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Heptachlor and Its Metabolite: Accumulation and Degradation in Sediment

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1. Introduction

1.1. Organochlorine pesticide and river delta

Chemical pesticides are substances that kill or control an uninvited organism, which all share the common property of blocking a vital metabolic process of the target to which they are toxic [1]. Practically pesticides have been a concern since their introduction, because of the potential impact on human health through chemical contamination and their accumulation in food chain and environment.

Organic pesticides were developed during and after World War II to displaced inorganic and metal organic substances such as sulfur, arsenic, sodium fluoride and boric acid, which used by society for thousands of year. Some of these pesticides were OCPs which are organic compounds that contain chlorine. These OCPs were preferred because of their effective against the target pests even if only small amount was applied to the environment. Neither small amounts of chemicals should enter the environment; however, the organic substances are generally much less toxic to human than the inorganic and metal organic compounds.

Many OCPs share several remarkable properties together with stability against decomposition or degradation in the environment and their very low solubility properties in water, unless oxygen or nitrogen is also present in the molecules. In addition, their high ability to dissolve in hydrocarbon-like environments, fatty material in living matter for example. And the important one is OCPs is relatively high toxicity to insects, but low toxicity to humans [1]. OCPs can enter the environment from direct application and runoff, disposal of contaminated wastes into landfills, emissions from waste incinerators, and releases from manufacturing plants that produce these chemicals. Some OCPs are volatile or can adhere to soil or particles in the air. In aquatic systems, OCPs are adsorbed onto sediments in water that can then bioaccumulate in fish and other marine mammals.

Massive volumes of OCPs have been widely used for more than two decades as the backbone of a pest control strategy. Their lipophilic nature and stability contribute to their high bioaccumulation potential and long persistence. Organochlorine compounds have become an interesting object of study all over the world and are monitored continuously because of their proven toxicity to human beings, animal and plant life, and also food chain. Residues of OCPs were detected in almost all environmental compartments including water bodies, food chain, as well as in humans. Soil is the main repository of these OCPs [2]. The contamination of soil and sediments with persistent OCPs may be related to point sources such as industrial discharges and waste plant effluents, but more frequently, it is attributed to diffuse sources, precipitation, agricultural runoff and particle transport.

Because of hydrophobic characteristics, OCPs are least soluble in water but show a high affinity for different surface area, and those with organic content show the highest adsorption capacity. The organochlorines bound with particulate matter ultimately sink, thereby enhancing the concentration of the pollutant in the bottom sediment. Therefore, sediment acts as one of the main sinks and potential sources for OCPs in the environment [3]. Various reports have already confirmed the contamination with OCPs from different parts of the world. Chang and Doong [4], reported the contamination of BHCs, aldrin, α - and β -endosulfan, dieldrin, endrin and DDTs in estuaries surface sediments of Taiwan. In the same year, Pandit et al. [5] also reported the distribution of BHCs and DDTs in coastal marine of Mumbai. In 2005, Wure and Obbard [6] studied the distribution of organochlorine compounds, BHCs and DDTs, in the sea surface microlayer, water column and sediment of Singapore's coastal environment. Additionally, Cheevaporn and Menasveta [7] reviewed and reported the water pollution in the Gulf of Thailand, which included some OCPs such as BHCs, DDTs, aldrin, dieldrin, α -endosulfan, heptachlor and heptachlor epoxide.

Although the major sink of organochlorine compounds is the sediment, such compounds can bioaccumulate in the biota, especially for the benthic organisms and then enter the food chain. Menone et al. [8] reported that the burrowing crabs, *Chasmagnathus granulatus*, showed bioaccumulation of OCPs from sediments. They suggested that the pesticide levels are more related to the physico-chemical characteristics (e.g. total organic carbon and particle size distribution) of the sediment where the pesticides remain. Boonyatumanond et al. [9] reported the concentration of OCPs compounds in green mussel, *Cara viridis*, the bioindicator for water assessment, in coastal waters along the Gulf of Thailand.

Agricultural pesticides most often are applied as liquids sprayed on the crop or the soil or as a seed treatment. An application of pesticide, depending on crop stage, formulation, intended target, application technique, and weather conditions is distributed between soil, plant foliage or crop residues, and losses due to drift. Chemicals used in the formulation of the pesticide can change the agronomic effects such as effectiveness and phytotoxicity of the formulated product. Chemicals also affect the environmental impact, as dispersion patterns may be altered and the functional activity period of the active ingredient may be lengthened or its degradation delayed. The pesticides that reach the soil or plant material in the target area begin to disappear by degradation or dispersion. Pesticides may volatilize into the air,

runoff or reach into surface water and groundwater, accumulate by plant or soil organisms or stay in the soil [10].

Human and ecological system exposure to micro-organic contaminants is related to their distribution between the various compartments of the environment (atmosphere, soils, surface fresh waters, ground waters, and oceans), to their transport between compartments, and to their availability for uptake and bioaccumulation by organisms. All the compartments have their importance but each has its own significance. The most obvious concern relating to the pollutants in the freshwater compartment is the possibility of adverse effects upon the freshwater ecosystem. In addition, micro-organics in rivers can be washed out to the seashore and so freshwater can also act as a major source of the pollutants to the oceans, where they may result in adverse ecological effects, particularly in the coastal zone. Human exposure can then occur through eating both freshwater and saltwater fish and other seafood. Within the freshwater compartment, it is particularly important to consider the sediment phase, because the largely hydrophobic nature of many micro-organic pollutants, which are known to associate strongly with natural sediments and dissolved organic matter. Sediments therefore have the strong potential to influence micro-organic pollutants fate in bed sediment, both freshwater and coastal marine.

2. Sources and transport of pesticides in freshwater sedimentary environments

The sources and transport of OCPs to and within freshwater sedimentary environments are obviously a crucial factor in determining the concentrations and the distribution of contaminants in freshwaters [11]. After applied to the soil zone, many pesticides transport to sedimentary systems, through leaching, surface run-off, spray drift, soil erosion and volatilization. A complex range of factors determines the fate of pesticides applied to agricultural land. These include the method of application of the active ingredient, and the weather conditions such as temperature, wind direction and speed, and rainfall following the application. The antecedent conditions, topography, soil type, farming practice and crop grown on the land, also affect water movement and dispersal of pesticides. These factors are reported to be more important than the physico-chemical parameters of the compound [12].

Other major routes of these organics compounds into freshwater sedimentary environments include direct discharges from industry, treated effluent discharge from both domestic and industrial sources, storm-water discharge from storm drain and aerial deposition. When wastewaters are treated before discharge to rivers and lakes, the concentration of a range of pesticide in the effluents is likely to be lower than in direct discharges because of possible sorption to solids and degradation during waste treatment. A huge range of the compounds is used and produced in industrial processes and may be discharged either from treatment plants or direct into freshwater.

In some situations, industrial effluents are a very complex mixture of the OCPs and it is impossible to know the entire chemical composition of even the commercial products used

in manufacturing processes. This is because many commercial formulations are not pure chemicals but contain by-products of the production process. This, together with the metabolites formed during sewage treatment, leads to a wide range of compounds delivered to freshwater from a single commercial-product source. Hence any investigation of a point-source discharge containing micro-organic compounds must consider not only compounds that have been designed to be toxic, such as pesticide, but a wide range of commercial and natural products (possibly containing impurities not essential for the product application) that may have partially degraded in the pipeline or in the wastewater treatment process. Moreover, storm-water discharges, overflow from roadside and other urban drains during heavy rainfall events, can be sources of a range of micro-organic compounds to freshwaters.

3. The association of pesticides with sedimentary material and dissolved organic matter

In freshwater, micro-organic contaminants from OCPs can exist in a variety of forms: as a freely dissolved phase, as a colloidal phase or associated with sedimentary material. In terms of the fate and effects of micro-organics between these various phases is a central issue. It strongly influences bed and suspended-sediment concentrations, freely dissolved concentrations (both in pore-waters and in the overlying water) and colloidally bound concentrations, and therefore also have a strong influence on sediment and water quality [11]. Natural sediments are complex mixtures of inorganic mineral offer environments, which may be favorable for micro-organics to become associated with. The association of micro-organics with sediments and soils is known as sorption, a general term, which covers two types of process, adsorption and absorption. Outstanding to the compositional complexity of sediments, sorption is not, however, the result of a single process, but may result from both adsorption and adsorption in/on a range of matrices.

Behavior of pesticides in soil, suspended sediment and bed sediment were determined by several processes including degradation by soil microorganism, chemical degradation (e.g. hydrolysis), sorption and binding by organic and mineral soil components, uptake by plant roots, volatilization and the diluting effects of water flow process.

Losses of pesticide in the soil via microbiological and chemical pathways are collectively termed degradation. Rate of degradation in soil usually increases with temperature and with soil water content [13]. Half-lives can be very long in dry soil. Degradation is often described satisfactorily by simple exponential decay, which assumes that the amount degraded per unit time is directly proportional to the amount present. The rate of degradation can be characterized by a half-life (DT_{50}). As pesticide degradation products (metabolites) may have environmentally undesirable characteristics, the evaluation of the environmental fate of a pesticide should also take the fate of its major metabolites into consideration. However, the pesticide properties of the chemicals remain unaffected.

Field-measured half-lives generally are shorter than those measured under controlled laboratory conditions because of first, multiple degradation pathways operating under field

conditions, resulting in more rapid degradation. The last reason is losses by volatilization and photodecomposition. Both processes are occurring in the field and not in the laboratory field-measured soil; half-lives may also include dissipation losses by runoff, leaching and uptake by plants, which are not degradation pathway.

The sorption of pesticide on soil reduces its mobility, with the extent of reduction dependent upon the physical and chemical properties of the soil as well as the molecular characteristics of the pesticide. Since soil organic matter is the primary soil constituent responsible for sorption of non-ionic pesticides, a sorption constant based on only the organic carbon present (K_{oc} , $\text{dm}^3 \text{kg}^{-1}$) can be used to assess pesticide mobility, $K_{oc} = K_d/oc$. Where K_d is a measure of the extent of pesticide sorption by the soil, and oc is the fraction of the organic C present in the soil [14]. A sorption constant expressed in this manner is dependent only on the pesticide and is essentially independent of soil type. However, in soils with extremely low or high organic C and for ionizable or ionic pesticides the use of K_{oc} to estimate K_d may be subject to large error.

A significant proportion, typically ranging from 20 to 70%, of a pesticide or its degradation products may remain in the soil as a persistent residue bound to the soil colloids [15]. In this bound state, these compounds are difficult to extract and characterize, and tend to lose their biological activities. Many pesticides formerly believed to be readily degraded and lost from the soil were later shown to form these bound residues. Although no firm evidence is available, concern has been expressed that these bound residues may be released and be taken up by crop plants or leach into groundwater.

In any water body there are areas of bed-sediment erosion and of sediment accumulation, largely determined by flow and wave patterns. Fine suspended sediment particles, weather from external influxes to the water body or from resuspended of bed sediments will be deposited, in the long term, in accumulation zones. In general, fine silty sediments will also have a higher organic C content than coarse sandy sediments. Because of these and because of their higher surface area to volume ratio, fine sediments are likely to contain higher concentrations of micro-organic compounds, on a weight for weight basis. The overall effect is that away from direct sources, bed-sediments in accumulation zones are likely to have a much higher loading of micro-organic compounds than bed sediments in other areas [11].

The effects of flow rate can also be very important in the transport of micro-organics in freshwaters. In relatively slow-flowing rivers such as the Rivers Aire and Calder in Yorkshire, bed and suspended sediments have been found to contain relatively high concentrations of a range of pesticides, notably including the synthetic pyrethroids [16]. In contrast, some fast-flowing rivers have high self-purification ability against pollution, with high water-discharge and sediment loads. This is the case for a number of rivers in some catchments in western China, where in spite of heavy industrial discharges of HCHs, DDT and PCBs, relatively low concentrations have been found in surficial river sediment (depth <3 cm) [17] compared with the concentrations found in other sediment surveys [18]. Where contaminated river have high purification ability because of rapid flushing and bed-scouring, compounds that are not found in river sediments may accumulate in coastal zones, estuaries and lakes.

Spatial variations in suspended-sediment-bound concentrations, as well as in bed sediment concentrations, can occur because of different sedimentation and flow regimes. Spatial variations in suspended-sediment-bound concentrations can also reflect source differences [16]. There is also likely to be a dilution of suspended sediments carrying contaminants by clean suspended material as the distance away from the source increases [19]. Temporal variations in non-tidal stretches of rivers usually result from changes in flow levels into and through the river, often varying with season [16]. Moreover, temporal variations can be complex if the source of the micro-organic compound is flow-related as in the case of resuspension of contaminated bed sediments, runoff from storm drains and erosion of contaminated soils, for example due to flooding. Otherwise, high flow rates giving rise to increased sediment transport will act to dilute suspended-sediment micro-organic compound concentrations.

4. Degradation of organochlorine pesticides in freshwater sedimentary environment

Degradation of OCPs contaminants in freshwater environments can occur either in the water column, or in the sediment bed following deposition. For pesticides in particular, compound half-lives and stabilities under various abiotic conditions are available from manufactures' information. However, the situation is complicated in natural waters by the presence of varied microbial populations, suspended sediments, dissolved ions, dissolved organic matter and the sediment bed. Sediment, in particular, has the potential to strongly influence degradation, because many micro-organic compounds are known to associate strongly with sediments. In addition, microbial populations are also known to be largely associated with surfaces in the environment rather than living free in solution.

