FATE AND BEHAVIOUR OF ISOPROPYL[N-(3-CHLOROPHENYL)CARBAMATE](CHLORPROPHAM) HERBICIDE IN THE ENVIRONMENT

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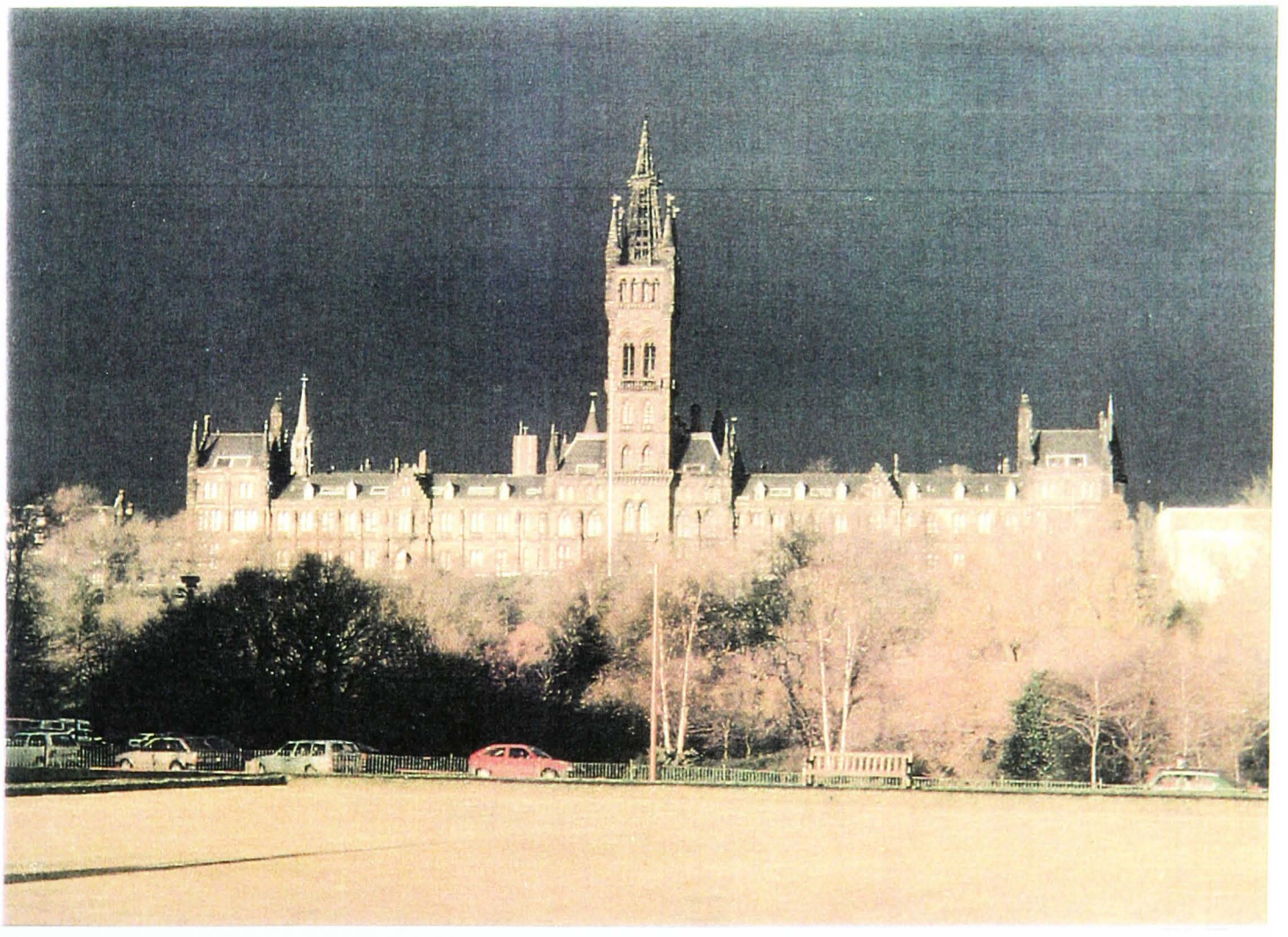
بسم الله الرحمن الرحيم

In the Name of **ALLAH**

"Most Gracious, Most Merciful"

UNIVERSITY *of* GLASGOW



DEPARTMENT OF CHEMISTRY (AFE)

To

MY MOTHER

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CHAPTER TWO : ADSORPTION-DESORPTION OF CHLORPROPHAM

LIST OF ABBREVIATIONS

AD	Air dried
CIPC	Chlorpropham
DCB	Dichlorobenzene
DI	Direct injection
DOM	Dissolved organic matter
EPA	Environmetal Protection Agency
FC	Field capacity
FDA	Federal Development Agency
HFC	Half field capacity
IPC	Propham
MDL	Mininmum detectable level
MQL	Minimum quantifiable level
NRC	National Research Council
OECD	Organisation for economic co-operation and development
QSAR	Quantitative Structure activity relationship
RT	Retention time

LIST OF CHEMICAL NAMES

Alachlor	2- chloro -2´, 6´- diethyl-*N*- (methoxymethyl) acetanilide.
Asulam	methyl 4-aminophenylsulphonylcarbamat
Azinphosmethyl	s-(3,4-dihydro-4-oxobenzo[*d*]-[1,2,3]-triazine-3- ylmethyl) O,O-dimethyl phosphorodithioate
Barban	4-chlorobut-2-ynyl 3-chlorophenylcarbamate
Carbaryl	1- nephthylmethlcarbamate.
Carbetamide	(R)-(-)-1-(ethylcarbomyl)ethylphenylcarbamate
Chlorpropham	Isopropyl *N*-3-chlorophenyl carbamate
2,4-D	2,4-dichlorophenoxy) acetic acid
Diazinone	*O,O*-Diethyl *O*-2-isopropyl-6-methylpyrimidine-4-yl phosphorothioate
DDT	Dichlorodiphenyl trichloroethane
Diquat	1,1′-ethylene-2,2′-dipyridylium
Diuron	3-(3,4 dichlorophenyl)-1,1- dimethylurea
Ethiofencarb	2-ethylthiomethylphenyl methylcarbamate
EPTC	s-ethyl dipropyl thiocarbamate
Fenuron	1,1-dimethyl-3-phenylurea
Hepatochlor	1,4,5,6,7,8,8-heptachlor-3a,4,7,7a-tetrahydro-4,7-methanoin-indene
Isoprocarb	2-isopropylphenyl methylcarbamate
Lindane	1,2,3,4,5,6-hexachlorocyclohexane
Isoproturon	3-(4 isopropylphenyl)-1,1-dimethyl urea
Methoxychlor	2,2-bis(*p*- methoxyphenyl)-1,1,1-trichloroethane
Metolachlor	2-chloro-6′-ethyl-*N*-(2-methoxy-1-methylethyl) Acet-*o*-toluidide
Monuron	3-(*p*-chlorophenyl)-1,1-dimethylurea.
MTBE	Methyl tertiarybutyl ether
Picloram	4-amino-3,5,6-trichloropicolinic acid
Promecarb	3-methyl-5-(1-methyl ethyl)phenyl methylcarbamate
Propham	Isopropyl phenyl carbamate
Simazine	2-chloro-4,6-bis(ethylamino)-s-triazine

Trifluralin	α,α,α,-trifluro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine

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SUMMARY

The work described in this thesis is mainly concerned with the environmental fate and analysis of 3-chloro isopropyl phenyl carbamate (chlorpropham), commonly used as herbicide and sprout suppressant in potato warehouses. Several phenyl carbamate pesticides including chlorpropham have carcinogenic and mutagenic properties. Such information when linked with the relative stability of these pesticides in natural waters and subsequently food chain, raise questions as to their future use and the need for adequate methods for their removal from drinking waters

In attempting to predict the fate of these pesticides in the environment, a full understanding of how the many parameters may influence the interaction of the pesticide with environmental compartments; soil, air and water and the ability to detect and determine the residue remaining in such compartments is essential to understand its impact upon the environment.

The work carried out here is basically a description of an attempt to meet the main objectives of the research project discussed at the end of chapter 1.

Chapter one, describes a comprehensive review of the existing literature pertaining to the impacts and dissipation of pesticides in the environment, in general, and with particular reference to chlorpropham.

Chapter two investigates the adsorption of chlorpropham on six different adsorbents including three soil types; the adsorption-desorption of chlorpropham from soil including the development of an analytical method suitable for the analysis of chlorpropham residues in drinking water. The analytical method involved preconcentration of chlorpropham residues on a solid sorbent (C18) followed by elution with a suitable solvent to achieve an environmentally safe and sensitive method for the detection and quantification

of chlorpropham. Octadecyl silylbonded silica cartridges (C18) proved to be very efficient for the determination of chlorpropham residues with a high recovery and reproducibility of 97%.

The adsorption study of chlorpropham was carried out on six different adsorbents including three soil types in an effort to find out their efficacy for the purification of chlorpropham polluted water. The studies were carried out using three types of soils , Downholland (peat), Midelney (clay), and Dreghorn (sand) and charcoal, bark, wheat straw, at three different temperatures and concentrations. The results showed generally, that charcoal had the greater adsorption efficacy followed by tree bark, wheat straw, Downholland (peat), Midelney (clay), and Dreghorn (sand) soil under all investigated temperatures and concentrations.

The desorption study was carried out to determine the extent of reversibility of the adsorption process for all the adsorbents under the same conditions of temperatures and concentrations. The results of the assessment indicated that desorption, in general, was more at higher temperature for all the studied adsorbents. However, for charcoal, adsorption was irreversible except at zero time at higher concentrations. For Downholland (peat), Midelney (clay) and tree bark, there was zero desorption at lower concentration levels.

Chapter three dealt with the volatility of chlorpropham from soil including the development of an analytical method appropriate for the determination of chlorpropham from the headspace of the heated soils. The method involved the use of Tenax adsorbent for the preconcentration of chlorpropham vapours followed by thermal desorption of the trapped vapours into GC-column to achieve an efficient and sensitive detection method.

These assessments were carried out in dynamic headspace model system using three soils; Midelney (clay), Downholland (peat), and sand (acid washed); under three moisture contents, two temperatures and two concentration levels.

These measurements, in general, showed a significant high volatility of chlorpropham for acid washed sand as compared to arable soil and relatively less from peat soil under all investigated temperatures, concentrations and moisture contents.

In addition, the volatility study revealed the formation of chlorpropham metabolites such as 3-chloroaniline and the corresponding alcohol and propham as a result of microbial degradation. More amounts of these products were formed from Downholland (peat) soil than from Midelney (clay) soil, and at high temperature and field capacity moisture content than at lower temperature and air dried conditions.

Chapter four describes the photodecomposition of chlorpropham in drinking water and in the presence of different soils, Downholland (peat), Midelney (clay), and acid washed sand. An attempt was also made to identify the possible photodecomposition products in water, and in the presence of different soils.

The photolysis rate was much more rapid in the presence of Midelney soil than in the presence of Downholland (peat) soil and water and much less in sand soil. The differences may be due to differences in refraction of light due to the presence of higher amounts of silt particles.

An attempt was made to identify the photoproducts in water. Ten chlorpropham photoproducts were identified using mass and GC-MS from water and soil fractions. Furthermore, for many bands isolated from TLC, it was very difficult to obtain a clear mass spectra.

Chapter five concludes the findings with recommendations for further monitoring of pesticide residue levels in the environment. It suggests that to reduce the risk from the chemical and to check that internationally recommended maximum residue levels are fully adhered to, search of new ways for the purification of pesticide polluted water is essential.

CHAPTER 1

INTRODUCTION

1.1 PESTICIDES: NEED

Ever since the dawn of civilisation man has continually endeavoured to improve his living conditions; in his effort to produce adequate supplies of food man has been opposed by the ravages wrought by insect pest and crop diseases. The blasting mentioned by Amos (760 BC) was the same cereal rust disease that is still responsible for enormous losses. History contains many references to seasons of high pest incidence, from the Biblical plaque of Egypt to the failure of the Irish potato crop in the middle of the last century (Cremlyn, 1991).

The major pests inhibiting the growth of agricultural crops are insects, fungi, and weeds, and the idea of combating these pests by the use of chemicals is not new; about AD 70 Pliny the Elder recommended that arsenic could be used to kill insects, and the Chinese used arsenic sulphide as an insecticide as early as the late sixteenth century.

The era of synthetic organic pesticides began about 1940 (van der Werf, 1996). The use of herbicides has been expanding more rapidly than other pesticides (fungicides or insecticides). The total world sales of pesticides in 1989 was $21 500 million. Even today almost half of the total agricultural production is lost; 35% of the crop to the weeds pests, and disease before harvest with a further 15% loss between harvest and sale. In the underdeveloped countries the losses are substantially greater, often 70% of the potential crop is lost (Cremlyn, 1991).

The world population continues to grow at about 2 percent each year. The current global population of 5.3 billion is expected to increase to 6.3 billion by the year 2000 (van der Werf, 1996), therefore, the need for more food and

control of human disease vectors will require even more use of pesticides which until now has played a more significant role than other tools in increasing food production and saving man's life.

1.2 RISK ASSESSMENT AND NEED FOR ENVIRONMENTAL QUALITY STANDARDS.

Pesticides are by design biologically active materials. Their usual effect is disruption of the normal biochemical balance of the target organisms. Each year about 2.5 million tons of pesticides are applied to agricultural crops world-wide (van der Werf, 1996). In most studies the proportion of pesticides applied reaching the target pest has been found to be less than 0.3 % , so 99.7 % went `somewhere else' in the environment (Pimentel, 1995). Since the use of pesticides in agriculture inevitably leads to exposure of non-target organisms including humans, undesirable side effects may occur on some species, communities or ecosystems as a whole. So, environmental pollution plays an ever increasing role in assessing risk and safety.

The NRC defined human health risk assessment as ``the characterisation of the potential adverse health effects of human exposures to environmental hazards" (Barnthouse , 1995). Risk assessment of human exposure to pesticides requires reliable exposure data, including both field measurements and models (laboratory and computer), evaluations of pesticide source, strength and drift. Risk assessment procedures should expand their scope beyond human health to include the effects of toxic chemicals in total ecosystems It is also necessary to determine the relative effects of various toxic compounds and their conversion products and to determine the relative distribution of toxins among various environmental compartments (Woodrow et al., 1990).

The EPA has responsibility for pesticides registration guideline in the USA. It includes a requirement to carry out six studies, which form basis for today`s environmental studies. The studies are designed to show : 1) the rate of dissipation in soil; 2) the mechanism of degradation of residues; 3) potential to leach in the soil; 4) potential to move in surface water; 5) whether the pesticide is bound or active; 6) the level that accumulates in fish, rabbit and bird tissue, and dose-related symptoms in these species. Toxicology studies (including acute and subacute toxicity, biochemical effect of metabolites, reproductive and teratogenic effects, long term toxicity, and mutagenic studies) are also designed and included in registration requirements. Along with pesticide registration, EPA administers programmes to control residue levels on food. In addition, the EPA has recently implemented a "reduced-risk pesticide initiative" and a "safer pesticide policy", both of which accelerates the registration process for new pesticides that pose lower risks than the currently registered alternatives (OECD, 1997).

Toxicity of a chemical is usually expressed as the effective concentration or dose of the material that would produce a specified effect in 50 % of population of test species (EC_{50} or ED_{50}). If the effect recorded is death the term LC_{50} or LD_{50} are used. The no observed effect level or concentration (NOEL or NOEC) is the dosage level immediately below the lowest dosage level eliciting any type of toxicological response in the same study (Severn and Ballard, 1990). Toxicity tests evaluate acute, subchronic, and chronic exposures and measure biological endpoints such as mortality, reproductive performance, growth and behavioural changes. Data from these tests are used in conjunction with information on water solubility, the effect of acid and alkali, octanol-water partition coefficient, soil adsorption/desorption properties and rate of hydrolysis. From these basic data, prediction can be made of the basic behaviour of herbicide in soil and water and its potential environmental

impacts. Further, laboratory studies are carried out to investigate degradation, metabolism and persistence in soil and water (Cooping et al., 1990). In Britain to protect the aquatic environment National River Authority (NRA) assesses water quality against Environmental Quality Standards (EQSs). An EQS is the concentration of a substance which must not be exceeded within the aquatic environment in order to protect it for its recognised uses. EQSs are specific to individual substances including pesticides and are produced using the best available environmental and ecotoxicological information (Eke et al., 1996; Killen, 1997).

The basic process in any hazard evaluation carried out in regulatory schemes involves assessment of pesticide exposure and effects. The exposure assessment involves developing an understanding of the dispersion of the chemical in the environment and estimating the predicted environmental concentration (PEC) to which organisms will be exposed. The effects assessment involves summarising data on the effects of chemical on selected representative organisms and using this data to establish the predicted no-effect concentration (PNEC) for a specific environmental compartment. The PEC and PNEC can be combined as a risk quotient (PEC/PNEC ratio),the value of PEC/PNEC is seen as a measure of the relative risk posed by a given use of the chemical (Klein et al., 1993; Linders and Luttik, 1995). The prediction of toxicity is done by using quantitative structure-activity relationship (QSR), and dispersion models to compare the potential impact on sensitive species serving as bioindicators, with the expected lethal concentrations for a specified environment. The predictive value of new chemicals in mesocosms, especially pesticides has been more recently developed in many countries and regulated by USEPA in late 1980 (Ramade, 1995).

Concerning the problems of human environment the United Nations conference was held in Stockholm in 1972, since then studies on pollution and

other environmental problems have been encouraged and supported in most countries, while the world organisations like FAO and WHO pay a lot more attention to these problems in their planning than previously. However positive the general attitude of human beings towards the environment will develop in the future, the technical problems of how to predict environmental hazards of pesticides and how to find safer alternatives will still remain. Predictive risk assessment both in USEPA and OECD are highly standardised. The objective of these assessments is to quickly and efficiently classify chemicals as being clearly harmless, clearly hazardous or potentially hazardous (Barnthouse, 1995).

There seems little likelihood of being able to dispense with the use of pesticides. However, future is looking brighter. New modelling techniques, EQS development, and the implementation of pesticide registration process, coupled with the development of newer, less persistent pesticides with lower dose rates all should help to reduce the risk of pesticide pollution.

Hopefully the techniques and the result of this work will be useful as a part of the information needs, in the world-wide concern about environmental quality.

1.3 INTERACTION OF PESTICIDES IN THE ENVIRONMENT

Pesticides enter into the environment by many direct and indirect routes. Most pesticide entry into the atmosphere comes from pesticide sprays for agricultural purposes to control soil inhabiting pests, weeds, as systemics to control phytophagous insects and systemic plant diseases. Other sources are from industrial plants, fumigation of ships, aircraft and buildings, factories manufacturing, storing or utilising pesticides and the burning of waste organic material containing pesticide residues. So, atmosphere is a key transport

medium and a vast reservoir for pesticides and their residues(Hill and Wright, 1978; Seiber et al., 1990).

Pesticides enter the atmosphere indirectly by missing the target, runoff, death of the treated plants and animals, green manure, faeces from treated animals and losses due to drift. Up to 50% may drift out of the target area when pesticides are applied from an aircraft (Pimentel and Levitan, 1986). Further, pesticides can enter the atmosphere in particulate or vapour forms at time of application, by after deposition on soil or adsorbed to wind-blown soil or plant particles (Hill and Wright, 1978).

Pesticide can enter the aquatic environment via a number of routes, including spillages, inappropriate disposal of dilute pesticides, and runoff into drains. Pollution from diffuse sources, such as spray drift into water courses and leaching from soil can also occur (Eke, et al., 1996) or they may be directly applied as aerial sprays or granules to control water inhabiting pests; movement via wind, water, and soil erosion. Generally the amounts originating from run-off from agricultural land and rain are less whereas massive amounts come from industrial effluents, emptying sheep dips, and emptying and washing of spraying equipment (Hill & Wright, 1978; Senesi and Chen, 1989).

Pesticide volatilisation from treated surfaces of soil, water and plants are responsible for a considerable proportion of the total residues of the pesticide in the environment. Air borne pesticide and its subsequent readsorption by dry-deposition and wet deposition are brought to the soil surface by rain. Reconcentration of vapour by adsorption into fog droplets, with redeposition on vegetation also occurs. However, pesticides entering the environment are transported and rapidly diluted to extremely low concentrations by air currents and wind (Spencer and Farmer, 1980; Glotfelty,et al., 1987).

Introduction of a pesticide into the environment results in the transport of the pesticide in the air, water, soil/sediment and biota. Movement of

pesticides and their transformation products within one compartment of the environment, or from one to another is not only a function of intrinsic physical-chemical properties of the pesticide and the environment but also of the prevailing climatic conditions (Haque, et al. 1980).

Pesticides are lost from the environment by scavenging, either by dry deposition or washout in rain, physical removal, volatilisation, leaching and runoff, uptake by plant and animals or by chemical, photochemical, and microbial degradation. Degradation of a pesticide in the environment depends on several factors, most important is adsorption to soil. Other factors include chemical and physical properties of the pesticide, formulation, application method, chemical and biological properties of the environment component (Robinson, 1973).

Since chlorpropham, which is under investigation in this study, is mainly used as a soil applied preemergence herbicide, therefore those pathways of pesticide dissipation in the soil environment mentioned above will be discussed in detail in next section of this chapter.

1.4 FATE OF PHENYLCARBAMATE HERBICIDES IN THE ENVIRONMENT

Carbamic acid (NH_2COOH) is the basic grouping of the carbamate herbicides. Urethanes, the ethyl esters of carbamic acid, have long been recognised as hypnotics and antipyretics in medicine. They are physiologically active in plants having been used to break dormancy. Other esters of carbamic acid have sedative and hypnotic properties.

Shaw and Swanson (1954) examined a wide range of substituted carbamates and found herbicidal activity highly correlated with substitution by chlorine, methyl and methoxy group, especially in the 3 and 6 position of the

benzene ring. IPC was eighteen in the list in terms of effectiveness and CIPC second.

Isopropyl N-phenylcarbamate (IPC) or propham, the first member of the group, found to have phytocidal activity, became widely used as a herbicide to control grasses in tolerant crops: including sugar beets, soyabeans, onions, garlic, sunflower, mustard. It was relatively harmless to many dicotyledonous crop plants and has proved toxic to oats, barley, wheat, etc.

In 1951, the chloro substituent of propham, chlorpropham (Isopropyl-[N-3-chloro phenyl] carbamate) was introduced. It is the most prominent compound in carbamate series of herbicides. It has been used world-wide as a highly selective pre-emergence or early post emergence herbicide and as a potato sprout suppressant. Chlorpropham is a mitotic poison and prevents the germination of susceptible weed, seed and kills roots by inhibiting cell division and inhibiting spindle formation. Table 1.1 shows the structure, chemical name, physical and chemical properties of chlorpropham. Phenyl carbamates accompanied by their structure and some of their physical and chemical properties are presented in Table 1.2.

1.4.1 Synthesis

The N-phenylcarbamates can be prepared by the reaction of the aromatic amine and alkyl chloroformate or by reaction of the appropriate phenylisocyanate with alcohol according to the following equations (Cremlyn, 1991).

$$Ar\text{-}NH_2 + ClCOOR \xrightarrow{\text{pyridine}} Ar\text{-}NHCOOR + HCl \qquad (1.1)$$

$$Ar\text{-}NCO + ROH \longrightarrow Ar\text{-}NHCOOR + HCl \qquad (1.2)$$

Table 1.1 General properties of chlorpropham.

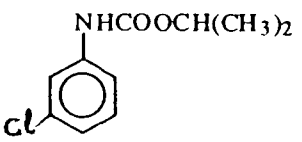
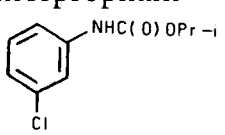
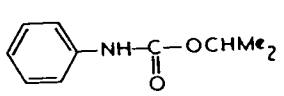
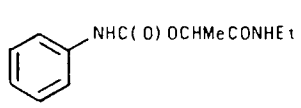
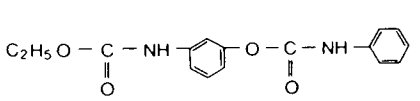
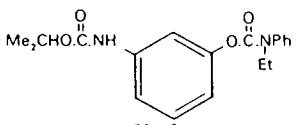
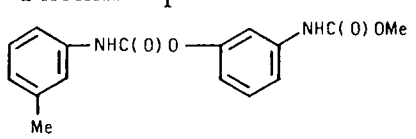
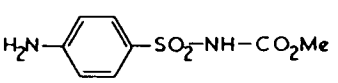
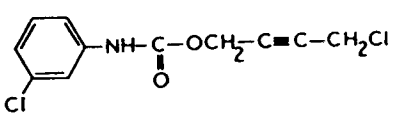
Common name:	chlorpropham
Chemical name:	isopropyl 3-chlorocarbamate (IUPAC) 1-methylethyl (3-chlorophenyl)carbamet (CA)
Other names:	CIPC; chloro-IPC; chlor-IFC (USSR)
structure:	
Physical form:	Colourless crystals
Melting point:	41.4 °C (pure); 38-40 (technical)
Boiling point:	247 °C (with decomposition)
Density:	1.180 at 30 °C
Refractive index:	n^{20}_{D} 1.5395 (supercooled)
Stability:	Very stable under normal conditions. Slowly hydrolyse by acids and alkalis
Corrosive:	Non-corrosive
Solubility:	In water at 25°C, 89 mg/l. Moderately soluble in mineral oils (10 % kerosene). Readily soluble in most organic solvents, e.g. alcohols, ketones, esters, chlorinated hydrocarbons.
Analysis of residues:	Extraction with petroleum ether, hydrolysis in strongly alkaline medium, distilling off the 3-chloroaniline, and photometric detrmination of the blue complex with hypochlorite, phenol, ammonium hydroxide, or diazotisation, coupling with *N*-(1-naphthyl) ethylene-diamine dihydrochloride, and colorimetric determination at 540 nm.

Table 1.2 Phenyl carbamates with some of their physical properties.

(The Agrochemical Handbook, 1983; Hance, 1990)

Name	MW	MP °C	Water sol	VP	$LD_{50} \times 10^{3}$
Chlorpropham 	213	40.7-41.1 25 °C	89 mgl^{-1} 20°C	0.001pa	3.15-7.5 mg/kg rat
Propham 	179.22	87-88	250 mg/l 20 °C	sublimes slowly at room temp.	5000 mg/kg acute oral rat
Carbetamide 	236.27	118(pure)	3.5g/l	< 10^{-5} m bar at 20° C	11000 mg/kg acute oral rat
Desmedipham 	300.32	120	7 mg/l	> 1.3×10 m bar at 25 °C	96000 mg/kg acute oral rat
Phenisopham 	342.4	109-110	insoluble		> 4000 mg/kg
Phenmedipham 	300.3	143-144	< 10 mg/ml	1.3×10^{-11}	> 800 mg/kg acute oral rat
Asulam 	230.24	143-44	0.5%	< 10^{-5} m bar at 20 °C	5000 mg/kg rats
Barban 	258.19	75-76	1.1 mg/100g 25 °C	very low	99 mg/kg acute oral rat

MW = molecular weight MP = melting point Water sol. = water solubility

VP = vapour pressure LD = lethal dose

1.4.2 Mode of action

Chlorpropham and propham are among soil applied herbicides, and are non translocated; they kill principally by contact action. They act by inhibiting oxidative phosphorylation, RNA synthesis, protein synthesis and the Hill reaction of photosynthesis as well as reducing the ATP content of tissues (Mitsunaka et. al., 1986). Degree of inhibition is related to susceptibility of the species.

The mode of action of carbamate herbicides vary with structure. Moreland and Hill (1959) screened a series of N-(3-chlorophenyl) carbamic acids and found the s-butyl to be most effective followed by n-butyl > n-propyl > isopropyl > amyl esters. Replacement of the imino hydrogen of ethyl phenylcarbamate by an ethyl, a phenyl, or a benzyl radical resulted in loss of inhibitory activity.

The effect of chlorpropham on protein synthesis was the main effect found by Mann et al., (1965) when they reported the inhibition of incorporation of C^{14}-labelled leucine in polymeric material in susceptible plants treated with chlorpropham and propham. It was further confirmed by Gruenhagen & Moreland (1971) that chlorpropham and propham inhibit RNA and protein synthesis by interfering with ATP production, chlorpropham being more effective (Lotlikar et al., 1968; Moreland et al., 1969).

Inhibition of cell division and mitosis has been reported by Davis et al., 1977, following treatment with chlorpropham. Fletcher & Kikwood (1982) reviewed that the 2-hydroxy derivative inhibited more than did chlorpropham and the 4-hydroxy derivative. Chlorpropham is also known to inhibit elongation and increase in radical expansion of root cells. Further, Vaughn and Lehnen (1991) reported that chlorpropham and other members of the group affected cell division by altering the organisation of the spindle microtubules so that multiple

spindles and thus multiple nuclei result. Chlorpropham inhibited the microtubule system so it blocks cell division in *Chlamydomonas* but not the growth of the cell (Fedtke, 1982).

Carbamate herbicides normally inhibit the Hill reaction of photosynthesis; being preemergence herbicides, this mechanism is not a major factor in their toxicity (Moreland, 1993). In inhibiting the Hill reaction, the imino hydrogen may take part in hydrogen bond formation with some electronegative constituent located at or near the reaction centre of the chloroplast.

It is worth mentioning that methyl carbamates and/or organophosphorus insecticides compete with phenylamide/ phenylcarbamates for the hydrolysing enzyme, thereby increasing the persistence and phototoxicity of these herbicides (Matsunaka, 1971; Hassall, 1983). However, in animals the insecticides deactivate cholinesterase resulting in the accumulation of acetylecholine and hence block the transmission of the nerve impulses (Hassall, 1983).

1.4.3 Toxicology

Chlorpropham is applied directly to a range of human food; vegetables and also used as potato sprout suppressant. So, it is important to investigate its toxicity to humans. It is difficult to judge the safe use of a chemical in this field since the available data has been derived from animals which are not necessarily directly applicable to human beings.

Chlorpropham is degradable and metabolised to water soluble products in higher plants which result from hydroxylation of either aromatic ring or of alkyl side chain. In animals in addition to hydroxylated derivatives, other metabolites are generated by the hydrolysis of the carbamate function. These metabolites are water soluble and excreted through urine.

Toxicity of chlorpropham is not well defined. Chlorpropham and propham seemed to have low mammalian toxicity, probably due to their ready adsorption and excretion after their administration (van Esch & Kroes, 1972).

Chlorpropham and propham are derivatives of mutagenic and carcinogenic urethanes (Barnes, 1976). Further, as chlorpropham could inhibit mitosis in plants, this, initiated some workers to explore whether chlorpropham inhibits mitosis in animal and human cells or not. van Esch et al., (1958) reported that chlorpropham and propham have weak tumour initiation action, similar to urethane. However, van Esch & Kroes (1972) reported that long-term exposure to either chlopropham or propham by subcutaneous injection or in diet produced no signs of carcinogenisis.

Woo (1983) and Benigni et al., (1989) evaluated mutagenicity of chlorpropham and reported various experiments with positive and negative results depending on the type of mutagenicity test studied. Sarivastava et al., (1992) carried out an experiment to evaluate the fetotoxic/teratogenic potential in albino rats. They found that at doses of 50 and 100 mg/kg/day administered orally to female rats during day 6-20 of gestation, they were devoid of such effects. Dolara et al., (1993) used a pesticide mixture containing chlorpropham to determine the toxocological effect on rats and humans. No mutagenic activity was observed in rat liver at concentrations up to 500 mg/plate, but they observed a slight but statistically significant increase in sister chromatid exchange at 1 mμg/ml, when applied on human lymphocytes in vitro. Furthermore, these authors also administered the mixture to Wistar rats at doses of 1, 10, and 100 mμg/kg, After 24 h the ratio between bone marrow polychromatic and norchromatic decreased but they did not observe a significant increase in the frequency of micronuclei. So, they concluded that the mixture did not have appreciable genotoxic activity in the assay.

It is known that under physiological conditions, chlorpropham had a cytolytic effect, modified membrane permeability and reduced intracellular ATP level. Carrera et al., (1995) investigated, after modulation of sulphonation and glucuronidation, the relationship between the changes in metabolism and cytotoxicity of chlorpropham, in isolated rat hepatocyte suspensions. They interpreted that the cytolytic effect was due to chlorpropham itself, whereas the effect on energytic metabolism was attributed to a metabolite.

Recently Hoffman (1995) and Hoffman and Michael (1996) for the first time reported that growth inhibition assay and immunoflorescence microscopy of HeLa cells shows that chlorpropham could weakly induce cytoskeletotoxicity in human cells.

The acute oral toxicity, LD_{50}, for rats and rabbits has been reported by Anon (1990) as 1200 mg/kg and 500 mg/kg respectively. Brown (1978) reported LD_{50} (24h) of propham for bluegill sunfish is 32 ppm and daphnia waterfleas is 32 and 10 ppm for propham and chlorpropham respectively.

International agency for research on cancer has re-evaluated the carcinogenic risk of chlorpropham to humans and experimental animals. From the re-evaluated data, chlorpropham and propham were both placed in group 3- agents not classifiable as to their carcinogenicity to humans (Anon, 1987).

In view of these findings and the scientific thinking which considers no level of carcinogens as safe, a point of risk associated with these chemicals and their metabolites should always be borne in mind.

1.5 ENVIRONMENTAL FATE OF CARBAMATE PESTICIDES

A number of physical, chemical and biological processes in the environment govern the fate and behaviour of pesticides Apart from the

biological factors which govern mineralization and transformation of pesticides, other influencing factors include; physio-chemical, formulations, and synergistic, environmental factors and the agricultural techniques.

1.5.1 Physio-chemical factors

The physiochemical nature of a herbicide generally determines its availability, movement and rate of degradation (Hartley and Graham-Bryce, 1980). Some of the major influencing physio-chemical properties which are used to predict the environmental behaviour of pesticides are discussed below.

1.5.2 Water and lipid solubility

Water solubility of a chemical is an intrinsic property which is important in determining the movement of chemical in soils, sediments, and ground-water aquifers (Haque et al., 1980; Malcom, 1989; Domine et al., 1992). Solubility values for phenylcarbamates are relatively low and decrease as the number of halogen substituents increases. Consequently these compounds are liable to partition out from water and accumulate in biota. This attitude is best described as octanol/water partitioning and expressed as K_{ow}. The role of n-octanol/ water partitioning coefficient (K_{ow}) for organic compounds is of paramount importance in predictive environmental studies. It is used in evaluative models for the prediction of distribution among environmental compartments, in equations for estimating bioaccumulation in animals and plants and in predicting toxic effects of a substance in QSAR studies (Finizio et al., 1997).

Kow is defined as the relative solubility of the chemical in pure octanol, (Co), to that in water, (Cw), i.e. $K_{ow} = Co/Cw$ (1.3)

The traditional method for the measure of K_{ow} is the shaking-flask method. In this method the tested chemical is mixed with an appropriate n-

octanol/water mixture and shaken until equilibrium between phases is achieved. After separation of the phases the concentration of the tested chemical in one or both phases is determined. This method is unreliable for substances having high lipophilicity (log K_{ow}>6), due to the formation of octanol emulsion in water. Finizio et al., (1997) has critically reviewed and compared different methods used in determining K_{ow}.

Various correlations have been observed between the solubility (s), K_{ow}, bioconcentration factor (K_{BCF}), absorption coefficient on to organic carbon (K_{OC}), melting point and ecological magnification (EM). Hance, (1980); Haque et al., (1980) and Briggs, (1981) have reported the following regression correlation respectively. These correlations facilitate the estimation of the value from the others.

$$\log BCF = 0.524 \log K_{ow} + 0.124 \quad (1.4)$$

$$\log EM = 0.6335 \log K_{ow} + 0.728 \quad (1.5)$$

$$\log K_{OC} = -0.782 \log [S] + 0.27 \quad (1.6)$$

$$\log K_{OC} = 0.52 \log K_{OW} + 0.62 \quad (1.7)$$

$$\log K_{OW} = -\log[S] - 0.01MP + 0.7 \quad (1.8)$$

1.5.3 Adsorption

The adsorption of pesticides to a soil surface is of particular environmental importance; as a mechanism of physical removal; it can reduce run-off erosion, leaching and volatilisation, and may also control both biological activity against the target pest and undesirable toxicological and ecological effects on non-target organisms (Hill & Wright, 1978; Riley & Eagle, 1990).

Various factors influence adsorption and desorption of pesticides in soil directly such as soil or colloid type, physiochemical nature of pesticide, soil

reaction, nature of the saturating cation on the colloid exchange site, soil moisture content, nature of formulation, and temperature; physical properties of soil however, act as a substrate and climate exerts a more indirect effect (Bailey & White, 1964; Hsu and Bartha, 1976; Huang, 1980). Haque et al., (1980) revealed that adsorption increases with increase of hydrophobicity of the adsorbate and/or with the increase of the organic content of the adsorbent while water solubility, temperature, soil moisture content especially above the sorption limit, all have inverse effect on adsorption (Parochetti & Warren, 1966).

Adsorption of herbicides varies greatly according to the nature of soil organic matter and is greatly conditioned by the ionic composition of the clay surface. Mineral and organic soil constituents are not stable and undergo various transformations as they age. In addition the fact that mineral and organic constituents are frequently associated, explains the difficulty in predicting soil adsorption behaviour simply from gross soil composition.

Adsorption of the pesticides is an equilibrium process (Osgerby, 1973; Khan, 1980) where the solute partitions itself between soil and water. This is described as the adsorption coefficient, Kd. The Kd is defined as the concentration of pesticide adsorbed to the soil particles divided by the concentration in the equilibrium solution; thus kd values are highest for strongly adsorbed chemicals. Adsorption-desorption phenomenon can be described with Langmuir, Freundlich, or Elovich equations.

The adsorption of pesticides to clay or humic matter may catalyse their degradation (Saltzman et al., 1976) or it may slow down their dissipation and/or transformation over a period of time (Schwarzenbach, et al., 1993; Bartha, 1980).

Adsorption of pesticides to mineral and organic soil particles is mostly a reversible process and volatilisation resumes when the soil is rewetted (Osgerby, 1973; Hill & Wright, 1978; Glotfelty et al., 1984)

Because the adsorption/desorption phenomenon is a very important factor determining the fate and behaviour of pesticides in soil, an attempt was made to study the adsorption-desorption behaviour of chlorpropham on different soil types and adsorbents (Chapter 2).

1.5.4 Volatilisation

Volatilisation is defined as the loss of chemicals from surfaces in the vapour phase; vaporisation followed by movement into the atmosphere (Spencer & Cliath, 1990).

Volatilisation of a pesticide is a dynamic process. Potential volatility of a pesticide is related to its inherent vapour pressure. However, many chemicals such as DDT and Phenylamides, despite their low or moderate vapour pressure, water solubility and low polarity were lost at rapid rates owing to high activity coefficients in solution (Spencer et. al., 1973; Mill, 1980).

The rate of vaporisation is affected by temperature, water solubility and air flow rate. The ratio of the vapour pressure to the water solubility of a pesticide is more important in volatilisation rate than its vapour pressure alone (Jury et. al., 1984; Spencer & Cliath, 1990). Mackay and Wolkoff (1973) proposed that an estimation of the air/water partitioning coefficient (H) can be obtained from the equation:

$$H = P\,[\,S\,] \qquad (1.9)$$

Where P, is vapour pressure of the chemical in mm Hg and [S] stands for molar solubility.

Adsorption of the pesticide to the soil lowers vapour pressure of the pesticide thereby decreasing evaporation (Spencer & Farmer, 1980; Hance, 1980). Moisture can enhance pesticide dissipation through volatilisation from soil because of the competition between water and herbicide for available adsorption sites (Parochetti & Warren, 1966; Riley and Eagle, 1990). Soil incorporation, plant cover,and relative soil temperature and humidity can all, decrease volatilization (Spencer et al., 1973; Spencer & Cliath, 1975).

There are few studies about volatilisation of phenyl carbamates, especially chlorpropham/propham, which are discussed in Chapter 3.

Bearing in mind the need for more studies on dissipation of chlorpropham in field and volatility in the laboratory (EPA, 1987), present work will help to fully assess the environmental fate of chlorpropham.

1.5.5 Leaching

The downward movement of pesticide in solution through the soil profile in the zone above the water table is termed as leaching (Hill & Wright, 1978).

Knowledge of the movement of the pesticide and its transformation products in the soil environment help us to understand the performance of soil applied pesticides and to evaluate the risk of leaching through the soil to ground water, and runoff to surface water.

Pesticides can be lost from the soil by leaching and runoff. The fraction removed by leaching is generally less. The extent of leaching is determined by many factors such as the solubility, adsorptive properties and rate of degradation of pesticide as well as by the amount and nature of water movement and the physical and chemical characteristics of the soil (Bailey & White, 1964; Robinson, 1973; Taylor & Spencer, 1990)

Leaching depends upon the partition of the pesticide between the soil constituents; organic and inorganic and water percolating through the soil. A fertile soil contains 40% solid particles and 60% pore space. Herbicides within soil aggregates or small pores (<100 μm diameter) through which water moves very slowly, are by-passed by water moving down the larger pores under gravity. Conversely, chemical present in larger pores can readily be leached (Riley, 1976; Riley & Eagle, 1990) .

The rate of pesticide leaching in soil decreases with increasing organic matter content and depth of surface zone with high biological activity, while the presence of macropores (cracks, worms, holes, root channels) enhance leaching. Leaching is directly related to the amount of precipitation or irrigation or both and inversely related to solubility, sorption, rate of decomposition and evapotranspiration. Further, progressively less pesticide is leached with successive leaching after application to the soil (Goring, 1972; Beven & German, 1982). Recently models have been developed to measure leaching (Hall, 1994).

Both methyl and phenyl carbamates resist leaching into the soil profile. Chlorpropham was highly resistant to leaching in three different soil types (Ogle & Warren, 1954). Over 90% of the recovered chlorpropham was found in the upper inch of the soil profile after 1.68 inches of rain (Pray & Witman, 1953).

Insufficient data are available to permit a reliable prediction of the leaching potential of chlorpropham. Taking into account chlorpropham's high solubility and relative stability in water, in addition to known mobility of a related chemical, propham, chlorpropham can be expected to leach. Chlorpropham is the subject of a ground water DCI notification and additional data is needed to fully characterise the potential for it to enter ground water (EPA, 1987).

1.5.6 Uptake by plants and animals

Pesticides are lost from the soil environment by uptake into cultivated and non-cultivated plants. The total amount and rate of uptake are related to the ability of the plant to adsorb the chemical and the availability of the pesticide to the plant roots. The role of plants in the removal of pesticides from soil is less significant (Hill & Wright, 1978).

Herbicides may move in a plant along pathways which are non-living (apoplast) or living (symplast) or both; all herbicides show some symplastic movement since they must enter living material in order to be toxic.

Uptake of pesticide from soil by plants is a major source of food chain accumulation and an important route of exposure to humans and animals (Paterson et. al., 1990). Foliar uptake of pesticide volatilized from soil contributes more to total plant residue than root uptake (Paterson et al., 1990).

The efficiency of plant uptake is influenced by a number of factors such as water solubility, herbicide concentration, nutrient and water, metabolic inhibitors, soil type, root aeration, presence of adventitious roots, soil pH and formulation (Fletcher & Kirkwood, 1982). In addition ,there are direct and indirect effects of light (Caseley & Walker, 1990). Fletcher & Kirkwood (1982) reviewed that uptake of chlorpropham by soybean seed is directly related to concentration and increased with rise in temperature.

The classical view that roots of the seedling are largely responsible for the uptake of herbicides from soil has been modified since it is known that some soil applied herbicides can enter the parts of the shoot system which are underground. Entry into shoot is essential for full effectiveness of the thiocarbamates herbicides EPTC and also responsible for the activity of CIPC because it has appreciable volatility (Caseley and Walker, 1990).

Baldwin et. al., (1954) were the pioneers of the studies on the absorption and translocation of the carbamate herbicides. They reported that propham was

absorbed through cut surfaces of leaves, cut surfaces of roots and intact roots in descending order. Further, they reported that plant leaf surfaces are a barrier to the adsorption of propham.

Comparison of the absorption and movement of C^{14}-ring or side chain labelled chlorpropham by foliage or root of redroot pigweed, pale smartweed, and parnsip revealed that absorption occurred by both routes though only apoplastic transport was evident (Prendeville et. al., 1968). Selectivity could not be attributed to interspecies variation in absorption or translocation. The absorption and translocation of chlorpropham by germinating seedlings of soyabean, maize, peanut and castor showed that the seed coat acts as a barrier for penetration and very little of the absorbed radioactivity is translocated and appears to move in the apoplast. Still and Mansager (1973 a) found that root treated cucumber could absorb, translocate and metabolize chlorpropham. However, these metabolites were not translocated once they were formed in the root or shoot.

Generally, chlorprophan enters the emerging shoots more readily than the roots. Chlorpropham enters the cotyledons of seeds rapidly, little transport from cotyledon occurs. The translocation studies suggest that carbamate herbicides are almost exclusively distributed via the apoplastic system (Ashton & Crafts, 1973; Fletcher & Kirkwood, 1982).

Depending on the available literature, it seems that the dissipation of chlorpropham from soil through uptake by plants is mostly extremely small and has no environmental significance.

There is no available literature concerning the uptake of chlorpropham by animals but generally speaking, since chlorpropham is a soil applied herbicide, the invertebrates in soil are capable of moving pesticide, whether in their outer surface over relatively small distances. When invertebrates contaminated with pesticide are eaten by mammals or birds, the distances over

which the chemical is transported can be increased enormously, even to a global scale.

1.5.7 Chemical decomposition

Pesticides in the environment are subjected to a number of biological, and non-biological transformations. The most important biotic processes that may act on a chemical include hydrolysis, pyrolysis, oxidation-reduction and photolysis (Mill, 1980; Draper and Wolfe ,1987).The factors governing chemical transformation in soil are pH and moisture content (Crosby, 1970).The studies of Plimmer and Kearney (1968) have indicated that free radicals may degrade pesticides and Jury et al., (1987) reported that major chemical losses for pesticides in the atmosphere are via reactions with O_3, $HO^{\cdot}$ and NO_3^{-} radicals.

In the environment non-biological hydrolysis is slow and negligible as compared with the enzymatic one. In water the reaction is enhanced by the involvement of HO^{-} or HO_3^{+}. In soil, although sorption to humic matter and clay may be regarded as a kind of sequestering , metal ions $[M]^{x+}$, such as Cu^{2+} , Ca^{2+} and Zn^{2+} and/or their ligand aqua complexes $[M(H_2O)(OH)L]^{x+}$ act as a carrier for H_2O or $HO,^{-}$ thereby catalysing the hydrolysis process (Saltzman et al., 1976; Mill & Maybe, 1988; Falah and Hammers, 1994).

Phenyl carbamates have been reported to undergo acid , neutral and alkaline hydrolysis. Alkaline hydrolysis is likely to occur at pH levels and temperatures common to the aquatic environment. The mechanism of carbamate alkaline hydrolysis has been characterised by several workers (Aly & El-Dib, 1971; William, 1972, 1973; Wolfe et al., 1978 a). Others have studied the kinetics of carbamate pesticides in natural and distilled water using structure-

reactivity relationship (Wolfe et al., 1978 a; Wolfe et al., 1978 b; Bergon & Calmon, 1983).

Phenylcarbamate hydrolysis of the carbamyl bond or the ester linkage preferentially results in the formation of the aniline precursor as follows:

$$\text{Ar-NHCOR} + \text{HOH} \xrightarrow{H_3O^+/OH^-} \text{Ar-NH}_2 + \text{RCOOH} \qquad (1.10)$$

Various factors such as steric, inductive, pH, temperature, water solubility and catalytic activity of the media have a direct effect on the rate of hydrolysis (Wolfe et al., 1978 b ; Hartley and Graham-Bryce, 1980; Wolfe et al., 1980). El-Dib and Aly (1976 a) reported that phenylamides hydrolyse very slowly and maintain their stability in natural water. The order of hydrolysis was as follows:

Phenylcarbamates > anilides > phenylureas

1.5.8 Photodecomposition

Pesticides are dissipated in the environment through various processes, viz: volatilisation, leaching, adsorption into soil colloids and through chemical, biological and photochemical transformations (Benson, 1974). Photochemical reactions of organic compounds in the environment are brought about directly or indirectly by absorption of solar radiation (Crosby and Li, 1969). The absorption might occur in the air, during spraying in water droplets and on the plant and soil surface (Hulpke et al., 1983).

Photolysis of the herbicide may result in increased biological activity, decrease in activity hence facilitates its removal as harmful residue, yields a compound with different biological activities or/and different significant mammalian toxicity (Day, 1991).

The absorption of light with subsequent excitation results in various chemical changes including reductive dehalogenation, oxidation, nucleophilic substitution, isomerisation, dimerisation and/or polymerisation (Menzie, 1988).

More details on the phototransformations of carbamates are discussed in Chapter 4.

1.5.9 Degradation of carbamate herbicides in plants

Plants influence the fate of pesticide in the environment both directly and indirectly. Chlorpropham is widely used in vegetable crops as a preemergence herbicide as well as a sprout suppressant in potato stores. It is therefore, an important reason to discuss this aspect in the literature section.

Plants can come in contact with pesticides by direct treatment, spray drift, uptake from soil and particle deposition on plant surfaces.

Pesticides applied to growing plants are subjected to a multiplicity of external and internal degradation. The degradation of herbicide by plants is an important mechanism of detoxification of the compound through the food chain and acting as an important basis for selective toxicity. Herbicide degradation in higher plants results from a wide variety of chemical reactions. Most of these are catalysed by specific enzymes; few are non enzymatic. By a combination of chemical processes the original herbicide molecule may be degraded completely to innocuous substances such as carbon dioxide, water, and ammonia (Fletcher & Kirkwood, 1982).

Plants metabolise pesticides as free compounds, conjugates and bound residues. Free compounds and conjugates are both extractable from plant tissues, although conjugates are generally more polar than most free compounds and are generally soluble in water or other highly polar solvents (Harvey, 1983).

For both carbamate herbicides and insecticides, chemical analysis shows that they are readily degraded.

Reiden & Hopkins (1962) found that barban, a phenyl carbamate was rapidly degraded in both resistant and sensitive wild oat to a water soluble substance(X) which released 3-chloroaniline on hydrolysis with alkali. Formation of 3-chloroaniline ruled out the prospect of ring hydroxylation. This 3-chloroaniline moiety is complexed into several water soluble derivatives. Lamouraux et al., (1971) reported the formation of a barban/glutathione conjugate. Still & Mansager (1972) reported that metabolites are formed by alteration of side chain and not by hydroxylation of the aromatic ring.

Earlier, rapid disappearance of certain carbamates suggested that hydrolysis may be the degradation pathway for chlorpropham in resistant plants. However, when only limited amounts were detected, along with, other products containing the intact carbamoyl linkage, this suggested that metabolic transformations other than hydrolysis may play an important role in the degradation of carbamates.

James and Prendeville (1969) found evidence of formation of water soluble metabolites when they applied chlorpropham to leaf surfaces of several plant species. They found no evidence of cleavage of the carbamate group, no hydroxylation of the ring and identified B-glucoside possibly linked through hydroxylation of alky side chain. On the other hand, Still and Mansager (1971, 1972) found no evidence of alteration of the isopropyl side chain in soyabean roots treated with C^{14} chlorpropham. They found ring hydroxylation to produce a hydroxy chlorpropham which was further metabolised to produce an O-glucoside. This was confirmed by acetylation, B-glucosidase hydrolysis and mass spectrometery (MS) and found to be isopropyl-5-chloro-2-hydroxy carbamate (2-OH-chlorpropham), 4-OH-chlorpropham was also found. There was no cleavage of the carbamate group.

Still & Mansager (1973) after examining the metabolism of chlorpropham in the resistant soyabean and in susceptible cucumber species calculated that the formation of two OH-chlorpropham metabolites and especially their further metabolism to glycosides and insoluble residues was associated with differences between resistant and susceptible species. Further, Russness & Still (1974a; 1974b; 1977) concluded that the rate of 4-OH chlorpropham conjugation was associated with susceptibility of cucumber to chlorpropham.

Lamoureux & Rusness (1982) isolated 4-hydroxy chlorpropham as a major water soluble metabolite from peanut cell suspension culture but mass spectrometry of the resulting derivative was inconclusive.

In the studies on soyabean, as described earlier, no evidence of side chain hydroxylation was reported. However, Wiedman et al., (1976) found that the major metabolite in soyabean was hydroxylated on the isopropyl side chain. They suggested that differences in the metabolites might be due to the fact that their plants were grown in soil and in all other studies, they used hydroponically grown plants. But it is in contrast with the results shown by Zurqiyah et al., (1976). They reported labelled propham applied to hydroponically grown alfalfa plants has been shown to produce almost equal amounts of 4-OH chlorpropham, 2-OH chlorpropham and 1-hydroxy-2-propyl 3-chlorocarbanilate. Further, Heikes (1985) found 4-methoxy chlorpropham as a metabolite in potatoes and Worobey and Sun, 1987 reported the presence of 3,3' dichloroazobenzene in the peel of chlorpropham treated potatoes.

