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Transport of Pesticides through Soil Columns from Al-Ain Area, United Arab Emirates

Huda Ateeq Al Hassani

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**United Arab Emirates University
Deanship of Graduate Studies
M. Sc. Program in Environmental Science**

**Transport of Pesticides through Soil
Columns from Al-Ain Area,
United Arab Emirates**

By

Huda Ateeq Al Hassani

**A thesis submitted to United Arab Emirates University in
partial fulfilment of the requirements for the
degree of M. Sc. in Environmental Science**

2004



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By

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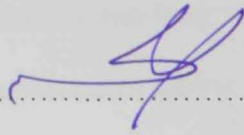
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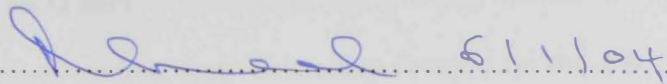
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ABSTRACT

Proper management of pesticides application in the UAE is greatly lacking, causing waste of resources and environmental concerns due to the excessive use of these chemicals. It has been reported that the rate of pesticides use in UAE reaches about 10 kg/hectare/yr, posing a potential threat to the quality of water in underlying aquifers. Little, however, is known about the mobility of applied pesticides in the UAE subsurface environment and the impact of these pesticides on soil and groundwater quality.

The aim of this study was to gain an understanding of the fate and mobility of pesticides in the UAE subsurface environment. This study focused on the role of mechanisms like advection, dispersion, degradation, and sorption that affect pesticides transport in the soil. The study was conducted in the laboratory using soil packed columns. Batch experiments were also conducted to assess the impact of some of the above mechanisms.

In this study, three pesticides that are commonly used in UAE were employed (i.e. dimethoate, metalaxyl and cymoxanil). Two sandy soils from Al Foah and Abu Samra areas in Al Ain district, Abu Dhabi Emirate were collected and utilized in the study. Both soils are alkaline with similar texture but have different organic matter content that ranges between 0.2% to 0.8%. Results showed that the pesticides are subject to various extent of degradation with cymoxanil undergoes the highest rate especially at high pH values. The study revealed that there was no influence of light and indigenous microorganisms on the degradation of the used pesticides within an experimental time of 3 days.

Pesticides sorption to soil is increased by the increased soil organic matter content with dimethoate and metalaxyl are being more readily sorbed on soil with high organic matter compared to sorption on soil with lower organic matter.

Pesticides sorption is also affected by the compound hydrophobicity with metalaxyl being more sorbed than dimethoate on a given soil. Both dimethoate and metalaxyl sorb linearly on soil with low organic matter, while metalaxyl undergoes nonlinear sorption on the soil with high organic matter. Cymoxanil sorption to both soils was not evaluated due to the loss of the chemical from solution by hydrolysis.

Generated breakthrough curves (BTCs) for the ideal tracer (bromide) and the employed pesticides were analysed using the nonlinear least-squares model (CXTFIT2.0). BTCs obtained for bromide were used to describe the dispersive behaviour of the two soils. It was found that the dispersivity of Abu Samra soil is 0.12 cm while that of Al Foah 0.34 cm. Generated BTCs for the used pesticides were analyzed by moment analysis to determine the retardation coefficient (R) and the first-order degradation rate constant (λ). Simulation of BTCs using the determined coefficients showed that the equilibrium model adequately described transport of dimethoate in Abu Samra soil, but failed to describe breakthrough data for metalaxyl. A good description of the BTC for metalaxyl we obtained when the two-site sorption nonequilibrium model was used. The mass-transfer rate coefficient for metalaxyl can be predicted using empirical relationships reported in the literature.

Comparison between transport parameters determined by moment analysis and those determined by curve fitting showed that the use of moment analysis is sufficient to obtain R and λ . It was also observed that the values of the sorption distribution coefficient (K_d) determined from the column studies were 2-10 times higher than their counterparts obtained from batch experiments. This study also revealed that there appears to be an enhanced degradation of the pesticides in a soil environment as compared to their hydrolysis in the aqueous solution.

To my great mother

with love

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ABBREVIATIONS

- a = Adsorption constant related to the binding energy
- A = Cross-sectional area
- b = The maximum amount of solute that can be absorbed by the solid
- C = Concentration
- C_e = Concentration of the solute in the aqueous phase
- C_o = Solute concentration in the influent solution
- D = Hydrodynamic dispersion coefficient
- D_{e^*} = Effective diffusion coefficient in the soil matrix
- DI water = Deionized water
- EC = European Community
- F = Fraction of sorbent for which sorption is instantaneous
- FAO = UN Food and Agriculture Organization
- FIFRA = Federal Insecticide, Fungicide, and Rodenticide Act
- HPLC = High performance liquid chromatography
- IC = Ion Chromatography
- k = First-order mass-transfer coefficient
- K and n = Freundlich constants
- K_d = Linear sorption distribution coefficient.
- K_H = Henry's Constant
- K_{oc} = Organic carbon based coefficient
- L = Column length
- M_o = Temporal moments from concentration breakthrough curve (area under the curve)
- OM = Organic matter

PAHO= Pan America Health Organization

Q = Flow rate

R = Retardation coefficient

r^2 = Correlation coefficient

S = Solubility

S/W = Soil/Water ratio

S_2 = Average sorbed concentration in the rate-limited domain

S_e = Amount of a solute sorbed onto the solid

T = Pore Volume

t = Travel time

$t_{1/2}$ = Field dissipation half-life

t_0 = Injection time

T_0 = Pore Volume Injected

US EPA = US Environmental Protection Agency

V_{total} = Total volume of the column.

v = Pore-water velocity

W_{empty} = Weight of column empty

WHO = World Health Organization

W_{packed} = Weight before saturation

W_{packed} = Weight of the packed column

W_{sat} = Weight of the saturated column

x = Distance

x = Distance

θ = Volumetric water content

θ = Moisture content

ρ = Soil bulk density

β and ω = Dimensionless parameters that specify the degree of nonequilibrium

α = Dispersivity of the soil

λ = Combined first-order degradation rate constant that accounts for degradation of solute in both liquid and solid phases

λ_l = First-order hydrolysis rate constant in the liquid phase

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Only 3% of all water on earth is fresh water and about 80% of this is unavailable as it is present as polar ice. This means that less than 1% of all water is potentially available and about 95% of this is present as groundwater. The remaining 5% (less than 0.05% of total water on earth) is surface fresh water in rivers, lakes, atmosphere, and soil moisture (Mandl et al., 1994).

Over the years, contamination of groundwater has been a major concern worldwide. Contaminants are introduced into the subsurface environment from various sources including domestic, agricultural and industrial activities. Contaminants introduced through agricultural activities are ranked number three in the United States in terms of their frequency of causing major threats to groundwater quality (Fetter, 1993). Among contaminants, nitrates and pesticides are considered the most critical ones (US EPA, 1990).

Once groundwater is contaminated, analyzing the problem and providing alternative water supplies can be quite expensive. Since the discovery in 1979 of aldicarb in Long Island groundwater, for example, more than \$3 million has been spent measuring aldicarb concentrations in Long Island wells (Trautmann et al., website 1.1). Moreover, activated carbon units have been installed in more than 2,500 affected households, and plans were made to replace individual wells with expensive community water supply systems (Trautmann et al., website 1.1). These huge expenses have helped to define and treat the problem, yet have not corrected the underlying groundwater contamination.

Another possible consequence of pesticide contamination of groundwater is losing the use of a particular pesticide. For example, aldicarb may no longer be used on Long Island. Other compounds such as DBCP and EDB (ethylene dibromide) were banned completely from agricultural use in the United States after their discovery in groundwater. Of the forty-six pesticides recently found in groundwater in different regions of the United States, twelve are no longer available for agricultural use (Trautmann et al., website 1.1).

Cleanup of groundwater contaminated by pesticides often is impossible, and the contamination may last for many years. The low microbial activity in groundwater causes pesticide degradation to occur more slowly than at the soil surface. The slow movement of groundwater means that it may take decades for the contaminated water to flow beyond the affected wells. Even determining which wells will be affected and for how long is a difficult problem, necessitating expensive long-range monitoring. Due to the potential groundwater contamination with commonly used pesticides, efforts have been directed in the last decade towards producing new pesticides that can be applied in small quantities and yet give good pest-resistance and are degradable.

Pesticides are widely used in the United Arab Emirates (UAE) and remain an essential component of crop production and control of pests. Although there is an increased emphasis on reducing inputs when feasible, over 90% of the acreage now used for major fruit and vegetable crops in the UAE continue to be treated with various classes of pesticides (Kaakeh et al., 2004). Proper management of pesticides application in the UAE is greatly lacking, causing a waste of resources and environmental concerns due to the excessive use of these chemicals.

Protection of groundwater resources from pesticides contamination in UAE is necessary since almost all the water consumed for irrigation comes from underlying

aquifers. Little also is known about the mobility of applied pesticides in the UAE subsurface environment and the impact of these pesticides on soil and groundwater quality. It is well established that water is one of the primary media in which pesticides are transported from application areas to other locations. However, there is no consensus yet of the major mechanisms that affect the transport of pesticides in the UAE subsurface environment.

Successful prediction of pesticides transport in the subsurface environment greatly depends on understanding the role of transfer and transformation processes controlling their movement. Research suggests that the movement of pesticides in the environment is complex, with transfer mechanisms occurring continually among the different environmental compartments. Transfer mechanisms may involve advection, dispersion, sorption, volatilization, and plant uptake. Transformation mechanisms play an important role in the fate of pesticides and may include biodegradation and chemical degradation. The latter may include photodegradation and hydrolysis.

Four major factors determine whether a pesticide is likely to reach groundwater, namely: (1) pesticide properties, (2) soil properties, (3) site conditions, and (4) management practices (Kaakeh et al. 2004). Worrall et al. (2002) concluded that both chemical properties and soil properties have a significant and independent effect on groundwater pollution by pesticides. Nevertheless, interaction between site and chemical factors represents the most important control on the occurrence of pesticide in groundwater (Worrall et al., 2002). Presence of pesticides in UAE aquifers has not been investigated. It is not even clear what transport mechanisms will predominate with soil materials typical to those of agricultural lands in the UAE.

1.2 OBJECTIVES

The overall objective of this study is to gain an understanding of the fate and mobility of pesticides in the UAE subsurface environment. Specifically, the study will focus on:

1. Investigating the role of advection and dispersion on the transport of pesticides
2. Investigating the role of pesticide/soil chemical interaction.
3. Investigating the role of degradation on pesticides mobility.
4. Model the mobility of selected pesticides in groundwater using laboratory-derived transport parameters.

It is anticipated that this study will have a significant impact on better understanding how selected pesticides through aquifer materials representative of the UAE subsurface environment and allows for prediction of pesticide mobility and accumulation in UAE groundwaters. Albeit indirect, this study should also benefit future efforts directed towards management of pesticides application and utilization in the country.

1.3 APPROACH

Identification of the role of each mechanism affecting the mobility of pesticides requires isolation of that mechanism. This approach has been taken by Maraqa and co workers (Maraqa et al., 1997; 1998; 1999a; 1999b; Voice et al., 1997) in investigating transport of volatile organic compounds in groundwaters. A similar approach will be followed in this study to investigate the transport of pesticides through columns packed with soil samples representative of Al Ain soil environment.

Batch studies will be conducted under specified conditions in order to gain an understanding of the role of hydrolysis, photodegradation, sorption, and

biodegradation. Miscible displacement studies will be performed on packed soil columns to assess the impact of advection and dispersion as well as other transfer and transform mechanisms.

Simulation of pesticide movement through saturated columns packed with natural soil materials from UAE will be conducted using the CXTFIT2.0 program of Toride et al. (1995).

1.4 SCOPE OF WORK

The present investigation was conducted using three different pesticides (Dimethoate, Cymoxanil and Metalaxyl) that are commonly used in UAE. This study involves the use of two soil materials that were collected from Al Foah and Abu Samra area in Al Ain city. The two soils are similar in texture but vary in their organic matter content. In all the experiments (batch and column), the soils were homogenized before use and the experiments were conducted under laboratory conditions using synthetic solution produced in the laboratory. Column experiments were conducted under steady state, saturated flow conditions. In the column experiments, the average pore-water velocity used (3-4 cm/hr) is may not be representative of pore-water velocities typical to those found in the field.

Although this study considers degradation of pesticides as a mechanism that affects the ultimate fate of these chemicals, the study does not address or investigate the nature of the degradation byproducts.

1.5 THESIS STRUCTURE

The thesis is organized into five chapters. Chapter 1 describes a general overview of groundwater contamination with pesticides and presents the rationale and objectives of this study. Chapter 2 reviews the literature pertaining to classifications

of pesticides and their health impact. Pesticides imported to UAE were explored in this chapter. Furthermore, Chapter 2 provides a review of the fate of pesticides in the environment and their subsurface transport mechanisms. Chapter 3 describes the materials and methods including soil materials and pesticides used as well as the different experiments employed. Chapter 3 also explores the analytical techniques adopted for the tracers used and highlights the method used to reduce and analyze the generated data. Results of this study are presented in Chapter 4 along with discussion of the obtained results. Finally, Chapter 5 concludes this study and sets some recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 CLASSIFICATION AND USES OF PESTICIDES

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) defined pesticides as: any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating insects, rodents, nematodes, fungi, or weeds, or any other form of life declared to be pests; and any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant (Marer et al., 1988). Thus, pests can be animals (like insects or mice), unwanted plants (weeds), or microorganisms (like plant diseases and viruses) (Kumar et al., 1996).

Pesticides are classified based on target pests and pesticide functions or they are classified according to chemical origin. Classification of pesticides based on target pests and pesticide functions is presented in Table 2.1. For example, insecticides control insects, herbicides control weeds, and fungicides control fungi. Also to regulate animal or plant growth, growth regulator pesticides are used. Pesticides are also grouped according to chemical origin (Table 2.2) (Marer et al., 1988).

Pesticides use has benefited modern society by improving the quantity and quality of the world's production while keeping the cost of that food supply reasonable. The use of pesticides is an important aspect of modern agriculture to control various living organisms that cause damage or economic loss, or produce diseases (Kumar et al., 1996). In Australian agriculture, for example, the benefits of pesticides are estimated to be in the range of \$A4-5 billion each year (Kookana et al., 1998).

Table 2.1 Pesticide Classification Based on Target Pests and Functions. (Marer et al., 1988)

Pesticide Type	Pests Controlled or Function	Examples of Pesticides
Acaricide	Mites	Propargite (Omite, Comite) Fenbutatin-oxide (Vendex)
Algaecide	Algae	Copper sulfate Dichlone Endothall (hydrothol 191)
Attractant	Attract pests	Pheromones Baits Miscellaneous chemicals
Avicide	Birds	Aminopyridine (Avitrol) Starlicide Omitrol
Bactericide	Bacteria	Oxytetracycline (mycoshield) Copper compounds
Defoliant	Remove plant foliage	Endothall (Accelerate) Thidiazuron (dropp) Tributyl phosphorotrithioate (folex)
Desiccant	Remove water from arthropod pests	Boric acid powder Silica gel Diatomaceous earth
Fungicide	Fungi	Benomyl (benlate) Copper sulfate Captan
Growth regulator	Regulates plants or animal growth	Gibberelic acid (Pro-Gibb) Chlorocarbamate (Sprout Nip) Methoprene (precor)
Herbicide	Weeds	Atrazine Bromoxynil (buctril) Trifluralin (treflan) Paraquat Petroleum oil
Insecticide	Insects	Diazinon Permethrin (ambush) Azinphos-methyl (guthion) Parathion
Molluscicide	Snails and slugs	Snarol Mesurol Triphenomorph (Frescon) Clonitralid (Bayluscide)
Nematicide	Nematodes	Carbofuran (Furadan) Phosphoramidate (nema-cur) Dichloropropene (Telone)
Piscicide	Fish	Rotenone Lampicide Antimycin (Fintrol)
Predacide	Mammal predators	Strychnine Zinc phosphide Compound 1080
Repellent	Repels animals or invertebrates	Deet Mesurol (methocarb) Avitrol Thiram
Rodenticide	Rodents	Chlorophacinone Strychnine Hydroxycoumarin (Warfarin) Diphacinone (diphacin) Bromadiolone (Maki)
Silvicide	Trees and woody shrubs	Tebuthiuron (Spike)

Table 2.2 Pesticide Classification Based on Chemical origin (Adopted partially from Marer et al., 1988)

Chemical Type	Examples	Mode of Action
INSECTICIDES		
Petroleum oils	Supreme oil, superior oil	Physical toxicants
Organochlorines	DDT Cyclodienes	Axonic poisons Central nervous system
Organophosphate -Aliphatic derivatives -Phenyl derivatives -Heterocyclic derivatives	Dimethoate Ethyl parathion Chlorpyrifos	Synaptic poisons Central nervous system
Carbamates	Carbaryl Aldicarb	Central nervous system
Dinitrophenols	Dinoseb	Metabolic inhibitors
Botanicals	Nicotine Pyrethrum	Postsynaptic poisons Axonic poisons
Pyrethroids	Permethrin Fenvalerate Allethrin	Axonic poisons (also inhibit mixed function oxidase when mixed with a synergist)
Inorganics	Silica gel, Boric acid Sulfur	Physical toxicants
Fumigants	Methyl bromide naphthalene	Narcotic and alkylating agents
Microbials	<i>Bacillus thuringiensis</i> Viruses Fungi	Various
Insect growth regulators	Methoprene Other chitin synthesis inhibitors	Influence growth and development
HERBICIDES		
Inorganics	Sodium chlorate	Desiccant
Petroleum oils		Physical toxicants
Organic arsenicals	MSMA, DSMA, cacodylic acid	Interfere with cellular respiration and metabolism and other functions
Phenoxyaliphatic acid	2,4-D, 2,4,5-T	Multiple actions
Amides	Propanil, alachlor, metolachlor	Inhibit root and shoot growth
Substituted ureas	Tebuthiuron	Block photosynthesis
Carbamates	Propham, barban	Block photosynthesis and interfere with cell division
Triazines	Atrazine, simazine	Block photosynthesis
Phenol derivatives	Dinoseb	Destroy cell membranes, also a desiccant
Microbials	<i>Phytophthora palmivora</i>	
PLANT GROWTH REGULATORS		
Auxins	IAA, 2,4-D, VAR	
Gibberellins		
Cytokinins		
FUNGICIDES		
Inorganic fungicides	Copper Sulfur	Enzyme inhibitor Metabolic inhibitor
Dithiocarbamates	Thiram	Enzyme inhibitor
Triazines	Anilazine	Inhibit metabolism and protein synthesis
Dicarboximides	Captan	Enzyme inhibitor
Oxathiins	Carboxin	Metabolic inhibitors
Acylalanines	Metalaxyl	
Aliphatic nitrogen compounds	Dodine	Inhibit metabolism and protein synthesis
Fumigants	Chloropicrin	
Antibiotics	Streptomycin, cycloheximide	

The US Environmental Protection Agency (US EPA) estimates that approximately 550 million kg of pesticides are sold annually in the United State. About 70% (380 million kg) of the pesticides applied are used for agricultural production of food and fiber. The largest user of agrochemicals in the world is the European Community (EC), and six of the individual countries are within the top ten. In the EC member states, the use of pesticides (in agriculture) amounts to about 320 million kg of active ingredients per year and this amount may vary from year to year due to weather conditions (van den Berg and van den linden, 1994).

2.2 HEALTH IMPACT

Contamination of soil and groundwater by pesticides poses a potential hazard and serious threat to human health and environment. UN Food and Agriculture Organization (FAO) and the World Health Organization (WHO) warned in a joint statement that around 30% of pesticides marketed in the developing countries do not meet internationally accepted quality standards. They are posing a serious threat to human health and environment (website 2.1). Also, the U.S. National Academy of Sciences estimates that tighter controls of pesticides would reduce the risk of cancer from pesticides in the United State by 80%. Persistent pesticides are bioaccumulated and magnified in food chains, eventually reaching toxic levels in top carnivores, include humans. One example of these pesticides is DDT, which had been forbidden (Cunningham and Saigo, 1992).