Those OCPs contaminants can undergo degradation, either abiotically, through purely chemical or photochemical pathways, or biologically, with the microorganism assistant. Degradation can be complete, with compounds being mineralized to form CO₂ and other simple chemical species, or partial, with the resultant degradation products more closely resembling the parent species. Different degradation pathways can occur simultaneously, with the relative importance of the various pathways being dependent upon the compound and the environmental conditions. Even if it is difficult to generalize because of the multitude of compound and types of environment, biotic degradation pathways are often found to be more important in the degradation of micro-organic contaminants. In particular, microbial pathways usually lead to complete mineralization of microorganism compounds.

5. Abiotic degradation pathways

The two most important types of abiotic chemical degradation reactions are hydrolysis, usually either acid or based-catalyzed and redox reactions. Hydrolysis can be a significant

degradation pathway for compounds containing ester, ether or amide functional groups, s-triazine and carbamate for example, and for substituted haloalkanes. In terms of chemical oxidation, the major oxidants present in the environment are O_2 , and Fe (III) and Mn (III) and (IV) oxides, with susceptible compounds including anilines and polyalkylated phenols. Whilst reduction is known to be a degradation route for a wide range of micro-organic compounds under appropriate environmental conditions, it is often difficult to identify the chemical reducing agents responsible. It is generally thought that low abundance but highly reactive species such as quinoid-type compounds, Fe porphyrines and some transition metal ions may be involved [11].

In terms of abiotic photochemical degradation or photolysis, there are few micro-organic contaminants including highly conjugated species such as polyene, nitroaromatics and some polyaromatic compounds, that will degrade directly following absorption of natural light. Indirect photolysis, in which dissolved natural organic matter becomes electronically excited after absorbing natural light, resulting in the production of a wide range of highly reactive species such as the hydroxyl radical (OH), which then may react with micro-organic pollutants. It is thought to be the more significant photolysis pathway for micro-organic compounds, with alkyl-substituted phenols, anilines, mercaptans, furans and other dienes being particularly susceptible [11].

6. Biotic degradation

Microbial populations are responsible for the vast majority of biotic transformations of micro-organics in the environment. Microorganisms involved in five basic types of transformation including, microbial metabolism, in which the compound serves as a growth substrate, which leads to mineralization and co-metabolism, in which the compound is transformed by metabolic processes, but does not serve as an energy source. The third transformation type is polymerization or conjugation, in which microbial reactions result in the polymerization of the compound with natural organic matter. The last two transformation types are accumulation, in which the compound is incorporated into the tissues of the organism itself, but not for growth, and secondary effect transformations, whereby transformation results from changes in redox potential or pH as a result of microbial reactions.

7. The study area

The study area is Mae Klong River basin, which is located in the central plain of Thailand. The climate in Thailand can be divided into 3 seasons including winter (October-February), summer (February-May) and rainy season (May-October). Approximate annual rainfall levels are up to 1,100 mm in the rainy season (85% in May to September). The temperatures are between 25-40°C. The humidity is around 56-79% [20].

The Mae Klong River basin is one of three major river basins in the Chao Phraya Delta, which are an important agricultural area in rice production and other agronomic in

Thailand for some centuries. The other two major river basins are the Chao Phraya and Tha Chin River basins. The Mae Klong River basin covers a total area of 30,800 km² in the west central of Thailand with the very flat delta. It is periodically flooded in rainy season (mostly during August to November) [21]. The most important farming activities in this region are rice paddies and orchards including coconut, lime, lychee and mango. The main waterway in this basin is Mae Klong River which ends at the Gulf of Thailand in Samut Songkhram Province, and has the length of 132 km. The river receives water from both the irrigation canal systems and natural tributaries, which flow through cultivated areas where OCPs are intensively used to improve crop yields [7,22]. The discharge of untreated waste from agriculture is a major source of OCPs contamination in this area, and has been a major concern to citizens and officials for more than two decades [7,20,22]. Some organochlorine pesticides accumulation and their degradation along Mae Klong River basin and some of its tributaries will be discussed in this chapter.

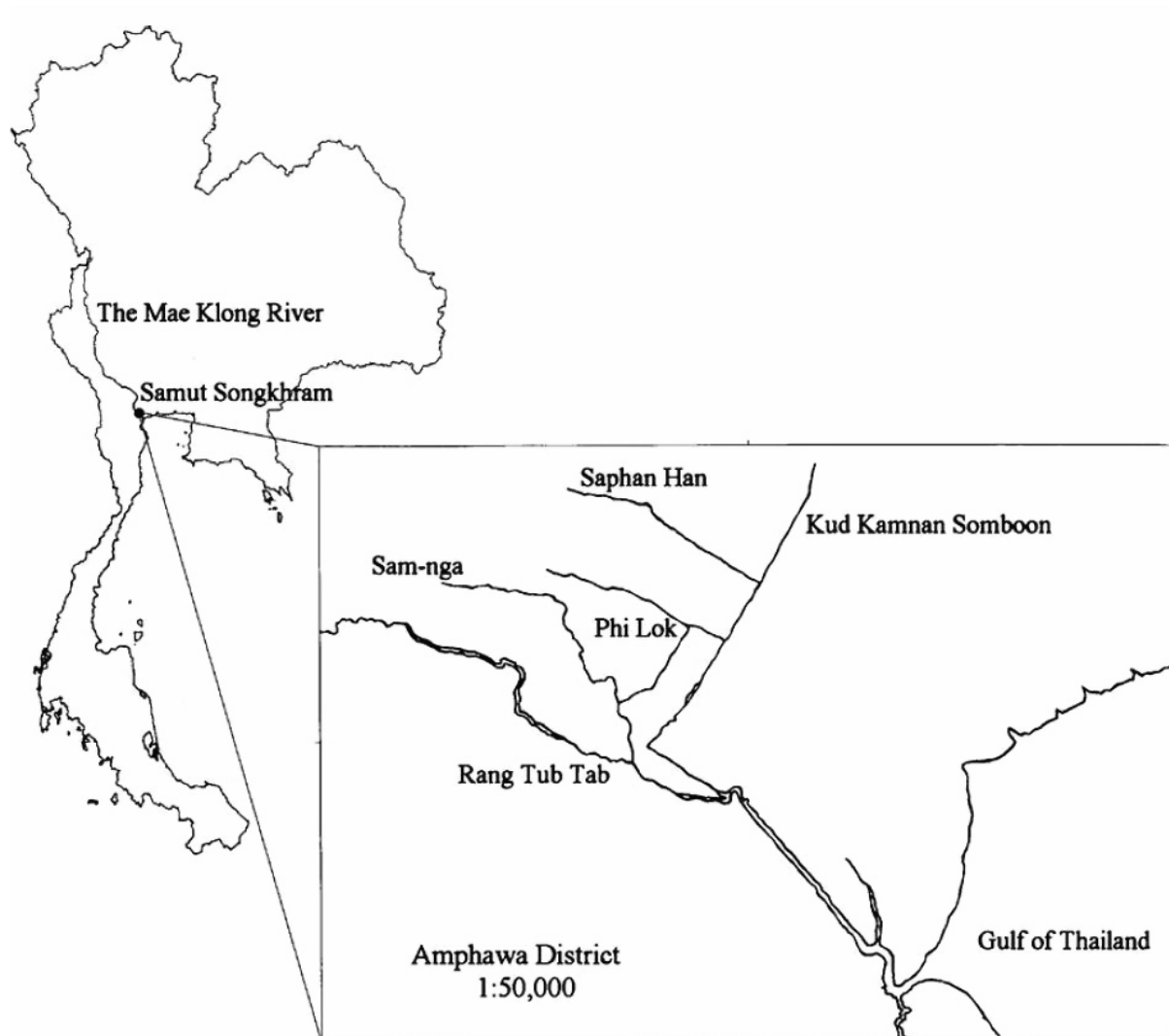


Figure 1. Map of Thailand showing the five tributaries of the Mae Klong River in the study area (Poolpak et al., 2008)

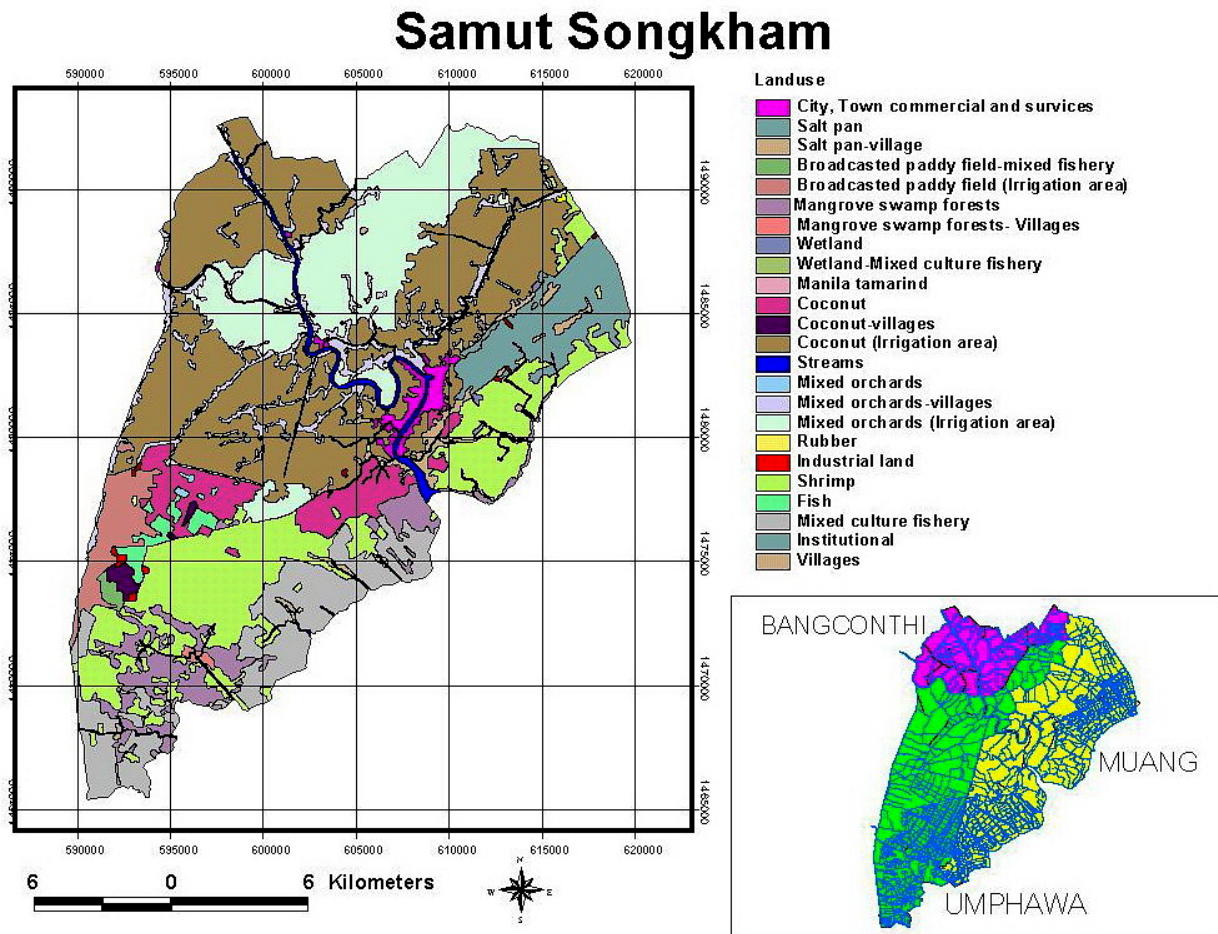


Figure 2. The land use in Mae Klong Basin in the area of Samut Songkram Province with the major land use is agricultural area (Poolpak et al., 2008)

The five sampling sites were on the Mae Klong River tributaries at Tumbon Prag Nam Dang, Amphawa, Samut Songkram Province (Figure 1). These tributaries are also major sources for household and industrial water supply in Samut Songkram Province. As showed in Figure 2, the areas surrounding the sampling sites are a traditional rice-cultivation area in which farmers cultivate rice twice per year. The first crop (rainy-season rice) cultivation typically starts in August and harvested in November or December. An irrigated dry-season crop is planted in April or May and ends in July or August. Five sites were chosen in such a way as to include hot spots of pollution discharges along the Mae Klong River such as industrial regions, paddy fields and orchards for the first year. For the second year of monitoring, sediment samples were collected from Rang Tub Tab canal (site R) and Phi Lok canal (site P), which is an important crossing point of several tributaries in study area. Site R is also the tributary connected to the Gulf of Thailand. Sediment samples were collected monthly for a period of two years, during August 2003 to February 2005. The study areas and sampling locations along the selected tributaries were illustrated in figure 3. Furthermore, the basic physico-chemical properties of natural surface sediment samples within the area are shown in Table 1.

