



Determination of carbendazim sorption-desorption in vietnamese soils with different pH, content of clay and organic carbon

Master's thesis 20 p.
(examensarbete)

by

Tran Van Dung

Department of Environmental Assessment
Swedish University of Agricultural Sciences
Box 7050, SE 750 07 Uppsala

Supervisors: Tomas Berglöf, Henrik Kylin, Ingvar Nilsson

Determination of carbendazim sorption-
desorption in vietnamese soils with different
pH, content of clay and organic carbon

© Dept. Env. Assessment

ISSN 1403-977X

Abstract

Four Vietnamese soils with various physical and chemical properties, one alluvial soil (AG), one acid sulphate soil (CT), one sandy soil (ST), and one high degradation soil (TG) were selected for sorption and desorption studies of carbendazim using the batch equilibration technique. Sorption coefficients (K_d) increased with increased organic carbon and clay content. K_d values for carbendazim sorption on AG, CT, ST, TG with the content of organic carbon at 1.1%, 9.8%, 0.3% and 1.0% were 12.5, 127, 8.1 and 9.6 mL/g, respectively. The organic carbon partition coefficients (K_{oc}) for AG, CT, ST and TG were 1136, 438, 270 and 960 mL/g respectively. The sorption constant (K_f) showed good correlation with organic carbon (OC) of each soil for carbendazim. Percent of carbendazim desorbed as percent of initially sorbed were about 2.2% for CT, 6.3% for CT, 12.2% for AG and 16% for ST. Carbendazim was strongly sorbed and the binding was less reversible in the CT soil than in the other soils.

The influence of pH on carbendazim sorption was studied in the ST and CT soil, the sorption was pH dependent, with ST and CT soils showing completely different behaviour. Sorption of carbendazim on the ST soil increased as the pH decreased ($R^2=0.93$), while sorption of carbendazim by the CT soil increased as pH increased.

Table of contents

Introduction	3
Objectives	4
Background	5
Sorption/desorption	5
Solubility	5
Polarity K_{ow} (octanol-water coefficient)	6
Soil organic matter sorption	6
Clay sorption	7
Amorphous minerals and the important of Al and Fe	7
Effect of sorbent surface and soil structure on sorption	8
Temperature	8
pH	8
The shape of sorption isotherms	9
The high-affinity type (H-type) isotherm	9
The Langmuir-type (L-type) isotherm	9
The solvent-affinity type (S-type) isotherm	10
The constant- partition types (C-type) isotherm	11
Summary	11
Use of carbendazim in the Mekong Delta (Vietnam)	11
Structure and sorption of carbendazim in soil	12
Material and Methods	13
Soils	13
Soil characteristic	13
Alluvial soil	13
Acid sulphate soil	13
High degradation soil	13
Preparation of soil samples for the experiment	14
Determination of dry weight	14
Chemical and solutions	15
Determination of K_d	15
Batch sorption/desorption experiment	15
Desorption experiment	16
Sorption/desorption isotherms	16
Effect of pH value on the sorption	17
Determination of carbendazim in the water phase	17
Spectrophotometric determination	17
Statistical analysis	17

Results	19
Effects of soil properties on sorption/desorption of carbendazim	19
Desorption of carbendazim	19
Sorption-desorption of carbendazim on 4 soils	21
Desorption isotherm of carbendazim	23
Effect of pH values on sorption	24
Discussion	25
The influence of soil properties on sorption	25
Organic matter versus clays as sorbent	26
Desorption of carbendazim	26
The sorption-desorption isotherm of carbendazim	26
Effect of pH on the sorption	27
Conclusions	28
Acknowledgement	28
References	30

Introduction

Pesticides play an important role in the effort of increasing food production in today's agriculture. Pesticides protect harvested food and control diseases, but, at the same time, they can cause environmental hazards and negative effects on public health because of their toxicity and some times high persistence. To avoid negative effects in the environment, more knowledge is necessary about the fate of individual pesticides. The environmental fate of pesticides and other pollutants in tropical areas is not well understood.

An understanding of the mechanisms involved in the binding of pesticides in soil may help to understand and predict the behaviour of pesticides in the soil system, and consequently, the potential risk for contamination of water resources and for human health. Some soil characteristics that have been found to influence the fate of pesticides are the content of clay and organic matter and the pH of the soil (Hayes, 1970; MacNamara and Toth, 1970; Lopatin and Erich, 1960). The tropical climate as well as the particular micro-organisms in the soils may also influence the fate of the pesticides in the soil.

Benomyl (Figure 1A) is a common fungicide throughout the world. It is also commonly used in the Vietnamese agriculture against a wide range of diseases in rice, vegetables and fruit. However, benomyl is rapidly converted to carbendazim (methyl benzimidazol-2-yl carbamate, Figure 1B) in the environment. The reported half-life for benomyl is 1 hour in water, 19 hours in soil (Pesticide Manual, 1997) and carbendazim is actually the active moiety of benomyl. The Environment Protection Agency in USA has pointed to the possible mutagenicity, teratogenicity and potential for the reduction in spermatogenic activity caused by benomyl and carbendazim under defined conditions. On the other hand, because of the slow rate of degradation and low solubility in water of carbendazim, this fungicide may remain in the soil for a long time in an immobilised state due to interactions with soil colloids. These facts emphasise the need for sorption studies with carbendazim, since sorption significantly affects its movement and persistence in the soil environment.

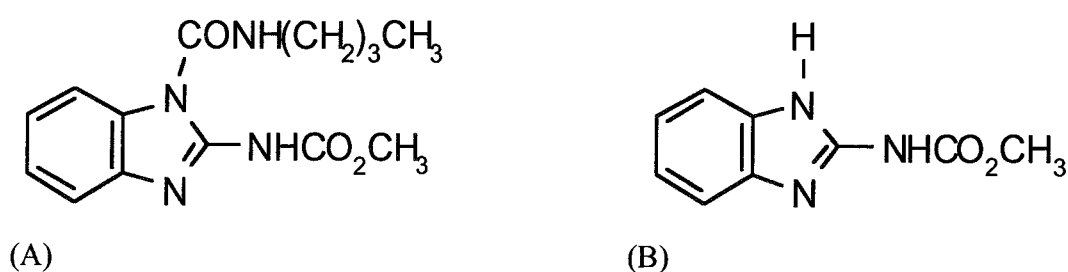


Figure 1. The chemical structure of (A): Benomyl; (B): Carbendazim

Objectives

The main goal of this work was to determine and compare the sorption/desorption isotherms of carbendazim of four Vietnamese soils with various physical and chemical properties.

A second goal was to study the affect of soil type, pH, clay content and organic matter contents on the sorption behaviour.

Background

Sorption/desorption

Compound characteristics, such as solubility, molecular weight, charge distribution, polarity, molecular configuration, and functional groups have been found to affect the degree and the amount of sorption of organic compounds on solid surfaces (Haque and Freed, 1974).

Bailey and White (1970) suggested that the structural factors that determine the chemical character of pesticide molecule and thus influence its sorption on soil colloids are:

- The nature of functional group(s) such as alcoholic (-OH), ketonic ($>C=O$), carboxylic acid (-COOH), or amine (-NH₂)
- Nature of substituting groups, which tend to alter the behaviour of functional groups
- Position of substituting groups with respect to the functional groups that may enhance or hinder intramolecular bonding

Carbendazim contains functional groups such as (-NH), and (-C=O), groups that are important for the sorption on soil surfaces.

Organic compounds can be sorbed by physical/chemical bonding mechanisms such as van der Waals forces, hydrogen bonding, dipole-dipole interactions, ion exchange, covalent bonding, protonation, ligand exchange, cation bridging, and water bridging with varying degrees of strengths of interactions. Sorption has also been described as a hydrophobic partitioning process between soil water and the organic matter phase for the sorption of hydrophobic (nonpolar) compounds (Chiou *et al.*, 1979), although the extent and importance of this mechanism is uncertain (Mingellgrin and Gerstl, 1983).

Sorption may be specific or non-specific (Osgerby, 1970). Specific sorption results when particular charged sites of a surface exert strong forces on the molecule or reactive units of molecules. The capacity for specific sorption is directly related to the number of bonding sites per unit of surface. Because of higher sorption energy, specific sorption will be take precedence, to the partial or total exclusion of non-specific sorption reactions.

Desorption is a dynamic process in which molecules are continually transferred from the solid phase to the bulk liquid phase (Bailet and White, 1970; Burchill *et al.*, 1981). Desorption is generally accompanied by hysteresis. The pesticide-organic complexes are stronger than clay-pesticide ones. Sorption usually increases as the temperature decreases, and the desorption is favoured by increasing temperature.

Solubility

Sorption is said to decrease as solubility in the solvent increases. Several workers have reported this effect (Hilton and Yuen, 1963). Ashton (1961) showed that the mobility of triazine herbicides increased in the order of their solubility. As the water solubility decreases, an increase in the hydrophobic character of the pesticide occurs, resulting in an increase in sorption by soil clays and organic matter (Coleman and Thomas, 1967; Barloe and Hadaway, 1955). On the other hand found no relationship between solubility and sorption and sorption

of substituted urea's Hance (1965a), and Weber (1966; 1970b) reported that solubility differences of s- triazines were not reflected in sorption differences. Similarly, when Harris and Warren (1964) compared herbicides differing widely chemically, they concluded that no general relationship exists between solubility and sorption.

Polarity K_{ow} (octanol-water coefficient)

The polarity of a substance can be estimated by studying the partition of the substance between n-octanol and water. The octanol/water partition coefficient K_{ow} is usually expressed as $\log K_{ow}$. K_{ow} has proved valuable for prediction of mobility and persistence in soil and of soil sorption (Wan and Koeng, 1994). The $\log K_{ow}$ of carbendazim is 1.38 (pH=5); 1.51 (pH=7) and 1.49 (pH=9). This compound is classified as moderately polar, which strong sorption on soils

Soil organic matter sorption

Sorption by organic matter is a key factor in the behaviour of many pesticides in soil. Because of for instance variation in composition and degree of cation saturation, sorption with soil organic matter varies from soil to soil (Hayes, 1970; McNamara and Toth, 1970). The sorption of carbofuran increased with an increase in soil organic matter, with peat and composts showing the highest sorption (Jamet and Piedallu, 1975b). Acetanilide herbicide sorption by Chinese soils was linearly correlated with soil organic matter (Qiquan *et al.*, 1999).

Humic substances in soil have an important role in sorption (Senesi, 1982). The NH and C=O functional groups in carbendazim may react with soil humus by cation exchange, hydrogen bonding or van der Waal forces (Sposito, 1989).

While soil organic matter plays an important role for sorption of organic compounds, it can rarely be used alone for predictive purposes (Meggett, 1970). Saltzam *et al.* (1972) suggested that the mineral organic matter interactions determine the sorptive capacity of each soil. Aharonson and Kafkafi (1975a,b) showed that clay minerals and organic matter play a prominent role in the sorption of this fungicide. Carbendazim sorption was thus greatest in mucky loam soil with a high humus content than in other soil. (Helweg, 1976).

