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อะโรมาติกไฮโดรคาร์บอนของอินทรีย์คาร์บอนในดิน



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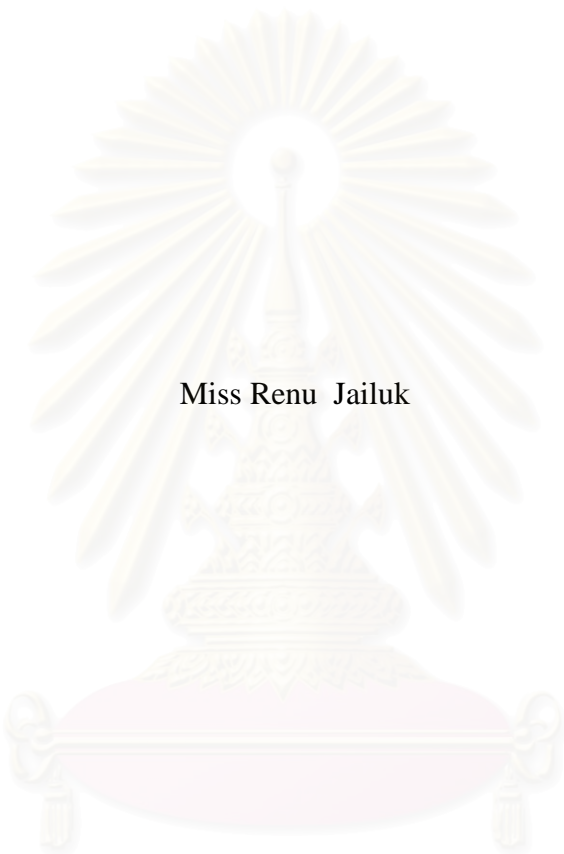
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DEVELOPMENT OF A QSAR MODEL TO PREDICT SOIL ORGANIC
CARBON-WATER PARTITION COEFFICIENTS OF POLYCYCLIC
AROMATIC HYDROCARBONS



Miss Renu Jailuk

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เรณู ใจหลัก : การพัฒนาควิซาร์โมเดลเพื่อทำนายค่าสัมประสิทธิ์การดูดซับสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนของอินทรีย์คาร์บอนในดิน. (DEVELOPMENT OF A QSAR MODEL TO PREDICT SOIL ORGANIC CARBON-WATER PARTITION COEFFICIENTS OF POLYCYCLIC AROMATIC HYDROCARBONS) อ. ที่ปรึกษา : ดร. เบญจลักษณ์ กาญจนเศรษฐ์, 73 หน้า. ISBN 974-17-2567-1.

การศึกษาดูดซับสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน (PAH) 9 ชนิด ได้แก่ แนพทาซีน อะเซแนพทีน ฟลูออรีน แอนทราซีน พีแนนทรีน ฟลูออแรนทีน ไพรีน เบนโซเอแอนทราซีน และเบนโซเอไพรีนซึ่งเป็นตัวแทนสาร PAH โดยมีค่า $\log K_{ow}$ อยู่ในช่วง 3.4-6.5 โดยทำการทดลองการดูดซับสาร PAH ของอินทรีย์คาร์บอนในดินบนตัวอย่างดิน 4 ตัวอย่างที่ระดับความเข้มข้นของสาร PAH 4 ความเข้มข้น โดยมีจุดประสงค์เพื่อประเมินพฤติกรรมของสาร PAH ระหว่างสารอินทรีย์คาร์บอนในดินและน้ำ เพื่อหาความสัมพันธ์ระหว่างค่า $\log K_{oc}$ กับค่า $\log K_{ow}$ มวลโมเลกุล ค่าการละลายน้ำ ค่าความดันไอ และค่าคงที่ของเฮนรี และเพื่อตรวจสอบความสามารถของโมเดลในการทำนายค่า $\log K_{oc}$ จากการศึกษาพบว่า ค่า $\log K_{oc}$ ที่ได้จากการศึกษานี้มีค่าใกล้เคียงกับค่า $\log K_{oc}$ จากงานวิจัยอื่นซึ่งค่า $\log K_{oc}$ มีค่าเพิ่มขึ้นตามน้ำหนักโมเลกุลและค่า $\log K_{ow}$ ที่มากขึ้น เมื่อเปรียบเทียบค่า $\log K_{oc}$ ที่ได้จากการศึกษานี้กับงานวิจัยอื่นๆ พบว่าโดยส่วนใหญ่มีค่าใกล้เคียงกันและบางค่ามีความแตกต่างกับงานวิจัยอื่นทั้งนี้อาจมีสาเหตุมาจากความแตกต่างของเงื่อนไขในการทดลอง อุณหภูมิในการทดลองแตกต่างกัน อิทธิพลของขนาดอนุภาคดิน สารละลายหรือสารคอลลอยด์อินทรีย์ การย่อยสลายสารโดยชีวภาพ และการย่อยสลายสารโดยแสง เป็นต้น จากการศึกษาพบว่า ความสัมพันธ์ระหว่างค่า $\log K_{oc}$ กับ $\log K_{ow}$ น้ำหนักโมเลกุล และค่าคงที่ของเฮนรี อยู่ในระดับสูง แสดงให้เห็นว่าคุณสมบัติของสารเหล่านี้สามารถใช้ทำนายค่า $\log K_{oc}$ ของ PAH ได้ โดยการตรวจสอบโมเดลโดยใช้สาร PAH ซึ่งมีค่า $\log K_{ow}$ อยู่ในช่วง 3.4-6.5 (สารชนิดที่ไม่ได้นำมาศึกษาเพื่อพัฒนาโมเดล) พบว่าค่า $\log K_{oc}$ ที่คำนวณจากโมเดลของการศึกษานี้ใกล้เคียงกับงานวิจัยอื่น โดยเฉพาะค่า $\log K_{oc}$ ที่ได้จากการสมการของ $\log K_{ow}$ สำหรับการตรวจสอบโมเดลโดยใช้สารที่มีคุณสมบัติใกล้เคียงกับสาร PAH คือ สาร PCDD และ PCB พบว่า ค่า $\log K_{oc}$ ที่ได้ไม่ดีเท่ากับเมื่อทดสอบโมเดลโดยใช้สาร PAH ยกเว้นค่า $\log K_{oc}$ ที่ได้จากการสมการของ $\log K_{ow}$ สำหรับความสัมพันธ์ระหว่างค่า $\log K_{oc}$ กับค่าการละลายน้ำและค่าความดันไอ อยู่ในระดับที่ต่ำกว่าซึ่งทำให้โมเดลสามารถทำนายค่า $\log K_{oc}$ ได้ไม่ดีเท่ากับโมเดลอื่นๆ ทั้งนี้อาจมาจากความหลากหลายของค่าการละลายน้ำและค่าความดันไอของสารซึ่งทำให้ค่าความสัมพันธ์ที่ได้อยู่ในระดับต่ำกว่าที่ควรจะเป็น

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RENU JAILUK: DEVELOPMENT OF A QSAR MODEL TO PREDICT SOIL
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The study focussed on the sorption of 9 PAH (NAP, ACE, FLU, ANT, PHE, FLA, PYR, BaA, and BaP) which was used as the representative for the PAH with $\log K_{ow}$ ranged from 3.4 to 6.5. The sorption of PAH was undertaken on four soil organic carbon contents over four concentrations of the compounds. The objectives were to evaluate the partitioning behavior of PAH between the soil and the water, to determine the relationships between $\log K_{oc}$ and $\log K_{ow}$, MW, $\log S$, $\log VP$, and $\log H$, and to validate the developed models. The soil organic carbon-water partition coefficients ($\log K_{oc}$) values of PAH obtained agree well with other studies. The values increased with increasing molecular weight and $\log K_{ow}$ of the compounds. Deviation of $\log K_{oc}$ values could be the influence of experimental condition, temperature, soil particle size, suspended or colloidal organic matter, biodegradation, and photodegradation. Good relationships of $\log K_{oc}$ which those of $\log K_{ow}$, MW, and $\log H$ were obtained which indicated these properties as good indicators for predicting the $\log K_{oc}$ values. This was evident by the values of $\log K_{oc}$ of other PAH with $\log K_{ow}$ ranged from 3.4 to 6.5 derived from the models were close to those in the literatures, especially, the $\log K_{oc}$ values derived from $\log K_{ow}$. The application of the models with similar physicochemical property, i.e. PCDD, PCB is not good as for PAH compounds except the model derived from $\log K_{ow}$. Therefore, the application of the models to these groups may be limited. Other models developed from the relationships of $\log K_{oc}$ with S , VP may not be appropriate since their correlation coefficients were not justified. This was probably due to variation in the S and VP values.

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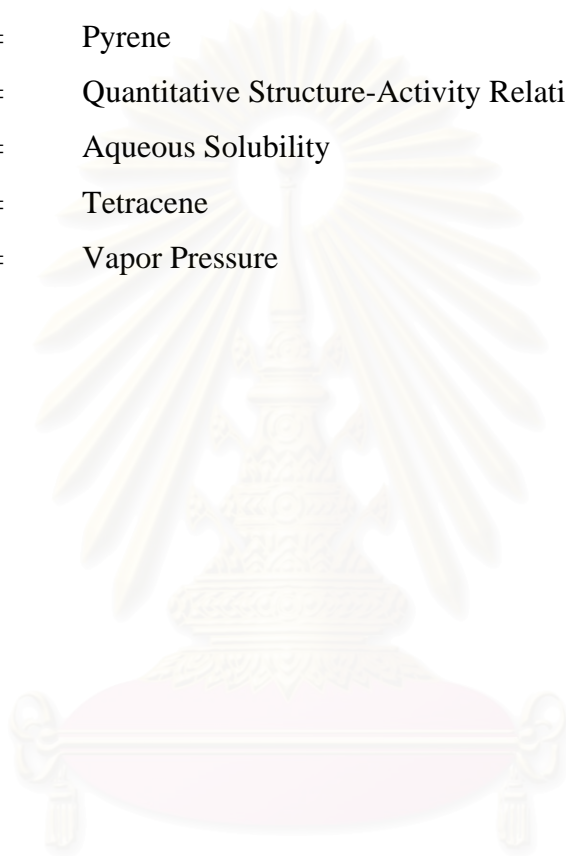


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LIST OF ABBREVIATIONS

1-ENAP	=	1-Ethyl-naphthalene
1-MNAP	=	1-Methyl-naphthalene
2-MNAP	=	2-Methyl-naphthalene
9-MANT	=	9-Methyl-anthracene
2-CDD	=	2-Chloro-dibenzo-p-dioxin
2-PCB	=	2-Chlorobiphenyl
2,2'-PCB	=	2,2'-Dichlorobiphenyl
2,3-DCDD	=	2,3-Chloro-dibenzo-p-dioxin
2,4'-PCB	=	2,4'-Dichlorobiphenyl
2,4,4-PCB	=	2,4,4-Trichlorobiphenyl
2,2',5,5'-PCB	=	2,2',5,5'-Tetrachlorobiphenyl
ACE	=	Acenaphthene
ACT	=	Acenaphthylene
ANT	=	Anthracene
BaA	=	Benzo (a) Anthracene
BaF	=	Benzo (a) Fluoranthene
BkF	=	Benzo (k) Fluoranthene
BaP	=	Benzo (a) Pyrene
CEC	=	Cation Exchange Capacity
CHRY	=	Chrysene
DBA	=	Dibenzo (a,h) anthracene
DMBA	=	7,12-Dimethylbenz (a) anthracene
FLA	=	Fluoranthene
FLU	=	Fluorene
H	=	Henry's law Constant
Kd	=	Soil-Water Partition Coefficients
Koc	=	Soil Organic Carbon-Water Partition Coefficients
Kom	=	Soil Organic Matter-Water Partition Coefficients
Kow	=	Octanol-Water Partition Coefficients
MCI	=	Molecular Connectivity Indices
MCT	=	3-Methylcholanthrene

MPHE	=	Methylphenanthrene
MW	=	Molecular Weight
NAP	=	Naphthalene
OC	=	Organic Carbon
PAH	=	Polycyclic Aromatic Hydrocarbons
PCDD/F	=	Chlorinated Dibenzofurans
PHE	=	Phenanthrene
PYR	=	Pyrene
QSAR	=	Quantitative Structure-Activity Relationships
S	=	Aqueous Solubility
TTC	=	Tetracene
VP	=	Vapor Pressure



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CHAPTER 1

INTRODUCTION

When chemicals are released from sources, they are subject to distribute into the environment. Since the environment can be divided into many compartments (e.g. air, soil, water), the chemicals transportation from one compartments to other compartments is depend on physicochemical properties of compound (e.g. octanol-water partition coefficients, water solubility, vapor pressure, molecular weight) (Office for Official Publications of the European Committee, 1996) and the properties of the environmental media (e.g. atmospheric conditions, organic carbon content in the soil (Gerstl, 1990)). Therefore, many studies on evaluation of fate and transport of chemicals have accumulated with the aim to determine the environmental concentrations of the compounds as a step to assess the environmental exposure (Sabljic, 2001). Generally, the partition coefficient of the compound can be used to characterize the likely environmental media the compounds will reside. For example, the soil-air partition coefficient describes the partitioning of the compounds between the soil and the air (Hippelein and McLachlan, 1998). However, the transport process can be influenced by a number of factors including photodegradation, biodegradation (Boethling and Mackay, 2000).

In the terrestrial environment, it seems that the soil is a sink of chemicals. This is evident by many studies. For example, the soil contains the vast majority of PAH in U.K (Wild and Jones, 1995). The soil-water partition coefficient (K_d) describes the distribution of the compounds in the soil and in the aqueous phase (Boethling and Mackay, 2000) and is regarded as one of the most important input parameters in the environmental fate models (Baker, Mihelcic, and Shea, 2000). The K_d help to predict the tendency of the compounds that will be leached to surface water or migrated to groundwater which lead to adverse affects on their quality. The determination of K_d can be generally obtained from laboratory experiment that is costly, time consuming and dealing with problems of error during the laboratory work. This is one of the reasons that the K_d values are not available for all compounds

or all PAH since there are approximately 10,000 compound members in the group of PAH (Wisconsin Department of Health and Family Service, 2000). These difficulties on the measurement of K_d have brought estimation methods, a quantitative structure activity relationship (QSAR) approach, useful tool for the prediction of K_d . Although there have been a lot of studies on these soil-water partition coefficients on many organic compounds including PAH and others with similar properties, e.g. PCB, PCDD. Most of data are not appropriate to apply since they lack some essential data such as environmental condition is not available, only one soil type and one compound concentration are undertaken in the experiments, some of the K_d values derived from various groups of compounds while others derived from a few compounds used in the experiments (Chiou, Porter, and Schmedding, 1983; Mean *et al.*, 1980).

This study is therefore focused on nine PAH which is treated as the representative for the PAH and undertaking the partitioning experiments on four soil organic carbon contents which is considered to play an important role on the adsorption of the compound and with four different concentrations of the compounds. The results obtained can be applied to predict the K_d of other PAH and to compounds of similar physicochemical properties.

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CHAPTER 2

OBJECTIVES AND STRATEGIES

The study has two main objectives as follows:

2.1 To evaluate the partitioning behavior of PAH between the soil and the water

To obtain the partitioning behavior, a partitioning experiment between the soil and the water is carried out. Four organic carbon contents in soil are studied over four concentrations of the test compounds to achieve the better K_d instead of undertaking on one organic carbon content over one concentration of the compound. To enable our K_d values to be comparable to other studies, the K_d values are normalized to the soil organic carbon-water partition coefficient (K_{oc}). The $\log K_{oc}$ values are compared with other studies.

2.2 To determine the relationship between the $\log K_{oc}$ and physicochemical properties

The $\log K_{oc}$ values obtained are plotted against $\log K_{ow}$ and comparison is made with results in the literature. Other physicochemical properties, i.e. MW, VP, S, and H are also plotted to investigate their relationships. Some PAH and other hydrophobic organic compounds are chosen to test the models.

CHAPTER 3

LITERATURE REVIEWS

3.1 PAH and their behavior

3.1.1 Sources

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental contaminants that are formed during incomplete combustion of organic materials and from geochemical formation of fossil fuels (Yang *et al.*, 1991). Primary natural sources are forest fires and volcanic activity, for example, in some geographical areas, forest fires and volcanoes (Benzo (a) Pyrene) are the main natural sources of PAH in the environment (Back *et al.*, 1992). In Canada, about 2,000 tons of airborne PAH per year are attributed to natural forest fires (The International Program on Safety [IPCS], 1998).

However, most of the PAH released into the environment arise from anthropogenic sources such as combustion of coal coking, petroleum refining, refuse burning, industrial processes, and motor vehicle exhausts.

During coal coking, PAH are released into the ambient air, for example, pyrene, benzo (a) pyrene, benzo (e) pyrene, benzo (a) anthracene, and fluoranthene (Broddin *et al.*, 1977). Petroleum refinery is one of important sources that released PAH, for example, naphthalene and its derivatives (IPCS, 1998). PAH are detected in the stack gases from a British municipal incinerator, for example, pyrene, benzo (a) anthracene, and fluorene (Colmsjö *et al.*, 1986a). There are several industrial industries that released PAH, such as naphthalene and benzo (ghi) perylene were released from aluminium production. In addition, the main compounds released from petrol-fuelled vehicles are fluoranthene and pyrene, while naphthalene and acenaphthene are abundant in the exhaust of diesel-fuelled vehicles (IPCS, 1998).

PAH molecules are made up of two or more benzene rings, which are fused with two neighboring rings sharing two adjacent carbon atoms (ToxProbe Inc. for Toronto Public Health [ToxProbe], 2002). In addition to PAH that are composed of carbon and hydrogen atoms only, some PAH contain heteroatom such as nitrogen and sulfur (IPCS, 1998). PAH are a group of approximately 10,000 compounds, but the most toxic members of this family known to date are PAH molecules that have four to seven rings (ToxProbe, 2002).

The U.S. Environmental Protection Agency has identified 16 unsubstituted PAH as priority pollutants considered to be representative of the class. They are including naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, fluorene, benzo (a) anthracene, benzo (b) fluoranthene, chrysene, fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, dibenzo (a,h) anthracene, indeno (1,2,3-d) pyrene, dibenzo (a,h) anthracene, and benzo (ghi) perylene (US.EPA, 1984a). The test compounds in this study are 9 of 16 priority pollutants.

3.1.2 Physicochemical properties

The relevant physicochemical properties including aqueous solubility, vapor pressure, octanol-water partition coefficient, molecular weight and Henry's law constant were described below.

Aqueous solubility is one of the most important physicochemical properties of a compound, there has been reported the high relationship between aqueous solubility and molecular volume of PAH. It is a direct measurement of hydrophobicity (Boethling and Mackay, 2000). PAH are hydrophobic compounds and generally characterized as "low to very low" aqueous solubility (tends to decrease with increasing molecular weight). The highest aqueous solubility in the group is 31.7 mg/L (NAP), and 0.0038 mg/L (BaP) for the lowest (Mackay, Shiou, and Ma, 2000).