The heavy use of agricultural insecticides in association with irrigation can induce or aggravate the resistance of malaria vectors due to contamination of surface water with these insecticides such as what has occurred with *Anopheles albimanus* in Central America and *A. quadrimaculatus* in Mexico and the United State (WHO 1985, PAHO 1991). This can diminish the effectiveness of insecticides, which

continues to be the principle malaria control measure in Latin America and the Caribbean (LAC) (Reiff, 1993).

Since the early 90s the UAE has witnessed a rapid development in the field of agriculture. This development, however, is not without its adverse effects. The excessive use of pesticides for the purpose of increasing crop yield may pose environmental hazards and health problems due to possible contamination of groundwater and the soil materials as well as due to plant uptake. Direct health impact of the use of pesticides in the country has been investigated by Beshwari et al. (1999). They concluded that the use of pesticides in the UAE has resulted in acute respiratory symptoms and changes in body metabolism.

2.3 PESTICIDES IMPORTED TO UAE

Pesticides used in the UAE fell under one of the following classes or groups according to their use: insecticides, fungicides, nematocides, acaricides, rodenticides, defoliant, growth regulators, etc. More than 2.5 million liters (or kg) of pesticides were imported to UAE during the three years 1996-1998 (Table 2.3). A total of 822 different types of pesticide were registered in the UAE during these years. Insecticide products (for agricultural use) have the greatest share in total amount and use in UAE at 46.4% for only 110 products out of 249 registered agricultural insecticides (Ministry of Agriculture and Fisheries-UAE, 1999). Fungicides account for the second largest category at 22.0% for only 67 products out of the 184 registered fungicides. Other types of pesticides constitute the remaining percentage (i.e., 28.2%) (Ministry of Agriculture and Fisheries-UAE, 1999).

The amount of pesticides imported to UAE differed during the years 1996-1998 as shown in Table 2.4. It is observed that the amount imported during 1998 is generally higher than the amount imported during the other two years. This is possibly

attributed to an expansion in the agricultural sector after 1997 as the cultivated area during the period 96-98 was about 57700, 66300, and 93600 ha, respectively.

Table 2.3 Number of registered pesticides and quantities imported during 96-98. (Ministry of Agriculture and Fisheries - UAE, 1999).

Pesticide type	No. of registered pesticides	Quantities (kg) imported during 96-98 (No. registered pesticides)
A. Insecticides: Agricultural	249	1,208,004 (110)
B. Soil insecticides/ nematicides	19	
C. Acaricides: Agricultural	34	83,609 (17)
D. Insecticides: Public Health	168	346,213 (38)
E. Fungicides	184	793,238 (67)
F. Bactericides	3	
G. Herbicides	20	2,500 (1)
H. Rodenticides	47	113,650 (11)
I. Nematicides	13	59,105 (6)
J. Molluscicides	4	
K. Insecticides & miticides (veterinary)	4	
L. Soil sterilants	9	
M. Plant hormones, growth regulators, etc.	13	
N. Spreaders, stickers, buffers, etc.	20	
O. Insect pheromone lures	13	
P. Active ingredients for local pesticides formulation	8	
R. Deodorizers	5	
S. Leaf-shine, fruit and veg. wax, disinfectants.	9	
Total	822	2,603,819

Kaakeh et al. (in press) estimated that the average amount of pesticides used in the UAE is 9.86 liter (or kg) per ha per yr. This number is relatively high compared to pesticides use in other countries including India (0.5 liter or kg/ha per yr), USA (1.5 liter/ha per yr), and Europe (1.9 liter/ha per yr), but comparable to the amount used in Japan (10 liter/ha per yr) as reported by Rao (1998). It should be noted that that rate of pesticide use in UAE as reported by Kaakeh et al. (in press) was based on the assumption that all imported pesticides were used during the years 1996-1998 on the specified cultivated area reported by the Ministry of Agriculture and Fisheries.

Table 2.4 Amount of selected agricultural insecticides and fungicides imported to UAE during 96-98. (Ministry of Agriculture and Fisheries - UAE, 1999).

Pesticide type	Commercial name	Quantities (liter) imported during:			
		1996	1997	1998	96-98
Agricultural insecticides	Actellic 50 EC	4,900	29,000	21,000	54,900
	Action 51 EC	27,754	32,600	70,200	130,554
	Aflix	11,000	13,000	10,000	34,000
	Decis 2.5 EC	6,000	7,000	8,500	21,500
	Dimeclor	-	3,000	2,000	5,000
	Dursban 4E	22,200	15,900	30,600	68,700
	Hostathion 40 EC	9,000	12,000	13,500	34,500
	Karate 2.5 EC	13,000	18,000	24,000	55,000
	Marshal 25% EC	3,000	13,824	39,494	56,318
	Rogodial 53 EC	5,000	2,000	7,949	14,949
	Rolfan 58% EC	20,000	4,600	14,480	39,080
	Total	121,854	150,924	241,723	514,501
Fungicides	Remiltine 50 WP	13,000	6,000	12,360	31,360
	Redomil MZ 72 WP	6,450	7,750	11,750	25,050
	Tichigaren 30 L	9,000	10,000	15,000	34,000
	Topsin - M 40 WP	1,000	4,000	7,000	12,000
	Total	29,450	27,750	46,110	102,410

2.4 FATE OF PESTICIDES IN THE SOIL

The fate of pesticides in the soil environment is viewed with a great concern today due to their leaching to aquifers and contamination of groundwater. Generally, the fate of pesticides is described by how and where it enters the environment, how long it lasts, and where it goes (Aylmore and Di, 2000).

Understanding the basic properties of pesticides and interactions with soils is a complex process. Pesticides represent a heterogeneous group of chemical substances, where properties such as polarity, charge and degradation rate greatly influence their mobility. Moreover, soil properties such as pH and content of natural organic matter, clay and Fe/Al oxides influence to a large extent the retention of pesticides in soils (Riise et al., 1997). In addition, moisture and temperature status of the soil influence pesticide behavior directly through their effects on pesticide adsorption, vaporization

and solubility, and indirectly through their influence on physiological processes in the plants and microbial and chemical decomposition of the chemicals (Weber and Weed, 1986).

As a result of many field and laboratory studies, the US EPA has compiled a list of key chemical and physical properties called threshold values (Table 2.5). Although the threshold values provide only a rough guide, compounds with properties that do not satisfy these limits warrant extra attention because of their relatively high potential for leaching to groundwater. The field dissipation half-life for a pesticide takes into account physical, chemical, and biological degradation, and plant uptake. The use of half-life requires caution since these estimates are highly dependent on the chemical, physical, and biological properties of the soil being tested.

Table 2.5 Threshold values indicating potential for groundwater contamination by pesticides

Chemical or physical property	Threshold value
Solubility (S)	> 30 ppm
Henry's Constant (K_H)	< 10^{-2} atm (mol/m ³) ⁻¹
Organic carbon based coefficient (K_{oc})	<500
Field dissipation half-life ($t_{1/2}$)	> 3 weeks

Figure 2.1, adopted from Kaakeh et al. (in press), shows some of the properties of the pesticides used in the UAE as compared to the threshold values in Table 2.5. The figure shows that three pesticides used in the UAE have the potential to leach to groundwater due to their solubility, which exceeds the threshold value. Five pesticides have the potential to leach due to their low vapor pressure (low K_H value). Four pesticides will possibly leach to groundwater due to their weak interaction with the soil. Finally, eight of the pesticides used in UAE will probably leach due to their relatively high field dissipation half-life.

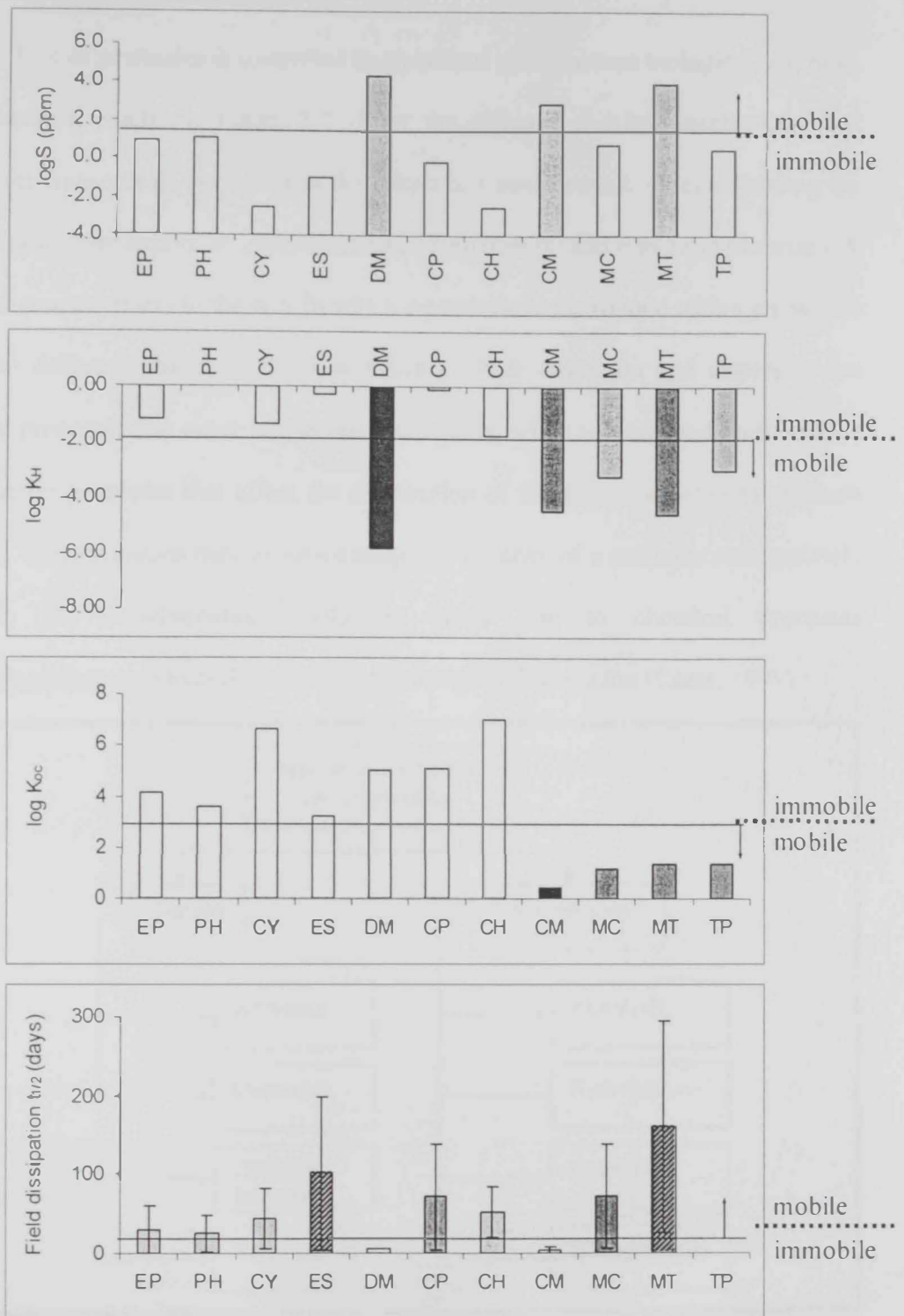


Fig. 2.1 Properties of pesticides used in the UAE in comparison with the threshold values (lines and arrows) indicating potential for groundwater contamination. EP= Ethyl pirimiphos, PH=Phentoate, CY=Cypermethrin, ES= Endosulfan, DM= Dimethoate, CP= Chlorpyrifos, CH=Cyhalothrin, CM= Cymoxanil, MC= Mancozeb, MT= Metalaxyl, TP= Thiophanate-methyl.

2.5 TRANSPORT MECHANISMS

Fate of pesticides is controlled by numerous simultaneous biological, physical, and chemical reactions. Figure 2.2 shows the different possible mechanisms that affect the transport of pesticides in the subsurface environment. Comprehending the fate of pesticides require an understanding of both transfer and transform processes. A transfer process refers to the way in which a pesticide is distributed within a phase or between different phases (solids and liquids). Both advection and dispersion are transfer processes that occur within the liquid phase, while sorption and volatilization are transfer processes that affect the distribution of the chemical between different phases. Transformation mechanisms change the structure of a pesticide or completely degrade it. Transformation could be either due to chemical processes (photodegradation or hydrolysis) or due to biological degradation (Coats, 1991).

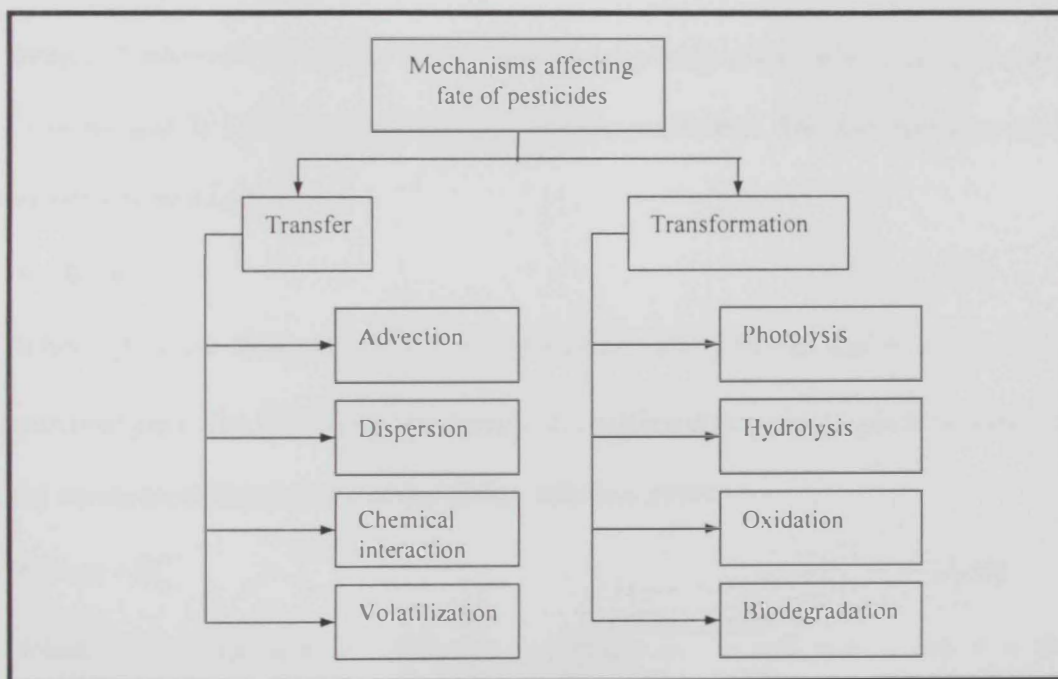


Fig. 2.2 Mechanisms affecting pesticides transport in the subsurface environment.

2.5.1 Advection and Dispersion

Advection refers to the movement of dissolved or very fine particulate material as they are carried by moving water within the pores. Dispersion is one of the important mechanisms that effect the spreading of pesticide in the subsurface environment (Schnoor, 1991). On a microscopic-scale, two processes cause hydrodynamic dispersion: mechanical mixing due to fluid advection and molecular diffusion driven by concentration gradient. On a macroscopic-scale, dispersion is mainly affected by the presence of large-scale heterogeneities within the medium that create variations in flow velocities and flow paths (Bedient et al., 1999).

The equation describing the transport of solutes under the effects of advection and dispersion in a one-dimensional flow field is written as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.1)$$

Where, C is the concentration, t is the travel time, x is the distance, v is the pore-water velocity, and D is the hydrodynamic dispersion coefficient. The average pore-water velocity is given as:

$$v = Q / \theta A \quad (2.2)$$

Where, Q is the flow rate, θ is the volumetric water content, and A is the cross-sectional area. The hydrodynamic dispersion coefficient is typically given as a sum of the mechanical dispersion and molecular diffusion terms:

$$D = \alpha v + D_e^* \quad (2.3a)$$

Where, D_e^* is the effective diffusion coefficient in the soil matrix and α is the dispersivity of the soil. The effective diffusion coefficient in soil is related to the diffusion coefficient in water (D_d) multiplied by a coefficient (ω) that is related to the tortuosity of the medium (Fetter, 1999):

$$D_e^* = \omega D_d \quad (2.3b)$$

2.5.2 Sorption

Sorption is defined as the association of a dissolved or gaseous contaminant with a solid material (Bedient et al., 1999). Sorption is a surface phenomenon that may be either absorption or adsorption, or a combination of the two. Adsorption is the association of a contaminant on the surface of a solid particle, whereas absorption is the association within a solid particle. The term sorption is used when the specific mechanism is not known (Web site 2.2)

Sorption of pesticides is controlled by the amount of total organic carbon as well as the quality of the organic matter (website 2.3). For soils that have high organic matter levels (>5%), the mobility of the pesticides has been related to the total organic matter content, with the nature of the organic matter having a little apparent influence on sorption processes (Jenks et al., 1998; Bekbolet et al., 1999). For soils with low organic matter contents, the mobility of the pesticide is often related to the active components of the inorganic fraction, which is predominantly the clay-sized fraction. An increase in the clay content results in decreasing mobility of the pesticide, with the composition of the clay and the identity of the major cations in the soil solution also being important (Welhouse and Bleam, 1992; Baskaran et al., 1996). Other factors that may influence their sorption to soil include chemical properties soil texture and pH (Gennari and Gessa, 1999).

Sorption of pesticides to soils has been studied extensively by batch methods (Mersie and Foy, 1985; Hermosin and Cornejo, 1987; Reddy and Grambell, 1987; Sanchez-Camazano and Sanchez-Martin, 1988; Kanazawa, 1989; Santos-Buelga et al., 1992). Sorption is determined experimentally by measuring how much of a solute can be sorbed by a particular sediment, soil, or rock type. The results of the experiment are plotted on a graph called an isotherm that shows the solute concentration versus the amount sorbed onto the solid. Travis and Etnier (1981) gave

a comprehensive review of sorption isotherms and kinetic models. If there is a direct, linear relationship between the amount of a solute sorbed onto the solid (S_e) and the concentration of the solute in the aqueous phase (C_e), a linear sorption isotherm results:

$$S_e = K_d C_e \quad (2.4)$$

Where, K_d is the linear sorption distribution coefficient.

There is, however, an increasing awareness that nonlinear sorption can play an important role in contaminant transport (Ball and Roberts, 1991; Jaekel et al., 1996; Abulaban et al., 1998; Abulaban and Nieber, 2000; Serrano, 2003). Evidence of nonlinear sorption of contaminants to soil and aquifer material has been documented both on a laboratory-scale (Appert-Collin et al., 1999; Chia et al., 2001) as well as in the field (Hutzler et al., 1986; Roberts et al., 1986; Brusseau and Srivastava, 1997). In many cases, it has been found that the Freundlich-type model better describes the sorption isotherm. The Freundlich model is written as:

$$S_e = K C_e^n \quad (2.5)$$

Where, K and n are constants. Values for the Freundlich exponent (n) could be as low as 0.5. Nonlinear sorption may also be described by the Langmuir model. This model was developed with the concept that a solid surface possesses a finite number of sorption sites. The Langmuir model is expressed as:

$$\frac{C_e}{S_e} = \frac{1}{ab} + \frac{C_e}{b} \quad (2.6)$$

Where, a is an adsorption constant related to the binding energy and b is the maximum amount of solute that can be absorbed by the solid.