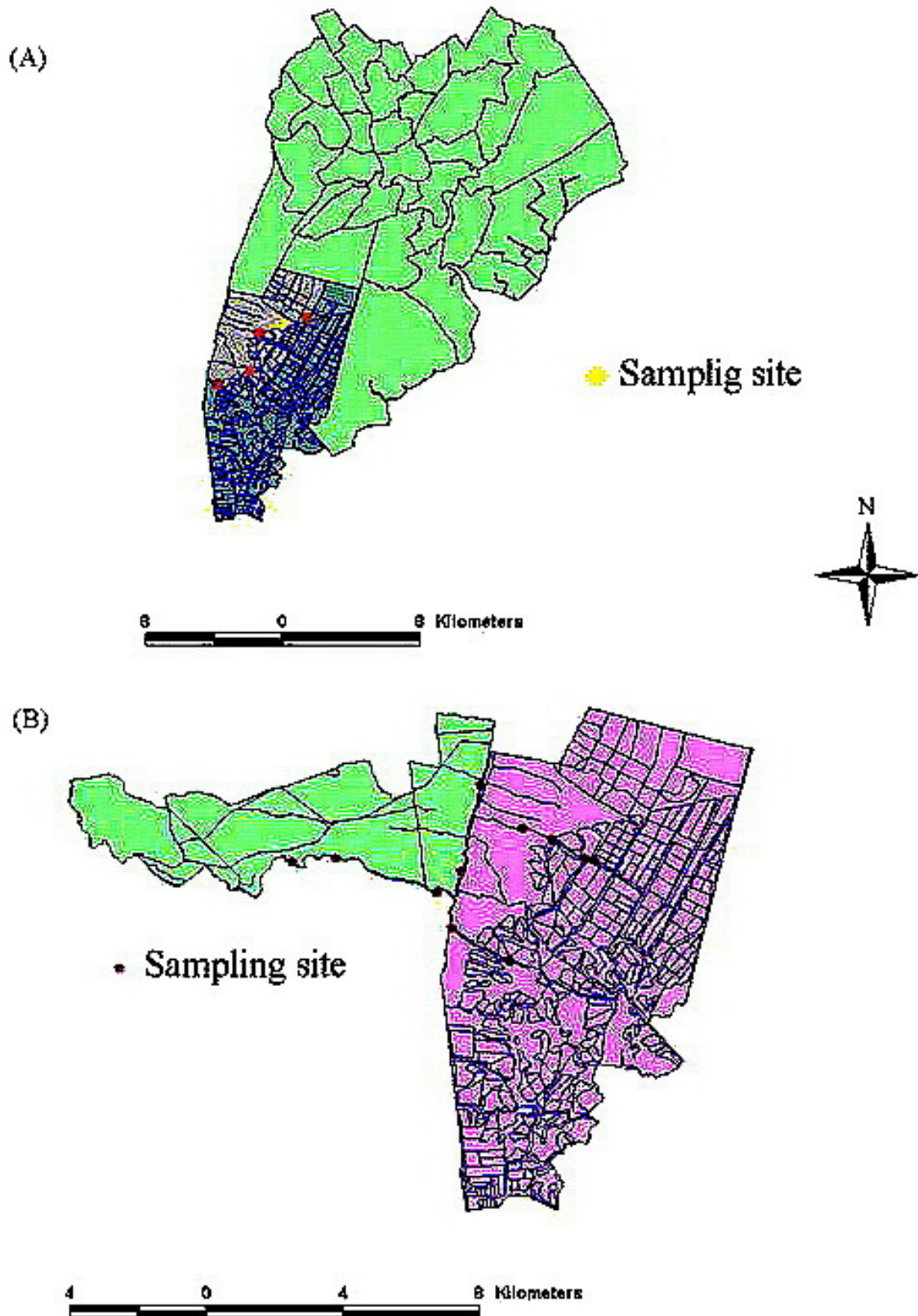


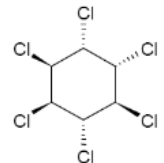
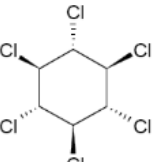
Figure 3. The study areas and sampling locations along the selected tributaries during August 2003 to July 2004 (A) and March 2004 to February 2005 (B) (Poolpak et al., 2008)

Sampling year	Sampling sites	Geographical coordinate	Water content (%)	pH	Sand (%)	Silt (%)	Clay (%)
2003	Kud Kamnan Somboon (K)	(598863N, 1475923E)	50.79	5.9	20	24	56
	Saphan Han (SP)	(598450N, 1475000E)	64.15	5.8	30	21	49
	Phi Lok (P)	(595992N, 1475052E)	56.88	5.7	25	23	52
	Sam-nga (SN)	(595235N, 1472125E)	64.41	5.6	32	20	48
	Rang Tub Tab (R)	(593496N, 1472125E)	61.79	5.8	29	30	41
2004	Phi Lok (P)	(595986N, 1472125E; 594718N, 1471496E; 595133N, 1475347E)	59.34	5.7	24	23	53
	Rang Tub Tab (R)	(588357N, 1474380E; 589628N, 1474503E; 592581N, 1473464E; 593310N, 1474090E; 593059N, 1472441E; 593899N, 1476626E)	42.44	5.8	29	30	41

Table 1. Sampling areas and codes of the tributaries of Mae Klong River, their coordinates and the basic physicochemical properties of natural surface sediment samples within the area

8. OCPs accumulation and their distribution in study area

The organochlorine compounds in this investigation were hexachlorocyclohexane (technical HCH including α -HCH, γ -HCH, β -HCH, δ -HCH), heptachlor and its epoxide, α -, β -endosulfan and endosulfan sulfate, DDT, DDE, and DDD. They were chosen in the subject of their persistence and their importance in agricultural activities. The chemical structures and some properties of the selected OCPs were presented in table 2 and 3.

Name	Molecular formula	Molecular weight	Chemical structure
α -HCH	$C_6H_6Cl_6$	290.83	
β -HCH	$C_6H_6Cl_6$	290.83	

Name	Molecular formula	Molecular weight	Chemical structure
γ -HCH	$C_6H_6Cl_6$	290.83	
δ -HCH	$C_6H_6Cl_6$	290.83	
DDT	$C_{14}H_9Cl_5$	354.49	
DDD	$C_{14}H_{10}Cl_4$	320.05	
DDE	$C_{14}H_{12}Cl_2$	318.03	
α -Endosulfan	$C_9H_6Cl_6O_3S$	406.93	
β -Endosulfan	$C_9H_6Cl_6O_3S$	406.93	
Heptachlor	$C_{10}H_5Cl_7$	373.32	
Heptachlor epoxide	$C_{10}H_5Cl_7O$	389.32	

Table 2. Organochlorine compound structures and their molecular properties

Substance	Melting Pt ^a	Boiling Pt ^a	Vapor pressure ^b	Water solubility ^c	Log P	Henry's law constant ^d	Atmospheric OH rate constant ^d
α -HCH	159.5	228 60 at	4.50E-05	2	3.80	1.22E-05	1.40E-13
β -HCH	314.5	5.80E-01 mmHg	3.60E-06	0.24	3.78	4.40E-07	5.73E-13
γ -HCH	112.5	323.4 60 at	4.20E-05	7.3	3.72	5.14E-06	1.90E-13
δ -HCH	141.5	3.40E-01 mmHg	3.52E-05	10	4.14	4.29E-07	5.73E-07
DDT	108.5	NA	1.60E-07	0.0055	6.91	8.32E-06	3.44E-12
DDD	109.5	350	1.35E-06	0.09	6.02	6.60E-06	4.34E-12
DDE	56	320	6.00E-06	0.04	6.51	4.16E-05	7.43E-12
α - Endosulfan	NA	NA	3.00E-06	0.51	3.83	7.09E-06	8.17E-12
β - Endosulfan	NA	NA	6.00E-07	0.45	3.83	3.91E07	8.17E-12
Endosulfan sulfate	181-182	NA	2.80E-07	0.48	3.66	3.25E-07	8.17E-12
Heptachlor	95.5	310	4.00E-04	0.18	6.10	2.94E-04	6.11E-11
Heptachlor epoxide	160	NA	1.95E-05	0.2	4.98	2.10E-05	5.17E-12

NA indicates that the property is not applicable

^a at 1 atmosphere, °C

^b at 25°C, mmHg

^c at 25°C, mg/L

^d at 25°C

Table 3. Physical and physico-chemical properties of some organochlorine pesticides

The variations of the OCPs levels for different rice-cropping seasons in surface sediments from the five tributaries during August 2003 and July 2004 are summarized in Table 4, whereas Tables 5 show the mean concentration of OCPs residues in the sediment samples taken along site P and site R during March 2004–February 2005. Despite the official ban and restriction on the usage of some OCPs, pesticide residues were detected in all sampling sites [20].

The range of total OCPs concentration in the sediments from five tributaries were 0.09-96.48 $\mu\text{g/g dw}$ at site K, 0.01-110.92 $\mu\text{g/g dw}$ at site SP, 0.06-102.05 $\mu\text{g/g dw}$ at site P, 0.11-84.00 $\mu\text{g/g dw}$ at site SN and 0.02-274.16 $\mu\text{g/g dw}$ at site R. In the second year of observation, sites P and R were then chosen for further monitoring. Total residue concentrations of OCPs ranged from 0.15 to 99.60 at site P and 0.14 to 129.82 at site R. Comparing with the others, site R was found to be the most OCPs contaminated site in this study.

The higher concentration of OCPs at five selected tributaries indicated the high irrigation of these compounds in and around the basin. These OCPs are believed to have originated from various pesticide-rich sources, mainly agricultural areas and household. The natural processes of leaching and runoff and irrigation are likely to enhance their transfer to the main course of these tributaries, especially during the rice cultivation season [20].

The relatively high pesticide levels at site R can be explained from the input of pollutants in discharge from agricultural fields. This tributary was connected to and received water from other tributaries so it may contain pesticides from extraneous areas as well as from the immediate surroundings.

OCPs residues in dry-season rice cultivation periods were higher than during the wet season in both years. This meant that some OCPs could be released from the surrounding areas to the tributaries in the irrigation from paddy fields. Moreover, the still water in dry season is one of the major basis. Decreased OCPs concentrations in the rainy-season cultivation can be explained in term of lower upstream discharge and dilution effects. Where non-agricultural activities in cool season infer to the low levels of the chemicals found in this sampling season [20].

Pesticides	Rainy –season cultivation ^a					Non-rice cultivation ^b					Dry-season rice cultivation ^c				
	K	SP	P	SN	R	K	SP	P	SN	R	K	SP	P	SN	R
α -HCH	0.05 (0.06)	0.25 (0.18)	0.12 (0.10)	0.25 (0.18)	0.33 (0.08)	0.28 (0.05)	0.28 (0.20)	0.26 (0.11)	0.25 (0.14)	0.30 (0.13)	0.26 (0.09)	0.39 (0.07)	0.35 (0.00)	0.41 (0.04)	0.33 (0.08)
β -HCH	0.11 (0.02)	0.18 (0.02)	0.13 (0.04)	0.17 (0.02)	0.21 (0.08)	0.17 (0.06)	0.02 (0.02)	0.17 (0.03)	0.18 (0.03)	0.23 (0.07)	0.21 (0.10)	0.18 (0.02)	0.15 (0.02)	0.19 (0.03)	0.33 (0.19)
γ -HCH	0.21 (0.05)	0.35 (0.00)	0.26 (0.05)	0.32 (0.06)	0.30 (0.05)	0.23 (0.04)	0.35 (0.00)	0.29 (0.00)	0.28 (0.09)	0.33 (0.00)	0.23 (0.04)	0.35 (0.00)	0.29 (0.00)	0.32 (0.06)	0.31 (0.06)
δ -HCH	0.54 (0.24)	0.91 (0.41)	0.76 (0.72)	0.68 (0.22)	3.31 (1.32)	0.86 (0.81)	1.28 (1.51)	1.15 (1.13)	1.67 (2.49)	1.99 (1.01)	2.64 (1.08)	2.89 (2.13)	1.96 (1.35)	1.85 (1.22)	2.95 (0.95)
Heptachlor	0.06 (0.07)	0.15 (0.10)	0.21 (0.19)	0.13 (0.10)	0.19 (0.14)	0.04 (0.04)	n/a	0.09 (0.07)	n/a	0.25 (0.19)	0.10 (0.04)	0.13 (0.05)	0.15 (0.11)	0.21 (0.12)	0.61 (0.91)
Heptachlor epoxide	11.61 (4.39)	13.99 (5.96)	16.52 (20.78)	9.23 (7.87)	63.22 (24.72)	20.41 (25.67)	20.82 (27.51)	29.79 (38.96)	33.01 (56.12)	58.77 (49.73)	64.46 (29.63)	76.11 (44.67)	55.74 (19.57)	41.76 (26.84)	152.17 (55.50)
Endosulfan I	0.12 (0.00)	0.16 (0.00)	0.13 (0.00)	0.16 (0.00)	0.15 (0.00)	0.11 (0.02)	0.15 (0.03)	0.13 (0.00)	0.16 (0.00)	0.16 (0.02)	0.10 (0.02)	0.17 (0.02)	0.11 (0.03)	0.16 (0.00)	0.12 (0.05)
Endosulfan II	0.03 (0.02)	n/a	0.05 (0.04)	0.01 (0.03)	0.05 (0.04)	0.03 (0.03)	0.01 (0.03)	0.04 (0.02)	0.01 (0.03)	0.14 (0.25)	0.03 (0.07)	n/a	0.05 (0.04)	0.09 (0.06)	0.07 (0.05)
Endosulfan sulfate	0.07 (0.06)	0.13 (0.03)	0.08 (0.05)	0.15 (0.04)	0.15 (0.03)	0.11 (0.05)	0.08 (0.08)	0.17 (0.08)	0.07 (0.10)	0.38 (0.46)	0.15 (0.01)	0.21 (0.07)	0.19 (0.02)	0.19 (0.02)	0.58 (0.51)
p,p'-DDE	0.08 (0.03)	0.04 (0.08)	0.09 (0.06)	0.06 (0.08)	0.11 (0.04)	0.09 (0.08)	0.17 (0.10)	0.13 (0.09)	0.12 (0.14)	0.16 (0.07)	0.10 (0.03)	0.21 (0.04)	0.12 (0.06)	0.18 (0.08)	0.16 (0.07)
p,p'-DDD	0.01 (0.02)	0.06 (0.12)	0.03 (0.03)	0.02 (0.03)	0.02 (0.03)	0.13 (0.05)	0.03 (0.04)	0.03 (0.03)	0.03 (0.06)	n/a	0.14 (0.10)	0.13 (0.27)	n/a	0.11 (0.18)	n/a
p,p'-DDT	0.13 (0.08)	0.17 (0.12)	0.14 (0.13)	0.26 (0.11)	0.08 (0.05)	0.26 (0.07)	0.31 (0.13)	0.25 (0.05)	0.38 (0.05)	0.20 (0.14)	0.37 (0.11)	0.35 (0.08)	0.22 (0.10)	0.37 (0.03)	0.63 (0.74)

n/a means no available

^a August 2003-November 2003

^b December 2003-March 2004

^c April 2004-July 2004

Table 4. Mean and standard deviation (S.D.) of OCPs ($\mu\text{g g}^{-1}$ dw) detected in the surface sediment in five tributaries of the Mae Klong river during August 2003-July 2004 (n=60/cultivation period)