In summary on the basis of the above literature, chlorpropham and other phenyl carbamates are degradable and metabolize into water soluble metabolites in higher plants.

1.5.10 Degradation of carbamate pesticides in animals

Animals are exposed to pesticides directly by both deliberate application and accidental contact or indirectly by eating treated or contaminated plants or other animals (Hill & Wright, 1978) The possibility that pesticides and their metabolites reach man through the food chain is well established. That reason gives more importance to the main purpose of this section of literature which describes the fate of chlorpropham in animals as a part of the environment.

Most animals appear to have systems capable of metabolism and excretion of xenobiotics. Herbicides have been regarded generally as less toxic to animals and more readily excreted than insecticides.

Degradative reactions of pesticides, in general, may involve hydrolysis, oxidative reduction and rearrangement. Generally, but not always, compounds may be degraded via the same pathways in plants and in animals and it has been shown that the reactions are mediated by similar enzymes in both plants and animals. Conjugation is the most interesting type of reaction during the degradation process, whereby the organism combines the pesticide, or its derivatives with a normal constituent of the organism to synthesise a new compound which is more readily eliminated from an animal, or bound into an inactive form in plant. Metabolism of pesticides usually results in detoxification, although in some cases into a more active or toxic form (Harvey, 1983).

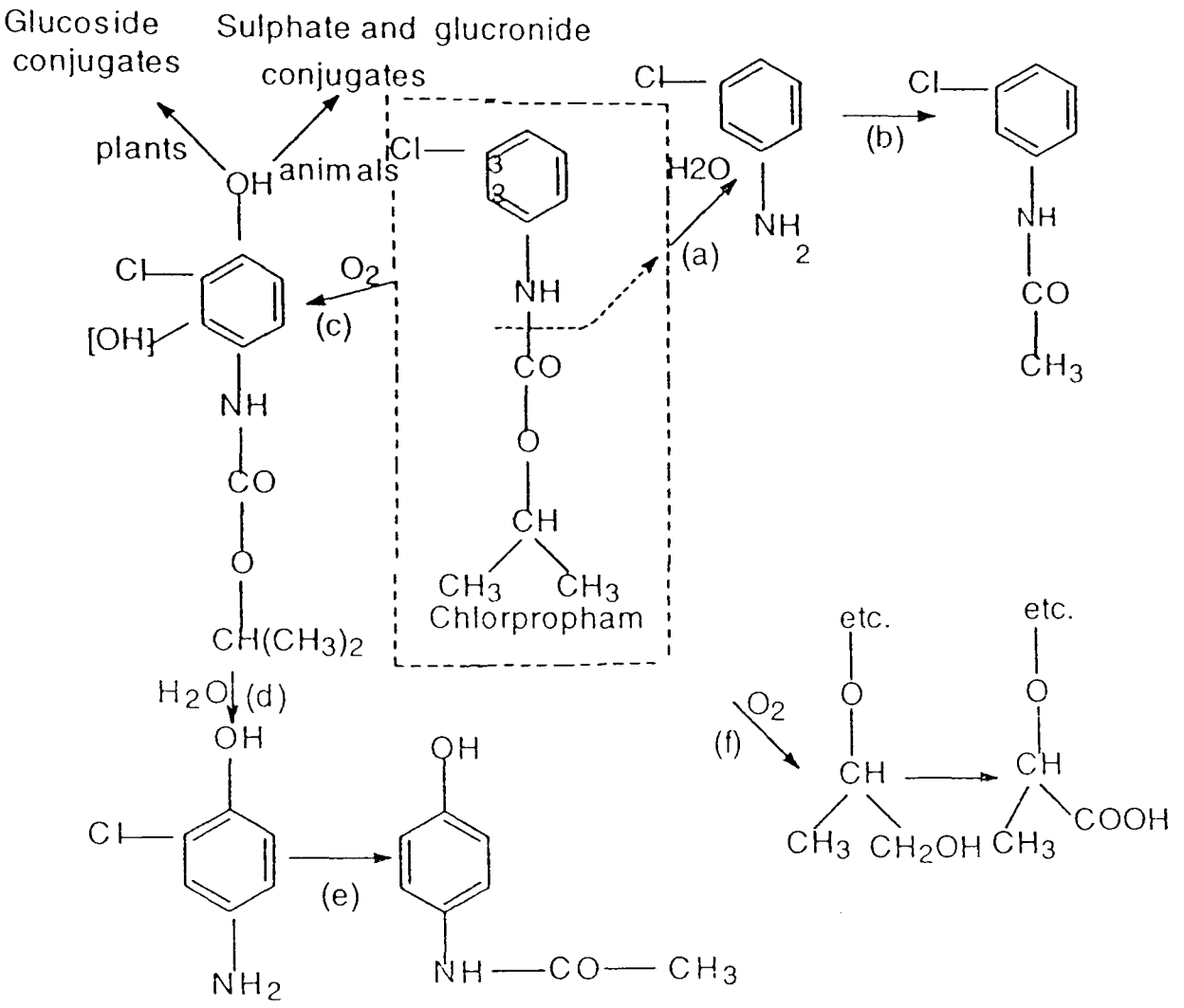
Ryan (1971) and Menzie (1978) reviewed the metabolism of carbamate pesticides. Little is available in the literature on the fate of chlorpropham or propham in animal systems. Most of the workers have emphasised feeding or dosing trials on animals such as rats, sheep, goats and chickens with single doses of C^{14} -labelled chlorpropham and propham and subsequent identification of possible metabolites. These experiments showed that orally administered chlorpropham to various animals such as rats (Holder and Ryan,

1968; Grunow et al., 1970; Fang et al., 1974), goats (Paulson et al., 1973), sheep (Paulson et al., 1975) or chicken (Paulson & Jacobson 1974) was readily absorbed, translocated and excreted as conjugated metabolites in their urine and faeces over a period of a few days after administration.

For chlorpropham the most common process for metabolising was found to be aryl hydroxylation resulting in the formation of isopropyl-N-(3-chloro-4-hydroxy phenyl) carbamate (Grunow et al., 1970; Bobik et al., 1972); both this substance and its N- acetylated hydrolysis product(3-chloro-4-hydroxy-acetanilide) are found in rat urine in the form of their glucuronide and sulphate conjugates (Grunow et al., 1970) . In addition, side chain alkyl hydroxylation resulted in the formation of 1-hydroxy-2-propyl-N-(3-chlorophenyl) carbamate. The hydroxylated metabolites once formed, were subject to conjugation and excretion as glucuronides and sulphate esters in the urine. It is worth noting that reported sulphate conjugates of m-hydroxy -3,4-dihydroxypropham and 2-aminophenol were specific metabolites for propham in chicken, since when chlorpropham was used instead of propham, these metabolites were not detected in animals or in plants (Bend et al., 1971; Paulson et al.,1972 ,1973). Recently Carrera et al., (1995) investigated the formation of metabolites of chlorpropham in isolated rat hepatocyte suspensions and reported that chlorpropham was metabolised by hepatocytes mainly into 4-OH chlorpropham sulphate (37%) and glucuronide conjugate (18 %).

Hydrolysis of the carbamate group resulting in 3-chloroaniline or producing metabolites derived from 3-chloroaniline, e.g. 2-amino-4-chlorophenol and 4-amino-2-chlorophenol has been reported (Grunrow et al., 1970; Fang et al., 1974; Still and Herrett, 1976). In rats up to 30% of an oral dose was split by hydrolysis to give chloroaniline and its N-acylated derivatives (Fig.1.1).

Figure 1.1 Metabolism of chlorpropham in animals (Hassall, 1990)



Chlorpropham uptake by animals is directly through forage and foodstuffs. Paulson et al., (1975) reported that when rats and sheep were fed with alfalfa which had been treated with C ^{14}-labelled propham; it was found that although alfalfa converts propham to a number of products, a substantial amount of the label remained unextractable. It was also noticed that of the label added to the roots and shoots, 26.4% and 77% of radioactivity was found to be insoluble respectively. The treated alfalfa was split into two portions, one of which was extracted to produce alfalfa containing mainly unextractable or

insoluble radioactive label. These two types of alfalfa were fed to the test animals. Analysis of the urine and faeces samples showed that non-polar and soluble radioactivity was extracted in urine; insoluble residues passed through the gut with apparently little uptake, suggesting that the insoluble metabolites produced by plants were not readily available to animal systems. In fish and crustacea, chlorpropham has been demonstrated to concentrate in their bodies (Erb et al., 1980).

As noted in the literature above, chlorpropham, when ingested by animals, was absorbed from the gut, followed by metabolism and elimination via urine and faeces. The major mode of detoxification of chlorpropham proceeds through hydroxylation of aryl moieties followed by conjugation with sulphuric and/or glucuronic acids. A minor route included hydrolysis with subsequent acylation, hydroxylation and conjugation.

1.5.11 Degradation of carbamate herbicides in soil and water.

Organic chemicals introduced into water or soil are subject to non biological and biological changes. Significant alteration in structure and properties of organic molecules may result from non-biological processes. The major and more often the only mechanism by which such compounds are converted to inorganic products is biological. Incomplete degradation is frequently of environmental concern because the products may be more toxic than the original substance, more persistent than the parent compound or subject to biomagnification or other biological changes different from those undergone by the precursor molecule (Alexander, 1980).

Micro-organisms have enzymatic potential to metabolise the majority of pesticides and are responsible for numerous transformations that cycle elements

and energy in nature. The microbial population exists in a dynamic equilibrium formed by the interaction of abiotic and biotic factors. Micro-organisms are able to degrade a wide variety of chemicals, from polysaccharides, amino acids, proteins, lipids etc. to more complex materials such as plant residues, waxes, rubbers (Haider, 1983). In soil and water, the rate and route of transformation of herbicides are influenced by environmental factors, agricultural techniques and the properties of the herbicides and pesticide combinations; losses by volatilisation, uptake by plants or animals and adsorption while in an aquatic system pressure may indirectly influence transformations (Herrett, 1969; Hill and Wright, 1978). Many of the organisms found in soil are often present in aquatic conditions, consequently, in an aquatic system the metabolism of the pesticide may be similar to that in soil (Hill, 1978). The degree of degradation varies from compound to compound. Some molecules can be utilised as sole sources of carbon, nitrogen, and energy for growth of a particular organism leading, in some but not all cases, to the complete metabolism of the substrate while others are degraded to non-metabolisable compounds; some are apparently completely resistant to microbial attack. Some micro-organisms metabolise the pesticide in the presence of alternative substrate (Cripps & Roberts, 1978). Some micro-organisms can co-metabolise certain substrates which do not serve as carbon and energy sources (Alexander, 1980).

Torstensson (1980) and Hill and Wright, (1978) reported that in microbial decomposition of herbicides two phenomenon are of particular interest; the mechanism by which a soil microbial population develops the capacity to degrade a herbicide (adaptation); the nature of incidental microbial transformation by peripheral metabolic processes (co-metabolism).

Hill (1978) reported that pesticides degrade after an initial lag phase so that micro-organisms could develop the ability to degrade pesticides by chance

mutation or enzyme adaptation. The absence of a 'lag phase' does not necessarily indicate the presence of constitutive enzymes but may be due to co-metabolic transformation of the pesticide, the alternative substrate from which the organism obtains its growth and energy already being present in the atmosphere. The co-metabolism (with no lag phase) has been found for long persistence herbicides while the initial lag phase behaviour has been found for short persistence herbicides in soil.

Hill and Arnold (1978) stated that the initial losses of pesticides are slow or absent but increase progressively with time and reach a steady state for a period of time. It is deemed likely that the observed effect results from enrichment of the soil with organisms able to transform the pesticide. Further applications of the pesticide may be transformed more rapidly, either without or with a reduced lag phase. The same information was reviewed by Alexander (1980) about the kinetics of the microbial transformation processes.

The principal reactions involved in pesticide metabolism include oxidation, oxidative dealkylation, thioether oxidation, phosphorothionate oxidation, epoxidation of carbon-carbon double bond, hydroxylation, aromatic ring cleavage, hydrolysis, dehalogenation, condensation and conjugate formation. Hydrolysis, reductive dechlorination and nitro-reduction are enhanced in flooded soils, dehydrochlorination and ring cleavage are less favoured. Hydrolytic cleavage of carbamates occurs in flooded and non-flooded soils but heterocyclic ring cleavage is considerably reduced by flooding (Hill, 1978).

Several workers reported the involvement of soil microflora and blue green algae in degradation of chlorpropham (Kauffman and Kearney, 1965; Kaufman, 1967; Clark and Wright, 1970; Kaufman and Black, 1973; Still and Herrett, 1976; Vega et al., 1985; Rouillon, 1989; Mochida et al., 1993). Many of the authors were able to isolate fungi and bacteria which degraded

chlorpropham and propham and used them as a sole source of carbon.

Soil bacteria shown capable of degrading chlorpropham include *Pseudomonas straita, Flavobacterium spp., Agrobacterium spp., and Achromobactor spp.* These organisms also readily degrade 3-chloroaniline (Upchurch, 1973). *Pseudomonas* degrades chlorpropham to 3-chloroaniline as an end product (Kearney and Kaufman, 1965) but *Arthrobactor* and *Achromobactor* can dechlorinate this breakdown product to aniline which in turn yields CO_2 (Clark & Wright, 1970; Brown, 1978). Vega et al., (1985) demonstrated that 3-chloroaniline degraded through catechol as a source of carbon and energy in a similar rate to chlorpropham itself. This is in contrast to the utilisation of dichloroanilines, which mineralise very slowly, probably due to their binding and or polymerisation with soil constituents (You and Bartha,1982). Wright and Maule (1982) reviewed that blue green algae *Anacystis nidulans* was capable of converting propham and chlorpropham to the corresponding aniline and 3-chloroaniline respectively. Marty et al., (1986) revealed that the bacterial strain *Pseudomonas alcanigenes* isolated from soil was able to hydrolyse chlorpropham, propham, BIPC and Swep to corresponding aniline and alcohol by co-metabolism. In the presence of low herbicide concentrations (18 $\mu molL^{-1}$) the chlorpropham has the highest degradation rate chlorpropham> propham> BIPC> Swep.The degradation rate depended on initial chlorpropham concentration. In contrast to You and Bartha (1982), Bachofer and Ligens (1965) were not able to study further metabolism of 3-chloroaniline to catechol or other products because the transformation of the phenylcarbamate to aniline or chloroaniline was stoichiometric. They observed an increase of the lag before herbicide degradation began. This observation suggested that chlorpropham induced the formation of an enzyme responsible for chlorpropham degradation. Weid (1972) and Hurle & Walker (1980) also reported the adaption of soil microorganisms to decompose chlorpropham. McClure (1970) reported that a

mixed culture adapted to propham also degrades chlorpropham and swep at an accelerated pace. Pure isolates of two bacterial and two fungal species obtained from this culture proved capable of breaking the benzene rings of propham, chlorpropham and propanil, but not of Swep (McClure, 1974).

Rouchaud et al., (1986, 1987) reported 10 and 14-17 days as the half life periods of chlorpropham in soils of lettuce culture and lettuce under field conditions respectively. They also reported 3-chloroaniline as the major metabolite which was bound to soil. Bollag (1974), Brown (1978) and Rajagolal et al., (1984) found that the persistence of chlorpropham may extend to eight weeks. This is in contrast to 104 days and six months, the calculated half life periods of chlorpropham in water and acid/base media at 70 °C respectively (Koivistonen & Karinpa, 1965; Wolf et al., 1978 a). Further El-Dib and Aly (1976 c) observed that in the aquatic environment chlorpropham/propham concentration remained constant for a period of more than four months however, active bio-degradation of propham was noticed after the addition of inoculum of *Bacillus cereus*. Aniline was liberated in the solution of propham. Chlorpropham on the other hand did not degrade in the presence of this bacterium. Rouillion (1989) found evidence that *Ectomycorrhizal* fungi could immobilise chlorpropham by adsorption and absorption and 3-chloroaniline as the degradation product of chlorpropham. Experiments carried out with the same sterilised mycellium showed that 3-chloroaniline was derived from the biological hydrolysis of chlorpropham.

Stepp et al., (1985) studied anaerobic microbial degradation of dihalogenated aromatic compounds. Isopropyl-3,4 dichlorocarbanilate (DCIPC) was dehalogenated to give chlorpropham after 85 days showing dehaloganation at the para position.

In general the predominant route for chlorpropham metabolism in soil and water is hydrolysis, yielding isopropanol, carbon dioxide and 3-

chloroaniline. 3-chloroaniline may principally be incorporated in soil organic matter (Kaufman, 1967) or be further metabolised via mineralisation (Vega et al., 1985), acylation (Tweedy et al., 1970), N-oxidation (Kaufman et al., 1973), hydroxylation (Fletcher & Kaufman, 1979) and/or condensation into products similar to its transformation in a peroxide model system (Bartha et al., 1968; Kearney et al., 1969; Martey et al., 1986).

1.12 OBJECTIVES OF THE THESIS

In addition to its use as a sprout suppressant for ware potatoes, chlorpropham is one of the world's most widely used herbicides and is, therefore, exposed to a wide range of environmental and climatic conditions. During the processing of potatoes, the washings are added directly to rivers, thus increasing the risk of exceeding the maximum residue limits set by Environment Protection Agency (EPA) and EEC. For chlorpropham NRA has set a maximum admissible limit of 10 µg/l. It is, therefore, important to investigate the effect of selected environmental factors on the fate and behaviour of chlorpropham in the environment, and to find a way to reduce these levels in the environment especially in the drinking water. Since the fate of chlorpropham is determined by such factors like adsorption, volatilisation, and photodecomposition, these processes will be investigated in this study.

This thesis was build up with the following aims.

A comprehensive study on the behaviour and fate of chlorpropham in the environment. This involved an insight into the most important dissipation routes, adsorption-desorption, volatilisation, and photodecomposition. The adsorption-desorption study pertains to the selection of suitable adsorbents for the removal of chlorpropham from polluted waters. The volatilisation study involves optimising the conditions of an analytical method to measure chlorpropham volatility additive to the sampling technique, sample storage and

thermal desorption technique using GC-FID. Photodecomposition study aims at determining the photolysis rate of chlorpropham in the natural system of water and suspended sediments, and in addition, to identify potential metabolites in different systems.

CHAPTER 2

ADSORPTION-DESORPTION OF CHLORPROPHAM

2.1 INTRODUCTION

Adsorption and desorption are the main retention phenomena, which determine the transport, transformation, and biological effects of pesticides in soil environment (Barriuso et al., 1994)

Adsorption is one of the major factors affecting pesticide-soil colloid interaction (Bailey et al., 1968). Adsorption/partition are the factors controlling the uptake of organic contaminants by soil (Ding and Wu, 1995). Adsorption strongly influences chemical transport to the atmosphere, ground waters (leachability) and a primary factor influencing the bioactivity, efficacy of soil-applied pesticide (Bailey & White, 1964; Horowitz, 1972) and affecting immobilisation of toxic fractions of hazardous waste (Sims et al., 1987). Sorption to soil may effect the rate of degradation (Aharonson and Katan, 1993). Sorption is a general term that includes adsorption, (surface binding), absorption and partitioning (Senesi, 1993).

Pesticide adsorption on soils and soil constituents has been extensively documented (Bailey and White, 1964; Hamaker and Thompson, 1972; Green, 1974; Weed and Weber, 1974; Calvet, 1980; Koskinen and Harper, 1990 ; Beck et al., 1993).

Physical and chemical factors that have been related to soil binding of chemicals are size, shape, configuration solubility, pK, and polarity and polarizability, ionic nature and charge distribution. Soil properties that play important roles in binding are organic carbon content, cation exchange capacity, particle size, pH, clay content, water content, and salt concentration (Chiou et

al., 1979; Haque et al., 1980; Senesi, 1993). In addition to the nature of adsorbent and that of the herbicide, adsorption depends on several characteristics of the experimental system: temperature, ionic composition of the solution, and soil water ratio (Calvet, 1980; Yeager and Halley, 1990), and formulation type (Hill and Wright, 1978).

Adsorption of environmental chemicals on solids is generally evaluated by the use of adsorption isotherms. An isotherm is a relation between the amount of a chemical adsorbed(at constant temperature) per unit weight of adsorbent and the concentration of the chemical (solute) in the solution at equilibrium (Choudhry, 1982). Isotherms are most frequently characterised by the Freundlich equation. Depending on the dominating mechanism(s) sorption isotherms may exhibit different shapes; S, L, H, or C (Beck et al., 1993). The Freundlich isotherm is a simple empirical relationship relating the solid concentration (S) to equilibrium solution concentration (C), a sorption strength index (K_f) frequently referred to as the Freundlich coefficient), and an index of linearity(1/n)

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

Where S = x/m = mass sorbate/mass sorbent

For simplicity, the logarithmic transformation (Equation 2) of Equation 1 is frequently used such that 1/n and K_f can be derived by linear regression of log S against log C

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

Where isotherms are S or L shaped, 1/n values will be >1 or <1, respectively. For C-type isotherm, 1/n is unity and consequently the characterisation of an isotherm can be reduced to a simple proportionality relationship (Equation 3). Where S is related to C by a single distribution coefficient (Kd)

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

which is frequently expressed on an organic carbon(Equation 4) or an organic matter (Equation 5) basis to compare sorption of contaminants by different soils.

$$K_{OC} = (K_d / \% \text{ organic carbon}) \times 100 \qquad (2.4)$$

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

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

At low pollutant concentration (aq.phase conc. being less than half the solubility) the isotherm for sorption of neutral hydrophobic sorbates (solute) onto sediments and soils are linear, reversible and characterised by partition coefficient (Chaudhry, 1982; Beck et al., 1993)

The adsorption behaviour of pesticides depends on the chemical characteristics of the compounds and thereby varies in the same soil from compound to compound. As with the soil surfaces, functional groups on an organic molecule influence the strength and mechanism of chemical retention. For example, substitution in the phenyl ring with a halogen (Cl^- or Br^-) or chlorophenoxy group, increasing the chain length of dialkyls, or substituting the dialkyls with the corresponding alkoxy derivative (Hance, 1965; Grover, 1975) increases the adsorption of phenylurea herbicides. The type (e.g. hydroxyl, methyl, halogen, or nitro), number, and placement of the functional groups determine the strength of bonding as well as the availability for bonding (Isaacson, 1985; Boyd, 1982).

Several workers have reported a significant relationship between physical or chemical characteristics such as solubility and sorption of pesticides or other organic compounds within a chemical category (Bailey et al., 1968; Briggs, 1969; Chiou et al., 1979; Haque et al., 1980) and Graham-Bryce and Hartley, (1980) reviewed and showed the existance of relationship between the quantity adsorbed and values of Hammett and Taft function for several

substituted ureas and homologous series of alkyl-N-phenyl carbamates. Hamaker and Thompson, (1972) and Chaudhry, (1982) have correlated adsorption to parachor (A quantity which may be regarded as the molecular volume of a substance when its surface tension is unity; in most cases it is independent of temperature.

Temperature affects adsorption by its effect (i) on surface-solute interactions and (ii) on water-solute interactions It is the balance between these two effects which determines the observed behaviour and this may result in adsorption increasing, decreasing or remaining unaffected as a consequence of a change in temperature (Calvet, 1980).

The water content of the system can influence adsorption either by modifying the aggregation of adsorbents and mayincrease or decrease the accessibility of surface to the solute (Grover and Hance, 1970). The water content can also affect the physio-chemical properties of the adsorbent. While the soil water serves primarily for chemical transport within the soil matrix, adsorption of a compound is effected by water as a solvent and solute and by other solutes contained in the water. An adsorbing solute such as a pesticide must compete with water molecules, anions or hydrophobic solutes for adsorbing sites available. The soil water also plays a direct role in many of the adsorption mechanisms such as water bridging and ligand exchange. Hydrolysis of the soil surface may change the types of the adsorption sites that are available (Koskinin and Harper, 1990).

The major factor governing the magnitude of adsorption of different basic chemical families is the dissociation constant of the adsorbate. Within a family or within an analogue series basic in character, the magnitude of adsorption is related to and governed by the degree of water solubility. The magnitude of adsorption of organic compounds with widely different character is governed by the degree of water solubility, the dissociation constant of the

adsorbate, and the pH of the clay system (Bailey et al., 1968). Ionic composition of the aqueous solution can effect adsorption due to the varying effect of hydrogen ions on solute molecules and on the adsorbents. Protons cause conformational modifications of humic substances and hydrolyse the clay lattice.

Natural organic chemicals sorb to soil or sediment by partitioning into the organic carbon fraction. Ding and Wu (1995) described that the soil behaved as a dual sorbent, in which the mineral matter functioned as a conventional solid adsorbent and the organic matter as a partition medium. A good correlation between the octanol/water constant (K_{OW}) and partition coefficient for sediments (K_{OC}) has been demonstrated (Haque et al., 1980; Mill and Mabey, 1988). Gauthier et al., 1987 reported that the magnitude of the K_{OC} values correlated strongly with characteristics of the humic material. Strong linear correlations between sorption of non-ionic organic chemicals and soil organic matter content has been demonstrated by Beck et al., (1993). Briggs (1981) indicated that despite the complexity of soil organic matter, K_{om} for a particular chemical is virtually constant. Log P value for chlorpropham was 3.1 (Domine et al.,1992). Reddy and Locke (1994) developed QSAR model to estimate K_{OC} of immediate metabolites of herbicides including propham and chlorpropham as representatives of phenyl carbamates. Using K_{OC} values they calculated multiple regression models to suggest a mechanism involved in the sorption process. They further suggested that for more polar dinitroanilies, triazines, and carboxylic acids, the sorption process (with relatively higher regression coefficient) is dominated by Van der Waals interactions, hydrophobic bonding and hydrogen bonding compared to less polar ureas, carbamates, and acid amides.

Adsorption-desorption is a dynamic process in which molecules are continuously transferred between the bulk liquid and solid surface. The different

intramolecular forces that can attract molecules to the interface and subsequently retain them on the surface have been classified as to the mechanisms (Bailey and White, 1970; Hill and Wright, 1978; Chaudhry, 1982; Mortland, 1970, 1986; Sposito, 1984). All of these interaction mechanisms will operate simultaneously, and the combination that dominates the overall solution-solid distribution will depend on the structural properties of the organic chemical and solid medium of interest (Schwarzenbach et al., 1993).

Adsorption has also been described as a hydrophobic partitioning process between the soil water and the soil organic matter phase for the sorption of hydrophobic (nonpolar) compounds (Chiou et al., 1979). Hydrophobic adsorption by organic matter is suggested to be important for phenyl carbamate herbicides (Briggs, 1969; Senesi, 1993). In addition to these, covalent binding is also described as a possible binding mechanism for phenyl carbamates (Hsu and Bartha, 1976).

For a given chemical, or family of chemicals, several of these mechanisms may operate in the bonding of the chemical to the soil. For any given chemical, an increase in polarity, ionic nature of the chemical, and number of functional groups will increase the number of potential adsorption mechanisms for the chemical. For instance, an organic molecule may be sorbed initially fairly fast by the sites that provide the strongest mechanism, followed by progressively weaker sites(slower penetration) as the stronger adsorption sites become filled (Haque et al, 1980; Koskinen & Harper, 1990). For instance, within triazine herbicides, it has been suggested that mechanisms involving van der Waals forces, charge transfer, hydrophobic bonds, cation exchange, and cation bridging are responsible for bonding to soil surfaces (Hayes, 1970).

The adsorptive capacity of soil organic and inorganic molecules is dependent on the number and type of the functional groups at accessible surfaces. The intimate association between different soil minerals and organic

matter, makes many functional groups inaccessible to adsorbate molecules (Figure 2.1a). Some functional groups are accessible only to molecules that move through tiny soil pores, clay interlayers, or the polymeric soil matrix. The major functional group on inorganic surfaces contributing to the adsorptive reactivity associated with metal (hydrous) oxides (Sposito, 1984), oxyhydroxides, and hydroxides.

Inorganic hydroxyl groups are the most abundant and reactive functional groups on soil clays, particularly since they are associated with the surfaces of the clay minerals. Their reactivity varies depending on the number and type of coordination to metal ions. A variety of organic functional groups are present in the humic substances of the soil. Humic substances are large aromatic polymers made up of heterocyles, quinones, phenols, and benzoic acids that occur as micelles in nature (Stevenson, 1972,). The functional groups of humic substances are known to include carboxylic, carbonyl, phenylhydroxyl, amino, imidazole, sulfhydryl, and sulphonic groups. Soil humic substances also contain a relatively high concentration of stable free radicals (Steelink and Tollin, 1967). Recent studies combining chemical analyses, infrared (IR), and nuclear magnetic resonance (NMR) have shown that humic substances contain a larger proportion of aliphatic material than previous studies using only elemental and functional group chemical analyses (Sciacovelli et al., 1977; Wilson et al, 1987). The variety of functional groups in soil organic matter and steric interaction between functional groups in soil organic matter leads to a continuous range of activities in soil organic matter.

The aqueous environment also is important in the amount of binding to soil. Factors such as pH and ionic strength of the water environment affect binding. Pesticides may also be adsorbed by aquatic life, including plankton, invertebrates, vegetation and fish. The surface area, volume characteristics of unicellular micro-organisms, coupled with the lipophilic nature of many

pesticides, explain the high and often rapid pesticide sorption capacities of micro-organisms (Hill and Wright, 1978).

The effective diffusion coefficient is reduced by the adsorption of the pesticide by soil. However, Letely and Farmer (1974) reviewed that increase in total surface area and organic matter content tend to increase the measured diffusion rate. Increase in water content could also cause increase in diffusion coefficient. Soil temperature affects the rate of diffusion and adsorption of chemicals in soils

Models have also been developed to simulate sorption-desorption kinetics. Most sorption rate models can be divided into various categories: first order rate models and two site rate models (Karickhoff, 1980; Weber et al., 1991; Lee et al., 1991); pore diffusion models (Wu and gschwend, 1986). In these cases, an apparent hysteresis would seem to be observed, assuming equilibrium is achieved during the sorption phase of an experiment but equilibrium is not attained during desorption.

Desorption is the reverse process of adsorption (Osgerby, 1973; U.S. FDA, 1987). Huang (1971) proposed that after adsorption, small amounts of pesticides are desorbed into the surrounding water, to maintain a dynamic equilibrium. Desorption usually occurs readily in short term, however, Hill and Wright (1978) mentioned that under field condition the rate of desorption is retarded, becoming particularly slow after cycles of wetting and drying.

Generally, the extent of desorption follows the Freundlich isotherm. Factors directly associated with desorption include the properties of both pesticide and soil (Harris and Warren, 1964), however, amount of leachate (soil/ water ratio) and the amount of constituent contaminating the soil (soil/constituent ratio) are inversely related to desorption (Sims et al., 1986).

Molecular structure indices have been used to predict the sorption of the non-ionic compounds to soil orglanic matter. Boyd (1982) used Hammet

constants, which are based on the reactivity of aromatic substituent groups, as a relative measure of phenol sorption in soil. Molecular connectivity indices, based on the topology of an organic molecule, have been successfully used to predict soil sorption coefficients for non-ionic compounds (Sabljic, 1984).

In the following, studies on the adsorption-desorption of chlorpropham are summarised.

2.2 ADSORPTION OF PHENYLCARBAMATE HERBICIDES

There are numerous studies on the adsorption of phenyl carbamates using different adsorbents. Some of the studies are cited below.

Bailey et al., (1968) studied the adsorption of organic herbicides including phenylcarbamates on montmorillonite. Propham was not adsorbed on Na-montmorillonite but was on H-montmorillonite. However, chlorpropham was adsorbed by both the Na and H-montmorillonite clay. They attributed higher adsorption efficiency of chlorpropham as compared to propham to the presence of highly electronegative group (Cl) on chlorpropham, which enhanced its ability to form hydrogen bonds. They further concluded that adsorption of organic compounds is governed by the degree of water solubility, the dissociation constant of the adsorbate, and the pH of the adsorbent system.

Further, dependence of adsorption of chlorpropham on nature of the adsorbent, pH, and temperature was supported by the results of Harris and Warren (1964). They studied the adsorption of chlorpropham and other herbicides from aqueous solution by muck (organic) soil, bentonite, an anion exchanger, and a cation exchanger. Lowering of pH resulted in increased adsorption by bentonite of chlorpropham. In addition, chlorpropham was adsorbed by both cation and anion exchangers. Of all the herbicides studied, chlorpropham was adsorbed more by muck soil followed by diquat. However

these authors could not find a relationship between water solubility and adsorption.

Babiker and Duncan (1977) investigated the adsorption of asulum, a phenylcarbamate was influenced by the soil depth. They reported that adsorption was inversely correlated with pH, but, comparatively higher amounts of asulum were retained by top soil samples than by their respective sub soil samples owing to great organic matter content of the top soil.

Briggs (1969) stated that the sorption behaviour of phenylcarbamates on soils can be accounted for on the basis of Hammet and Taft constants. He studied adsorption of a homologous series of alkyl phenyl carbamates on four neutral soils containing 1 to 4% organic matter and concluded that sorption is caused by increasing lipophilicity with increasing length of alkyl chain. He observed a linear relationship between log K and π, Hansch's constant and described that sorption is an accumulation at hydrophobic sites at the organic matter interface in a way similar to surface active agents. In addition he demonstrated an inverse relationship with water solubility and sorption of phenylcarbamates. The partition coefficient for chlorpropham was 51. In this context Dominie et al., (1992) calculated multivariate structure-property relationship for chlorpropham to help predict sorption coefficient. Further, Jeng et al., (1992) reported a soil sorption coefficient of 5.9 E+02 L/kg.

During this decade attempts have been made to use molecular connectivity (MC), a topological description of organic compounds, for the estimation of adsorption of organic pesticides including chlorpropham by soils. Gerstle and Helling (1987) used K_{om} and K_{ow} of chlorpropham to calculate MC which gave a reasonable estimate of chlorpropham sorption. The value of MC for chlorpropham is 24-53.

Balaynnis (1988) presented the relationship between the adsorption of chlorpropham and the thermodynamic constants, Gibbs free energy, entropy and

the enthalpy of pesticide-water solution. The author reported that the distribution coefficient, K_d, of chlorpropham was significantly higher in low temperature to those obtained in higher ones. Further, desorption of chlorpropham from the studied soil (sandy clay loam) was less which was depicted by low exothermic free energy indices for chlorpropham. However, the high value of free energy obtained confirmed the high adsorption affinity of chlorpropham for the soil.

Helling (1971) reported that adsorption of chlorpropham was highly correlated with soil organic matter and total clay content. Furthermore, adsorption of chlorpropham was negatively correlated with mobility. Chlorpropham's adsorption was less correlated with its own mobility than with the mobility of three other herbicides under study (diuron, azinphosmethyl, diquat). The authors attributed the results to the extensive diffusion chlorpropham undergoes. In this context, Letley and Farmer (1974) reported that the diffusion coefficient for chlorpropham increased as the soil water increased, thereby increasing its adsorption.

Scott and Weber (1967) revealed that the phytotoxicity of chlorpropham was affected by adsorption. They studied the phytotoxicity of chlorpropham in the presence of four adsorbents; anion resin (Amberlite IRA 400), montmorillonite and Kaolinite clays, and a peat muck soil. The phytotoxicity of chorpropham was significantly reduced by the addition of anion resin and organic soil. This additive effect was attributed to the fact that the anion-exchange resin/organic matter adsorbed chlorpropham from the solution phase significantly and thereby reduced the rate at which the herbicide was absorbed by the plant.

The above survey revealed that adsorption of chlorpropham was effected by factors such as, temperature, pH, soil organic matter and soil clay content. Keeping in mind the environmental quality standards set for water in 1995 it

was demanding a need to study the effect of concentration, time, adsorbent and temperature on the adsorption of chlorpropham. This chapter was set up to fulfil the following objectives.

1- To develop a sensitive and reproducible analytical method which could efficiently be used for the detection of low levels of chlorpropham in waters.

2- To evaluate the adsorption capacity of various adsorbents, and select a cheaper, more commonly available one, which could be used on large scale for the removal of chlorpropham from polluted waters.

3- During the processing of potatoes, potatoes are washed and washings are added directly to river waters. An attempt was made to assess the effect of different temperatures on the adsorption of chlorpropham.

4- Desorption studies were conducted with all the adsorbents and under the same conditions to check the extent of reversibility of the adsorption.

2.3 EXPERIMENTAL

This section deals with the development of a sensitive analytical method which involves the use of solid phase extraction as a means of environmentally safe analysis of chlorpropham from soils and other adsorbents.

2. 3.1 Chemicals, apparatus, methods

Chlorpropham(CIPC) technical grade 99.5% pure was obtained from Greyhound Chromatography and Allied Chemical.

Hexane (HPLC grade), Acetone, Methanol (Analytical grade) were obtained from Fisher Scientific Ltd. Isopropanol, Diethyl ether, Dichloromethane, MTBE, were obtained from Rathburn (Scotland). All these solvents used were of analytical grade.

Anhydrous sodium sulphate, sodium chloride and calcium chloride were purchased from BDH Ltd.

Solid-phase extraction cartridges were obtained from Alltech Associates, Inc.

Granulated charcoal was purchased from Merck, Germany.

Wheat straw and tree bark were obtained from a local farm.

Drinking water was used in the experiment. The water was filtered through Millipore filter apparatus (47mm) using 0.2 μ GFC filter.

2.3.2 Adsorbents

Adsorbents are one of the important factors effecting adsorption of a pesticide. By studying the adsorption of a chemical on well defined adsorbents, information on the type of bonding mechanism possible for particular chemical can be estimated. Besides using soils a variety of adsorbents have been employed to determine the adsorption of chlorpropham from water; powdered nylon, cellulose triacetate, and cellulose (Ward and Upchurch, 1965), Montmorillonite (Bailey et al., 1968) and Kaolinite clays, Amberite IRA-400 and a high organic matter content soil (60% OM) (Scott and Weber, 1967), powdered carbon (El-Dib and Aly, 1977), activated carbon, graphatized carbon black (Leopold et al., 1965; Mangani and Bruner, 1983), Tenax, SI C18, Porapak Q, Separon SE 50/50, and Separon SI C 18 (Tatar and Popl, 1985).

The adsorbents used in this study include charcoal, wheat straw and tree bark in addition to three different soil types. The structures of charcoal, wheat straw and tree bark are illustrated in Figure 2.1 b and Figure 2.2. a, b respectively.

The soil samples chosen for this study represent major soil types prevailing in farming areas in West-Central Scotland and England. Soil descriptions are as follows.

Soil no.1. Midelney

The site is located at Bank Farm, Norfolk, England. Grid reference no. is TF 588022. The soil is used for intensive arable crop production. e.g. wheat, potatoes and sugar beet. It belongs to the Midelney series which is developed from calcareous alluvial clay material. The series has been classified as a ground water gley.

Soil no. 2. Downholland

The site is located at Bank Farm, Norfolk, England. Grid reference no. TF 586021. The soil is used for intensive cultivation of wheat, potatoes and sugar beet. It belongs to the Downholland series which originated from peat remnant cultivated into the fen clay to produce an organic matter rich soil. The series has been classified as a humic gley.

Soil no. 3. Dreghorn

The site is situated at West of Scotland College of Agriculture, Auchincruive, Ayr, Scotland. Grid reference No. is NS 373232. The soil is under permanent grass adjacent to greenhouses. It belongs to the Dreghorn Association which is developed from raised beach deposits. The series is Dreghorn which has been classified as freely drained brown forest soil.

Sand, silt, clay and C.E.C. values were obtained from Khan (1987), total carbon and LOI were estimated by the method of the above author. The relevant analytical data is given in Table 2.1.

Table 2.1 SOIL PROPERTIES

	MIDELNEY (clay)	DOWNHOLLAND (peat)	DREGHORN (sand)
Total C %	4.4	12.5	2.3
LOI %	14.7	31.2	6.7
pH Water	7.4	5.1	5.8
pH $CaCl_2$	7.0	4.6	4.8
Total N %	0.55	0.92	0.45
% Coarse sand	1.5	8.0*	46.9
% Fine sand	7.4		25.9
% Silt	50.8	2.1	19.0
% Clay	40.4	47.5	8.1
Textural class	Silty Clay	Clay	Sandy Loam

*Total sand as coarse and fine sand content of these samples were not determined individually.

Coarse sand > 0.18 mm, fine sand = 0.18-0.05 mm, silt= 0.05-0.02 mm and clay < 0.002mM

Figure 2.1(a): Interaction of a clay particle and an organic molecule (Koskinen and Harper, 1990)

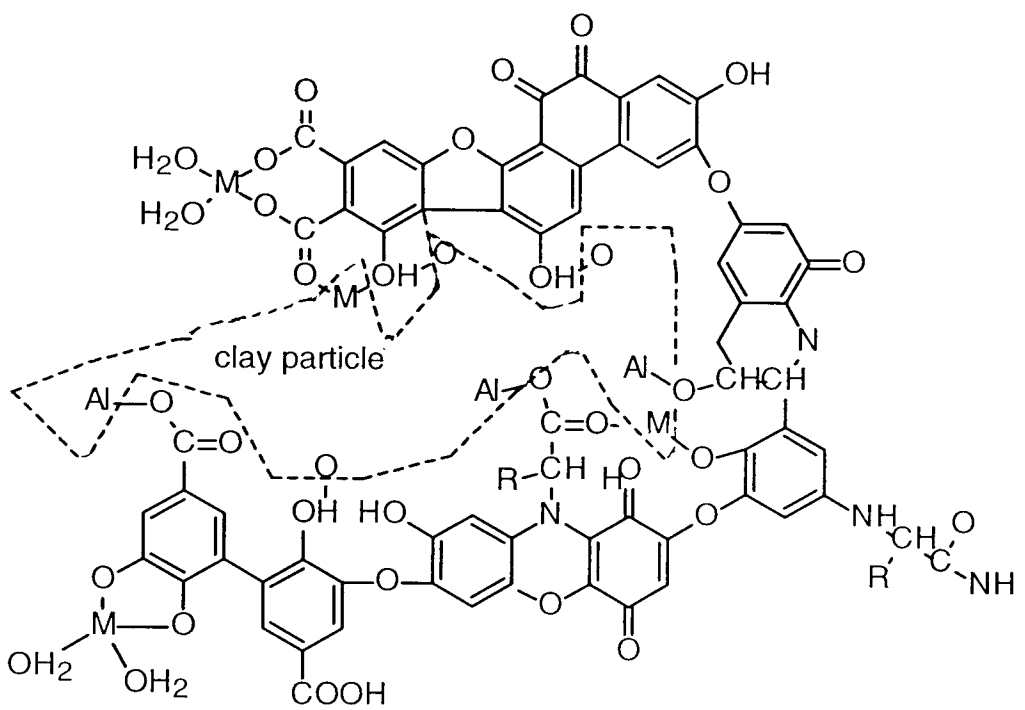


Figure 2.1(b): Structure of charcoal (Weber et al., 1965)

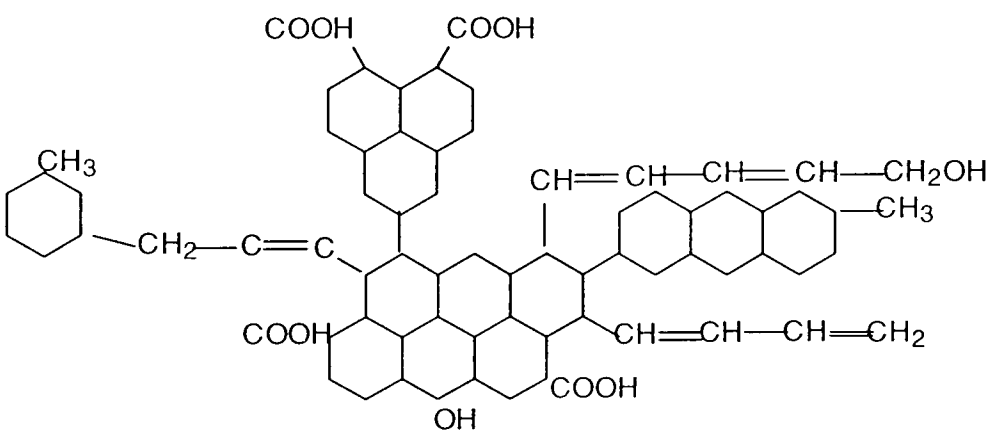


Figure 2.2(a): Structure of wheat straw (Staniforth, 1979)

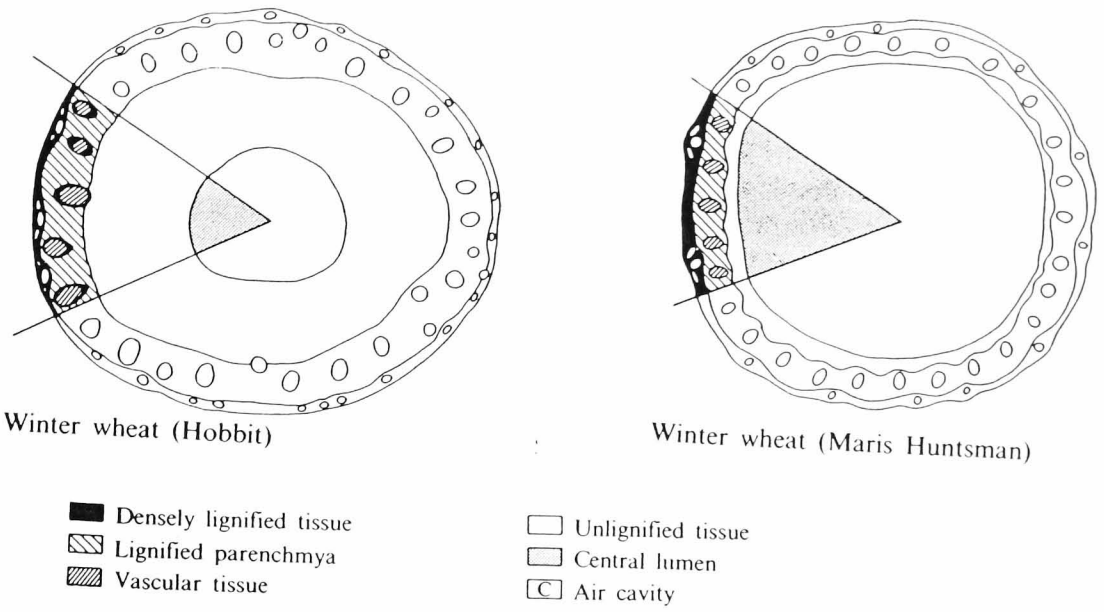
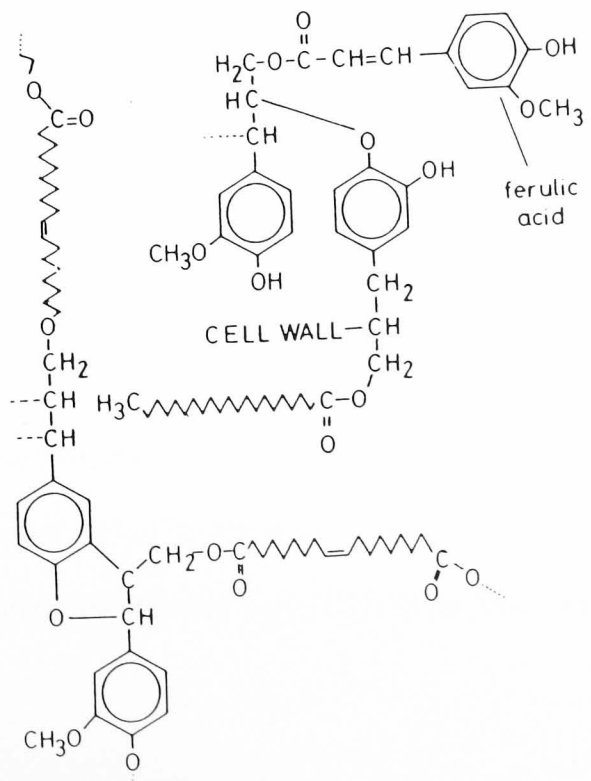


Figure 2.2(b): Structure of Suberine



2.3.3 Preparation of adsorbents

The soils were air dried, and sieved through a 2mm sieve. Wheat straw, and tree bark were cut and passed through mill (Glen Creston Ltd.) equipped with 2mm sieve.

Granulated activated carbon (Merck, Germany) was washed with double distilled water, dried at 120 °C overnight and finally kept in closed bottles.

2.3.4. Preparation of solutions

Solutions of standards of chlorpropham 10 µg/ml, 50 µg/ml, 100 µg/ml were prepared in analytical grade methanol to enhance the solubility of chlorpropham. All the standards were refrigerated when not in use.

2.3.5. Retention time, linearity, and MDL/MQL of GC-FID

An assessment was carried out to measure the linearity of response of Flame Ionisation Detector to the recovery of chlorpropham as well as minimum detectable level of chlorpropham using FID. A series of chlorpropham standard solutions 10, 20, 30, 40, 50 µg/ml were made up in glass distilled n-hexane. The solutions were kept in stoppered volumetric flasks when not in use. 5µl of each standard solution was injected onto the GC column. Each standard was injected in triplicate. The linearity of the detector was determined by plotting peak area against concentration. The MDL/MQL for FID was calculated as three/five times of the chlorpropham peak observed at zero attenuation.

2.3.6 Analysis of chlorpropham in soil/water

Different methods for the extraction and detection of chlorpropham from soil and water have been used. Some of these are mentioned below.

2.3.6.1 Extraction

Various solvent systems are used in liquid-liquid extraction to extract chlorpropham/ phenyl carbamates from water such as dichloromethane (Edgell et al., 1991; Tonogai et al., 1992), ethylacetate (Tonogai et al., 1992), chloroform (Erb et al., 1980), acetone and methanol (Voznakova, et al., 1988), isooctane (Steen et al., 1980) and acetone-methanol (1:1) (Bertrand et al., 1991).

Recently the use of solid sorbent for the extraction of chlorpropham from water is becoming popular. These include polymeric sorbent Wofatit Y 77 (Dedek et al., 1991), Sep-Pak cartridges (Wolkoff and Creed, 1979), Separon SI C18 (Tatar and Popl, 1985; Voznakova et al., 1988), graphitised carbon black (carbographs) (Capplello et al., (1994), C18 (Volmer et al., 1994).

2.3.6.2 Detection

Various detection methods have been adopted to quantify chlorpropham residues from water. Among those are:

Colorimetric methods of Harris and Warren, 1964; Baily et al., 1968; Leopold et al., 1965; Helling, 1971; Siek et al., 1975; El-Dib 1972, El-Dib et al., 1978; and Aaron Jean-Jaequs, 1993.

High Pressure Liquid chromtography with different detectors has been frequently employed for the detection of chlorpropham from water samples.

Among these are UV-HPLC (Wolkoff and Creed, 1979; Erb et al., 1980; Steen et al., 1980).

Mass Spectrometric (LC-MS) detection (Mestres et al., 1977) has also been used with different interfacing system such as Particle beam interface (Capplello et al., 1994), Thermospray (Volmer et al., 1994), Ammonia and methane chemical ionisation-MS (Kalinkoski et al., 1986; Cairns et al., 1984; Cairns et al., 1992), moving belt interface (Games et al., 1981).

Gas chromatographic methods using different detectors has also been used for the detection of chlorpropham in environmental samples e.g. FID-GC (Erb et al., 1980; Voznakova et al., 1988), NPD-GC (Laski, 1983; Ripley and Braun, 1983; Draper, 1995), FTD-GC (Tonogai et al., 1992).

Mass Spectrometry and GC-MS has been employed for the analysis and identification of chlorpropham in water and sediments (Mestres et al., 1977; Volmer et al., 1994; Tonogai et al., 1992; Mangani and Bruner, 1983; Kalinkoski et al., 1986).

In addition TLC was used by El-Dib (1970). El-Dib (1976 d) and Scott and Weber (1967) adopted bioassay techniques for the detection of chlorpropham.

The procedure adopted for the extraction and detection was developed in this study to accommodate available supplies and equipment.

2.3.7 Analytical method development

Although most official methods for analysis in water still use liquid-liquid extraction (LLE). Some disadvantages have been noticed: they are laborious, time-consuming, and expensive, are subject to problems arising from the formation of emulsions, the evaporation of large solvent volumes and the disposal of toxic or inflammable solvents. In the past few years, as alternative to

liquid partitioning the method of combined extraction and preconcentration of organic compounds in water by adsorption on proper solid material followed by desorption with a small quantity of an organic solvent has been employed extensively for trace determination of contaminants in environmental waters.