The impact of sorption is to reduce the average velocity of the contaminant relative to that of water. For a sorbing solute, Eq. (2.1) is written as:

$$R \frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) - v \frac{\partial C}{\partial x} \quad (2.7)$$

Where, R is the retardation factor given for the case of linear sorption as:

$$R = 1 + \frac{\rho K_d}{\theta} \quad (2.8)$$

Where ρ is the bulk density of the soil. Whereas, for the case of a Freundlich sorption, R is expressed as:

$$R = 1 + \frac{\rho n K C^{n-1}}{\theta} \quad (2.9)$$

Proper determination of R can have a significant impact on managing and preventing groundwater contamination. In the laboratory, retardation coefficients are determined by either batch or packed column experiments. Kool et al. (1989) and Jackson et al. (1984) discussed the advantage and disadvantage of the two techniques. Maraqa and co-workers (Maraqa et al., 1998; Altfelder et al., 2001; Maraqa, 2001) reported discrepancy between batch and column determined retardation coefficients.

2.5.3 Pesticides Degradation

Once introduced into the environment, pesticides may be degraded chemically or biologically. Chemical (abiotic) degradation of pesticides within the soil includes all reactions not mediated by soil microorganisms, fauna, or flora (Burnside, 1986). Such reactions may include hydrolysis and photolysis. The 1-D advection-dispersion equation that includes retardation and a degradation term is written as:

$$R \frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) - v \frac{\partial C}{\partial x} - \lambda C \quad (2.10a)$$

Where λ is the combined first-order degradation rate constant that accounts for degradation of solute in both liquid and solid phases and is defined as:

$$\lambda = \lambda_l + \frac{\rho K_d}{\theta} \lambda_s \quad (2.10b)$$

where, λ_l is the hydrolysis rate constant in the liquid phase and λ_s is the hydrolysis rate constant in the solid phase.

2.5.3.1 Hydrolysis

It is a common chemical reaction by which a pesticide reacts with a water molecule. For many pesticides molecules, hydrolysis reaction is a primary route of degradation. Due to catalysis of the hydrolysis reaction by sorption, it occurs more rapidly in soil than in comparable soil-free aqueous systems (Armstrong and Konrad, 1986; Coats, 1991)

Cleavage by hydrolysis is pH sensitive. In many pesticides, as the pH increases, the rate of chemical hydrolysis in the soil increases (Aly and El-Dib, 1971; Lamoreaux and Newland, 1978; Jackson et. al., 1990). Al-Mughrabi et al. (1992) studied the effect of pH of water on the stability of cypermethrin (insecticide) using four pHs (canal water pH8.38, distilled water pH6.2, phosphoric acid-treated canal water pH6, and propionic acid-treated canal water pH 6). The results showed that, the highest percentage of hydrolysis of cypermethrin after 24hr treatment was found in canal water and in distilled water but at a slightly slower rate than in the canal water. Liu et al., (2001) reported that pH alone cannot be used as a single parameter to extrapolate hydrolysis rate constants obtained in the laboratory onto estimated rates under field conditions.

2.5.3.2 Photodegradation

Photodegradation (photolysis) involves the breakdown of pesticides by direct or indirect energy from sunlight. Crosby, 1969 and Smith et al. (1978) measured the photodegradation rate and showed in laboratory studies that sunlight has the ability to

detoxify certain pesticides. However, the practical significance of this method of dissipation under field condition has been questioned (Burnside, 1986).

2.5.3.3 Biological Degradation

In the environment, it is well established that microorganisms are the major or frequently the only means of degradation/detoxification of several pesticides. Also, this mechanism has a great advantage due to its ability to completely degrade a wide variety of pesticides, even under mild condition compared with degradation through physical and chemical means (Kumar et al., 1996)

Pesticides applied to soil may ultimately be degraded by microorganisms. Many studies indicated that microorganisms have a great role for the degradation and enhancing the degradation of pesticides in soil (Cain and Mitchell, 1996, Struthers et al., 1998, Hole et. al., 2001, Bhadbhade, 2002). However, before these processes are complete, the pesticide and its metabolites may be leached into the groundwater (website 2.4). In groundwater system, indigenous bacteria are generally the organisms that carry out this process (Bedient et al., 1999). Torstensson (1987) indicated that the degradation of pesticides in soil is mainly due to biological transformations and is thus controlled by the availability of the organic chemical and by the activity of the soil microflora.

2.5.4 Schematic Representation of Transport Mechanisms

The impact of some of the above mentioned mechanisms on the transport of a dissolved chemical are presented in Fig. (2.3). Advection is the mechanism by which chemicals are transported by the bulk motion of the flowing phase. As illustrated in Fig. (2.3a), a nonreactive chemical present in the water phase moves at average velocity equals to the average pore-water velocity. Due to hydrodynamic dispersion,

however, part of the chemical plume migrates in a period of time that is shorter than the time calculated based on average flow velocity, part of the plume moves in a longer period of time as shown in Fig. (2.3b).

The effect of sorption is demonstrated in Fig. (2.3c). Sorption reduces the average velocity of the sorbates with respect to that of the water molecules. Sorption may also have an effect on many natural transformation processes. Microorganisms, for example, are unable, or less able, to assimilate and transform sorbed molecules compared to those in soil solution (Orgam et al., 1985). Moreover, chemical reactions may also be affected by sorption (Macalady and Wolfe, 1985). The effect of degradation is to reduce the area under the curve as some mass of the induced chemical will be degraded (Fig. 2.3d).

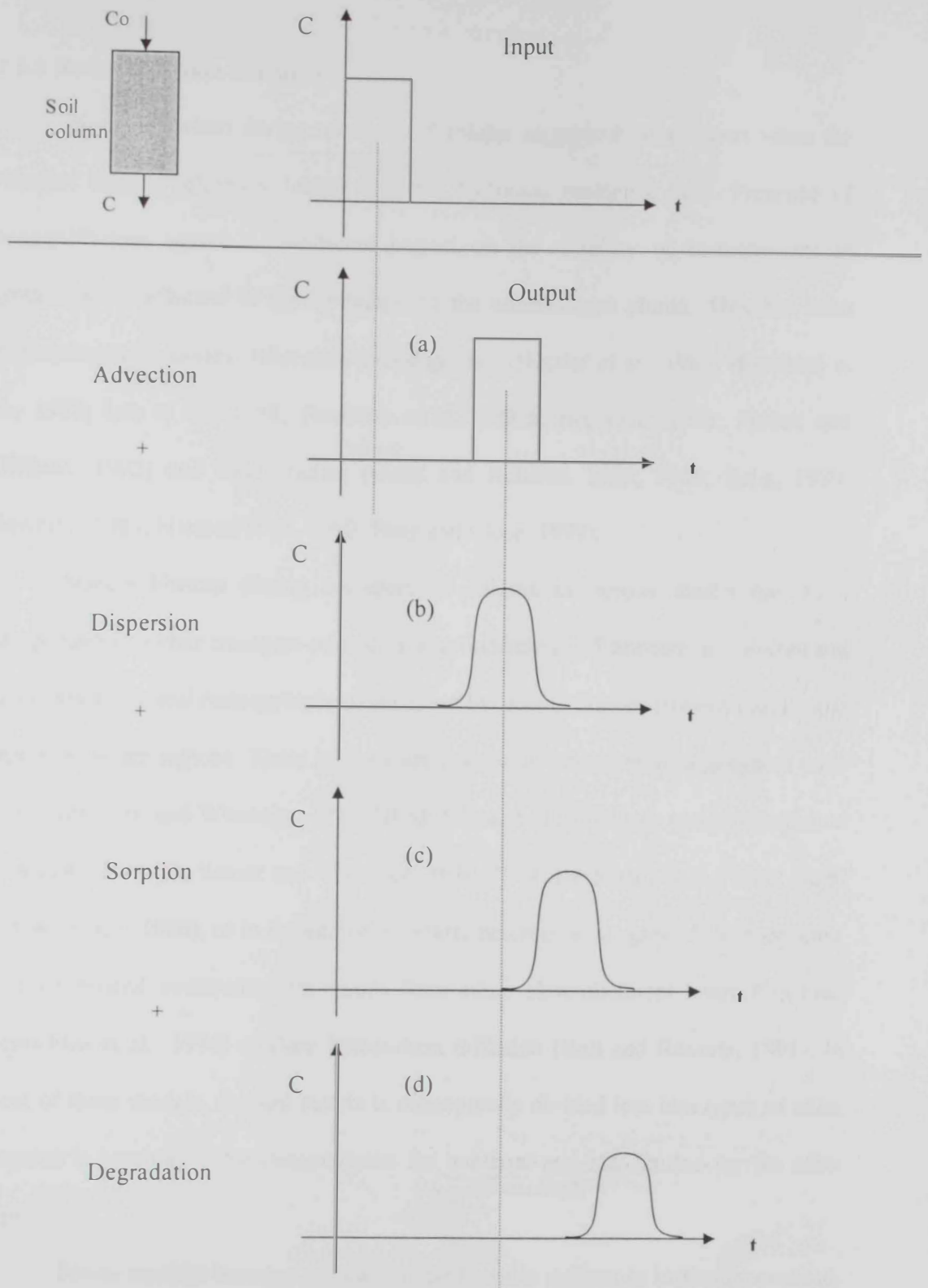


Fig. 2.3 Impact of transfer and transform processes on movement of a dissolved chemical in saturated soil column.

2.5.5 Nonequilibrium Sorption

Nonequilibrium during transport of solutes in groundwater occurs when the reaction time is relatively longer than the hydraulic residence time. Presence of nonequilibrium causes a significant impact on the mobility of contaminants in groundwater, reflected in the spreading of the contaminant plume. This has been demonstrated by several laboratory investigations (Hutzler et al., 1986; Bouchard et al., 1988; Lee et al., 1988; Brusseau et al., 1991a; Brusseau, 1992; Ptacek and Gillham, 1992) and field studies (Goltz and Roberts, 1986; 1988; Bahr, 1989; Bowman, 1989; Harmon et al., 1992; Pang and Close, 1999).

Nonequilibrium during transport of solutes in porous media has been categorized as either transport-related or sorption-related. Transport nonequilibrium (also called physical nonequilibrium) is caused by slow diffusion between mobile and immobile water regions. These regions are commonly observed in aggregated soils (van Genuchten and Wierenga, 1976; Nkedi-Kizza et al., 1983), or under unsaturated flow conditions (De Smedt and Wierenga, 1979; 1984; De Smedt et al., 1986; Bond and Wierenga, 1990), or in layered or otherwise heterogeneous groundwater systems. Sorption-related nonequilibrium results from either slow chemical interaction (van Genuchten et al., 1974) or slow intrasorbent diffusion (Ball and Roberts, 1991). In most of these models, the soil matrix is conceptually divided into two types of sites; sorption is assumed to be instantaneous for one type and rate-limited for the other type.

Solute transfer between mobile/immobile water regions or instantaneous/rate-limited sorption sites is commonly described by a first-order rate expression. The dimensionless equations of the first-order, two-site nonequilibrium model for the case of linear sorption are given as:

$$\beta R \frac{\partial \mathcal{C}^*}{\partial T} + (1 - \beta) R \frac{\partial \mathcal{S}^*}{\partial T} = \frac{vL}{D} \frac{\partial^2 \mathcal{C}^*}{\partial X^2} - \frac{\partial \mathcal{C}^*}{\partial X} \quad (2.11)$$

$$(1 - \beta) R \frac{\partial \mathcal{S}^*}{\partial T} = \omega (C^* - S^*) \quad (2.12)$$

Where,

$$X = x/L \quad (2.13a)$$

$$T = vt/L \quad (2.13b)$$

$$C^* = C/C_0 \quad (2.13c)$$

$$S^* = \frac{1}{(1-F)K_D} \frac{S_2}{C_0} \quad (2.13d)$$

$$R = 1 + \frac{\rho K_d}{\theta} \quad (2.13e)$$

$$\beta = \frac{\theta + F\rho K_d}{\theta + \rho K_d} \quad (2.13f)$$

$$\omega = \frac{kL}{v} (1 - \beta) R \quad (2.13g)$$

Where C is the aqueous solute concentration, C_0 is the solute concentration in the influent solution, x is distance, L is the column length, t is time, v is the average pore-water velocity, D is the hydrodynamic dispersion coefficient, S_2 is the average sorbed concentration in the rate-limited domain, R is the retardation coefficient, K_D is the linear sorption distribution coefficient, ρ is the soil bulk density, θ is the moisture content, F is the fraction of sorbent for which sorption is instantaneous, and k is the first-order mass-transfer coefficient. β and ω are the dimensionless parameters that specify the degree of nonequilibrium in the system.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Soils

Two soil samples were collected from Al Foah and Abu Samra areas in Al Ain district, Abu Dhabi Emirate. Soil samples were air dried and disgraded to pass the 0.85-mm sieve. Soil samples were characterized for grain-size distribution, pH, and organic matter (OM) as shown in Table 3.1. The pH of the soil samples was determined using a 1:1 and a 1:2.5 soil/water ratio (Eckert, 1988) and the organic matter was determined by the wet digestion technique (Schulte, 1988). Both samples are classified as sandy soil with more than 97% sand. The two soil samples vary in their organic matter content (OM) from ~ 0.2 to ~0.8%.

Table 3.1: Characteristics of soil samples

Soil sample	Sand %	pH		Organic matter (OM %)
		s/w 1:1	s/w 2.5:1	
Al Foah	>97.5	8.03	8.34	0.835
Abu Samra	>99.8	8.59	9.24	0.207

Soil characterization was conducted at the Department of Agricultural Land laboratory at the College of Food Systems, UAE University. Note: S/W is soil/ water ratio by weight.

3.1.2 Pesticides

Three pesticides were selected (dimethoate, metalaxyl, and cymoxanil). These pesticides are commonly used in Al-Ain for agricultural purposes. The three pesticides were selected based on their relatively high solubility value and they are available in different commercial forms. The commercial pesticides used that contain the active ingredient are Dimeclor that contain dimethoate, Remiltine contains cymoxanil, and Ridomil contains metalaxyl (Table 3.2).

Table 3.2: Properties of selected pesticides

Name	M.wt. (g/mol)	Chemical formula	Solubility ¹ (g/l)	K _{oc} ²	Half life ¹ (d)	Commercial Product
Dimethoate	229.2	C ₅ H ₁₂ NO ₃ PS ₂	25	9-34	7-12	Dimeclor
Cymoxanil	198.2	C ₇ H ₁₀ N ₄ O ₃	1	39-238	<7	Remiltine
Metalaxyl	279.3	C ₁₅ H ₂₁ NO ₄	7.1	30-284	70	Ridomil

¹ Pesticide Manual,

² K_{oc} is the organic carbon distribution coefficient (reference: www.arsusda.gov).

Kaakeh et al. (in press) evaluated the potential for pesticides used in the UAE to leach to groundwater. The authors found that among several pesticides used in UAE, metalaxyl is the single pesticide that exceeds all threshold values indicating a high potential to leach to groundwater. Although cymoxanil has three properties (solubility, vapor pressure, and soil interaction) that favor leaching to groundwater, its field dissipation is low indicating a fast degradation rate that may not allow substantial amount of this chemical to reach groundwater. This same argument applies well for dimethoate. Hence, the three compounds have been chosen to assess their mobility through soil samples representative of the UAE subsurface environment.

3.2 METHODS

The interaction of pesticides with soil including sorption; chemical degradation (hydrolysis and photodegradation) and biological degradation was tested using two types of experiments: batch and column experiments. Brouwer (1994) indicates that mobility studies must include both batch equilibration and column leaching experiments to assess the groundwater pollution potential of a given compound. The impact of advection and dispersion on the transport of these pesticides was tested using a column experiment and employing bromide as an ideal tracer.

3.2.1 Analytical Techniques

The three selected pesticides were analyzed using the high-performance liquid chromatography (HPLC) located at the Central Laboratory Units on the UAE University campus. The instrument has a column with a C18 packing material that has a grain-size of 220nm. The flow rate employed was 1.5 ml/min and the mobile phase was 35% acetonitrile and 65% water. A stock solution of pesticides (0.01g of each pesticide used) was prepared in 100ml sodium acetate buffer solution (pH 5.5) resulting in a concentration of 100 ppm of each pesticide. Five standard solutions (0.5, 1, 5, 25, 50 and 100 ppm) were prepared and utilized for HPLC calibration. A buffer acetate sample with no pesticide was utilized as blank. Figure 3.1 shows a chromatogram of the three pesticides under the analytical conditions stated above.

Bromide was used as an ideal tracer in the column experiment to study the dispersive behavior of the soil. Bromide was analyzed using ion chromatography (Dionex IC) at Dubai Municipality.

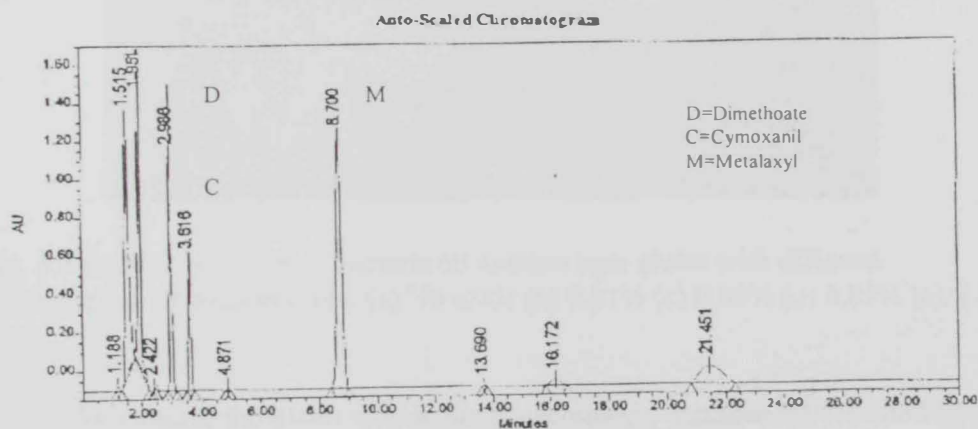


Fig. 3.1 Example chromatogram for the three pesticides.

3.2.2 Determination of Biocide Concentration

Biocide was employed to inhibit biodegradation so that the impact of this process would be isolated. This was necessary to allow investigation of the role of other mechanisms like hydrolysis and sorption.

Sodium azide (NaN_3) was selected as an inhibitor. The biocide concentration needed to inhibit biodegradation was determined by conducting an experiment over a range of biocide concentration and monitor the growth on the plates. One of the microorganisms isolated from the soil was streak-inoculated along of five nutrient agar plates. The first plate containing no azide, but the others contained (0.01, 0.03, 0.05, and 0.1% sodium azide). The plates were then incubated at 37°C for 24 hrs (Fig.3.2).

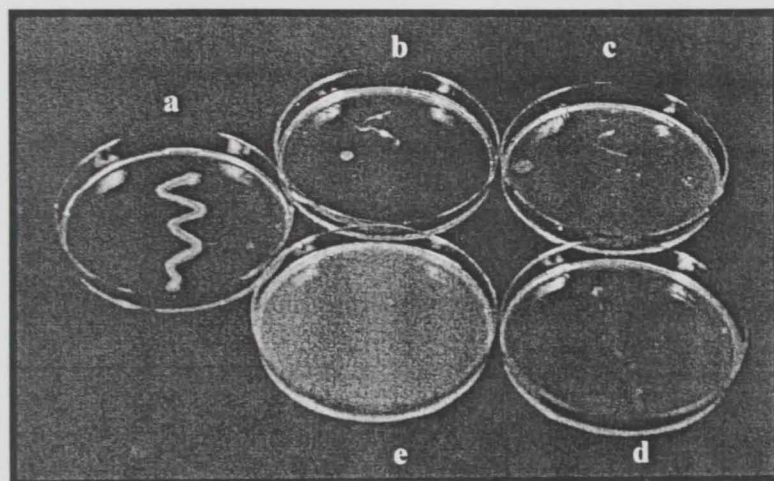


Fig. 3.2 Growth behavior of bacteria on nutrient agar plates with different concentration of sodium azide. (a) No azide (b) 0.01% (c) 0.03% (d) 0.05% (e) 0.1%.