Pesticides	Dry-season cultivation ^a		Rainy-season rice cultivation ^b		Non-rice cultivation ^c	
	P	R	P	R	P	R
α -HCH	0.21 (0.15)	0.28 (0.15)	0.32 (0.06)	0.02 (0.03)	n/a	0.33 (0.08)
β -HCH	0.93 (0.83)	3.66 (3.29)	0.12 (0.02)	0.09 (0.02)	0.11 (0.02)	0.08 (0.19)
γ -HCH	0.18 (0.08)	0.21 (0.12)	0.08 (0.13)	0.05 (0.08)	0.02 (0.02)	0.01 (0.06)
δ -HCH	5.50 (3.32)	10.09 (6.31)	1.08 (1.28)	0.82 (0.94)	0.64 (0.23)	0.43 (0.95)
Heptachlor	0.53 (0.59)	2.16 (2.61)	0.04 (0.09)	0.04 (0.04)	0.04 (0.03)	0.02 (0.02)
Heptachlor epoxide	72.43 (30.90)	110.39 (56.79)	19.51 (28.43)	14.84 (21.82)	7.66 (3.41)	4.59 (1.50)
Endosulfan I	0.07 (0.05)	0.18 (0.12)	0.10 (0.05)	0.06 (0.02)	0.02 (0.01)	0.01 (0.05)
Endosulfan II	0.07 (0.04)	0.10 (0.03)	0.06 (0.04)	0.07 (0.03)	0.02 (0.01)	n/a
Endosulfan sulfate	0.17 (0.07)	4.62 (7.47)	0.04 (0.02)	0.05 (0.03)	0.01 (0.01)	n/a
p,p'-DDE	0.66 (0.12)	0.11 (0.05)	0.03 (0.01)	0.03 (0.03)	0.03 (0.01)	n/a
p,p'-DDD	1.03 (0.63)	0.17 (0.09)	0.02 (0.02)	0.02 (0.01)	0.01 (0.01)	n/a
p,p'-DDT	1.05 (0.85)	2.99 (2.59)	0.05 (0.04)	0.05 (0.02)	0.02 (0.02)	n/a

n/a means no available

^a March 2004-June 2004

^b July 2004-October 2004

^c November 2004-February 2005

Table 5. Mean and standard deviation (S.D.) of OCPs ($\mu\text{g g}^{-1}$ dw) detected in the surface sediment at site P and R during March 2004-February 2005 (n=36/cultivation period)

Even though usage of some imported pesticides such as DDT was officially banned in 1983, there is the official report presented that these OCPs were parts of organochlorine insecticides active ingredients not included in the ban list. That is why they were still detected in sediment samples along with their metabolites [22-24]. Additionally, the appearance of some OCPs such as endosulfan and heptachlor in the sediment may indicate continued usage of these pesticides despite the official ban. Illegal smuggling of these pesticides from the neighborhood countries has been reported several times in local newspapers. Furthermore, some pesticides are still used in some developing countries around the tropical belt [25,26] which demonstrates the degradation persistence of these substances, even in tropical environment [27].

Heptachlor epoxide was found at the highest concentration in sediments from station R. The enzymatic epoxidation of heptachlor to heptachlor epoxide in soil and animals is most likely responsible for the significant greater incidence of heptachlor epoxide than heptachlor [28]. This chemical was also extensively used for termite control in Thailand in the past, and additionally, was used in seed treatments and control of soil insects such as ants. Although the usage of heptachlor was officially banned in 1988, the observed high residue concentrations of heptachlor epoxide at all sampling sites could come either from persistence in the environment or from continued use reflecting either illegal smuggling or use of old stocks [20]. Heptachlor and its epoxide were also detected in both water samples

[23] and agricultural soil samples [24] from the Chao Phraya Basin. Furthermore, the other unlikely sources of heptachlor and its metabolite may be chlordane which is widely used against termite infestation and could be released into the environment primarily from its application as an insecticide [9]. It has the main components including α - and γ -chlordane, γ -nonachlor and heptachlor and generally metabolized in the environment and in the human body to oxychlordane and may be heptachlor epoxide found in the absence of either oxychlordane or γ -nonachlor [29].

In the case of endosulfan, the concentration of its α -isomer (the main component of the commercial product) was higher than β -endosulfan (a secondary component) at all sampling sites during the two years. Total endosulfan showed values in the range >0.001 - $1.34 \mu\text{g/g dw}$ in 2003, with 0.05 - $0.20 \mu\text{g/g dw}$ for the α -isomer and only >0.001 - $0.51 \mu\text{g/g dw}$ for the β -isomer. Endosulfan sulfate, an endosulfan degradation by-product, was found in large concentration in the sediment samples (range >0.001 to $1.34 \mu\text{g/g dw}$). The total endosulfan in 2004 was $22.60 \mu\text{g/g dw}$ with the highest proportion as endosulfan sulfate (>0.001 - $15.72 \mu\text{g/g dw}$) [20].

Endosulfan was extensively used to control golden apple snails in rice fields in this area and was officially banned in 2004. Endosulfan and its by-products, endosulfan sulfate, were found in relatively high concentrations, both during the dry and rainy-rice cultivation seasons. These data reflects the wide use of endosulfan in the surrounding agricultural areas over a long period [20]. Moreover, during warehouse storage, β -endosulfan can be slowly converted to α -endosulfan, which has higher toxic insecticidal properties than the β -isomer [30].

For some OCPs, chemical transformation and microbial decomposition may occur, e.g. DDT is transformed to DDE and δ -HCH to α -HCH. However, complete mineralization of organochlorine compounds does usually either not takes place, or is an extremely slow process [3]. Composition of DDT metabolites and HCH isomers were examined in detail because their differing composition in the environment could indicate different sources of contamination [31].

9. DDTs

In the first year of monitoring, levels of DDTs were found elsewhere, for example, between 0.08 and $1.83 \mu\text{g/g dw}$ in sediment from site R. The ratios of $(\text{DDE}+\text{DDD})/\sum\text{DDT}$ in surface sediments ranged from 0.21 to $0.61 \mu\text{g/g dw}$ in 2003 and from 0.10 to $1.00 \mu\text{g/g dw}$ during 2004 (Figure 4 and 5). Most values were less than 0.5 for the first year, whereas they were greater than 0.5 for the second year. As to the individual DDTs, the concentrations in surface sediment were generally found in the order of $\text{DDT} > \text{DDE} > \text{DDD}$ in most sampling sites and sampling seasons (Figure 6). The same trend was also reported for the second year (Figure 7) except for sites P and R (non-rice cultivation areas), at which DDE showed the highest percentage. In addition, DDE was usually present at a higher concentration than DDD [20].

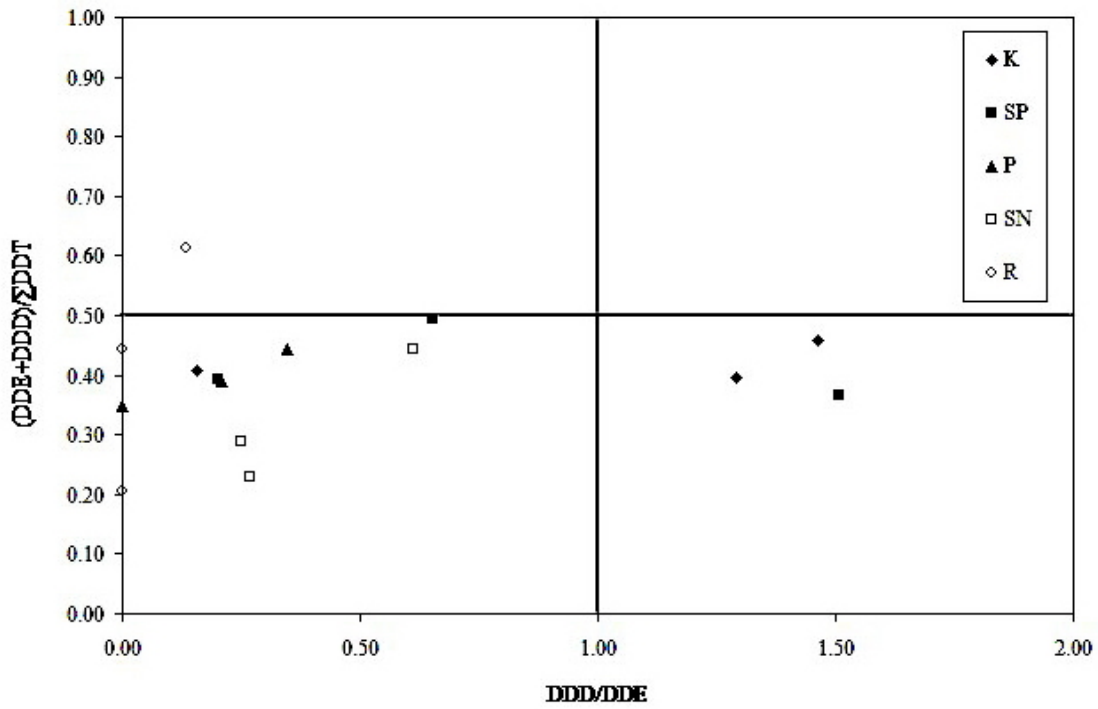


Figure 4. Relationship between $(DDE+DDD)/\Sigma DDT$ and DDD/DDE in surface sediments during August 2003 to July 2004 (Poolpak et al., 2008)

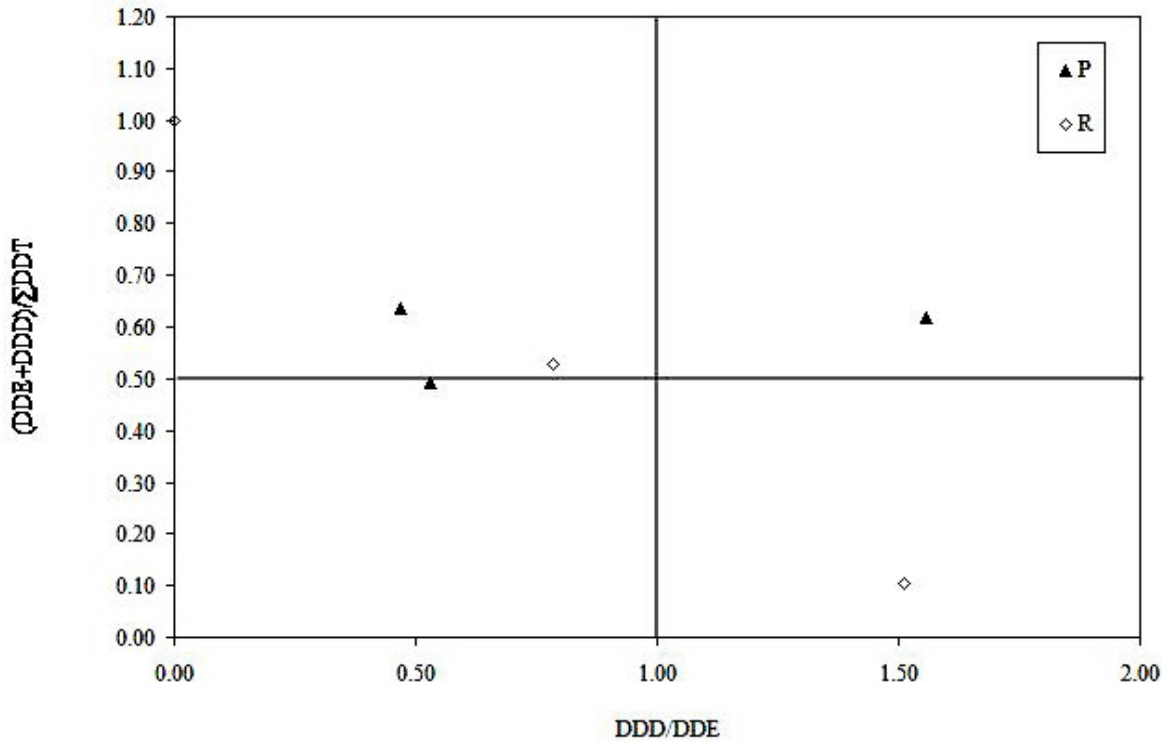


Figure 5. Relationship between $(DDE+DDD)/\Sigma DDT$ and DDD/DDE in surface sediments during March 2004 to February 2005 (Poolpak et al., 2008)