There are only a few studies involving the use of solid sorbent such as Wofatit Y 77 (Dedek et al, 1991), for the extraction of chlorpropham from water samples.

In the light of these views a comparison of LLE and SPE method was made for the the extraction of chlorpropham from drinking water using octadecyl-silyl bonded silica (C18) cartridges.

A number of preliminary experiments were carried out during the development of SPE method.

1- An experiment was carried out to compare the adsorption efficiency of C8 and C18 cartridges (200 mg) for the extraction of chlorpropham from drinking water (Table 2.2).

2- To determine pesticide collection efficiency of the cartridge, two 200 mg cartridges were connected in tandem to analyse the front and back cartridges separately to look for breakthrough of pesticide to the back cartridge. This tandem cartridge set up provides an opportunity to measure pesticide retention on the cartridge (or conversely, pesticide breakthrough) by comparing the mass of pesticide found on the back cartridge relative to that collected on the front trap by the relation (Foreman, et al., 1993)

Percent breakthrough = (mass on back cartridge/mass on front cartridge)×100 (2.5)

Breakthrough data calculated using above equation for the drinking water spike-recovery experiments for two amounts of adsorbent are shown in Table 2.3.

3- In order to select the best extracting reagent, different solvents were tested on the basis of increasing polarity. Results in terms of percent recovery are presented in Table 2.4.

4- During the course of analysis it was found that the water remained in the cartridge after nitrogen blowdown and it substantially reduced the recovery of chlorpropham from the analytes, therefore, vacuum drying was employed. An effort was made to elucidate the effect of cartridge drying time on the recovery of chlorpropham from spiked water samples. The results are shown in Table 2.5.

5- Finally, experiments were carried out to compare liquid-liquid (LLE) and solid-phase extraction (SPE) techniques (Table 2.6).

The procedures adopted for liquid-liquid and solid-phase extraction were as follows:

2.3.7.1 Liquid-liquid extraction

The procedure adopted was a modification of Edgell et al., (1991). 1 littre of filtered drinking water was spiked with 110µg/ml of chlorpropham solution in methanol. The entire sample was poured into 2 L separatory funnel. The sample was adjusted to pH 7 by adding 50 mL phosphate buffer. 100 g NaCl was added to the sample, sealed, and shaken to dissolve salt. 60 mL CH_2Cl_2 was added to sample bottle, sealed and shaken the bottle for 30s to rinse inner walls. Solvent was transferred to separatory funnel and sample was extracted by vigorously shaking funnel for 2 min with periodic venting to release excess pressure. The organic layer was allowed to separate from the water phase for >10 min. If the emulsion interface between layers was more than one-third volume of the solvent layer, the phase separation was completed mechanically. CH_2Cl_2extract was collected in 500 ml Erlenmeyer flask containing ca 5g anhydrous Na_2SO_4. A second 60 ml portion of CH_2Cl_2 was

added to the sample bottle and the extraction procedure was repeated. A third extraction was performed in the same manner, combining the extracts in Erlenmeyer flask. The flask was swirled to dry the extract and the flask was left for 15 min. The original volume was determined by refilling sample bottle to the mark and transferring water to a 1000 ml graduated cylinder. The sample volume was recorded to the nearest 5 mL.

2.3.7.1(i) Extract concentration

A K-D concentrator was assembled by attaching a 25 ml concentrator tube to a 500 mL evaporation flask. CH_2Cl_2 was decanted into the concentrator. The remainig Na_2SO_4 was rinsed with two 25 ml portions of CH_2Cl_2 and decanted the rinses into concentrator. 1or 2 clean boiling stones were added to the evaporating flask and macro-Snyder column was atthached. The column was prewetted by adding ca 1 ml CH_2Cl_2 to top. The K-D apparatus was placed on 65-70 water bath so that concentrator tube was partially immersed in hot water and the entire lower, rounded surface of the flask was bathed with hot vapour. The vertical position of the apparatus and water temperature was adjusted as required to complete concentration in 15-20 min. At proper rate of distillation, balls of column actively chattered. When apparent volume of the liquid reached 2 ml, K-D apparatus was removed, drained and cooled > 10 min. The Snyder column was removed; the flask and its lower joint was rinsed with 1-2 ml MTBE, the rinse was collected in concentrator tube. 5-10 ml MTBE and fresh boiling stone were added. Micro-Snyder column was attached to concentrator tube and column was prewetted by adding ca 0.5 ml MTBE to top. Micro K-D apparatus was placed on water bath so that concentrator tube was partially immersed in hot water. Vertical position of apparatus and water temperature was adjusted as required to complete

concentration in 5-10 min. When apparent volume of liquid reached 2 mL, apparatus was removed from bath and drained and cooled. 10 mL MTBE and boiling stone were added and concentrated to 2ml. The process was repeated three times and volume was adjusted to 5.0 ml with MTBE, and chlorpropham recovery was determined using GC.

2.3.7.2. Solid-phase extraction

1 litre of filtered drinking water was spiked with 1ml of 110µg/ml chlorpropham in methanol. The spiked water was passed through octadecylsilyl-bonded silica (C18) cartridges The cartridge was conditioned with 3 ml of methanol followed by 3 ml of deionized water prior to the extraction.

The sample was extracted at a flow rate of 4-5 ml/min to isolate and preconcentrate the analyte on the solid sorbent`. Upon completion of extraction step, the sorbent cartridges were rinsed with 3 ml of distilled water. The sorbent cartridges were initially dewatered by vacuum drying for 1 h. The analyte was eluted from the sorbent cartridge with 2 ml acetone and analysed by FID-GC. Comparison of LLE and SPE methods is shown in Table 2.6.

2.3.8. Procedure

Soil samples, 20 g air-dried, sieved, were weighed into glass stoppered 500 ml flasks and 250 ml of filtered drinking water was added. The soils were spiked with 1 ml of 10 mg/ml, 50 mg/ml, and 100 mg/ml chlorpropham solution in methanol. The total volume of the suspensions was always 250 ml.The flasks were put in orbital incubator shaker (Gallenkamp) at 100 rpm for 1 min (0 h), 24 h, and 72 h at 10 °C, 20 °C, and 30°C. The slurry was then filtered through Buckner funnel using Whatman filter paper no. 42. I ml of 0.1M $CaCl_2$ solution

was added to the soil slurries to help filtration. The filtrate was further processed by the SPE method mentioned below.

All measurements were carried out in duplicates. For each replicate measurement, duplicate gas chromatographic injections were done. Since the variability between the duplicate experiments was comparable with the variability between duplicate GC injections for each replicate. Therefore, adsorption values were determined as a mean of four values for each set of conditions. Blanks were run for all the treatments and adsorption was corrected for blanks at all treatments.

Adsorption was expressed as the percentage of the initial applied as well as the distribution coefficient K_d where

$$K_d = \frac{\text{Amount adsorbed per unit weight of adsorbent } (\mu g\ g^{-1})}{\text{Concentration in solution } (\mu g\ ml^{-1})}$$

Similar experiments were carried out with other adsorbents; charcoal, wheatstraw, and tree bark except that the amount of adsorbent used was 1 g.

2.3.8.1 Instrumentation

The analysis was carried out using GC. The GC used was Pye Unicam, PU 4500 chromatograph, fitted with flame ionisation detector (FID), and a 2m 4 mm i.d. glass column packed with a semipolar 3% OV 17, supported on 100/120 mesh WHP. GC conditions used were; injector temperature: 200 °C, detector temperature: 250 °C, carrier gas nitrogen at flow rate 30 ml/min, Hydrogen and Oxygen gas at 30 and 80 ml/min. The FID signals were recorded on a chromatographic integrator, Spectra-Physics (4290).

2.4. RESULTS AND DISCUSSIONS

2.4.1 Analytical method development

Many experiments were carried out to develop an efficient and sensitive method using solid-phase extraction technique for the analysis of chlorpropham residues from drinking water. The assessments are as follows:

(1) Effect of cartridge type

As a first step of analytical method development, the effect of cartridge type on the recovery of chlorprpham from water was determined. The results demonstrated clearly that C 18 cartridges could be used for the extraction of chlorpropham from water (see Table 2.2)

(2) Effect of cartridge size

Data from breakthrough experiments (Table 2.3) demonstrated that 99.99 % of the applied chlorpropham could be adsorbed/ eluted from an 500 mg adsorbent cartridge as compared to a 200 mg adsorbent cartridge where only 67 % could be recovered. These results suggested that a 500 mg cartridge might be necessary for isolation of chlorpropham from water.

(3) Effect of solvent

In an effort to select efficient solvent for the elution of adsorbed chlorpropham from the cartridges, a number of solvents and solvent systems ranging in increasing polarity were tested using two 200 mg cartridges in series.

Acetone proved to the best solvent with 87.88% recovery. The results are shown in Table 2.4.

(4) Drying time

Following the initial procedure of solid-phase extraction, which involved the nitrogen blowdown for 30 minutes for the removal of water solution from the cartridge, it was observed that water still remained in the cartrige resulting in a turbid solution with a low recovery (78.69 %) of chlorpropham. Attempts were, therefore, made to dewater the cartridge by vacuum drying. Various time intervals were used to improve the recovery of chlorpropham. Based on the results (Table 2.5) of drying time effect on the recovery of chlorpropham from C18 cartridges, one hour was taken as an appropriate drying time for extracted cartridges and followed throughout the experiment.

(5) Comparison of the efficiency of LLE/SPE

The analysis of chlorpropham residues from water samples using Liquid-Liquid/Solid-phase extraction methods was also carried out. The results are presented in Table 2.6.

In an attempt to find the minimum detectable/ quantifiable level by FID, it was calculated that chlorpropham samples could be detected down to 2 to 5ng.

From these findings it follows that maximum recoveries of chlorpropham from water could be obtained using 500 mg C18 cartridges with acetone as an eluting solvent at 1h cartridge drying time. Therefore, another set

of experiments was carried out to further confirm the method. The results are presented in Table 2.7.

The results of the above series of experiments clearly demonstrated that the solid-phase extraction method provides an excellent technique for the isolation and preconcentration of chlorpropham from water samples with 97-100% recovery. Thus, the solid-phase extraction method was adopted for the analysis of chlorpropham from water during this study.

Adsorption/desorption experiments were carried out on different soils, charcoal, bark and straw and the results are discussed in the following.

Table 2.2 Effect of cartridge type on the recovery of chlorpropham (110μg/ml) using acetone as eluting solvent

Sample No.	chlorpropham added (μg)	cartridge used (200mg)	amount(μg) recovered	% Recovery
1	110	C8	4.09	3.72
2			4.41	4.01
3			4.34	3.95
4			4.89	4.45
5			3.91	3.56
		Mean	4.32	3.93
1	110	C18	74.06	67.33
2			77.15	70.14
3			76.63	69.67
4			75.88	68.99
5			77.97	70.89
		Mean	76.33	69.39

Table 2.3 Mean analyte recovery and cartridge breakthrough data for chlorpropham spiked water (105 μg/ml) by SPE method.

Sample No.	cartridge used (C18)	Front cartridge	Total = Front+ Back+Rinse	Mean percent breakthrough
1	200 mg	67.33	97.14	42.16
2		65.02	96.99	46.82
3		68.32	98.62	42.23
	Mean	66.89	97.58	43.73

Table 2.4 Effect of solvent on the recovery of chlorpropham from drinking water using two (200+200 mg) C 18 cartridges.

Chlorpropham (added µg)	Eluting solvent	Amount recovered	% Recovery
50	Hexane	1.69	3.39
		1.07	2.14
		1.88	3.76
	Mean	1.54	3.09
	Methanol	28.98	57.97
		29.55	59.1
		29.76	59.52
	Mean	29.43	58.86
	Ethylacetate+Isopropanol (5:5)	36.22	72.44
		36.44	72.89
		34.62	69.24
	Mean	35.76	71.52
	Cyclohexane+Isopropanol (7:3)	36.52	73.04
		36.48	72.96
		37.00	74.00
	Mean	36.66	73.33
	Acetone	43.77	87.54
		44.07	88.14
		43.99	87.98
	Mean	43.94	87.88

Table 2.5 Effect of cartridge drying time on the recovery of chlorpropham (using 500 mg C 18 cartridges and acetone as eluting solvent)

Sample no.	Drying time (min)		Amount recoverd (µg)	% recovery
1	10		68.49	65.22
2			63.28	60.26
		Mean	65.88	62.74
1	20		66.67	63.49
2			64.23	61.17
		Mean	65.45	62.33
1	30		84.98	80.93
2			82.63	78.69
		Mean	83.80	79.81
1	60		100.08	95.31
2			102.78	97.88
		Mean	101.43	96.55
1	90		82.72	78.78
2			80.45	76.61
		Mean	81.58	77.69

Table 2.6 Comparison of liquid-liquid/solid-phase extraction methods for the analysis of chlorpropham spiked water samples

Sample No.	Chlorpropham added (µg)	Method used	Amount recovered	% Recovery
1	110	LLE	96.18	87.43
2			93.35	84.86
3			88.83	80.75
4			94.43	85.84
5			93.73	85.20
		Mean	93.30	84.82
1	105	SPE	101.59	96.66
2			100.13	95.36
3			102.57	97.68
4			105.11	100.10
5			103.82	98.87
		Mean	102.64	97.75

Table 2.7: Recovery of chlorpropham (105 µg/ml) from water using SPE method

Sample no.	cartridge used (C18)	Amount recovered	% Recovery
1	500 mg	102.41	97.54
2		103.04	98.14
3		102.88	97.99
	Mean	102.78	97.88

2.4.2 Adsorption of chlorpropham on different adsorbents

The adsorption/desorption of chlorpropham was carried out using six adsorbents including three soils. To assess the effect of various factors on adsorption, experiments were conducted at three different temperatures, concentrations and time. The results of adsorption and desorption of chlorpropham from different adsorbents at studied concentration and temperatures are shown in Figure 2.3-2.8. The analysis of variance showed a highly significant difference ($p < 0.05$) over all times and concentrations for all the six adsorbents. However, effect of temperature was not significant in most cases except for wheat straw and Midelney soil. The results are shown in Table i-vi (see appendix)

2.4.2.1 Adsorption on soils.

2.4.2.1.1 Effect of soil type

The results for the adsorption of chlorpropham on soils are presented in Figures 2.3-2.5 (Table i-iii in appendix). The data shows that adsorption values for Downholland (31.2 % LOI), Midelney (14.7 % LOI), and Dreghorn soil (6.7 % LOI) at 100 µg/ml dose were 3.68 µg/g, 3.20 µg/g and 2.19 µg/g respectively at 10 °C and 72 h. Similar trends are seen at 20 °C and 30 °C and at concentrations of 50 and 10 µg/ml. These results are as expected and theoretically accepted when compared with the information reviewed by Bailey et al., (1968). Theoretically, for non-ionic or weakly polar herbicides, soil organic matter is the most important factor in controlling adsorption/desorption (Hamaker and Thompson, 1972; Kenaga and Goring, 1980; Karickhoff, 1981;

McCall et al., 1981, Briggs, 1981; Schwarzenach et al., 1993). There is a linear relationship between organic matter content of the soil and adsorption of organic compounds. The retention mechanism of non-ionic organic chemicals in soil is a partitioning of the chemical between the aqueous phase and the hydrophobic organic matter (Chiou et al., 1979). The soils under study differ in O.M. content, they exhibited various adsorption efficiencies.

The results in this study are further supported by the results obtained by Scott and Weber (1967) as they reported that addition of organic soil to the growth media significantly decreased the phytotoxicity of chlorpropham highly significantly because of high adsorption of chlorpropham by the soil organic matter. In addition Babiker and Duncan (1977) reported comparatively larger adsorption values of Asulam, a phenyl carbamate herbicide; they attributed this finding to the larger organic matter content of the top soil. Similarly Yen et al., (1994) reported that K_f of alachlor decreased with soil depth partly due to difference in soil organic matter content. In this context, Grover (1975) reported that relative adsorption of phenylurea on various soil types was significantly correlated with the soil organic matter content. Arienzo et al., (1994) revealed that Freundlich's constant k and K_d for diazinon were found to be highly significantly correlated ($P< 0.001$) with the organic matter (OM) content when all soils or only those with OM content above 2% were considered. In addition, Farmer and Aochi (1973) reported that the value of k for picloram adsorption increased with increasing soil organic matter content, and the range in k was 3-fold between soils with the highest to lowest organic matter. Furthermore, Helling (1971) revealed that adsorption to soil was highly correlated with soil organic matter content: simazine (0.671**), diuron (0.916**), chlorpropham (0.884**). However,Yeager and Halley (1990) during the adsorption of efrotomycin on soils, revealed that the sorption distribution coefficient was not correlated with soil organic matter content. Helling (1971) revealed that

Figure 2.3(a) : Adsorption / desorption of chlorpropham fom Downholland soil at 100 μg/ml.

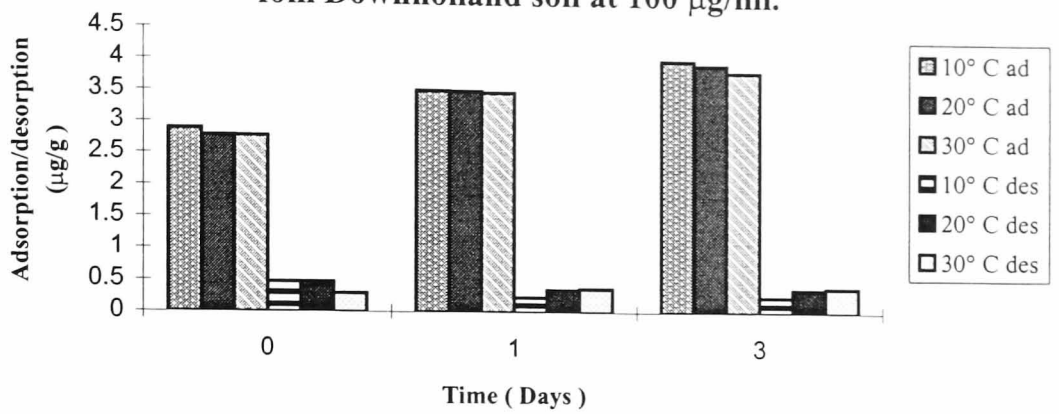


Figure 2.3(b) : Adsorption /desorption of chlorpropham from Downholland soil at 50 μg/ml.

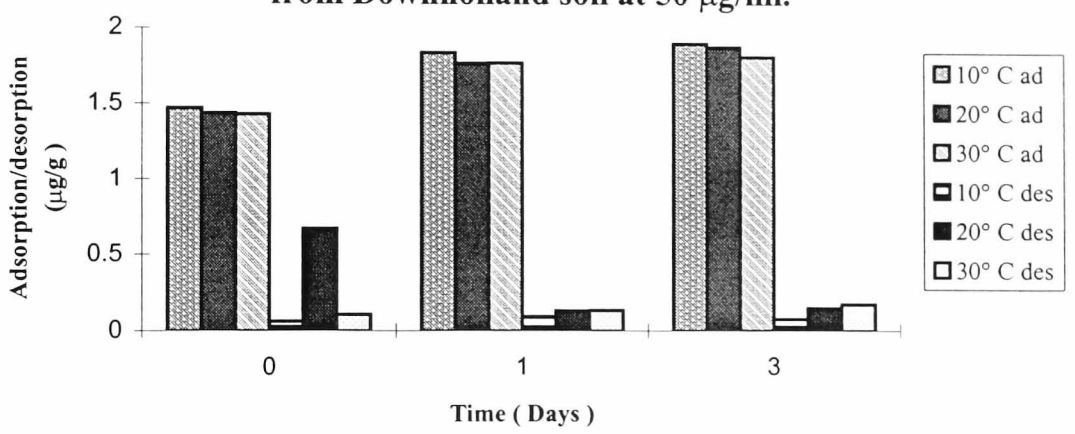
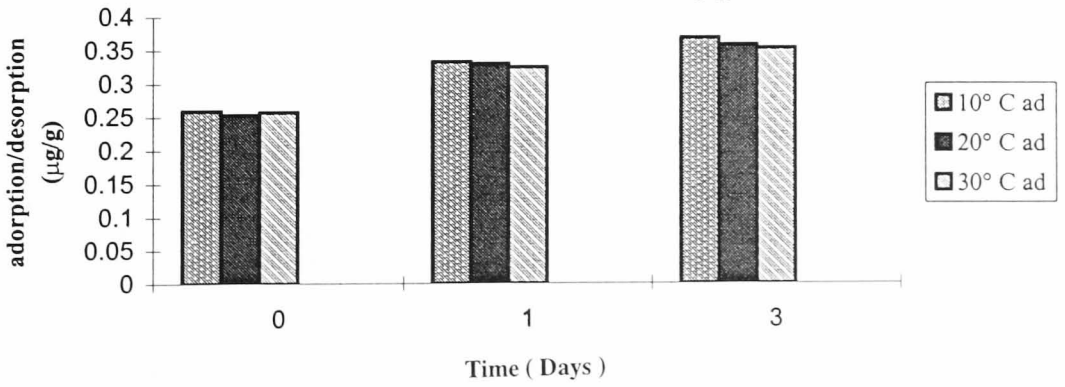


Figure 2.3(c) : Adsorption/desorption of chlorpropham from Downholland soil at 10μg/ml



ad = adsorption des = desorption

Each value is mean of four replicates

Figure 2.4(a) : Adsorption/desorption of chlorpropham from Midelney soil at 100 μg/ml.

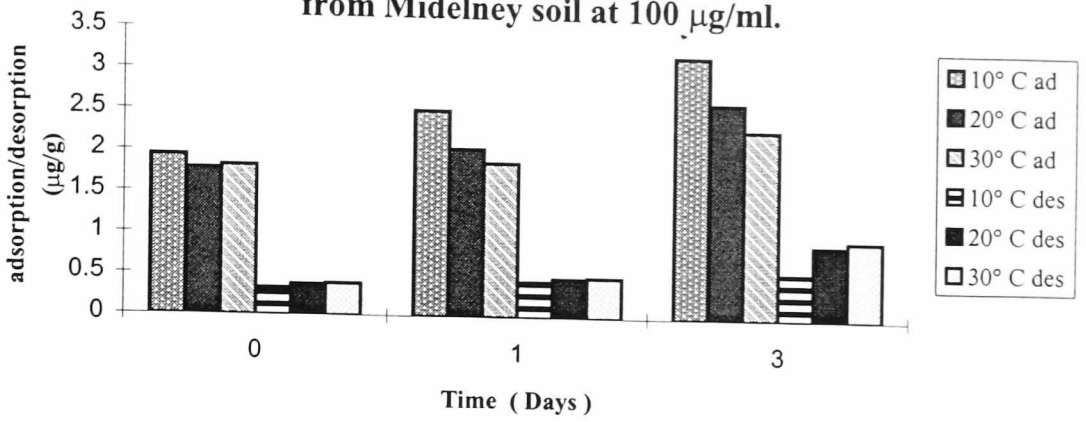


Figure 2.4(b) : Adsorption/desorption of chlorpropham from Midelney soil at 50 μg/ml.

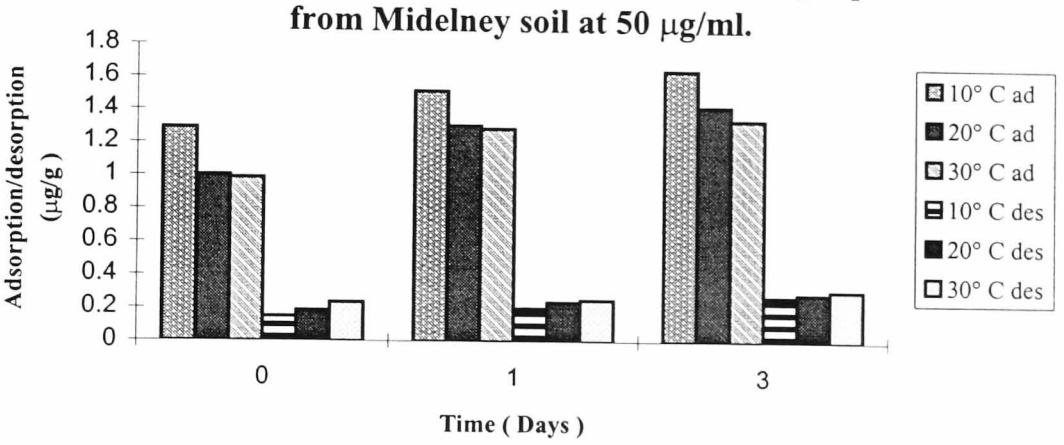
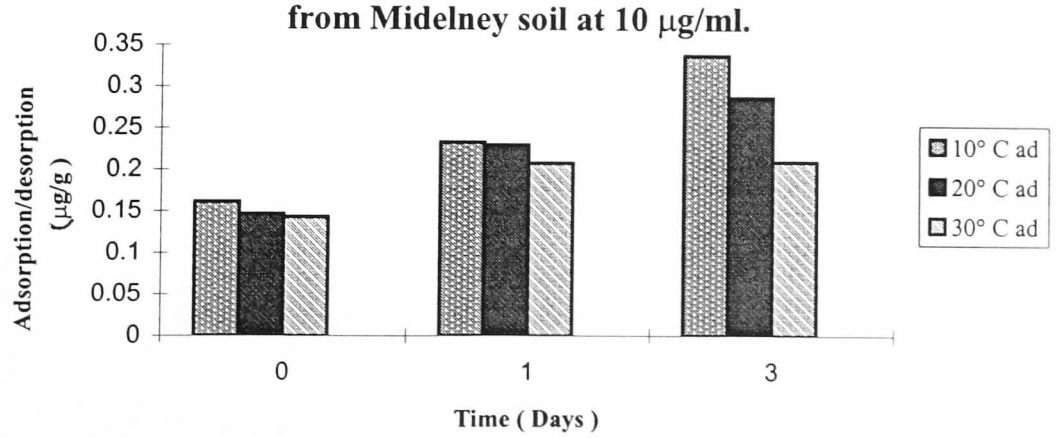


Figure 2.4(c) : Adsorption/desorption of chlorpropham from Midelney soil at 10 μg/ml.



ad = adsorption des = desorption

Each value is mean of four replicates

Figure 2.5(a) : Adsorption/desorption of chlorpropham from acid washed sand at 105 μg/ml.

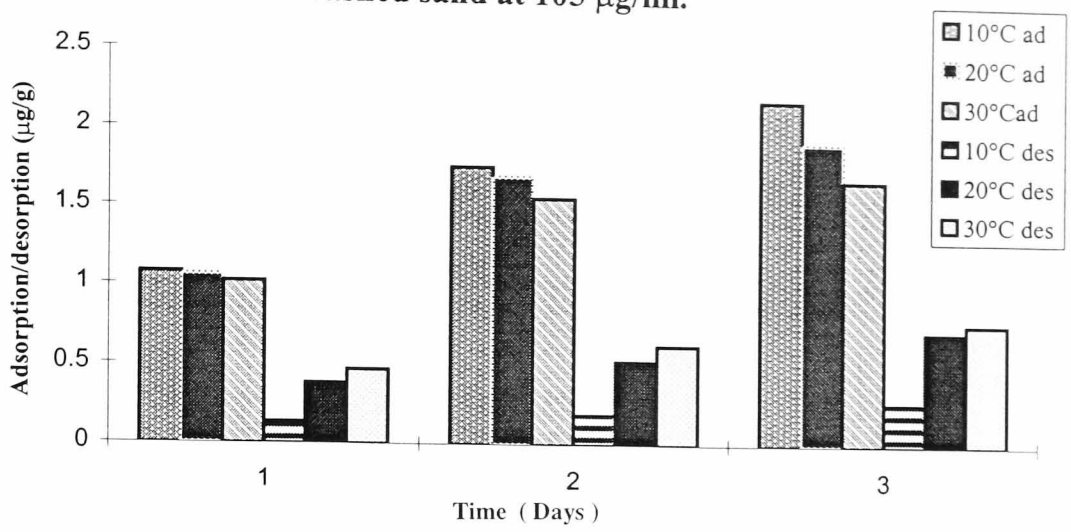


Figure 2.5(b) : Adsorption/desorption of chlorpropham from acid washed sand at 50 μg/ml.

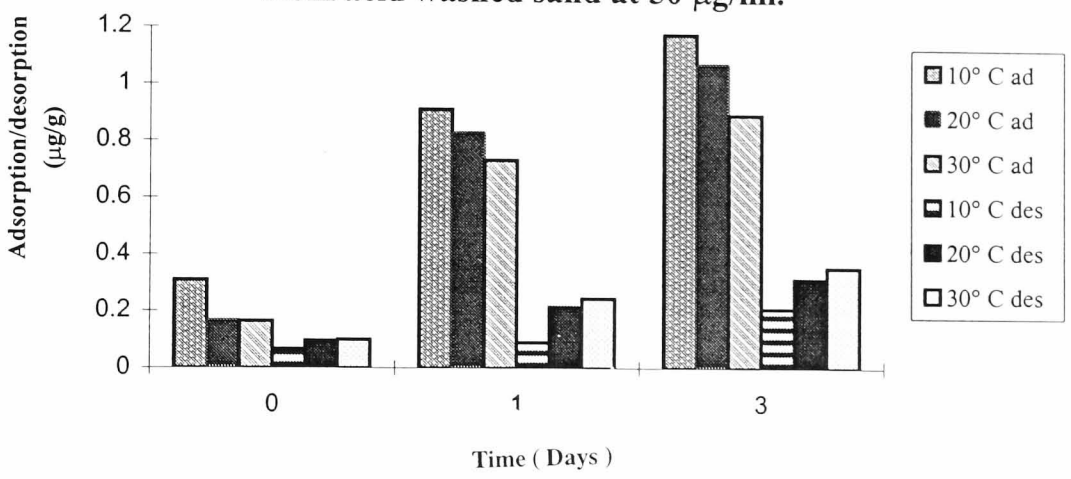
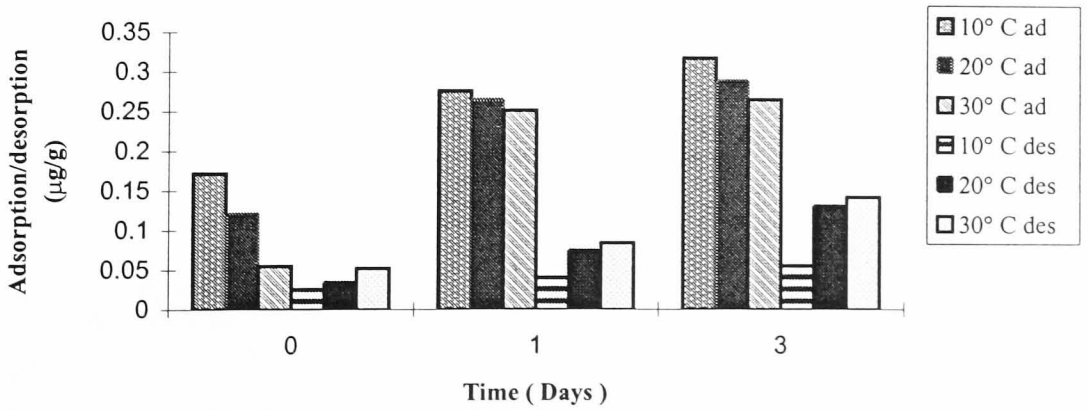


Figure 2.5(c) : Adsorption/desorption of chlorpropham on acid washed sand at 10 μg/ml.



ad = adsorption des = desorption

Each value is mean of four replicates

Figure 2.6(a) : Adsorption/desorption of chlorpropham on wheat straw at 100 μg/ml.

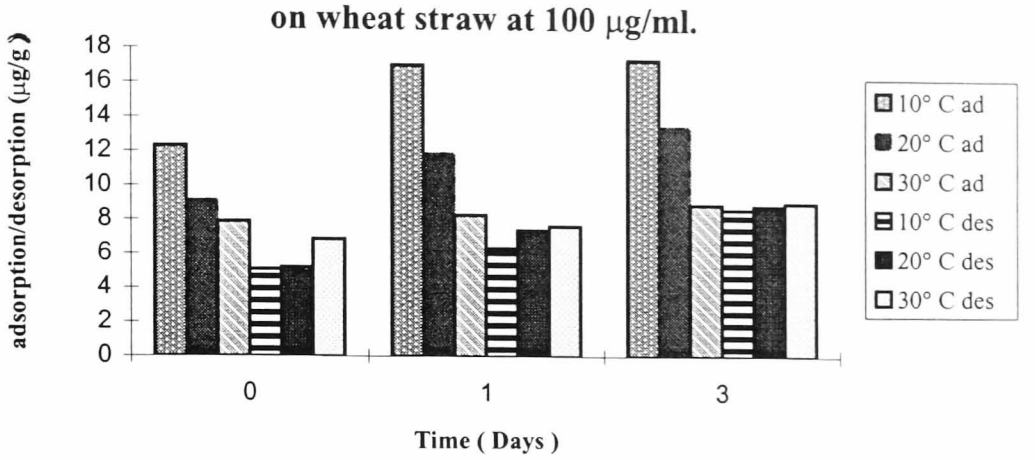


Figure 2.6(b) : Adsorption/desorption of chlorpropham on wheat straw at 50 μg/ml.

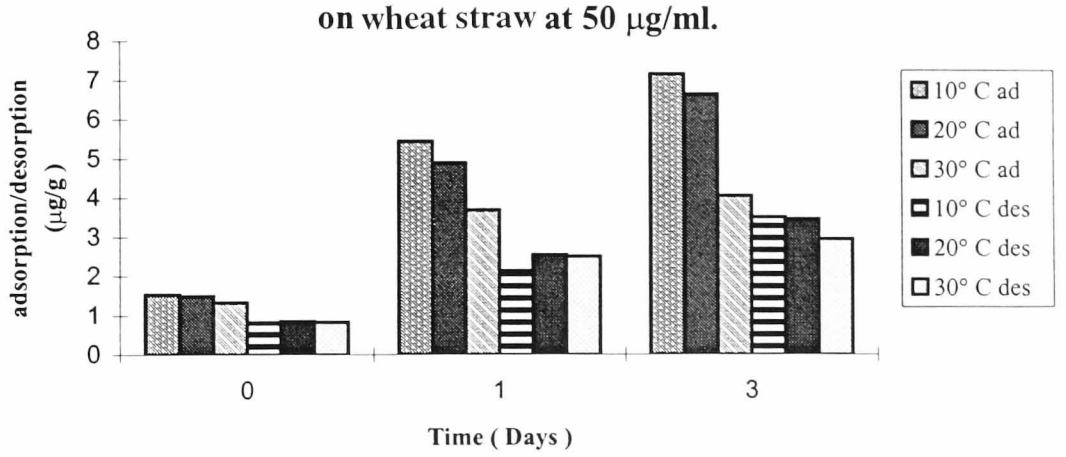
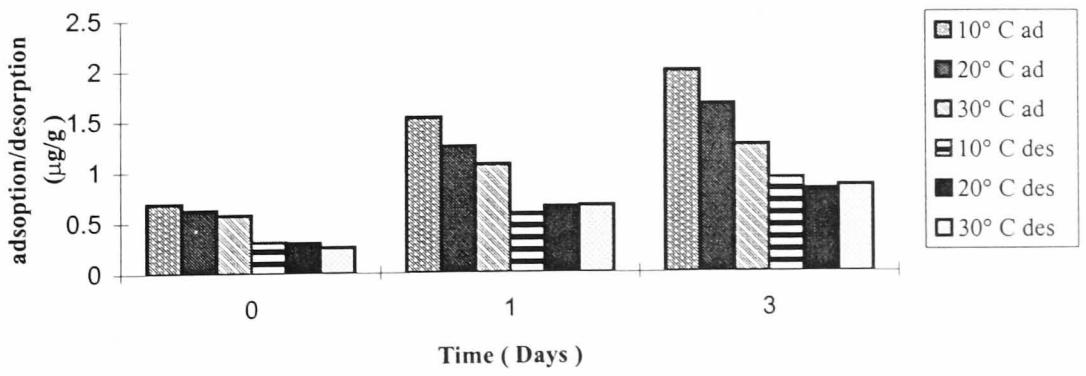


Figure 2.6(c) : Adsorption/desorption of chlorpropham onwheat straw at 10 μg/ml



ad = adsorption des = desorption

Each value is mean of four replicates

Figure 2.7(a) : Adsorption/desorption of chlorpropham from Treebark at 100μg/ml.

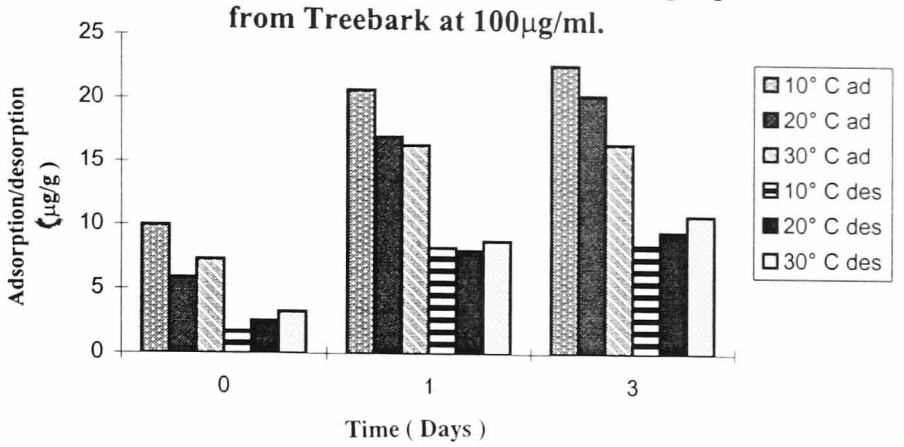


Figure 2.7(b) : Adsorption/desorption of chlorpropham from Treebark at 50 μg/ml.

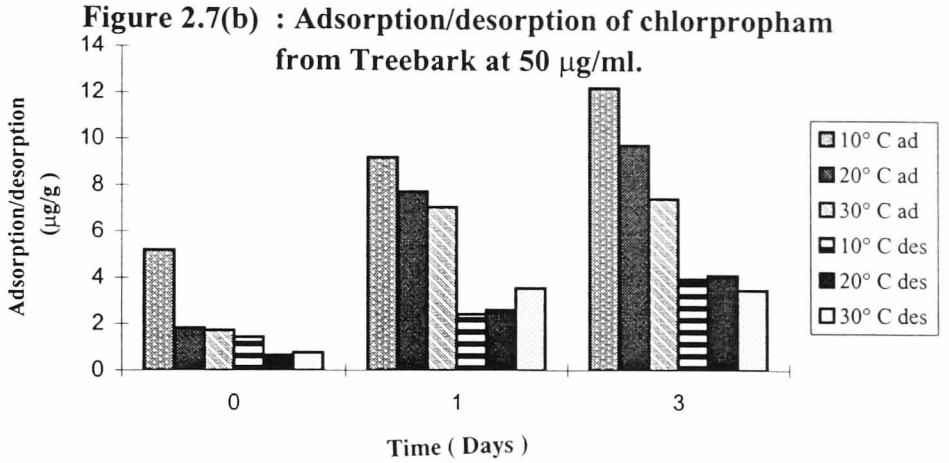
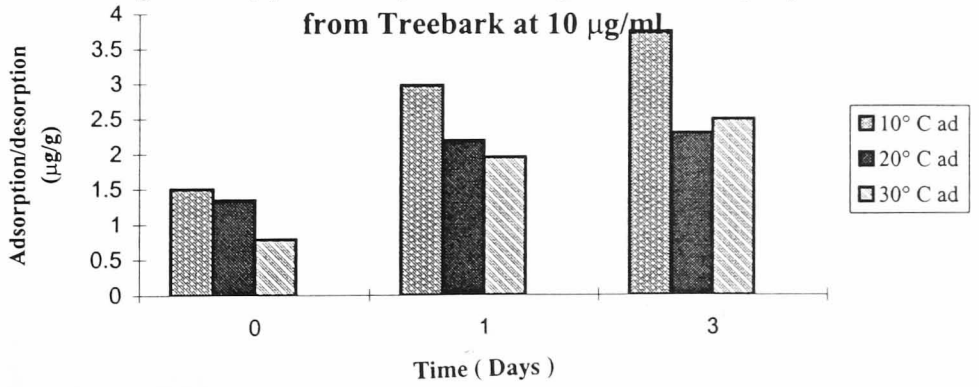


Figure 2.7(c) : Adsorption /desorption of chlorpropham from Treebark at 10 μg/ml



ad = adsorption des = desorption

Each value is mean of four replicates

Figure 2.8(a) Adsorption/desorption of chlopropham from charcoal at 100 μg/ml

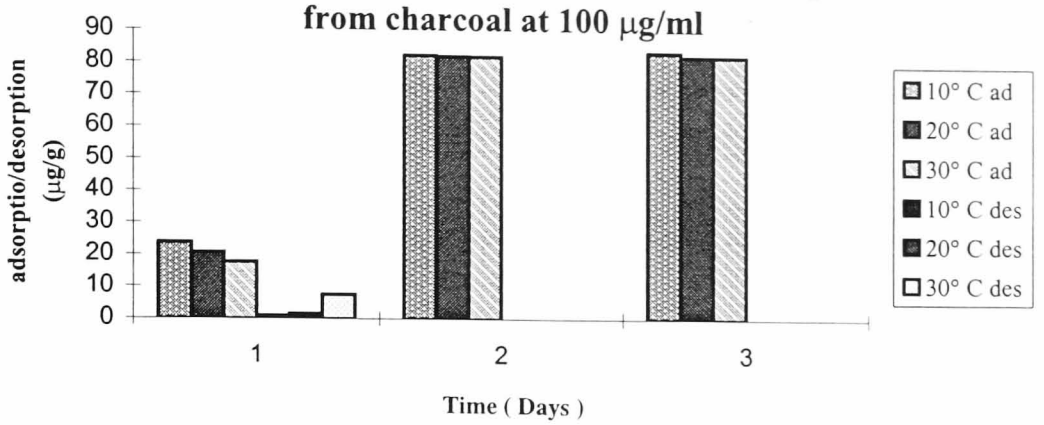


Figure 2.8(b) Adsorption/desorption of chlorprpham from charcoal at 50 μg/ml.

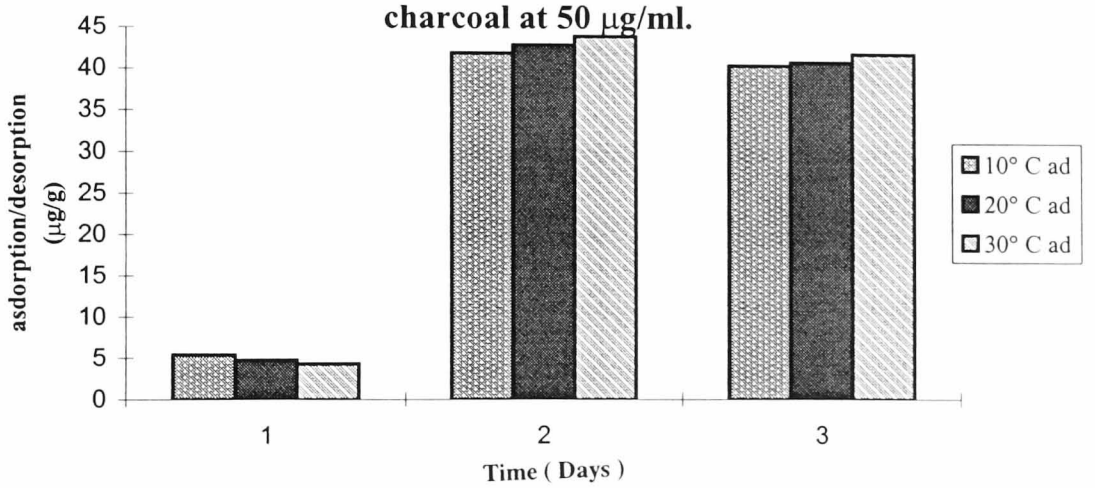
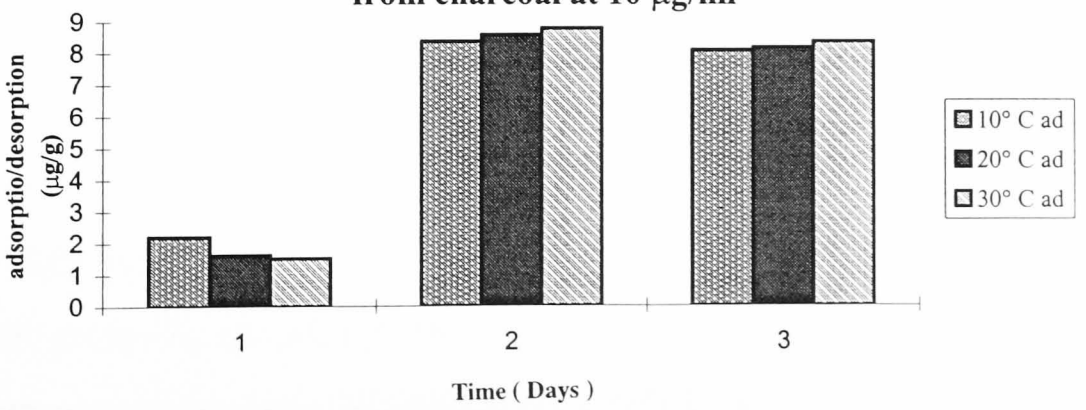


Figure 2.8(c) Adsorption/desorption of chlorpropham from charcoal at 10 μg/ml



ad = adsorption des = desorption

Each value is mean of four replicates

adsorption of diuron (0.695**) and chlorpropham (0.650**) was related to total clay content.

Closer examination of the adsorption data shows that the two soils under study ; Downholland (peat) and Midelney (clay), though significantly different in their OM content, yet exhibited comparable adsorption efficiency and this effect was more prominent at lower temperatures. Adsorption values of chlorpropham on peat and arable soils were 0.369 µg/g and 0.339 µg/g respectively at the 10 µg/ml application level, at 10 °C and 72h. For other studied temperatures and concentration levels similar results were observed (see appendix. Table i-ii).

The results of this study could be explained on the basis that Downholland and Midelney have a closer number of hydrophobic sites resulting in more adsorption of chlorpropham on Midelney soil than would be expected.. The clay and silt contents for Downholland) and Midelney soils were 46.9% and 2.1% and 40.4% and 50.8% respectively. Clay minerals are coated, at least partially, with mixtures of polymeric oxides and hydroxides of iron, aluminium and manganese and/or with humic substances which give hydrophobic properties to the clay surface (Fusi et al.,1993; Koskinen and Harper, 1990; Yaron et al., 1967). The Si-O-Si bonds at clay mineral surfaces are hydrophobic and are potential sites for the adsorption of non-polar compounds (Sonon and Schwab, 1995). Chlorpropham may have adsorbed on the clay mineral fraction of these soil.

In this regard, Bailey et al., (1968) reported that the combined effect of the COOR group and the phenyl ring would lead to enhanced stability of the chlorpropham molecule and a weakening of the N-H bond, which would in turn favour the formation of stronger hydrogen bonds with the oxygen of the clay mineral surface. Similarly, Helling (1971) revealed that adsorption of diuron (0.695**) and chlorpropham (0.650**) was significantly related to total clay

content. In this context, Arienzo et al., (1994) reported that there was a significant correlation ($p<0.01$) of K and K_d values with the silt plus clay content soil with OM content below 2%. It appears that comparable adsorption rates in the case of the two soils resulted from the cumulative effect of OM and clay contents of these soils. However, Grover (1975) reported that relative adsorption of urea herbicides on various soil types was significantly correlated with the soil organic matter, but not with the clay content. Sonon and Schwab (1995) however, reported a poor correlation with organic carbon ($r^2=0.15$) and higher correlation with silt content ($r^2=0.48$) suggesting a greater role of mineral surface area rather than organic matter in the retention of the herbicides.

In this regard Green and Karickhoff (1990) reviewed that sorption potential of mineral surfaces in natural surface soil is blocked by organic matter. The extent to which clay minerals contribute to sorption depends both on the ratio of the clay mineral to organic carbon fractions of the soil or sediment and on the nature of organic sorbate. The type of soil clay becomes increasingly important when soil organic contents are low. In this connection Bansal and Chaturvedi (1993) reported that adsorption of benalate on Zn-, Cu-, Cd-, and Mn-montmorillonite decreased progressively as more humic acid was added due to the preferential adsorption of organic matter on clay. In this context, El-Dib et al., (1978) reported variation in the adsorption capacity of clay mineral. The value of k was higher in the case of bentonite as compared with that for kaolinite owing to the large surface area of bentonite (600-800 $m^2\ g^{-1}$) as compared with that of kaolinite (7-30 $m^2\ g^{-1}$).

2.4.2.2 Adsorption on charcoal, bark and wheat straw

Among the adsorbents studied charcoal proved to be the most effective followed by tree bark and wheat straw for the removal of chlorpropham. The

amounts of chlorpropham adsorbed on charcoal, bark, and wheat straw were 83 µg/g, 23.56 µg/g, and 17.53 µg/g respectively at 100 µg/ml, 10°C and 72h. Tree bark and wheat straw followed a similar trend at 50 µg/ml and other studied temperatures. Chlorpropham was completely adsorbed by both charcoal and bark at the lowest concentration levels (10 µg/ml) employed at the three studied temperatures after 24h and 72 h; while for charcoal no chlorpropham was detected after 24h and 72 h at the 50 µg/ml level. The corresponding results are presented in Tables iv-vii (see appendix).

Figure 2.1(b) illustrates the theoretical structure of charcoal as discussed by Weber et al., (1965). Some of the groups which are present on charcoal are similar to those found in soil organic matter (i.e. -COOH, -OH, $-CH_3$, etc.) and hence adsorption by the two substances might be similar for organic compounds. Activated carbon has been successfully used for the removal of phenylamides from the polluted waters. El-Dib and Aly, (1977) reported that adsorption of phenylcarbamates on carbon increased in the order: CIPC > IPC. They reported that carbon doses required to remove 1 mg/litre chlorpropham from drinking waters are 57 mg and 27 mg for propham and chlorpropham respectively. The results of this study showed that only 83 µg of chlorpropham are removed by 1 g of charcoal from 250 ml of chlorpropham spiked water. These differences in the amount of carbon required to remove chlorpropham could be due to the variation in the relative activity and surface areas of carbons used, since the above authors used powdered carbon with a large surface area, while the carbon used in this study was granulated with less surface area.

Maximum adsorption capacities of wheat straw (17.35 µg/g) and tree bark (23.56 µg/g) were observed for chlorpropham at 100 µg/ml application rate and 10 °C after 72 h. Similar results were seen under other studied conditions (Figure 2.6(a)-2.7(a). Observing the 'like dissolves like' principle it seemed that

hydrophobic interactions were mainly responsible for the adsorption of chlorpropham on tree bark and wheat straw. The effect may be due to the presence of hydrophobic components, such as cutin, waxes, suberin and lignin in tree bark and wheat straw, which make up the outer layer of their cell walls respectively (Brett and Waldron, 1990) (Figure 2.2. a , b). However, comparatively significantly higher amounts adsorbed per gram of the wheat straw and tree bark could be due to the higher adsorbate-adsorbent ratio (100 µg/g) as compared to the soils where the corresponding ratio was 100 µg/20g. Table 2.8 shows adsorption of all the adsorbents at 10 °C and at 72 h.

Table 2.8 Summary of adsorption of Chlorpropham at 10 °C and after 72 h for each adsorbent.

	Amount of chlorpropham added (µg/ml)		
Adsorbent	100	50	10
Downholland	3.68	1.81	0.36
Midelney	3.20	1.61	0.33
Dreghorn	2.19	1.18	0.31
Wheat straw	17.35	7.20	3.58
Tree bark	23.56	11.03	2.51
Charcoal	83.70	40.50	8.10

2.4.3 Effect of time on adsorption

Analysing the effect of time on the adsorption of chlorpropham on various studied adsorbents revealed that in all the studied temperatures and

concentrations, adsorption increased with time; comparatively more chlorpropham was adsorbed during the first 24 h as compared to that adsorbed during the next 48 h showing the system was approaching equilibrium. Generally, this effect was more pronounced in the case of Dreghorn (sand) than for Downholland (peat) and relatively less for Midelney (clay) at all concentrations and temperatures. While tree bark showed greater effect than wheat straw and less for charcoal (Figures 2.3-2.8).

The results showed that for sand soil there was a 1.62 fold increase in adsorption during first 24 h while only a 1.25 fold increase was observed during the next 48 h at 100 μg/ml and 10 °C. However, for peat soil this increase was 1.21 and 1.04 fold for the first 24 h and next 48 h respectively under the same conditions. Similarly tree bark and wheat straw demonstrated a 2.07 and 1.13 and 1.37 and 1.02 fold increase at 100 μg/ml, at 10 °C for the first 24 h and 48 h respectively (Table i-vi appendix).