The vapor pressure of a chemical is the pressure its vapor exerts in an equilibrium with its liquid or solid phase. The vapor pressure can be considered as an influencing factor governing the fate of the compound. As a general rule, vapor pressure tends to decrease with increasing molecular weight. The vapor pressure of

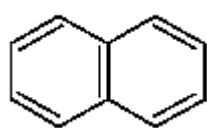
PAH under environmental conditions is very low: the maximum at room temperature is 10.4 Pa for naphthalene, and the minimum is 7×10^{-7} Pa for benzo (a) pyrene (Mackay *et al.*, 2000). Vapor pressure is temperature dependence, therefore, it is describe to apply the data at the same temperature.

Octanol-water partition coefficient (K_{ow}) is defined as the equilibrium ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase. It provides a direct estimate of lipophilicity and partitioning tendency from water to organic media such as lipids, waxes, and natural organic matter. The log K_{ow} values range from 3.4 for naphthalene to 6.5 for benzo (a) pyrene (Mackay *et al.*, 2000), indicating the potential for bioaccumulation. K_{ow} is constant under defined conditions and usually measured at 20 °C or 25 °C. K_{ow} is a common parameter mostly used in the investigation of QSAR with bioconcentration.

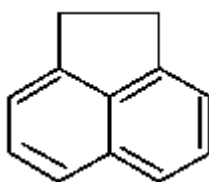
Henry's Law Constant is the partition coefficient for the distribution of a chemical in the gas phase to that in the aqueous phases. Little is volatilized from water phase owing to their low Henry's law constant: the Henry's law constant value range from 48.9 Pa.m³/mol for naphthalene to 0.034 Pa.m³/mol for benzo (a) pyrene (Mackay *et al.*, 2000).

In addition, molecular weight of the compounds is the one important property. Molecular weight from 128.2 for naphthalene to 252.3 for benzo (a) pyrene (IPCS, 1998). At ambient temperatures, PAH are solids. The general characteristics common to the class are high melting and boiling points, low vapor pressure, and very low water solubility with tends to decrease with increasing molecular weight. PAH are soluble in many organic solvents and are highly lipophilic. They are chemically rather inert, photodegradation, and reactions with nitrogen oxides, nitric acid, sulfur oxides, sulfuric acid, ozone, and hydroxyl radicals.

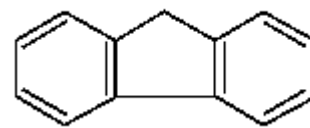
The structures of PAH covered in this study are shown in Figure 3.1 and the relevant physicochemical properties are shown in Table 3.1.



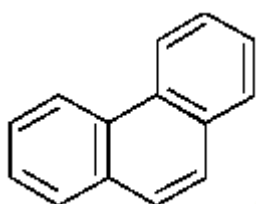
Naphthalene



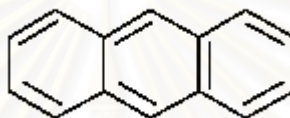
Acenaphthene



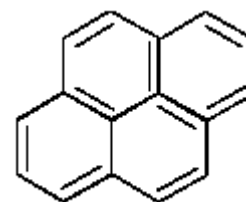
Fluorene



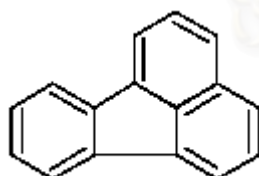
Phenanthrene



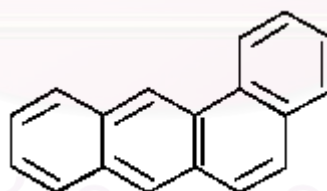
Anthracene



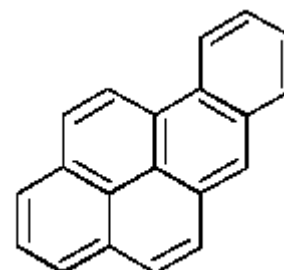
Pyrene



Pyrene



Benzo (a) Anthracene



Benzo (a) Pyrene

Figure 3.1 the structures of test compounds

Table 3.1 The relevant physicochemical properties of test compounds

PAH	CAS registry	Chemical Formula	Molecular Weight	Aqueous Solubility (mg/l at 25 °C)	Vapor Pressure (Pa at 25 °C)	Log Kow at 25 °C	Henry's Law Constant (Pa.m ³ /mol) at 25°C
NAP	91-20-3	C ₁₀ H ₈	128.2	31.7	10.4	3.4	48.9
ACE	83-32-9	C ₁₂ H ₁₀	154.2	3.93	2.9x10 ⁻¹	4.07	14.79
FLU	86-73-7	C ₁₃ H ₁₀	166.2	1.98	8.0x10 ⁻²	4.18	10.13
ANT	120-12-7	C ₁₄ H ₁₀	178.2	0.073	8.0x10 ⁻⁴	4.5	6.59
PHE	85-01-8	C ₁₄ H ₁₀	178.2	1.29	1.6x10 ⁻²	4.6	3.98
FLA	206-44-0	C ₁₆ H ₁₀	202.3	0.26	1.2x10 ⁻³	5.22	0.957
PYR	129-00-0	C ₁₆ H ₁₀	202.3	0.135	6.0x10 ⁻⁴	5.18	1.1
BaA	56-55-3	C ₁₈ H ₁₂	228.3	0.014	2.8x10 ⁻⁵	5.6	0.0902
BaP	50-32-8	C ₂₀ H ₁₂	252.3	0.0038	7.0x10 ⁻⁷	6.5	0.034

Source: Mackay *et al.* 2000

3.1.3 Harmful effect of PAH

The health effects of PAH have been widely reviewed in IPCS, 1998; ATSDR, 1995; and IARC, 1998. Brief summary is provided here. PAH have been shown to induce a number of toxic effects. Several PAH have caused death in rodents. On the other hand, eye irritation (anthracene and naphthalene), respiratory mucosa irritation, photophobia and skin toxicity such as dermatitis and kerotosis (e.g. benzo (a) pyrene, phenanthrene, pyrene, and fluorene), have been demonstrated to cause occupational exposure to PAH. Adverse respiratory effects, including acute and subacute inflammation, and fibrosis, have been demonstrated experimentally.

Carcinogenic PAH has been reported to suppress immune reaction in rodents. IARC (1998) recommended that BaA and BaP are human carcinogenic. In addition, US.EPA classified the carcinogenicity as following: the probable human carcinogen but limited human data are available (e.g. BaA, BaF, BaA, B_jF, B_kF, and BaP. The possible human carcinogens are including BaP and NAP. Exposure to PAH can have a number of adverse effects on both female and male reproductive systems and on fetal development. A large amount of data is available for rodent fetal development. Although no human data are available, reproductive and developmental effect may be important in humans.

Genotoxic effects have been repeatedly demonstrated both in *in vivo* tests in rodents and *in vitro* tests using mammalian including human (e.g. benzo (a) anthracene, benzo (a) pyrene , and fluoranthene). A genotoxic effect event is postulated as a required step in the carcinogenicity process and may play a role in some forms of developmental toxicity (ToxProbe, 2002).

3.1.4 Fate and transport of PAH in soil

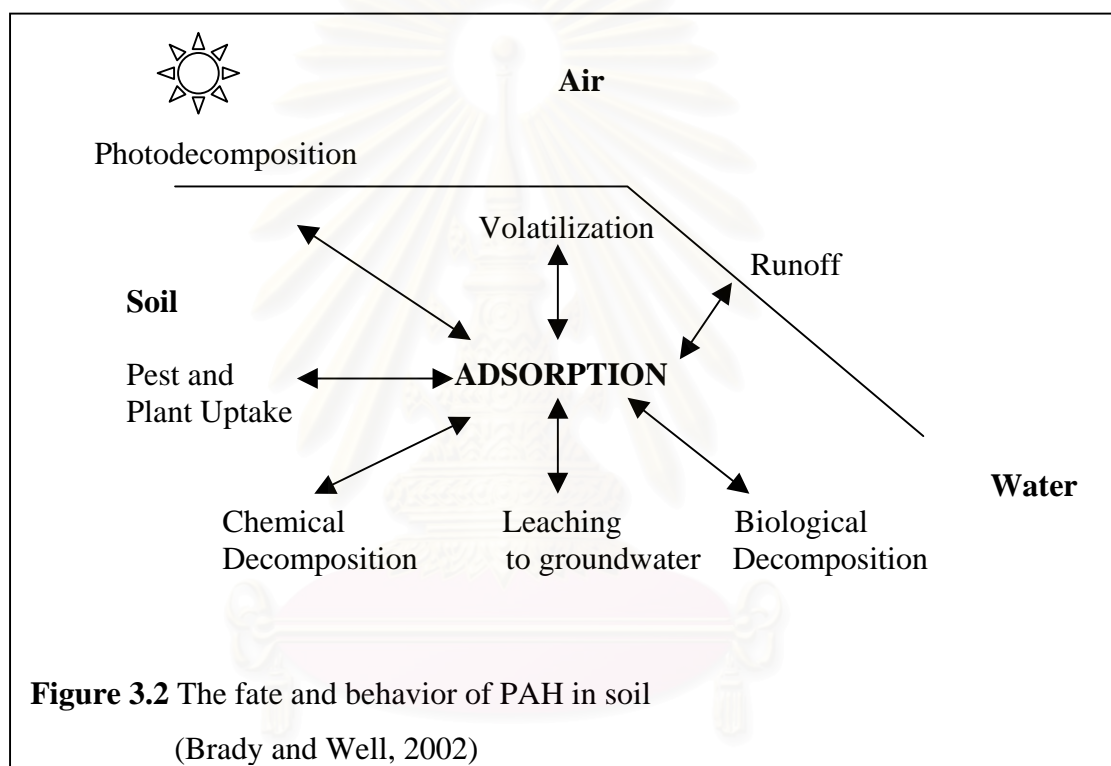
The main sources of PAH in soil are atmospheric deposition after emission, long-range transport and pollution from combustion gases emitted by industries, power plants, domestic heating, and automotive exhausts and from natural combustion like forest fires (Wania and Mackay, 1996). For example, the study of Cousins and Jones (1998) found that atmospheric deposition essentially supplies the vast majority of PAH and PCDD/F entering soils. Moreover, the PAH concentration in soil correlate significantly with the corresponding level in air (Vogt *et al.*, 1987), house dust (Chuang *et al.*, 1995), urban street dust (Takada, Onda, and Orgura, 1990). Trapido (1999) studied the distribution and accumulation of PAH in Estonian soil. He found that PAH concentration were significant higher in the central part of the city probably, due to intense traffic than in other part of the city.

Another sources of PAH in soil is deposition from sewage (sewage sludge and irrigation water) and particulate waste products (IPCS, 1998).

The extent of soil pollution by PAH also depends on factors such as use of the soils and its content of humic substances. Humus is a mixture of residues left after partial decay of organic substances in and on top of soils. Several researchers (Karickhoff *et al.*, 1979; Mean *et al.*, 1980; and Abdul *et al.*, 1987) showed that there is a correlation between the organic content of a soil and the hydrophobic organic compounds concentration in the soil.

Once they reached the soil, further dissipation of PAH from contaminated soil are via vaporization into the atmosphere (Brady and Well, 2002). For example, Cousins and Jones (1998) examined the air-soil exchange of semi-volatile organic compounds in the U.K. The study provided evidence that the soil may be a source of some lighter weight PAH in the atmosphere, and a long-term sink for the heavier weight PAH and PCDD. The compounds may move downward into the groundwater and be lost from the soil by leaching. They may be washed into streams and rivers via surface runoff, and taken up by plants or animals. Yang *et al.* (1991) observed that only the four lowest molecular weight compounds, PHE, ANT, FLA, and PYR were detected in grass. They indicated that PAH with lower molecular

weight are more readily taken up by vegetation than those with higher molecular weight, and finally into the food chain. McLanahan (1995) and Welsch-Pausch and McLanahan (1998) said that the terrestrial agricultural food chain supplies the majority of human exposure to PCDD/F via the pathway air-deposition-crop/pasture/soil-grazing animals-meat/dairy-human diet. Since PCDD/F and PAH have somewhat similar physicochemical properties, such accumulation through food chain of PAH would be expected. The fate and transport of PAH in soil (Brady and Well, 2002) is shown in Figure 3.2.



3.1.5 Partitioning behavior

Once, pollutants discharged into the environment, they can be distributed through environmental compartments (e.g., air, soil, water) as the results of various transport processes (Mackay *et al.*, 2000). The transport of pollutants from one compartment to another can be quantified by appropriate partition coefficients. Since, the partition coefficients, K_{ij} , is defined as the ratio of the equilibrium concentration of a pollutant in one environmental compartment with respect to another environmental compartment, therefore (Equilibrium partitioning of pollutants in the environment, 2002).

$$K_{ij} = C_i / C_j \quad (3.1)$$

Where C_i is the concentrations in compartment i and C_j is the concentration in compartment j .

In the soil system, the distribution of a hydrophobic organic compound between water and soil can be described similarly that it involved the amount of chemical sorbed to soil to the amount in the water at equilibrium. Equilibrium adsorption data are presented in the form of an adsorption isotherm, a diagram that depicts the distribution of the test chemical between a solid sorbent and the solution at equilibrium over a 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).

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).

$$K_d = C_s / C_w \quad (3.2)$$

Where C_s and C_w are the concentrations of the organic chemical sorbed by the solid phase (mg/kg) and dissolved in aqueous phase (mg/L), respectively. Units of K_d typically are given as L/kg, mL/g, or cm^3/g .

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

$$C_s = K_f C_w^N \quad (3.3)$$

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

For a given organic chemical, sorption coefficients (K_d or K_f) vary considerably from soil to soil or sediment to sediment, depending on the properties of the sorbent (Karickhoff *et al.*, 1979). However, for many organic chemicals, and in particular neutral hydrophobic organic, sorption is directly proportional to the quantity of organic matter associated with the solid (Chiou *et al.*, 1979; Mean *et al.*, 1980; Karickhoff *et al.*, 1979). Thus, an Equation (3.3) shows, normalizing soil or sediment specific sorption coefficients to the organic carbon content of the sorbent yields a new coefficient, K_{oc} , that is considered a unique property or “constant of the organic chemical being sorbed:

$$K_{OC} = \frac{K_{d,f} \times 100}{OC\%} \quad (3.3)$$

Where K_{OC} is the soil organic carbon-water partition coefficient, K_d and K_f are the linear and Freundlich sorption coefficients specific to particular sorbent and chemical combination, and OC% is the organic carbon content of that sorbent expressed in percent (Gawlik *et al.*, 1997).

Since determination of K_{oc} is difficult and time consuming, Quantitative Structure-Activity Relationships (QSAR) have developed. QSAR is well known scientists/engineers because they can help understand and predict the impact of organic chemicals due to very little environmental data. The method is primarily based on the structure or property of the substances using the statistical correlation techniques. They have been developed on the basis of experimental data on model substances (Office for Official Publications of the European Committees, 1996). The general goal of QSAR is to quantitatively relate a property or activity of a given set of chemicals to characteristics (structure or property), sometimes called descriptors, of these chemicals (Sawyer, McCarty, and Parkin, 1994).

A variety of physicochemical properties have been used to correlate with the hydrophobicity of the chemical's activity. The basic property often used is the octanol/water partition coefficient (K_{ow}) and aqueous solubility (S) (i.e., Karickhoff *et al.*, 1979; Mean *et al.*, 1980; Abdul *et al.*, 1987; Sabljic *et al.*, 1995). These regression models are usually expressed by relating $\log K_{oc}$ to $\log K_{ow}$ or $\log S$.

These two physicochemical properties are highly interrelated and, consequently, these two groups of QSAR models can be considered as identical or parallel models (Sabljić *et al.*, 1995). Many studies on the relationship between the $\log K_{oc}$ of PAH and related compounds and physicochemical properties are summarized below.

Karickhoff *et al.* (1979) studied the sorption of aromatic hydrocarbons and chlorinated hydrocarbons (pyrene, methoxychlor, tetracene, anthracene, 9-methylanthracene, phenanthrene, naphthalene, 2-methylnaphthalene, benzene, and 2,4,6,2', 4',6'-hexachlorobiphenyl) on pond and river sediments. Special emphasis was placed on the sorption role of sediment particle size and organic matter content and upon the correlation of sorption with sorbate aqueous solubility (S) and octanol/water partition coefficients (K_{ow}). They have found that the sorption isotherms were linear over a broad range of aqueous phase pollutant concentrations. The K_{oc} correlation with octanol/water partition coefficient was more excellent than water solubility. The differences in sorption within the silt and clay fractions were largely related to differences in organic carbon content.

Mean *et al.* (1980) investigated the sorption behavior of four PAH compounds (Pyrene, 7,12-dimethylbenz (a) anthracene, 3-methylcholanthrene, and 1,2:5,6-dibenzanthracene) on a group of 14 sediments and soils. The soil characteristics were including the pH ranged from 4.54 to 8.34. Cation exchange capacity (CEC) ranged from 3.72 to 33.01 mequiv/100 g, and percent organic carbon ranged from 0.01 to 2.38%. The clay content of the sample ranged from 6.8% to 69.1%. They found that a highly significant negative correlation was observed between $\log K_{oc}$ and $\log S$.

Chiou *et al.* (1983) examined the sorption of 12 aromatic compounds (benzene derivatives and PCB) from both single-solute and binary-solute aqueous solutions on a woodburn soil (1.9% organic matter, 68% silt, 21% clay, and 9% sand, and CEC of 14 mequiv/100 g). They also found a good linear relation of $\log K_{om}$ vs. $\log S$, and $\log K_{om}$ vs. $\log K_{ow}$.

Schellenberg, Leuenberger, and Schwarzenbach (1984) established quantitative relationships for the describing the overall sorption of chlorinated phenols by sediments and aquifer materials. The tested compounds were 2,3-DCP, 2,4-DCP, 2,4,6-TCP, 2,4,5-TCP, 3,4,5-TCP, 2,3,4,6-TeCP, 2,3,4,5-TeCP, and PCP.

Abdul *et al.* (1987) examined the partition coefficient for nonpolar organic contaminants (pyrene, benzene, toluene, m-xylene, o-xylene, p-xylene, trichloroethylene, and tetrachloroethylene) between aquifer organic carbon and water. The results were shown that the adsorption coefficient could be estimated from the measurement of the aquifer organic carbon (f_{oc}) and from the known octanol-water partition coefficient (K_{ow}) or aqueous solubility (S) of the contaminants.

Gerstl (1990) summarized work conducted on methods for estimating the K_{oc} of non-ionic organic compounds by soils and sediments. He collected and analyzed sorption data for > 400 compounds and divided into 13 groups of chemical including acetanalides, acids, amides, halogenated and non-halogenated aromatic hydrocarbon, carbamates, dinitroanilines, halogenated non-aromatic hydrocarbons, organophosphorous pesticides, PAH, triazines, triazoles, and ureas. It was found that the relationship ($\log K_{oc}$ vs either $\log S$ or $\log K_{ow}$) for individual chemical groups were preferred over the general equation for all chemicals. The use of MCI alone was inadequate for predicting sorption values with the exception of a few homologous groups.

Sabljić *et al.* (1995) evaluated the quality and reliability of the quantitative relationships between the soil sorption coefficients and the octanol-water partition coefficients ($\log K_{oc}$ vs. $\log K_{ow}$). They studied on predominantly hydrophobic chemicals 81 compounds including PAH.