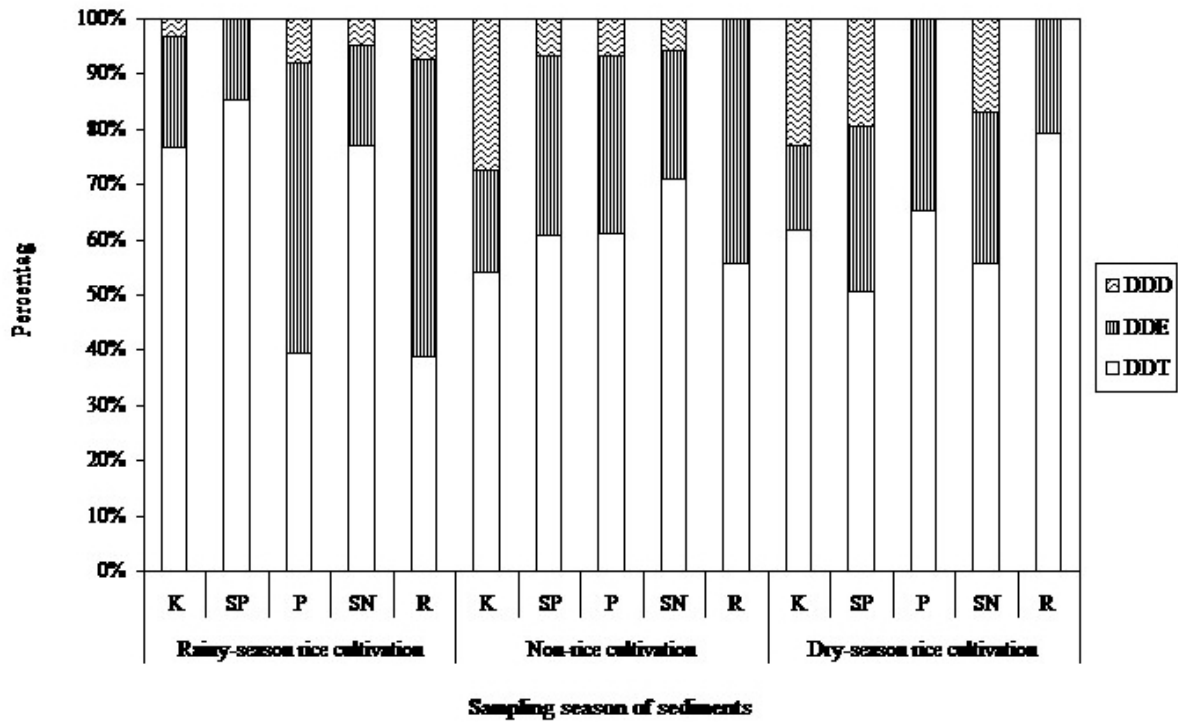


Figure 6. Composition of DDTs in surface sediments, during August 2003 to July 2004 (Poolpak et al., 2008)

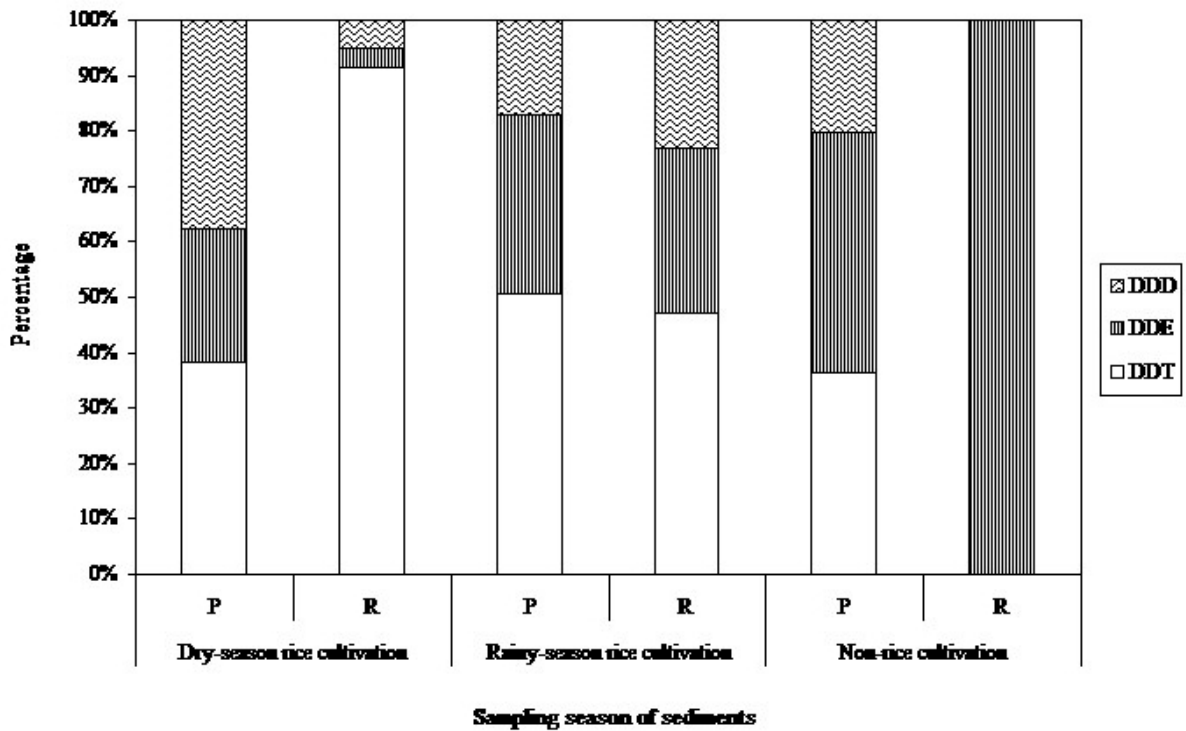


Figure 7. Composition of DDTs in surface sediments, during March 2004 to February 2005 (Poolpak et al., 2008)

The result showed that DDE was usually present in a higher concentration than DDD, suggesting that the most DDT was transformed into DDE [32]. The higher occurrence of DDD and DDE are the results of DDT degradation and the higher stabilities of the metabolites [33-35]. The metabolite DDE is produced from DDT under aerobic conditions such as that occurs in upland soils. On the other hand, DDT is converted to DDD with a half-life of a few days under anaerobic conditions such as in the aquatic sediment [3]. Microbial degradation of DDTs is generally slow resulting in environmental persistence of these compounds [36]. The relative concentrations of the parent DDT and its metabolites can indicate whether DDTs input are from the former or present uses [26,34,37].

Data from the relative concentrations of the parent DDT and its metabolites (DDE and DDD) shows that most values were less than 0.5 for the first year (2003), whereas they were greater than 0.5 for the second year (2004) [20]. The ratios of $(DDE+DDD)/\sum DDT > 0.5$ are reported to indicate long-term weathering [26,38-41]. This suggested that the DDT compounds in sediments collected in 2003 were from the current use whereas the 2004 values which were mostly > 0.5 indicated that degraded metabolites formed a significant proportion of total DDT compounds and the contamination of the area has started long time ago. Since the DDD/DDE ratios were less than the unity at both sampling sites, this indicates that the sediment samples were dominated by the products of aerobic degradation and the contamination of the area is fairly recent. It also indicates that the ongoing use of DDT and its metabolites were derived under aerobic conditions before transported by surface runoff to the waterways sediment [20]. This may be explicable by the relatively higher transportability of DDE than the other form in the atmosphere [18].

10. HCHs

The concentrations of HCH isomers detected in this study in 2003 were in the sequence β -HCH< α -HCH< γ -HCH< δ -HCH at most sampling sites, where the order in 2004 was α -HCH< γ -HCH< β -HCH< δ -HCH. In addition, β -HCH represented the lowest proportion (7.61% of the total HCHs compared to 11.2% and 12.0% for α - and γ -isomers, respectively during 2003 (Figure 8). On the other hand, the decreased proportion of α -HCH and the increased proportion of β -HCH in 2004 were detected (Figure 9). Among HCH isomers analyzed, γ -HCH (lindane) contributed 12% and then 2.22% of the total HCH concentrations in sediment samples in 2003 and 2004, respectively [20].

HCH residues are among the most widely distributed and frequently detected organochlorine contaminants in the environment [36]. Technical HCH was formerly used as a broad-spectrum pesticide for agricultural purpose in Thailand until it was banned in 1980 [9] whereas the γ -isomer, commonly known as lindane, (the only isomer with insecticidal activity) was used for controlling agricultural and medical pests [43] and banned in 2001. Generally, the most common isomers of HCHs in the environment are α -HCH, β -HCH and γ -HCH [44]. Whereas there were high concentrations of δ -HCH in sediments at most sampling sites in the present study, the results are similar to the levels detected at Beijing Guanting reservoir, where the possible reasons of contamination are still unclear [44]. The

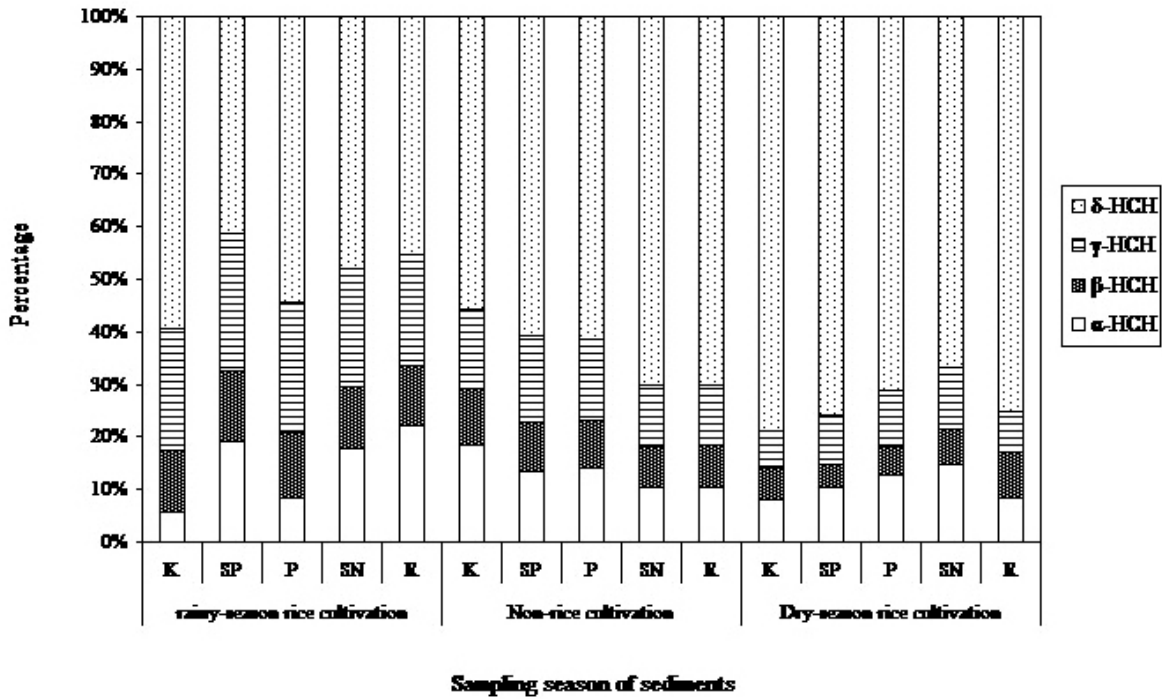


Figure 8. Composition of HCHs in surface sediments, during August 2003 to July 2004 (Poolpak et al., 2008)

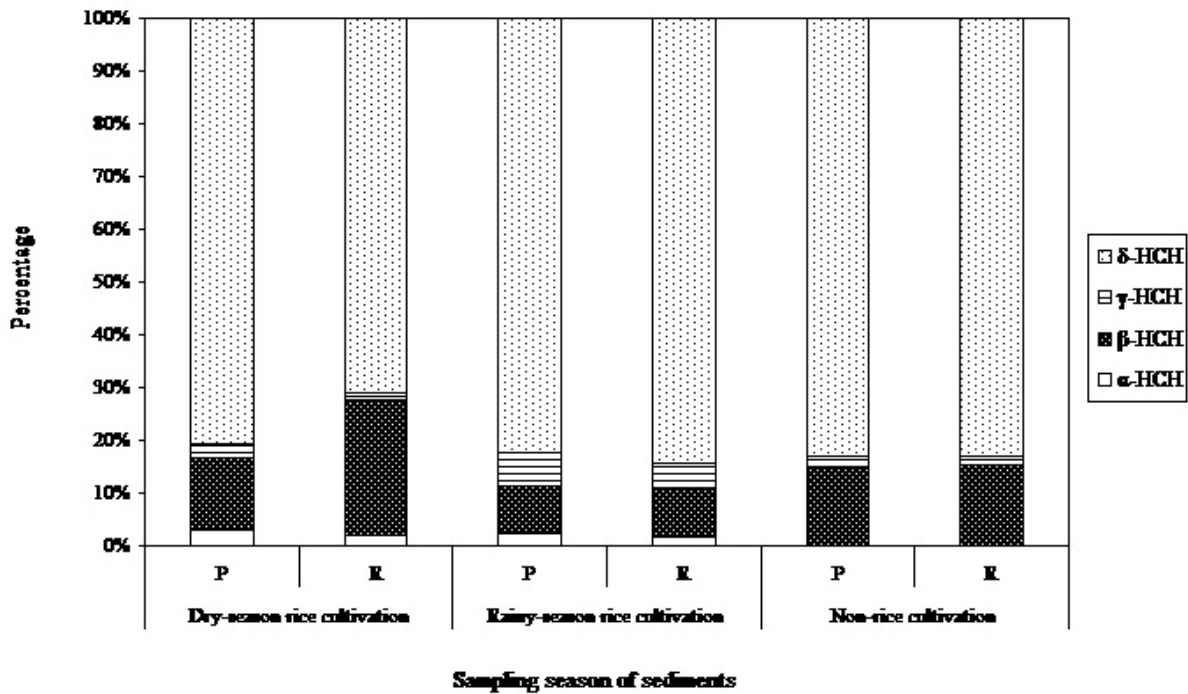


Figure 9. Composition of HCHs in surface sediments, during March 2004 to February 2005 (Poolpak et al., 2008)

typical technical HCH generally contains all four isomers and their physico-chemical properties are different. The most stable β -HCH, relatively resistant to microbial degradation due to its lowest water solubility and vapor pressure, represents a good indicator of contamination [31,33,43,45]. Many studies have reported that β -isomer was dominant in sediments from river or estuary environment after long-term migration and transformation [38,46,47]. In addition, α -isomer is typically predominant in ambient air as well as ocean waters and can be converted into the β -isomer in the environment [31,42].

