



CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Endosulfan

Most pesticides used in agriculture have the potential to affect non-target organisms and to contaminate water resources. Endosulfan, a hydrophobic chemical (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzo(e)dioxathiepin-3-oxide) is a chlorinated hydrocarbon of the cyclodiene group (organochlorine). It is a broad spectrum insecticide currently used throughout the world for the control of numerous insects in both food and non-food crops. In Thailand, endosulfan has been used extensively for the eradication of Japanese apple snails in paddy fields and for the control of thrip, bollworm, aphid, and leafhopper in vegetable and fruit farms. Because of abundant usage and potential transport, endosulfan is frequently detected in the atmosphere, soils, sediments, and surface waters at high levels (Schulz, 2004).

Technical endosulfan is a mixture of two isomers, alpha (α) and beta (β) endosulfan in a ratio of 7:3, and endosulfan sulfate is derivative of parent endosulfan. Endosulfan is a cream to brown crystalline solid with a melting point of 70-100 °C, a water solubility (20 °C) of 500 $\mu\text{g L}^{-1}$, and a vapor pressure (25 °C) of 1×10^{-5} mmHg. The α -isomer is more toxic than the β -isomer while the endosulfan sulfate is as toxic as the β -isomer (Barnes and Ware, 1965; Devi *et al.*, 1981; Barry *et al.*, 1995).

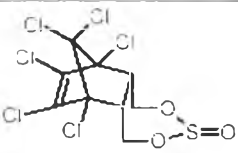
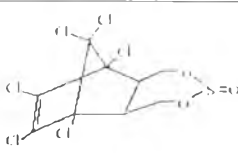
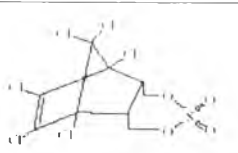
According to ESCAP/EC (1994) and IAEA-TECDOC-695 (1991) they found that endosulfan is very toxic for fish and its LD₅₀ is 1-10 µg L⁻¹.

2.1.1 Properties

The α - and β -isomers of endosulfan have half-lives of only few days in water, but the endosulfan sulfate (Martens, 1976; Chopra and Mahfouz, 1977; Katayama and Matsumura, 1993) has an aqueous half-life of several weeks (Miles and Moy, 1979; Peterson and Batley, 1993). Both isomers and the sulfate metabolite of endosulfan are more persistent when sorbed to soil and sediment (Van Dyk and Van der Linde, 1976; Rao and Murty, 1980). Half-lives of total endosulfan toxic residues (α - and β -endosulfan and the sulfate product) were 1.6 days in foliage and 7.1 days in soil, and could be explained by the rapid volatilization of the parent isomers in the first 5 d (up to 70% of endosulfan volatilizes) (Kennedy *et al.*, 2001). It should be noted that β -endosulfan is slowly converted to α -endosulfan (Hapeman *et al.* 1997).

Technical-grade endosulfan contains at least 94% of two pure isomers, α - and β -endosulfan (German Federal Environment Agency, 2004). Endosulfan sulfate is a reaction product found in technical endosulfan; it is also found in the environment due to photolysis and in organisms as a result of oxidation by biotransformation. The chemical formula, structure, physical and chemical properties for endosulfan, α -endosulfan, β -endosulfan, and endosulfan sulfate are listed in Tables 2.1.

Table 2.1 Molecular formula and selected properties of α -endosulfan, β -endosulfan, and sulfate endosulfan (source: ATSDR, 2000).

Property	α -Endosulfan	β -Endosulfan	Sulfate Endosulfan
Chemical structure			
Molecular formula	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_3S$
Molecular weight	406.93	406.93	422.9
Color	Colorless	Cream or tan	Brown
Physical state	Crystalline solid	Crystalline solid	Crystalline solid
Melting point:	108-110 °C	207-209 °C	198-201 °C
Density at 20°C	1.735 g cm ⁻³	No data	No data
Solubility:			
Water at 25 °C	0.53 mg L ⁻¹	0.28 mg L ⁻¹	0.22 mg L ⁻¹
Organic solvent at 20 °C			
Hexane	24 g L ⁻¹	Soluble in most	No data
Acetone	200 g L ⁻¹	organic solvent	No data
Partition coefficients:			
Log K _{ow}	3.83	3.52	3.66
Log K _{oc}	3.55	No data	No data
Vapor pressure at 25 °C	1x10 ⁻⁵ mmHg	1x10 ⁻⁵ mmHg	1x10 ⁻⁵ mmHg
Henry's law constant at 24.8 °C	1x10 ⁻⁵ atm m ³ mol ⁻¹	1.91x10 ⁻⁵ atm m ³ mol ⁻¹	2.61x10 ⁻⁵ atm m ³ mol ⁻¹