Baker *et al.* (1997) evaluated the estimation methods for $\log K_{oc}$ using three types of descriptor. They compared the three types of descriptors including octanol-water partition coefficients (K_{ow}), molecular connectivity (mX_t), and linear solvation energy relationships (LSERs). The best results were obtained by estimating $\log K_{oc}$ from $\log K_{ow}$.

Another approach for estimating K_{oc} , especially when experimental values of K_{ow} and S are unavailable, is to employ correlation between MCI and $\log K_{oc}$ (Sabljic, 1987; Gerstl, 1990; Meylan, Howard, and Boethling, 1992; Baker *et al.*, 1997; Sabljic, 2001). Molecular connectivity is a method of bond counting from which topological indices can be derived from chemical structures. One significant advantage of using MCI- K_{oc} regression models is that, once the model has been developed, only the structure of the chemical of interest is required as input, and no additional experimental parameters are needed (Boethling and Mackay, 2000). However, Gerstle (1990) said that the use of MCI alone were inadequate for predicting sorption values with the exception of a few homologous groups.

In addition to MCL, several other structurally derived parameters have been correlated with $\log K_{oc}$, such as parachor (Briggs, 1981), linear solvation energy relationships (LSERs) (Baker *et al.*, 1997) and molecular weight (Kanazawa, 1989). Experimental retention times or capacity factors generated by high performance liquid chromatography (Chin, Peven, and Weber, 1988) also have been correlated with $\log K_{oc}$. These correlation are especially valuable when experimental K_{ow} and S values are unavailable (Boethling and Mackay, 2000).

3.2 Characteristics of soil

3.2.1 Physicochemical properties

The physical properties of a soil include soil texture, soil structure, soil density, soil strength, and soil color, which are dominant factors that affect the use of a soil. These properties are concerned with the size and content of the particle that make up the soil, how the particles are arranged into larger units or aggregates, and how the units and individual particles affect other soil properties (Hassett and Banwart, 1992; Miller and Gardiner, 2001).

Soil texture is the 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); 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.

Soil structure is the arrangement of soil particles into aggregates. Soil structural units (peds) are described by three characteristics: type (shape), class (size), and grade (strength of cohesion). Soil structure influence many important properties of the soil, such as the rate of infiltration of water and air.

Bulk density, the weight of a volume of soil, is related to pore space in the soil.

Soil color indicates many soil features which provide valuable clues to the nature of others soil properties and conditions. The major factors have the greatest influence on the color of soil: (1) its organic matter content, (2) its water contents, and (3) the presence and oxidation states of iron and manganese oxides.

Soil strength refers to a soil's response to mechanical, forces. For example, a soil specimen may be soft or hard when dry. Soil may be friable, firm, or rigid when wet. These characteristics can be described as resistance to rupture.

The chemical properties of soil include soil reaction (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, are colloidal, and most clays are crystalline. The various kinds of clays posses different properties, for example, montmorillonite and vermiculte 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 held 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 the 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).

3.2.2 Composition of soil

Soil consists of three major classes of components: solids, liquids, and gases. The solids component is composed of inorganic minerals and organic matter. The liquid component is composed of water, dissolved ions, molecules, and gases and is collectively known as the soil solution. The soil's gaseous component, that is, the soil atmosphere, is composed of gases similar to those in the atmosphere above the soil, but often in very different proportions.

An ideal soil would contain about 50% pore and 50% solid space. The solid space would be subdivided into 45% inorganic minerals and 5% organic matter, while the pore space would be equally divided between larger pores that drain free of water and contain the soil atmosphere and smaller pores that retain water against the pull of gravity (Hassett and Banwart, 1992).

CHAPTER 4

EXPERIMENTAL PROCEDURES

The characteristics of the soil samples were determined. The method evaluations were carried out to cover calibration curve, percent recovery and detection limit. Then, the partitioning experiments were done mixing the soil samples, PAH standard, and deionized water until equilibrium time reached. Soil and water phases were separated and then, the soil was extracted using microwave-assisted extraction and the water was extracted using liquid-liquid extraction. Before the PAH compounds are quantified by GC/FID, the extracted solution was isolated by passing through the silica gel packed column. The concentration of test compounds in the soil and water was quantified and the soil-water partition coefficient (K_d) was calculated by the ratio of PAH concentration in soil to the concentration in water. K_d can be normalized by organic carbon content in the soils to the soil organic carbon-water partition coefficient (K_{oc}). The relationships were determined by plotting physicochemical properties of the compound against the log K_{oc} values obtained in the study (Figure 4.1).

4.1 Apparatus

1. Hydrometer
2. pH meter
3. Analytical Balance
4. Blending Machine
5. Thermometer
6. Mortar
7. Orbital Mixer Incubator (OM15 Ratek)
8. Oven (Carbolite AAF 1100)
9. Sorvall Biofuge Stratos (Heraceus)
10. Rotary Vacuum Evaporator (EYELA NE-1)
11. Microwave Extraction System (Milestone ETHOS SEL)
12. Gas Chromatography with FID detector
(Agilent Technologies 6890N)

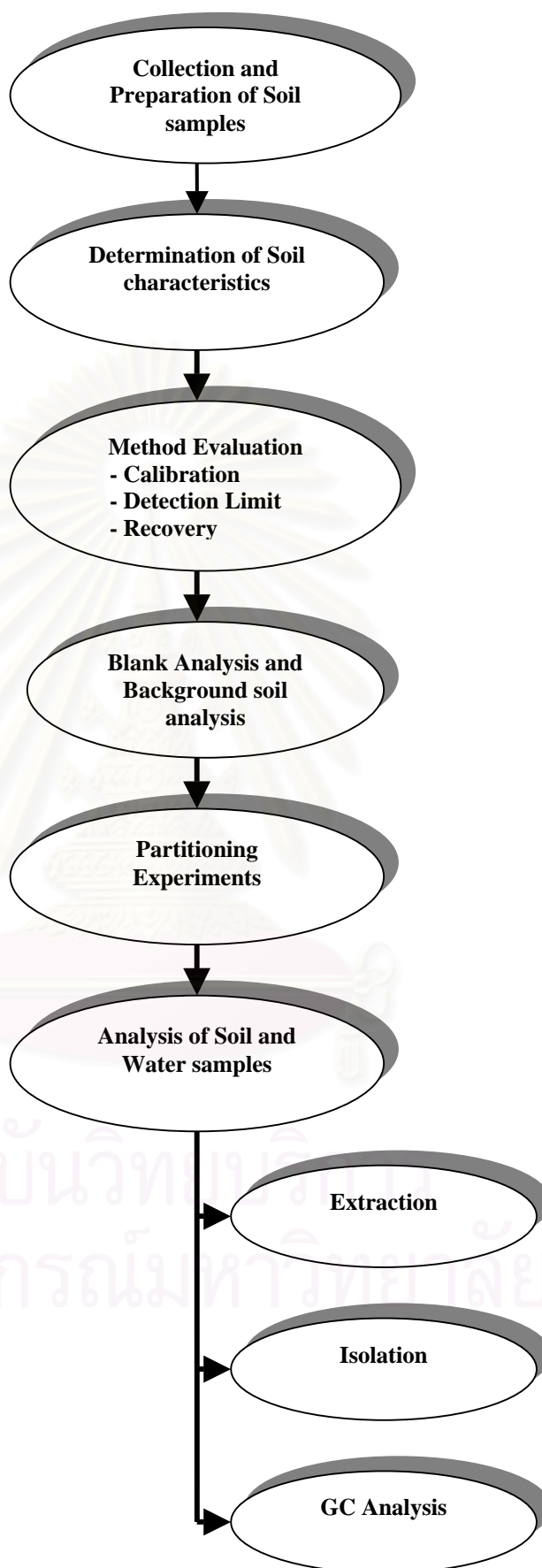


Figure 4.1 Scheme of the overall experimental procedure

4.2 Materials

1. Test compounds: Naphthalene, Acenaphthene, Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene, Benzo (a) anthracene, and Benzo (a) pyrene. PAH Standards with 99% purity were purchased from SUPELCO.

2. Internal standard: Methylphenanthrene purity of 99.5 % from SIGMA.

3. Solvents and chemicals: Hexane, Acetone, Dichloromethane (DCM), Sodiumsulphate (Na_2SO_4), Calciumchloride (CaCl_2), Sodium metaphosphate (NaPO_3)_x. Na_2O), Ammonium acetate (NH_4OAC), Ammonium chloride (NH_4Cl), Sodium hydroxide (NaOH), Sodium chloride (NaCl), Sulphuric acid (H_2SO_4), Boric acid (Boric acid), Bromocresol green-methyl red indicator, Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), Ferrous sulphate (FeSO_4), O-phenantroline indicator, and Silica Gel 60 (0.063-0.200 mm).

4. Glassware: Beaker, glass bottle, separating funnel, weighing funnel, volumetric flasks, erlenmeyer flasks, suction flasks, glass column, buret, pipet, syringe, leaching tube, cylinder, kjeldahl flask.

5. Glass wool, glass microfibre filter (GF/C)

6. Deionized water.

All glassware used in this study was specially cleaned to minimize contamination. Glassware was washed with water and was soaked overnight with Extran MA 03 Phosphatefree. Then, glassware was washed with water and rinsed with deionized water. Glassware was dried in an oven and rinsed with hexane before use.

4.3 Method

4.3.1 Determination of soil characteristics

The soil sample were analyzed for a number of physicochemical properties including pH, moisture content, cation exchange capacity, organic carbon content, and soil texture (Black *et al.*, 1969 and Tan, 1996). The methods of determination of soil characteristics were presented in Table 4.1 and the details of the method were presented in Appendix A.

Table 4.1 The methods of determination of soil characteristics

Parameters	Methods
PH	Soil:water 1:1
Moisture content	Gravimetric method
Cation exchange capacity	Ammonium saturation method
Organic carbon content	Wet oxidation method
Soil texture	Hydrometer

4.3.2 Extraction

(1) PAH extraction from soils (microwave-assisted extraction method)

The soil was transferred into an extraction vessel. The soil was extracted with 30 ml 1:1 of acetone: hexane solution. The vessel containing the soil and the solvent was sealed and heated in microwave extraction system. The temperature program was as follows: an initial temperature of 20 °C ramped to 120 °C in 10 minutes and held at this temperature for 20 minutes. The mixture was allowed to cool. Then, the vessel was opened and the contents were filtered passing through a GF/C. The resulting solution were combined and proceeded for isolation step (US. EPA, 2000).

(2) PAH extraction from water (liquid-liquid extraction method)

The water was transferred into a 2 L separating funnel. The water was extracted with 20 ml of hexane and shook vigorously for 10 minutes. Allowed the solution separated, drain the part of hexane that floats on the water passing through glass funnel with Na₂SO₄. The resulting solution was combined and proceeded for concentration.

4.3.3 Isolation

The glass column used was 40 cm high with a diameter of 2 cm. The absorbent used was silica gel which was activated in an oven at 500 °C for 4 hours before use, then allowed to cool to room temperature in a desiccator. The drying agent was sodium sulfate, which was treated in an oven at 450 °C for 6 hours before use. The eluent used to elute the PAH was 20% DCM in hexane. The glass column was plugged with glass wool at the bottom and packed with 1-2 cm thick of sodium sulfate. Slurry of 15 g activated silica gel in hexane and was poured into the column. Drain the hexane until just above the silica gel layer. Then, the column was washed with 20 ml of 20% DCM in hexane. The extracted sample was then transferred to the top of the column. The solution was eluted with 50 ml of 20% DCM in hexane, the cleaned up solution was collected and concentrated using a rotary evaporator (Jaouen-Madoulet et al., 2000).

4.3.4 Gas chromatographic analysis

PAH was quantified using a Hewlet Packard 6890 series GC-FID, which was coupled to an autosampler and fitted with HP-5 capillary column (30 m x 320 µm id) 5% Phenyl Methyl Siloxane with a film thickness of 0.25 µm. The temperature program was as follows: an initial column temperature of 80 °C ramped to 160 °C at a rate of 25 °C/min. The temperature was held at 160 °C for 3 min, then, ramped to 300 °C at 3 °C/min, and held at this final temperature for 2 min. Each sample was run for a period of 60 minutes. Injection was made in the splitless mode

4.3.5 Confirmation of PAH identity

PAH compounds can be detected in FID detector within the specific range of retention time for particular compound. It was noticed that other contaminants are also found in the time ranges. To overcome this interference for identifying the compounds, injection of the standard solutions was done prior to injection of the sample. Figure 4.2 showed a typical chromatogram of standard PAH.

The x-axis shows the retention times of different PAH compounds (Table 4.2). The peak area of the PAH detected in the eluted sample is shown on y-axis. Based on the retention time identified through standard solutions injection, the concentration of each of the PAH compounds is matched with the peak area identified in the chromatographs.

Table 4.2 Mean retention times of test compounds and internal standard

Compounds	Mean Retention time (minute)
NAP	5.0 (SD = 0.05)
ACE	8.3 (SD = 0.06)
FLU	10.0 (SD = 0.04)
ANT	14.2 (SD = 0.08)
PHE	14.3 (SD = 0.08)
MPHE	17.7 (SD = 0.05)
FLA	21.3 (SD = 0.05)
PYR	22.6 (SD = 0.05)
BaA	31.3 (SD = 0.05)
BaP	40.7 (SD = 0.05)

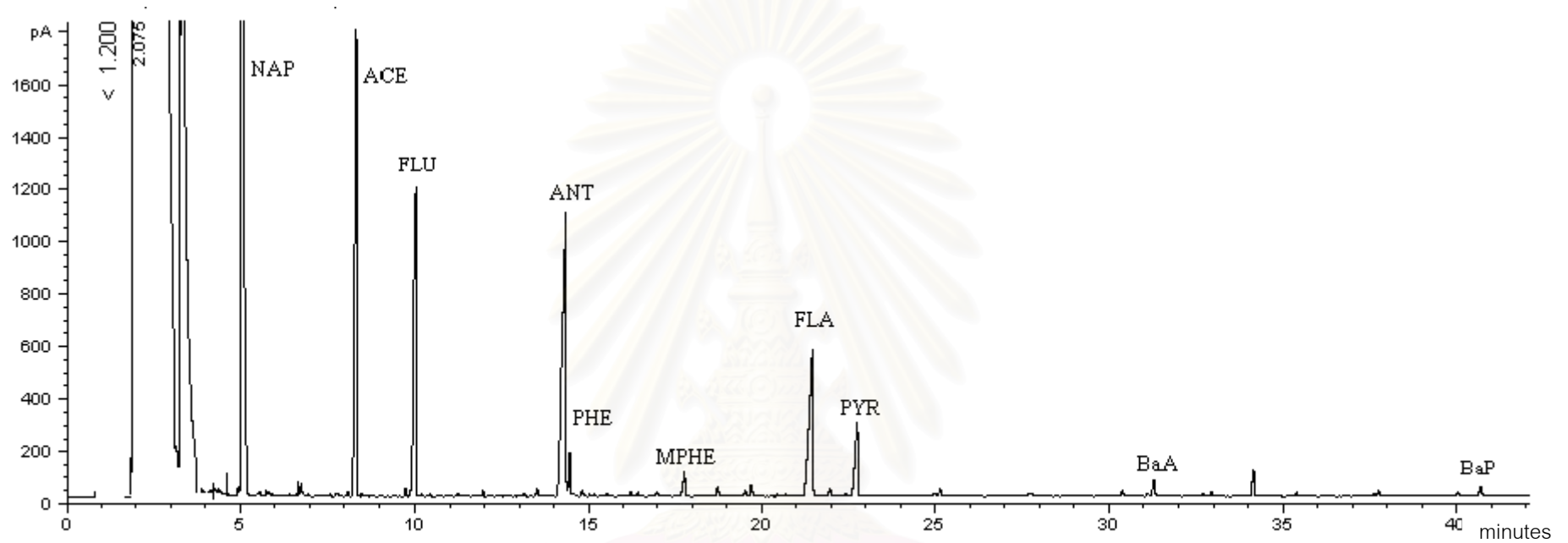


Figure 4.2 A typical chromatogram of PAH standard

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4.4 Method evaluation

4.4.1 Contaminated and blank procedure

All soil samples and water were checked for any contamination prior to use. Blank analyses were determined in the same manner as the sample determination, but without the PAH standard. Three blank analyses were carried out in each soil and water analyses.

Three grams of soil and two liters of water were used for blank analysis. MPHE (internal standard) was added for quantification of test compounds. Then the soil was extracted using microwave-assisted extraction and the water was extracted using liquid-liquid extraction method. The combined extract was proceeded for isolation, concentration, and injection steps.

The results were found that there was no tested compound in the soil samples.

4.4.2 Calibration

(1) Stock standard solutions

Five PAH standards (NAP, ACE, FLU, FLA, and PHE) were dissolved in hexane and in acetone at a concentration of 250(0.25S) (S = aqueous solubility of compound) and a concentration of other four PAH standards (ANT, PYR, BaA, and BaP) 2500(0.25S). Then, the stock standard solutions were diluted to obtain in 0.25S, 0.18S, 0.12S, and 0.05S in 500 ml volumetric flask. The stock solutions were stored in the dark at 4 °C.

(2) Calibration curve

A calibration curve was developed for both the soil and the water by spiking PAH in mixture on the soil and the water separately. This was carried out with four concentration of PAH (0.25S, 0.18S, 0.12S, and 0.05S) and was repeated three

times each. A fixed concentration of MPHE was added to each spiking concentration. The spiked soil and spiked water were analyzed by the same procedures the samples. Good linear regression equations between the compound concentrations and peak area ratio (peak area of the test compound/peak area of internal standard) were obtained. The standard curves for 9 PAH compounds in the soil and the water were presented in Appendix B. Concentrations of the test compounds in the sample were obtained using calibration curve which were constructed based on the peak area ratio. The slope, y-intercept and r^2 of above regression equation were presented in Table 4.3.

Table 4.3 The regression equations and regression coefficients of the calibration curves

Compounds	Soil		Water	
	Equation	r^2	Equation	r^2
NAP	$y = 0.21x - 60.33$	0.90	$y = 69.66x - 31.47$	0.99
ACE	$y = 0.26x - 5.15$	0.94	$y = 75.95x + 6.58$	0.99
FLU	$y = 0.29x - 3.07$	0.97	$y = 77.58x + 3.29$	0.99
ANT	$y = 4.97x + 0.33$	0.98	$y = 1303.5x + 1.26$	0.98
PHE	$y = 0.014x + 0.05$	0.99	$y = 3.05x + 0.24$	0.96
FLA	$y = 0.31x - 0.08$	0.99	$y = 88.18x - 0.02$	0.95
PYR	$y = 0.28x + 0.08$	0.99	$y = 74.59x + 0.25$	0.90
BaA	$y = 0.38x + 0.01$	0.92	$y = 86.10x + 0.06$	0.94
BaP	$y = 0.58x + 0.01$	0.93	$y = 225.08x - 0.06$	0.97

4.4.3 Recovery

Recoveries of the compounds were determined and repeated three times to determine the extraction procedure efficiencies.