The sequence of HCHs in this study can be explained by the resistance to chemical degradation of these isomers in this environmental condition and the recent use of technical HCH in this area [45]. Various technical HCH formulations have different amounts of the α -, β -, and γ -isomers; however, the long range atmospheric transport favors α -HCH, the most volatile isomer [48]. On the other hand, the decrease in proportion of α -HCH and the increase in proportion of β -HCH in 2004 implied that the HCHs contamination in the sediment samples might have originated from a relatively distant source or long-term accumulation. Additionally, this data indicates the use of technical HCHs rather than lindane (γ -HCH) and may be explained by the degradation of γ -HCH in this environmental condition because γ -HCH is degraded by microorganisms [49,50] and photochemically isomerized to the α -isomer [45,51]. Although, the predominance of α -isomer in some environmental samples reflects the recent use of technical HCH [52], the higher concentration of α -isomer than γ -isomer in this study may establish the evidence of lindane usage in the past. Since there is no historical data concerning HCHs contamination in this central plain, thus the data presented here can be used to establish a baseline for the future monitoring and management of pesticides in this area [20].

11. Degradation of heptachlor by soil microcosm

According to Poolpak [53], the biodegradation of heptachlor and its oxidative metabolite, epoxide in the microcosm were selected in the mean of their highest contamination in the filed study. The effect of initial concentrations and kinetic study of heptachlor, biodegradation in the sediment, effect of additional carbon sources, soil:water ratio and temperature on degradation of heptachlor were studied to assess its degradation in the fresh water environment. Sediments in degradation study were collected from Rang Tub Tab canal to determine the biodegradation behavior of the indigenous microorganisms in studied site.

12. The effects of initial concentrations of heptachlor on microcosm activities

The effects of different initial concentrations of heptachlor on the degradation and rate of metabolism of soil microcosms were performed in the liquid culture at the heptachlor concentrations of 50, 100 and 150 $\mu\text{g/mL}$ at temperature of 30°C, 150 rpm for 7 days. The decline of different concentrations of heptachlor and the transformation of heptachlor epoxide, the oxidative metabolite, were examined. The liquid cultures without heptachlor but with 1% yeast extract were used as control. Degradation of heptachlor and heptachlor epoxide formation at various initial concentrations was illustrated in figure 10.

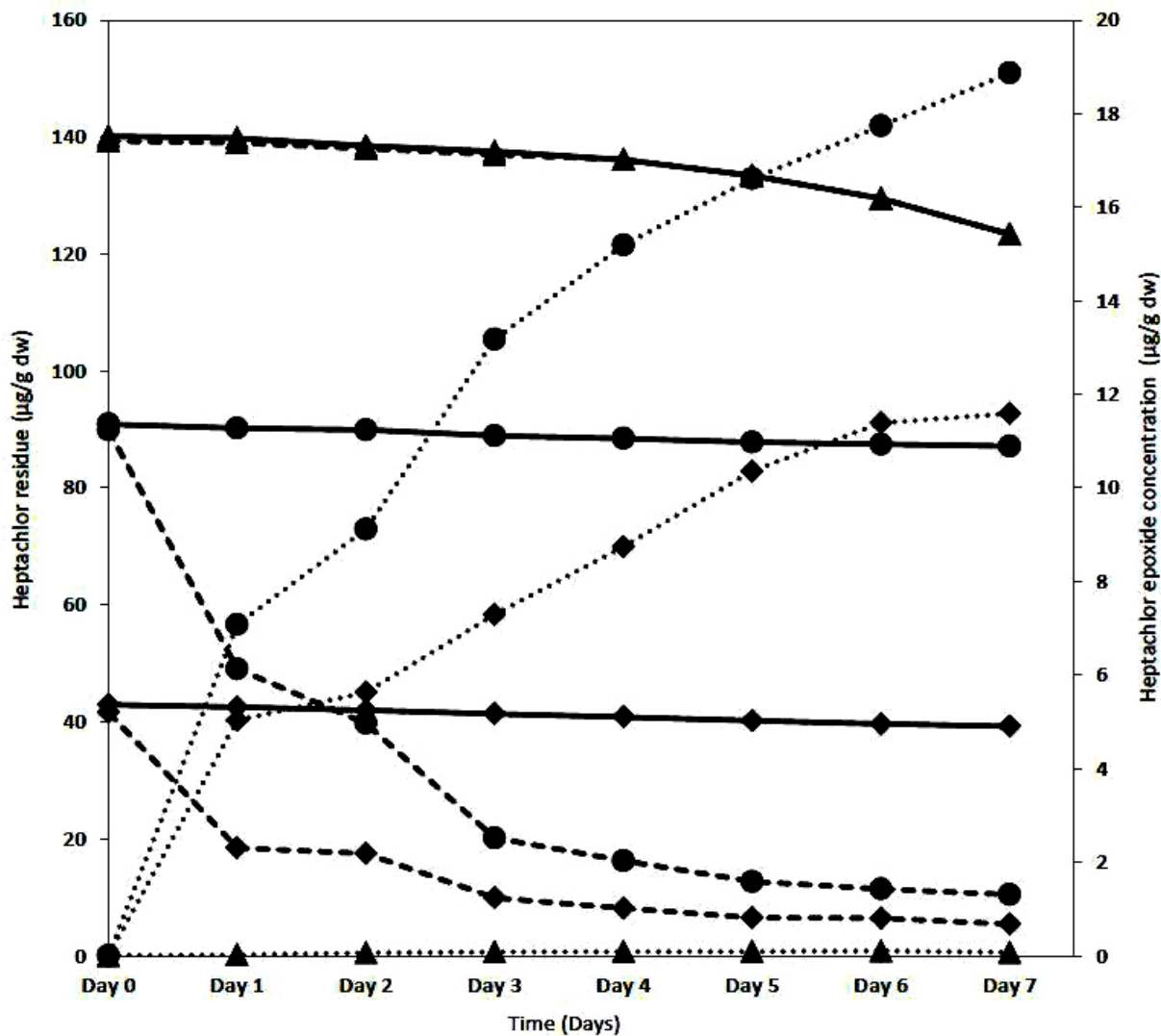


Figure 10. Degradation of heptachlor and heptachlor epoxide formation at various initial concentrations (Heptachlor residue at \blacklozenge 50 $\mu\text{g}/\text{mg}$ heptachlor (abiotic); \bullet 100 $\mu\text{g}/\text{mg}$ heptachlor (abiotic); \blacktriangle 150 $\mu\text{g}/\text{mg}$ heptachlor (abiotic); $-\blacklozenge-$ 50 $\mu\text{g}/\text{mg}$ heptachlor; $-\bullet-$ 100 $\mu\text{g}/\text{mg}$ heptachlor; and $-\blacktriangle-$ 150 $\mu\text{g}/\text{mg}$ heptachlor. Heptachlor epoxide concentration at $\bullet\blacklozenge\bullet$ 50 $\mu\text{g}/\text{mg}$ heptachlor; $\bullet\bullet\bullet$ 100 $\mu\text{g}/\text{mg}$ heptachlor; and $\bullet\blacktriangle\bullet$ 150 $\mu\text{g}/\text{mg}$ heptachlor) (Modified from Poolpak, 2008)

The highest degradation efficiencies were observed in 100 $\mu\text{g}/\text{mL}$ heptachlor as 88.36%, whereas at the concentration of 150 $\mu\text{g}/\text{mL}$ heptachlor, the efficiencies were lower. Accordingly, 100 $\mu\text{g}/\text{mL}$ heptachlor were conditioned in further experiments. Transformation of heptachlor to heptachlor epoxide in liquid culture was evaluated and showed that its metabolite was mostly found in 50 $\mu\text{g}/\text{mL}$ heptachlor treatments or 27.85% of parent heptachlor with the positive values of redox potential suggesting the oxidative activities of microorganisms. Lu et al. [54] reported the transformation of heptachlor into 1-hydroxychloridene and 1-hydroxychloridene epoxide was relatively rapid but small proportion of heptachlor epoxide was formed which suggested that heptachlor epoxide formed environmentally largely *in vivo* by microsomal multifunction oxidase action.

Growth of microorganism represented inhibition of higher heptachlor concentrations, which may decrease the degradation efficiencies of the chemical in this study. Similar results were presented in degradation of DDT by *Serratia marcescens* [55] and biodegradation of heptachlor and DDT by sediment microbial [56]. In addition, Chiu et al. [56] reported that 100 µg/mL heptachlor and DDT were completely inhibited anaerobic microorganisms and no metabolite was found.

pH and redox potential of different concentrations of heptachlor in liquid culture were measured to evaluate the relationship between growth and metabolic activities of the microcosms and pesticide concentrations. The culture pH was slightly decreased to an acidic range in early treatments before slightly increased to neutral at the end of the experiment in all treatments except for the liquid culture at 150 µg/mL heptachlor concentration where the pH was decreased to acidic range until the end of the experiment. This phenomenon may be due to the metabolic activities of the growing microorganisms. The decreased of pH in liquid culture in biodegradation experiment were also reported [56,58]. In addition, the redox potential values of the liquid culture were positive earlier then decreased to the negative value at the end of the experiment.

The effects of abiotic factors such as temperature, pH and organic matter on degradation of heptachlor in sediment were also determined at 30°C for 28 days. Heptachlor was degraded in sediment only 19.62% in abiotic control compared to 51.17% in biotic control. Furthermore, its metabolite, heptachlor epoxide was not detected under abiotic condition, whereas its concentration under biotic condition was 21.13 ± 1.62 µg/g dw or 25.58% of the parent heptachlor. Because of heptachlor epoxide can be degraded by oxidative reaction by organisms, as a result abiotic control presented no concentration of heptachlor epoxide. Additionally, heptachlor epoxide concentration in this studied was 25.58% of the parent heptachlor which higher than that reported by Bidleman et al. [59] who suggested that heptachlor epoxide accounted for about 20% of the original heptachlor. They also suggested heptachlor degradation in soil proceeded at by at least two routes, 1-hydroxy chlordane and the more persistent, epoxide which subsequently volatilized. Consequently, the oxidation product of indigenous microbial in this study was heptachlor epoxide. This result is relatively similar to the field survey data which the major contaminant in the tributaries of the Mae Klong River was heptachlor epoxide [20].

The pH values were slightly acidic in biotic than abiotic condition. The redox potentials were positive in both conditions, except for later incubation, when those of biotic condition showed the negative value. Microorganisms were increased in number when the incubation time was increased. The positive redox potential was related to the microbial metabolism employing oxidative activities. DeLaune et al. [60] reported that soil generally had a redox range from -250 to +700 mV. In the flooded soil, oxygen is consumed and disappears at a redox potential of approximately +350 mV. Accordingly, aerobic soils represent a redox range of +350 to +700 mV, and anaerobic soil a range of -250 to +350 mV.

13. Effects of additional carbon source on heptachlor degradation

The additional carbon sources other than the target compounds may influence the degradation rates in the system, so the effects of additional carbon sources including sodium succinate, sodium acetate and glucose supplements at 1% concentration were performed and compared with abiotic control (no additional carbon source) to observe heptachlor degradation and heptachlor epoxide evolution.

Higher heptachlor residue in the experiment amended with 1% glucose, without additional carbon sources and 1% succinate (40.33 ± 2.06 , 40.33 ± 1.79 and 39.84 ± 0.77 $\mu\text{g/g dw}$, respectively), where 1% sodium acetate showed the least heptachlor (37.13 ± 0.39 $\mu\text{g/g dw}$) as showed in figure 11. The results illustrated that without carbon supplement, the degradation efficiency was at its highest, whereas 1% of sodium succinate and sodium acetate addition increased the efficiency of degradation. In contrast, many studied reported the inhibition of the degradation of pesticides by microbial when the presence of the more favorable carbon sources has been found [55,56,61]. Moreover, increasing organic contents by adding carbon sources made sediment microorganisms more vigorous in consuming oxygen and turned the incubating condition into anaerobic condition [62].