Since sorption reactions do not always involve only weak, reversible bonding, hysteresis is often observed in sorption/desorption studies in the soil. A desorption hysteresis coefficient is calculated as the percentage of the ratio between desorption and sorption isotherm slopes ($H=(1/n_{des})/(1/n_{ads}) \times 100$). In some cases organic matter sorption is partially irreversible (Swanson, 1973; Moyer, Kercher and Hance, 1972). For example, when paraquat (cation) was sorbed on soil organic matter in amounts below the saturation, desorption was slower than for clays even in the presence of high solution concentrations of cationic salts (Burns, *et al.*, and Stacey, 1973b). Prometryne desorption from soils by water varied with soil organic matter and texture (Lafleur, 1976). Graham-Bryce (1967) showed that desorption of disulfoton was reversible soon after sorption. However, complete desorption was not obtained if the soil was allowed to dry after sorption.

Clay sorption

The potential for clays to bind organic chemicals depends on their surface area and cation exchange capacity (Miathyantha *et al.*, 1975). The smectite group of the mineral, including montmorillonite, has the highest potential for interacting with pesticides.

An organic compound must have some polarity in order to penetrate into the basal surfaces of montmorillonite (Grim, 1968). Many organic pesticides are polar in nature and are subject to sorption between two tetrahedral sheets. This is sometimes referred to as interlayer sorption. Pesticides sorbed in this manner are not active and are frequently shielded from microbial degradation (Weber and Scott, 1966).

The interaction of a basic organic chemical (like carbendazim) with organic and inorganic soil colloids (like clay) usually involves more than one mechanism, including chemical sorption, physical sorption, hydrogen bonding, protonation, or ion exchange (Weber, 1966, 1970a; Bailey *et al.*, 1968). Aharonson and Kafkafi (1975a,b) suggested that carbendazim may be sorbed on montmorillonite and soil by ion exchange. However, Cancela *et al* (1992) showed that the correlation of K (Freundlich constants) of carbendazim with the clay content of the soil ($R^2=0.85$) was weaker than that with organic matter content. This finding may be related to the fact that the soil was low in montmorillonite and high in illite, which has a low affinity for carbendazim.

Amorphous minerals and the important of Al and Fe

Huang, Grover, and McKercher (1984) studied the relative importance of organic matter, sesquioxides and different particle size fractions of soil in the sorption of atrazine. They found that aluminium, iron, and probably other mineral elements present in soil fractions ranging from clay to sand provided sorption sites for atrazine. The removal of aluminium and iron oxides from soils significantly decreased the amount of atrazine sorbed and changed the sorption kinetics. However, the amount of extractable Al and Fe in the different particle size fractions was not proportional to the extent of sorption, suggesting that different forms of sesquioxides could have different reactivities for atrazine.

Sorption of anions by hydrous Fe and Al oxides in soil can be specific or non-specific (Hingston *at el.*, 1968; Hingston *at el.*, 1967). In specific sorption, the anion is incorporated as a ligand in the coordination shell of a Fe or Al atom. Non-specific sorption refers to sorption of anions by coulombic interactions with positively charged on $Al_2O_3H^+$ or $Fe_2O_3H^+$ groups. In a soil system, specifically sorbed anions are not leached with solutions containing other anions such as chloride (Wada and Harward, 1974).

Al and Fe in soil can influence pesticide behaviour by acting as exchangeable ions on the exchange complex as well as colloidal materials (Adams, 1973). The hydrated oxides of Fe and Al adsorb Picloram more strongly than clays (Hammker, Goring and Youngson, 1966). Sorption of organoarsenical herbicides is strongly correlated with iron oxide content of soil (Wanchope, 1975). The oxides of Fe and Al, and soil organic matter are important soil

constituents in the sorption of 2,4,5-T (O'Connor and Anderson, 1974). Fe and Al saturated clays adsorb more glyphosate than Na or Ca -saturated clays (Sprankle, Meggitt and Penner, 1975b; Chaussidon and Calvet, 1975).

Effect of sorbent surface and soil structure on sorption

Bailey and White (1964) concluded that both total charge and surface area decrease in the series: organic matter > vermiculite > montmorillonite > illite > kaolinite. Total surface area decreased from 800 m²/g for montmorillonite to 10 m²/g for kaolinite (Weber, 1972; Chaussidon and Calvet, 1975). Humic acid sorbed =70 times more linuron and malathion than K-montmorillonite under comparable experimental conditions, and the difference was even wider for clays with different saturating cations. Thus, soil organic matter can play important role in the sorption of organic compounds and has been cited as playing a major role of triazine herbicides (Walker and Crawford, 1968).

Temperature

Sorption is an exothermic process, hence, it should decrease with increasing temperature. Thus, sorption of some herbicides on minerals was reported to be less at 50 °C than at 0 °C (Harris and Warren, 1964). Farmer *et al.*, (1966) reported a fourfold increase in the rate of volatilisation of dieldrin with an increase in temperature from 20 °C to 30 °C, with lower sorption at the higher temperature. However, sorption of parathion by soil from aqueous solution showed no appreciable temperature influence (Yaron and Saltzman, 1972). The herbicidal effect of 2,4-D was greater at 26 °C than at 10 and 5 °C due to lower sorption at the high temperature (Muzik and Mauldin, 1964). Similar temperature effects were also noted for 1,3-dichloropropene and 1,2-dibromoethane in soils (Kenry and Thomason, 1974). The sorption of carbendazim decreased when the temperature increased from 20°C to 30 °C (Cancela *at el.*, 1992). In the Mekong Delta, Vietnam, the temperatures are relatively high, average monthly temperature vary between 25 °C and 28 °C. The difference between the hottest and coolest month is less than 5 °C. The temperature factors in the Mekong Delta should be unfavourable for sorption of carbendazim, due to lower sorption at higher temperatures (Muzik and Mauldin, 1964).

pH

The action of solute, solvent and absorption surface may be the pH-dependent (Lopatin and Eirich, 1960). Maximum sorption of many organic compounds reportedly occurs when pH=pKa, when the two forms are of nearly equal concentration (Aharoson and Kafkafi, 1975a). The pH at maximum sorption can be acidic or alkaline, depending on the nature of the organic compound and the corresponding reactive complexes. Therefore, some compounds such as atrazine (McGlamery and Slife, 1966), metribuzin (Ladlie, 1975; King and McCarty, 1968), s-triazines (Weber, 1970a), and pentachlorophenol (Vallett, Calvet and Chaussidon, 1973) are more strongly sorbed by clays under acidic conditions. Other compounds are better bound under weakly acidic to weakly alkaline condition (pyridine, purines and nucleosides), depending on their interaction with inorganic cations (Lailach, Thompson and Brindley, 1968b).

Pesticides that tend to protonate in acid soils are more biologically active in neutral soils (Weber and Best, 1972), which correlates with reports that pesticides with low sorption in alkaline soils break down faster (Hermanson and Forbes, 1966). Some workers report reduced sorption under acid conditions, leading to faster degradation (Nearpass, 1965) other find that pH does not influence the behaviour of pesticides in the soil (Leopold, Schaik and Neal, 1960). Thiabendazole and 2-benzimidazolecarbamic acid ionise at a low pH value of approximately 5.8, and their sorption on soil particles is by a cation exchange process (Aharonson and Kafkafi, 1975b). Peter and Avis (1991) studied the influence of pH on carbendazim sorption. The results showed that sorption of carbendazim increased to K_d values greater than 10 as pH decreased, this behaviour being typical of a base in which the positive charge of the protonated form is subject to aromatic delocalisation.

The shape of sorption isotherms

A sorption isotherm is obtained by plotting the amount of substance (sorbate) sorbed on a solid (sorbent) at constant temperature against the amount of substance remaining in solution at constant temperature (equilibrium conditions). Sorption isotherms of the type presented in Figure 2 are normally obtained for most pesticides on soil or soil constituents (Weber and Miller, 1989)

The high-affinity type (H- type) isotherm

H-type isotherm occurs when the substance is preferentially sorbed to such an extent that no measurable amount remains in solution. The initial portion of the isotherm is therefore vertical. The sorbed species are often charged and undergo ion-exchanges with other species of similar charge but with lower affinity for the surface. Organic cations such as the quaternary N compounds diquat and paraquat exchange for inorganic cations on the surface of clays minerals (Weber, Perry and Upchurch, 1965). The pesticide /soil reaction occurs until the reacting surface becomes limiting, i.e., the CEC of the clay mineral is exceeded, at which time the remaining pesticide remains in solution and the curve becomes a flat plateau.

The Langmuir-type (L-type) isotherm

The Langmuir-type (L-type) isotherm has an initial slope that is curvilinear and convex with respect to the amount of substance sorbed. The substance has a preferential sorption initially-compared to the solvent or other solutes, with sorption decreasing as more substance is sorbed because of the difficulty for a substance molecule to find a vacant site. This is the most common type of pesticide sorption isotherm, and occurs when weakly basic pesticides, such as triazine herbicides atrazine and prometyrn interact with the surfaces of organic matter and/or clays mineral in soils. Other examples are when acidic As or P pesticides, such as glyphosate, complex with clays or metallic hydrous oxides in soils (Weber and Miller, 1989), or when non-ionic moderate to low water soluble organic pesticides sorb

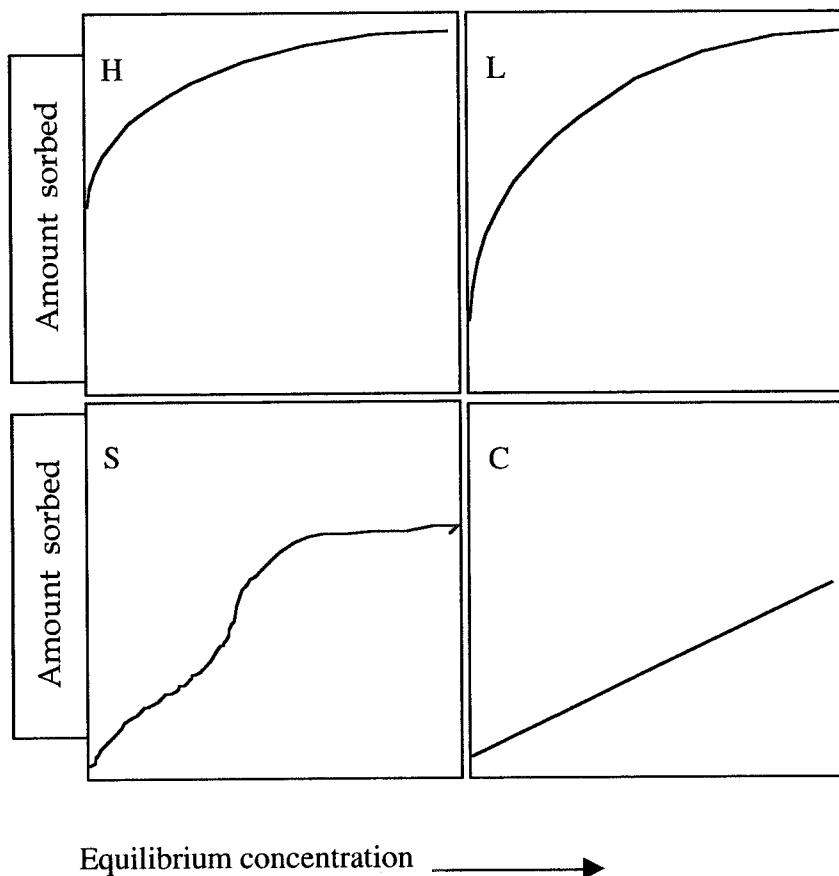


Figure 2. Classification of adsorption isotherms

to organic matter surfaces in soils. The Freundlich equation is usually used to describe the data in the L-type isotherm

$$x/m = K_f C^{1/n}$$

x/m : amount of pesticide sorbed ($\mu\text{g/g}$)

K_f : constant (indicates sorption capacity)

C : equilibrium concentration ($\mu\text{m/l}$)

$1/n$: constant (the slope of the isotherm)

The Freundlich equation normally describes L-type isotherms adequately except at very low and very high concentrations and the resulting $1/n$ value is equal to or less than 1.0.