It appeared that equilibrium was never achieved during 72 h for the studied adsorbents. In fact, many laboratory and field investigations have demonstrated that in most cases sorption reactions are not fast enough to reach equilibrium, and nonequilibrium conditions prevail during solute/pesticide transport. Sorption can, in fact, continue for several days (Wauchope and Myers, 1985; Kookana et al., 1992), taking even months to achieve (Zhou et al., 1997). Similar informations have been provided by Gaillardon (1996) where 70% adsorption occurred after first day for diuron and isoproturon but equilibration required about one month. Brusseau and Reid (1991) reported that in sorption of organic chemicals by five aquifier materials, all with an organic carbon content less than 0.05 %, exhibited similar non-equilibrium behaviour.

The results further revealed that adsorption was affected by chlorpropham concentration. It was noted that at lower sorbent concentrations the rate of adsorption was faster for all adsorbents. Downholland (peat) soil

demonstrated a 1.28 and 1.10 fold increase in adsorption after first 24 h and next 48 h respectively at 10 μg/ml and at 10 °C showing a rapid rate of adsorption at lower concentration (Table i appendix).

Sorption equilibrium has also been shown to be influenced by sorbent concentration (Van Hoof and Andren, 1991; Zhou et al., 1997). Time required to reach equilibrium increases with sorbent concentration as the solute diffusion rate decreases with solid (Van Hoof and Andren, 1991). Wu and Gchwend, (1986) also showed that compounds with a higher value of k_{ow} showed slower sorption. In addition a low rate of attaining equilibrium indicates that the process is only partly of chemical nature.

Adsorption in soil is generally controlled by the rate of molecular diffusion into soil aggregates and the rate of reaction (rate of adsorption) at the soil water interface. Diffusion has been found to be a rate limiting step (Leenheer and Alrichs, 1971; Khan; 1973; Wauchope and Myers, 1985) with solute movement from the mobile pore water limiting the initial rate of adsorption and solute diffusion within a soil particle dominating the rate of adsorption as adsorption slows (Leenheer and Ahlrich, 1971; Koskinen and Harper, 1990).

A similar explanation could be afforded for the results in this study. It appears that the initial rate was controlled by the herbicide movement to adsorbent surface involving a physical type of adsorption. This transference rate is dependent upon solute diffusion surrounding the adsorbent particles and on the stirring and mixing rate of the suspension. As adsorption proceeds, the rate slows as adsorption becomes governed by the solute diffusing within the adsorbent particle, intraparticle transport is the dominant rate-limiting step.

In this regard Khan (1973) revealed that there was an initial rapid rate of adsorption of the pesticide 2,4-D and picloram on humic acid at the two studied temperatures followed by slower rates at longer times. Similarly Weber and

Gould (1966) studied adsorption of 2,4-D and several other organic pesticides from dilute aqueous solution by porous activated charcoal and suggested a mechanism involving intraparticulate transport of the solute in the pores and capillaries of the adsorbent.

It has been postulated that the structure of humic substance/organic matter is a three dimensional network of randomly oriented polymer chains, and of porous structure (Schnitzer, 1978; Kookana et al., 1992). A pesticide molecule will have to diffuse to the reaction sites before it can be sorbed.

2.4.4 Effect of temperature on adsorption

Temperature did not have a great effect on adsorption. Generally, more chlorpropham was adsorbed at lower temperature (10°C) than at higher temperature (20 °C) and relatively less at 30 °C for all the adsorbents at all studied concentrations (Fig. 2.3-2.8). The average K_d values at 30 °C, 20 °C and 10 °C were 7.31, 10.31, and 13.55 for Dreghorn (sand) soil at 100 µg/ml dose and at 72 h while, for tree bark the respective values were 66.44, 77.55 and 96.85. (See Table iii appendix). Similar trends were observed for other adsorbents at all studied concentrations (appendix, Table i-vi). Adsorptive processes are exothermic; therefore, an increase in temperature should reduce adsorption (Harris and Warren, 1964). Further, the effect of temperature may be due to its effect on the Van der Waals forces, with the result that less adsorption occurs at higher temperature due to the greater molecular vibration (Weber et al., 1965).

The results in this study are in agreement with the results reported by Harris and Warren (1964) who reported that adsorption of chlorpropham on bentonite was greater at 0°C than at 50°C. Further, Balayannis (1988) revealed that more chlorpropham (77 µg/g) was adsorbed on a sandy loam soil at 3°C

than at 27°C (61.6 µg/g). Similar trends were depicted by K_d values of chlorpropham i.e. K_d value at 3°C was 26.4 and 17.4 at 27°C. Similarly Farmer and Aochi (1973) investigated that increasing temperature from 10 to 20 to 30 °C generally resulted in decreased adsorption of picloram by the three soils examined. In addition, Cancella et al., (1990) reported a decrease in adsorption of cyanazine by an increase in temperature from 20°C to 30°C which, they attributed to two factors: (i) weakening of attraction between the pesticide and peat surface causing a decrease in physical adsorption and a change in pesticide solubility due to a change in temperature. Similar results have been reported by Bladel and Moreale (1974) for the adsorption of monuron on montmorillonite. Furthermore, the soil temperature effects the rate of diffusion and adsorption of chemicals in soil (Sonon and Schwab, 1995). Gonzalez et al., (1995) revealed that endrin and heptachlor epoxide showed reduced sorption on chitin at high temperature. Further, endrin sorption-desorption process shows a non-reversible behaviour which is higher at lower temperature. These workers explained that temperature could potentially affect the sorption rate because temperature changes the partition coefficients and consequently changes the effective diffusion which determine the sorption rates.

The amounts of chlorpropham adsorbed as percentages, were approximately the same at all the applied doses suggesting that sorption might be roughly proportional to herbicide dose (Gaillardon, 1996).

2.5 DESORPTION OF CHLORPROPHAM

The results from desorption studies are shown in Fig. 2.3-2.8 (Table i-vi appendix). The results demonstrate that chlorpropham was desorbed from all six adsorbents at 0 h time and at all three studied temperatures (10 °C, 20 °C, and 30 °C) at higher concentrations i.e. 100 µg/ml and 50 µg/ml except for

charcoal which showed desorption only at the 100 µg/ml dose at 0 h at all temperatures and concentrations. At the lowest concentration of 10 µg/ml desorption was seen only in the case of wheat straw and Dreghorn (sand) soil for 0h, 24h, and 72h at all the studied temperatures. There was no desorption from Downholland (peat) and Midelney (clay) soils, charcoal and bark at all the temperatures and times. However, chlorpropham was desorbed from Dreghorn (sand) and wheat straw at 0 h, 24 h, 72 h and at all studied temperatures.

Of the total amount initially adsorbed 50.23 % and 101.46 %, 48.98 % and 72.85 %, and 26.03 % and 69.00 % was desorbed from wheat straw at 100 µg/ml, 50 µg/ml, and 10 µg/ml after 72 h at 10 °C and 30 °C respectively. On the other hand, of the amount initially adsorbed on tree bark only 36.29 % and 59.64 %, 35.88 % and 41.49 % was under the same conditions of temperature for 100 µg/ml and 50 µg/ml dose . However, there was no desorption at 10 µg/ml application dose for tree bark (see Table iv-v appendix).

Of the studied soils chlorpropham was easily desorbed from Dreghorn (sand) soil which is low in OM content (6.7% LOI), but not from high organic Downholland (peat) soil (LOI 31.2%). In Dreghorn (peat0 desorption did not exceed more than 10 % at both 100 µg/ml and 50 µg/ml doses, with no desorption at all at the lower dose of 10 µg/ml. While for Midelney (clay) soil desorption was 41.87 and 20.30 % after 72 h at 100 µg/ml and 50 µg/ml doses and all the three studied temperatures with no desorption at the 10 µg/ml dose. However, Dreghorn (sand) soil showed reversibility of adsorption at all temperatures and concentrations in the order ranging from 12.26 %, 17.80 %, 17.52 %, and 47.91 % 39.6 % 53.64 % at 100, 50 and 10 µg/ml dose after 72h and 30 °C. Further, the above data displayed that desorption increased with rise in temperature from 10°C to 20°C to 30°C, though the effect was not very prominent in the case of all studied adsorbents. Desorption increased, generally, with time for wheat straw and bark at all the studied conditions of temperature

and concentration. However, for soils desorption was more at 0 h, decreased after 24h and then increased after 72h. Table 2.9 shows percent desorption of chlorpropham from all the adsorbents at different temperatures and after 72 h.

Table 2.9 Percent desorption of chlorpopham from the studied adsorbents.

		Amount of chlorpropham added (µg/ml)		
Adsorbent	Temp.(°C)	10	50	10
Downholland	10	6.62	4.30	ND
	20	10.06	8.32	ND
	30	10.74	9.76	ND
Midelney	10	14.05	17.06	ND
	20	34.54	11.10	ND
	30	41.87	20.30	ND
Dreghorn	10	12.26	17.80	17.52
	20	37.35	29.48	45.34
	30	47.91	39.66	53.64
Wheat straw	10	50.28	48.98	26.03
	20	66.098	52.21	50.33
	30	101.46	72.85	69.00
Tree bark	10	36.29	35.88	ND
	20	47.57	40.13	ND
	30	59.64	41.49	ND
Charcoal	10	ND	ND	ND
	20	ND	ND	ND
	30	ND	ND	ND

*ND = no desorption

It appears that the nature of adsorption/desorption equilibria and also the forces involved in soil of high OM content may be quite different from those soils with low (Dreghorn, 6.7%) and medium (Midelney 14.7%) OM contents. These results are in accordance with the findings of Grover (1975). The author reported that all six urea herbicides were easily desorbed from the low to medium OM content soil, but not from the high organic matterMelfort loam soil (OM 10.49%). Furthermore, there was a marked decrease in percent desorbed with each successive rinse, a portion of the chemical being very difficult to remove even after six rinses. Further, Thaper et al., (1995) observed similar results in the adsorption/ desorption study of dimethoate on different soils. They reported that dimethoate was adsorbed more to clay mineral and was then slowly desorbed. Half-lives decreased in the order sandy clay > clay > clay loam. They inferred that adsorption controls the release of pesticide. In another study it was noticed that carbaryl desorbed in significant amounts in the order, sand > sandy loam > sediment i.e. desorption was proportional to sand content.

Barriuso et al., (1994) revealed that in soil low in organic matter, pesticide adsorption-desorption by clay minerals may strongly influence the fate of pesticides in soil environment. The workers reported that adsorption of atrazine by smectite was reversible suggesting that atrazine is primarily retained on the surface of smectites through relatively weak Van der Waals or H bonds. The author also reported a little hysteresis for adsorption-desorption of non-ionic pesticide on a mineral surface. Furthermore, Bailey et al., (1968) reported that the combined effect of COOR group and the phenyl ring would lead to enhanced stability of the molecule and a weakening of N-H bond, which would in turn favour the formation of stronger hydrogen bonds with the oxygen of the clay mineral surface. Furthermore, the adsorption of neutral organic molecules on the clay-water interface is due to stronger interaction with the interfacial

water than with the water in the bulk solution, without any evidence of a direct bonding of molecules to clay surfaces (Zhang et al., 1990).

An increase in temperature should increase desorption as desorption is endothermic. The results of this study are in agreement with this observation and follow the order 30 °C > 20 °C > 10 °C for all adsorbents. Leopold et al.,(1965) in this context revealed that heating the carbon to 95 °C resulted in the releases of 50 percent of the adsorbed 2,4-D to the solution in about 2 minutes and complete release after 60 minutes. The worker suggested that this heat lability is expected from a simple adsorption system not involving chemical bonding.

The irreversibility of chlorpropham in solution from charcoal, Downholland (peat), Midelney (clay), and bark at lower concentrations might be due to the factors discussed by Koskinen and Harper (1990) that compounds that are strongly bound to the soil surface have little or no desorption, particularly at lower rates of chemical application. These appear to be the cases where the compound reacts irreversibly with the soil surface or else equilibrium is not established because the kinetics of the desorption are far slower than the adsorption.

With sufficient time, even weakly adsorbed chemical can react with the soil surface to become more strongly adsorbed or bound compared to when they were firstly applied. Desorption coefficients for cyanazine and metribuzin measured 56 and 121 d after application were two to three and six to eight times greater, respectively, than when measured 1 d after application (Boesten and van der Pas, 1983). Further, Appleton et al., (1980) reviewed that higher degree of desorption was obtained from samples in which DCB had been in contact with sediment for one day than with those where contact had been maintained for several days.

Conclusion

Generally the amount of chlorpropham adsorbed per gram of the adsorbent was more at longer time (72 h) and at low temperature (10° C) for all the adsorbents. Of all the studied adsorbents charcoal displayed the highest adsorption capacity while sand soil exhibited the lowest value for adsorption of chlorpropham under all investigated temperatures, times, and concentrations. The order of chlorpropham adsorption for different adsorbents was as follows: charcoal > tree bark > wheat straw > Downholland (peat) soil > Midelney (clay) soil > Dreghorn (sand) soil under all temperatures, times and concentrations.

The faster rate of adsorption, the reversibility of adsorption of chlorpropham on wheat straw, tree bark, arable and sand soil tend to rule out chemisorption and point rather to physical adsorption with formation of Van der Waals bonds between hydrophobic portion of the adsorbate molecules and the adsorbent surface in the aqueous system.

The rate of adsorption, the reversibility of adsorption and high adsorption capacities on hydrophobic surfaces tend to point to physical adsorption with the formation of Van der Waals bonds between the hydrophobic portion of the adsorbate molecules and the adsorbent surface in aqueous solution. Further, the higher degree of irreversibility in organic soils as well as in charcoal and tree bark especially at the lower concentration of 10 μg/mL suggested the efficacy by which the latter could be used for the removal of chlorpropham from the polluted waters.

CHAPTER 3

VOLATILISATION OF CHLORPROPHAM FROM SOIL

3.1 INTRODUCTION(GENERAL)

Herbicides dissipate through various routes; degradation, adsorption on soil colloids, leaching, absorption by plants and through volatilisation.

Volatilisation is a major dissipation route for many pesticides used in agriculture (Taylor 1978; Cliath et al., 1980; Spencer and Cliath, 1990) and is an especially important mechanism affecting transport to the atmosphere (Plimmer, 1976). Entry to the atmosphere is dependent on such factors as the method of application, type of formulation, pesticide physiochemical properties, and meteorological conditions at the application site (Woodrow et al., 1990; Diaz Diaz et al., 1995). The rate of the loss by volatilisation often exceeds that by chemical degradation (Taylor and Spencer, 1990). The importance of volatilisation in transport of pesticides from treated areas has been established by direct field measurements (Taylor, 1978; Glotfelty et al., 1984). Spencer and Cliath (1975), Spencer and Farmer (1980), and Spencer et al.(1973) reviewed the literature on volatilisation of pesticide from soil.

Volatilisation is the resultant of interchange process between pesticides sorbed onto soil and the soil organic matter, dissolved in the pore water, and present in the soil atmosphere (Diaz Diaz et al, 1995). Organic chemicals applied to land as pesticides range in volatility from gaseous fumigants to herbicides with vapour pressure below 10^{-8}mm Hg. The tendency of an organic compound to volatilise is related to its inherent vapour pressure, but actual vaporisation rate will depend on environmental conditions and all factors that

control the chemical at the soil-air-water interface (Spencer et al.,1973; Haque et al., 1980; Spencer and Cliath, 1990).

Volatilisation rates of pesticides from inert/non adsorbing surfaces/surface deposits are directly proportional to their relative vapour pressures and external conditions that effect movement of the chemical away from the evaporating surface such as surface roughness, wind speed, air turbulence, etc. (Nash, 1983; Spencer and Farmer 1980; Spencer et al., 1988). The rate of movement away from the evaporating surface is diffusion controlled. Air movement is reduced to zero close to the evaporating surface and the vaporised substance is transported from the surface through the stagnant air layer to the region of turbulent mixing only by molecular diffusion.

Factors that influence the loss of a soil incorporated pesticide include the vapour pressure of the pesticide, its concentration, water solubility, mass flow in water and by diffusion, adsorption to soil, the soil temperature and moisture content and the velocity and humidity of air above the soil surface (Plimmer, 1976; Hance, 1980; Taylor and Spencer, 1990; Grass et al., 1994). Volatilisation is greatly reduced by incorporation into the soil, where the rate becomes dependent on the movement of the residues to the soil surface by diffusion or convective transport by soil water.

Vaporisation from the aqueous system depends not only on the vapour pressure of the chemical, but also on its water solubility which for a given chemical concentration depends on its air-water-partition, or Henry`s law constant. Generally, chemicals volatilise more readily from water than from soil, because adsorption in the latter medium slows the rate of movement to the surface. Consequently, no single physiochemical property can describe and predict the probable vapour behaviour and fate of a chemical in the environment or its likely method of transport in the atmosphere (Spencer and Farmer, 1980). However, relative vaporisation rates useful for environmental indices can be

calculated from basic physical properties of vapour pressure, water solubility, adsorption and persistence, if reliable values are known for each of these properties at various temperatures.

Vapour density of a chemical is a reflection of its inherent vapour pressure, its water solubility, and its adsorption to the soil. Vapour density of a soil applied herbicide is a major factor in determining the volatility of a weakly adsorbed material (Spencer and Cliath, 1969). In addition Taylor and Spencer (1990) discussed that the interaction between temperature, soil moisture content, and the fugacity of pesticide residues is of major importance in controlling losses of pesticides from soil surfaces. Soil water content has an influence on vapour loss of pesticide from soil allowing greater volatilisation losses from wet than from dry soil (Glotfelty et al., 1984). This effect is mainly due to an increase in vapour pressure resulting from displacement of chemical from soil surface by water (Spencer et al., 1969; Spencer and Cliath, 1970; 1973)

Vaporisation rates are greatly influenced by temperature because of its effect on vapour pressure (Baker and Johnson, 1984). The response usually follows the relationship $\log_{10} P = A - B/T$ where A and B are constants. T is the temperature and P is the vapour pressure. The value of A and B in any particular circumstances depends not only on heat of vaporisation but also on the heats of solution and adsorption. The vapour pressure of many organic chemicals of environmental interest increase three to fourfold for each 10°C increase in temperature. For soil-incorporated pesticide temperature influences volatility through its effect on movement of pesticide to the surface by diffusion or mass flow in evaporating water, or through its effect on the soil water adsorption/desorption equilibrium. For all these effects increase in temperature is associated with increase in volatilisation rate.

Plimmer (1976) pointed out that codistillation phenomenon has incorrectly been associated with increased rate of volatilisation at high soil moisture content. There is in fact no enhancement of the volatility of a material due to the evaporation of water, but reduction of soil moisture increases the sites available for adsorption on soil particles invariably reducing pesticide vapour density and volatility (Igue et al., 1972). Volatilisation will occur whether or not water is evaporating from the soil, but, if the moisture content of the soil falls, the ratio of volatilisation is influenced.

Adsorption is a function of soil as well as herbicide properties. Adorption behaviour of a soil also characterises the evaporation tendencies of soil applied herbicide. Briggs (1969) has shown that soil adsorption characteristics of non-ionic substances are well predicted by octanol-water partition ratios (P) using the relationship logQ = 0.52 log P + 0.62 where Q is given by 100K = K, K being the soil: water partition ratio. The proportion of the chemical in soil that will be lost by volatilisation depends on the resistance of the chemical to the adsorption (Plimmer, 1976).

Volatilisation behaviour of a chemical is controlled mainly by the ratio of its solution to vapour concentration or Henry`s Law constant (K_H), which determines the extent to which the air boundary layer restricts volatilisation from soil and consequently whether or not the chemical will volatile as fast as it moves to the surface by convection in evaporating water. Spencer et al., 1988; Jury et al., 1987 investigated that volatilisation of chemicals with low K_H ($< 2.65\times10^{-5}$) is controlled within the air-boundary layer above the soil surface. Such compounds are much less volatile, with volatility increasing with time (Jury et al. 1984; Clendening et al., 1990), whereas compounds with K_H much greater than 2.65×10^{-5} are volatile, with control of volatilisation within the soil and volatility decreasing with time.

Partition of pesticide between the vapour, solid, and solution phase is an important factor in the process of diffusion; which provides one of the mechanisms for the movement of pesticide through soil. Vapour phase diffusion in the soil is controlled by the same factors that control vapour pressure, that is temperature, adsorption and soil water content. Other factors involved are soil porosity, hence bulk density, the tortousity of soil pores and the number of blocked pores. Soil porosity, together with the soil water content gives a measure of the air space available for vapour diffusion. For molecules the size of herbicides, diffusion as vapour is 10^4 or more times faster than diffusion in water so that effect of soil water content on overall diffusion rate depends very much on the air-water partition ratio of a compound. Calculations based on these results by Letely and Farmer (1974) suggested a possible vapour phase component in the diffusion of chlorpropham. The estimated vapour pressure for chlorpropham is 3.1×10^{-5} m bar at 25°C and distribution ratio liquid/ gas is 7×10^5 (Hamaker, 1972). The coefficient indicates what proportion of chemical is in the vapour and thus gives some idea of the potential for volatilisation.

An important source of pesticide volatilisation from soil system is an advection process, the `Wick Effect' in which mass movement of dissolved herbicide to the surface by capillary action accelerates the evaporation of dissolved chemicals because it is more rapid than vapour diffusion. The impact of this wick effect varies from compound to compound and is a function of soil adsorption characteristics, water solubility, and partition coefficient in the air, soil and water phases (Hartley and Graham-Bryce, 1980; Sims et al., 1986). The proportion of the chemical in soil that will be lost by volatilization depends on the resistance of the chemical to the degradation and adsorption (Hance, 1980).

Vaporisation of pesticides in soil can be predicted from considerations of the physical and chemical factors controlling concentration at the soil surface. Screening models are developed for assessing volatility, mobility, and

persistence of pesticides in soil. Jury et al., (1984) described and applied a screening model to classify pesticides for their environmental behaviour based on their physical and chemical properties such as vapour pressure, solubility and Henry`s law constant, organic carbon partition coefficient and degradation. An important parameter calculated by Jury et al., (1984) with the screening model is volatilisation half-life.The volatilisation half-life of a given chemical was a function of temperature, water content, water flux, and depth of incorporation. The relative size of this half-life compared to the chemical half-life provided an indication of the extent to which a pesticide exposed to the environment would volatile rather than degrade. Models of the volatilisation process currently available have been tested only under controlled conditions in the laboratory. and do not take into account the complexity of the many interacting factors encountered under field conditions; soil type, surface roughness, ground cover, weather, method of incorporation of the chemical into the soil, leaching, rainfall etc. Success in predicting pesticide volatilisation compared with other pathways of dissipation depends on the availability of reliable values of vapour pressure, water solubility, adsorption coefficient, and persistence of organic chemicals in environmental systems such as soil, water and sediment.

3.2 VOLATILITY OF PHENYL CARBAMATE HERBICIDES

There are a few studies regarding the volatility of phenyl carbamates. In the following available studies will be reviewed.

Parochetti and Warren (1966,67) reported that propham, the dechlorinated counterpart of chlorpropham, proved more volatile than chlorpropham under controlled laboratory conditions. They revealed that temperature, air flow rate moisture, and cation exchange capacity of soil were important factors influencing volatility. Vapour losses increased with increasing

air-flow rate and temperature; losses were negligible from spray application on dry soil but were considerably greater at field capacity. In addition they stated that vapour losses of propham from granules were much higher than from a surface spray but chlorpropham losses were about the same for the granules as from the spray. The above authors also evaluated the effect of incorporation depth of chlorpropham in soil i.e covering the soil-applied herbicide with 1/8 to 1/4 inch of soil was effective in reducing vapour pressure.

The volatilisation of chlorpropham from a micro-encapsulated formulation was compared with that of a conventional emulsion in a field study by Turner et al., (1978). The formulation was a chlorpropham solution contained in 25 μm nylon capsules suspended in water and applied as a water-based spray to the surface of a bare silt loam under otherwise identical conditions. The specific volatilisation rate of the encapsulated formulation was between 12 and 26% of the conventional during the first 8 days of the experiment. Over 50 days about one half of the disappearance of the conventional formulation and about one-fourth of that of the encapsulated material were due to volatilisation. The similarities in volatilisation pattern suggested that the volatilisation of encapsulated formulation was not controlled by direct release from the capsules themselves, but was associated with re-volatilisation of chlorpropham that had been adsorbed on to the soil surface after its release from the capsules. Field evaluations showed that the formulation used by Turner et al. (1978) was herbicidally effective for a significantly longer period than the commercial emulsions owing to more adsorption and low volatility. Earlier Danielson (1959) observed that chlorpropham disappeared more rapidly from certain granules which were exposed to moisture. In addition Dawson (1979) compared the effect of granules and liquid formulation of chlorpropham on dodder seedlings. They applied clay granules in moist and dry soils. Dodder seedlings were killed in

moist soil by the vapours of chlorpropham showing more volatility of chlorpropham in moist than in dry soil.

Sensi (1993) reported that chlorpropham and propham are readily volatilised from soil systems, but terbutol and carbaryl are not. Further, vapour losses of propham and chlorpropham from moist soils decrease as the percentage of O.M. increases.

From the abovementioned survey it is evident that volatility is a significant pathway for chlorpropham losses from soil to the atmosphere. This subject is very interesting from both environmental point of view and analytical technique which concerns a lot of chemicals including pesticides as air pollutants. The reviewed studies indicate that the major factors affecting chlorpropham volatility are soil moisture, soil type, temperature, and formulation type. Since volatility is a major dissipation pathway for chlorpropham from soil, the main medium in which chlorpropham is used, a volatility study of chlorpropham under certain conditions of temperature, moisture content and concentration was considered very important. Chlorpropham is used as sprout suppressant in potato stores at quite low temperatures. In addition it is used as a weedicide in different vegetables throughout the world. Because of the specific climatic conditions experienced viz both hot and dry weathers, three levels of moisture content (air dried, half field capacity, and field capacity) under two different temperature (10 and 25°C) were chosen as experimental conditions. To meet the requirements set by EQS two concentration levels (10 μg/g and 100 μg/g) were also selected. To evaluate the effect of soil type on the volatility of chlorpropham under the investigated conditions three soil types were chosen.

3.3 MATERIALS AND METHODS

This section involves the use of the dynamic head space system designed and assembled in this laboratory. It also includes the development of a thermal desorption technique as a means of sensitive analytical method for the detection of chlorpropham vapours from the experimental soils.

3.3.1 Chemicals and apparatus

Chlorpropham technical grade 99% was purchased from Alltech Associates (U.K.). Tenax TA 80-100 mesh was purchased from Jones Chromatography, UK. Hexane, Acetone, Dichloromethane, methanol were purchased from Rathburn Chemicals Ltd, Scotland. All organic solvents and chemicals used in this experiment were of analytical grade.

Sodium Sulphate anhydrous (Analytical Reagent Grade) was purchased from BDH Chemicals Ltd, England. Activated charcoal was purchased from Aktivkohle, Germany. Air cylinders were obtained from B.O.C. Glasgow.

3.3.2 (i) Dynamic headspace model system

The system included an air cylinder fitted with a pressure regulator, charcoal trap, glass manifold, fine flow rate adjustment (Porter Instrument Company, Hatfield, PA, USA), reaction chamber (modified vessel), Tenax trap and a controlled temperature water bath. Charcoal trap consisted of a cylindrical glass bottle with a gas purifier with internal volume of 200 cm^3 connected through a water bottle containing distilled water to obtain clean and humid air.

The air cylinder fitted with pressure regulator was connected to the activated charcoal trap to allow a flow of clean and humid air. The air flow rate

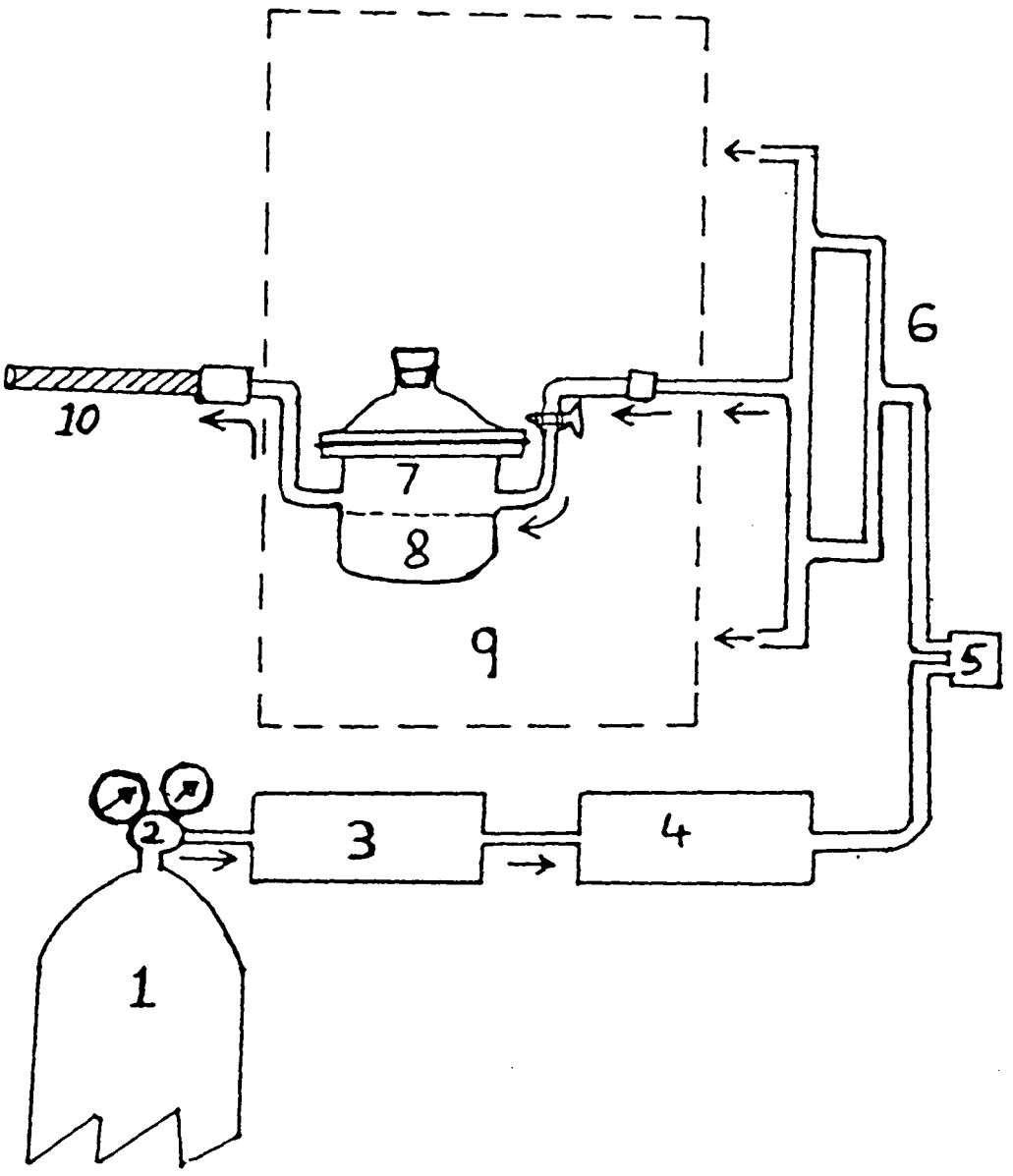
was adjusted, using a fine flow rate adjustment, which was connected to a glass manifold to distribute the air among the reaction chambers containing treated soils. A soap bubble flow meter was used to measure the air flow rate from the end of the Tenax trap. The flow was maintained at 10^{-12} cm^3 min^{-1}. The air was used to sweep the chlorpropham vapours from the headspace over the treated soil onto the Tenax trap. The reaction chamber was a modified reaction vessel, with 80 mm in depth and 100 mm internal diameter. Two glass tubes with 10mm outer diameter were attached at 50 mm from the bottom of the vessel for flow of air in and out of the vessel. The first tube was connected to the Tenax trap by a PTFE tube with 6 mm internal diameter. The reaction chamber had a removable cover of 40 mm in depth and with 100 mm internal diameter. The two parts were sealed using a PTFE ring of 110 mm outer diameter and 0.5 mm thick and metal clips to form a headspace volume of 549.8 cm^3 over the treated soil. The reaction chambers were covered with aluminium foil to avoid any photolysis of chlorpropham by U.V. The vessels were kept in heated waterbath to maintain a particular temperature during the experiment. The schematic diagram of the system is depicted in Figure 3.1.

3.3.2. (ii) Heating block

The heating block was constructed as follows:

A block of aluminium 200 mm long, 75 cm deep, and 100 mm wide was drilled with eight equally spaced 7mm diameter holes into which the precolumns were inserted. The whole block was surrounded with 10mm maranite heat insulation. The block was placed in an asbestos lined box and surrounded by sand to provide further thermal insulation. A manifold was constructed from 1/4 inch O.D. copper tubing to enable eight tenax traps to be purged with N_2 during cond itioning. The precolumns were connected to the manifold with 1/2 inch

Figure 3.1 Schematic diagram of dynamic head space system.



1- Air cylinder 2- Pressure regulator 3-Activated charcoal

4- Air humidifier 5- Fine flow rate adjustment 6- Manifold

7- Soil headspace 8- Treated soil 9- Water bath 10- Tenax trap.

couplings (Dralim, Phase Separations Ltd). When operational, the heating block was maintained at a temperature of 310-330°C.

3.3.3 Tenax trap preparation

Thermal conditioning was used according to the method of Kraish (1990) to prepare and purify Tenax traps.

1- A borosilicate glass tube (100 mm long, 6.5 mm outer diameter) was kept in concentrated hydrochloric acid for 24 h and then rinsed thoroughly with deionised water followed by acetone to remove all impurities. The tubes were kept in an oven at 220°C for 2 h. The tubes were packed with 100 mg of Tenax G.C. 80-100 mesh which was held in place with plugs of silanised glass wool. The pre columns were conditioned, by heating at 280-300°C for 2 h using a heated block (mentioned above). Nitrogen gas was purged through the precolumns during heating at 20-30 $cm^3 min^{-1}$. The traps were then removed and allowed to cool to room temperature under N_2 gas flow. The traps were then removed and sealed with PTFE (30 mm in length and 10 mm outer diameter drilled upto a depth of 20 mm with a 6 mm drill) or PTFE film. The traps were stored in refrigerator till use. This method was used throughout the work while re-conditioning of the used traps was carried out from time to time as required before sampling.

3.3.4 Comparison of direct injection/thermal desorption

An experiment was carried out to assess whether chlorpropham was quantitatively and reproducibly desorbed from a Tenax G.C. precolumn in comparison to conventional direct injection of chlorpropham made up in a

solvent onto the top of the G.C. column. The experiment was devised as follows:

Five freshly conditioned precolumns were injected with 5 mm^3 of 5000 $\mu g\ cc^{-1}$ chlorpropham in hexane, which gave 1 μg of chlorpropham injected onto the column. The injections were made so that the chlorpropham was injected onto the Tenax G.C. in the middle of the pre-column. After the injection was made the pre-column was sealed with PFTE caps and allowed to equilibrate for 30 minutes before the analysis. These operations were performed sequentially. One pre-column was injected with chlorpropham and analysed at a time. 5 cm^3 of injection was made of the above standard chlorpropham solution directly on to the G.C. column alternative with the standard solution injected by desorption. Peak areas for chlorpropham were calculated for both injection methods.

3.3.5 Analysis of Tenax trap

(i) Sampling

Chlorpropham vapours ware collected from the system onto a Tenax trap every 48 hours for a period of 12 days. The headspace of the treated soil was 549.8 cm^3 corresponding to 26.39 litre sample volume every 48 h. The traps were sealed immediately after sampling using either PTFE caps or PTFE film. The traps were analysed on the day of sampling or within 2-3 days after sampling. In case of delayed analysis the samples were stored in refrigerator in sealed polyethylene bags.

(ii) Analysis

A thermal desorption technique was chosen as the most appropriate method for the transferral of chlorpropham volatiles from the precolumn. The details of the procedure are as follows:

Chlorpropham vapours were trapped and preconcentrated on Tenax traps. The traps were connected to the top of the packed column with the 1/4 inch coupling, the desorption block was placed round the precolumn and the carrier gas connected to the top of the precolumn. All these operations were carried out as quickly as possible, usually within 30 seconds, to minimise the interruption of the carrier gas flow to the GC column.

(iii) Gas chromatography

G. C:	Schimadzu (Schimadzu Ltd.).
Column:	2 meter glass column, 6mm O.D., 4mm I.D packed with 3% OV 17(Phase Separations Ltd.) on WHP 120 mesh (Phase Separations Ltd.)
Temperature:	Initial: 100 °C 10 min
	Rise: 12 °C min^{-1}
	Final: 220 °C 20 min
	Injection port: 200 °C
	Detector F.I.D.: 250 °C
Detector:	H_2 45 cm^3 min^{-1}
	O_2 210 cm^3 min^{-1}
	N_2 43 cm^3 min^{-1}

These conditions were used for all of the analyses in this section of the project.

Spectro-physics, SP 4290 integrator was used for all calculations such as calibration and integration. Standard solutions were run at the start, middle and at the end of the daily analysis.

(iv) Assessment of linearity, retention time, and chlorpropham recovery from the Tenax trap

To assess the linearity of the thermal desorption of chlorpropham from Tenax traps a series of chlorpropham standard solutions 10, 20, 40, 60, 80, 100, 200, 1000, 2000, 5000, and 10000 $\mu g\ cm^{-3}$ were made up in glass distilled n-hexane. 5 mm^3 from each solution was injected onto the middle of the Tenax trap, using a 10 mm^3 syringe (Hamilton, Switzerland). Tenax traps were allowed to equilibrate for 30 minutes at room temperature and then analysed. The same volume from the same standard solution was injected directly into the GC column to compare the linearity and retention time of both techniques. Each treatment was done in duplicate. All the standard solutions were refrigerated when not in use. The recovery of chlorpropham from the Tenax trap was calculated as a percentage of the peak areas from the duplicate injection based on the mean of the duplicates from the direct injection. The results are shown in Table 3.1. Comparison of the linear response of the flame ionisation detector to chlorpropham, using the direct injection and thermal desorption technique is shown in Fig. 3.3.

(v) Storage life of chlorpropham pre-columns

Twenty freshly prepared Tenax precolumns were injected with 1000 $\mu g\ cm^3$ chlorpropham in n-hexane in the middle of the trap using 1 µl syringe (Hamilton-Bonaduz, Switzerland). The traps were sealed with PTFE caps. Ten

precolumns were stored in a fridge in a sealed bag. Five of the stored precolums were analysed after five days while rest of the five precolumns were analysed after 10 days. To assess the effect of temperature, the remaining 10 precolumns were stored at room temperature ($22^{\circ}C \pm 3$) and were analysed after the same interval time. Recoveries were made by comparing mean of the peak areas of three traps analysed prior to the experiment.

3.3.6. Soil preparation

Three types of soils used in the volatility study were Downholland (peat), Midelney (clay), and acid washed sand. Dreghorn (sand) soil was replaced by acid washed sand in this study and was used as a control. The soil samples were mixed homogeneously and were air dried then they were screened through a 2mm mesh sieve prior to treatment.

3.3.6.1 Determination of field capacity water content

The field capacity water content was determined using the following procedure. Air dried soil was placed on a grade 3 porosity sintered glass funnel on filter paper in a Haines apparatus. The soil was wetted at a tension of 5cm then the burett was raised to saturate the soil. The soils were brought to equilibrium at a height difference 52 cm by lowering the burette. Water in soils corresponds to soil water potential at -0.05 bar (F.C.). The soils were weighed at this water content, air dried and weighed. The difference corresponds to the field capacity water content of the soil.

3.3.6.2 Autoclaving the soil

The procedure was as follows: 300 g of sieved, air dried soil was autoclaved for 30 minutes at 120°C and 15 lb $in.^{-2}$ The procedure was repeated after 3-days to prevent any microbial germination causing biodegradation of chlorpropham.

3.3.6.3 Soil treatment

Standard solutions of 1000 and 10,000 µg cm^{-3} of chlorpropham in hexane were prepared in glass distilled hexane in a volumetric flask. 3 ml of the standard solution were added in three portions to 300 g of air dried soil in a 750 cm^3 glass jar to provide 10 µg/g and 100 µg/g concentration of chlorpropham respectively. After each addition the solution was thoroughly mixed with a glass rod followed by shaking the jar for 10 minutes. After the final addition of the solution the homogeneous distribution of chlorpropham was assured by shaking the jar for 30 minutes using a roller shaker (Lukham Ltd.). Calculated amounts of distilled water were added to bring the soils to full or half field capacity. Treated soils were put in pre-described vessels and Tenax pre-columns were connected immediately after sealing the vessels. All the vessels were covered with aluminium foil to avoid any photodegradation. The vessels were placed in a water the bath at required temperatures of 10°C and 25°C. An appropriate control treatment was included.

3.3.6.4 Recovery of chlorpropham from soils

20 g of air dried soil were spiked with 1ml of 50µg chlorpropham in cyclohexane in a beaker. The soil was covered with cyclohexane and left

overnight to allow homogeneous mixing of chlorpropham. The treatment was done in three replicates. The treated soil was then transferred to a paper thimble and put in a glass extractor and fluxed for 6 hours with 150 ml of hexane. After fluxing hexane was passed through anhydrous sodium sulphate. The filtrate was evaporated to dryness under vacuum using a rotary evaporator (Buchi). The residue was dissolved in 2 ml of hexane and analysed using a gas chromatograph equipped with flame ionisation detector using the conditions mentioned earlier. Chlorpropham residues were calculated by integrating the injected amounts of the sample with the standard solution using Spectro-Physics 4290 integrator. The recoveries from the soils are shown in Table 3.4.

The soils were analysed at the start and end of the experiment. Zero time readings were used to calculate the residues of chlorpropham.

3.4. RESULTS AND DISCUSSION

3.4.1 Development of the headspace analytical method

A series of experiments were carried out to assess the efficiency of Tenax adsorbent to collect chlorpropham vapours through the headspace sampling method and to desorb it thermetically. The factors assessed are as follows:

(i) Adsorption ability of Tenax traps

The ability of Tenax adsorbent to trap chlorpropham vapours was determined. Tenax demonstrated an excellent ability to trap chlorpropham vapours when the headspace of chlorpropham crystals in sealed bottles were drawn through the tenax precolumns, using a syringe. Typical chromatograms

of direct injection onto G. C. columns, thermal desorption through the Tenax traps and the blank sample are shown in Figure 3.2.

(ii) Linearity of flame ionization detector

The linearity of response of flame Ionisation Detector (FID) to chlorpropham was evaluated for both direct injection and thermal desorption. The recovery of chlorpropham from the Tenax trap was calculated as a percentage of the peak areas from the duplicate injection based on the mean of the duplicates from the direct injection. The results are shown in Table 3.1. A linear relationship between chlorpropham concentration and detector response was observed (Figure 3.3).

(iii) Comparison of the direct injection and thermal desorption techniques

A comparison was made between the direct injection and thermal desorption technique. From these assessments it was concluded that both systems were satisfactory. Furthermore there was no appreciable difference between retention time for chlorpropham when desorbed from the tenax trap using the thermal desorption technique and also when injected directly into the G.C. column (Table 3.2).

(iv) Effect of storage time

The effect of storage time on the recovery of chlorpropham from Tenax traps was assessed under different temperature conditions (Table 3.3). The calculation of the recovery values were based on the mean of the peak areas of five fresh injections which were carried out at the same time as the stored trap

analysis. The results show that the precolumn could be stored in a fridge (4°C±1) for upto five days with no appreciable loss in injected amount. After 10 days storage in a fridge the loss was slightly more. However at room temperature the losses were quite significant after 5 and 10 days.

In addition Boyd (1984) assessed that chlorpropham was quantitatively (99.8%) introduced into the column using the desorption method and it was introduced within 2-4 min. Furthermore, the orientation of the precolumn during desorption made no difference to the levels of chlorpropham that were determined.

(v) The adsorption capacity of the soils under study was also evaluated. The corresponding results are presented in Table 3.4.

3.4.2 VOLATILITY OF CHLORPROPHAM FROM SOIL

A preliminary experiment using Midelney (clay) soil was conducted in duplicate to estimate the effect of temperature, moisture content and concentration on the volatility of chlorpropham. Downholland (peat) soil was selected to evaluate the effect of soil type on the volatility of chlorpropham and Sand (acid washed) was selected as a control treatment. Due to the high cost of the material and unavailability of the equipment, duplicate treatments were carried out randomly for different conditions of temperature and soil moisture content for both concentration levels applied.

The results of chlorpropham volatility under different conditions of temperature and moisture contents at both applied concentrations are presented in Figures 3.6 (a,b)-3.8(a,b). The overall picture of the results is presented in Figures 3.4(a,b)-3.5(a,b). The analysis of variance did not show a significant difference between Downholland (peat) and Midelney (clay) soils. However,

Figure 3.2: Gas chromatographs of chlorpropham

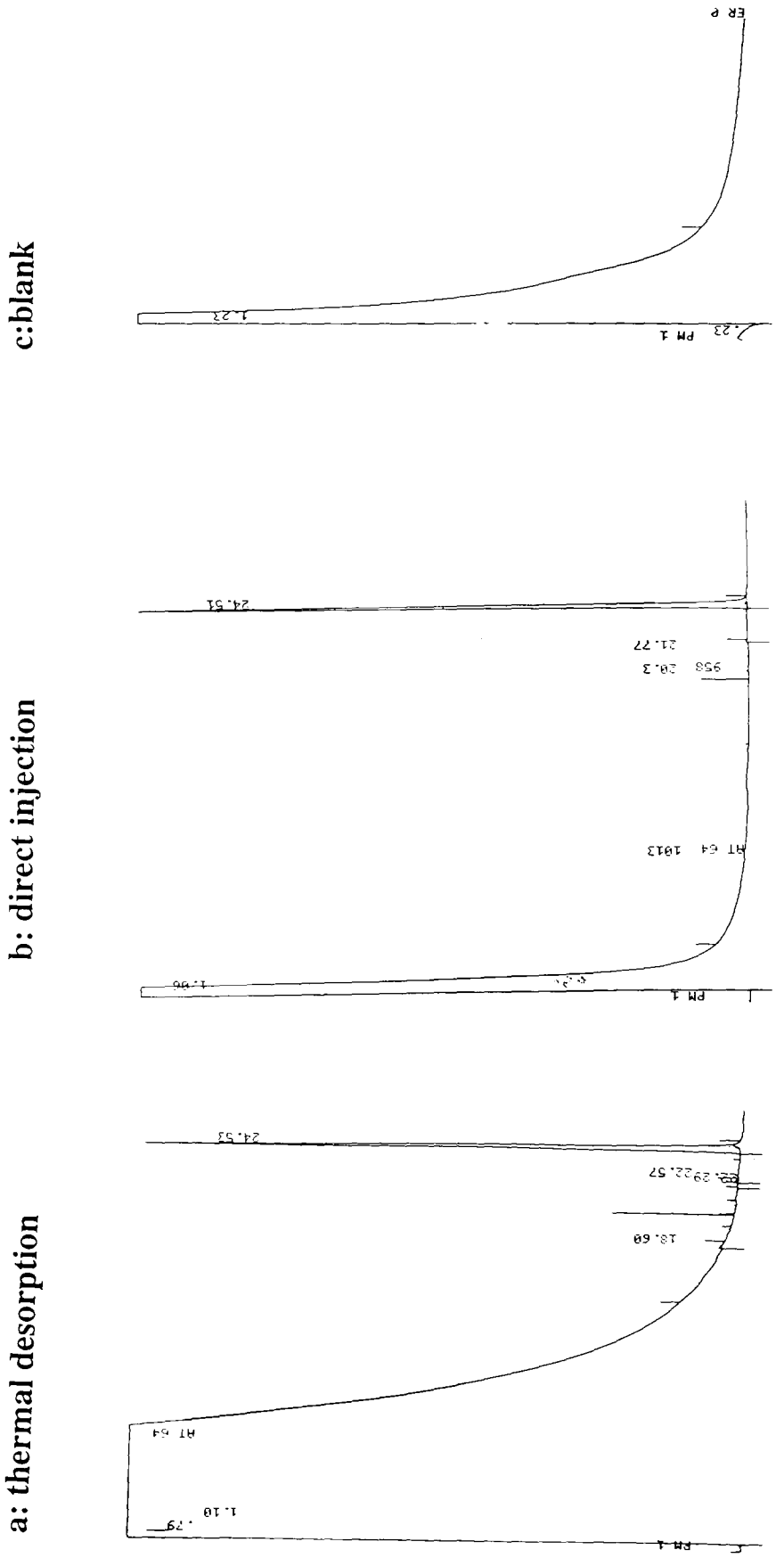


Figure 3.3 Comparison of the direct injection and thermal desorption techniques.

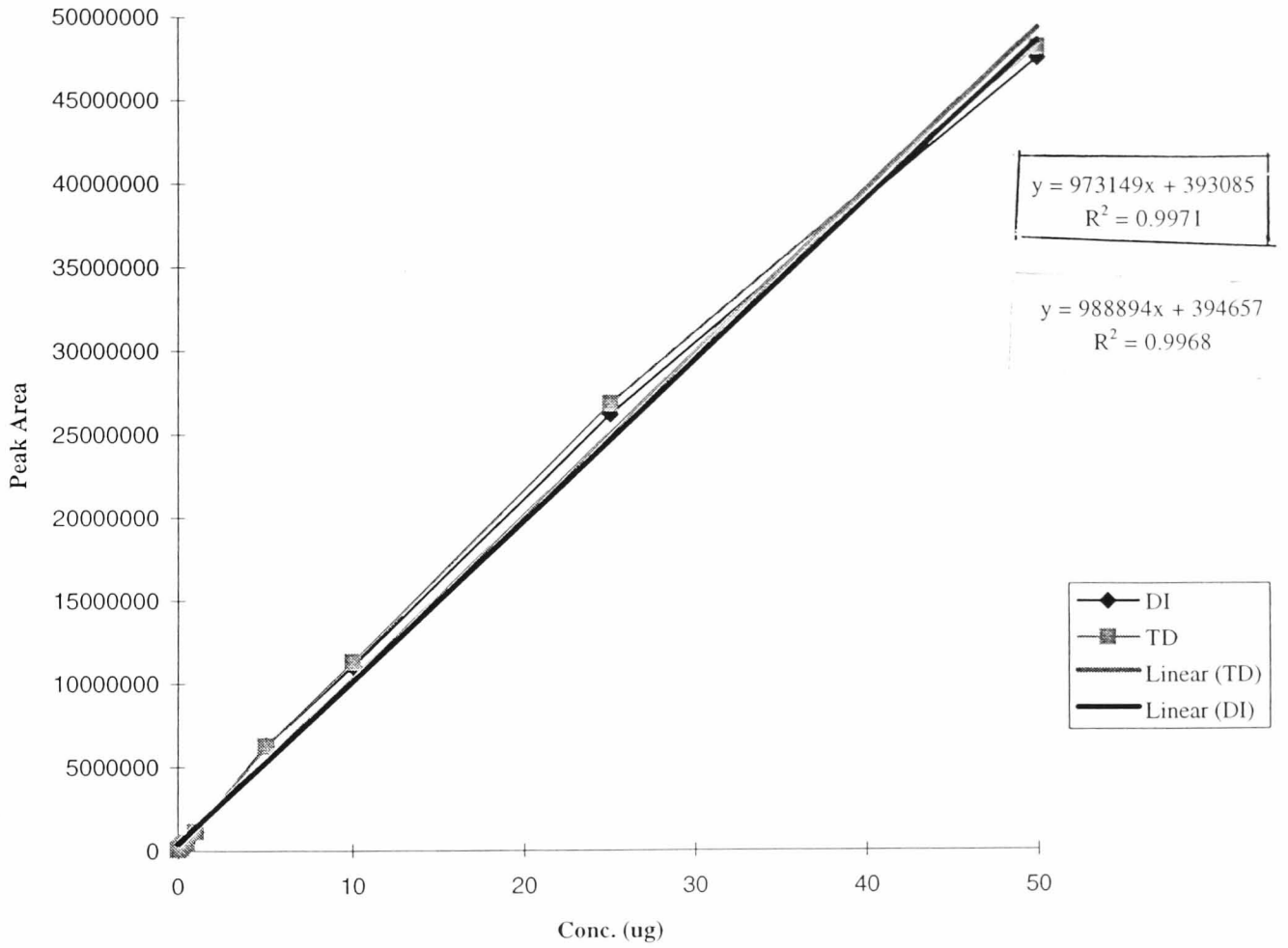


Table 3.1. Comparison of peak area and retention time (RT) for thermal desorption (TD)/direct injection (DI) techniques:

Inj. No.	Amount added	DI	RT	TD	RT
1	(1 µg)	1057646	24.51	1027587	24.32
2		1100567	24.12	989792	24.21
3		1000111	24.01	1057697	24.11
4		1067677	24.49	1199988	24.39
5		1023567	24.21	1099879	24.19
	Mean	1049914	24.26	1074989	24.24
	S.D.	±73991	±0.22	±80698	±0.11
	t value	mean DI – mean TD = 0.59		not significant	
1	(5 µg)	6301335	24.42	6225699	24.49
2		6023567	24.11	5999788	24.11
3		5927012	24.31	6059345	24.354
4		6127290	24.28	6058998	24.40
5		6259730	24.56	6157780	24.29
	Mean	6127787	24.11	6100322	24.29
	S.D	±57083	±0.16	±90159	±0.17
	t value	mean DI – mean TD = 0.66		not significant	

Table 3.2. The recovery of chlorpropham from the Tenax precolumn using thermal desorption technique.

