophoresis/UV has given promising results in terms of sensitivity and selectivity (Dinelli et al., 1993). Capillary electrophoresis coupled to ion spray MS also has been used to analyse sulfonylureas in the selected-ion monitoring (SIM) mode with positive-ion detection (Garcia and Henion, 1992). However, this technique is not widely used in the determination of pesticides.

2.9 Sequestration, Release and Bioavailability of Pesticides

In recent years, evidence has accumulated that the bioavailability of certain organic pesticides changes as the compounds reside in soil for some time, a phenomenon known as "aging" or "sequestration". This phenomenon, by which the molecules become sequestered, is of vital environmental significance, but is poorly understood. In this review, the term "aging" is used to mean prolonged contact time between the compound and soil. Aged residues are not to be confused with bound residues. As defined in literature, bound residues are those residual fractions that can not be extracted by procedures that do not appreciably alter the nature of those residues which are usually converted to the original compounds by vigorous hydrolysis. In contrast, aged residues can be extracted by organic solvents and are thus subject to regulation if the original compounds are toxic in nature.

Several hypotheses have been presented to explain the sequestration process and consequent lack of bioavailability of organic compounds in soil. A redistribution of chemical from weaker to stronger sorption sites and incorporation into the organic fraction of soil has been suggested as a mechanism of their sequestration (Alan, 1989; Brusseau and Rao, 1989). The entrapment of organic molecules in micropores has also been theorised as a mechanism of their sequestration in soil (Steinberg et al., 1987). However, these organic compounds can slowly leach out over years to groundwater with concentrations that may be considered significant to human health. A soil fumigant, 1,2-dibromoethane (EDB), was found to persist (1-32 ng g^{-1}) in agricultural top soils for 19 years after its last application, despite its high volatility and potential for degradation (Steinberg et al., 1987). Steinberg et al. (1987) also found EDB residue concentrations of 130, 125, and 27 ng g^{-1} after 0.9, 3 and 13 years after the last application. The long persistence of some organic compounds is evident from the Table 2.2.

Few studies on desorption of organic compounds from long-term contaminated soils have been reported in the literature. Pavlostathis and Jaglal (1991) investigated the desorption of trichloroethylene (TCE) that had been present in silty clay soil with low organic matter content (0.13%) for at least 18 years. Using a short column, continuous desorption of TCE showed an initial fast rate and a subsequent slower rate. Approximately 27% of the TCE initially present in the soil resisted desorption. However, partitioning of TCE by organic C alone could not be explained due to low soil organic C, and they proposed that the soil inorganic fraction should also be considered. In another study by Deitsch and Smith (1995), the effect of soil chemical-contact time on the desorption of TCE from a soil containing 24% organic C was investigated in a continuous-flow stirred tank reactor (CFSTR). Prior to the desorption experiment, the soil and the chemical were allowed to equilibrate for 1 or 4 weeks in the CFSTR. The results revealed that desorption of TCE was greater (65% of the initial) for 1 week equilibrium time than after an equilibrium time of 4 weeks (54% was desorbed), which indicates that longer contact time between TCE and the soil resulted in less desorption.

Studies of pesticides release from soil that has been exposed to pesticides for extended periods of time (e.g. decades) are scarce. However, Pignatello and Huang (1991) found that soils collected from a field with a previous history of atrazine application (2 to 15 months) contained a large fraction of the contaminant in a slowly reversible sorbed state and that this fraction increased with time. Also in column elution studies, freshly injected atrazine and metolachlor were much more mobile than 7 month aged residues (Pignatello et al., 1993). Scribner and co-workers (1992) observed that a residual fraction of simazine behaved strikingly differently with increased exposure time. The results underscore the need to carry out the experiments on other nonionic pesticides with residence time of decades or so in soils, to elucidate the mechanisms of constrained release.

In addition to the constrained release with aging, the desorption-resistant fraction of microbially-degradable compounds may have a major influence on remediation through biodegradation. For microbial degradation of organic compounds in soils, the compound must be present in a form available to the microorganisms. Although much attention has been given to the effect of sorption on biodegradation, those studies typically do not consider the effect of aging. In a long-term contaminated soil, much of the fraction of sorbed chemical may not be available for microbial degradation. Fu et al. (1994) found that less desorption-resistant styrene was degraded than the freshly added compound.

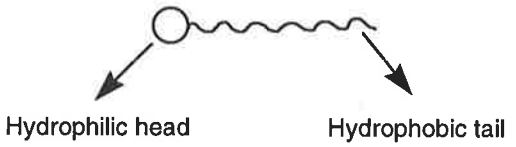
Pesticide contaminated sites are a common problem. Organic chemicals reach soils at these sites by spills, leaks, tank rupture and disposal options. At such sites, after a long contact time of pesticide with the soil, one is concerned about the extent and magnitude of the risk posed by the aged pesticide and about the remediation of the soils. Even low amounts of aged residues of persistent pesticides in soil may potentially be hazardous, because remobilization could eventually lead to leaching to the groundwater and toxic effects. Therefore, information about the rate of release of such pesticides is needed to understand the mobility of these pesticides in soil and their possible off site migration. From the stand point of remediation of contaminated sites, means of enhancing bioavailability need to be understood.

2.10 Effect of Surfactants on the Release and Bioavailability of Pesticides

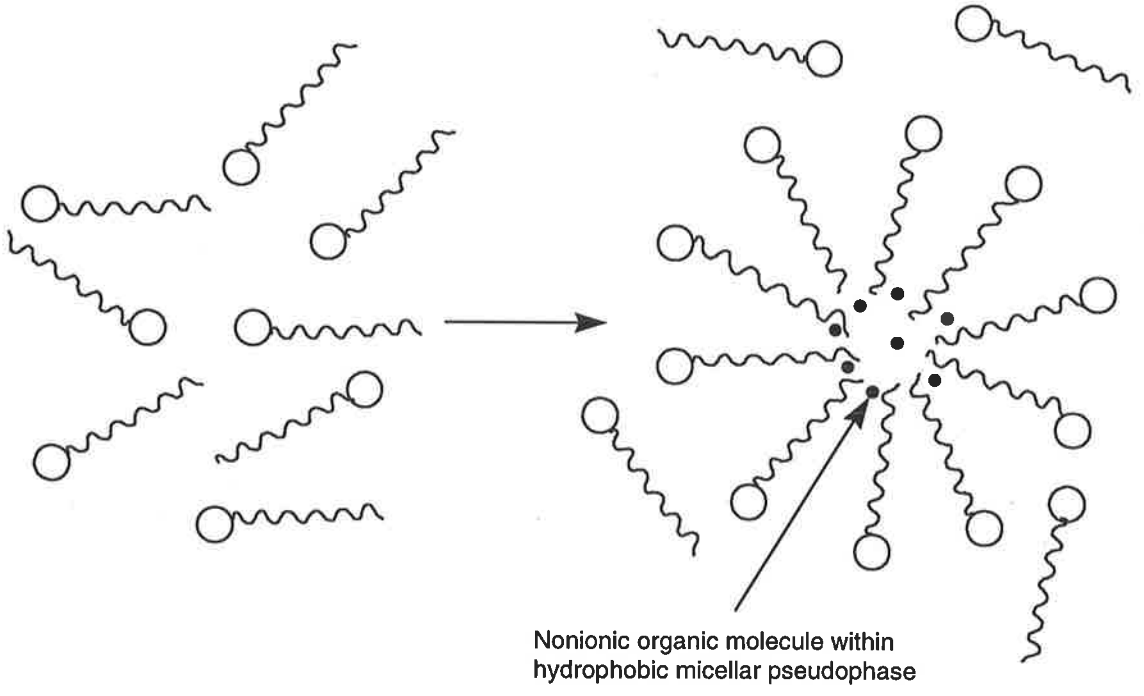
2.10.1 Surfactants

Surfactants are organic compounds having a molecular structure with two-components that have different characteristics - a polar or ionic hydrophilic moeity (head) and a nonpolar hydrophobic moeity (tail) (Smith et al., 1991). The head imparts water solubility, but the hydrophobic tail would prefer to dissolve in nonpolar materials. As a result of their amphiphilic nature, surfactants exhibit special properties when present in an aqueous solution.

On reaching the limit of their solubility in water, the surfactant molecules do not precipitate as do conventional solutes, but begin to clump together in "micelles" (Figure 2.8). Micelle formation is of great importance, not only because a number of other important interfacial phenomena such as solubilization and detergency depend on it, but also because it influences other phenomena that do not directly involve micelles, such as reduction in interfacial tension (Rosen, 1989). Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for every surfactant (Rosen, 1989). CMCs of surfactants typically range between 0.1 and 10 mM for most synthetic surfactants (West and Harwell, 1992). Surfactants in aqueous solution exist predominantly in the monomeric state below the CMC with some fraction of the monomers positioned at water-air or water-solid interfaces (Edwards et al., 1991; Smith et al., 1991). Above the CMC, the concentration of monomers remains constant at the CMC while the excess surfactant leads to the formation of pseudophase micelles. In a micelle, the individual monomers are oriented with their hydrophilic moieties in contact with the aqueous phase and their hydrophobic moieties tucked into the interior of the aggregate (Figure 2.8). This corresponds to minimizing the free energy of the system.



Surfactant molecule amphiphilic structure



Surfactant concentration below CMC (surfactant monomers)

Surfactant concentration above CMC (surfactant monomers and micelle)

Figure 2.8 Schematic diagram of the amphiphilic structure of a surfactant molecule. Additional illustrations portray the existence of surfactant molecules in monomeric form at concentrations below the critical micelle concentration, and in monomeric/micellar form at concentrations above the critical micelle concentration (after DiCesare and Smith, 1994)

The CMC of surfactants can be detected by changes in solution properties e.g. surface tension. Figure 2.9 shows the changes in some properties of an aqueous solution of surfactant in the neighbourhood of the CMC.

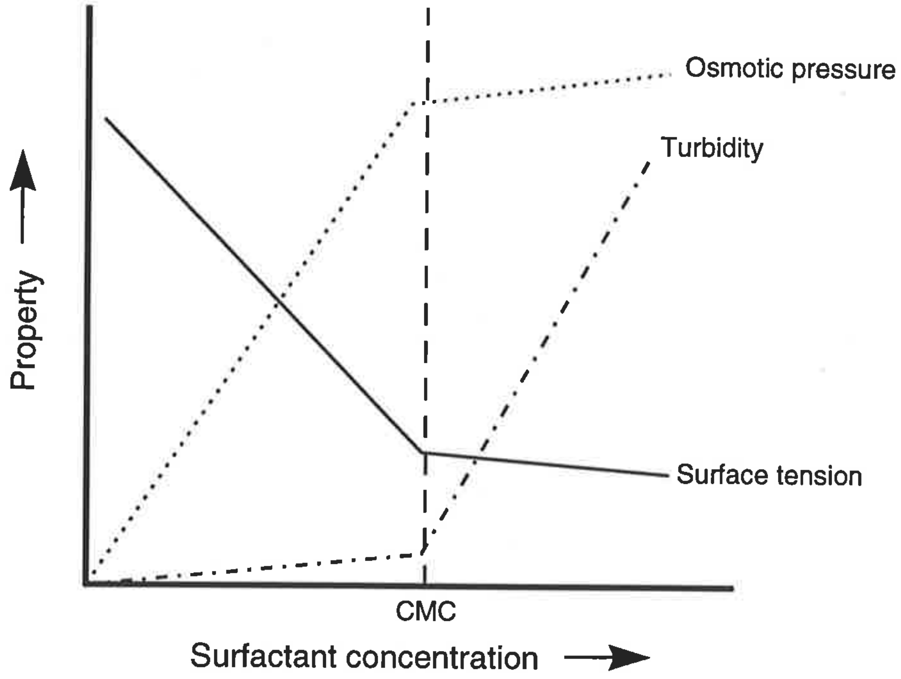
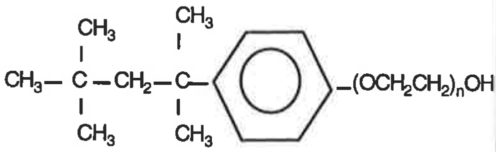
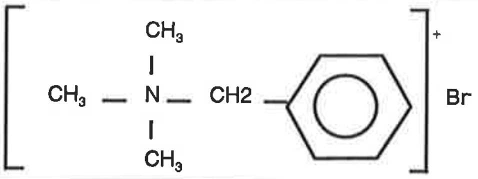


Figure 2.9 Changes in some properties of an aqueous solution of surfactant near the critical micelle concentration (After Connell et al., 1997)

Surfactants are broadly classified into four categories based on the charged nature of the hydrophillic portion (head group) of the molecule. The head group may carry a negative charge (anionic), a positive charge (cationic), both negative and positive charges (amphoteric or zwitterionic), or no charge, though highly polar (nonionic). Some examples of synthetic surfactants in the four classes are illustrated in Table 2.5.

Table 2.5 Some synthetic surfactants in the four surfactant types

Common name	Ionic type	Molecular structure
Sodium dodecylbenzene-sulphonate (DDBS)	Anionic	
Triton series Triton X-100 ave n=9.5 Triton X-114 ave n=7.5 Triton X-405 ave n=40.0	Nonionic	
Fatty alcohol ethoxylates	Nonionic	R—(OCH$_2$CH$_2$)n OH (R=C$_{8-18}$, n = 9-70)
Benzyltrimethyl-ammonium bromide	Cationic	
B-N-alkyl aminopropionic acid	Zwitterionic/amphoterics	RN$^+$H$_2$CH$_2$COO$^-$

2.10.2 Application of Surfactants to Enhance Remediation

Hydrophobic organic compounds (HOCs) are common in many contaminated sites. In these environments, HOCs are often strongly sorbed onto the soils and their persistence is a major impediment to successful remediation of the sites. Laboratory studies have demonstrated that most of these chemicals are either biodegradable or decomposed by hydrolysis but their bioavailability is limited by low water dissolution rates. Moreover, remediation methods such as the conventional pump-and-treat approach are generally not successful due to the low aqueous solubility of the chemicals and their slow desorption from soils in old contaminated sites. The limitations in remediating contaminated aquifers has been subject of several publications (e.g. Hunt et al., 1988; Mackay and Cherry, 1989).

Partitioning into the native SOM may be the additional factor that may protect these hydrophobic contaminants from microbial attack. Over long time periods, changes in properties such as pH, ionic strength, and wetting and drying of soil may cause rearrangement of alkyl and aryl functional groups in SOM (DiCesare and Smith, 1994). This may result in trapping a fraction of the sorbed organic compound. Therefore, it is conceivable that changes in soil solution chemistry (by the addition of cosolvents and surfactants) can potentially enhance the solute mass transfer rate from soil to solution, thus reducing the diffusional tortuosity of the SOM.

The apparent solubility and diffusion rate of pollutants sorbed to the contaminated aquifers can be enhanced by washing with aqueous solutions of surfactants which have been shown to be effective for the removal of hydrocarbons, or polychlorinated biphenyls from soil (Abdul and Gibson, 1991). Some laboratory soil column studies have also shown that surfactants have the capability to remove significant amount of contaminants from soil by solubilising them (Abdul et al., 1990; Edwards et al., 1991; Abdul et al., 1992). Surfactants can also decrease the water-SOM interfacial tension and can cause swelling of the SOM. A recent laboratory study on sorption-desorption and transport conducted by Sahoo and Smith (1997) on long-term TCE-contaminated soil found that the nonionic surfactant Triton X-100 caused a modest increase in the desorption rate of TCE. Another study has investigated the effect of surfactants on the rate of TCE desorption from laboratory-contaminated soil (Deitsch and Smith, 1995). The study reported that Triton X-100 increases the mass transfer coefficient for organic solute desorption from the soil.

There are two general mechanisms by which surfactants can enhance the removal of hydrophobic organic compounds; solubilisation into the aqueous phase and mobilisation of highly sorbed hydrophobic organic compounds from the soil. From an engineering point of view, the easiest approach is solubilisation, which is a result of micelle formation. Mobilisation depends on the tendency of surfactants to lower interfacial tension.

Solubilisation

Surfactants are capable of enhancing the apparent solubility of hydrophobic compounds in water. In pump-and-treat remediation schemes, this enhancement in the solubility is extremely important since a great fraction of the contaminant will be present in the soluble form and can be removed. When a surfactant is added to the aqueous phase, the organic interior of micelles acts as an organic pseudophase into which the organic contaminant can be partitioned. This phenomenon is called solubilisation. It has been demonstrated that the solubility of the organic contaminants can be enhanced many times by aqueous surfactants (Kile and Chiou, 1989; Grimberg et al., 1996). At the CMC, the aqueous solutions of surfactants show a greatly enhanced ability to dissolve chemicals that are otherwise sparingly soluble in water. The enhanced solubilisation potential of surfactants is examplified by 3.5 g of PCE solubilised per each gram of the nonionic surfactant polyoxyethylene nonylphenyl ether, in comparison with its aqueous solubility of 0.002g g^{-1} of water (Saito and Shinoda, 1987). In an aqueous system, the extent to which a compound will concentrate in a micelle can be related to its octanol-water partition coefficient (Edwards et al., 1991), such that larger the K_{ow} of a compound, the greater will be its tendency to concentrate inside the micelle.

A model for solubility enhancement of a solute by surfactants above and below the CMC has been proposed by Kile and Chiou (1989):

$$S_w{}^*/\,S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc}$$

where $S_w{}^*$ is the apparent solute solubility at the total surfactant concentration X, S_w is the intrinsic solubility in pure water, X_{mn} is the concentration of surfactant as monomers, K_{mn} is the partition coefficient of the solute between monomers and water, X_{mc} is the concentration of the surfactant in micellar form, and K_{mc} term is the partition coefficient of the solute between micelles and water.

The solubilisation capacity of a surfactant can be expressed as a molar solubilisation ratio (MSR), defined by Edwards et al. (1991) as:

$$MSR = \frac{C_o - C_{o,cmc}}{C_{surf} - C_{surf,cmc}}$$

where C_o is the molar concentration of the organic in solution, $C_{o,cmc}$ is the molar concentration of organic compound at the CMC, C_{surf} is the molar concentration of surfactant in solution and $C_{surf,cmc}$ is the molar concentration of surfactant at the CMC. Although the values of $C_{o,cmc}$ and $C_{surf,cmc}$ may not be known, the MSR can be obtained from the slope of the solubility curve above the CMC. The MSR has been widely used to characterise the solubility of hydrocarbons in micellar solutions.

Solubility Enhancement above the Surfactant's Critical Micelle Concentration:

The apparent solubility of hydrophobic compounds can be dramatically enhanced in aqueous solutions of surfactants at concentrations above CMC, (Kile and Chiou, 1989; Valsaraj and Thibodeaux, 1989; Edwards et al., 1991). For example, in the case of trichloroethylene (TCE), which has an aqueous solubility of 980 mg L^{-1} at 15°C (Verschueren, 1983), a 20-fold increase in solubility in 0.5 M sodium dodecyl sulphate solution at 15°C has been quoted by West and Harwell (1992). The increased micelle volume present in the bulk solution provides an increased volume of micellar pseudophase available for partitioning of the nonionic organic compound. This partitioning is supported by the demonstration by Edwards et al. (1991) of linear relationships between log K_{mc} (micelle-water partition coefficient) and log K_{ow} for a variety of hydrophobic organic compounds in micellar solutions. This study demonstrated significant increases in the apparent solubilization of polycyclic aromatic hydrocarbons (PAHs). Fountain et al. (1991) also reported a great solubility enhancement of most organic non-aqueous phase liquid (NAPL) contaminants by surfactants at concentration above the CMC.

Solubility Enhancement below the Surfactant's Critical Micelle Concentration:

At aqueous surfactant concentrations below the CMC, surfactant molecules exist in monomeric form. Although the ability of surfactants to enhance the apparent solubility of nonionic compounds above the CMC is extensively reported, and attributed to the presence of pseudophase micelles, the effectiveness of surfactants below the CMC has received very little attention and only been reported for an extremely water insoluble compound, DDT. As the solubility enhancement effect by surfactants at concentrations below their CMCs is comparable in magnitude to the effect with the aquatic humic substances (Kile and Chiou, 1989), the investigation of the water solubility enhancement of hydrophobic pesticides by surfactants below their CMCs is of great importance.

2.11 Effect of Surfactant Micelles on the Alkaline Hydrolysis of Hydrophobic Compounds

Many organic compounds in soil can be degraded through abiotic pathways involving one or more chemical reactions. Hydrolysis can be the dominant pathway for the transformation of many organic compounds (Cowart et al., 1971; Mabey and Mill, 1978). The rates at which the chemicals undergo transformation, however, depend on their physical and chemical properties that vary greatly from compound to compound. Certain pesticides, such as carbamates and organophosphates, are also reported to undergo hydrolysis (e.g. Boulding, 1995). Khan (1980) reported that many organophosphorus pesticides characteristically undergo alkaline hydrolysis in which the hydroxide ion (OH^-) attacks a specific group at a rate which is proportional to the hydroxide ion concentration. The hydrolysis of pesticides has been studied extensively and many of the details of the mechanisms and kinetics of such reactions have been elucidated in well defined buffered systems under laboratory conditions (Burkhard and Guth, 1981; Sabadie, 1996).

Surfactants have been shown to enhance significantly the cleanup of old contaminated sites by enhancing the desorption rate in pump-and-treat schemes. The enhanced solubility of hydrolysable hydrophobic compounds in the presence of surfactants may lead to enhanced breakdown in an alkaline environment. However, such information on pesticides in the presence of surfactants is limited. A study on kinetics of hydrolysis of dicarboximide fungicides (procymidone, iprodione, vinclozolin and chlozolinate) in micellar solutions of anionic, cationic, and nonionic surfactants by Villedieu et al. (1995) showed little influence of nonionic micelles on the hydrolysis of the fungicides. However, they concluded that it is possible to increase or decrease the rate of degradation of fungicides in micellar media by changing the type of surfactant and varying its concentration. In another study, Sundaram et al. (1995) reported that hydrolysis of azadirachtin-A isomer is considerably retarded by the presence of surfactants in the formulation compared with the hydrolysis of the chemical in pure form in aqueous buffered solution at different pH. Most of the studies (e.g. Tentsova et al., 1986; Devos et al., 1993; Yamato et al., 1993) conducted on pharmaceuticals indicate that incorporation of surfactants greatly enhances the chemical stability of drugs by reducing the hydrolysis in aqueous solutions.

Humic substances, like surfactants, enhance the solubility of certain hydrophobic pesticides such as DDT and affect the kinetics of reaction in water (Carter and Suffet, 1982). Highly hydrophobic compounds sorb to the humic substances in a ‘partition-like’ interaction, similar to that with surfactant micelles, where sorbates are partitioned into a microscopic organic phase (Chiou, 1989). An enhancement in hydrolysis rate constants of 2, 4-D esters by dissolved organic materials in aqueous solutions has been reported by Struif et al (1975). Later studies by Perdue and Wolfe (1982) on the rate of alkaline hydrolysis of *n*-octyl ester of 2,4-D (2,4-DOE) in the presence and absence of soluble humic materials in water revealed that the second-order rate constant for hydrolysis in the presence of humic substances was lower than in distilled water. They suggested that a fraction of 2,4-DOE partitioned to the humic material did not undergo alkaline hydrolysis. They attributed the enhanced rate of hydrolysis of 2,4-D esters observed by Struif et al. (1975) to microbially mediated hydrolysis.

In summary, it is evident that surfactants may offer potential to enhance the removal of pesticides from soils by solubilising significant amount of contaminants. They may also be useful in mobilising the contaminants from aquifers by decreasing the interfacial tension between the organic and water phases. However, only limited experimental data are available on use of surfactants to remediate sites contaminated with pesticides, including their effect on the rate of alkaline hydrolysis of the pesticides.

2.12 Summary

Sorption and release phenomena are pivotal in controlling the fate and behaviour of organic pesticides in soils. Knowledge concerning sorption and release is essential for the assessment of the fate of pesticides in the environment, and for the assessment of potential adverse impacts. There are comparatively few published data dealing with the behaviour of pesticides in Australian soils and the information on Pakistani soils is even more scarce. The registration authorities in Pakistan rely mostly on the data from overseas. However, this approach may not be appropriate as soils in Pakistan as well as in Australia differ in many respects from those on which the bulk of the research on pesticides has been undertaken. The most important factors controlling behaviour of pesticides, are the amount and nature of SOM and the environmental conditions. Most of the Australian and

Pakistani soils are low in organic matter and they perhaps differ in nature of the organic matter as well, due to nature of vegetation and the peculiarities of the environment in which the soils developed. Consequently, it is unlikely that the data obtained from overseas and prediction on sorption and release behaviour of organic pesticides is directly applicable to the soils of Australia and Pakistan.

There are also considerable gaps in our knowledge in the influence of the nature of SOM on the sorption of nonionic pesticides, release of sequestered pesticides and the influence of surfactants on the mobilisation and release of pesticides from historically contaminated soils.

CHAPTER 3

General Materials and Methods of Pesticide Analysis

3.1 Introduction

In this chapter, the general methods and materials used in the experiments, including the soils, pesticides and their properties, and the development/optimisation of analytical methods of pesticides have been described. Other methods specific to various experiments have been described in respective chapters.

A variety of analytical techniques are currently available for the determination of pesticides, including gas chromatography (GC), capillary electrophoresis, high performance liquid chromatography (HPLC), immunoassay and bioassay. Gas chromatography is commonly coupled with a variety of detectors like flame ionisation detector (FID), flame photometric detector (FPD) electron capture detector (ECD), nitrogen-phosphorus detector (NPD) and mass spectrometer (MS) (Keith, 1996). In recent decades, HPLC has become an important technique for analysis of pesticides (Singh, 1989; Sherma, 1995; Powley and Bernard, 1998). The increasing use of HPLC is mainly due to its suitability for analysis of thermally labile pesticides (e.g. carbamates), and polar pesticides and their metabolites that require derivatisation prior to GC analysis (Sherma, 1995). A further advantage of liquid chromatography may lie in the need for less expensive cleanup of samples before determination than required with gas chromatographic methods or even no cleanup. Given the mildness of the technique and the plethora of high efficiency columns currently available, HPLC appears to be ideally suited for pesticide analysis. However, HPLC methods are not available in the literature for quantitative determination of all commonly used pesticides.

In this chapter, the general materials and the analytical methods that provided the quantitative determination of 13 commonly used pesticides using reversed-phase HPLC with UV/Visible detector are presented. Other specific materials and methods are described in the relevant chapters.

3.2 Soils

In sorption studies, a total of 48 soils were used. They were collected from several locations in Pakistan, Australia, and the UK. The soils used were chosen because their characteristics span a wide range of soil properties. The soils had no known recent pesticide use.

3.2.1 Pakistani Soils

Thirteen Pakistani soils were collected from three main agricultural zones. Soils Pk2, Pk4, Pk6 and Pk18 were collected from an area under intensive agriculture in the central Punjab province. Soils Pk7, Pk8, Pk9 and Pk10 were sampled at the Rice Research Institute, Kalashah Kaku, representing the rice zone of the Punjab. Soils Pk11, Pk12, Pk13, Pk15 and Pk16 were taken from the Cotton Research Station and a Model Farm in Multan, and represent the cotton zone where pesticide use is abundant and frequent during the cropping season. Together these soils cover a wide range of soil types of Pakistan.

3.2.2 Australian Soils

A total of twenty six Australian soils were used in various experiments. Among the Australian soils, SS6, SS7, SS8, ACU1, B211, N19, URB-P, Buckelboo and Qld had various origins and were generously provided by Dr J. Skjemstad of CSIRO Land and Water. Soils Avon1, Avon2, Mt. Mary and Pinnaroo soils were agricultural soils from South Australia, and soils 1413, 1416, 1418, 1422, 1428, 1432, 1433, 1433A2, 1437, and 1440A2 were from the Mt. Crawford Forest in South Australia. Soil WAV was a virgin soil and WAC was from an area under vegetables: both belonged to the Bassendean association of Swan Coastal Plain in Western Australia. Soil WFS was a water repellent soil from the area in Western Australia.

3.2.3 UK Soils

Soils from the UK were collected at the Rothamsted Experimental Station to represent long term land uses of different types. They included two soils from the Highfield, one (Highfield Grass) from under old grassland, a site that has been under grass for at least

130 years and the other (Highfield Fallow) from the area uncropped since 1960. Five soils were taken from the Broadbalk experiment, four were from arable plots within Section 3 of the Continuous Wheat Experiment: plot 22 which has received farmyard manure annually since 1843; plot 03 which received no manure or inorganic fertiliser since 1843; plot 05 which has received P and K fertilisers but no N since 1852 and plot 08 which has P, K, and N fertilisers applied annually. The fifth sample was from the wooded section of Broadbalk Wilderness, which was arable until 1881 when it was reverted to deciduous woodland. Two soils were from Geescroft, one from Geescroft arable field and one from Geescroft Wilderness which was reverted to deciduous woodland in 1881.

3.3 Measurement of Soil Properties

The soil samples were air dried and passed through a 2 mm stainless steel sieve. The soils were characterised for their physical and chemical properties following standard procedures. Particle size distribution was determined by the international pipette method as outlined by Black (1965). The total organic C content was determined on a microprocessor-controlled LECO induction furnace (LECO CR 12 carbon analyser, manufactured by the LECO Corporation, USA) as described by Merry and Spouncer (1988) and corrected for carbonate-C determined by a volumetric calcimeter method (Allison and Moodie, 1965) where appropriate. The pH values of the soils were determined in 0.01M $CaCl_2$ at a soil to solution ratio of 1:5. The clay minerals were identified by X-ray diffraction (XRD). The clay suspension was pipetted onto a 0.025 µm millipore membrane filter under suction to remove water and to obtain oriented specimens. Samples were then saturated with 1M $MgCl_2$. The excess $MgCl_2$ was removed by washing with deionised water prior to treatment of the sample with 20% glycerol in methanol. The oriented samples were glued onto aluminium plates and dried at room temperature. The samples were examined with a Philips PW 1729 X-ray diffractometer. X-ray diffraction data were collected and stored by an IBM-compatible PC using a control system developed by Self (1989) and were analysed using the software package XPLOT (Raven, 1990). The XRD spectra of the soils characterised are given in Appendix 3.1. Clay mineralogy of Pakistani soils was dominantly illite and that of Australian soils was kaolinite. The dominant mineral in the UK soils was kaolinite (P. Powlton, Pers. Comm.).

Among the other properties, organic C ranged from 2.8-22.2, 3.0-138.0 and 7.0-86.0 g kg^{-1}, pH ranged from 7.56-8.56, 4.30-8.02 and 3.74-7.34; clay ranged from 140-320, 12-755 and 232-427 g kg^{-1} in Pakiatani, Australian and the UK soils, respectively. All Pakistani soils were alkaline in nature. The physical and chemical properties of the soils are presented in Table 3.1.

3.4 Pesticides Used

Thirteen pesticides, namely, ametryn, atrazine, bifenthrin, carbaryl, dichlorvos, dicrotophos, ethion, imazethapyr, methomyl, monocrotophos, phosalone, thiodicarb and trifluralin, were selected for the development of analytical methods by HPLC. These pesticides are representatives of the classes of pesticides commonly used in agriculture. Of these, seven pesticides, namely, ametryn, imazethapyr, carbaryl, phosalone, bifenthrin, dichlorvos and monocrotophos were used in sorption studies. Pesticide contaminated soils of known history from Pakistan were screened for a range of pesticides by Australian Government Analytical Laboratories (AGAL) in combination of following the methods of analysis of the above mentioned pesticides developed in laboratory. Ethion found in an historically contaminated soil from a cattle tick dip site in Australia and carbaryl in an old pesticide storage site in Pakistan were selected for release studies (Chapter 7). Technical grade chemicals (>98% purity except trifluralin which had 95% purity) were used. Imazethapyr and dicrotophos were puchased from Chem Service, West Chester, PA, USA; trifluralin and atrazine were purchased from Sigma-Aldrich Pty. Ltd, NSW, Australia; carbaryl, methomyl and thiodicarb were donated by Rhône-Poulenc Rural Australia Pty Ltd, Australia; bifenthrin was a gift from FMC International A. G., Australia; and ametryn, phosalone, dichlorvos, monocrotophos and ethion were obtained from the Pesticide Division of the Plant Protection Institute, Faisalabad, Pakistan, where these compounds were originally supplied by international pesticide marketing companies. Some selected properties of the pesticides are given in Table 3.2 and the structural formulae are depicted in Figure 3.1.

For development of the methods, a standard stock solution containing 1000 mg L^{-1} of each of the compounds was prepared in methanol or acetonitrile and serially diluted as required with the respective solvent to obtain final working standard solutions of known

Table 3.1 Some pertinent physical and chemical properties of the soils used

Soil#	Soil name	Location[A]	Depth	OC(Leco)	pH	Sand	Silt	Clay	Clay Minerals[B]
			(cm)	(g kg^{-1})	(1:5 $CaCl_2$)	(g kg^{-1})			
A. Pakistani Soils									
1	Pk2	Jhumra, Faisalabad	0-15	3.88	8.16	653	95	252	I>K>V=RIM/Q
2	Pk4	Mamoon Kanjan, Faisalabad	0-15	6.66	8.07	129	715	156	I>K>V>Q
3	Pk6	Satiana, Faisalabad	0-15	13.82	8.56	221	511	268	I>K>V>Q=RIM
4	Pk7	RRI, Kalashah Kaku	0-15	6.84	8.08	107	741	152	I>K>V:Q(minor)
5	Pk8	RRI, Kalashah Kaku	15-30	3.88	8.35	101	759	140	I>K>V:Q(minor)
6	Pk9	RRI, Kalashah Kaku	0-15	6.54	7.80	224	620	156	I>K>V=RIM
7	Pk10	RRI, Kalashah Kaku	15-30	2.79	8.07	217	603	180	I>K>V=RIM
8	Pk11	CRS, Multan	0-15	6.92	8.30	84	624	292	I>K>V=Q=RIM
9	Pk12	CRS, Multan	15-30	6.18	8.51	82	746	172	I>K>V>RIM
10	Pk13	CRS, Multan	0-15	9.70	8.20	98	610	292	I>K>Q=V>RIM
11	Pk15	Gohar Model Farm, Multan	15-30	6.50	8.03	128	552	320	I>K>Q=V>RIM
12	Pk16	Gohar Model Farm, Multan	0-15	22.20	7.56	215	493	292	I>K>V=Q>RIM
13	Pk18	AARI, Faisalabad	0-15	5.72	8.47	245	583	172	I>K>V=RIM>Q

Table 3.1 Some pertinent physical and chemical properties of the soils used.(continued)

Soil#	Soil name	Location^A	Depth (cm)	OC(Leco) (g kg^{-1})	pH (1:5 $CaCl_2$)	Sand	Silt	Clay	Clay Minerals^B
						(g kg^{-1})			
B. Australian Soils									
14	SS6	Tallagalla, Qld	0-5	70.1	5.40	212	309	479	K, I, Q*
15	SS7	Toowoomba,Qld	0-5	138.0	4.69	121	719	160	K, G, Ha*
16	SS8	Waco, Qld	0-10	23.2	7.21	40	281	679	S, K, Q*
17	Buckelboo	Kimba, SA	0-10	12.9	7.29	626	114	260	K>RIM
18	Avon1	Avon, SA	0-10	12.9	7.38	731	139	130	K>I>RIM
19	Avon2	Avon, SA	10-20	3.8	8.02	719	101	180	K>RIM
20	Mt.Mary	Mt. Mary, SA	0-10	10.2	7.63	681	109	210	K>I>RIM
21	Pinnaroo	Pinnaroo, SA	0-5	12.0	7.54	759	59	182	K>I
22	ACU1	Gumeracha, SA	0-10	25.6	4.72	94	694	212	IK/S,Q**
23	B211	Toowoomba, Qld	0-5	34.3	5.94	33	213	755	Not determined
24	N19	Narayan, Qld	0-15	44.8	5.92	75	222	703	Not determined
25	URB-P	Adelaide, SA	0-10	26.7	4.90	145	683	172	I, K, Q*
26	Qld	Chinchilla, Qld	0-10	38.4	5.20	94	391	515	Not determined
27	1413	Mt.Crawford Forest, SA	0-10	8.0	5.10	910	60	30	K>I>Q>RIM

Table 3.1 Some pertinent physical and chemical properties of the soils used.(continued)

Soil#	Soil name	Location[A]	Depth (cm)	OC(Leco) (g kg^{-1})	pH (1:5 $CaCl_2$)	Sand	Silt	Clay	Clay Minerals[B]
						(g kg^{-1})			
28	1416	Mt.Crawford Forest, SA	0-15	15.0	4.40	700	190	110	K>V>Q>RIM
29	1418	Mt.Crawford Forest, SA	0-5	20.0	5.10	860	100	40	K>I>Q>V
30	1422	Mt.Crawford Forest, SA	0-10	25.0	4.80	790	90	110	K>RIM=V>I>Q
31	1428	Mt.Crawford Forest, SA	0-10	23.0	4.60	880	80	40	K>I>Q
32	1432	Mt.Crawford Forest, SA	0-10	26.0	4.40	820	120	60	K>V=I>RIM>Q
33	1433	Mt.Crawford Forest, SA	0-10	58.0	4.60	630	160	210	K>I=RIM=V=Q(Minor)
34	1433-A2	Mt.Crawford Forest, SA	20-30	21.0	4.40	650	160	190	K>I=RIM=V=Q(Minor)
35	1437	Mt.Crawford Forest, SA	0-15	12.0	4.30	920	40	40	K=RIM>I>Q
36	1440-A2	Mt.Crawford Forest, SA	20-30	3.0	4.40	920	50	30	V=RIM>K>I>Q
37	WAV	Swan Costal Plain, WA	0-10	10.0	4.69	966	22	12	K***
38	WAC	Swan Costal Plain, WA	0-10	16.0	4.67	954	18	28	K***
39	WFS	Western Flat, WA	0-10	7.0	5.05	957	27	16	Not determined

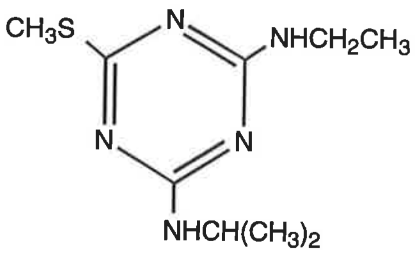
Table 3.1 Some pertinent physical and chemical properties of the soils used (continued)

Soil#	Soil name	Location[A]	Depth (cm)	OC(Leco) (g kg^{-1})	pH (1:5 CaCl$_2$)	Sand	Silt	Clay	Clay Minerals[B]
						(g kg^{-1})			
C. UK Soils									
40	Highfield Grass	IACR, Rothamsted	0-15	20.0	5.72	121	475	404	K dominated
41	Highfield Fallow	IACR, Rothamsted	0-15	10.0	4.57	102	666	232	K dominated
42	Broadbalk Plot 22	IACR, Rothamsted	0-15	19.0	7.16	177	455	367	K dominated
43	Broadbalk Plot 03	IACR, Rothamsted	0-15	7.0	7.34	145	561	296	K dominated
44	Geescroft Wilderness	IACR, Rothamsted	0-15	41.0	3.74	142	447	411	K dominated
45	Geescroft Arable	IACR, Rothamsted	0-15	22.0	6.20	160	472	368	K dominated
46	Broadbalk Wilderness	IACR, Rothamsted	0-15	86.0	5.10	184	389	427	K dominated
47	Broadbalk Plot 05	IACR, Rothamsted	0-15	11.0	7.06	154	566	280	K dominated
48	Broadbalk Plot 08	IACR, Rothamsted	0-15	10.0	7.14	172	488	340	K dominated

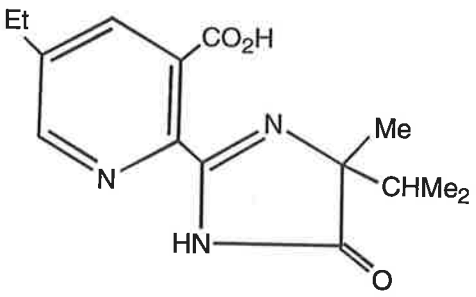
[A] Qld=Queensland, SA=South Australia, WA=Western Australia; RRI=Rice Research Institite; CRS=Cotton Research Station; AARI=Ayub Agricultural Research Institute; IACR=Institute of arable Crops Research

[B] I = illite, K = kaolinite, V = vermiculite, Q = quartz, G = gibbsite, Ha = haematite, S = smectite, RIM = randomly interstratified materials

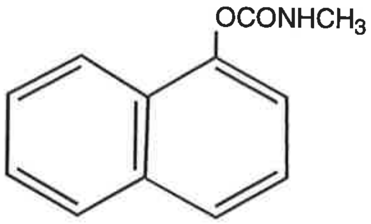
* Skjemstad et al. (1994); ** Skjemstad et al. (1996); ***Kookana and Aylmore (1993)



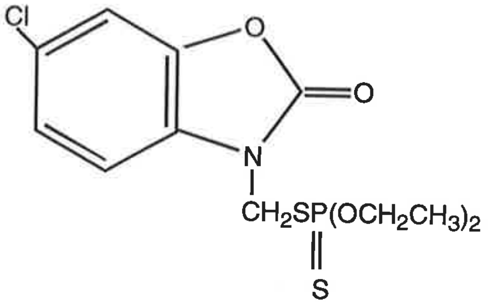
Ametryn



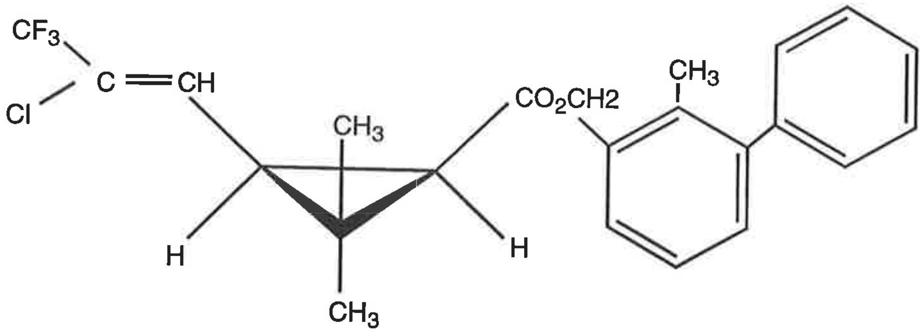
Imazethapyr



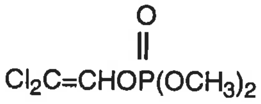
Carbaryl



Phosalone

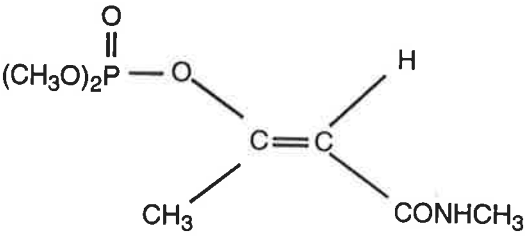


Bifenthrin

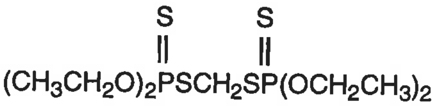


$Cl_2C{=}CHO\overset{\overset{O}{\|}}{P}(OCH_3)_2$

Dichlorvos

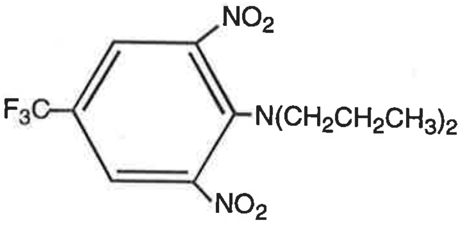


Monocrotophos

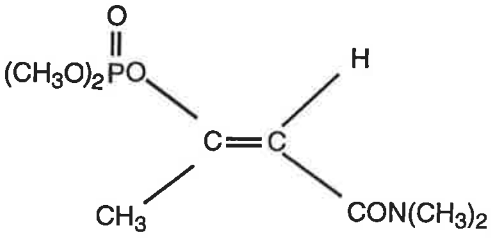


$(CH_3CH_2O)_2\overset{\overset{S}{\|}}{P}SCH_2S\overset{\overset{S}{\|}}{P}(OCH_2CH_3)_2$

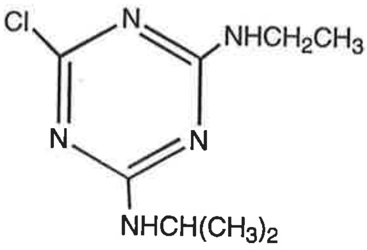
Ethion



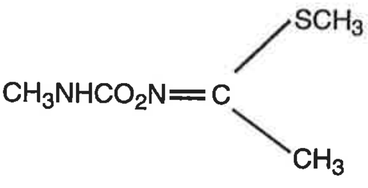
Trifluralin



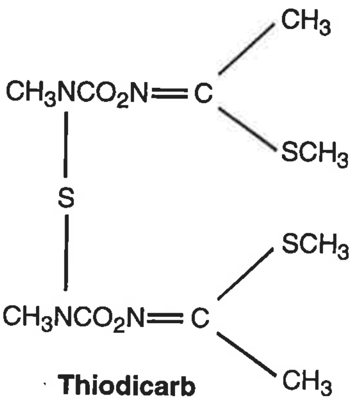
Dicrotophos



Atrazine



Methomyl



Thiodicarb

Table 3.2 Some selected properties of the pesticides used

Common name	Chemical name	Chemical formula	Chemical family	Molecular weight	Aqueous solubility	Ionizability (pKa)	Vapour pressure
Ametryn	N^2-ethyl-N^4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine	$C_9H_{17}N_5S$	Triazine	227.3	200 mg L^{-1}(20 °C)	4.1	0.365 mPa (25 °C)
Imazethapyr*	(RS)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid	$C_{15}H_{19}N_3O_3$	Imidazolinone	289.3	1.4 g L^{-1} (25 °C)	2.1, 3.9**	-
Carbaryl	1-naphthyl methylcarbamate	$C_{12}H_{11}NO_2$	Carbamate	201.2	120 mg L^{-1}(20 °C)	Nonionic	4.1×10^{-2} mPa (23.5 °C)
Phosalone	S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl O,O-diethyl phosphorodithioate	$C_{12}H_{15}ClNO_4PS_2$	Organophosphorus	367.8	3.05 mg L^{-1} (25 °C), 10 mg L^{-1} (rt)***	Nonionic	<0.06 mPa (25 °C)
Bifenthrin	2-methylbiphenyl-3-ylmethyl (Z)-(1RS, 3RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate	$C_{23}H_{22}ClF_3O_2$	Pyrethroid	422.9	0.1 mg L^{-1}	Nonionic	0.024 mPa (25 °C)
Dichlorvos	2,2-dichlorovinyl dimethyl phosphate	$C_4H_7Cl_2O_4P$	Organophosphorus	221.0	18 g L^{-1} (25 °C),	Nonionic	2.1×10^{3} mPa (25 °C)
Monocrotophos	dimethyl (E)-1-methyl-2-(methylcarbamoyl) vinyl phosphate	$C_7H_{14}NO_5P$	Organophosphorus	223.2	Completely miscible	Nonionic	2.9×10^{-1} mPa (20 °C)
Ethion	O,O,O′,O′-tetraethyl S,S′-methylene bis (phosphorodithioate)	$C_9H_{22}O_4P_2S_4$	Organophosphorus	384.5	2 mg L^{-1} (25 °C)	Nonionic	0.2 mPa (25 °C)
Dicrotophos	(E)-2-dimethylcarbamoyl-1-methylvinyl dimethyl phosphate	$C_8H_{16}NO_5P$	Organophosphorus	237.2	100% (miscible)	Nonionic	9.3 mPa (20 °C)
Trifluralin	α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-*p*-toluidine	$C_{13}H_{16}F_3N_3O_4$	Dinitroaniline	335.3	0.184 (pH5), 0.221 (pH7), 0.189 (pH9) all in mg L^{-1}	Nonionic	6.1 mPa (25 °C)
Atrazine,	6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine	$C_8H_{14}ClN_5$	Triazine	215.7	33 mg L^{-1} (pH7, 22 °C)	1.7	3.85×10^{-2} mPa (25 °C)
Methomyl	S-methyl N-(methylcarbamoyloxy) thioacetimidate	$C_5H_{10}N_2O_2S$	Carbamate	162.2	57.9 g L^{-1} (25 °C)	Nonionic	0.72 mPa (25 °C)
Thiodicarb	3,7,9,13-tetramethyl-5,11-dioxa-2,8,14-trithia-4,7,9,12-tetra-azapentadeca-3,12-diene-6,10-dione	$C_{10}H_{18}N_4O_4S_3$	Carbamate	354.5	35 mg L^{-1} (25 °C)	Nonionic	5.7 mPa (20 °C)

All information from Tomlin (1988) except where otherwise indicated. * Hartley, 1987; ** Hornsby et al., 1996; ***Kenaga, 1980, room temperature concentrations. Both methanol and acetonitrile have been widely demonstrated to provide good, reproducible analytical separation of pesticides.

3.5 Reagents

HPLC grade solvents were used. The acetonitrile and methanol (HiperSolv^{TM} BDH, England) used in the mobile phase were degassed in a sonicating water bath prior to use. Water was obtained from a Milli-Q $_{plus}$ Ultra-Pure Water System (Milford, M. A., USA).

3.6 Instrumentation

For absorbance spectra, a Varian liquid chromatograph was used with a polychrom diode array (PDA) UV detector (Model 9065), a pump (Varian 9012), an autosampler (Varian 9100) and Star Chromatography Workstation for processing the spectra. The wavelength for absorption of each pesticide was established initially. The PDA detector provids an opportunity to explore all wavelengths in the UV range and select the wavelength which maximises the instrumental sensitivity during monitoring.

A high performance liquid chromatograph (Waters Chromatography Division) equipped with a variable wavelength UV detector (Lambda-Max Model 481), a degasser (Model ERC-3310, ERMA Optical Works, Tokyo), an HPLC pump (Model 510) and an autosampler (Model 710B WISP) was utilised to analyse the samples. Data was processed using the Millennium^{TM} Chromatography Manager (Version 2.1).

The pesticides were separated on a Waters Radial-Pack C18 cartridge (100 mm × 5.0 mm ID, 4 μm partcle size). A Nova-pack guard column (Waters) was used as a precolumn. The separation of pesticides was carried out using isocratic elution at a flow rate of 1.0 mL min^{-1} (except for imazethapyr where flow rates were 1.0, 1.5 and 2.0 mL min^{-1}) with injection volume of 15 μl. The chromatographic operating conditions are given in Table 3.3.

3.7 Results and Discussion

The absorbance spectra of selected pesticides are given in Appendix 3.2. The optimum wavelengths used for the compounds are tabulated in Table 3.3. Wavelengths <205 nm were avoided due to serious drawbacks of UV detection of pesticides arising from high UV absorbance shown by solvents and matrix interferences below this wavelength.

The typical chromatograms of the compounds under the best conditions (shaded columns in Table 3.3) are given in Figure 3.2 through 3.5. The solvent blanks were also performed and the chromatograms are given in the Figure 3.5. The figure shows that there were no contribution in the absorbance of the solvents in the region of retention times of the various pesticides studied.

The separation of the compounds was done using isocratic conditions. The compositions of mobile phases were selected from various proportions of organic solvents and water tried for optimum separation and suitable retention times. Given the structural diversity among the pesticides studied, no retention time relationship between them was expected nor was observed.

Acetic acid (0.5% V/V) was used in the mobile phase solvent mixture for imazethapyr. An acetonitrile-water mobile phase was found unsuitable for good separation of monocrotophos, dicrotophos and methomyl due to their very high aqueous solubilities, but methanol-water mobile phase yielded good resolution with a ratio of 25:75. Table 3.3 summarises the results obtained with various methanol + water and acetonitrile + water mixtures as the mobile phase. Retention times and peak areas of the pesticides under test after different times of storage showed no significant difference.

A mixture containing dichlorvos, atrazine and ametryn was also separated using acetonitrile:water (35:65) with retention times of 4.6, 6.8 and 11.7 min using wavelength of 220 nm. Phosalone and ethion mixture was also done together using acetonitrile :water (75:25) as a mobile phase at wavelength of 205 with retention times of 3.4 and 5.8 min, respectively. However, at the same HPLC conditions, trifluralin showed the same

Table 3.3 Representative HPLC retention times of the pesticides under different experimental conditions (The shaded row shows the selected mobile phase and wavelength)

Pesticide	Mobile phase	Composition	Wavelength	Flow rate (mL min^{-1})	Retention time (min)
Ametryn	Methanol:water	80:20	220	1.0	No separation
	Methanol:water	70:30	220	1.0	4.38
	Methanol:water	60:40	220	1.0	8.52
	Acetonitrile:Water	80:20	220	1.0	No separation
	Acetonitrile:Water	60:40	220	1.0	3.25
	Acetonitrile:Water	40:60	220	1.0	6.48
	Acetonitrile:Water	35:65	220	1.0	11.68
Imazethapyr	Methanol:Water:Acetic acid	40:60:0.5%	254	1.0	6.72
	Methanol:Water:Acetic acid	40:60:0.5%	254	1.5	5.30
	Methanol:Water:Acetic acid	40:60:0.5%	254	2.0	3.98
Carbaryl	Methanol:water	60:40	220	1.0	3.23
	Acetonitrile:Water	35:65	220	1.0	6.60
Phosalone	Methanol:Water	70:30	205	1.0	8.97
	Acetonitrile:Water	80:20	205	1.0	2.73
	Acetonitrile:Water	75:25	205	1.0	3.42
	Acetonitrile:Water	70:30	205	1.0	4.35
	Acetonitrile:Water	60:40	205	1.0	10.93
Bifenthrin	Methanol:Water	88:12	205	1.0	8.57
	Acetonitrile:Water	85:15	205	1.0	7.92
Dichlorvos	Methanol:Water	80:20	205	1.0	No separation
	Methanol:Water	70:30	205	1.0	No separation
	Methanol:Water	60:40	205	1.0	2.83
	Methanol:Water	40:60	205	1.0	10.30
	Acetonitrile:Water	80:20	205	1.0	No separation

Table 3.3 Representative HPLC retention times of the pesticides under different experimental conditions (continued)

Pesticide	Mobile phase	Composition	Wavelength	Flow rate (mL min^{-1})	Retention time (min)
	Acetonitrile:Water	60:40	205	1.0	2.03
	Acetonitrile:Water	40:60	205	1.0	3.91
	Acetonitrile:Water	35:65	205	1.0	4.58
Monocrotophos	Methanol:Water	80:20	220	1.0	No separation
	Methanol:Water	70:30	220	1.0	No separation
	Methanol:Water	60:40	220	1.0	No separation
	Methanol:Water	40:60	220	1.0	2.13
	Methanol:Water	25:75	220	1.0	5.33
	Methanol:Water	20:80	220	1.0	7.93
	Acetonitrile:Water	80:20	220	1.0	No separation
	Acetonitrile:Water	60:40	220	1.0	No separation
	Acetonitrile:Water	40:60	220	1.0	No separation
	Acetonitrile:Water	20:80	220	1.0	2.58
Ethion	Methanol:Water	80:20	205	1.0	5.95
	Acetonitrile:Water	80:20	205	1.0	4.27
	Acetonitrile:Water	75:25	205	1.0	5.85
	Acetonitrile:Water	72:28	205	1.0	6.13
	Acetonitrile:Water	70:30	205	1.0	8.06
	Acetonitrile:Water	60:40	205	1.0	27.51
Dicrotophos	Methanol:Water	25:75	205	1.0	7.18
	Acetonitrile:Water	60:40	205	1.0	No separation
	Acetonitrile:Water	35:65	205	1.0	No separation
	Acetonitrile:Water	25:75	205	1.0	No separation

Table 3.3 Representative HPLC retention times of the pesticides under different experimental conditions (continued)

Pesticide	Mobile phase	Composition	Wavelength	Flow rate (mL min^{-1})	Retention time (min)
Trifluralin	Acetonitrile:Water	80:20	205	1.0	4.21
	Acetonitrile:Water	75:25	205	1.0	5.75
	Acetonitrile:Water	72:28	205	1.0	6.06
	Acetonitrile:Water	70:30	205	1.0	8.06
	Acetonitrile:Water	60:40	205	1.0	27.33
Atrazine	Methanol:Water	80:20	220	1.0	No separation
	Methanol:Water	70:30	220	1.0	2.65
	Methanol:Water	60:40	220	1.0	4.27
	Methanol:Water	40:60	220	1.0	19.58
	Acetonitrile:Water	80:20	220	1.0	No separation
	Acetonitrile:Water	60:40	220	1.0	2.53
	Acetonitrile:Water	40:60	220	1.0	7.88
	Acetonitrile:Water	35:65	220	1.0	6.80
Methomyl	Methanol:Water	70:30	234	1.0	No separation
	Methanol:Water	25:75	234	1.0	3.73
	Acetonitrile:Water	35:65	234	1.0	No separation
	Acetonitrile:Water	25:75	234	1.0	No separation
Thiodicarb	Methanol:Water	70:30	234	1.0	No separation
	Acetonitrile:Water	60:40	234	1.0	No separation
	Acetonitrile:Water	35:65	234	1.0	4.55

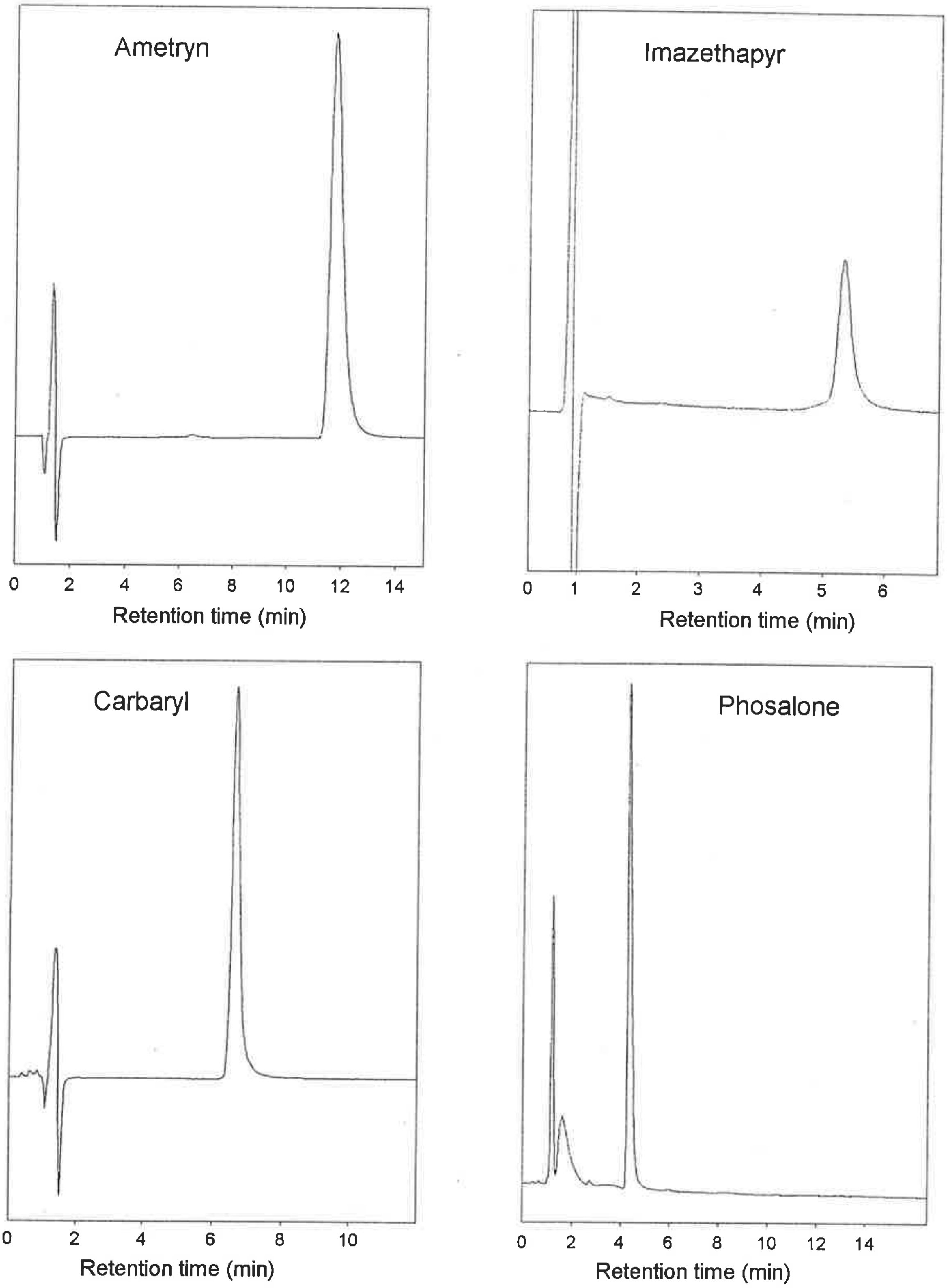


Figure 3.2 Typical chromatograms for ametryn, imazethapyr, carbaryl and phosalone

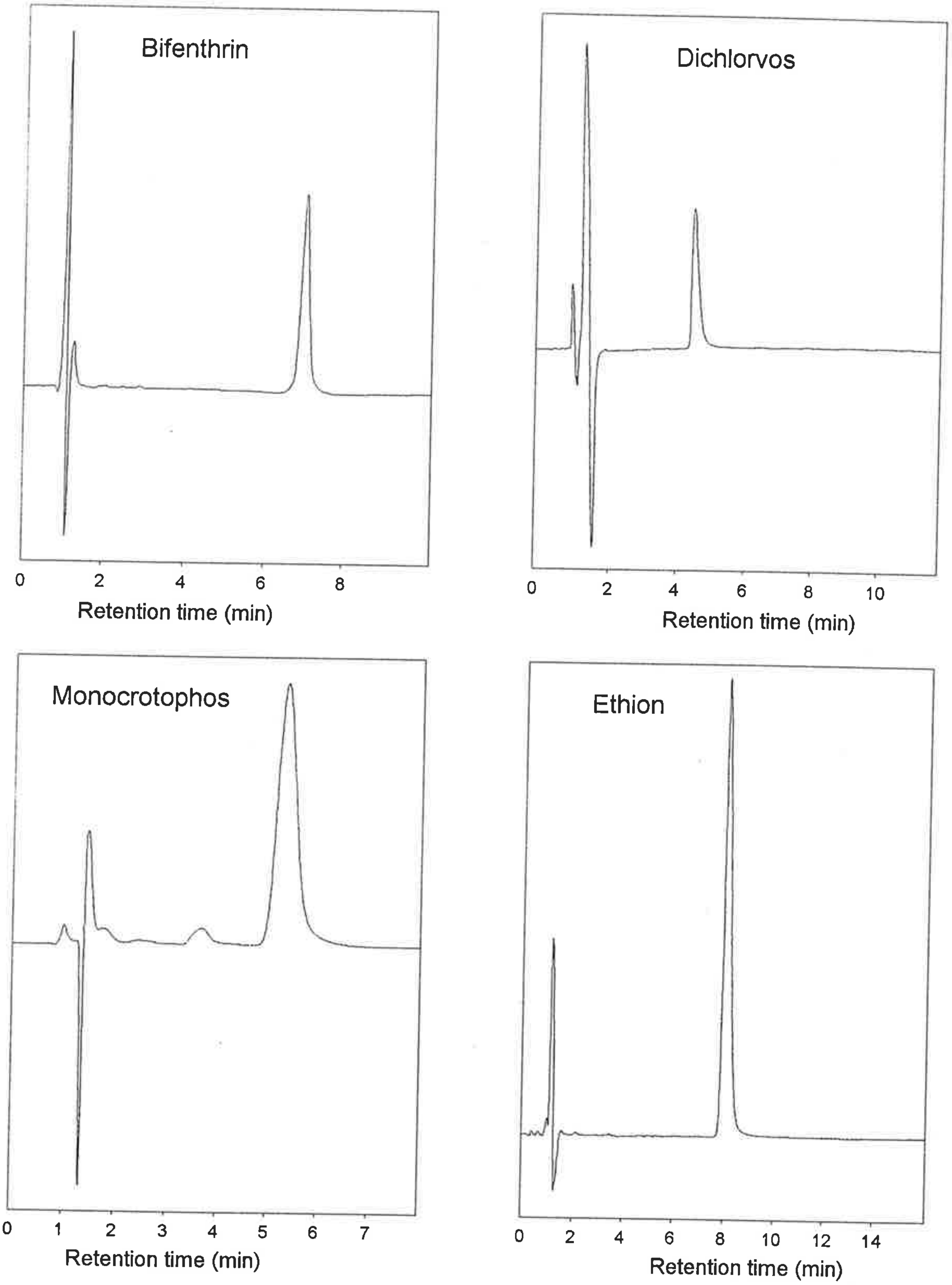


Figure 3.3 Typical chromatograms for bifenthrin, dichlorvos, monocrotophos and ethion

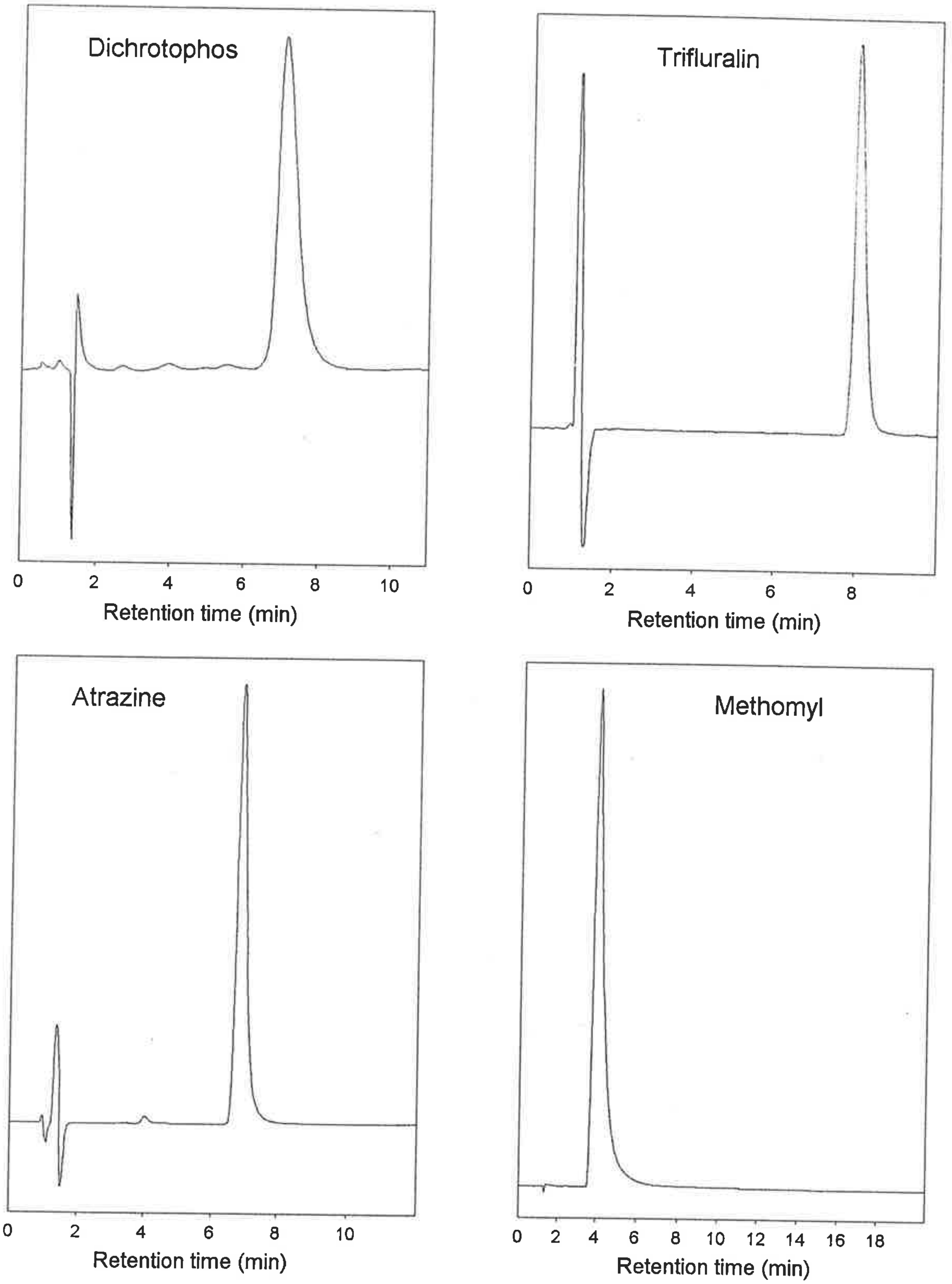


Figure 3.4 Typical chromatograms for dicrotophos, trifluralin, atrazine and methomyl

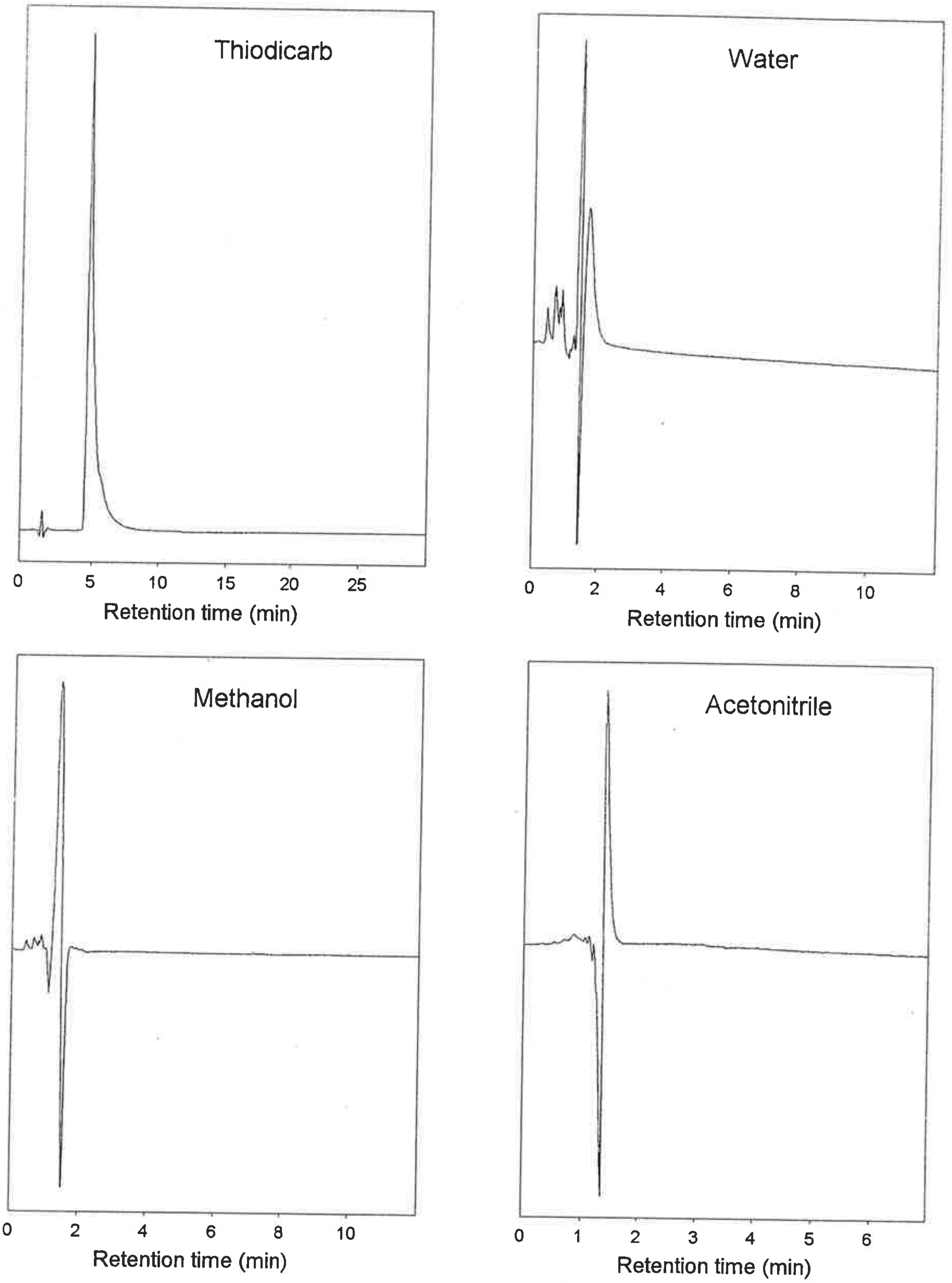


Figure 3.5 Typical chromatograms for thiodicarb, water, methanol and acetonitrile

retention time as that for ethion and peaks of the both compounds in mixed standard merged together.