As a result, the plates with azide concentration less than 0.05% showed some growth. Thus, a concentration of 0.05% was selected to inhibit the biodegradation of the used pesticides in some of the experiments.

3.2.3 Batch Experiments

Batch experiments were utilized to investigate the role of several transport mechanisms including photodegradation, hydrolysis, sorption, and biodegradation. In all these experiments, 20-ml glass vials with Teflon-lined caps were utilized. The pesticide solution, in these experiments, was prepared from commercial pesticides (0.8 ml Dimeclor + 2.5 g Ridomil + 1.0 g Remiltine) using 1-L deionized water containing 0.05M CaCl₂. Such solution results in dimethoate, cymoxanil, and metalyxel concentration of about 114, 15, 120 ppm, respectively. The solution also contained 0.05% sodium azide in all the experiments except that related to the investigation of the role of biodegradation. Detailed description of the batch experiments is presented below.

3.2.3.1 Hydrolysis

For this test, twelve dry, fixed glass vials were prepared. The first six vials were filled with 15ml of pesticide solution prepared using DI water (pH 7.2). The other six vials were filled by a solution of pesticides dissolved in sodium acetate buffer (pH 5.5) (Table 3.3). This was conducted to investigate the impact of pH on the hydrolysis rate of the selected pesticides. Each vial from the two sets was sampled at a different time (1 hr, 6 hrs, 12 hrs, 24 hrs, 3 days, and 7 days) and analyzed by the HPLC.

Later experiment was done using two flasks containing phosphate buffer, one with pH 8 and the other with pH 9 (Table 3.3). The samples were taken at different time from each flask (1 hr, 6 hrs, 19 hrs, 23 hrs, 47 hrs and 71hrs) and analyzed by the HPLC.

Table 3.3 Buffer Preparation

Buffer pH	Method
5.5	Add 40 g of sodium acetate powder to 500 ml deionized water. Mixed well. Take 50 ml of the previous solution and mix with 15ml HCl (1N). Adjust the volume to 250ml with deionized water.
8	Prepare 0.25M sodium phosphate, dibasic solution (initial pH approx. 9.25). Adjust pH to 8 with slow addition of 0.25M potassium phosphate, monobasic in water.
9	Prepare 0.25M sodium phosphate, dibasic solution (initial pH approx. 9.25). Adjust pH to 9 with slow addition of 0.25M potassium phosphate, monobasic in water.

3.2.3.2 Photodegradation

Twelve dry, fixed glass vials were prepared. Six of them were covered and filled with 10ml of the pesticides solution, and the others were uncovered and filled with 10ml of the same solution. Samples had been taken at different times from each vials (1 hr, 6 hrs, 12 hrs, 24 hrs, 3 days, and 7 days) and were analyzed by the HPLC.

3.2.3.3 Sorption rate

For sorption rate, 13 covered glass vials were prepared. One of them represents the control (10ml of pesticides solution only). Six of the vials were filled with 15g of Al Foah soil amended with 10ml of the pesticides solution. The other six vials were filled with 25g of Abu Samra soil and 10ml of the pesticides solution. All the vials were capped with Teflon screw caps. After being filled with the solution, the vials were rotated end-over-end at 20 rpm. Each vial was sampled at a specific time (1 hr, 6 hrs, 12 hrs, 24 hrs, 3 days, and 7 days). The samples were analyzed using the HPLC.

3.2.3.4 Sorption isotherm

Ten, dry, covered fixed glass vials were prepared. Five of the vials were filled with 14g of Al Foah soil. These vials were filled with a pesticides solution of various concentrations. The same was done for Abu Samra soil but using 25g soil. The vials were capped with Teflon screw caps and were then mixed end-over-end until equilibrium was reached. After mixing, all vials were centrifuged for 30min. at 3000 rpm. The aqueous phase was filtered and analyzed for the target pesticides using the HPLC. The solid phase concentration was determined by difference after accounting for the effects of hydrolysis.

Table 3.4 Some conditions of the isotherm experiments.

Soil	Soil mass (g)	S/W ratio	Approximate initial concentration (ppm)
Al Foah	14	1:1	0.5-200
Abu Samra	25	2:1	0.5-200

3.2.3.5 Biodegradation

In this test, a solution containing the three pesticides with 0.05 M CaCl_2 was prepared without adding sodium azide. The solution was prepared using soil extract that contains some of the microbes originally present on soil. For both soils, soil extract was prepared by adding 100g of the soil to 1L deionized water. Pesticides were added to soil extract afterward.

Twelve dry, covered fixed glass vials were prepared. Six of them were filled with 10ml of Al Foah extract, and the others with 10ml of Abu Samra extract. Samples were taken at different times (1 hr, 6 hrs, 12 hrs, 24 hrs, 3 days, and 7 days) and analyzed for pesticide level using the HPLC.

3.2.4 Column Experiment

Miscible displacement experiment for ideal tracer and target pesticides were conducted in separate experiments using stainless-steel columns. The column length is 25 cm and the internal diameter is 2.2 cm. The columns were packed with the soil material and flushed with CO₂ to displace air and achieve full saturation upon the introduction of the aqueous phase. The columns were then saturated using 0.05M CaCl₂-azide solution at low flow rates (2 ml/hr). The characteristics of the packed columns are presented in Table 3.5. Bulk density (ρ) was determined gravimetrically from the weight of the packed column (W_{packed}) and that when the column was empty (W_{empty}) as follows:

$$\rho = \frac{W_{\text{packed}} - W_{\text{empty}}}{V_{\text{total}}} \quad (3.1)$$

where V_{total} is the total volume of the column. The porosity of the column was also determined gravimetrically from the weight of the saturated column (W_{sat}) and the weight before saturation (W_{packed}) as follows

$$\theta = \frac{W_{\text{sat}} - W_{\text{packed}}}{V_{\text{total}}} * \rho_{\text{water}} \quad (3.2)$$

ρ_{water} was assumed equal 1g/ml

Table 3.5 Characteristics of the packed columns

Soil		ρ g/cm ³	θ	Q ml/hr	Injected PV T _o
Al Foah	Br	1.749	0.339	6	1.302
	Pesticides	1.400	0.441	5	1.400
Abu Samra	Br	1.633	0.384	6	0.989
	Pesticides	1.570	0.381	6	1.990

A schematic diagram of the column setup is shown in Fig. 3.3. A peristaltic pump (MasterFlex) was used to inject the solution into the columns. Effluent samples were collected using a fraction collector (Spectra/Chrom CF1). All connecting tubes are made of Teflon but those used with the pump are made of Tygon.

In the ideal tracer experiment, a bromide solution with known concentration (Table 3.6) was injected into the soil packed columns with a pulse input of 6 hrs at a flow rate of 6 ml/hr. The columns were then displaced by a CaCl₂-azide solution free of Br. Effluent samples were analyzed for bromide using ion chromatography (IC) with a AS-17 column. The flow rate employed was 1 ml/min and the mobile phase was 100% de-ionized water.

Table 3.6 Concentration (mg/l) of bromide and pesticides injected in the soil columns

Soil	Br	Dimethoate	Cymoxanil	Metalaxyl
Abu Samra	110	96	43	124
Al Foah	102	14	3	60

The input concentration of the three pesticides injected into Abu Samra and Al Foah soil columns are also shown in Table 3.5. After injection of the pesticides solution through these columns with the conditions outline in Table 3.4, the columns were leached with a pesticide-free solution. Effluent samples were collected at specified time intervals and were analyzed for the target compounds immediately after collection.

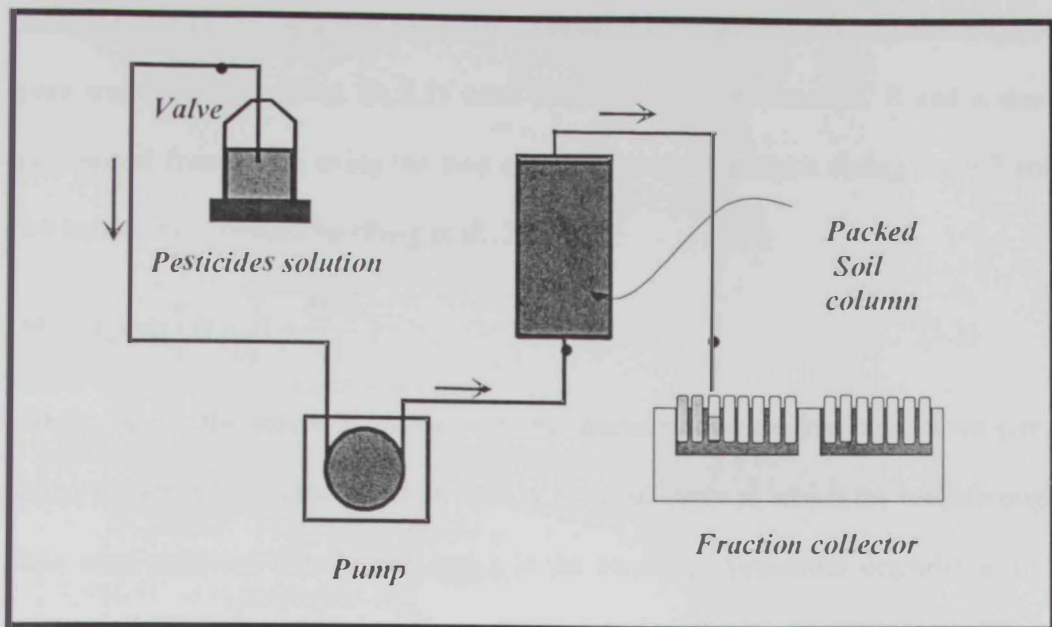


Fig. 3.3: A schematic diagram of the column setup.

3.3 DATA ANALYSIS

Breakthrough curves (BTCs) generated from the column experiments were analyzed using CXTFIT version 2.0 code by Toride et al. (1995). The model employs least-squares analysis in the prediction of transport parameters from breakthrough data. There are several limitations accompanied with the CXTFIT code including the assumption of a linear sorption behavior, the assumption of a first-order degradation, and the assumption of a constant first-order mass transfer coefficient.

Dispersion coefficients were determined using the generated BTCs of bromide. The advection-dispersion model with no degradation term (Eq. 2.9) was used to analyze bromide BTCs. In this case, the pore-water velocity was determined using Eq. 2.2 and the retardation coefficient (R) was set equal to 1.0 as the solute is believed to act as an ideal tracer (no sorption). The dispersion coefficient was thus determined from the best fit of the breakthrough data.

Pesticides BTCs were analyzed using the advection-dispersion model with degradation using either the equilibrium or the nonequilibrium sorption model (Eq.

2.10 or Eq. 2.12). Dispersion coefficient (obtained from the bromide experiment) and pore water velocity (from Eq.2.3) were used as known parameters. R and λ were determined from BTCs using the zero and first moment analysis (using Eq. 3.3 and 3.4 below) as described by (Pang et al., 2003).

$$M_o = t_o \exp \frac{v}{x} \left(1 - \sqrt{1 + \frac{4D\lambda}{v^2}} \right) \quad (3.3)$$

Where, M_o is the temporal moments from concentration breakthrough curve (area under the curve), t_o is the injection time, x is the distance at which the breakthrough data were collected (i.e. 25 cm) and λ is the combined first-order degradation rate constant that accounts for degradation of solute in both liquid and solid phases.

$$Mu_1 = \frac{t_o}{2} + \frac{xR}{\sqrt{v^2 + 4D\lambda}} \quad (3.4)$$

Where a nonequilibrium model is been used, the parameters β and ω were obtained by curve fitting as there is no independent technique to determine these parameters. The mass transfer coefficient (k) and the fraction of instantaneous sorption sites (F) were then determined from the best fit values of β and ω and Eqs. (2.13f and 2.13g). The procedure used for analyzing the pesticides BTCs is schematically shown in Fig. 3.4.

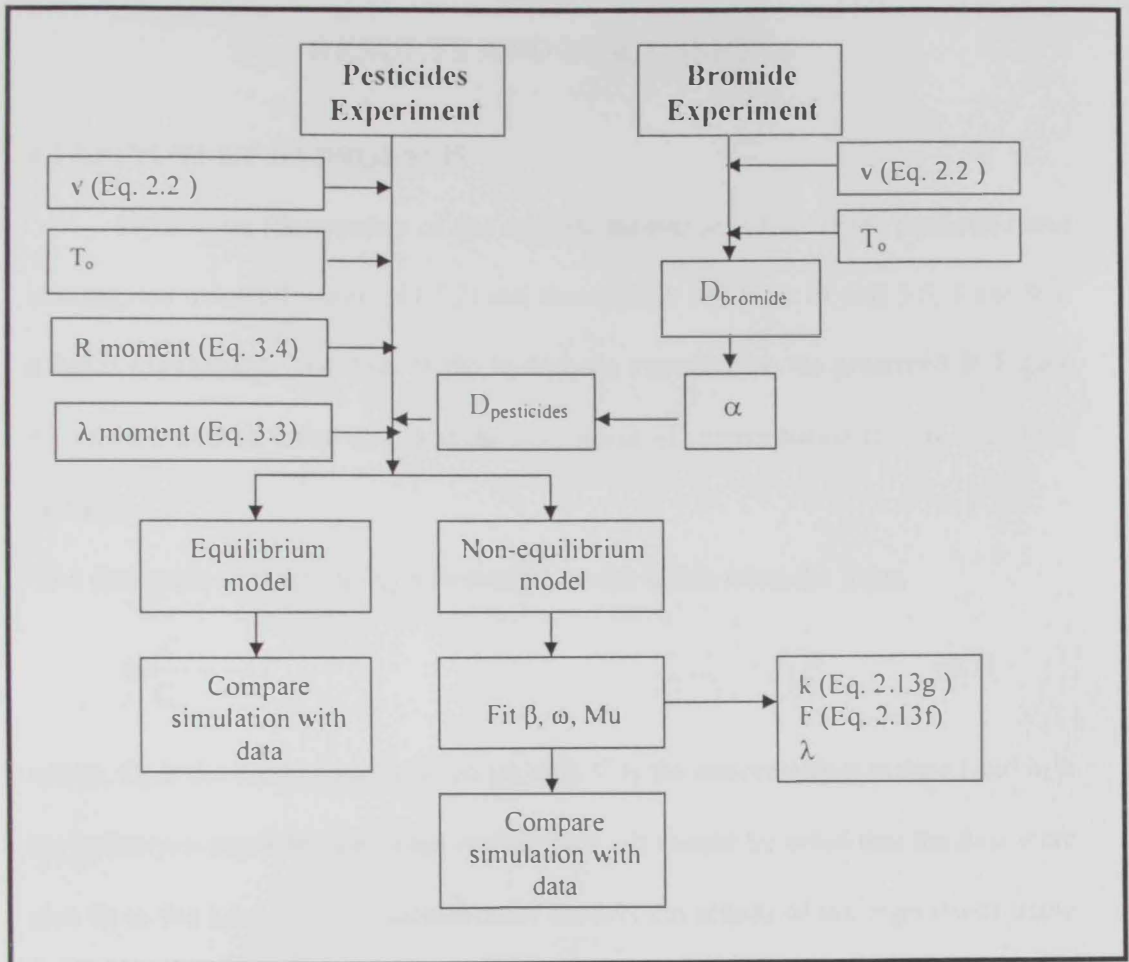


Fig. 3.4 Schematic diagram of the analysis of pesticides breakthrough data.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 EFFECTS OF HYDROLYSIS

Hydrolysis (destruction of the original substance) of the three pesticides was investigated using DI water (pH 7.2) and three buffer solutions of pHs 5.5, 8 and 9 in a batch experiment. The data of the hydrolysis experiments are presented in Figure 4.1 and the best fit value of λ_1 and the coefficient of determination (r^2) are presented in Table 4.1.

The data were analyzed using a first-order model which takes the form:

$$\ln \frac{C}{C_0} = -\lambda_1 t \quad (4.1)$$

where, C_0 is the initial concentration (at $t=0$), C is the concentration at time t and λ_1 is the hydrolysis rate constant in the liquid phase. It should be noted that the data were also fit to the zero- and the second-order models but results of the regressions using these models were not better than those obtained by the first-order model.

Table 4.1 Results of fitting hydrolysis data to the first-order degradation model.

Pesticide	Solution pH	λ_1 (1/hr)	r^2
Dimethoate	5.5	0.0015	0.87
	7.2	0.0015	0.87
	8.0	0.0018	0.968
	9.0	0.0047	0.978
Cymoxanil	5.5	1×10^{-4}	0.11
	7.2	0.023	0.99
	8.0	0.079	0.936
	9.0	0.819	NA*
Metalaxyl	5.5	5×10^{-6}	0.11
	7.2	0.0014	0.75
	8.0	2×10^{-5}	0.028
	9.0	2×10^{-5}	0.003

* Regression was based on two points since the concentration at periods longer than 6 hrs was not detected.

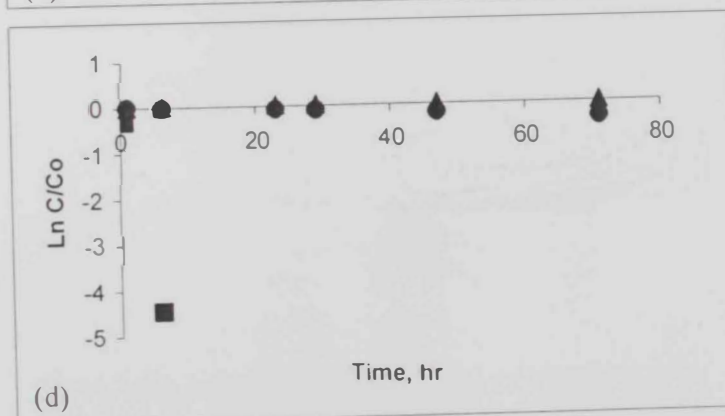
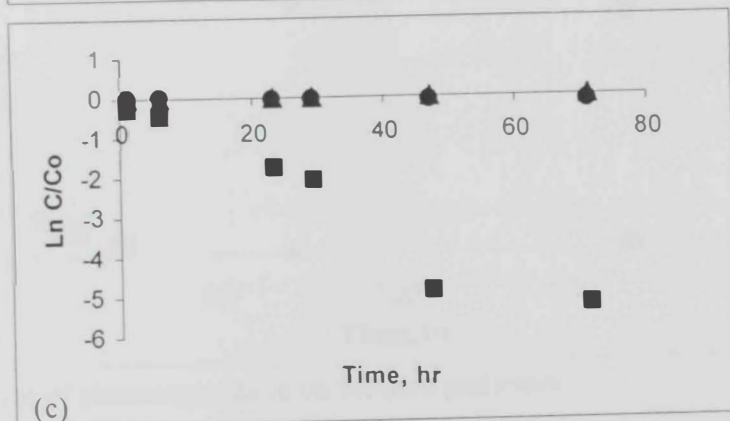
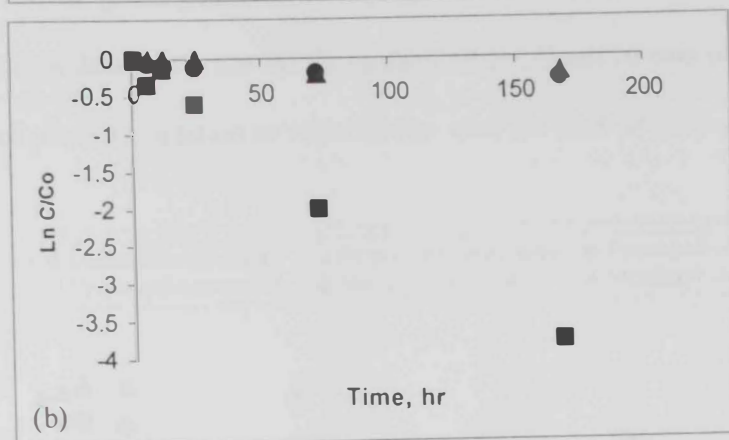
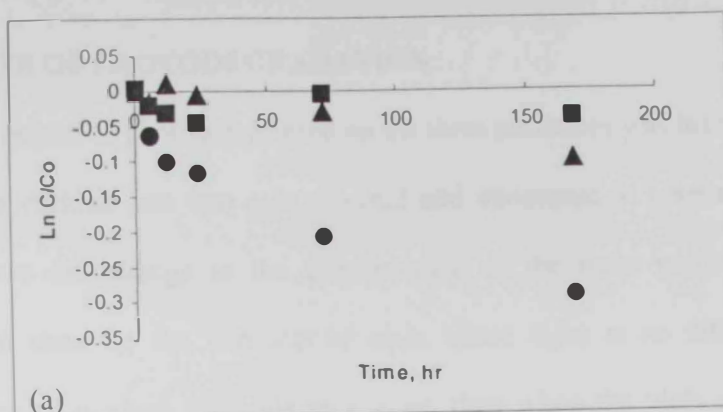


Fig. 4.1 Effect of hydrolysis on the three pesticides at (a) pH 5.5, (b) pH 7.2, (c) pH 8, and (d) pH 9. Circles for dimethoate, rectangles for cymoxanil and triangles for metalaxyl.