Percent recovery was determined according to the following

$$\% \text{ Recovery} = \frac{\text{Amount recovered}}{\text{Original amount spiked}} \times 100$$

Generally, reasonable recoveries were obtained for the 9 PAH as shown on Table 4.4.

Table 4.4 Mean percentage recovery of test compounds

Compounds	% recovery in soil	% recovery in water
NAP	86	75
ACE	87	83
FLU	96	86
ANT	89	82
PHE	80	85
FLA	94	84
PYR	92	82
BaA	97	92
BaP	90	86

4.4.4 Detection limits

The detection limits were determined from the standard deviation of the compounds above blank, where detection limit = 3SD of response/blank factors. The results obtained reflected the min amount of the compounds that can be detected by the method. The SD was determined from triplicate analyses of each compound concentration and then plotted against the corresponding concentration for each PAH (Table 4.5).

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Table 4.5 Detection limits of the experimental procedure

Compounds	Detection limit	
	Water ($\mu\text{g/L}$)	Soil (mg/kg)
NAP	904	11.72
ACE	35	2.28
FLU	9	2.71
ANT	0.3	0.21
PHE	244	4.95
FLA	0.7	0.11
PYR	0.1	0.30
BaA	0.2	0.02
BaP	1.0	0.03

4.5 Soil sampling and preparation

The soil samples used in this study were collected from soil surface (0-5 cm.) in the rural area of Thungkok, Songphenong, Suphanburi province (northern of Bangkok). The location of sample no.1, no.3, and no.4 are located on the agricultural land (sugar cane plant) and the sample no.2 is located on the residential area.

The samples were air-dried at temperature not exceeded 35°C to avoid the change in its characteristics and any possible reaction (Tan, 1996).

The samples were then ground by mortar and sieved through a 1 mm sieve in order to reduce heterogeneity and to provide maximum surface area for physical and chemical reaction (US.EPA, 2000).

The soils used for the partitioning experiments were prewashed to remove nonsettling micro and macroparticles. This washing was done by suspending the soils in deionized water in a glass bottle, shaking for 48 hours, centrifuging at

15,000 rpm for 10 minutes, and discarding the supernatant. After several (approximately five) washes, the samples were ready for the partitioning experiments (Gschwend and Wu, 1985).

4.6 Partitioning experiments

Prior to the partitioning experiments, the steady state attainments are determined under the same condition of partitioning experiment. Two bottles were removed at the end of the shaking time at 6, 12, 24, 36 and 48 hour and then, amount of PAH in the soil were analyzed. The plot of the PAH concentration in soil against the shaking time indicated the steady state was reached at 24 hrs (Appendix C).

Partitioning experiments were determined for four concentrations of each compound on each soil sample. The experiments were repeated two times using three g soil in two liters of standard solution at the concentration of 0.25S, 0.18S, 0.12S, and 0.05S in 0.01 M CaCl₂. The batch cells were sealed and brought to the steady state by shaking for 24 hours. When steady state was reached, the soil and water phase were separated by centrifuging at 15,000 rpm for 10 minutes. The soil and the water samples were analyzed according to the method in section 4.3.2 to 4.3.4.

4.7 Data analysis

Statistical analysis in this study was processed in Microsoft Excel 2000. The software provided a wide range of statistical analyses including mean, standard deviation, linear regression, polynomial regression, equations and correlation coefficient, that were mostly used in this study.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characteristics of soil

Some physicochemical properties of the four soil samples were determined in according to the method described in section 4.3.1. The results are shown in Table 5.1. Percent moisture content of soil samples ranged from 0.48 to 1.95. pH (1:1 water:substrate) of the soils were slightly acid to neutral (ranged from 6.3 to 7.2) (Sparks, 1995). Cation exchange capacity (CEC) which is a general term used for describing the soil fertility, ranged from 7.3 to 14.0 $\text{cmol}_c\text{kg}^{-1}$. A soil may have a CEC of 15 $\text{cmol}_c\text{kg}^{-1}$, indicating that 1 kg of the soil can hold 15 cmol_c of H^+ ions and can exchange this number of charges from H^+ ions for the same number of charges. Soil sample no.1 and no.3 with organic carbon content of 8.9 and 7.3 $\text{cmol}_c\text{kg}^{-1}$, respectively, had low CEC while other samples had the medium CEC. Soil under study had percent organic carbon content ranged from 0.40% to 2.05%. The results presented the %OC that lower than 1.5 (sample no.1 and no.2) are explained that the soil fertility are low, and those more than 1.5% (sample no.3 and no.4) can be explained that the soil fertility is medium (Land Development Department, 1998). The percent of organic carbon content is the most important factor that described the soil sorption of hydrophobic organic compounds. Moreover, the soil texture was determined by separating the particle size of soil. The soil texture is classified according to their particle size. Soil sample no.1 (48% sand, 30% silt, and 22% clay) is loam sand that can be defined as a mixture of sand, silt, and clay particles that exhibit the properties of those separates in about in equal proportions. Soil sample no.2 is clay (28% sand, 32% silt, and 40% clay) that can be defined as the soil which the particles smaller than 0.002 mm and have a very large specific surface area, giving them a capacity to adsorb water and other substances. Soil sample no.3 (70% sand, 18% silt, and 12% clay) and no.4 (60% sand, 20% silt, and 20% clay) are sandy loam that is the loam soil in which sand is dominant.

However, this study is mainly focusing on the percent organic carbon content due to the sorption of hydrophobic compounds are strongly dependent on the organic carbon content in the soil. The other soil properties are no significant.

Table 5.1 Characteristics of soil samples

Sample	Moisture content (%)	pH	CEC (cmol _c kg ⁻¹)	OC (%)	Sand (%)	Silt (%)	Clay (%)	Soil Texture
1	1.95	7.2	8.9	0.40	48	30	22	Loam
2	1.33	6.3	14.0	1.03	28	32	40	Clay
3	0.48	7.2	7.3	1.57	70	18	12	Sandy loam
4	1.27	6.6	11.2	2.05	60	20	20	Sandy loam

5.2 Evaluation of the soil organic carbon-water partitioning behavior

5.2.1 Soil organic carbon-water partition coefficients

The soil-water partition coefficients (K_d) were calculated in according to section 3.1.5 covering four organic carbon contents and four compound concentrations (Appendix D). The K_d values were then normalized by organic carbon content to the soil organic carbon-water partition coefficients (K_{oc}). The K_{oc} values obtained from the experiments on four soils with four concentrations were averaged and calculated to obtain $\log K_{oc}$ as shown in Table 5.2.

NAP has the lowest $\log K_{oc}$ (3.46) while BaP has the highest (5.70). This is seen that the $\log K_{oc}$ values of 9 PAH increase with increasing molecular weight and their $\log K_{ow}$ (shown in Table 3.1). The results are in line with other studies. For example, Chiou *et al.* (1983), examined the sorption of 12 aromatic compounds (benzene derivatives and PCB) of which $\log K_{ow}$ ranging from 2.13 to 5.62, the soil organic matter-water distribution coefficients (K_{om}) values were increased with increasing $\log K_{ow}$ which $\log K_{om}$ range from 1.26 to 4.38. The same results were presented by Mean *et al.*(1980). They investigated the sorption of PAH including PYR, DMBA, MCT, and DBA ($\log K_{ow}$ range from 5.18 to 7.11). The results showed that the average $\log K_{oc}$ values increased

from 4.79 to 6.22. Another similar results was performed by Karickhoff *et al.* (1979), they studied the sorption of aromatic hydrocarbons and chlorinated hydrocarbons (log K_{ow} range from 2.11 to 6.34) on natural sediments.

Table 5.2 The values of log K_{oc} of the test compounds in this study

Compounds	log K_{oc}				Average log K_{oc}
	0.40% OC	1.03% OC	1.57% OC	2.05% OC	
NAP	3.73	3.45	3.32	3.32	3.46
ACE	3.77	3.75	3.58	3.66	3.69
FLU	4.09	3.77	3.59	3.79	3.81
ANT	3.69	3.88	3.74	4.14	3.86
PHE	4.93	4.73	4.56	4.64	4.72
FLA	4.86	4.59	4.69	4.83	4.74
PYR	4.56	4.73	4.59	4.64	4.63
BaA	5.42	5.29	5.28	5.38	5.34
BaP	5.79	5.73	5.66	5.62	5.70

5.2.2 Comparison with other investigations

There have been limited data on PAH sorption in soil. Therefore, only few PAH in the literature can be compared. Similar study was carried out by Mean *et al.* (1980). They studied the sorption of PYR, DMBA, MCT, and DBA (log K_{ow} ranged from 5.18 to 7.11) over 11 sediments and 3 soils that were collected from sites along the Missouri, Ohio, Wabash, and Mississippi Rivers. The sediment and soil samples studied by Mean *et al.* (1980) have the characteristics as following; pH ranged from 4.54 to 8.34, CEC ranged from 3.72 to 33.01 mequiv/100 g, and percentage of nitrogen and percentage of organic carbon ranged from 0.010 to 0.195 and from 0.11 to 2.38, respectively. The clay, sand, and silt content of the sample ranged from 6.8% to 69.1%, 0 to 82.4%, and 10.7 to 55.4%, respectively. Only PYR in the study of Mean *et al.* (1980) can be compared to this study of which log K_{oc} value of PYR was 4.66. The result of log K_{oc} (4.63) in this study agrees with the result of Mean *et al.* (1980).

The similar result obtained from Abdul *et al.* (1987) was shown by the log K_{oc} of PYR which was 4.66 while the result in this study was 4.63 (Table 5.3). They examined the partition coefficient of eight nonpolar organic contaminants (pyrene, benzene, toluene, m-xylene, o-xylene, p-xylene, trichloroethylene, and tetrachloroethylene) on three sandy aquifer materials in batch equilibrium experiments. Their samples were collected from Borden, Canada; Flint, Michigan; and Warren, Michigan and the aquifer sample have a fraction of organic carbon range from 0.0002 to 0.0225 which were in the same range of this study.

Meylan *et al.* (1992) investigated nonpolar organic compounds including PCB, phenol, aldrin, PAH (BaP, BaA, FLU, FLA, derivatives of NAP, CHRY and ANT) etc. They calculated log K_{oc} values from MCI. Log K_{oc} values obtained in this study are in line of their study. For instance, log K_{oc} value of BaA in this study (5.34) close to their study (5.36) and log K_{oc} of BaP (5.70) close to their study (5.90).

Karickhoff *et al.* (1979) studied on the natural sediments that collected from Doe Run, Hickory Hill, Oconee River. Log K_{oc} values of NAP, ANT, and PHE (3.46, 3.86, and 4.72, respectively) obtained in this study were slightly difference to their study (3.11, 4.41, and 4.36, respectively). The differences may be due to particle size specific of the compounds. As previously described sand, silt, and clay have difference size, i.e. 0.05-2.0 mm, 0.002-0.05 mm, <0.002 mm, respectively. According to study of Krauss and Wilcke (2002), they found that the log K_{oc} values of PAH and PCB were different among particle size fractions. For PAH, they were highest in silt fraction where PAH accumulate preferentially while PCB were highest in clay fraction. The K_{oc} values of PAH and PCB varied by the studied soils and particle size fractions illustrating that they are not a compound specific constant but depend on properties of the soils and particle size fractions. On the contrary, the experimental soils in this study composed of sand, silt, and clay in varying proportion. Therefore, the deviation of the result from their study can be expected.

For the study of Pavlou (1987) that cited in Mackay *et al.* (2000), the log K_{oc} (3.67) is close to 3.69 that obtained in this study. However, conclusion can not be made when compared to Pavlou (1987) due to the detail of the experiment in their work is not known.

However, the comparison of $\log K_{oc}$ values can be difficult. Part of the difficulty may be due to variation in the physicochemical properties, for example, $\log K_{ow}$ of NAP can range from 3.01 to 4.70, of ACE range from 3.32 to 4.49 and of PHE range from 3.60 to 4.67 (Mackay *et al.*, 2000).

Table 5.3 Comparison of $\log K_{oc}$ values obtained in this study to those in the literatures

Compounds	$\log K_{oc}$ (this study)	$\log K_{oc}$ (literatures)
NAP	3.46	2.74 ^(a) , 3.11 ^(b)
ACE	3.69	3.67 ^(c)
FLU	3.81	3.70 ^(a) , 4.05 ^(d)
ANT	3.86	4.27 ^(a) , 4.41 ^(b)
PHE	4.72	3.72 ^(a) , 4.36 ^(b)
FLA	4.74	4.62 ^(a) , 4.85 ^(d)
PYR	4.63	4.66 ^(e) , 4.66 ^(f)
BaA	5.34	5.36 ^(d)
BaP	5.70	5.90 ^(d)

(a) Abdul and Gibson (1986), aquifer materials (b) Karickhoff *et al.*(1979), natural sediments. (c) Pavlou (1987), cited in Mackay *et al.* (2000) (d) Meylan *et al.* (1992) (e) Abdul *et al.* (1987), sandy aquifer materials. (f) Mean *et al.* (1980), sediments and soils.

Although, the results in this study are similar to Pavlou, 1987, cited in Mackay *et al.* (2000), Meylan *et al.* (1992) Abdul *et al.* (1987), Mean *et al.*(1980) and slightly difference to Karickhoff *et al.*(1979) as earlier described, there are also some other unknown detail in those studies which have an influenced on the $\log K_{oc}$ values. These are soil particle size, temperature, dissolved or colloidal organic matter, biodegradation and photodegradation.

Particularly, the influenced of soil particle size has already mentioned. The difference of temperature in the laboratory experiments may be influenced to the $\log K_{oc}$ values. According to the review of ten Hulscher and Cornelissen (1996) found that the sorption coefficient for the most compounds decrease with increasing temperature. However, the increased sorption at higher temperatures can be expected for compounds

for which solubility decreases at higher temperature. This was observed by Chiou *et al* (1979) for 1,1,1-trichloroethane.

In their experimental design, there was no evidence clean soil used in the partitioning experiments, which the present of dissolved or colloidal organic matter in the partitioning experiments has been shown to influence sorption. Hegeman *et al* (1995) found that the dissolved organic matter could effect the value of $\log K_{oc}$ for BaP and PHE. Because of their high specific surface area, and high affinity for hydrophobic organic compounds. The present of dissolved or colloidal organic matter result in a higher apparent solubility of hydrophobic organic compounds in the liquid phase. The resulting of the presence of dissolved organic matter, the sorption partition coefficient would be lower than the true sorption partition coefficient. Gschwend and Wu (1985) also observed that sorption partition coefficients of PCB were decreased when increasing the dissolved organic matter.

In addition, factor including biodegradation and photodegradation could also vary the $\log K_{oc}$ values, particularly during the soil-water partitioning experiments. PAH with up to four aromatic rings are biodegradable under aerobic conditions but the biodegradation rate of PAH with more aromatic rings is very low. The rate of biodegradation in soil depends on several factors including the characteristic of the soil and its microbial population and the properties of the PAH present. Temperature, pH, oxygen content, soil type, nutrients, and the presence of other substances that can act as co-metabolites are also important (IPCS, 1998). According to the study of Nagpal (1993) found that PAH could be degraded through the process of photodegradation. PAH differ in their sensitivity to photooxidation. ANT, PHE, and BaA were the most sensitive PAH, whereas CHRY, FLU, PYR, and BaP were relatively resistant to photodegradation. Therefore, these processes may degrade the test compounds that resulting in the error for determination of PAH concentration in the soil or/and the water.

5.3 Relationships between soil organic carbon-water partition coefficients (K_{oc}) and physicochemical properties

Physicochemical properties under study are octanol-water partition coefficient (K_{ow}), aqueous solubility (S), Vapor pressure (VP), Henry'law Constant (H),

and Molecular weight (MW). Each property (Table 3.1) was plotted against $\log K_{oc}$ obtained from soil-water partitioning experiments (see section 5.2.1). The results and discussion were described as follows.

5.3.1 Octanol-water partition coefficients (K_{ow})

The octanol-water partition coefficient (K_{ow}) is a measure of the hydrophobicity of a chemical (Boethling and Mackay, 2000). As such, $\log K_{ow}$ is a key parameter in the assessment of environmental fate and transport. Since the soil adsorption behavior is similar to the octanol-water partition behavior, K_{ow} for hydrophobic compounds is considered as one of the most important physicochemical characteristics related to sorption on soils and sediments. Therefore, K_{ow} is frequently used to predict how well the sorption in soil is.

In this evaluation, the K_{ow} values of the compounds are plotted against $\log K_{oc}$ obtained in this study (Figure 5.1). The plots indicated a linear relation between $\log K_{oc}$ and $\log K_{ow}$ and linear regression equation obtained (Equation 5.1) has a slope of 0.8 and an intercept of 0.58.

$$\log K_{oc} = 0.8\log K_{ow} + 0.58 \quad (r^2 = 0.90) \quad (5.1)$$

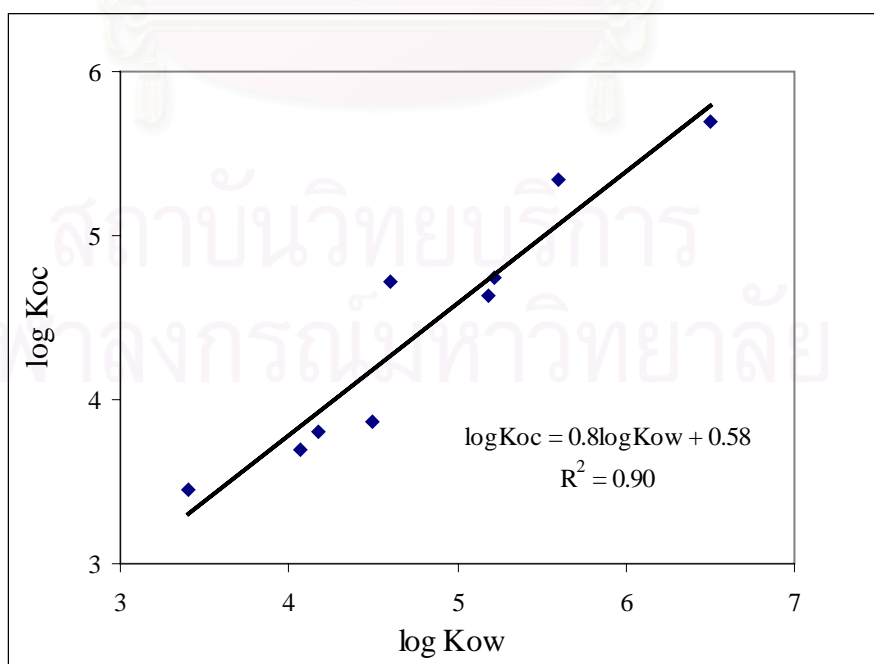


Figure 5.1 The linear relationship between $\log K_{oc}$ obtained in this study and $\log K_{ow}$

If $\log K_{ow}$ is good representative for $\log K_{oc}$, the slope of the relationship between $\log K_{ow}$ and $\log K_{oc}$ should be close to 1 and the intercept should be zero. Since the slope of the plot (0.8) of $\log K_{ow}$ against $\log K_{oc}$ is close to unity (1) and the intercept (0.58) is close to zero, the equation of the relationship between $\log K_{oc}$ and $\log K_{ow}$ obtained in this study is reasonable.