The great advantage of these methods is the simplicity of analysis, without any sacrifice of time for lengthy cleanup procedures necessary with other methods using the GC technique. The HPLC methods described above are also equally applicable for the formulated pesticides and can be used for quality testing of pesticides for monitoring. The UV detector in liquid chromatography is the most common, and the C18 column is readily available.

Linearity of the response using peak area at the respective wavelength *v* concentration was studied by using successive injections of 15 μL at a range of concentrations (0.1 μg to 2.0 μg; ethion 1-100 μg). The calibration curves of the selected pesticides had good linearity, with correlation coefficients of 0.979-0.999. The linear calibration equations are given in Table 3.4.

Table 3.4 The standard linear calibration equations of the pesticides studied

No	Pesticide name	Linear calibration equation*	r^2
1	Ametryn	A=134671[C]+1967	0.998
2	Imazethapyr	A=66672[C]+383	0.998
3	Carbaryl	A=268951[C]–5297	0.997
4	Phosalone	A=61256[C]–258	0.999
5	Bifenthrin	A=122499[C]–169	0.992
6	Dichlorvos	A=14324[C]–467	0.988
7	Monocrotophos	A=83791[C]+1190	0.997
8	Ethion	A=16620[C]+977	0.979

*A is peak area and C is concentration in μg.

3.8 Conclusions

Conditions have been established for HPLC determination of ametryn, imazethapyr, carbaryl, phosalone, bifenthrin, dichlorvos, monocrotophos, ethion, dicrotophos, trifluralin, atrazine, methomyl and thiodicarb — pesticides in common use. Reversed-phase chromatography with a C18 column was found suitable for separating and measuring the pesticides studied. HPLC offers advantages compared with GC in that aqueous extracts of soil can be directly injected without clean up and partitioning into an organic solvent. The characterisation of the range of soils for use in studies revealed a range of organic C, pH, mineralogy and texture for a broad representation of different soil types.

CHAPTER 4

Sorption of Ionic and Nonionic Pesticides in Selected Soils From Three Countries

4.1 Introduction

Groundwater contamination by organic pesticides has become an international problem. With the steady increase in use of pesticides in agriculture, there is increasing concern over their potential threat to the soil, water quality and environmental health. Therefore, a complete understanding of the processes that affect the transport and fate of these contaminants is crucial to assess the potential groundwater contamination and to develop efficient and cost-effective site management and soil remediation strategies.

Sorption is the primary process governing the transport and fate of ionic and nonionic organic pesticides in the soil environment. The increasingly frequent occurrence of pesticides in the surface and groundwaters of various countries (Hallberg, 1989; Leistra and Boesten, 1989; Legrand et al., 1991; Funari et al., 1995) and the significant impact of pesticide sorption on soil remediation (Krishnayya et al., 1994) has made sorption a major topic of soil-pesticide research.

The main factors controlling sorption include the hydrophobicity of the chemical, the soil organic C (SOC) content, pH and mineral content. However, the mineral phase in soil is generally considered as inert with regard to sorption of nonionic pesticides as numerous studies (e.g. Hamaker and Thompson, 1972; Karickhoff et al., 1979; Rao and Davidson, 1980; Johnson and Sims, 1993) have shown that sorption of nonionic hydrophobic pesticides is solely dependent on the SOC content. Based on this, the distribution coefficient (K_d) of pesticides is usually expressed as per unit organic C as $K_{oc} = K_d/f_{oc}$ (Hamaker and Thompson, 1972; Mackay and Paterson, 1981). The K_{oc} of a given nonionic pesticide has often been reported to be the same for different soils (Chapter 2).

Soil-pesticide interactions have been examined extensively, particularly in Europe and North America. In Australia, studies on sorption behaviour of different pesticides have been conducted by several researchers (e.g. Briggs, 1981a; Gerritse et al., 1996; Kookana et al.,1997). However, the behaviour of pesticides in Australian soil environment remains poorly understood (Kookana et al., 1998a). In Pakistan, at present there are no significant data available to allay the mounting concern of farmers and the public over the increased use of pesticides and potential adverse impact on environment.

Although the soils, climates and cropping systems in Australia and Pakistan are different from those in the U.S.A. and Europe, pesticide persistence and behaviour in soil is often extrapolated from overseas studies. Particularly, the pesticide registration authorities of Pakistan rely heavily on the data from overseas studies. However, the behaviour of a pesticide can vary greatly depending on the soil type and environmental conditions. Therefore, it is imperative that studies on pesticides be conducted on soils of Australia and Pakistan to better understand the sorption behaviour of pesticides in these soils.

Since information on the sorption behaviour of pesticides in soil is essential in predicting their leaching potential and contamination of groundwater, studies were conducted on the sorption of selected ionic and nonionic pesticides in 48 soils from Australia, Pakistan and the UK, covering a range of physical and chemical properties. Inclusion of 9 soils from UK in sorption study of two nonionic pesticides, carbaryl and phosalone, was aimed at comparing the behaviour of these pesticides, and to determine if overseas data were applicable to the soils of Pakistan and Australia.

The main objectives of the study were to evaluate the sorption characteristics of two ionic (ametryn and imazethapyr herbicides) and five nonionic (carbaryl, phosalone, bifenthrin, monocrotophos, and dichlorvos) pesticides on a variety of soils and to evaluate the soil characteristics that influence sorption of these pesticides.

4.2 Materials and Methods

4.2.1 Soils

Forty eight soils, with no recent history of application of the pesticides, were collected from Australia, Pakistan and the UK. The soils used were chosen because their characteristics span a wide range of soil properties (OC, 2.8 - 138.0 g kg^{-1}; pH, 3.74- 8.56; clay, 12 - 755 g kg^{-1}). The description and pertinent characteristics of the soils have been given in Chapter 3 (Table 3.1). For determination of C contents in the particulate form (53 µm - 2 mm), 5 g soil (2 mm) was weighed into 50 mL centrifuge tube and 17.5 ml of Na hexametaphosphate (Calgon-T, 5g/L) was added. The tubes were shaken end-over-end overnight. The contents were sieved using a 53 µm sieve with the aid of a gentle flush of water. The fraction remaining above the sieve was transferred into a crucible and dried at 70°C in an oven. The total C contents in the particulate (53 µm - 2 mm) fraction of soils was performed on a Leco C analyser. The inorganic C contents were determined by the calcimeter method (Allison and Moodie, 1965). The difference in the total C and inorganic C gave the total organic C content. The difference between the OC in the whole soil (2 mm) and that in the 53 µm - 2 mm gave the OC content of the <53 µm fraction.

4.2.2 Pesticides

Seven pesticides, all important for pest control, were used in this study [ametryn (N^2-ethyl-N^4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine), imazethapyr ((RS)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid), carbaryl (1-naphthyl methylcarbamate), phosalone (S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl O,O-diethyl phosphorodithioate), bifenthrin (2-methylbiphenyl-3-ylmethyl(Z)-(1RS,3RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate), monocrotophos (dimethyl(E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate, and dichlorvos (2,2-dichlorovinyl dimethyl phosphate)]. The pesticides include both ionisable (ametryn and imazethapyr) and nonionic (carbaryl, phosalone, bifenthrin, monocrotophos, and dichlorvos) and are representative of a large spectrum of pesticide chemical properties (refer to Chapter 3). All the pesticides used in the study had >99% purity.

4.2.3 Evaluation of Syringe Microfilters

Materials used in sorption studies can potentially sorb some pesticides. Indeed, preliminary studies showed that there were significant sorptive losses to syringe filters. Therefore, an evaluation of 9 types of syringe filters was carried out in to find appropriate filters that could be used in sorption studies with minimal sorption of pesticides from the aqueous phase onto the filter membrane or its housing. The details of the filters used are given in Table 4.1.

Table 4.1 Specifications of the filters tested for their suitability

Sr No	Filter code	Membrane type	Housing material	Diameter (mm)	Pore size (μm)
1	PTFE	Polytetrafluoroethylene	Polypropylene	25	0.45
2	Nylon	Nylon	Polypropylene	25	0.45
3	SS	Cellulose acetate	Polycarbonate	25	0.45
4	SLHV	Durapore*	EASTAR**	25	0.45
5	RC	Regenerated cellulose	Polypropylene	25	0.45
6	B101	316 stainless steel	Polypropylene	3	0.50
7	SLS Frit	316 stainless steel	Stainless steel holder	25.4	0.50
8	Polypure	Polypropylene	Polypropylene	13	0.45
9	AGS	Nylon	Polypropylene	25	0.45

*Durapore is a trademark of Millipore Corporation or affiliated company.
**EASTAR is a trademark of Eastman Chemical Company.

An aliquot of ~1 mL (triplicate) of each pesticide solution containing 2 mg L^{-1} in 0.01M $CaCl_2$ was passed through various types of syringe filter directly into the HPLC autosampler vials and an unfiltered sample was used as a reference. Bifenthrin solution was prepared in 0.01M $CaCl_2$ containing 0.5% acetone owing to its low aqueous solubility. The samples were analysed immediately for the pesticide contents. The sorption by filters was calculated from the concentration difference between the reference and filtered solutions.

4.2.4 Pesticide Sorption Equilibria

To establish when pesticide sorptions reached equilibrium in the soil systems, 10 mL of pesticide solution in 0.01M $CaCl_2$ was added to 2 g of air dried soils (1:5 soil solution ratio) in 14 mL glass tubes fitted with Teflon-lined screw caps. A soil solution ratio of 1:10 was used for bifenthrin due to its very high sorption on to soils. The same ratio was applied for phosalone sorption studies in Australian soils due to their higher organic C contents. This was necessitated for better precision in the measurement of the pesticide concentration in the solution phase. For imazethapyr, a soil solution ratio of 1:2 was employed due to its very low sorption and to avoid errors due to small changes in the solution concentrations after equilibration. Duplicate samples plus blanks (no soil) were shaken for 0.5, 1, 2, 4, 8, 16, 20 and 24 h. The tubes were centrifuged for 20 min at 1800 rpm. Suitable aliquots were syringe filtered (using standardised syringe filters) and analysed on HPLC for the pesticide concentrations. B101 filter was used for bifenthrin, RC filter for phosalone and carbaryl while nylon membrane filters were used for the other pesticides according to their suitability as discussed in Section 4.3.1. Shaking times were assessed to be sufficient to reach the sorption equilibrium.

4.2.5 Pesticide Sorption Measurements

Sorption of the pesticides from aqueous solution was determined at ambient laboratory temperature (22 ± 2 °C) employing a standard batch equilibration method. This method has become the most widely used for characterising the sorptive properties of chemicals and sorbents (Brusseau et al., 1991) and it is accepted for pesticide registration purpose (USEPA, 1975). Sorption was measured at various field-representative concentrations, using 0.01M $CaCl_2$ as a background electrolyte to minimise changes in ionic strength and promote flocculation. For example, at a pesticide application rate of 0.5 kg ha^{-1} (active ingredient), a 10-cm top layer of saturated soil would have a concentration of about 1 mg L^{-1} in the soil solution. Two sets of measurements were made in duplicate. The first set, for determination of sorption isotherms used four solution concentrations (0.5, 1.0, 1.5, and 2.0 mg L^{-1}) for all pesticides except bifenthrin (5, 10, 15, and 20 mg L^{-1} in the presence of 2% acetone) and imazethapyr (0.5, 1.0, and 1.5 mg L^{-1}) The second set, for determination of K_{oc}, employed a single concentration (1.5 mg L^{-1}) for each pesticide. Isotherm measurements from the first set allowed an evaluation of the assumption of sorption linearity that is inherent in the calculation of K_{oc} (Green and Karickhoff, 1990). Duplicate soil samples were equilibrated with pesticide solutions at the soil solution ratios given in Section 4.2.4 by shaking for 2 h (phosalone and bifenthrin), 4 h (carbaryl), or 16 h (ametryn and imazethapyr) in glass tubes sealed with teflon-lined caps. Glass tubes with teflon liners in caps are very commonly reported not to sorb ionic and nonionic compounds (e.g. Zytner et al., 1992; Baskaran, 1994). At the end of shaking time, the suspension was centrifuged at 1800 rpm for 20 minutes to obtain a clear solution and ~1 mL of the clear supernatant was filtered directly into the HPLC autosampler vials through specific syringe filters (B101 for bifenthrin, RC for carbaryl and phosalone, and nylon for the others). The pesticide concentrations in solution were measured on HPLC following the methods described in Chapter 3. Differences between initial and equilibrium concentrations were assumed to be sorbed and the values were used to calculate sorption. In selected soil samples, the pesticides remaining after the experiment were extracted and measured to check if there was any loss of pesticides through degradation during the equilibration time. Blanks which included each of the soils with only 0.01M $CaCl_2$ solution (no test chemical) and a single control of the test chemical solution with no soil were also performed to check for analytical interference due to soil extracts and for interaction between chemical and the tubes. Appropriate corrections were applied as necessary.

4.2.6 Determination of Sorption Coefficients (K_d, K_{oc})

The sorption coefficient, K_d was determined either from the slope of the linear plots of sorbed *v* aqueous pesticide concentrations or from the single solution concentration of the pesticide as:

$$K_d = \frac{\text{pesticide sorbed (mg / kg of soil)}}{\text{pesticide in solution (mg / L)}}$$

The K_d values are quoted as L kg^{-1}.

Sorption coefficient normalised on the basis of SOC (K_{oc}) was derived as

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

where K_d is the sorption coefficient and f_{oc} is the mass fraction of OC present in the soil sample.

4.3 Results and Discussion

4.3.1 Evaluation of Various Syringe Microfilters on Concentrations of Pesticides in Solution

A comparison between various filters for their sorption capacities for different pesticides is made in Table 4.2. As evident from the table, there were significant losses from the filtered solutions of pesticides. The complete recovery of pesticides from the filters by the extraction with organic solvent (data not shown) suggested that the decrease in solution concentration was due to sorption on the filter membrane and/or housing material. As the membrane and housing of syringe filters were used as one sealed unit, it was not possible to distinguish between proportions of the pesticides retained on the membrane and housing separately. The loss through sorption by filters was in the order of SLVH (95%) > SS (87%) > AGS (82%) > Nylon (79%) > PTFE (64%) > SLS-Frit (55%) = RC (55%) > Polypure (28%) > B101 (1%) for bifenthrin, SLVH (79%) > SS (75%) > Nylon (66%) > PTFE (51%) > SLS-Frit (11%) > B101 (0.3%) = RC (0.2%) for phosalone, and SS (25%) > PTFE (10%) > Nylon (9%) >SLS-Frit (1%) > B101 (0.5%) = RC (0.3%) for carbaryl. Nylon and PTFE filters which are very frequently used in pesticide studies showed significant amounts of sorption of the more hydrophobic pesticides.

It is obvious that the pesticides in the order of decreasing sorption were: bifenthrin (95%) > phosalone (79%) > ametryn (41%) > carbaryl (25%) > dichlorvos (12%), irrespective of the filters used. Higher efficiencies (<1% loss) were observed for imazethapyr and monocrotophos for all filters, except for some loss of monocrotophos on B101 (2.8%) and SLS-Frit (5.35%). It appeared that some decomposition of monocrotophos on steel material occurred as evident from a slight corrosion of the frit. Monocrotophos is reported to corrode stainless steel (Charles and Hance, 1991) and such filters are clearly not suitable for monocrotophos. The other pesticides studied are non-corrosive to stainless steel. The SS filter showed high sorption during filtration of aqueous solutions of dichlorvos and ametryn (the loss from solution being 12% and 41% for dichlorvos and ametryn, respectively), whereas other filters were found compatible to these chemicals.

Table 4.2 Average loss (%) of pesticide solutions filtered through various syringe filters. Standard errors (±) are shown in parentheses, n = 3.

Pesticide	PTFE*	Nylon	SS	SLVH	RC	B101	SLS-Frit	Polypure	AGS3125
Bifenthrin	63.8 (±4.4)	78.8 (±3.9)	87.3 (±4.3)	94.8(±2.5)	54.7 (±3.2)	0.9 (±0.4)	55.1 (±3.0)	27.6 (±2.8)	82.4 (±2.1)
Phosalone	51.2 (±1.4)	66.3 (±2.7)	75.4 (±3.7)	79.4 (±0.6)	0.2 (±0.2)	0.3 (±0.3)	10.8 (±1.7)	N.T.	N.T.
Carbaryl	10.4 (±2.1)	9.3 (±1.0)	25.1 (±1.5)	N.T.	0.3 (±0.3)	0.5 (±0.3)	0.8 (±0.3)	N.T.	N.T.
Ametryn	2.4 (±1.1)	1.1 (±0.6)	40.6 (±3.2)	N.T.	0.4 (±0.3)	0.4 (±0.2)	0.2 (±0.4)	N.T.	N.T.
Imazethapyr	0.2 (±0.2)	0.2 (±0.2)	0.3 (±0.2)	N.T.	0.2 (±0.2)	0.7(±0.4)	0.6 (±0.9)	N.T.	N.T.
Monocrotophos	0.3 (±0.3)	0.3 (±0.2)	0.5 (±0.3)	0.3 (±0.2)	0.1 (±0.1)	2.8 (±0.3)	5.3 (±0.5)	N.T.	N.T.
Dichlorvos	N.T.	0.6 (±0.2)	12.4 (±3.3)	2.0 (±0.4)	0.7 (±0.4)	0.2 (±0.7)	1.0 (±0.6)	N.T.	N.T.

N.T. = not tested

* For types of filters see Table 4.1.

The differences in sorption by various filters were due to the different types of organic polymers used in the filter membranes and their housings, which may react with the organic compounds in solution. As evident from the Table 4.1, the SS filter, which showed maximum sorptive capacity for the more hydrophobic compounds, has a cellulose acetate membrane and a polycarbonate housing. The high interaction of pesticides with the SS filter is supported by the study on sorption of pesticides to centrifuge tubes conducted by Baskaran (1994) who observed 63 and 68% sorption of phorate and terbufos from their aqueous solutions onto the polycarbonate tubes after shaking time of 4 h.

It is noteworthy that the extent of sorption of pesticides by filters was greater for more hydrophobic compounds like bifenthrin and phosalone. Bifenthrin was highly retained by the all filters tested except B101. The stainless steel frit used with a stainless steel holder gave a loss of 55% for bifenthrin, whereas the B101 syringe filter containing polypropylene housing and a stainless steel frit of the same material as that in the SLS frit (316 stainless steel) gave highest efficiency (>99%) even for highly hydrophobic compounds. Further Investigation on this anomaly revealed that the stainless steel frit was heat passivated, whereas the B101 filter frit was heat passivated in the presence of hydrogen (hydrogen passivated). It is likely that the hydrogen passivation changed the characteristics of the material such that a high recoveries of the pesticides were possible.

A major source of analytical error which may be encountered in sorption studies is sorption losses to the tubes and caps, and sorption to the filters and their housings during filtration prior to analysis of the pesticides in solution. Significant sorption of atrazine and metolachlor herbicides from aqueous solution onto materials used for tubes and flasks was reported by Topp and Smith (1992). A retention of up to 28% was observed by Hinckley and Bidleman (1989) using glass-fibre filters for chlordane and fenvalerate, compounds with aqueous solubilities of 0.1 and <1 mg, respectively. However, a literature search showed that information on the compatibility of filters with pesticides in aqueous solutions is scarce. General guidelines regarding membranes and filter housing are provided by the manufacturers. However, there are no specifications available for their compatibilities with various pesticides in aqueous solutions.

The results of this study cautioned that the sample filtration may be a major source of error in the determination of pesticides and suggested that suitability of filters to aqueous solution must be determined before their use in research involving organic pesticides, particularly for those with low aqueous solubilities.

4.3.2 Sorption Kinetics

Changes in solution concentration with time for ametryn, imazethapyr, carbaryl, phosalone, and bifenthrin used in this study are shown for selected soils in Figure 4.1. The kinetic study results indicated that >90% of carbaryl, phosalone and bifenthrin was sorbed within the first 0.5 h and ametryn and imazethapyr within 2 h. On the basis of these experiments, equilibrium seemed to complete in 1 h for phosalone and bifenthrin, 2 h for carbaryl, 8 h for ametryn and 12 h for imazethapyr (Figure 4.1) as there were no changes observed in concentrations of the pesticides in solution after these time periods. Sorption equilibrium times to be used in the subsequent studies are shown by the open symbols in the figures. Full attainment of equilibrium for carbaryl has been reported to occur within 2 h (Rajagopal et al., 1984) and 3 h (Jana and Das, 1997). Briggs (1981a) employed a shaking time of 2 h for sorption studies of nonionic organic chemicals and pesticides, including carbaryl, in Australian soils. Earlier determinations of sorption coefficients were based on 4 h equilibrations for ametryn (Green et al., 1993) and 10 h (Renner et al. (1988) or 15 h (Stougaard et al., 1990) for imazethapyr with no significant changes in solution concentrations beyond 4 h. A equilibrium time of 2 h for phosalone and bifenthrin, 4 h for carbaryl and 16 h for ametryn and imazethapyr were used in the sorption studies.

4.3.3 Sorption of Ionic Pesticides

The sorption isotherms for ametryn and imazethapyr (Figure 4.2 & 4.3) were linear over the concentrations used and showed good fit to the measured data (r^2 = >0.96) which suggested that the K_d is appropriate to use for these chemicals. The K_d values for ametryn and imazethapyr determined for 25 soils are reported in Table 4.3. The magnitude of the K_d values is indicative of moderate to strong sorption for ametryn and weak to moderate binding for imazethapyr. For ametryn, value of K_d for 13 Pakistani soils varied from 0.59 L kg^{-1} (Pk4) to 4.30 L kg^{-1} (Pk16) whereas in Australian soils, it varied from 0.97 L kg^{-1}

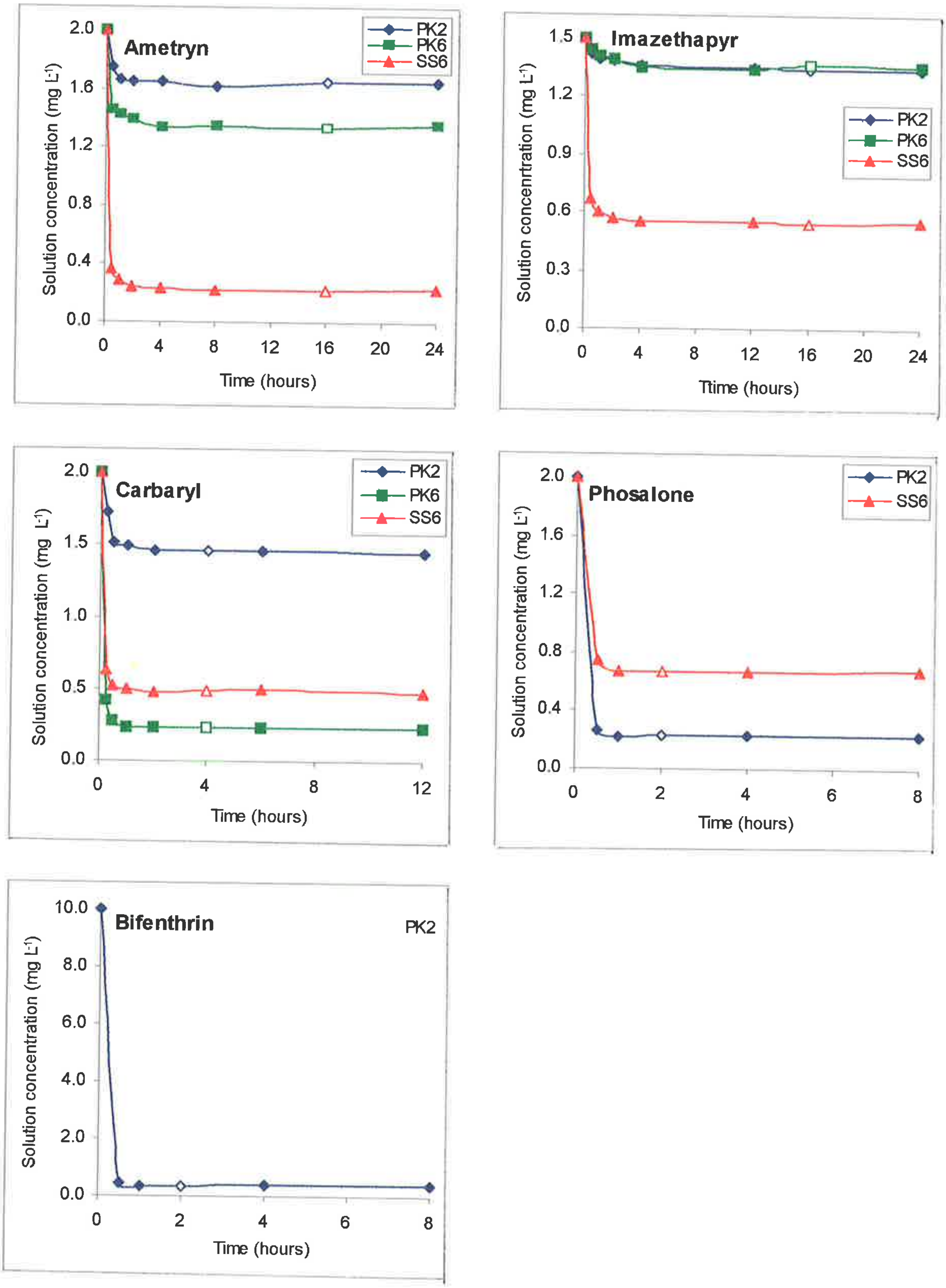
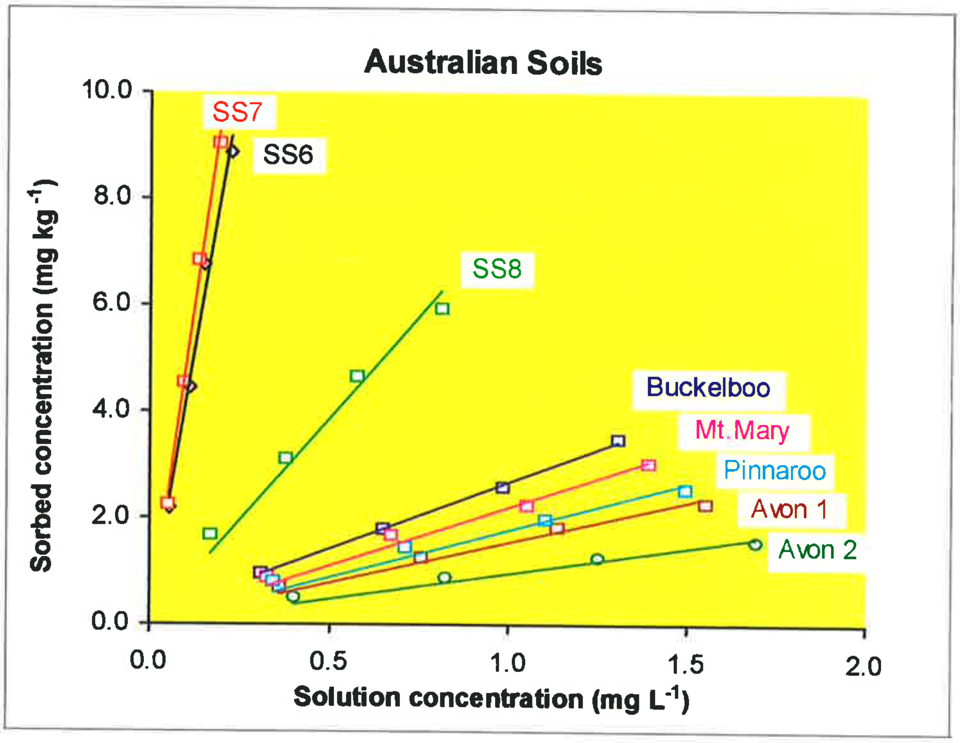


Figure 4.1 The effect of time on sorption of ametryn, imazethapyr, carbaryl, phosalone and bifenthrin in selected soils. Open symbols indicate equilibration times used in subsequent experiments.



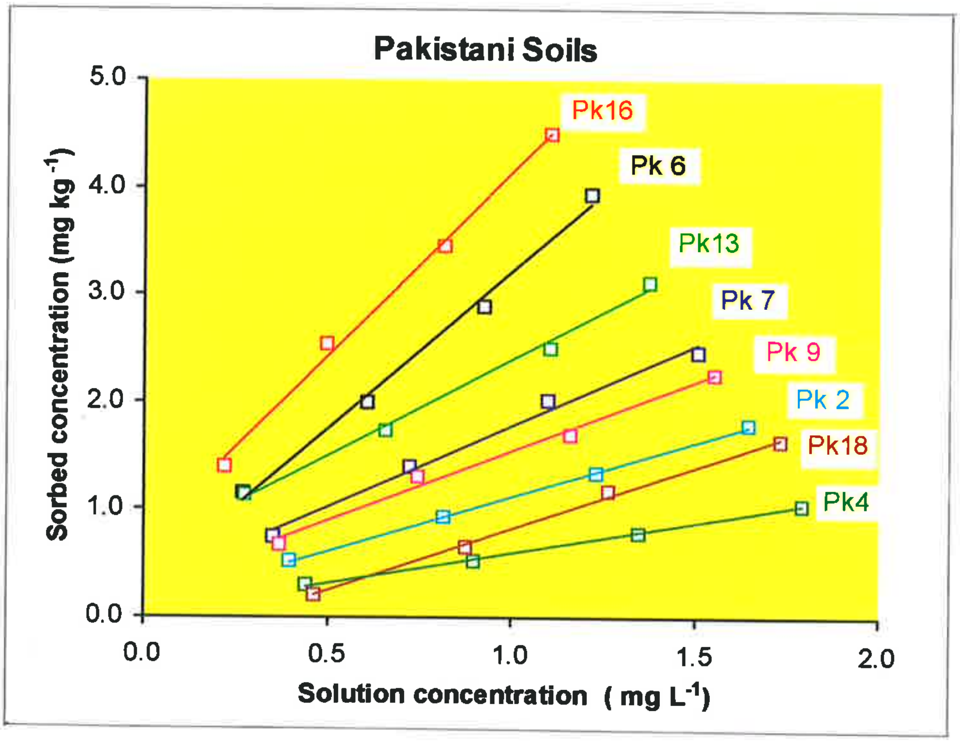


Figure 4.2 Sorption isotherms of ametryn in some Australian and Pakistani soils

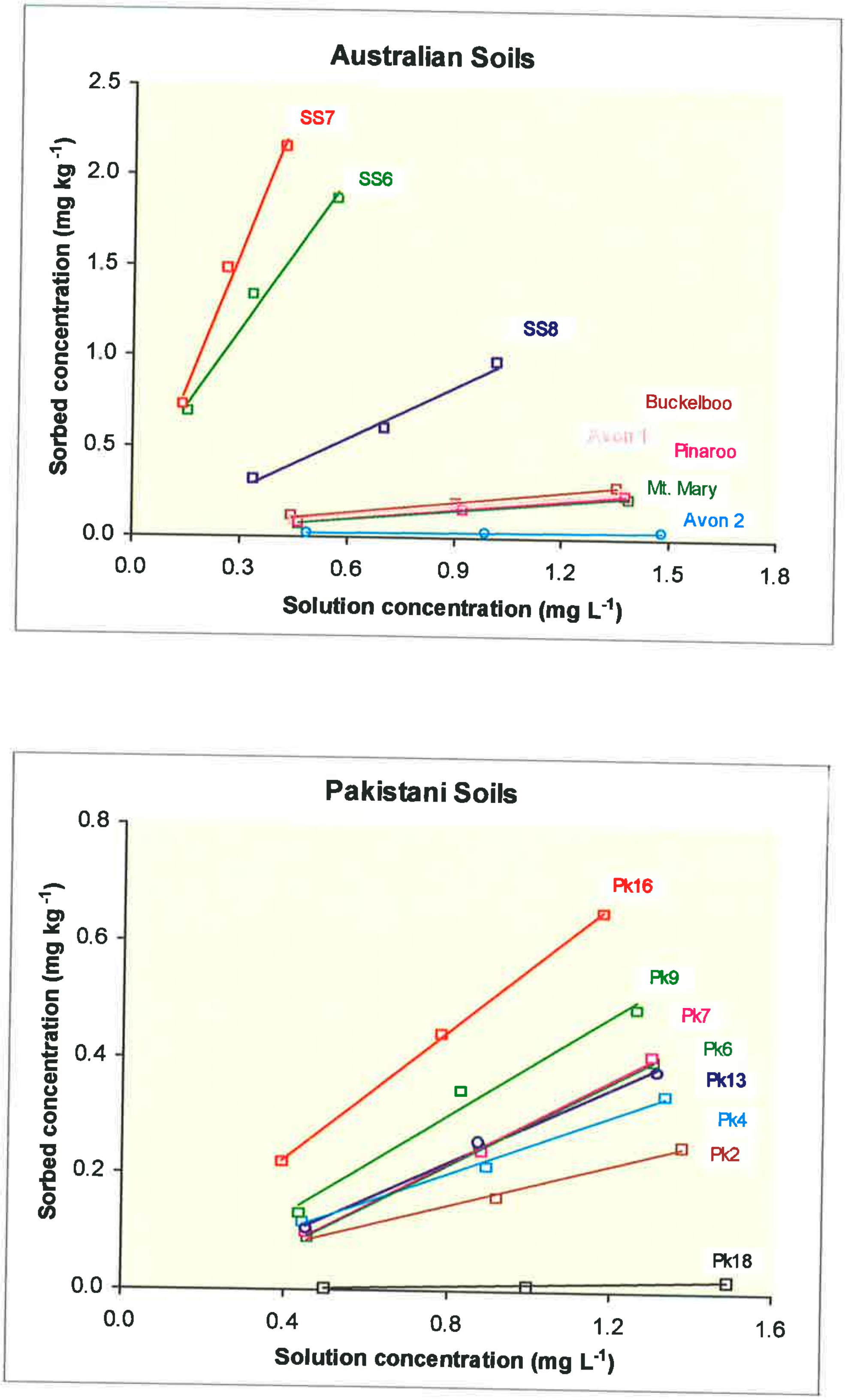


Figure 4.3 Sorption isotherms of imazethapyr in some Australian and Pakistani soils

Table 4.3 Soil sorption coefficients (K_d) for ametryn and imazethapyr in 25 soils from Australia and Pakistan

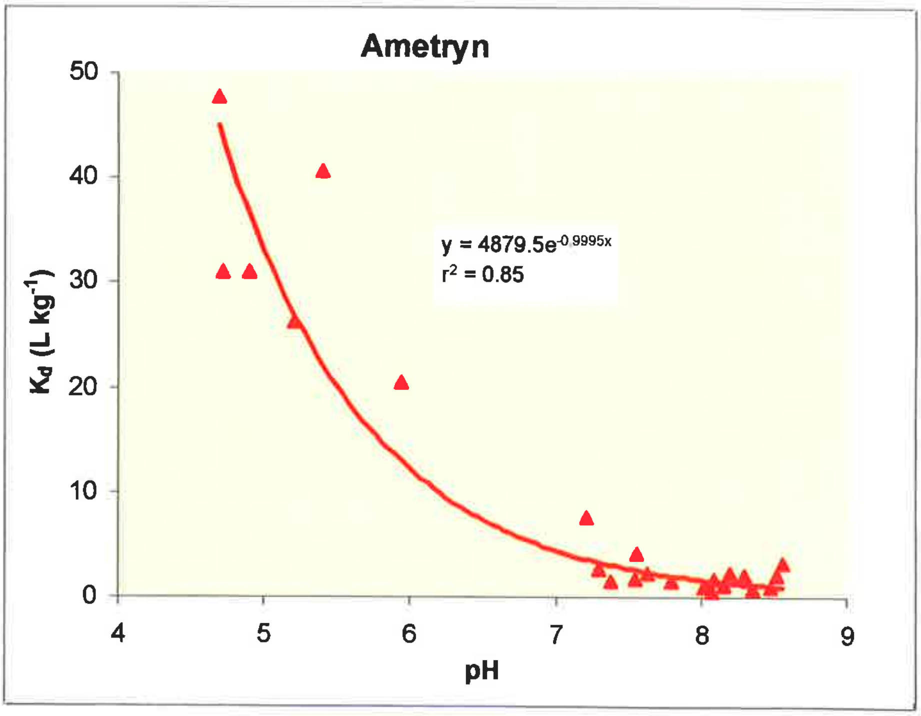
No	Soil name	SOC (Leco) (g kg^{-1})	pH (1:5 $CaCl_2$)	Clay (g kg^{-1})	K_d (Ametryn) (L kg^{-1})	K_d (Imazethapyr) (L kg^{-1})
Pakistani Soils						
1	Pk2	3.88	8.16	252	1.10	0.17
2	Pk4	6.66	8.07	156	0.59	0.25
3	Pk6	13.82	8.56	268	3.25	0.36
4	Pk7	6.84	8.08	152	1.75	0.36
5	Pk8	3.88	8.35	140	0.85	0.16
6	Pk9	6.54	7.80	156	1.51	0.43
7	Pk10	2.79	8.07	180	0.63	0.13
8	Pk11	6.92	8.30	292	2.16	0.22
9	Pk12	6.18	8.51	172	2.07	0.13
10	Pk13	9.70	8.20	292	2.36	0.32
11	Pk15	6.50	8.03	320	1.05	0.31
12	Pk16	22.20	7.56	292	4.30	0.55
13	Pk18	5.72	8.47	172	0.90	0.02
Australian Soils						
14	SS6	70.10	5.40	479	40.55	2.84
15	SS7	138.00	4.69	160	47.62	4.98
16	SS8	23.20	7.21	679	7.68	0.97
17	Buckelboo	12.94	7.29	260	2.65	0.19
18	Avon1	12.90	7.38	130	1.53	0.18
19	Avon2	3.84	8.02	180	0.97	0.02
20	Mt. Mary	10.20	7.63	210	2.21	0.16
21	Pinnaroo	12.00	7.54	182	1.78	0.18
22	ACU1	25.60	4.72	212	31.02	6.94
23	B211	34.30	5.94	755	20.45	4.72
24	Qld	38.40	5.20	515	26.23	5.64
25	URB-P	26.70	4.90	172	31.06	6.44

(Avon2) to 47.62 L kg^{-1} (SS7). For imazethapyr the K_d varied from ~0 (Pk18) to 0.55 L kg^{-1} (Pk16) in Pakistani soils and from ~0 (Avon2) to 6.94 L kg^{-1} (ACU1) in Australian group of soils. Variations in the K_d values show that these soils varied widely in their intrinsic capacities to sorb these herbicides. In the case of both pesticides, the soils from Pakistan showed relatively lower K_d than the Australian soils. This is probably due to Pakistani soils all being alkaline. This aspect is discussed further in Section 4.3.3.1. The mean K_d for ametryn (9.45 L kg^{-1}) was greater than that for imazethapyr (1.47 L kg^{-1}). The findings are in agreement with their hydrophobicity represented by the K_{ow} values.

These results support the comment by Calvet (1989) about the use of the octanol-water partition coefficients to predict the sorption of organic compounds in soils, which is valid only if the mineral constituents do not play an important role. Moreover, interactions with the organic matter may cause deviations from the predicted behaviour of an ionic pesticide. Therefore, the role of soil pH, SOC, and clay contents in sorption of ametryn and imazethapyr are discussed in the following sections.

4.3.3.1 Influence of Soil pH

Soil pH is expected to influence the K_d for ametryn and imazethapyr, both being ionisable. Therefore, the K_d values were plotted against pH for ametryn and imazethapyr in Figure 4.4. Sorption of both herbicides to soil increased with the decrease of soil pH from 8.6 to 4.7 as expected for the interaction of ionisable pesticides with SOC (Nicholls and Evans, 1991). Ametryn showed much higher sorption than imazethapyr across all pH levels (Table 4.3). As can be seen from Figure 4.4, there is a good negative correlation between K_d and pH for ametryn ($r^2 = 0.85$) and imazethapyr ($r^2 = 0.76$). Very low sorption occurred at soil pH >8, particularly for imazethapyr. One Pakistani soil Pk18 and an Australian soil Avon2 showed very little sorption for imazethapyr (K_d, 0.02). In case of ametryn, soil Pk4 (K_d, 0.59) and Avon2 (K_d, 0.97) were lowest in Pakistani and Australian group, respectively. All these soils with lower K_d values had pH >8. These results are in consistent with the reported decrease in imazethapyr activity at lower pH, attributed to decreased sorption resulting from dissociation of acidic molecules resulting in anions at pH ≥ pK_a (Stougaard et al., 1990; Mangels, 1991; Che et al., 1992). In the case of



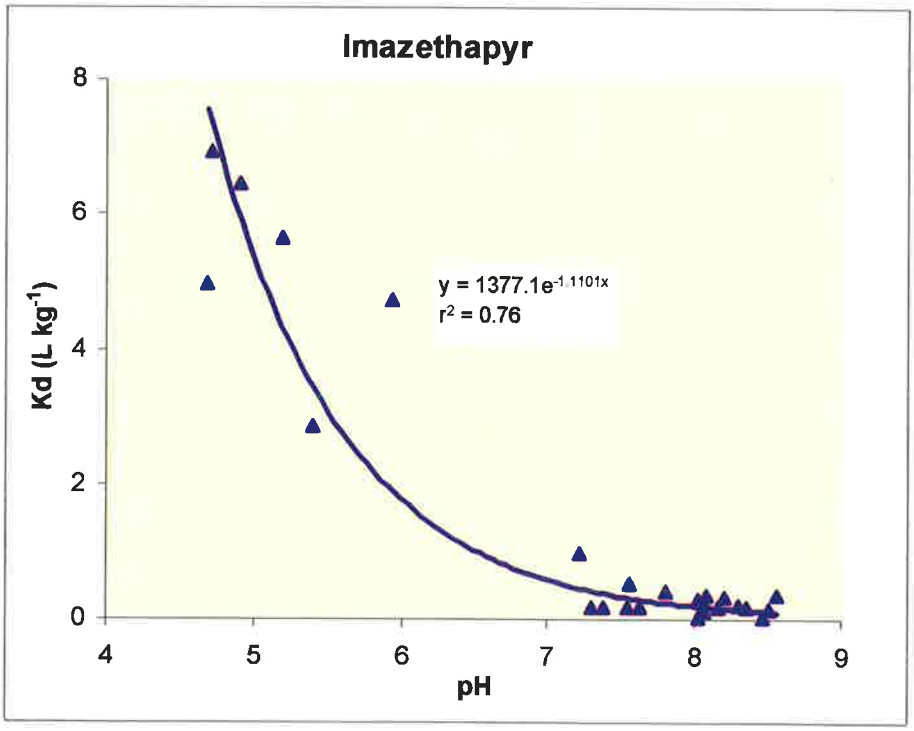


Figure 4.4 Relationship of K_d values of ametryn and imazethapyr with soil pH in some Pakistani and Australian soils

ametryn, a basic compound, the decrease in pH causes protonation and formation of cations at pH $\leq$ pK_a. However, Gan et al. (1994) did not observe any significant difference in the behaviour of imazethapyr in four Minnesota soils in the pH range of 4.8 to 7.1 which is contrary to the reports that greatest change in sorption occurs when pH decreases below 6, with little or no response occurring above 6 (Renner et al, 1988; Stougaard et al., 1990). In another study by Mark et al. (1989), sorption of imazethapyr showed that sorption was greater at pH below 6 than at higher pH, which is in accord with the studies reported here.

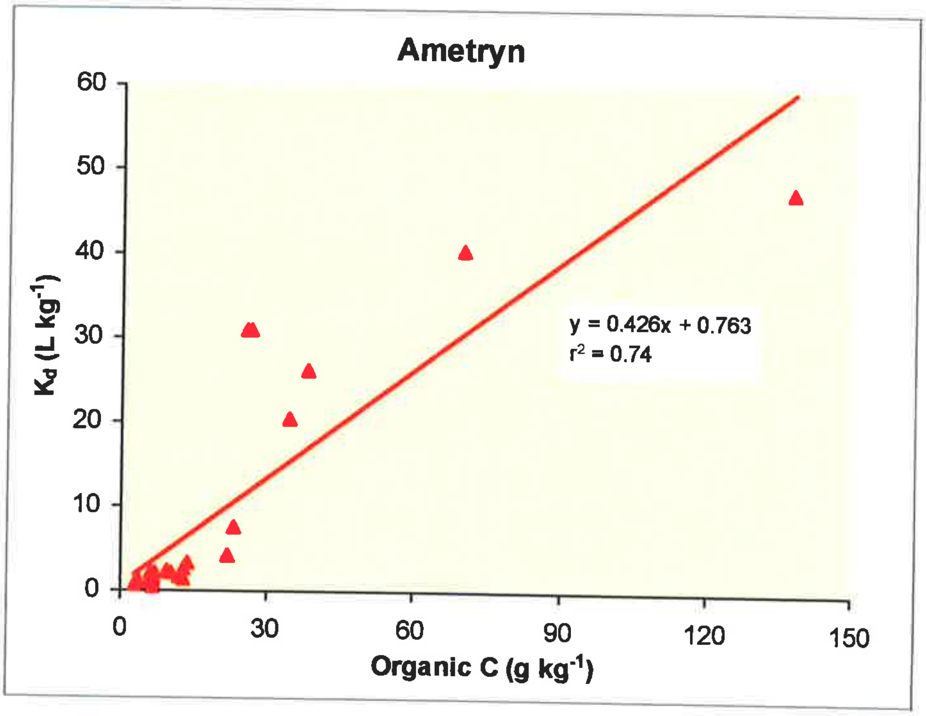
The sorption is generally characterised by an envelope showing a maximum sorption at a pH in the vicinity of the dissociation constant (pK_a) of weakly acidic (e.g. imazethapyr) and weakly basic (e.g. ametryn) compounds (Weber, 1970b; Hingston et al., 1972; Barriuso et al., 1992). The soil pH influences sorption by influencing the degree of ionisation of herbicides. Imazethapyr is an amphoteric compound because of the presence of acidic and basic functional groups (Basham et al., 1987). Ionisable carboxyl group for imazethapyr has acidic and basic pK_a values of 3.9 and 2.1, respectively (Basham et al., 1987). Therefore, it should be predominantly in anionic form at pH values greater than the pK_a value. Because of its anionic form, the molecule is repulsed by negatively charged clay and organic surfaces, and little or no sorption was observed in soils having high pH. Protonation of imidazolinone nitrogens may occur at low pH, resulting in a positively charged or even undissociated molecule with a potential for the binding the herbicide molecule to the soil (Mark et al., 1989; Strougaard et al., 1990). Moreover, the water solubility of acidic compounds generally decreases with increasing pH and resultantly an increase in their K_{ow}. This increase in K_{ow} of imazethapyr at low pH could have resulted in its higher sorption.

The dependence of imazethapyr sorption on soil pH is similar to the sorption of acidic herbicides. The characteristics of imazethapyr sorption is somewhat similar to those of chlorsulfuron, an acidic herbicide with pK_a of 3.58 (Shea, 1986). Chlorsulfuron sorption decreases as the soil pH increases, and pH changes below 6 have the greatest influence on its sorption (Mersie & Foy, 1985; Thirunarayanan et al., 1985).

Basic herbicides like ametryn also protonate as the soil pH decreases and the resulting cations are sorbed to the negatively charged soil colloids (Green, 1974). Reduced protonation of ametryn in soils with high pH is likely to have been responsible for its low sorption. The pK_a value for ametryn is 4.1 (Hornsby et al., 1996). Relationships between increased sorption with decreasing soil pH have been reported for other weak base herbicides such as terbutryn (Barriuso et al., 1992) and atrazine (Baskaran et al., 1996).

4.3.3.2 Influence of Soil Organic Carbon

Sorption distribution coefficients of ametryn and imazethapyr varied between soils also because of the varying quantities of SOC, an important soil component from the standpoint of sorption. This was particularly ~~one~~ the case for Pakistani soils which had a narrow pH range. The high SOC contents of Pk16, SS6, SS7, ACU1, B211, Qld and URBP are most likely responsible for the high sorption of both chemicals by these soils observed for the both chemicals (Hamaker and Thompson, 1972). In soils with low SOC e.g. Pk18 (OC, 5.7 g kg^{-1}) and Avon2 (OC, 3.8 g kg^{-1}), the sorption of ametryn and imazethapyr herbicides was very low (<1 and 0.02 L kg^{-1}, respectively). In case of the soils with low OC contents, contribution of other properties (e.g. pH) to sorption becomes more important, and should not be overlooked (Hance, 1987). The soils Pk18 and Avon2, which had very low SOC contents and pH >8, showed almost zero sorption of imazethapyr. Sorption of ametryn was highest in soils SS6 and SS7 with highest OC (70 and 138 g kg^{-1}, respectively) and acidic pH (5.4 and 4.7) compared with other acidic soils (ACU1, B211, Qld, and URBP) with medium OC. It seems that the contribution of SOC in addition to pH, plays a greater role in sorption of ametryn than of imazethapyr. Moreover, it is evident from Table 4.3 that soil SS7, containing much higher C content (138 g kg^{-1}), did not contribute accordingly to the sorption of the herbicides as compared with the other soils (ACU1, B211, Qld, URB-P) having pH in the same range but OC much lower. It appears that besides amount, differences in the physical and chemical composition of SOC between soils may be playing an important role in the sorption of the herbicides. Pakistani soil Pk6, sorbed a high amount of ametryn (3.2 L kg^{-1}) in spite of having high pH (8.6) and only a medium amount of OC (13.8 g kg^{-1}). It appears that SOC is more important than pH in sorption of ametryn whereas soil pH seems to be more important in sorption of



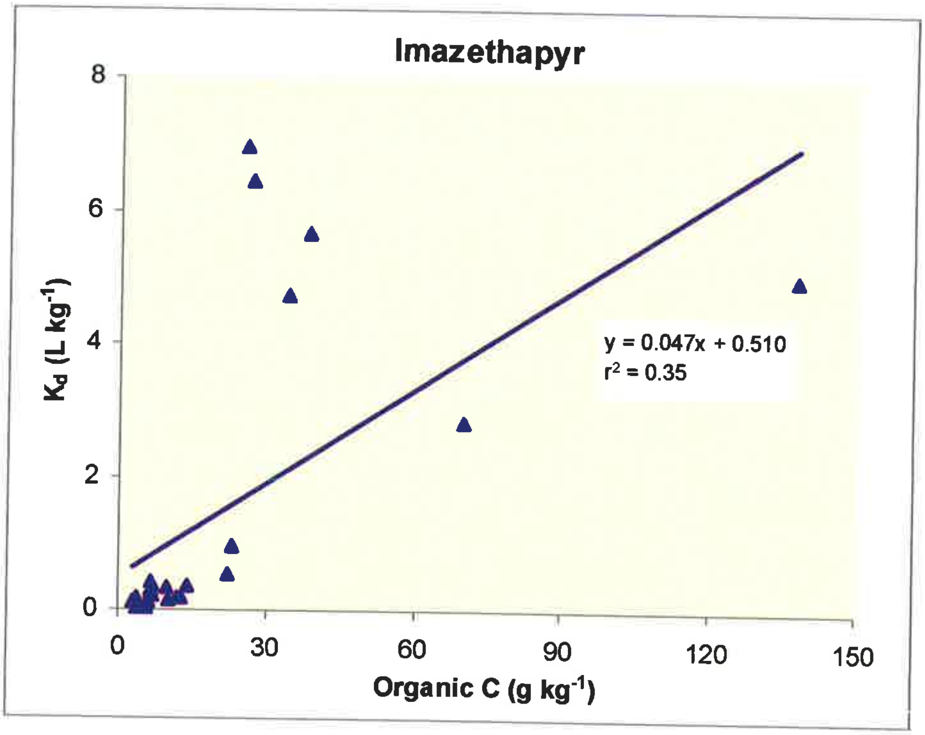


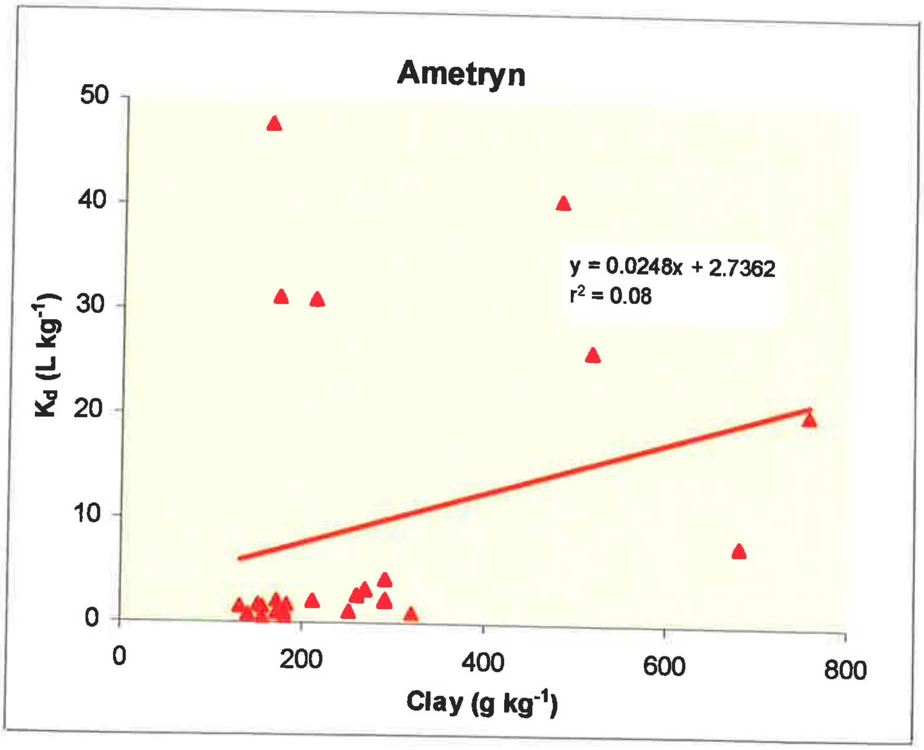
Figure 4.5 Relationship of K_d values of ametryn and imazethapyr with SOC

imazethapyr. This is clear from Figure 4.5 which shows poor correlation ($r^2 = 0.35$) of SOC with K_d of imazethapyr and a better correlation ($r^2 = 0.74$) for ametryn.

Further investigations of the quality and properties of organic C in soils of different origins are necessary to elucidate the mechanisms responsible for the differences in sorption. This aspect is discussed in detail in Chapter 6.

4.3.3.3 Influence of Clay

No correlation was found between K_d values of the soils for each of the herbicides and the clay content (Figure 4.6). The soil SS7 (clay, 160 g kg^{-1}) and URBP (clay, 172 g kg^{-1}) which has lower clay content showed very high sorption for ametryn (47.6 and 31.1 L kg^{-1}, respectively) and imazethapyr (5.0 and 6.4 L kg^{-1}, respectively). This shows that the K_d of both herbicides appeared to be independent of the clay contents of soils. Valverde-Garcia et al. (1989) also found no correlation between the K_d of atrazine (a herbicide belonging to the same family as that of ametryn) and clay content, but found a strong correlation between the illite content and K_d. However, studies conducted by Seybold et al. (1994) on influence of the type of clay on sorption of atrazine showed no significant correlation between any of the individual clay minerals including illite. Another study, by Loux et al. (1989), showed that imazethapyr sorption on soils was correlated with soil clay content. Che et al. (1992) observed greater sorption of imazethapyr on illite and kaolinite at pH 3.0, compared with that on hectorite (OC, 0.1%), which was consistent with the higher C contents of illite (OC, 0.17%) and kaolinite (OC, 0.16%). In this study, Pakistani soils contained illite as the most dominant clay type, followed by kaolinite. However, they were generally lower in sorption of both herbicides than the Australian soils, which might be due to the lower SOC contents and higher pH of the Pakistani soils. Dolling (1985) concluded that the availability of imidazolinone herbicides was unlikely to be affected by the soil clay content because of their overall weak affinity for clays. Clearly the sorption is determined by interactions of several factors such as pH, SOC and mineral matter.



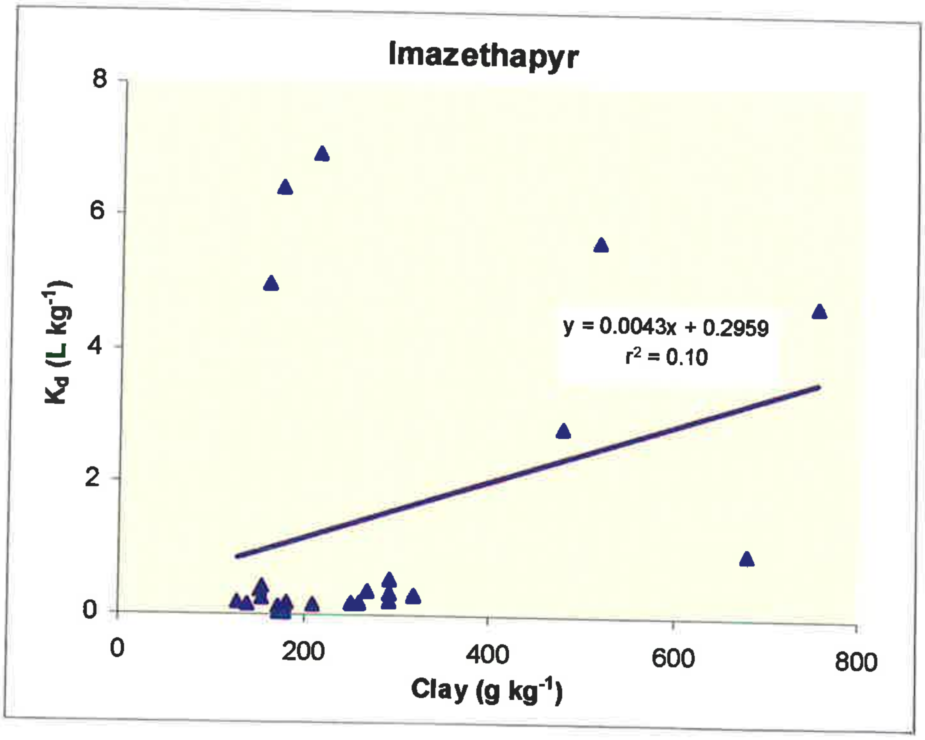


Figure 4.6 Relationship of K_d values of ametryn and imazethapyr with clay contents

4.3.3.4 Multiple Linear Regression

As the soil properties are frequently interrelated (Burchill et al., 1981), a multiple regression analysis was carried out. Two soil parameters, SOC and soil pH, accounted for 94% of the total variance in ametryn sorption by 25 soils.

$$\text{Ametryn } (K_d) = 58.0 + 0.1889 \text{ SOC} - 7.195 \text{ pH} \qquad r^2 = 0.94, \quad p < 0.001$$

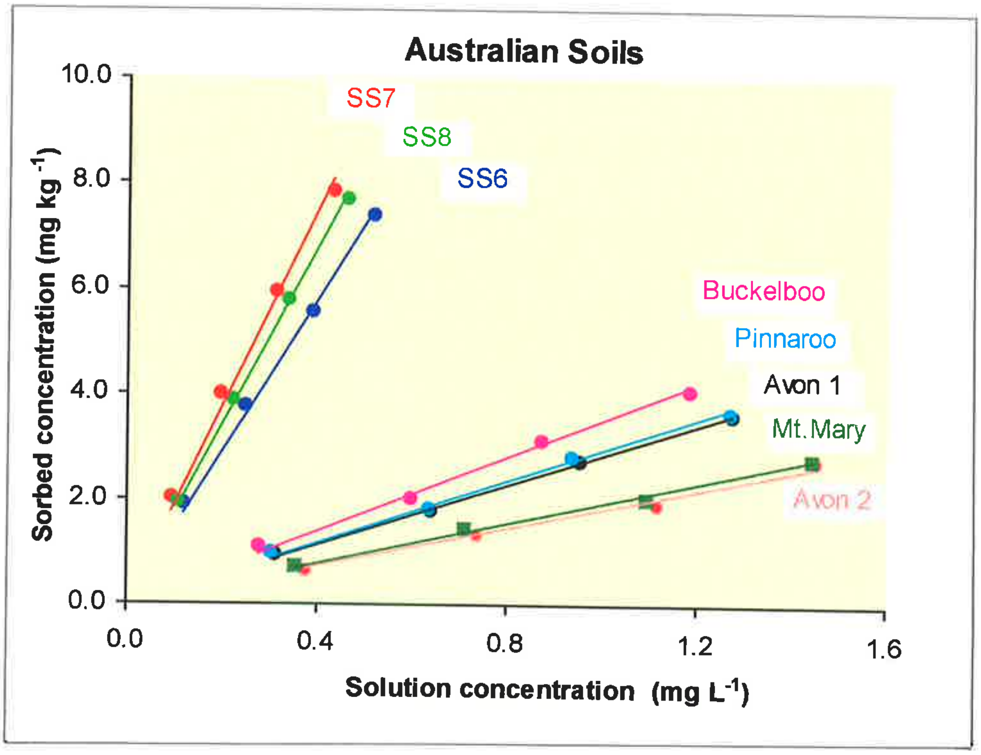
$$\text{Imazethapyr } (K_d) = 15.63 - 0.0157 \text{ SOC} - 1.901 \text{ pH} \qquad r^2 = 0.89 \quad p > 0.05$$

The correlation suggests that the combination of a high SOC content and a low pH value could have been responsible for the K_d values of SS6, SS7, ACU1, B211, Qld, and URB-P soils from Australia being significantly higher than the others. It shows that the sorption of ametryn is dependent both SOC and pH, and that both parameters are needed to be considered to explain variations in K_d of ametryn in various soils. By contrast, the K_d of imazethapyr was not significantly ($p<0.05$) related to SOC and pH.

Pakistani soils, after years of intensive cultivation resulting in low SOC, exhibit low sorption of weakly basic herbicides such as ametryn. Sorption of acidic chemicals such as imazethapyr depends greatly on pH of the soil. As most of the Pakistani soils are alkaline in nature (pH >7.5), they have very low capacities of retaining acidic herbicides like imazethapyr and eventually their leaching is likely to cause contamination of the groundwater.

4.3.4 Sorption of Nonionic Pesticides

Sorption isotherms of carbaryl, phosalone and bifenthrin in selected soils of Australia, and Pakistan are depicted in Figures 4.7, 4.8 and 4.12. As evident from the figures, the isotherms obtained were linear. Equilibrium sorption of hydrophobic organic compounds on suspended solid matter in an aqueous phase has usually been described with linear sorption isotherms (Chiou et al., 1979; Wijayarante and Means, 1984). As the isotherms for these soils were linear, the K_d values for all other soils were estimated from sorption



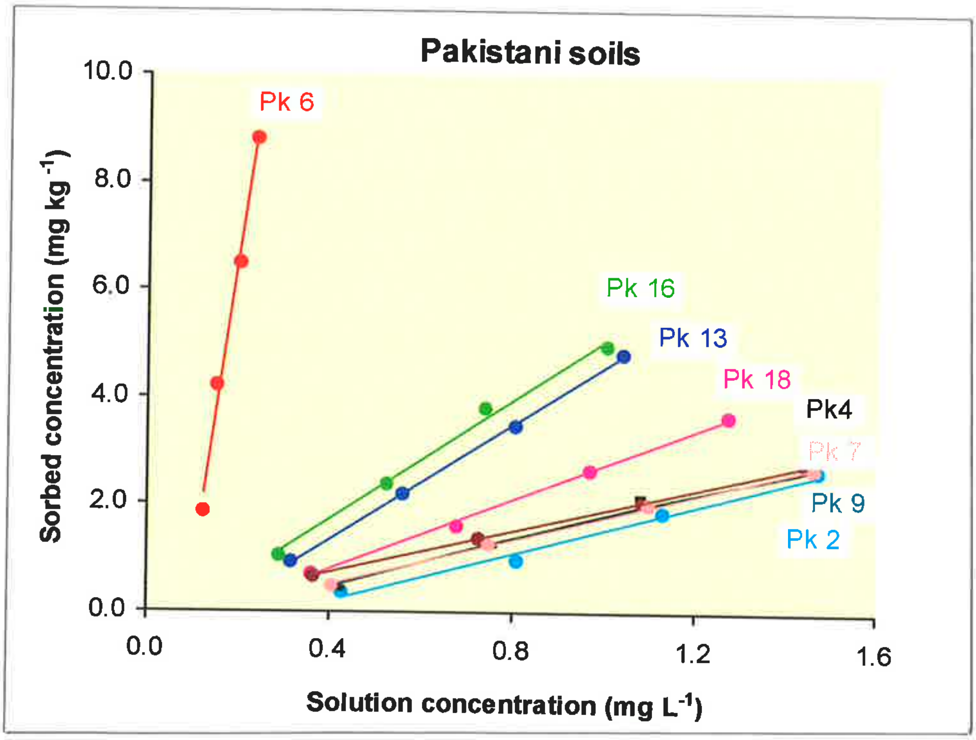
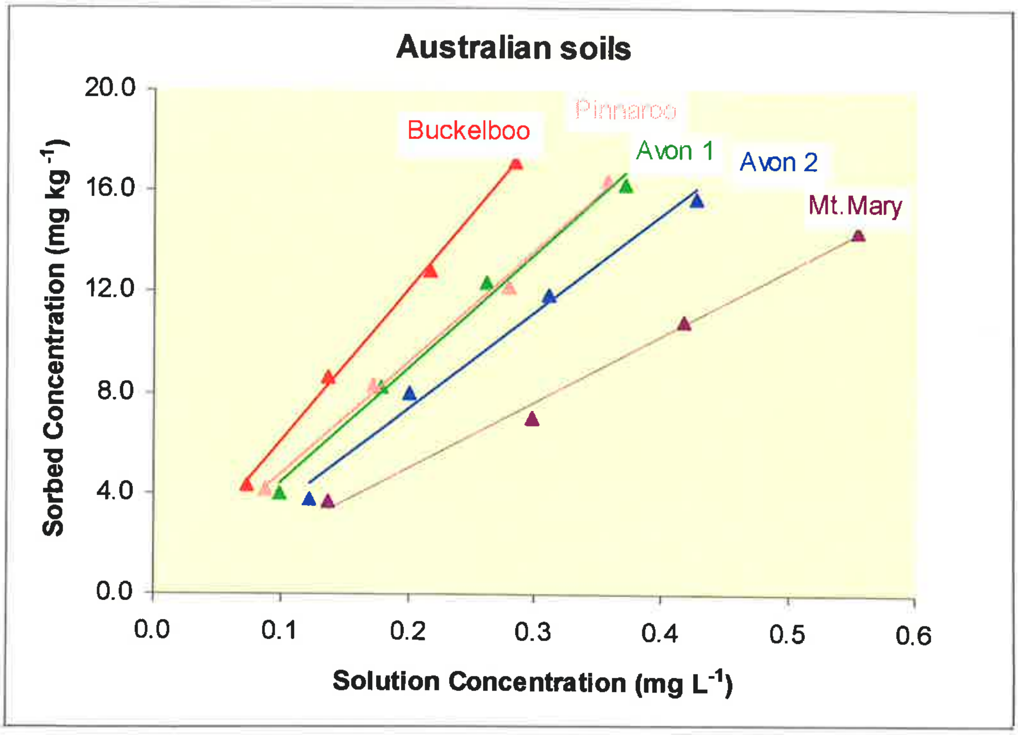


Figure 4.7 Sorption isotherms of carbaryl in some Australian and Pakistani soils



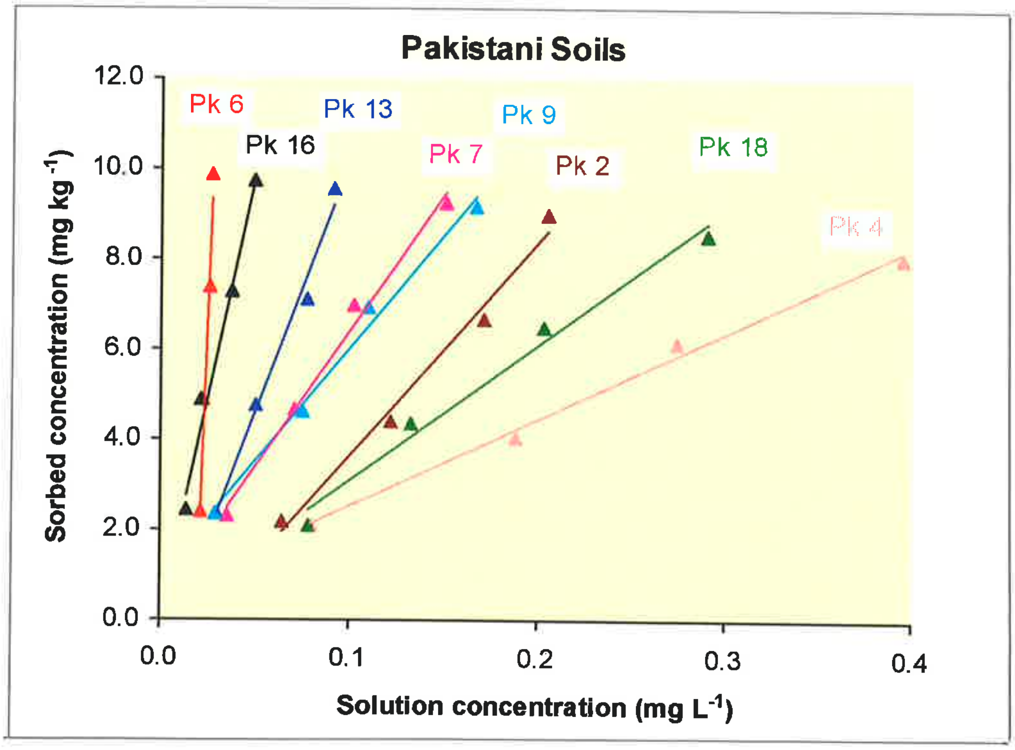


Figure 4.8 Sorption isotherms of phosalone in some Australian and Pakistani soils

measured at a single solution concentration. Single solution concentration for measuring the sorption coefficient (K_d) has been implied in many studies (e.g. Barriuso et al., 1992; Mallawatantri and Mulla, 1992; Baskaran et al., 1996). In total, the extent of sorption (K_d) of carbaryl and phosalone by 48 soils from Australia (26), Pakistan (13), and UK (9) were determined. For bifenthrin, it was not possible to determine sorption using aqueous solution because of its very low aqueous solubility (0.1 mg L^{-1}). Therefore, its sorption was determined in 21 soils from Australia and Pakistan using 2% acetone as a cosolvent. The results and discussion on sorption of bifenthrin follow that for carbaryl and phosalone.