4.2 EFFECTS OF PHOTODEGRADATION

The impact of photodegradation on the three pesticides was investigated using similar vials divided into two sets: covered and uncovered at constant pH of 7.2. Fig.4.2 shows the change in the concentration of the three pesticides over the experimental time for the two sets of vials. Since there is no difference in the concentration of a given pesticide at a given time when the vials are covered or uncovered (some data points are overlying each other), it can be concluded that there is no effect of photodegradation or vaporization over the time of the experiment.

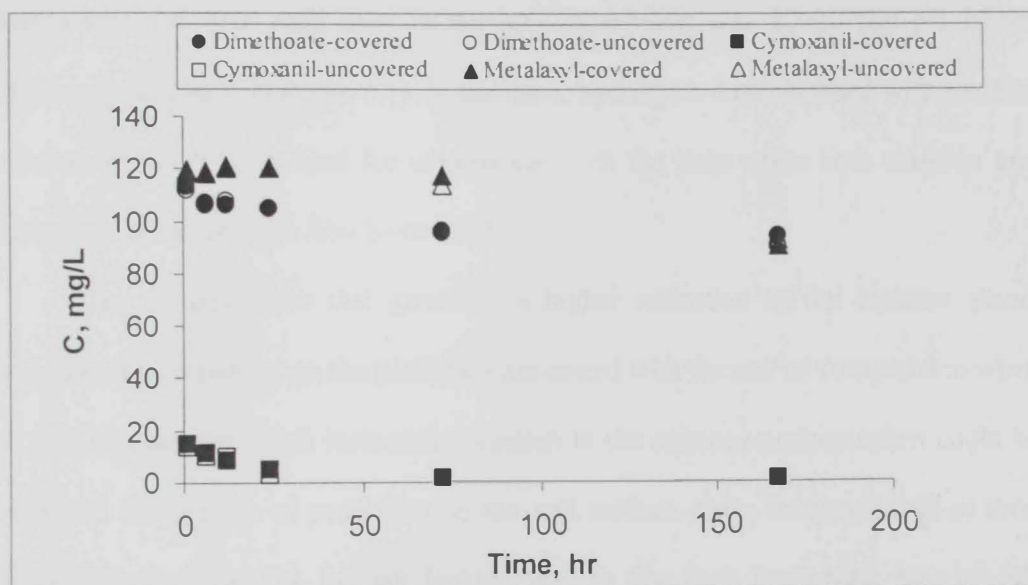


Fig. 4.2 Effect of photodegradation on the used pesticides.

4.3 EFFECTS OF SORPTION

4.3.1 Sorption Rate

The results of the batch sorption rate study for dimethoate, cymoxanil and metalaxyl on Al Foah and Abu Samra soils are presented in Figures 4.3 and 4.4, respectively. Also shown on the figures are the hydrolysis data at the pH of the soil solution (Table 3.1). For Al Foah soil the S/W ratio used in the rate experiment was 1.5:1. The pH of such solution would fall between 8.03 and 8.34 (table 3.1). In this case, the hydrolysis data obtained with a buffer solution of pH 8 were employed for comparison with the data when both sorption and hydrolysis occurred. As for Abu Samra soil, the S/W ratio used in the rate experiment was 2.5:1. The pH of the solution would be 9.24 (table 3.1). In this case, hydrolysis data obtained with a buffer solution of pH 9 were used for comparison with the data when both sorption and hydrolysis occurred with Abu Samra soil.

The figures show that generally a higher reduction in the aqueous phase concentration occurs when the pesticides are mixed with the soil as compared to when no soil was present. Such increased reduction in the aqueous concentration could be attributed to sorption of pesticides on the soil surface. Data for cymoxanil at time periods greater than 24 hrs are lacking due to the high hydrolysis rate of this pesticides in addition to its sorption on the soil. The combined effect caused disappearance of the chemical from the solution.

Figures 4.3 and 4.4 show that it is reasonable to assume that equilibrium sorption for dimethoate and metalaxyl occurs after approximately 3 days since there is a slight change in the aqueous-phase concentration of the compounds with time afterwards.

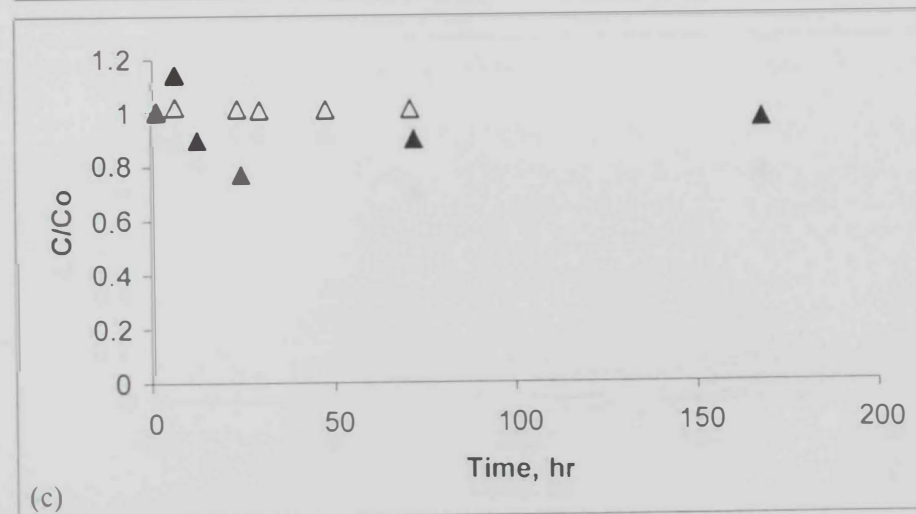
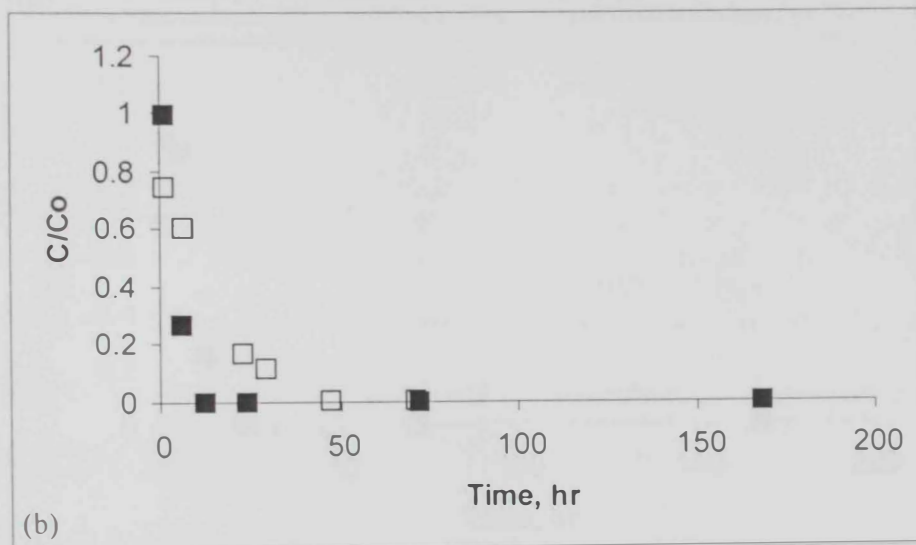
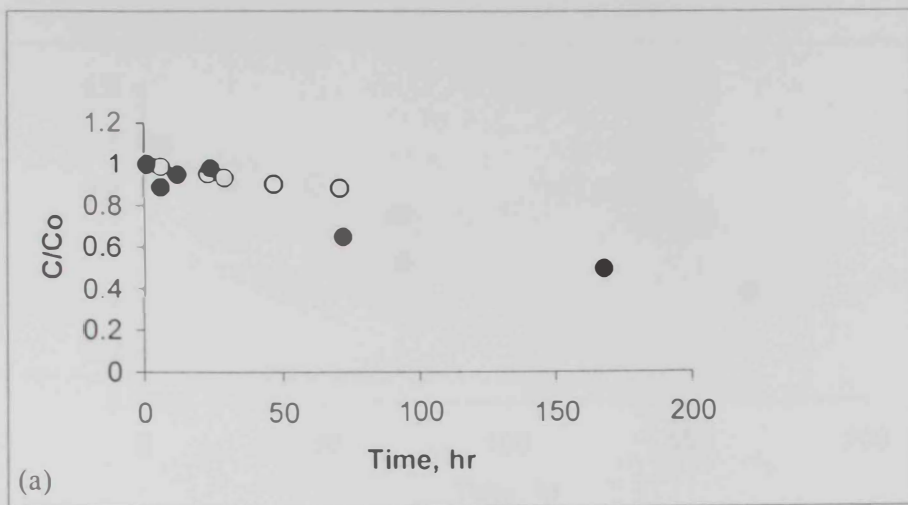


Fig. 4.3 Sorption rate of (a) dimethoate (b) cymoxanil and (c) metalaxyl on Al Foah soil (S/W=1:1). Open symbols represent the hydrolysis data. Closed symbols represent both hydrolysis and sorption.

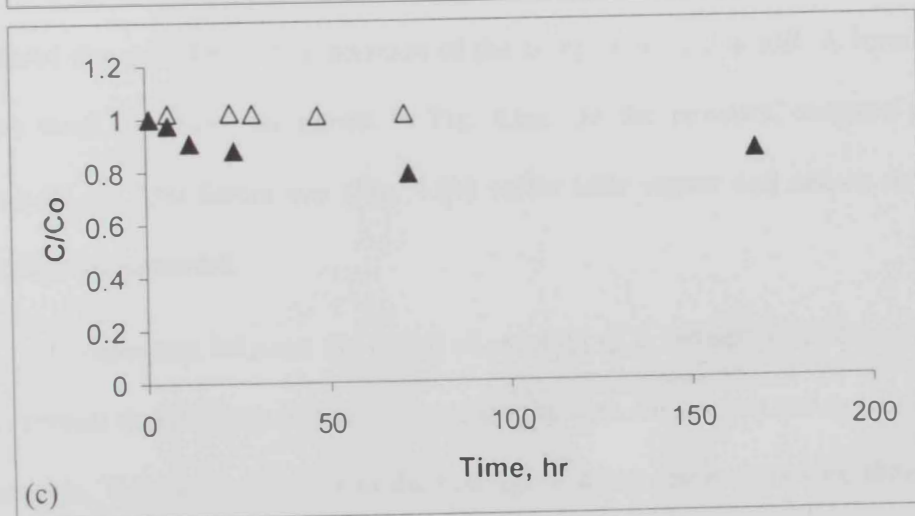
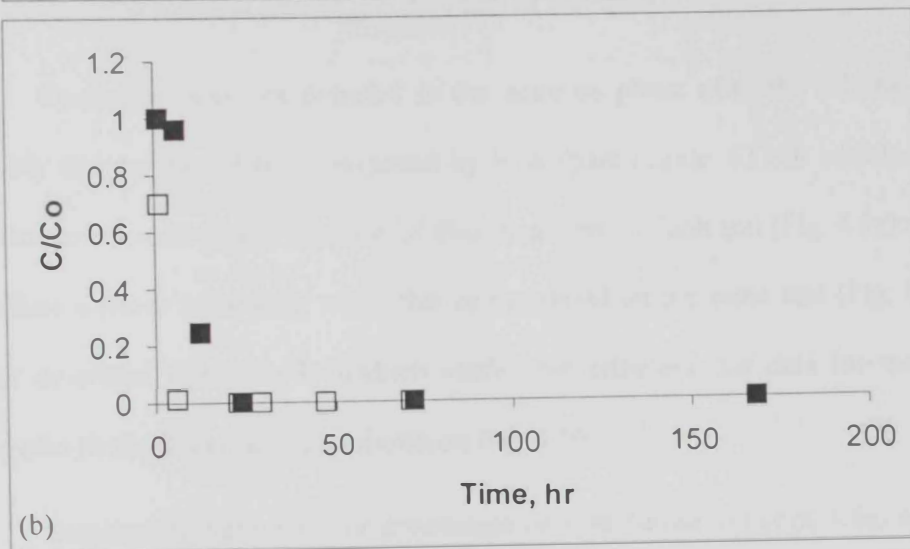
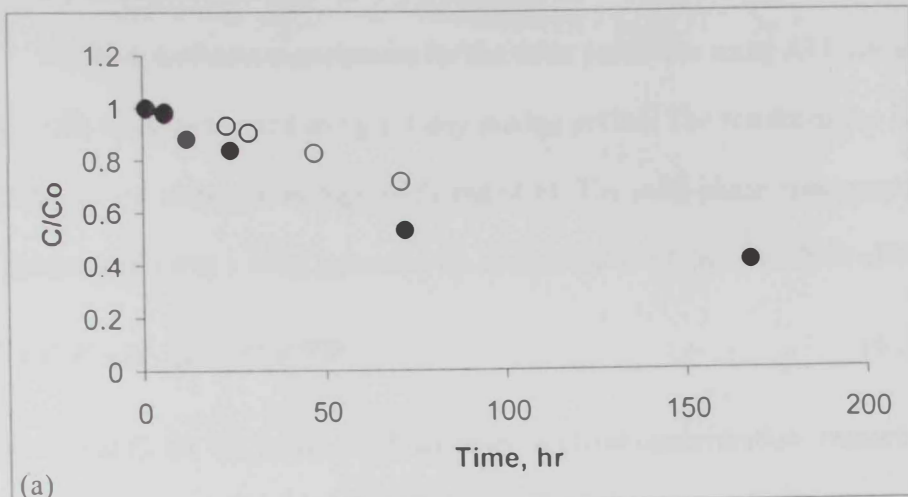


Fig. 4.4 Sorption rate of (a) dimethoate (b) cymoxanil and (c) metalaxyl on Abu Samra soil (S/W=2.5:1). Open symbols represent the hydrolysis data. Closed symbols represent both hydrolysis and sorption.

4.3.2 Sorption Isotherm

Sorption isotherm experiments for the three pesticides using Al Foah and Abu Samra soils were conducted using a 3-day mixing period. The results of the isotherm experiments are presented in Figs. (4.5) and (4.6). The solid-phase concentration (S_e) was determined using a mass balance with consideration of the hydrolysis effect:

$$C_oV = C_eV + M_{soil}S_e + C_o e^{-k_d t} V \quad (4.2)$$

where C_o and C_e are the initial and final aqueous-phase concentration, respectively. V is the volume of solution and M_{soil} is the mass of soil used.

Cymoxanil was not detected in the aqueous phase after the mixing period possibly due to loss of this compound by hydrolysis (Table 4.1) in addition to its sorption to the solid phase. Sorption of dimethoate on Al Foah soil (Fig. 4.5a) appears to follow a linear behaviour, while that of metalaxyl on the same soil (Fig. 4.5b) is better described using the Freundlich model. Nevertheless, the data for metalaxyl were also fit the linear model as shown on Fig. 4.5b.

Sorption isotherm data for dimethoate on Abu Samra soil (Fig. 4.6a) is highly scattered due possibly to low sorption of the compound on this soil. A linear trend, albeit weak, is drawn as shown in Fig. 4.6a. On the contrary, sorption data of metalaxyl on Abu Samra soil (Fig. 4.6b) suffer little scatter and can be described using the linear model.

Comparison between the extent of sorption of a certain pesticide on the two soils reveals that Al Foah soil has higher capacity than Abu Samra soil to absorb these chemicals. This is consistent with the findings of many researchers who showed that as the organic matter content of the soil increases so does its sorption capacity. Based on the linear fit equations (Figs. 4.5 and 4.6), it can be seen that sorption of dimethoate on Al Foah soil is almost 15 times higher than that on Abu Samra soil,

while that of metalaxyl is 36 times higher. These numbers are even higher than the ratio of the organic matter content of the two soils (i.e. 4.0).

Based on the range of values of K_{oc} reported in the literature for the three compounds (Table 3.2), values of the linear sorption distribution coefficient (K_d) can be determined as:

$$K_d = K_{oc} \times f_{om} \times 0.59 \quad (4.3)$$

where f_{om} is the fraction of organic matter on the soil and the coefficient 0.59 is used to convert organic matter to organic carbon (Fetter, 1999). Values of K_d determined using (4.3) are listed in Table 4.2 along with corresponding values for the compounds shown on Fig. 4.5 and 4.6. Apparently, values of K_d found in this study for the compounds using Abu Samra soil fall within the range of values predicted using Eq. 4.3. However, values found for the pesticides using Al Foah soil are beyond the upper range of those predicted by Eq. 4.3.

Table 4.2 Predicted versus determined K_d values for the pesticides.