This relationship was compared to other studies of similar compounds (Table 5.4), e.g., Karickhoff *et al.* (1979) and Gerstl (1990) which has a slope and intercept in line with the theory.

5.3.2 Molecular Weight (MW)

The molecular weight of the compounds is of interest properties because it is the property that easy to obtain. Plotting molecular weight against $\log K_{oc}$ is presented in Figure 5.2.

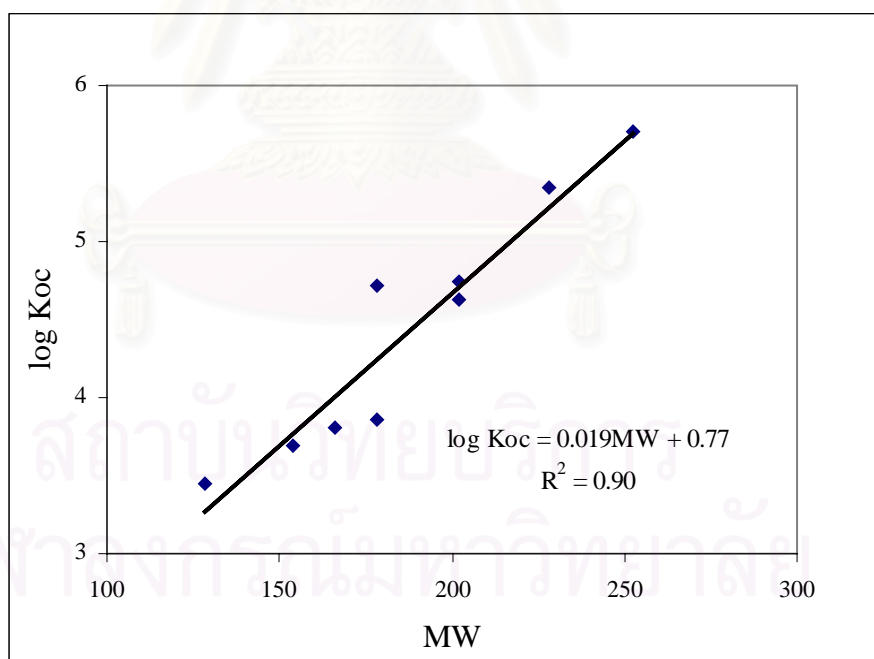


Figure 5.2 The linear relationship between $\log K_{oc}$ obtained in this study and MW

Table 5.4 Models derived from log Kow in the literatures

Equation	r ²	Chemical classes	n	Sorbent	References
$\log K_{oc} = 0.903\log K_{ow} + 0.094$	0.91	Wide variety	72	No specify	Baker <i>et al.</i> , 1997
$\log K_{oc} = 0.81\log K_{ow} + 0.10$	0.887	Hydrophobics	81	No specify	Sabljić <i>et al.</i> , 1995
$\log K_{oc} = 0.762\log K_{ow} + 1.051$	0.898	PAH	20	No specify	Gerstl, 1990
$\log K_{oc} = 0.722\log K_{ow} + 0.417$	0.855	Halogenated aromatic hydrocarbon	38	No specify	
$\log K_{oc} = 0.402\log K_{ow} + 1.071$	0.69	Pesticides	15	Soils	Kanazawa, 1989
$\log K_{oc} = 1.04\log K_{ow} - 0.84$	0.99	Nonpolar organic (eg. Pyrene, benzene, toluene)	13	Sandy aquifer materials	Abdul and Gibson, 1986 Abdul <i>et al.</i> , 1987
$\log K_{oc} = 0.82\log K_{ow} + 0.02$	0.98	Chlorinated phenols	8	Sediments and aquifer materials	Schellenberg <i>et al.</i> , 1983
$\log K_{oc} = 0.904\log K_{ow} - 0.779$	0.989	Benzene, and derivatives, and PCB	12	Wood burn soil	Chiou <i>et al.</i> , 1983
$\log K_{oc} = 1.00\log K_{ow} - 0.21$	1.00	PAHs e.g. PYR, ANT, NAP, and 2-MNAP, and aromatics e.g. benzene.	10	Natural sediments	Karickhoff <i>et al.</i> , 1979

The relationship between molecular weight and $\log K_{oc}$ is shown as the following equation:

$$\log K_{oc} = 0.019MW + 0.77 \quad (r^2 = 0.90) \quad (5.2)$$

The relationship between the $\log K_{oc}$ and molecular weight was found in the study of Kanazawa (1980). The equation in this study agrees with his study that has similar relationship and the linear regression obtained was $\log K_{oc} = 0.0085MW + 0.132$ ($r^2 = 0.793$). The results of his study were observed on 15 pesticides (such as dimethoate, propoxur, molinate, lindane, diazinon, and trifluralin) that $\log Kow$ in the range of 1.52 to 5.34 and carried out on two soil samples having organic carbon content of 4.24% and 1.35 %.

5.3.3 Aqueous Solubility (S)

Aqueous solubility is a measurement of hydrophobicity. Since a fair linear relationship between $\log K_{oc}$ and $\log S$, the negative slope of the linear regression can be expected (Figure 5.5). $\log S$ (unit of mole/L) was plotted against with $\log K_{oc}$. Regression of $\log K_{oc}$ as a function of $\log S$ for PAH yield the following equation:

$$\log K_{oc} = -0.5\log S + 3.06 \quad (r^2 = 0.72) \quad (5.3)$$

Other studies on the relationships between $\log K_{oc}$ obtained in this study and $\log S$ is presented in Table 5.5.

Table 5.5 Models derived from log S in the literatures

Equation	r ²	Chemical classes	n	Sorbent	References
log K _{oc} = -0.439log S + 1.91 (S in mol/L)	0.851	PAH	20	No specify	Gerstl, 1990
log K _{oc} = -0.475log S + 1.318 (S in mol/L)	0.839	Halogenated aromatic hydrocarbon	38	No specify	
logK _{oc} = -0.74logS + 4.0	0.98	Nonpolar organic (eg. Pyrene, benzene, toluene)	13	Sandy aquifer materials	Abdul et al., 1987
log K _{om} = -0.729log S + 0.001 (S in mol/L)	0.996	Benzene, and derivatives, and PCB	12	Wood burn soil	Chiou et al., 1983
log K _{oc} = -0.594log S - 0.197 (S in mole fraction)	0.94	PAH	5	Natural sediments	Karickhoff et al., 1981
logK _{OC} = -0.82logS + 4.070 (S in µg/mL)	1.00	PAH: PYR, DMBA, 3-MC, and DBA	4	Sediments and soils	Mean et al., 1980
logK _{OC} = -0.54logS + 0.44 (S in mole fraction)	0.94	PAHs e.g. PYR, ANT, NAP, and 2-MNAP, and aromatics e.g. benzene.	10	Natural sediments	Karickhoff et al., 1979
log K _{oc} = -0.56logS+4.28 (S in µmol/L)	0.98	Chlorinated hydrocarbon	15	Silt loam soils	Chiou et al., 1979
log K _{oc} = -0.356logS + 3.01 (S in ppm)	0.79	Pesticides	15	Soils	Kanazawa, 1989

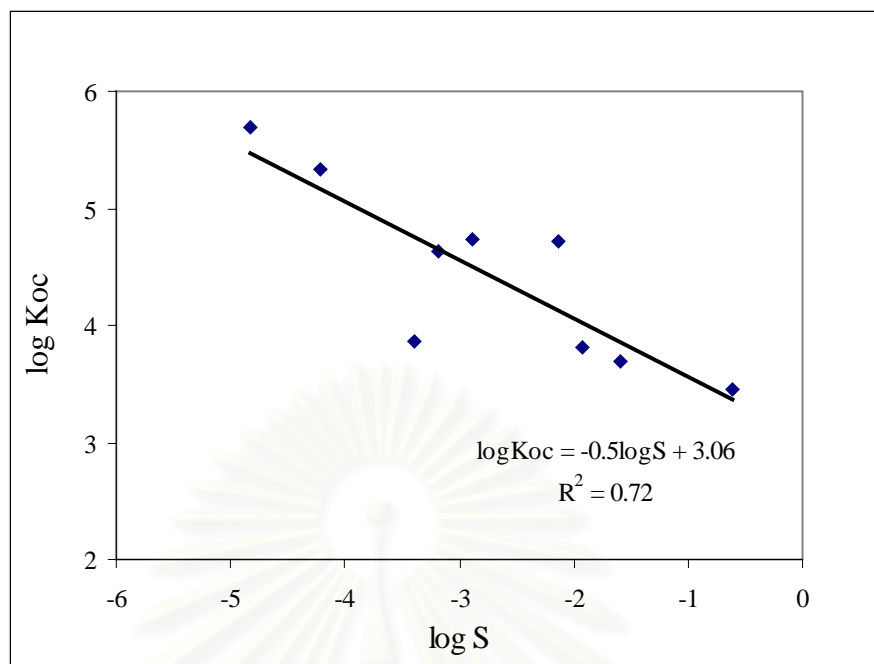


Figure 5.3 The linear relationship between $\log K_{oc}$ obtained in this study and $\log S$

The slope and intercept of the relationship between $\log K_{oc}$ and $\log S$ in this study are -0.5 and 3.06, respectively. As compared to those obtained from Karickhoff *et al.* (1979) (-0.54 and 0.44), Karickhoff *et al.* (1981), (-0.594 and -0.197), Mean *et al.* (1980) (-0.82 and 4.07) and Gerstl (1990) (-0.439 and 1.91), respectively. The equation of the relationship between the $\log K_{oc}$ and $\log S$ obtained in this study is reasonable. The variation could occur from the test compounds, properties of soils and experimental design under the study. Karickhoff *et al.* (1979) investigated the sorption of PAH and aromatic hydrocarbons on natural sediments and Karickhoff *et al.* (1981) studied for 5 PAH compounds on natural sediment. For the study of Mean *et al.* (1980), slope of the line was higher (-0.82) than the studies. The reason may be due to they studied on only 4 PAH.

5.3.4 Vapor Pressure (VP)

The vapor pressure is an importance in the environmental work resulted from its effects on the transport and partitioning of chemicals among the environmental components. The $\log VP$ was plotted against with $\log K_{oc}$. The relationship between $\log K_{oc}$ and $\log VP$ presented in Figure 5.3 and the regression equation as following:

$$\log K_{oc} = -0.32\log VP + 3.64 \quad (r^2 = 0.79) \quad (5.4)$$

A fair linear relationship between $\log K_{oc}$ and $\log VP$ was observed. The negative slope (-0.32) was indicated that $\log K_{oc}$ increase with decreasing vapor pressure. The relationship between $\log K_{oc}$ and $\log VP$ has not been much studied in the literature reviews. However, the linear correlation coefficient was considered, the result was demonstrated that vapor pressure can be used to predict the $\log K_{oc}$ of PAH compounds.

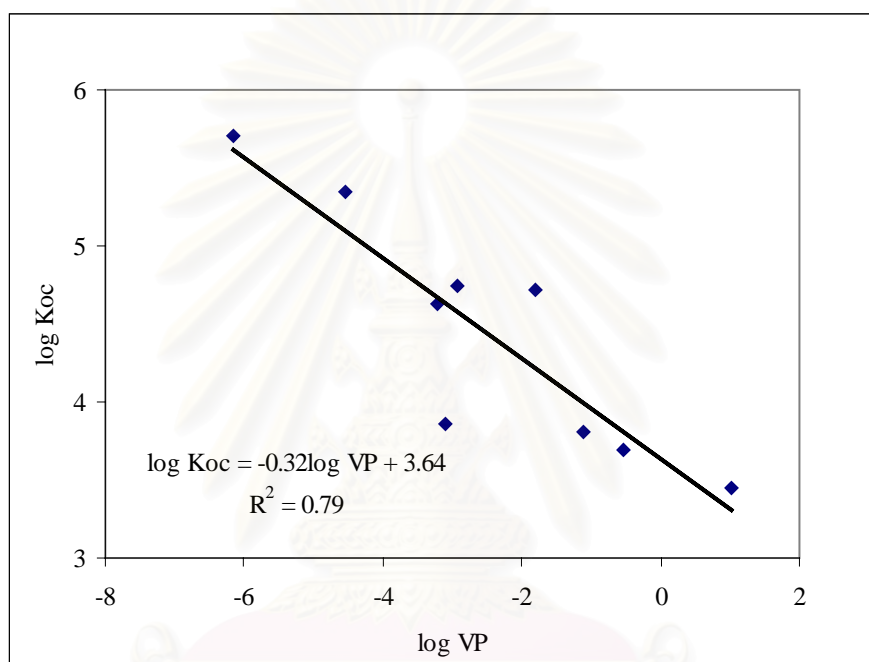


Figure 5.4 The linear relationship between $\log K_{oc}$ obtained in this study and $\log VP$

5.3.5 Henry's Law Constant (H)

Henry's law constant is the partition coefficient for the distribution of a chemical between the air and water compartments. Since air and water are the major compartments of most model ecosystems, and water is considered to act as the link between all of the compartments. Therefore, it is expected that there is a relationship between K_{oc} and Henry's Law constant (unit of $\text{Pa}\cdot\text{m}^3/\text{mol}$) (Figure 5.5). The result is shown as the following equation

$$\log K_{oc} = -0.73\log H + 4.66 \quad (r^2 = 0.93) \quad (5.5)$$

The good linear correlation coefficient was observed. It is indicated that $\log K_{oc}$ increase with decreasing Henry's law constant. The relationship between $\log K_{oc}$ and $\log H$ has not been in the literature reviews. However, the slope of the line is -0.73 and the relationship between the $\log K_{oc}$ and $\log H$ is good. This demonstrated that Henry's law constant could be used as the estimator for predicts the $\log K_{oc}$ of PAH compounds.

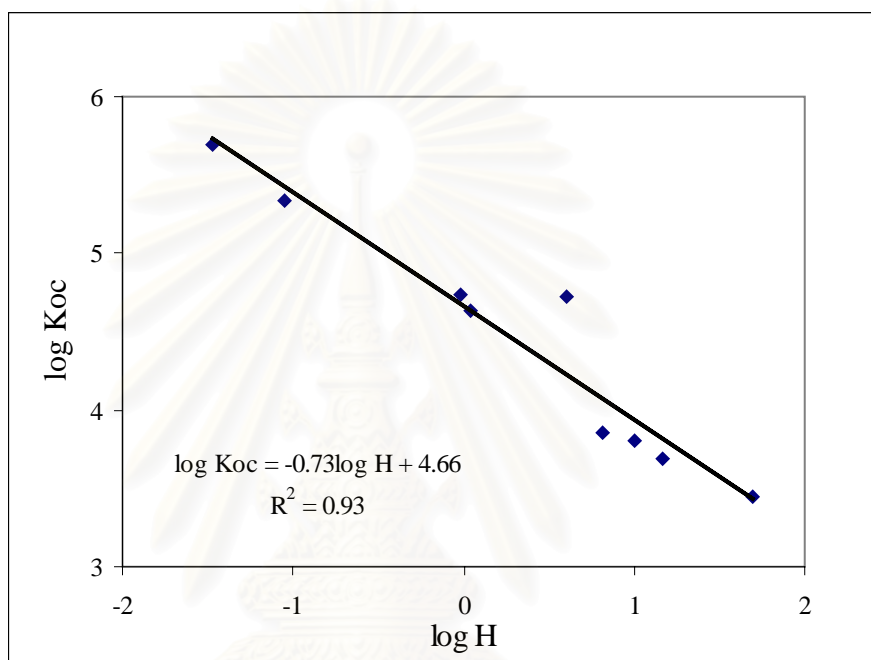


Figure 5.5 The linear relationship between $\log K_{oc}$ obtained in this study and $\log H$

5.3 Model Validations

To validate the models developed from the relationships of $\log K_{oc}$ and physicochemical properties as shown on Equation 5.1 to Equation 5.5, some PAH outside the studies and other organic compounds with similar physicochemical properties are used to test models. As a general rule, the models are best applied to the compounds of similar properties of which the models based on. Therefore, the selected compounds (PAH, PCDD, and PCB) are those in the same range of $\log K_{ow}$ where the models developed from. Properties of the selected compounds (K_{ow} , MW, S, VP, and H) obtained from Mackay *et al.* (2000) were then put into the models and the results are shown in Table 5.6 including the $\log K_{oc}$ values obtained from other studies. In considering model

in equation 5.1 - 5.5, it seems models of equations 5.1, 5.2, and 5.5 are more promising due to their regression correlation coefficients (r^2) ≥ 0.90 . This demonstrates that these models would better predict $\log K_{oc}$ than those models developed from aqueous solubility and vapor pressure ($r^2 \leq 0.79$). However, lower r^2 may be due to the difficulty in measuring these properties since the compounds have relatively low aqueous solubility and low vapor pressure. Therefore, there are wide ranges of these values in the database. This would cause the relationships between $\log K_{oc}$ and $\log VP$, and $\log S$ lower than it should be.

In addition, such models of high r^2 probably reflect their behavior between phases (in these cases; octanol-water and air-water phases) while the rest exhibit their properties in a media (S-solubility in an aqueous phase, VP-volatility in the atmosphere). Thus, K_{ow} is more likely a good descriptor for the QSAR model to predict the $\log K_{oc}$, though H described the compound behavior between the air and the water but air phase is somewhat different from organic carbon in soil. For instances, the values of $\log K_{oc}$ (derived from model of $\log K_{ow}$) of 2-MNAP, BkF, DMBA (3.67, 5.73 and 5.36, respectively) which these values are more close to the value from the literature than the K_{oc} values that derived from the other physicochemical properties.

The selected PAH used to test the models have $\log K_{oc}$ derived from the models fairly close to each other and to that collected from literature, for example, the values of $\log K_{oc}$ of ACT in model (model of K_{ow} , MW, S, VP, and H i.e. 3.78, 3.66, 3.85, 3.91, and 3.88, respectively) are close to the $\log K_{oc}$ from the literature (3.75). It should be noted that K_{oc} values from literature used as reference were also reviewed from literature. A slight deviation of $\log K_{oc}$ values could be as a result of the varied values of each compound property as mentioned earlier.

Generally, PAH, PCDD, and PCB share similar physicochemical properties; low aqueous solubility, lipophilic, low vapor pressure. However, in Table 5.6, PCDD and PCB with $\log K_{ow}$ ranged from 3.75 to 6.09, which is in the $\log K_{ow}$ range the models developed from, have somewhat different properties of aqueous solubility and vapor pressure from PAH group. This is due to chlorination of the compounds, i.e. an increase of chlorine in the molecule leading to the decreases in S and lipid solubility and increase of $\log K_{ow}$ causing these compounds somewhat different from PAH compound.