4.3.4.1 Sorption of Carbaryl and Phosalone

The results of the sorption experiments with carbaryl and phosalone in 48 soils are given in Table 4.4. Phosalone was sorbed to a greater extent than carbaryl by all soils, which is consistent with the octanol-water partition coefficients (K_{ow}) of the pesticides. The K_d values of carbaryl ranged from 0.19 to 26.94 L kg^{-1} in Australian soils, 0.99 to 59.67 L kg^{-1} in Pakistani soils, and 1.09 to 8.8 L kg^{-1} in UK soils. The K_d values for phosalone varied from 4.8 to 294 L kg^{-1} in Australian soils, from 15.5 to 1182 L kg^{-1} in Pakistani soils, and from 18.1 to 205.2 L kg^{-1} in UK soils. Such a wide range of K_d values suggests weak to very high sorption capacities of the soils for the pesticides.

Despite the fact that carbaryl has a long history of use as a broad-spectrum carbamate insecticide against over 150 major agricultural pests (Back, 1965) on over 100 field, vegetable and fruit crops (Kuhr, 1970), there are few other studies reported on carbaryl sorption with which to compare these results. Caro et al. (1974) and Sharom et al. (1980) reported that sorption of carbaryl to the soil surface was greater than that of carbofuran. The Freundlich k values were 2.20 and 0.51 for carbaryl and carbofuran, respectively (Caro et al., 1974). However, the studies conducted by Helling et al. (1971) found carbaryl to be mobile in soils.

Table 4.4 Soil distribution coefficients (K_d) and organic C normalised distribution coefficients (K_{oc}) for carbaryl and phosalone in soils of Australia, Pakistan and the UK

Soil #	Soil Name	SOC (Leco)	Carbaryl		Phosalone	
		(g kg soil^{-1})	K_d (L kg soil^{-1})	K_{oc} (L kg C^{-1})	K_d (L kg soil^{-1})	K_{oc} (L kg C^{-1})
Australian soils						
1	SS6	70.1	14.50	207	190.0	2711
2	SS7	138.0	18.88	137	268.6	2500
3	SS8	23.2	16.98	732	292.5	12608
4	Buckelboo	12.9	3.51	272	60.2	4670
5	Avon1	12.9	2.86	221	45.2	3503
6	Avon2	3.8	1.82	475	38.5	10035
7	Mt. Mary	10.2	1.92	189	26.4	2587
8	Pinnaroo	12.0	2.93	245	44.5	3711
9	ACU1	25.6	13.55	529	223.2	8717
10	B211	34.3	11.80	344	173.9	5069
11	N19	44.8	21.38	415	294.2	6566
12	URB-P	26.7	11.23	322	151.7	5680
13	Qld	38.4	26.94	265	168.1	4379
14	1413	8.0	2.69	397	55.7	6962
15	1416	15.0	4.44	297	92.1	6138
16	1418	20.0	6.69	335	121.6	6078
17	1422	25.0	12.90	516	230.8	9233
18	1428	23.0	8.20	356	136.6	5941
19	1432	26.0	7.39	284	139.9	5381
20	1433	58.0	23.02	397	442.7	7633
21	1433A2	21.0	3.65	174	50.0	2381
22	1437	12.0	4.38	365	80.5	6710
23	1440A2	3.0	0.19	64	4.8	1586
24	WAV	10.0	6.01	601	118.9	11890
25	WAC	16.0	8.68	542	171.2	10701
26	WFS	7.0	3.48	497	76.3	10907
Pakistani soils						
27	Pk2	3.9	2.22	572	47.6	12266
28	Pk4	6.7	2.30	349	21.3	3210
29	Pk6	13.8	59.67	4318	1182.0	85528
30	Pk7	6.8	1.90	278	64.1	9375
31	Pk8	3.9	1.05	270	15.5	3993
32	Pk9	6.5	2.07	316	58.3	8920
33	Pk10	2.8	0.99	354	16.6	5952
34	Pk11	6.9	2.55	368	49.0	7088
35	Pk12	6.2	2.38	385	43.5	7038
36	Pk13	9.7	5.30	546	97.9	10095
37	Pk15	6.5	1.67	257	22.7	3492
38	Pk16	22.2	5.53	249	198.6	8948
39	Pk18	5.7	3.26	570	30.5	5322
UK soils						
40	Highfield grass	20.0	1.78	326	46.1	2519
41	Highfield fallow	10.0	1.09	123	21.1	2374
42	BBK-22	19.0	2.80	157	77.8	4500
43	BBK-3	7.0	1.35	162	20.3	2417
44	Geesecraft-wilder	41.0	4.76	125	159.1	4189
45	Geesecraft-arable	22.0	2.09	109	62.1	3238
46	BBK-wilder	86.0	8.80	105	205.2	2448
47	BBK-05	11.0	1.26	205	18.4	3000
48	BBK-08	10.0	1.54	153	18.1	1506

Sorption of hydrophobic compounds has very often been reported to be highly correlated with the SOC content and is relatively independent of the other soil properties (Karickhoff et al., 1979; Hassett et al.,1980a; Xing et al., 1994). It is often suggested (e.g. Hamaker and Thompson, 1972) that one should obtain essentially the same or a narrow range of K_{oc} value for a given pesticide within a group of soils. In contrast, the K_{oc} values obtained for different soils in the present study did not parallel increases in SOC. There was a variation of 11-fold (64 to 732 L kg^{-1}), 17-fold (249 to 4318 L kg^{-1}) and 3-fold (105 to 326 L kg^{-1}) in the K_{oc} values of carbaryl in Australian, Pakistani and UK soils, respectively. A similar trend for phosalone sorption was observed. It is worth noting that in addition to SS8, the other three sandy soils (WAV, WAC, WFS) from Australia showed very high K_{oc} values whereas the soils 1433A2 and 1440A2, which were sub-surface soils, gave very low K_{oc} values for the both pesticides. Previously, Gerritse et al. (1996) reported K_{oc} values of atrazine in 5 sandy soils from Western Australia higher (by an order of magnitude) than other values reported on Australian soils. Briggs (1981a) studied the sorption of carbaryl in 6 Australian soils and reported that K_{oc} of carbaryl ranged from 93 to 221 L kg^{-1}. An average value of 264 L kg^{-1} was obtained from 9 different sources cited by Hornsby et al. (1996) and a mean value of 252 L kg^{-1} in 4 Indian soils has been reported by Jana and Das (1997). In the present study, mean K_{oc} values for carbaryl were 349 L kg^{-1} for Australian, 376 L kg^{-1} (excluding Pk6) for Pakistani and 163 L kg^{-1} for UK soils. The mean values of K_{oc} for Pakistani and Australian soils are higher than the foregoing values from the literature. For phosalone, mean values of 6318 L kg^{-1} for Australian soils, 7142 L kg^{-1} (excluding Pk6) for Pakistani soils and 2910 L kg^{-1} for UK soils were obtained in the study, which clearly indicates that the soils of Pakistan and Australia are more reactive than those collected from UK in terms of sorption with nonionic pesticides. Since clay minerals are generally assumed to be inert towards the sorption of nonionic pesticides such as carbaryl and phosalone, the differences in K_{oc} values among the soils might be attributed to the different potential of soils for sorbing these pesticides due to the differences in the quality of organic C.

The relationships of SOC with the K_d values of carbaryl and phosalone in individual group of soils (Figure 4.9) gave good fit for linear relations. The strength of correlation decreased in the order: UK (r^2, 0.97 and 0.89) > Pakistani (r^2, 0.53 and 0.83) > Australian soils (r^2, 0.24 and 0.08). The relationships of SOC with K_d in all soils of the three

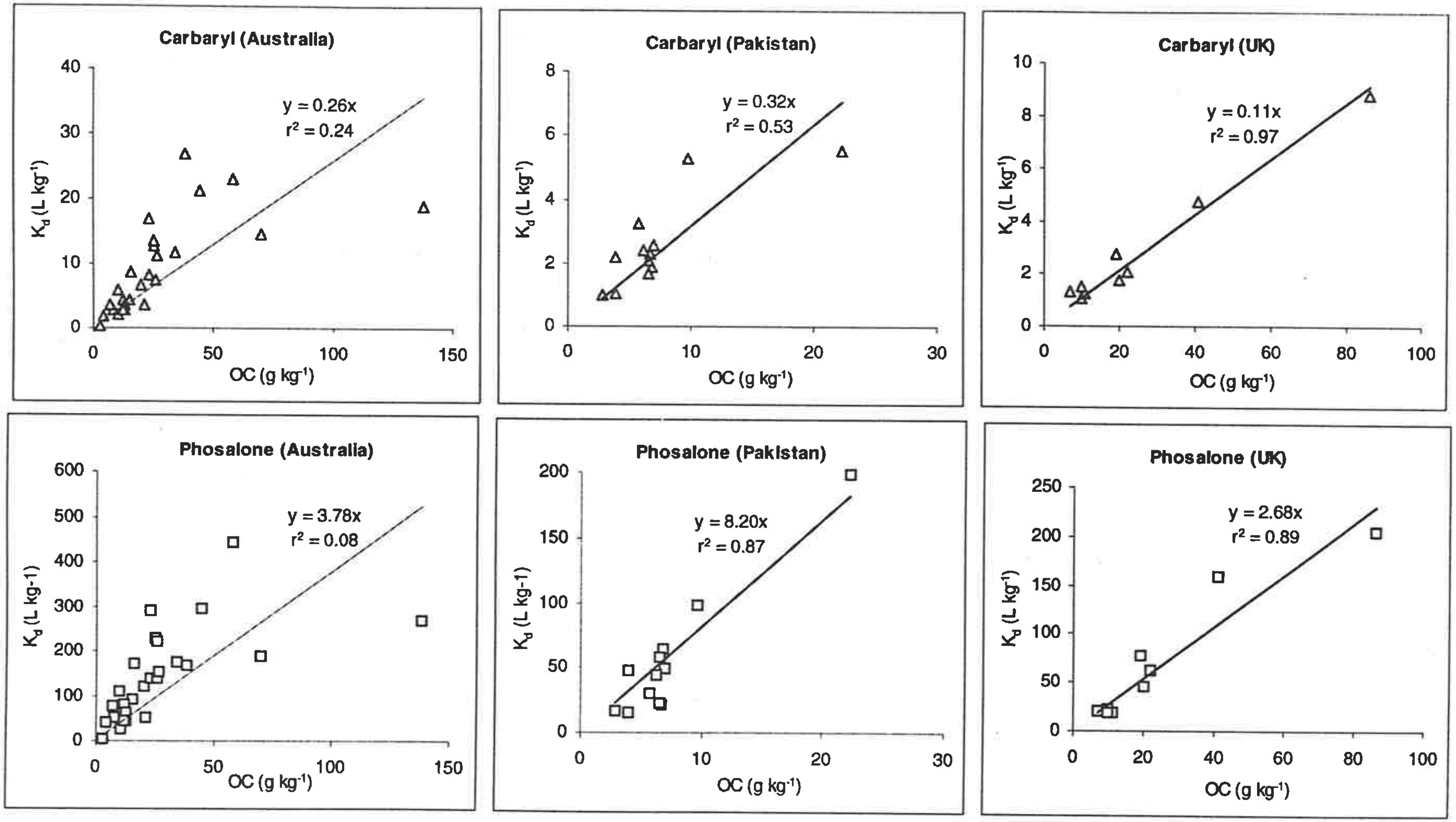
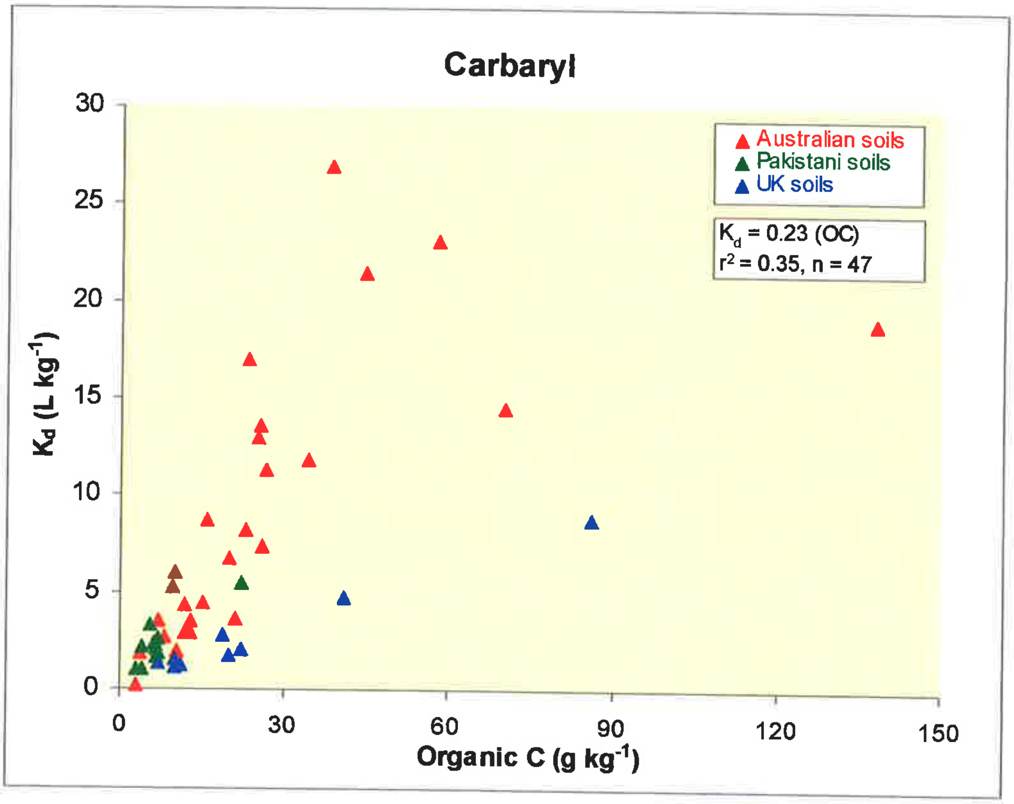


Figure 4.9 Relationships of OC and K_d values of carbaryl and phosalone in Austalian, Pakistani and UK soils

countries (excluding one soil, Pk6, which had an exceptionally high K_d value) gave r^2 values of 0.35 and 0.30 for carbaryl and phosalone, repectively (Figure 4.10). The results indicate that better relationships may be obtained with soils from within a region or country, than with comparisons made across regions. However, the subset of soils from Australia gave a lower r^2 value than those for the Pakistani and the UK soils. This indicates that the K_{oc} values of nonionic pesticides can also vary between soils of the same region, probably due to different affinities of SOC for the pesticides or interplay of other properties. The Australian subset was larger and had wider coverage of soil properties. This is supported by the substantial variations reported in the sorption of linuron and fenamiphos in some Western Australian soils (Singh et al., 1990).

It is also evident from the Figure 4.10 that the Pakistani soils generally had higher sorption of carbaryl and phosalone per unit OC than the Australian soils. The soils from UK, with generally much higher SOC, were lowest in their sorption capacities for the two pesticides on the basis of SOC. The higher SOC contents of the soils show accumulation of OC in prevailing colder climate in the region. Decomposition of SOC might have been more rapid in the warmer climates of Australia and Pakistan, which might have caused the higher sorption capacities per unit OC of these soils. The other major difference is the land use and particular type of vegetation being the source in the case of UK soils.

That sorption of the pesticides by the soils of Pakistan and Australia differed from that in the UK soils cautions against placing undue reliance on overseas data for prediction of pesticide sorption behaviour in Australian and Pakistani soils.



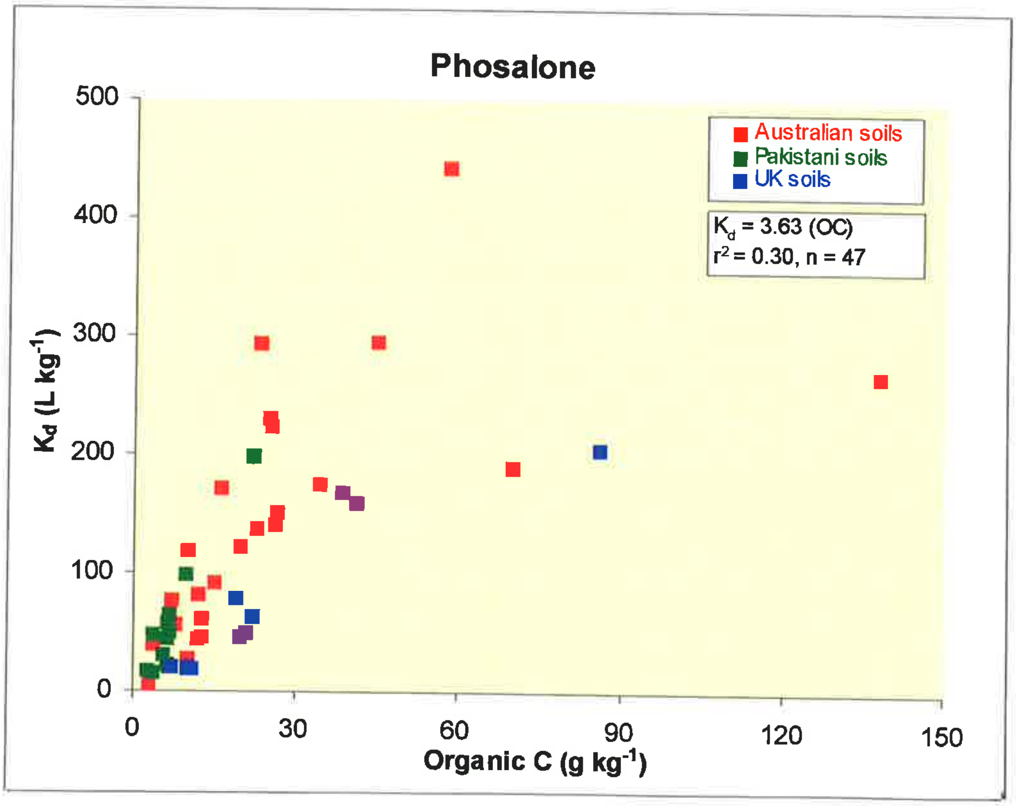


Figure 4.10 Relationships between SOC and K_d of carbaryl and phosalone in 47 soils from three countries

4.3.4.2 Sorption of Bifenthrin in Selected Soils of Australia and Pakistan

Initial sorption studies with bifenthrin did not yield reproducible results even in the presence of up to 20% (V/V) of methanol as a cosolvent, owing the low solubility of bifenthrin in methanol. Therefore, 2% (V/V) acetone was used as a cosolvent in these studies. In Figure 4.11, the sorption coefficients estimated from batch equilibrium studies for soil Pk7 are plotted against the volume fraction of acetone (f_c). As evident from the figure, K_d values of bifenthrin from the aqueous organic binary mixtures decreased exponentially with increasing f_c. This decrease in sorption was expected, as the increase in the fraction of cosolvent such as acetone causes an increase in solubility of hydrophobic compounds such as bifenthrin. This is in accord with the previously reported studies (Nkedi-Kizza et al., 1985; Nkedi-Kizza et al., 1987).

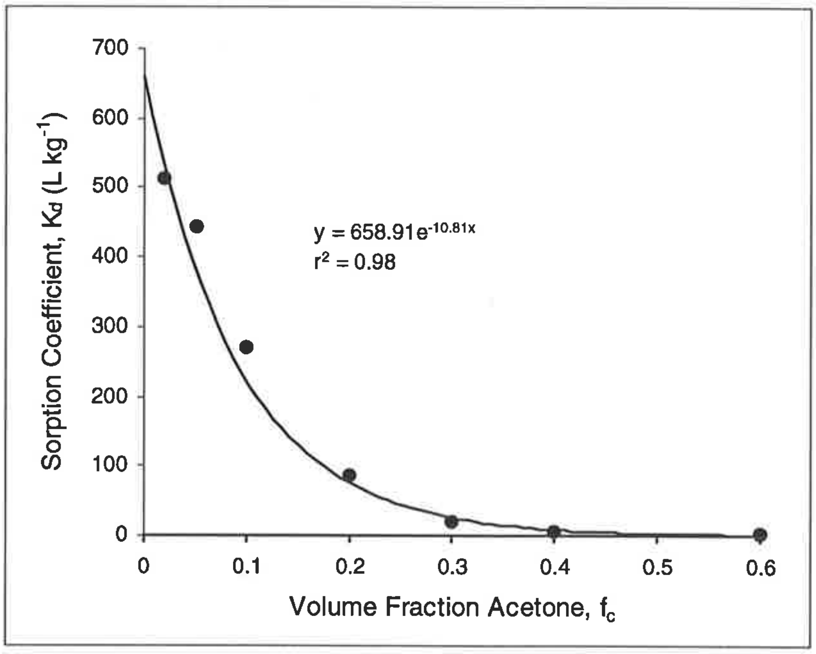
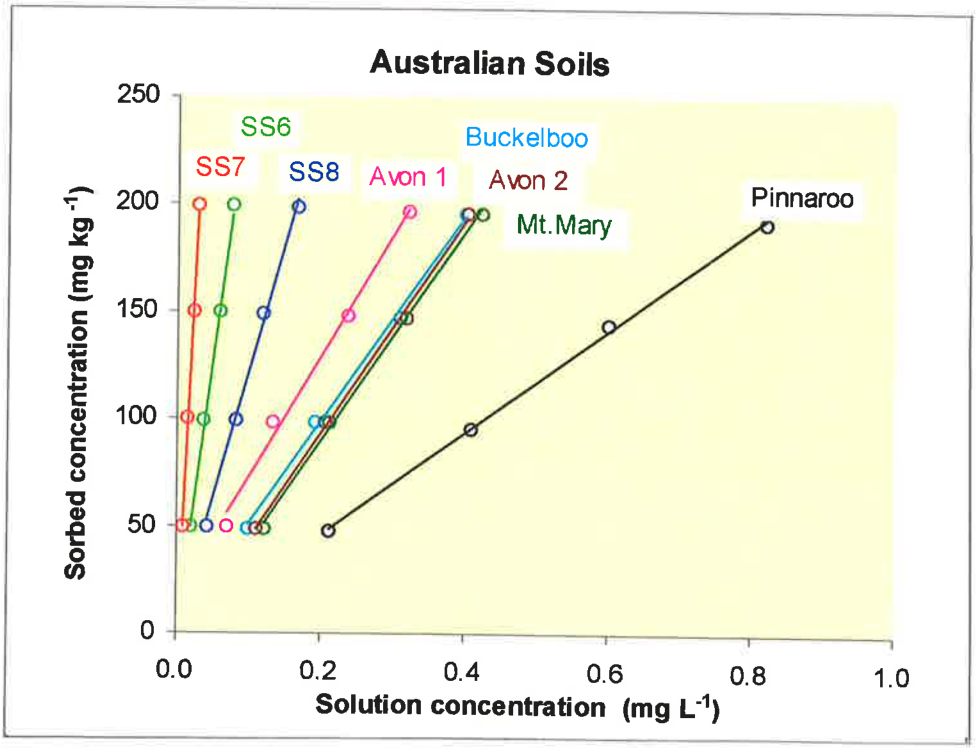


Figure 4.11 Relationship between K_d of bifenthrin and fraction of cosolvent

The relationship between fraction of cosolvent and K_d values in Figure 4.11 shows that 2% acetone in solution caused ~22% decrease in K_d values. The sorption isotherms in the presence of 2% (v/v) of acetone as a coslovent in 0.01M $CaCl_2$ are presented in Figure 4.12 and the results obtained are summarised in Table 4.5. The soils varied widely in their



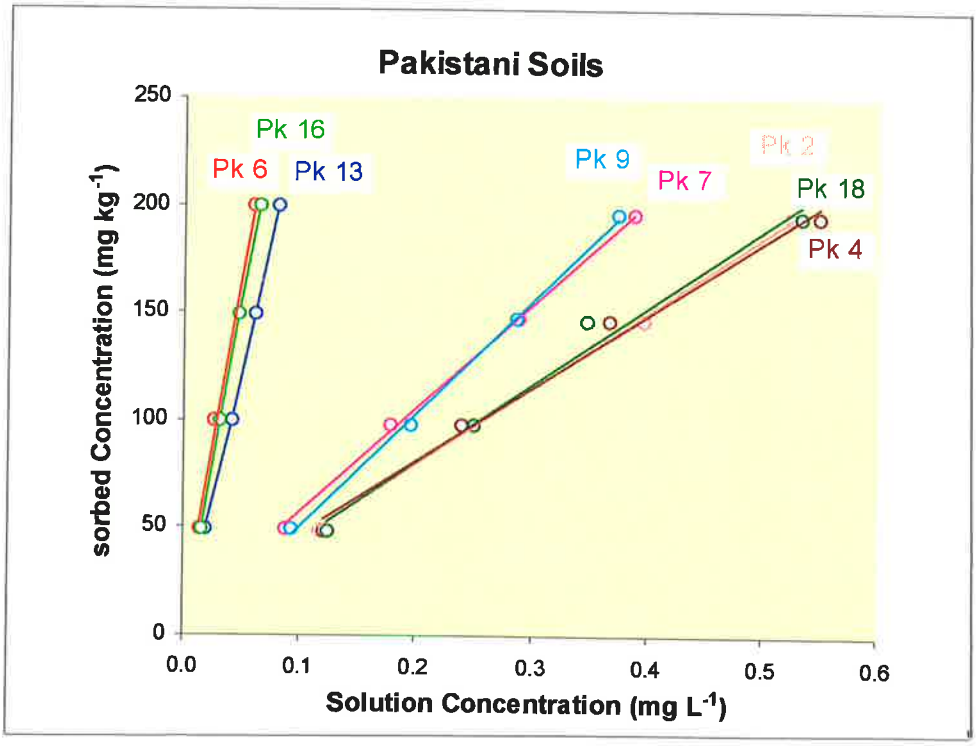


Figure 4.12 Sorption isotherms of bifenthrin in some Australian and Pakistani soils

Table 4.5 Sorption coefficients (K_d, K_{oc}) of bifenthrin in the presence of 2% acetone as a cosolvent.

Sr #	Soil Name	SOC	Bifenthrin sorption	
			K_d	K_{oc}
		(g kg soil^{-1})	(L kg soil^{-1})	(L kg C^{-1})
Australian soils				
1	SS6	70.1	2596	37031
2	SS7	138.0	6717	48672
3	SS8	23.2	1211	52190
4	Buckelboo	12.9	487	37663
5	Avon1	12.9	630	48867
6	Avon2	3.8	476	123987
7	Mt. Mary	10.2	464	45444
8	Pinnaroo	12.0	236	19664
Pakistani soils				
9	Pk2	3.9	376	96781
10	Pk4	6.7	374	56621
11	Pk6	13.8	3333	241143
12	Pk7	6.8	513	75038
13	Pk8	3.9	287	73962
14	Pk9	6.5	517	79047
15	Pk10	2.8	243	87036
16	Pk11	6.9	460	66460
17	Pk12	6.2	447	72409
18	Pk13	9.7	2450	252629
19	Pk15	6.5	428	65831
29	Pk16	22.2	3146	141707
21	Pk18	5.7	383	66944

K_d and K_{oc} values. In Australian soils, K_{oc} varied six-fold whereas in Pakistani soils, there was a variation of four-fold. These results show that the range of K_{oc} values for bifenthrin was narrower than those for carbaryl and phosalone as reported above (Table 4.4). It is interesting to note that soil SS8 from the Australian group and Pk6 from the Pakistani group which had the highest K_{oc} values for carbaryl and phosalone, did not exhibit a particularly high sorption capacity for bifenthrin. Also, the pattern of sorption of bifenthrin in other soils was not consistent with those of carbaryl and phosalone. This may be due to the cosolvent altering the organic matter, perhaps changing its conformation in a way that affected sorption of bifenthrin. Direct competition between the pesticide and solvent for sorption sites, pesticide-cosolvent interactions via hydrophobic bonds, as reported by Arienzo et al. (1993) for diazinon which like bifenthrin, may also be involved. Freeman and Cheung (1981) suggested that rate of desorption of hydrophobic organic compounds from sediments may be influenced by the presence of organic cosolvents, which may induce swelling or shrinking of the organic C gel matrix. Solvent-SOM and pesticide-SOM interactions are poorly understood and require further investigation.

These results show that the use of cosolvents can facilitate determination of the sorption of very hydrophobic pesticides. However, the presence of a cosolvent may change the sorption behaviour of such pesticides possibly by changing the properties of the SOM, and care must be taken when making predictions or assumptions about the sorption and transport behaviour of hydrophobic pesticides from the data obtained in the presence of cosolvents.

4.3.5 Influence of the Particulate OC on Sorption of Nonionic Pesticides

As K_d values of nonionic pesticides do not converge to a similar K_{oc} value when normalised by the fraction of SOC, it is likely that different components of SOC differ in their sorptive capacities. Therefore, the relationship between K_d and different particle size fractions of SOC was examined. The Pakistani soils Pk6 was not included in the relationship due to its exceptional high K_d value.

Figure 4.13 shows that K_d for carbaryl and phosalone was only slightly better correlated with the 53 μm - 2 mm than with the <2 mm fraction of SOC, and there was no significant difference for ametryn and bifenthrin. The results shows that there is no significant difference between sorption of these pesticides by the particulate SOC and that in dissolved form. Carter et al. (1982) also found no difference between the binding of DDT to dissolved humic acids from binding to particulate organic C on the basis of per unit OC. This indicates that the specific nature of the soil organic materials rather than the size of particles may be a determining factor in the wide variation of K_{oc} values of the nonionic pesticides.

4.3.6 Sorption of Monocrotophos and Dichlorvos

Sorption of monocrotophos and dichlorvos in 8 Pakistani soils was determined using the batch equilibrium method, and the results are given in Table 4.6. Sorption of the both pesticides varied greatly among soils, and the K_{oc} values were much higher than the estimated values of 1 and 30 L kg^{-1} for monocrotophos and dichlorvos, respectively reported by Hornsby et al. (1996). Lee et al. (1990a) studied ^{14}C monocrotophos in four different soil types using batch equilibrium method and reported K_{oc} values to vary from 7.9 - 30.8 μg g^{-1} organic matter with an average of 18.9. The hydrophilic character of monocrotophos is responsible for its low sorption in soils.

As mentioned earlier in this chapter, K_d is computed in the batch equilibrium method from the amount of pesticide sorbed to the soil or its constituents and that in the solution at equilibrium, assuming that there is no significant loss due to degradation or evaporation of the chemical. However, measurement of the pesticides remaining in the soils after sorption experiment revealed that substantial loss of dichlorvos (21-64%) and monocrotophos (up to 19%) occurred during the shaking periods of 2 h and 16 h, respectively (Table 4.6). Studies with the batch procedure were discontinued, and a new method was adapted for determining the sorption of dichlorvos, and monocrotophos (Chapter 5).

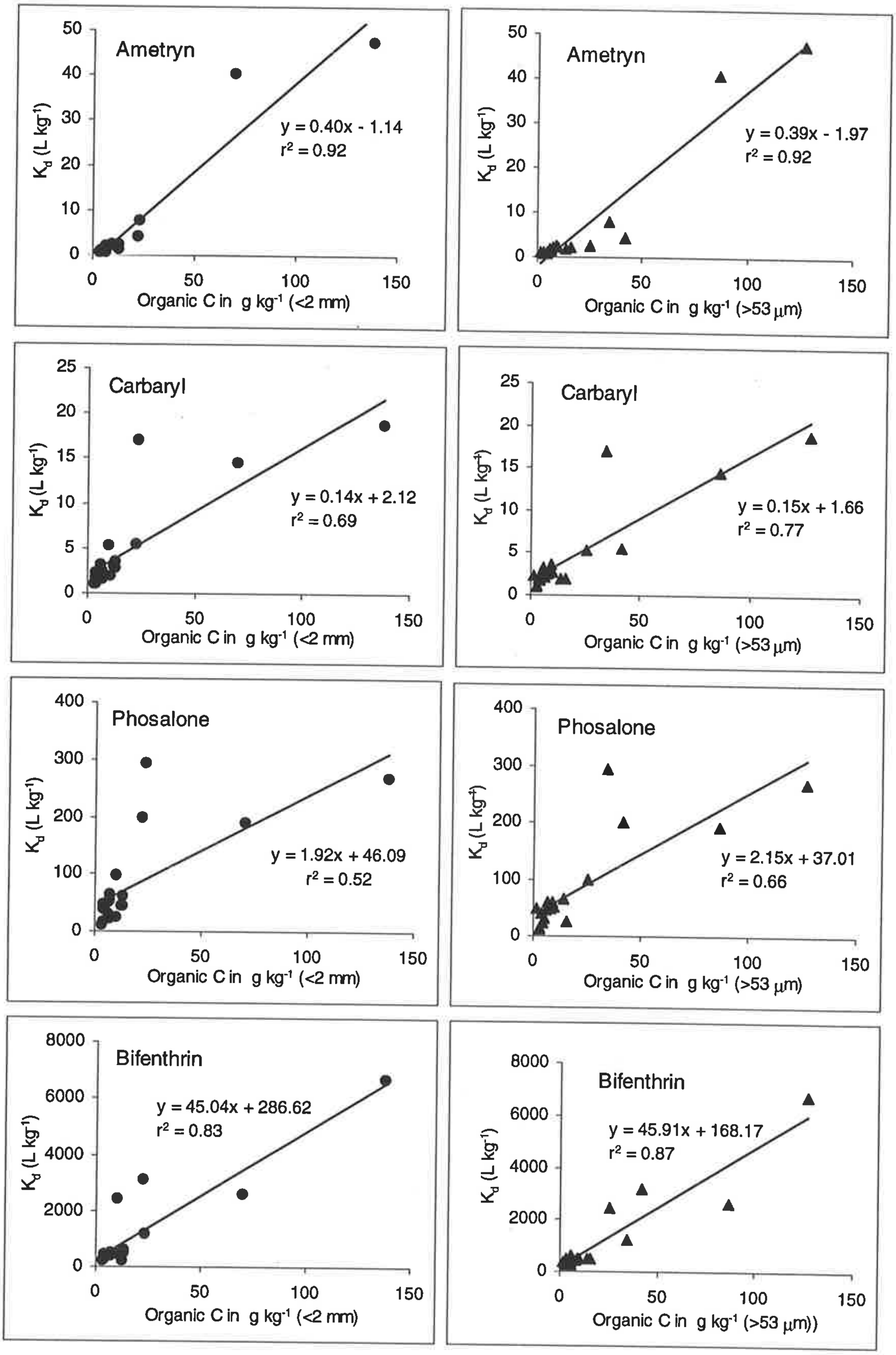


Figure 4.13 Relationship of K_d of ametryn, carbaryl, phosalone, and bifenthrin with SOC (<2 mm and 53 μm - 2 mm) in selected soils from Pakistan and Australia

Table 4.6 K_d and K_{oc} values of dichlorvos and monocrotophos, and extent of their losses during batch equilibration time

Soil	K_d (L kg^{-1})	K_{oc} (L kg^{-1})	% loss
Dichlorvos			
Pk2	5.84	1505	61.4
Pk4	2.89	434	64.4
Pk6	1196.94	86609	21.3
Pk7	4.45	651	53.4
Pk9	4.11	628	59.1
Pk13	5.22	538	52.7
Pk16	30.83	1389	43.5
Pk18	1.44	251	57.2
Monocrotophos			
Pk2	0.09	22	N.D.
Pk4	0.07	10	N.D.
Pk6	1.47	106	10.1
Pk7	0.27	39	N.D.
Pk9	0.09	14	N.D.
Pk13	0.46	48	15.7
Pk16	1.23	55	18.8
Pk18	0.25	43	N.D.

N. D.= not determined

4.4 Conclusions

Based on the above study, following conclusions were drawn.

- Filtration can be an important source of error in the determination of pesticide concentration in sorption studies. The choice of filter during sorption experiments is crucial.

- Of the ionisable pesticides studied, ametryn was sorbed more strongly than imazethapyr. Both soil pH and organic C were correlated significantly with the sorption of ametryn, whereas, pH was the only strong determinant of imazethapyr sorption. No correlation was found between the K_d values of both pesticides and the clay contents of the soils.

- Soils varied widely in their sorption capacities for nonionic pesticides. The K_{oc} of bifenthrin, phosalone and carbaryl varied by an order of magnitude among the soils and increased in the order listed.

- The sorption capacities of the soils from different countries for carbaryl and phosalone were in the order of Pakistan > Australia > UK. Therefore, undue reliance on overseas data for pesticide behaviour is likely to be erroneous.

- The K_d values of carbaryl and phosalone were poorly correlated with the OC contents of the 47 soils. Although, there was a slightly better correlation of K_d with the OC 53 µm - 2 mm than with OC <2 mm.

- The sorption data indicated that the chemical nature of SOC, in addition to the amount, may be important in the sorption of nonionic compounds. This is the focus of Chapter 6.

- The batch equilibration method could not be used to determine the sorption of monocrotophos and dichlorvos, due to degradation losses of both the pesticides during the equilibration time. This led to the adaptation of a new method of determining sorption of rapidly degrading and highly soluble pesticides, which is the subject of the following chapter (Chapter 5).

CHAPTER 5

Measuring Sorption of Pesticides by a Transient, Unsaturated Flow Method

5.1 Introduction

Conventional batch equilibration is by far the most commonly used approach to obtain the sorption data of the organic compounds by soil in the laboratory. As mentioned in the preceding chapter, sorption of a compound is measured in this method from the difference between initial and final concentrations in solution. However, this method can produce erroneous results in case of relatively fast degrading pesticides such as dichlorvos, due to degradative losses during equilibration (see Chapter 4). Moreover, for highly soluble and weakly sorbed pesticides such as monocrotophos, the common analytical methods of determining the pesticide concentration in the supernatant solution may lead to large errors due to the relatively small changes in concentration that occur during the equilibration. These limitations of measuring sorption with the classical batch method necessitated development/adaptation of more accurate and reliable method for measuring the sorption of weakly sorbed and rapidly degradable organic compounds.

An unsaturated flow method was originally suggested by Katou et al. (1998) for determination of adsorption of exogenous, weakly reactive inorganic ions by variable-charge soils without causing appreciable desorption of indigenous ions. They applied this method to Cl^{-1} adsorption by an Andisol subsoil and recommended this method for the soils where adsorption of ions is predominantly due to an increase in the exchange capacity of the soil. The approach is based on displacement of antecedent solution by invading water, as observed in unsaturated soil. Water is absorbed into a horizontal column packed with soil which has been premixed with a salt solution. The amount of solute adsorbed by the soil and the equilibrium solution concentrations prior to the water absorption are acquired from a plot of the solute content against the soil water content in a region beyond the 'plane of separation' (Smiles and Philip, 1978).

The purpose of the present study was to use the unsaturated flow method originally developed by Katou et al. (1998) for adsorption of ions and later adapted by Kookana et al. (1998a) for pesticides, to measure the sorption of two organic pesticides, dichlorvos and monocrotophos, possessing low sorption affinities and relatively fast degradation in soils. This was to determine if the method could provide more accurate sorption data for the two pesticides under realistic conditions.

Theory

It has been well established that during miscible displacement, the water present in a homogeneous soil is pushed ahead by the invading water and the fraction of solute present in the displaced antecedent water accumulates beyond the 'plane of separation', x^* (Smiles and Philip, 1978). The plane that identifies the front of invading water is given by the relation

$$\int_{\theta_n}^{\theta_s} x d\theta = \int_0^{x^*} \theta dx$$

where x is the distance, θ_n the initial water content, θ_s the water content at the proximal end of the soil column and θ is the volumetric water content. Eventually, the mass of solute in soil in this region is increased (Figure 5.1). The change in the solute content in this region is merely due to the change in the water content. Therefore, a plot of mass of solute *v* water content in the region beyond the 'plane of separation' is expected to yield a linear relationship (Katou et al., 1998) expressed by:

$$M = Q_n + C_n (\theta/\rho) \qquad (1)$$

where M denotes the mass of solute (mg kg^{-1}), Q_n the solid phase concentration (mg kg^{-1}), θ the volumetric water content (m^3 m^{-3}), ρ the bulk density (kg m^{-3}) of soil, and C_n is solution concentration (mg m^{-3}) prior to the imbibition of water.

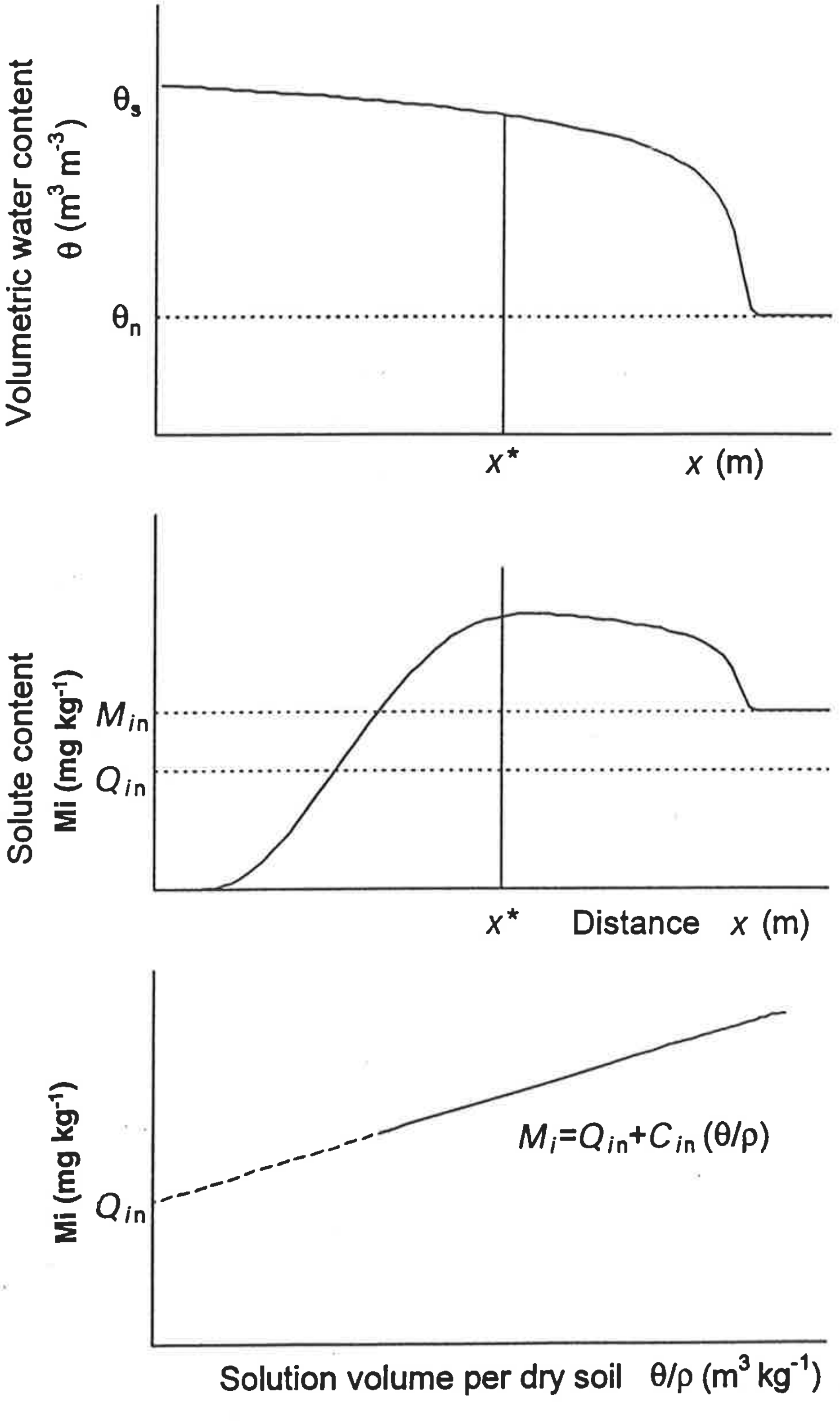


Figure 5.1 Schematic representation of the theory (after Katou et al., 1998)

θ_n=initial water content; θ_s=water content at proximal end; M_{in}=initial solute content; ρ=bulk density; x^*=plane of separation
Initial liquid phase concentration of the solute species i, C_{in}, and initial adsorption by soil, Q_{in}, are obtained from the Mi v θ/ρ plot

5.2 Material and Methods

5.2.1 Horizontal Infiltration Experiments

One-dimensional horizontal infiltration experiments were carried out at a constant flow rate to determine the sorption of dichlorvos and monocrotophos (characteristics given in Chapter 3). The columns, made of acrylic, were 20 cm long and had an internal diameter of 19.1 mm (Plate 5.1).

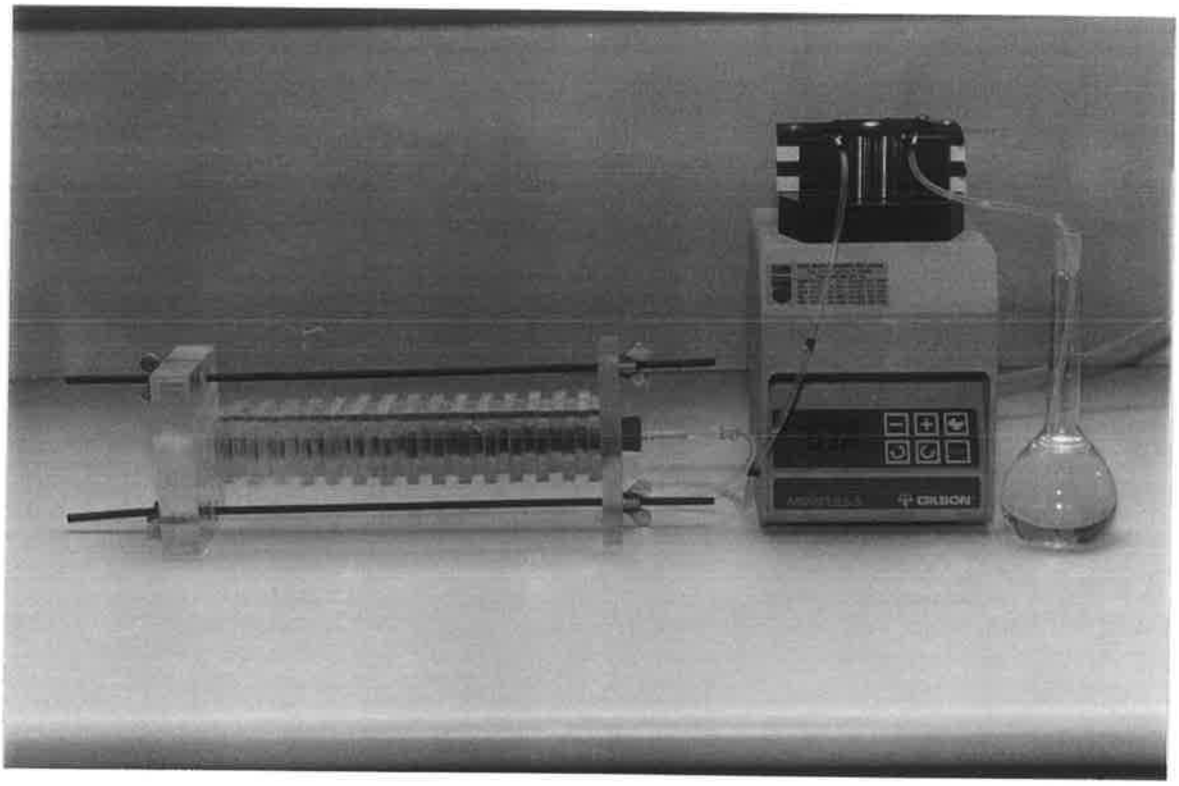


Plate 5.1 The column apparatus used in the experiments

The Pinnaroo soil, with 0.182 kg kg^{-1} clay and 0.012 kg kg^{-1} OC, air dried and sieved to <2 mm, was used for these experiments. Other characteristics of the soil are given in Table 3.1. The soil was spiked with an aqueous solution of either dichlorvos (6 mg kg^{-1} soil) or monocrotophos (2.5 mg kg^{-1} soil), distributed dropwise by spraying over a thin layer of the soil at a water content of 0.08 kg kg^{-1} soil to give an initial gravimetric water content ~0.10 kg kg^{-1}. Sorption of monocrotophos was also studied at soil water content of

0.16 kg kg^{-1} (initial gravimetric water content ~0.19 kg kg^{-1}). The spiked soil was mixed thoroughly in a sealed polyethylene bag to obtain uniform distribution of the pesticide. The soil was packed uniformly into the sectionable acrylic column by adding small increments while gently tapping the sides of the column and pressing with the use of a glass rod until each increment occupied the same volume. After the column was packed, the average bulk density of the soil was calculated from the internal dimension of the column and the actual mass of soil added. The experimental conditions are given in Table 5.1.

Table 5.1 Summary of the experimental conditions during the one-dimensional, horizontal imbibition experiments

Pesticide	Bulk density (kg m^{-3})	Water content (kg kg^{-1})	Initial pesticide concentration (mg kg^{-1})	Flow rate (m s^{-1})	Elapsed time (s)	Plane of separation (cm)
Dichlorvos	1604	0.08	6.0	0.1164	2160	7.5
Monocrotophos	1370	0.08	2.5	0.0582	4380	6.7
	1632	0.16	2.5	0.0582	3600	4.4

The column experiments were conducted in the laboratory at an ambient temperature (24±2°C) by feeding a pesticide-free solution (Milli-Q water) from a volumetric flask into the packed column with spiked soil at a constant flow using a peristaltic pump (Minipuls 3, Gilson, John Morris Scientific Pty Ltd, Australia). After the wetting front had moved about 15 cm, the flow was terminated and the elapsed time was noted. The column was quickly sectioned, a portion of soil from each section (approximately 1.5 g) was immediately transferred to a preweighed glass tube containing $CH_3OH:H_2O$ (90:10) and weight of the tube containing the extracting solution plus soil was recorded. Dichlorvos and monocrotophos was extracted by shaking the tube for one hour. The samples were centrifuged at 1800 rpm for 10 min, filtered and analysed for the pesticide (sorbed plus solution concentration) following the HPLC methods described in Chapter 3. The remaining soil from each 8 mm section of the column was transferred into a pre-weighed container and its water content was measured gravimetrically.

The pesticide contents in the soil samples taken from the region beyond the plane of separation, where the antecedent water accumulated, were plotted against water contents (θ/ρ) and the initial aqueous phase concentration (C_n), and the initial sorption by soil (Q_n) were deduced from linear regression analysis for the pesticides. The sorption coefficient, K_d, of each pesticide was obtained from the quotient of Q_n and C_n.

5.2.2 Pesticide Sorption to Column Material

To determine if the pesticides sorbed onto the column material, segments of the column were immersed in aqueous solutions of dichlorvos (6.0 mg L^{-1}) and monocrotophos (2.5 mg L^{-1}) for two hours. At the end of this time, the concentrations of each pesticide were determined by HPLC and compared with the concentrations in control solutions.

5.2.3 Batch Experiments

Batch studies with dichlorvos and monocrotophos in the Pinnaroo soil were also carried out to enable comparison of the K_d values obtained from batch and flow methods. Five mL (6 mg L^{-1}) of an aqueous solution of dichlorvos (in triplicate) and 5 ml of aqueous solutions containing 0.25, 0.5, 1.0, 2.0 and 3.0 mg L^{-1} of monocrotophos were added to 5 g portions of soil in glass tubes with teflon caps. The soil suspensions were shaken for one hour, centrifuged at 1800 rpm and an aliquot of the supernatant was filtered and analysed for the respective pesticide. The K_d value of dichlorvos was determined from one point sorption while the K_d value of monocrotophos was estimated from the sorption isotherm constructed from the range of the pesticide concentrations.

5.3 Results and Discussion

5.3.1 Sorption of Dichlorvos and Monocrotophos to the Column Material

The tests to determine if there was sorption of the pesticides to the column material (acrylic) during the experiment showed that there was no significant sorption loss of dichlorvos (<1.0%) or monocrotophos) (<0.5%) to the column material compared with the control. These results confirm the suitability of acrylic materials for the manufacture of columns for experiments with compounds having low hydrophobicity. The suitability of acrylic materials for making columns is also supported by the studies of Topp and Smith (1992) on sorption of atrazine and metolachlor (more hydrophobic than dichlorvos and monocrotophos) by a variety of tubing materials. The authors found that neither of these pesticide was significantly sorbed by acrylic plastic.

5.3.2 Sorption at Low Initial Water Content by Flow Method

Figure 5.2 shows the water content profiles for dichlorvos and monocrotophos following water absorption as the flow proceeded. The water content of the soil at the time of spiking the dichlorvos and monocrotophos was 0.08 kg kg^{-1}. In the figure, the gravimetric water content, θ_n, of 0.1 kg kg^{-1} denotes the initial water content after addition of pesticides. The planes of separation (x^*) were found to be 7.5 cm and 6.7 cm for dichlorvos and monocrotophos, respectively.

Figure 5.3 shows the measured dichorvos and monocrotophos content profiles upon imbibition of water into the Pinnaroo soil premixed with the pesticides. The soils had initial concentrations of 6 mg kg^{-1} and 2.5 mg kg^{-1} soil of dichlorvos and monocrotophos, respectively. Upon imbibition of water, monocrotophos was almost completely removed from the soil near the column inlet but a small amount of dichlorvos (~ 0.09 mg kg^{-1}) was detected. Dichlorvos is less hydrophilic than monocrotophos, which accounts for the difference in behaviour.

In Figure 5.4, the pesticide contents in the region beyond the plane of separation are plotted against the water contents on weight basis (θ/ρ) of the soil premixed with pesticide. A straight line relationship was obtained for both dichlorvos and monocrotophos ($r^2 = 0.97$). This shows that the variations in the total concentration of each pesticide in these sections of the column were related solely to the variation in the soil water content, which is in accordance with the theory (Katou et al., 1998). The intercept, therefore, represented the sorption of the pesticide and the slope represented the concentrations in solution. The sorption coefficient of each pesticide is represented by

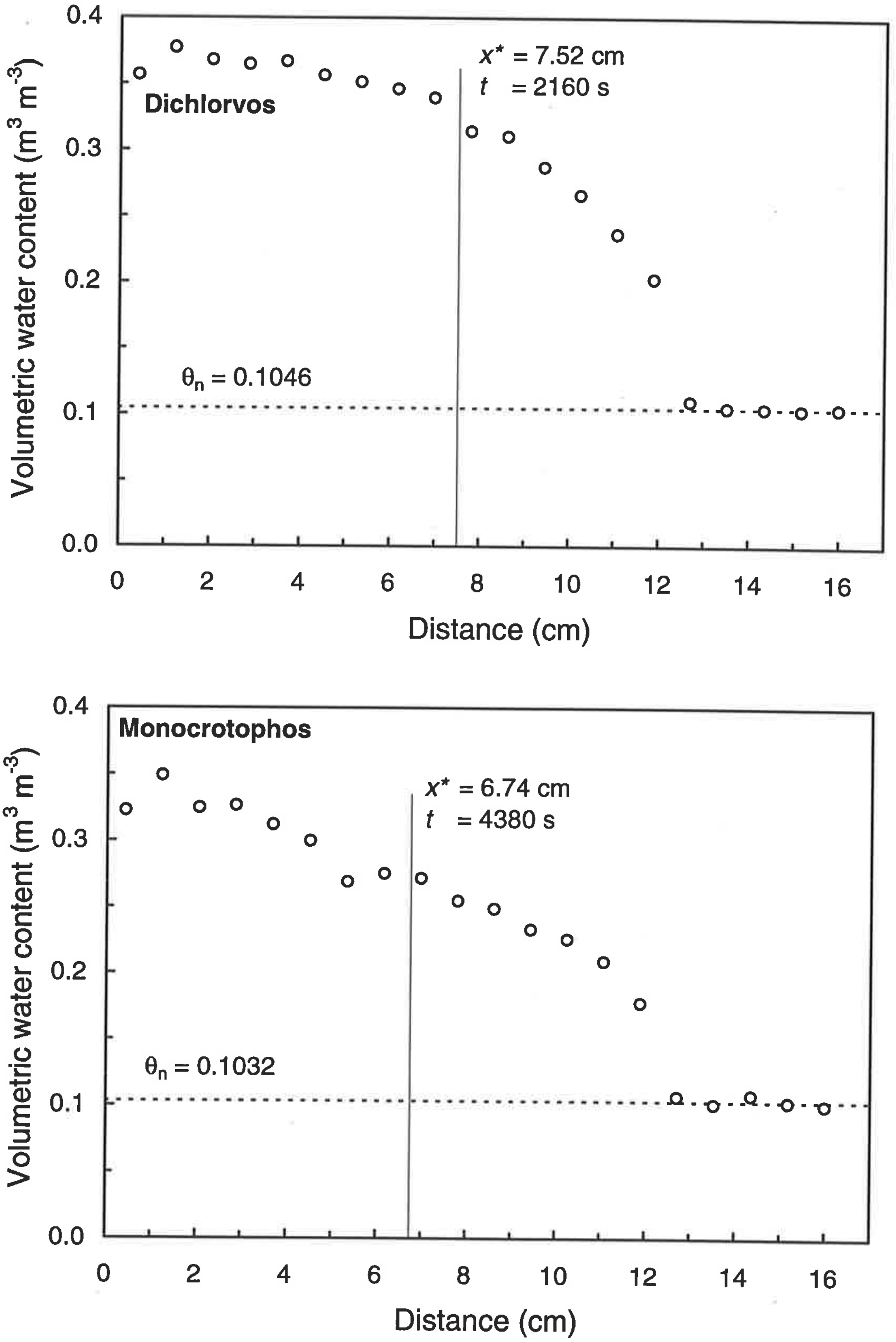
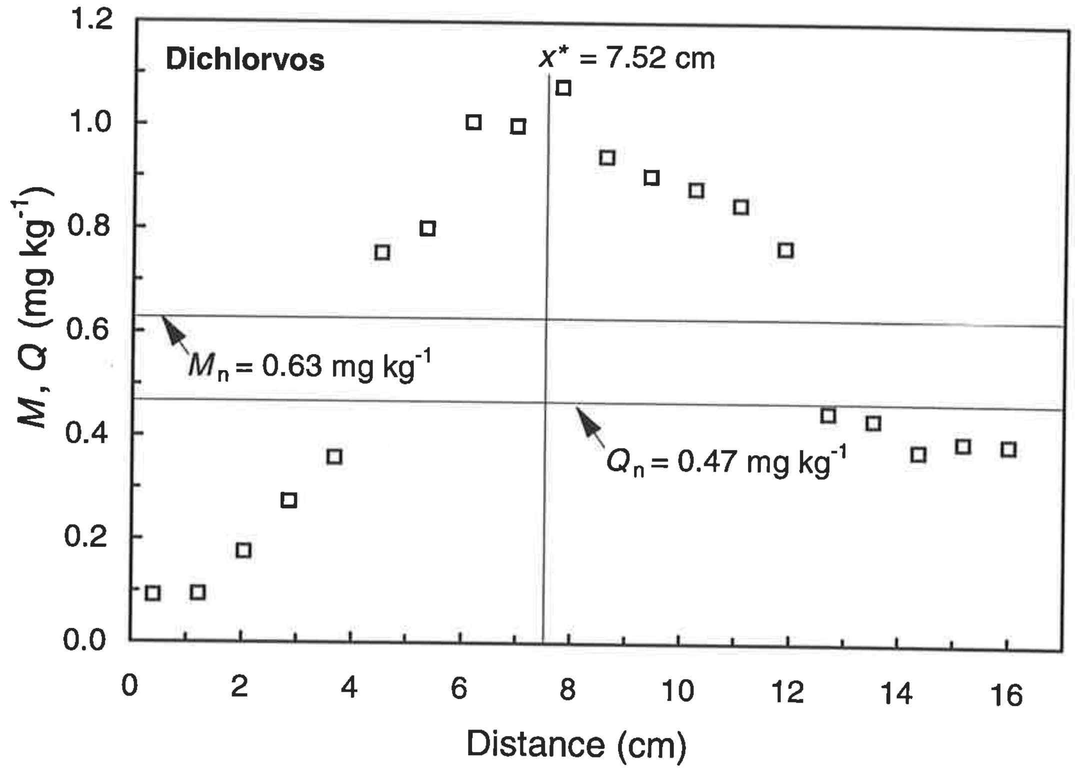


Figure 5.2 Plots of volumetric water contents and distance for dichlorvos and monocrotophos



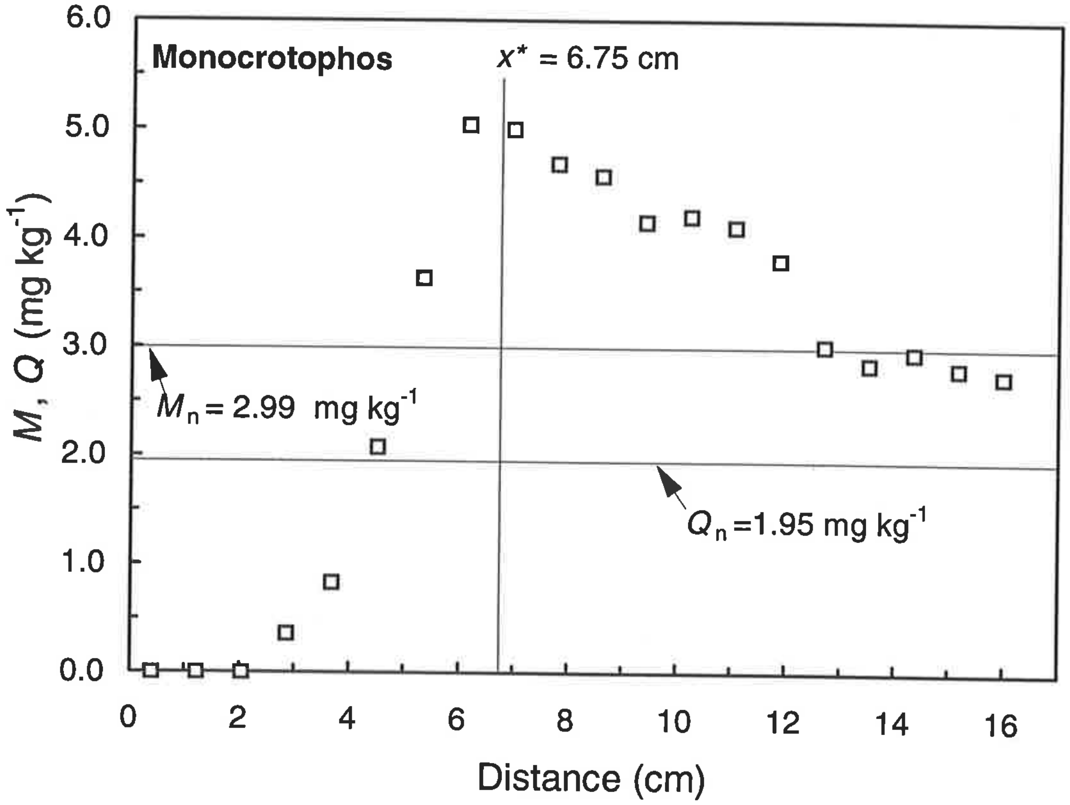
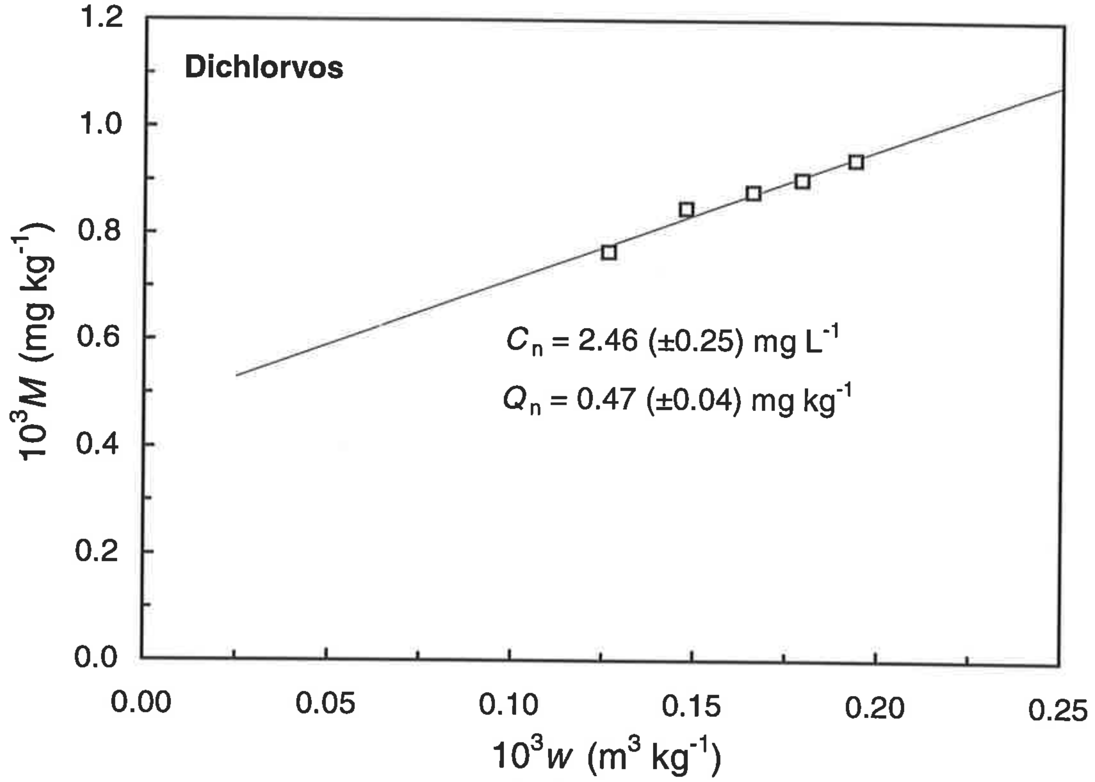


Figure 5.3 Profiles of dichlorvos and monocrotophos contents upon imbibition of water into the soil premixed with the pesticides.



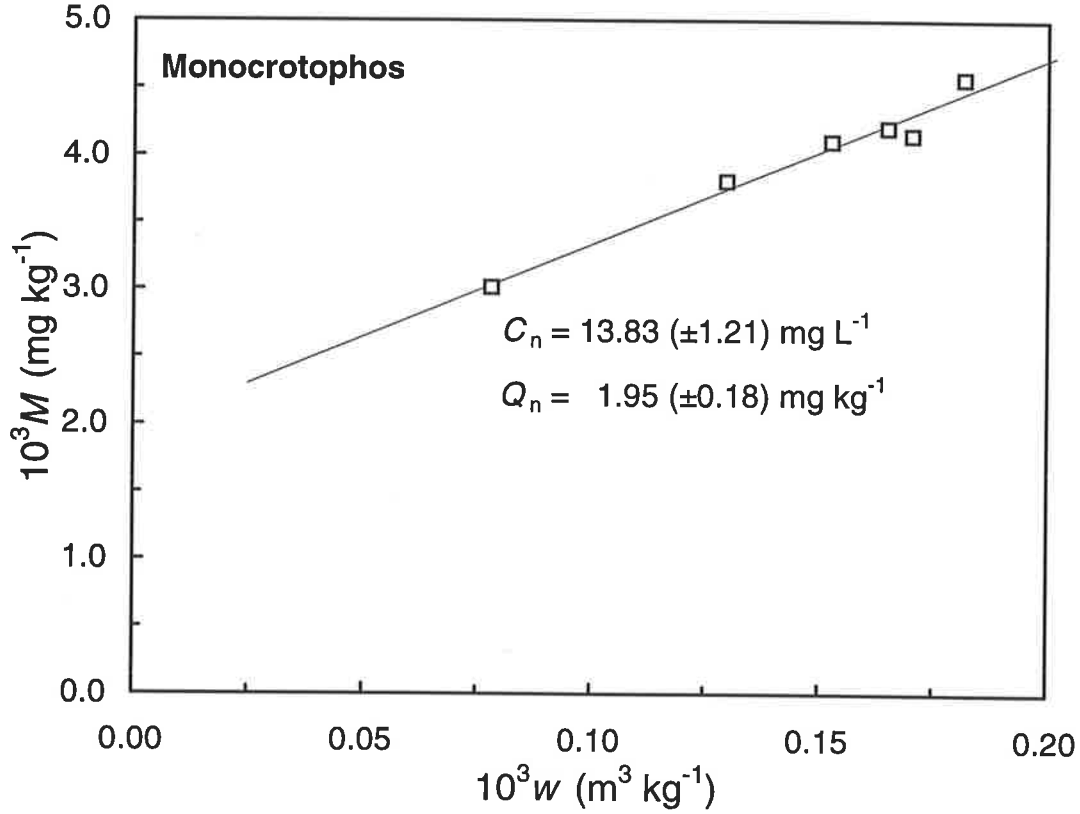


Figure 5.4 Relationships of mass and water content in the region beyond the plane of separation for dichlorvos and monocrotophos

the ratio of the intercept to slope (Q_n/C_n). The values of Q_n were found to be 0.47 (± 0.04) and 1.95 (± 0.18) mg kg^{-1} for dichlorvos and monocrotophos, respectively. The values of C_n obtained were 2.46 (± 0.25) and 13.83 (± 0.1.21) mg L^{-1} for dichlorvos and monocrotophos, respectively. Thus, the sorption coefficients for dichlorvos and monocrotophos ($K_d = Q_n/C_n$) were 0.19 L kg^{-1} for dichlorvos and 0.14 L kg^{-1} for monocrotophos (see Appendices 5.1 and 5.2 for detailed data).

A similar experiment with monocrotophos conducted under the same experimental conditions yielded reproducible results, with a K_d value of 0.15 L Kg^{-1} derived from Q_n (1.76 ± 0.18) mg kg^{-1} and C_n (11.95 ± 1.02) mg L^{-1}. The detailed results and figures are given in Appendix 5.3.