Pesticide	Soil	K_d (Eq. 4.3)	K_d (Figs. 4.5 and 4.6)
Dimethoate	Al Foah	0.044-0.167	0.22
	Abu Samra	0.011-0.042	0.015
Cymoxanil	Al Foah	0.19-1.17	NA
	Abu Samra	0.048-0.29	NA
Metalaxyl	Al Foah	0.148-1.4	9.1
	Abu Samra	0.037-0.35	0.253

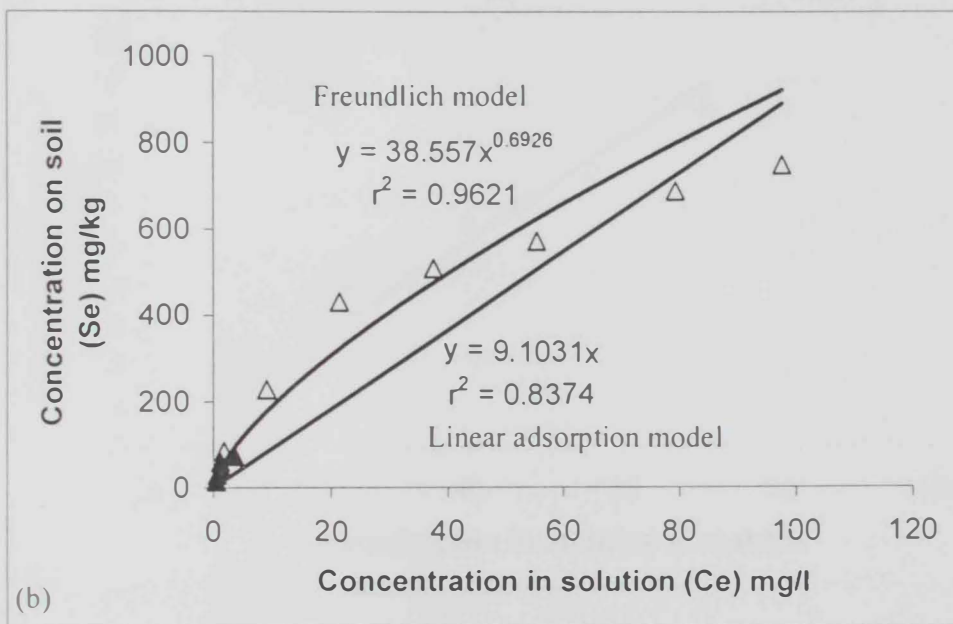
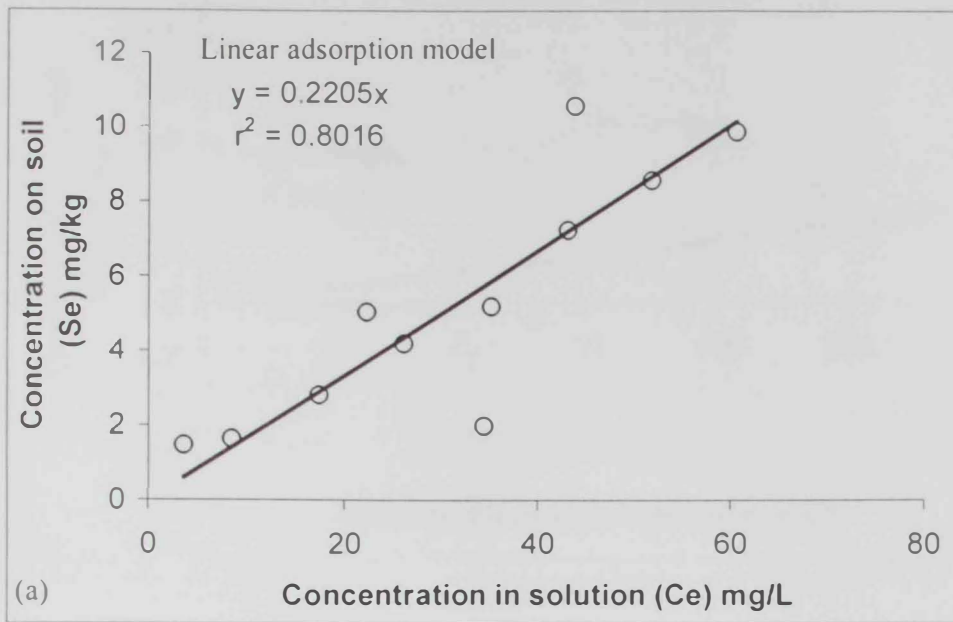


Fig. 4.5 Sorption isotherm of (a) dimethoate and (b) metalaxyl on Al Foah soil.

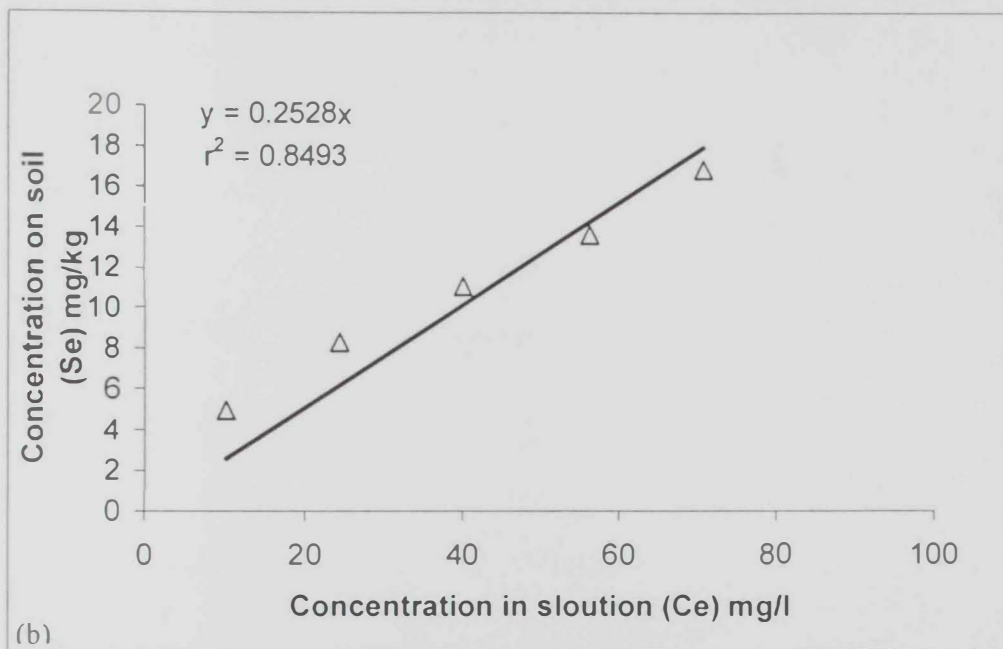
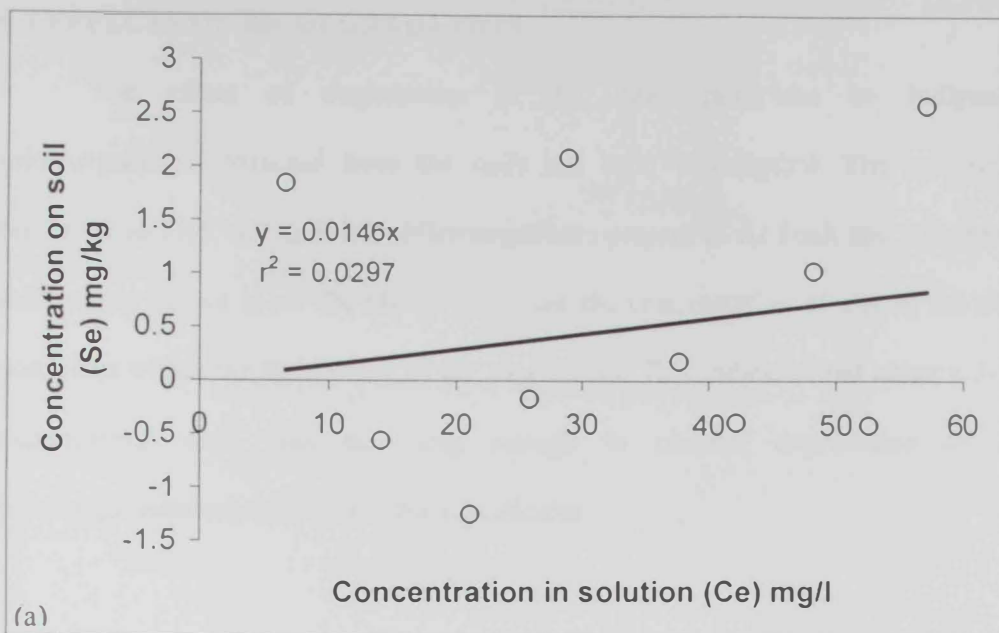


Fig. 4.6 Sorption isotherm of (a) dimethoate and (b) metalaxyl on Abu Samra soil.

4.4 EFFECTS OF BIODEGRADATION

The effect of degradation of the three pesticides by indigenous microorganisms extracted from the soils has been investigated. The results are presented in Figs. 4.7 and 4.8. Microorganisms present in Al Foah and Abu Samra soil extract do not show the ability to reduce the concentration of any of the three pesticides within the time frame of the experiment. This indicates that either a 3-day experimental time was not long enough to observe degradation or soil microorganisms cannot degrade these pesticides.

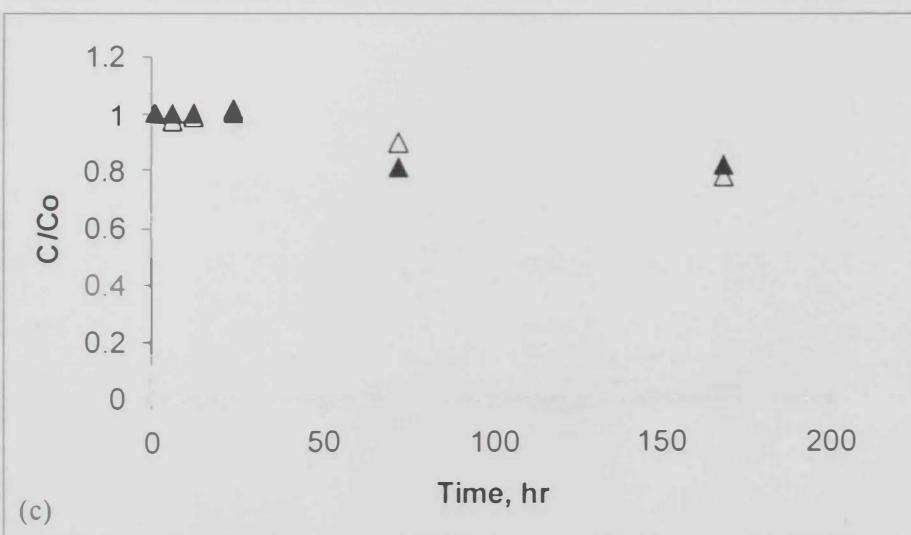
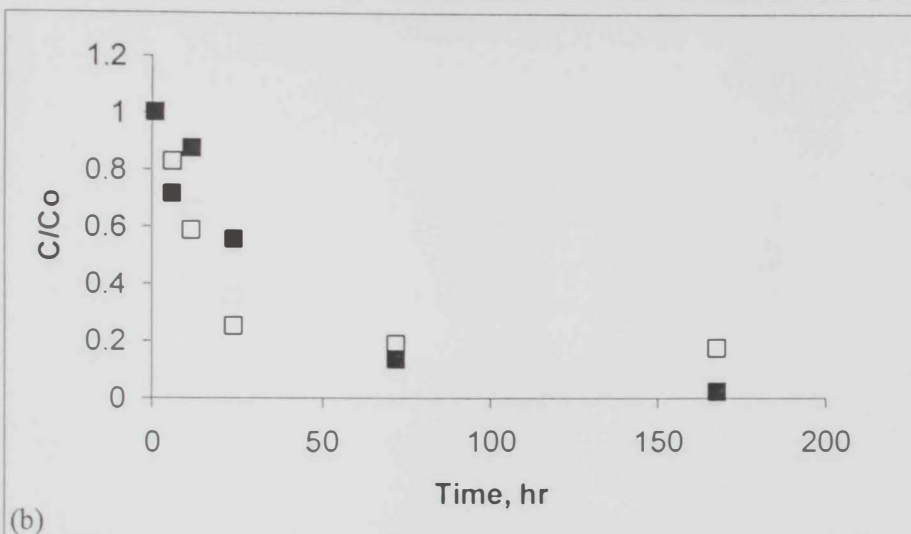
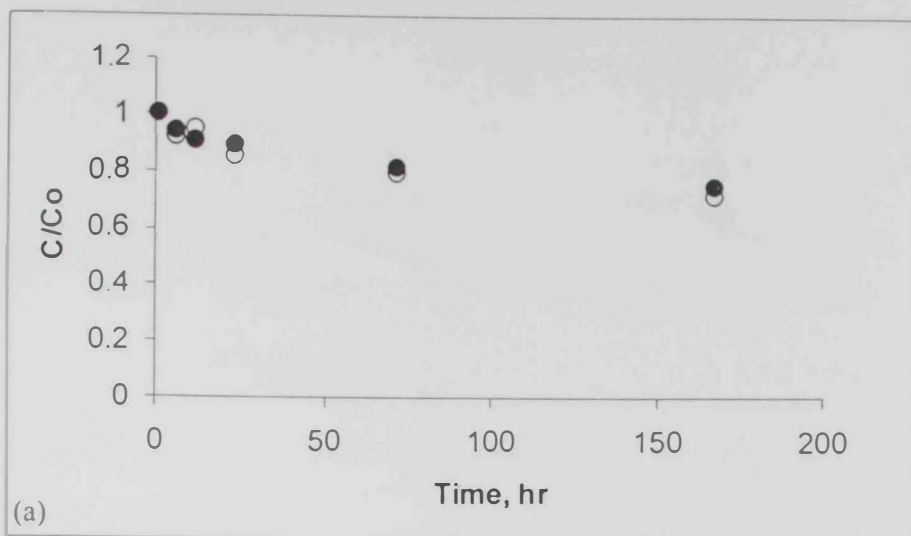


Fig. 4.7 Effect of using indigenous microorganism in Al Foah soil extract on degradation of (a) dimethoate (b) cymoxanil and (c) metalaxyl. Closed symbols represent effect of hydrolysis. Open symbols represent hydrolysis and biodegradation.

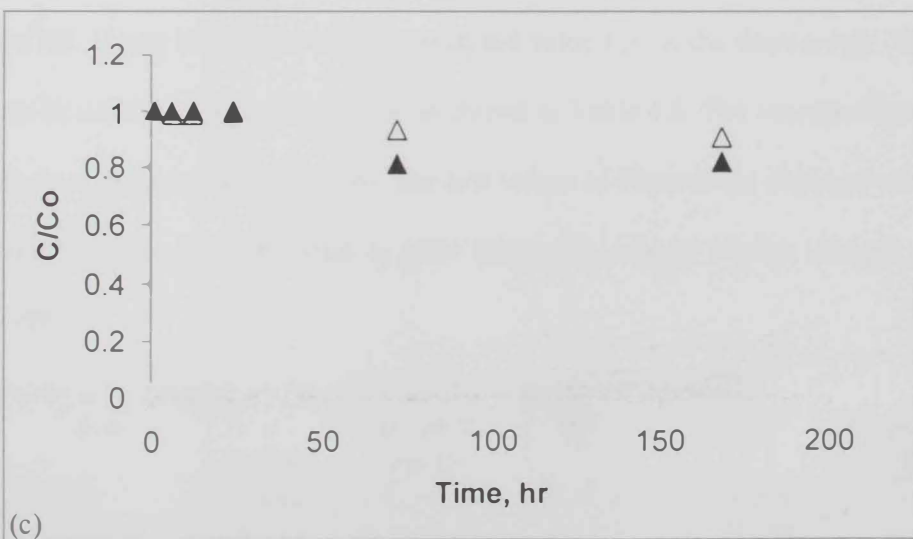
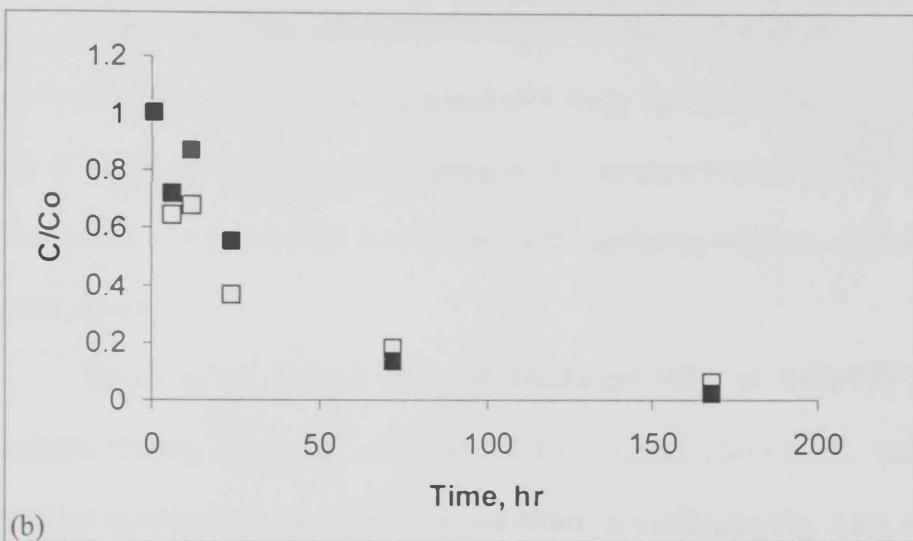
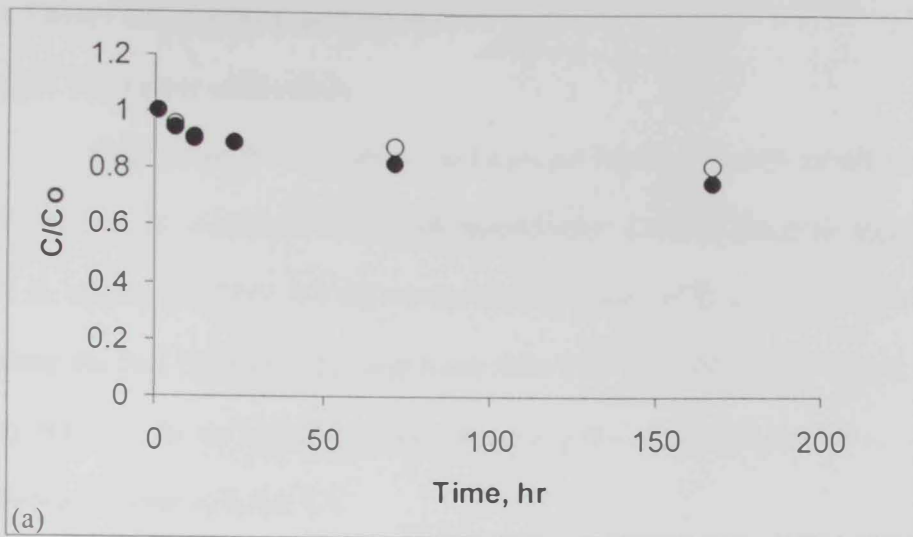


Fig. 4.8 Effect of using indigenous microorganism in Abu Samra soil extract on degradation of (a) dimethoate (b) cymoxanil and (c) metalaxyl. Closed symbols represent effect of hydrolysis. Open symbols represent hydrolysis and biodegradation.

4.5 MISCIBLE DISPLACEMENT

4.5.1 Transport of Bromide

Normalized BTCs of Br on Al Foah and Abu Samra soils are shown in Figure 4.9. Dispersion coefficients were determined using CXTFIT assuming that both D and R as unknowns. Table 4.3 shows the best fit values of D and R. Simulations of Br using the best fit values of D and R are shown by the solid lines in Figure 4.9 (a and b). BTCs of Br are adequately described using the optimized parameters as reflected by the r^2 values in Table 4.3.

Inspection of the values of R in Table 4.3 shows that Br acts as a near ideal tracer (R is close to 1.0). Small deviation of R from 1.0 for bromide could possibly be due to interaction with the solid matrix or due to experimental uncertainties in the determination of some of the known parameters including moisture content and pore-water velocity.

Based on an aqueous diffusion coefficient value of 2.01×10^{-9} m²/sec for bromide (Fetter, 1999) and an ω of 0.7 for columns packed with uniform sand (Perkins and Johnson, 1963), the effective diffusion coefficient (Eq. 2.3b) will be 0.05 cm²/hr. Using this value and the predicted value for D, the dispersivity of the media can be calculated using Eq. (2.3a) as shown in Table 4.3. The average dispersivity for the two packed soils is 0.23 cm. The low values of dispersivity obtained are consistent with what has been reported in other laboratory column studies (Beigel and Pietro, 1999).

Table 4.3 Summary of the results of the bromide experiments.