Table 5.6 Comparison of log Koc values derived from the models in this study with these from the literatures.

compounds	log Kow	log Koc derived from the model					log Koc from literature
		1	2	3	4	5	
PAH							
1-MNAP	3.87	3.68	3.47	3.41	3.34	3.43	3.36 ^(a)
2-MNAP	3.86	3.67	3.47	3.43	3.33	3.56	3.64 ^(a)
1-ENAP	3.87	3.68	3.74	3.66	3.51	3.81	3.78 ^(a)
9-MANT	5.14	4.69	4.42	4.49	4.49	-	4.81 ^(c)
DMBA	5.98	5.36	5.64	5.07	5.29	-	5.35 ^(b)
ACT	4.00	3.78	3.66	3.85	3.91	3.88	3.75 ^(d)
2-ENAP	4.38	4.08	3.74	3.71	3.48	3.26	3.76 ^(e)
TTC	6.02	5.40	5.11	5.86	6.08	-	5.81 ^(c)
CHRY	5.60	5.06	5.11	5.35	5.37	4.91	4.89 ^(f)
BbF	6.50	5.78	5.56	5.67	5.66	5.60	5.74 ^(g)
BkF	6.44	5.73	5.56	5.81	5.97	5.66	5.74 ^(g)
PCDD							
2-CDD	4.20	3.94	4.92	4.42	4.21	3.86	3.92 ^(h)
2,3-DCDD	5.60	5.06	5.58	5.00	4.73	4.06	4.73 ^(h)
PCB							
2-PCB	3.75	3.58	4.35	3.82	3.51	3.31	3.47 ^(a)
2,2'-PCB	3.76	3.59	5.01	4.10	3.83	3.54	3.92 ^(a)
2,4'-PCB	4.47	4.16	5.01	4.10	3.82	3.64	4.14 ^(a)
2,4,4-PCB	5.11	4.67	5.66	4.73	4.14	3.71	4.62 ^(a)
2,2',5,5'-PCB	6.09	5.45	6.32	5.08	4.47	3.54	5.41 ⁽ⁱ⁾

$$1 \log Koc = 0.8 \log Kow + 0.58 \quad (r^2 = 0.90)$$

$$2 \log Koc = 0.019MW + 0.77 \quad (r^2 = 0.72)$$

$$3 \log Koc = -0.5 \log S + 3.06 \quad (r^2 = 0.90)$$

$$4 \log Koc = -0.32 \log VP + 3.64 \quad (r^2 = 0.79)$$

$$5 \log Koc = -0.73 \log H + 4.66 \quad (r^2 = 0.93)$$

(a) Sabljic, 1995; (b) Mean *et al.*, 1980; (c) Karickhoff *et al.*, 1979;

(d) Chiou *et al.*, 1983 (e) Vowles and Mantoura, 1987, cited in Mackay *et al.*, 2000

(f) Pavlou, 1987, cited in Mackay *et al.*, 2000

(g) Mabey *et al.*, 1982, cited in Mackay *et al.*, 2000

(h) Fiedler and Schramm, 1990, cited in Mackay *et al.*, 2000

(i) Paya-Perez *et al.*, 1991, cited in Mackay *et al.*, 2000

Thus, varying $\log K_{oc}$ values for PCDD and PCB derived from the models other than those derived from $\log K_{ow}$ can be expected. However, some derived $\log K_{oc}$ values from $\log K_{ow}$ for these PCDD and PCB close to the values from the literature are observed.



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CHAPTER 6

CONCLUSIONS

Development of QSAR models in this study for PAH in the $\log K_{ow}$ range from 3.4 to 6.5 by investigating the partitioning behavior of PAH between the soil and the water over four concentrations of compounds and four soil organic carbon contents is appropriate. Since the models give reasonable $\log K_{oc}$ values for PAH of the same range of $\log K_{ow}$ of which the models developed from. Roughly, these models for the relationships of $\log K_{oc}$ with $\log S$ and $\log VP$ seem less reliable than these relationships with $\log K_{ow}$, $\log H$, and MW due to the relationships between them are not good. In addition, the difficulty in measuring these properties since the compounds has relatively low aqueous solubility and low vapor pressure. Therefore, there are wide ranges of these values in the database. This would cause the relationships between $\log K_{oc}$ and vapor pressure, and aqueous solubility lower than it should be.

As the models were tested, it can be concluded that the application of the models is best for PAH in the range of $\log K_{ow}$ 3.4-6.5. PAH with $\log K_{ow}$ outside this range or other compounds with similar physicochemical properties (i.e. PCDD, PCB, and derivatives PAH) would give promising $\log K_{oc}$ values for estimation purpose.

However, there might have some factor influencing the partitioning system and affect $\log K_{oc}$ values. Such factors include variation of physicochemical properties, temperature, dissolved or colloidal organic matter, biodegradation, and photodegradation.

The models are adequate for estimation $\log K_{oc}$ values and better understanding of a chemical's partitioning behavior in the environment to enable decisions and action for environmental protection to proceed in a timely manner. A further benefit of the use of estimated values for selected properties of organic

chemicals is significant saving in both time and expenses. Actual measured values of many properties may take considerable time and the cost can be prohibitive.

Caution should be made applying the models particularly for new compounds produced into the markets since the models would fit well to compounds of similar physicochemical properties. It should be aware the range of physicochemical properties the models developed from. Application of the models fit well with PAH family of the same range of $\log K_{ow}$, however, may not be good for PCDD and PCB except the model derived from $\log K_{ow}$.

Since there have been varying values of individual organic compound property, the reliable properties as an input to the models would therefore improve better relationship of these properties to the $\log K_{oc}$ values and better application of the models. Furthermore, the models could extend to cover more compounds with the method developing in the study using test compounds having $\log K_{ow}$ larger than 6.5.



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REFERENCES

- Abdul A.S. and Gibson T.L. 1986. Hazardous Waste & Hazardous Materials 3(2):125.
- Abdul A.S., Gibson T.L., and Rai D.N. 1987. Statistical correlation for predicting the partition coefficients for nonpolar organic contaminants between aquifer organic carbon and water. Hazardous Waste & Hazardous Materials 4(3):211-222.
- Alloway, B.J and Ayres, D.C. 1997. Chemical principles of environmental pollution. 2 nd ed. London: Black academic and professional.
- ATSDR. 1995. Toxicological profile for polycyclic aromatic hydrocarbons (PAHs) [Online] Available from: <http://www.stsdr.cdc.gov> Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. [2001, June 22].
- Back S.O., Goldstone M.E., Lester J.N., and Perry R. 1992. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate, and behavior. Water Air Soil Pollut. 60 : 279-300.
- Baker J.R., Mithelcic J.R., Luehrs D.C., and Hickey J.P. 1997. Evaluation of estimation methods for organic carbon normalized sorption coefficients. Water Environment Research 69(2) : 136-145.
- Baker J.R., Mihelcic J.R., and Shea E. 2000. Estimating K_{OC} for persistent organic pollutants : limitations of correlation with K_{OW} . Chemosphere 41 : 813-817.
- Black C.A., Evans D.D., White J.L., Ensminger, and Clark F.E. 1969. Method of Soil Analysis Part 2 Chemical and Microbiological properties. 2 Vols. 2 nd ed.
- Boethling R.S. and Mackay D. 2000. Handbook of Property Estimation Methods for Chemicals: Environmental and Health Science. USA: Lewis Publishers.
- Brady N.C and Well R.R. 2002. The nature and properties of soils. 13 th ed. New Jersey : Prentice-Hall.
- Briggs G.G. 1981. Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficient, water solubility, bioconcentration factors and the parachor. J.Agric.Food.Chem. 29: 1050-1059.
- Broddin G., Van Vaeck L., and Van Gauwenberghe K. 1977. On the size distribution of polycyclic aromatic hydrocarbon containing particles of a coke oven emission source. Atmos.Environ. 11:1061-1064.

- Chin Y.P., Peve C.S., and Weber JR W.J. 1988. Estimating soil/sediment partition coefficients for organic compounds by high performance reverse phase liquid chromatography. Wat.Res. 22(7): 873-881.
- Chiou C.T., Peters L.J., and Freed V.H. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206: 831-832.
- Chiou C.T., Porter P.E., and Schmedding. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ.Sci.Technol. 17(4): 227-231.
- Chiou C.T. , Mcgroddy S.E., and Kile D.E. 1998. Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environ.Sci.Technol. 32(2): 264-269.
- Chuang J.C., Callahan P.J., Menton R.G., and Gordon S.M. 1995. Monitoring methods for polycyclic aromatic hydrocarbons and their distribution in house dust and track-in soil. Environ.Sci.Technol. 29(2): 494-500.
- Colmsjö A.L, Zebühr Y.U, and Ostman C.E. 1986. Polynuclear aromatic hydrocarbons in the gases and ambient air in the vicinity of a municipal incineration plant. Atmos. Environ. 20 : 2279-2282.
- Cousins I.T. and Jones K.C. 1998. Air-soil exchange of semivolatile organic compounds (SOC_s) in the UK. Environ. Pollut. 102: 105-118.
- Equilibrium partitioning of pollutants in the environment. [Online] Available from <http://polysep.ucla.edu> [2002, June 13]
- Gawlik B.M., Sotirou N., Feicht E.A., Schulte-Hostede S., and Kettrup A. 1997. Alternatives for the determination of the soil adsorption coefficient, K_{oc} , of non-ionic organic compounds-A review. Chemosphere 34(12): 2525-2551.
- Gerstl Z. 1990. Estimation of organic chemical sorption by soils. J.of Contaminant Hydrology 6: 357-375.
- Gschwend P.M. and Wu S. 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ.Sci.Technol. 19(1): 90-96.
- Hassett J. J. and Banwart W. L. 1992. Soils and their environment. New Jersey: Prince-Hall.
- Hegemen W.J.M, Van Der Weijden C.H., and Gustar Loch J.P. 1995. Sorption of benzo (a) pyrene and phenanthrene on suspended harbor sediment as a

- function of suspended sediment concentration and salinity: A laboratory study using the cosolvent partition coefficient. Environ.Sci.Technol. 29(2): 363-371.
- Hippelein M. And McLachan M.S. 1998. Soil/air partitioning of semivolatile organic compounds. 1. Method development and influence of physical-chemical properties. Environ.Sci.Technol. 32: 310-316.
- IARC Monographs Program on the Evaluation of Carcinogenic Risks to Humans and Their supplements.[Online] Available form: <http://193.51.164.11/default.html> [1998, March 26]
- Jaouen-Madoulet A., Abarnou A., Le Guellec A.M., Loizeav V., and leboulenger. 2000. Validation of an analytical procedure for polychlorinated biphenyls, coplanar polychlorinated biphenyls and polycyclic aromatic hydrocarbons in environmental samples. J.of Chromatography A. 886: 153-173.
- Jones K.M and Tiller C.L. 1999. Effect of solution chemistry on the extent of binding of phenanthrene by a soil humic acid: A comparison of dissolved and clay bound humic. Environ.Sci.Technol. 33(4): 580-587.
- Kanazawa J. 1989. Relationship between the soil sorption constants for pesticides and their physicochemical properties. Envi. Toxi. and Chem. 8: 477-484.
- Karickhoff S.W., Brown D.S., and Scott T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. Wat. Res.13: 241-248.
- Karickhoff S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10(8): 833-843.
- Krauss M. and Wilcke W. 2002. Sorption strength of persistent organic pollutants in particle-size fractions of urban soils. Soil. Sci. Soc. Am. J. 66: 430-437.
- Land Development Department. 1998. Soil survey of Suphanburi Province Report. vol. 660. Ministry of Agriculture and Cooperatives.
- Mackay D., Shiou W.Y., and Ma K.C. 2000. Physical-chemical properties and environmental fate Handbook [CD-ROM].
- McLachlan M.S. 1995. Bioaccumulation of hydrophobic chemicals in agricultural foodchains. Environ. Sci. Tehnol. 30: 252-259.
- Means J.C., Wood S.G., Hassett J.J. and Banwart W.L. 1980. Sorption of polycyclic aromatic hydrocarbons by sediments and soils. Environ.Sci.Technol. 14(12): 1524-1528.

- Meylan W., Howard P.H., and Boethling R.S. 1992. Molecular topology/fragment contribution method for predicting soil sorption coefficients. Environ.Sci.Technol. 26(8): 1560-1567.
- Miller R.W. and Gardiner D.T. 2001. Soil in Our Environment 9 th ed. New Jersey : Prentice-Hall.
- Müller S., Wilcke W., Kanchanakool N., and Zech W. 2000. Polycyclic aromatic hydrocarbon (PAH_s) and polychlorinated biphenyls (PCB_s) in particle-size separates of urban soils in Bangkok, Thailand. Soil Science 165(5): 412-419.
- Nagpal N.K. 1993. Ambient water quality criteria for polycyclic aromatic hydrocarbons (PAHs) [Online] Ministry of environment, lands, and parks province of British Columbia. Available from: <http://Wlapwww.gov.bc.ca> [2003, January 26]
- Office of official publications of the European Committees. 1996. Technical guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No. 1488/94 on risk assessment for existing substances Part III: Guidance Document on QSAR version 1, 1995[Online]. Luxembourg. Available from:<http://www.ecb.ei.jrc.it> [2002, May 20]
- Raymond W. Miller and Duane T. Gardiner. 1998. Soils in our environment. 8 th ed. New Jersey: Prentice-Hall.
- Sabljić A. 1984. Predictions of the nature and strength of soil sorption of organic pollutants by molecular topology. J Agri Food. Chem. 32: 243-246.
- Sabljić A. 1987. On the prediction of soil sorption coefficients of organic pollutants from molecular structure: application of molecular topology model Environ.Sci.Technol. 21: 358-366.
- Sabljić A. , Gusten H., Verhaar H., and Hermens J. 1995. QSAR modeling of soil sorption (Improvement and systematic of log K_{oc} vs log K_{ow} correlations). Chemosphere 31 (11/12): 4489-4514.
- Sabljić A. 2001. QSAR models for estimating properties of persistent organic pollutants required in evaluation of their environmental fate and risk. Chemosphere 43 : 363-375.
- Sawyer C.N., McCarty P.L., and Parkin G.F. 1994. Chemistry for Environmental Engineering. 4 th ed. Singapore: McGraw-Hill.

- Schellenberg K., Leuenberger C., and Schwarzenbach. 1984. Sorption of chlorinated phenols by natural sediments and aquifer materials. Environ. Sci. Technol. 18 (9): 652-657.
- Sparks D.L. 1995. Environmental soil chemistry. USA: Academic Press.
- Tan K.H. 1996. Soil sampling, preparation, and analysis. USA: Marcel Dekker.
- Tan K.H. 1998. Principles of Soil Chemistry. 3rd ed. USA: Marcel Dekker.
- Takada H., Onda T., and Ogura N. 1990. Determination of polycyclic aromatic hydrocarbons in urban street dust and their source material by capillary gas chromatography. Environ. Sci. Technol. 24: 1179-1186.
- ten Hulscher Th.E.M. and Cornelissen. 1996. Effects of temperature on sorption equilibrium and sorption kinetics of organic micropollutants - a review. Chemosphere 32(4): 609-626.
- The International Programme on Chemical Safety (IPCS). 1998. Environmental Health Criteria 202 : Selected Non-heterocyclic Polycyclic Aromatic Hydrocarbons. World Health Organization. Geneva, Switzerland.
- Toxprobe Inc. for Toronto Public Health. 2002. Benzo (a) pyrene and other polycyclic aromatic hydrocarbons. [Online] Available from: <http://www.city.toronto.on.ca> [2003, January 10]
- Trapido M. 1999. Polycyclic aromatic hydrocarbons in Estonian soil : contamination and profiles. Environ.Pollut. 105: 67-74.
- U.S.EPA. 1984a. Guidelines establishing test procedures for the analysis of pollutants under the clean water act : method 610. Polycyclic aromatic hydrocarbons. Fed Reg, 49(209): 43344-43352 (40 CFR part 136).
- U.S.EPA. 1986. Method 8100 Polycyclic Aromatic Hydrocarbons. U.S.Environmental Protection Agency. Washington D.C., US.
- U.S.EPA. 2000. Method 3546 Microwave Extraction. U.S.Environmental Protection Agency. Washington D.C., US.
- Vogt N.B., Brakstad F., Thrane K., Nordenson ssS., Krane J., Aamot E., Kolset K., Esbensen K., and Steinnes E. 1987. Polycyclic aromatic hydrocarbons in soil and air: statistical analysis and classification by the SIMCA methods. Environ. Sci.Technol. 21: 34-44.
- Wania F. And Mackay D. 1996. Tracking the distribution of persistent organic pollutants. Environ.Sci.Technol. 30 : 390a-396a.

- Welsch-Pausch K. And McLachlan M.S. 1998. Fate of airborne polychlorinated dibenzo-p-dioxins and dibenzofuran in an agricultural ecosystem. Environ. Pollut. 102: 129-137.
- Wild S.R. and Jones K.C. 1995. Polynuclear Aromatic Hydrocarbons in the United Kingdom Environment: a preliminary source inventory and budget. Environ. Pollut. 88: 91-108.
- Wisconsin Department of Health & Family Services. 2000. Fact sheet of polycyclic aromatic hydrocarbon [Online]. Available from: www.dhfs.state.wi.us [2002, May 6]
- Yang S.Y.N., and Connell D.W., Hawker D.W., and Kayal S.I. 1991. Polycyclic aromatic hydrocarbons in air, soil, and vegetation in the vicinity of an urban roadway. The Science of the Total Environment 102: 229-240.



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APPENDICES

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APPENDIX A

Determination of soil characteristics

(1) pH (soil : water 1:1)

10 g of soil was weighed in a beaker and 10-ml of distilled water was added. The slurry was stirred for about an hour. Then the pH was measured using a pH meter.

(2) Moisture content

5 g of soil was weighed in a preweigh flask (PF). Then the flask and its content was dried at 103-110 °C for 24 hour in an oven. At the end of the 24 hours, allowed the flask to cool down in a desiccator and weighed the flask and its content again (F). The moisture content is calculated based on the equation below.

$$\% \text{ moisture} = \frac{(PF-F) \times 100}{PF}$$

(3) Cation exchange capacity (ammonium saturation method)

10 g of soil was weighed and added 250 ml of neutral 1N ammonium acetate (NH₄OAC). The flask was shaken thoroughly and allowed it to stand overnight. The soil was filtered with light suction using buchner funnel. The soil was leached with the neutral ammonium acetate reagent (NH₄OAC) until no trace of calcium found in the effluent solution. The leachate was combined for the determination of exchangeable bases. Then the soil was leached four times with 1 N ammonium chloride (NH₄Cl) and once with 0.25N ammonium chloride (NH₄Cl) and washed out the electrolyte with 150 to 200 ml of 99% isopropyl alcohol. Determined the adsorbed ammonium (NH₄) by leaching the ammonium-saturated soil with 10% acidified sodium chloride (NaCl) until 225 ml have passed through the samples. The leachate was transferred quantitatively to kjeldahl flask, added 25 ml of 1N sodium hydroxide (NaOH), and distilled 60 ml of the solution into 50 ml of 2% boric acid (H₃BO₃). 10 drops of bromocresol green-methyl red mixed indicator was added, and titrated the boric acid solution with standard 0.1N H₂SO₄. The color change is from bluish green

through bluish purple to pink at the end point. Run blanks on the reagents. Corrected the titration figure for the blanks, and calculate the centimoles of cations per kilogram of dry soil (cmol_c/kg).