Chlorpropham (µg)	%Recovery ± SD	Chlorpropham (µg)	%Recovery ± SD
0.05	96.79 ± 0.75	1.0	97.38 ± 3.20
0.1	96.54 ± 1.22	5.0	98.79 ± 1.34
0.2	93.61 ± 0.99	10.0	97.6 ± 2.60
0.3	93.70 ± 1.89	25.0	94.53 ± 1.01
0.4	95.98 ± 4.59	50.0	98.28 ± 0.10
0.5	97.21 ± 2.67		

Table 3.3 Storage life of chlorpropham precolumns under different temperature conditions.

	% Recovery of chlorpropham			
Tenax precolumn	Refrigerator (5°C+1) Days		Room Temperature (20°C+4) Days	
	5	10	5	10
1	98.2	96.8	90.0	89.06
2	100.6	94.0	89.6	88.67
3	102.2	98.95	92.6	85.41
4	97.6	94.7	91.8	84.74
5	99.4	95.6	90.2	78.48
Mean	99.60	96.01	90.84	85.27
S.D.	± 1.85	±1.94	±1.29	±4.29

Table 3.4 Percent recovery of chlorpropham from different soils at 50μg/ml

Soil type	Replicate No.	Detected(μg)	% Recovery
Midelney	1	47.89	95.78
(clay)	2	46.42	92.84
	3	48.04	96.08
	Mean	47.44	94.90
Downholland	1	43.98	87.96
(Peat)	2	45.09	90.18
	3	42.02	84.04
	Mean	43.69	87.39
Sand	1	51.04	102.08
(Acid washed)	2	49.90	99.80
	3	50.43	100.86
	Mean	50.45	100.91

both soils showed a significant ($p< 0.001$) difference at 0.05% confidence level from acid washed sand which is not a real soil.

3.4.2.1 Effect of soil type

Comparison of the results show that at both applied concentrations (10µg/g and 100µg/g) the amount of chlorpropham vapours trapped was in the order Acid washed sand > Midelney > Downholland under all investigated temperature and moisture contents. These results could be attributed to different organic matter content of the soils under investigation. Soil organic matter causes the partitioning of chemical between the soil/vapour phase and a reduction in compound diffusion coefficient due to a reduction in its vapour density which in turn lowers vapour pressure. This reduction in vapour pressure decreases significantly vaporisation rate of the compound (Sims et al., 1986). Since the investigated soils differ significantly in their organic matter content they exhibited different amounts of vapour losses. The maximum vapour losses were 16.48%, 1.42%, 1.32% from acid washed sand (0.00% O.M.), Midelney (clay) soil (14.7 % LOI) and Downholland (peat) soil (31.2% LOI) respectively under field capacity moisture content at 25°C and at 100µg/g. The minimum losses were 2.77%, 0.53%, and 0.140% from sand (acid washed), Midelney (clay) and Downholland (peat) soil respectively under air dried condition, 10°C and 10µg/g application level.

These results are in accordance with the reviews presented by Taylor and Spencer (1990). They reported that vapour densities over both wet and dry soils were inversely related to the soil organic content. In this context Watanabe (1993) revealed that the air/soil partition coefficient (Ka/s) increased as the water content in soil increased or as the organic matter content in soil decreased. The Ka/s value for chlorpropham at a third of saturation and 5%

Figure 3.4 (a): Total Vapour loss from different soils at 10° C (10μg/g) under different moisture contents in 12- day period

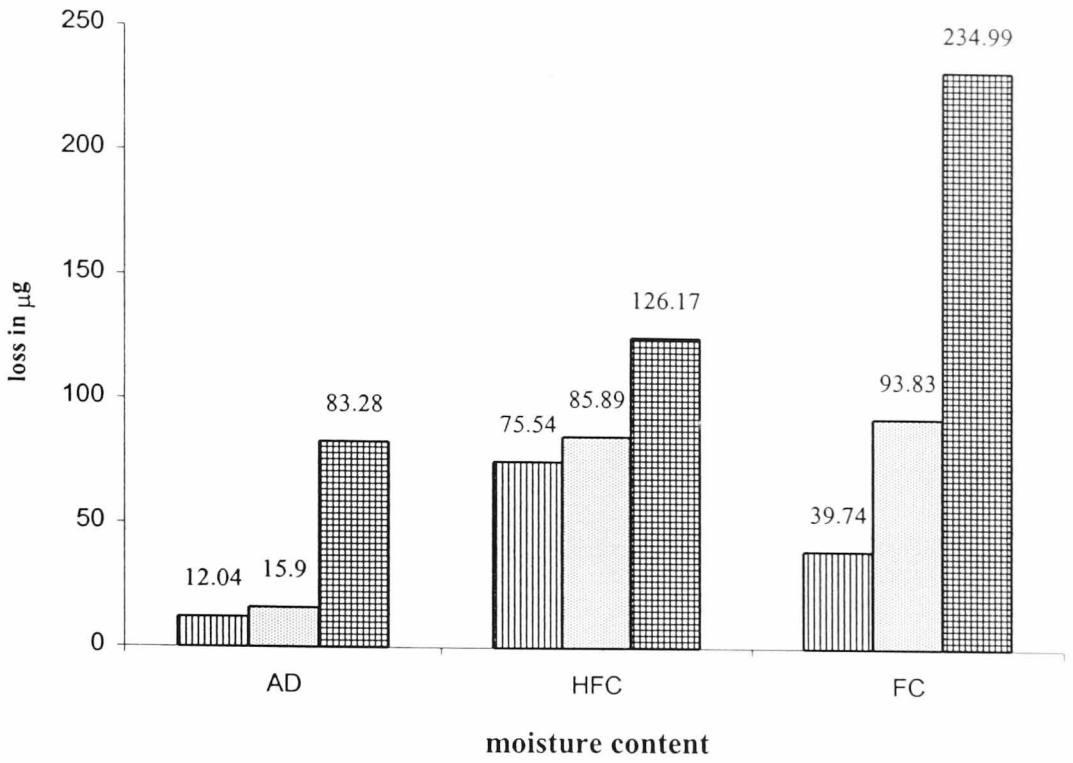
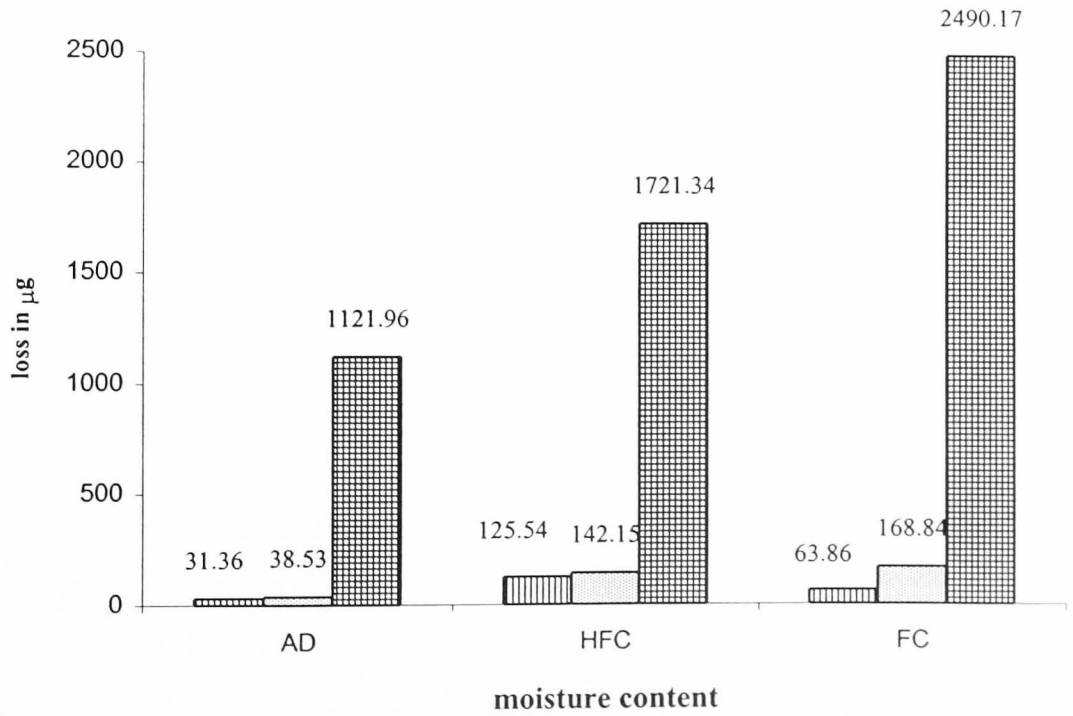


FIgure 3.4 (b): Total vapour loss of chlorpropham from three soils at 10° C (100μg/g) under different moisture contents in 12-day period.



= Downholland = Midelney = acid washed

AD= air dried HFC= Half field capacity FC= Field capacity

Figure 3.5 (a): Total vapour loss of chlorpropham from three soils at 25° C (10μg/g) under different moisture contents in 12-day period

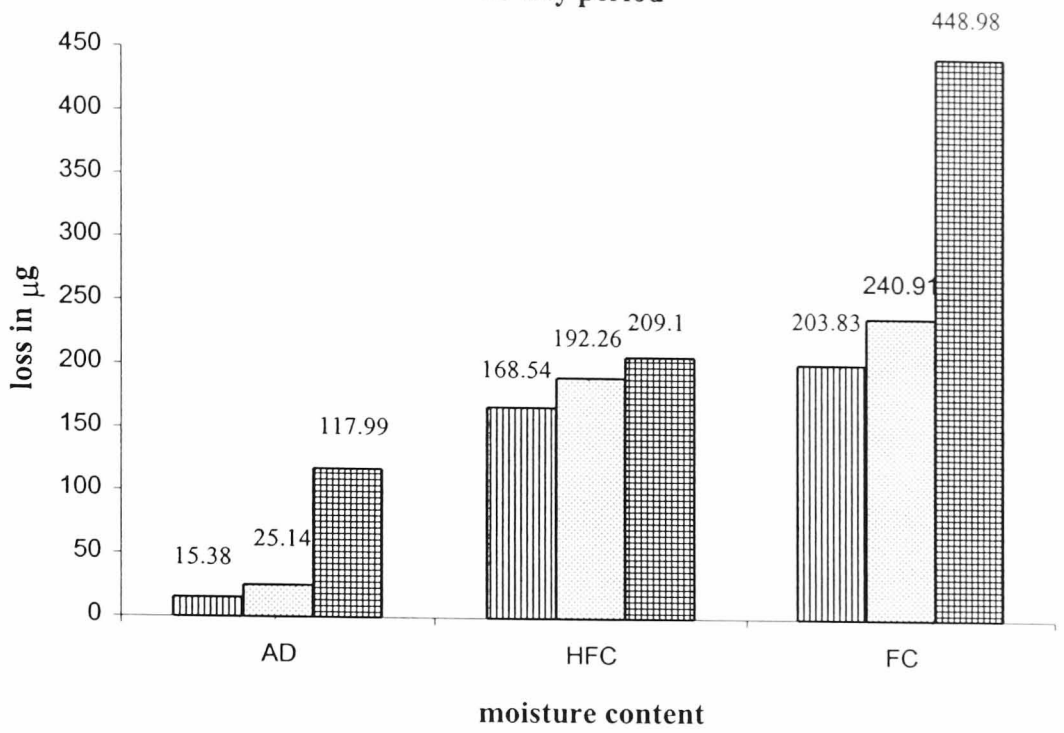
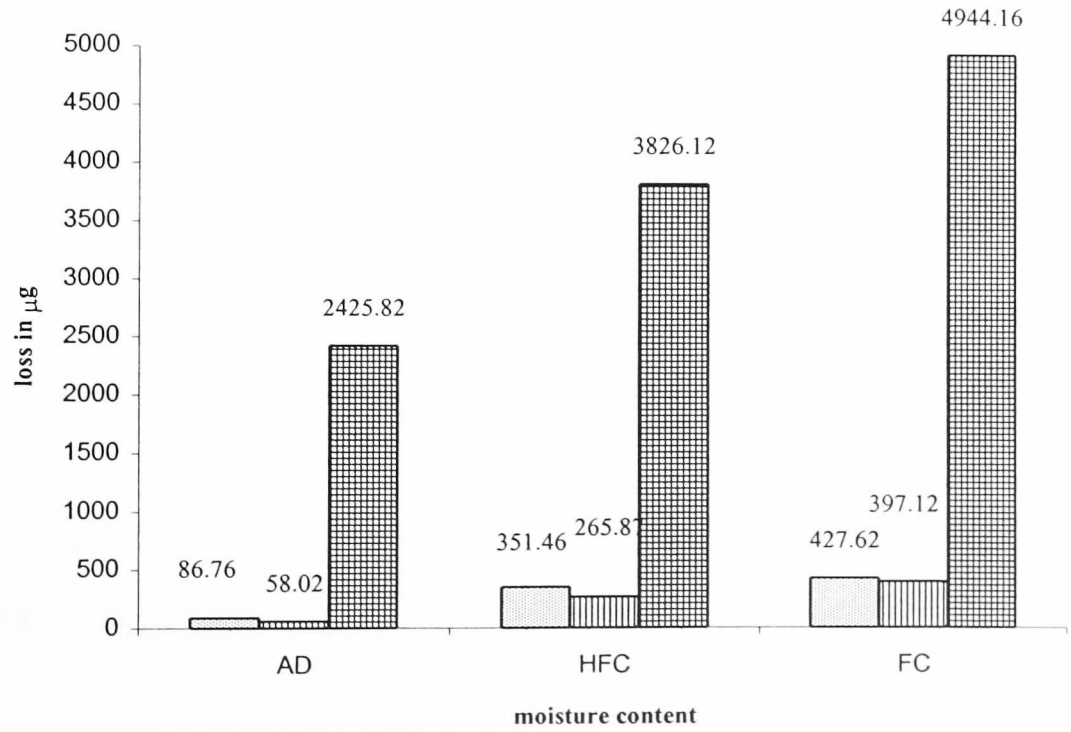


Figure 3.5(b): Total vapour loss of chlorpropham from three soils at 25° C (100μ/g) under different moisture contents in 12-day period



Downholland Midelney acid washed

AD = Air dried HFC = Half field capacity FC = Field capacity

organic matter content was 3.4×10^{-6}. In addition, they demonstrated that there was a positive correlation between air/soil partition coefficient and vapour pressure. Furthermore, Plimmer (1976) reported that the diffusion coefficient decreased with increased percentage of organic matter. The diffusion coefficients were highest in quartz sand where there is little interaction between the medium and the pesticide. In addition Gan et al.,(1996) reported similar findings i.e. the cumulative volatilisation losses of pesticide were 89% and 90% from carssetas (0.22% O.M.) and greenfield soils (0.92% O.M.). However, with the Linne clay loam (2.99% O.M.) under the same conditions, only 44% of the applied pesticide was emitted via volatilisation. In another study it was reported that EPTC was lost by vaporisation most rapidly from moist silty clay and builders sand (O.M. 2% and <1%) and slowest from the moist peat and heavy clay soils (O.M. 34% and 5%). In this context Wheatly (1976) reported that pesticides disappear as vapour most rapidly from sand or soils containing little organic matter. In soil containing little organic matter adsorption onto the mineral complex, particularly clays is an important factor affecting volatilisation.

Dependence of volatilisation of pesticide from soil on organic matter is further supported by the results of Parochetti and Warren (1966) who studied the volatility of chlorpropham on different soil types ranging from quartz sand (0.00% O.M.) to muck (74% O.M.) and reported that losses of propham and chlorpropham from quartz sand and soils decreased with an increase in percent organic matter and clay or both. In addition, McGrath and McCormack (1979) reported that toxicity of chlorpropham is related to O.M. content of the soil.

3.4.2.2 Effect of moisture content

In the present study, the most important factor affecting chlorpropham volatility is soil moisture content (Figures 3.6-3.8). The minimum volatility within each soil is displayed under air dried conditions at both concentration levels. The volatility increases appreciably with increase in soil moisture content. However, exception to this trend was observed for Downholland (peat) soil at full field capacity and 10°C at both concentration levels. This trend may be due to high clay (47.5%) and organic matter (31.2% LOI) contents of the Downholland (peat) soil which retains a high moisture at 10°C as compared to 25°C. The reduction in volatility at high moisture content could be explained by the fact that the high moisture content reduces the soil porosity, which in turn reduces the diffusion of chlorpropham through the soil. In contrast this behaviour was not observed at 25°C under the same moisture content probably due to faster evaporation of water.

Earlier Parochetti and Warren (1966) reported parallel observations during the volatility of chlorpropham. They stated that increasing the moisture content from field capacity to saturation did not greatly increase the losses of chlorpropham from quartz sand, silt loam and silty clay. While for muck soil volatility of chlorpropham decreased as moisture content exceeded field capacity. In another study with similar findings Parochetti and Warren (1967) explained that diffusion of herbicide decreased at moisture contents greater than field capacity.

The overall results of this study (Fig 3.4(a,b) -3.5(a,b) show that, volatilisation of chlorpropham increased with increasing moisture content at both temperatures and concentrations except in the case of Downholland (peat) soil at 10°C at field capacity These observations are in agreement with the results of Letey and Farmer (1974). They stated that diffusion coefficients for

Figure 3.6 (a): Total vapour loss of chlorpropham from Downholland soil under different temperatures and moisture contents at treatment level 10 μg/g .

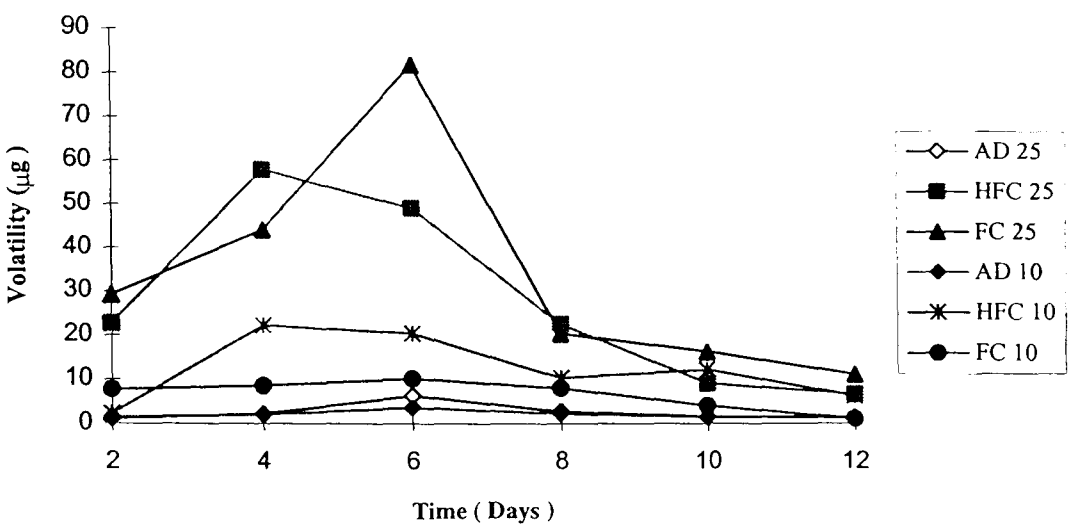
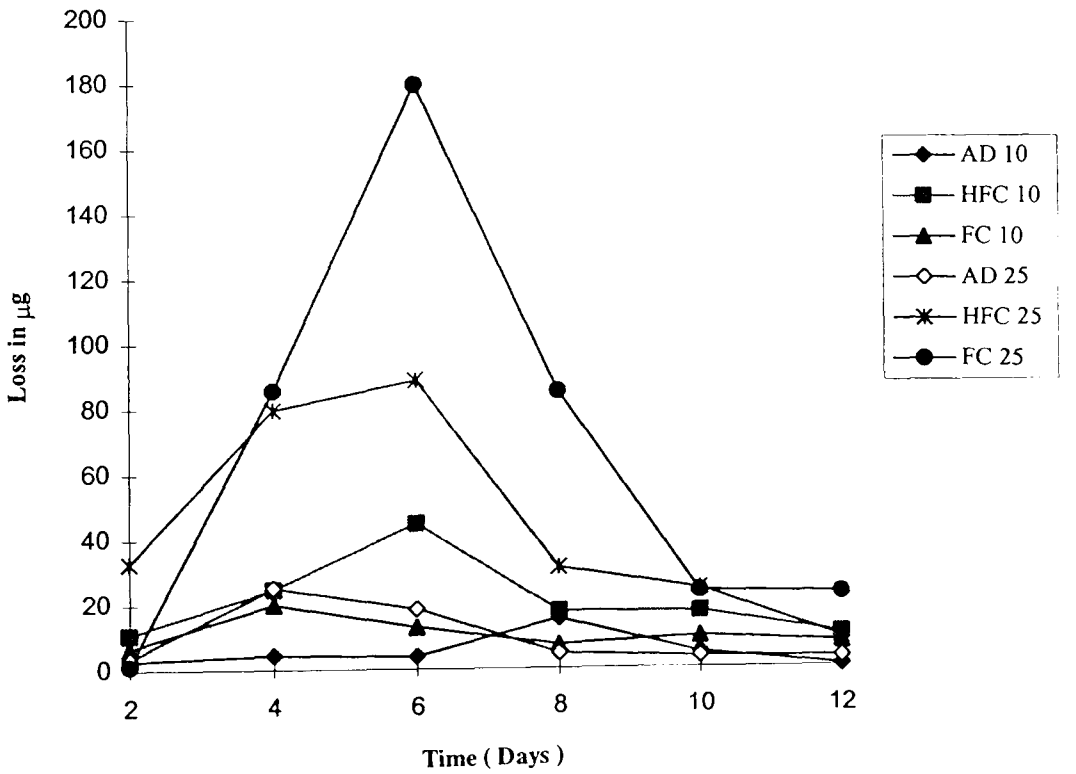


Figure 3.6 (b): Total vapour losses of chlorpropham from Downholland soil at different conditions of temp. and moisture content at 100 μg/g.



AD = air dry 1/2 FC = half field capacity FC = field capacity

Figure 3.7 (a): Total vapour loss of chlorpropham from Midelney soil under different temperatures and moisture contents at treatment level 10 μg/g .

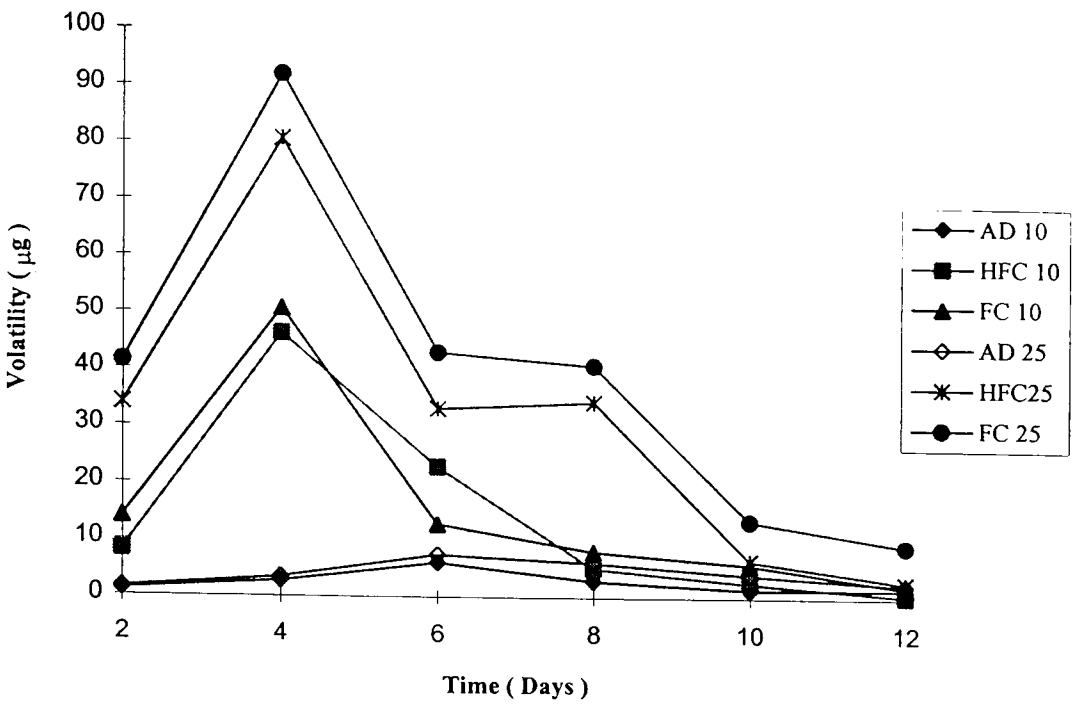
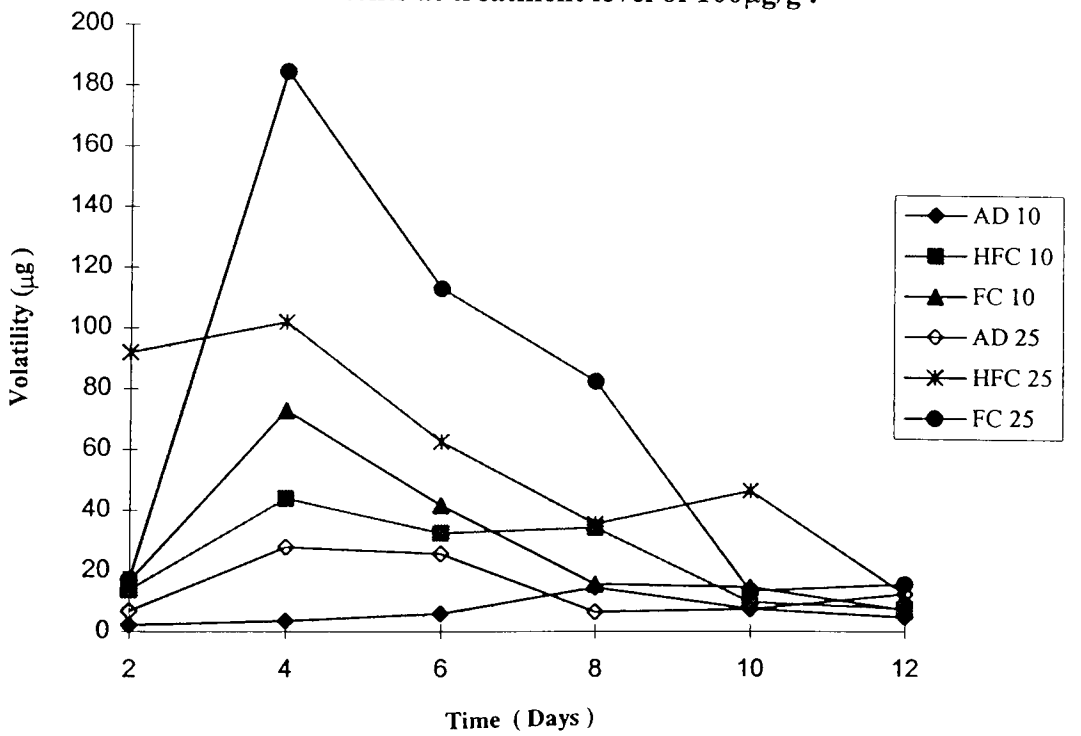


Figure 3.7 (b): Total vapour loss of chlorpropham from Midelney soi under different temperatures and moisture contents at treatment level of 100μg/g .



AD = air dry HFC = half field capacity FC = field capacity

Figure 3.8 (a): Total vapour loss of chlorpropham from acid washed sand under different tempeatures and moisture contents at 10μg/g treatment level

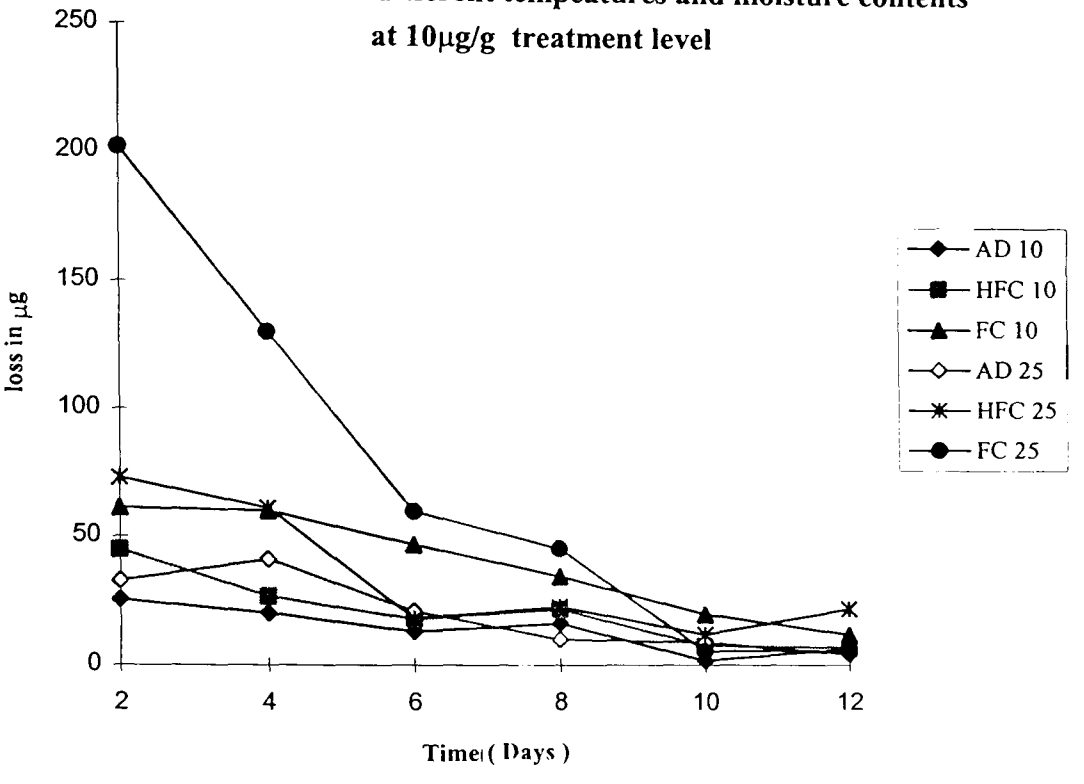
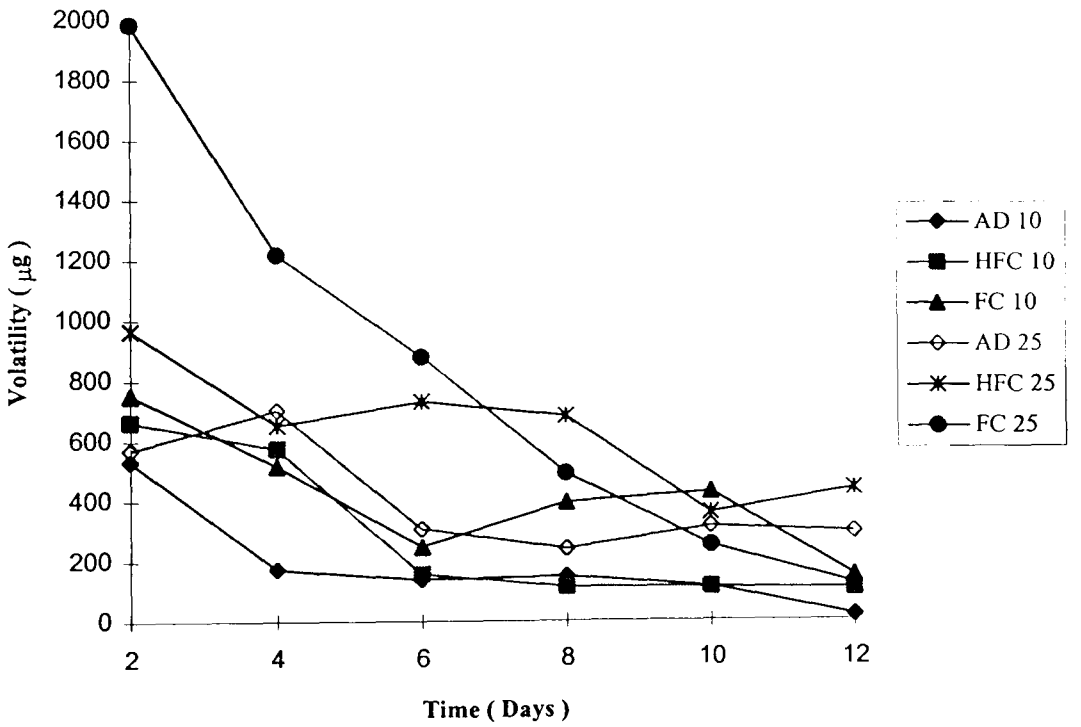


Figure 3.8 (b): Total vapour loss of chlorpropham from acid washed sand under different temperatures and moisture contents at treatment level 100μg/g .



AD = air dry HFC = half field capacity FC = field capacity

chlorpropham from silty clay loam soil increased as soil moisture content increased from half field capacity to field capacity. They assumed that since chlorpropham has a relatively high vapour pressure so vapour phase diffusion could be expected. Furthermore, these results are supported by the results of Turner et al., (1978) where the losses of chlorpropham decreased steadily (29.4 g/hec/h to 10.4 g/hec/g) from a bare dry soil despite continuous sunshine and steady wind as the moisture applied in the spray was evaporated. However despite a 4°C decrease in air temperature a marked rise in chlorpropham losses was observed after the soil was moistened by a rain shower. In addition, when the soil moisture content was raised to 18% by rain the volatilisation exceeded that of the first day i.e. 29.4%. In addition Glotfelty et al., (1989) stated that volatilisation was dramatically reduced when the surface layer of the soil became dry near noon and the highest rate occurred in the morning or afternoon as the soil surface was remoistured by dew formation or the upward movement of soil moisture to the cooler surface.

It appears that the soil moisture content has a pronounced effect on the volatility of chlorpropham among all the treatments within each soil type at both investigated temperatures and concentrations. The effect was more obvious in the case of the Downholland (peat) soil (13.25 and 6.84 times) treatment than the Midelney (clay) soil (9.58 and 4.92 time) treatment and comparatively less with acid washed sand treatments (2.38 and 2.03 times) at both concentrations at 25 °C. Similar trends were observed for both concentrations for all moisture contents. These differences in losses could be related to the influence of moisture content on the adsorption of chlorpropham on soil O.M. The adsorption studies (Chapter 2) have shown that adsorption of chlorpropham is directly related to the O.M. content of the soil. The LOI of the soils under investigation were 31.2%, 14.7%, and 0.00% for peat, arable and acid washed sand respectively. Accordingly, the adsorption behaviour of the soils followed

the same pattern i.e. Downholland (peat)> Midelney (clay)> sand (acid washed). Since chlorpropham competes with water molecules for adsorption onto the soil O.M., this competition is expected to be highest in the case of Downholland (peat) soil than in the Midelney (clay) soil and the lowest in the acid washed sand. Thus the effect of moisture content on adsorption is reflected to a different extent in different soils ultimately affecting the degree of chlorpropham losses from different soils. In addition, these results are in accordance with the findings of Nair et al. (1992) who mentioned that flooding significantly enhanced volatilisation, and the effect was maximal in the soil, which had the highest organic carbon. Further, Beetsman and Deming (1974) reported that the rate of volatilisation from continuously moist soils under similar exposure conditions was 3 to 20 times greater than volatilisation from air dried soils.

3.4.2.3 Effect of temperature

The measured volatilisation rates indicated an enhancement of chlorpropham volatility with increase in temperature from 10°C to 25°C from all the investigated soils at all moisture contents and both concentration levels. In comparing the factors governing the volatilisation from soil, the effect of temperature is relatively less significant as compared with other factors such as soil moisture and soil type except in the case of peat soil where increase in temperature at field capacity moisture content caused a significant increase in chlorpropham volatility. Temperature causes an increase in vapour pressure, water advection rates, soil/water/air partition coefficients, and biodegradation rates (Hamaker, 1972 a); increase in temperature increases the vapour pressure of chlorpropham, in turn diffusion depends directly on vapour pressure, thus increasing the temperature enhances the volatility of chlororopham. The results

are in accordance with the findings of Hussain et al., (1994) where an increase in temperature from 35°C to 45°C caused a 1.8 fold increase in volatility of DDT.

In this context, Spencer and Cliath (1990) mentioned that temperature influences volatility of soil incorporated pesticide through its effect on movement of pesticides to the surface by diffusion or mass flow in evaporating water, or through its effect on the soil water adsorption/desorption equilibrium. For all these effects increases in temperature are associated with increase in volatilisation rate. However, in some cases increase in temperature is associated with a decrease in volatility because of an increase in the drying rate of the soil surface.

The increase in volatility due to increase in temperature from 10°C and 25°C (at field capacity moisture content) was, on average, not more than 1.91, 1.98 and 2.56, 2.53 times for sand (acid washed) and Midelney (clay) soil at 10μg/g and 100μg/g concentration levels respectively. While for Downholland (peat) soil it was 5.12 and 6.21 times at the 10μg/g and 100μg/g application rates. In this context, Nash and Gish (1989) reported that volatilisation increased 1.8 times from sandy loam soil for each 10°C rise in temperature. The higher rate of increase in the case of peat soil is most likely due to high clay and organic matter contents (47.5 and 31.2%), the soil which lowers the rate of water evaporation as compared to that from Midelney (clay 40.4, LOI 14.7%). The higher clay content of peat soil may be responsible for prolonging the effect of moisture on volatility of chlorpropham.

There were substantial water losses from all treated soils especially at 25°C at both concentration levels. The water losses are presented in Table 3.5. It is evident that from the data (Fig. 3.6(a,b)-3.8(a,b)) that there was an appreciable decrease in volatility after 2, 4, and 6 days from the sand, Midelney and Downholland soils respectively at all 25°C treatments at both concentration

levels This behaviour is in agreement with the explanation given by Wheatly, (1976). Water molecules compete more than pesticide for adsorption sites, and moisture thereby reduces the adsorption tendency of the pesticide. As more water is lost at high temperature so competition of water molecules becomes less with chlorpropham, resulting in more adsorption of chlorpropham on adsorption sites. Similar results have been reported by Taylor and Glotfelty (1988) and Spencer, (1970) where they observed a decrease in volatilisation with increase in temperature. In this context Nash (1983) stated that when soil moisture decreases on soil surface to an amount equal to one monomolecular layer amount [Harper et al., 1976 (cit. Nash (1983) places this at a three molecular layer] the effective vapour pressure and thus volatilisation is reduced. In addition, Taylor (1978) reportd that adsorption of many pesticides including chlorpropham is very strongly influenced by soil moisture. Under very dry conditions strong adsorption reduces the vapour pressure of the residues to negligible values, but when sufficient moisture is present to cover the surface of the soil colloids to a depth of a few molecular layers, the vapour pressure rises to values closer to those of the pure compounds. The moisture contents at which this transition takes place varies from soil to soil depending on clay and O.M. content.

3.4.2.4 Effect of time

There was a rapid decrease in the volatilisation rate of chlorpropham with time especially at 25°C (Fig.3.6(a,b)-3.8(a,b). The effect could be due to less chlorpropham concentration left at 25°C after more losses at high temperature. Nash and Gish (1989) also found a decrease in flux rate of pesticides with time as the amount of pesticide remaining was reduced through volatilisation and degradation.

Table: 3.5. Water loss from the soils during the experiment

Soil type	Temp. (°C)	% initial moisture content	% moisture after 12 days (100µg/g)	% moisture after 12days (10µg/g)
Downholland (peat)				
	10	8.85(AD)	8.03	7.67
		30.83(1/2FC)	20.22	20.64
		61.67(FC)	31.47	32.36
	25	8.85(AD)	6.16	6.60
		30.83(1/2FC)	9.29	9.04
		61.67(FC)	10.71	11.88
Midelney				
(clay)	10	4.95(AD)	5.57	5.05
		24.05(1/2FC)	16.15	16.39
		48.1 (FC)	25.71	26.45
	25	4.95(AD)	4.67	4.29
		24.05(1/2FC)	5.01	5.08
		48.1 (FC)	9.37	10.23
Sand	10	0.04(AD)	0.04	0.05
(Acid washed)		12.98(1/2FC)	1.92	2.02
		25.97(FC)	3.68	4.09
	25	0.04(AD)	0.04	0.04
		12.98(1/2FC)	0.04	0.04
		25.97(FC)	0.30	0.25

AD = air dry 1/2 FC = half field capacity FC = field capacity

Another reason for the rapid decrease in the rate of evaporation was probably due to diffusion of chlorpropham to the soil surface becoming the limiting factor controlling volatility as the surface soil chlorpropham concentration was depleted. Taylor (1978) has reviewed and investigated that at lower pesticide concentration adsorption becomes more important and less sensitive to water content and the volatilisation of pesticide is greatly restricted, becoming dependent on the rate of upward movement of the soil to the surface.

Rapid losses of water from soil at 25°C than at 10°C means more adsorption of chlorpropham on adsorption sites which mainly affects diffusion rather than volatility. In this regard Spencer et al., (1973) explained that owing to the strong adsorption forces that develop, diffusive movement in a dry soil layer is very slow and volatilisation is almost ceased.

3.4.2.5 Effect of concentration

Investigations of the influence of the application dose (Table 3.6) on soil volatilisation shows that at lower application doses, the amount volatilized (calculated as percentage of the initial amount) was higher than with the higher dose. However, if volatilisation is expressed in terms of mass flow, a higher volatilisation was observed using a higher chlorpropham concentration. This trend is seen for Downholland (peat) and Midelney (clay) soils at all temperatures, and moisture contents. This effect could be interpreted as the result of the saturation with chlorpropham of the air mass which was in contact with the soil, the uptake by the air was hindered, although more chlorpropham was accessible for volatilisation. Similar results have been reported Waymann and Rude (1995), during the volatilisation of lindane at higher concentration. In addition, Lichtenstein (1972) mentioned that by increasing concentration of dyfonate (40-160ppm), no increase in volatilisation occurred.

Table 3.6: Volatilisation of chlorpropham during 12 day period: Effect of different application doses.

	ADA1	ADA11	HFCA1	HFCA11	FCA1	FCA11
Downholland 10°C						
Obs.(µg)	31.36	12.04	125.54	75.54	63.86	39.74
% of initial applied	0.10	0.40	0.41	2.51	0.21	1.32
Midelney 10°C						
Obs.(µg)	38.53	15.9	142.15	85.89	168.84	93.83
% 0f initial applied	0.12	0.53	0.47	2.86	0.56	3.12
Acid washed sand 10°C						
Obs.(µg)	1121.96	83.23	1721.34	126.17	2490.17	234.99
% of initial applied	3.73	2.77	5.75	4.20	8.30	7.83
Downholland 25°C						
Obs.(µg)	58.02	15.38	265.87	168.54	397.12	203.83
% of initial applied	0.19	0.51	0.88	5.61	1.32	6.79
Midelney 25°C						
Obs.(µg)	86.76	25.14	351.46	192.26	427.62	240.9
% 0f initial applied	0.28	0.83	1.17	6.40	1.42	8.03
Acid washed sand 25°C						
Obs.(µg)	2425.82	117.99	3825.35	209.1	4944.16	448.9
% of initial applied	8.08	3.93	12.75	6.97	16.48	14.94

AD=Air Dried FC=Field Capacity A1=100µg/g A11=10µg/g

Downholland (peat) Midelney (clay) sand (Acid washed)

3.4.3 Biological degradation

Although an attempt was made to sterilise the soils under treatment by autoclaving using the conditions mentioned in section 3.3.6.2. however, during the course of study some fungal growth was noticed on soils at half field and full field capacity treatments. This urged me to look for any potential metabolites produced by microbial degradation. In this context Khafif et al., (1983) mentioned the presence of microbial populations in sterilised soil following three autoclavings (20 min-120 °C). The results of biological degradation are presented in Figure 3.9(a,b,c)-3.10(a,b,c). The metabolites which were detected during the study were 3-chloroaniline, and propham. The identification of these metabolites was done by running the synthetic standards and comparing the retention times with those of the retention times of the metabolites. Another peak corresponding to RT 9.0 min is expected to be isopropanol since chlorpropham has been reported to be hydrolysed to 3-chloroaniline and the corresponding alcohol by Ectomycorrhizal fungi (Rouillion, 1989). Formation of propham as a result of microbial degradation could be explained on the basis of the reports of Stepp et al., (1985). These authors found that isopropyl-3,4 dichlorocarbanilate (DCIPC) was microbially tranformed to chlorpropham resulting from dehalogenation at the para position and appeared as a transitory intemediate. However, the authors reported that the second degradation product was not propham (IPC). In the present study the metabolites could not be detected from the soils at air dried condition and low application level i.e. 10µg/g under both studied temperatures. The effect could be due to increased adsorption under the mentioned conditions. These results are supported by reports of Hurle and Walker (1980) that herbicides were more persistent in the cooler and drier conditions than in hot and wet ones. In addition Singh et al. (1990a) mentioned that lowering the concentration

effectively leads to stronger sorption which, in turn, could result in lowering the overall degradation rate. The approximate formation of 3-chloroaniline and isopropanol (Table 3.7) followed the order Downholland (peat) FC 25°C, > Downholland (peat) HFC 25°C, > Downholland (peat) FC 10°C, Downholland (peat) HFC 10°C, and Midelney (clay) FC 25°C, > Midelney (clay) HFC 25°C.

Table 3.7 Microbial degradation of chlorpropham from different soils.

Soil type	Temp. (°C)	Moisture content	Approximate biological degradation (%)
Downholland (peat)	10	1/2 FC	2.04
		FC	6.32
	25	1/2 FC	6.60
		FC	28.25
Midelney (clay)	10	1/2 FC	1.17
		FC	2.19
	25	1/2 FC	3.95
		FC	9.83

1/2 FC = half field capacity FC = field capacity

Figure 3.9 (a): Profile of 3- chloroaniline formation in Downholland soil during 12 days under different temperatures and moisture contents

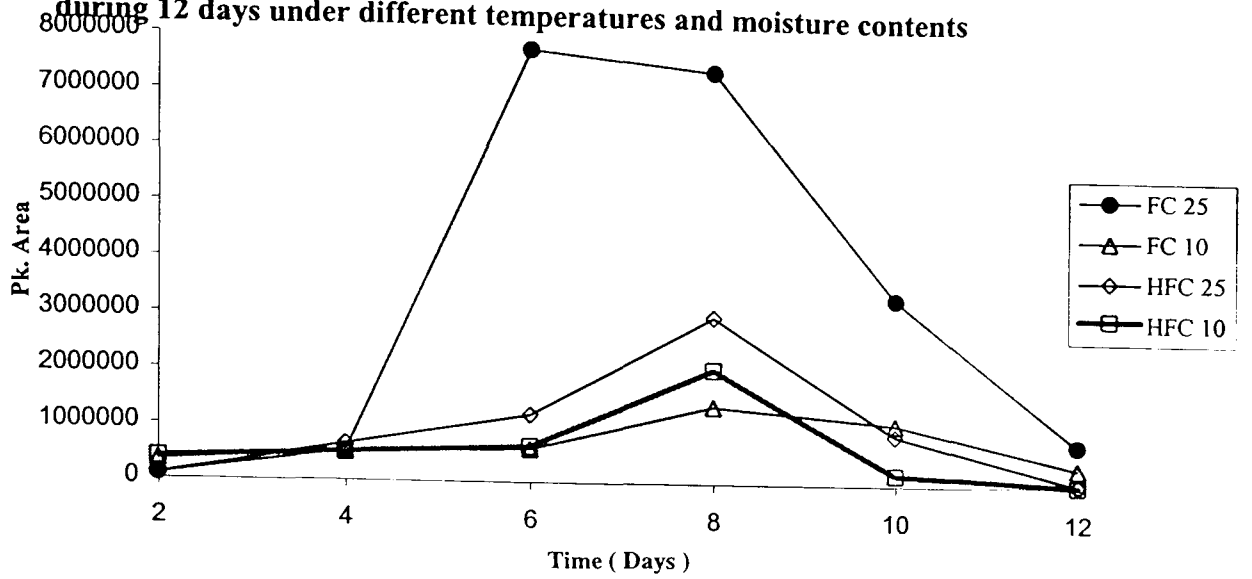


Figure 3.9 (b): Rate of isopropanol formation in Downholland soil during 12 days under different temperatures and moisture contents.

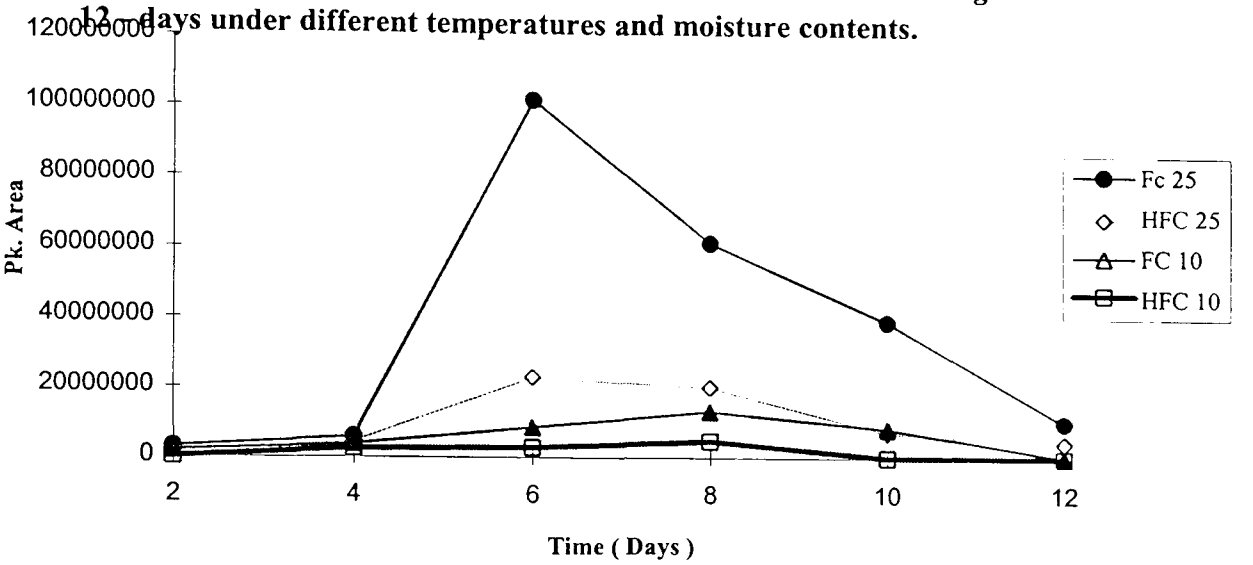
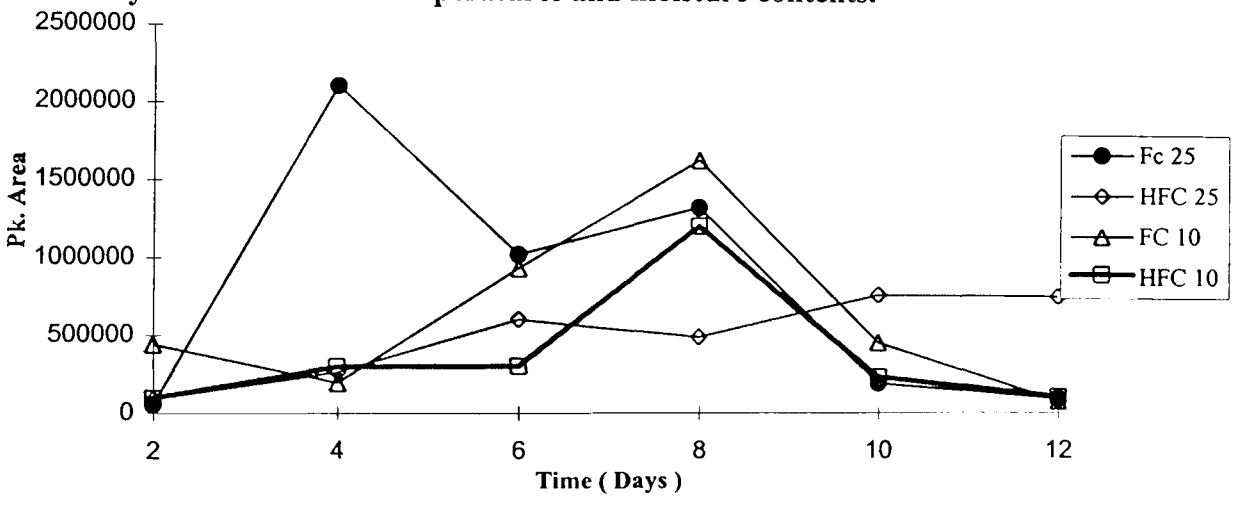


Figure 3.9 (c): Propham(IPC) formation in Downholland soil during 12 days under different temperatures and moisture contents.