Soil	v cm/hr	D (\pm CI), cm ² /hr	R (\pm CI)	r^2	Dispersivity cm
Al Foah	4.645	1.62 (0.142)	1.07(0.142)	0.9943	0.338
Abu Samra	4.115	0.55(0.071)	1.12(0.071)	0.9985	0.122

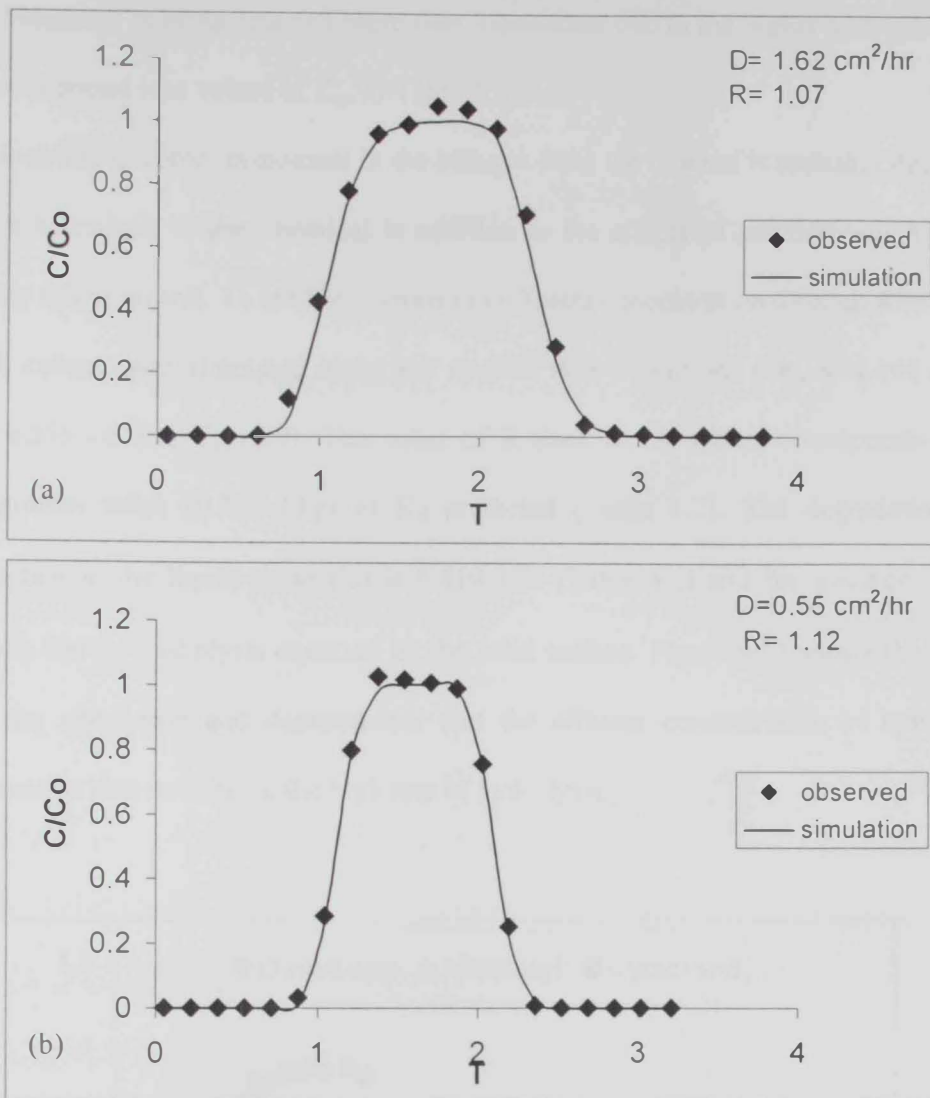


Fig. 4.9 BTCs of Br using columns packed with (a) Al Foah and (b) Abu Samra soil samples.

4.5.2 Qualitative Analysis of Pesticides BTCs

Normalized effluent concentration of the injected pesticides through Abu Samra soil column are shown in Fig. 4.10. Both dimethoate and metalyxal appeared in the effluent from the soil column within the time frame of the experiment (i.e. 48 hrs), but cymoxanil did not appear in the effluent during the experimental time interval. The following two observations can be drawn from Fig. 4.10:

1. Metalaxyl is being retarded more than dimethoate due to the higher hydrophobicity of compound (see values of K_{oc} in Table 3.2).

2. Inability to detect cymoxanil in the effluent from the column is probably due to the high hydrolysis of this chemical in addition to the effects of sorption which causes delay of cymoxanil. To see this, cymoxanil effluent concentration through Abu Samra soil column was simulated under the applied flow conditions (i.e., $v=4.144$ cm/hr, $D=0.555$ cm²/hr, $T_0=1.99$). The value of R used is 1.2 which corresponds to the minimum value (0.253 l/kg) of K_d predicted (Table 4.2). The degradation rate constant in the liquid-phase (λ_l) is 0.819 1/hr (Table 4.1) and the assumption was made that no hydrolysis occurred on the solid surface. Figure 4.11 shows the results of the simulation and demonstrates that the effluent concentration of cymoxanil cannot be detected due to the high rate of hydrolysis.

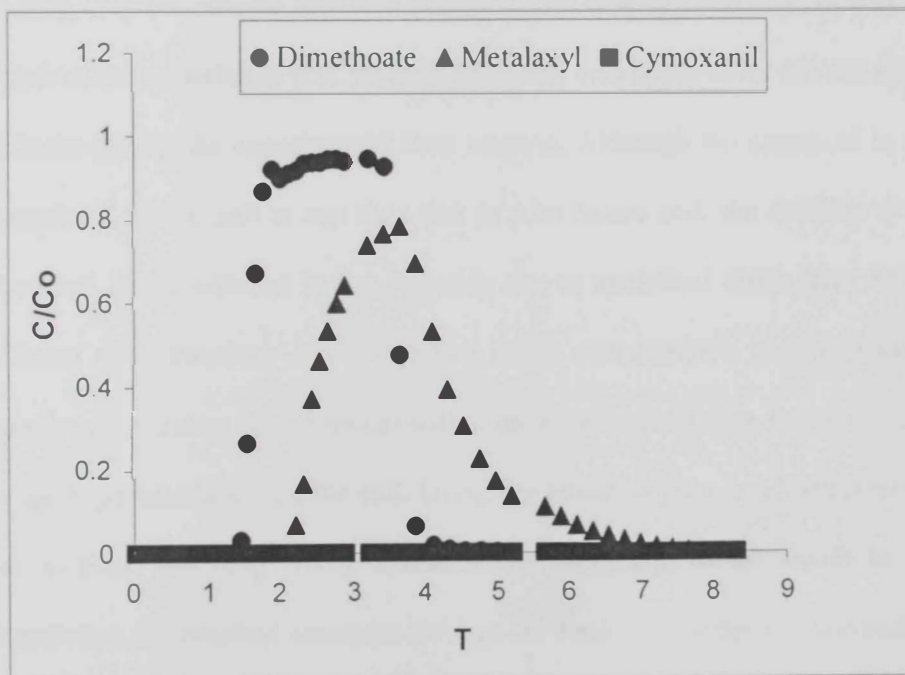


Fig. 4.10 BTCs of the used pesticides through Abu Samra soil column.

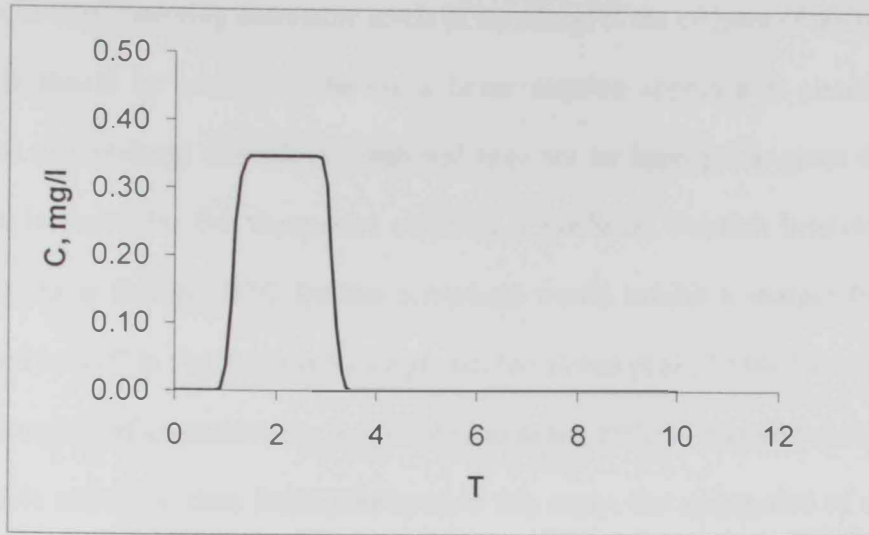


Fig. 4.11 Simulated BTCs for cymoxanil through Abu Samra soil.

Normalized effluent concentration of the injected pesticides through Al Foah soil column is shown in Figure 4.12. For this soil which has high organic matter (0.8%), only dimethoate appeared in the effluent from the soil column within the time frame of the experiment (i.e. 50 hrs). The other two compounds did not appear in the effluent during the experimental time interval. Although the extent of hydrolysis of cymoxanil in this soil is less than that in Abu Samra soil, the inability to detect the chemical in the effluent is due probably due to analytical difficulties detecting low effluent concentrations due to the low initial concentration (3 mg/L) used. As for metalaxyl, to detect this chemical within the experimental time frame is probably due to the high retardation on the soil. Using the linear sorption coefficient for metalaxyl on Al Foah soil (Fig. 4.5b), a retardation coefficient of 40 would be estimated. Simulation of metalxyl transport through Al Foah soil under the conditions $v=2.98$ cm/hr, $D=1.04$ cm²/hr, $T_0=1.4$, and $R=40$ was done as shown in Fig. 4.13. The value of λ used to generate the simulation is 0.00002 1/hr (Table 4.1) and the assumption was made that no hydrolysis occurred on the solid surface. The figure shows that

samples should have been collected for about 25 pore volume (approximately 6 days) in order to start observing detectable levels of metalaxyl in the effluent of the column.

It should be noted that the use a linear sorption approach to simulate the transport of metalaxyl through Al Foah soil may not be appropriate given that the sorption isotherm for this compound exhibited a nonlinear sorption behavior. The expectations is that the BTC for this compound would exhibit a sharper front (as compared to BTC in Fig. 4.13) and a longer tail (Abulaban et al., 1998). Nevertheless, for the purpose of demonstrating the inability to detect effluent concentration within the sample collection time frame employed in this study, the assumption of a linear sorption behavior would be sufficient.

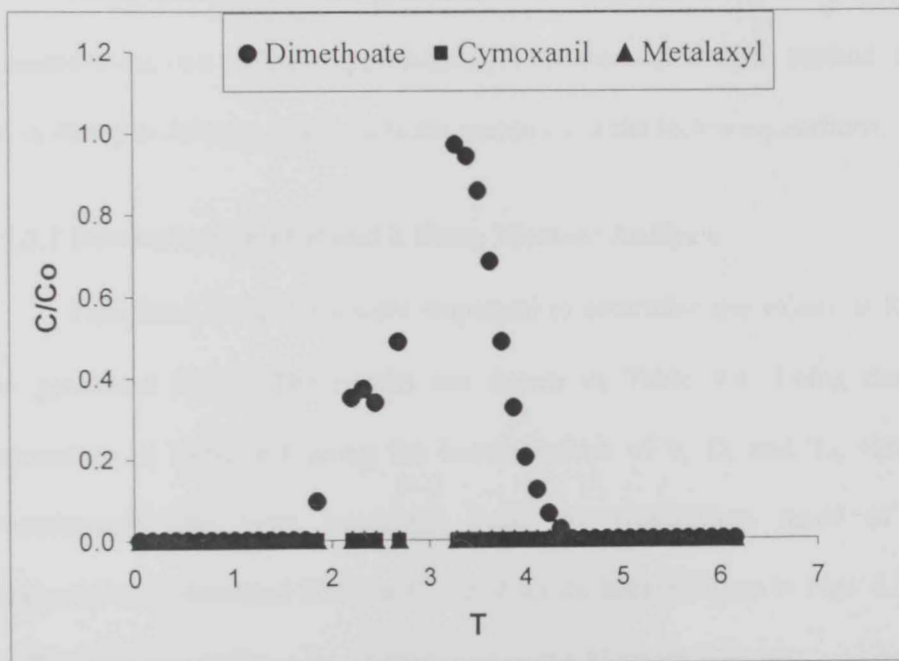


Fig. 4.12 BTCs of the used pesticides through Al Foah soil column.

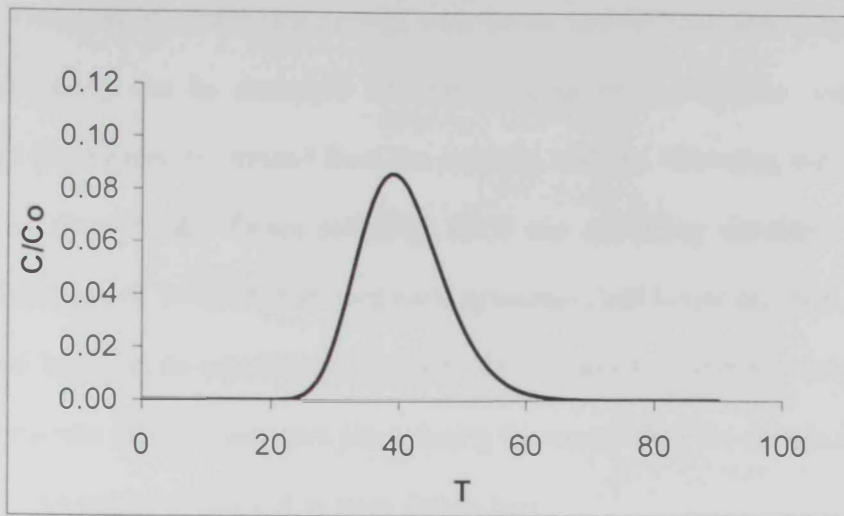


Fig. 4.13 Simulated BTC for metalaxyl using Al Foah soil.

4.5.3 Simulation of the Breakthrough Data

Generated BTCs of the pesticides were simulated using transport parameters obtained using two different approaches: (1) the moment analysis method, and (2) the curve fitting technique. The results are presented in the following sections.

4.5.3.1 Determination of R and λ Using Moment Analysis

Equations 3.3 and 3.4 were employed to determine the values of R and λ for the generated BTCs. The results are shown in Table 4.4. Using the transport parameters in Table 4.4 along the known values of v , D , and T_0 , simulation of breakthrough data were conducted using the equilibrium mode of CXTFIT. Comparison of simulated BTCs with the observed data is shown in Figs. 4.14-4.16.

Table 4.4: Values of R and λ Determined by the Moment Method

Soil	Pesticide	R	λ (1/hr)	K_d
Abu Samra	Dimethoate	1.597	0.0056	0.145
	Metalaxyl	3.171	0.055	0.770
Al Foah	Dimethoate	2.43	0.021	0.450

Transport of dimethoate through Abu Samra and Al Foah soil columns (Fig. 4.14 and 4.16) can be described adequately using the equilibrium model with transport parameters determined from the moment analysis. However, movement of metalaxyl through Abu Samra soil (Fig. 4.15) can not being simulated with the equilibrium model. Metalaxyl showed early appearance and longer tail than could be described based on an equilibrium transport. This behavior is probably due to a rate limited transfer process that takes place during the transport of the chemical through the soil. This point is discussed in more details later.

Table 4.4 shows that the retardation coefficient of metalaxyl through Abu Samra soil is almost twice as higher as that of dimethoate. Dimethoate through Al Foah soil showed higher sorption than on Abu Samra soil due to higher soil organic matter content. Comparison between the ratio of the two K_d values for this compound on Al Foah and Abu Samra soils (~ 3.1) showed that this ratio is comparable to the ratio of organic matter on the two soils (i.e. 4.0).

Comparison between K_d values determined by the miscible displacement study (Table 4.4) and corresponding ones obtained by sorption isotherm (Table 4.1) showed that the K_d values determined from the column studies are 2-10 times higher. This could be due to the assumption made that equilibrium in the batch tubes has been reached in 3 days while it takes longer for the compounds to reach equilibrium. Under such conditions the determined value of K_d would be lower than the actual one.

Table 4.4 also shows that the hydrolysis rate coefficient for dimethoate and metalaxyl determined by moment analysis are higher than the corresponding values of λ_1 in Table 4.1. Since λ determined by moment analysis is a combined degradation rate constant, higher values of λ determined by moment analysis as compared to λ_1 (Table 4.1) suggests that there is an enhanced hydrolysis with sorption. The extent of

differences between the combined λ and λ_i is amplified by the extent of retardation of the compound.

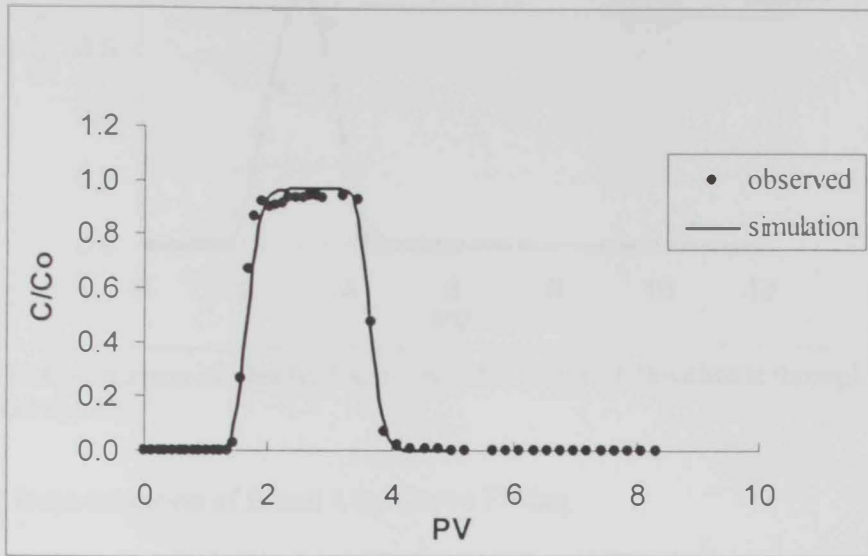


Fig. 4.14 Comparison of observed and simulated BTCs of dimethoate through Abu Samra soil column

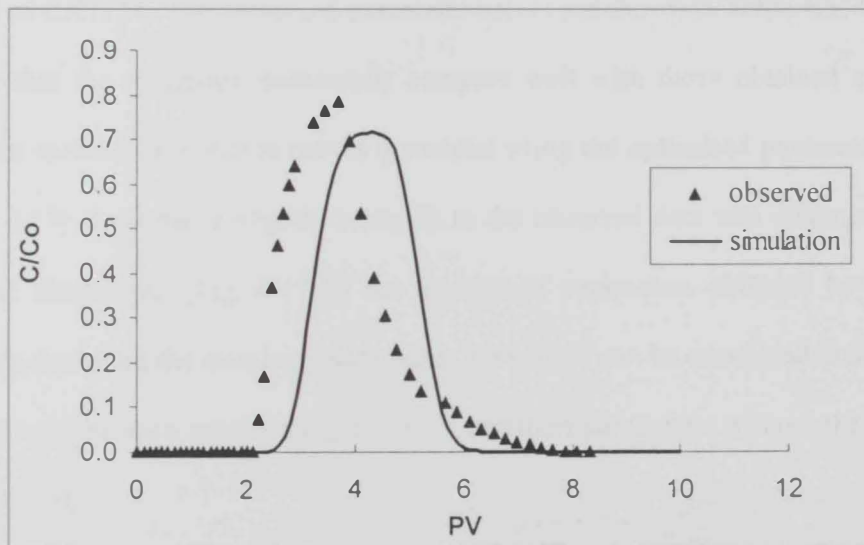


Fig. 4.15 Comparison of observed and simulated BTCs of metalaxyl through Abu Samra soil column.