5.3.3 Sorption at High Initial Water Content by Flow Method

To determine the influence of water content on the sorption of monocrotophos using the flow method, the experiment was repeated at the higher water content of 0.16 kg kg^{-1} (volumetric water content, θ, 0.19). The results are represented in Figures 5.5 to 5.7. Details are given in Appendix 5.4. The K_d calculated from Q_n (1.16 ± 0.15) mg kg^{-1} and C_n (11.01 ± 0.94) mg L^{-1} was 0.11 L kg^{-1} which is slightly lower than the value from the experiment with the low water content ($\theta = 0.1$). This shows that the initial water content has little influence on sorption coefficient of the pesticide.

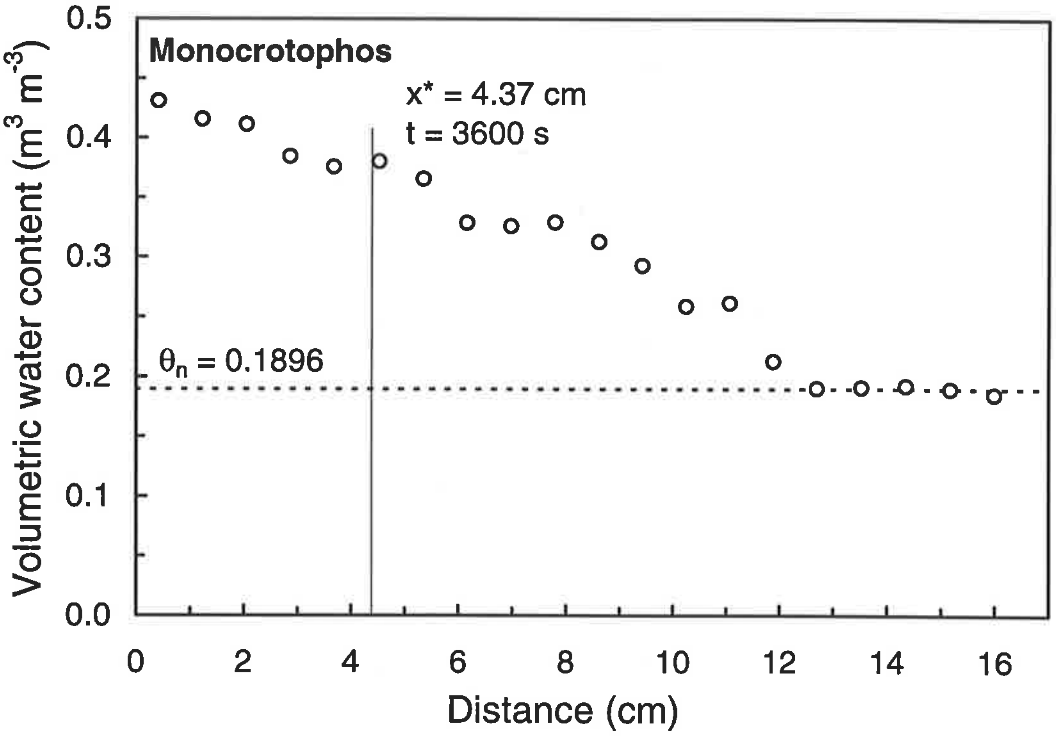


Figure 5.5 Plot of volumetric water content and distance of monocrotophos at high initial soil water content ($\theta = 0.19$)

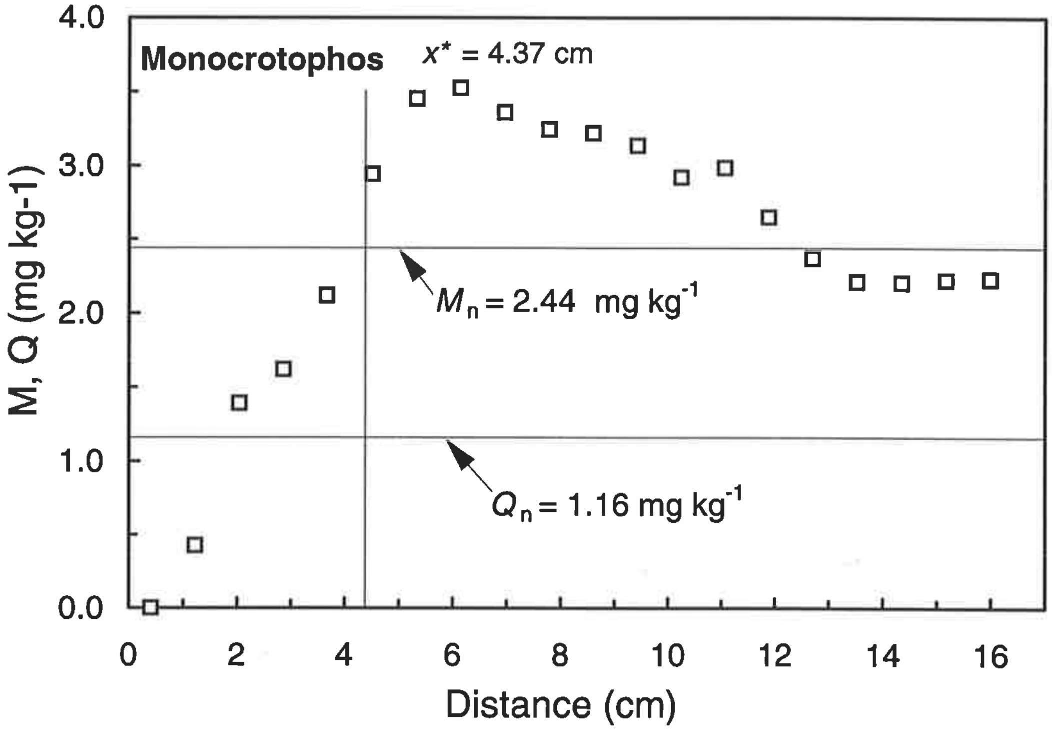


Figure 5.6 Monocrotophos contents profile upon imbibition of water into the soil mixed with monocrotophos at high initial soil water content ($\theta = 0.19$)

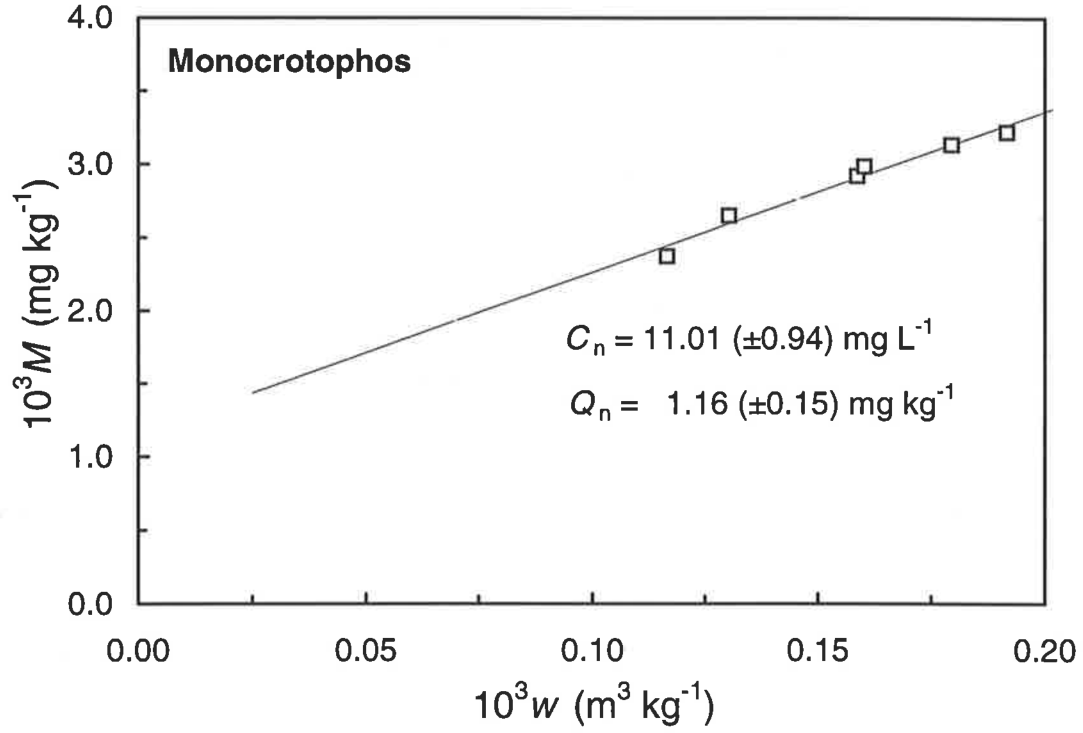


Figure 5.7 Relationships of mass and water content for monocrotophos at high initial soil water content (θ = 0.19)

5.3.4 Comparison With Batch Sorption Coefficients

The batch studies conducted for determination of sorption of the pesticides gave K_d values of 3.22 L kg^{-1} (average value from one-point concentration) and 0.25 L kg^{-1} (determined from the 5-point isotherm in Figure 5.8) compared with 0.19 and 0.14 L kg^{-1} by the unsaturated flow method for dichlorvos and monocrotophos, respectively.

It is clear from these results that the K_d value for dichlorvos obtained from batch studies is 17-fold greater and that for monocrotophos two-fold greater than the respective values obtained with the unsaturated flow method. The batch values are, therefore, wrong. The much higher K_d value for dichlorvos using batch method was due to its much greater loss during the shaking time, which was attributed to the sorbed phase concentration. These results showed that the batch values for these pesticides were not comparable with those from unsaturated flow method due to the degradation/volatilisation during the experiment as evident from the studies presented in Chapter 4 (Section 4.3.6).

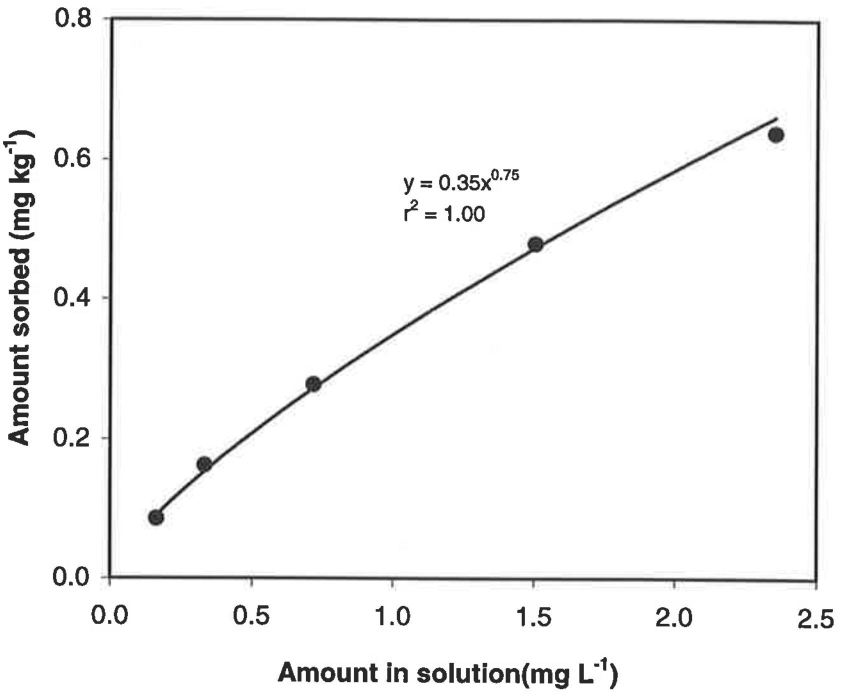


Figure 5.8 Sorption isotherm for monocrotophos obtained with the batch method

5.3.5 Comparison of Sorption Coefficients With Literature Values

The results of these studies showed that the K_{oc} value of dichlorvos obtained by the unsaturated column method is comparable with values reported in the literature (Table 5.2). However, it should be noted that the published values for dichlorvos given in the table are only calculated values, as compiled by Hornsby et al. (1996). No sorption values from the actual studies on soils were found in the literature search.

Table 5.2 Comparison of sorption coefficient values in the literature

Pesticide	Unsaturated column		Batch equilibration		Literature
	K_d	K_{oc}	K_d	K_{oc}	K_{oc}
Dichlorvos	0.19	15.8	3.22	268.0	28, 22, 18*
Monocrotophos	0.14, 0.15	11.7	0.25	20.8	19**

*Hornsby et al. (1996); ** Lee et al. (1990a)

For monocrotophos, the average K_{oc} value of 19 L kg^{-1} reported by Lee et al. (1990a), obtained from laboratory batch studies in four different soil types, was higher than the column value obtained in this study (11.7 L kg^{-1}) but comparable with the batch value (20.8 L kg^{-1}) obtained in the present studies.

5.4 Implications and Advantages

This study has shown that the unsaturated flow technique is a good method for measuring the sorption of relatively fast degrading and highly water soluble pesticides in soils. Sorption is calculated from the concentrations of pesticide extracted from both the solid and solution phases, the data are exempt from errors resulting from any degradation losses that occur during the measurement. Moreover, the method is based on unsaturated flow conditions, which are more representative of the field situation. The technique is simple and not time consuming. However, the method is best suited to relatively water soluble pesticides and is not likely to be applicable to the more hydrophobic pesticides.

CHAPTER 6

Influence of the Chemical Nature of Soil Organic Matter on the Sorption of Nonionic Pesticides

6.1 Introduction

Soil organic matter (SOM) is the most important component of the soil matrix in terms of binding of nonionic pesticides (Chiou, 1989; Koskinen and Harper, 1990; Xing et al. 1994). There is a substantial body of evidence that SOM acts as a medium into which the nonionic compounds partition (e.g. Chiou et al., 1979; Gschwend and Wu, 1985; Chiou, 1990) and that the uptake of nonionic organic compounds by soil from water is highly correlated with SOM content (e.g. McCall et al., 1980; Means et al., 1980; Xing et al., 1994).

As discussed in Chapter 2, the degree of sorption from solution onto the solid phase of the soil may be described by a soil-water partitioning coefficient (K_p). The sorption can also be expressed on the basis of organic C as K_{oc}, which is K_p divided by the organic C content (f_{oc}) of the soil (Mackay and Paterson, 1981). The value of K_{oc} for a nonionic organic compound has often been reported to be nearly the same for different soils or size fractions of soil (Chiou, 1981; Karickhoff, 1981; Schwarzenbach and Westall, 1981). However, the sorption coefficient, K_{oc}, does not take into account the nature of SOM which can affect the sorption of nonionic organic compounds.

Several linear equations have been developed to predict distribution coefficients for pesticides in soils (See in Chapter 2, Section 2.5.2). These equations are based on the octanol/water partition coefficients, $K_{ow,}$ or aqueous solubility, $S_{w,}$ of the pesticide (e.g. Means et al., 1980; Briggs et al., 1981a) and sometimes employ a single soil characteristic, such as f_{oc}.

In predicting sorption of pesticides in soils using these empirical equations, it is generally assumed that soils have the same reactivity for a nonionic compound per unit mass of organic C. However, such uniform behaviour of organic matter among different types of soils is unlikely, because not only the quantity but also the quality of the organic constituents varies between soils (Grathwohl, 1990; Schnitzer, 1991; Krosshavn et al., 1992; Preston and Newman, 1992; Kögel-Knabner,1993). Xing et al. (1994) reported a pronounced difference between K_{oc} values predicted on the basis of K_{ow}, and laboratory-measured K_{oc} values. This disparity in K_{oc} values raise the question whether the variations in structure and composition of SOM influence the sorption of nonionic pesticides.

To probe into the composition of SOM without altering its chemistry, solid-state ^{13}C CP/MAS NMR spectroscopy can be used to assess quantitatively the structural environment of each C atom in organic materials found in soils. The NMR spectra may also be interpreted to infer various molecular components.

6.2 Objectives

The objectives of this study were:

1) to characterise the chemical nature of SOM in a diverse group of soils from Australia and Pakistan on the basis of

  a) C types as derived from ^{13}C CP/MAS NMR spectra, and
  b) molecular components inferred from the NMR spectra using a simple molecular mixing model, and

2) to determine the relationship between K_{oc} of two different nonionic pesticides (carbaryl and phosalone) and the nature of the organic matter in this group of soils.

6.3 Materials and Methods

6.3.1 Soils Used

Some pertinent properties of 22 soils from Australia, and 5 soils from Pakistan used in this study are summarised in Chapter 3. Carbon and N concentrations in HF-treated soils were determined using gas chromatography/mass spectrometry (GC MS). The dried soil samples were finely ground, sealed into tin capsules and combusted. The reaction products were separated by GC to give pulses of pure N and CO_2 for analysis of total N and total C by the mass spectrometer (20-20, Europa Scientific, Crewe, UK). Molar N:C ratios were calculated from the N and organic C contents of the soils. The values are tabulated in Table 6.1.

6.3.2. Carbon Chemistry as Determined by Solid-state Cross-polarisation Magic-angle ^{13}C NMR Spectroscopy

Prior to NMR analysis, soil samples were treated with HF (Skjemstad et al., 1994) to concentrate the C and remove paramagnetic materials. Finely ground (<0.2 mm) soil samples (3 g) were weighed into 50 mL centrifuge tubes and 50 mL aliquots of 2% HF were added. The samples were shaken for one hour, centrifuged at 2000 rpm for 20 min and the supernatant discarded. Any light organic fraction in the supernatant, which was not centrifuged down with the soil residue was collected on a Millipore 5 μm Durapore membrane filter. This procedure of HF-treatment was repeated five times and then followed by four more similar HF treatments using longer shaking times (3×16 h and 1×64 h). After the final treatment, the residues were washed five times with deionised (Milli-Q) water, combined with the light organic fractions, and freeze dried.

^{13}C CP/MAS NMR spectra of HF-treated soil samples were obtained on a Varian Unity200 spectrometer. The freeze-dried and powdered soil samples were confined in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000 Hz in a Doty Scientific MAS probe. The magnetic field was 4.7 T, giving a ^{13}C resonance frequency of 50.3 MHz. A 1 ms contact time and a 2 s recycle delay were used. The spectra were partitioned by chemical shifts into the following functional group regions (Wilson, 1987): 0-45 ppm, alkyl C (C-H); 45-110 ppm, O-alkyl C (C-O); 110-140 ppm, aryl C (Ar)); 140-165 ppm, O-aryl C (Ar-O); 165-190 ppm, carboxyl C (C=O) and 190-220 ppm, aldehyde/ ketone C (ketone) as shown previously in Figure 2.5. The proportional contribution of these types of C was determined by integration of the spectra (Ogner, 1985; Oades et al., 1988; Inbar et al., 1989; Fründ et al., 1989). Aromaticity of organic C in each soil was calculated by dividing the fraction of aromatic C (aryl plus O-aryl C) by the sum of the fractions of all components of C as given below.

$$\text{aromaticity} = \frac{(\text{aryl C}) + (\text{O - aryl C})}{(\text{alkyl C}) + (\text{O - alkyl C}) + (\text{aryl C}) + (\text{O - aryl C}) + (\text{carboxyl C}) + (\text{aldehyde / ketonic C})} \text{ x } 100$$

Table 6.1 Organic C and N contents of the HF-treated soils

S. No	Soil name	%N	%C	N:C
1	SS6	3.77	40.16	0.09
2	SS8	3.01	37.93	0.08
3	Buckelboo	2.46	24.97	0.10
4	Avon_1	0.15	1.56	0.10
5	Mt.Mary	0.29	2.73	0.11
6	Pinnaroo	0.11	1.24	0.09
7	ACU1	3.12	33.93	0.09
8	B211	3.26	35.56	0.09
9	Qld	3.58	40.97	0.09
10	Urb-P	3.37	36.49	0.09
11	1413	0.05	1.33	0.04
12	1416	0.18	2.28	0.08
13	1418	0.13	2.6	0.05
14	1422	0.15	3.83	0.04
15	1428	0.31	7.52	0.04
16	1432	0.17	3.07	0.06
17	1433	0.37	9.20	0.04
18	1437	0.09	1.62	0.06
19	WAC	0.07	1.07	0.07
20	WAV	0.02	0.57	0.04
21	WFS	0.02	0.48	0.04
22	Pk10	0.15	1.54	0.10
23	Pk11	0.35	3.26	0.11
24	Pk12	0.27	2.48	0.11

6.3.3 Molecular Components of Organic Matter Inferred from ^{13}C MAS NMR Spectra

The NMR spectra were interpreted using the Model Components and Simultaneous Equations (MCSE) method developed by Nelson et al. (1999) to assess the molecular nature of the SOM. The method compares NMR spectra and N:C ratios of the samples with spectra and N:C ratios of their most likely components. The most likely molecular components are assumed to be the compounds produced in largest quantities by plants and microorganisms: cellulose and other carbohydrates; protein (structural and enzymes); lignin; cutin, suberin and aliphatic membrane components; chitin; and mucopolysaccharides and glycoproteins. Charcoal is an additional component of soil organic matter which also contributes to NMR spectra (Skjemstad, 1996). These compounds were classed to six model molecular components having characteristic and known solid-state ^{13}C NMR spectra and N:C ratios:

A) hexose

B) amino acid

C) lignin

D) cutin

E) pure carbonyl, and

F) charcoal.

On the basis of NMR spectra and N:C ratios, chitin can not be distinguished from a mixture of amino acid and hexose, so it was not included as a model component.

The ^{13}C MAS NMR spectra of each of the HF-treated soil samples was divided into 7 chemical shift regions: carbonyl (210 – 162 ppm), O-aromatic (162 – 143 ppm), aromatic (143 – 113 ppm), O_2-alkyl (113 – 93 ppm), O-alkyl (93 – 60 ppm), N-alkyl (i.e. α C of amino acids, peptides and proteins) or methoxy (60 – 46 ppm), and alkyl (46 – -10 ppm) and the distribution of signal intensity in these regions for the samples and six model components was calculated.

The model calculates the proportion of each model component for the sample by solving the simultaneous equations (6.1 – 6.6) for each sample.

$$a + b + c + d + e + f = 1 \qquad (6.1)$$

$$a (n_A) + b (n_B) + c (n_C) + d (n_D) + e (n_E) + f (n_F) = n_{sample} \qquad (6.2)$$

$$a (\alpha_A) + b (\alpha_B) + c (\alpha_C) + d (\alpha_D) + e (\alpha_E) + f (\alpha_F) = \alpha_{sample} \qquad (6.3)$$

$$a (\beta_A) + b (\beta_B) + c (\beta_C) + d (\beta_D) + e (\beta_E) + f (\beta_F) = \beta_{sample} \qquad (6.4)$$

$$a (\chi_A) + b (\chi_B) + c (\chi_C) + d (\chi_D) + e (\chi_E) + f (\chi_F) = \chi_{sample} \qquad (6.5)$$

$$a (\delta_A) + b (\delta_B) + c (\delta_C) + d (\delta_D) + e (\delta_E) + f (\delta_F) = \delta_{sample} \qquad (6.6)$$

where a, b, c, d, e and f are the proportions of the component A (hexose), B (amino acid), C (lignin), D (cutin), E (carbonyl) and F (Charcoal) in the model. α, β, χ, and δ equal the proportions of C (carbon) in the specified components (or sample) that resonate in the 46 – -10, 93 – 60, 210 – 162, and 143 – 113 ppm chemical shift regions, respectively (e.g. α_A equals the proportion of total signal in the 46 – -10 ppm region in the hexose component. n is the N:C ratio of the component (or sample) specified (e.g. n_A equals the N:C ratio of the hexose component. The N:C ratio (molar) was 0.3205 for amino acid component and zero for all other components.

The proportions so calculated were multiplied by the percent C in each spectral region for that component, and the resultant values added together to give a model spectral distribution. The difference between the modelled and actual spectral distributions (error) was expressed by the sum of the absolute value of the differences (in %C) between them for each spectral region.

6.3.4 Scanning Electron Microscopy

Micromorphology of two selected Pakistani soils was examined by mounting the whole soils on aluminium stubs, coated with Au-Pd alloy, using a Philips XL 20 scanning electron microscope.

6.3.5 Sorption Measurement

Sorption isotherms for carbaryl and phosalone in soils were obtained by the batch equilibrium method as outlined in Chapter 4. The sorption coefficient, K_p, was calculated either from the slope of the linear isotherm, or measured at a single solution concentration given the linearity of the isotherms of both pesticides. The K_{oc} value was calculated by dividing K_p by the fraction of soil organic C, f_{oc}.

6.3.6 Statistical Analysis

The relationship between pesticide sorption parameters and SOM quality, as described by C chemistry and molecular components, was examined using stepwise multiple regression. In addition, variation amongst the soil samples in terms of the C chemistry variables or molecular components was examined using principal component analysis (PCA). All statistical analyses were accomplished using Genstat for Windows (Genstat 5 Release 4.1, Lawes Agricultural Trust, IACR-Rothamsted, 1997).

6.4 Results and Discussion

6.4.1 Carbon Chemistry of the Soils

^{13}C NMR spectra for 25 soils are depicted in Figure 6.1. 6.2, 6.3 and 6.4. For a quantitative comparison, the spectral distribution into six chemical shift ranges is shown in Figure 6.5. The figure shows that C resonating in the 45 – 110 ppm region of the spectra (N- and O-alkyls and acetals) dominates in almost all the soils studied, while alkyl C (-10 – 45 ppm) was the second, and aromatic C (110 – 165) the third quantitatively most important C types seen by ^{13}C NMR. The alkyl C peak centred around 31-33 ppm,

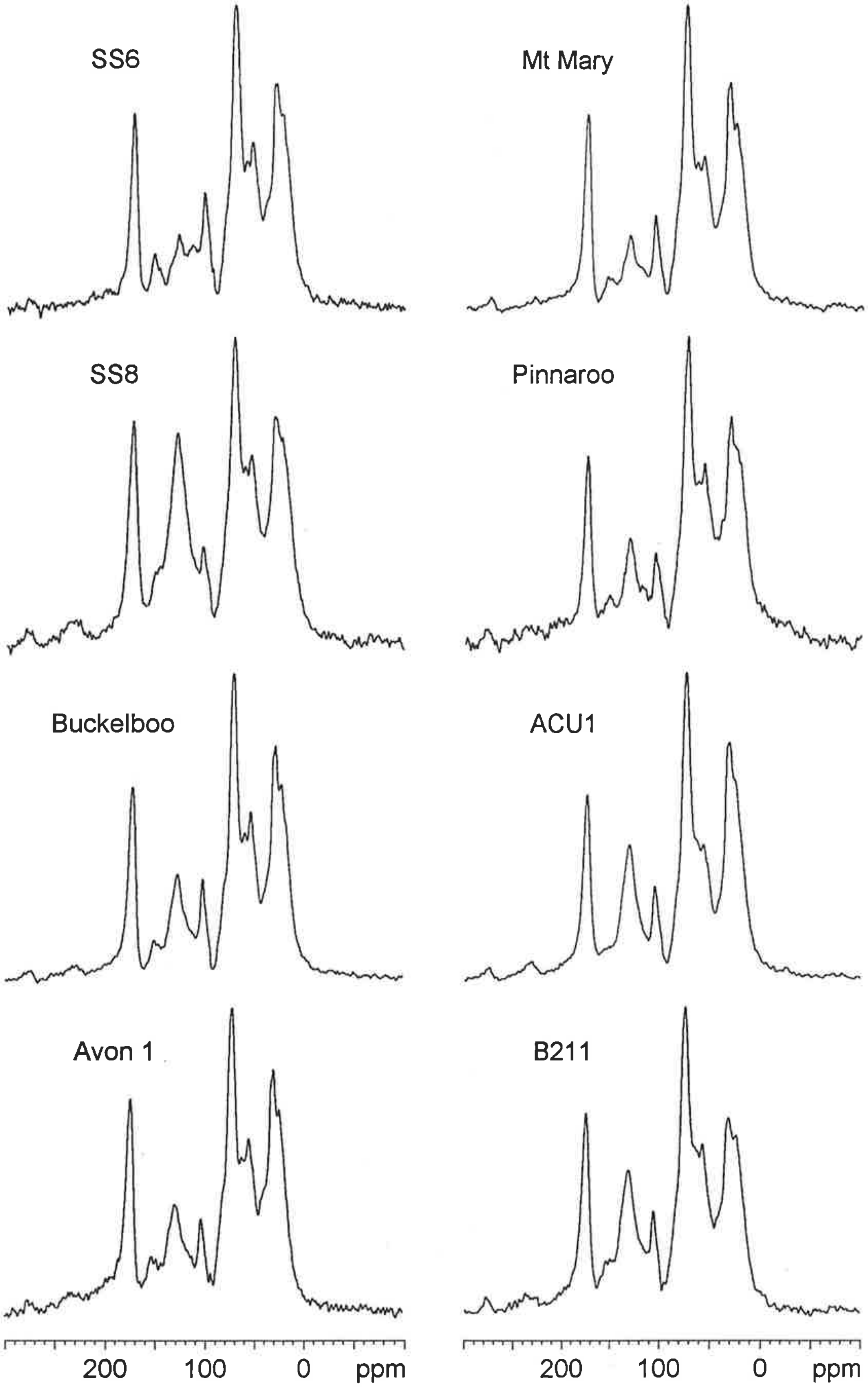


Figure 6.1 Solid state ^{13}C CP/MAS NMR spectra of soils SS6, SS8, Buckelboo, Avon1, Mt. Mary, Pinnaroo, ACU1 and B211

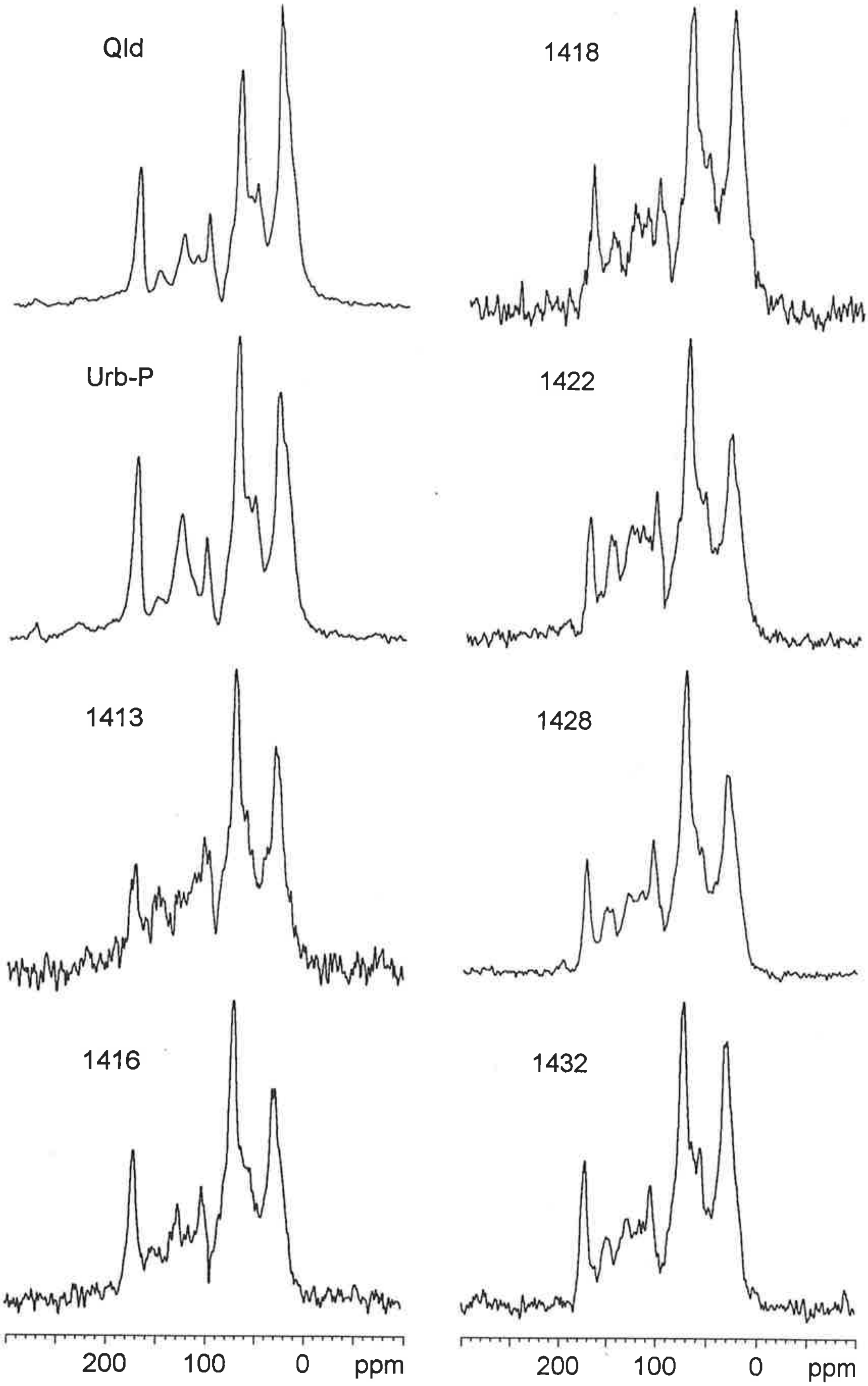


Figure 6.2 Solid state ^{13}C CP/MAS NMR spectra of soils Qld, Urb-P,1413, 1416, 1418, 1422, 1428 and 1432

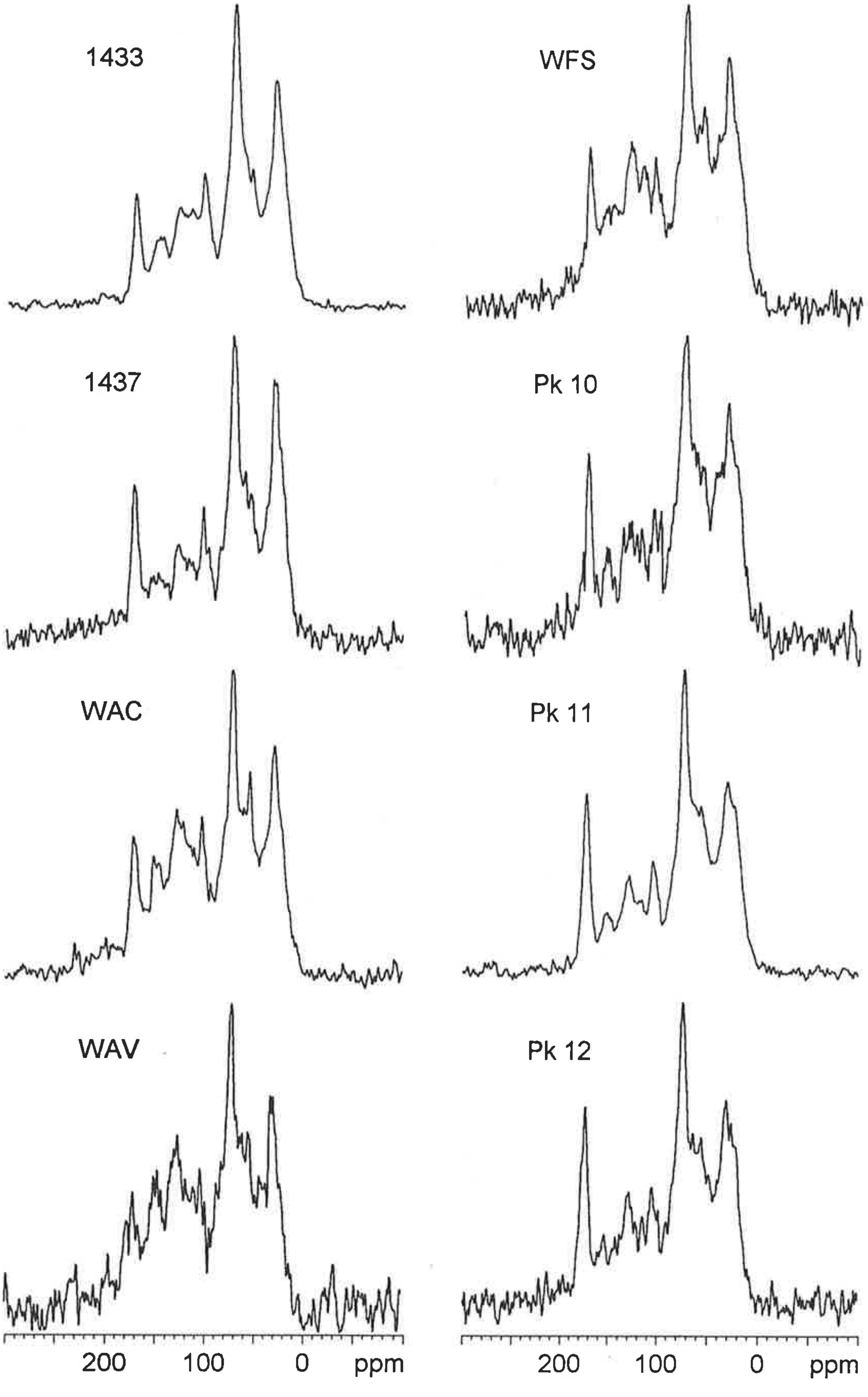


Figure 6.3 Solid state ^{13}C CP/MAS NMR spectra of soils 1433, 1437, WAC, WAV, WFS, Pk10, Pk11 and Pk12

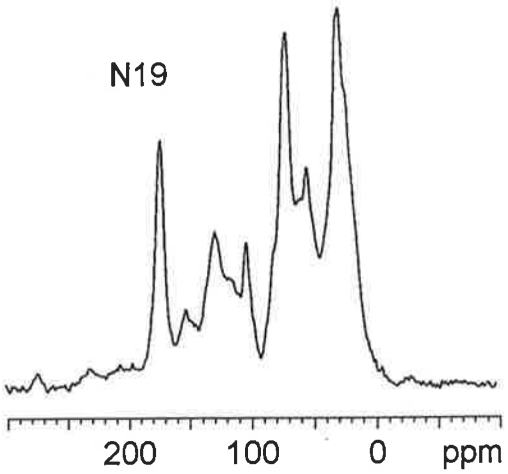


Figure 6.4 Solid state ^{13}C CP/MAS NMR spectrum of soil N19

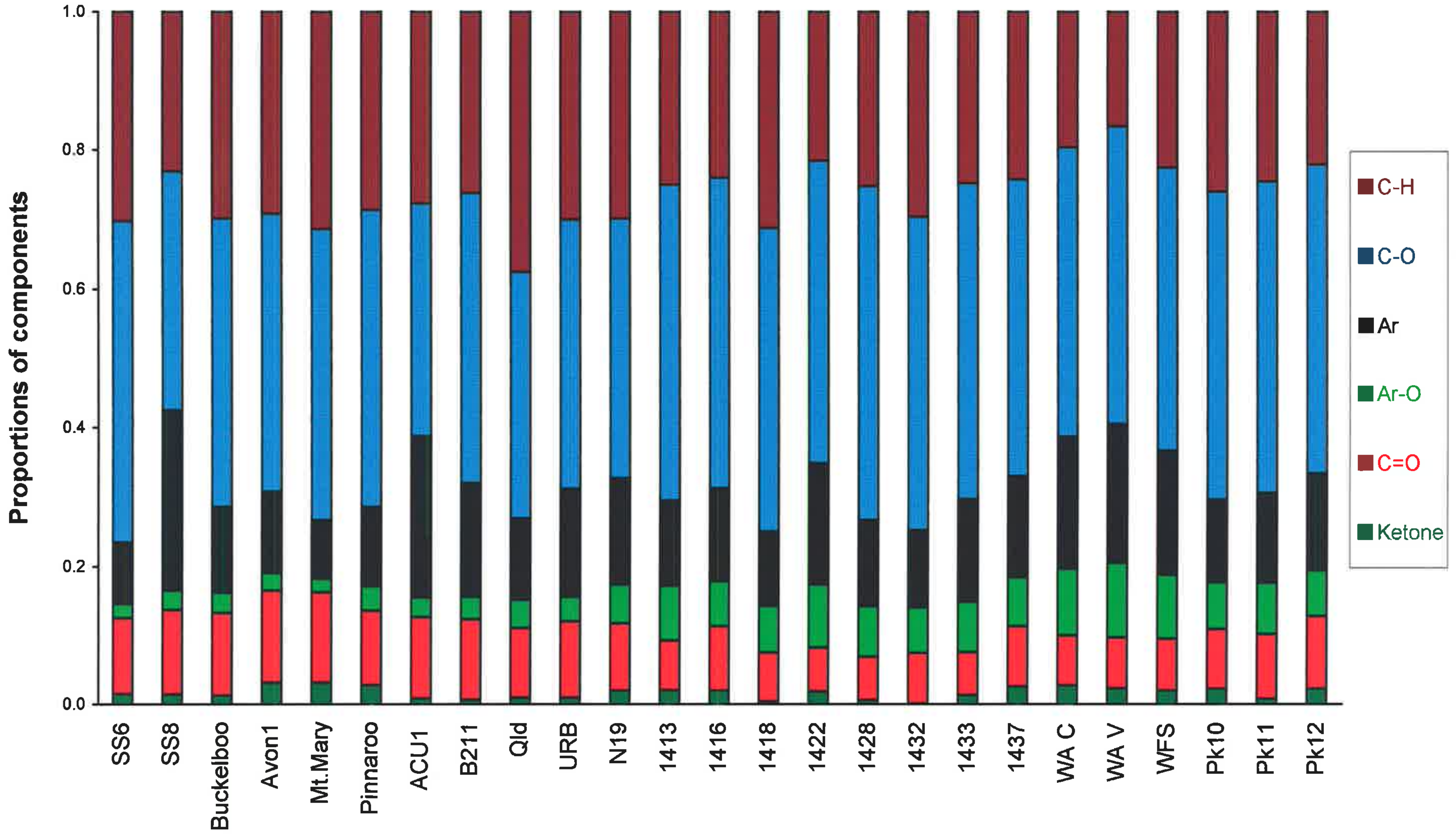


Figure 6.5 Relative proportions of C in different regions of the ^{13}C CP/MAS NMR spectra of 25 soils

indicating a dominance of CH_2 groups. The chemical-shift range for aromatic or olefinic C (110 to 165 ppm) is dominated by signals at 130 and 150 ppm. The peak at 130 ppm is characteristic of C-substituted aromatic C and that at 150 ppm is attributed to O-substituted aromatic C (phenolic C) (Kögel-Knabner et al., 1991). In most soils, the large peak at 150 ppm indicated that most of the aromatic C was derived from lignin. In all soils except Qld there was a higher proportion of O- alkyl C than alkyl C. The dominance of carbohydrates has been documented for samples studied from soils differing widely in term of soil orders (Baldock et al., 1992). In the present study, alkyl C (-10 – 45 ppm) was found to be the second most abundant C type in all but soils SS8, 1422, WAV, WAC, and WFS (lower in alkyl than aromatic (Ar + Ar-O)) C. In contrast, Randall et al. (1995) observed aromatic C to be the second most important type in soils from the Broadbalk Experiment at Rothamsted, UK (monoculture of winter wheat since 1843) and the Lermarken site of the Askov Long-Term Experiment on Animal Manure and Mineral Fertilizers (arable rotation since 1894). In many other soils, alkyl C appears to contribute more than aromatic C and studies combining chemical analyses, infrared (IR) and NMR have demonstrated that humic substances contain a larger proportion of alkyl C than indicated by previous studies employing only elemental and functional chemical analysis (Sciacovelli et al., 1977; Hatcher et al., 1981; Wilson et al., 1987). Generally, carbonyl C (165-220 ppm) contributed the smallest proportion to the SOM. All the forest soils, WAV, SS6, and 3 Pakistani soils appear to be slightly enriched in O-alkyl C. Overall, the proportion of O-alkyl C in the soils studied varied from 33.6 to 46.3%, alkyl C from 16.6 to 37.6, and the aromatic C ranged from 10.4 to 30.7%. Mahieu et al. (1999), on the basis of NMR data on >300 soils collected from literature, reported that O-alkyls are the most abundant group followed by alkyls and aromatics. The carbonyls are always the least abundant group.

Principal component analysis of the data (Figure 6.6) displays two sets of information, namely, soil samples (Nos 1 to 25) and explanatory variables (vectors). Along the first principal component axis, which contrasts CH with Ar and Ar-O (note that the vector for CH runs near parallel to the x-axis), samples towards the right hand side of the plot [Nos. 9 (Qld), 5 (Mt. Mary), 1 (SS6), 4 (Avon-1), 3 (Buckelboo), 13 (1418), 6 (Pinnaroo), 16 (1432), 10 (Urb-P), and 25 (N19)] have above-average levels of alkyl and carbonyl, below-average levels of aromatic C and a range of above average to below average concentrations of O-alkyl C. Along the second principal component, which mainly shows differences in O-alkyl C amongst the samples (note that the vector for C-O runs nearly parallel to the y-axis), soils No 2 (SS8) and 7 (ACU1) are very different (containing higher proportion of aryl component) from the other samples. The vectors show the approximate correlation amongst the explanatory variables. (Note that the point of reference is the origin from where the vectors radiate and that angles <90° indicate positive correlation, angles >90° negative correlation and angles ~ 90° indicate near zero correlation). The principal components 1 and 2 altogether accounted for 89.6% (50.6 + 39.0) of the total variation.

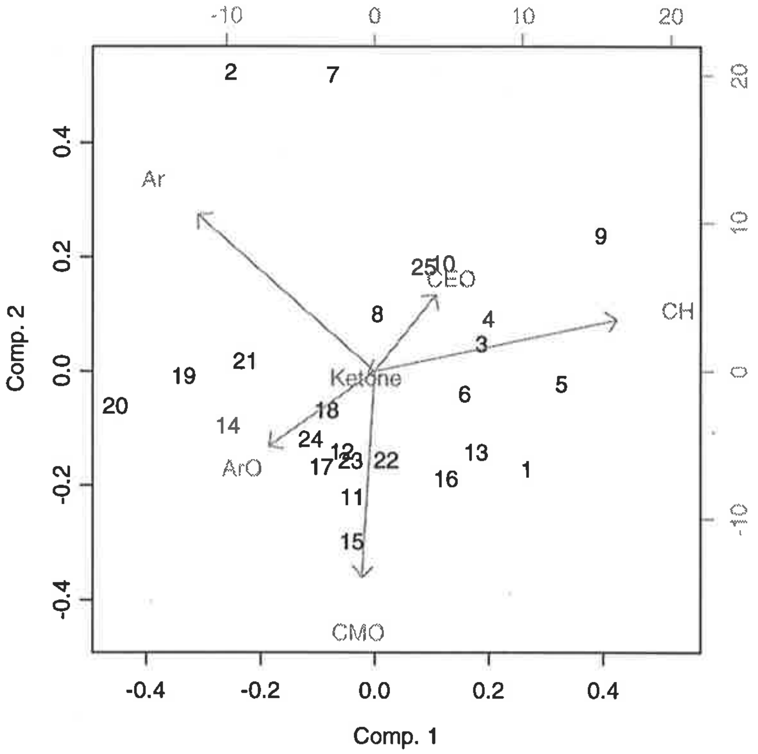


Figure 6.6 Biplot for principal components one and two for functional groups of SOM (Note: CEO stands for C=O and CMO for C-O)

The relative accumulation of alkyl structures in soils is likely due to *in situ* enrichment because of the selective decomposition of carbohydrates (Baldock et al., 1989, 1990). Alkyl C components of SOM are reported to be more concentrated in the clay fraction. Skjemstad et al. (1986) found higher concentrations of alkyl C in the higher density fractions of SOM (2.0 to 2.4 Mg m^{-3}), indicating that sorption to clay minerals can increase the stability of materials with highly aliphatic structures. Higher concentrations of alkyl C can also be found in oxisols with higher C and clay content (Baldock et al., 1992) than soils of lower C and clay contents. The 3 sands (WAC, WAV, and WFS) investigated in this study contained more aromatic C than long chain alkyl C. Capriel (1997) reported that the organic matter of sandy soils contained more aliphatic C-H units than in clayey soils which is probably due to differences in sources of organic matter.

The type of vegetation from which the SOM originates affects the chemical composition of soil appreciably, but the other important factor appears to be the degree of decomposition of the SOM (Kögel et al., 1988; Baldock et al., 1997). O-alkyl C tends to decrease with decomposition, while the proportion of O-alkyl C tends to increase and aromatic C may increase or decrease, depending on the situation (Baldock et al., 1997). The soils used in the present study originated from different regions, and the organic matter in these soils differed in chemical composition due to degree of decomposition, origin, parent materials and environmental factors.

6.4.2 Inferred Molecular Components of SOM

The MCSE model was successfully fitted to the samples (sum of differences or error between actual and modelled spectral distributions ranged from 1.1 – 6.2%). In some cases the proportions of particular components were negative, but the negative values were <2%. The actual and modelled distributions of the signal intensities for 24 samples are presented in Figure 6.7. (Soil N19 could not be interpreted because N:C ratio was not determined). The relative proportions of various molecular components inferred from the model are depicted in Figure 6.8. A significant proportion of organic matter appeared to be composed of hexose and amino acids or protein. Free amino acids are present at low concentrations in soils as they are readily decomposable, and are usually present in polymeric structures such as peptide, protein, amino acid-phenol, protein-phenol, or glycoprotein (Nelson et al., 1999). The MCSE method can not discriminate between these different compounds. As mentioned in the Materials and Method section, the amino acid and hexose components may consists partly of chitin. The forest soils (1413, 1416, 1418, 1422, 1428, 1432, 1433, 1437) and sands (WAC, WAV, WFS) contained comparatively

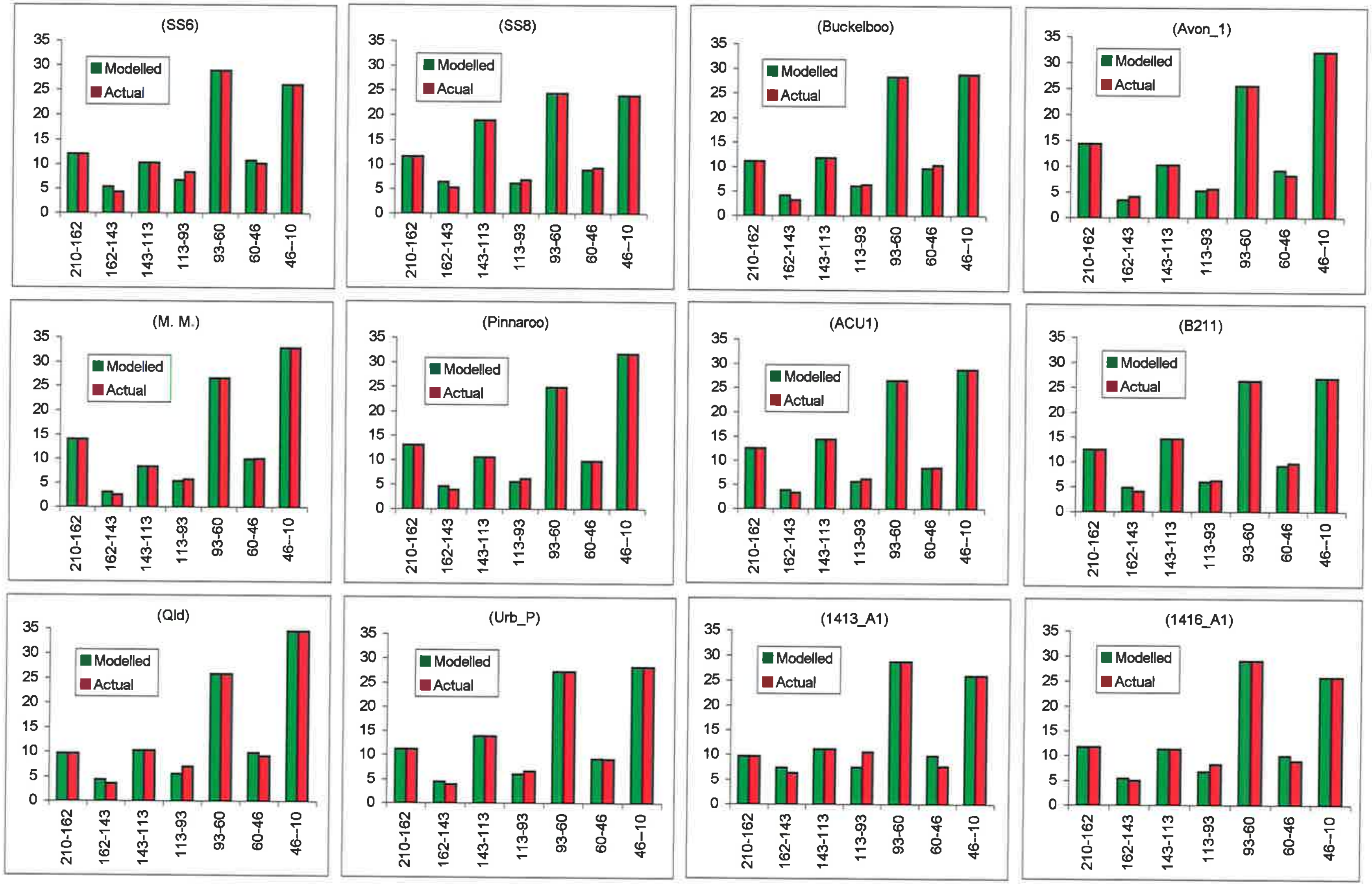


Figure 6.7 The actual and modelled distributions of the signal intensities for 24 soils

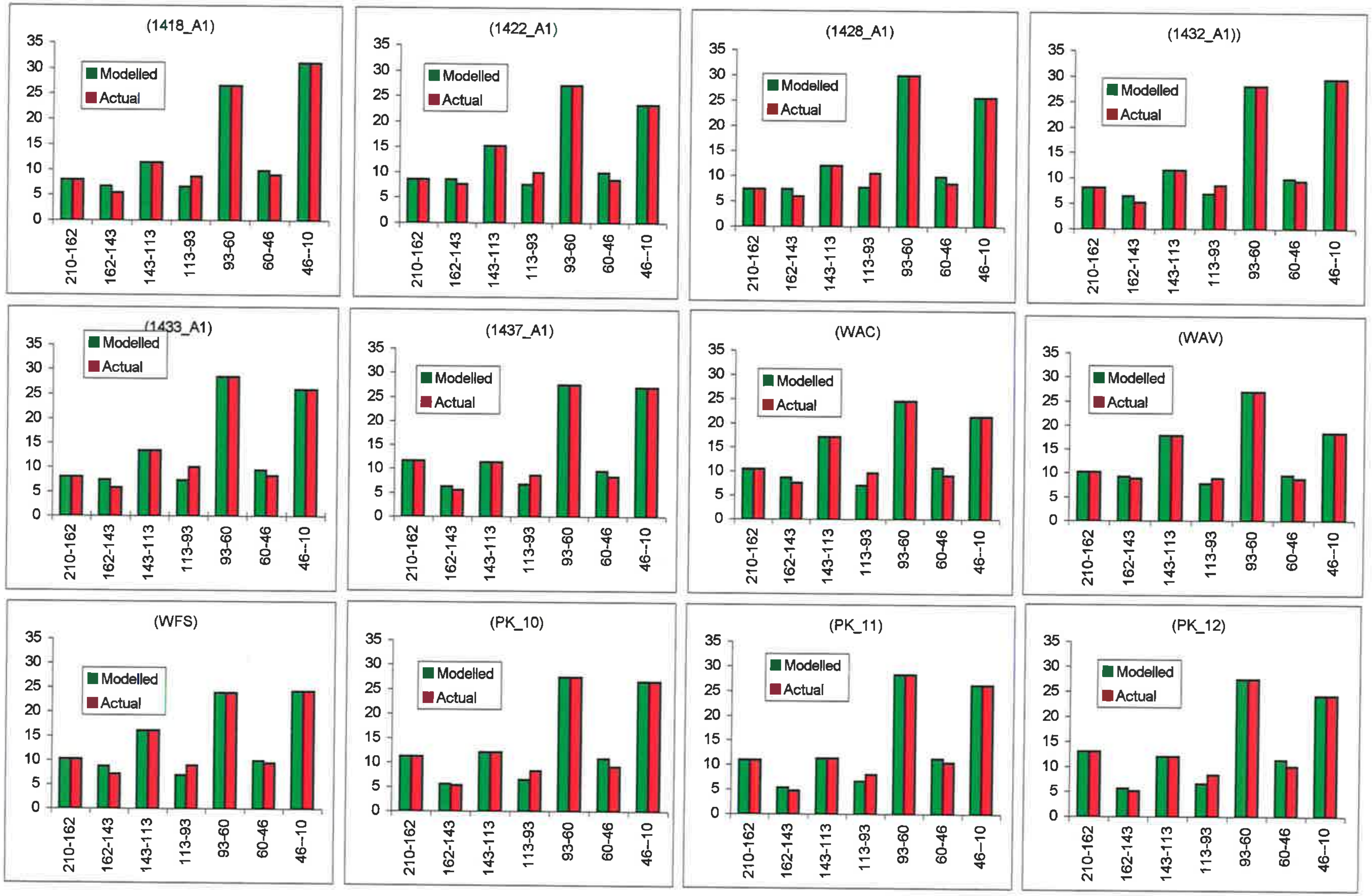


Figure 6.7 The actual and modelled distributions of the signal intensities for 24 soils (continued)

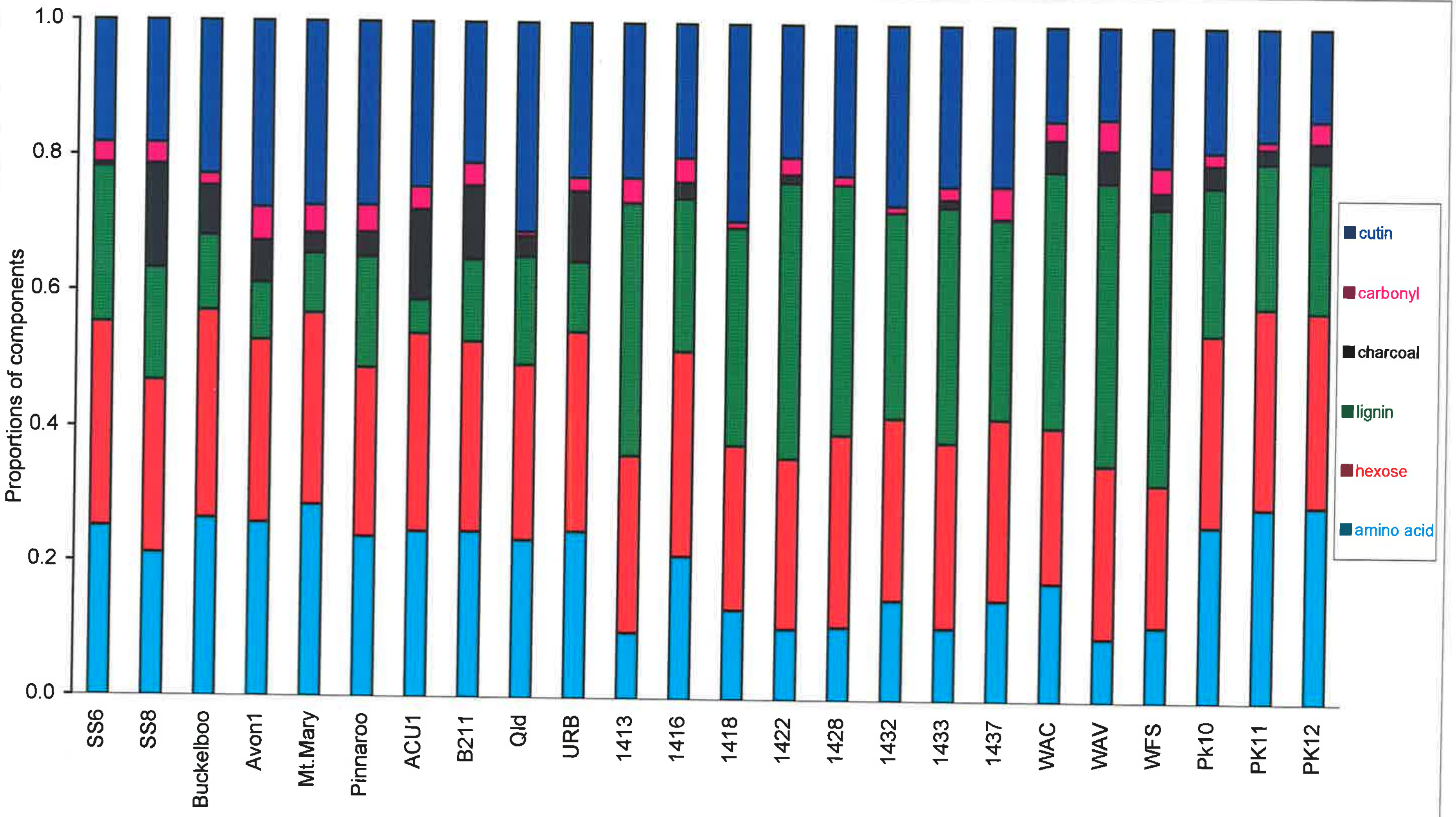


Figure 6.8 Components of soil organic matter as estimated using model components and simultaneous equations (MCSE)

less amino acids than the other Australian and Pakistani soils. Hexose was chosen to represent all carbohydrates, but the underestimate of signal in the 113-93 ppm indicated that pentoses were also present in all samples. In general, the three sandy soils WAC, WAV and WFS contained the highest proportions of lignin or lignin derived materials followed by the forest soils. The forest soils contained much less (or no) charcoal compared with the other soils. The remaining Australian soils contained appreciable amounts of charcoal, SS8, ACU1, B211, and Urb-P being fairly high in charcoal contents. The three Pakistani soils contained much higher lignin than charcoal. Lignin is generally considered to be one of the major precursors of aromatic C in humic substances (Stevenson, 1982). It is composed of cross-linked phenyl- propane monomers such as guaiacyl/vanillyl, syringyl, and *p*-hydroxyphenyl units (Kögel- Knabner et al. 1991).

The results of principal component analysis using the MCSE data set are shown as a biplot in Figure 6.9. Along the first principal component axis which contrasts lignin and

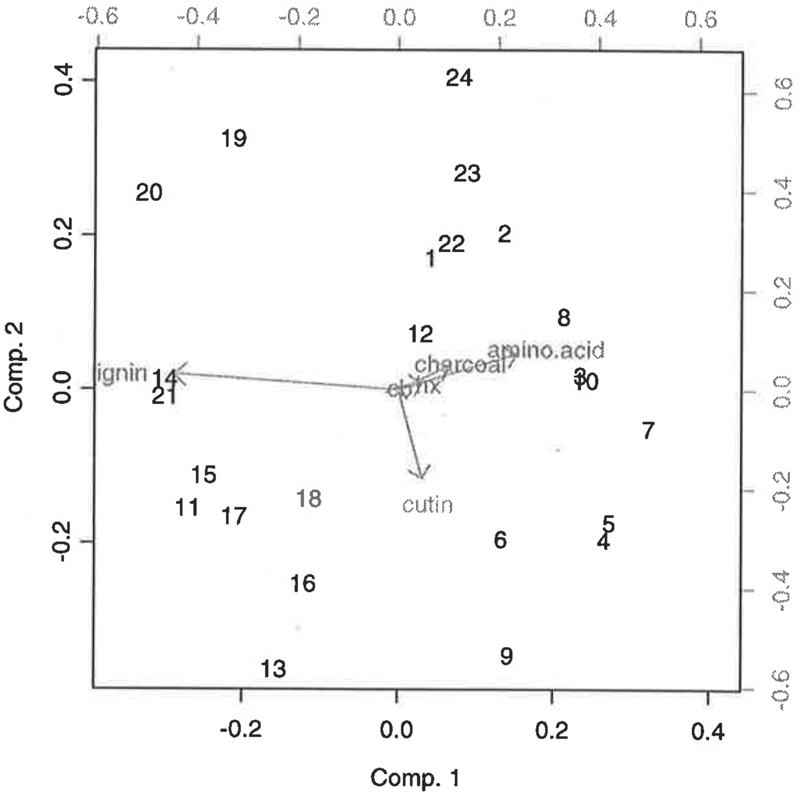


Figure 6.9 Biplot for principal components one and two for molecular components of SOM (Note: cb = carbonyl and hx = hexose)

amino acid (note that their vectors run near parallel to x -axis), samples towards the left hand side of the plot (20, 14, 21, 11,15, 17, 19, 13, 16, 18) have above average levels of lignin, below average levels of amino acid and a range of above average to below average levels of cutin.

Along the second principal component, which mainly shows differences in cutin amongst the samples (note that the vector for cutin runs near parallel to the y-axis), samples 19, 20 and 24, 23, 22, 1, 2, and 12 have below average levels of cutin. The principal component 1 and 2 accounted for 90.9% (79.0 + 11.9) of the total variation.

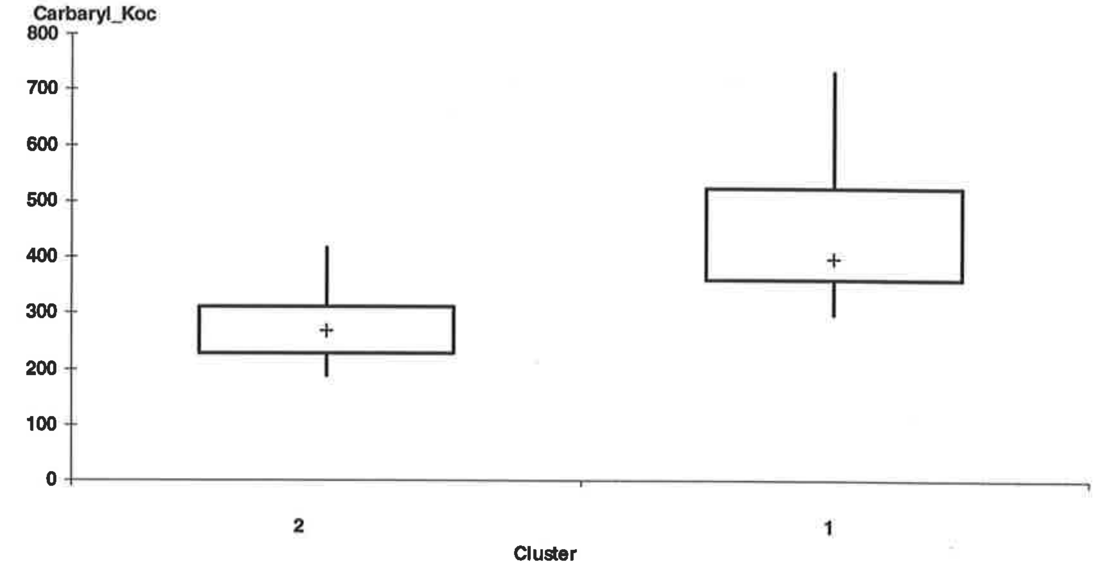
6.4.3 Correlation of C Chemistry and Molecular Components with Sorption of Carbaryl and Phosalone

The linear sorption isotherms of carbaryl and phosalone were previously presented in Chapter 4. The K_{oc} values (sorption coefficients, K_p, normalised per unit organic C) varied by as much as an order of magnitude (Table 6.2). Investigations through box (Whisker) plot distribution of measurements found that the left hand side cluster of the biplot from the principal component analysis (Figure 6.6) had significantly higher K_{oc} values for both pesticides ($p < 0.001$) (Figure 6.10). The wide range of the K_{oc} values of both pesticides indicates that the nature of SOM is a determining element of the sorption capacity of a soil.

Regression of K_p for carbaryl and phosalone against the total organic C content of 47 soils from 3 countries (Australia, Pakistan, and UK) could account for only 35 and 30% of the variance in K_p, respectively (Figure 4.10 in Chapter 4). One Pakistani soil, Pk6, which had exceptionally high sorption values for both pesticides was excluded from the regression. Therefore, the roles of various components of SOM were examined by the use of simple correlation between K_{oc} of the pesticides and the organic matter components (Table 6.3).

Table 6.2 K_p and K_{oc} values of carbaryl and phosalone for the soils studied

S. No	Soil name	Carbaryl		Phosalone	
		K_p (L kg^{-1})	K_{oc} (L kg^{-1})	K_p (L kg^{-1})	K_{oc} (L kg^{-1})
1	SS6	14.5	207	190.0	2711
2	SS8	17.0	732	293.0	12608
3	Buckelboo	3.5	272	60.0	4670
4	Avon_1	2.9	221	45.0	3503
5	Mt.Mary	1.9	189	26.0	2587
6	Pinnaroo	2.9	245	45.0	3711
7	ACU1	13.5	529	223.2	8717
8	B211	11.8	344	173.9	5069
9	Qld	26.9	265	168.1	4379
10	Urb-P	11.2	322	151.7	5680
11	1413	2.7	397	55.7	6962
12	1416	4.4	297	92.1	6138
13	1418	6.7	335	121.6	6078
14	1422	12.9	516	230.8	9233
15	1428	8.2	356	136.6	5941
16	1432	7.4	284	139.9	5381
17	1433	23.0	397	442.7	7633
18	1437	4.4	365	80.5	6710
19	WAC	8.7	542	171.2	10701
20	WAV	6.0	601	118.9	11890
21	WFS	3.5	497	76.3	10907
22	Pk10	1.0	354	16.6	5952
23	Pk11	2.6	368	49.0	7088
24	Pk12	2.4	385	43.5	7038
25	N19	21.4	415	294.2	6566
26	Pk4	2.3	349	21.3	3210
27	Pk6	59.7	4318	1182.0	85528



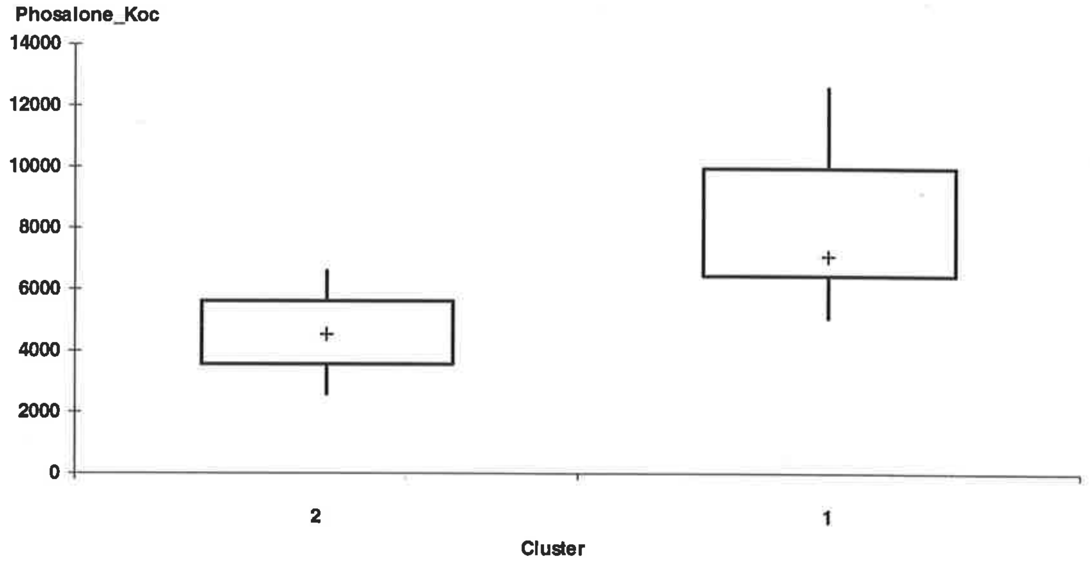


Figure 6.10 Boxplot distribution of C type data presented in Figure 6.3 with respect to the variations in the K_{oc} values of carbaryl and phosalone

(The groups of soils are significantly different at $p<0.001$)
Group 1 - 2, 7, 8, 11, 12, 14, 15, 17, 18, 19, 20, 21, 22, 23, 24
Group 2 - 1, 3, 4, 5, 6, 9, 10, 13, 16, 25

- The "+" sign indicates the medians
- The box goes from the 1st to the 3rd quartile
- Data points that are further than 1.5 times the interquartile range from the boxes are indicated with a "*" as possible outliers.
- Lowers whisker (vertical line coming out of box) is the next smaller than the 25th quartile + 1.5*the interquartile range.
- Upper whisker (vertical line coming out of box) is the next value greater than the 75th quartile + 1.5*the interquartile range.