The solvent-affinity type (S-type) isotherm

The isotherm has an initial slope that is curvilinear and concave with respect to the amount of pesticides sorbed. Initial sorption of the pesticide is low compared with the solvent or other solute, and increases as the number of pesticide molecules on the surface increases. S-type

isotherms occur when moderate to highly water soluble weakly acidic pesticides (such as dicamba and bromacil) are weakly bounded to hydrophobic surfaces, or when low to high water soluble nonionizable pesticides (such as aldrin and fensulfothion) are weakly bounded to clay minerals (Weber and Miller, 1989). S-type isotherms are normally adequately described by the Freundlich equation, except at very low and very high concentrations, the resulting $1/n$ values are greater than 1.0.

The constant-partition type (C-type) isotherm

The isotherm has a linear slope typical of the partitioning of a solute between two immiscible solvents. The isotherm is commonly observed when the concentration range over which sorption is being carried out is very narrow. It has also been observed to occur when nonionizable pesticides (such as the herbicide chlorpropham and diuron) were sorbed to specific sorbents such as ethyl cellulose (Weber and Miller, 1989). In addition, sorption of pesticides with very low water solubility has been reported to be of the C-type and has been attributed to sorption by the organic matter only (Werber, Perry and Upchurch, 1965; Karickhoff, Brown and Scott, 1979). The Freundlich equation adequately describes the C-type isotherm and resulting $1/n=1$, the K_f can be calculated as:

$$K_f = \frac{x/m}{C^{1.0}}$$

Summary

In most cases, sorption isotherms are of L- and S-type, except where ionic bonding or precipitate reaction occurs and the isotherm is of the H-type. The Freundlich equation normally adequately describes L-,S-, and C-type isotherms, and $1/n$ values range from less than 1.0.

The K_d (pesticides/soil distribution coefficient) is normally calculated as follows (Hammker and Thompson, 1972; Lambert, 1968; Karickhoff, Brown and Scott, 1979):

$$K_d = \frac{C_s}{C_w}$$

C_s = pesticides sorbed in soils ($\mu\text{g/g}$)

C_w = pesticides in solution ($\mu\text{g/mL}$)

Use of carbendazim in Mekong Delta (Vietnam)

Several types of pesticides have been widely used for agricultural production in the Mekong delta, Vietnam. Carbendazim (methyl benzimidazol-2-ylcarbamate), with the commercial names: benlate, fundozol or copper B was introduced in 1967 as a wide spectrum fungicide effective against different disease types on different kinds of crops (Edginton *et al.* 1980). Carbendazim is a systemic fungicide with protective and curative action, that absorbs through

the leaves and roots, with translocation acropetally (The Pesticide Manual, 1997). Nowadays, in the Mekong Delta, carbendazim is commonly used in agriculture and horticulture because the cost is low and the pesticide is easy to find in the market as a wettable powder containing the active ingredients carbendazim (Hai, T.V. 1998). Carbendazim is effectively used against a wide range of diseases such as blast, sheath blight, yellowing, grain discoloration in rice; anthracnose, powdery mildew, stem rot, damping out in vegetable; leaf spot, gray mold in fruit. It is also effective against mites, primarily as an ovicide, and is also used as pre-harvest spray. Typical application rates of benomyl in the Mekong delta on the rice field and vegetable crops are: 2 kg a.i./ ha; on tree crops 550-1100 g a. i. /ha; for post-harvest uses, 25-200 g/h (Hai, T. V. 1998).

Structure and sorption of carbendazim in soil

Carbendazim is a moderately weak base ($pK_a=4.2$), the Mol. Wt 191.2.

Solubility in water = 29 (pH 4), 8 (pH 7) or 7 (pH 9) (mg/L at room temperature). Solubility in chloroform is 0.1, dimethylformamide 5, acetone 0.3, xylene 10, ethanol 0.3, ethyl acetate 0.14, dichloromethane 0.07, benzene 0.04 (g/kg at 25 °C)

Stability: decomposed by strong acids and strong alkalis, decomposed slowly in the presence of moisture.

Carbendazim is strongly sorbed by soils, particularly in a protonated form (Graham-Bryce and Coutts, 1971; Gunther, 1970). Carbendazim forms complexes with simple, hydrated and basic metal ions including calcium, iron, manganese and aluminium ions (Klopping, 1960).

Sorption of unionised carbendazim, assuming that it behaves like other non-ionic chemicals in soil, would be predominantly on soil organic matter (Briggs, 1973). Bailey and White (1970) suggested that the structural factors that determine the chemical character of pesticide molecules and thus influence its sorption on soil colloids are the nature of functional group(s) such as alcoholic (-OH), ketonic (>C=O), carboxylic acid (-COOH), or amine (-NH₂). The carbendazim containing NH and C=O groups. The NH groups in carbendazim can form hydrogen bonding with soil organic matter, while C=O groups in carbendazim can form hydrogen bonding with NH of organic matter.

Materials and Methods

Soils

Four soils from the Vietnam Mekong Delta, Soc Trang, An Giang, Can Tho, and Tien Giang soils, were used in this study (Table 1).

Table 1. Classification and some physical, chemical properties of soils used in this study

Soil	FAO classification	Organic carbon (%)	Clay content (%)	pH(H ₂ O) (1:5)	pH(KCl) (1:5)
An Giang	Eutric Fluvisols	1.1	37.9	4.7	3.7
Can Tho	Umbric-epi-orthithionic Fluvisols	9.8	49.8	2.9	2.9
Soc Trang	Typic Arenosols	0.3	26.3	5.4	5.2
Tien Giang	Umbric Gleysols	1.0	17.3	3.6	3.4

Soil characteristics

The four studied soils belonged to four major soil groups of the Mekong Delta (Figure 3), one alluvial soil (An Giang), one acid sulphate soil (Can Tho), one sandy soil (Soc Trang) and one high degradation soil (Tien Giang).

Alluvial soil

The soil was collected in the An Giang province, situated along the Mekong river. The soil has no sulphuric or sulfidic horizons.

Acid sulphate soil

The soil was collected in the Can Tho province, situated in an area with an even topography. The soil has a sulphuric horizon occurring in the upper 50 cm of the soil profile.

Sand soil

The soil was collected in the Soc Trang province, situated in a location with steeper topography. The soil has a sandy texture.

High degradation soil

The soil was collected in the Tien Giang province, situated in a location with steep topography. The profiles is strongly developed, with sandy texture (Ve and Anh, 1990). Soil

used for the experiment An Giang, Can Tho, Soc Trang and Tien Giang is abbreviated as AG, CT, ST, and TG respectively.

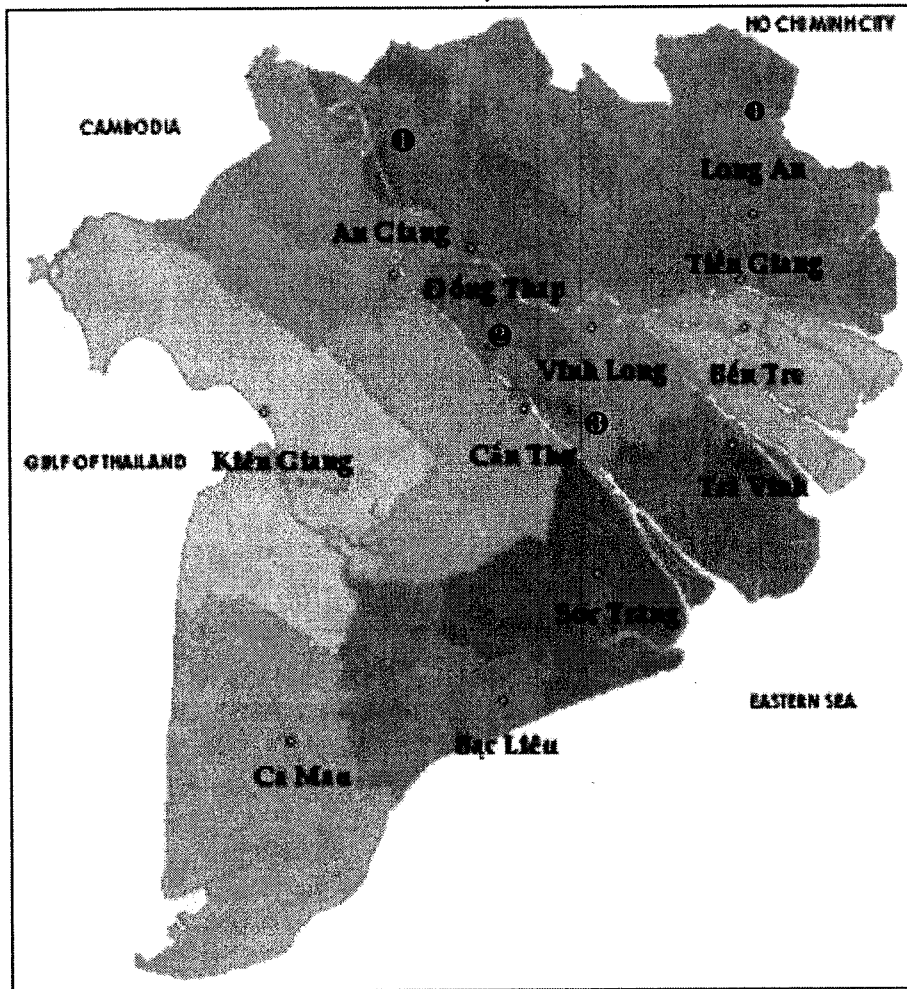


Figure 3. The maps of Mekong Delta and the site of soil sampling: AG (①); CT (②); ST (③) and TG (④).