2.1.2 Harmful effects

2.1.2.1 Acute toxicity

Endosulfan is a highly toxic substance and carries the signal word DANGER on the label. Toxicity is partly dependent on the manner with which the pesticide is administered (National Institute for Occupational Safety and Health, 1985-86). Undiluted endosulfan is slowly and incompletely absorbed into the body whereas absorption is more rapid in the presence of alcohols, oils and emulsifiers.

Stimulation of the central nervous system is the major characteristic of endosulfan poisoning (Meister, 1994). Symptoms of acute exposure are indistinguishable from symptoms from other cyclodienes (US Department of Health and Human Services, 1990). They include incoordination, even a loss of the ability to stand. Other signs of poisoning include gagging, vomiting, diarrhea, agitation, convulsions and loss of consciousness. Blindness has been documented for cows which grazed in a field sprayed with the compound. The animals completely recovered after a month following the exposure (US Department of Health and Human Services, 1990). In an accidental exposure, sheep and pigs grazing on a sprayed field suffered a lack of muscle coordination and blindness.

The oral LD50 in rats ranges from 18 - 220 mg kg⁻¹. Some other oral LD50 values are: mice 7.36 mg kg⁻¹, hamsters 118 mg kg⁻¹, cats 2 mg kg⁻¹, and dogs 76.7 mg kg⁻¹. The dermal LD50 for rats is 74 mg kg⁻¹ while for rabbits figures from 200 to

359 mg kg⁻¹ are recorded ESCAP/EC (1994). As noted before, the solvents and emulsifiers used to dissolve endosulfan influence its toxicity. Rats have an inhalation LC50 of 8.0 mg m⁻³ for four hours.

2.1.2.2 Chronic toxicity

Several chronic effects have been noted for animals exposed to endosulfan. The pesticide is most likely to affect kidneys, liver, blood chemistry and the parathyroid gland (Meister, 1994).

(1) Reproductive Effects

Rats fed low doses of endosulfan (2.5 mg kg⁻¹ day⁻¹) for three generations showed no ill effects. The same dose in dogs, however, produced vomiting, tremors, and convulsions. These are the symptoms of acute endosulfan poisoning. Higher doses of endosulfan (5.0 mg kg⁻¹ day⁻¹) caused death in rat dams, increased resorption and caused skeletal deformities in the rat fetuses. Female mice fed the compound for 78 weeks (0.1 mg kg⁻¹ day⁻¹) had damage to their reproductive organs (US Department of Health and Human Services, 1990).

(2) Teratogenic Effects

When moderate to high levels of endosulfan (5 or 10 mg kg⁻¹ day⁻¹) were given orally to female rats on days 6 to 14 of pregnancy, no soft tissue defects were found in their offspring. Some delayed bone formation occurred, however. It is possible that chronic exposure to endosulfan may result in reproductive and/or

developmental difficulties in humans. There is no direct evidence of this in humans though.

(3) Mutagenic Effects

Endosulfan is mutagenic to bacterial cells and to yeast cells. The metabolites of endosulfan have also shown the ability to cause cellular changes (US Department of Health and Human Services, 1990). This compound has also caused mutagenic effects in two different mammalian species. It is possible that it would induce these changes in humans.

(4) Carcinogenic Effects

In a national cancer institute study done with both mice and rats, the males of both groups experienced such a high mortality rate that no conclusions could be drawn (National Cancer Institute, 1978). However, the females of both species failed to develop any carcinogenic conditions 78 weeks after being fed diets containing up to 445 ppm (about 23 mg kg⁻¹). There are no reports of cancer in humans exposed to endosulfan. The EPA has placed endosulfan in the "not classifiable" category due to the lack of data on its carcinogenicity.

2.2 Fate and transport

Fate and transport of endosulfan were widely studied. For example, Kennedy *et al.* (2001) found the majority of endosulfan losses on-field occurred by volatilization in first week after application. The portion of soil losses that were accounted by volatile fluxes was ordered 34.5% of α -endosulfan and 14.5% of β -endosulfan (Rice *et al.*, 2002).