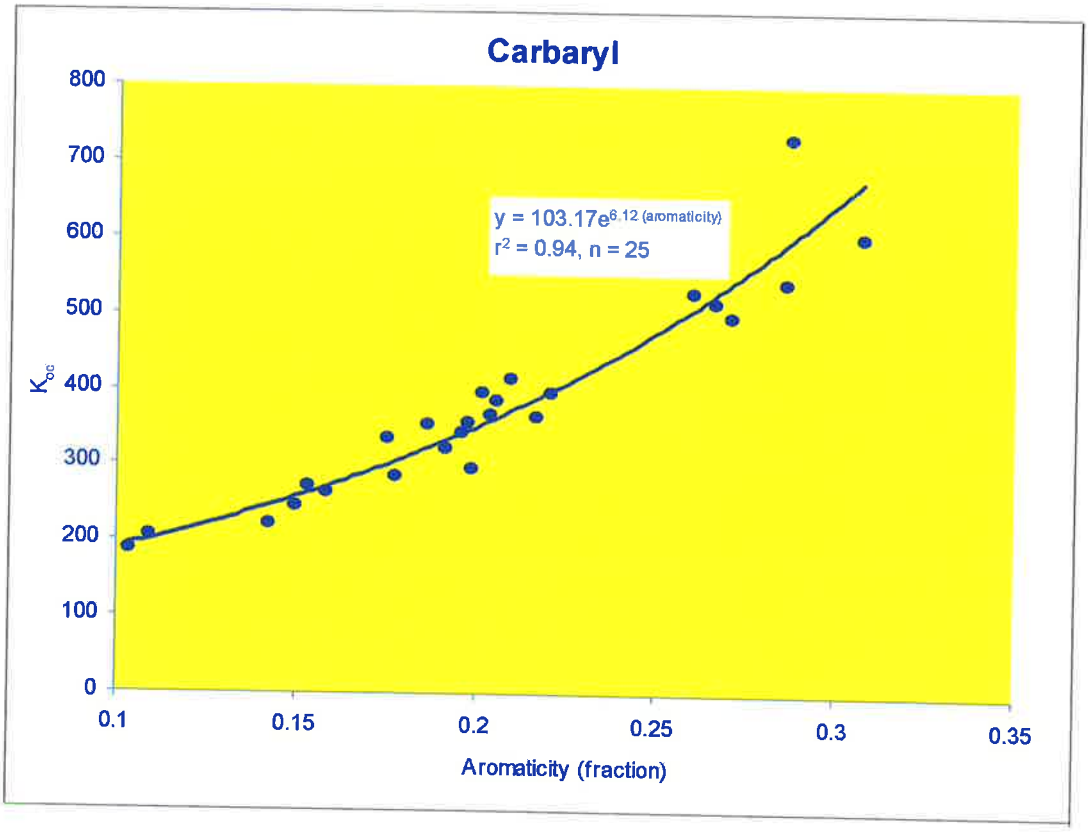
Among the C types in SOM, the K_{oc} values of carbaryl and phosalone were best correlated with aryl (r = 0.92***and 0.86***, respectively) and O-aryl (r = 0.46* and 0.61**, respectively). The K_{oc} of both pesticides increased with decreasing alkyl C. Single-variable regression of K_{oc} *v* aryl C yielded r^2 values of 0.83 and 0.72 for carbaryl and phosalone respectively, and that *v* O-aryl gave r^2 values of 0.18 and 0.34, respectively.

Table 6.3 Simple correlation coefficients (r) between K_{oc} of pesticides and components of SOM

Organic matter component	K_{oc} (Carbaryl)	K_{oc} (Phosalone)
A) Carbon Type		
Ketone/aldehyde	-0.02NS	0.01NS
Carboxyl	-0.29NS	-0.41*
Aryl	0.92***	0.86***
O-aryl	0.46*	0.61**
O-alkyl	-0.35NS	-0.24NS
Alkyl	-0.69***	-0.76***
B) Molecular components predicted from MCSE		
Carbonyl	0.13NS	0.12NS
Charcoal	0.42*	0.28NS
Cutin	-0.54**	-0.57**
Hexose	-0.45*	-0.52**
Lignin	0.39®	0.51**
Amino acid	-0.42*	-0.50*

NS = not significant; * $p<0.05$; ** $p<0.01$; *** $p<0.001$; ®significant at $p<0.051$

It is evident from the Figure 6.11 that aromaticity of SOM has a significant impact on sorption of the two pesticides. A good positive exponential correlation of aromaticity (aryl + O-aryl) with the K_{oc} values ($r^2 = 0.94$ and 0.95 for carbaryl and phosalone, respectively) was found (Figure 6.11), which suggests that aromaticity is likely the key structural parameter that regulates sorption of nonionic pesticides.



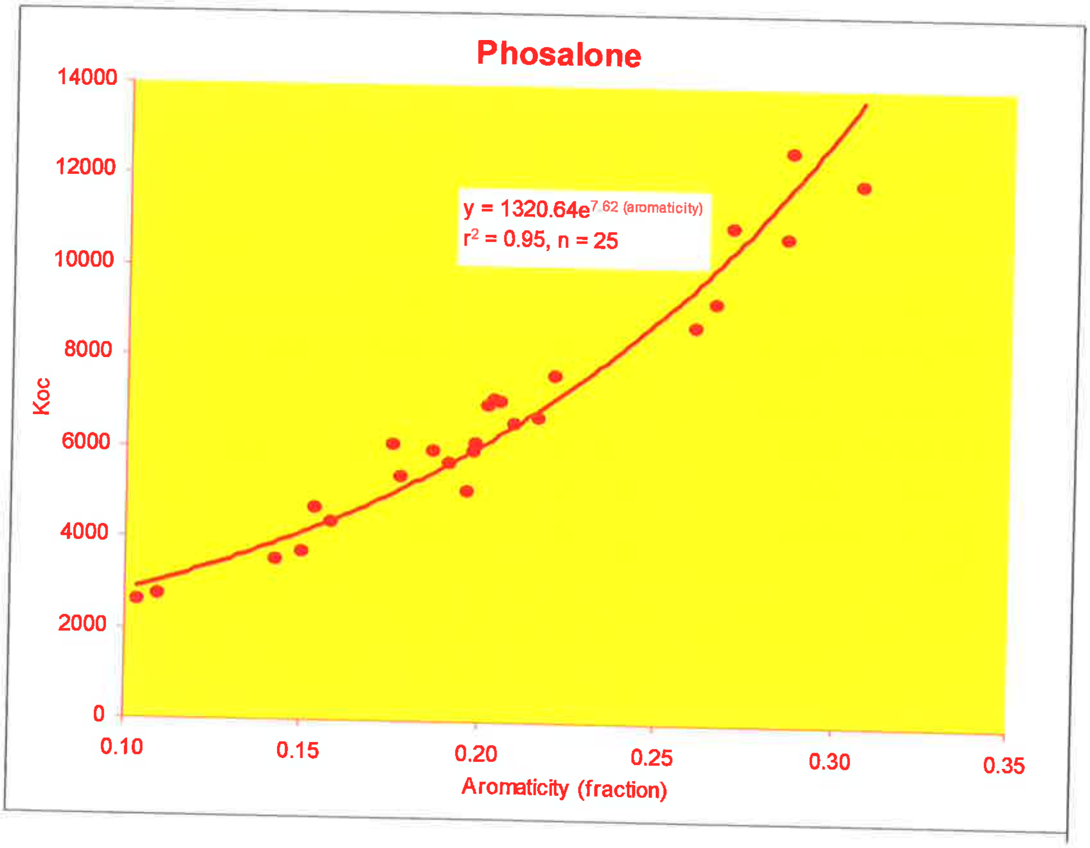


Figure 6.11 Relationship between aromaticity and K_{oc} of carbaryl and phosalone

Simple correlation of K_{oc} with the molecular components predicted from MCSE (Table 6.3) showed that lignin was positively correlated with K_{oc} of phosalone (significant at $p<0.01$) and carbaryl (significant at $p<0.051$). The K_{oc} of both pesticides decreased with increase in cutin, hexose or amino acids. The relatively low correlation coefficients with molecular components suggested that sorption was influenced by chemical structures at sub-molecular scale. Further investigation, through box plot distribution of measurements (Figure 6.12) indicated that the soil samples in the left hand side cluster (LHS) of the biplot from principal component analysis (Figure 6.6) had a higher K_{oc} for both carbaryl and phosalone (samples 11, 13, 14, 15, 16, 17, 18, 19, 20, 21) than the soil samples on the right hand side cluster (RHS) (samples 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 22, 23, 24) ($p<0.05$). Two-sample t-tests were used to determine if the cluster means for K_{oc} were significantly different.

Stepwise multiple linear regression procedure for the components determined by NMR was used to ascertain if a multivariable model might better explain the data sets. The results suggest that the K_{oc} values for both carbaryl and phosalone are adequately predicted using aryl C together with either O-aryl ($p<0.001$ or carboxyl C ($p<0.001$). Note that the interchangeability of O-aryl and carboxyl C is indicative of the high correlation between them (-0.88). The results from multiple regression also suggest that sorption of both pesticides is adequately predicted using lignin and charcoal as explanatory variables ($p<0.001$). The models are summarised below.

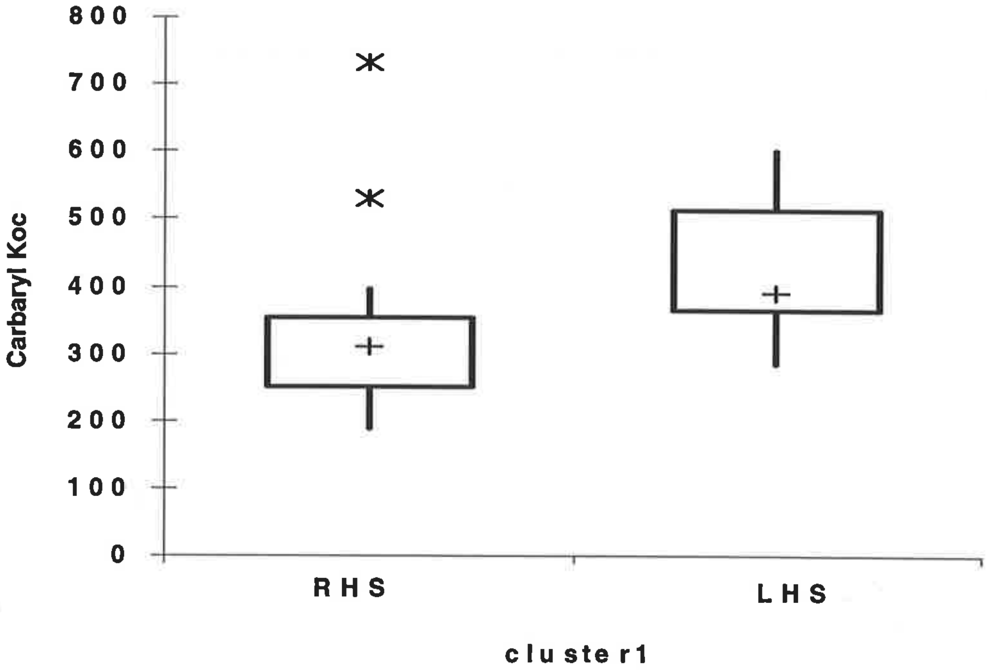
<u>Carbaryl Prediction</u>

Model 1: $K_{oc\ (Carbaryl)} = -99.3 + 2689\ (Ar) + 1496\ (ArO)$ adjusted $r^2 = 0.92$

Model 2: $K_{oc\ (Carbaryl)} = 119.6 + 2852\ (Ar) - 1644\ (C{=}O)$ adjusted $r^2 = 0.91$

Multiple regression based on the inferred molecular components yielded the following model.

$K_{oc\ (Carbaryl)} = -40.9 + 1172\ (lignin) + 3245\ (charcoal)$ adjusted $r^2 = 0.83$



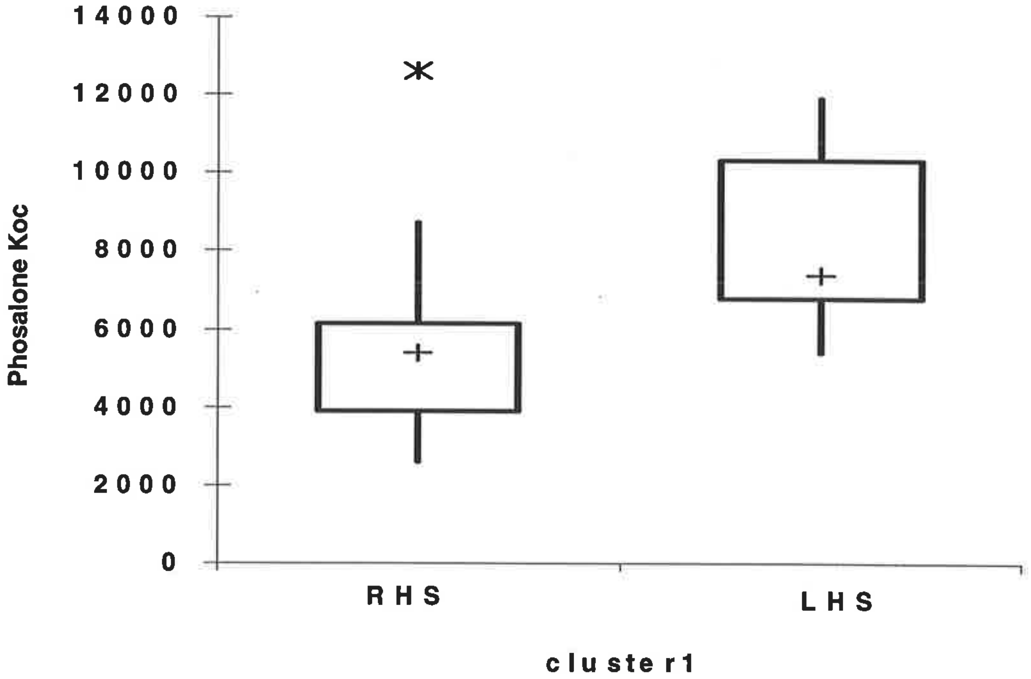


Figure 6.12 Boxplot distribution of molecular component data presented in Figure 6.6 with respect to the variations in the K_{oc} values of carbaryl and phosalone

(Groups are significantly different at p=0.04 and 0.008 for carbaryl and phosalone, respectively)

LHS-11, 13, 14, 15, 16, 17, 18, 19, 20, 21
RHS-1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 22, 23, 24

Phosalone prediction

Model 1: $K_{oc\ (Phosalone)} = -3253 + 49640\ (Ar) + 47890\ (ArO)$ adjusted $r^2 = 0.94$

Model 2: $K_{oc\ (Phosalone)} = 3327 + 54890\ (Ar) - 48180\ (C{=}O)$ adjusted $r^2 = 0.89$

Multiple regression based on the inferred molecular components yielded the following model.

$K_{oc\ (Phosalone)} = -1964 + 25583\ (lignin) + 60784\ (charcoal)$ adjusted $r^2 = 0.82$

The role of different components of the SOM in determining pesticide sorption has been clearly observed in this study. While the importance of SOM in influencing sorption of nonionic contaminants is well documented, the role of different components of the SOM is not well understood. Hartley (1960) speculated that the "oily" constituent of the SOM might be responsible for uptake of nonionic compounds by soil. The existence of such a lipid phase was supported by Schnitzer and Khan (1972), who reported the presence of fatty acids and alkanes at the surface of the SOM resulting from long alkyl chains projecting from the surface. They suggested that interactions such as hydrogen bonding may be important in uptake of nonionic pesticides by this lipid fraction. The hydrophobicity of the SOM has generally been reported to originate from aromatic and alkyl domains of the organic matter component (Wershaw, 1986). Murphy and Zachara (1995) suggested the presence of heterogeneous sorption sites on the humic substances and considered the most hydrophobic domains as the most energetic and strong binding sites. The K_{oc} values in the present study were strongly dependent on aromaticity and negatively correlated with the alkyl C and cutin components. Previously, the binding of pyrene to dissolved humic and fulvic acids was reported to be modified to a significant extent by the degree of aromaticity in humic substances (Gauthier et al., 1987). However, humic and fulvic acids are not necessarily representative of organic matter in soil. In another study conducted by Chin et al. (1997), it was found that the humic substances rich in aliphatic 1 type moieties would be less capable of binding pyrene. The negative significant correlation of alkyl C with K_{oc} values of carbaryl and phosalone ($r = -0.69^{***}$ and -0.76^{***}, respectively) noted in the present study is also supported by the findings of

Dunigan and McIntosh (1971) who suggested that fats, oils, and waxes had a negligible capacity to sorb atrazine. A small increase rather than a decrease in atrazine sorption was observed by these workers after removal of ethyl ether-extractable components of SOM. Such an increase in sorption was attributed to an unblocking of active sites which had previously been masked by these materials. Barriuso and Koskinen (1996) found that nonhumified organic matter in the size fractions coarser than 50 μm had larger sorption capacities for atrazine than humified organic matter of finest fractions isolated from the same soil The higher capacity of nonhumified organic matter was assumed due to the different nature of the fraction of organic matter.

Multiple regression analysis shows that relationships using both lignin and charcoal contents of SOM, as predicted from MCSE, were highly correlated with K_{oc} values of both carbaryl and phosalone (r^2 being 0.83 and 0.82, respectively). Lignin, a possible precursor for humic substances in soil, has been reported to show high sorption capacities for other organic pollutants (Riggle and Penner, 1988). Xing et al. (1994) have reported higher sorption of phenol on lignin compared with cellulose. Earlier, Tompkins et al. (1968) reported that the phytotoxic effect of atrazine on oats (*Avena sativa* L.) was significantly reduced when 1% lignin was incorporated into a sand culture. However, very little effect was noted when sand contained 1% cellulose. Abnormally high retention of pesticides in burned-over fields and those containing wind-blown carbon particles has been reported (Hilton and Yuen, 1963). This is in accord with a high sorption capacity of charcoal-containing soils. Moreover, the higher correlation of K_d of carbaryl with charcoal agree well with the suggestion of Weber et al. (1993) that activated C additions would be effective as a remediation treatment for soils contaminated with carbamate pesticides.

Two soils from Pakistan, Pk4 and Pk6, were conspicuously different from the other soils shown in Figure 6.1 through 6.4, in their NMR spectra as evident from Figure 6.13. Soil Pk4 exhibited generally lower sorption capacities for carbaryl (K_{oc}, 349 L Kg^{-1}) and phosalone ($K_{oc,}$ 3210 L Kg^{-1}) than most of the other soils. Sharp resonances at 115, 121, and 130 ppm in the NMR spectra of Pk4 indicate the presence of tannin-like materials. The bark and leaves of some trees like spruce contain high amounts of tannins (Fengel and Wegener, 1984; Harborne, 1989). As the soil was sampled from an agricultural area in Pakistan with a variety of trees including eucalyptus trees, it is likely that the tannins or tannin-like structures originated from that source. High tannin content may explain the lower K_{oc} values of both pesticides in this soil. A low capacity of tannic acid employed as commercial organic sorbent, for sorption of two nonionic volatile organic pollutants, toluene and trichloroethylene (TCE) was observed by Garbarini and Lion (1986).

By contrast, soil Pk6 showed extremely high sorption of both pesticides (K_{oc} was 4318 and 85528 L kg^{-1} for carbaryl and phosalone, respectively). The NMR spectrum (Figure 6.13) is substantially different from those of the other soils studied (Figures 6.1-6.4). It indicates the presence of abundant alkyls (33 ppm) and methoxy groups (56 ppm), and the soil may also be rich in proteinaceous material (the NMR signal at 175 ppm). Considering the small role apparently played by alkyl groups in sorption of carbaryl and phosalone by the other soils studied, it is suggested that the alkyl component of organic matter in this soil is different not only in amount but also in reactivity. The aliphatic component alone or in combination with high contents of proteinaceous material and methoxy C might have strongly influenced the sorption of both pesticides in this soil. The nature of the proteinaceous material in this soil might also differ from that of the other soils. Piccolo et al. (1998) observed the role of a high content of proteinaceous material (revealed by NMR) present in one of the four humic fractions extracted from soils by different extractants on the sorption of atrazine. This fraction rich in aliphatic amines, despite a much lower aliphatic C content (which they found a controlling factor for higher sorption of atrazine), showed sorption comparable to that with the fraction rich in aliphatic C. The role for proteins in the high sorption capacity of a soil was also noted by Dunigan and McIntosh (1971). They studied sorption of atrazine, an ionisable compound, on model compounds of the soil organic fractions, and observed 2-4 times higher sorption affinity of protein (egg albumin) for atrazine than that of polysaccharides. They theorised that the sorption of atrazine was high because the protein compounds contained reactive functional groups. They stated that still the lower sorption values were probably due to unavailability of potential reactive sites due to intermolecular bonding of this compound.

An examination of Pk6 under a Scanning Electron Microscope (SEM) suggested the presence of waxy materials cementing soil particles and forming round shaped aggregates. (Plate 6.14, a). These organic coating and cementing lipids/waxes, due to their distinct

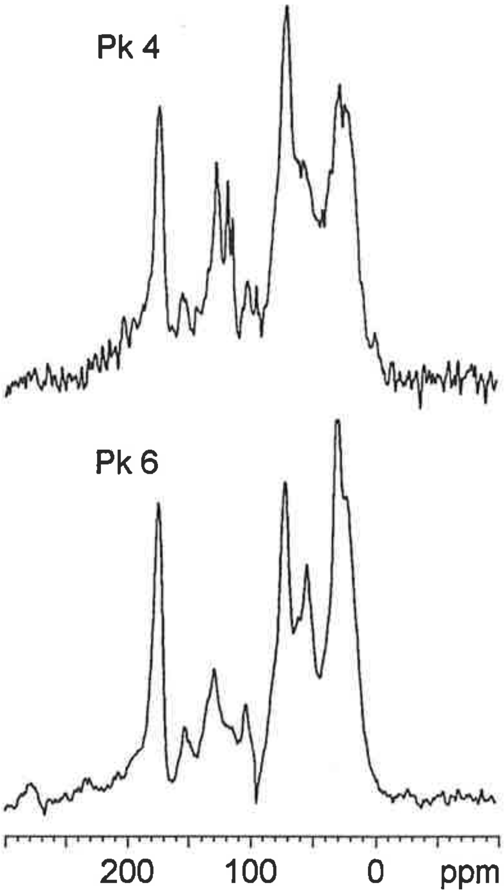
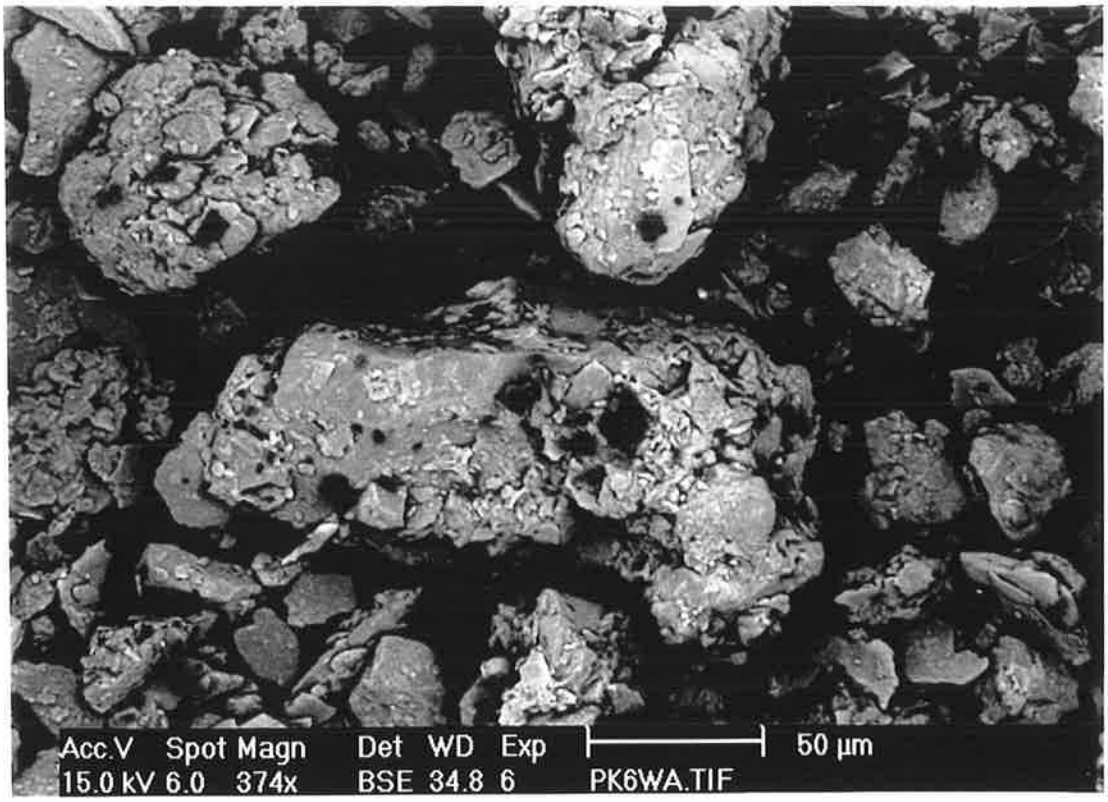
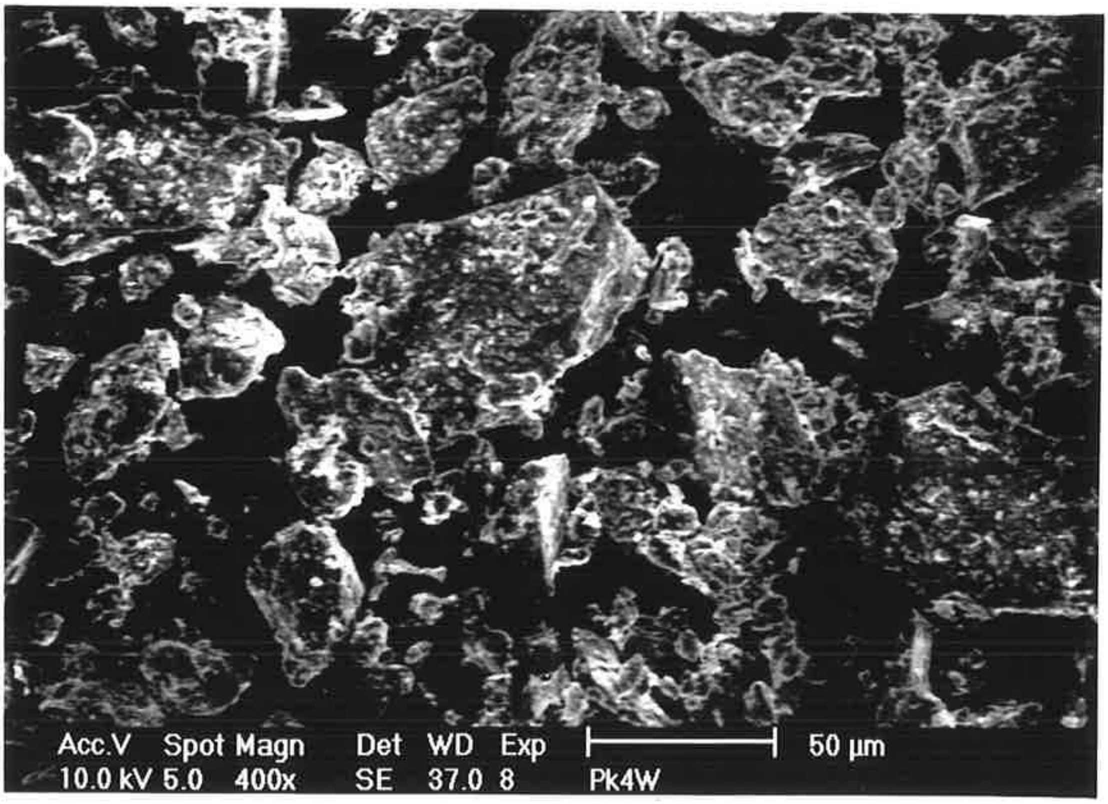


Figure 6.13 Solid state ^{13}C CP/MAS NMR spectra of soils Pk4 and Pk6

Plate 6.1 Electron micrographs of two Pakistani soils Pk6 (top) and Pk4 (bottom), contrasting in NMR spectra


Acc.V Spot Magn Det WD Exp
50 µm
15.0 kV 6.0 374x BSE 34.8 6 PK6WA.TIF


Acc.V Spot Magn Det WD Exp
50 µm
10.0 kV 5.0 400x SE 37.0 8 Pk4W

chemical composition, may have been responsible for the exceptionally high sorption of the both pesticides in this soil.

6.5 Conclusions

This study of soils collected from different environments revealed substantial variations in the structural and chemical composition of SOM, as characterised by NMR. The sorption behaviour of carbaryl and phosalone was related to these variations in the nature of SOM. There was a good correlation of the K_{oc} values of carbaryl and phosalone with aromaticity (aryl plus O-aryl carbon) alone or with aryl-C and carboxylic C of the SOM. Among the molecular components of SOM as predicted from MCSE, lignin and charcoal were the most important contributors to the sorption capacity of the SOM. Variations in the nature of SOM may also be important for sorption of other contaminants, and worth further investigation.

The study also showed that the use of K_{ow} to predict K_{oc} for nonionic pesticides may give rise to misleading results because it fails to account for variations in the chemical composition of SOM. It is reasonable to expect variations in the nature of SOM from different environments and consequent dissimilarities in their sorption affinities. Prediction equations for pesticide sorption using parameters like water solubility, K_{ow}, or a single soil characteristic such as $f_{oc,}$ do not reflect differences in the nature of SOM. Therefore, there is a need to develop better approaches for estimation of sorption of pesticides based on not only the quantity but also the quality of organic matter. Simpler methods of characterising SOM in terms of degree of its aromaticity may prove valuable in such a pursuit.

CHAPTER 7

Release Behaviour of Carbaryl and Ethion in Historically Contaminated Soils

7.1 Introduction

There are few reports on the release behaviour of pesticides in soils that have been exposed to pesticides for extended periods: much of the research on release behaviour has been carried out on freshly added pesticides and the information such studies provide may be inadequate to determine environmental toxicity and enable bioremediation of the contaminated soils. There is evidence that the release or bioavailability of organic compounds decreases with their increased residence times in soil environment, a process called ‘aging’ or ‘sequestration’(Robertson and Alexander, 1998). Bioavailability is of great importance because it frequently accounts for the persistence of compounds that are biodegradable and that might otherwise be assumed to be readily decomposed. It may also be a major constraint to bioremediate contaminated sites.

In Australia, there are over 1600 cattle and sheep dip sites in Northern New South Wales (NSW) alone, where the soils are massively contaminated with various pesticides such as ethion and DDT. Such sites are likely to be present in other regions of Australia. Similarly, in Pakistan, there are around 1900 contaminated storage sites in the Punjab province alone. The extent and magnitude of the risk posed by pesticides at these long-contaminated sites is unknown and consequently there are unanswered questions about the cleanup levels or remediation of such sites that could be achieved. Knowledge concerning the rate of release of these compounds from soil into the aqueous phase is essential to answer to such questions.

It was hypothesised that surface-active agents (surfactants) reduce the water-SOM interfacial tension and eventually enhance the release of hydrophobic pesticides. Therefore, the study was extended to examine the use of nonionic surfactants to enhance the release of ethion and carbaryl from the historically contaminated soils. Much research has been conducted on enhancing recovery of crude oil from oil reservoirs by the use of aqueous surfactant solutions (Abdul et al., 1990; Peters et al., 1992) and also for other organic compounds from soils (Lopes et al., 1992). However, there are few documented studies of the removal of hydrophobic pesticides by the use of surfactants from long term-contaminated soils (Pignatello and Xing, 1996).

As reported in the literature review (Chapter 2), many organic compounds, particularly the carbamates (e.g. carbaryl) and organophosphates (e.g. ethion) are transformed by alkaline hydrolysis. Conceivably, the enhanced solubilisation of hydrolysable hydrophobic pesticides in the presence of surfactants could facilitate availability and such hydrolysis. While studies on hydrolysis of pesticides in aqueous alkaline solutions have been reported extensively, reports on the hydrolysis of soil-extracted pesticides such as carbaryl and ethion in the presence of surfactants are not available.

7.2 Objectives

The investigation was designed:

1) to study the release behaviour of carbaryl and ethion from historically contaminated (aged) soil samples collected from a pesticide storage place and a cattle dip site, respectively,

2) to explore the reasons of long persistence of carbaryl (a relatively rapidly degradable pesticide) and to explore the mechanisms of sequestration/aging of carbaryl and ethion,

3) to evaluate the extent to which aqueous solutions of five nonionic surfactants could enhance removal of carbaryl and ethion from the historically contaminated soils, and

4) to investigate the kinetics of alkaline hydrolysis of carbaryl and ethion in a nonionic surfactant micellar solution and compare with the kinetics in aqueous media.

7.3 Materials and Methods

7.3.1 Soils

A contaminated soil was collected from the area around the scooping mound and adjacent to the dip bath in the splash zone of a cattle dip site located at Coraki town of NSW (Australia). A typical layout of the cattle tick dip site is shown in Figure 7.1 and a picture of one of the sites is given by Plate 7.1. Ethion was used at the site from 1962 to 1973 when the use was halted. Another soil was obtained from an old pesticide storage place in Pakistan located at Mamoon Kanjan since 1965. Leaking pesticide containers caused some soil contamination. No further contamination of this site with carbaryl was recorded since 1984. The soils were passed through a 2 mm sieve to remove debris. After sieving, each sample was thoroughly mixed by shaking the jars half-filled with soils overnight. The soils were stored at -14°C. When the soils were screened for contaminants, ethion was found to be the major pesticide in the soil collected from dip site and carbaryl in the soil taken from the pesticides storage place. Some selected physico-chemical properties of the soils are given in Table 7.1.

Table 7.1 Some pertinent properties of the soils used in the study

Soil	pH (1:5 $CaCl_2$)	Clay (g kg soil^{-1})	Organic C content (g kg soil^{-1})	Total contaminant concentration (mg kg soil^{-1})
Coraki	4.01	56	35.8	1001 (Ethion)
MK3	7.15	252	22.0	88 (Carbaryl)

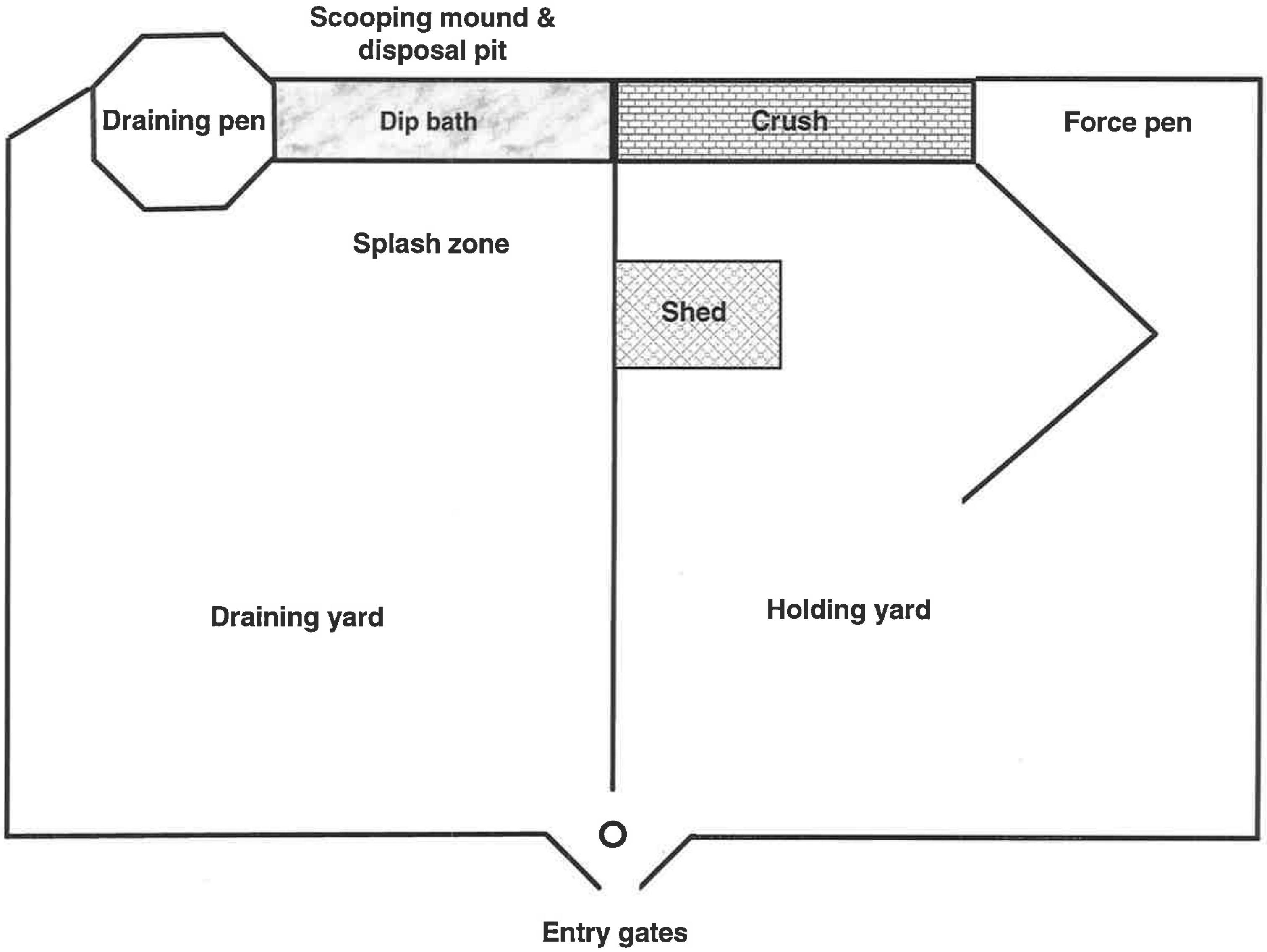


Figure 7.1 Diagramatic representation of a cattle tick dip site

Plate 7.1 A cattle dip site located in New South Wales

7.3.2 Determination of Contaminants

The ethion content of the dip site soil and the carbaryl content of the soil from the storage place were extracted with 1:10 (soil:methanol) and 1:5 (soil:ethanol), respectively and determined by HPLC following the analytical methods given in Chapter 3. The purity of the peaks in the chromatograms were verified using polychrom diode array detector (PDA) and pure standard of carbaryl (Appendix-7.1). PDA provides complete spectral and chromatographic peak processing. This was necessary for carbaryl because the retention time of carbaryl was the same as that for atrazine following the HPLC conditions. Carbaryl was also confirmed to be present in the contaminated soil from Pakistan by an independent accredited analytical laboratory, Australian Government Analytical Laboratories (AGAL) South Australia. The contents of pesticides in the soils are given in Table 7.1.

7.3.3 Biological Characterisation of Carbaryl Contaminated Soil: Microbial Population and Dehydrogenase Activity

Bacterial and fungal populations in the carbaryl-contaminated soil were estimated following the method described by Megharaj et al. (1998), using LB agar medium for bacteria, and Martin's Rose Bengal agar medium for fungi. The populations were enumerated as colony forming units from 10-fold serial dilutions of the soils plated out in triplicate on agar plates. The colonies were counted after 5 days incubation at 28°C.

Dehydrogenase activity in the carbaryl-contaminated soil was estimated by incubating the soil at 37°C for 24 h with 2, 3, 5-triphenyltetrazolium chloride for the production of 2,3,5-triphenyltetrazolium formazan (Casida et al., 1964).

7.3.4 Release Kinetics

A batch method was used to determine the rate and extent of release of carbaryl and ethion from soils to the aqueous phase. A series of soil suspensions (1 g of ethion-contaminated soil and 10 mL of water in the presence of 60% CH_3OH and 2 g carbaryl-contaminated soil with 10 mL of water in glass tubes with Teflon-lined screw caps) were shaken at ambient temperature (22±2°C). Duplicate tubes were removed at various designated periods of time and centrifuged at 1800 rpm and filtered through RC25 and B101 microfilters for carbaryl and ethion, respectively. The filtrates were analysed following the RP-HPLC method, as described in Chapter 3.

To study the influence of mechanical break-up of the soil on release of carbaryl and ethion, and also on microbial degradation of carbaryl, samples of each soil were transferred to the capsule of a ball mill and pulverised for 0.5, 1, 2, 4, 6, and 8 minutes prior to use in these experiments.

7.3.5 Biodegradation of Carbaryl

To investigate if the aged carbaryl was amenable to the microbial degradation, carbaryl contaminated soil was extracted with water by shaking for 24 h. After centrifugation, the supernatant was decanted and transferred to a flask for biodegradation studies. The remaining soil was extracted twice with autoclaved Milli-Q water by shaking for 1 h and centrifuged to remove any remaining water-extractable fraction of carbaryl. The extracted soil, referred to as 'washed soil', was then air dried. For determination of microbial degradation in 'unwashed' and 'washed soils', 2 g soil from each group (in duplicate) was transferred to sterilised (autoclaved) glass culture tubes with Teflon-lined screw caps and the following treatments were applied.

1. Control (2 g soil + 0.3 mL autoclaved water)
2. Soil (2 g) + mixed bacterial culture in water (0.3 mL)
3. Soil (2 g)+ mixed bacterial culture + mineral medium (total = 0.3 mL)
4. Soil (2 g)+ mixed bacterial culture + mineral medium + yeast extract (0.1%) (total = 0.3 mL)

The composition of mineral medium (M9 Minimal medium) used was that given by Eisenstadt (1994). The purpose of adding the various nutrients was to determine if nutrient deficiency was restricting microbial degradation. The mixed bacterial culture (two *Pseudomonas* spp.) was enriched from another contaminated soil, and was known to use carbaryl as a sole source of C (Megharaj, unpublished). The bacteria added to the soils were at a level of 10^6-10^7 cells g^{-1} dry soil.

To determine the effect of pulverising the soil on the biodegradation of the aged carbaryl, 1 g samples (in duplicate) of soil samples milled for 0, 2, 4 and 8 min, were treated with a total 0.3 mL bacterial culture + mineral medium +yeast extract (0.1%).

To investigate if the soil conditions at the contaminated site were toxic to the microbes, aliquots (in duplicate) of undiluted aqueous extract of carbaryl-contaminated soil were transferred to a series of glass tubes and the following treatments (in a final volume of 5 mL) were applied.

1. Control (undiluted aqueous extract of carbaryl-contaminated soil)
2. Undiluted aqueous extract of carbaryl-contaminated soil (4.5 mL) + mixed bacterial culture (0.5 mL) + yeast extract (0.1%)
3. Undiluted aqueous extract of carbaryl-contaminated soil (4.5 mL) + mixed bacterial culture (0.5 mL) + glucose (0.5%)

Five millilitres of fresh aqueous solution of carbaryl (5 mg L^{-1}) was also transferred to tubes and the following treatments (0.5 mL) applied.

1. Aqueous carbaryl + mineral medium + glucose + mixed bacterial culture
2. Aqueous carbaryl + mineral medium + yeast extract + mixed bacterial culture
3. Aqueous carbaryl + mineral medium

To establish if there was any abiotic degradation during the experimentation, 5 mL of 5 mg L^{-1} carbaryl solution was spiked with autoclaved cells of carbaryl degrading bacteria.

All samples were incubated for one week at ambient temperature (22±2°C), and duplicate tubes were taken and the samples were extracted with ethanol and determined by HPLC following the conditions given in Chapter 3.

7.3.6 Surfactant Enhanced Release of Ethion and Carbaryl from Long-contaminated Soils

7.3.6.1 Characteristics of Surfactants Used

Five nonionic ethoxylate surfactants were used in the study. Triton X-100 and Brij35 were purchased from Sigma Chemical Company, Australia and three commercially available surfactants, Ethylan GE08, Ethylan CD127 and Ethylan CPG660 were a gift from Akross Chemicals, UK. The detail and pertinent characteristics of the surfactants are given in Table 7.2. Milli-Q water was used for preparing the solutions.

Table 7.2 Selected properties of the surfactants used in the study

Trade name	Chemical makeup	Water solubility	Specific gravity	CMC (mg L^{-1})*
Triton X-100	POE(10) octyl phenol	Clear to faint yellow solution at 1mL plus 10 mL of water	1.07 (25°C)	175
Brij35	POE(23) lauryl ether	Clear colourless solution at 1 g plus 10 mL of water	-	70
Ethylan GE08	POE (20) sorbitan mono-oleate	Complete	1.10 (25°C)	100
Ethylan CD127	Synthetic C12 primary alcohol ethylene oxide condensates	Complete	1.002 (20°C)	175
Ethylan CPG660	Modified alcohol ethoxylate	Complete	0.988 (20°C)	60

* Critical micelle concentration, measured in laboratory

7.3.6.2 Determination of Critical Micelle Concentration for the Surfactants

Critical micelle concentration (CMC) of each of the nonionic surfactants used in the study was determined by measuring the surface tension of the aqueous solution of each surfactant over a wide range of concentrations and noting the inflection in the plot of surface tension versus log surfactant concentration. The plotted surface tension value was taken when stable readings were obtained for a given concentration of surfactant. Surface tension of the surfactant solutions were determined with a surface tensiometer assembled in the laboratory.

7.3.6.3 Surfactant Enhanced Release Studies

The rate and extent of release of ethion and carbaryl from long contaminated soils in the presence of surfactants were measured in batch studies. Aqueous solutions of various concentrations of surfactants below and above their CMCs (50 mg L^{-1} to 20 g L^{-1}) were prepared in Milli-Q water. Ten millilitre aliquots of surfactant solutions were added to a series of 14-mL glass vials with Teflon-lined caps, each containing 1 g of the contaminated soil and the vials were shaken mechanically. After given time intervals, the soil suspensions were centrifuged at 1800 rpm for 20 min. An aliquot of the supernatant was withdrawn and filtered using B101 microfilter for ethion and RC25 for carbaryl. The soils were washed twice with aqueous solutions of the surfactants (each cycle was of 24 h duration), to determine the cumulative removal of each pesticide from the soil. The concentrations of ethion and carbaryl in the supernatant solutions were determined by HPLC following the analytical methods described in Chapter 3.

7.3.6.4 Kinetics of Alkaline Hydrolysis of Ethion and Carbaryl

The kinetics of alkaline hydrolysis of ethion and carbaryl were investigated using the surfactant ethylan CPG 660. Solutions of ethion (1.1 mg L^{-1}) and carbaryl (10 mg L^{-1}) were made in 0.2 g L^{-1} aqueous solution of the surfactant in autoclaved water. The concentrations of these pesticides are much lower than their water solubilities (Table 3.2). The pH of these solutions was adjusted to 11 with Na_2CO_3. The influence of pH on hydrolysis of ethion was studied with another set of solutions. Solutions of ethion (20 mg L^{-1}) containing 10 g L^{-1} CPG660 were adjusted to pH 4, 8, 9, and 11 with Na_2CO_3 and CH_3COOH. No change in the pH was observed in these solutions during the studies. The glass apparatus was sterilised prior to use by autoclaving to avoid microbial degradation during the incubation. The solutions were kept in an incubator at 25°C. After specified time intervals, aliquots of the solution were taken and the concentrations of the pesticides were determined immediately using HPLC with a UV detector following the methods outlined in Chapter 3.

7.4 Results and Discussion

7.4.1 Release of Carbaryl

7.4.1.1 Release Kinetics

Release of carbaryl from the contaminated soil (MK3, Table 7.1) followed a biphasic pattern i.e. a fast initial release for 2 h followed by a slow release (Figure 7.2). The amount released in 2 h was equivalent to 45% of the total concentration present in soil, while a total of about 51% was released by the end of 72 h period.

A biphasic release of many organic compounds showing a rapid phase followed by a period of slow release have been observed (e.g. Connaughton et al., 1993). From published studies, it appears that the longer a pesticide remains in soil, lesser the amount is released into water (McCall and Agin, 1985: Pignatello and Huang, 1991). Pavlostathis and Mathavan (1992) reported that trichloroethylene (TCE), a volatile organic compound, remaining in the soil after successive equilibrations for a period of 12 days increased from 10 to 45% for corresponding residence times of 2.5 and 15.5 months. Most of the available fraction of TCE was released during first 24 h.

In the present studies, the residence time of carbaryl in the soil was >12 years. The data on release of carbaryl showed that following an initially rapid release, presumably from the sites very near to the particles-water interface, a slow release of the compound into the solution resulted. The slowly released carbaryl originated presumably from less accessible sites at some distance from the interface. The release after 24 h in this study was small. This might be due to very long (>12 years) soil-pesticide contact time, which may have permitted the molecules to diffuse into even more remote sites. Therefore, it is conceivable that the aging of carbaryl was associated with the slow diffusion of the pesticide molecules into more remote sites where they were retained and diffusion of the molecules from these sites might have been retarded by the tortuous path through the micropores. Other processes of SOM-carbaryl interactions could also be involved.

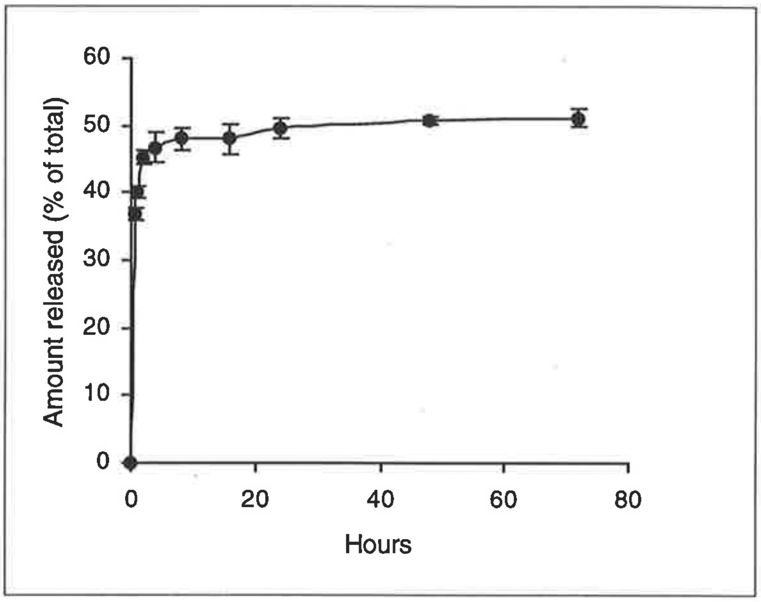


Figure 7.2 Release pattern of carbaryl from contaminated soil. Bars indicate ± standard deviation from the mean

7.4.1.2 Effect of Pulverisation on the Release of Carbaryl

If aging of carbaryl molecules was associated with diffusion into soil micropores, crushing of the soil aggregates should enhance the release of sequestered carbaryl. In this study, pulverisation of the soil for different time intervals showed an increase in release of carbaryl into solution phase (Figure 7.3). There was a 19% increase in the release of carbaryl after 8 h of shaking with pulverisation time of 8 minutes compared with the release from unpulverised soil. It can be inferred from this result that a fraction of carbaryl was indeed entrapped in inaccessible regions which were exposed by the break-up of soil particles. However, substantial proportion of carbaryl (33%) was still resistant to release. It is possible that this part of the sequestered carbaryl was closely associated with SOM which might have restrained its release into the aqueous phase, even after pulverisation. It has been hypothesised that aging is due to partitioning into SOM, to strong surface adsorption, or to a combination of these processes (Brusseau and Rao, 1991). Humic materials consist of phenolic and benzenecarboxylic acids joined by hydrogen bonding to form a molecular sieve type polymeric structure of considerable stability (Schnitzer and Khan, 1972). One of the characteristics of this proposed structure is that it contains voids of different molecular dimensions which can trap organic molecules such as carbaryl. It is

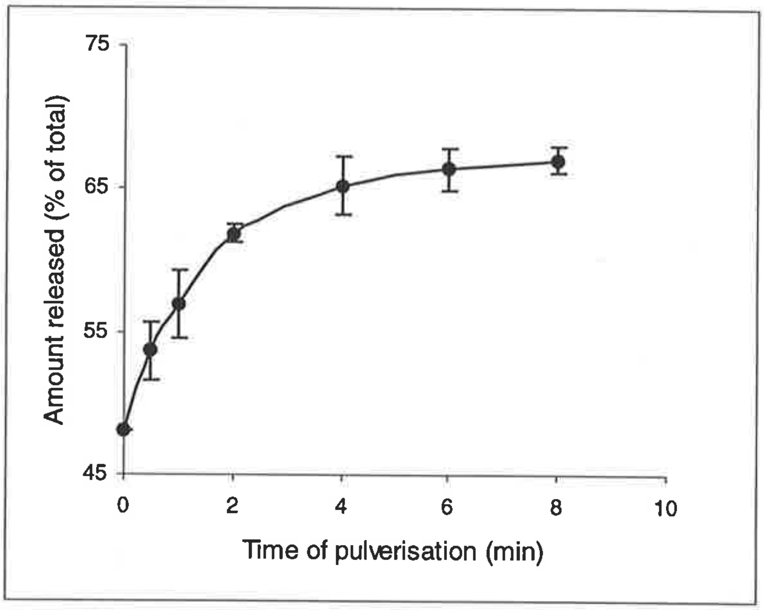


Figure 7.3 Effect of pulverisation on the release of carbaryl from contaminated soil. (0 min represent unpulverised soil). Bars indicate ± standard deviation from the mean

possible that the carbaryl (33%) retained by the soil after pulverisation is held entrapped within the polymer-like matrix of the SOM. Sequestration, regardless of the mechanisms involved, has major implications for assessing the toxicity and bioavailability of pesticides such as carbaryl in the soil.

7.4.1.3 Biodegradation of Aged Carbaryl

As carbaryl is a relatively easily degradable pesticide, it was unusual that carbaryl was present in the soil at such high concentration after more than a decade since its last spill. There can be several reasons for the lack of biodegradation of carbaryl at the site: i) the concentration of carbaryl might be so high that microbial proliferation and metabolism is precluded; ii) one or more nutrients needed for microbial growth are at levels too low to permit appreciable growth; and iii) carbaryl may not be in a form that is readily available for microorganisms.

Attempts to enhance degradation of aged carbaryl in contaminated soil with addition of active mixed bacterial culture did not significantly improve the degradation beyond the water extractable fraction of carbaryl (Figure 7.4). Less than 5% of the non-extractable carbaryl was degraded in washed soil after an incubation time of one week: a small portion of this may have been from the soluble fraction left after decanting. It appears that the carbaryl which resists release into water is also not available for microbial degradation.

To test if the conditions at the contaminated site were toxic to the microorganisms capable of degrading carbaryl, the water extracted carbaryl was incubated for one week with the mixed culture of bacteria capable of degrading carbaryl with different treatments of nutrients. The results showed that there was almost complete degradation of the water extracted carbaryl in the solution during the incubation period, with or without nutrients (Table 7.3). Even the additionally spiked freshly prepared 5 mL of carbaryl solution (5 mg L^{-1}) was degraded by the bacteria.

It is clear from these studies that microbial degradation of carbaryl was not restricted by toxicity problems (due to other contaminants and carbaryl itself) or nutrient deficiency.

The bacterial culture introduced in the contaminated soils were capable of degrading only the portion of carbaryl which was in the readily extractable form but not the unavailable (aged) portion, as apparent from the very limited degradation in the washed soil (Figure 7.4). At the contaminated site, even if most of the carbaryl had been available, it may not have degraded rapidly as the microbial population in the soil was low and not at all active. The carbaryl contaminated soil contained an average of 43×10^5 colony-forming units g^{-1} soil as determined by the bacterial count. However, there was no dehydrogenase activity and fungi were not detected in the soil.

Table 7.3 Degradation after 7 days incubation of aqueous carbaryl extracted from the contaminated soil

Treatment	Carbaryl degradation (%)
Control (undiluted water extract)	-
Undiluted aqueous carbaryl extract + mixed bacterial culture + yeast extract	99.5
Undiluted aqueous carbaryl extract + mixed bacterial culture + glucose	98.5
Carbaryl (5 mg L^{-1}) + mineral medium + glucose + mixed bacterial culture	100.0
Carbaryl (5 mg L^{-1}) + mineral medium + yeast extract + mixed bacterial culture	100.0
Carbaryl (5 mg L^{-1}) + mineral medium	4.0
Carbaryl (5 mg L^{-1}) + autoclaved cells before incubation	0.0
Carbaryl (5 mg L^{-1}) + autoclaved cells	3.2

As stated previously, aging of organic compounds can involve their diffusion into soil micropores, partitioning into SOM or strong surface adsorption, all of which may have limited the degradation of carbaryl. There was a considerable (9-11%) increase in bacterial mineralisation of carbaryl in the contaminated soil after its pulverisation for 2 and 4 minutes followed by a non-significant increase in degradation in the soil sample after 8 minute of pulverisation (Figure 7.5).

A considerable part of the pore volume within soil particles is composed of micropores with diameters of 20 nm or less (Pignatello, 1989; Farrell and Reinhard, 1994). These pores are too small to permit the penetration of bacteria (Alexander, 1995). In the present

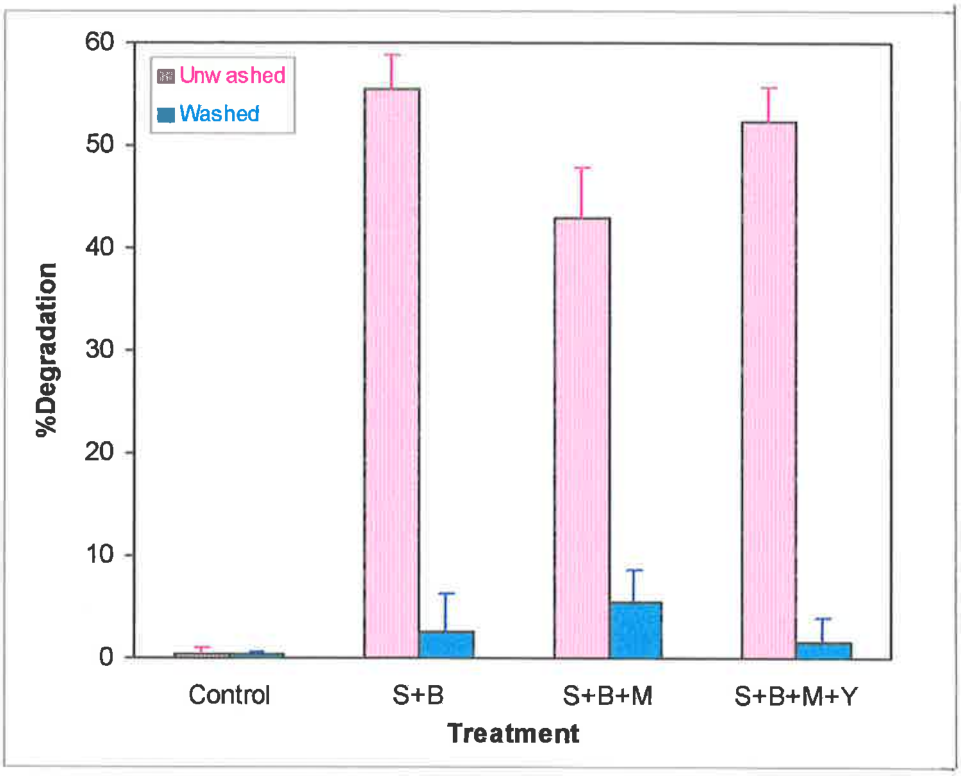


Figure 7.4 Microbial degradation of carbaryl in unwashed and washed soil after one week of incubation. Bars indicate ± standard deviation from the mean. (S = soil, B = Mixed bacterial culture, M = Mineral medium, Y = Yeast extract)

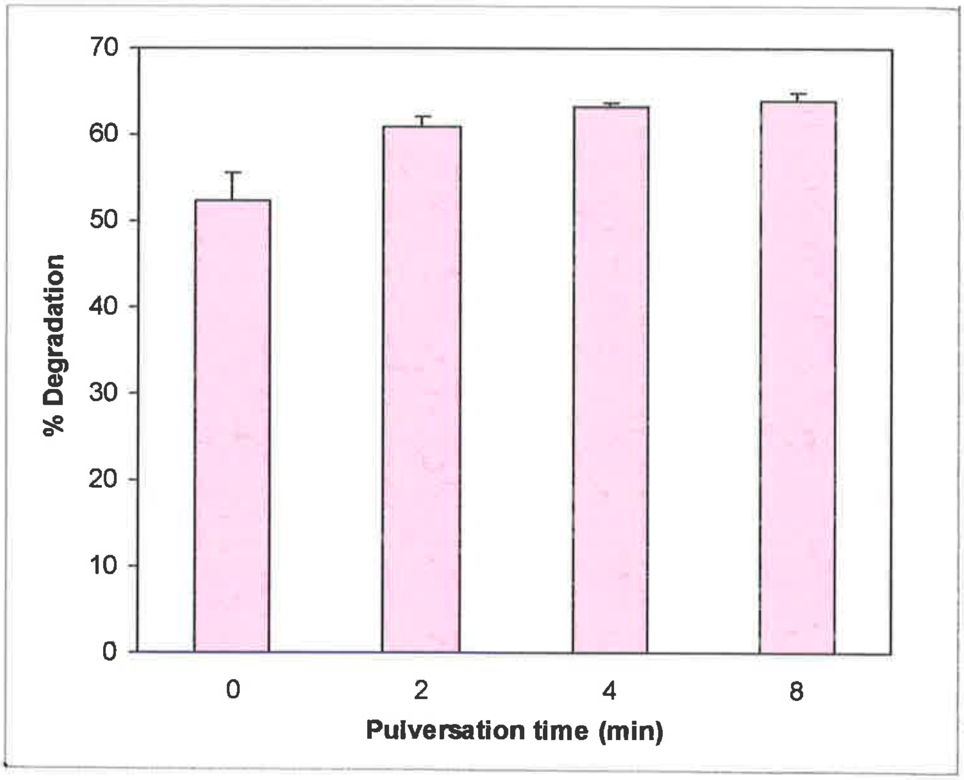


Figure 7.5 Effect of pulverisation on the microbial degradation (with mineral medium and yeast extract) of aged carbaryl after one week of incubation. Bars indicate ± standard deviation from the mean.

study only a portion (~12%) of carbaryl residing in these pores was exposed due to pulverisation. However, there was still a large proportion (~36%) of the chemical which was not bioavailable. Clearly, the fraction extractable in aqueous solution was truly bioavailable. Organic compounds have been reported to penetrate and bind at the expandable inter layer regions of 2:1 types of clays (Burchill et al., 1981). Analysis of the soil containing carbaryl by X-ray diffraction showed that illite, which does not have expandable inter layers, was the dominant clay (Appendix-7.2). Therefore, it is possible that the remaining fraction was partitioned deeply in the matrix of the SOM by intraorganic matter diffusion. Over a long period of time, the diffusional paths might have been blocked due to configurational changes in SOM due to rearrangement of the alkyl or aryl functional groups in response to changes in pH, ionic strength or temperature. For example, Murphy et al. (1994) noted that, depending on factors such as pH and ionic strength, structural orientation of humic substances may change from a coiled configuration to a more open configuration. Therefore, it can be suggested that the entrapment of carbaryl within these cages or dead-end pores could be one of the mechanisms of carbaryl aging in the soil. As the bacterial cells are too large (> 0.2 µm) to fit into the organic matter matrix, it seemed unlikely that the bacteria had the ability to attack these remote molecules of carbaryl. However, further research is crucial to elucidate the mechanisms involved in aging.

The outstanding feature of these results is that virtually all the carbaryl remaining in soil after aqueous extraction of the soil could not be accessed by carbaryl-degrading microorganisms. The microbes were capable of degrading only the free or loosely bound carbaryl. On milling the soil, only the exposed fraction of carbaryl was degraded. These results indicate that the release of nonionic pesticides such as carbaryl from soils may be strongly impeded by the hypothesised cage effects or a ‘lock-in’ mechanism. Therefore, the total pesticide concentration in a soil may not be an adequate indicator of the bioavailability of the compounds residing in the soil for a long period of time. Moreover, these results raise questions about the effectiveness of the bioremediation techniques used for decontamination of sites that contain aged residues of pesticides such as carbaryl.

7.4.2 Release of Ethion

As ethion is sparingly soluble in water (2 mg L^{-1}), CH_3OH was used as a cosolvent in this study. Figure 7.6 shows an exponential relationship ($r^2 = 0.97$) of the solubility of ethion with the fraction of cosolvent. Figure 7.7 shows the influence of the cosolvent on the release of ethion from the contaminated soil (Coraki soil, Table 7.1). The contaminated soil contained a high concentration of ethion (1001 mg kg^{-1}), and to avoid solubility limitation 60% CH_3OH in aqueous solution was used in the release studies.

The release of ethion in 60% CH_3OH from the contaminated soil is presented in Figure 7.8. It is evident that a fraction of ethion (143 mg $kg^{-1} \equiv 14\%$) was not released into the solution even after 1440 h (60 days) of shaking. It is likely that the presence of CH_3OH aided the release of ethion, not just by increasing its solubility, but also by causing the soil organic matter matrix to swell. The influence of solvents on the swelling of SOM has been well documented. For example, citing increased rates of herbicide release from soil during miscible-displacement column experiments with increasing volume fractions of methanol, Nkedi-Kizza et al. (1989) hypothesised that methanol may cause swelling of the SOM and thereby increased the rate of solute diffusion out of SOM and into the bulk solution. Later, Lyon and Rhodes (1991) found from a study on swelling of different types of organic matter in 37 organic solvents and water, that the values of the volumetric swelling parameter (the ratio of swollen volume of the organic matter to its unswollen or dry volume) ranged from 0.9 for water up to 2.7 for the organic solvents. Brusseau et al. (1991) reported that methanol causes SOM to expand and eventually enhances the rate of diffusion of organic compounds in the SOM. At present, there is no significant body of literature on the release of hydrophobic organic compounds such as ethion from long contaminated soils in the presence of organic solvents. Explanations about the behaviour of aged hydrophobic pesticides in soil remain speculative.

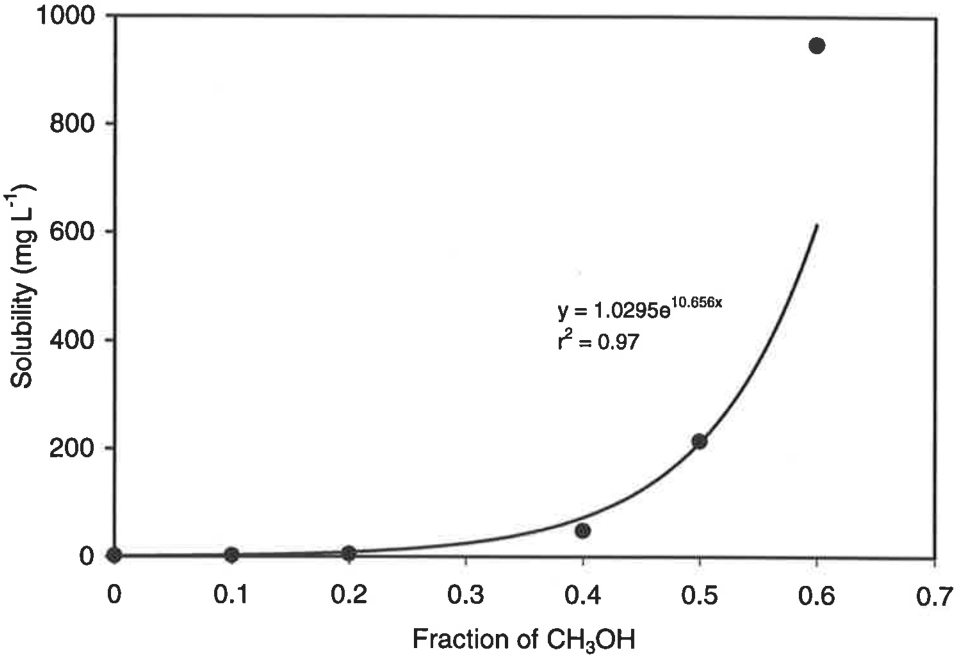


Figure 7.6 Solubility of ethion in water with CH_3OH as a cosolvent

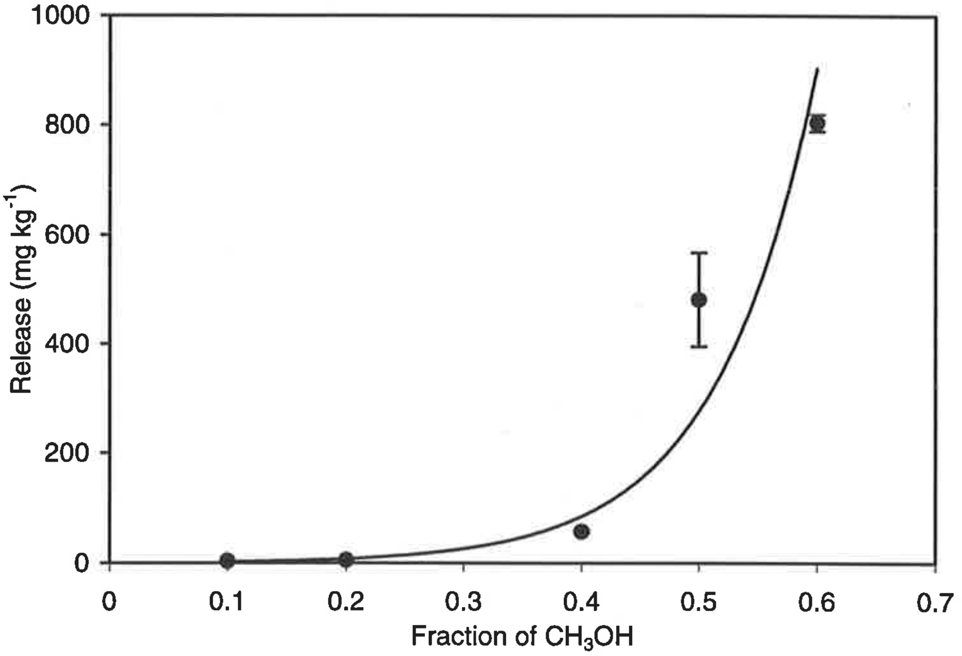


Figure 7.7 Release profile for ethion from contaminated soil after using different fractions of CH_3OH (shaking time = 24 h). Bars indicate ± standard deviation from the mean.