AD = air dry HFC = half field capacity FC = field capacity

Figure 3.10 (a): Profile of 3 -chloroaniline formation in Midelney soil during 12-days under different temperatures and moisture contents.

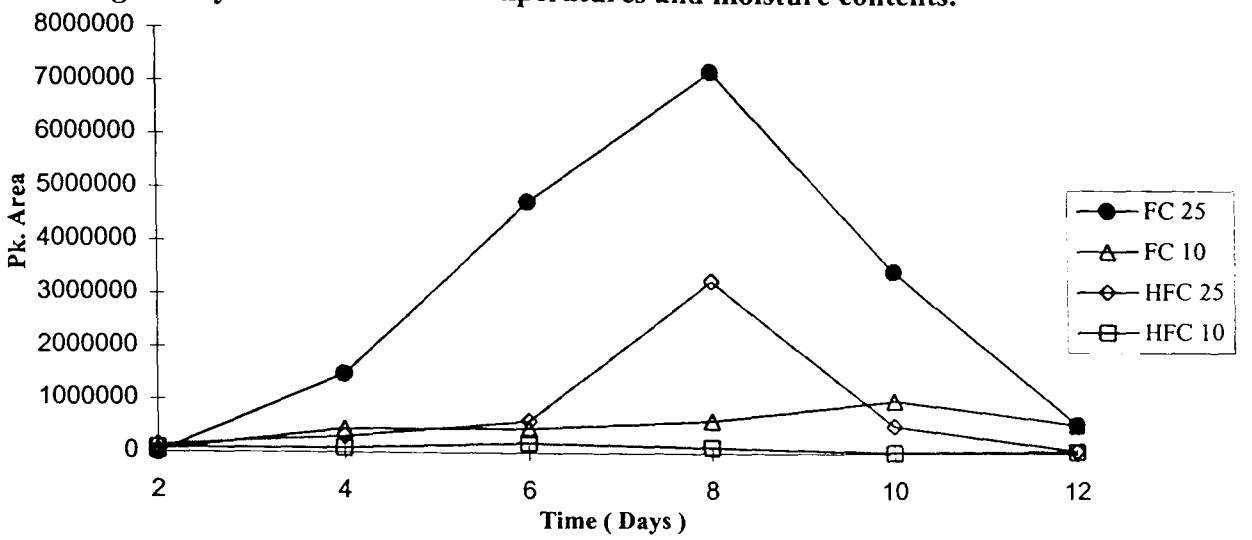


Figure 3.10 (b): Profile of isopropanol formation in Midelney soil during 12-days under different conditions of temperature and moisture contents.

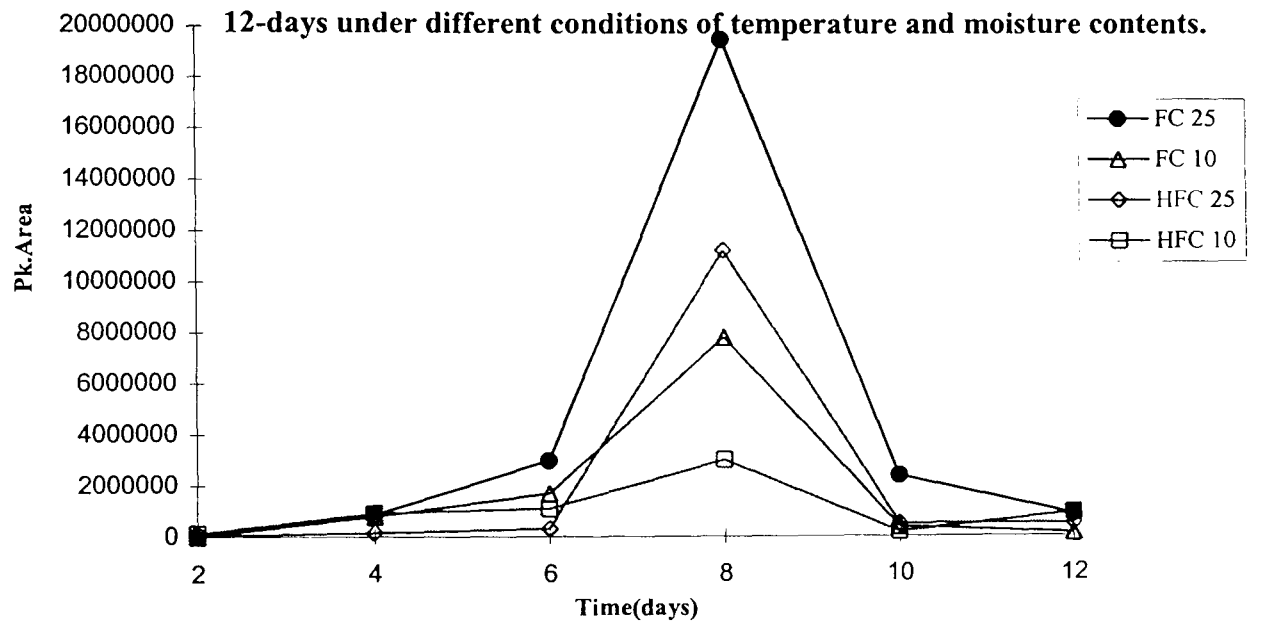
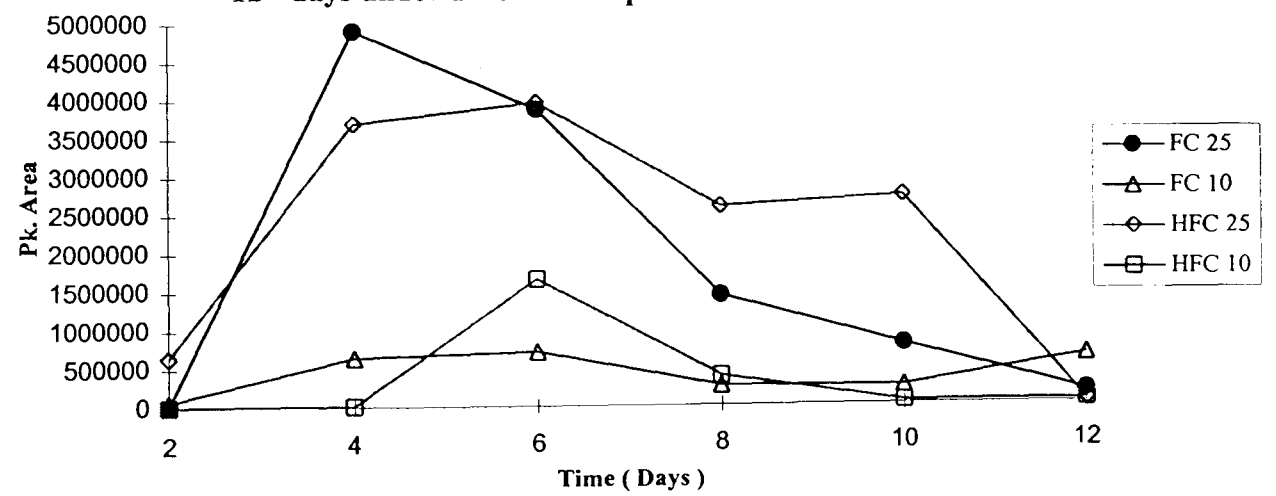


Figure 3.10 (c): Propham (IPC) formation in Midelney soil during 12 - days under different temperatures and moisture contents.



AD = air dry HFC = half field capacity FC = field capacity

Midelney (clay) FC 10 °C, > Midelney (clay) HFC 10°C, 100 µg/ml dose under the mentioned conditions.

Increasing the moisture content from air dry conditions to half field capacity and field capacity and temperature from 10°C to 25°C increased the formation of propham, 3-chloroaniline and isopropanol in both peat and arable soils. The results of this study are in agreement with the results of Freed (1951) who observed rapid breakdown of IPC at elevated temperature from 42°F to 70°F. Singh et al., (1990b) also reported an increase in EPTC degradation because of increased microbial activity at higher moisture content. Similarly Gan et al., (1996) explained that enhanced degradation in moist soils was a result of reduced pesticide diffusion and extended retention in soil.Further, Chapman and Harris (1990) demonstrated that enhanced microbial activity to pesticides was not generated at low temperatures (3°C), low soil moistures or with low pesticide concentrations (< 1 ppm). Hurle and Walker (1980) explained that adequate water as well as temperature is essential for microbial activity. In addition, water acts as a solvent and transport agent, a reaction medium for both biological and non-biological processes and is a reagent in hydrolytic processes. Furthermore, Horowitz (1972) mentioned that conditions favouring microbial activity in the soil, enhance the rate of breakdown. The investigations in the present study are consistent with this hypothesis.

The resulting effect of soil type on the microbial degradation is evident in the present work. Higher amounts (based on comparison of integrated peak area) of 3-chloroaniline and isopropanol were obtained from peat soil than from arable soil. The effect is more likely to be due to different organic matter content of these soils. Similar reports have been given by Ogle and Warren (1954) that persistence of many herbicides including chlorpropham decreased progressively from a light sandy soil to reports have been given by Ogle and Warren (1954) that persistence of many herbicides including chlorpropham

decreased progressively from a light sandy soil to a silt loam to an organic soil. Similar results were reported by Gan et al. (1996). They found that 49% of the applied pesticide was degraded in the Linn soil (O.M. 2.99%) while the degradation in Caretas (O.M. 0.22%) and Greenfield (O.M. 0.92%) soils was approximately 10%. They explained that enhanced degradation of pesticide in Linn clay loam is likely to be due to its higher organic matter content. Hance (1980), reported evaluated that soil organic matter might be expected to have effect on degradation since microbial activity is often high in more organic soils. However, adsorption of most herbicides also increases with an increase in soil organic matter and since adsorption reduces the amount of herbicide available in soil, it might provide protection from degradation. For this reason, Hamaker (1972) suggested that an increase in organic matter might increase rate of increase in mineral soils to limiting value, above which the rate of loss would be retarded. The data in Fig. 3.9 (a,b,c) - 3.10 (a,b,c) show that there was little microbial degradation during the first 4 days from the treated soils. However, after this time rapid formation of 3-chloroaniline and isopropanol was observed. This delay in breakdown of chlorpropham is more likely to be due to the fact that a soil microbial population develops the capacity to degrade a herbicide (Torstensson, 1980) due to the synthesis of inducible enzymes by responsible micro-organisms.

In this context, Hance and McKone (1971) suggested that reduced rates at higher initial concentrations might result from a limitation in the number of reaction sites in the soil or toxic effects on micro organisms or enzyme inhibition might be involved (Hurle and Walker, 1980).

A balance sheet was constructed from chlorpropham remaining on the soil and loss to air (Table 3.8(a) and 3.8(b) alongwith apparent pesticide loss through degradation and possibly binding. As expected maximum residues

Table 3.8(a): Balance sheet after 12 days.

Soil type	Temp. (°C)	Moisture content	Component, % of application(10µg/g) Soil	Air	Unknown
	10°C	AD	97.5	0.40	2.10
		HFC	93.7	2.51	3.79
Downholland (peat)		FC	94.8	1.32	3.88
	25°C	AD	94.2	0.51	5.29
		HFC	89.9	5.61	4.49
		FC	83.5	6.79	9.71
	10°C	AD	96.4	0.53	3.07
		HFC	92.8	2.86	4.34
Midelney (clay)		FC	87.7	3.12	9.14
	25°C	AD	93.6	0.83	5.57
		HFC	89.1	6.40	4.50
		FC	82.4	8.03	9.57
	10°C	AD	79.5	2.77	17.73
		HFC	74.2	4.20	21.60
Sand (Acid washed)		FC	71.9	7.83	20.27
	25°C	AD	74.9	3.93	21.17
		HFC	70.2	6.97	22.83
		FC	69.1	14.96	15.94

AD = air dry HFC = half field capacity FC = field capacity

Table 3.8(b) continued: Balance sheet after 12 days

Soil type	Temp. (°C)	Moisture content	Component, % of application(100µg/g) Soil	Air	Unknown
Downholland		AD	95.92	0.10	3.98
(Peat)	10°C	HFC	91.02	0.41	8.57
		FC	92.88	0.21	6.91
		AD	92.34	0.19	7.47
	25°C	HF	85.37	0.88	13.75
		FC	80.55	1.32	18.13
Midelney		AD	96.85	0.12	3.03
(clay)	10°C	HFC	91.12	0.47	8.41
		FC	89.43	0.56	10.01
		AD	90.61	0.28	5.57
	25°C	HFC	87.37	1.17	11.46
		FC	82.4	1.42	16.18
		AD	77.95	3.73	18.32
Sand	10°C	HFC	73.42	5.73	20.85
(Acid washed)		FC	70.91	8.33	20.79
		AD	75.49	8.08	16.43
	25°C	HFC	70.92	12.75	16.33
		FC	66.91	16.48	16.61

AD = air dry HFC = half field capacity FC = field capacity

remaining on soil occurred at lower temperature, air dried condition, and lower concentrations while maximum volatilisation occurred at higher temperature, field capacity moisture content and higher concentration. Microbial degradation was highest in the case of Downholland (peat) soil followed by Midelney (clay) soil presumably due to the higher organic matter content of Downholland (peat) soil. In addition high moisture content and high temperature favoured microbial degradation. Apparent higher losses in case of acid washed sand could be due to the loss of chlorpropham during soil treatment, changing of Tenax traps etc. absorption to glass (Wheatly, 1976). Such type of losses have been reported by Nash (1983) where 35% of the applied hepatochlor and trifluralin could not be accounted for. The possibility of microbial degradation is ruled out as none of the afore mentioned metabolites were observed in the case of acid washed sand.

Conclusion

The results of the volatility study demonstrated that volatility is an important pathway of chlorpropham loss from soil to the atmosphere. The study further revealed that the factors which determine the extent of volatility of chlorpropham are (1) nature of the soil (2) soil moisture content and (3) temperature. The nature of the soil and water content of the soil had a pronounced effect on volatility as compared to temperature and concentration. In addition, due to the presence of 3-chloroaniline and possibly isopropanol in significant amounts, it was concluded that biological degradation is also an important route for the removal of chlorpropham depending on the type of soil.

CHAPTER 4

PHOTODECOMPOSITION OF CHLORPROPHAM

4.1 INTRODUCTION

A pesticide that has entered into the environment is subjected to various transformations influencing its residual fate. Pesticide may be "lost" from the environment viz leaching, volatilisation, adsorption into the soil colloids and through transformation. These transformations may be biological, chemical and photochemical (Crosby, 1969; Adityachaudhary et al., 1994). In practice the products of biological, chemical and photochemical activity on pesticides are often the same or similar and it is not easy to distinguish which of the three agencies has caused a specific transformation or to establish their relative involvements (Benson, 1974; Hill and Wright, 1978).

Phototransformation caused by sunlight is a very important route for dissipation of pesticides in various environments and a considerable portion of a pesticide may be transformed by solar radiation especially those compounds which absorb radiations in UV-visible region of solar spectrum (Crosby, 1969; Brown, 1978). Rapid losses and conversion of pesticide in sterilised soil (Fletcher and Kaufman, 1980) and enhancement of their efficiency by shading (Crosby, 1972) suggests that photodecomposition of pesticides occurs under field conditions (Plimmer, 1972 ; Brown, 1978). Further, photochemical transformation of pesticide can cause both bioactivation and deactivation (Crank and Mursyidi, 1992; Adityachaudhary et al., 1994). The power of solar radiations is observed since ancient times in many naturally occurring phenomena ; photosynthesis, synthesis of vitamin-D, photochemical smog, ozone depletion, sunburn, rancidity of fats and fading of clothes and dyes,

which led to extensive corrective research in the case of the latter, one result of which has been the development of successful colour photography. In addition are the examples of use of sunlight in water purification, phototherapy of rickets and jaundice in new-born infants (Crosby, 1976; Pfoertner, 1984; Acher and Saltzman, 1989).

The photochemistry of herbicides and other xenobiotic compounds by sunlight has rapidly become an integrated part of studies concerning the environmental transformation of pollutants present in rivers, lakes, soil matrics and the atmosphere (Marcheterre et al, 1988).

Chlorpropham is used world-wide as a herbicide and/or potato sprout suppressant in store. As potatoes are washed during the processing of different products and washings added directly to the river causing a risk of contaminating the river water above the limits set for environmental quality standards. Since, there is the possibility of exposure to sunlight especially in hot regions where sunlight is prolonged it was important and relevant not only from public health point of view but also from environmental safety interest to study photochemical fate of chlorpropham In addition, it cannot be presumed that environmental products of a pesticide present a lesser ecological and public health hazard, so it is important to identify the products that are formed in model environmental systems.

This chapter was set up with the following aims:

1. To assess the rate of chlorpropham photolysis in water and in the presence of different soil/sediment suspensions at different concentrations.
2. To study the mechanism of phototransformation of chlorpropham in water and/or on soil.
3. To identify the possible photoproducts of chlorpropham and to predict their environmental fate.

Since involvement of light is essential in the phenomenon, therefore, a brief description of basics is given below for a better understanding of the process.

4.2 PHOTOCHEMISTRY(GENERAL)

Photochemistry is the study of the interaction of "photon" or light quantum" of electromagnetic energy with an atom or molecule, and of the resulting chemical and related physical changes that occur, while environmental photochemistry is a study of these processes relevant to environmental conditions (Roof, 1982).

Light is electromagnetic in character. It exists in both particulate and wave form. Radiant energy occurs in discrete parcels or quanta. The energy (E) of each quantum in ergs is related to wavelength or frequency by

$$E = h\nu = hc/\lambda \qquad (4.1)$$

Where h is Plank's constant (6.62×10^{-27}ergsec^{-}) and c is the velocity of light.

Energy of excitation of each absorbing particle is the same as the energy of quantum given by Planks relation (3.1) and the excitation energy per mole is obtained by multiplying this molecular excitation energy by N,

$$E = N\,h\nu = N\,hc/\lambda \qquad (4.2)$$

N, here, represents Avagadro's number (6.02×10^{23}mole^{-1})

4.2.1 Radiation-matter interaction

The emission spectra of sun is very broad; it ranges from long radiation waves of low frequency to very short gamma and ultraviolet radiation of high energy content. Sunlight is bounded by the UV cut off of the ozone absorption spectrum about 290 mμ (413 kj $mol^{-1)}$ on one end and the low energy limit for the activation of bond breaking on the other. Therefore, only radiations at this narrow range, are responsible for photolytic reactions (Crosby, 1976).

Ultraviolet light is considered to include wavelengths between 40 and 400 A^{o}(4-400 mμ), but most chemical experiments have been restricted to the middle (200-300 mμ) and near (300-400 mμ) UV. The energy required to bring about photochemical transformations amounts to about 143 kcal/mole at 200 mμ, 95 kcal/mole at 300 mμ and 68 kcal/ mole at 420 mμ. Although bond strengths vary widely depending upon the type of molecule, physical state, and reaction mechanism. It is apparent that UV light is sufficiently energetic to bring about many kinds of chemical transformations.

Quantum energy continues to fall off as wavelength increases. In the majority of herbicides, light of wavelength greater than about 450 mμ (blue-violet) representing energies less than 65 kcal/mole would not be expected to bring about chemical changes under most circumstances even if the compound was extremely efficient at absorbing energy in this region. Energy absorption by a molecule is dependent on its degree and wavelength on chemical structure; a majority of herbicides exhibit rather intense absorption in the UV region e.g maximum UV absorption of propham in water is 234 nm (Bailey and White, (1965)

Energy absorption is the prime requisite for a photo chemical reaction. In the UV region the absorbed energy causes excitation of non-bonded (n) or pi (π) electrons from its singlet ground state to the respective non-bonded or

antibonded empty orbitals of δ^*or $\pi.^*$ If unquenched, the excited singlet electrons may undergo intersystem crossing to a long-lived triplet state. The majority of herbicides exhibit intense adsorption in the UV region. Herbicides absorb low energy infra-red radiation which is sufficient only to increase the amplitude of vibration, rotation or tumbling of the molecule and is lost as heat. For a photochemical reaction the absorption of a photon leads to electronic excitations. Thermal energy, however, is distributed about all modes of excitation including translational, rotational, vibrational as well as electronic excitations. For a thermally electronic excitation, the relative number of particles, n_1 and n_2, in two equally degenerate levels 1 and 2, separated by an energy gap ΔE are given by Boltzman' distribution law (Bailey et al., 1978; Wayne, 1988);

$$\frac{n_2}{n_1} = e^{-\Delta E / KT} \qquad (4.3)$$

Where n_2 and n_1 stands for number of particles in the excited and ground state respectively, ΔE is the minimum amount of energy that a particle should possess for excitation to start a chemical change (activation energy); K, Boltzman's constant (1.3805×10^{-23} kj) and T, the absolute temperature.

The fraction, n_2/n_1 , of O_2 molecules, with energy of activation > 429 kj mol^{-1} at 1500 k is approximately 7×10^{-18}, from eq. (3.4) this is too small to lead to even the most efficient thermal reaction involving oxygen atoms. Many reactions such as this one that are not feasible thermally can, however, be initiated by light (Bailey et al., 1978).

4.2.2 Photochemical reaction; fate of electronic excitations

A molecule that has absorbed a quantum of radiation, becomes `energy rich' or `excited'. Absorption in the wavelength region of photochemical interest

leads to electronic excitations of the absorber. Once a molecule is promoted to an excited state, it does not remain there for long. There are several physical processes by which an excited species may return to the ground state (Rosen et al., 1970; Roof, 1982; Schwarzenbach et al., 1993).

1. A species in the first excited state may convert to higher vibrational levels of the ground state, and then "cascade" down through the vibrational levels of the ground state by giving off its energy in small increments of heat to the environment, called internal conversion.

2. An excited molecule (singlet) may directly or after undergoing intersystem crossing (triplet), drop to low vibrational levels of ground state all at once giving off the energy in the form of light. These luminescent processes are called fluorescence (singlet) and phosphorescence (triplet) respectively.

3. An excited species may transfer its excess energy to another molecule in the environment in a process called photosensitization or quenching.

4. Alternatively, there are a variety of chemical reactions that an excited species may undergo, depending on the structure of the chemical, its concentration, the neighbouring molecular species and kind of photolysis i.e. direct or sensitised (Plimmer and Kearney, 1969; Roof, 1982 ; March, 1985; Schwarenbach et al., 1993).

The extent of these various processes is somewhat dependent upon the medium on which the molecule finds itself; dissolved in a liquid, vapour phase, adsorbed on a solid (Choudhry and Webster, 1985).

4.3 PHOTOTRANSFORMATIONS IN WATER AND SOIL SYSTEM

The transformation processes in the aquatic environment include hydrolysis, oxidation, microbial degradation and photolysis. Two different types

of photochemical processes lead to the transformation of xenobiotics in the aquatic environment; photolysis may be direct or indirect.

4.3.1 Direct photolysis

In this type of photolysis a pollutant/xenobiotic absorbs light itself and undergoes transformation. Compounds that strongly absorb at wavelengths greater than 320 nm have the potential to rapidly undergo direct photolysis in sunlight (Zepp, 1982; Wolf et al., 1990).

The kinetic expression for direct photolysis in an aquatic system is given mathematically by first order rate expression (Roof, 1982; Zepp, 1982):

$$-\left(\frac{dP}{dt}\right)_{\lambda} = \phi_{\lambda} k_{a\lambda}[P] \qquad (4.4)$$

Where k_a equals $\Sigma k_{a\lambda}$, the sum for all wavelengths of sunlight that are absorbed by the pollutant. Whereas, ϕk_a is expressed in units of reciprocal time. Zepp and Cline (1977) provided an expression for the calculation of photolytic half-life ($t_{1/2}$) of chemical in sunlight:

$$t_{1/2} = \frac{0.693}{k_a \phi} \qquad (4.5)$$

Where ϕ is the quantum yield and k_a is the amount of light of a certain wavelength absorbed by the molecule.

Since the value of ϕ is not likely to exceed unity, it follows that:

$$t = < \frac{0.693}{K_a} \qquad (4.6)$$

The life time of chemical undergoing direct photo transformation in the aqueous environment depends not only on the absorption spectrum of the

compound but also on light intensity, spectral distribution of day light and penetration of light into water (Mansour et al., 1988).

In this context, Parlar (1980) reported that prediction of direct photolysis rate of xenobiotics sorbed to a solid sample is impeded by the fact that a compound may be shielded from the light. In addition the UV/vis spectrum of a given compound may be significantly different in the sorbed state as compared to dissolved state.

4.3.2 Indirect or sensitized photolysis

The second type of photochemical process is indirect photolysis; which follows two routes (Draper and Wolfe, 1987; Schwarzenbach et al., 1993). In the first route sensitised photodegradation by which a molecule, after absorption of light energy becomes excited and on contact with a xenobiotic, transfers the excitation energy to the molecule that undergoes transformations as it has acquired energy directly. The donors are called sensitizers (S) and acceptor molecules(A) quenchers, which undergo photoreaction.

$$Sens(S_o) + h\nu \quad \text{-----} \quad Sens\ (S_1) \qquad (4.7)$$

$$Sens(S_1) + ISC \quad \text{-----} \quad Sens\ (T_1) \qquad (4.8)$$

$$sens(T_1) + A\ (S_o) \text{ -----} \quad Sens(S_o) + A\ (T_1) \qquad (4.9)$$

For a photosensitization process to occur a sensitizer should have:

1. Efficiency of intersystem crossing (ISC).
2. The ability to transfer energy.
3. It should absorb light at higher wavelength than the acceptor will absorb i.e. the excited triplet state (T_1) of the sensitizer should be energetically higher than that of the receptor (Roof, 1982; Harriman, 1995).

In the second route, photoinduced degradation, involves degradation of the chemical through its reaction with photochemically generated intermediates

(Choudhry and Webster, 1985). Various transient reagents such as singlet oxygen (Zepp et al., 1977; Haag and Hoigne, 1986; Wayne, 1994), alkyl peroxy radicals RO_2 (Mill et al., 1980), and OH radical (Draper and Crosby, 1984; Zepp et al. 1992; Mazellier, 1997), aqueous electrons as well as superoxide anion O^{-}_2 and H_2O_2 (Draper and Crosby, 1981; Cooper et al., 1989) are responsible for indirect photolysis (Zepp, 1980). Some salts of zinc, iron , cobalt, could also enhance the photochemical process (Crosby and Li, 1969).

In natural water and soil these short lived species ($O^{\cdot}H$, $RO^{\cdot}_2$, $O_2{}^{1)}$ are formed by the absorption of light by humic or fulvic material, dissolved organic matter (DOM), nitrate, nitrite (Crosby, 1970; Gohre and Miller, 1983; Zepp et al. 1987 b ; Schwarzenbach et al., 1993; Aguer and Richard, 1996; Mabury and Crosby, 1996). In natural water humic substances are the largest fraction of dissolved organic matter (DOM 40-60%) and the molecular interactions of DOM are dependent on temperature, pH, ion strength and type of ions present in solution (Schlautman and Morgan, 1993)

Swallow (1969) calculated that sunlight wavelength below 325 nm could generate hydrated electrons in the oceans at the rate of as much as 3×10^{12} e^{-}_{aq} /gram/s, equivalent to 10^{19} e^{-}_{aq}/litre/h or about 0.026 mM of reducing power per litre for every daylight hour.

In natural water and soil surfaces the concentration of singlet oxygen, hydrated electrons and free radicals such as carbonate, chloride, alkoxy, alkylperoxide, and superoxide anion results from a balance between the rate of production and consumption by natural scavangers and on the concentration of the dissolved organic and inorganic matter (Draper and Wolfe, 1987).

Herbicides decompose under the influence of radiation; the factors involved include light sources and intensities, physical state, sensitisation , and physical and chemical properties of the compounds themselves. All regulate the rate of decomposition and nature of the products and all these factors should be

taken into account while predicting the photolytic fate of a xenobiotic. The wavelength of the light source involved also influences the rate of photodegradation with more change occuring at the lower wavelengths (Bertrand and Barcelo,1991; Romero, et al., 1994; Mazellier et al., 1997). Light attenuation in soil and natural waters can substantially reduce photolytic rates. In addition, vertical mixing can be important determinants of photolytic rates, especially in aquatic and soil environments, where light is completely absorbed in the upper layer (Miller and Zepp, 1983). In solution, pathways and rates of photochemical transformation depend on solvent (Kopf and Schwack, 1995), on solution composition e.g. pH oxygen concentration, ionic strength (Mill and Mabey, 1985). Further, duration of irradiation also effects the rate and routes of photolysis (Crosby, 1976).

The physical state of irradiated chemical has a direct effect on rate of photolysis e.g. the rate of acetone photolysis increases dramatically in going from solution to gas phase because radical recombination is minimized (Mill, 1980). Alternatively, photo-oxidation efficiency is favoured by the electron donation and inhibited by electron withdrawing nuclear substituents (Bocco et al., 1994).

Polarity of the solvent affects the wavelength of the absorption band. Polar solvents reduce the amount of energy associated with π–π^* transitions (red shift) as compared to the π-π^* (blue shift), e.g. in ketones (Wayne, 1988). In addition, solvents can stabilise certain intermediate species, resulting in the concentration of the product or they may associate with the reacting species thereby decreasing its formation; solvent may be involved directly in the photoreaction (solvolysis) (Mill, 1980).

The composition of water varies from source to source. The factors ininclude temperature, pH, conc. of oxygen, and the organic and inorganic content, the presence of nucleophiles, oxidising and reducing agents, natural

sensitisers and quenchers and hydrated electrons. All these may direct the photochemical fate of aquatic pollutant. Water itself may act as a medium for both oxidative, reductive , or nucleophilic reactions, but also participate as a reagent.

Other materials in the media may act as sensitisers or quenchers. Surfactants can act as sensitisers; they increase the herbicide solubility and shift its UV spectra to longer wavelength. They may also increase the total amount of energy absorbed and thereby increase the rate of photo-reaction (Tanaka, 1989). Dissolved organic matter/ humic acid may act as both sensitizers and quenchers. Humic substances contain ketonic and quinonoid functional groups which strongly absorb in the ultraviolet region and can transfer their excitational energy to chemicals present in the environment, thereby acting as photosensitisers. On the other hand the aromatic polycyclic structures in humic acid may act as quenchers by accepting the excitational energy of the environmental chemicals (Chaudhry, 1982).

4.4 PHOTOLYSIS OF CARBAMATE PESTICIDES

N- or O-aryl carbamates are reported to yield their respective aminobenzoates and hydroxybenzamides as major photoproducts on irradiation with ultraviolet light , similar to photo-Fries intramolecular rearrangements of aryl esters, anilides and ureides (Trecker et al., 1968). In this context they mentioned that polar solvents inhibited phenyl carbamate photo-Fries rearrangement due to the inter-molecular hydrogen bond between the carbamate and the protic solvent. Following the above, Beachell and Chang (1972) revealed that photolysis of ethyl N -phenyl carbamates involved photo-Fries rearrangment via homolysis of the amide bond and hydrogen abstraction. In addition the presence of oxygen and photosensitisers favour the formation of

related diethyl 4,4- azo benzene dicarboxylate. Moreover, Masilmani et al., (1976) investigated that photoconversion of N-phenyl cabamate was concentration dependent. At low concentration, aniline was the sole product through free radical hydrogen abstraction from the solvent, which in turn underwent dimerisation. At high concentration, however, photo-Fries rearrangement was enhanced by the cyclic or chain aggregates or hydrogen-bonded clusters of the carbamate molecule. Schwack and Kopf (1992) investigated photodegradation of propoxur in organic solvent and reported that photolysis was more rapid in the presence of protic solvent. Photolysis in isopropanol resulted in the formation of isopropyl phenyl ether. As a trace component 2-isopropoxy phenol was detected. In the presence of cyclohexene on the other hand photomineralisation was found to be the main degradation pathway. Climent and Miranda (1996) revealed that the photolysis of the carbamate pesticides, isoprocarb and promecarb, in aqueous solution resulted in the photo-Fries rearrangement to the ortho and para hydroxy benzamide.

Since photo-Fries rearrangements have been mentioned above for carbamate herbicides, a brief description of the photo-Fries reaction follows as given by Masilmani et al.,(1976) (For reaction see appendix).

Photo-Fries rearrangements are fairly general for aromatic systems linked to a carbonyl or sulfonyl group through a heteroatom, particularly O, N, or S. Scheme 1 depicts the overall reaction type with the mechanism involving initial light induced homolytic cleavage of the X-Y bond followed by rearrangement of the resulting biradical to the observed ortho and para products. In addition, cleavage products resulting from hydrogen abstraction by the intermediate radicals usually accompany the rearrangement products.

4.4.1 Phototransformations of chlorpropham/propham

The photolysis of chlorpropham/propham under ultra-violet light has been studied by several workers. Mitchel (1961) revealed that UV light caused little or no change in propham when 10 mmg of propham was irradiated on filter paper at 253.7 nm. In contrast to propham, chlorpropham exhibited photodegradation under the same conditions with the formation of four photoproducts which could not be identified. Afterwards, Crosby and Li (1969) and Crosby (1976) reported that propham was photolysed by two routes. By one route it decomposed through reversal of the reaction and provided phenyl isocyanate and 2-propanol. The other elimination reactions resulted in propylene and the carbamic acid which immediately underwent decarboxylation to aniline and carbon dioxide. Aniline and phenyl isocyanate then reacted to form s-diphenyl urea. Such reactions were recognised from its thermal decomposition. Crosby (1976) revealed that chlorpropham, barban and swep may be expected to photolyse in the same fashion as propham at least by the formation of correspo- nding isocyanate and aliphatic alcohol.

Wolfe et al., (1977) compared the rates of photolysis , hydrolysis and biolysis for propham and chlorpropham and reported that propham and chlorpropham underwent photolysis very slowly as compared to microbial degradation. Furthermore, Wolfe and co-workers (1978 b) revealed that propham and chlorpropham underwent direct photolysis in distilled water very slowly even during summer time, with a half life of 254 days for propham and 121 days for chlorpropham. They suggested the possibility of a photoreaction similar to photo-Fries type rearrangement. However, they were unable to isolate or identify potential photo- products, due to the formation of non-volatile, high molecular weight products by polymerisation.

Irradiation of 4 ppm solution of chlorpropham in distilled water at 25° C for 104 h yielded a half life period of 130 h with 3-hydroxy chlorpropham as the major photoproduct. The light source was a Hanovia 654 A°high pressure lamp, filtered with a Hanovia 7740 pyrex to simulate noon day sunlight. Extensive photolysis of the herbicide led to the formation of the polymeric material of molecular weight estimated at 3000 to 30,000. However, a 30 fold faster rate with half life of 3 h and a second major extractable photoproduct was obtained when a solution containing 124 ppm chlorpropham in 1 dm^3 of 2 % aqueous acetone was irradiated for 7 hours. The additional photoproduct was identified as 2-isopropoxy-carbonylamino-1,4-benzoquinine (Guzik et al., 1978)

Tanaka (1989) and Tanaka et al. (1981) reported that photodegradation of chlorpropham and propham in aqueous solution increased in the presence of 0.2 % heterogenous surfactant Tergitol TMN-10. In addition, the aryl surfactant X-100 demonstrated a significant photosensitisation effect in barban, chlorpropham, and dichlormate. They concluded that surfactant may cause an increase in photodegradation rate of the herbicides having low water solubilities. Further, Tanaka et al., (1985) revealed the formation of monohydroxylated biphenyl derivative under 300 nm sunlight lamp in aqueous solution, in a manner similar to the formation of chlorinated biphenyl from monuron or propanil. The photoreaction proceeded via the coupling of two herbicide molecules with concomitant loss of hydrogen chloride.

Finally Larson and Zepp (1988) reported that the carbonate radical generated by the photolysis of H_2O_2 at 313 nm in aqueous sodium bicarbonate (pH 8.3, 0.09 M Na_2CO_3) reacted with propham with a half life of 180 minutes suggesting that the carbonate radical may play a significant role in the removal of propham from the aquatic environment especially in carbonate rich water.

4.5 EXPERIMENTAL

4.5.1 Chemicals

Chlorpropham (CIPC), with 99.8 % purity was purchased from Greyhoud Chemicals Co.

Hexane, glass distilled, from Rathburn chemical company (Scotland).

Other solvents such as acetone, dichloromethane, and methanol were analytical grade and were used as such.

Silica gel 60 F- 254 was obtained from Fluka, Germany.

Acid washed sand was purchased from BDH .

4.5.2 Instrumental

The photoproducts were analysed by GC-Pye Unicam, PU 4500 chromatograph, equipped with a flame ionization detector and 2mm × 4 mm i.d. glass column, packed with 3 % OV-17 supported on 100/120 mesh WHP (Altech associates). All calculations such as integration were achieved using a spectra physics SP 4290 integrator.

The photochemical apparatus was a three-necked pear shaped vessel of 1050 cm^3 capacity equipped with a 125 watt Hanovia medium pressure mercury vapour lamp (England Hanovia lamp Ltd.) and a magnetic stirring bar. The lamp was housed in a double jacket quartz immersion well containing circulating water to prevent heat transfer to the solution being irradiated. A pyrex thimble was used as a filter to prevent radiation of wavelength shorter than 300 nm from reaching the sample. The following table shows ultraviolet output at outer wall of thimble, measuring at midpoint of the arc.

Table 4.1 Ultraviolet output at outer wall of pyrex thimble.

Wavelength	mw/cm^2	Wavelength	mw/cm^2
254	2.9	366	10.5
265	4.1	405	5.7
297	3.2	436	9.29
303	4.4	546	9.1
313	7.6		

4.5.3 Chromatographic conditions

GC conditions were as follows: oven temperature 175 °C, injection port and detector temperature was 200 °C and 250 °C respectively, nitrogen carrier gas flow rate 30 ml/min. Hydrogen and oxygen gases were at 30 and 80 ml /min respectively.

4.5.4 Identification of photoproducts

The mass spectra for identification of photoproducts were made on a GC and/or mass spectrometer using positive electron impact and direct injection technique.

4.5.5 Photolysis rate assessment

Photodecomposition rate of chlorpropham was assessed in aqueous media at different concentrations and in the presence of three different soil types.

4.5.5.1 Photolysis of chlorpropham in aqueous solution

100, 50, and 10 mg/ml of chlorpropham was dissolved using 1 ml of methanol to enhance the solubility and added to 1 litre of distilled water while stirring which was continued for half hour.The solution was filtered through a Whatman filter no.1 and then transferred to the predescribed vessel and subjected to irradiation at wavelength (253.7 nm) with constant stirring at room temperature (for three hours). Aliquots of 25 ml were withdrawn at zero time and at intervals of 10, 20, 30, 45 60, 90, 120, 150, and 180 minutes and were passed through the pre-activated cartridge at the rate of 5 ml/min to adsorb chlorpropham. The cartridge was then dried for 30 minutes under vacuum, eluted with 2 ml methanol to desorb chlorpropham and the eluate was analysed by GC-FID for the disappearance of chlorpropham or build up of any metabolites. The remaining amount of chlorpropham in each sample was determined as a percentage, based on the amount of chlorpropham detected at zero time sample. The photolysis rate plot was obtained by plotting the percentage of remaining chlorpropham against time. A controlled experiment was also conducted under dark conditions and analysed by GC-FID.

After termination of the irradiation, the remaining solution which turned into a pale yellow colouration, was extracted three times with 30 ml of dichloromethane in the presence of 5 g NaCl. The combined organic extract was washed with distilled water and dried over anhydrous Na_2SO_4, filtered, and

transferred into a 250 cm^3 round bottom flask and evaporated almost to dryness under vacuum. The brown-red residue was dissolved in 2 ml methanol and analysed on GC and/or GC-MS for any build up of photoproducts.

To examine the effect of different soil types and concentrations on the photolysis of chlorpropham in distilled water, three photoexperiments were done; 1- in the presence of arable soil, 2- in the presence of peat soil and 3- in the presence of acid washed sand. All these experiments were conducted with the following concentrations: 100, 50 10 mg chlorpropham per litre water and 20 grams of sterilised soil. Respective control experiments were also carried out under dark conditions and analysed by GC-FID.

4.5.5.2 Photolysis of chlorpropham in suspended soil

A standard solution of 100 mg/ml of chlorpropham was made in distilled water according to the pre-mentioned procedure.The solution was transferred into the photoreactor followed by the addition of 20 g of soil and irradiated at 253.7 nm, with constant stirring at room temperature for three hours. A 25 ml sample was taken as zero time reading and subsequent samples were drawn periodically as described earlier. The samples were filtered through Whatman filter no. 1. One ml of 0.1 M $CaCl_2$ was added to each sample prior to filtration in order to encourage aggregation of soil particles. The filtrate was passed through the activated C-18 cartridge which was eluted with 2ml methanol and analysed on GC to assess the rate of chlorpropham photolysis and/or detect any potential metabolites.

The photolysate bulk, which eventually acquired a brownish yellowish and pale yellow colour in the case of peat and arable soil respectively was filtered with the addition of 8 ml of 0.1M $CaCl_2$. The filtrate was processed as mentioned earlier, while the soil fraction was treated according to modified

Mcleese et al., (1982) method; soil was dried three times with 20 ml of acetone. Acetone from the washings was brought to at least 100 ml with distilled water and partitioned with hexane (3×10 ml). The dried soil was extracted with 150 ml of hexane in a soxhlet apparatus for 6 hours. The combined hexane extracts were evaporated on a roto-evaporator to dryness and dissolved in 2ml of hexane and analysed on GC and/or GC-MS for photodecomposition products.

4.5.6 Separation and identification of photoproducts

Thin layer chromatography was used for the separation of chlorpropham photoproducts. The photolysate concentrate from different experiments was carefully chromatographed on 20× 20 cm glass plates of 2mm thickness coated with silica gel 60 F-254 containing a fluorescent indicator. The prepared TLC plates were activated at 110 °C overnight before use. The plates were developed in a binary solvent system of hexane:diethyl ether 5:5 (v/v). To avoid overlapping bands TLC plates were developed twice in the same solvent system. After development the plates were examined under UV light. The bands were scraped off and eluted with methanol, evaporated by blowing N_2 and finally analysed by mass spectrometer.

The identification of photoproducts was done by comparison of the mass spectra of chlorpropham degradative products with the available literature. Due to the small amount of the products further confirmatory studies could not be carried out.

4.7 RESULTS AND DISCUSSIONS

The rate of chlorpropham phototransformation and estimation of its half life period was carried out by conducting photolysis of chlorpropham in

aqueous media. Effects of suspended matter and concentration on the rate and route of photolysis were also determined. The rate of chlorpropham photolysis was estimated by the detection of the percentage of chlorpropham remaining in solution at different intervals.

In this study water was chosen as a model medium because it is the one that is most available in nature. Since water is highly variable in composition; distilled water was selected to evaluate photolysis of chlorpropham The rate of photochange of chlorpropham in water at various concentrations is shown in Fig. 4.1(a,b). The chlorpropham photolysis in water could be fitted to a first order equation

$$dc/dt = -kC \qquad (4.10)$$

where C = concentration, t = time, and k is the first order rate constant. Using int- egrated form $c/c_0 = e^{-kt}$ of the equation and taking natural log (ln) of this equation

$$\ln c/c_0 = -kt \qquad (4.11)$$

which describes a linear relationship, plot of ln c/c0 against t gives a straight line with slope -k. The half life could be calculated from the relation using the equation $t_{1/2} = \ln (2)/k$. The half life values of chlorpropham in aqueous media and in the presence of suspended solids in water at different concentrations were obtained by plotting the natural logarithmic values of the remaining chlorpropham against time and applying linear regression to obtain the rate constant of photolysis.

After 3 h of irradiation the remaining amounts of chlorpropham in water were 2.05 mg at 180 min, 1.90 mg at 150 min and 1.68 mg at 30 min with corresponding half lives 0.54 h (32.54 min), 0.28 h (17.15 min), and 0.08 h (5.13 min) at 100, 50, and 10 mg/l respectively. Similar trends are seen in the case of all soils with the highest rate of change at lower concentration.(see Figures 4.1a,b-4.5a,b). The half lives for the photolysis of chlorpropham in the

presence of Midelnney (clay), Downholland (peat) and sand (acid washed) soil are 1.65 h, 1.51 h, 0.38 h, at 100 ppm, 1.48 h, 1.40 h, 0.27 h at 50 ppm, and 1.25 h, 1.17 h, 0.11 h, at 10 ppm respectively. The photoirradiation of chlorpropham in water and in the presence of three different soils at 100ppm is demonstrated in fig 4.5. It shows the highest rate of photolysis in the presence of acid washed sand and the lowest rate in the presence of Midelney (clay) soil. With Downholland (peat) soil the rate is more than that in the presence of Midelney (clay) soil but less than that in water and/or in acid washed sand soil. The faster rate of photolysis in the presence of acid washed sand is in accordance with the results obtained by Miller and Zepp (1979 b), who demonstrated that the photolysis rates of the dissolved pollutants were more rapid in turbid than in clear water. Enhanced photolysis rates were attributed to increased diffuseness of light caused by scattering.

Similarly, Mansour et al., (1988) reported that photolysis of carbetamide in aqueous solution was more rapid in the presence of humic acid than in water alone. Further soil organic and inorganic materials are reported to accelerate the photodegradation by energy transfer reaction, by photoinduced oxidation, or by efficient light scattering (Miller and Zepp, 1979 (a,b); Roof, 1982; Zepp , 1982; Larson et al., 1991; Katagi, 1993; Kochany and Maguire, 1994). In this context, Mathew and Khan (1996) reported that the half-life of herbicide metolachlor in water under UV irradiation at pH 7 was longer in the absence of soil constituents. The nature of suspended/ dissolved material had strong effect on rate of photolysis; the amount of metolachlor degraded was more in the presence of mineral soil ($t_{1/2}$ = 1.03 h at unadjusted pH) and fulvic acid ($t_{1/2}$ = 1.07 h at pH 7) than with water alone ($t_{1/2}$ = 2.58 h at pH 7). They argued that iron and/or Ti present on the surfaces of soil minerals might have generated hydroxyl radicals and other active oxygen species that assisted in increasing rate of photodegradation of metolachlor.

Figure 4.1(a): Rate of phototransformation of chlorpropham in water at different concentrations.

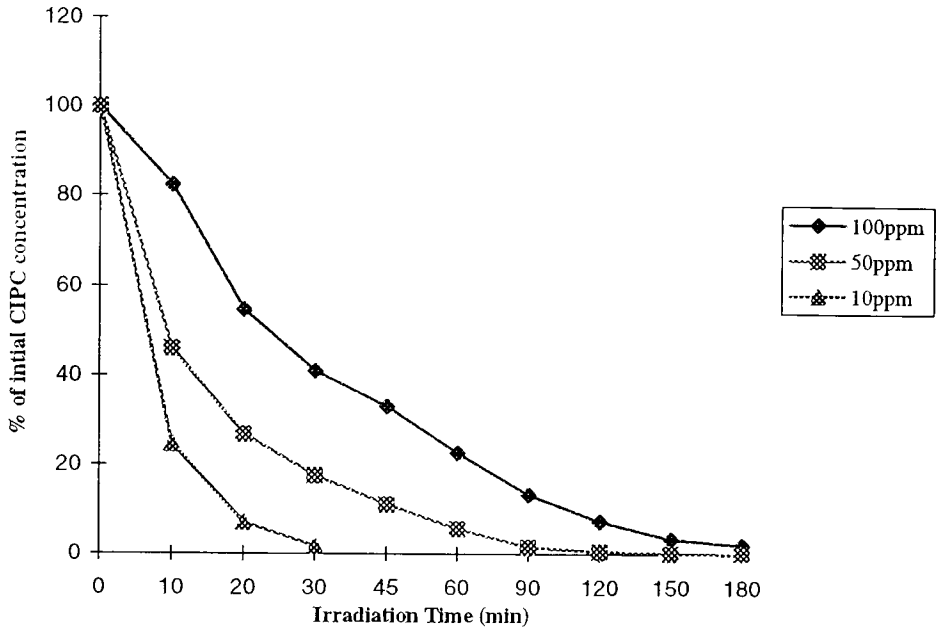


Figure 4.1 (b)

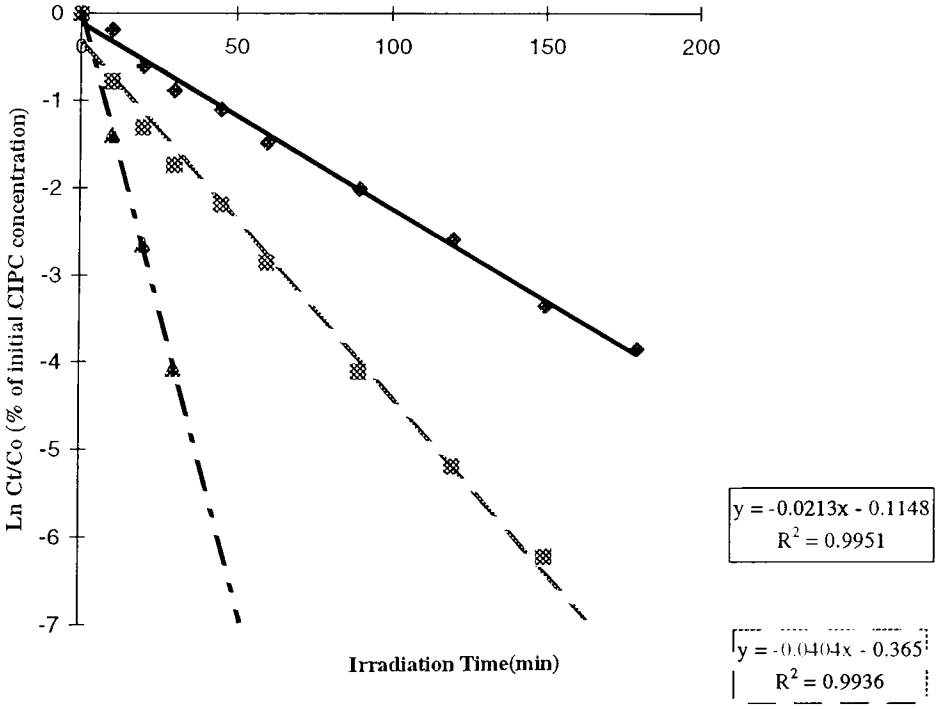


Figure 4.2 (a): Rate of chlorpropham photoirradiation in the presence of Downholland soil at different concentrations.