Preparation of soil samples for the experiments

Ten fresh surface soil (0-15 cm) samples were randomly collected from each sampling location. The samples were transported to the laboratory in plastic bags. The soils were air-dried at room temperature ($< 40\text{ }^{\circ}\text{C}$), and litter material was thrown away. The soil was sieved to a particle size $< 2\text{ mm}$. Prior to weighing a sample, the soil was homogenised by shaking. Samples were stored at room temperature until the time for analysis.

Determination of dry weight

Soil moisture content was determined by drying approximately 30 g of fresh soil over night at $105\text{ }^{\circ}\text{C}$. Dried samples were weighed and percentage dry weight was calculated.

Chemicals and solutions

Pure analytical carbendazim (97% purity) was obtained from Dr. Ehrenstorfer (GmbH). A standard stock solution was prepared by dissolving carbendazim (4.04 mg/L) in a 0.01 M solution of calcium chloride in distilled water.

Hydrochloric acid (HCl) concentrated, HCl solution (0.1 M); Sodium hydroxide (NaOH) solution (6.5 M); Ethyl acetate.

Determination of K_d

The K_d for carbendazim in the different test soils was determined according to the OECD guidelines (OECD guidelines for testing of chemicals, 1996).

$$K_d = \frac{\text{Carbendazim sorbed in soil } (\mu\text{g/g})}{\text{Carbendazim in solution } (\mu\text{g/mL})}$$

Since the distribution of carbendazim between soil and water phases is highly dependent on the organic matter content, the distribution coefficient was recalculated per amount of organic carbon. The new coefficient (K_{oc}) was defined as:

$$K_{oc} = \frac{K_d}{F_c} \times 100$$

F_c is the percent fraction of organic carbon in the soils.

Batch sorption/desorption experiments

Air dried soil samples (10 g) were equilibrated with 0.01 M CaCl_2 (100 mL) overnight before the day of experiment. The soil/water mixture was centrifuged and as much as possible of the water phase was removed (about 5 mL water remained in the soil). 50 mL of a carbendazim solution prepared in 0.01 M CaCl_2 was added to the soil. Four concentrations of carbendazim were used for the Soc Trang, Tien Giang and An Giang soils (Table 2). Five higher concentrations of carbendazim were used for the Can Tho soil (Table 3). Initial carbendazim concentrations below 7.5 $\mu\text{g/g}$, carbendazim in soil solution could not be determined in the CT soil after equilibration. The mixture was shaken for 24 hours. After a period of agitation, the mixture was centrifuged, and the aqueous phase was recovered as completely as possible and the volume was measured. All experiments were performed in triplicate, and one blank sample was included in every sample batch.

Desorption experiments

Desorption experiments were performed after the sorption experiments were finished. The soil/water mixture was centrifuged and as much as possible of the aqueous phase was withdrawn (approx. 50 mL). 30 mL of clean 0.01 M CaCl₂ solution (without carbendazim) was added and the mixture was shaken for another 24 hours. The aqueous phase was separated by centrifugation and 30 mL removed for analysis. This desorption cycle was repeated twice for each sample.

Table 2. Concentrations of carbendazim used for the Soc Trang, Tien Giang and An Giang soils

Code	Concentration ($\mu\text{g/g}$ soil)
C1	1
C2	2.5
C3	7.5
C4	20

Table 3. Concentrations of carbendazim used for the Can Tho soil

Code	Concentration ($\mu\text{g/g}$ soil)
C1	20
C2	25
C3	30
C4	35
C5	45

Sorption/desorption isotherms

The results from the sorption-desorption experiments were evaluated by the Freundlich equation, rewritten as:

$$\log x/m = \log K_f + 1/n \log C$$

Where x/m is the amount of carbendazim sorbed to the soil (difference between initial carbendazim concentration and concentration after equilibrium was assumed to sorbed on the soil, $\mu\text{g/g}$ soil), C is the concentration of carbendazim in the water phase after equilibrium ($\mu\text{g/mL}$), K_f is the Freundlich sorption coefficient, and $1/n$ is the slope of the sorption isotherm.

Effect of pH value on the sorption

Two soils (ST and CT) with the lowest and highest sorption coefficients were selected for studying the influence of pH on sorption. Initial pH of ST, and CT soils was 5.4, and 2.9, respectively. Soil samples (10 g) were spiked with carbendazim solution as described above. pH of the samples was adjusted to around 3 and 7 by adding concentrated HCl, and Ca(OH)₂ (ST soil), and increased to around 5 and 7 by adding Ca(OH)₂ (CT soil).

Determination of carbendazim in the water phase (analytical procedure, see Figure 4)

-Transfer water, approximately 25 mL (measure the volume) to the separatory funnel.

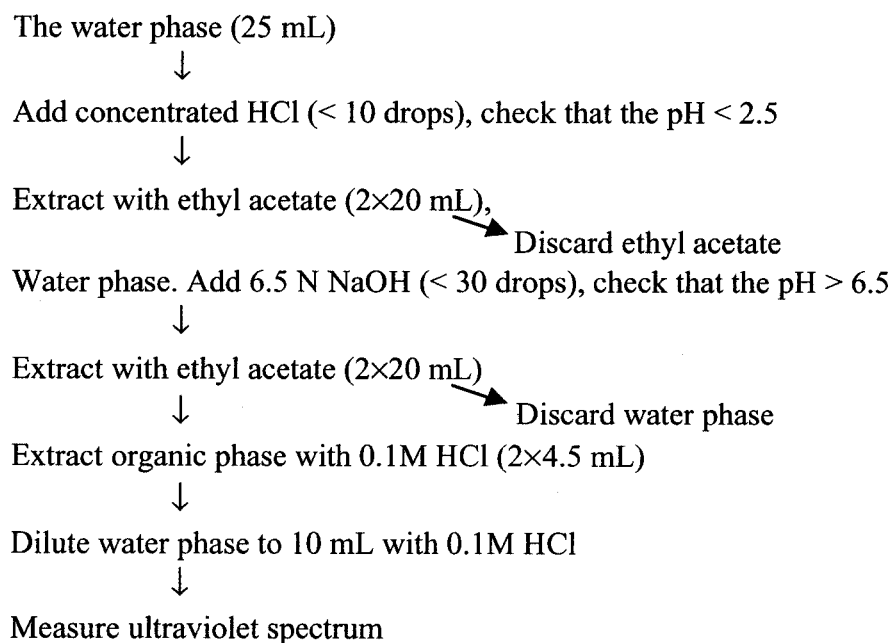


Figure 4. Analytical procedure for carbendazim in water phase.

Spectrophotometric determination

Determination of carbendazim was made by second derivative spectrophotometry at the absorbance maximum of carbendazim ($\lambda = 282$ nm) using a Shimadzu 1601 UV spectrophotometer (Figure 5).

Statistical analysis

Statistical evaluations of the results included regression analysis, comparison of slopes, and calculation of 95% confidence intervals for the intercept ($\log K_f$), standard deviation of K_d and standard error of the slope ($1/n$).

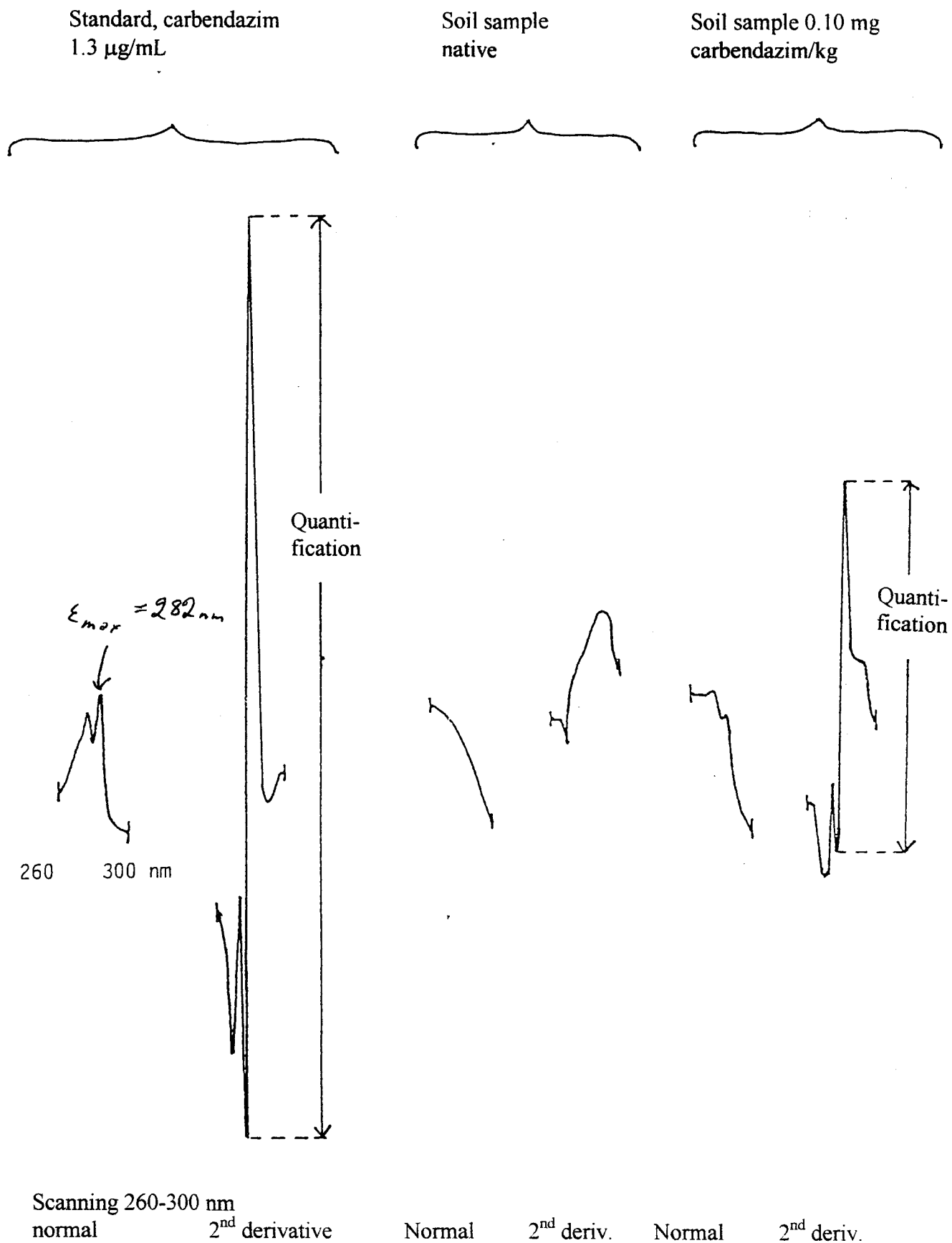


Figure 5. UV-spectra and second deviation of standard and a sample.

Results

Effects of soil properties on sorption/desorption of carbendazim

The obtained sorption coefficient (K_d) of carbendazim on the four soils, the ST, TG, AG, and CT was 8.1, 9.6, 12.5, and 127 mL/g respectively (Table 4).

Table 4. Sorption of carbendazim on four soils.