(4) Organic carbon content (wet oxidation method)

2 g of soil was transferred into an erlenmeyer flask. Added 10 ml of 1N potassium dichromate (K₂Cr₂O₇) and swirled the flask gently to disperse the soil in the solution. Then rapidly added 10 ml of concentrated H₂SO₄, directing the stream into the suspension. Immediately swirl the flask gently until soil and reagents were mixed, then swirled more vigorously for a total of 1 minutes. Allowed the flask to stand for 30 minutes. Then added 100 ml of water to the flask, added 3 to 4 drops of o-phenanthroline indicator, and titrated the solution with 0.5N ferrous sulphate (FeSO₄). As the endpoint was approached, the solution takes on a greenish cast and then changed to dark green. At this point, added the ferrous sulfate drop by drop until the color changes from blue to red. Made a blank determination in the same manner, but without soil, to standardize the Cr₂O₇²⁻.

(5) Soil Texture (hydrometer)

100 g of soil was weighed and transferred into a blender cup. Filled the blender cup with distilled water to within 10 cm of the top and added 10 ml of sodium metaphosphate solution (NaPO₃)_x.Na₂O). Attached the cup to a blending machine and blend mechanically for 15 minutes. Transferred the soil suspension into an ASTM soil-testing cylinder. Made up the volume in the cylinder with water to the 1205-ml level. Mixed the suspension thoroughly by stirring with a stirring rod. Record the exact time when stirring was stopped.

Placed a hydrometer into the suspension, and exactly 40 second after the stirring was stopped, read the nearest 0.5 scale division the top of the meniscus on the hydrometer. Stirred the suspension again and repeated the analysis of the 40 second reading. The average of the 2 reading was taken as the result, which equals the amount of silt + clay in grams. Determined and recorded the temperature of the suspension after removed the hydrometer. Stirred the suspension again thoroughly.

Take a third hydrometer and temperature reading after 120 minutes of settling time.
This reading will measure the amount of clay in grams.