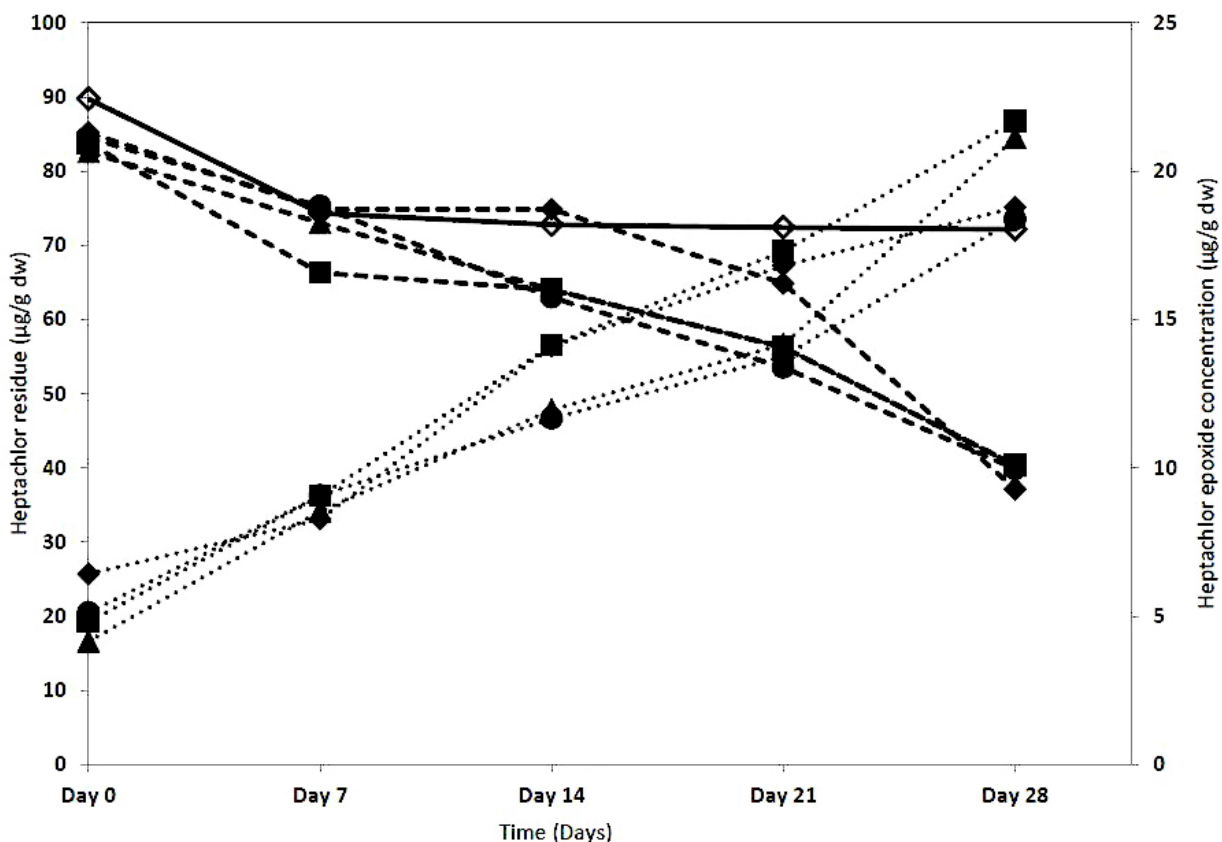


Figure 11. Degradation of heptachlor and heptachlor epoxide formation at various additional carbon sources (Heptachlor residue at \blacklozenge abiotic control; $--\blacksquare--$ w/o carbon source; $--\blacktriangle--$ 1% glucose; $--\bullet--$ 1% sodium succinate; and $--\blacklozenge--$ 1% sodium acetate. Heptachlor epoxide concentration at $\bullet\bullet\blacksquare\bullet\bullet$ w/o carbon source; $\bullet\bullet\blacktriangle\bullet\bullet$ 1% glucose; $\bullet\bullet\bullet\bullet$ 1% sodium succinate; and $\bullet\bullet\blacklozenge\bullet\bullet$ 1% sodium acetate) (Modified from Poolpak, 2008)

Heptachlor epoxide appeared in experiments with adding sodium succinate (21.73% of the parent heptachlor) and sodium acetate (22.02% of the parent heptachlor) was lower than the other two (25.87% and 25.58% for glucose added and without carbon source added, respectively). By means of heptachlor epoxide concentrations decreased when carbon sources were added, the degradation product of heptachlor was no longer heptachlor epoxide. The anaerobic degradation of heptachlor by study of Chiu et al. [56] indicated that sodium acetate increased the anaerobic degradation of heptachlor in river sediment better than glucose and chlordane was produced as the product of degradation. Accordingly, heptachlor could be metabolized to chlordane and 1-hydroxychlordene-2,3-epoxychlordene under anaerobic condition [63].

Microorganisms grew well with 1% glucose as compared to other carbon sources. With sodium succinate added, the pH was increased with the increase in incubation time whereas the number of microorganisms and redox potential values were decreased. The same trend was observed in sodium acetate addition experiment, less microorganism and redox potential values were found.

14. Effect of soil:water ratio on the heptachlor degradation

The effect of water volume on heptachlor degradation in sediment, the 1:1, 1:2 and 1:4 soil:water (w/v) ratio experiments were determined and the biodegradation effects were presented in figure 12. When the soil:water ratio was decreased, the degradation rate was decreased. Together with higher heptachlor residues in the 1:1 soil:water ratio (47.89 ± 1.52 $\mu\text{g/g dw}$), heptachlor epoxide concentration was also decreased when soil:water ratio was increased to 1:1 w/v (18.81% of the parent heptachlor). The degradation efficiencies of heptachlor were also decreased when more sediment was added. Degradation of α - and γ -HCH in the soil slurry by Siddique et al. [57] showed that the soil:water ratio significantly decreased the rate of degradation at 4 weeks of chemical incubation. In addition, the study of Castro and Yoshida [64] found that heptachlor had degraded readily in flooded soil than under upland conditions.

The fate of heptachlor in the environment is influenced by environmental factors including soil/water ratio. Decreasing the soil:water ratio decreased the degradation of heptachlor in the sediment, which might be due to the adsorption of heptachlor to the soil particles, decreasing their bioavailability to the microorganisms. Furthermore, the conditions in sediments are principally controlled by the diffusion of dissolved oxygen from the overlying water into the sediment bed, which aerobic bacteria dominate, and oxidation reactions both abiotic and biotic relatively easy occurred [11].

The decrease in heptachlor epoxide productivity when soil:water ratio decreased, suggested that less oxidative metabolism by bacterial activities with the confirmation by negative redox potential. The redox profile is expected to have the greatest effect on OCPs degradation in bed sediments, since compounds will be degraded at different rates and may be degraded through different pathways under different redox conditions. In general, the degradation rates in soils and sediments have been observed to be significantly faster under

aerobic conditions, atrazine degradation in oxidizing conditions [60] and HCH degradation by microbial consortium [61,65]. This studied shows the same trend as previous studies as redox potential since 1:4 soil:water ratio were more positive than the others. Moreover the degradation efficiency of this soil:water ratio was better than other treatments.

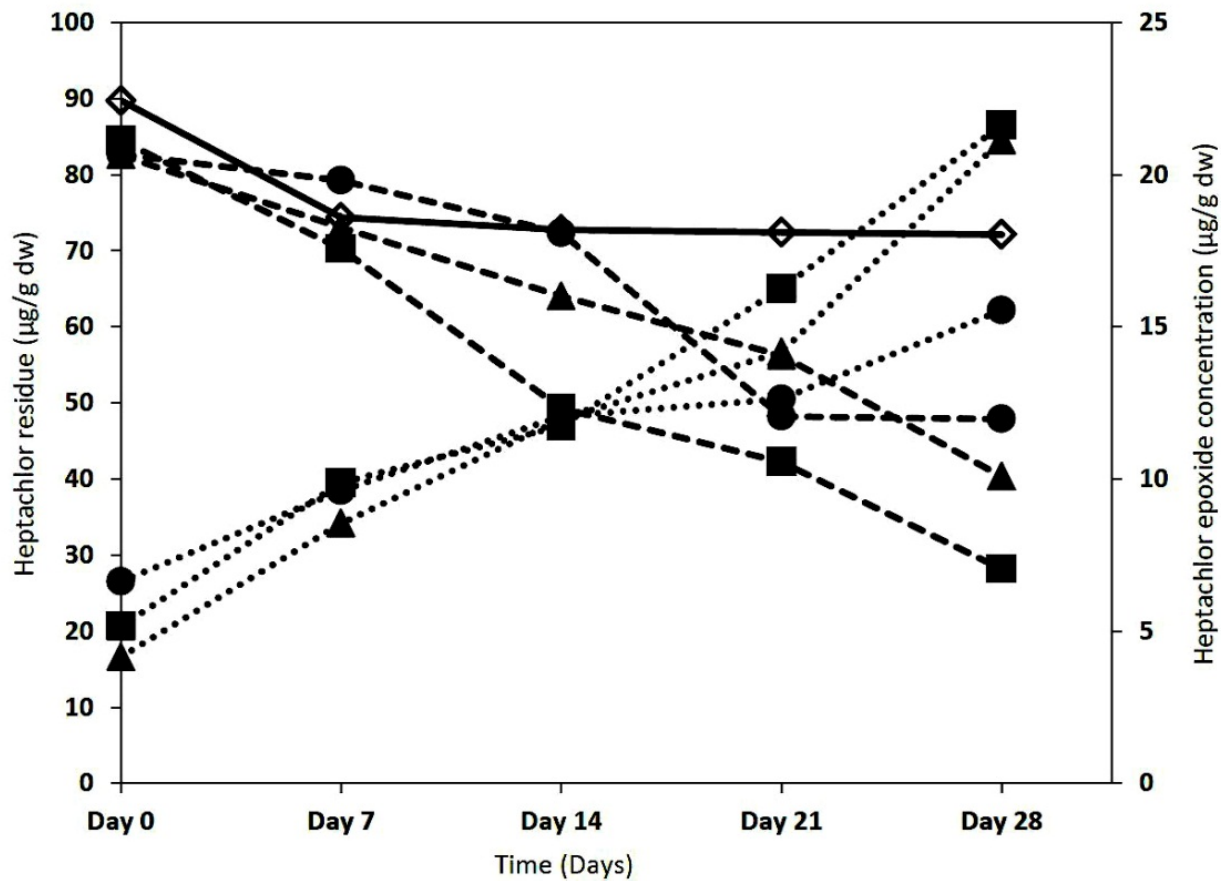


Figure 12. Degradation of heptachlor and heptachlor epoxide formation at various soil:water ratio (Heptachlor residue at \blacklozenge abiotic control; $--\blacksquare--$ 1:4 soil:water ratio; $--\blacktriangle--$ 1:2 soil:water ratio; and $--\bullet--$ 1:1 soil:water ratio. Heptachlor epoxide concentration at $\bullet\bullet\blacksquare\bullet\bullet$ 1:4 soil:water ratio; $\bullet\bullet\blacktriangle\bullet\bullet$ 1:2 soil:water ratio; and $\bullet\bullet\bullet$ 1:1 soil:water ratio) (Modified from Poolpak, 2008).

Even though degradation was slow under reducing or anaerobic condition, the anaerobic degradation of chlordane [66], atrazine [60] and endosulfan [67] were observed.

15. Effect of incubation temperature on heptachlor degradation

The influence of incubation temperatures on heptachlor degradation and heptachlor epoxide transformation was studied at 20°C and 30°C to evaluate the degradation efficiencies of the microcosm. A smaller amount heptachlor residue was presented at 30°C (40.33 ± 2.06 µg/g dw) than that of 20°C (65.70 ± 2.41 µg/g dw). Heptachlor epoxide concentration was decreased when the temperature was decreased, 25.58% and 14.75% of parent heptachlor at 30°C and 20°C, respectively (figure 13). Furthermore, the higher percentage of biodegradation at 30°C was also better than that of 20°C (51.17% and 26.30%, respectively).