Soil	pH (KCl)	Organic carbon (%)	Clays (%)	K_d (mL/g) (Distribution coefficient)
AG	3.7	1.1	37.9	12.5(± 2.3) ^a
CT	2.9	9.8	49.8	127(± 13.5)
ST	5.2	0.3	26.3	8.1(± 1.1)
TG	3.4	1.0	17.3	9.6(± 1.6)

^a Numbers in parentheses are standard deviation about the mean K_d

The carbendazim sorption increased (from 8.1 in the ST soil to 127 in the CT soil) with increasing organic carbon content (from 0.3 in the ST soil to 9.8% in CT soil). A linear relationship between K_d for the soils, and organic carbon (OC) content was obtained ($R^2 = 0.99$), while K_d was only slightly correlated with clay content ($R^2 = 0.66$), and poorly correlated with pH ($R^2 < 0.5$).

The K_{oc} ($= (K_d / \% \text{ organic carbon}) \times 100$) coefficient allows a comparison of sorption on soils with different organic carbon content. K_{oc} has been used for prediction of the mobility of different chemicals in soil (Swan *et al.*, 1983). Obtained K_{oc} values correspond to results reported in the literature (Lambert and Omega, 1968; Briggs, 1973). Based on the K_{oc} values, The mobility of carbendazim in the AG, and CT soils was expected to be low to very low, the mobility in the ST soil very low to immobile and the mobility in the TG soil low to immobile (Table 5).

Desorption of carbendazim.

Profiles of carbendazim sorption (SE) and desorption (D1 – D3) equilibration's obtained for the soils are shown in Figure 6. Calculated average K_d values increased through three desorption (D1 – D3) equilibration's for the AG (62.2 to 86.8, CV = 11.1%), Soc Trang (47.8 to 57.3, CV = 10.0%) and CT (281 to 742, CV = 5.9%), K_d of the TG soil was relatively constant; 145; CV = 9.7%. In general, as the desorption K_d increased, CV decreased.

Table 5. Expected mobility of carbendazim based on K_{oc} values

Soil	Initial Concentration ($\mu\text{g/g}$)	$K_d(\text{mL/g})$	$K_{oc}(\text{mL/g})$	Expected mobility (Torstensson, 1993)
AG	1	11.3	1030	Low
	2.5	20.6	1870	Low
	7.5	47.3	4300	Very low
	20	12.5	1140	Low
CT	20	127	1300	Low
	25	43.8	450	Medium
	30	42.9	440	Medium
ST	1	47.5	15830	Immobile
	2.5	38.7	12900	Immobile
	7.5	55.6	18530	Immobile
	20	8.1	2700	Very low
TG	1	45.5	4550	Very low
	2.5	63.8	6380	Immobile
	7.5	64.5	6450	Immobile
	20	9.6	960	Low

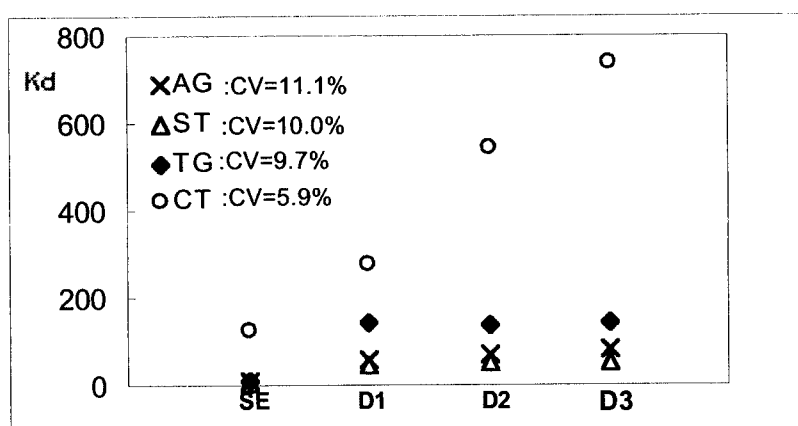


Figure 6. Sorption coefficient (K_d) values from sorption equilibration's (SE) and desorption equilibration's (D1 to D3) for (X) AG; (Δ) ST; (\blacklozenge) TG and (O) CT soils.

The amounts of carbendazim desorbed from the soil, expressed as percentage of initially sorbed carbendazim are shown in Figure 7. Desorbable amounts of carbendazim from the CT, TG, AG, and ST soils were about 2.2, 6.3, 12.2, and 16 %, respectively. The results shows a high correlation between the percentage desorbable amount and K_{oc} ($R^2=0.8$). The percentage of carbendazim desorbed from the soils increased in the order from $CT < TG < AG < ST$, this corresponds to an increase in K_{oc} (from 438 for the CT soil to 2700 for the ST soil).

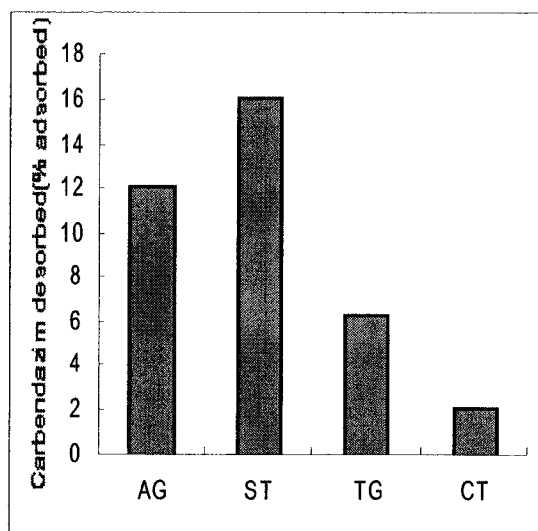


Figure 7. Desorption as percent of initially sorbed carbendazim from AG, CT, ST and TG soils.

Sorption-desorption isotherms of carbendazim on 4 soils.

Sorption-desorption isotherms of carbendazim on the 4 soils are shown in Figure 8. In generally, the L-shaped sorption isotherm (Giles *et al.*, 1960) was obtained for all soils, indicating a high affinity to carbendazim.

The Freundlich equation was used for the description of the sorption isotherms of pesticides. K_f and $1/n$ are important parameters in many models of environmental fate and transport of pesticides in soils (Mervosh *et al.*, 1995). The values of K_f and $1/n$ and the correlation coefficients are given in Table 6. It was concluded that the Freundlich equation was rather good to fit the data in the sorption isotherm of carbendazim on soils.

The sorption coefficients K_f as well as K_d increased in the following order $ST < TG < AG < CT$. The relationship between K_f and organic carbon gave a high correlation ($R^2=0.99$). The correlation between K_f and % clay contents was 0.73. However, no significant correlation with pH was obtained ($R^2=0.35$). The average slope of the line ($1/n_{ads}$) for sorption of carbendazim on AG, CT, ST and TG soils was 0.91, 0.33, 0.58 and 0.57, respectively. A $1/n$ less than 1 indicates that the sorption is concentration dependent, *e.g.* the percentage of carbendazim sorbed on the four soils decreased as the initial concentration increased (Table 6).

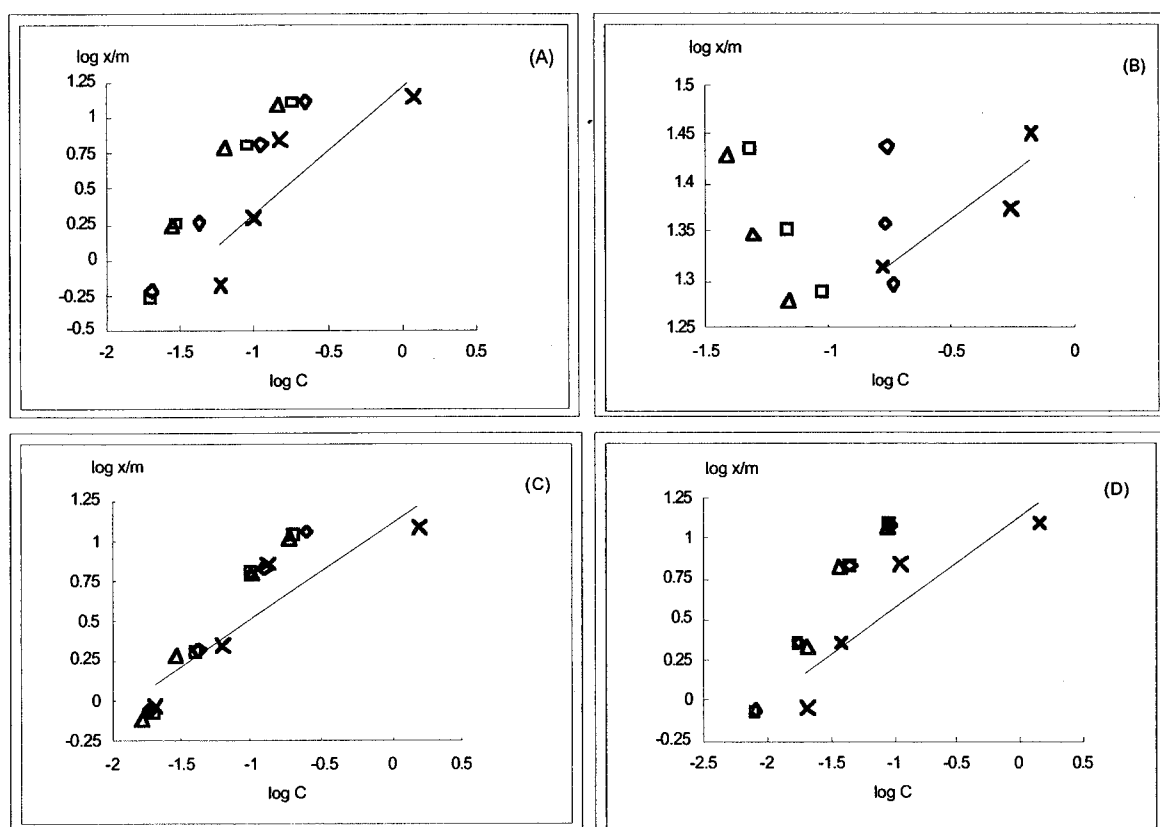


Figure 8. Sorption-desorption of carbendazim on (A) AG, (B) CT, (C) ST, and (D) TG soils. (X) Adsorption; (◇) Desorption1; (□) Desorption2; (Δ) Desorption3.

Table 6. The Freundlich constants ($K_{f,ads}, 1/n_{ads}$) and correlation coefficients for sorption of carbendazim on soils.

Soil	$K_f (\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n})$	$1/n$	R^2
AG	15.8(± 0.7) ^a	0.91(± 0.23) ^b	0.77
CT	34.7(± 0.8)	0.33(± 0.05)	0.80
ST	12.3(± 0.7)	0.58(± 0.23)	0.86
TG	13.5(± 0.7)	0.57(± 0.20)	0.84

^a Numbers in parentheses are standard error about the mean K_f

^b Numbers in parentheses are \pm standard deviation

Desorption isotherm of carbendazim

The desorption isotherm values of K_{fdes} , $1/n_{des}$ and hysteresis coefficients $H = (1/n_{des}) / (1/n)$ are given in table 7. As the initial concentration of carbendazim increased, the K_{fdes} increased. Higher K_{fdes} indicates that a greater proportion of the carbendazim was retained by the soil. The K_{fdes} values for CT soil were greater than for the other soil types. This indicates that a lower amount of carbendazim in Can Tho soil was desorbable than in the other soils. Desorption isotherm $1/n_{des}$ were lower than sorption $1/n$ indicating hysteresis. The low hysteresis coefficients observed in the CT and TG compared with AG and ST soils indicate irreversibility of strongly bound chemical to soil colloidal components.