According to Awasthi *et al.* (2000), the study of factors influencing the degradation of endosulfan isomers found that were carbon sources, pH, moisture content, concentration of endosulfan, and size of inoculum.

Leonard *et al.* (2001) studied fate of endosulfan and found that loss of endosulfan is due to volatilization and/or chemical hydrolysis of endosulfan. Endosulfan sorption was significantly greater in the largest (>63 μm) particle size fraction than in the smaller size fractions (<5 μm and 5-24 μm) for two field-contaminated sediment samples.

From the study of Laabs *et al.* (2000), the high Koc pesticide such as trifluraline, λ -cyhaloturin, chlopyrifos, and endosulfan remained immobile in soil. That means the Koc value of pesticide influence the transportation. Similar findings were reported for endosulfan using cotton-soil under sub-tropical conditions (Kathpal *et al.*, 1997).

The persistence of endosulfan was studied by Sethunathan *et al.* (2002). They found that the persistence of added endosulfan sulfate was examined in non-flooded and flooded soil samples, unamended and amended with straw. There was no appreciable decrease in the concentration of endosulfan sulfate in any of the treatments during 120-day incubation. Consequently, endosulfan sulfate persisted under both moisture conditions, even after organic addition.

According to Ghadiri and Rose (2001), the degradation of endosulfan in a clay soil was studied. Soil moisture content and temperature are the two most influential factors on the degradation of both α -, β -endosulfan, and endosulfan sulfate. α -endosulfan degradation appears to be more affected by changes in soil water content, while the β -endosulfan is more influenced by temperature.

2.2.1 Partitioning behavior

Reese (1972) indicated that pesticide contamination is originated by spraying of pesticide in agricultural fields to the atmosphere and widely dispersed to the environment. Most of the sprayed pesticide is deposited onto plants, soil, and water. It is transported into the environment via leaching and runoff water. Figure 2.1 shows how pesticide can contaminate the environment. The arrows show the transportation of pesticide into each media. In this diagram, water plays a significant role in mediating the fate and transport of pesticide in the environment.

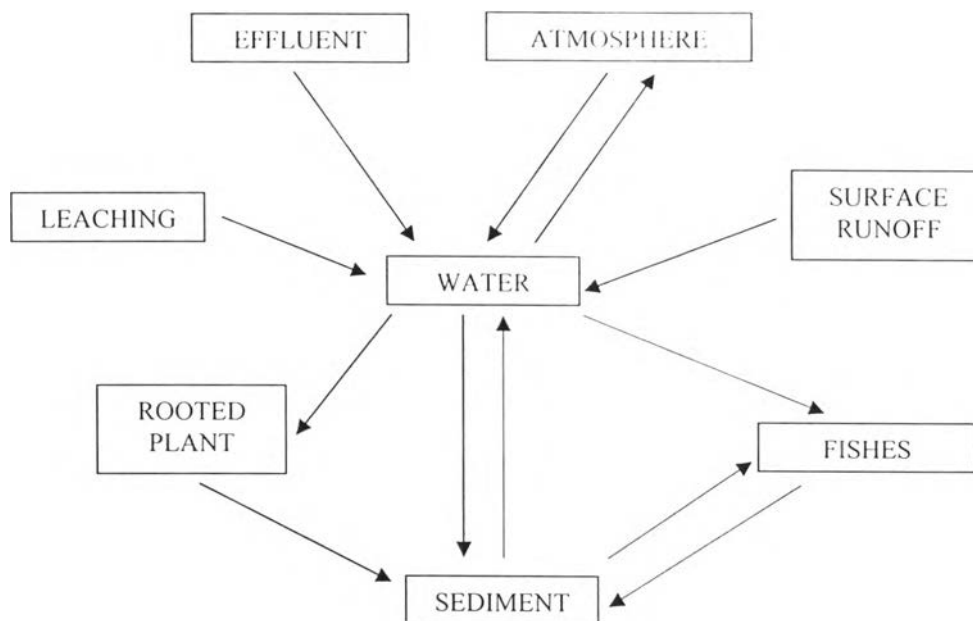


Figure 2.1 Fate and transport of pesticide in the environment.