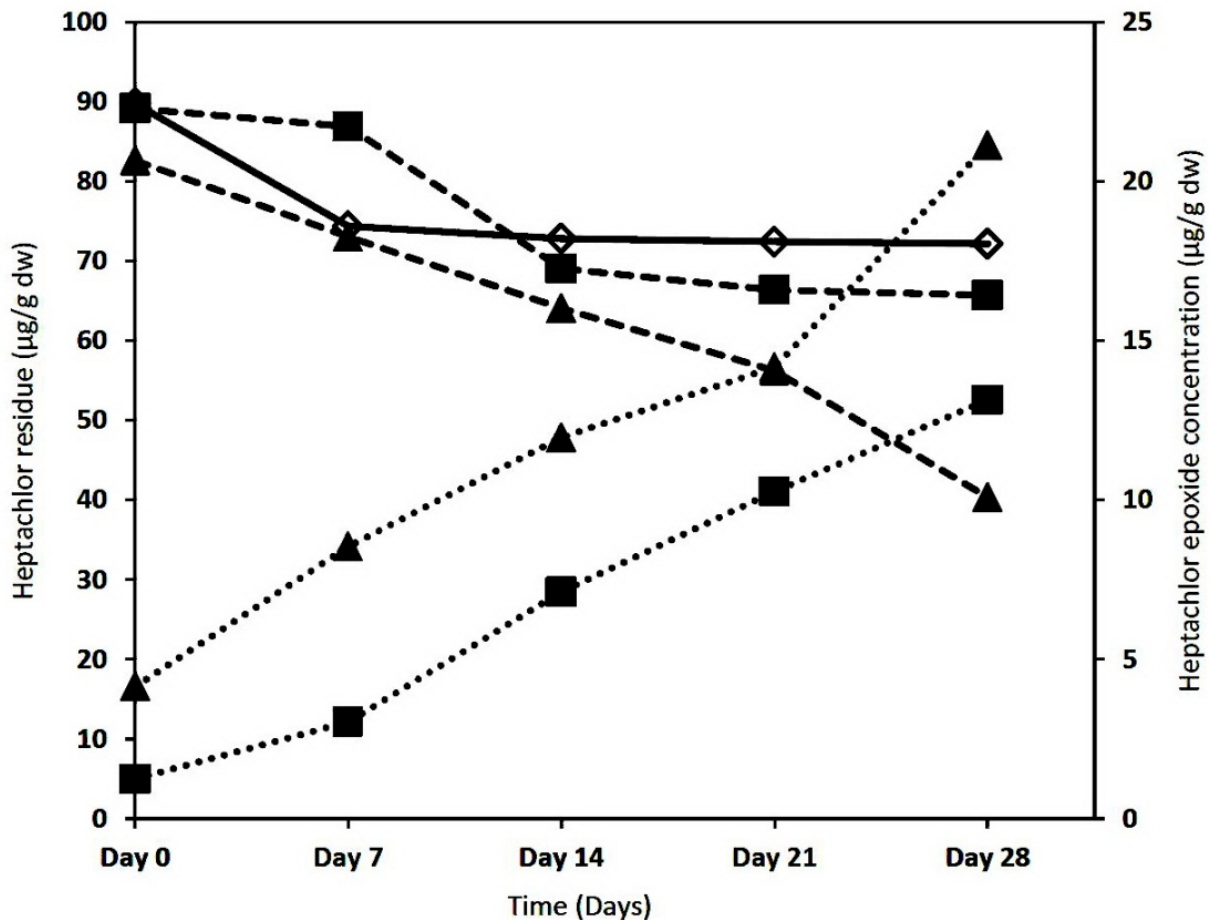


Figure 13. Degradation of heptachlor and heptachlor epoxide formation at various temperature (Heptachlor residue at ◆ abiotic control; --■-- 20°C; and --▲-- 30°C. Heptachlor epoxide concentration at ●■● 20°C; and ●▲● 30°C) (Modified from Poolpak, 2008).

Many studies reported that the temperature of 30°C was suitable for chemical biodegradation including biodegradation of HCH isomer in soil slurry [57] and DDT and heptachlor degradation in river sediment of Taiwan [56]. Moreover, biodegradation of endosulfan by soil bacteria [68], abiotic degradation of endosulfan in a clay soil [70] and degradation of DDT by soil bacteria [54] yielded the maximum values at temperature of 30°C. However, microorganisms have the ability to degraded pesticides in a wide range of temperatures. For example, *Serratia marcescens* DT-1P can degrade DDT at the temperature from 4°C up to 50°C [55].

16. Rate of heptachlor degradation

In liquid culture and sediment, the degradation rate at the heptachlor concentration of 100 µg/g soil dw by indigenous microorganism fitted well with the second-order reaction and first order-reaction, respectively. The constant heptachlor degradation rate in liquid culture with the degradation rate constant, $k = 0.0125 \mu\text{g}/\text{mL}\cdot\text{day}$. The degradation acted as the

concentrations of one second-order reactant, or two first-order reactants. Heptachlor degradation in sediment hold the degradation rate constant (k) of $3.106 \times 10^4 \mu\text{g/g dw}\cdot\text{day}$ and acted as the first-order reaction. A first-order reaction depended on the concentration of only one reactant. Other reactants could be present but in zero-order reaction.

The reaction rate of heptachlor biodegradation in both liquid culture and sediment was slightly decreased when the incubation time was increased. This may be due to the decrease in bacterial number when the incubation time was increased. Additionally, the conditions of the experiment were unfavorable for metabolic activities for microorganisms.

Since the degradation rate in liquid culture fits to the second-order reaction, it indicates that not only bacterial activities affected heptachlor degradation but also other factors should be involved as well. Even though, degradation of sorbed pesticides in the soil is a complicated process affected by many factors, the degradation rate of heptachlor in sediment fitted well with first-order reaction. This suggests that microbial degradation of pesticide was the major factor in sediment degradation. Ghadiri et al. [70] reported the degradation rates of aldrin, dieldrin, endrin and chlordane were first-order, the same as rate of atrazine degradation in reactors studied by Ghosh and Philip [71].

17. Dominant microorganism in heptachlor degradation experiment

In all experiment of heptachlor biodegradation by soil microorganisms collected from Rang Tub Tab canal. Three indigenous microorganisms, which dominated in the biodegradation experiment in both liquid culture and sediment, were identified by 16S rDNA sequencing as *Bacillus subtilis* RS-01, *Bacillus cereus* RS-02 and *Pseudomonas putida* RS-03. Although, the numbers of bacteria were low at earlier incubation, it was increased when the incubation time increased. Additionally, degradation rate increased when the number of bacteria was increased.

Despite the fact these three bacteria were dominant in the experiment during heptachlor degradation; it is difficult to interpret the role that the bacteria play in the transformation process of heptachlor in view of the fact that the physiological actions of these isolates are still unknown. However, biodegradation of endosulfan contaminated soil and water in laboratory scale reactors by *B. circulans*-I and II enriched from contaminated soil of endosulfan processing industry has been reported by Kumar and Philip [71]. In addition, *P. fluorescens*, *B. cereus* and *Bacillus* sp. were the consortium successful for *ex-situ* biodegradation of chlorobenzenes in soil [73]. Ambrosoli et al. [74] studied the degradation of carbofuran by bacterial population; the results showed that genera *Pseudomonas* and *Bacillus* rapidly degraded carbofuran in soil as carbon source. Furthermore, heptachlor epoxide concentrations in all biotic experiments represented oxidative metabolism of these bacterial population. The evidences suggest that these three bacteria might be responsible for the heptachlor degradation in sediment. The proposed pathways of heptachlor metabolism in this study were summarized in Figure 14.

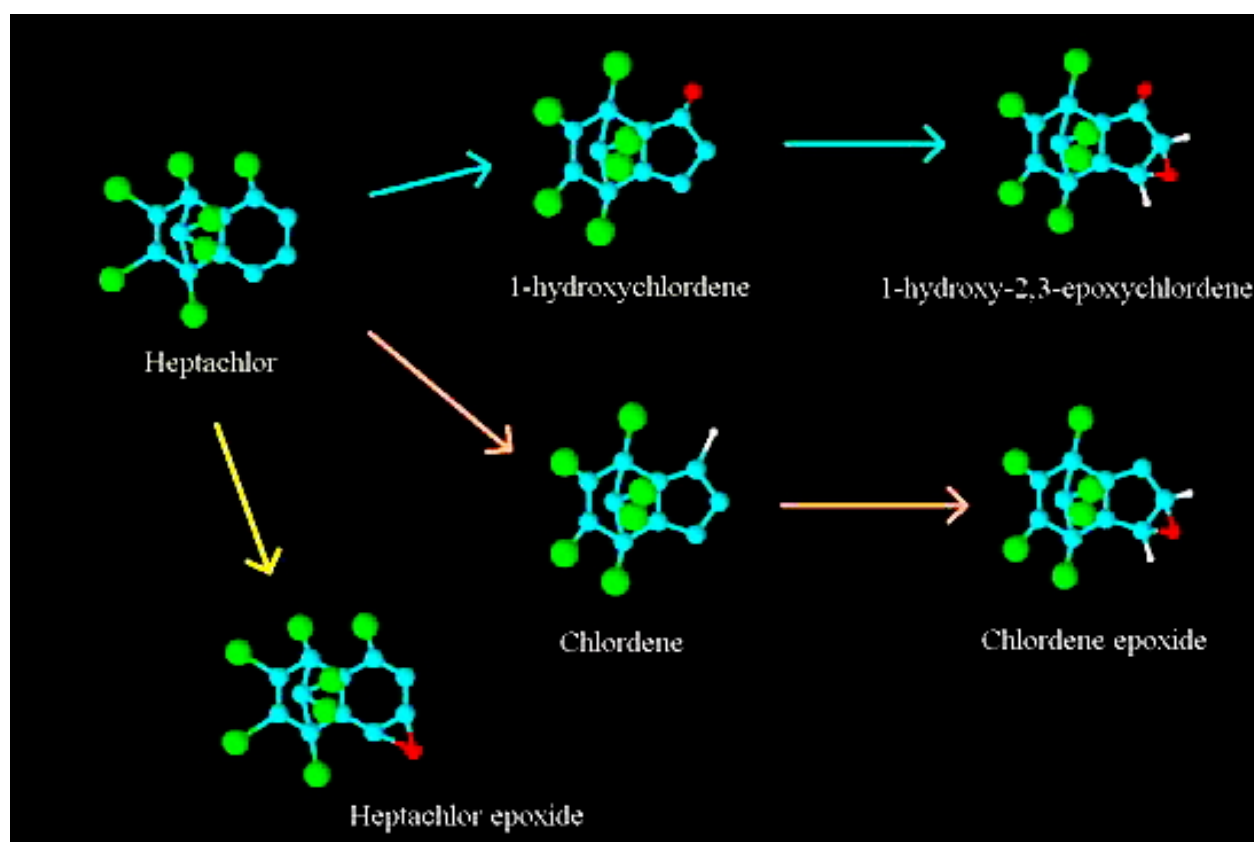


Figure 14. Pathways of heptachlor metabolism by indigenous microorganisms (T. Poolpak, 2008; modified from Lal and Saxena, 1982).

The first route of heptachlor degradation is the chemically hydrolysis of heptachlor to 1-hydroxychlordeane in soil, and microbial attack on this product results in the production of 1-hydroxy-2,3-epoxychlordeane. The second is microbial dechlorination of heptachlor produce chlordene, which undergoes microbial epoxidation to form the corresponding chlordene epoxide. The last route of biodegradation is oxidation of heptachlor by microorganism converts heptachlor to its epoxide by mixed-function oxidase system [63].

18. Conclusion

The surface sediment in the tributaries of Mae Klong River is polluted by the OCPs and relatively high levels of these compounds were observed in most study areas which summer was the season that highest OCPs residues were found in both sampling years. Heptachlor epoxide presented the highest concentration among detected OCPs. In addition, Σ DDT and HCHs were found in slightly elevated levels representing a recent input of these two OCPs into the study area.

For heptachlor biodegradation in liquid cultures, the highest degradation efficiency (88.36%) was observed in 100 $\mu\text{g/mL}$ heptachlor where at 150 $\mu\text{g/mL}$ heptachlor, the efficiency was lower. Moreover, growth of microorganism was inhibited at higher heptachlor concentration; as a result the degradation efficiency was decreased. In addition, heptachlor

epoxide, the oxidative product of heptachlor by microorganism was found at the highest concentration in the 50 µg/mL heptachlor treatments. This evidence enhanced the idea of inhibition of bacterial growth at high concentration of heptachlor.

In abiotic condition of heptachlor biodegradation and the transformation to heptachlor epoxide in sediment, there was no detection of heptachlor epoxide. Confirms microorganisms play a major role in heptachlor oxidation to heptachlor epoxide. In contrast, heptachlor degradation was detected in biotic degradation; heptachlor epoxide concentration in this study was 25.58% of the parent heptachlor.

A number of external parameters including additional carbon sources affected the degradation rates in this study. Without carbon supplement, the degradation efficiency was high. Moreover, when 1% of sodium succinate and sodium acetate was added, the efficiency of degradation was even higher. However, heptachlor epoxide concentrations decreased when these carbon sources were added and the degradation product of heptachlor was changed to chlordane instead of heptachlor epoxide.

For soil:water ratio experiments, as the soil:water ratio was decreased, the degradation rate of heptachlor decreased. At 1:4 soil:water ratio, the redox potential values were more positive and higher degradation efficiency was observed. Also both degradation efficiency and transformation of heptachlor to epoxide at 20°C were lower than those at 30°C, these may be due to 30°C was the most favorable temperature for bacterial growth and heptachlor degradation.

The degradation rate in liquid culture fitted to the second-order reaction where the degradation rate of heptachlor in sediment fitted well to the first-order reaction. Decrease of reaction rate as incubation time increased was seen in both liquid culture and sediment. This may be as a result of the decrease in bacterial number and the shortage of food source toward time.

Three dominant bacteria were isolated and identified as *B. subtilis* RS-01, *B. cereus* RS-02 and *P. putida* RS-03. Degradation rate of heptachlor and heptachlor epoxide evolution increased when the number of bacteria was increased. Although these three bacteria were dominant in the experiment during heptachlor degradation, it is difficult to interpret the role that the bacteria play in the transformation process of heptachlor in view of the fact that the physiological actions of these isolates are still unknown. Nonetheless, heptachlor epoxide, oxidative products from microorganism metabolism, presented in biotic treatments, suggests that these bacteria might be responsible for the heptachlor degradation in sediment.

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