Table 7. Desorption coefficients (K_f) the slope ($1/n$) and $H = (1/n_{des}) / (1/n)$ for carbendazim on four soils

Soil	Initial Concentration ($\mu\text{g/g}$)	K_{fdes} ($\mu\text{g}^{1-1/n}\text{g}^{-1}\text{mL}^{1/n}$)	$1/n_{des}$	R^2	H
AG	1	1.0(± 0.51) ^a	0.15(± 0.04) ^b	0.72	16
	2.5	2.7 (± 0.62)	0.12(± 0.01)	0.91	13
	7.5	9.3 (± 0.68)	0.14(± 0.02)	0.97	15
	20	34.7(± 0.64)	0.05(± 0.06)	0.82	5.5
CT	20	22.4(± 0.83)	0.06(± 0.01)	0.70	18.2
	25	24(± 0.86)	0.02(± 0.01)	0.98	6.1
	30	25.2(± 0.91)	0.02(± 0.09)	0.97	6.1
ST	1	7.9(± 0.69)	0.57(± 0.01)	0.51	98
	2.5	4.4(± 0.64)	0.23(± 0.01)	0.90	39.6
	7.5	17.7(± 0.66)	0.45(± 0.01)	0.88	77.6
	20	12.5(± 0.60)	0.06(± 0.02)	0.60	10.3
TG	1	1.1(± 0.85)	0.04(± 0.01)	0.75	7.0
	2.5	2.8(± 0.75)	0.05(± 0.01)	0.40	8.8
	7.5	7.8(± 0.79)	0.05(± 0.01)	0.79	8.8
	30	25.2(± 0.91)	0.02(± 0.09)	0.97	3.5

^a Numbers in parentheses are standard error about the mean K_f

^b Numbers in parentheses are \pm standard deviation

Effect of pH values on sorption in the ST and CT soils.

Sorption of carbendazim is reported to be pH dependent (Peter and Avis, 1991), with stronger sorption at lower pH values when the molecule is protonated.

Sorption of carbendazim by the ST soil increased as the pH decreased, ($R^2=0.93$). This corresponds to results presented in the literature (Austin and Briggs, 1976; Aharonson and Kafkafi, 1975; Singh and Thapliyal, 1987; Peter and Avis, 1991).

In contrast, sorption of carbendazim by the CT soil increased as the pH increased ($R^2=0.99$).

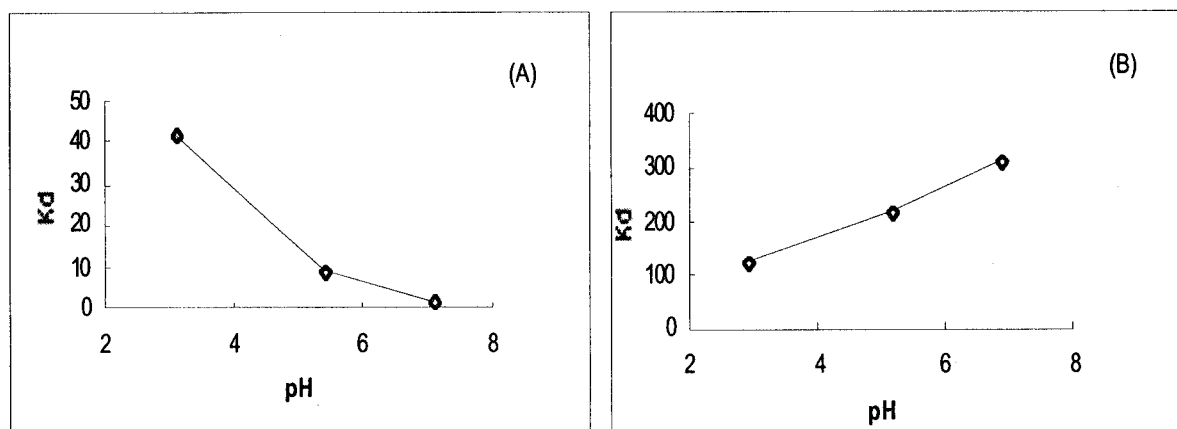


Figure 9. Effect of pH on the sorption: (A) ST soil; (B) CT soil.

Discussion

The influence of soil properties on sorption

The correlation between sorption and soil properties can be used either to predict the sorption of pesticides in different soils, or help to determine soil properties that dominate in the sorption process (Pusino, Liu and Gessa, 1992; Mallawatantri, Macconkey and Mulla, 1996; Pusino, Lui and Cargo, 1994). The soils used in this study covered a wide range of organic carbon and clay content. The results indicate that both organic carbon (OC) and clay contents influenced the carbendazim sorption, although, sorption was more influenced by OC than clay content.

Carbendazim was strongly sorbed ($K_d > 8$) by all soils studied. Earlier studies of carbendazim sorption on different soils gave K_d values > 3 (Autin and Briggs, 1975). Similar results were reported by Peter and Avis (1991), who studied the sorption of weak bases including carbendazim on soils and their results showed that carbendazim was strongly sorbed (K_d 9-35) at low pH. The higher and lower organic carbon content of the soil used (0.3 to 9.8) may account for the lower or higher K_d values compared with the K_d values reported by Autin and Peter.

Many studies of the sorption of basic pesticides by soil have shown that the most important soil fraction related to sorption is the organic carbon. Cancela *et al* (1992) investigated the sorption of carbendazim on soil showing that the correlation between organic matter content and sorption coefficient was high ($R^2=0.92$). Several sorption mechanisms were postulated for the very complex process of interaction between organic colloids and basic pesticides (Weber, Weed and Ward, 1969).

The interaction of organic substances with clays depends on the physical, chemical, and biological properties of the soil matrix. Organic compounds that are weakly basic may be sorbed to clay particles after protonation, a process in which an organic molecule assumes a positive charge by accepting an H^+ ion (Jacks, 1963).

Aharonson and Kafkafi (1975) suggested that sorption of carbendazim on clay surfaces is due to protonation of the basic organic molecule, and therefore dependent upon the acidity of the clay surface. Thus, the pH dependence of the sorption of carbendazim derivatives by soils may also be due to protonation of the molecules on the soil surface. The authors suggested that carbendazim may be sorbed on montmorillonite and soils by ion exchange. In this study, the correlation of clay content with K_d ($R^2=0.66$) was weaker than that with the organic carbon content. This rather poor correlation may be due to the fact that the soil from TG has a lower clays content, but higher organic carbon content than the ST soils, resulting in a greater sorption on the ST soil due to its higher organic carbon content.

The poor correlation found between K_d and soil pH may simply reflect the narrow range of pH values in the soil studied (from 2.9 to 5.2)

Organic carbon versus clay as a sorbent

Walker and Crawford (1968) suggested that, up to an organic carbon content of about 8 percent, organic and mineral surfaces are both involved in sorption; at higher organic carbon content, sorption occurs mostly on organic surfaces. Consequently, the ST, TG and AG soils sorbed carbendazim on both the organic carbon and soil mineral surfaces, while the sorption of carbendazim on CT soil was mainly influenced by the organic carbon content.

Desorption of carbendazim

K_d desorption increased for all soils with increasing desorption equilibrium steps, the increase was significantly higher for the CT soil. The CT soil has the highest OC and clay content of the soils investigated, and consequently a greater number of sorption sites with different binding strengths. Therefore, the increase in K_d is probably due to the removal of more readily desorbable carbendazim during the first extraction step, while at later equilibration steps less carbendazim desorbed from the more strongly sorbing sites.

Desorbable amounts of carbendazim from the soils were in the order CT<TG<AG<ST. One explanation may be that desorption of organic compounds from soil organic matter is slower than from clay (Harris and Warren, 1964; Helling, Kearney and Alexander, 1971; Jamet and Piedallu, 1975a; McGlamery and Slife, 1966). In some cases, organic carbon sorption is partially irreversible (Swanson and Dutt, 1973; Moyer, McKercher and Hance, 1972). In our case, the organic carbon keeps the most important role in the CT soil to sorb carbendazim, and a result, the lowest amount of carbendazim was desorbable. In contrast, in ST soil, organic carbon was less important in the sorption process, the result being that a larger proportion of carbendazim was desorbable than in the CT soil

In the case of TG and AG soil, the effect of organic carbon and clay cannot easily be separated. One explanation to the lower desorption from TG than from AG soil could be that in TG soil, organic carbon plays the most important role for sorption of carbendazim, whereas in AG soil both organic carbon and clay are important for sorption. The higher proportion of carbendazim sorbed to organic carbon may be caused by less the amount of desorption in TG soil than in AG soil.

The sorption-desorption isotherms of carbendazim

The Freundlich equation can reasonably describe the sorption of carbendazim on the investigated soils, AG ($R^2 = 0.77$), CT ($R^2 = 0.8$), ST ($R^2 = 0.86$), and TG ($R^2 = 0.84$). The sorption coefficient, K_f was highest in CT soil ($K_f = 34.7$), indicating that CT soils sorbed carbendazim stronger than in the other soils. The results correspond with results obtained in a previous study by Canleda (1992) who investigated the sorption of carbendazim on soil with different organic carbon content, and obtained a correlation coefficients between K_f and organic carbon content of 0.92.

The average slope ($1/n$) for the sorption of carbendazim on AG, CT, ST, and TG soils were, 0.91, 0.33, 0.58 and 0.57 respectively. Slopes were <1 , indicating a convex, or L-type isotherm (Giles, *et al.*, 1960). The slope of the isotherms steadily decreased with increasing solute concentration, because vacant sites became less accessible as the surface was progressively covered. The curvilinear slopes suggest that the number of available sites for sorption was limiting factor.

The slopes of all desorption isotherms ($1/n_{des}$) were less than their sorption ($1/n_{ads}$) values, indicating hysteresis. The most likely cause for hysteresis is the relatively higher organic carbon content in CT soil than in the other soils. Carbendazim bonded on soils (nondesorbable), has depending on sorption strength been characterised as water, acetone or ammonium chloride extractable (Austin and Brigg, 1976), thus, acetone and ammonium chloride are commonly used to extract the most strongly sorbed carbendazim residues from the soil.

Desorption hysteresis has been reported for a large number of soil-organic compound systems, and several explanations, such as chemical or biological transformation, nonequilibrium conditions, and high-energy bonding, have been proposed (Clay and Koskinen, 1990). This study did not indicate that degradation was taking place during desorption experiments, although further studies would be needed to understand this hysteresis phenomenon.