McEwen and Stephenson (1979) indicated that many factors are known to influence the behavior and fate of pesticides after contact with soil (Figure 2.2). These include:

- (1) Adsorption to clay and organic matter
- (2) Leaching with the downward percolation of water
- (3) Volatilization to the atmosphere
- (4) Uptake by soil organisms or plants
- (5) Movement with runoff water or eroded soil
- (6) Microbial degradation
- (7) Chemical degradation
- (8) Photolysis

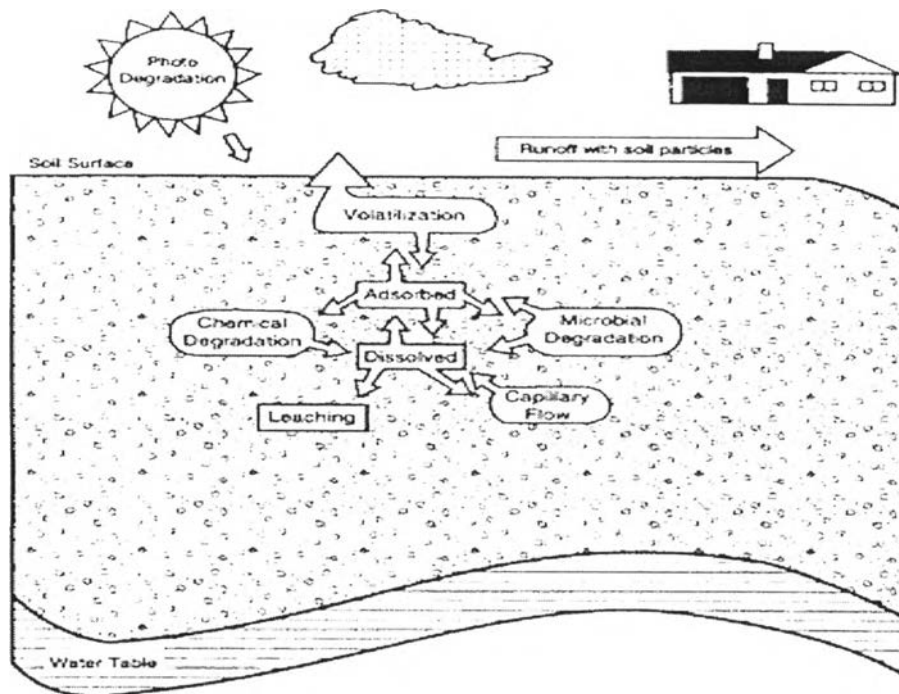


Figure 2.2 General fate of pesticides used in soil (modified from McEwen and Stephenson, 1979).

2.2.2 Sorption and desorption process

Once discharged into the environment, pollutants can be distributed through environmental compartments (e.g., air, soil, and water) as the results of various transport processes (Mackay *et al.*, 1989). The sorption of contaminant on the subsurface media will retard the movement of the contaminant. Adsorption, absorption and sorption are three terms that refer to similar phenomena. Adsorption is the accumulation occurring at an interface, absorption is the partitioning between two phases and sorption is included both processes (Weber, 1972; Weber *et al.*, 1991).

The distribution of a hydrophobic organic compound between water and soil media can be described by the amount of chemical sorbed to soil and the amount in the water at equilibrium. Equilibrium adsorption data are presented in the form of the test chemical between solid sorbent and the solution at equilibrium over the range of concentrations at constant temperature. These isotherms can be linear or nonlinear, depending on the properties of the test chemical and solid on the aqueous phase concentration of the chemical. In many cases, sorption isotherms are linear at low concentration but tend to become nonlinear as the concentration of chemical in the aqueous phase increases (Boethling and Mackay, 2000).

When the measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, a graph is obtained called the adsorption isotherm (Yaron *et al.*, 1996). Three adsorption models are used to describe three different isotherms as shown in Figure 2.3.

A straight-line plot of adsorption implies that the process of adsorption is not affected by solute concentration and that surface of the solid has unlimited capacity for adsorption. Linear adsorption isotherm is appropriate for many species at low solution concentration, but they are not appropriate at higher concentrations when the surface sites for adsorption become saturated (Deutsch, 1997).