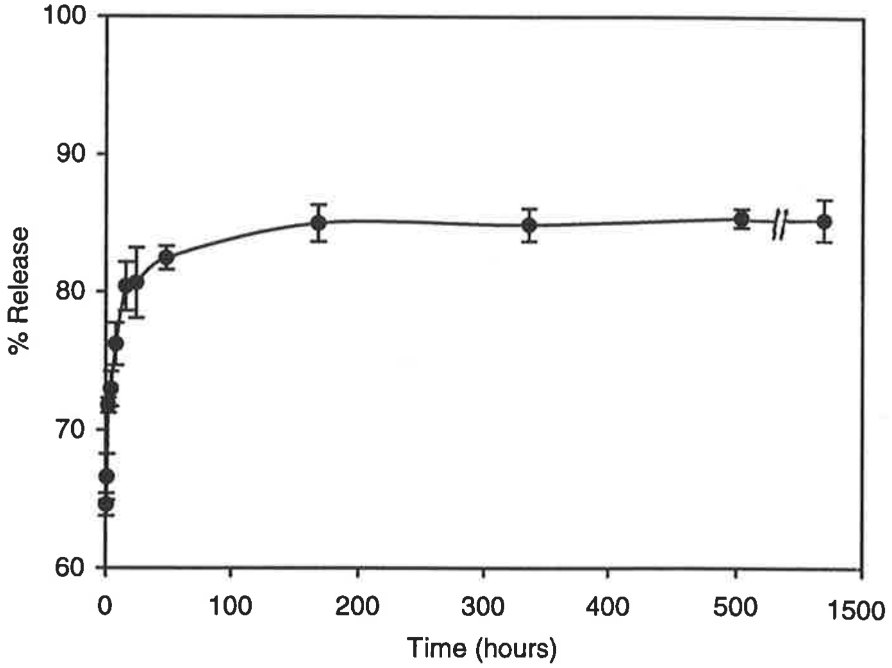


Figure 7.8 Release pattern of ethion from contaminated soil. Bars indicate ± standard deviation from the mean.

Table 7.4 shows that pulverisation of the soil had no significant effect of on the release of ethion, which contrasts sharply with the significant increase in release of carbaryl (Figure 7.3) where only water was used as the extractant. It appears that the CH_3OH used in the ethion studies was able to penetrate to the microsites and enable release from these remote sites, so that milling the soil did not have any further effect on removal of ethion. However, it should be noted that the ethion-contaminated soil had a low clay content (56 g kg^{-1}) and probably far fewer micropores than the carbaryl-contaminated soil (clay content 252 g kg^{-1}). The remaining 14% fraction seemed to be tightly complexed to the soil matrix and unavailable for its release with the given concentration of CH_3OH as a cosolvent. Carroll et al. (1994), while studying the release of 2-2′, 5,5′-CB from contaminated Hudson River sediment, observed that 45% fraction of the sorbed mass resisted desorption, whereas heat treatment of the sediment enhanced the release of the resistant fraction. They attributed the cause of the slow release to be slow desorption from a condensed phase of SOM. It appears that the thermal treatment of organic matter weakens the structure by eliminating the functional groups which in turn permits the release of the fraction trapped in the structure of organic matter.

Another difference in the ethion contaminated soil and the carbaryl contaminated soil is ofpH. Carbaryl contaminated soil has a pH of 7.2 but ethion contaminated soil is acidic (pH 4.0). At higher pH, as in case of carbaryl, the hydration and concomitant repulsion of ionised acidic groups of humic molecule may lead to more expanded conformations and thus may decrease the extent of non-polar regions available for the interactions with the hydrophobic chemicals (Senesi, 1993). This might be another reason that release of ethion from the contaminated soil was more compared with the carbaryl release from the soil. It is concluded from the study that the sequestration of highly hydrophobic compounds such as ethion is associated with the organic matter component of the soil.

Table 7.4 Effect of pulverisation on release of ethion from contaminated soil after 8 hour of shaking time (± standard deviation of the mean

Pulverisation Time (Min)	Release (%)
0.0	76.20 (±1.54)
0.5	76.11 (±1.98)
1.0	77.83 (±3.41)
2.0	75.59 (±1.79)
4.0	76.24 (±2.08)
6.0	75.36 (±3.93)
8.0	76.01 (±1.26)

7.4.3 Surfactant Enhanced Release of Ethion and Carbaryl From Long Contaminated Soils

7.4.3.1 Critical Micelle Concentrations

CMC values of surfactants were determined in the laboratory through a conventional plot of the surface tension versus the logarithm of the concentration of the surfactant in aqueous solution (Figure 7.9). The concentration at which a pronounced break of the slope occurs is the CMC. The CMC values for Triton X-100, Brij35, Ethylan GE08, Ethylan CD127, and Ethylan CPG660 were 175, 70, 100, 175, and 60 mg L^{-1}, respectively. The CMC is an important property in terms of remediation because above this concentration, surfactants may greatly increase the water solubility of organic contaminants due to the increased number of micelles (Rosen, 1989). On the basis of above CMC values selected, concentrations of surfactants below and above their critical values were used in the studies.

7.4.3.2 Release of Ethion and Carbaryl

The effects of the surfactants on release of ethion and carbaryl are presented in Figure 7.10. The release of ethion, which is very hydrophobic compound, was dramatically enhanced by the aqueous concentrations of surfactants above their CMC values. This is attributed to solubility enhancement through incorporation of the highly hydrophobic compound within surfactant micelles (Edwards et al., 1991). A concentration of 10 g L^{-1} of various surfactants released >70% of the ethion from the soil irrespective of the surfactant. Three surfactants Ethylan GE08, Ethylan CD127, and Ethylan CPG660 had a higher potential for releasing ethion than Triton X-100 and Brij35.

For carbaryl, a generally similar pattern of release was observed, but the effects were not as sharp as those observed for ethion. The ethylan surfactants had a higher potential for release of carbaryl than Triton X-100 or Brij35. The reason for the difference in behaviour between the two pesticides could be the relatively high water solubility of carbaryl (120 mg L^{-1}). As reported earlier, 49.7 mg carbaryl kg^{-1} was released from the contaminated soil by water in 24 h. A significant amount of release (up to 32%) was contributed by the surfactants. However, there was still a significant portion of strongly bound carbaryl left in soil. It is worth noting that at concentration above 10g L^{-1}, the surfactants did not further increase the release of carbaryl possibly due to the formation of large micelles which clogged the soil micropores.

The addition of surfactants enhanced the release possibly by reducing the tortuosity of the SOM. This might be due to two mechanisms. Firstly, the addition of a surfactant to water reduces the surface tension of the water until CMC is reached. The surfactants might have reduced the interfacial tension between water and SOM, allowing the water to wet the hydrophobic regions of the SOM. Therefore, the water content was increased, and the

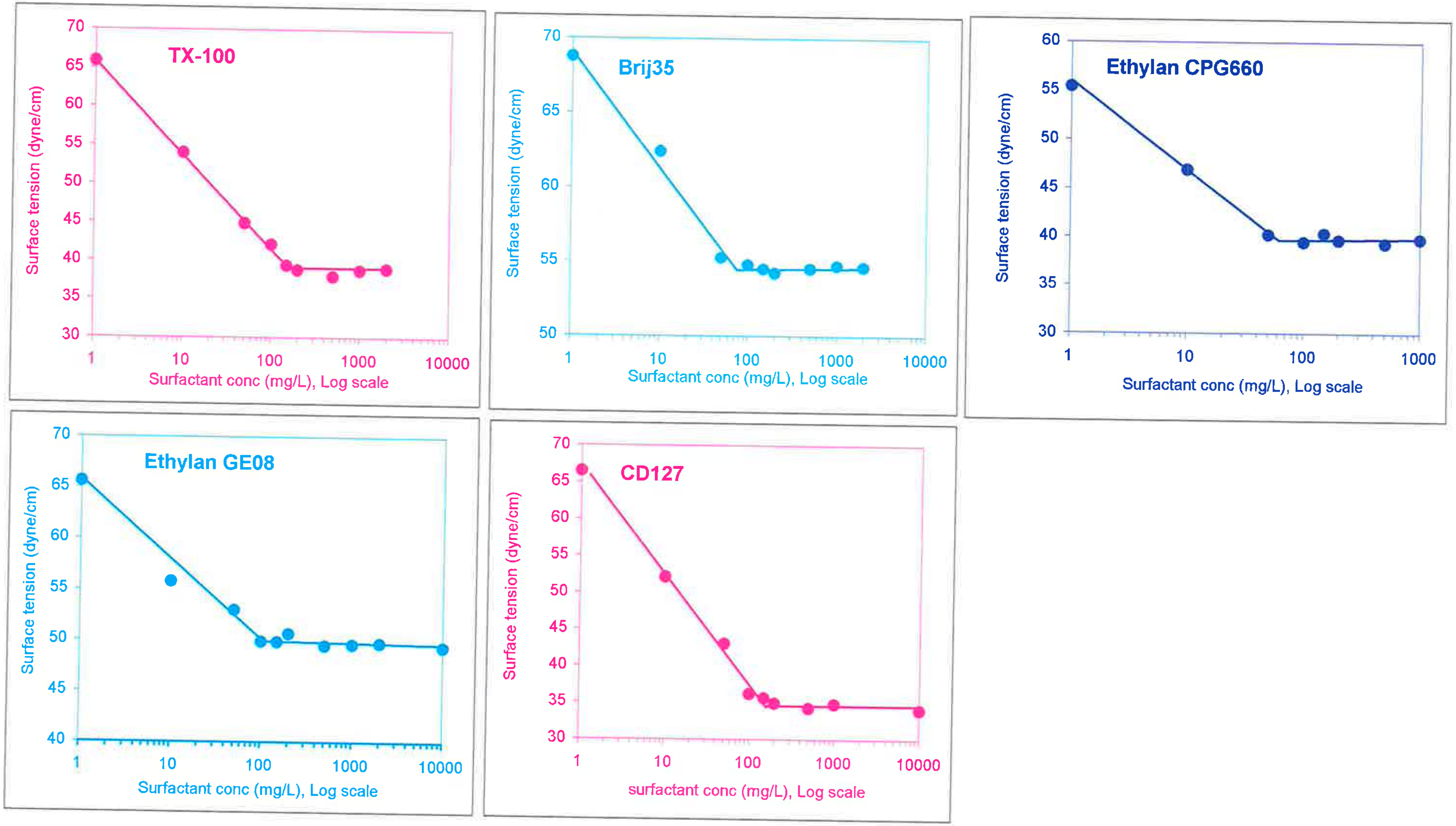


Figure 7.9 Plots of surface tension (n=3) versus the logarithm of surfactant concentration for TX-100, Brij35, ethylan GE08, ethylan CD127 and ethylan CPG660

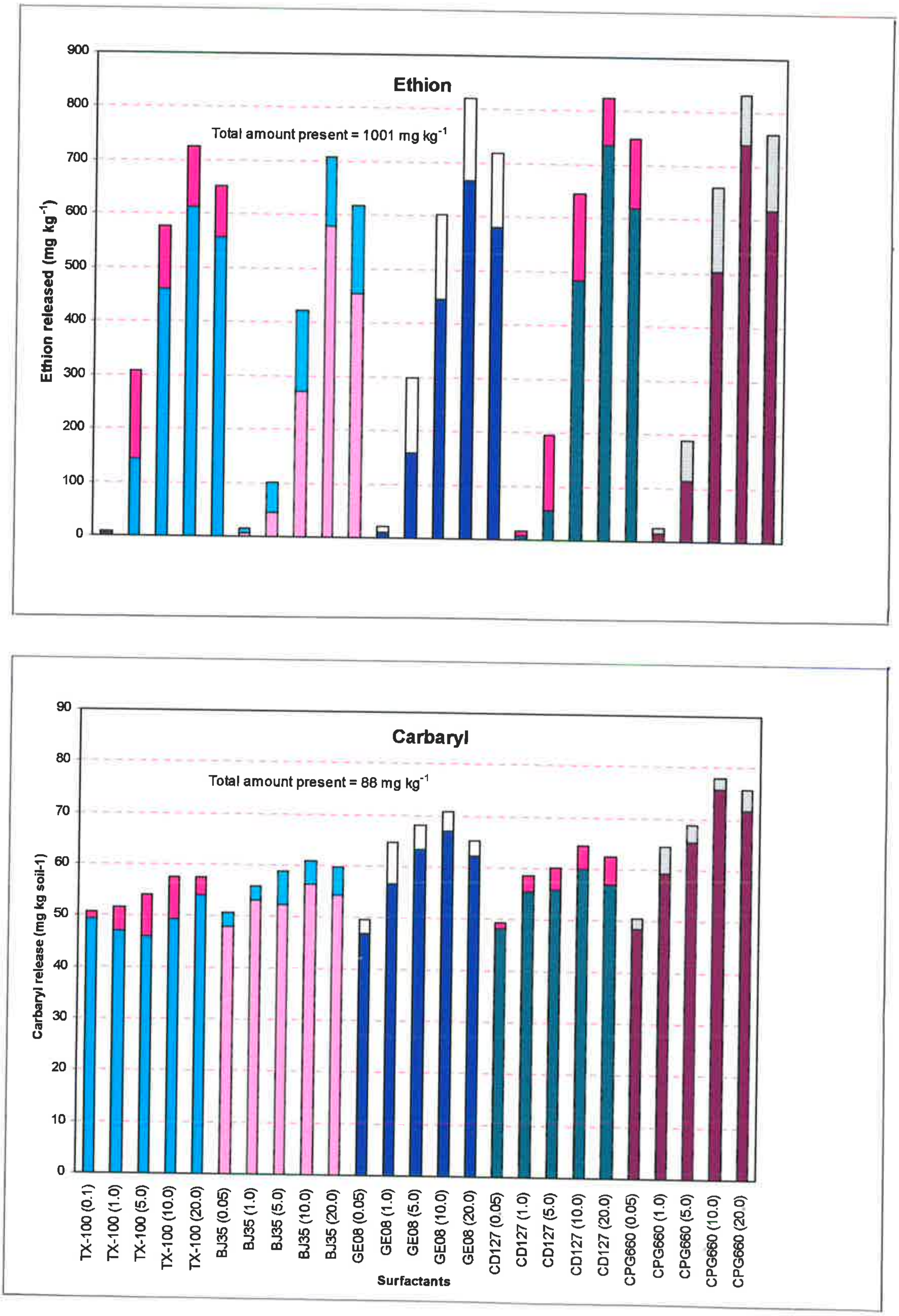


Figure 7.10 Surfactant enhanced release of ethion and carbaryl in long contaminated soils. The lower and upper sections of each bar represent release by first and second washing, respectively. Figures in parentheses are concentrations of surfactants in g L^{-1}.

tortuosity of the SOM was reduced. Secondly, the surfactants might have caused the organic matrix to expand and reduce the tortuosity.

The study also showed that there must be an optimal concentration of each surfactant to enhance the mass transfer coefficient. At some threshold concentration level, it appears that additional surfactant started to inhibit the mass transfer of solute from the SOM into the water. A possible explanation for this phenomenon is that increased sorption of surfactant to the SOM might have blocked more diffusive paths that were open. Therefore, selection of a surfactant for remediation should attempt to minimise its sorption to the contaminated soil. It is also clear from the studies that even the use of surfactants may not result in complete cleanup. However, surfactants can be used to decrease the time that is needed for cleanup to achieve to an acceptable level. Other surfactants may be more effective in promoting release.

7.4.3.3 Release of Ethion and Carbaryl at Below and Above CMC of the Surfactants

A close examination of Figure 7.10 reveals that there was some enhancement of release of ethion below the CMC of the surfactants, the observed order of release being CPG660 > GE08 > CD127 > Brij35 > Triton X-100. However, there was no evidence that the aqueous surfactants affected the release of carbaryl below their CMC. This was attributed to much higher water solubility of carbaryl compared with ethion, which in essence reduces its partition efficiency with the dissolved surfactant. In a study to determine the effect of several surfactants on the release of phenanthrene from soil, Aronstein et al. (1991) observed that Triton X-100 did not enhance the extent of desorption of phenanthrene at the concentrations below its CMC whereas the extent of release of phenanthrene from the contaminated soil was appreciably increased by two nonionic alcohol ethoxylate surfactants, Alfonic 810-60 and Novel II 1412-56 at concentrations below their CMC

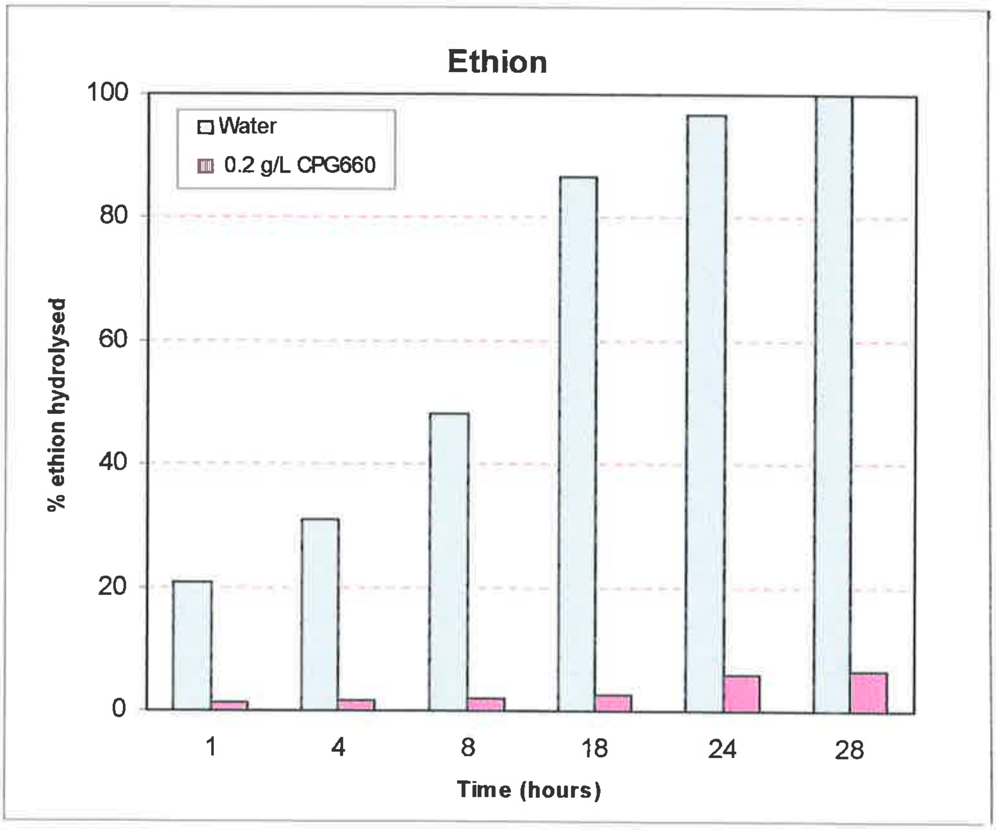
The sharp enhancement of ethion release above the CMC of surfactants indicate that micelles were more effective in solubilising ethion because of the wider extent of the organic environment in a pseudophase state. The inner region of the hydrophobic micellar pseudophase was capable of solubilising ethion by partitioning of the compound into this region (Valsaraj et al., 1988; Valsaraj and Thibodeaux, 1989). However, in case of carbaryl, there was a comparatively less enhancement in the release beyond the release with water (without surfactant) at above the CMC values of the surfactants. The physical state of organic matter in these soils due to variation in pH may be in part responsible for these differences.

Considering the impact of surfactants on the mobility of contaminants, it is apparent from this study that at low concentrations of nonionic surfactants, as generally found in waste waters, the effect should be largely insignificant for the relatively water soluble contaminants. However, it might be important for sparingly soluble contaminants such as ethion. At concentrations far above the CMC, surfactants would have considerably greater impact on release of a wide range of organic pollutants. However, the toxicity of the surfactants to the pesticide-degrading microbes may reduce the effectiveness of higher surfactant concentration. Therefore, the concentration of the surfactant may determine whether biodegradation of the contaminant would be promoted or not.

7.4.4 Kinetics of the Alkaline Hydrolysis of Ethion and Carbaryl in Aqueous and Micellar Media

Figure 7.11 shows the degree of alkaline hydrolysis of ethion and carbaryl as influenced by the nonionic surfactant (200 mg L^{-1} aqueous CPG660). It is clear that hydrolysis was greatly influenced by the presence of the surfactant. After 24 h for example, at pH 11, only 5.9% of ethion was hydrolysed in the presence of the surfactant compared with 96.6% in its absence. The corresponding figures for carbaryl were 9.3 and 75.6%. The comparatively higher rate of hydrolysis of carbaryl in the presence of the surfactant may be related to its lower hydrophobicity compared with that of ethion. As the relatively greater water solubility of carbaryl reduces its partition efficiency with the surfactant, a greater fraction of the dissolved carbaryl might be available for hydrolysis.

It is evident from the results that incorporation of the surfactant slowed the alkaline hydrolysis of both ethion and carbaryl. The inhibitory effect of the surfactant may be related to micelle formation and the partitioning of the pesticide molecules into micelles (Edwards et al., 1991). Therefore, the inhibition of the reaction was likely due to



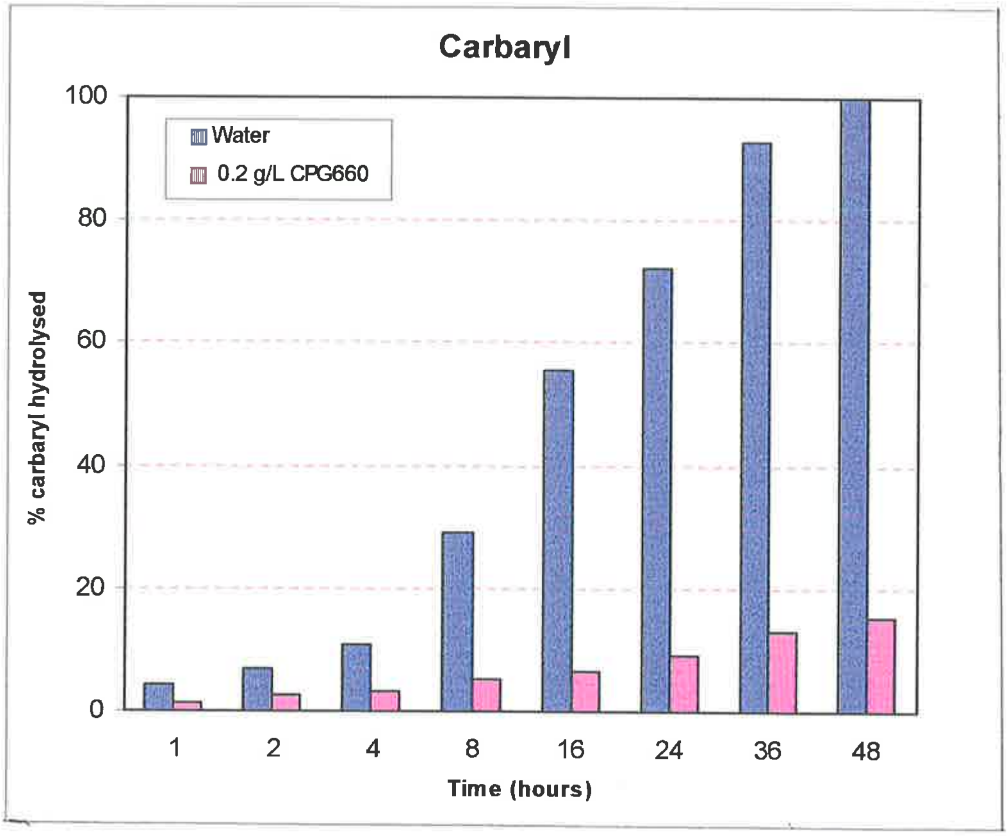


Figure 7.11 Hydrolysis of ethion and carbaryl in water with and without surfactant CPG660 at pH 11

electrostatic effects severely reducing the -OH concentration around the micelle. The rapid hydrolysis of both ethion and carbaryl at alkaline pH suggests that chemical hydrolysis might be a major pathway for the disappearance of these chemicals in an alkaline environment. The idea behind this study was that after having released the compounds from the contaminated soils with the aid of nonionic surfactants like CPG660, alkaline aqueous solutions can be injected to break down the compounds. However, there seems to be little advantage by this approach if alkaline hydrolysis of the compounds is inhibited by the presence of surfactants. Since most of the pesticide is partitioned into the miceller phase, the rate of biodegradation may decrease in the presence of surfactants above their CMC. Therefore, the biodegradability of the surfactants may be one of the key criteria for the practical use of remediation of contaminated soils. Not all surfactants may be as inhibitory as CPG660, and further investigation is required.

A study conducted on the effect of pH on hydrolysis of ethion (Table 7.5) using a 10 g L^{-1} aqueous solution of CPG660 revealed that the hydrolysis was greatly inhibited at this concentration of surfactant, which is much higher than the CMC (60 mg L^{-1}). The inhibition of hydrolysis in the studies is indirectly supported by a few studies (e.g. Devos et al.,1993; Yamato et al., 1993) which suggested that incorporation of surfactants into drugs reduces the hydrolysis occurring in aqueous solutions and consequently enhances their stability during storage.

Table 7.5 Percent Hydrolysis of ethion in the presence of 10 g L^{-1} ethylan CPG660 solutions of various pH

Time (h)	pH4	pH8	pH9	pH11
1	0.00	0.14	0.00	0.00
2	0.00	0.00	0.00	0.37
4	0.17	0.00	0.12	0.00
8	0.13	0.40	0.39	0.68
16	0.64	0.28	0.38	0.57
24	0.77	0.25	0.94	0.85
48	0.75	0.54	0.89	0.97

Many studies on the hydrolysis of pesticides use technically pure (i.e. unformulated) materials (e.g. Cowart et al., 1971; Dierberg and Pfeuffer, 1983; Cambon and Bastide, 1996). However, this study has shown that hydrolysis may be greatly affected by surfactants and the hydrolysis rates of analytical grade chemicals may give inaccurate rates of hydrolysis of the formulated pesticides. The results also indicated that a fraction of hydrophobic pesticides can partition to the humic materials in soils akin to that of a surfactant micelle, and may not undergo hydrolysis. Their persistence has the potential to cause long term pollution.

7.5 Conclusions

- Aged carbaryl is resistant to release into aqueous solution and microbial degradation, even after pulverisation in a ball mill for 8 min. Partitioning of carbaryl deeply into the interior regions of the SOM and entrapment of the molecules within soil micropores are likely mechanisms of its sequestration.

- A considerable fraction of ethion was also unavailable for its release into a binary solvent (H_2O:CH_3OH), which showed its sequestration in the SOM.

- Bioavailability is one of the key constraints for effective bioremediation of historically contaminated sites containing the compounds studied here.

- The use of surfactants to enhance the release of carbaryl and ethion from long contaminated soils into aqueous solution is potentially a viable remediation technique. Optimal surfactant concentration for increasing the release of the contaminants need to be established..

- Above the CMC, ethylan CPG660 exhibited an inhibitory effect on the alkaline hydrolysis of carbaryl and ethion. Therefore, while surfactants can enhance the release of a pesticide into solution, they can potentially constrain the chemical decontamination options such as hydrolysis. This needs further investigation.

CHAPTER 8

General Discussion, Future Research and Conclusions

8.1 General Discussion

The preceding chapters (3-7) have described development/optimisation of analytical methods for the determination of 13 pesticides, the sorption behaviour of selected pesticides in a range of soils from Australia, Pakistan and UK, the influence of the chemical nature of soil organic matter (SOM) on sorption of nonionic pesticides, the determination of sorption of rapidly degrading pesticides by an unsaturated flow method, the release of carbaryl and ethion from historically contaminated soils, and mechanisms involved in their sequestration, and finally enhanced release of carbaryl and ethion by the use of surfactants. While the results and discussion in association with various experiments have been included in each chapter, in this chapter the results are integrated and discussed generally in relation to the aims of the project outlined in Chapter 1.

While development of methods was not the prime objective of this study, it was necessary to develop/optimise analytical methods for pesticides using high performance liquid chromatograph (HPLC) to avoid the lengthy cleanup procedures necessary for other techniques e.g. gas chromatograph. The methods of pesticide analysis developed gave good reproducibility using reversed-phase HPLC with a UV detector, and they were used throughout in the determination of pesticides in the solution phase for sorption and release studies.

Many studies on sorption and release of pesticides in soil, as well as analytical procedures (e.g. solid/ liquid extraction), require filtration of the sample prior to the analysis of the pesticide in solution. In these studies, filtration is an essential step to remove solid particles from the soil solution prior to the pesticide analysis by HPLC. While sorption of pesticides from aqueous solutions onto the materials used in sorption studies has been fairly well documented (Topp and Smith, 1992), little attention has been given to filters and information on the compatibility of microfilters is scarce. During the preliminary sorption studies, it was observed that a considerable amount of pesticide loss from solution was occurring due to the microfilters. Significant differences were noted between filtered and unfiltered aqueous pesticide solutions and between different filters. Such variations in sorption affinities of pesticides for these filters were due to different chemical make-up of membranes and housing of the filters. The mechanisms of sorption are unknown but were not the focus of these studies. The extent of sorption of pesticides from aqueous solutions on to the filter membranes was greater for the more hydrophobic pesticides. It is surprising to note that while the stainless steel filter B101 was the most compatible filter for all pesticides, the stainless steel frit composed of the same material showed a significant amount of sorption for hydrophobic pesticides. This shows that subtle differences in preparation of seemingly inert materials such as stainless steel may make the materials unsuitable for use in experiments on pesticides. The studies stress the need for preliminary experiments on compatibility of filters for a specific pesticide in aqueous solution prior to their use.

Another important experimental issue for pesticide studies is the suitability of batch method in calculating pesticide sorption. In the conventional batch method, K_d values of the pesticides are computed from the difference between initial concentration and the final concentration of the pesticide in the solution phase at equilibrium. However, for pesticides having high vapour pressures and rapidly degrading pesticides, the batch method is not valid due to significant losses which may occur during the experimental time. Hydrophilic pesticides showing low sorption in soil may also give erroneous results for K_d with batch method, due to the very small changes in concentration of the pesticides in the solution phase. This is evident from the sorption studies of dichlorvos and monocrotophos in some Pakistani soils using batch technique (Chapter 4). Sorption by the batch method was overestimated due to loss of pesticides (e.g up to 64% for dichlorvos and ~19% for monocrotophos in the studies reported in Chapter 4) during the shaking time. These errors can be overcome using more appropriate methods of determining sorption of pesticides. The study reported in Chapter 6 on dichlorvos (a rapidly degradable pesticide) and monocrotophos (a hydrophilic pesticide) in a sandy loam soil showed that an unsaturated flow method (Katou et al., 1998) gave satisfactory estimation of sorption of these pesticides. The 17-fold greater K_d value of dichlorvos with the conventional batch method cautions against the use of the batch technique for the determination of sorption of rapidly degrading pesticides.

Information on the sorption behaviour of commonly used pesticides in soils is necessary in estimating their surface water and groundwater pollution potentials. The studies on the sorption of ionic and nonionic pesticides of different chemical nature using a range of soils from Australia, Pakistan and the UK showed a wide variation in their sorption capacities for individual pesticides. A wide range of K_{oc} values of the nonionic pesticides, carbaryl, phosalone were observed. Generally, the soils from Pakistan and Australia were more reactive in terms of their sorption per unit mass of organic matter than those from the UK. This difference in SOM reactivity can be explained on the basis of the climatic variations among the regions, as warmer climates of Pakistan and Australia cause faster decomposition and turnover of SOM compared with the colder climate of the UK where the SOM contents of soils are higher. Variations in the quality of SOM preclude the extrapolation of data between countries and regions. For ionisable pesticides such as ametryn, it was observed that pH is a strong determinant of sorption. Generally the alkaline soils of Pakistan had much lower sorption coefficients than the more acidic soils of Australia. Data for soils from predominantly acidic soils in high rainfall areas may be unapplicable to alkaline soils of the arid regions.

In numerous documented studies, it has been reported that sorption of the nonionic pesticides in soils and sediments is well correlated with the quantity of SOM (e.g. Means et al., 1980; Xing et al., 1994). It has been generally assumed that the SOM behaves similarly in its sorption affinity for the nonionic pesticides, and information in the literature concerning the role of various components of SOM in sorption of pesticides is relatively scarce. Those few studies (Garbarini and Lion, 1986; Chiou et al.,1987; Benoit et al., 1996) have used commercially available organic materials and extracted soil fractions as sorbents, which are not likely to be truely representative of the components of natural SOM. Attempts to investigate the compositional effect of SOM on sorption are usually hindered by the possible compositional changes of SOM associated with the chemical agents used to remove the organic matter from the soil. The extremes in pH generated by the extractants may also create artefacts (Hayes and Swift, 1978; Tate and Theng, 1980). Therefore, nondestructive means of SOM characterisation are more attractive.

Quantitative characterisation of the SOM of the whole soil material by a non-destructive method (^{13}C CP/MAS NMR) was carried out on 25 soils. NMR clearly revealed substantial dissimilarities in structural composition of the organic matter of the soils collected from different origins and environments. This evidence of variations in the SOM composition was supported by micromorphological examination of two soils contrasting in their sorption capacities. The variation in pesticide sorption (K_{oc}) observed for various soils could be explained only when the variations in the aromatic components of SOM were taken into consideration. The highly significant correlations of the components of SOM with the K_{oc} values of carbaryl and phosalone ($r^2 = 0.94$ and 0.95, respectively) revealed that the aromatic component of the SOM is a good indicator of a soil's ability to bind nonionic pesticides. It has been speculated in the literature that the solvent action of waxy or oily constituents of the SOM might be responsible for high sorption capacities of soils for nonionic pesticides (Hartley, 1960; Schnitzer and Khan, 1972).By contrast, in the studies reported in this thesis, the few soils with higher aliphatic contents of SOM were not particularly reactive towards nonionic pesticides. It is possible that the abundance of alkyl component in the soils has masked the more active sorption sites.

Although, the results of solid-state ^{13}C NMR can be used to assess quantitatively the structural environment of each C atom, little information pertaining to how the various C atoms are joined together into molecular structure is obtained. One must know the molecular nature of SOM to understand the processes of sorption in which it is involved. As, there had been no study reported on investigations of the molecular components of SOM in relation to the sorption of nonionic pesticides, the molecular nature of the SOM was estimated from the NMR data for structural components by the use of a model (Nelson et al., 1999). Of the various molecular components of SOM in soils estimated from the model, the contents of lignin and charcoal were found to be strongly correlated with sorption of carbaryl and phosalone. These unique studies linking pesticide sorption with nature of SOM, characterised by NMR and MCSE model, demonstrated that the variations in the SOM are strong determinants of pesticide sorption.

One of the important outcomes of these studies is the recommendation that while the extrapolation of data may hold well for groups of closely related soils in a country or a region, it is unlikely that the data will be appropriate for other countries or regions. The studies have demonstrated that the dissimilarities in the chemical nature of the SOM due to their varying origins and degrees of humification must be considered while estimating the sorption capacities of soils for nonionic pesticides. The empirical equations that are commonly used in prediction of pesticide sorption (K_{oc}) from K_{ow} or water solubility have limited applicability to a range of soils with differences in SOM. Instead, the use of models for estimation of K_{oc} which employ aromaticity or charcoal and lignin contents is likely to be more accurate and reliable.

The utility of the NMR technique in characterising SOM seems to be unequivocal. However, few laboratories have access to this technique for characterising SOM. Use of infrared analysis and elemental analysis (atomic H/C and N/C ratios) to correlate chemical and spectral properties of SOM to its sorption affinity for pesticides may be an alternative to NMR characterisation of SOM. Clearly there is a need to develop simple techniques to characterise SOM and further establish the role of certain components of SOM in determining pesticide sorption from studies on soils covering much wider area.

Following sorption of pesticide in soil, a decrease in solution concentration of pesticide in solution disturbs the equilibrium leading to release of the sorbed pesticide in solution. While numerous studies have been carried out on the release behaviour of pesticides in freshly spiked soils, release of pesticides from long-term contaminated soils is poorly understood. The release behaviour of aged pesticides in soils is extremely difficult to predict due to the complex nature of SOM and its relationship with the pesticides. The literature shows that even those pesticides whose use stopped long ago can still be found to persist in some soils (See Chapter 2, Table 2.2). Organophosphorus pesticides, which are generally less persistent than organochlorine pesticides, also show relatively slow degradation rates at historically contaminated sites. The characteristics of a pesticide in combination with properties of the soils, particularly SOM and biological activity, mainly determine the persistence and release potential of the pesticide. Therefore, an understanding of the mechanisms by which nonionic pesticides are sequestered in soil over time is of profound environmental significance. It needs to be established whether chemicals sorbed to soil for a long period of time are available for microbial degradation, and if not how their bioavailability may be enhanced.

The results of the study (Chapter 7) on the release of carbaryl and ethion from the historically contaminated soils showed that the two followed a biphasic pattern of release. The initial rapid release of the compounds into solution appears to originate from sites readily accessible to water while the slow release of the compounds arises from less accessible sites. This hypothesis is supported by the additional release of carbaryl that occurred after pulverisation of the soil, which indicates that a fraction of the pesticide was entrapped in the soil micropores. Soils are known to have an abundance of pores with diameters appreciably smaller than 1 µm (Alexander, 1995) and it is suggested that the pesticides which penetrate these nanopores become resistant to release (Barriuso and Koskinen, 1996; Pignatello and Xing, 1996). However, only a fraction of the compound could be released into solution by pulverising the soil. As the extent of sorption of nonionic pesticides is directly related to SOM, the rest (33%) of the total carbaryl is likely to be associated with the SOM, which is the major determinant of sequestration. The soil had a low organic C content (22 g kg^{-1}), and it is possible that soils with higher organic C contents might sequester even higher proportions of carbaryl.

The finding of significant residues of carbaryl (88 mg kg^{-1}) in a historically contaminated soil showed that pesticides which are considered to be readily degraded in soil may persist for a much longer period of time than expected. It is important in such cases to determine if the persistence is due to lack of bioavailability or due to absence of microorganisms capable of biodegradation. Biodegradation studies in carbaryl-contaminated soil using carbaryl degrading isolates showed that the bacteria degraded only the water-extractable fraction of the pesticide. After pulverising the soil, only an additional ~12% of carbaryl was biodegraded indicating that a significant proportion of carbaryl in the soil was not bioavailable. The contact time of the pesticide had been more than a decade, which may have allowed the chemical to penetrate deeply into organic matter in the soil. Another possibility is that alterations in configuration of SOM might have blocked desorption of the pesticides. These results are important from the point of view of bioremediation, because they demonstrate that in old contaminated soils, a considerable amount of pesticide residue can be sequestered and become unavailable to microorganisms. Clearly, measurements of the effectiveness of bioremediation which are most commonly tested on freshly added pesticides, may not be suitable predictors of the effectiveness under field conditions.

To remediate contaminated sites, surfactants can be used to enhance the release and availability of pesticides. Much of the environmental research on surfactants has been concerned with the efficiency of surfactant solubilisation of contaminants other than pesticides such as PCBs and petroleum products (e.g. Abdul et al., 1990; Abdul et al., 1992; Peters et al., 1992) and little is known about the remediation of a site historically contaminated with pesticide residue. The studies described earlier have suggested that a proportion of soil-bound pesticides are unavailable to pollutant-degrading bacteria and release of these compounds into the aqueous phase is a prerequisite for microbial degradation. Nonionic surfactants were found to be effective in removing a relatively water soluble pesticide (carbaryl) and a poorly water soluble pesticide (ethion) in the long-contaminated soil at concentrations above their CMCs. Laboratory tests using representative soil samples from contaminated sites can be used to determine the optimum concentration of surfactants.

It was surprising that even concentrations of surfactants below their CMC also showed a potential to release a significant amount of ethion. This has important implications for mobility of pesticides. Natural waters that commonly contain surfactants at low concentrations might have no effect on the release of relatively hydrophilic compounds. However, the low concentrations of surfactants may be important for relatively insoluble compounds. The run-off waters following the application of formulated pesticides could potentially give micellar concentrations of surfactants high enough to facilitate pesticide transport.

It is known that organophosphorus and carbamate pesticides undergo alkaline hydrolysis (Khan, 1980; Boulding, 1995). However, the hydrolysis of pesticides in the presence of organic surfactants has rarely been studied. An important finding of the present study is that use of surfactants in remediation can retard the process of alkaline hydrolysis in the extracted solution. The inhibition of hydrolysis is possibly due to the partitioning of pesticide molecules into the micelles. Therefore, once the pesticide is removed from the contaminated soil with surfactant solution, the surfactant needs to be degraded first to enhance the alkaline hydrolysis. This may also mean that the use of analytical grade materials in the studies on pesticide hydrolysis may not be appropriate, as they are not representatives of the formulated materials containing surfactants. However, there was only one surfactant tested in the present studies and more work is needed before definite conclusion can be reached about the effectiveness of surfactants in the remediation process.

Undoubtedly, pesticides will continue to play a key role in global agriculture. Due to larger number of available pesticides together with variations in soil and climatic conditions, it is difficult to obtain adequate local site specific pesticide data. Therefore, reliance on extrapolated data will continue. However, the present studies on soils of three countries in different continents have revealed that extrapolation of data from one country to another may lead to erroneous conclusions. Caution is needed by pesticide registration authorities of Australia, Pakistan and elsewhere in utilising imported data on pesticide sorption from other regions in support of registration of new products in their countries.

8.2 Future Research Needs and Directions

It is clear from the above discussion that many questions remain unanswered. Some specific suggestions for further research needs arising out of the current studies are listed in the following section.

- As the sorption of nonionic pesticides is strongly dependent on the nature of organic matter, further research is needed to probe the links among the structural and molecular parameters of the SOM complex to understand their role in determining pesticide sorption. Furthermore, there is need for a comparative study of the compositional effects of organic matter in soils and sediments.

- Sorption and release of pesticides may be related to the molecular geometry or physical conformation of the SOM. Hence, further studies on pesticide sorption to the soils and sediments should be oriented towards this area.

- The expansion/swelling of SOM in the historically contaminated soils in the presence of water, surfactants and organic cosolvents needs to be investigated. The effect of wetting and drying cycles of the soils on SOM configurations needs attention to examine further the sequestration mechanisms of the aged pesticides.

- The current level of understanding of the sequestration and formation of the microbially resistant fractions of pesticides in soils is inadequate The difficulty in identifying aging mechanisms is often hindered by fundamental gaps in our knowledge of the *in situ* structural and chemical composition of SOM. There is a pressing need for collaborative research by soil organic chemists, physical chemists and soil microbiologists.

- Studies on release, mobility, and hydrolysis of contaminants in the presence of more organic surfactants are suggested. The release studies of pesticides using surfactants at concentrations below their CMCs should also be investigated. This can be important for organic compounds at land treatment sites, and even in intensive agricultural systems which receive higher input of formulated pesticides and irrigation (e.g. cotton regions of Pakistan).

- From a practical point of view, more convenient and accurate methods of determining sorption of highly hydrophobic pesticides are needed. There is a scope for development of better methods, free from errors due to losses during experimentation.

8.3 General Conclusions

- In the sorption and other environmental studies of pesticides, filtration of extracts prior to analysis can be a potential source of error. The study raised a serious concern about the compatibility of syringe microfilters in filtration of aqueous samples containing pesticides particularly with low aqueous solubilities.

- An unsaturated flow method gave more reliable values of sorption of readily degradable and water-soluble pesticides than the batch technique and is proposed for application to such pesticides.

- Soils from the Australia, Pakistan and the UK varied greatly in their sorption capacities for ionic and nonionic pesticides due to variations in their physical and chemical characteristics. The variations in sorption of the nonionic pesticides were found to be closely related to the differences in structural and chemical composition of SOM. There was a strong positive correlation of K_{oc} values of carbaryl and phosalone with aromaticity (aryl+O-aryl component) of SOM. Among the molecular components of SOM, lignin and charcoal are important indicators of the sorption capacities of the soils studied.

- Predictions based on data collected from one country or region may not be reliable when extrapolated to another region. The extrapolation of data may hold well for groups of closely related soils in a region but as the compositional similarity of SOM from other geological region diminishes, so does the reliability of the extrapolated data. The study emphasises the need for local data.

- Inoculation of soil with specific carbaryl degraders showed that aged carbaryl was resistant to release and was not available for microbial degradation. The results have major implications for the way soil-pesticide partitioning is modelled. Models which do not take into account the resistant fraction present in soils may give erroneous results.

- Sequestration of carbaryl and ethion was found to be responsible for long term persistence of the compounds in soils. Whether the pesticide molecules are present in a soil micropores, partitioned into SOM or both, this physical remoteness of aged pesticides and their diffusion to the microbially inaccessible sites are key considerations in the risk assessment of pesticides in soils.

- Use of surfactants could enhance the release of pesticides from long-term contaminated soils. However, their presence could inhibit subsequent hydrolysis of some pesticides.

REFERENCES

AAVCC. 1990. Australian Agricultural and Veterinary Chemical Council. Annual Report 1989-90. Australian Government Publishing Services, Canberra.

Abdul, A. S. and Gibson, T. L. 1991. Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyls from sandy material. *Environmental Science and Technology* **25**, 665-671.

Abdul, A. S., Gibson, T. L., Ang, C. C., Smith, J. C. and Sobczynski, R. E. 1992. In situ surfactant washing of polychlorinated biphenyls and oils from a contaminated site. *Ground Water* **30**, 219-231.

Abdul, A. S., Gibson, T. L. and Rai, D. N. 1990. Selection of surfactants for the removal of petroleum products from shallow sandy aquifers. *Ground Water* **28**, 920-926.

Alan, R. R. 1989. The occurrence and significance of bound pesticide residues in soil. *Residue Reviews* **108**, 71-103.

Alexander, M. 1995. How toxic are toxic chemicals in soil? *Environmental Science and Technology* **29**, 2713-2717.

Ali, M. and Jabbar, A. 1991. Effect of pesticides and fertilizers on shallow groundwater quality. Final Technical Report, January, 1990 - September, 1991. Pakistan Council of Research in Water Resources, Ministry of Science and Technology, Government of Pakistan.

Allison, L. E. and Moodie, C. D. 1965. Carbonate. pp. 1379-1396. *In* Black C. A., Evans D. D., Ensminger L. E., White, J. L. and Clark, F. E. (ed.). Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. American Society of Agronomy, Inc. Madison, Wisconsin, USA.

Almendros, G. 1995. Sorptive interactions of pesticides in soils treated with modified humic acids. *European Journal of Soil Science* **46**, 287-301.

Appleyard, S. J. 1993. Resourcing the investigation and management of groundwater contamination in Western Australia - a case study of contamination from herbicide manufacture near Perth. *AGSO Journal of Australian Geology and Geophysics* **14,** 177-181.

Appleyard, S. J. 1995. Investigation of groundwater contamination by fenamiphos and atrazine in residential area: source and distribution of contamination. *Ground Water Monitoring Review* **Fall**, 110-113.

Arienzo, M., Sánchez-Camazano, M., Crisanto, H. T. and Sánchez-Martin, M. J. 1993. Effect of organic cosolvents on adsorption of organophosphorus pesticides by soils. *Chemosphere* **27**, 1403-1417.

Aronstein, B. N., Calvillo, Y. M. and Alexander, M. 1991. Effect of surfactants at low concentrations on the desorption and biodegradation of sorbed aromatic compounds in soil. *Environmental Science and Technology* **25**, 1728-1731.

Augustijn-Beckers, P. W. M., Hornsby, A. G. and Wauchope, R. D. 1994. The SCS/ARS/CES pesticide properties database for environmental decision-making II. Additional compounds. *Reviews of Environmental Contamination and Toxicology* **137**, 1-23.

Australian Commodity Statistics. 1998. Australian Bureau of Agricultural and Resource Economics, Canberra.

Back, R. C. 1965. Significant developments in eight years with Sevin insecticide. *Journal of Agricultural and Food Chemistry* **13**, 198-199.

Bailey, G. W. and White, J. L. 1970. Factors influencing the adsorption, desorption and movement of pesticides in soils. *Residue Reviews* **32**, 29-92.

Baldock, J. A. and Nelson, P. N. 1999. Soil organic matter. *In* Sumner M. E. (ed.) Handbook of Soil Science. CRC Press Boca Raton, Florida (in press).

Baldock, J. A., Oades, J. M., Nelson, P. N., Skene, T. M., Golchin, A. and Clarke, P. 1997. Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. *Australian Journal of Soil Research* **35**, 1061-1083.

Baldock, J. A., Oades, J. M., Vassallo, A. M. and Wilson, M. A. 1989. Incorporation of uniformly labelled ^{13}C-glucose into the organic fraction of a soil. Carbon balance and CP/MAS ^{13}C NMR measurements. *Australian Journal of Soil Research* **27**, 725-746.

Baldock, J. A., Oades, J. M., Vassallo, A. M. and Wilson, M. A. 1990. Solid-state CP/MAS ^{13}C NMR analysis of particle size and density fractions of a soil incubated with uniformly labelled ^{13}C-glucose. *Australian Journal of Soil Research* **28**, 193-212.

Baldock, J. A., Oades, J. M., Waters, A. G., Peng, X., Vassallo, A. M. and Wilson, M. A. 1992. Aspects of the chemical structure of soil organic materials as revealed by solid-state 13C NMR spectroscopy. *Biogeochemistry* **16**, 1-42.

Ball, W. P. and Roberts, P. V. 1991. Long-term sorption of halogenated organic chemicals by aquifer material. 1. Equilibrium. *Environmental Science and Technology* **25**, 1223-1237.

Barners, C. J., Lavy, T. L. and Talbert, R. E. 1992. Leaching, dissipation and efficacy of metolachlor applied by chemigation or conventional methods. *Journal of Environmental Quality* **21**, 232-236.

Barriuso, E., Feller, Ch., Calvet, R. and Cerri, C. 1992. Sorption of atrazine, terbutryn and 2,4-D herbicides in two Brazilian oxisols. *Geoderma* **53**, 155-167.

Barriuso, E. and Koskinen, W. C. 1996. Incorporating nonextractable atrazine residues into soil size fractions as a function of time. *Soil Science Society of America Journal* **60**, 150-157.

Basham, G., Lavy, T. L., Oliver, L. R. and Don Scott, H. 1987. Imazaquin persistence and mobility in three Arkansas soils. *Weed Science* **35**, 576-582.

Baskaran, S. 1994. Sorption and Movement of Ionic and Non-Ionic Pesticides in Selected Soils of New Zealand. Ph. D. Dissertation, The Massey University, New Zealand.

Baskaran, S, Bolan, N. S., Rahman, A. and Tillman, R. W. 1996. Pesticide sorption by allophanic and non-allophanic soils of New Zealand. *New Zealand Journal of Agricultural Research* **39**, 297-310.

Bauld, J. 1996. Groundwater quality: human impact on a hidden resource. pp. 143-147. *In* Proceedings of the 23rd Hydrology and Water Resources Symposium, Hobart, 21-24 May.

Bauld, J., Evans, W. R. and Sandstrom, M. W. 1992. Groundwater quality under irrigated agriculture: Murray Basin, southern Australia. *In* Jin, F. (ed.) Groundwater and Environment. Proceedings of International Workshop on Groundwater and Environment, Beijing, China. Seismological Press, Beijing.

Bayer, D. E. 1967. Effect of surfactants on leaching of substituted urea herbicides in soils. *Weeds* **15**, 249-252.

Benoit, P., Barriuso, E., Houot, S. and Calvet, R. 1996. Influence of the nature of soil organic matter on the sorption-desorption of 4-chlorophenol, 2-4 dichlorophenol and the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). *European Journal of Soil Science* **47**, 567-578.

Biggar, J. W., Mingelgrin, U. and Cheung, M. W. 1978. Equilibrium and kinetics of adsorption of picloram and parathion with soils. *Journal of Agricultural and Food Chemistry* **26**, 1306-1312.

Black, C. A. 1965. Methods of Soil Analysis. p. 9. *In* American Society of Agronomy Monograph.

Blacklow, W. M. and Pheloung, P. C. 1992. Sulphonylurea herbicides applied to acidic sandy soils, movement, persistence and activity within the growing season. *Australian Journal of Agriculture Research* **43**, 1157-68.

Boesten, J. J. T. I. 1990. Influence of solid/liquid ratio on the experimental error of sorption coefficients in pesticide/soil systems. *Pesticide Science* **30**, 31-41.

Boesten, J. J. T. I. and van der Linden, A. M. A. 1991. Modelling the influence of sorption and transformation on pesticide leaching and persistence. *Journal of Environmental Quality* **20**, 425-435.

Boulding, J. R. 1995. Remediation of contaminated groundwater. pp. 761-804. *In* Practical Handbook of Soil, Vadose Zone, and Ground-Water Contamination: Assessment, Prevention and Remediation. CRC Press, Inc. Boca Raton.

Bowman, B. T. and Sans, W. W. 1977. Sorption of parathion, fenitrothion, methylparathion, aminoparathion and paraoxon by Na, Ca, and Fe montmorillonite suspensions. *Soil Science Society of America Journal* **41**, 514-519.

Bowman, B. T. and Sans, W. W. 1985. Partitioning behaviour of insecticides in soil-water systems. II. Desorption hysteresis effects. *Journal of Environmental Quality* **14**, 270-273.

Bowmer, K. H. 1991. Atrazine persistence and toxicity in two irrigated soils of Australia. *Australian Journal of Soil Research* **29**, 339-350.

Briggs, G. G. 1981a. Adsorption of pesticides by some Australian soils. *Australian Journal of Soil Research* **19**, 61-68.

Briggs, G. G. 1981b. Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors and parachor. *Journal of Agricultural and Food Chemistry* **29,** 1050-1059.

Brown, D. S. and Flagg, E. W. 1981. Empirical prediction of organic pollutant sorption in natural sediments. *Journal of Environmental Quality* **10**, 382-386.

Brownawell, B. J., Chen, H., Collier, J. M. and Westall, J. C. 1990. Adsorption of organic cations to natural materials. *Environmental Science and Technology* **24**, 1234-1241.

Brusseau, M. L. and Rao, P. S. C. 1989. Sorption nonideality during organic contaminant transport in porous media. *Critical Reviews in Environmental Control* **19,** 33-99.

Brusseau, M. L. and Rao, P. S. C. 1991. Influence of sorbate structure on nonequilibrium sorption of organic compounds. *Environmental Science and Technology* **25**, 1501-1506

Brusseau, M. L., Wood, A. L. and Rao, P. S. C. 1991. Influence of organic cosolvents on the sorption kinetics of hydrophobic organic chemicals. *Environmental Science and Technology* **25**, 903-910.

Burchill, S., Hayes, M. H. B. and Greenland, D. J. 1981. Adsorption. pp. 221-400. *In* Greenland, D. J. and Hayes, M. H. B. (ed.) The Chemistry of Soil Processes. Wiley, New York.

Burkhard, N. and Guth, J. A. 1981. Chemical hydrolysis of 2-chloro-4,6-bis(alkylamino)-1,3,5-triazine herbicides and their breakdown in soil under the influence of adsorption. *Pesticide Science* **12**, 45-52.

Burnside, O. C., Wicks, G. A. and Fenster, C. R. 1971. Dissipation of dicamba, picloram and 2,3,6-TBA across Nebraska. *Weed Science* **19**, 323-325.

Buxton, D. S. and Green, R. E. 1987. Desorption and leachability of DECP residues in soils. Agronomy abstracts. p. 167. ASA , Madison, WI.

Calvet, R. 1980. Adsorption-desorption phenomena. pp. 1-30. *In* Hance, R. J. (ed.) Interactions Between Herbicides and the Soil. Academic Press Inc.

Calvet, R. 1989. Adsorption of organic chemicals in soils. *Environmental Health Perspective* **83**, 145-177.

Cambon, J. and Bastide, J. 1996. Hydrolysis kinetics of thifensulfuron methyl in aqueous buffer. *Journal of Agricultural and Food Chemistry* **44**, 333-337.

Capriel, P. 1997. Hydrophobicity of organic matter in arable soils: influence of management. *European Journal of Soil Science* **48**, 457-462.

Capriel, P. and Haisch, A. 1983. Persistenz von Atrazine Seiner metaboliten im bodennach einmaliger Herbizidanwendung, Zeitschrift fuer pflanzenernachrung und Bodenkunde **146**, 474.

Caro, J. H. Freeman, H. P. and Turner, B. C. 1974. Persistence in soil and losses in run off of soil-incorporated carbaryl in a small watershed. *Journal of Agricultural and Food Chemistry* **22**, 860-863.

Carringer, R. D. Weber, J. B., and Monaco, T. J. 1975. Adsorption-desorption of selected pesticides by organic matter and montmorillonite. *Journal of Agricultural and Food Chemistry* **23,** 568-572.

Carroll, K. M., Harkness, M. R., Bracco, A. A. Balcarcel, R. R. 1994. Application of permeant/polymer diffusional model to the desorption of polychlorinated biphenyls from Hudson River sediments. *Environmental Science and Technology* **28**, 253-258.

Carski, T. H., and Sparks, D. L. 1985. A modified miscible displacement technique for investigating adsorption-desorption kinetics in soils. *Soil Science Society of America Journal* **49**, 1114-1116.

Carter, C. W. and Suffet, I. H. 1982. Binding of DDT to dissolved humic materials. *Environmental Science and Technology* **16**, 735-740.

Carvalho, F. P., Fowler, S. W., Villeneuve, J. P. and Horvat, M. 1997. Environmental behaviour of crop protection chemicals. pp. 35-57. *In* Proceedings of an international symposium on the use of nuclear and related techniques for studying environmental behaviour of crop protection chemicals. International Atomic Energy Agency Vienna.

Casida, Jr. L. E., Klein, D. and Santoro, T. 1964. Soil dehydrogenase activity. *Soil Science* **98**, 371-376.

Celorie, J. A., Woods, S. L., Vinson, T. S. and Istok, J. D. 1989.A comparison of sorption equilibrium distribution coefficients using batch and centrifugation methods. *Journal of Environmental Quality* **18**, 307-313.

Charles, R. W. and Hance, R. J.1991. The Pesticide Manual. A World Compendium. 9th edition. The British Crop Protection Council.

Che, M., Loux, M. M., Traina, S. J. and Logan. T. J. 1992. Effect of pH on sorption and desorption of imazaquin and imazethapyr on clays and humic acid. *Journal of Environmental Quality* **21**, 698-703.

Chesters, G., Simsiman, G. V., Lavy, J., Alhajjar, B. J., Fatulla, R. N. and Harkin, J. M. 1989. Environmental fate of alachlor and metolachlor. *Reviews of environmental Contamination and Toxicology* **110**, 1-73.

Chin, Y.P., Aiken, G. R. and Danielsen, K. M. 1997. Binding of pyrene to aquatic and commercial humic substances: The role of molecular weight and aromaticity. *Environmental Science and Technology* **31**, 1630-1635.

Chiou, C. T. 1981. Partition coefficient and water solubility in environmental chemistry. pp. 117-153. *In* Saxena J. and Fisher F.(ed.) Hazard Assessment of Chemicals; Current Developments. Academic Press, New York.

Chiou, C. T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. pp. 1-29. *In* Sawhney, B. L. and K. Brown (ed.) Reactions and Movement of Organic Chemicals in Soils. Soil Science Society of America. Madison, Wisconson.

Chiou, C. T. 1990. Roles of organic matter, minerals, and moisture in sorption of nonionic compounds and pesticides by soil. pp. 111-160. *In* McCarthy, P., Clapp, C. E., Malcolm, R. L. and Bloom, P. R.(ed.) Humic Substances in Soil and Crop Sciences; Selected Readings. Soil Science Society of America, Madison, Wisconson.

Chiou, C. T., Kile, D. E., Brinton, T. I., Malcolm, R. L., Leenheer, J. A. and MacCarthy, P. 1987. A comparison of water solubility enhancement of organic solutes by aquatic humic materials and commercial humic acids. *Environmental Science and Technology* **21**, 1231-1234.

Chiou, C. T., Peters, L. J. and Freed, V. H. 1979. A physical concept of soil-water equilibria for non-ionic organic compounds. *Science* **206**, 831-832.

Chiou, C. T. and Schmedding, D. W. 1982. Partitioning of organic compounds in octanol-water systems. *Environmental Science and Technology* **16**, 4-10.

Chisholm, D. 1975. Persistence of chlorfenvinphos in soil and its uptake by some crops. *Canadian Journal of Soil Science* **55**, 177-180.

Clay, S. A. and Koskinen, W. C. 1990. Characterisation of alachlor and atrazine desorption from soils. *Weed Science* **38**, 74-80.

Colbert, F. O., Volk, V. V. and Appleby, A. P. 1975. Sorption of atrazine, terbutryn and GS-14254 on natural and lime amended soils. *Weed Science* **23**, 390-394.

Collins, H. P., Paul, E. A., Paustian, K. and Elliott, E. T. 1997 Characterization of soil organic carbon relative to its stability and turnover. pp. 51-72. *In* Paul, E. A., Paustian, K., Elliott, E. T. and Cole, C. V. (ed.) Soil Organic Matter in Temperate Agroecosystems. CRC Press Inc.

Connaughton, D. F., Stedinger, J. R., Lion, L. W., and Shuler, M. L. 1993. Description of time-varying desorption kinetics: release of naphthalene from contaminated soils. *Environmental Science and Technology* **27**, 2397-2403.

Connell, D. W., Hawker, D. W., Warne, M. S. J. and Vowles, P. P. 1997. Soaps and Detergents. pp. 221-241. *In* Basic Concepts of Environmental Chemistry. Lewis Publishers, Boca Raton, Florida.

Cooper, B. 1996. Central and North West Regions Water Quality Program 1995/96 Report on Pesticides Monitoring. Land and Water Conservation, Parramatta, NSW, Australia.

Cowart, R. P., Bonner, F. L., and Epps E. A. 1971. Rate of hydrolysis of seven organophosphate pesticides. *Bulletin of Environmental Contamination and Toxicology* **6**, 231-234.

Cribb, J. 1989. 'Fertilizer Industry', Australian Fertilizer Manufacturers' Committee in Australian Agriculture: The Complete Reference on the Rural Industry, National Farmers Federation, Morescope Pty Ltd, Camberwell, Victoria.

Croll, B. T. 1991. Pesticides in surface waters and groundwaters. *Journal of Institution of Water and Environmental Management* **5**, 389-395.

Cros~~s~~by, D. G. 1976. Nonbiological degradation of herbicides in soil. pp. 65-98. *In* Audus, L. J. (ed.) Herbicides Physiology Biochemistry Ecology. New York Academic Press.

Curl, R. L. and Keoleian, G. A. 1984. Implicit-adsorbate model for apparent anomalies with organic adsorption on natural adsorbents. *Environmental Science and Technology* **18**, 916-922.

Cys, T., Cyr, N. and Haque, R. 1977. Spectroscopic methods. pp. 75-98. *In* Zweig, G. and Sherma, J. (ed.) Analytical Methods for Pesticides and Plant Growth Regulators, IX. Academic Press New York.

Deitsch, J. J. and Smith, J. A. 1995. Effect of Triton X-100 on the rate of trichloroethene desorption from soil to water. *Environmental Science and Technology* **29**, 1069-1080.

Devos, A., Vervoort, L. and Kinget, R. 1993. Solubilization and stability of indomethacin in a transparent oil-water gel. *International Journal of Pharmaceutics (Amsterdam)* **92**, 191-196.

DiCesare, D. and Smith, J. A. 1994. Surfactant effects on desorption rate of nonionic organic compounds from soil to water. *Reviews of Environmental Contamination and Toxicology* **134**, 1-29.

Dierberg, F. E. and Pfeuffer, R. J. 1983. Fate of ethion in canals draining a Florida citrus grove. *Journal of Agricultural and Food Chemistry* **31**, 704-709.

Dinelli, G., Vicari, A., and Catizone, P. 1993. Use of capillary electrophoresis for detection of metsulfuron and chlorsulfuron in tap water. *Journal of Agricultural and Food Chemistry* **41**, 742-746.

Dios-Cancela, G. Romero, T. E., Sánchez-Rasero, F. 1990. Adsorption of cyanazine on peat and montmorillonite clay surfaces. *Soil Science* **150**, 836-843.

DIPMAC. 1992. Report on the management of contaminated waste at cattle dip sites in North Eastern, New South Wales. Cattle Tick Dip Site Management Committee. New South. Wales, Government Task Committee.

Dolling, A. M. 1985. Studies of interactions of some imidazolinone herbicides with clays. M. Sc. thesis. Department of Chemistry. University of Birmingham, UK.

Dragun, J. 1998. Adsorption and mobility of organic chemicals. pp. 480-537 *In* The Soil Chemistry of Hazardous Materials. Amherst Scientific Publishers, Massachusetts.

Dunigan, E. P. and McIntosh, T. H. 1971. Atrazine-soil organic matter interactions. *Weed Science* **19**, 279-282.

Eagle, D. J., Jones, J. L. O., Jewel, E. T. and Paxton, R. P. 1991. Determination of pesticides by gas chromatography and high pressure liquid chromatography. pp. 547-601. *In* Smith, K. A. (ed.) Soil Analysis. Modern Instrumental Techniques. Marcell Dekker inc., New York.

Edwards, D. A. Luthy, R. G. and Liu, Z. 1991. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions. *Environmental Science and Technology* **25**, 127-133.

Egler, F. E. 1964. Pesticides in our ecosystem. *American Scientist* **52**, 110-136.

Eisenstadt, E., Carlton, B. C. and Brown, B. J. 1994. Gene Mutation. pp. 297-313. *In* Gerhardt, P., Murray, Wood, W. A. and Krieg, N. R. (ed.). Methods for General and Molecular Bacteriology. American Society of Microbiology, Washington, D. C.

Eke, K. R., Barnden, A. D. and Tester, D. J. 1996. Impact of agricultural pesticides on water quality. pp. 43-56. *In* Hester, R. E. and Harrison, R. M. (ed.) Issues in Environmental Science and Technology: Agricultural Chemicals and the Environment. Royal Society of Chemistry, Hertz , UK.

Ellgehausen, H., D'Hondt, C. and Fuerer, R. 1981. Reversed-phase chromatography as a general method for determining octanol-water partition coefficients. *Pesticide Science* **12**, 219-227.

Farrell, J. and Reinhard, M. 1994. Desorption of halogenated organics from model solids, sediments, and soil under unsaturated conditions. 1. Isotherms. *Environmental Science and Technology* **28**, 53-62.

Felsot, A. and Dahm, P. A. 1979. Sorption of organophosphorus and carbamate insecticides by soils. *Journal of Agricultural Food and Chemistry* **27**, 557-559.

Fengel, D. and Wagener, G. 1984. Wood: Chemistry, Ultrastructure Reactions. De Gruyter, Berlin.

Ferris, I. G. and Haigh, B. M. 1993. Herbicides persistence and movement in Australian soils. Implications for agriculture. pp. 134-60. *In* Altman, J. (ed.) Pesticide Interactions in Crop Production. CRC Press, Boca Raton, Florida.

Fleming, F., Simmons, F. W., Wax, L. M., Wing, R. E. and Carr, M. E. 1992. Atrazine movement in soil columns as influenced by starch-encapsulated and acrylic polymer additives. *Weed Science* **40**, 465-470.

Fountain, J. C., Klimek, A., Beikirch, M. G. and Middleton, T. M. 1991. The use of surfactants for in situ extraction of organic pollutants for a contaminated aquifer. *Journal of Hazardous Materials* **28**, 295-311.

Freeman, D. H. and Cheung, L. S. 1981. A gel partition model for organic desorption from a pond sediment. *Science* **214**, 790-792.

Friesel, P., Milde, G., Stock, R. and Ahlsdorf, B. 1986. Impact of agricultural pesticide application on groundwater in Western Germany–Latest results and an attempt of assessment. pp. 856-871. *In* Proceedings of 13th Congress International Soil Science Society, Hamburg.

Fründ, R., Lüdemann, H. D., Gonzalez-Vila, F. J., Almendros, G., Del Rio, J. C. and Martin, F. 1989.Structural differences between humic fractions from different soil types as determined by FT-IR and Carbon 13-NMR studies. *Science of Total Environment* **81-82,** 187-194.

Fruhstorfer, P., Schneider, R. J. and Niessner, R. 1993. Factors influencing the adsorption of atrazine on montmorillonite and kaolinite clays. *Science of the Total Environment* **138**, 317-328.

Fryer, J. L. Hance, R. J. and Ludwig, J. W. 1975. Long term persistence of paraquat in sandy loam soil. *Weed Research* **15**, 189-194.

Fu, M. H., Mayton, H. and Alexander, M. 1994. Desorption and biodegradation of sorbed styrene in soil and aquifer solids. *Environmental Toxicology and Chemistry* **13**, 749-753.

Funari, E., Donati, L., Sandroni, D. and Vighi, M. 1995. Pesticide levels in groundwater: value and limitations of monitoring. pp. 3-44. In Vighi, M and Funari, E. (ed.) Pesticide Risk in Groundwater. CRC Press, Boca Raton, Florida.

Gan, J., Weimer, M. R., Koskinen, W. C., Buhler, D. D., Wyse, D. L. and Becker, R. L. 1994. Sorption and desorption of imazethapyr and 5-hydroxyimazethapyr in Minnesota soils. *Weed Science* **42**, 92-97.

Garbarini, D. R. and Lion, L. W. 1986. Influence of the nature of soil organics on the sorption of toluene and trichloroethylene. *Environmental Science and Technology* **20**, 1263-1269.

Garcia, F. and Henion, J. 1992. Fast capillary electrophoresis- ion spray mass spectrometric determination of sulfonylureas. *Journal of Chromatography* **606**, 237-247.

Gauthier, T. D., Seitz, W. R. and Grant, C. L. 1987. Effects of structural and compositional variations of dissolved humic materials on pyrene K_{oc} values. *Environmental Science and Technology* **21**, 243-248.

Genstat for Windows. 1997. Genstat 5 Release 4.1, Lawes Agricultural Trust, IACR-Rothamsted.

Gerritse, R. G., Beltran, J. and Hernandez, F. 1996. Adsorption of atrazine, simazine and glyphosate in soils of the Gnangara mound, Western Australia. *Australian Journal of Soil Research* **34**, 599-607.

Gerstl, Z., Saltzman, S. and Yaron, B. 1981. Distribution of herbicides in soil in a simulated drip irrigated system. *Irrigation Science* **41**, 1-12.

Gerstl, Z., Saltzman, S. and Yaron, B. 1983. Behaviour of bromacil and naproamide in soils. II. Distribution after application from a point of source. *Soil Science Society of America Journal* **47**, 478-483.