Effect of pH on the sorption

Effects of the pH change on the sorption of organic chemical are commonly used to determine bonding mechanism of acidic and basic organic chemical. Weakly basic compound like carbendazim may adsorb by cation exchange while weakly acidic compounds may adsorb by anion exchange (Khan, 1974; Burns *et al.*, 1973). Sorption of carbendazim on ST soil types in the range pH 3-7 was strong and increased to values of $K_d > 40$ at the lower pH. As mentioned above, Soc Trang soil type content only 0.3% organic carbon, so that the sorption of carbendazim on soil is dominated by clay content (Walker and Crawford, 1968). As the pH decreased the sorption of carbendazim was enhanced by protonation of the carbendazim molecules and the ensuing cation sorption

In the case of CT soil, K_d values increased with increasing pH. The reason for the increase in K_d with increased pH is not entirely understood. One explanation may be that solubility of carbendazim decreases with increased pH (solubility of carbendazim in water (24°C), decrease from 29mg/l at pH4, to 8mg/L at pH7), (The Pesticide Manual, 1997). Sorption is said to decrease as solubility in water increases. This effect has been reported by several workers (Hilton and Yuen, 1963; Bailey, White and Rothberg, 1968).

The CT soil had a very low initial pH combined with high organic carbon content. When pH increases, the humic molecules will deprotonate and increase their negative charge. Also, Al ions initially complexed to the organic matter will start to hydrolyse and eventually precipitate as $Al(OH)_3$. These processes will also contribute to the increase in negative charge. At least to some extent, the increasing exposure of negative charge on humic molecules with increasing pH may over compensate the declining positive charge of the carbendazim molecules.

Conclusions

The results obtained in this study showed that:

- Sorption of carbendazim on soil is affected by soil properties, sorption increased with increased soil organic carbon and clay contents.
- Carbendazim sorption follows the Freundlich sorption equation under the experimental condition used.
- The influence of pH on sorption of carbendazim on CT soil and ST soil showed completely different behaviour. Sorption of carbendazim on ST soil increased as the pH decreased. In contrast, sorption of carbendazim by CT soil increased as the pH increased
- Desorption as percent of initially sorbed carbendazim decreased with increased organic carbon content.
- Most acid sulphate soils in the Mekong Delta, Vietnam have very high organic carbon and clays contents (organic carbon from 2.7 to 9.8%, and clays contents from 30 to 50%). Consequently, sorption of carbendazim on the CT soil was high and desorption low. Carbendazim remains in the CT soil in large amounts during long times, in an immobilised state due to interaction with soil colloids. On the other hand, sandy soil in this region are low in both organic carbon and clay contents (organic carbon <1%; clays content < 30%) and potentially may leach carbendazim that could contaminate underground and surface waters.

Acknowledgements

First of all, I would like to thank to Dr. **Tomas Bergl f**, Dr **Henrik Kylin** my main supervisor for all their help, for directing me to this new research field, for all stimulating discussions and encountering criticism of my work during my entire stay in Sweden.

I am very grateful to Professor **Ingvar Nilsson** for all kinds of help and support during the time I stayed and studied in Sweden. The knowledge in soil chemistry he gave me is very valuable.

I am deeply indebted to Dr. **Tran Kim Tinh** for his support and encouragement, for understanding my problem and giving me a wide range of solutions to the problem, for helping me to select the site for my experiments

A lot of thanks to:

Mrs. **Gunborg Alex** and Mr **Tomas Bergl f** for training me to analyses pesticides in soil in my preliminary experiment.

Mr **Vo Tong Anh**, thank a lot for your help to classificate the soil in my experiment. Mr **Pham Van Dung**, thank you very much for your assistance during the laboratory work. Mr **Ha Gia Xuong**, thank you a lot for your providing facilities and chemical when I needed, Mr **Ngo Tan Phu**, for helping me to take all soil sampling in the field. **Tran Ba Linh**, thank you very much for analysing soil physics and Mr **Tran Ngoc Dinh** for helping me a lot when I got the problems with UV

Mr **Pham Van Quang** Mr. **Ragnar Persson** for ready help when I got some troubles with computer.

Mrs. **Anna Hedlund** and her family for their kindness and hospitality.

Mrs. **Evi Marklund**, my apartment-owner at my last time in Sweden. Thanks to her for being my company at dinners, she is so helpful to me.

I also would like to thank all the teachers at the Swedish University of Agricultural Sciences ,SLU for giving me a lot of knowledge in Agriculture. To the students I worked with and the people I met in Uppsala for their hospitality and all great fun we all had.

I thank the Swedish International Development Agency – SAREC/SIDA and SLU for funding this MSc project.

All my Vietnamese students in Sweden, previously or at present, they are **Tran Kim Tinh, Chau Minh Khoi, Do Quang Minh, Nguyen Phan Duy Thai, Nguyen Nhut Xuan Dung, Bui Huy Nhu Phuc, Minh Ha Fagertröm, Thuy Olsson, Nguyen Thi Mui, Nguyen Thanh Hoi, Pham Van Quang, Nguyen Van Thu, Bui Xuan Men, Le Duc Ngoan, Ngo Van Man, Nguyen Van Sanh, Nguyen Ha Khoa, Dao Nguyen Hoai Nam, Lam Quang Nga, Le Van An, Tran Duc Chinh** and his family for the parties and pleasures we shared.

To my teachers and colleagues in Cantho University – Vietnam:

I am deeply indebted to Mrs.**Vo Thi Guong**, Heat of Department for all kinds of help, support and facilities during the laboratory work at the Soil Science Department.

Warm thanks to my teachers, staffs and my classmate colleagues at the College of Agriculture and the Department of Soil Science, Can Tho University for all help, fun and moral support.

I wish to express my gratitude to my parents. Thank you parents that you gave me my life and education in Viet Nam, my parents-in-law and my brother, my brother-in law, my sister and my sister-in law for their commitment, inspiration and throughout the period.

Finally my deepest gratitude to my wife **Nguyen Thi My Tien** and my daughter **Tran Nguyen Kha Vy** who encouraged and gave spiritual and moral support during the time to carry out this thesis.

References

- Adams, R. S. Jr. 1973. Factors influencing soil adsorption and bioactivity of pesticides. *Res. Rev.* 47, 1-54.
- Aharonson, N. and Kafkafi, U. 1975a. adsorption of benzimidazole fungicides on montmorillonite and kaolinite clay surface. *J. Agric. Food Chem.* 23, 434-437.
- Aharonson, N. and Kafkafi, U. 1975b. Adsorption, mobility and persistence of Thiabendazole and methyl 2-benzimidazolecarbamate in soil. *J. Agric. Food Chem.* 23, 720-724.
- Ashton, F. M. 1961. Movement of herbicides in soil with simulated furrow irrigation. *Weed* 9: 612-619.
- Austin, D. G. and Briggs, G. G. 1976. A new extraction method for benomyl residues in soil and its application in movement and persistence studies. *Pes. Sci.* 7, 201-210.
- Bailey, G. D., and White, J. L. 1964. Soil pesticides relationships, Review of adsorption and desorption of organic pesticides by soil colloids, with implication concerning pesticides in soil bioactivity. *J. Agric. Food chem.* 12, 324-332.
- Bailey, G. W. and White, J. L. 1970. *Residue Rev.* 32,29.
- Bailey, G. W., White, J. L. and Rothberg, T. 1968. Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. Proc.* 32, 222-234
- Barlow, F. and Hadaway, A. B. 1955. Studies on aqueous suspensions of insecticides. Part V. the sorption of insecticides by soils. *Bull. Ent. Res.* 46, 547-559.
- Bingham, F. T., Sims, J. R. and Page, A. L. 1965. Retention of acetate by montmorillonite. *Soil Sci. Soc. Am. Proc.* 29, 670-672.
- Brigg, G. C. 1973. *A simple relationship between soil adsorption of organic chemicals and their octanol/partition coefficient*, Proc. Br. Insectic. Fungic. Conf. 7, 83-86.
- Burchill, S., Heyer, M. H. B. and Greenland, D. J. 1981. *The chemical of soil processes*. John Wiley and Sons, Chichester, England. p, 221-400
- Burns, I. G., Hayer, M. H. B. and Stacey, M. 1973a. Some physicochemistry interactions of Paraquats with soil organic materials and model compounds. I. Effect of temperature, lime and adsorbate degradation on Paraquat adsorption. *Weed Res.* 13, 67-138.
- Cancela, G. D., E. R. Taboada and Rasero, F.S. 1992. Carbendazim adsorption on montmorillonite, peat and soils. *J. Soil. Sci.* 43, 99-111.
- Chaussidon, J. and Calvet, R. 1975. *Catalytic reaction on clay surfaces*. In F. Coulson and F. Korte (eds.) Pesticides. Environ. Qty. Saf. Suppl. 3, 230-236.
- Chiou, C. T., Peter, L. T. and Freed, V. H. 1979. A physical concept of soil-water equilibria for noninonic organic compound. *Science.* 206, 831-832.
- Clay, S.A. and Koskinen, W. C. 1990a. Characterisation of alachlor and atrazine desorption from soil. *Weed Sci.* 38, 74-80.
- Coleman, N. T. and Thomas, G. W. 1967. The basic chemistry of soil acidity. *In Soil Acidity and Liming*, Am. Soc. Agron. Monograph #12. Madison, Wisconsin.
- Edginton, L. V., Martin, R. A., Bruin, G.C. and Parsons, I. M. 1980. *Ph.D dis.*, 64,16
- Farmer, V. C. and Mortland, M. 1966. An infrared study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite. *J. Chel. Soc. A.* pp. 344-351. *Geochim. Cosmochim. Acta. Soil Sci.* 83, 487-496.