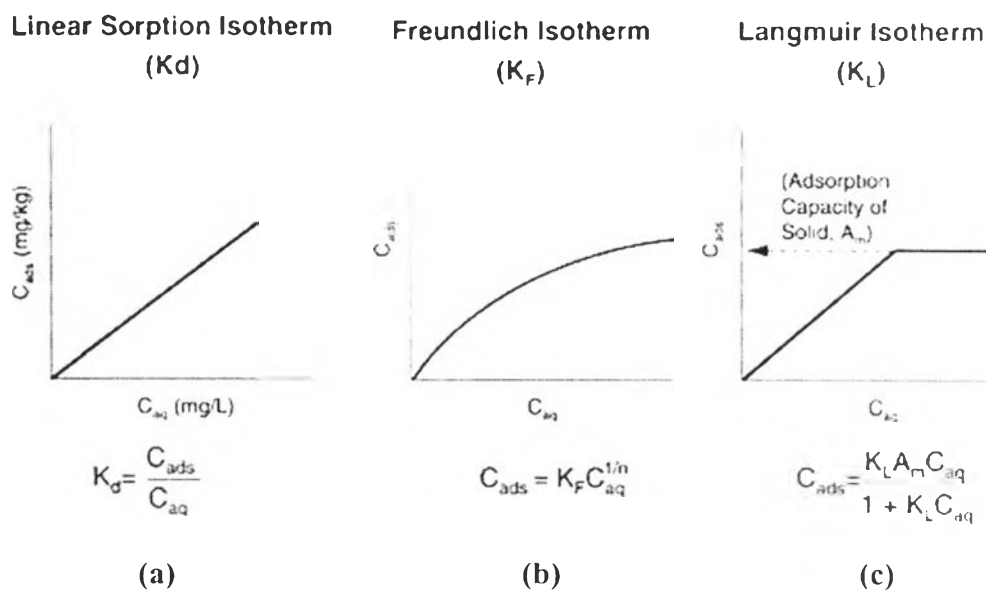


Figure 2.3 Sorption isotherms (a) Linear sorption isotherm (b) Freundlich Isotherm (c) Langmuir Isotherm (Source: Robert *et al*, 1993).

Each of the isotherms is linear at low adsorbate concentration; however, the slope of Freundlich and Langmuir isotherms will be changed at higher adsorbate concentrations. The Freundlich isotherm becomes a curve at higher concentrations reflecting lower adsorption at these values as the adsorption sites become saturated. However, there is no total capacity term in the Freundlich isotherm equation, so there is no upper limit on adsorption. The Langmuir isotherm has a capacity term (A_m) in its definition. Once the concentration of adsorbed species reaches this capacity term, adsorption decrease to zero and any additional increase in species solution concentration remains in solution (Deutsch, 1997).

If the sorption isotherm is linear, the concentration of chemical sorbed by solids is directly proportional to the concentration of the chemical in water, and the slope of the isotherm is referred to as the linear sorption coefficient (K_d) (Tan, 1998).

$$K_d = C_s / C_w \quad (3.1)$$

Where C_s and C_w are the concentrations of the organic chemical sorbed by the solid phase (mg kg^{-1}) and dissolved in aqueous phase (mg L^{-1}), respectively. Units of K_d typically are L kg^{-1} , mL g^{-1} , or $\text{cm}^3 \text{g}^{-1}$.

For nonlinear isotherms, the Freundlich isotherm is often used to describe the relationship between the sorbed (C_s) and the solution phase concentration (C_w):

$$C_s = K_f C_w^N \quad (3.2)$$

Where K_f is the Freundlich sorption coefficient and N is a constant (Tan, 1998).

For the organic content, many studies show that the greater the organic content of the soil media, the greater the sorption potential. Thus, sorption can be characterized in many cases, particularly for hydrophobic organics, on the basis of the organic content of the porous medium of soil media by following linear expression.

$$K_d = K_{oc}f_{oc} \quad (3.3)$$

Where f_{oc} = organic carbon fraction of the porous medium.

K_{oc} = organic carbon partition coefficient of the chemical constituent.

Desorption is sorption reversible process. This can occur when more water enters the soil through rain or irrigation, the sorbed pesticide molecules may be detached from soil particles through a desorption process. The solubility of pesticide and its sorption on soil are inversely related; that is increased solubility result in less sorption.

2.2.3 Factors influencing the persistence of pesticides in soil

Organic matter content is assumed to be the primary factor correlated to pesticide sorption in soils for neutral and weakly ionizable compound (Harper, 1994). This notion was confirmed for Oxisols by Barriuso *et al.* (1992).

According to White (1976), the physico-chemical properties of a pesticide will govern its behavior in the soil and its biological activity. Molecular size, ionisability, water solubility, lipophilicity, polarizability and volatility are all key properties, but generally one or two properties have a dominating influence.

Pignatello and Xing (1996) stated that the extent of adsorption depends on the properties of soil and compound, which include size, shape, configuration, molecular

structure, chemical functions, solubility, polarity, polarizability and charge distribution of interacting species, and acid-base nature of the pesticide molecule.