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APPENDIX B

Calibration curves of the test compounds

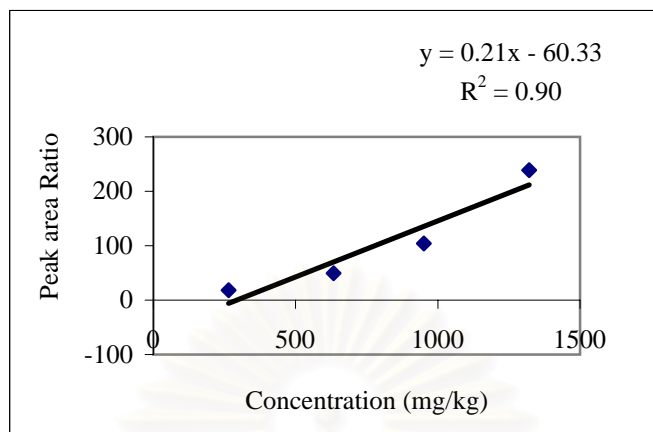


Figure B.1 Calibration curve of NAP in soil

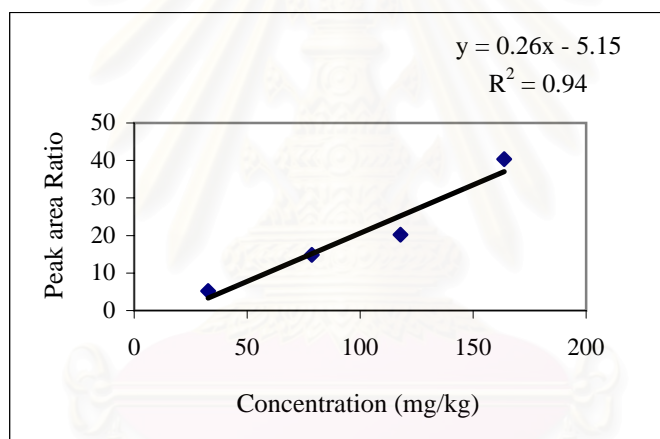


Figure B.2 Calibration curve of ACE in soil

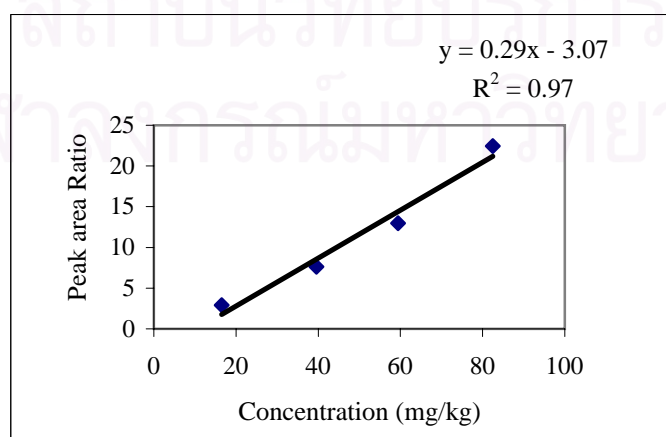


Figure B.3 Calibration curve of FLU in soil

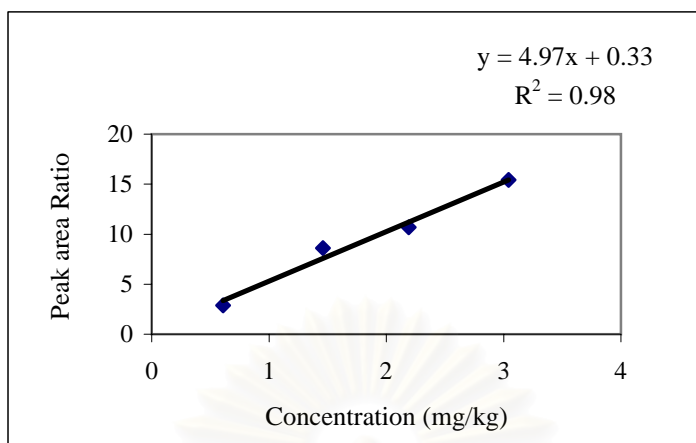


Figure B.4 Calibration curve of ANT in soil

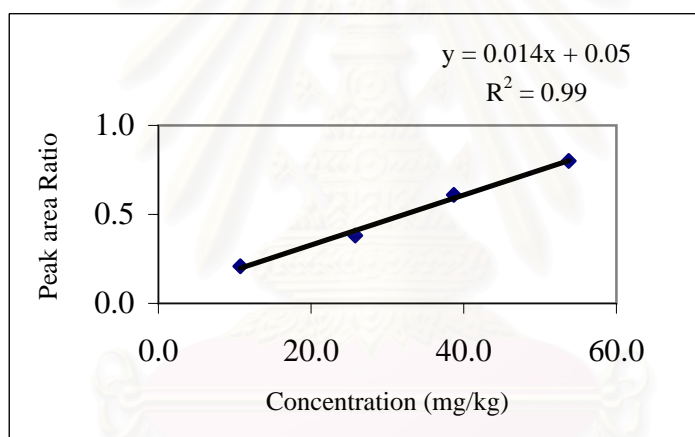


Figure B.5 Calibration curve of PHE in soil

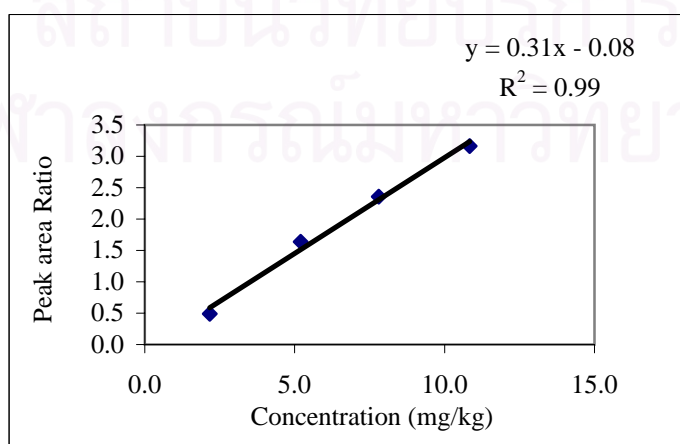


Figure B.6 Calibration curve of FLA in soil

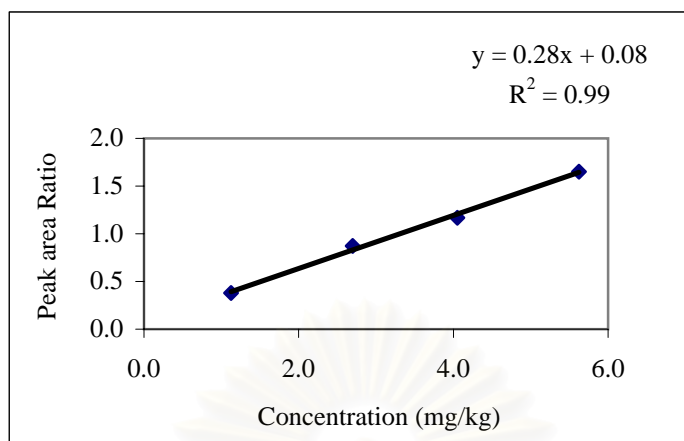


Figure B.7 Calibration curve of PYR in soil

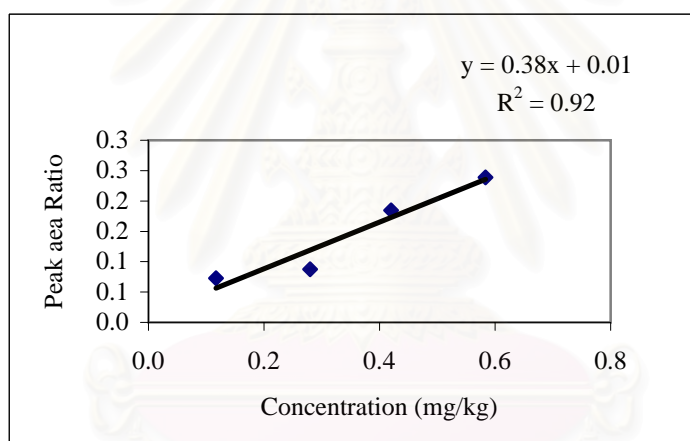


Figure B.8 Calibration curve of BaA in soil

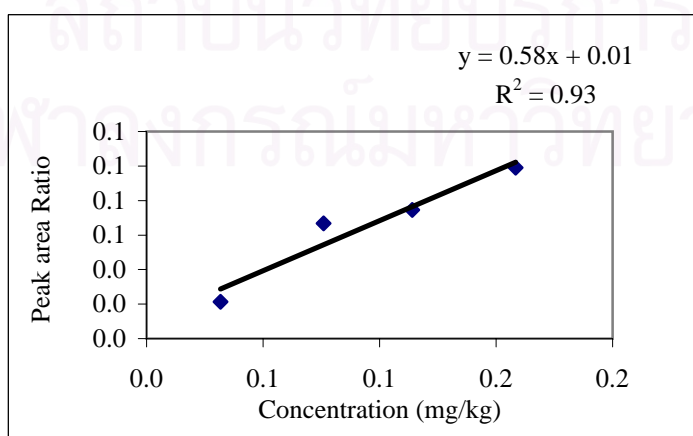


Figure B.9 Calibration curve of BaP in soil

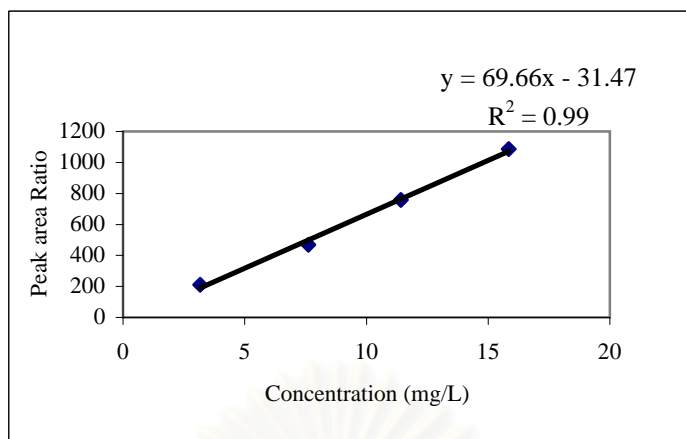


Figure B.10 Calibration curve of NAP in water

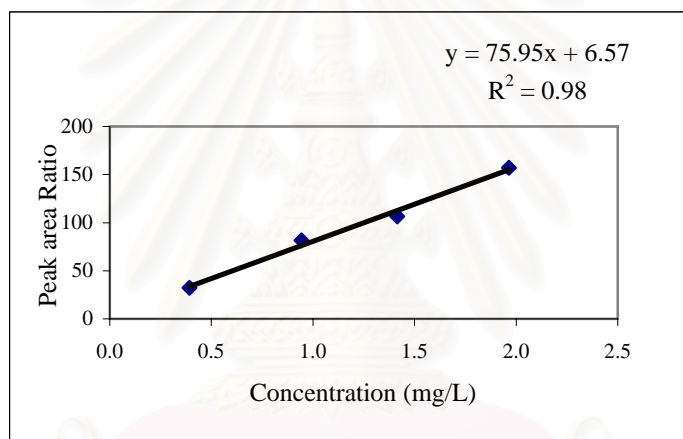


Figure B.11 Calibration curve of ACE in water

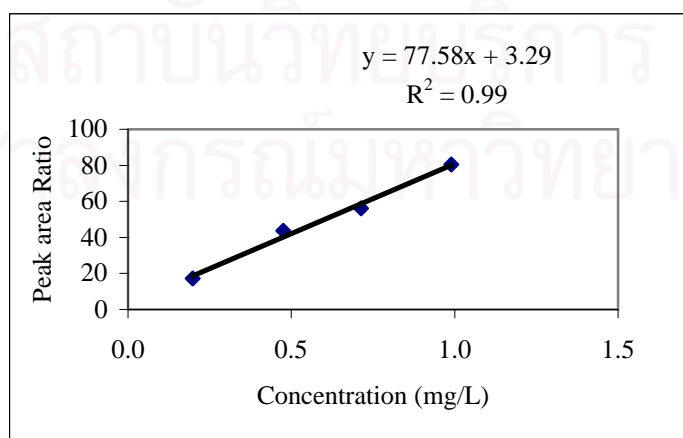


Figure B.12 Calibration curve of FLU in water

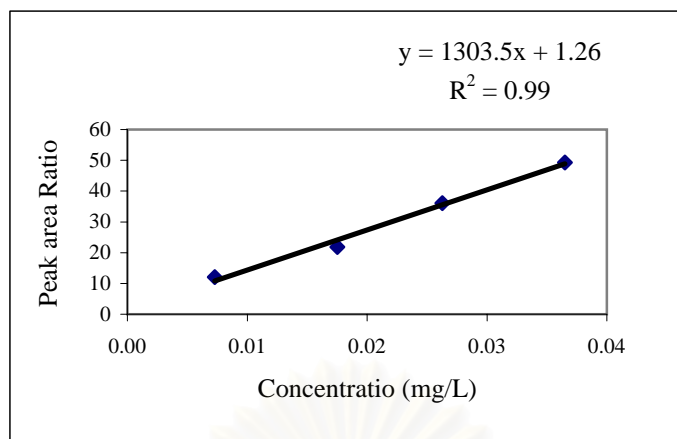


Figure B.13 Calibration curve of ANT in water

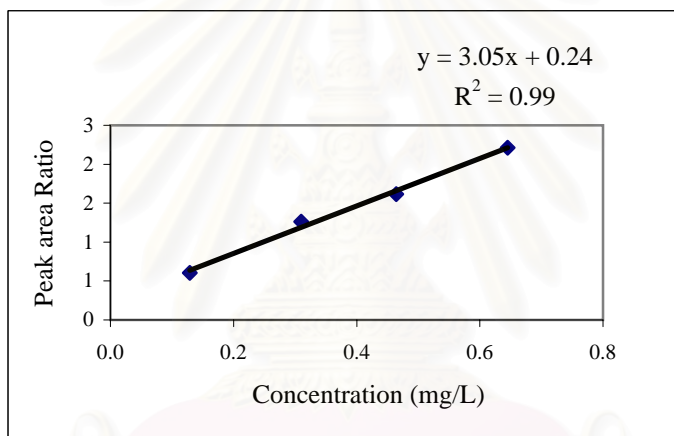


Figure B.14 Calibration curve of PHE in water

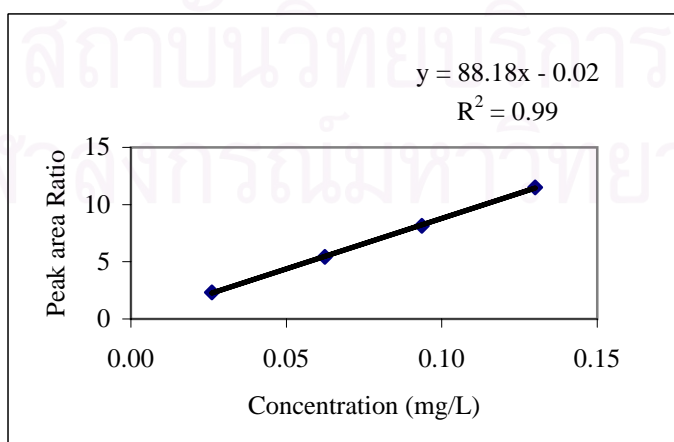


Figure B.15 Calibration curve of FIA in water

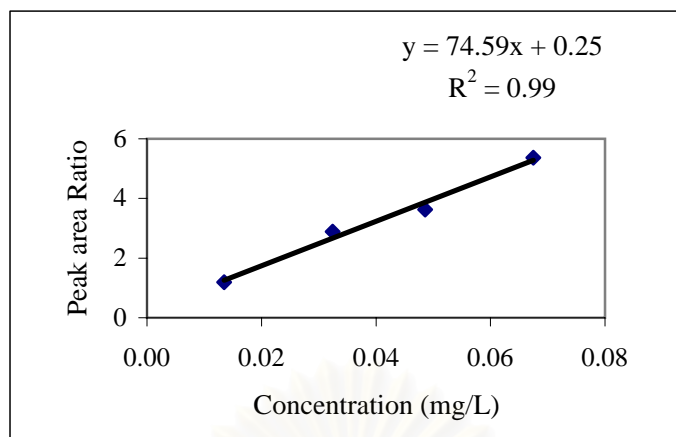


Figure B.16 Calibration curve of PYR in water

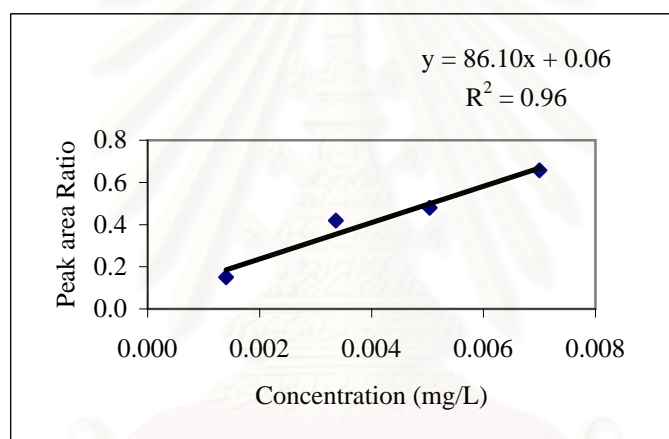


Figure B.17 Calibration curve of BaA in water

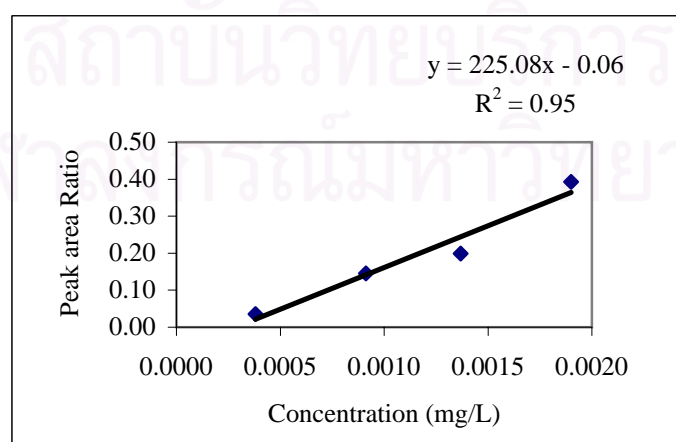


Figure B.18 Calibration curve of BaP in water

The steady state attainment experiments

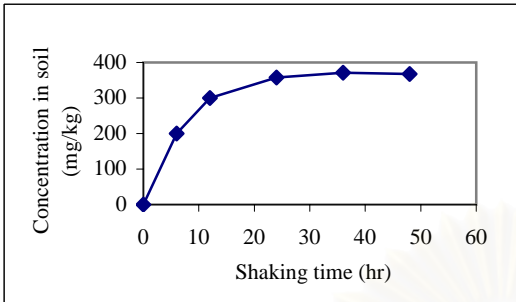


Figure C.1 the steady state attainment experiment of NAP

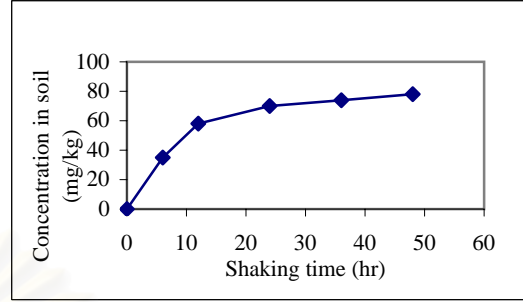


Figure C.2 the steady state attainment experiment of ACE

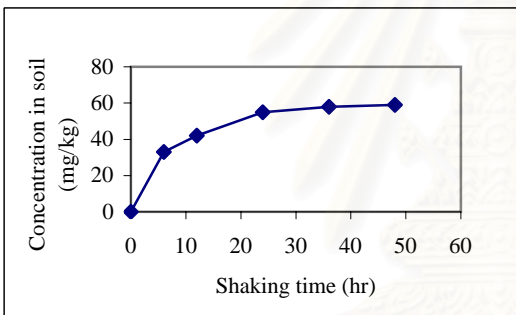


Figure C.3 the steady state attainment experiment of FLU

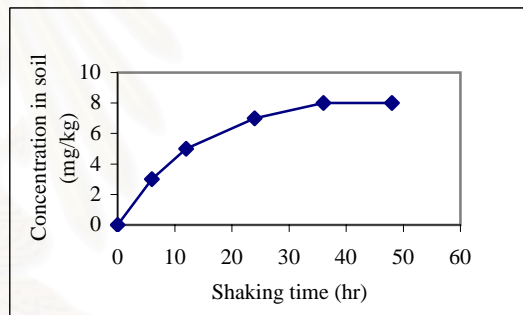


Figure C.4 the steady state attainment experiment of ANT

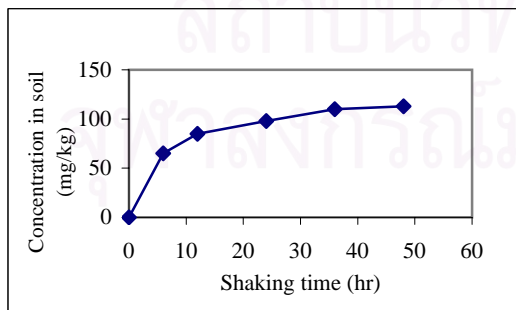


Figure C.5 the steady state attainment experiment of PHE

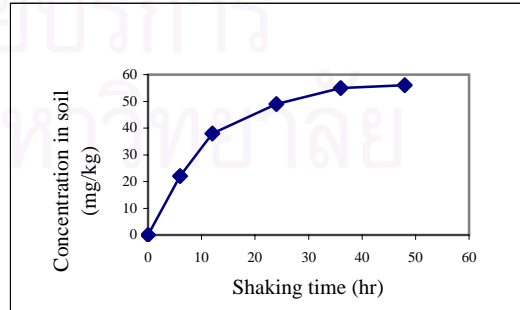


Figure C.6 the steady state attainment experiment of FLA

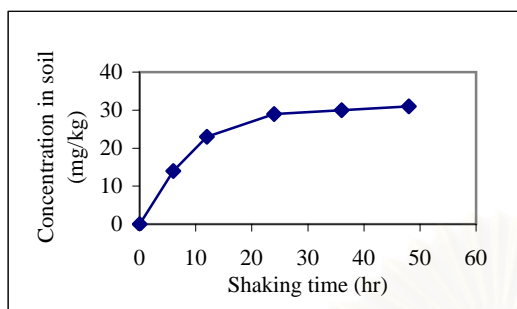


Figure C.7 the steady state attainment experiment of PYR

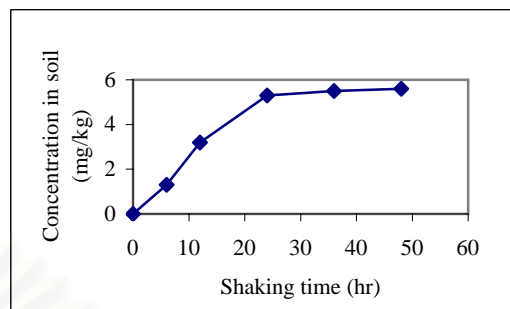


Figure C.8 the steady state attainment experiment of BaA

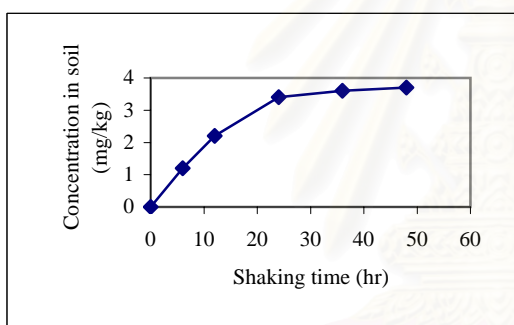


Figure C.9 the steady state attainment experiment of BaP

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APPENDIX D

The results of the partitioning experiments for each compounds

Naphthalene

%OC	Conc.	C _s (mg/kg)	C _w (mg/L)	K _d (L/kg)	K _{oc} (L/kg)	log K _{oc}
0.4	0.05S	290.46	11.46	25.35	6338.29	3.80
	0.12S	293.77	11.13	26.40	6600.59	3.82
	0.18S	298.72	15.27	19.56	4890.02	3.69
	0.25S	305.57	19.55	15.63	3907.00	3.59
1.03	0.05S	294.05	9.26	31.77	3084.47	3.49
	0.12S	296.47	9.13	32.46	3151.37	3.50
	0.18S	298.59	10.23	29.20	2835.04	3.45
	0.25S	350.30	14.26	24.57	2385.69	3.38
1.57	0.05S	293.36	7.26	40.43	2574.89	3.41
	0.12S	294.32	9.13	32.22	2052.51	3.31
	0.18S	295.28	11.37	25.97	1654.23	3.22
	0.25S	400.71	12.26	32.70	2082.57	3.32
2.05	0.05S	295.82	5.27	56.17	2740.06	3.44
	0.12S	296.43	7.26	40.85	1992.73	3.30
	0.18S	314.87	9.26	34.01	1658.94	3.22
	0.25S	431.52	9.90	43.60	2127.03	3.33
					Average	3.45

Acenaphthene

%OC	Conc.	C _s (mg/kg)	C _w (mg/L)	K _d (L/kg)	K _{oc} (L/kg)	log K _{oc}
0.4	0.05S	20.85	1.90	10.96	2738.88	3.44
	0.12S	21.42	1.41	15.18	3795.72	3.58
	0.18S	22.81	0.45	50.91	12726.97	4.10
	0.25S	29.81	0.80	37.26	9314.13	3.97
1.03	0.05S	22.20	0.21	103.30	10028.65	4.00
	0.12S	30.84	0.47	65.78	6386.67	3.81
	0.18S	25.81	0.58	44.49	4319.82	3.64
	0.25S	27.23	0.75	36.41	3535.43	3.55
1.57	0.05S	21.45	0.18	117.85	7506.34	3.88
	0.12S	24.14	0.53	45.73	2912.61	3.46
	0.18S	26.87	0.49	54.34	3461.22	3.54
	0.25S	32.48	0.77	42.33	2696.09	3.43
2.05	0.05S	27.28	0.20	137.97	6730.29	3.83
	0.12S	31.58	0.29	107.31	5234.64	3.72
	0.18S	46.18	0.72	64.31	3137.16	3.50
	0.25S	78.26	0.93	83.72	4083.96	3.61
					Average	3.69

Fluorene

%OC	Conc.	C _s (mg/kg)	C _w (mg/L)	K _d (L/kg)	K _{oc} (L/kg)	log K _{oc}
0.4	0.05S	11.48	0.18	65.42	16355.54	4.21
	0.12S	12.14	0.31	39.35	9837.05	3.99
	0.18S	13.40	0.26	51.71	12926.74	4.11
	0.25S	18.95	0.43	43.70	10924.04	4.04
1.03	0.05S	13.44	0.14	96.20	9340.23	3.97
	0.12S	19.78	0.29	68.16	6617.71	3.82
	0.18S	16.83	0.34	49.85	4839.68	3.68
	0.25S	17.79	0.44	40.28	3910.37	3.59
1.57	0.05S	13.25	0.11	116.47	7418.49	3.87
	0.12S	15.76	0.30	51.74	3295.49	3.52
	0.18S	19.15	0.34	57.12	3638.04	3.56
	0.25S	22.79	0.57	40.30	2566.69	3.41
2.05	0.05S	19.11	0.11	167.80	8185.17	3.91
	0.12S	23.25	0.16	141.16	6885.87	3.84
	0.18S	37.05	0.40	92.39	4506.87	3.65
	0.25S	61.51	0.51	121.34	5918.88	3.77
					Average	3.81

Anthracene

%OC	Conc.	C _s (mg/kg)	C _w (mg/L)	K _d (L/kg)	K _{oc} (L/kg)	log K _{oc}
0.4	0.05S	0.16	0.02	8.32	2081.16	3.32
	0.12S	0.29	0.02	12.62	3154.23	3.50
	0.18S	0.43	0.01	36.13	9032.27	3.96
	0.25S	0.69	0.02	39.29	9823.45	3.99
1.03	0.05S	0.52	0.01	76.58	7434.87	3.87
	0.12S	1.32	0.01	99.85	9693.98	3.99
	0.18S	1.05	0.01	73.35	7120.89	3.85
	0.25S	1.25	0.02	65.43	6352.78	3.80
1.57	0.05S	0.44	0.01	76.25	4856.58	3.69
	0.12S	0.88	0.01	66.00	4203.73	3.62
	0.18S	1.29	0.01	156.29	9954.80	4.00
	0.25S	1.71	0.02	69.19	4406.75	3.64
2.05	0.05S	1.14	0.00	230.58	11247.59	4.05
	0.12S	1.59	0.01	240.00	11707.15	4.07
	0.18S	4.44	0.01	296.01	14439.73	4.16
	0.25S	7.26	0.02	389.45	18997.62	4.28
					Average	3.86

Phenanthrene

%OC	Conc.	C_s (mg/kg)	C_w (mg/L)	K_d (L/kg)	K_{oc} (L/kg)	log K_{oc}
0.4	0.05S	29.79	0.07	421.96	105489.79	5.02
	0.12S	31.54	0.11	294.28	73569.74	4.87
	0.18S	32.87	0.09	384.64	96161.23	4.98
	0.25S	40.74	0.14	288.45	72112.78	4.86
1.03	0.05S	32.36	0.05	597.80	58038.61	4.76
	0.12S	32.77	0.04	871.43	84604.37	4.93
	0.18S	37.14	0.09	428.48	41599.96	4.62
	0.25S	51.35	0.13	407.08	39522.05	4.60
1.57	0.05S	37.02	0.04	944.15	60136.63	4.78
	0.12S	44.51	0.06	795.90	50694.29	4.70
	0.18S	48.38	0.15	319.49	20349.80	4.31
	0.25S	84.69	0.19	454.78	28966.60	4.46
2.05	0.05S	26.57	0.02	1074.44	52411.56	4.72
	0.12S	43.33	0.04	996.70	48619.40	4.69
	0.18S	102.88	0.12	879.97	42925.25	4.63
	0.25S	127.53	0.18	700.28	34159.91	4.53
					Average	4.72

Fluoranthrene

%OC	Conc.	C_s (mg/kg)	C_w (mg/L)	K_d (L/kg)	K_{oc} (L/kg)	log K_{oc}
0.4	0.05S	3.19	0.01	261.67	65416.26	4.82
	0.12S	6.40	0.02	257.82	64455.23	4.81
	0.18S	10.03	0.03	294.90	73724.47	4.87
	0.25S	14.77	0.04	356.31	89076.46	4.95
1.03	0.05S	6.15	0.02	399.04	38742.00	4.59
	0.12S	12.45	0.03	441.24	42839.16	4.63
	0.18S	11.76	0.03	373.95	36305.83	4.56
	0.25S	15.07	0.04	390.04	37868.25	4.58
1.57	0.05S	11.64	0.01	819.15	52175.14	4.72
	0.12S	15.77	0.02	788.62	50230.47	4.70
	0.18S	32.61	0.04	740.15	47143.45	4.67
	0.25S	40.74	0.06	699.49	44553.33	4.65
2.05	0.05S	14.34	0.01	1129.04	55075.24	4.74
	0.12S	17.33	0.01	1369.49	66804.59	4.82
	0.18S	39.78	0.03	1523.91	74337.17	4.87
	0.25S	56.19	0.03	1708.73	83352.86	4.92
					Average	4.74

Pyrene

%OC (L/kg)	Conc. (L/kg)	C_s (mg/kg)	C_w (mg/L)	K_d (L/kg)	K_{oc} (L/kg)	log K_{oc}
0.4	0.05S	2.29	0.0201	114.27	28567.85	4.46
	0.12S	2.94	0.0271	108.50	27126.12	4.43
	0.18S	3.25	0.0175	185.64	46411.10	4.67
	0.25S	4.89	0.0260	187.92	46980.34	4.67
1.03	0.05S	3.32	0.0057	586.56	56948.03	4.76
	0.12S	6.74	0.0119	566.96	55044.96	4.74
	0.18S	7.86	0.0154	511.65	49674.44	4.70
	0.25S	10.38	0.0182	568.73	55216.55	4.74
1.57	0.05S	3.42	0.0050	682.31	43459.25	4.64
	0.12S	8.03	0.0122	660.07	42042.90	4.62
	0.18S	10.31	0.0182	566.05	36054.11	4.56
	0.25S	13.10	0.0247	529.51	33727.06	4.53
2.05	0.05S	3.80	0.0052	729.43	35582.11	4.55
	0.12S	6.27	0.0073	861.36	42017.37	4.62
	0.18S	17.87	0.0174	1024.90	49995.34	4.70
	0.25S	25.31	0.0250	1013.20	49424.60	4.69
					Average	4.63

Benzo (a) Anthracene

%OC	Conc.	C_s (mg/kg)	C_w (mg/L)	K_d (L/kg)	K_{oc} (L/kg)	log K_{oc}
0.4	0.05S	1.75	0.0016	1091.49	272873.12	5.44
	0.12S	1.83	0.0019	953.21	238302.77	5.38
	0.18S	2.18	0.0020	1102.00	275500.01	5.44
	0.25S	2.58	0.0025	1027.60	256900.59	5.41
1.03	0.05S	1.87	0.0010	1922.07	186608.85	5.27
	0.12S	2.73	0.0012	2345.26	227695.03	5.36
	0.18S	2.52	0.0010	2522.96	244947.96	5.39
	0.25S	2.86	0.0020	1456.87	141443.24	5.15
1.57	0.05S	2.21	0.0006	3426.02	218218.10	5.34
	0.12S	3.29	0.0012	2718.63	173160.94	5.24
	0.18S	3.76	0.0015	2568.79	163617.04	5.21
	0.25S	4.11	0.0012	3458.42	220281.21	5.34
2.05	0.05S	2.41	0.0006	4192.29	204501.89	5.31
	0.12S	3.33	0.0007	4954.18	241667.18	5.38
	0.18S	4.57	0.0008	5436.48	265194.34	5.42
	0.25S	6.41	0.0012	5540.91	270288.06	5.43
					Average	5.34

Benzo (a) Pyrene

%OC	Conc.	C_s (mg/kg)	C_w (mg/L)	K_d (L/kg)	K_{oc} (L/kg)	log K_{oc}
0.4	0.05S	0.74	0.0004	1998.15	499537.58	5.70
	0.12S	1.10	0.0004	2820.45	705113.49	5.85
	0.18S	1.96	0.0008	2425.03	606257.58	5.78
	0.25S	2.35	0.0009	2764.71	691176.47	5.84
1.03	0.05S	1.60	0.0003	5318.62	516370.74	5.71
	0.12S	1.56	0.0003	5196.53	504517.80	5.70
	0.18S	1.90	0.0004	4746.75	460849.51	5.66
	0.25S	2.97	0.0004	7421.33	720516.99	5.86
1.57	0.05S	2.00	0.0003	6662.18	424342.68	5.63
	0.12S	2.76	0.0004	6270.43	399390.56	5.60
	0.18S	3.03	0.0004	7563.60	481757.96	5.68
	0.25S	4.57	0.0006	8308.70	529216.79	5.72
2.05	0.05S	2.33	0.0003	7068.18	344789.36	5.54
	0.12S	2.89	0.0004	7596.16	370544.29	5.57
	0.18S	3.86	0.0004	9642.00	470341.46	5.67
	0.25S	5.70	0.0005	10752.26	524500.69	5.72
					Average	5.70

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BIOGRAPHY

Miss Renu Jailuk was born on July 10, 1974 in Suphanburi Province, Thailand. She graduated from Matthayomthanbin Kamphangsan School in Nakornpathom Province in 1993. She received her Bachelor's Degree in Environmental Science from Faculty of Science, Silpakorn University in 1996. She worked as Environmental Scientist at System Engineering Co., Ltd. since 1996 to 2000 and then, she worked as of Researcher Assistant at Environmental Research Institute, Chulalongkorn University since 2000 to 2001. She pursued her Master Degree study in the International Postgraduate Programs in Environmental Management, Inter-Department of Environmental Management, Chulalongkorn University, Bangkok, Thailand in May 2001. She finished her Master Degree of Science in Environmental Management in May 2003.



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