- Giles, C. H., McEwan, J. H., Nakhwa, S. N. and Smith, D 1960. Studies in adsorption .XI. A system of classification of solution adsorption isotherm and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of soils. *J. chem. So.* 3973-3993.
- Graham-Bryce, I. J and Cotts. 1971. *J. Proc. 6th Br. Insectic. Fungic. Conf.* 2,419.
- Graham-Bryce, I. J. 1967. Adsorption of diflufenoxuron by soil. *J Sci. Food Agric.* 18, 72-77.
- Grim, R. E. 1968. *Clay mineralogy*. McGraw Hill, New York.
- Gunter, F.A. 1970. *Residues Rev*, 32, 12.
- Hai, T. V. 1998. Personal communication, Department of Plant Protection, Can Tho University.
- Hammer, J. W. and Thomson, J. M. 1972. *Organic chemistry in the soil environment*. vol., Marcel Decker, New York. pp, 49-143.
- Hammer, J. W., Goring, C. A. I. and Youngson, C. R. 1966. Sorption and leaching of 4-amino-3,5,6-trichloropicolinic acid in soil. *Adv. Chem. Ser.* 60, 23-37.
- Hance, R. J. 1965a. the adsorption of urea and some of its derivatives by a variety of soils. *Weed Res.* 5, 98-107.
- Haque, R. and Freed, V. 1974. Behaviour of pesticides in the environment-environment chemodynamic. *Res. Rev.* 52, 89-116.
- Harris, C. I. and Warren, C. F. 1964. Adsorption and desorption of herbicides by soil. *Weeds.* 12, 120-126.
- Hayes, M. H. B. 1970. Adsorption of triazine herbicides on soil organic matter, including a short review on soil organic matter chemistry. *Res. Rev.* 32, 131-171.
- Helling. C. S., Kearney, P. C. and Alexander, M. 1971. Behaviour of pesticides in soil. *Adv. Agron.* 23, 174-240.
- Helweg, A. 1976. Degradation and adsorption of carbendazim and 2-aminobenzimidazole in soil. *Pestic. Sci.* 8, 71-78.
- Hermanson, H. P. and Forbes, C. 1966. Soil properties effecting Dieldrin toxicity to *Drosophila melanogaster*. *Soil Sci. Soc. Am. Proc.* 30, 748-751.
- Hilton, H. W. and Yuen, Q. H. 1963. Adsorption of several permanence herbicides by Hawaiian sugar cane soils. *J. Agric. Food Chem.* 11, 230-234.
- Hingston, F. J., Atkinson, R. J. Poener, A. M. and Quirk, J. P. 1967. *Specific adsorption of anion*. *Nature* 215, 1459-1461.
- Hinston, F. J., Atkinson, R.J. Posner, A. M. and Quirk, J.P. 1968. *Specific adsorption of anions on goethite*. *Trans. 9th Int. Congr. Soil Sci. Australia.* 1, 669-678.
- Huang, P.M., Grover, R. and McKercher, R. B. 1984. Components and particle size fraction involved in atrazin adsorption by soil. *Soil. Sci.* 138, 20/24
- Jack, G. V. 1963. *Soil. Fert.* 26, 147
- Jamet, P. and Piedallu, M. A. 1975a. Adsorption and desorption of Pyrazon (5-amino-4-chloro-2-phenyl-1,3-(2H)-pyridazinone) by different types of soils. *Weed Res.* 15, 113-121.
- Jamet, P. and Piedallu, M. A. 1975b. Movement of Carbofuran in different types of soil, Study of the adsorption and desorption of Carbofuran. *Phytiatr. Phytopharm.* 24, 297-295.
- Karickhoff, S. W., Brown, D. S. and Scott, T. A. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 13, 241-248.
- Khan, S. U. 1974. Interaction of biryridylum herbicides with organoclay complex. *J. Soil. Sci.* 24, 244-248.

- King, P. H. and McCarty, P. L. 1968. A chromatographic model for predicting pesticide migration in soils. *Soil Sci.* 106, 248-261.
- Klopping, H. L. 1961. Abstracted in *Chem. Abstr.* 55,3617
- Ladlie, J. S. 1975. *Effect of soil pH on Metribuzin activity and fate in soil. Ph.D Dissertation.* Michigan State Uvi. East Lansing, Michigan.
- Lafleur, K. S. 1976. Prometryne desorption and movement in soil columns. *Soil Sci.* 121, 9-15
- Lailach, G. E., Thomson, T. D. and Brindley, G. W. 1968b. adsorption of pyridine, purines and nucleosides by Co, Ni, Cu, Fe(III)- montmorillonite. *Clays and clay Miner.* 16, 295-231.
- Lambert, S. M. and Omega. 1968. A useful index of soil sorption equilibria. *J. Agric. Food Chem.* 16, 340-340.
- Leopold, A. C., Schaik, P. V. and Neal, M. 1960. Molecular structure and herbicide adsorption. *Weeds.* 8, 48-54.
- Lopatin, G. and Eirich, F. J. 1960. *The adsorption of poly methacyclic acid (PMAA).* Proc. 3rd Int. Cong. Surface activity, Cologne. 2, 97-103.
- MacNamara, G. M. and Toth, S. J. 1970. Adsorption of Linuron and Malathion by soil and clay minerals. *Soil Sci.* 109, 234-240.
- Mallawatantri, A.P., Maccconkey, B. G. and Mulla, D. J. 1996. Characterisation of pesticides sorption, desorption in macropore linings and soil horizons of Thatuna silt loam. *J. Environ Qual.* 25, 227-235.
- McGlamery, M. D. and Slife, F. W. 1966. The adsorption and desorption of Atrazine as effected as pH, temperature and concentration. *Weeds* 14, 237.239.
- Meggitt, W. F. 1970. *Pesticides in Soil, Ecology, Degradation and movement.* Michigan State University Press, East Lansing.
- Mervosh, T. L., Sim, G.K., Stoller, E. W. and Ellsworth, T.L. 1995. Clomazone sorption in soil: incubation time, temperature, and soil moisture effect. *J. Agric Food Chem.* 43, 2295-2300.
- Mithyantha, M. S., Rao, K. B. Biddappa, C. C. Lillaram, N. T. and Perur, N. G. 1975. Paraquat adsorption and clay minerals. *Bull. Indian Natl. Sci. Acad.* 50, 293-298.
- Moyer, J. R., McKercher, R. B. and Hance, R. J. 1972. Desorption of some herbicides from montmorillonite and peat. *Can. J. Soil. Sci.* 55, 439-447.
- Muzik, T. J. and Mauldin, W. G. 1964. Influence of environment on the response of plants to herbicides. *Weeds* 12, 142-145.
- Nearpass, D. C. 1965. Effect of soil acidity on the adsorption, penetration and persistence of Simazine. *Weeds* 13, 341-346.
- O'Connor, G. A. and Anderson, J. U. 1974. Soil factors effecting the adsorption of 2,4,5-T. *Soil Sci. Soc. Am. Proc.* 38, 433-436.
- OECD guidelines for testing of chemicals (1996). *Adsorption /desorption using a Batch Equilibrium Method.*
- Osgerby, J. M. 1970. Sorption of unionised pesticides by soil. In sorption and transport Processes in *Soil. Soc. Chel. Ind. Monograph* 37, 63.78. London.
- Peter, H. N. and Avis, A. E, 1991. Sorption of ionisable organic compounds by fields soil. Part 2: cation, bases and zwitterions. *Pes. Sci.* 33, 331-345.
- Pusino, A., Liu, W and Carlo, G. Adsorption of tricolopyr on soil and some it component. *J. Agric Food Chem.* 42, 1026-1029.
- Pusito, A., Liu, W and Gessa, G. 1992. Influence of organic matter and its clay complexes on metolachlor adsorption on soil. *Pes. Sci.* 36, 283-286.

- Quiquan, W., Weichun, Y and Weiping, L. 1999. Adsorption of acetanilide herbicides in soils and its correlation with soil properties. *Pes. Sci.* 55, 1103-1108
- Saltzman, S., Kliger, L. and Yaron, B. 1972. Adsorption, desorption of Malathion as effected by soil organic matter. *J. Agric. Food chem.* 20, 1226-1229.
- Sensini, N and Testini, C. 1982. Physical-chemical investigation of interaction mechanisms between s-triazin herbicides and soil humic acids. *Elsevier Science Publishers.* 28, 129-146.
- Singh, P and P. N. Thapliyal. 1987. Effect of some factors on persistence and adsorption of carbendazim in soil. *Indin Phytopath.* 40, 88-92.
- Sposito, G. 1989. *The chemistry of soils.* Oxford University press, Inc. pp, 42-61.
- Sprankle, P., Meggitt, W. F. and Penner, D. 1975b. Adsorption, mobility and microbial degradation of glyphosate in the soil. *Weed. Sci.* 23, 229/234.
- Stevenson, F. J. 1982. *Humis chemistry: Genesis, composition, reactions.* Wiley- interscience, New York.
- Swan, R. L. and Eschenroeder, A. 1983. *The fate of chemical in the environment*, ACS symposium Series No.225. Am. Chem. Soc. Washington.
- Swanson, R. A. and Dutt, G. R. 1973. Chemical and physical processes that effect Atrazine distribution in soil system. *Soil Sci. Soc. Am. Proc.* 34, 872-876.
- The Pesticides Manual (1997), eleventh edition, British crop protection council, editor C D S Tomlin.
- Torstenson, L. (1993). *Herbicides.* Swedish University of Agricultural Sciences
- Wada, K. and Harward M. E., 1974. Amorphous clay constituents of soils. *Adv. Agron.* 26, 211-260.
- Walker, A. C. and Crawford, J. V. 1968. The role of organic matter in adsorption of triazine herbicides by soil. In *Isotopes and Radiation of Soil Organic Matter Studies.* Proc. 2nd symp., Int. Atomic Energy Agency, Vienna. pp. 91-105.
- Vallett, M., Calvet, R. and Chaussidon, J. 1973. Addition remarks on several physical- chemical aspects of the adsorption of Atrazine by montmorillonite. In *herbicides in soil.* Proc. European Weed Pes. Council Symp. Versailles, France.
- Wan, H. B. Koeng, M. and Moh, C.Y. 1994. *J. Agric. Food Chem.*, 42, 2625.
- Wanchope, R. D. 1975. Fixation of arsenical herbicides, phosphates and aresennate in alluvial soils. *J. Environ. Qual.* 4, 355-358.
- Ve, N. B. and Anh, V. T. 1990. *Soil map of the Mekong Delta based on the soil taxonomy, scale 1/25000.* National project 60B. Soil Science Department. Can Tho University.
- Weber, J. B. 1966. *Molecular structure and pH effects on the adsorption of 13 s-triazine by montmorillonite clay.* Am. Miner. 51, 1657-1670.
- Weber, J. B. 1970a. Mechanisms of adsorption of s-triazine by clay colloids and factor effecting plant availability. *Res. Rev.* 32, 93-130.
- Weber, J. B. 1970b. Adsorption of s-triazine by montmorillonite as a function of pH and molecular structure. *Soil Sci. Soc. Am. Proc.* 34, 401-404.
- Weber, J. B. and Miller, C. T. 1989. Organic chemical movement over and through the soil. In reaction and movement of organic chemicals in soil. *Soil. Sci. Soc. Am.* Madison.WI. pp. 305-334.
- Weber, J. B. and Scott, D. C. 1966. Availability of a cationic adsorption herbicide sorbed on clay minerals to cucumber seeding. *Soil Sci* 152, 1400-1402.

Weber, J. B. and Best, J. A. 1972. Activity and movement of 13 soil applied herbicides as influenced by soil reaction. *Proc. South. Weed Sci. Soc.* 25, 403-413.

Weber, J. B., Perry, P. W. and Upchurch. 1965. The influence of temperature in time on the adsorption of Paraquat, Diquat, 2,4-D and prometone by clays, charcoal, and an anion-exchange resin. *Soil Sci. Soc. Am. Proc.* 29, 678-688.

Weber, J. B., Weed, S. B. and Ward, T. M. 1969b. Adsorption of s-triazine by soil organic matter. *Weed Sci.* 17, 417-421.

Yaron, B. and Saltzman, S. 1972. Influence of water and temperature on adsorption of Parathion by soils. *Soil Sci. Soc. Am. Proc.* 36, 583-586.