2.2.3.1 Soil Characteristics

The physical properties of a soil include soil texture, soil structure, and soil density, which are dominant factors that affect the use of a soil. These properties are concerned with the size and content of particle that make up the soil, how the particles are arranged into larger units or aggregates, and individual particles affect other soil properties (Miller and Gardiner, 2001).

(1) Soil Texture and soil structure

Soil texture is physical property of particular importance that is the term used to indicate the proportions of sand, silt, and clay in each soil. The soil texture control water contents, water intakes, aeration, and some chemical properties. The soil texture is classified according to their particle size. Soils that are predominantly clay are called clay (< 0.002 mm); those with high silt content are called silt (0.002-0.05 mm); those with a high sand percentage are called sand (0.05-2.0 mm). A soil does not exhibit the dominant physical properties of any these three groups is called loam. Clay and organic matter contents are important characteristics influencing pesticide sorption mechanism. Clay and organic matter in soil can vary from less than 1 percent in sand to well over 50 percent in heavy clay soils. The vertical and horizontal distribution of pesticides is dependent upon the interaction with soil particles through processes called adsorption and desorption (Miller and Gardiner, 2001).

Adsorption is the binding of a pesticide to the surface of soil particles, especially clay and organic matter. Desorption is the release of adsorbed chemicals from a soil particle surface. Depending on many factors in a soil profile, such as moisture, pH, temperature, etc., compounds may adsorb and desorb from soil particle surfaces as they migrate down through the soil. It is also important to consider the clay, sand and silt content of soils because insecticides generally do not migrate as readily in soils with high clay and organic matter contents. The mineral content of soil is also an important factor in determining the persistence of pesticides by either catalyzing decomposition or affecting the adsorption rate. Because groundwater contamination is an extremely important issue to the general public, understanding how compounds bind to soil particles is an important part of evaluating whether a pesticide will leach. However, there are no conclusive research data to determine how adsorption/desorption affects pesticide efficacy and application rate in different soils. It is generally assumed that since termites come in contact with soil particles, it may not be necessary to adjust pesticide dilution rates for most soils. Additional research is needed to accurately determine if variable rates are needed.

(2) Soil chemical properties

The chemical properties of soil include pH, cation exchange capacity (CEC), clay, humus, and buffering action. The chemical properties of soils are more influenced by the colloids (clay and humus) than by equal weight of the larger silt and sand particles. Clay, the active mineral portion of soils, is colloidal, and most clay is crystalline. The various kinds of clays possess different properties, for example, montmorillonite and vermiculite are swelling-shrinking clays that absorb large

amounts of cations and water. Humus is a temporary intermediate product left after considerable decomposition of plant and animal remains. Clay and humus are the sites of most chemical reaction in soils. The quantity of cations that can hold by a given amount of soil is the cation exchange capacity of that soil.

The pH is a measured of acidity or alkalinity. Soil pH ranges from, about pH 4.0 to about pH 10.0. Buffering capacity is the ability to resist a change in pH of soil. The buffering capacity increases as the cation exchange capacity increase. The most important property of soil is soil organic matter that is a complex and varied mixture of organic substances. It provides much of the cation exchange and water-holding capacities of surface soils. Certain components of soil organic matter are largely responsible for the formation and stabilization of soil aggregates (Miller and Gardiner, 2001). The soil pH is known to have a major impact on performance of pesticides because it affects how rapidly a compound degrades. In general, pesticides used today persist longer in acidic soil than in alkaline soil (Kamble, 1996).

(3) Soil temperature and moisture

For the most part, pesticides will remain more efficacious and persistent in soils with low temperatures and low moisture content. Warm soil temperatures and moist conditions can enhance the activity of insecticide-degrading microorganisms, thereby increasing degradation of compounds (Kamble, 1996).

(4) Soil Microorganisms

Microbial degradation is another process in which soil microbes utilize insecticides as substrate (food source) for growth and maintenance. However, little information is available on how microbial degradation of registered pesticides occurs in various soils (Kamble, 1996).

2.2.3.2 Pesticide characteristics

The second major element affecting pesticide performance involves the chemical characteristics of each pesticide.

(1) Solubility

Solubility of pesticides in water is an important factor affecting their distribution and mobility in soil, but it is not necessarily the best indicator of performance. For example, soluble compounds may have strong affinity to adsorb to soil particles, subsequently limiting their mobility through soil. Ultimately, a combination of factors determines the pesticide mobility in soil (Kamble, 1996).