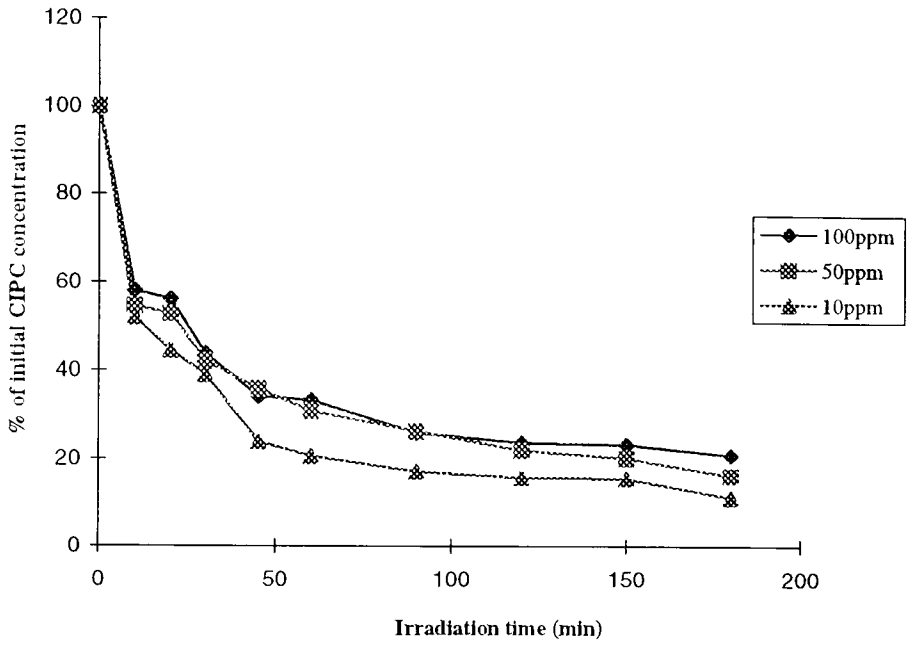


Figure 4.2 (b)

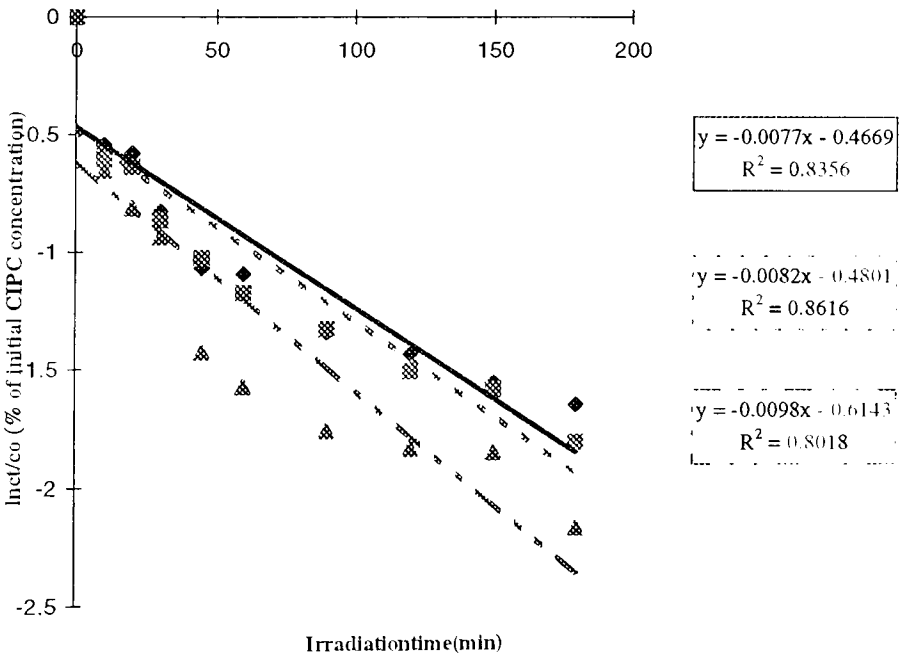


Figure 4.3 (a): **Photochange of chlorpropham in the presence of Midelney soil at different concentrations**

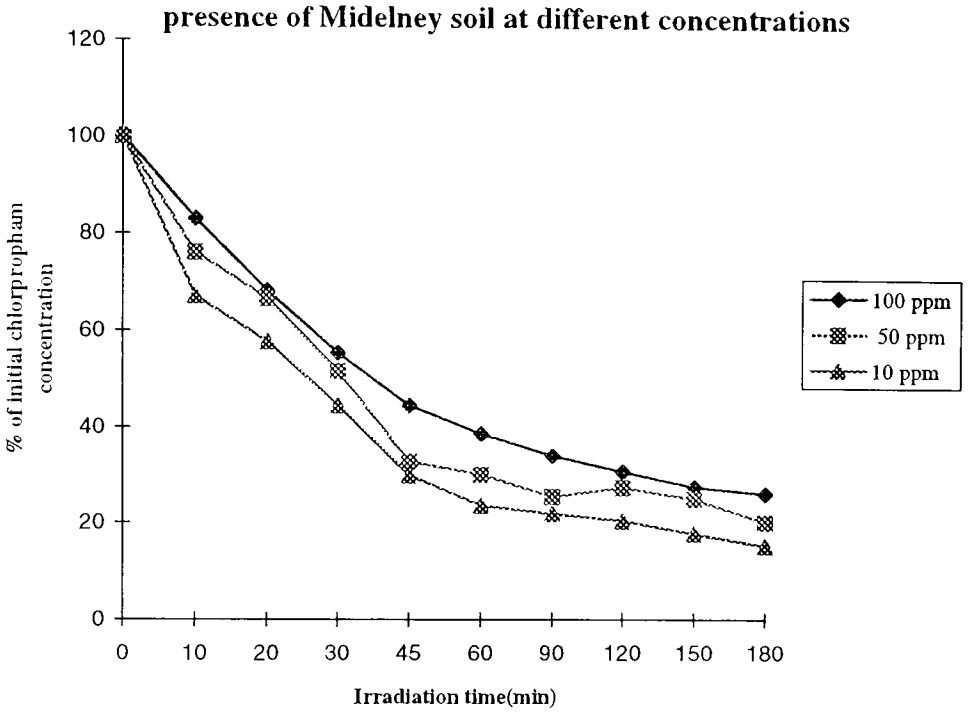


Figure 4.3 (b)

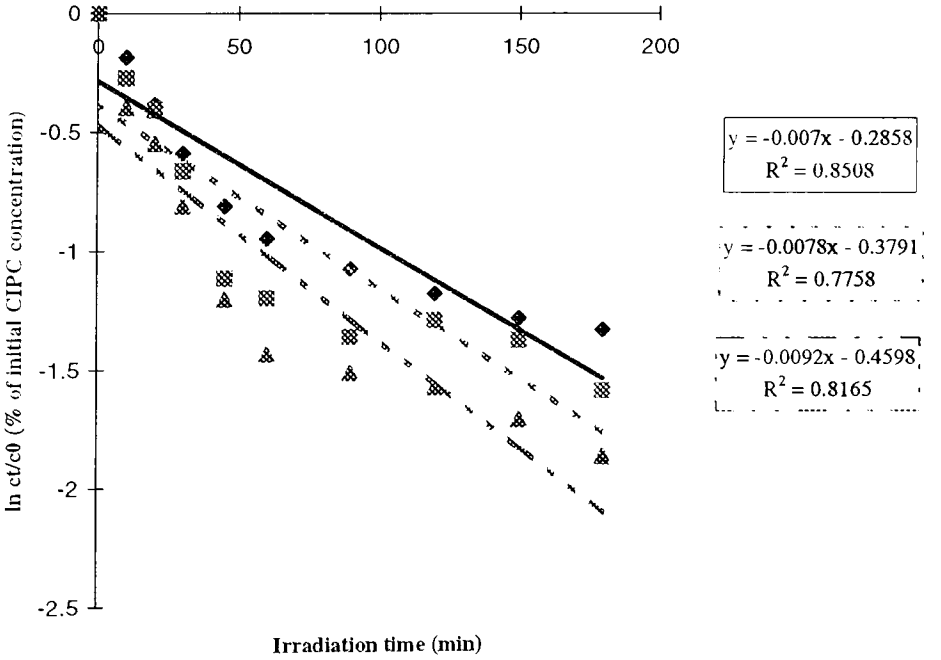
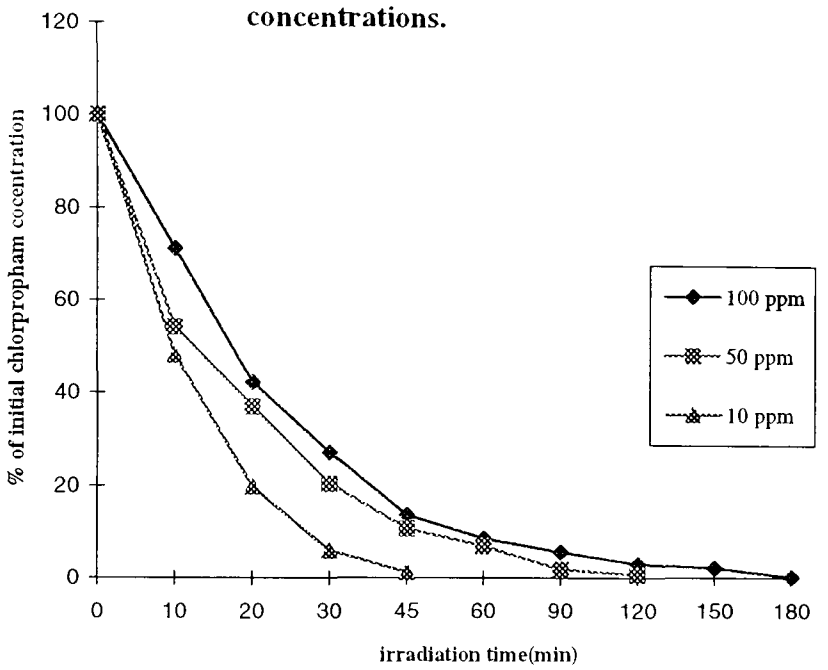


Figure 4.4 (a): Rate of photoirradiation of chlorpropham in the presence of acid washed sand at different concentrations.



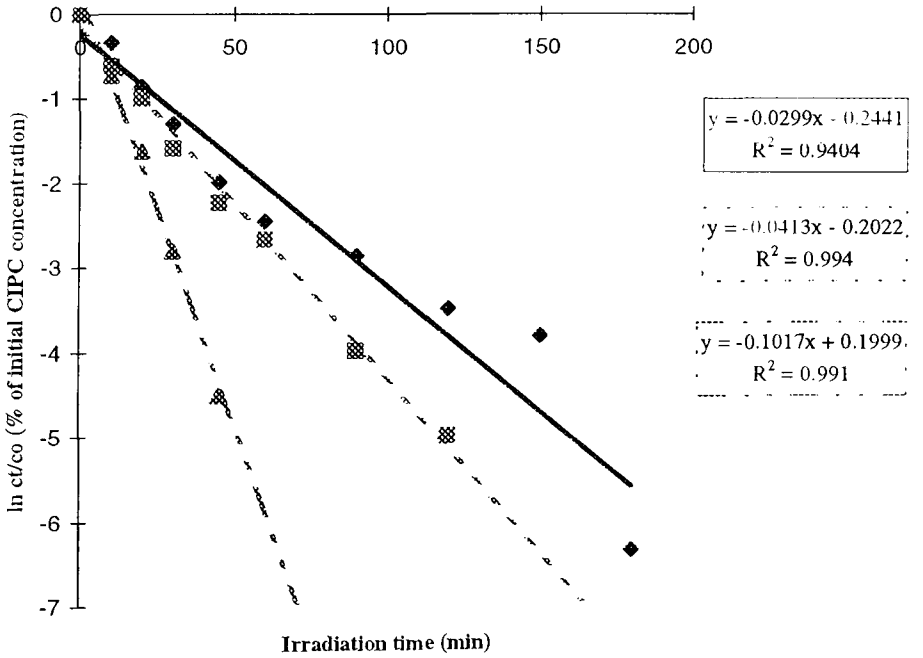


Figure 4.4 (b)

Figure 4.5 (a): Rate of photolysis of chlorpropham in water and in the presence of different soils at 100 mg/l.

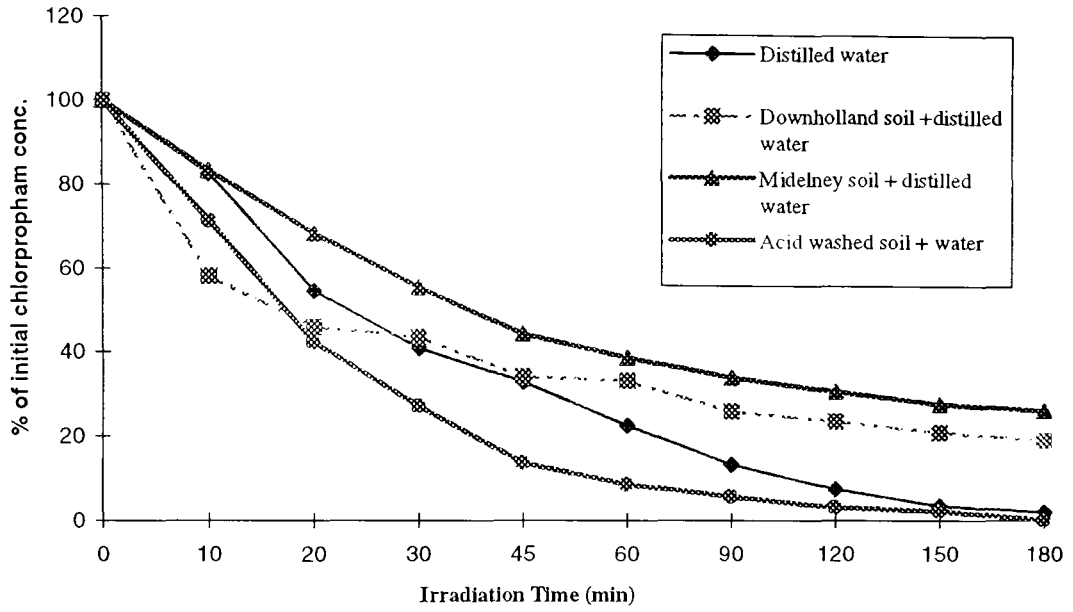
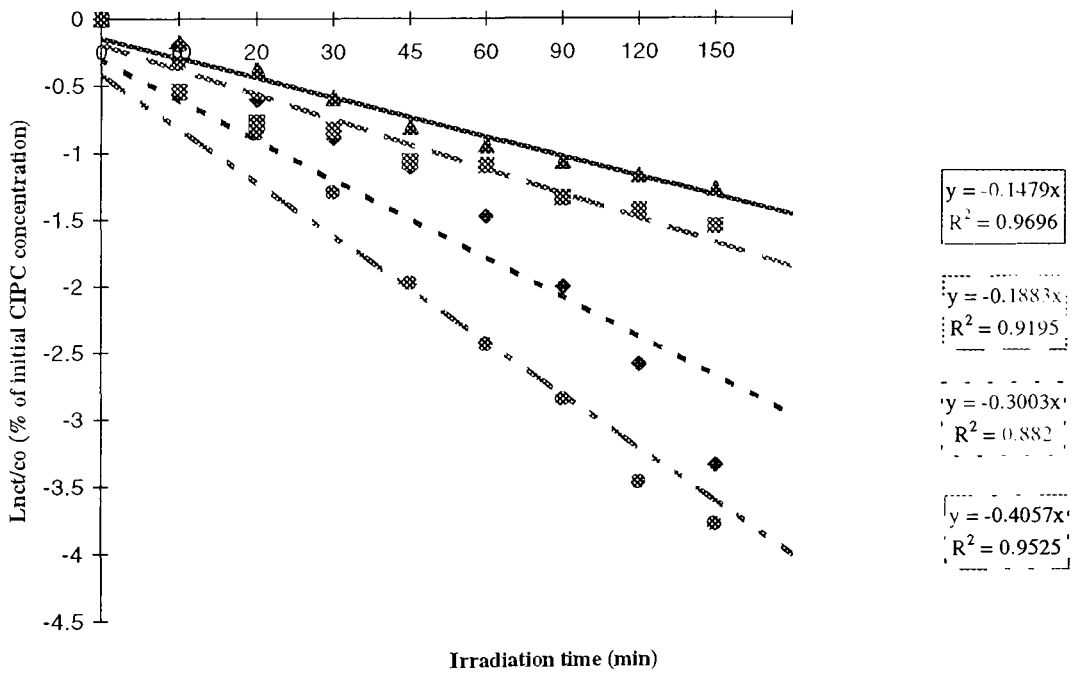


Figure 4.5 (b)



Furthermore, Chiron et al., 1995 reported similar results insofar that the addition of 4 mg/l humic matter to natural water solution of alachlor decreased the half life by 56 minutes (84 min.) as compared to that in natural water alone (140 min.) They interpreted that reaction proceeds through the formation of ·OH radicals. As the soil is an acid washed sand with low organic matter content, it seems that increased diffuseness of light caused by scattering is a more favourable mechanism than ·OH radical generation for the increased rate of photolysis of chlorpropham in the presence of acid washed sand. The inhibition of photolysis in the case of Midelney
(clay) and Downholland (peat) soil could be attributed to both, the shielding effect of suspended solids from available light. and/ or the adsorption of chlorpropham on the soil.

The two soils, Downholland (peat) and Midelney (clay) vary considerably in their organic matter content (LOI 31.2 % and 14.7 % respectively). In Downholland (peat) soil photolysis was initially considerably faster i.e. 42 % and 57 % of the applied chlorpropham was photolysed in first 10 and 20 minutes respectively: then it slowed down and only 22 % was photolysed in the next 150 minutes. It seemed that in first 30 minutes both processes i.e. photolysis and adsorption compete for chlor- propham with adsorption dominating and subsequently leaving less chlorpropham available for photolysis.

Zepp and Schlotzhaver, (1981) reported that adsorption of chemicals to clays during photolysis may interfere with the kinetics/rate of photolysis. A parallel explanation could be afforded for an even slower rate of photolysis in the presence of Midelney (clay) soil. However, adsorption did not seem dominating in the photolysis process since Midelney soil is low in organic matter content as compared to Downholland soil i.e. LOI 14.7% and 31.2% respectively. The lesser adsorption efficiency of Midelney soil was depicted by

the studies described in Chapter 2. Alternatively, the shielding effect of light could be responsible for the decreased rate of photolysis. Midelney soil is silty clay, with 53% silt as compared to Downholland which contains only 2.2% silt; consequently more shielding of light by the high silt content of Midelney soil resulting in lesser photolysis as compared to Downholland soil can not be ruled out. In this context, Crosby (1976) reported that the thickness of the liquid layer is of prime importance in effecting the rate of photolysis. The high concentration of suspended material influences the absorption of light and consequently the degree of photodegradation (Samanidou et al.,1988).

Similarly, Oliver et al, (1979) revealed that rate of photolysis of methoxychlor was considerably decreased in the presence of two soils with a large difference in organic carbon content (21% and 4.1%). The extinction coefficient (3.3) at the wavelength used was in close approximation to the ratio of the slope of the half-life vs. concentration plot (3.8). Consequently, they believed that suspended solid shielded methoxychlor from the available light. In this regard, Kochany and Maguire (1994) reported that addition of 5 mg/l of DOM increased the half-life of metolachlor in lake water from 11 to 22 days and 77 to 231 days in summer and winter respectively ; DOM retarded the photodecomposition by a factor of 2-3 depending on season. Furthermore, Aguer and Richard (1996) reported that addition of humic acid to a solution of fenuron resulted in a decrease of the rate of fenuron disappearance as photons could be absorbed by both fenuron and humic acid resulting in a reduced rate of fenuron disappearance.

The photodecomposition of chlorpropham in water and in the presence of different soils at 253.7nm yields 3-hydroxy propham as a major product, alongwith the dechlorinated counterpart, propham. The formation of 3-hydroxypropham has already been reported by Guzik (1978). In Figure 4.6 the

Figure 4.6: Photolytic OH-IPC formation in distilled water at different concentrations of chlorpropham

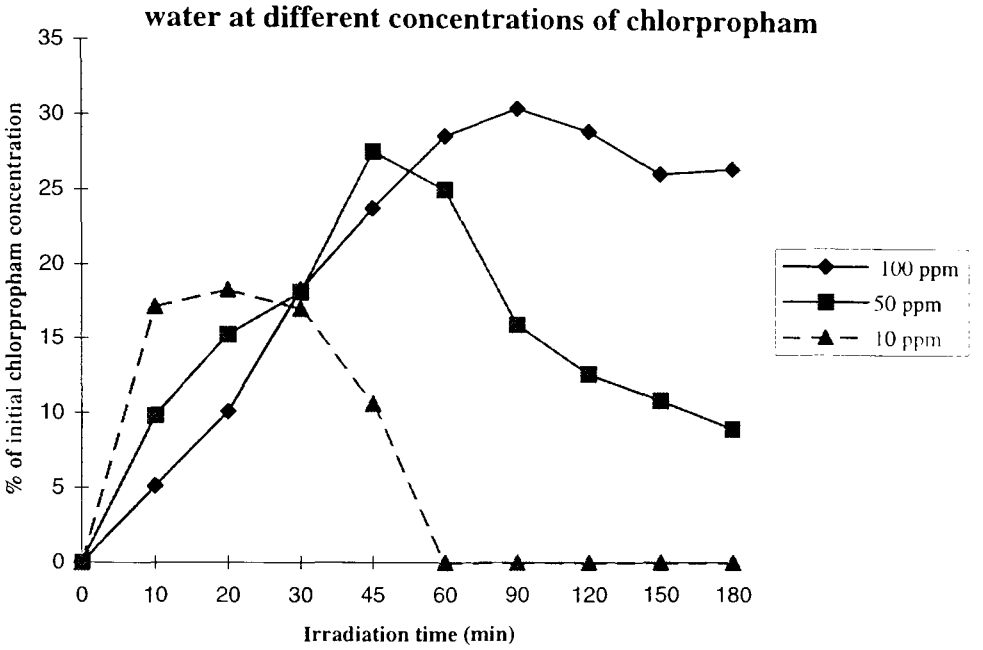


Figure 4.7: Rate of formation of OH-propham in the presence of Downholland soil at different concentrations of chlorpropham

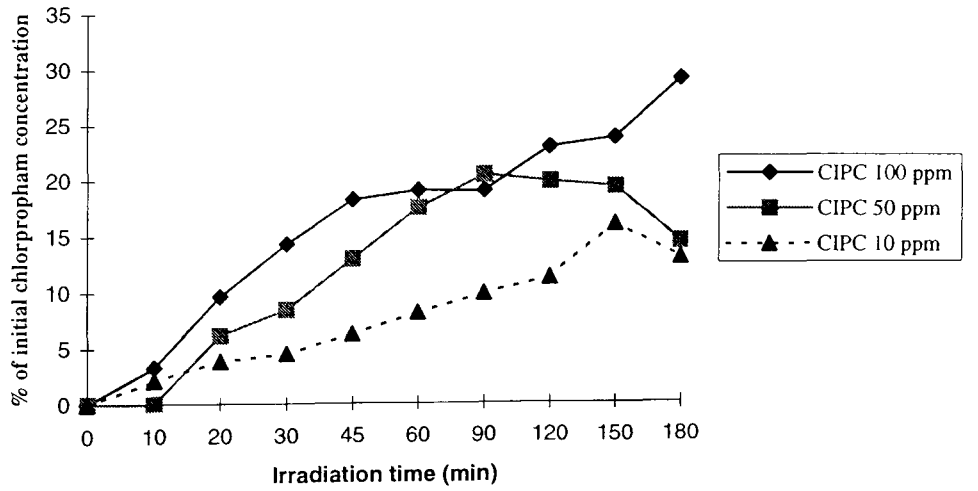


Figure 4.8: Formation of OH-propham in the presence of Midelney soil at different concentrations of chlorpropham

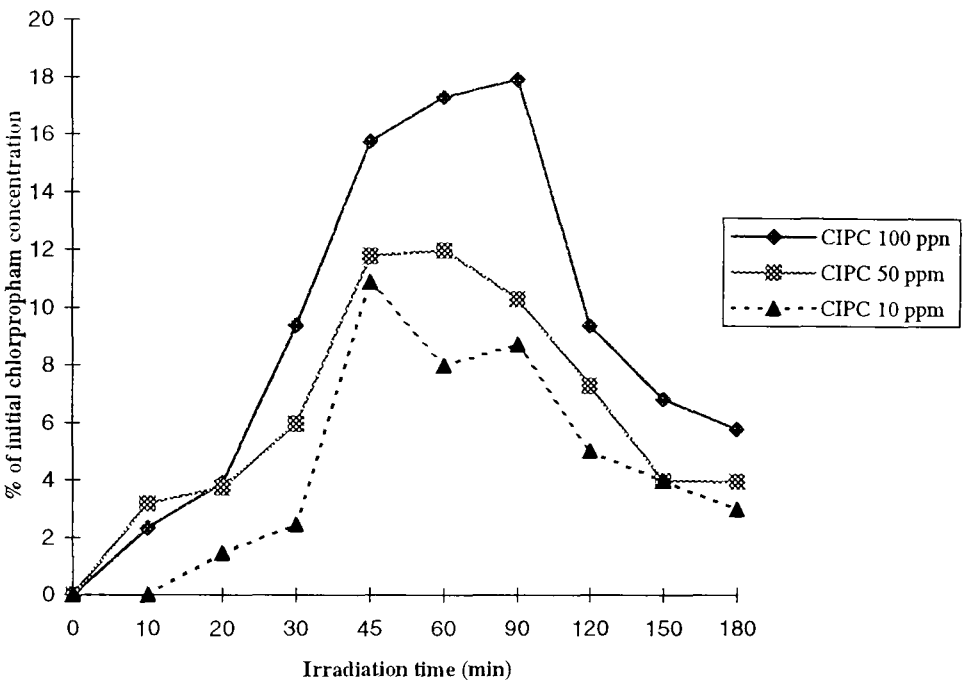


Figure 4.9: Profile of OH-propham formation in the presence of acid washed sand at different concentrations of chlorpropham

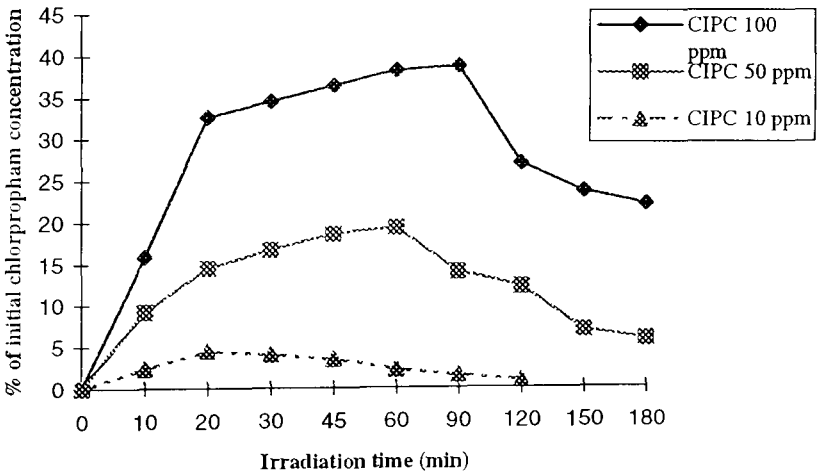


Figure 4.10: Formation of OH-propham in the presence of different soils at 100 ppm chlorpropham.

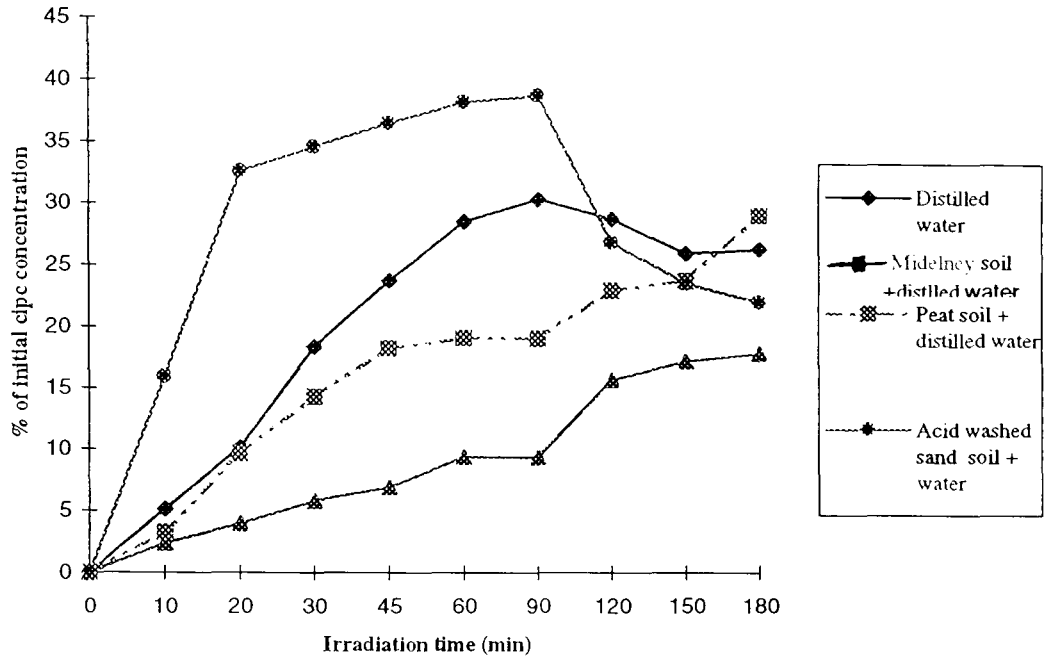
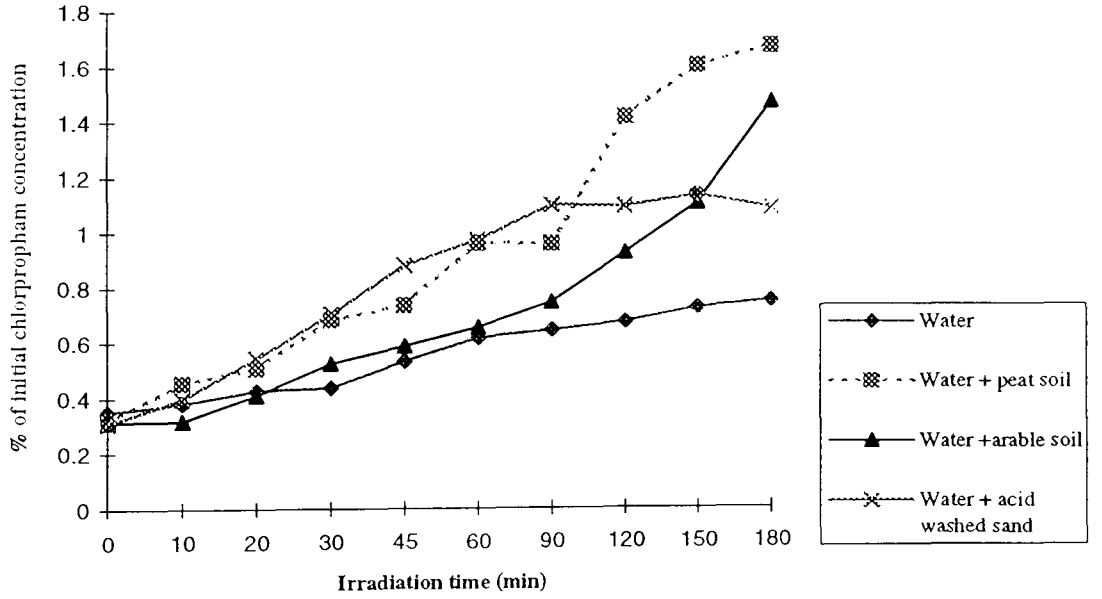


Figure 4. 11: Fomation of propham (IPC) during photolysis of chlorpropham (100 ppm) in the presence of water and different soils



formation of hydroxy chlorpropham at various concentrations in water is presented. Respective curves for Midelney (clay), Downholland (peat), and Acid washed sand soil are given in Figures 4.7-4.9. Profiles of formation of hydroxypropham at different concentrations revealed that formation of the compound is concentration dependent, i.e. more hydroxypropham is formed at higher concentrations of chlorpropham. It is in accordance with the results demonstrated by Masilmani et al., (1976). Comparison of the rate of formation of 3-hydroxychlorpropham in water and in the presence of the soils at 100 ppm (Figure 4.10) revealed that the rate of formation was in the following order acid washed sand > water > Downholland (peat) > Midelney (arable) at all concentrations. This trend may be due to the same reason mentioned earlier, the different soil type can shield chlorpropham from available light to different extents thus effecting the rate of photolysis. The decrease in the concentration of OH-propham with time further reveals that the compound is vulnerable to degradation by UV light.

From the presented data it is apparent that chlorpropham phototransformation is concentration dependent with the greatest rate at lowest concentration. It is evident that the nature of soil predominantly effects the photolytic behaviour of chlorpropham. The presence of different soils effect the rate and route of photolysis differently depending on to the extent to which the soil could shield chlorpropham from the available UV light.

4.8 IDENTIFICATION OF PHOTOPRODUCTS

Distilled water and three soils in aqueous media were selected to investigate the photolytic fate of chlorpropham and to compare the effect of soil type on the nature of chlorpropham photoproducts in aquatic environment.

The identities of the photoproducts in the investigated media were determined from retention time of the available standards and either by matching their mass spectra with mass spectra of chlorpropham photoproducts and metabolites which are available in literature or were identified by GC-MS library search. The selected mass and/or GC-MS of chlorpropham photoproducts are presented in Figure 4.12.

In distilled water, after concentration and chromatographic separation by TLC followed by gas chromatographic, mass and GC-MS analysis, the photolysate yielded a variety of products; 3-hydroxyropham at M/Z 195 as a major product and propham of M/Z 179 as a second major product. The formation of 3- hydroxy propham is in agreement with the results obtained by Guzik (1978). The presence of a hydroxy group was confirmed by the formation of acetate derivatives while the meta position of the hydroxy group was inferred from its mass spectrum as compared to that reported by Guzik (1978). In addition, the absence of a mass fragment at 107 which is typical of iminoquinone from ortho or para derivative only, confirmed the meta position.

The formation of propham was confirmed by comparing the GC retention time as well as by the comparison of the MS of the synthetic compound with that of the photoproduct.

Among other products identified from water were; 3-chlorophenyl isocyanate (M/Z 153); 3-chloroaniline (M/Z 127) and the methyl ester of chlorpropham. These compounds were identified from the GC-MS spectra as compared to their literature analogues using GC-MS libraray search.

The formation of 3-chlorophenyl isocyanate is similar to the formation of phenyl isocyanate during the photolysis of propham (Crosby, 1976). In addition Paramauro et al., (1993) reported 4-chlorophenyl isocyanate as a major reaction intermediate during the light-induced degradation of monuron in aqueous solution containing TiO_2 suspension.

Anilines have been reported as photolysis products of N-phenylcarbamates in organic solvents (Masilmani et al., 976) as well as during the photolysis of phenylurea in aqueous solution (Tanaka et al., 1982 a,b). However, Guzik (1978) did not observe the formation of chloroaniline during the photolysis of chlorpropham in water. This was based on the inability to detect chloroaniline by extraction/TLC AR of the photolysis solution after it was made strongly basic.

The formation of methyl N-3-chloro carbanilate involves substitution of a methoxy group for the isopropoxy one in chlorpropham. This may have resulted either thermally on the GC column or photochemically due to the presence of methanol which was used to dissolve chlorpropham. Similar formation of methoxy analogues of the photodegradation products of cyanazine in distilled water has been reported by Durand et al., (1991), as they dissolved the pesticide in methanol for solubility reasons. Alkoxy substitution for N,N-dimethyl group in monuron, a phenylurea herbicide has been reported photochemically in alcohol solution or thermally on the GC-column during its analysis (Gaylord and Stroog, 1953; Lee and Fang, 1971; Mazzochi and Rao, 1972)

Formation of propham in this study resulted from the dechlorination of the meta carbon-chlorine bond. In this context, Kearney et al., (1987) stated that photodehalogenation reactions can occur in a variety of ways, the most common being homolytic bond cleavage to give a chlorine radical and an organic radical. Reaction with oxygen or nucleophilic solvent, either immediately or subsequently to electron transfer affords alcohol. Pinhey and Rigby (1969) also supported homolytic cleavage during the photolysis of chlorobenzene to benzene. A less likely possibility is the reduction of the organic radical resulting in the formation of an aryl cation intermediate. This aryl cation formation produced by the heterolytic cleavage of the meta carbon-chlorine bond has been

reported by Miller et al., (1979) during the photolysis of 3,4-dichloroaniline in water. Alternatively, under certain conditions the proper donor is present, the halogenated molecule can undergo photoinduced electron transfer. The resultant radical anion can lose an halide anion and upon reaction with solvent forms alcohol.

Another product in this study was monohydroxy biphenyl with M/Z 372. The same product has been reported by Tanaka et al., (1985) during the photolysis of chlorpropham in aqueous solution. The formation of monohydroxy biphenyl proceeds via photo dechlorination to yield isopropyl 3-hydroxycarbanilate. Thus, photoexcited chlorpropham , preferentially couples with isopropyl 3-hydroxycarbanilate from the photolysis of chlorpropham to yield a hydroxylated biphenyl compound. However they suggested that sunlight is capable of producing chlorinated biphenyl from carbamate herbicides in aqueous solution.

The formation of a chlorpropham-propham diamer has not been reported in the literature but similarities did exist for structural analogues; Tanaka et al., (1982 (a); 1984) revealed the formation of monuron-fenuron and fenuron-fenuron biphenyl upon UV-irradiation of monuron in aqueous solution. They also observed the formation of biphenyls from carbamates and anilide herbicides in aqueous solution. Investigating the mechanism of formation of diamers these authers suggested three possible pathways. As a first possibility they proposed generation of phenyl radicals which add readily to an intact molecule forming a fenuron-monuron molecule which is in agreement with the formation of W8 in this study or to its dechlorinated product forming a fenuron-fenuron product and as a last possibility the coupling of photoexcited fenuron molecules. They supported the first pathway for the formation of chlorinated biphenyl and rejected the photocoupling of two photoexcited fenuron molecules. They failed to obtain a fenuron-fenuron molecule which is also in

Table 4.2(a): Fragment pattern of chlorpropham photoproducts in water accompanied by their assigned name and as determined by massand/or GC-MS.**

Code	Proposed name	M^{+} ; M/Z (% intensity)
W_1	3-chlorophenyl Isocyanate	153(100); 125(32); 90(32); 63(20); 50(5); 45(4)
W_2	3-chloroaniline	127(10); 92(10); 65(26); 63(10); 45(4)
W_3	Propham (IPC)	179(36); 137(32); 120(26); 93(100); 77(10); 65(22); 43(100); 41(28)
W_4	Methyl-N-chloro carbanilate	185(100); 187(15); 153(38); 140(50); 99(80; 63(12); 59(44)
W_5	3-OH propham**	195(20); 153(20); 136(12); 109(57); 81(18); 65(8); 59(4); 53(13); 43(100)
W_6	Chlorpropham**(CIPC)	213(29); 171(18); 154(16); 127(58); 99(6); 90(4) ;75(4); 63(4);43 (100)
W_7	Monohydroxy biphenyl**	372(10); 312(10); 286(8); 270(8); 226(10); 200(18); 154(5); 109(6)
W_8	Chlorpropham-propham** Diamer	390(8); 330(8); 218(10); 182(5); 109(6); 69(8); 57(12); 43(100).

Table 4.2 continued(b): In Midelney soil and water fraction.

Code	assigned name	$M^{`+}$; M/Z (% intensity)
AW_1	Benzene, 1-chloro-4-isocyanato	153(100); 125(33); 98(2); 90(38); 76(4); 73(4); 63; (24); 52(20; 49(4)
AW_2	m-Chloroaniline	127(100); 100(8); 92(15); 73(3); 65(30); 63(13); 46(8)
AW_3	Propham(IPC)	179(37); 137(29); 120(23); 93(99); 77(3); 65(15); 43(100).
AW_4	Methyl N-3-chloro Carbanilate	185(100); 153(43); 140(71); 126(12); 99(27);90(13);75(6); 63(15); 59(50)
AW_5	Chlorpropham+**	213(27); 171(17); 154(15); 127(59); 111(3); 99(7); 75(4); 63(8); 43(100)
AW_6	3-OH propham**	195(23); 153(24); 136(17); 109(61); 92(2); 81(16); 65(7); 59(4);53(11); 43(100)
AS_1	2-isopropoxy carbonyl amino-1,4-benzoquinone (IBQ)	209(5); 167(7); 150(9); 121 (6); 123(2); 104(10); 95(3) 43(70); 41(71)
AS_2	Chlorpropham**	213(22); 185(2); 171(15); 154(19); 127(54); 99(10); 91(8); 75(10); 59(7); 43(100)

AS = arable soil fraction AW = water fraction of arable

Table 4.2 continued(c): In Downholland soil and water fraction

Code	assigned name	M`+ ; M/Z (% intensity)
PW_1	Benzoxazole-2-one	135(100); 107(6); 79(20); 68(10); 52(34)
PW_2	3-hydroxyphenyl** isopropyl carbanilate	195(51);153(45); 136(29);109(89); 81(15); 68(4); 65(6); 43(100)
PW_3	Chlorpropham**	213(12); 171(9); 154(10); 127(37); 99(5); 93(8); 75(3); 63(8); 100)
PS_1	2-isopropoxy carbonyl** amino-1,4-benzoquinone (IBQ)	209(16); 167(12); 150(20); 123 (10);109(20); 97(27); 95(29); 85(33);69(47); 59(88); 43(100); 41(55)
PS_2	Chlorpropham**	213(12); 171(10); 154(9); 127 (37);99(8);92(3);90(6);75(4);63(9);43(100)

PS = Peat soil fraction PW = water fraction of Peat

Table 4.2 continued(d): In acid washed sand soil and water fraction(SW)

Code	assigned name	M`+ ; M/Z (% intensity)
SW_1	3-OH propham**	95(29); 154(31); 136(21) 109 (73) ;91(2); 81(15); 65(7); 57(5); 52(13);43(100)
SW_2	Chlorpropham**	213(11);179(9); 137(8); 127(19); 93(28); 74(5); 65(8); 60(19); 59 (6); 43(100); 41(37).
SW_3	Monohydroxy biphenyl**	372(7); 312(7); 286(8); 270(5); 226(9); 200(18); 109(3); 95(7); 81(11); 69 (17); 55(23); 43(100)
SW_4	Chlorpropham-propham** diamer	388(8); 328(4); 302(4); 260(7); 216(5); 199(16); 95(8); 81(12); 69(20); 59(25); 43(100)

agreement with the present study as there was no evidence of formation of the propham-propham diamer. Table 4.2 (a, b, c, d) represents the mass spectral data of chlorpropham photoproducts in water, Midelney (clay), Downholland (peat) and sand (acid washed) soil respectively. The photolysis of chlorpropham in distilled water in the presence of Midelney (clay) soil yielded six photoproducts from solution fraction and only one from the soil fraction. The products identified were the same as obtained from distilled water alone with the exception of monohydroxy biphenyl and chlorpropham-propham diamer. The formation of two dimeric compounds; 2-isopropoxy carbonylamino-1,4-benzoquinone (IBQ) and benzoxazole-2-one in Midelney (clay), Downholland (peat) and Downholland (peat) soil respectively. The absence of both dimers from the solution fraction of Midelney (clay) soil may be attributed to the adsorption effect of the soil, which left less chlorpropham available for photolytic conversion. In this context, Zepp (1982) stated that photoproducts in water are concentration dependent and dimerisation occurs efficiently only at higher concentrations.

The photoirradiation of chlorpropham in the presence of the Downholland (peat) soil resulted in the formation of only two compounds from the solution fraction; 3-hydroxypropham, and benzoxazole-2-one. and one from the soil fraction; 2-isopropoxycarbonylamino-1,4-benzoquinone (IBQ).

Benzoxazole 2-one has not been previously reported as a photoproduct of chlorpropham. However, Still and Herrett (1976) stated that, the hydroxylated chlorpropham metabolite in soyabean plants, underwent rapid thermal degradation to yield 5-chloro-2-benzoxazolinone. Accordingly, the formation of benzoxazole-2-one could be attributed to the thermal cyclization ofmass spectral data of chlorpropham photoproducts in water, Midelney (clay),

a monohydroxylated propham ortho to the nitrogen group. The ortho position of the OH group was deduced from the presence of a mass fragment at M/Z 107, which corresponds to imminoquinone from the ortho to para position only.

The only product from the soil fraction of both Downholland (peat) and Midelney (clay) soil was identified as 2-isopropoxycarbonylamino-1,4-benzoquinone (IBQ). The conformation of the structure was done by comparing its mass spectra to that reported by Guzik (1978). The author reported the formation of this compound during the photolysis of chlorpropham in aqueous solution in the presence of 2% acetone. Since acetone has been suggested as a triplet sensitiser that can mimic the sensitising effect of dissolved materials present in natural water (Train, 1975)

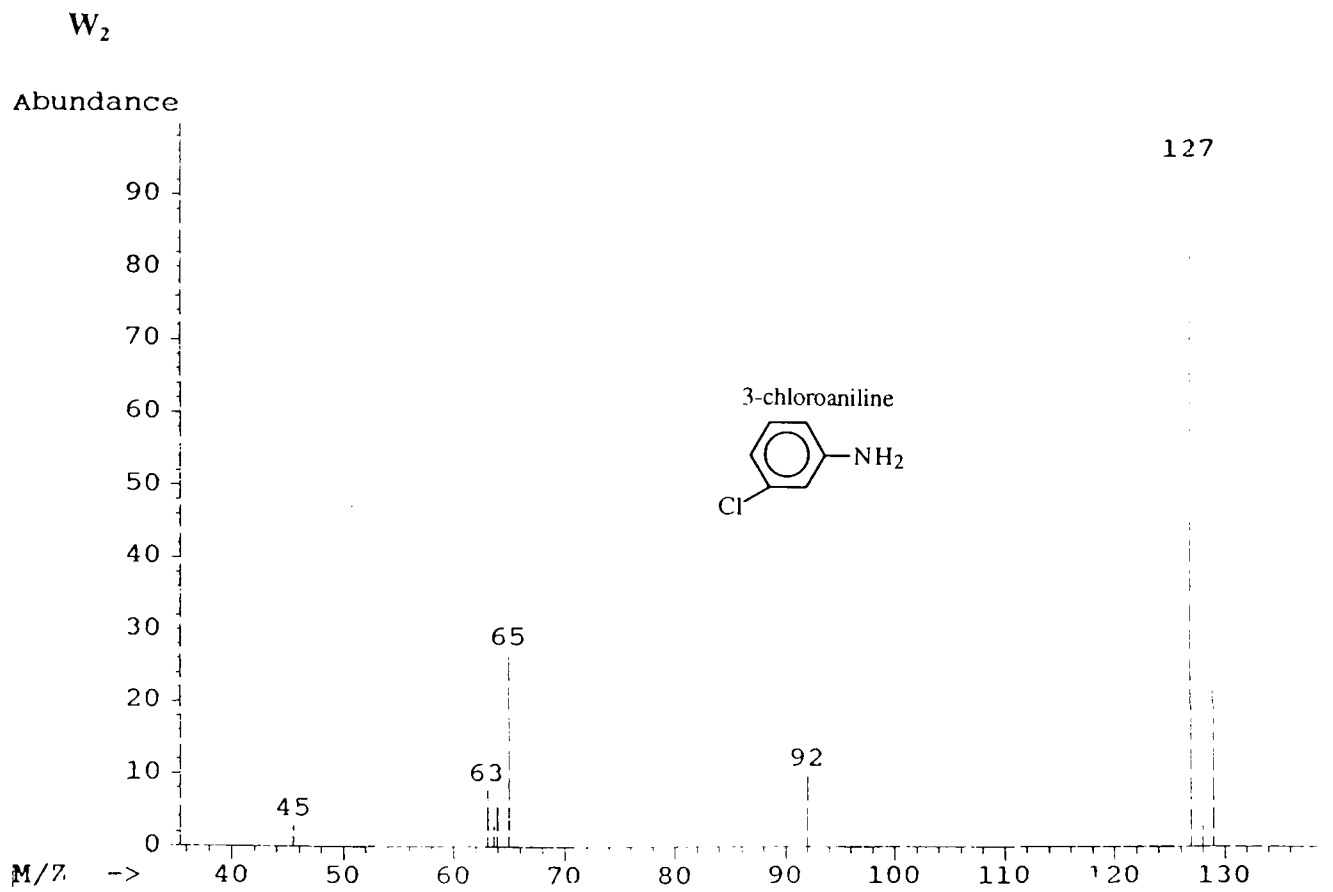
the possibility of formation of IBQ in the presence of Downholland and Midelney soils, particularly in the presence of peat soil could not be ruled out as Downholland (peat) is high in organic matter content (31.2% LOI).

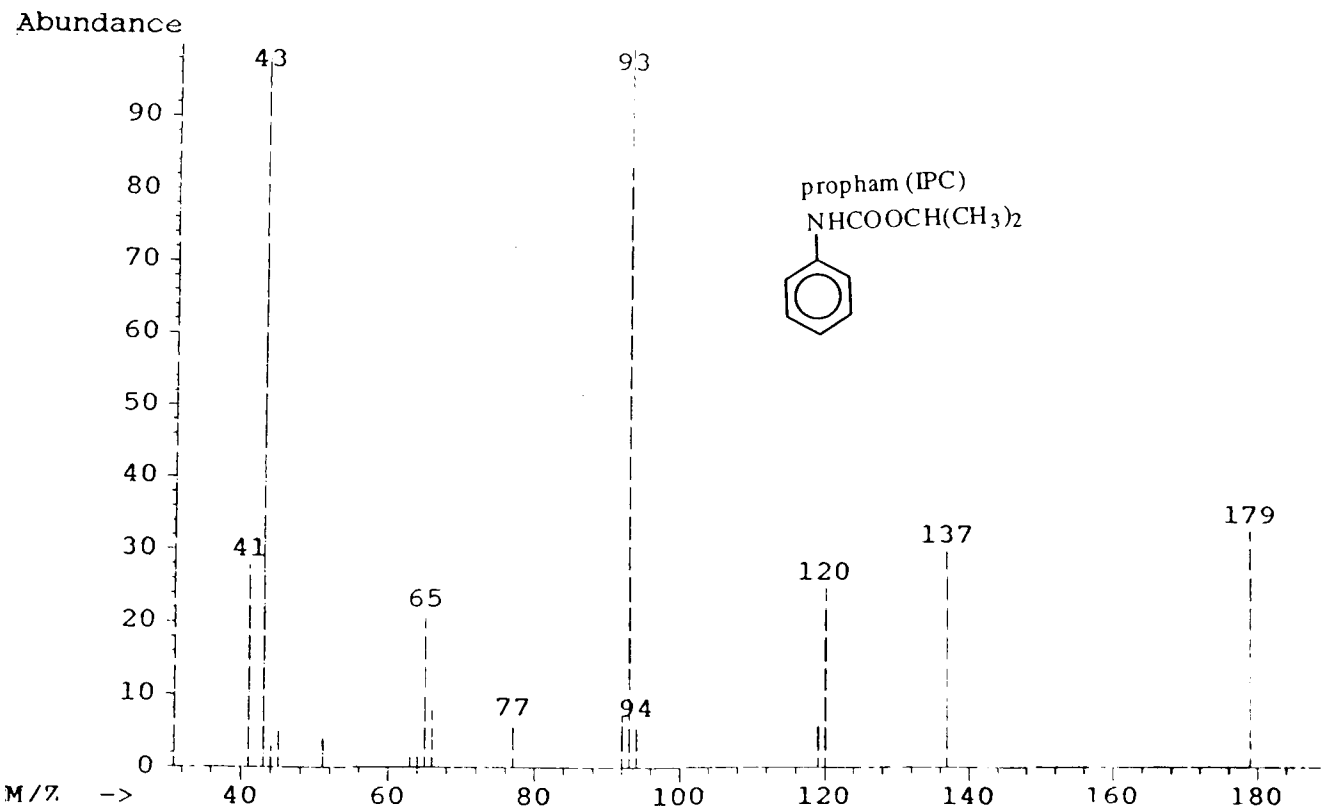
Photolysis of chlorpropham in aqueous solution in the presence of acid washed sand afforded three products; 3-hydroxypropham; monohydroxy biphenyl; and chlorpropham-propham diamer. The formation of diamers as a major product suggested that the nature of the soil had an influence on the photolytic route, in that, acid washed sand, which had lower adsorption efficiency than Midelney (clay) and Downholland (peat) soil could afford more chlorpropham for photolysis and resulted in the formatiom of diamers. Further support for the possibility came from the observation that the rate of formation of hydroxypropham was most rapid in the presence of acid washed sand as compared to that in the presence of other soils in the following order Acid washed sand > water > Downholland (peat) > Midelney (clay) (Figure 4.10). The same trend was seen for the disappearance of chlorpropham.

Conclusion

It appeared from this study that in all the treatments photolysis followed first order kinetics with respect to concentration of chlorpropham. The highest photoirradiation of chlorpropham in the presence of sand soil was persumably to be due to low adsorption of chlorpropham and increased diffuseness of light caused by scattering. For Downholland (peat) and midelney (clay) soils, in addition to the shielding effect of clay and silt contents of the two soils, adsorption of chlorpropham on the soils reduced the amount available for photolysis and so the rate of photolysis. Further, the formation of propham and OH-propham is concentration dependent. It appeared that significant amounts of OH-propham are formed during the photolysis of chlorpropham. However the decrease in concentration of OH-propham with time is quite interesting and indicated that the particular compound itself is also susceptible to degradation by UV light. A number of chlorpropham photoproducts were obtained. Identification of the photoproducts revealed that chlorpropham undergoes dechlorination, hydroxylation, alkoxylation, and rearrangement reactions under the effect of UV light.

Figure 4.12: Selected GC-MS/mass** spectra of chlorpropham photoproducts.