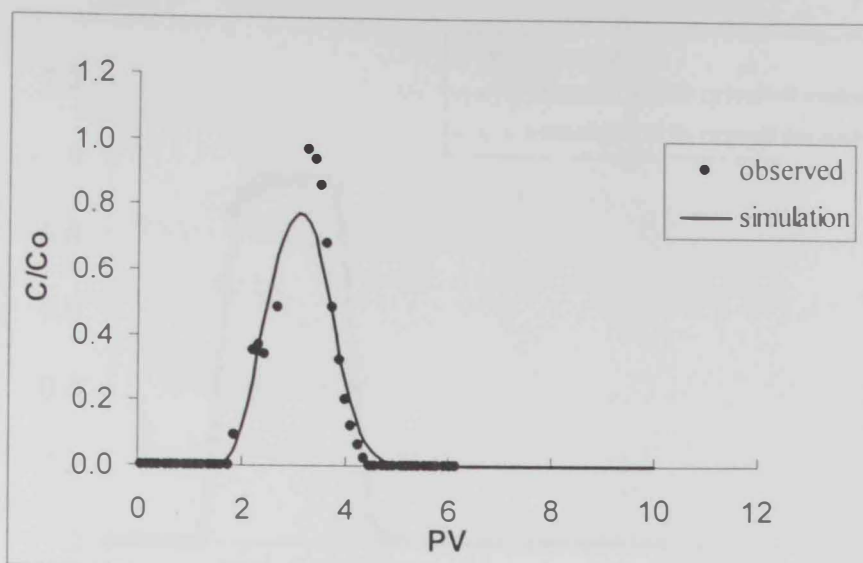


Fig. 4.16 Comparison of observed and simulated BTCs of dimethoate through Al Foah soil column.

4.5.3.2 Determination of R and λ by Curve Fitting

Transport parameters R and λ for dimethoate on Abu Samra and Al Foah soils were also determined by curve fitting using the inverse mode of the equilibrium model of CXTFIT. The optimized parameter values are shown in Table 4.5. The table shows that the optimized parameters compare well with those obtained using the moment method. Simulation curves generated using the optimized parameter values (Figs. 4.17) show that a slightly better fit to the observed data was obtained for the case of dimethoate (Fig. 4.17 b) but the use of parameters obtained by moment analysis described the metalaxyl data better. Overall, it can be concluded that moment analysis can be used satisfactorily to obtain transport parameters without the need for curve fitting.

Table 4.5 Comparison of parameter values of R and λ for dimethoate determined by optimization and moment analysis.

Soil	Method	R	λ , 1/hr	SSQ	r^2
Al Foah	Curve fitting	2.46	0.0624	0.185	0.942
	Moment analysis	2.43	0.021	NA	NA
Abu Samra	Curve fitting	1.65	0.0419	0.056	0.993
	Moment analysis	1.67	0.0056	NA	NA

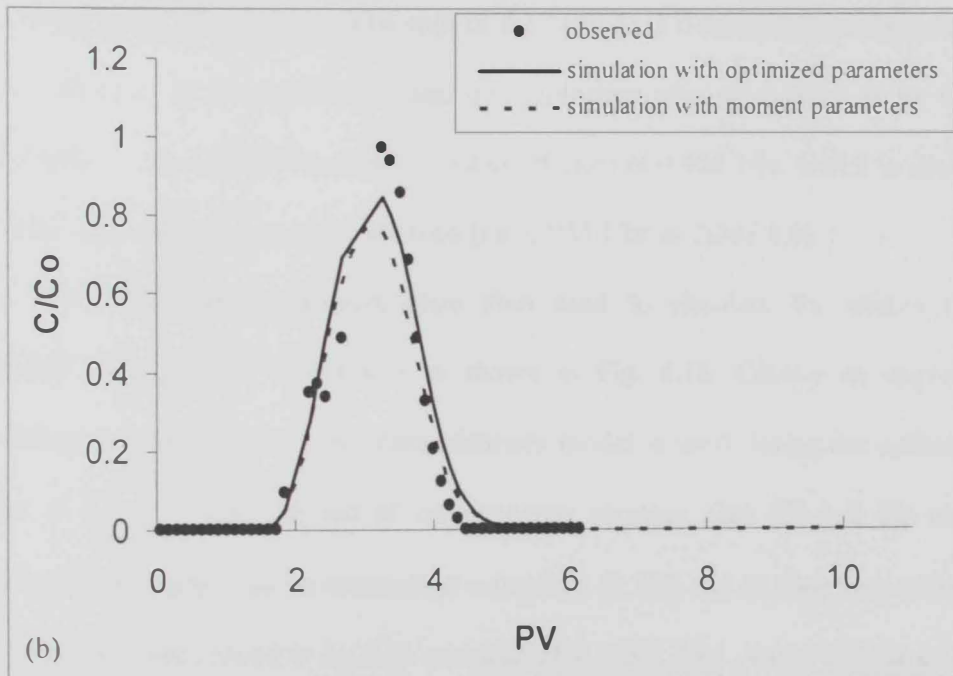
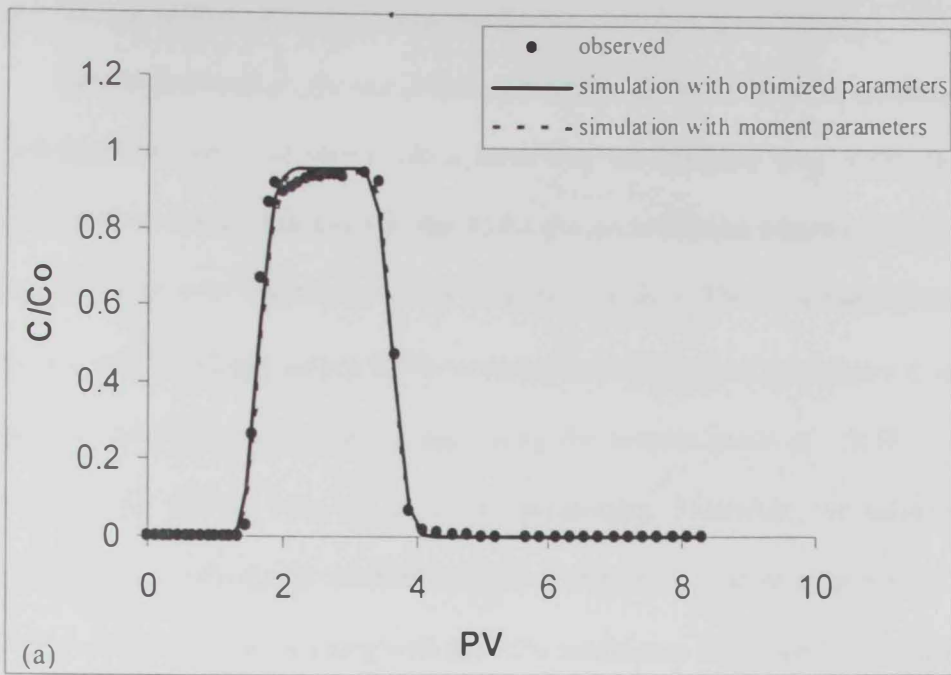


Fig. 4.17 Simulated and observed BTCs for dimethoate transport through (a) Abu Samra and (b) Al Foah soils.

4.5.3.3 Determination of Nonequilibrium Parameters by Curve Fitting

As indicated before, the use of the equilibrium model to describe the transport of metalaxyl through Abu Samra soil column was not adequate (Fig. 4.15). It was speculated that such inadequacy was due to the presence of mass transfer process that causes early appearance and long tail of breakthrough data. Thus, the nonequilibrium model was used to obtain values for the nonequilibrium transport parameters β and ω along with the degradation rate constant using the inverse mode of CXTFIT. The values of v , D , and T_0 were set as known parameters. Moreover, the value of R determined independently by moment analysis was used as a known parameter. The optimized values of β and ω along with the 95% confidence limits were $0.747 \pm (0.28)$ and $0.49 \pm (0.47)$, respectively. The sum of the optimized dimensionless degradation rate coefficients in the equilibrium and nonequilibrium sites was found to be 0.39. This results in a combined degradation rate coefficient of 0.056 1/hr, which is close to the value determined by moment analysis (i.e. 0.055 1/hr in Table 4.4).

The optimized parameters were then used to simulate the transport of metalaxyl through Abu Samra soil as shown in Fig. 4.18. Clearly an improved simulation is obtained when the nonequilibrium model is used. Using the optimized values of β and ω , the fraction of instantaneous sorption sites (F) and the mass-transfer coefficient (k) can be determined using Eqs. (2.13f) and (2.13g), respectively. The value of F was found to be 0.63 and that of k 0.082 1/hr. Value of F is a little higher than what Karickhoff (1980) and Karickhoff and Morris (1985) reported. These authors found that approximately 50% or less of the sorption sites were in equilibrium.

Maraqqa (2001) developed an empirical relationship relating the sorption mass-transfer coefficient to some system parameters:

$$k = 1.72 \left(\frac{LR}{v} \right)^{-0.93}, r^2 = 0.84 \quad (4.4)$$

Substituting the know values of L, R and v for metalaxyl on Abu Samra soil, the value of k predicted using Eq. (4.4) would be 0.11 l/hr. This value compares well with the value determined experimentally.

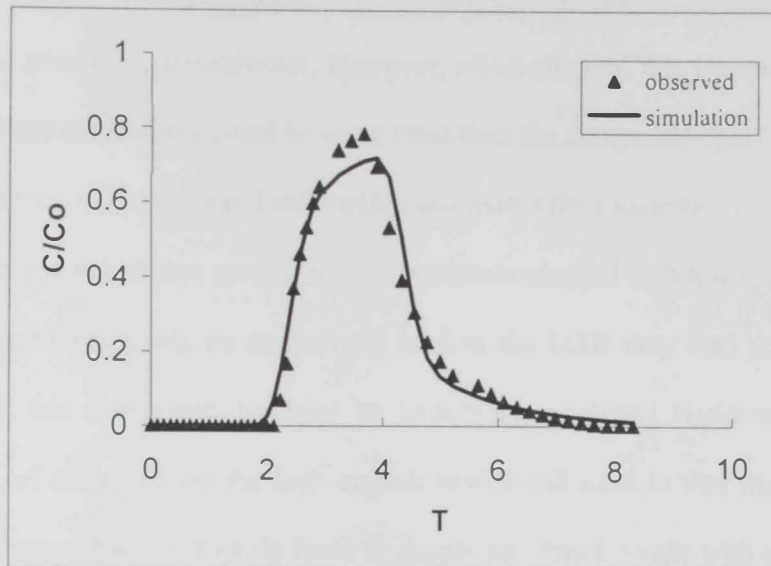


Fig. 4.18 Simulation of breakthrough data of metalaxyl through Abu Samra soil using the nonequilibrium transport model.

4.6 PRACTICAL IMPLICATIONS

With the reported field hydraulic conductivity of 1 m/day and the hydraulic gradient of 0.001 in several areas in the UAE (Wood et al, 2003), the average linear

velocity ($v = \frac{K}{\theta} \frac{dh}{dL}$), for a typical moisture content of 0.35, will be 1.04 m/yr.

Assuming that the dispersivity in the field does not deviate from that found in the laboratory (i.e. 0.23 cm), the mechanical dispersion part will be 0.0024 m²/yr. This value is very small, indicating that the magnitude of molecular diffusion cannot be ignored in the field. Thus, spreading of pesticides in groundwater will not extend far

beyond the application points under natural gradient flow conditions. In such case, efforts directed towards investigation of pesticides contamination of groundwater should focus on testing underlying aquifers below the agricultural areas. However, extensive pumping of groundwater will increase the gradient and may enhance the spreading of pesticides.

The high hydrolysis rate of cymoxanil implies that this compound will unlikely be present in groundwater. However, metabolites of this compound will be present. These metabolites could be more toxic than the compound itself. Hence, it is important to identify cymoxanil metabolites and assess their toxicity.

The low retardation coefficient of dimethoate coupled with low hydrolysis rate and high application rate on agricultural land in the UAE may lead to substantial amount of this compound leaching to underlying aquifers. However, the high retardation of metalaxyl on the high organic matter soil used in this study suggests that the compound will not easily leach to deeper aquifers for soils with a subsurface layer characterized as Al Foah soil. This compound may accumulate in the root zone leading to plant uptake as mechanism that affects its transport in the environment.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Based on the results obtained in this study, it was concluded that:

1. The three pesticides used are subject to various extent of hydrolysis with cymoxanil undergoes the highest rate of hydrolysis especially at high pH.
2. There was no effect of light and indigenous microorganisms on the degradation of the used pesticides within an experimental time of 3 days.
3. Pesticides sorption to soil is influenced by the soil organic matter with dimethoate and metalaxyl are being more sorbed on the high organic matter soil as compared to sorption on the low organic matter soil.
4. Pesticides sorption is affected by the compound hydrophobicity with metalaxyl being more sorbed than dimethoate on a given soil.
5. On the low organic matter soil, both dimethoate and metalaxyl sorb linearly, while on the high organic matter soil metalaxyl undergoes nonlinear sorption.
6. The dispersivity of the packed soil columns is in the order of 0.2cm.
7. The use of moment analysis to determine transport parameters R and λ were comparable to those found by curve fitting.
8. Transport of dimethoate through the soil columns can be adequately described using an equilibrium model. However, metalaxyl appears to exhibit nonequilibrium during its transport.
9. The mass-transfer coefficient for metalaxyl can well be predicted using empirical relationships reported in the literature.

10. The values of sorption distribution coefficient determined from miscible displacement study were higher than their corresponding values determined using the batch technique.

11. There appears to be an enhanced hydrolysis of the used pesticides in a soil environment as compared to there hydrolysis in the aqueous solution.

5.2 RECOMMENDATIONS

1. The high hydrolysis rate of cymoxanil necessitates identification of cymoxanil metabolites and their level of toxicity. Although it is not anticipated that cymoxanil will be present in alkaline soils and groundwater typical to UAE subsurface environment, its metabolites may be present.

2. Research should be also directed towards investigating pesticides uptake by plants especially with pesticides that have high retardation coefficient and for plants grown on high organic matter soil.

3. Efforts should be directed towards monitoring groundwater for pesticides especially in aquifers underlying agricultural lands.

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للكوث في الماء. حيث وجد ان الميتالاكسيل تقوم التربة بامتصاصه اكثر من الدايميثاويت. وجد ايضا ان كلا من الدايميثاويت والميتالاكسيل يمكن وصف امتصاصهما للتربة بأن خطي في التربة ذات المحتوى العضوي الاقل، بينما يتخذ الميتالاكسيل وصف غير خطي في التربة ذات المحتوى العضوي العالي. لم يتم تقييم السيموكسانيل في كلا التربتين بسبب الفقدان الكبير له في المحلول عن طريق خاصة التحلل المائي.

تم استخدام منحنى الاختراق الذي تم الحصول عليه للمادة المثالية (عنصر البروميد) والمبيدات المختارة عن طريق نموذج برنامج يسمى (CXTFIT 0.2 سي اكس تي فيت ٠,٢). المنحنيات الخطية التي تم الحصول عليها من البروميد استطاعت وصف خاصية التحرك في كلا التربتين. من خلال النتائج وجد ان خاصية التحرك في تربة ابو سمرة كانت تقدر ب ٠,١٢ سم وكانت ٠,٣٤ سم في تربة الفوعة. المنحنيات الخطية المولودة من المبيدات المستخدمة تم تحليلها باستخدام التحليل اللحظي لتحديد معامل التأخير (R) و معامل التكرس (λ). المنحنيات الخطية المفترضة والمستخدمه لتحديد وصف المبيدات في التربة اظهرت ان بالنسبة للدايميثاويت في تربة ابوسمرة يمكننا استخدام نموذج متوازي لوصف حالته اما للميتالاكسيل فقد فشل البرنامج لعمل وصف له، لذلك استخدم نموذج غير متوازي. معدل الانتقال الكبير لمعامل الاعاقه للميتالاكسيل يمكن التنبأ به جيدا وذلك باستخدام علاقات تجريبية و معادلات وردت في دراسات سابقة.

ان المقارنة بين العوامل المؤثرة في حركة المبيدات المحددة عن طريق التحليل اللحظي و التي تم تحديدها عن طريق وضع منحنى مناسب اظهرت ان استخدام التحليل اللحظي يعتبر كفاء وكافي لتحديد معامل التأخير (R) و معامل التكرس (λ). وقد تم ملاحظة ان القيم الخاصة بمعامل التوزيع بالنسبة للامتصاص في التربة (K_d) والتي تم تحديدها من الاعمدة الترابية وكانت معدلها اعلى بنسبة ١٠-٢ مرات من تلك التي تم تحديدها عن طريق التجارب المعملية. وقد كشفت الدراسة ايضا انه يبدو ان هناك تعزيز للتحلل المائي للمبيدات على التربة مع مقارنتها في المحلول المائي.

حركة المبيدات خلال أعمدة ترابية من منطقة العين-دولة الإمارات العربية المتحدة

ملخص

تفتقر دولة الإمارات العربية المتحدة إلى وجود إدارة وتنظيم لاستخدام المبيدات، مما أدى إلى ضياع المصادر البيئية والطبيعية بسبب الاستخدام المفرط لهذه المواد الكيميائية. وقد ورد أن معدل استخدام المبيدات الحشرية في الإمارات قد وصل إلى 10 كجم/هكتار، مما قد يؤدي إلى تهديد محتمل إلى تعرض جودة المياه الجوفية للتلوث. وبالرغم من ذلك فإن القليل هو المعروف في دولة الإمارات عن حركة وانتقال المبيدات في الطبقة تحت السطحية للبيئة، وتأثير هذه المبيدات على التربة وجودة ونقاء المياه الجوفية.

إن الهدف من هذه الدراسة هي فهم مصير وقابلية تحرك المبيدات في الطبقة تحت السطحية للتربة، وهذه الدراسة تركز على دور بعض العوامل التي تؤثر على حركة المبيدات في التربة مثل: خاصية التحرك، خاصية الانتشار، التحلل و خاصية الامتصاص. تمت الدراسة تحت الظروف المعملية باستخدام اعمدة ترابية. وقد تم أيضا اختبار تأثير العوامل التي سبق ذكرها بعمل الكثير من التجارب.

تم في هذه الدراسة اختيار ثلاثة أنواع من المبيدات المستخدمة في دولة الامارات العربية المتحدة وهي (الدايميثاويت، السيموكسانيل والميتالاكسيل). استخدم أيضا نوعان من التربة الرملية تم تجميعها من منطقة الفوعة ومنطقة ابو سمرة في مدينة العين، في اماره ابوظبي. كلا التريبتين قلوية وله تركيب مشابهة للاخرى ولكن لهما محتوى من المواد العضوية مختلف ويعادل من 0,2% الى 0,8%. أظهرت النتائج ان المبيدات معرضة الى حد مختلف ومتنوع التكسر عن طريق التحلل المائي. وقد وجد ان السيموكسانيل عرضة اكثر من غيره لتحلل عالي، وخاصة عند كلما ارتفع معدل القلوية للتربة. اظهرت الدراسة ايضا انه لا يوجد تأثير للضوء او التكسر عن طريق الاحياء الدقيقة الموجودة في التربة على المبيدات خلال مدة التجارب (3 ايام).

إن خاصية الامتصاص في التربة تتأثر بوجود المواد العضوية الموجودة في التربة. ومثال على ذلك، وجد ان عملية الامتصاص للدايميثاويت والميتالاكسيل تكون عالية في التربة ذات المحتوى العالي من المواد العضوية عن الأفقر منها. تتأثر أيضا عملية امتصاص المبيدات في التربة بتركيب المادة الكيميائية وحبها



جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج ماجستير علوم البيئة

حركة المبيدات خلال أعمدة ترايبية
من منطقة العين-دولة الإمارات العربية المتحدة

رسالة مقدمة من الطالبة

هدى عتيق الحساني

رسالة مقدمة إلى
جامعة الإمارات العربية المتحدة
استكمالاً لمتطلبات الحصول على درجة الماجستير في علوم البيئة

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