(2) Degradation

Pesticide efficacy and persistence are primarily affected by the degradation rate of that compound. Once the pesticides are applied to soils, their fate relies on degradation processes. As the pesticide degrades, it is transformed into other compounds that may be more or less toxic than the parent insecticide (Kamble, 1996).

Photodegradation: The breakdown of chemicals due to exposure to sunlight is not a major factor because pesticides are usually applied below the soil surface.

Chemical degradation: The most important process affecting pesticides is chemical degradation which involves hydrolysis, oxidation and reduction. This process directly affects the half life or residual of insecticides in soil.

Hydrolysis is a chemical process in which an insecticide reacts with water, resulting in splitting of the water molecules to form less toxic compounds. There is generally enough moisture in soil to initiate this reaction.

Oxidation is a chemical reaction through which an oxygen atom is added to the parent molecule of an insecticide. Initially, it may not appear that an oxidation reaction results in degradation of insecticides, but a more oxidized form of a molecule may be necessary for further microbial or chemical degradation.

Reduction is the third aspect of chemical degradation. An insecticide molecule is considered to be reduced if its hydrogen content increases or its oxygen content decreases. However, similar to oxidation, reduction may be a preliminary step toward further degradation by other processes. Reduction reactions generally occur under conditions where oxygen is limited (anaerobic environment). Reduction reactions may increase if a soil becomes flooded. As a result, pesticides applied to water-saturated soils may degrade rapidly, rendering the treatment unsuccessful. Areas with excessive water problems should always be corrected prior to pesticide application.

(3) Volatilization

This process involves transforming chemicals from solid or liquid into a gas or vapor. Several factors influence the tendency of pesticides to volatilize and leave soil as a vapor. The structure of the chemical is important because this determines its vapor pressure as well as its solubility in soil water and its tendency to be adsorbed. Cool and dry conditions in soils with high organic matter or clay content normally result in very little loss of even the most volatile chemicals from the soil. Conversely, warm and moist conditions contribute to great desorption and greater volatilization losses (Kamble, 1996). There are many studies described about the factors influencing volatility. They were aqueous solubility, vapor pressure, Henry's law constant, solid-phase partitioning, soil moisture, organic carbon content, and modes of application (Wania and Mackey, 1996; Jury *et al.*, 1984).

2.2.4 Bound pesticide residues

After sorption, pesticide residues may bind tightly to soil particles. Bound residues are defined as chemical species originating from pesticides, those are unable to extract by methods which do not significantly change the chemical nature of these residue (Roberts, 1984). Adsorption is probably the most important mode of interaction between soil and pesticides and control the concentration of the bound residues in the soil liquid phase. Fuhr *et al.* (1998) expanded the definition to include reference to the structure of the matrix: "Bound residues represent compounds in soil, plant or animal, which persist in the matrix form of the parent substance or its metabolites after extraction. The extraction method must not substantially change the

compounds themselves or the nature of the matrix. The nature of the bond can be clarified in part by matrix altering extraction methods and analytical techniques. For example, covalent, ionic and sorptive bonds as well as entrapments have been identified in this way. In general the formation of bound residues reduces the bioaccessibility and bioavailability significantly”.

The nature of the binding forces involved and the types of mechanisms operating in the adsorption process of pesticides onto the soil humic substances. These include ionic, hydrogen and covalent bonding, charge-transfer or electron donor-acceptor mechanisms, van der Waal forces, ligand exchange, and hydrophobic bonding or partitioning (Berry and Boyd, 1985; Calderbank, 1989; Bollag, 1992; Dec and Bollag, 1997). It must be noted that not all mechanisms occur simultaneously; however, two or more may occur simultaneously depending on the nature of functional group and the acidity of the system. Each of mechanisms are described;

Hydrophobic adsorption by soil organic matter and humic substances is suggested as an important mechanism for organochlorine pesticides (Lenheer and Aldrichs, 1971). Hydrophobic retention need not be an active adsorption mechanism, but can also be regarded as a partitioning between a solvent and non-specific surface. The partitioning theory, which treats soil organic matter as a water-immiscible liquid phase, has been used to explain the hydrophobic interaction between pesticides and soils (Karickhoff, 1981).