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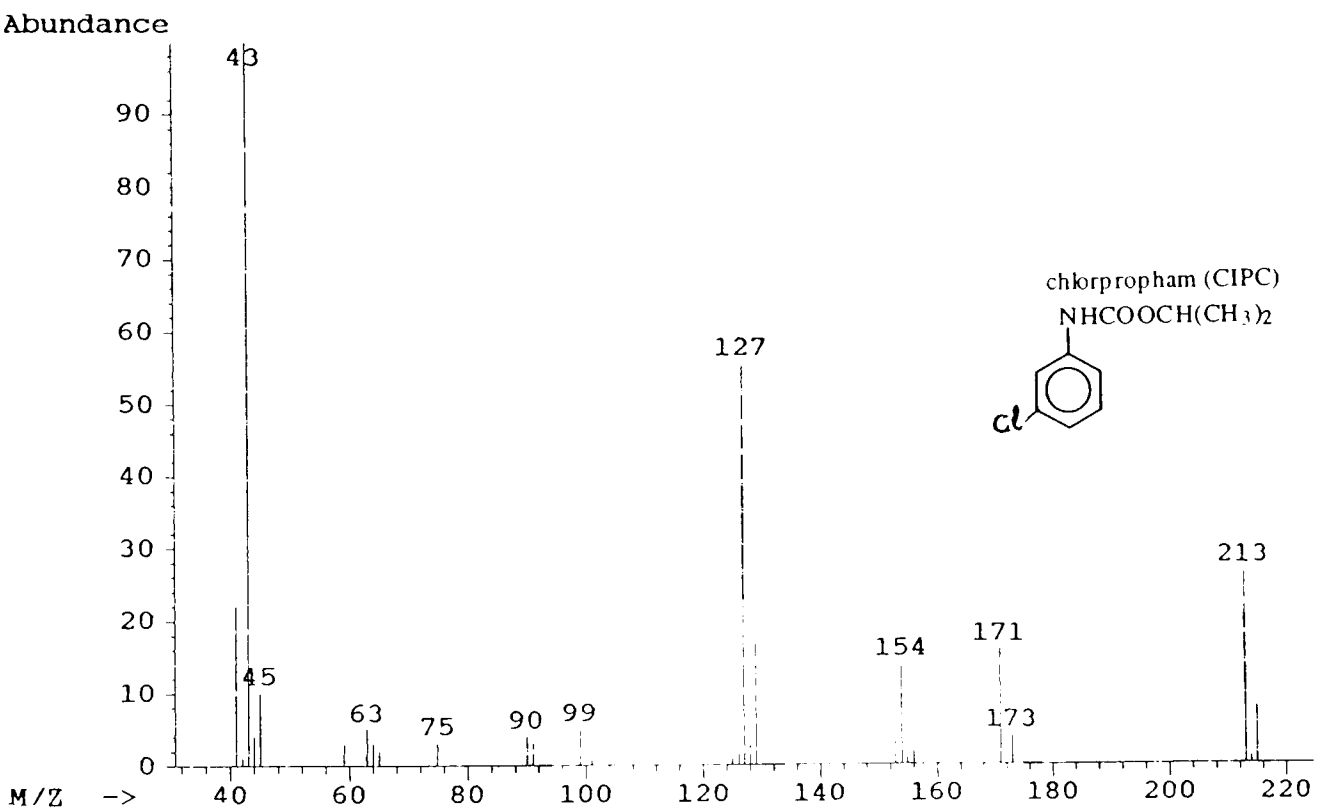
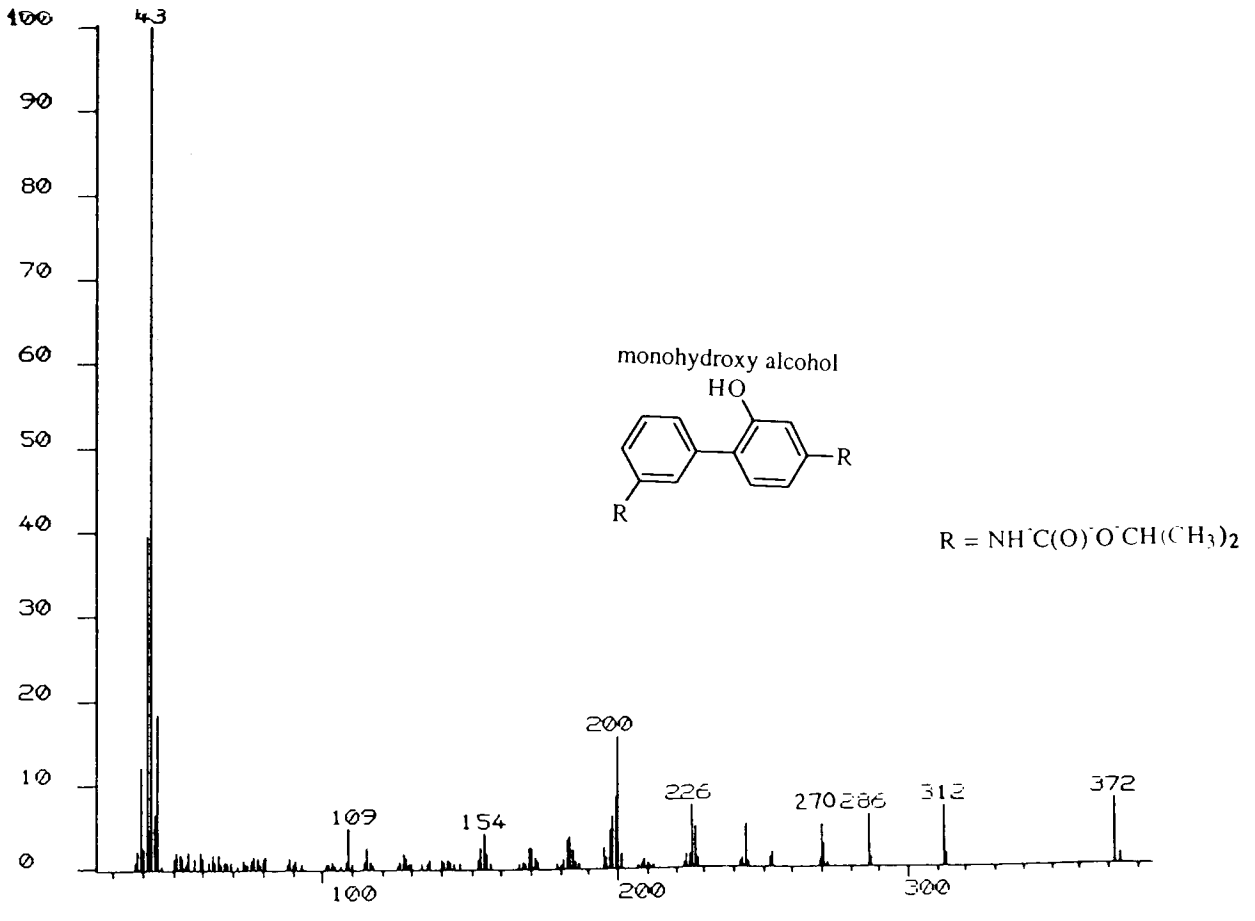
W_6

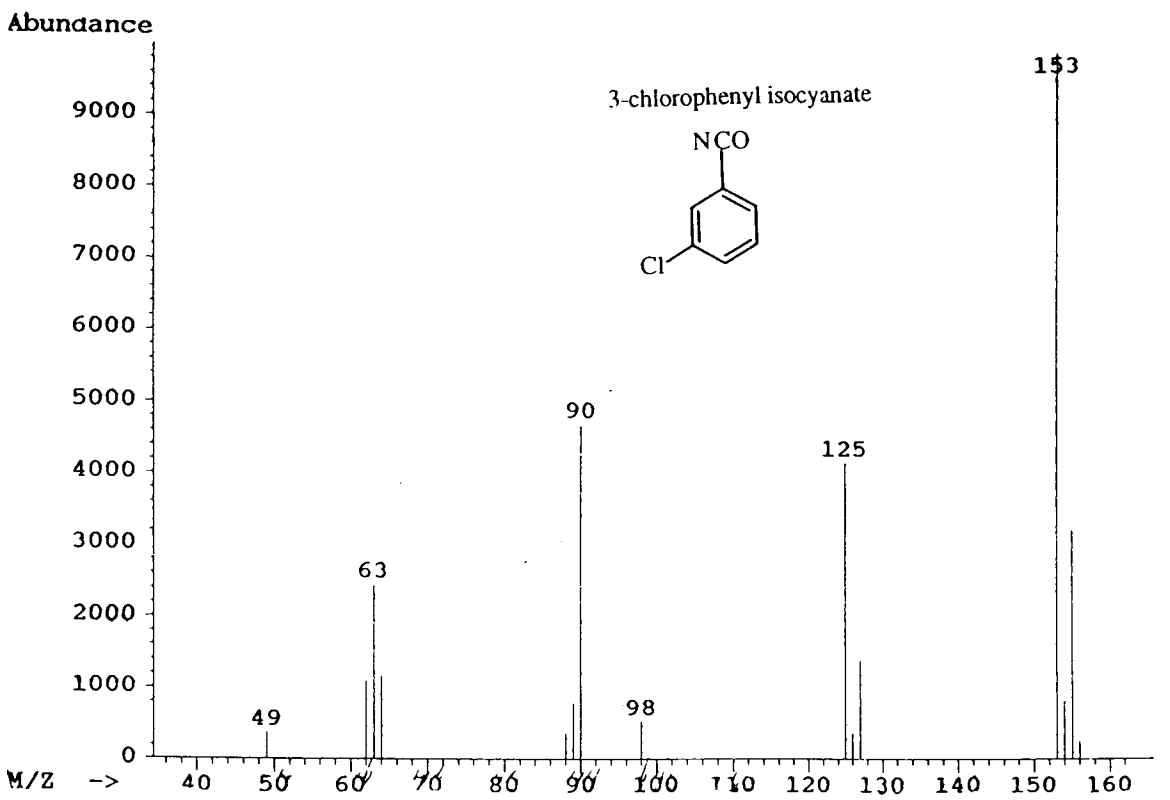


W_7

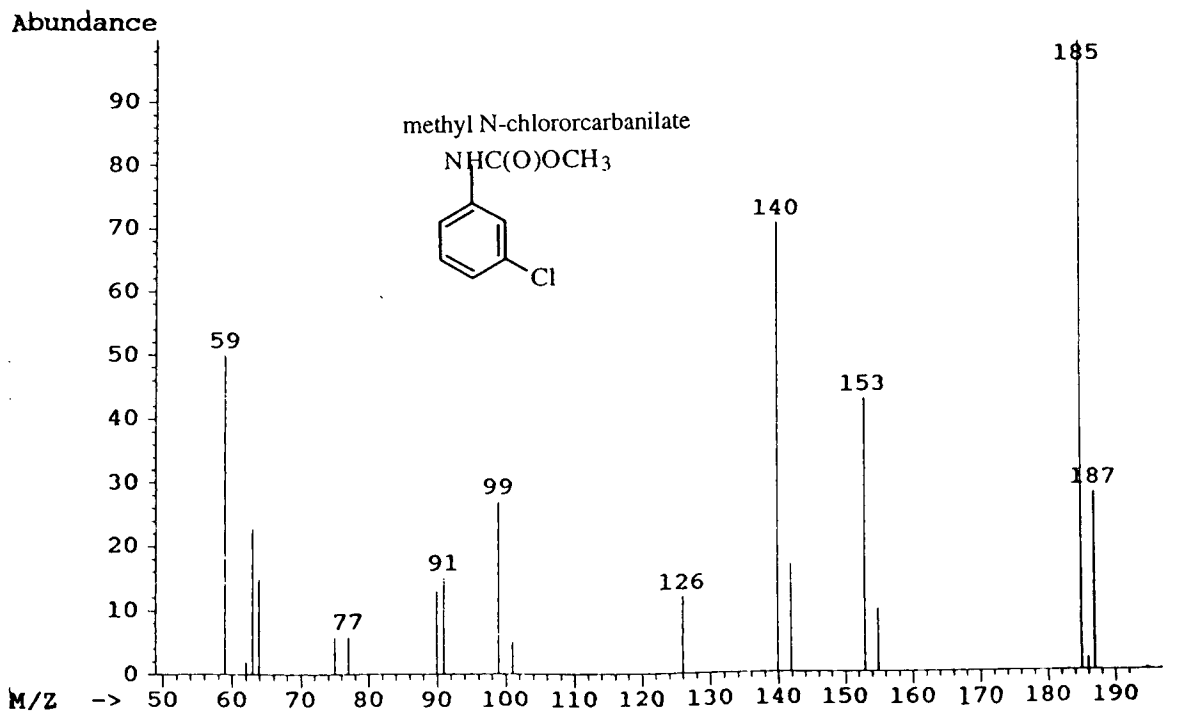


Continued.4.12:

AW_1



AW_4



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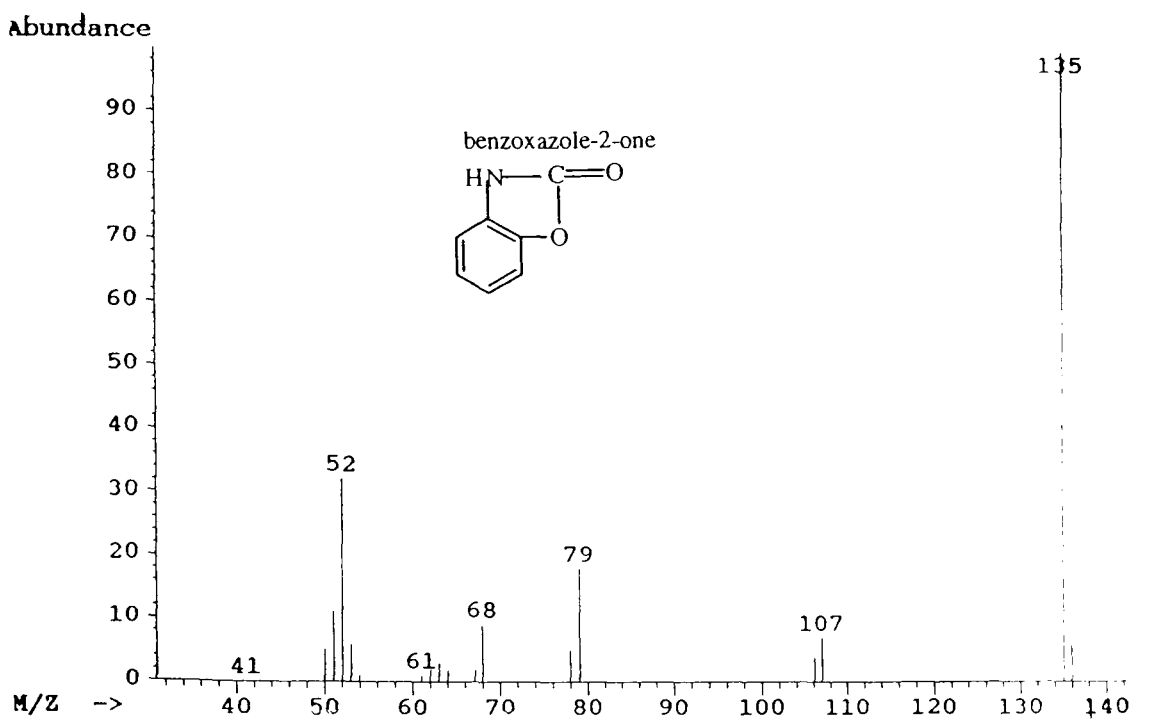
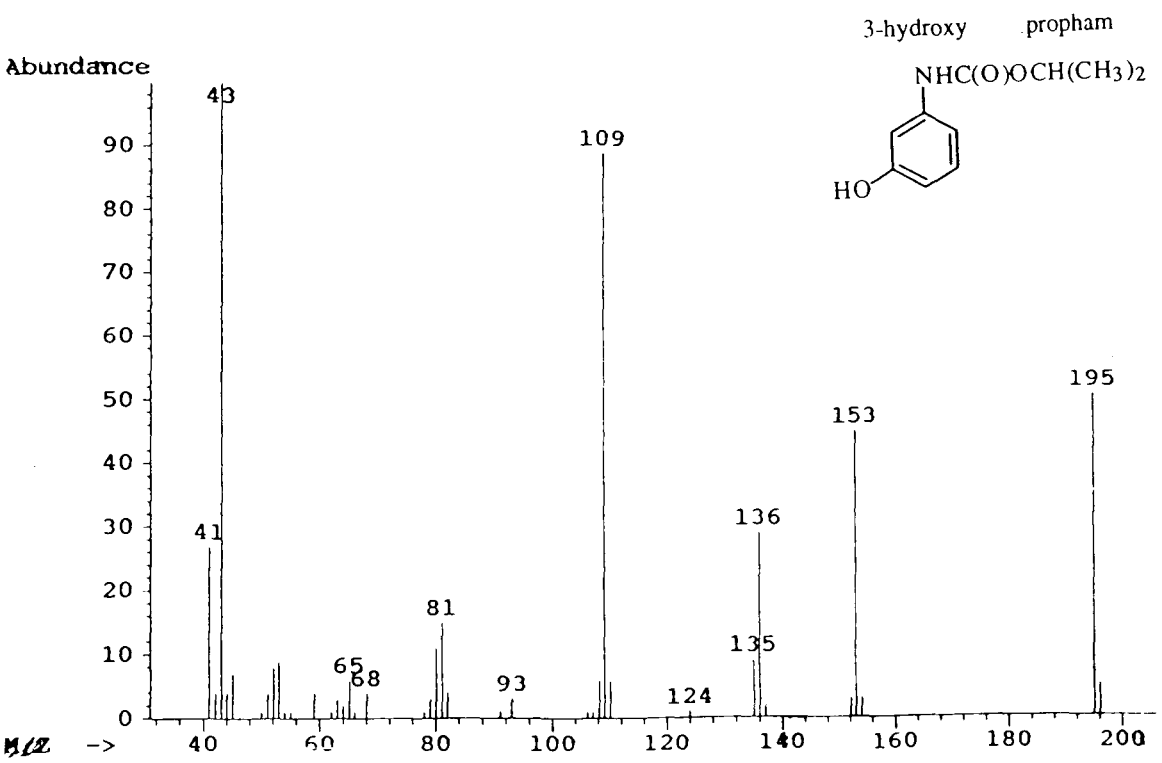
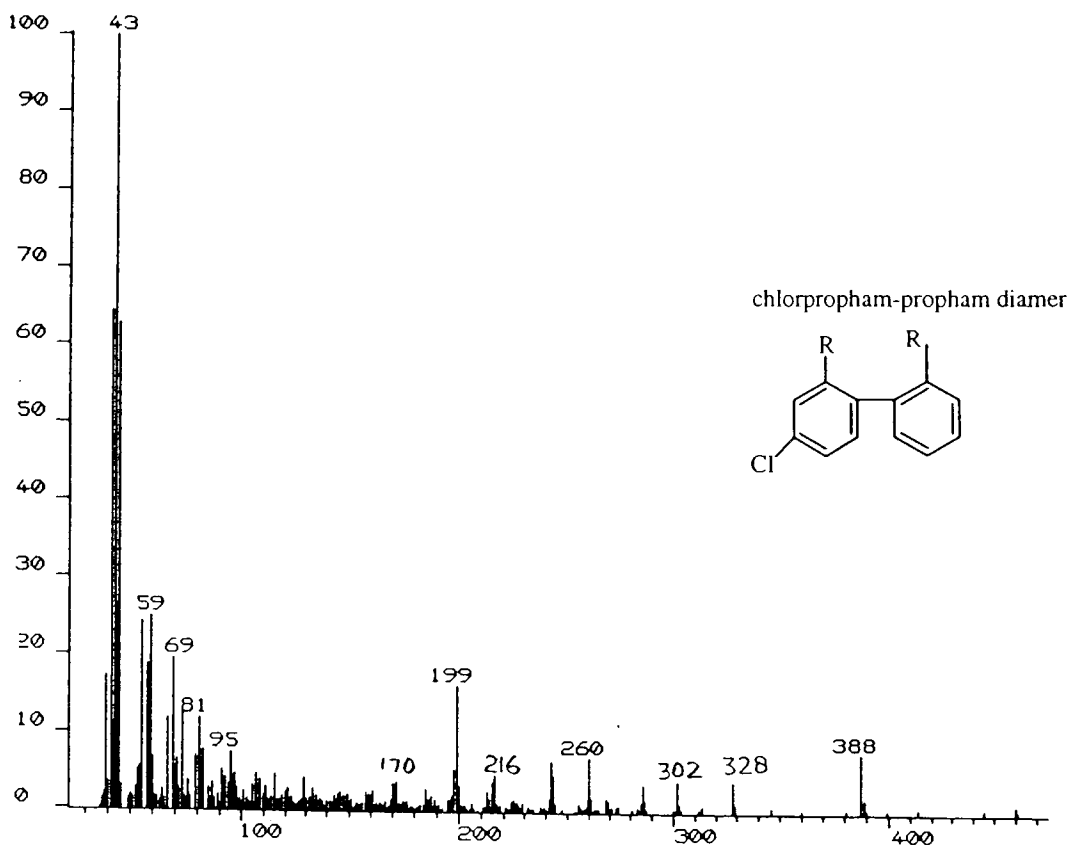
PW_1



PW_2



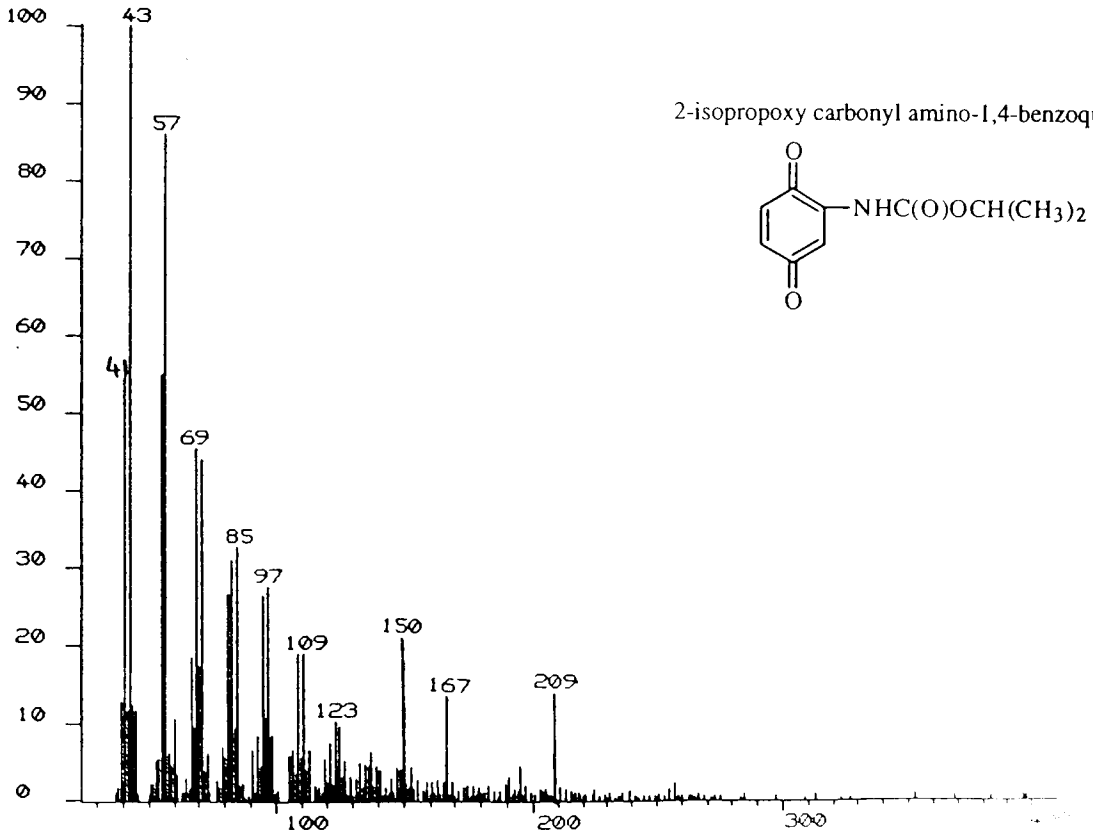
SW_4



chlorpropham-propham diamer

R = $NH^{-}C(O)^{-}O^{-}CH(CH_3)_2$

PS_1



2-isopropoxy carbonyl amino-1,4-benzoquinone (IBQ)

CHAPTER 5

GENERAL DISCUSSION

The main objective of this thesis, as mentioned in Chapter one, was to investigate the environmental fate of the phenylcarbamate compound chlorpropham. In addition to its use in potato warehouses as a sprout suppressant, this compound is used throughout the world as a herbicide. Therefore the compound is exposed to different climates which determine its fate in the environment.

In Chapter one, literature was reviewed which clearly demonstrated that three most important routes affecting the fate of chlorpropham in the environment. These are: 1- Adsorption to the soil in which chlorpropham is usually incorporated, 2- It is also potentially volatile from the treated surface especially soil, 3- Moreover, the compound is prone to photodecomposition as this is sensitive to ultraviolet light. Thus, these dissipation pathways are extremely important in determining the efficacy of chlorpropham in controlling weeds under both cold as well as hot climate conditions.

Hence, in order to develop a deeper understanding of these processes, it was necessary to critically review the existing literature pertaining to the subject in general. Although conclusions had been drawn at the end of each chapter in terms of results and discussions; it was found necessary to draw a general conclusion concerning the above objectives of the whole project and to point out the areas which would benefit from further research.

All over the world, herbicides are used for controlling weeds in major agricultural crops. As a consequence of agriculture practices, herbicidal chemicals are likely to enter into soil, air and aquatic environments. These

herbicidal chemicals are subjected to different dissipation processes, as discussed in Chapter one. From these different processes, three have been chosen and studied in this project.

In recent years, a lot of research has been carried out concerning the use of herbicides and their environmental fate. However, the bulk of the literature regarding chlorpropham behaviour on soil and in water is relatively limited and old. It needs further updating, review and expansion.

In chapter two, adsorption of chlorpropham to different adsorbents has been studied. Sorption is extremely important because it may dramatically affect the fate and impact of chemicals in the environment. Sorption studies were carried out using charcoal, tree bark, wheat straw and three soils varying in organic matter contents. The study was carried out at three different temperatures and at three concentration levels.

It was essential to adopt a sensitive, reliable and environmentally safe analytical method to detect chlorpropham quantitatively from water samples in order to meet requirements set by EQS. For this purpose, a solid-phase extraction method using octadecylsilyl-bonded silica C18 cartridges was adopted. It was found that the method could be used for the detection of chlorpropham up to 5 ng level with a recovery as well as reproductivity of 97%.

From the results of the adsorption/desorption study, it was concluded that the main determinant factors for the extent of adsorption/desorption are the soil type , time period and concentration of the applied chemical. Charcoal showed the greatest adsorption efficiency under all studied conditions of temperature , time period and concentration followed by bark and wheat straw respectively. Since charcoal and bark showed irreversibility of adsorption at lower application doses, it was concluded that these adsorbents could be successfully used for the removal of chlorpropham from the polluted water.

In another study in this laboratory on the adsorption of metals on different types of tree barks it was noted that tree bark could efficiently adsorb different metals. However it was revealed that different bark show different adsorption abilities. Tree bark could be successfully used for the removal both of organic and inorganic pollutants.

From the studied soils, it was also concluded that soil organic matter is an important factor in determining the sorption of chlorpropham followed by clay contents. Therefore, adsorption on Downholland (peat) soil (LOI 31.2%, 40.4% clay) was greater as compared with on Midelney (clay) soil (LOI 14.7% and 47.5% clay) and relatively less on Dreghorn (sand) soil (LOI 6.7%, clay 8.1%). This organic matter effect was further depicted in desorption studies when chlorpropham was not desorbed from Downholland (peat) and Midelney (clay) soils especially at lower concentrations. Thus, these soils can serve as an excellent source for the decontamination (purification) of water polluted with chlorpropham.

In the study, the effect of time period was found to be significant over all adsorbent types. The adsorption increased with increasing time period. The effect of time period was found to be dependent on nature of the adsorbent. Thus, for Downholland (peat) soil the effect of time period was more prominent as compared to Midelney (clay) while for straw , it was the least. For soils, this effect could be due to intra-molecular diffusion followed by physical adsorption.

Increasing the temperature did not significantly affect the adsorption of chlorpropham under all the studied conditions. An increase in temperature decreased the adsorption of chlorpropham on all the studied adsorbents. However, the effect was less as compared to the individual effects of adsorbent types, time period and concentration. Therefore, from the results it was inferred

that adsorption could follow the similar pattern under hot as well as cold climates.

The effect of concentration on the adsorption of chlorpropham was significant for all the adsorbents and under all temperatures as well as time periods. Almost the whole of the applied chlorpropham was adsorbed especially at lower temperatures. Furthermore, irreversibility of adsorption at lower concentrations for charcoal, tree bark, Downholland (peat) and Midelney (clay) soil displayed the efficacy with which these could be used for the purification of polluted water in order to enable us to fulfil the standards set by EQS, which is 10 mg/litre for chlorpropham.

In Chapter three, volatilization of chlorpropham from soil was studied. Volatilization is a major pathway of primary importance for the rapid dispersion of volatile pesticides into the environment. To study volatilization of chlorpropham from soil, three soils varying in textural class were selected. The study was conducted under different temperatures, molecular contents and concentrations.

In order to detect and quantify chlorpropham vapours in headspace of treated soil, it was vital to develop a sensitive analytical method. A sampling technique involving a preconcentration of chlorpropham vapours in order to reach the detection level of the GC instrument was adopted. For this purpose, a thermal desorption technique was selected, as it eliminates the use of solvents and other handling operations. This is also more sensitive than the solvent desorption technique. Therefore, higher sensitivity was achieveable since the whole sample could be injected at one time. Polymeric adsorbent Tenax-GC, proved to be an excellent collection material for use with thermal desorption. The recovery was in the range of 96-99%. From the linear response of GC-FID

for thermal desorption technique, it was concluded that head space analytical method was satisfactory.

Chlorpropham was quantitatively introduced onto a gas chromatography column with recoveries ranging from 96-99%. Moreover, samples on Tenax precolumns could be stored without significant loss for up to 5 days in a refrigerator. The result facilitates the transport of the samples from the sampling sites, which may be at some distance from the laboratory.

The results of the volatility study showed that soil type is the major determinant of the volatility and this effect is mainly due to the organic matter content. The total losses of chlorpropham were much higher in acid washed sand (0.00 O.M.) than from Midelney (clay) soil (14.7% LOI) and much less from Downholland (peat) soil (31.2 % LOI). The effect of organic matter content on volatility was further supported by the results of the adsorption study on the respective soils, where the adsorption order was Downholland (peat) > Midelney (clay) > acid washed sand.

The effect of temperature on volatility of chlorpropham was not significant. An increase in temperature increased vapour losses from all the studied soils under all conditions of moisture content at both concentration levels but the effect was less as compared to the effect of soil type and moisture content.

The results also indicated that moisture content of the soils had a significant effect on volatility which was more than that either of soil type or temperature. Increasing the moisture contents increased the volatility of chlorpropham. In addition, it was inferred that increase in volatility varied with soil type. Thus Downholland (peat) soil showed less losses at field capacity level than at half field capacity, persumably due to reduction in soil porosity at high moisture content.

Increasing concentration of the applied chlorpropham resulted in more losses. This effect was observed under all conditions of temperature and moisture contents as well as for all soil types. The trends of vapour losses were the same for different soils at both concentrations. However, results showed that for peat and arable soil at lower application doses, the amount volatilized (in terms of percentage of the initial amount) was higher than that at higher doses. This effect may be due to the saturation with chlorpropham of the air mass in contact with the soil.

Results of biological degradation of chlorpropham revealed the formation of 3-chloroaniline and isopropanol. In addition propham was also found as metabolite. The amount of these metabolites was found to be affected by temperature, soil type, and moisture content. The highest amount of 3-chloroaniline were observed in Downholland (peat) soil at 25 °C and field capacity moisture content while the lowest occured in Midelney (clay) soil at 10 °C and half field capacity. These trends may be due to the reason that the conditions favouring the microbial activity in soil, enhance the rate of biodegradation.

Phototransformations caused by sunlight is a route of utmost importance for the dissipation of herbicide in various environments. Interest in the aqueous environment is because of environmental and health related importance of water as well as to water being a condensed, homogeneous system that behaves in a generally predictable fashion except when suspended substances are present. Based on this a photodecomposition study of chlorpropham was carried out (Chapter 4). The study was conducted in distilled water and in the presence of different soil types at different concentrations. Further, identification of possible photoproducts in different media was also carried out. The photolysis study was accomplished at wavelength (253.7 nm) i.e. closer to that possibly reaching the earth surface.

From the results of photolysis in Chapter 4, it was concluded that the nature of soil has a remarkable effect on the rate and route of photolysis. The results showed the highest rate of photolysis in the presence of acid washed sand and lowest rate in the presence of Midelney (clay) soil. While in the presence of Downholland (peat) soil, the rate was more than that of in the presence of Midelney soil but less than that of in water and/or in acid washed sand soil. Different photolysis rates may be due to increased diffusness of light caused by the scattering effect or shielding effect of suspended solids from available light. For all the studied soils, photolysis followed first order kinetics. From the photolysis study in distilled water, Midelney (clay), Downholland (peat) and sand (acid washed) soil, it was concluded that the rate of chlorpropham photolysis was dependent on the medium and nature of suspended sediments present in the media.

From the identification of photoproducts, it was concluded that photolysis of chlorpropham followed three major routes i.e dechlorination, hydroxylation and dimerisation of the phenyl ring.

A total of ten chlorpropham photoproducts were identified from water and three studied soils. Among them, nine were found in distilled water and water fractions of different soils, while only one was obtained from soil fractions. However, for many others, it was quite difficult to get clear mass spectra in order to identify them. Hence, further studies are required to identify all remaining chlorpropham photoproducts in order to determine their toxicological/ biological effects on the environment. A summary of identified products of chlorpropham obtained by various routes is presented in Table 5.1.

A diagram showing putative fate of chlorpropham is presented in Figure 5.1.

From the results obtained in this study a few conclusions can be drawn.

(1) The SPE technique developed in this study affords a reliable method for the detection and analysis of low levels of chlorpropham in waters.

(2) The head space analytical method used in this study provides an efficient

method for monitoring of chlorpropham headspace and could be introduced as a management tool for trapping volatile chemicals in potato stores as well as for other stored products.

(3) Tree bark showed excellent scavanging properties for the adsorption of chlorpropham from contaminated waters. These results are quite promising for potato processors to help clean the river waters. Since tree bark provides an easily available, cheap material, it could be efficiently used for the removal of pollutants from waters.

(4) The formation of 3-chloroaniline and isopropanol as metabolites of chlorpropham provides interesting information in that if chlorpropham is not completely adsorbed on the soil, it is biologically degradable , thus referring less danger to the environment.

(5) Formation and subsequent disappearance of OH-propham during the photolysis of chlorpropham showed that OH-propham is also degradable by UV light.

The study also opens new areas for future reseach.

(1) The similar adsorption behaviour of Downholland (peat) and Midelney (clay) soils suggests the inclusion of soils varying widely in their textural class in the adsorption study, which could help to fully understand the role of silt, soil organic matter, and clay contents in the adsorption process. Further, adsorption studies could be extended using a wide range of chemical concentrations to evaluate the adsorption capacities of other cheap and easily available materials , to help remove the pollutants from the environmental compartments.

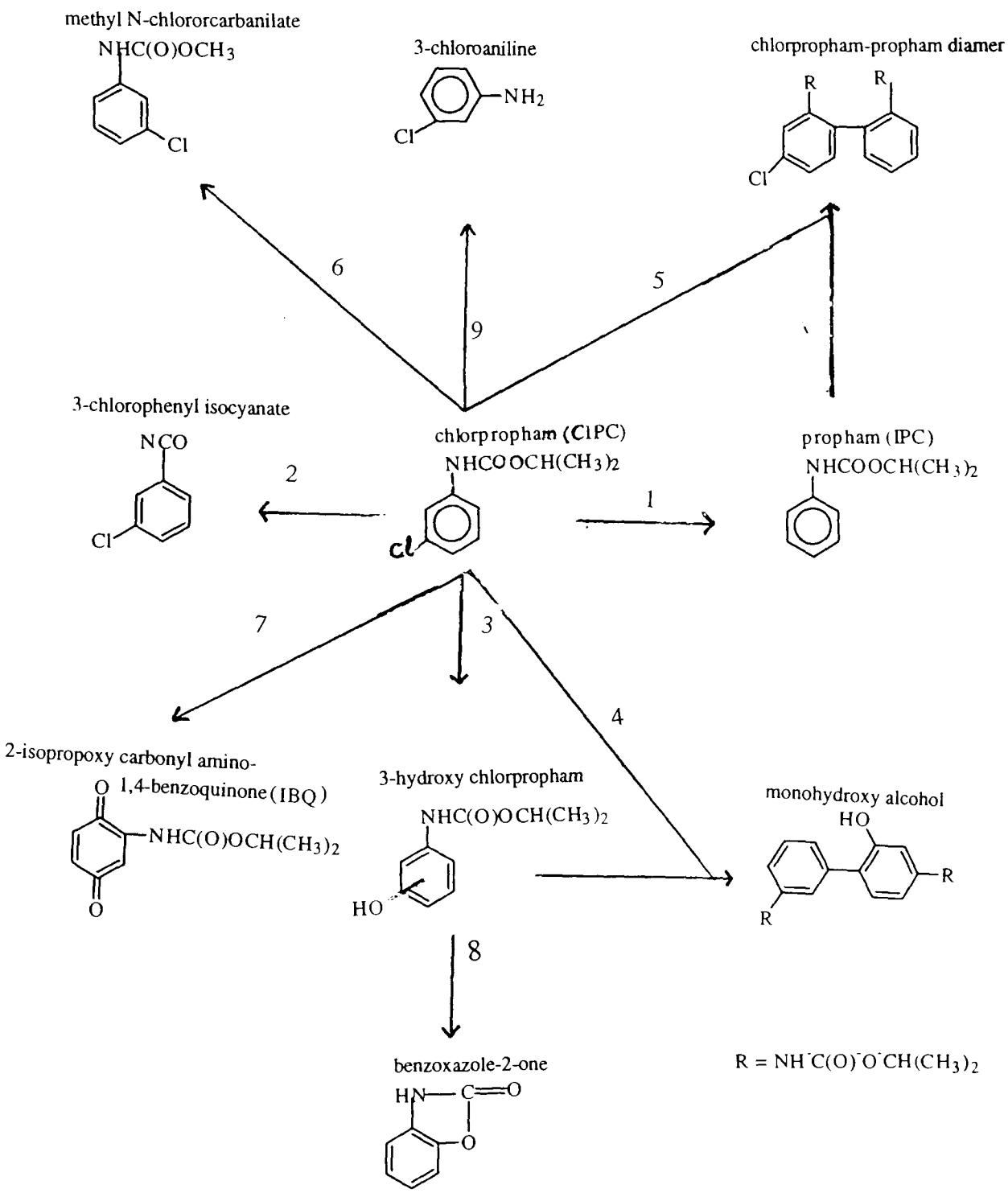
The headspace method used in the volatility study could be successfully used at a small scale to get initial information about the volatility of a compound. Due to the unavailability of the material, random replicates were used in the volatility study. Further studies could be carried out using many replicates. In addition formation of isopropanol as a metabolite needs to be confirmed.

Photodecomposition of chlorpropham yielded many metabolites; these need to be fully assessed for their toxicological effects on the environment.

Table 5.1 Summary of the identified products of chlorpropham

Compound	Microbial breakdown Product	Photochemical breakdown product	
	Soil	Water	Soil
3-OH propham		+	
Propham	+	+	
3-chloroaniline	+	+	
Isopropanol	+		
3-chlorophenyl isocyanate		+	
Methyl-N-chlorocarbanilate		+	
Chlorpropham		+	+
Monohydroxy biphenyl		+	
Chlorpropham-propham diamer		+	
2-isopropoxy carbonyl amino-1,4-benzoquinone(IBQ)			+

Figure 5.1 Environmental fate of chlorpropham



1- Dechlorination 2,9- Dealkylation + decarboxylation 3- Hydroxylation

4,5- Dimerisation 6- Alkoxy subsitution. 7- Photo-oxidation 8- Rearrangement

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APPENDIX

Table i: The effect of time, temperature and concentration on the adsorption/desorption of chlorpropham on Midelney (clay) soil.

Time (hrs)	Temp. (C°)	Conc. (μg/ml)	Adsorption (μg/g)	Desorption (μg/g)	% desorption	Kd
0			1.944±0.072	0.852±0.029	43.912±2.678	8.143±0.5
24	10		2.507±0.020	0.271±0.023	10.830±0.993	16.817±0.3
72			3.209±0.023	0.451±0.041	14.052±1.383	39.755±1.1
0			1.789±0.089	0.873±0.035	48.935±4.005	6.948±0.5
24	20	100	2.049±0.023	0.358±0.018	17.476±0.698	10.556±0.2
72			2.643±0.020	0.913±0.011	34.540±0.414	20.429±0.4
0			1.824±0.039	0.888±0.034	48.693±1.438	6.377±0.2
24	30		1.884±0.040	0.493±0.028	26.174±1.726	8.733±0.3
72			2.318±0.054	0.971±0.013	41.873±0.459	14.188±0.7
0			1.292±0.018	0.138±0.009	10.686±0.589	15.033±0.4
24	10		1.521±0.023	0.142±0.006	9.325±0.336	33.036±1.8
72			1.614±0.007	0.276±0.014	17.065±0.867	49.173±1.0
0			1.005±0.014	0.145±0.007	14.465±0.696	8.974±0.2
24	20	50	1.310±0.037	0.150±0.012	11.419±0.918	19.562±1.3
72			1.439±0.031	0.160±0.013	11.106±0.777	29.752±2.0
0			0.987±0.032	0.311±0.014	31.496±1.864	7.696±0.4
24	30		1.292±0.017	0.276±0.016	21.356±1.096	17.787±0.5
72			1.348±0.023	0.274±0.020	20.303±1.384	22.595±1.0
0			0.162±0.008			6.499±0.5
24	10		0.234±0.019	ND		15.982±3.2
72			0.339±0.004			64.081±5.0
0			0.147±0.019			5.538±1.0
24	20	10	0.231±0.010	ND		14.534±1.4
72			0.288±0.020			30.621±7.1
0			0.143±0.015			4.808±0.7
24	30		0.208±0.024	ND		11.440±2.5
72			0.210±0.011			12.640±1.2

Table ii: The effect of time, temperature and concentration on the adsorption/desorption of chlorpropham on Downholland(peat) soil.

Time (hrs)	Temp. (C°)	Conc. (μg/ml)	Adsorption (μg/g)	Desorption (μg/g)	% desorption	Kd
0			2.893±0.026	0.473±0.016	16.359±0.627	17.756±0.385
24	10		3.510±0.040	0.232±0.013	6.612±0.370	51.089±2.967
72			3.681±0.022	0.244±0.023	6.620±0.580	85.599±3.927
0			2.785±0.030	0.477±0.016	17.130±0.711	15.644±0.383
24	20	100	3.504±0.020	0.354±0.027	10.105±0.791	45.034±1.173
72			3.662±0.036	0.368±0.004	10.060±0.141	76.688±5.427
0			2.779±0.024	0.296±0.007	10.649±0.328	13.152±0.235
24	30		3.478±0.030	0.372±0.021	10.695±0.532	39.373±1.441
72			3.647±0.019	0.392±0.028	10.748±0.728	63.803±2.062
0			1.469±0.022	0.061±0.004	4.171±0.255	20.463±0.803
24	10		1.789±0.006	0.094±0.004	5.243±0.184	72.358±1.795
72			1.813±0.012	0.078±0.022	4.306±1.179	107.165±6.614
0			1.436±0.021	0.067±0.010	4.679±0.665	18.530±0.680
24	20	50	1.769±0.016	0.131±0.011	7.414±0.699	58.427±2.949
72			1.789±0.008	0.149±0.002	8.327±0.161	87.571±3.123
0			1.429±0.024	0.107±0.002	7.498±0.175	15.364±0.574
24	30		1.772±0.022	0.134±0.004	7.571±0.197	51.867±3.319
72			1.778±0.010	0.174±0.010	9.767±0.609	70.441±2.812
0			0.259±0.006			15.187±0.770
24	10		0.333±0.004	ND		47.890±2.898
72			0.369±0.004			130.575±15.15
0			0.254±0.001			13.939±0.090
24	20	10	0.330±0.008	ND		41.610±4.297
72			0.359±0.005			90.202±10.056
0			0.257±0.004			12.345±0.394
24	30		0.325±0.004	ND		35.429±1.820
72			0.354±0.012			70.542±15.269

Table iii: The effect of time, temperature and concentration on the adsorption/desorption of chlorpropham on s Dreghorn (sand) soil.

Time (hrs)	Temp. (C°)	Conc. (µg/ml)	Adsorption (µg/g)	Desorption (µg/g)	% desorption	Kd
0			1.077±0.081	0.137±0.018	12.724±1.157	3.50±0.335
24	10		1.753±0.018	0.189±0.005	10.772±0.266	8.374±0.146
72			2.194±0.042	0.269±0.020	12.266±0.749	13.553±0.540
0			1.058±0.055	0.383±0.010	36.297±2.370	3.349±0.220
24	20	100	1.692±0.025	0.530±0.020	31.313±1.530	7.595±0.182
72			1.926±0.007	0.720±0.030	37.353±1.536	10.317±0.069
0			1.021±0.038	0.469±0.021	46.034±3.615	2.914±0.133
24	30		1.559±0.036	0.628±0.012	40.287±1.491	6.448±0.227
72			1.611±0.021	0.772±0.007	47.914±0.952	7.318±0.148
0			0.310±0.034	0.167±0.006	54.683±8.075	1.884±0.236
24	10		0.913±0.048	0.229±0.018	25.217±3.292	9.660±0.896
72			1.180±0.034	0.210±0.013	17.808±1.081	17.472±1.152
0			0.168±0.043	0.096±0.006	60.069±14.997	0.941±0.265
24	20	50	0.832±0.026	0.217±0.010	26.098±1.073	7.900±0.401
72			1.075±0.041	0.317±0.013	29.481±1.584	13.887±1.172
0			0.165±0.037	0.100±0.004	62.438±12.068	0.852±0.206
24	30		0.734±0.029	0.245±0.002	33.453±1.179	6.264±0.373
72			0.896±0.024	0.355±0.002	39.661±1.133	9.359±0.432
0			0.172±0.001	0.026±0.004	14.976±2.284	7.144±0.067
24	10		0.277±0.007	0.041±0.003	14.772±1.287	24.368±1.867
72			0.319±0.009	0.056±0.004	17.521±1.675	46.928±6.405
0			0.122±0.025	0.035±0.003	29.276±3.517	4.289±1.143
24	20	10	0.266±0.028	0.075±0.006	28.635±4.714	21.161±5.734
72			0.291±0.003	0.132±0.010	45.346±3.379	30.660±0.966
0			0.055±0.053	0.052±0.002	103.17(;64	1.971±1.352
24	30		0.252±0.008	0.085±0.002	33.514 5	16.852±1.170
72			0.266±0.002	0.143±0.008	53.645: 1	21.828±0.520

Table iv : The effect of time, temperature and concentration on the adsorption/desorption of chlorpropham on wheat straw.

Time (hrs)	Temp. (C°)	Conc. (µg/ml)	Adsorption (µg/g)	Desorption (µg/g)	% desorption	Kd
0			12.324±0.357	5.097±0.659	41.370±5.371	35.710±1.182
24	10		16.998±0.534	6.341±0.118	37.340±1.631	60.355±2.363
72			17.358±1.190	8.675±0.298	50.235±5.053	64.819±5.581
0			9.100±0.401	5.193±0.168	57.087±1.120	24.968±1.213
24	20	100	11.868±0.341	7.414±0.438	62.575±5.261	38.206±1.268
72			13.498±1.107	8.890±0.246	66.098±4.022	47.108±4.608
0			7.891±0.477	6.866±0.044	87.229±4.915	19.711±1.291
24	30		8.308±0.870	7.648±0.419	93.088±13.861	24.944±2.883
72			8.962±0.489	9.073±0.022	101.464±5.526	28.628±1.732
0			1.538±0.486	0.817±0.029	56.965±16.524	8.420±2.763
24	10		5.460±0.481	2.149±0.748	40.296±16.068	37.435±3.790
72			7.200±0.390	3.529±0.483	48.980±5.735	54.085±3.548
0			1.493±0.274	0.855±0.115	57.917±7.386	8.013±1.516
24	20	50	4.908±0.588	2.555±0.439	53.383±14.768	32.284±4.392
72			6.683±0.398	3.487±0.400	52.214±5.534	48.858±3.437
0			1.333±0.065	0.827±0.101	62.019±6.338	6.596±0.330
24	30		3.705±0.675	2.515±0.366	69.924±18.958	23.046±4.618
72			4.077±0.193	2.963±0.131	72.859±5.952	26.964±1.414
0			0.692±0.111	0.308±0.140	47.159±29.099	19.755±3.405
24	10		1.537±0.448	0.585±0.058	39.875±9.836	57.116±21.131
72			3.584±0.131	0.932±0.100	26.031±2.998	147.087±6.503
0			0.377±0.069	0.235±0.087	61.125±13.021	10.520±2.094
24	20	10	1.248±0.506	0.651±0.105	63.827±40.631	43.514±20.086
72			1.670±0.387	0.823±0.154	50.337±9.630	64.968±18.787
0			0.577±0.245	0.257±0.079	52.428±29.394	14.886±6.768
24	30		1.071±0.332	0.663±0.113	66.968±27.019	35.039±12.618
72			1.263 ±0.182	0.8585±0.1607	69.007±15.75	44.5535±7.3940

Table v : The effect of time, temperature and concentration on the adsorption/desorption of chlorpropham on tree bark

Time (hrs)	Temp. (C°)	Conc. (µg/ml)	Adsorption (µg/g)	Desorption (µg/g)	% desorption	Kd
0			9.985±0.574	1.716±0.433	17.316±4.835	28.175±1.800
24	10		20.715±0.285	8.296±0.820	40.022±3.539	77.641±1.403
72			23.561±0.096	8.552±0.113	36.296±0.558	96.850±0.551
0			5.481±0.358	2.528±0.467	46.523±10.593	14.465±0.997
24	20	100	17.003±0.589	8.067±0.297	47.519±3.124	58.622±2.498
72			20.170±0.620	9.589±0.125	47.574±1.663	77.552±3.119
0			7.345±0.499	3.245±0.042	44.317±2.738	18.174±1.324
24	30		16.373±0.667	8.829±0.652	53.965±4.188	54.392±2.716
72			18.300±1.327	10.883±0.555	59.642±4.303	66.441±6.165
0			5.190±0.533	1.435±0.087	28.000±4.644	30.824±3.511
24	10		9.225±0.272	2.426±0.139	26.321±1.776	70.471±2.650
72			11.035±0.356	3.963±0.393	35.882±2.908	92.951±5.403
0			2.204±0.275	0.649±0.090	29.913±6.234	12.007±1.576
24	20	50	7.734±0.326	2.613±0.176	33.808±2.348	54.892±2.811
72			10.265±0.558	4.118±0.214	40.132±1.305	83.852±6.084
0			1.628±0.201	0.770±0.149	47.127±5.197	8.106±1.033
24	30		7.072±0.599	3.550±0.191	50.395±4.101	47.947±4.898
72			8.440±0.568	3.488±0.319	41.495±5.142	63.167±5.388
0			1.499±0.045			47.062±1.684
24	10		2.143±0.060	ND	ND	85.758±3.248
72			2.512±0.248			112.878±15.84
0			1.345±0.215			40.763±7.474
24	20	10	1.683±0.220	ND	ND	61.149±10.188
72			1.779±0.191			69.670±9.527
0			0.790±0.419			21.027±11.862
24	30		1.456±0.438	ND	ND	50.354±17.578
72			1.576±0.341			58.537±16.159

Table vi: The effect of time, temperature and concentration on the adsorption/desorption of chlorpropham on charcoal.

Time (hrs)	Temp. (C°)	Conc. (µg/ml)	Adsorption (µg/g)	Desorption (µg/g)	% desorption	Kd
0			23.743±0.142	0.959±0.034	4.043±0.146	79.28±0.62
24	10		82.540±0.432	ND		4136.75±277.1
72			83.708±0.104	ND		31732.1±529
0			20.686±1.268	1.533±0.324	7.449±1.770	65.074±5.01
24	20	100	82.253±0.457	ND		2836.45±184.4
72			82.548±0.465	ND		7946.80±1501
0			17.755±0.888	7.536±0.351	42.509±2.558	49.20±2.931
24	30		82.208±0.392	ND		2141.58±74.29
72			82.650±0.240	ND		4391.57±223.4
0			5.442±0.082			32.480±0.554
24	10		41.960±0.000	ND		
72			40.500±0.000			
0			4.765±0.423			27.500±2.705
24	20	50	42.970±0.000	ND		
72			40.900±0.000			
0			4.345±1.127			22.986±6.46
24	30		43.992±0.000	ND		
72			41.880±0.000			
0			2.205±0.206			76.180±9.304
24	10		8.390±0.000	ND		
72			8.100±0.000			
0			1.636±0.058			51.249±2.198
24	20	10	8.590±0.000	ND		
72			8.180±0.000			
0			1.530±0.217			41.258±2.915
24	30		8.798±0.000	ND		
72			8.376±0.000			

Photo-Fries rearrangements as given by Masilmani and Hutchison (1976)