Glotfelty, D. E., Leech, M. M., Jersy, J. and Taylor, A. W. 1989. Volatilization and wind erosion of soil surface applied atrazine and toxaphene. *Journal of Agricultural and Food Chemistry* **37**, 546-551.

Glotfelty, D. E., Taylor,A. W., Turner, B. C. and Zoller, W. H. 1984. Volatilization of surface applied pesticides from fallow soil. *Journal of Agricultural and Food Chemistry* **32**, 638-643.

Golab, T., Bishop, C. E., Donoho, A. L., Manthey, J. A. and Zornes, L. L. 1975. Behaviour of ^{14}C Oryzalin in soil and plants. *Pesticide Biochemistry and Physiology* **5**, 196.

Graham-Bryce, I. J. 1968. Movement of systemic insecticides through soil to plant roots. pp. 251-267. *In* Physico-chemical and biophysical factors affecting the activity of pesticides. Society of Chemical Industry Monograph No.29.

Graham-Bryce, I. J. 1969. Diffusion of organophosphorus insecticides in soils. *Journal of the Science of Food and Agriculture* **20**, 489-494.

Grathwohl, P. 1990. Influence of organic matter from soil and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{oc} correlations. *Environmental Science and Technology* **24**, 1687-1693.

Green, R. E. 1974. Pesticide-clay-water interactions. pp. 3-37. *In* Guenzi, W. D. (ed.). Pesticides in Soil and Water. Soil Science Society of America. Inc., Madison, Wisconsin.

Green, R. E. and Karickhoff, S. W. 1990. Sorption estimates for modeling. pp. 80-101. *In* Cheng, H. H. (ed.) Pesticides in the Soil Environment: Processes, Impacts, and Modeling. Soil Science Society of America Book Series:2. Soil Science Society of America Madison, Wisconson.

Green, R. E., Schneider, R. C., and Gavenda, R. T. 1993. Utility of sorption and degradation parameters from the literature for site-specific pesticide impact assessments. pp. 209-225. *In* Sorption and Degradation of Pesticides and Organic Chemicals in Soil. Soil Science Society of America Special Publication no. 32.

Grice, R. E. and Hayes, M. H. B. 1972. A continuous flow method for studying adsorption and desorption of pesticides in soil colloid systems. pp. 784-790. *In* Proceedings of 11th British Weed Control Conference.

Grimberg, S. J., Miller, C. T. and Aitken, M. D. 1996. Surfactant-enhanced dissolution of phenanthrene into water for laminar flow conditions. *Environmental Science and Technology* **30**, 2967-2974.

Grover, R. 1974. Adsorption and desorption of trifluralin, triallate and diallate by various asdorbents. *Weed Science* **22**, 405-408.

Gschwend, P. M. and Wu, S. C. 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environmental Science and Technology* **19**, 90-96.

Guth, J. A. 1981. Experimental approaches to studying the fate of pesticides in soil. pp. 85-114. *In* Hutson, D. H. and Roberts, T. R. C. (ed.) Progress in Pesticide Biochemistry. John Wiley and Sons, Ltd.

Haigh, B. M. and Ferris, I. J. 1991. Predicting herbicide persistence using the CALF model. pp. 50-60. *In* Moore, I. D. (ed.) Modelling the Fate of Chemicals in the Environment. CRES, Australian National University, Canberra.

Hallberg, G. R. 1989. Pesticide pollution of groundwater in the humid United States. *Agriculture, Ecosystems, and Environment* **26**, 299-367.

Hamaker, J. W. and Thompson, J. M. 1972. Adsorption. pp. 49-144. *In* Goring, C. A. I. and Hamaker, J. W.(ed.) Organic Chemicals in the Soil Environment. Marcel Dekker Inc., New York.

Hance, R. J. 1987. Herbicide behaviour in soil, with particular reference to the potential for groundwater contamination. pp. 223-247. *In* Hutson, D. H. and Roberts, T. R. (ed.) Herbicides. John Wiley and Sons Ltd.

Hance, R. J. 1988. Adsorption and bioavailability. P.1. *In* Grover, R. (ed.) Environmental Chemistry of Herbicides. Vol. 1. CRC Press Boca Raton, Florida.

Harborne, J. B. 1989. Recent advances in chemical ecology. *Natural Product Reports* **6**, 85-109.

Harris, C. I. and Warren, G. F. 1964. Adsorption and desorption of herbicides by soil. *Weeds* **12**, 120-126.

Hartley, D. 1987. The Agrochemicals Handbook. The Royal Society of Chemistry, England.

Hartley, G. S. 1960. Phyico-chemical aspects of the availability of herbicides in soils. pp. 63-78. *In* Woodford, E. K. and Sager, G. R. (ed.) Herbicides and the Soil. Blackwell Scientific Publishing Company, Oxford.

Hartley, G. S. and Graham-Bryce. 1980. *In* Physical Principles of Pesticide Behaviour. 2 Volumes, Academic Press, New York.

Hassett, J. J., Banwart, W. L., Wood, S. G. and Means, J. C. 1981. Sorption of alpha-Naphthol: Implications concerning the limits of hydrophobic sorption. *Soil Science Society of America Journal* **45**, 38-42.

Hassett, J. J., Means, J. C., Banwart, W. L. and Wood, S. G. 1980a. Sorption Properties of Sediments and Energy-related Pollutants. EPA Report 600/3-80-041.

Hassett, J. J., Means, J. C., Banwart, W. L., Wood, S. G., and Khan A. S. 1980b. Sorption of dibenzothiophene by soils and sediments. *Journal of Environmental Quality* **9**, 184-186.

Hata, U. and Isozaki, Y. 1980. The influence of soil properties on the adsorption and the phytotoxicity of piperophos. *Journal of Pesticide Science* **5**, 23-27.

Hatcher, P. G., Schnitzer, M. Dennis, L. W., and Maciel, G. E. 1981. Aromaticity of humic substances in soils. *Soil Science Society of America Journal* **45**, *1089-1094.*

Hayes, M. H. B. 1985. Extraction of humic substances from soil. pp. 329-362. *In* Aiken, G. R., Mcknight, D. M. and Wershaw, R. L. (ed.) Humic Substances in Soil, Sediment, and Water. John Wiley and Sons, New York.

Hayes, M. H. B. and Swift, R. S. 1978. The chemistry of soil organic colloids. pp. 179-320. *In* Greenland, D. J. and Hayes, M. H. B (ed.). The Chemistry of Soil Constituents. Wiley, Chichester, UK.

Helling, C. S. 1970. Movement of s-triazine herbicides in soil. *Residue Reviews* **32**, 175-210.

Helling, C. S. 1971. Pesticides mobility in soils. II. Application of soil thin-layer chromatography. *Soil Science Society of America Proceedings* **35**, 737.

Hilton, H. W. and Yuen, Q. H. 1963. Adsorption of several pre-emergence herbicides by Hawaiian sugar cane soils. *Journal of Agricultural and Food Chemistry* **11**, 230-234.

Hinckley, D. A. and Bidleman, T. F. 1989. Analysis of pesticides in seawater after enrichment onto C_8 bonded-phase cartridges. *Environmental Science and Technology* **23**, 995-1000.

Hingston, F. J., Posner, A. M. and Quirk, J. P. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *Journal of Soil Science* **23**, 177-192.

Hornsby, A. G., Wauchope, R. D. and Herner, A. E. (ed.). 1996. *In* Pesticide Properties in the Environment. Springer-Verlag New York, Inc.

Huang, P. M., Grover, R. and McKercher, R. B. 1984. Components and particle size fractions involved in atrazine adsorption by soils. *Soil Science* **138**, 20-24.

Huggenberger, F., Letey, J. and Farmer, W. J. 1973. Effect of two nonionic surfactants on adsorption and mobility of selected pesticides in a soil system. *Soil Science Society of America Proceedings* **37**, 215-219.

Hunt, J. R., Sitar, N. and Udell, K. S. 1988. Nonaqueous phase liquid transport and cleanup. 1. Analysis of mechanisms. *Water Resources Research* **24**, 1247-1258.

Hussain, Z., Chaudhry, M. R., Zuberi, F. A., Hussain, Q. and Sharif, M. 1996. Contaminants and the Soil Environment of Pakistan. pp. 629-646. *In* Proceedings of the First Australasia-Pacific Conference on Contaminants and the Soil Environment in the Australasia Pacific Region, held in Adelaide, Australia, 18-23 February, 1996.

Inbar, Y., Chen, Y. and Hadar, Y. 1989. Solid-state carbon-13 nuclear magnetic resonance and infra-red spectroscopy of composed organic matter. *Soil Science Society of America Journal* **53**, 1695-1701.

Jana, T. K. and Das, B. 1997. Sorption of carbaryl (1-naphthyl N-methyl carbamate) by soil. *Bulletin of Environmental Contamination and Toxicology* **59**, 65-71.

Johnson, J. A. and Farmer, W. J. 1993. Batch versus column method for determining distribution of organics between soil and water phases. *Soil Science* **155**, 92-99.

Johnson, R. M. and Sims, J. T. 1993. Influence of surface and subsoil properties on herbicide sorption by Atlantic and Coastal plain soils. *Soil Science* **155**, 339-348.

Jolly, A. and Johnstone, P. 1994. Degradation of trifluralin in three Victorian soils under field and laboratory conditions. *Australian Journal of Experimental Agriculture* **34**, 57-65.

Karickhoff, S. W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* **10**, 833-846.

Karickhoff, S. W., Brown, D. S. and Scott, T. A. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research* **13**, 241-248.

Katou, H., Uchimura, K. and Clothier, B. E. 1998. An unsaturated transient flow method for determining adsorption isotherms for exogenous solutes in variable-charge soils. Proceedings 16th World Congress of Soil Science, Montpellier, France. Symposium No 3.

Kaufman, D. D. and Kearney, P. C. 1976. Microbial transformation in the soil. pp. 29-64. *In* Audus, L. J. (ed.) Herbicides physiology Biochemistry Ecology. London Academic Press.

Kay, B. D. and Elrick, D. E. 1967. Adsorption and movement of lindane in soils. *Soil Science* **104**, 314-322.

Keith, L. H. 1996. Compilation of EPA's Sampling and Analysis Methods. 2nd ed. Lewis Publishers Bocca Raton, Florida.

Kenaga, E. E. 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. *Ecotoxicology and Environmental Safety* **4**, 26-38.

Kenega, E. E. and Goring, C. A. I. 1980. Relationship between water solubility, soil sorption, octanol-water partitioning, and bioconcentration of chemicals in biota. *In* Eaton, J. C., Parrish P. R. and Hedricks A. C.(ed.) Aquatic Toxicology. ASTM STP 707. Philadelphia, PA. American Society for Testing and Materials.

Khan, S. U. 1980. Pesticides in the Soil Environment. Elsevier Scientific Publishing Company, The Netherlands.

Khan, Z. A., Misra, B. M. and Raghu, K. 1996. Thermodynamics of interaction of lindane on silty loam and silty clay loam Indian soils. *Journal of Environmental Science and Health* **31**, 1015-1027.

Kile, D. E. and Chiou, C. T. 1989. Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. *Environmental Science and Technology* **23**, 832-838.

Kinchesh, P., Powlson, D. S., and Randall, E. W. 1995. ^{13}C NMR studies of organic matter in whole soils: I. Quantitation possibilities. *European Journal of Soil Science* **46**, 125-138.

King, P. H. and McCarty, P. L. 1968. A chromatographic model for predicting pesticide migration in soils. *Soil Science* **106**, 248-261.

Knight, M. J. 1993. Organic chemicals contamination of groundwater in Australia - An overview to 1993. *AGSO Journal of Australian Geology and Geophysics* **14**, 107-22.

Kögel-Knabner, I. 1993. Biodegradation and humification processes in forest soils. *Soil Biochemistry* **8**, 101-105.

Kögel-Knabner, I., Hatcher, P. G. and Zech, W. 1991. Chemical structural studies of forest soil humic acids: aromatic carbon fraction. *Soil Science Society of America Journal* **55**, 241-247.

Kögel, I., Hempfling, R., Zech, W., Hatcher, P. G. ,and Schulten, H. R. 1988. Chemical composition of the organic matter in forest soils: 1. Forest litter. *Soil Science* **146**, 124-136.

Kolpin, D. W., Barbash, J. E. and Gilliom, R. J. 1998. Occurrence of pesticides in shallow groundwater of the United States: Initial results from the National Water-Quality Assessment Program. *Environmental Science and Technology* **32**, 558-566.

Kookana, R. S. and Aylmore, L. A. G. 1993. Retention and release of diaquat and paraquat herbicides in soils. *Australian Journal of Soil Research* **31**, 97-109.

Kookana, R. S., Aylmore, L. A. G. and Gerritse, R. G. 1992a. Time-dependent sorption of pesticides during transport in soil. *Soil Science* **154**, 214-225.

Kookana, R. S., Baskaran, S., Ahmad, R., Katou, H. and Bond, W. J. 1998a. Measuring sorption of organic compounds in soil by an unsaturated flow method. Proceedings 16th World Congress of Soil Science, Montpellier, France. Symposium No 7.

Kookana, R. S., Baskaran, S. and Naidu, R. 1998b. Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. *Australian Journal of Soil Research* **36**, 715-764.

Kookana, R. S., Di, H. J. and Aylmore, L. A. G. 1995. A field study of leaching and degradation of nine pesticides in a sandy soil. *Australian Journal of Soil Research* **33**, 1019-1030.

Kookana, R. S., Gerritse, R. G. and Aylmore, L. A. G. 1990. Effect of organic cosolvent on adsorption and desorption of linuron and simazine in soil. *Australian Journal of Soil Research* **28**, 717-725.

Kookana, R. S., Gerritse, R. G. and Aylmore, L. A. G. 1992b. A method for studying nonequilibrium sorption during transport of pesticide in soil. *Soil Science* **154**, 344-349.

Kookana, R. S., Rogers, S. L. and Oliver, D. 1997. Sorption and desorption behaviour of strychnine rodenticide in soils. *Australian Journal of Soil Research* **35**, 491-502.

Koskinen, W. C. and Cheng, H. H. 1983. Effects of experimental variables on 2,4,5-T adsorption-desorption in soil. *Journal of Environmental Quality* **12**, 325-330.

Koskinen, W. C. and Harper, S. S. 1990. The retention process: mechanisms. pp. 305-349. *In* Cheng, H. H. (ed.) Pesticides in the Soil Environment: Processes, Impacts and Modelling. Soil Science Society of America, Madison, Wisconsin.

Krishnayya, A. V., Williams, D. R., Agar, J. G. and O'Connor, M. J. 1994. Significance of organic adsorption in soil and groundwater remediation. *Journal of Soil Contamination* **3**, 191-201.

Krosshavn, M., Southon, T. E. and Steinnes, E. 1992. The influence of vegetational and degree of humification of organic soils on their chemical composition, determined by solid-state ^{13}C NMR. *Journal of Soil Science* **43**, 485-493.

Kuhnt, G. 1995. Long-term fate of pesticides. pp 123-133. *In* Salomons, W.M. and Stigliani W. M. (ed.) Biogeodynamics of Pollutants in Soils and Sediments. Risk Assessment of Delayed and Non-Linear Responses. Springer-Verlag Berlin Heidelberg.

Kuhr, R. J. 1970. Metabolism of carbamate insecticide chemicals in plants and insects. *Journal of Agricultural and Food Chemistry* **18**, 1023-1030.

Kyle, B. G. 1981. Soil-water equilibria for nonionic organic compounds. *Science* **213**, 683-684.

Ladlie, J. S., Meggitt, W. F., and Penner, D. 1977. Effect of pH on metribuzin activity in the soil. *Weed Science* **24**, 505-507.

Laird, D. A. Yen, P. Y., Koskinen, W. C. Steinheimer, T. R. and Dowdy, R. H. 1994. Sorption of atrazine on soil clay components. *Environmental Science and Technology* **28**, 1054-1061.

Lambert, S. M. 1968. Omega (Ω), a useful index of soil sorption equilibria. *Journal of Agricultural and Food Chemistry* **16,** 340-343.

Lee, P. W., Fukuto, J. M., Hernandez, H. and Stearns, S. M. 1990a. Fate of monocrotophos in the environment. *Journal of Agricultural and Food Chemistry* **38**, 567-573.

Lee, L. S., Rao, P. S. C., Nkedi-Kizza, P., and Delfino, J. J. 1990b. Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol-water and soil-water systems. *Environmental Science and Technology* **24**, 654-661.

Legrand, M. F., Costentin, E. and Bruchet, A. 1991. Occurrence of 38 pesticides in various French surface and ground waters. *Environmental Technology* **12**, 985-996.

Leistra, M. 1980. Transport in solution. pp. 32-58. *In* Hance, R. J. (ed.) Interactions Between Herbicides and the Soil. Academic Press, London.

Leistra, M. and Boesten, J. J. T. I. 1989. Pesticide contamination of groundwater in Western Europe. *Agriculture, Ecosystems, and Environment* **26**, 369-389.

Lopes, A., Macanita, A. L., Pina, F. S., Melo, E. and Wamhoff, H. 1992. Multiequilibria of 2-(2′-furanyl)-1H-benzimidazole neutral and protonated forms in the presence of amphiphilic aggregates. *Environmental Science and Technology* **26**, 2448-2453.

Loux, M. M., Liebl, R. A. and Slife, F. W. 1989. Adsorption of imazaquin and imazethapyr on soils, sediments, and selected adsorbents. *Weed Science* **37**, 712-718.

Luthy, R. G., Aiken, G. R., Brusseau, M. L., Cunningham, S. D., Gschwend, P. M., Pignatello, J. J., Reinhard, M., Traina, S. J., Weber, Jr., W. J. and Westall, J. C. 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science and Technology* **31**, 3341-3347.

Lyon, W. G. and Rhodes, D. E. 1991. The swelling properties of soil organic matter and their retention to sorption of nonionic organic compounds. USEPA Project Summary, EPA/600/S2-91/033, Robert, S. Kerr Environmental Research Laboratory, Ada, OK, August, 1991.

Ma, L. Southwick, L. M. Wills, G. H. and Salim, M. H. 1993. Hysteresis characteristics of atrazine adsorption-desorption by Sharkey soil. *Weed Science* **41**, 627-633.

Mabey, W. and Mill, T. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. *Journal of Physical Chemistry* **7**, 383-415.

MacIntyre, W. G. and Smith, C. L. 1984. Comment on "Partition equilibria of nonionic organic compounds between soil organic matter and water". *Environmental Science and Technology* **18**, 295-97.

Mackay, D. M. and Cherry, J. A. 1989. Groundwater contamination: pump and treat remediation. *Environmental Science and Technology* **23**, 630-636.

Mackay, D. and Paterson, S. 1981. Calculating fugacity. *Environmental Science and Technology* **15**, 1006-1014.

Madhun, Y. A., Young, J. L. and Freed, V. H. 1986. Binding of herbicides by water-soluble organic materials from soil. *Journal of Environmental Quality* **15**, 64-68.

Mahieu, N., Powlson, D. S. and Randall, E. W. 1999. Statistical analysis of published carbon-13 CPMAS NMR spectra of soil organic matter. *Soil Science Society of America Journal* **63**, 307-319.

Malcolm, R. L. and MacCarthy, P. 1986. Limitations in the use of commercial humic acids in water and soil research. *Environmental Science and Technology* **20**, 904-911.

Mallawatantri, A. P. and Mulla, D. J. 1992. Herbicide adsorption and organic carbon contents on adjacent low input versus conventional farms. *Journal of Environmental Quality* **21**, 546-551.

Mangels, G. 1991. Behaviour of imidazolinone herbicides in soil: a review of literature. pp.191-209. *In* Shaner, D. L. and O'Connor, S. L. (ed.) The Imidazolinone Herbicides. Boca Raton, Florida: CRC Press.

Mark, M. L., Rex, A. L. and Fred, W. S. 1989. Adsorption of imazaquin and imazethapyr on soils, sediments, and selected adsorbents. *Weed Science* **37**, 712-718.

Martin, M. J. S. and Camazano. 1991. Relationship between the structure of organophosphorus pesticides and adsorption by soil components. *Soil Science* **152**, 283-288.

Maxin, C. R. and Kögel-Knabner, I. 1995. Partitioning of polycyclic aromatic hydrocarbons (PAH) to water-soluble soil organic matter. *European Journal of Soil Science* **46**, 193-204.

McCall, P. J. and Agin, G. L. 1985. Desorption kinetics of picloram as affected by residence time in the soil. *Environmental Toxicology and Chemistry* **4**, 37-44, McCall, P. J., Swann, R. L., Laskowski, D. A., Unger, S. M., Vrona, S. A. and Dishburger, H. J. 1980. Estimation of chemical mobility in soil from liquid chromatographic retention times. *Bulletin of Environmental Contamination and Toxicology* **24**, 190-195.

McCarthy, J. F. and Jimenez, B. D.. 1985. Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: Binding and dissociation. *Environmental Science and Technology* **19**, 1072-1076.

McLennan, W. 1996. Australian Agriculture and the Environment. Australian Bureau of Statistics, Canberra.

Means, J. C., Wood, S. G., Hassett, J. J. and Banwart, W. L. 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soil. *Environmental Science and Technology* **14**, 1524-1528.

Means, J. C., Wood, S. G., Hassett, J. J. and Banwart, W. L. 1982. Sorption of carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science and Technology* **16**, 93-98.

Megharaj, M., Singleton, I. and McClure, N. C. 1998. Effect of pentachlorophenol pollution towards microalgae and microbial activities in soil from former timber processing facility. *Bulletin of Environmental Contamination and Toxicology* **61**, 108-115.

Merry, R. H. and Spouncer, L. R. 1988. The measurement of carbon in soils using a microprocessor-controlled resistance furnace. *Communications in Soil Science and Plant Analysis* **19**, 707-720.

Mersie, W. and Foy, C. L. 1985. Phytotoxicity and adsorption of chlorsulfuron as affected by soil properties. *Weed Science* **33**, 564-568.

Mills, A. C. and Biggar, J. W. 1969. Solubility-temperature effect on the adsorption of gamma-and beta-BHC from aqueous and hexane solutions by soil materials. *Soil Science Society of America Proceedings* **33**, 210-216.

Mingelgrin, U. and Gerstl Z. 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *Journal of Environmental Quality* **12**, 1-11.

Morita, H. 1976. Linuron adsorption and the degree of decomposition of peats as measured by rubbed fiber content and pyrophosphate index. *Canadian Journal of Soil Science* **56**, 105-109.

Morrill, L. G., Mahilum, B. C. and Mohiuddin, S. H. 1982. *In* Organic compounds in soils: Sorption, degradation and persistence. Michigan: Ann Arbor Science.

Murphy, E. M. and Zachara, J. M. 1995. The role of sorbed humic substances on the distribution of organic and inorganic contaminants in groundwater. *Geoderma* **67,** 103-124.

Murphy, E. M., Zachara, J. M., Smith, S. C., Phillips, J. L. and Wietsma, T. W. 1994. Interaction of hydrophobic organic compounds with mineral-bound humic substances. *Environmental Science and Technology* **28**, 1291-1299.

Nash, R. G. and Harris, G. W. 1973. Chlorinated hydrocarbon insecticide residues in crops and soil. *Journal of Environmental Quality* **2**, 269-273.

Nelson, P. N. and Baldock, J. A. 1999. Common biomolecules can explain the chemical composition of natural organic materials. *Nature* (submitted)

Nelson, P. N., Baldock, J. A., Clarke, P., Oades, J. M. and Churchman, G. J. 1999. Dispersed clay and organic matter in soil: their nature and associations. *Australian Journal of Soil Research* **37**, 289-315.

Nicholls, P. H. 1988. Factors influencing entry of pesticides into soil water. *Pesticide Science* **22**, 123-137.

Nicholls, P. H. and Evans, A. A. 1991. Sorption of ionisable organic compounds by field soils. Part 1: Acids. *Pesticide Science* **33**, 319-330.

Nkedi-Kizza, P., Rao, P. S. C. and Hornsby, A. G. 1985. Influence of organic cosolvents on sorption of hydrophobic organic chemicals by soils. *Environmental Science and Technology* **19**, 975-979.

Nkedi-Kizza, P., Rao, P. S. C. and Hornsby, A. G. 1987. Influence of organic cosolvents on leaching of hydrophobic organic chemicals through soils. *Environmental Science and Technology* **21**, 1107-1111.

Nkedi-Kizza, P., Brusseau, M. L., Rao, P. S. C. and Hornsby, A. G. 1989. Nonequilibrium sorption during displacement of hydrophobic organic chemicals and ^{45}Ca through soil columns with aqueous and mixed solvents. *Environmental Science and Technology* **23**, 814-820.

Oades, J. M. Waters, A. G., Vassallo, A. M., Wilson, M. A. and Jones, G. P. 1988. Influence of management on the composition of organic matter in a red brown earth as shown by 13C nuclear magnetic resonance. *Australian Journal of Soil Research* **26**, 289-299.

Ogner, G. 1985. A comparison of four different raw humus types in Norway using chemical degradation and CP MAS carbon-13 NMR spectroscopy. *Geoderma* **35**, 343-353.

Ogram, A. V. Jessup, R. E., Ou, L. T. and Rao, P. S. C. 1985. Effects of sorption on biological degradation rates of (2,4-dichlorophenoxy) acetic acid in soils. *Applied Environmental Microbiology* **49**, 582-587.

PAPA Bulletin. 1991. Press Corporation of Pakistan, Karachi.

PAPA Bulletin. 1994. Press Corporation of Pakistan, Karachi.

PAPA Bulletin. 1995. Press Corporation of Pakistan, Karachi.

Parr, J. F. and Smith, S. 1973. Degradation of trifluralin under laboratory conditions and soil anaerobiosis. *Soil Science* **115**, 55-63.

Parveen, Z. and Masud, S. Z. 1988. Organochlorine pesticide residues in cattle drinking water. *Pakistan Journal of Scientific and Industrial Research* **31**, 53-56.

Parvez, T. 1993. Pesticide residue and cancer. pp. 86-87. *In* Hafiz, S. (ed.) Pakistan Agricultural Handbook-1993: Food and Agriculture. Press Corporation of Pakistan.

Pavlostathis, S. G. and Jaglal, K. 1991. Desorptive behaviour of trichloroethylene in contaminated soil. *Environmental Science and Technology* **25**, 274-279.

Pavlostathis, S. G. and Mathavan, G. N. 1992. Desorption kinetics of selected volatile organic compounds from field contaminated soils. *Environmental Science and Technology* **26**, 532-538.

Perdue, E. M. and Wolfe, N. L. 1982. Modification of pollutant hydrolysis kinetics in the presence of humic substances. *Environmental Science and Technology* **16**, 847-852.

PESKEM PC. 1995. PESKEM PC for Windows^{TM}, Version 1.1. User's Guide. An Australian Directory of Registered Pesticides. The Centre for Pesticide Application and Safety. The University of Queensland, Gatton College, Lawes, Queensland, Australia.

Peters, R. W., Montemagno, C. D. Shem, L. and Lewis, B. G. 1992. Surfactant Flooding of Diese-Fuel-Contaminated Soil. pp. 85-98. *In* Vandegrift, G. F., Reed, D. T. and Tasker, I. R. (ed.). Environmental Remediation: Removing Organic Metal Ion Pollutants. American Chemical Society, Washington, DC.

Piatt, J. J., Backhus, D. A., Capel, P. D. and Eisenreich, S. J. 1996. Temperature-dependent sorption of naphthalene, phenanthrene, and pyrene to low organic carbon aquifer sediments. *Environmental Science and Technology* **30**, 751-760.

Piccolo, A., Conte, P., Scheunert, I. and Paci, M. 1998. Atrazine interactions with soil humic substances of different molecular structure. *Journal of Environmental Quality* **27**, 1324-1333.

Pignatello, J. J. 1989. Sorption dynamics of organic compounds in soils and sediments. pp. 45-80. *In* Sawhney, B. L. and Brown, K. (ed.). Reactions and Movement of Organic Chemicals in Soils. Soil Science Society of America and American Society of Agronomy, Madison, Wisconsin.

Pignatello, J. J. 1990. Slowly-reversible sorption of aliphatic halocarbons in soils. I. Formation of residual fractions. *Environmental Toxicology and Chemistry* **9**, 1107-1115.

Pignatello, J. J., Ferrandino, F. J. and Huang, L. Q. 1993. Elution of aged and freshly added herbicides from soil. *Environmental Science and Technology* **27**, 1563-1571.

Pignatello, J. J. and Huang, L. Q. 1991. Sorptive reversibility of atrazine and metolachlor residues in field soil samples. *Journal of Environmental Quality* **20**, 222-228.

Pignatello, J. J. and Xing, B. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology* **30**, 1-11.

Pimental D. and Levitan, L. 1986. Pesticides: amounts applied and amounts reaching pests. *Bioscience* **36**, 86-91.

Pimental D., McLaughlin, L., Zepp, A. and Lakitan, B. 1991. Environmental and economic effects of reducing pesticide use. *Bioscience* **41**, 402-409.

Postel, S. 1988. Controlling toxic chemicals. pp. 118-36. *In* State of the World 1988. A Worldwide Institute Report on Progress Toward a Sustainable Society, Norton and Company.

Powley, C. R., Bernard, P. A. 1998. Screening method for nine sulfonylurea herbicides in soil and water by liquid chromatography with ultraviolet detection. *Journal of Agricultural Food and Chemistry* **46**, 514-519.

Preston, C. M. 1996. Applications of NMR to soil organic matter analysis: history and prospects. *Soil Science* **161,** 144-166.

Preston, C. M. and Newman, R. H. 1992. Demonstration of spatial heterogeneity in the organic matter of de-ashed humin samples by solid-state ^{13}C CP/MAS NMR. *Canadian Journal of Soil Science* **72**, 13-19.

Qualls, R, and Haines, B. L. 1992. Measuring adsorption isotherms using continuous, unsaturated flow through intact soil cores. *Soil Science Society of America Journal* **56**, 456-460.

Rajagopal, B. S., Brahmaprakash, G. P., Reddy, B. R., Singh. U. D. and Sethunathan, N. 1994. Effect and persistence of selected carbamate pesticides in soil. *Residue Reviews* **93**, 85-198.

Randall, E. W., Mahieu, Powlson, D. S. and Christensen, B. T. 1995. Fertilization effects on organic matter in physically fractionated soils as studied by ^{13}C NMR: Results from two long-term field experiments. *European Journal of Soil Science* **46**, 557-565.

Rao, P. S. C. and Davidson, J. M. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. *In* Overcash, M. R. and J. M. Davidson (ed.) Environmental Impact of Nonpoint Source Pollution. Ann Arbor, MI: Ann Arbor Science publishers, Inc.

Rao, P. S. C., Hornsby, A. G., Kilcrease, D. P. and Nkedi-Kizza, P. 1985. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: model development and preliminary evaluation. *Journal of Environmental Quality* **14**, 376-383.

Raven, M. D. 1990. XPLOT Version 3.2-User manual. Manipulation of powder X-ray diffraction data. CSIRO Division of Soils Technical Memorandum No. 1/1989.

Renner, K. A., Meggit, W. F. and Penner, D. 1988. Effect of soil pH on imazaquin and imazethapyr and sorption to soil and phytotoxicity to corn (*Zea mays*). *Weed Science* **36**, 78-83.

Riggle, B. D. and Penner, D. 1988. Controlled release of three herbicides with the Kraft lignin PC940C. *Weed Science* **36**, 131-136.

Roberts, A. H. C., Cameron, K. C., Bolan, N. S., Ellis, H. K. and Hunt, S. 1996. Contaminants and the soil environment. pp. 579-628. *In* Proceedings of the First Australasia-Pacific Conference on Contaminants and the Soil Environment in Australasia Pacific Region, held in Adelaide, Australia, 18-23 February, 1996.

Robertson, B. K. and Alexander, M. 1998. Sequestration of DDT and dieldrin in soil: disappearance of acute toxicity but not the compounds. *Environmental Toxicology and Chemistry* **17**, 1034-1038.

Rosen, M. J. 1989. Micelle formation by surfactants. pp. 108-169. *In* Surfactants and Interfacial Phenomena, 2nd ed. A Wiley-Interscience Publication, John Wiley and Sons New York.

Sabadie, J. 1996. Alcoholysis and chemical hydrolysis of bensufuron-methyl. *Weed Research* **36**, 431-440.

Sahoo, D. and Smith, J. A. 1997. Enhanced trichloroethene desorption from long-term contaminated soil using Triton X-100 and pH increases. *Environmental Science and Technology* **31**, 1910-1915.

Saito, H. and Shinoda, K. 1987. The solubilisation of hydrocarbons in aqueous solutions of nonionic surfactants. *Journal of Colloid and Interface Science* **24**, 10-15.

Sarmah, A. K., Kookana, R. S., and Alston, A. M. 1998. Fate and behaviour of sulfonylurea herbicides in soil environment: a review. *Australian Journal of Agricultural Research* **49**, 775-790.

Schnitzer, M. 1991. Soil organic matter–the next 75 years. *Soil Science* **151**, 41-58.

Schnitzer, M. and Khan, S. U. 1972. Reactions of humic substances with organic chemicals, N-containing compounds, and physiological properties of humic substances. pp. 281-304. *In* Humic Substances in the Environment. Marcel Dekker Inc., New York.

Schwarzenbach, R. P. and Westall, J. 1981. Transport of nonpoint organic compounds from surface water to groundwater. Laboratory sorption studies. *Environmental Science and Technology* **15**, 1360-1367.

Sciacovelli, O., Senesi, N., Solinas, V. and Testini, C. 1977. Spectroscopic studies on soil organic fractions I. IR and NMR spectra. *Soil Biology and Biochemistry* **9**, 287-293.

Scow, K. M. 1993. Effects of sorption-desorption and diffusion processes on the kinetics of biodegradation of organic chemicals in soil. pp. 73-114. *In* Sorption and Degradation of Pesticides and Organic Chemicals in Soil. Soil Science Society of America, Madison. W. I.

Scribner, S. L. Benzing, T. R., Sun, S. and Boyd, S. A. 1992. Desorption and bioavailability of aged simazine residues in soil from a continuous corn field. *Journal of Environmental Quality* **21**, 115-120.

Self, P. G. 1989. PC-PW1800-User manual. PC based system for the control of Philip PW1800 X-ray diffraction system. CSIRO Division of Soils Technical Memorandum No 1/1989.

Senesi, N. 1993. Nature of interactions between organic chemicals and dissolved humic substances and the influence of environmental factors. pp. 73-101. *In* Beck, A. J., Jones, K. C., Hayes, M. H. B. and Mingelgrin, U. (ed.) Organic Substances in Soil and Water: Natural Constituents and Their Influences on Contaminant Behaviour. The Royal Society of Chemistry, Cambridge, UK.

Seybold, C. A., McSweeney, K. and Lowery, B. 1994. Atrazine adsorption in sandy soils of Wisconsin. *Journal of Environmental Quality* **23**, 1291-1297.

Sharom, M. S., Miles, J. R. W., Harris, C. R. and McEwen, F. L. 1980. Persistence of 12 insecticides in water. *Water Research* **14**, 1089-1094.

Shea, P. J. 1986. Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. *Weed Science* **34**, 474-478.

Sherma, J. 1995. *Pesticides Analytical Chemistry* **67**, 5R.

Shin, Y., Chodan, J. J. and A. R. Walcott. 1970. Adsorption of DDT by soils, soil, fractions and biological materials. *Journal of Agricultural and Food Chemistry* **18**, 1129-1133.

Singh, R. 1989. Simultaneous determination of fenamiphos, its sulphoxide and sulphone in water by high-performance liquid chromatography. *Analyst* **114**, 425-427.

Singh, R., Gerritse, R. G. and Aylmore, L. A. G. 1990. Adsorption-desorption behaviour of selected pesticides in some Western Australian soils. *Australian Journal of Soil Research* **28**, 227-243.

Skjemstad, J. O., Clark, P., Golchin, A., and Oades, J. M. 1997. Characterization of soil organic matter by solid-state ^{13}C NMR spectroscopy. pp. 253-271. *In* Cadisch, G. and Giller, K. E. (ed.) 'Driven by Nature: Plant Litter Quality and Decomposition'. CAB International, Wallingford, UK.

Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M. and McClure, S. G. 1996. The chemistry and nature of protected carbon in soil. *Australian Journal of Soil Research* **34**, 251-271.

Skjemstad, J. O., Clark, P., Taylor, J. A., Oades, J. M. and Newman, R. H. 1994. The removal of magnetic materials from surface soils. A solid state ^{13}C CP/MAS n.m.r. study. *Australian Journal of Soil Research* **32**, 1215-1229.

Skjemstad, J. P., Dalal, R. C. and Barron, P. F. 1986. Spectroscopic investigations of cultivation effects on organic matter of Vertisols. *Soil Science Society of America Journal* **50**, 354-359.

Skjemstad, J. O., Janik, L. J. and Taylor, J. A. 1998. Non-living soil organic matter: what do we know about it? *Australian Journal of Experimental Agriculture* **38**, 667-80.

Skoog, D. A., West, D. M. and Holler, F. J. 1988. Gas Liquid Chromatography. P. 626-642. *In* Analytical Chemistry. Saunders College Publishing, New York.

Smiles, D. E. and Philip, J. R. 1978. Solute transport during absorption of water by soil: Laboratory studies and their practical implications. *Soil Science Society of America Journal* **42**, 537-544.

Smith, A. E. 1988. Transformation in soil. pp. 171-200. *In* Grover, R. (ed.) Environmental Chemistry of Herbicides. Vol. I. Boca Raton, Florida: CRC Press Inc.

Smith J. A., Harte, P. T. and M. A. Hardy. 1987. Trace-metal and organochlorine residues in sediments of the upper Rockway River, New Jersey. *Bulletin of Environmental Contamination and Toxicology* **39**, 465-473.

Smith, J. A., Tuck D. M., Jaffe, P. R. and Mueller, R. T. 1991. Effects of surfactants on the mobility of nonpolar organic contaminants in porous media. pp. 201-203. *In*

Baker, R. (ed.) Organic Substances and Sediments in Water, Vol I. Lewis Publishers, Chelsea, MI.

Smith, J. A., Witkowski, P. J. and Chiou, C. T. 1988. Partition of nonionic organic compounds in aquatic systems. *Reviews of Environmental Contamination and Toxicology* **103**, 127-151.

Spencer, W. F., Cliath, M. M. and Yates, S. R. 1995. Soil-pesticide interactions and their impact on the volatilisation process. pp. 371-381. *In* Huang, P. M., Berthelin, J. Bollag, J. M., McGill, W. B. and Page, A. L. (ed.) Environmental Impact of Soil Component Interactions: Natural and Anthropogenic Organics. Lewis Publishers, Boca Raton.

Stadter, F. A., Emmett, A. and Dillon, P. 1992. Occurrence of atrazine in groundwater in the Southeast of South Australia. CSIRO Australian Centre for groundwater Studies, Report No. 45.

Steinberg, S. M. Pignatello, J. J. and Sawhney, B. L. 1987. Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environmental Science and Technology* **21**, 1201-1208.

Stevenson, F. J. 1982. *In* Humus Chemistry: Genesis, Composition and Reactions. Wiley, New York.

Stevenson, F. J. 1976. Organic matter reactions involving pesticides in soil. pp. 180-207. *In* Kaulfman, D. D. Still. G. G., Paulson G. D. and Bandal, S. K. (ed.) Bound and Conjugated Pesticide Residues. ACS Symposium Series 29. American Chemical Society Washington, DC.

Stevenson, F. J. 1982. Soil lipids. pp.172-194. *In* Humus Chemistry: Genesis, Composition, Reactions. John Wiley and Sons, Inc. New York.

/ Stevenson, F. J. 1994. Organic matter reactions involving pesticides in soil. pp. 453-471. *In* Humus Chemistry: Genesis, Composition, Reactions. 2nd ed. John Wiley and Sons, Inc. New York.

Stougaard, R. N., Shea, P. J. and Martin, A. R. 1990. Effect of soil type and pH on adsorption, mobility and efficacy of imazaquin and imazethapyr. *Weed Science* **36**, 67-73.

Struif, B., Weil, L. and Quentin, K. E. 1975. The behaviour of herbicides phenoxy acetic acids and their esters in waters. *Wom Wasser* **45**, 53-73.

Sundaram, K. M. S., Sloane, L. and Curry, J. 1995. Kinetics of azadirachtin hydrolysis in model aquatic systems by high-performance liquid chromatography. *Journal of Liquid Chromatography* **18**, 363-376.

Swift, R. S. 1985. Fractionation of soil humic substances. p. 387. *In* Aiken, G. R., Mcknight, D. M., and R. L. Wershaw (ed.) Humic Substances in Soil, Sediment, and Water. John Wiley and Sons, New York.

Swoboda, A. R. and Thomas, G. W. 1968. Movement of parathion in soil columns. *Journal of Agricultural and Food Chemistry* **16**, 923-927.

Tate, K. R. and Theng, B. K. G. 1980. Organic matter and its interactions with inorganic soil constituents. pp. 225-249. *In* Theng, B. K. G (ed). Soils with Variable Charge. New Zealand Society of Soil Science, Lower Hutt, New Zealand.

Taylor, A. W. and Glotfelty, D. E. 1988. Evaporation from soil and crops. p.89. *In* Grover, R. (ed.) Environmental Chemistry of Herbicides. Vol 1. CRC Press Inc. Boca Raton, Florida.

Taylor, J. A., Skjemstad, J. O. and Ladd, J. N. 1996. Factors influencing the breakdown of sulfonylurea herbicides in solution and in soil. CSIRO Division of Soils, Divisional Report No 127, 1-12.

Taylor, A. W. and Spencer, W. F. 1990. Volatilization and vapour transport processes. pp. 213-269. *In* Cheng, H. H. (ed.) Pesticides in the Soil Environment: Processes, Impacts and Modelling. Soil Science Society of America, Madison, Wisconson.

Tentsova, A. I., Frik, L. P., Izhendeeva, T. V. and Pudel, M. E. 1986. Stability of dicaine solutions in the presence of surfactants. *Farmatsiya (Moscow)* **35**, 22-26.

Thirunarayanan, K., Zimdahl, R. L. and Smika, D. E. 1985. Chlorsulfuron adsorption and degradation in soil. *Weed Science* **33**, 558-563.

Thoma, K. 1990. Pilot survey of pesticides residues in streams draining horticultural catchment, Piccadilly Valley, South Australia. South Australian Department of Agriculture, Adelaide.

Tomlin, C. D. S. 1998. The Electronic Pesticide Manual. The British Crop Protection Council.

Tompkins, G. A., McIntosh, T. H. and Dunigan, E. P. 1968. Use of the Standford-DeMent bioassay to study atrazine-soil reactions. *Soil Science Society of America Proceedings* **32**, 373-377.

Topp, E. and Smith, W. 1992. Sorption of the herbicides atrazine and metolachlor to selected plastics and silicone rubber. *Journal of Environmental Quality* **21**, 316-317.

Triegel, E. K. and Gue, L. 1994. Overview of the fate of pesticides in the environment, water balance; runoff vs. leaching. pp. 1-13. *In* Honeycutt, R. C. and Schabacker, D. J.(ed.) Mechanisms of Pesticide Movement into Groundwater. Lewis Publishers. CRC Press, Boca Raton, Florida.

Troiano, Garretson, J. C., Krauter, C. K., Brownell, J. and Hutson, J. 1993. Soil processes and chemical transport influence of amount and method of irrigation water application on leaching of atrazine. *Journal of Environmental Quality* **22**, 290-298.

U. S. Environmental Protection Agency. 1975. Guidelines for registering pesticides in the United States. Chemodynamic parameters – adsorption. *Federal Register* 40 (123), 26881-26882. U.S. Government Printing Office, Washington DC.

U. S. Environmental Protection Agency. 1990. National Survey of Pesticides in Drinking Water Wells Phase I Report. US EPA Offices of Water and of Pesticides and Toxic Substances, November 1990, 570/9-90-015.

Valsaraj, K. T. Gupta, A., Thibodeaux, L. J. and Harrison, D. P. 1988. Partitioning of chloromethanes between aqueous and surfactant micellar phases. Water Research **9**, 1173-1183.

Valsaraj, K. T. and Thibodeaux, L. J. 1989. Relationships between micelle-water and octanol-water partition constants for hydrophobic organic compounds of environmental interest. *Water Research* **23**,183-189.

Valverde-Garcia, A., Gonzalez-Pradas, E., Villafranca-Sanchez, M., del Rey Bueno, F. and Garcia-Rodriguez, A. 1988. Adsorption of thiram and dimethoate on Almeria soils. *Soil Science Society of America Journal* **52,** 1571-1574.

Valverde-Garcia, A., Gonzalez-Pradas, E., Villafraca-Sanches, M., del Rey-Bueno, F. and Garcia-Rodriguez, A. 1989. Adsorption of linuron and atrazine on Almeria soils. *Agrochimica* **33**, 389-395.

Verschueren, K. 1983. *In* Handbook of Environmental Data on Organic Chemicals. 2nd ed. Van Nostrand, Reinhold, New York.

Villedieu, J. C., Desavignac, A. and Calmon, J. P. 1995. Kinetics and mechanisms of hydrolysis of dicarboximide fungicides in micellar media. *Journal of Agricultural and Food Chemistry* **43**, 1948-1953.

Walker, A. and Bond, W. 1977. Persistence of the herbicide AC92,553, N-(1 ethylpropyl)-2,6 dinitro-3,4-xylidine in soils. *Pesticide Science* **8**, 359-365.

Wang, Z, Gamble, D. S. and Langford, C. H. 1992. Interaction of atrazine with Laurentian soil. *Environmental Science and Technology* **26**, 560-565.

Weber, J. B. 1970a. Mechanisms of adsorption of s-triazines by clay colloids and factors affecting plant availability. *Residues Reviews* **32**, 93-130.

Weber, J. B. 1970b. Adsorption of s-triazines by montmorillonite as a function of pH and molecular structure. *Soil Science Society of America Proceedings* **34**, 401-404.

Weber, J. B. 1993. Ionization and sorption of fomesafen and atrazine by soils and soil constituents. *Pesticide Science* **39**, 31-38.

Weber, J. B., Best, J. A. and Gonese, J. U. 1993. Bioavailability and bioactivity of sorbed organic compounds. pp. 153-196. *In* Sorption and Degradation of Pesticides and Organic Chemicals in Soil. Soil Science Society of America Special Publication no 32. Soil Science Society of America and American Society of Agronomy, Madison, Wisconson.

Wershaw, R. L. 1986. A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water and sediment-water systems. *Journal of Contaminant Hydrology* **1**, 29-45.

West, C. C. and Harwell, J. H. 1992. Surfactants and subsurface remediation. *Environmental Science and Technology* **26**, 2324-2330.

White, J. L. 1976. Clay pesticide interactions. pp. 180-207. *In* Kaulfman, D. D. Still, G. D. and Bandal, S. K. (ed.) Bound and Conjugated Pesticide Residues. ACS Symposium Series.

Wienhold, B. J. Sadeghi, A. M. and Gish, T. J. 1993. Effect of starch encapsulated and temperature on volatilization of atrazine and alachlor. *Journal of Environmental Quality* **22**, 162-166.

Wijayaratne, R. D. and Means, J. C. 1984. Affinity of hydrophobic pollutants for natural estuarine colloids in aquatic environments. *Environmental Science and Technology* **18**, 121-123.

Williams, D. H. and Fleming, I. 1989. *In* Spectroscopic Methods in Organic Chemistry. McGraw-Hill Book Company, UK Limited.

Wilson, M. A. 1987. *In* NMR Techniques and Applications in Geochemistry and Soil Chemistry. Pergamon press, Oxford, U.K.

Wilson, M. A., Vassallo, A. M., Perdue, E. M. and Reuter, J. H. 1987. Compositional and solid-waste nuclear magnetic resonance study of humic and fulvic acid fractions of soil organic matter. *Analytical Chemistry* **59**, 551-558.

Wolfe, N. L., Mingelgrin, U. and Miller, G. C. 1990. Abiotic transformations in water, sediments and soil. pp. 103-168. Cheng, H. H. (ed.) *In* Pesticides in the Soil Environment: Processes, Impacts and Modelling. Soil Science Society of America, Madison, WI.

Worobey, B. L. and Barrie Webster, G. R. 1981. Indigenous ^{13}C NMR structural features of soil humic substances. *Nature* **292**, 526-529.

Wu, C. H., Buehring, N., Davidson, J. M. and Santelmann, P. W. 1975. Napropamide adsorption, desorption and movement in soils. *Weed Science* **23**, 454-457.

Xing, B., MacGill, W. B., Dudas, M. J., Maham, Y. and Hepler, L. 1994. Sorption of phenol by selected biopolymers: isotherm, energetics, and polarity. *Environmental Science and Technology* **28**, 1139-1144.

Xing, B. and Pignatello, J. J. 1997. Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. *Environmental Science and Technology* **31**, 792-799.

Yamane, V. K. and Green, R. E. 1972. Adsorption of ametryn and atrazine on an oxisol, montmorillonite and charcoal in relation to pH and solubility effects. *Soil Science Society of America Proceedings* **36**, 58-64.

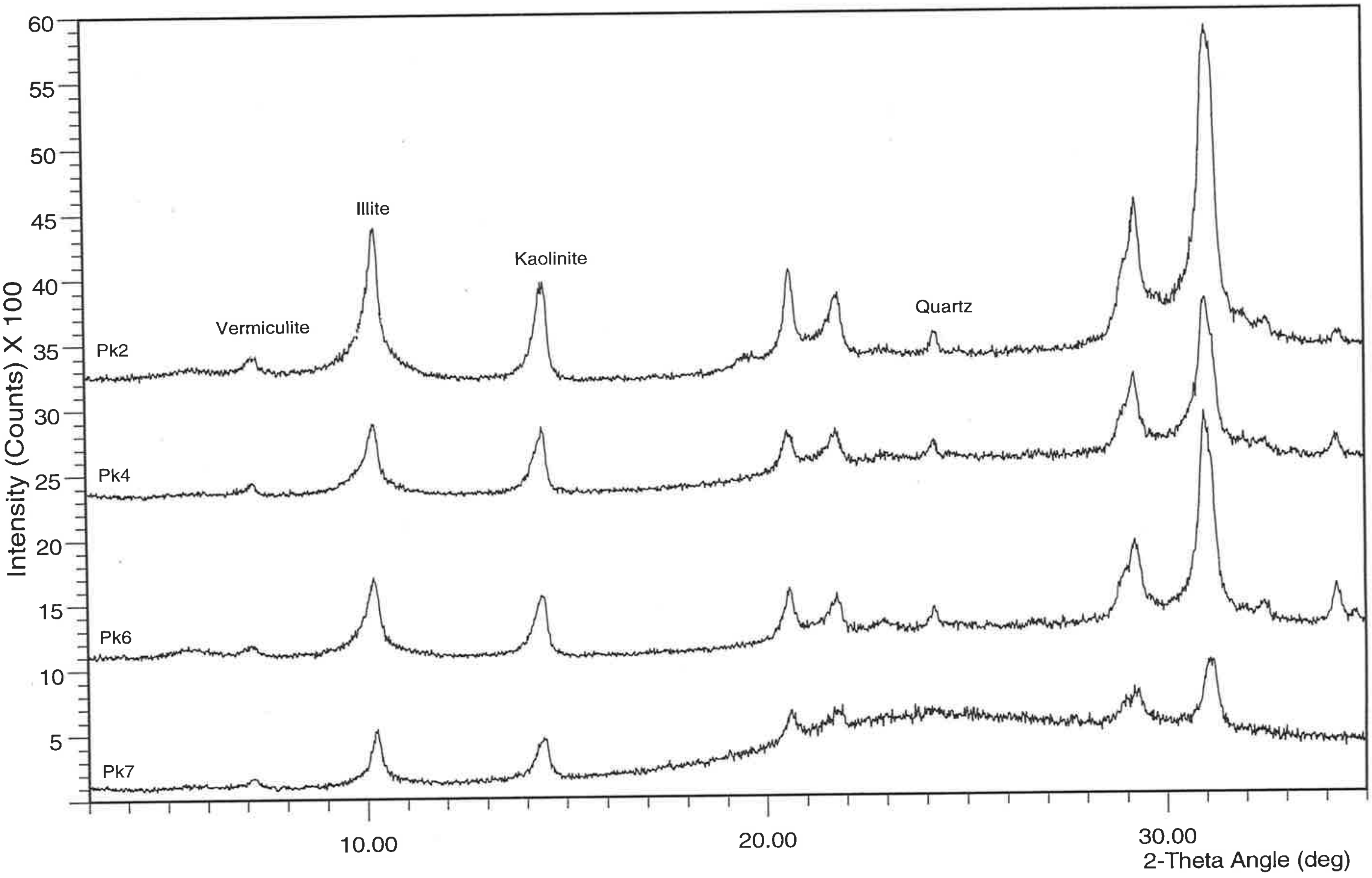
Yamato, A., Amemiya, T., Kumoura, M., Kondo, M. and Sanda, S. 1993. Effect of additives on stability of icariin in Epimedium extract. *Yakuzaigaku* **53**, 116-123.

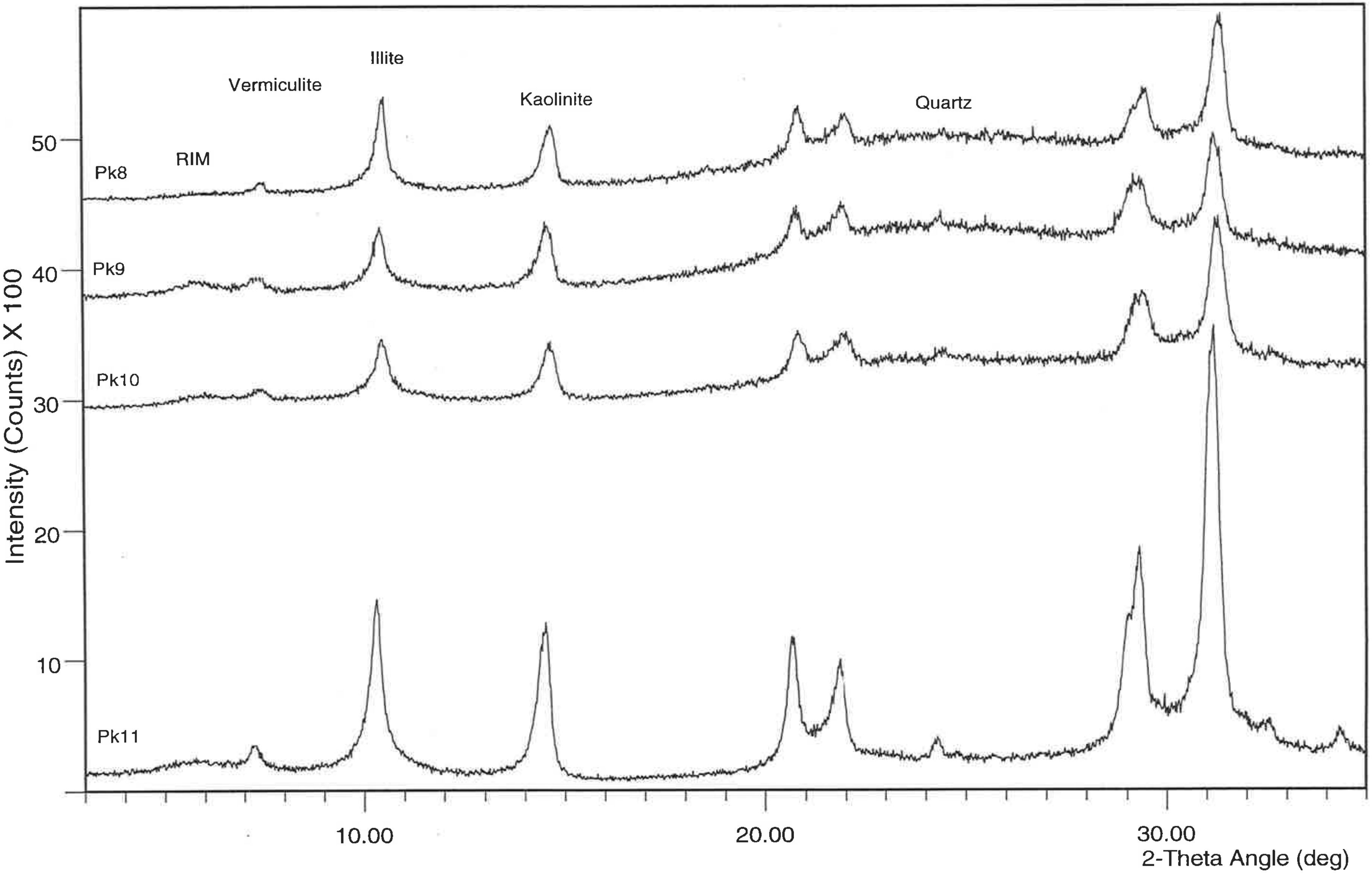
Yaron, B. and Saltzman, S. 1972. Influences of water and temperatureon adsorption of parathion by soils. *Soil Science Society of America Proceedings* **36**, 683-586.

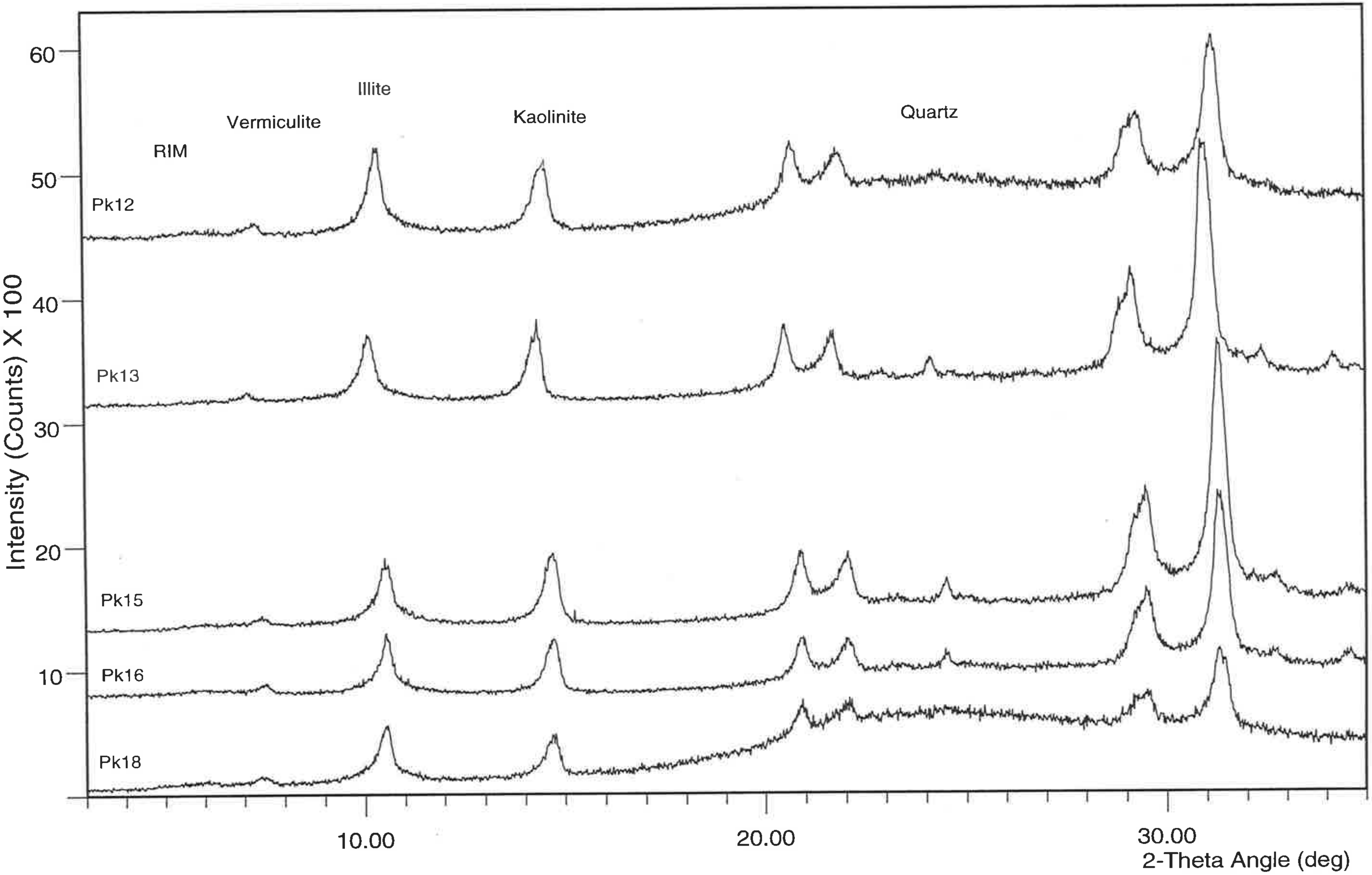
Zwieten, L.V. and Grieve, A. 1995. Remediation options for contaminated dipsites. *Agricultural Science*. November-December, 40-42.

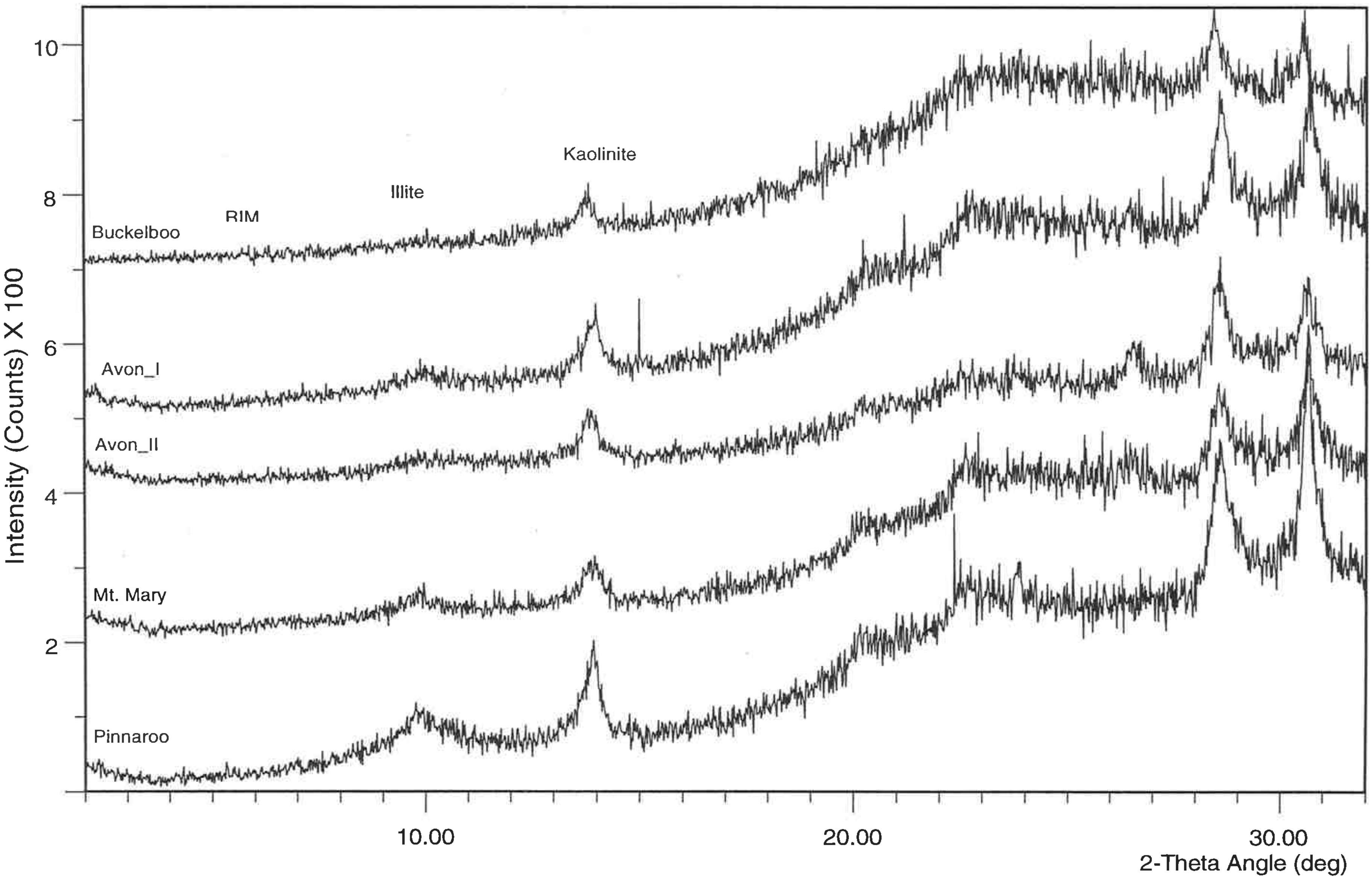
Zytner, R. G. 1992. Adsorption-desorption of trichloroethylene in granular media. *Water, Air and Soil Pollution* **65**, 245-255.