2.3 Application of wastewater treatment sludge for pesticide sorption

Application of wastewater treatment sludge to soil is a common practice in many countries. The use of treated municipal sewage sludge for soil amendment in agriculture is often considered more desirable than incineration or ocean and surface water dumping. Simultaneously, they can improve soil properties such as organic matter and plant nutrients (Golueke, 1977; Clapp *et al.*, 1986). Nutrients in sludge are used to replace or supplement commercial chemical fertilizers, while sludge organic matter has been seen to improve soil structure, reduce soil erosion and improve crop yield (Metzger and Yaron, 1987; Tester, 1990).

Soil amendment by sludge also affects pesticide binding, pesticide transport, and ultimate distribution in soil profile (Jin and O'Conner, 1990; O'Conner *et al.*, 1990; Bellin *et al.*, 1990). The effects of sludge on sorption of pesticide are probably due to the changes in soil structure and transport characteristics, including increased retention and changes in pore size distribution (Metzger *et al.*, 1987). Examples of studies using sludge for pesticide sorption are as follows.

Guo *et al.* (1991, 1993) studied the sorption of atrazine and alachlor on soils freshly amended with carbon-rich waste materials and found that the sorption coefficient (K_d) for these compounds increased when compared between amended versus unamended soils. Meanwhile, atrazine dissipation from the surface (0-10 cm) of sludge amended soil was not significantly different from non-amended soil in a field experiment (Barriuso *et al.*, 1995). The study added atrazine to the soil five

months after spreading sludge on the field. After one year, there was no apparent difference in distribution of atrazine at lower soil depths in the control field versus the sludge-amended fields.

Jin and O'Connor (1990) found that sludge additions increased toluene adsorption in two soils because of the increased organic C content. The source of organic C (soil or sludge) and soil clay content also influenced toluene adsorption. Toluene adsorption-desorption was reversible in one soil sample, but slightly hysteretic in other soil samples. An air-flow incubation system was used to evaluate toluene volatilization and degradation.

In 1990, O'Connor *et al.* studied the fate of 2,4-Dinitrophenol (DNP) in high pH soils. The adsorption and degradation behavior of DNP in two sludge-amended, calcareous soils was determined and used to explain DNP uptake by plants grown in the soils in the greenhouse. The DNP adsorption was minor in both soils and was only slightly affected by sludge. The DNP degradation was rapid in both soils and was unaffected by sludge. Thus, despite limited soil adsorption, plant uptake of DNP was minor in all crops. The main contribution of plant was to enhance soil DNP degradation.

Bellin *et al.* (1990) studied the sorption and degradation of pentachlorophenol (PCP) by two alkaline and one acid soil in the presence and absence of sewage sludge. The PCP sorption increased with increasing sludge additions. Desorption in the alkaline soils were completely reversible and no irreversible residues were formed.

Leaching of PCP would be most likely in the unamended alkaline soils. However, longer PCP residence times in the acid soil increase the possibility for plant uptake.

From previous studies, the application of sludge for pesticide sorption is seem promising; however environmental problems maybe occur due to the present of trace toxic metals in sludges. Meanwhile, sludges from different sources contain various amounts of toxic metals and have different compositions. We may prevent the contamination problem by selecting sludge from wastewater treatment plants that contain high amount of organic C but low amount of toxic metals. In this study, three types of sludge were used to represent the different sources of wastewater. Pig farm WWTS, municipal WWTS, and food industrial WWTS are represented the wastewater from animal, human activities, and plant, respectively.

2.4 Endosulfan contamination in Thailand

In Thailand, many reports have confirmed the presence of pesticide residues in soil, water, and agricultural products throughout Thailand. The studies of pesticides mostly focus on their accumulation and transportation in the environment. Pesticide concentration levels in soil were much higher than those in water. For example, the maximum concentrations of endosulfan in water and soil in 1997 were 0.001-0.460 $\mu\text{g L}^{-1}$ and 0.011-8.818 $\mu\text{g kg}^{-1}$, respectively (Thapinta and Hudak, 2000). Endosulfan residue was found at significant amounts in water, soil, and rice products (Suwaparp *et al.*, 1999). In addition, a study in Supanburi and Patumthani showed the accumulation of endosulfan residues on paddy fields after application for 100 days

(Agricultural Toxic Substances Division *et al.*, 2000). According to Siriwong (2001), dissolved ozone in water can reduce the endosulfan residues on Chinese cabbage. However, this is not feasible for mitigating endosulfan contamination in the environment. This study was therefore focused on the application of wastewater treatment sludge for endosulfan sorption. Consequently, the process would reduce the discharge of endosulfan into the environment.