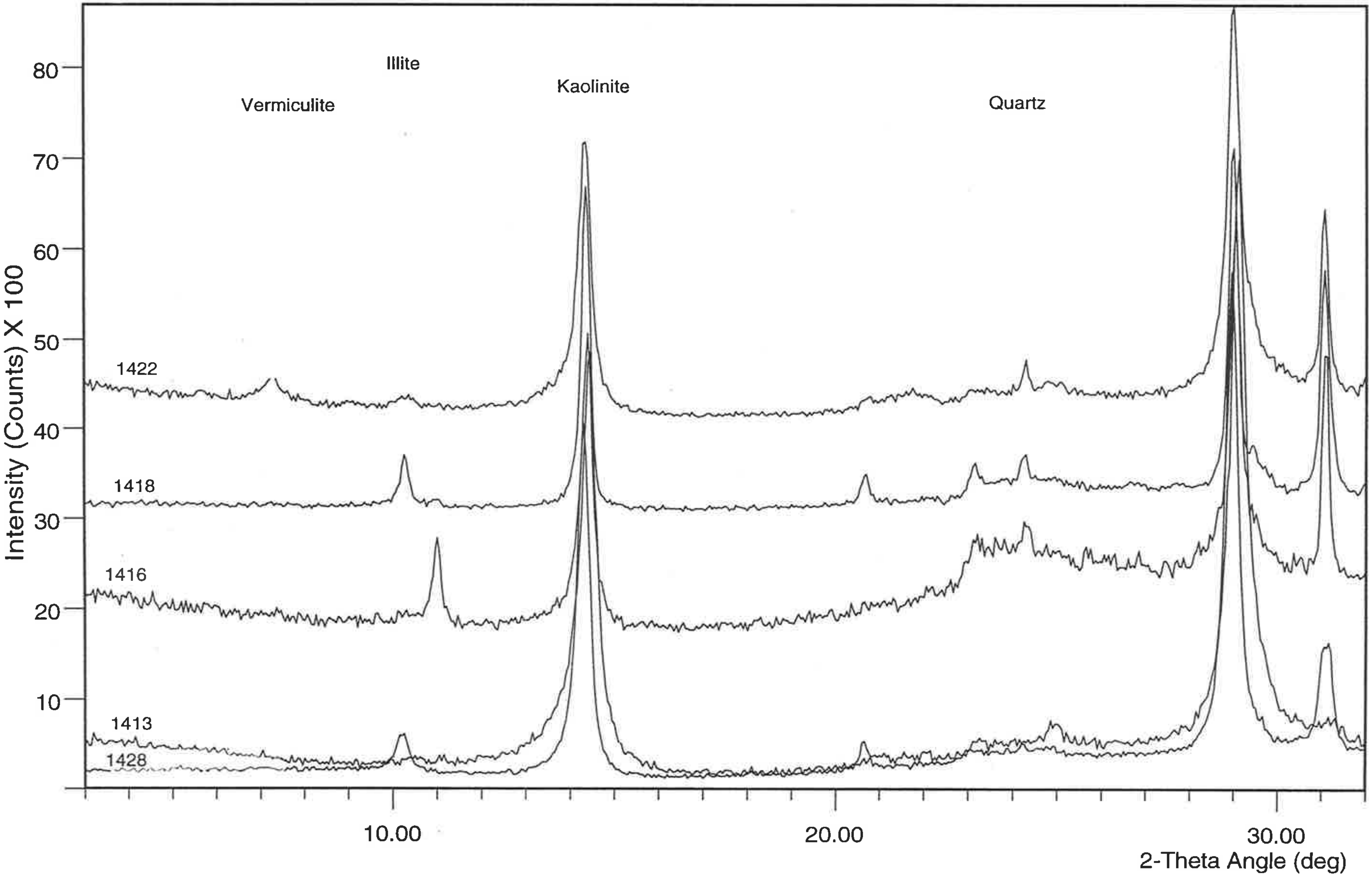
Appendix 3.1 X-ray diffraction patterns of some soils

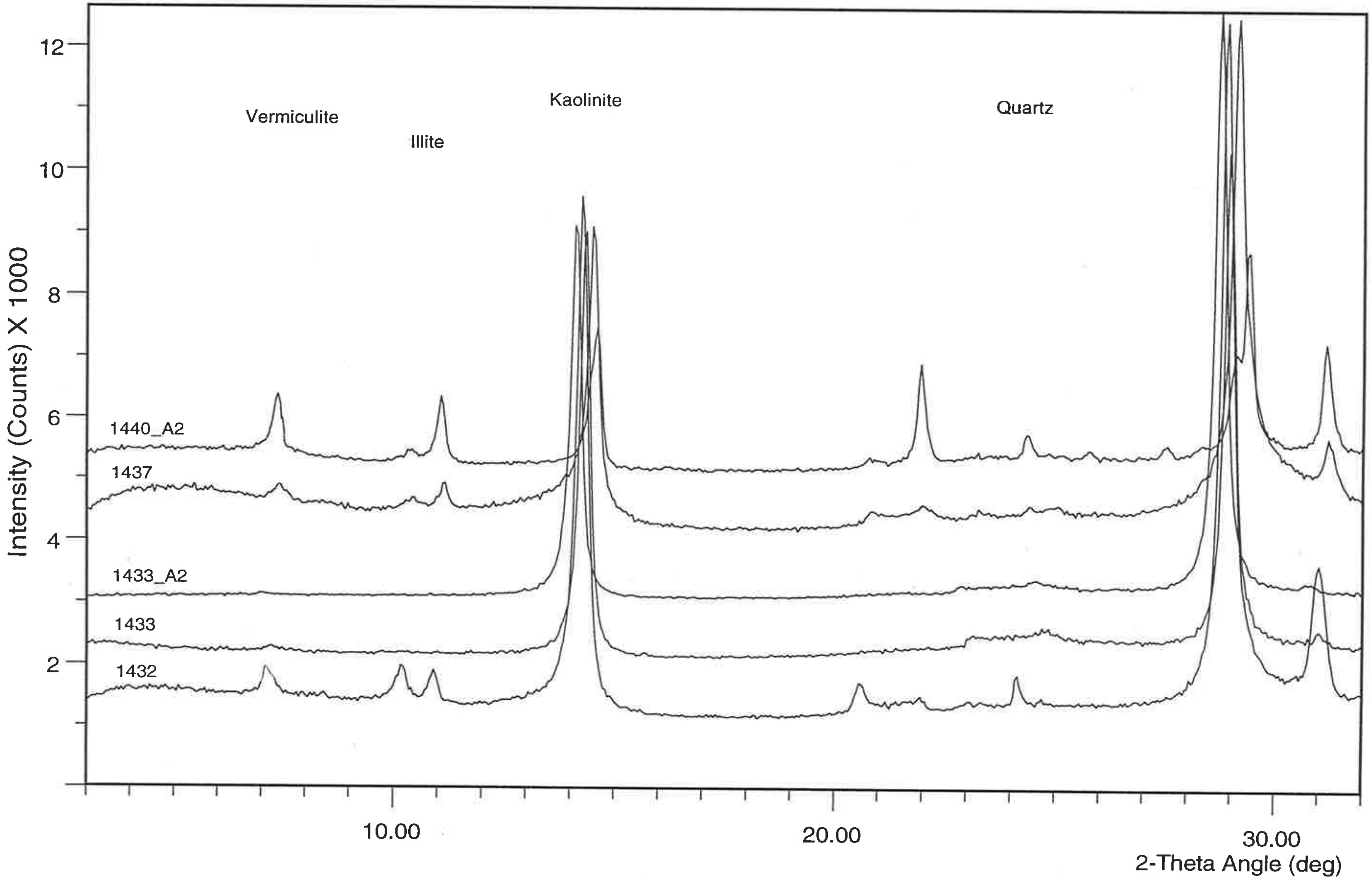



Illite
Vermiculite
Kaolinite
Quartz
RIM
Pk8
Pk9
Pk10
Pk11
50
40
30
20
10
Intensity (Counts) X 100
10.00
20.00
30.00
2-Theta Angle (deg)


60
50
40
30
20
10
Intensity (Counts) X 100
RIM
Vermiculite
Illite
Kaolinite
Quartz
Pk12
Pk13
Pk15
Pk16
Pk18
10.00
20.00
30.00
2-Theta Angle (deg)

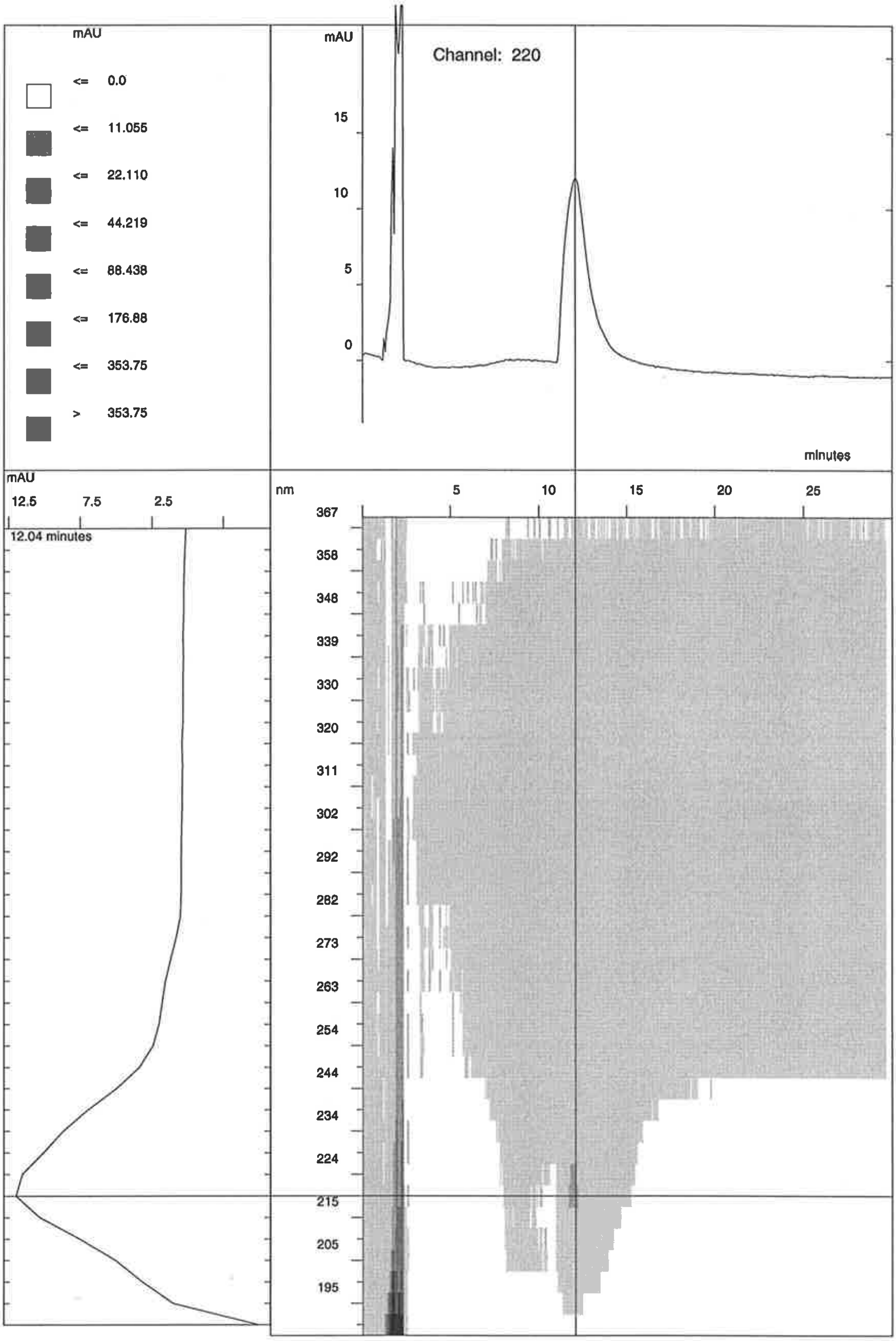

Kaolinite
Illite
BIM
Buckelboo
Avon_I
Avon_II
Mt. Mary
Pinnaroo
Intensity (Counts) X 100
10
8
6
4
2
10.00
20.00
30.00
2-Theta Angle (deg)


Vermiculite
Illite
Kaolinite
Quartz
80
70
60
50
40
30
20
10
Intensity (Counts) X 100
1422
1418
1416
1413
1428
10.00
20.00
30.00
2-Theta Angle (deg)

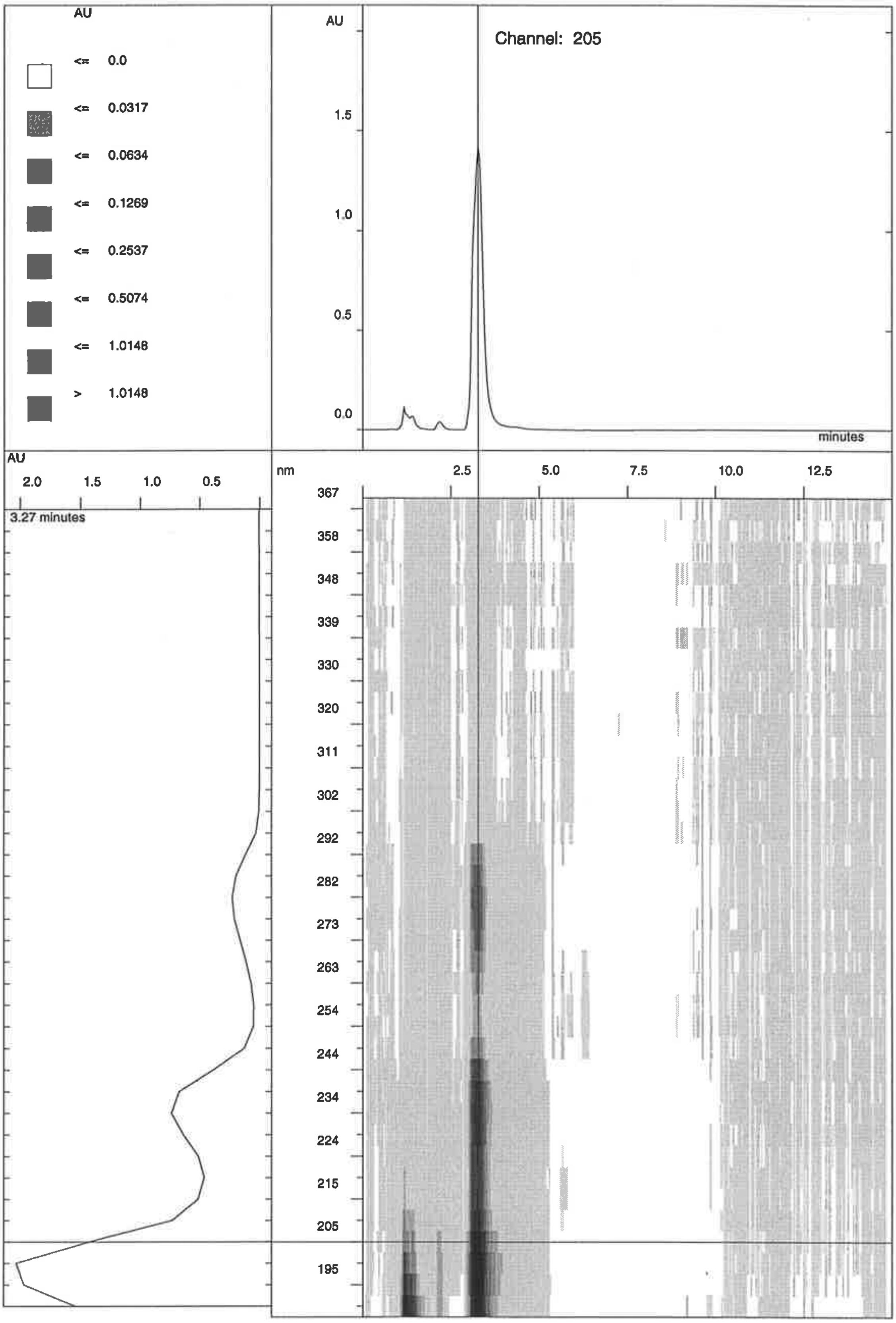

Vermiculite
Illite
Kaolinite
Quartz
1440_A2
1437
1433_A2
1433
1432
Intensity (Counts) X 1000
12
10
8
6
4
2
10.00
20.00
30.00
2-Theta Angle (deg)

Appendix 3.2 Poly-diode-array (PDA) spectra of the pesticides at different wavelengths

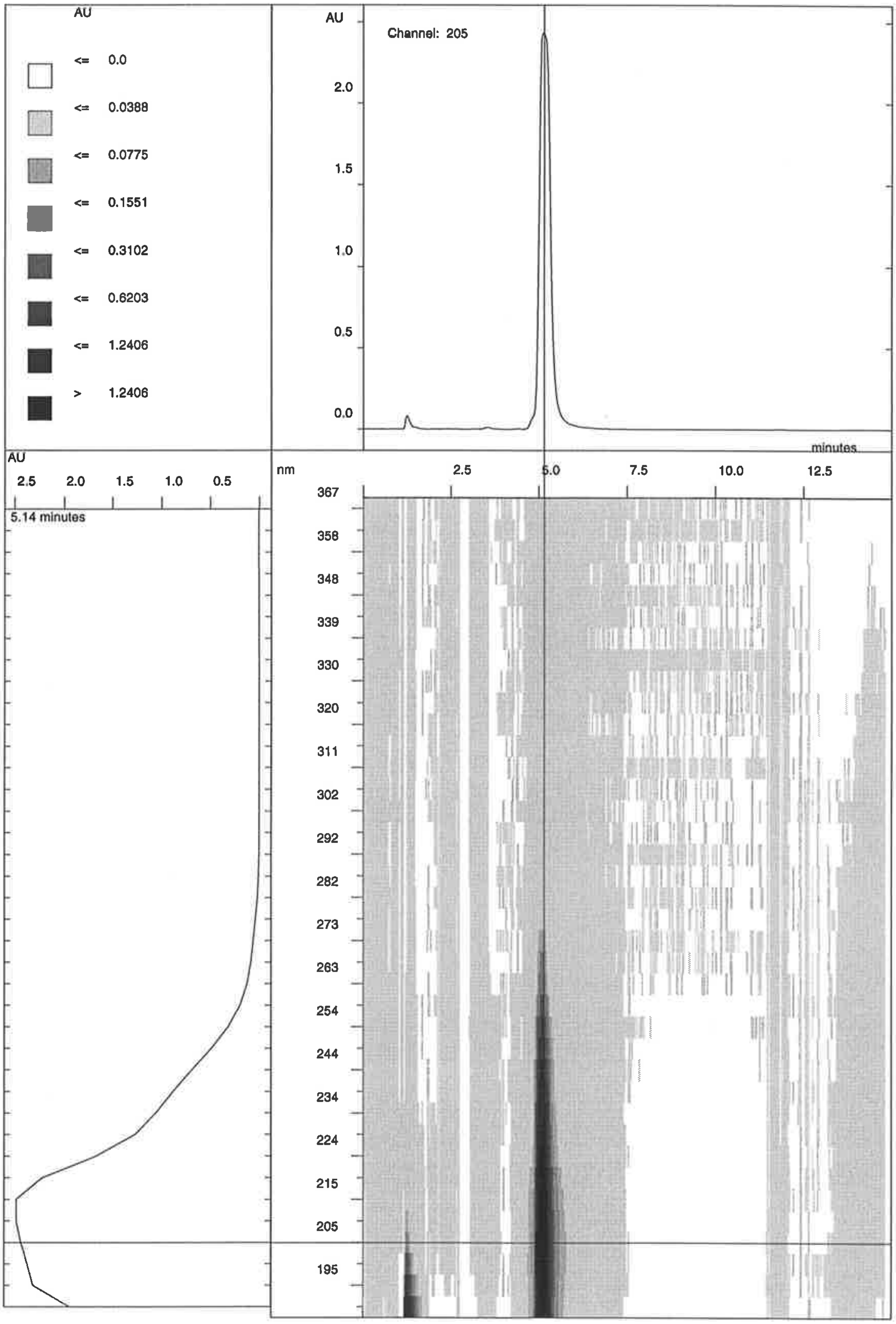
Ametryn



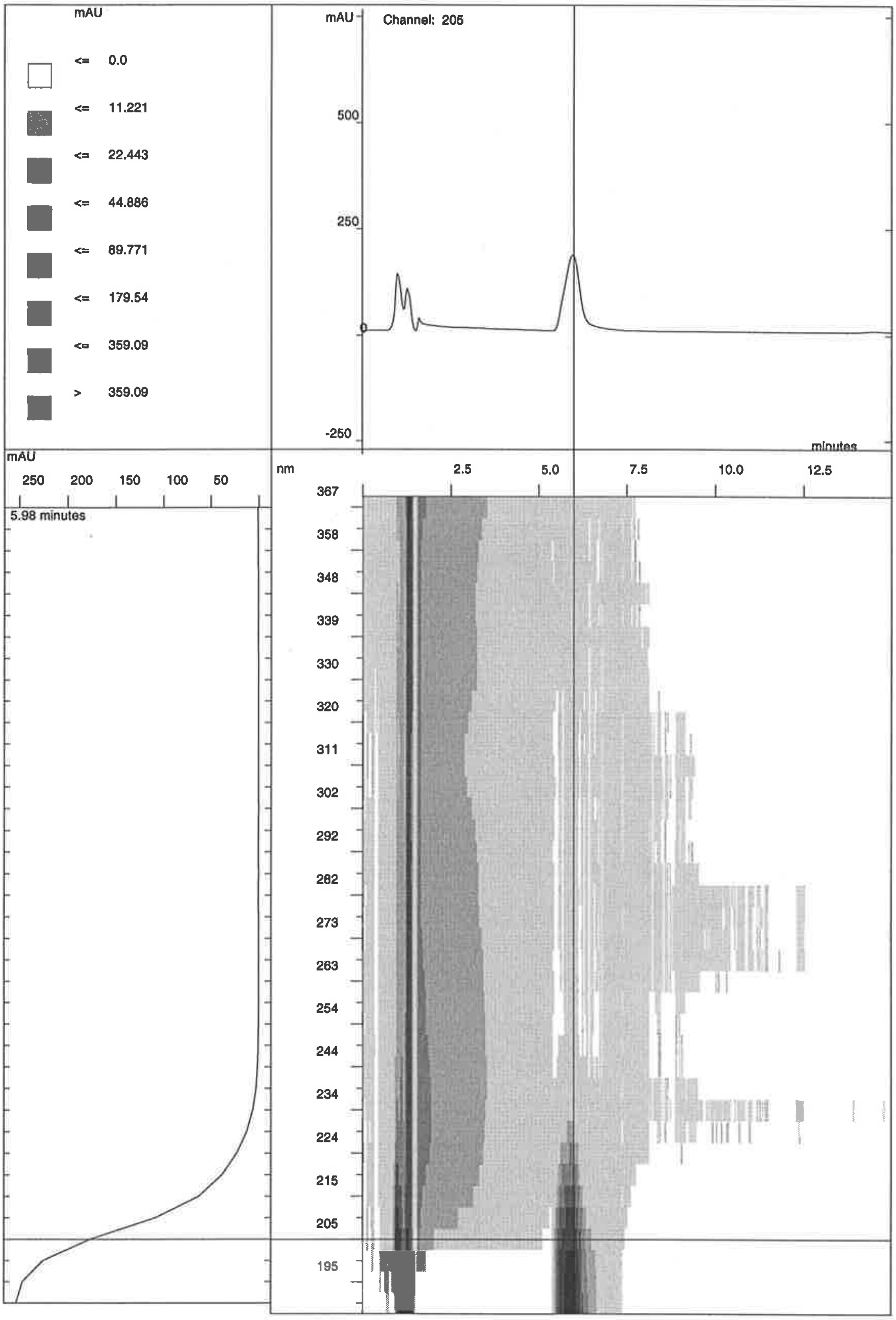
Phosalone


AU
<= 0.0
<= 0.0317
<= 0.0634
<= 0.1269
<= 0.2537
<= 0.5074
<= 1.0148
> 1.0148
AU
1.5
1.0
0.5
0.0
Channel: 205
minutes
AU
2.0
1.5
1.0
0.5
3.27 minutes
nm
2.5
5.0
7.5
10.0
12.5
367
358
348
339
330
320
311
302
292
282
273
263
254
244
234
224
215
205
195

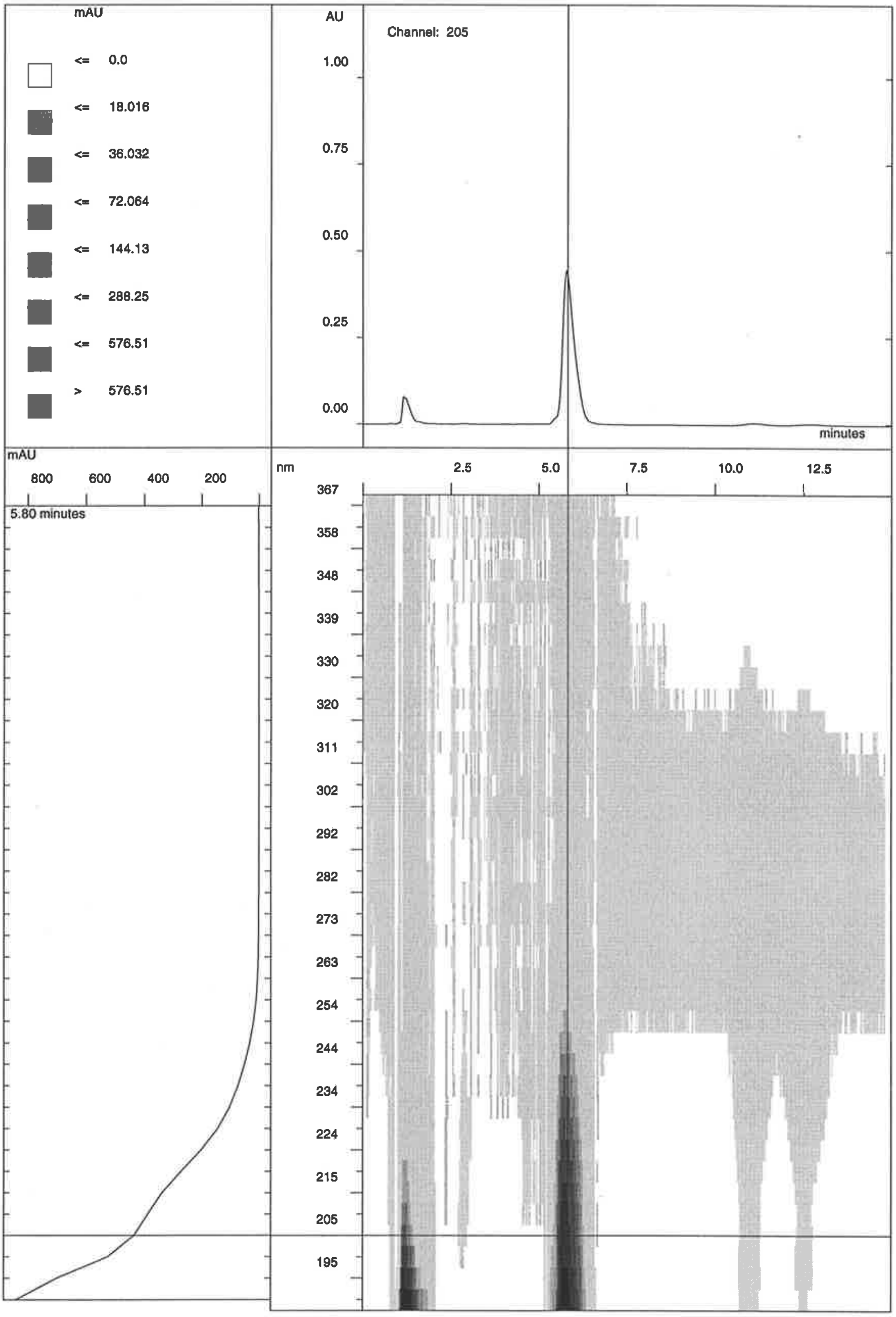
Bifenthrin


AU
<= 0.0
<= 0.0388
<= 0.0775
<= 0.1551
<= 0.3102
<= 0.6203
<= 1.2406
> 1.2406
AU
Channel: 205
2.0
1.5
1.0
0.5
0.0
minutes
AU
2.5
2.0
1.5
1.0
0.5
5.14 minutes
nm
2.5
5.0
7.5
10.0
12.5
367
358
348
339
330
320
311
302
292
282
273
263
254
244
234
224
215
205
195

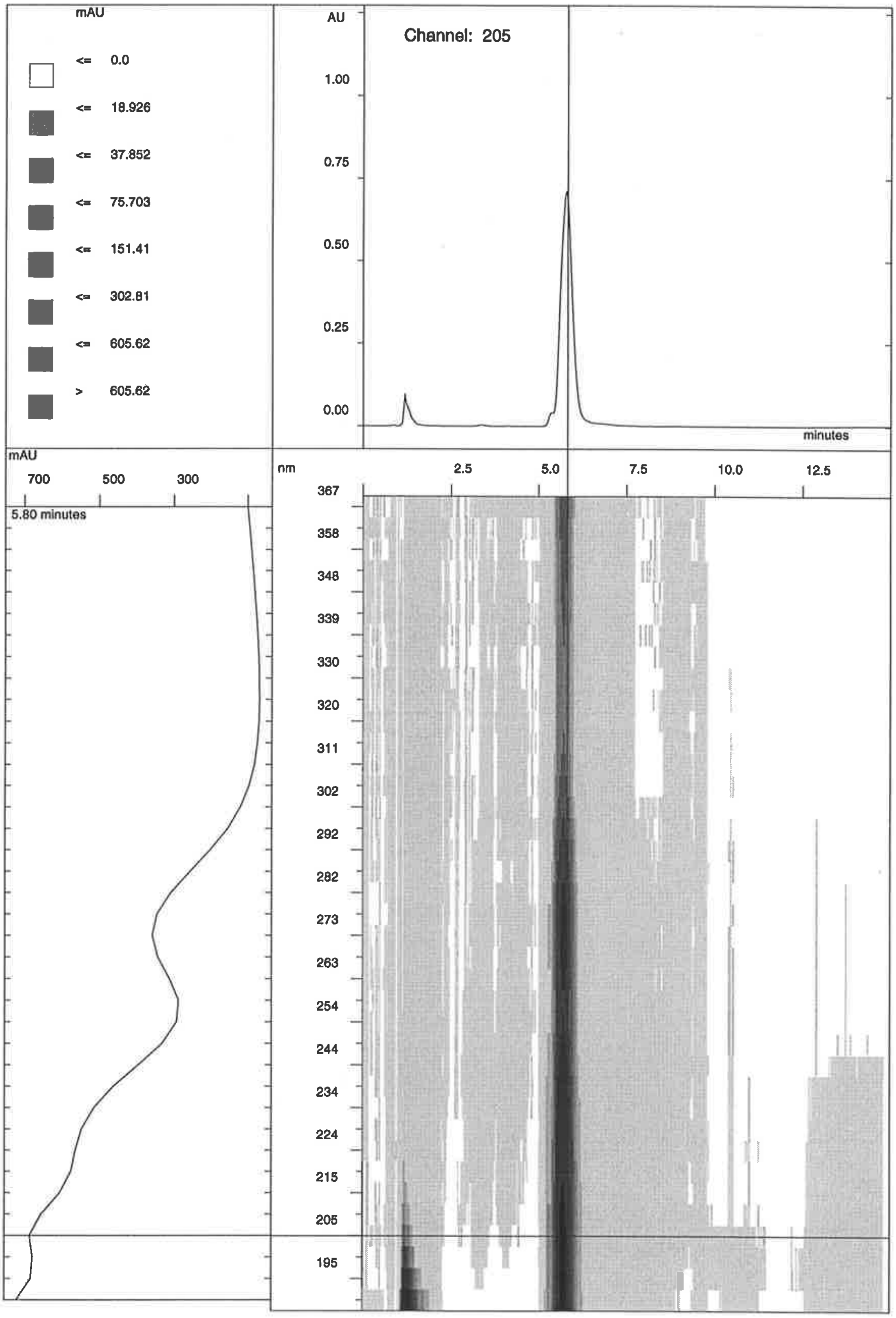
Dichlorvos


mAU
<= 0.0
<= 11.221
<= 22.443
<= 44.886
<= 89.771
<= 179.54
<= 359.09
> 359.09
mAU
Channel: 205
500
250
0
-250
minutes
mAU
250
200
150
100
50
5.98 minutes
nm
2.5
5.0
7.5
10.0
12.5
367
358
348
339
330
320
311
302
292
282
273
263
254
244
234
224
215
205
195

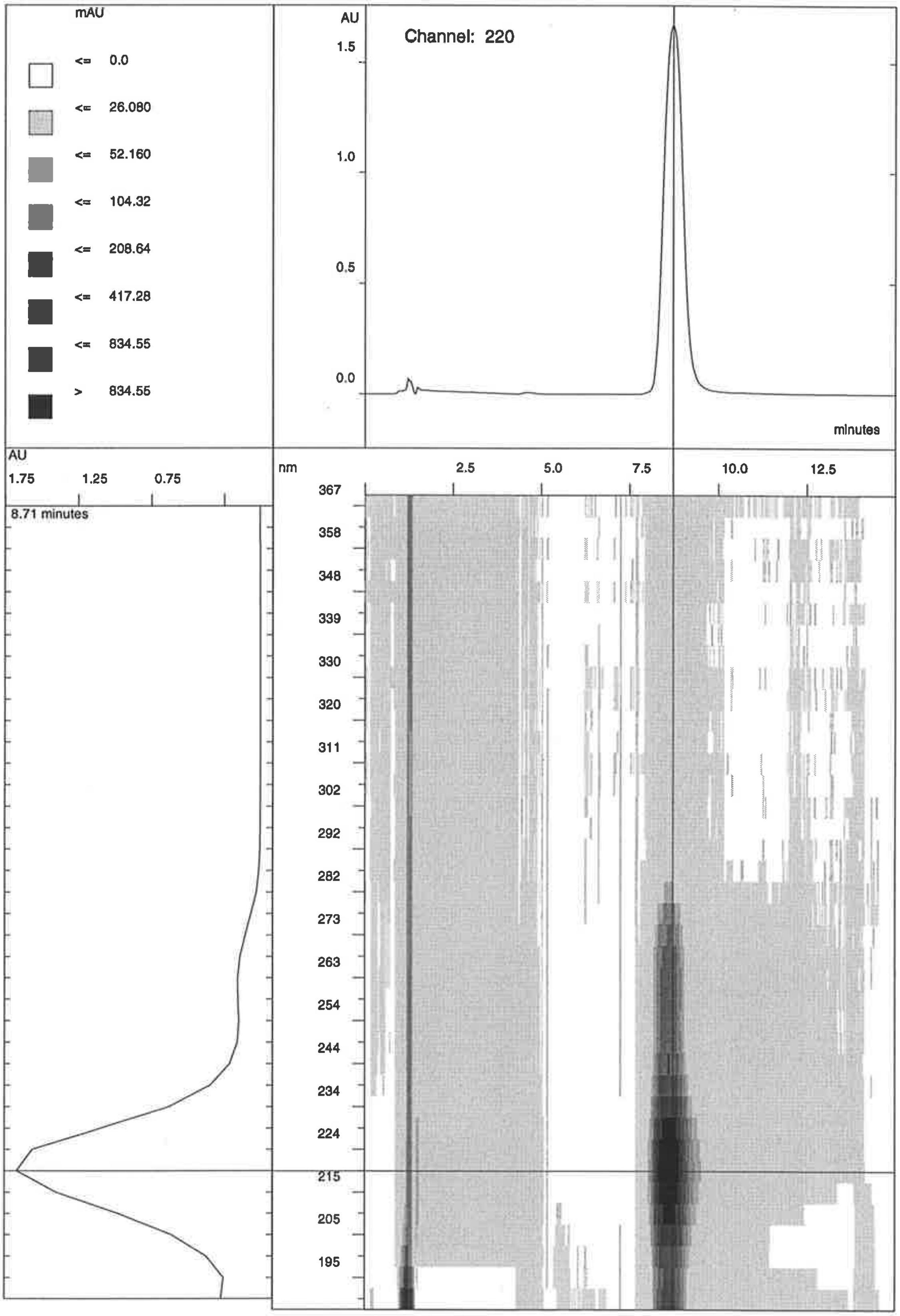
Ethion


mAU
<= 0.0
<= 18.016
<= 36.032
<= 72.064
<= 144.13
<= 288.25
<= 576.51
> 576.51
AU
Channel: 205
1.00
0.75
0.50
0.25
0.00
minutes
mAU
800
600
400
200
5.80 minutes
nm
2.5
5.0
7.5
10.0
12.5
367
358
348
339
330
320
311
302
292
282
273
263
254
244
234
224
215
205
195

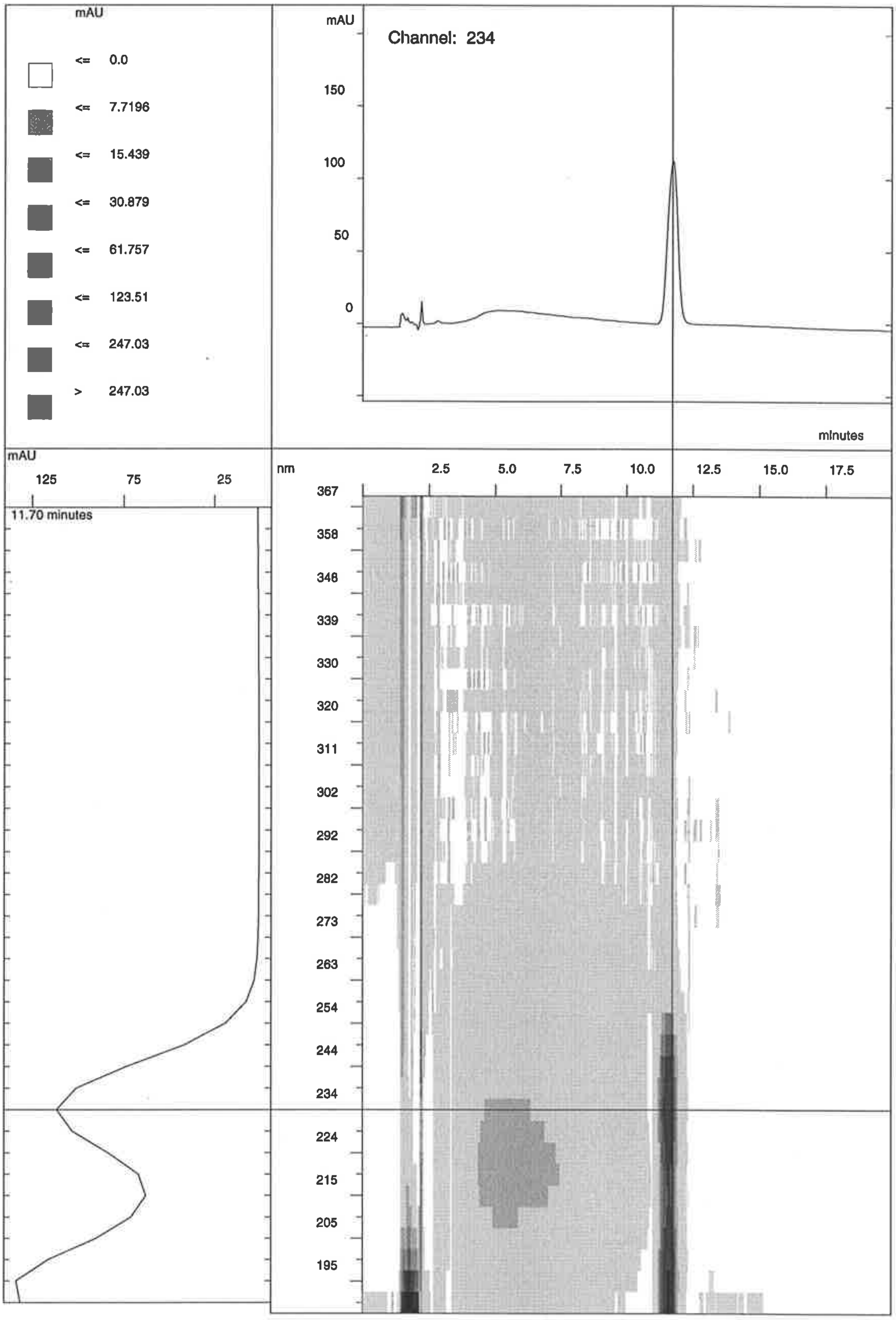
Trifluralin



Atrazine


mAU
<= 0.0
<= 26.080
<= 52.160
<= 104.32
<= 208.64
<= 417.28
<= 834.55
> 834.55
AU
1.5
1.0
0.5
0.0
Channel: 220
minutes
AU
1.75
1.25
0.75
8.71 minutes
nm
2.5
5.0
7.5
10.0
12.5
367
358
348
339
330
320
311
302
292
282
273
263
254
244
234
224
215
205
195

Thiodicarb


mAU
<= 0.0
<= 7.7196
<= 15.439
<= 30.879
<= 61.757
<= 123.51
<= 247.03
> 247.03
mAU
Channel: 234
150
100
50
0
minutes
mAU
125
75
25
11.70 minutes
nm
2.5
5.0
7.5
10.0
12.5
15.0
17.5
367
358
348
339
330
320
311
302
292
282
273
263
254
244
234
224
215
205
195

Appendix 5.1 Dichlorvos sorption by the unsaturated flow method

time = 2160 (s) column diameter = 1.910 (cm)
I = vo*t = 2.513 (cm) or 7.200 (cm^3) water flux at the column in 1.16E-03 (cms^{-1})
I (recovered) = 2.692 (cm) or 7.712 (cm^3) sity (g cm^{-3})= 1.604 mass(g)= ? /100g airdry soil
total amount of dichlorvos incorporated: #VALUE! total mass of salt (g)= #VALUE!

Section No	thickness (cm)	distance (cm)	bulk density (g cm^{-3})	mass wetness (g g^{-1})	volume wetness (cm^3 cm^3)	Integral [mid] (cm)	Integral2 [mid] (cm)
1	0.813	0.41	1.604	0.223	0.357	0.103	0.145
2	0.819	1.22	1.604	0.235	0.377	0.317	0.445
3	0.823	2.04	1.604	0.229	0.368	0.537	0.751
4	0.818	2.86	1.604	0.228	0.365	0.752	1.051
5	0.819	3.68	1.604	0.229	0.367	0.966	1.351
6	0.835	4.51	1.604	0.222	0.357	1.178	1.650
7	0.827	5.34	1.604	0.219	0.351	1.386	1.944
8	0.808	6.16	1.604	0.216	0.346	1.585	2.230
9	0.827	6.98	1.604	0.212	0.340	1.780	2.510
10	0.816	7.80	1.604	0.196	0.314	1.963	2.779
11	0.817	8.61	1.604	0.194	0.311	2.133	3.034
12	0.818	9.43	1.604	0.179	0.287	2.292	3.278
13	0.818	10.25	1.604	0.166	0.266	2.432	3.504
14	0.819	11.07	1.604	0.148	0.237	2.552	3.710
15	0.822	11.89	1.604	0.126	0.203	2.647	3.890
16	0.821	12.71	1.604	0.069	0.110	2.689	4.019
17	0.825	13.53	1.604	0.066	0.105	2.692	4.108
18	0.827	14.36	1.604	0.065	0.105	2.692	4.194
19	0.817	15.18	1.604	0.065	0.104	2.692	4.280
20	0.820	16.00	1.604	0.065	0.105	2.692	4.365

Column length		7.52 = x*	avg.rho	total mass of soil	Wn	theta-n	plane of separation
	16.409	7.52 cm	1.604 g/cm^3	75.389 g	0.0652	0.1046	7.519 cm

time(s) = 2160

Dichlorvos Section No.	Distance (cm)	Content (mg kg^{-1})	Integral A*M*rhodx (mg)	WatAcross (cm^3)	Integral desorbed (mg)	avg C (mg L^{-1})
1	0.41	0.091	0.0003	7.12	0.0019	0.27
2	1.22	0.093	0.0007	6.48	0.0038	0.59
3	2.04	0.175	0.0014	5.86	0.0054	0.92
4	2.86	0.273	0.0024	5.25	0.0066	1.27
5	3.68	0.358	0.0037	4.64	0.0076	1.63
6	4.51	0.753	0.0066	4.03	0.0070	1.73
7	5.34	0.800	0.0097	3.45	0.0062	1.80
8	6.16	1.006	0.0134	2.89	0.0047	1.63
9	6.98	0.999	0.0172	2.33	0.0032	1.37
10	7.80	1.075	0.0212	1.84	0.0014	0.76
11	8.61	0.940	0.0247	1.36	0.0001	0.09
12	9.43	0.903	0.0281	0.93	-0.0010	-1.08
13	10.25	0.879	0.0314	0.55	-0.0021	-3.72
14	11.07	0.848	0.0346	0.24	-0.0030	-12.27
15	11.89	0.766	0.0375	0.01	-0.0036	
16	12.71	0.449	0.0392	0.00	-0.0030	
17	13.53	0.435	0.0409	0.00	-0.0024	
18	14.36	0.376	0.0423	0.00	-0.0016	
19	15.18	0.393	0.0438	0.00	-0.0008	
20	16.00	0.389	0.0452	0.00	0.0000	

total dichlorvos incorporated (mg) = #VALUE! recovery = 0.956

Mn (=Cn*wn+Qn) = 0.628

Mn (incorporated) = #VALUE!

Mn [recovered](mgkg^{-1}) = 0.600

(adsorption and equilibrium solution concentration for lambda > lambda*)

type: Content(mg kg^{-1}) = Cn(mg L^{-1})*w(L kg^{-1}) + Qn(mg kg^{-1})

type: Content(mg kg^{-1}) = a*w(L kg^{-1}) + b

<for Dichlorvos>

Section No.	Y Cont. (mg kg^{-1})	X w(L kg^{-1})	Calc. (mg kg^{-1})	relative error
11	0.940	0.194	0.944	0.004
12	0.903	0.179	0.908	0.006
13	0.879	0.166	0.875	-0.004
14	0.848	0.148	0.830	-0.021
15	0.766	0.126	0.778	0.016
<for graph>		0.25	1.082	
		0.025	0.529	

a	b	2.46	0.468
SEa	SEb	0.25	0.041
r^2	SEy	0.9704	0.013
F	degfrd	98.3	3
SSreg	SSresid	0.02	0.00

Cn =	2.46	(± 0.25)	(mg L^{-1})
Qn =	0.468	(± 0.041)	(mg kg^{-1})
Mn =	0.628	(± 0.013)	(mg kg^{-1})
K_d =	0.1902	(± 0.0358)	(L kg^{-1})

avg. rho	theta-n	plane of separation
1.604 g cm^{-3}	0.1046	7.519 cm

time (s)= 2160

total amount of dichlorvos incorporated: #VALUE!

<for graph>

Section No.	distance (cm)	mass wetness (kg kg^{-1})	volume wetness (m^3 m^{-3})	Dichlorvos-content (mg kg^{-1})	plane of separation for M,Q	plane of separation for theta	theta-n	x>x* Qn (mg kg^{-1})	x>x* Mn (mg kg^{-1})
1	0.41	0.223	0.357	0.091					
2	1.22	0.235	0.377	0.093					
3	2.04	0.229	0.368	0.175					
4	2.86	0.228	0.365	0.273					
5	3.68	0.229	0.367	0.358					
6	4.51	0.222	0.357	0.753					
7	5.34	0.219	0.351	0.800					
8	6.16	0.216	0.346	1.006					
9	6.98	0.212	0.340	0.999					
10	7.80	0.196	0.314	1.075					
11	8.61	0.194	0.311	0.940					
12	9.43	0.179	0.287	0.903					
13	10.25	0.166	0.266	0.879					
14	11.07	0.148	0.237	0.848					
15	11.89	0.126	0.203	0.766					
16	12.71	0.069	0.110	0.449					
17	13.53	0.066	0.105	0.435					
18	14.36	0.065	0.105	0.376					
19	15.18	0.065	0.104	0.393					
20	16.00	0.065	0.105	0.389					
plane of	7.52				0	0			
separation	7.52				1.1	0.362			
for Mn,Qn,	0						0.1046	0.468	0.628
theta-n	17						0.1046	0.468	0.628
space									
for	16								
legend	17								
for Gr(M)	20		0.7	114					
for Gr(total)	15								
for Cn	8.02								
(x>x*)	23.85								
1	0.15								
80	23.85								

Appendix 5.2 Monocrotophos sorption by the unsaturated flow method (R1)

time = 4380 (s) column diameter = 1.910 (cm)
I = vo*t = 2.548 (cm) or 7.300 (cm^3) water flux at the column inlet = 5.82E-04 ($cm\ s^{-1}$)
I (recovered) = 2.098 (cm) or 6.011 (cm^3) density ($g\ cm^3$)= 1.370 mass(g)= ? /100g airdry soil
total amount of monocrotophos incorporated: #VALUE! total mass of salt (g)= #VALUE!

Section No.	thickness (cm)	distance (cm)	bulk density ($g\ cm^{-3}$)	mass wetness ($g\ g^{-1}$)	volume wetness ($cm^3\ cm^{-3}$)	Integral [mid] (cm)	Integral2 [mid] (cm)
1	0.813	0.41	1.370	0.236	0.323	0.089	0.131
2	0.819	1.22	1.370	0.255	0.349	0.279	0.406
3	0.823	2.04	1.370	0.237	0.325	0.471	0.682
4	0.818	2.86	1.370	0.238	0.327	0.654	0.949
5	0.819	3.68	1.370	0.228	0.312	0.831	1.211
6	0.835	4.51	1.370	0.219	0.300	0.999	1.464
7	0.827	5.34	1.370	0.196	0.269	1.149	1.701
8	0.808	6.16	1.370	0.201	0.275	1.287	1.923
9	0.827	6.98	1.370	0.198	0.272	1.427	2.147
10	0.816	7.80	1.370	0.186	0.255	1.558	2.363
11	0.817	8.61	1.370	0.182	0.249	1.680	2.569
12	0.818	9.43	1.370	0.170	0.233	1.792	2.766
13	0.818	10.25	1.370	0.165	0.226	1.896	2.954
14	0.819	11.07	1.370	0.153	0.209	1.989	3.132
15	0.822	11.89	1.370	0.130	0.178	2.063	3.290
16	0.821	12.71	1.370	0.078	0.107	2.095	3.407
17	0.825	13.53	1.370	0.074	0.101	2.096	3.493
18	0.827	14.36	1.370	0.079	0.108	2.097	3.580
19	0.817	15.18	1.370	0.075	0.103	2.099	3.666
20	0.820	16.00	1.370	0.073	0.101	2.098	3.750

Column length	6.74 = x*	avg.rho	total mass of soil	Wn	theta-n	plane of separation
16.409	6.74 cm	1.370 $g\ cm^{-3}$	64.406 g	0.0754	0.1032	6.745 cm

time(s) = 4380

Monocrotophos Section No.	Distance (cm)	Content (mg kg^{-1})	Integral A*M*rhodx (mg)	WatAcross (cm^3)	Integral desorbed (mg)	avg C (mg L^{-1})
1	0.41	0.000	0.0000	5.50	0.0091	1.65
2	1.22	0.000	0.0000	4.92	0.0182	3.70
3	2.04	0.000	0.0000	4.40	0.0274	6.22
4	2.86	(.357)	0.0011	3.88	0.0353	9.11
5	3.68	0.826	0.0038	3.39	0.0418	12.35
6	4.51	2.075	0.0106	2.91	0.0443	15.20
7	5.34	3.634	0.0224	2.52	0.0417	16.55
8	6.16	5.038	0.0384	2.12	0.0348	16.37
9	6.98	4.997	0.0546	1.72	0.0277	16.09
10	7.80	(4.681)	0.0696	1.37	0.0218	15.96
11	8.61	4.570	0.0842	1.03	0.0163	15.85
12	9.43	4.151	0.0976	0.72	0.0121	16.71
13	10.25	4.204	0.1111	0.44	0.0077	17.68
14	11.07	4.103	0.1243	0.19	0.0036	19.44
15	11.89	3.804	0.1365	0.01	0.0005	
16	12.71	3.013	0.1462	0.00	0.0000	
17	13.53	2.846	0.1555	0.01	-0.0001	
18	14.36	2.951	0.1650	0.00	-0.0004	
19	15.18	2.809	0.1740	0.00	-0.0003	
20	16.00	2.740	0.1829	0.00	0.0000	

total monocrotophos incorporated (n #VALUE! recovery = 0.948

Mn (=Cn*wn+Qn) = 2.994

Mn (incorporated) = #VALUE!

Mn [recovered](mg/kg) = 2.839

(adsorption and equilibrium solution concentration for lambda > lambda*)

type: Content(mmolc/kg) = Cn(mg L^{-1})*w(L kg) + Qn(mg kg^{-1})

type: Content(mg kg^{-1}) = a*w(L kg^{-1}) + b

<for Monocrotophos>

Section No.	Y Cont. (mg kg^{-1})	X w(L kg^{-1})	Calc. (mg kg^{-1})	relative error
11	4.570	0.182	4.465	-0.023
12	4.151	0.170	4.307	0.038
13	4.204	0.165	4.233	0.007
14	4.103	0.153	4.063	-0.010
15	3.804	0.130	3.746	-0.015
16	3.013	0.078	3.032	0.006
<for graph>		0.250	5.409	
		0.025	2.298	

a	b	13.83	1.952
SEa	SEb	1.21	0.182
r^2	SEy	0.9704	0.102
F	degfrd	130.9	4
SSreg	SSresid	1.37	0.04

Cn =	13.83	(± 1.21)	(mg L^{-1})
Qn =	1.952	(± 0.182)	(mg kg^{-1})
Mn =	2.994	(± 0.102)	(mg kg^{-1})
K_d =	0.1412	(± 0.0255)	(L kg^{-1})

avg. rho	theta-n	plane of separation
1.370 g cm^{-3}	0.1032	6.745 cm

time (s)= 4380

total amount of monocrotophos incorporated: #VALUE!

					<for graph>				
Section No.	distance (cm)	mass wetness (kg kg^{-1})	volume wetness (m3 m^{-3})	Monocroto- content (mg kg^{-1})	plane of separation for M,Q	plane of separation for theta	theta-n	x>x* Qn (mg kg^{-1})	x>x* Mn (mg kg^{-1})
1	0.41	0.236	0.323	0.000					
2	1.22	0.255	0.349	0.000					
3	2.04	0.237	0.325	0.000					
4	2.86	0.238	0.327	0.357					
5	3.68	0.228	0.312	0.826					
6	4.51	0.219	0.300	2.075					
7	5.34	0.196	0.269	3.634					
8	6.16	0.201	0.275	5.038					
9	6.98	0.198	0.272	4.997					
10	7.80	0.186	0.255	4.681					
11	8.61	0.182	0.249	4.570					
12	9.43	0.170	0.233	4.151					
13	10.25	0.165	0.226	4.204					
14	11.07	0.153	0.209	4.103					
15	11.89	0.130	0.178	3.804					
16	12.71	0.078	0.107	3.013					
17	13.53	0.074	0.101	2.846					
18	14.36	0.079	0.108	2.951					
19	15.18	0.075	0.103	2.809					
20	16.00	0.073	0.101	2.740					
plane of	6.74				0	0			
separatior	6.74				5.47	0.335			
for Mn,Q	0						0.1032	1.952	2.994
theta-n	17						0.1032	1.952	2.994
space									
for	16								
legend	17								
for Gr(	20		0.7	114					
for Gr(t	15								
for Cn	7.24								
(x>x*)	23.85								
1	0.15								
80	23.85								

Appendix 5.3 Monocrotophos sorption by the unsaturated flow method (R2)

time = 4574 (s) column diameter = 1.910 (cm)

I = vo*t = 2.661 (cm) or 7.623 (cm^3) water flux at the column inlet = 5.82E-04 ($cm\ s^{-1}$)

I (recovered) = 2.833 (cm) or 8.117 (cm^3) density ($g\ cm^{-3}$)= 1.404 mass(g)= ? /100g airdry soil

total amount of monocrotophos incorporated: #VALUE! total mass of salt (g)= #VALUE!

Section No.	thickness (cm)	distance (cm)	bulk density ($g\ cm^{-3}$)	mass wetness ($g\ g^{-1}$)	volume wetness ($cm^3\ cm^{-3}$)	Integral [mid] (cm)	Integral2 [mid] (cm)
1	0.813	0.41	1.404	0.274	0.384	0.117	0.156
2	0.819	1.22	1.404	0.264	0.371	0.347	0.464
3	0.823	2.04	1.404	0.253	0.356	0.566	0.763
4	0.818	2.86	1.404	0.275	0.386	0.792	1.067
5	0.819	3.68	1.404	0.248	0.348	1.014	1.368
6	0.835	4.51	1.404	0.247	0.347	1.221	1.655
7	0.827	5.34	1.404	0.252	0.353	1.433	1.946
8	0.808	6.16	1.404	0.239	0.336	1.636	2.228
9	0.827	6.98	1.404	0.230	0.323	1.826	2.497
10	0.816	7.80	1.404	0.236	0.331	2.015	2.765
11	0.817	8.61	1.404	0.215	0.302	2.195	3.023
12	0.818	9.43	1.404	0.214	0.301	2.363	3.270
13	0.818	10.25	1.404	0.202	0.284	2.523	3.509
14	0.819	11.07	1.404	0.178	0.249	2.662	3.727
15	0.822	11.89	1.404	0.154	0.216	2.775	3.918
16	0.821	12.71	1.404	0.076	0.107	2.828	4.050
17	0.825	13.53	1.404	0.068	0.096	2.832	4.134
18	0.827	14.36	1.404	0.068	0.096	2.832	4.213
19	0.817	15.18	1.404	0.070	0.099	2.833	4.293
20	0.820	16.00	1.404	0.067	0.094	2.833	4.371

Column length	8.01 = x*	avg.rho	total mass of soil	Wn	theta-n	plane of separation
16.409	8.01 cm	1.404 $g\ cm^{-3}$	66.009 g	0.0685	0.0962	8.012 cm

time(s) = 4574

Monocrotophos Section No.	Distance (cm)	Content (mg kg^{-1})	Integral A*M*rhodx (mg)	WatAcross (cm^3)	Integral desorbed (mg)	avg C (mg L^{-1})
1	0.41	0.000	0.0000	7.45	0.0071	0.95
2	1.22	0.000	0.0000	6.80	0.0142	2.09
3	2.04	0.084	0.0003	6.19	0.0211	3.40
4	2.86	0.175	0.0009	5.51	0.0276	5.01
5	3.68	0.354	0.0020	4.92	0.0335	6.82
6	4.51	0.776	0.0046	4.32	0.0382	8.85
7	5.34	0.674	0.0069	3.71	0.0431	11.63
8	6.16	2.376	0.0146	3.15	0.0424	13.46
9	6.98	2.807	0.0239	2.62	0.0403	15.39
10	7.80	3.966	0.0369	2.07	0.0344	16.61
11	8.61	4.284	0.0510	1.59	0.0274	17.25
12	9.43	4.253	0.0650	1.11	0.0205	18.50
13	10.25	4.379	0.0794	0.67	0.0132	19.73
14	11.07	3.783	0.0919	0.31	0.0078	25.39
15	11.89	3.599	0.1038	0.03	0.0031	
16	12.71	2.676	0.1126	0.00	0.0014	
17	13.53	2.633	0.1214	0.00	-0.0002	
18	14.36	2.170	0.1286	0.00	-0.0002	
19	15.18	2.217	0.1359	0.00	-0.0004	
20	16.00	2.040	0.1426	0.00	0.0000	

total monocrotophos incorporated (m #VALUE!   recovery = 0.838

Mn (=Cn*wn+Qn) = 2.579

Mn (incorporated) = #VALUE!

Mn [recovered](mg kg^{-1}) = 2.160

(adsorption and equilibrium solution concentration for lambda > lambda*)

type: Content(mg kg^{-1}) = Cn(mg L^{-1})*w(L kg^{-1}) + Qn(mg kg^{-1})

type: Content(mg kg^{-1}) = a*w(L/kg) + b

<for monocrotophos (R2)>

Section No.	Y Cont. (mg kg^{-1})	X w(L kg^{-1})	Calc. (mg kg^{-1})	relative error
11	4.284	0.215	4.329	0.010
12	4.253	0.214	4.319	0.016
13	4.379	0.202	4.174	-0.047
14	3.783	0.178	3.884	0.027
15	3.599	0.154	3.600	0.000
16	2.676	0.076	2.667	-0.003
<for graph>		0.25	4.749	
		0.025	2.059	

a	b	11.95	1.760
SEa	SEb	1.02	0.183
r^2	SEy	0.9718	0.121
F	degfrd	137.7	4
SSreg	SSresid	2.02	0.06

Cn =	11.95	(± 1.02)	(mg L^{-1})
Qn =	1.760	(± 0.183)	(mg kg^{-1})
Mn =	2.579	(± 0.121)	(mg kg^{-1})
K_d =	0.1473	(± 0.0279)	(L kg^{-1})

theta-n plane of separation

1.404 g cm^{-3} 0.0962 8.012 cm

time (s)= 4574

total amount of monocrotophos incorporated: #VALUE!

Section No.	distance (cm)	mass wetness (kg kg^{-1})	volume wetness (m^3 m^{-3})	Monocroto- content (mg kg^{-1})	<for graph> plane of separation for M,Q	plane of separation for theta	theta-n	x>x* Qn (mg kg^{-1})	x>x* Mn (mg kg^{-1})
1	0.41	0.274	0.384	0.000					
2	1.22	0.264	0.371	0.000					
3	2.04	0.253	0.356	0.084					
4	2.86	0.275	0.386	0.175					
5	3.68	0.248	0.348	0.354					
6	4.51	0.247	0.347	0.776					
7	5.34	0.252	0.353	0.674					
8	6.16	0.239	0.336	2.376					
9	6.98	0.230	0.323	2.807					
10	7.80	0.236	0.331	3.966					
11	8.61	0.215	0.302	4.284					
12	9.43	0.214	0.301	4.253					
13	10.25	0.202	0.284	4.379					
14	11.07	0.178	0.249	3.783					
15	11.89	0.154	0.216	3.599					
16	12.71	0.076	0.107	2.676					
17	13.53	0.068	0.096	2.633					
18	14.36	0.068	0.096	2.170					
19	15.18	0.070	0.099	2.217					
20	16.00	0.067	0.094	2.040					
plane of	8.01				0	0			
separation	8.01				4.63	0.4			
for Mn,Qn	0						0.0962	1.760	2.579
theta-n	17						0.0962	1.760	2.579
space									
for	16								
legend	17								
for Gr(M	20		0.7	114					
for Gr(tot	15								
for Cn	8.51								
(x>x*)	23.85								
1	0.15								
80	23.85								

Appendix 5.4 Monocrotophos sorption by the unsaturated flow method at high initial water content

time = 3600 (s) column diameter = 1.910 (cm)

I = vo*t = 2.094 (cm) or 6.000 (cm3) water flux at the column inlet = 5.82E-04 (cm s^{-1})

I (recovered) = 1.840 (cm) or 5.273 (cm3) density (g cm^{-3})= 1.632 mass(g)= ? /100g airdry soil

total amount of monocrotophos incorporated: #VALUE! total mass of salt (g)= #VALUE!

Section No.	thickness (cm)	distance (cm)	bulk density (g cm^{-3})	mass wetness (g g^{-1})	volume wetness (cm3 cm^{-3})	Integral [mid] (cm)	Integral2 [mid] (cm)
1	0.813	0.41	1.632	0.264	0.431	0.098	0.175
2	0.819	1.22	1.632	0.255	0.415	0.289	0.520
3	0.823	2.04	1.632	0.252	0.411	0.472	0.860
4	0.818	2.86	1.632	0.236	0.384	0.643	1.186
5	0.819	3.68	1.632	0.230	0.375	0.799	1.497
6	0.835	4.51	1.632	0.233	0.380	0.954	1.809
7	0.827	5.34	1.632	0.224	0.365	1.107	2.119
8	0.808	6.16	1.632	0.201	0.329	1.235	2.403
9	0.827	6.98	1.632	0.200	0.326	1.348	2.670
10	0.816	7.80	1.632	0.202	0.329	1.461	2.939
11	0.817	8.61	1.632	0.192	0.313	1.568	3.201
12	0.818	9.43	1.632	0.179	0.293	1.661	3.449
13	0.818	10.25	1.632	0.159	0.259	1.731	3.674
14	0.819	11.07	1.632	0.160	0.262	1.789	3.887
15	0.822	11.89	1.632	0.130	0.213	1.828	4.082
16	0.821	12.71	1.632	0.117	0.190	1.838	4.247
17	0.825	13.53	1.632	0.117	0.191	1.839	4.404
18	0.827	14.36	1.632	0.118	0.192	1.841	4.563
19	0.817	15.18	1.632	0.116	0.190	1.842	4.720
20	0.820	16.00	1.632	0.113	0.185	1.840	4.873

Column length			avg.rho	total mass of soil	Wn	theta-n	plane of separation	
	4.37	= x*						
16.409	4.37	cm	1.632 g cm^{-3}	76.715 g	0.1162	0.1896	4.372	cm

time(s) = 3600

Monocrotophos Section No.	Distance (cm)	Content (mg kg^{-1})	Integral A*M*rhodx (mg)	WatAcross (cm^3)	Integral desorbed (mg)	avg C (mg L^{-1})
1	0.41	0.000	0.0000	4.71	0.0092	1.95
2	1.22	0.426	0.0016	4.18	0.0168	4.01
3	2.04	1.393	0.0070	3.66	0.0207	5.66
4	2.86	(1.619)	0.0132	3.20	0.0237	7.41
5	3.68	2.119	0.0213	2.77	0.0249	8.99
6	4.51	2.942	0.0328	2.31	0.0228	9.87
7	5.34	3.453	0.0461	1.89	0.0188	9.91
8	6.16	3.525	0.0594	1.57	0.0146	9.27
9	6.98	3.360	0.0724	1.25	0.0109	8.74
10	7.80	(3.245)	0.0848	0.92	0.0077	8.38
11	8.61	3.221	0.0971	0.64	0.0047	7.33
12	9.43	3.135	0.1091	0.39	0.0019	4.82
13	10.25	2.920	0.1203	0.23	0.0000	-0.19
14	11.07	2.986	0.1317	0.06	-0.0022	-36.15
15	11.89	2.649	0.1419	0.01	-0.0031	
16	12.71	2.372	0.1510	0.01	-0.0030	
17	13.53	2.213	0.1595	0.00	-0.0022	
18	14.36	2.207	0.1681	-0.01	-0.0014	
19	15.18	2.224	0.1766	-0.01	-0.0007	
20	16.00	2.231	0.1851	0.01	0.0000	

total monocrotophos incorporated #VALUE! recovery = 0.989

Mn (=Cn*wn+Qn) = 2.440

Mn (incorporated) = #VALUE!

Mn [recovered](mg kg^{-1}) = 2.413

(adsorption and equilibrium solution concentration for lambda > lambda*)

type: Content(mg/kg) = Cn(mg L^{-1})*w(L kg^{-1}) + Qn(mmolc kg^{-1})

type: Content(mg kg^{-1}) = a*w(L kg^{-1}) + b

<for monocrotophos>

Section No.	Y Cont. (mg kg^{-1})	X w(L kg^{-1})	Calc. (mg kg^{-1})	relative error
11	3.221	0.192	3.271	0.015
12	3.135	0.179	3.137	0.001
13	2.920	0.159	2.908	-0.004
14	2.986	0.160	2.926	-0.020
15	2.649	0.130	2.597	-0.020
16	2.372	0.117	2.445	0.031
<for graph>		0.25	3.913	
		0.025	1.436	

a	b	11.01	1.161
SEa	SEb	0.94	0.149
r^2	SEy	0.9716	0.060
F	degfrd	137.1	4
SSreg	SSresid	0.49	0.01

Cn =	11.01	(± 0.94)	(mg L^{-1})
Qn =	1.161	(± 0.149)	(mg kg^{-1})
Mn =	2.440	(± 0.060)	(mg kg^{-1})
K_d =	0.1055	(± 0.0225)	(L kg^{-1})

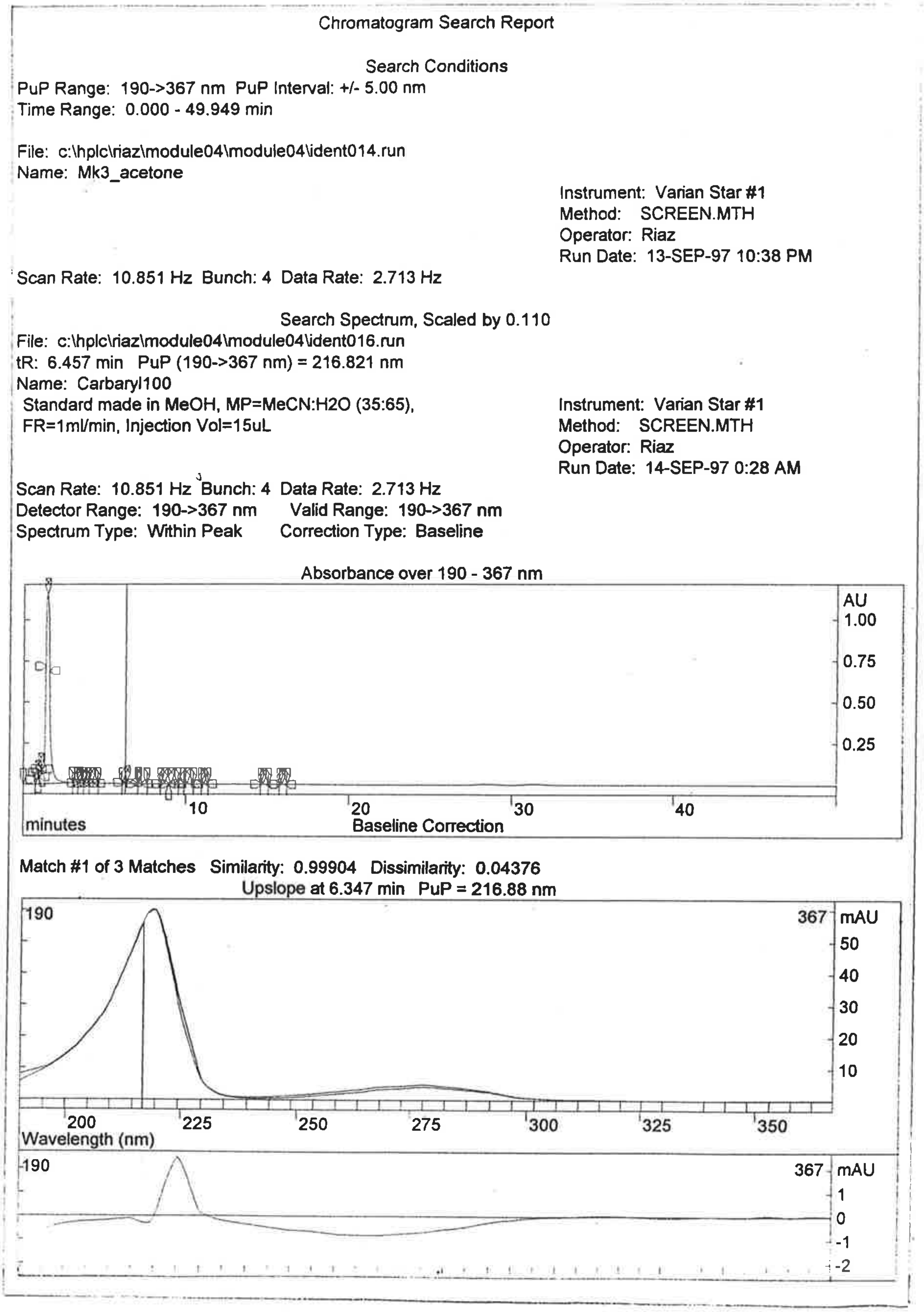
avg. rho	theta-n	plane of separation
1.632 g cm^{-3}	0.1896	4.372 cm

time (s)= 3600

total amount of monocrotophos incorporated: #VALUE!

Section No.	distance (cm)	mass wetness (kg kg^{-1})	volume wetness (m3 m^{-3})	Monocroto- content (mg kg^{-1})	<for graph> plane of separation for M,Q	plane of separation for theta	theta-n	x>x* Qn (mg kg^{-1})	x>x* Mn (mg kg^{-1})
1	0.41	0.264	0.431	0.000					
2	1.22	0.255	0.415	0.426					
3	2.04	0.252	0.411	1.393					
4	2.86	0.236	0.384	1.619					
5	3.68	0.230	0.375	2.119					
6	4.51	0.233	0.380	2.942					
7	5.34	0.224	0.365	3.453					
8	6.16	0.201	0.329	3.525					
9	6.98	0.200	0.326	3.360					
10	7.80	0.202	0.329	3.245					
11	8.61	0.192	0.313	3.221					
12	9.43	0.179	0.293	3.135					
13	10.25	0.159	0.259	2.920					
14	11.07	0.160	0.262	2.986					
15	11.89	0.130	0.213	2.649					
16	12.71	0.117	0.190	2.372					
17	13.53	0.117	0.191	2.213					
18	14.36	0.118	0.192	2.207					
19	15.18	0.116	0.190	2.224					
20	16.00	0.113	0.185	2.231					
plane of	4.37				0	0			
separation	4.37				3.51	0.408			
for Mn,Qn,	0						0.1896	1.161	2.440
theta-n	17						0.1896	1.161	2.440
space									
for	16								
legend	17								
for Gr(M)	20		0.7	114					
for Gr(tota	15								
for Cn	4.87								
(x>x*)	23.85								
1	0.15								
80	23.85								

Appendix-7.1 High performance liquid chromatogram search report for carbaryl in contaminated soil (MK3) from Pakistan using polydiode array detector (PDA)



Chromatogram Search Report

Search Conditions

PuP Range: 190->367 nm PuP Interval: +/- 5.00 nm
Time Range: 0.000 - 49.949 min

File: c:\hplc\riaz\module04\module04\ident014.run
Name: Mk3_acetone

Instrument: Varian Star #1
Method: SCREEN.MTH
Operator: Riaz
Run Date: 13-SEP-97 10:38 PM

Scan Rate: 10.851 Hz Bunch: 4 Data Rate: 2.713 Hz

Search Spectrum, Scaled by 0.110
File: c:\hplc\riaz\module04\module04\ident016.run
tR: 6.457 min PuP (190->367 nm) = 216.821 nm
Name: Carbaryl100
Standard made in MeOH, MP=MeCN:H2O (35:65),
FR=1ml/min, Injection Vol=15uL

Instrument: Varian Star #1
Method: SCREEN.MTH
Operator: Riaz
Run Date: 14-SEP-97 0:28 AM

Scan Rate: 10.851 Hz Bunch: 4 Data Rate: 2.713 Hz
Detector Range: 190->367 nm Valid Range: 190->367 nm
Spectrum Type: Within Peak Correction Type: Baseline

Absorbance over 190 - 367 nm

Match #1 of 3 Matches Similarity: 0.99904 Dissimilarity: 0.04376
Upslope at 6.347 min PuP = 216.88 nm

```
                    Page 1 - Chromatogram Search Report

Match  Similarity  Dissimilarity  PuP (nm)  Event       tR (min)
-----  ----------  -------------  --------  -----       -------
  1     0.99904     0.04376       216.879   Upslope       6.347
  2     0.99886     0.04783       216.810   Peak Apex     6.463
  3     0.99854     0.05402       216.808   Downslope     6.598

                           Search Conditions
PuP Range:  190->367 nm  PuP Interval: +/- 5.00 nm
Time Range:  0.000 - 49.949 min
Maximum Dissimilarity:  0.30

File:  c:\hplc\riaz\module04\module04\ident014.run
Name:  Mk3_acetone
                                               Instrument:  Varian Star #1
                                               Method:    SCREEN.MTH
                                               Operator:  Riaz
                                               Run Date:  13-SEP-97 10:38 PM
Scan Rate:  10.851 Hz  Bunch: 4  Data Rate:  2.713 Hz

                            Search Spectrum
File:  c:\hplc\riaz\module04\module04\ident016.run
tR:  6.457 min   PuP (190->367 nm) = 216.821 nm
Name:  Carbaryl100
Standard made in MeOH, MP=MeCN:H2O (35:65),   Instrument:  Varian Star #1
FR=1ml/min, Injection Vol=15uL                Method:    SCREEN.MTH
                                               Operator:  Riaz
                                               Run Date:  14-SEP-97 0:28 AM
Scan Rate:  10.851 Hz  Bunch: 4  Data Rate:  2.713 Hz
Detector Range:  190->367 nm      Valid Range:  190->367 nm
Spectrum Type:  Within Peak       Correction Type:  Baseline
```

Appendix-7.2 X-ray diffraction spectrum of carbaryl contaminated soil (MK3) from Pakistan