จุฬาลงกรณ์มหาวิทยาลัย

ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช
รายงานวิจัย

การประเมินความเสี่ยงจากการหายใจสารก่อมะเร็งพวก PAH ประเมินจากค่าความเข้มข้นของสารในใบไม้

โดย
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Assessment of Risk Posed by Inhalation of Carcinogenic PAH-Assessment from PAH Concentrations in Leaves

By

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บทคัดย่อ

ศึกษาพฤติกรรมการแพร่กระจายของสารพอลิไซคลิกอะโรแมติคไฮโดรคาร์บอน 16 ชนิด ระหว่างใบเข็ม น้ำ และอากาศ เพื่อสร้างโมเดลของใบไม้กับอากาศ พิสูจน์ความเหมาะสมในการใช้ใบเป็นดัชนีชี้วัด วัดความเข้มข้นของสารในอากาศ และการประเมินความเสี่ยงที่จะเป็นมะเร็งในผู้ใช้ถนนในเขตกรุงเทพมหานครเนื่องจากการหายใจสารดังกล่าว ทำการทดลองหาสัมประสิทธิ์การกระจายในช่วงเวลา 36 ชั่วโมงโดยใช้ความเข้มข้นของสาร 4 ความเข้มข้นในรูปของสารผสม ผลการทดลองเข้ากันได้ดีกับสัมประสิทธิ์การแพร่กระจายในออคตานอล-น้ำและคุณสมบัติอื่นของสาร สัมประสิทธิ์การแพร่กระจายในใบ-อากาศที่ได้ต่ำกว่าค่าที่ได้จากการศึกษาของผู้อื่นเนื่องจากเกิดการย่อยสลายของสารทางชีวภาพ สภาพอากาศ และโมเดลที่ใช้ ความสัมพันธ์ที่ดีระหว่างความเข้มข้นอากาศที่ได้จากการวัดในภาคสนามและที่คำนวณจากความเข้มข้นในใบแสดงให้เห็นถึงศักยภาพของการใช้ใบเป็นดัชนี จากกราฟชี้ให้เห็นว่าสารในสภาพก๊าซมีบทบาทสำคัญมากในการสะสมของสารในใบและพบว่ามีอยู่ในอากาศและในใบมากกว่าสารที่อยู่สภาพเกาะกับอนุภาค การประเมินความเสี่ยงของการเกิดมะเร็งในตำรวจจราจร คนขับรถ คนขายของ และคนเดินถนนนั้น คำนวณจากสถานการณ์ของระยะเวลารับสัมผัสต่างๆ รวมทั้งความเป็นพิษของสารแต่ละตัวโดยใช้เทคนิค TEF (Toxic equivalence factor) และนำค่าความมีอยู่ในชีวภาพ มาพิจารณาด้วย จำนวนการเกิดมะเร็งมากที่สุด เท่ากับ 2 ใน ล้านคน และเกิดกับผู้ที่ใช้เวลาอยู่ในถนน 12 ชั่วโมงต่อวัน 5 วันต่อสัปดาห์ เป็นเวลา 30 ปี ที่บริเวณถนนเกษมราษฎร์ ณ ความเข้มข้นเฉพาะเจาะจงนั้น ความเชื่อถือได้ของผลการศึกษาขึ้นอยู่กับค่าที่ใช้ในการคำนวณว่ามีความใกล้เคียงกับประชากรศึกษาอย่างใด เช่น ค่าตอบสนองต่อปริมาณ อัตราการหายใจ น้ำหนักตัว เป็นต้น

Project Title: Assessment of Risk Posed by Inhalation of Carcinogenic PAH-Assessment from PAH Concentrations in Leaves

Investigator: Dr Benjalak Karnchanasest

Year: January 2003

ABSTRACT

Partitioning behavior of 16 PAH between the leaves (*Ixora chinensis Lamk*), the water and the air were investigated to develop a leaf-air model, validate the use of leaf as a bioindicator, measure air concentrations, and assess cancer risk in Bangkok road users due to inhalation of PAH. The partitioning experiments were conducted over 36 h on four concentrations in a mixture. The results fitted reasonably well with octanol-water partition coefficients and other compound properties. The leaf-air partition coefficients obtained found lower than other comparable finding due to biodegradation, atmospheric conditions and model basis. Reasonably good relationships between the calculated air from leaf concentration and the measured air indicated the potential use of leaves. According to the plots, gas phase played a major role in bioconcentration process and found relatively abundant than particle phase. Cancer risks in traffic police, taxi drivers, venders and pedestrians based on different exposure scenario were estimated and covered individual PAH toxicity using TEF approach taken into account for compound bioavailability. The highest cancer cases were 2 out of a million found in road users who spent 12h day^{-1}, 5 $days\ week^{-1}$ for 30 years at KR site with that particular concentrations. The result reliability depended on how well the input data represented the actual human situation under the study, e.g. dose/response relationship, inhalation rate, body weight, etc.

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A	Gas-phase concentration
A	Slope of the linear regression
amu	Atomic mass units
AT	Averaged exposure period
atm	Atmosphere
B	Intercept of linear regression
BA	Bioavailability factor
BA_{IHG}	Bioavailability factor of BaP for inhaled gas
BA_{IHP}	Bioavailability factor of BaP for inhaled particle
BaP_{equi}	Toxicity equivalent concentrations relative to BaP
BCF	Bioconcentration factor
bw	Body weight
C	Exposure concentration
C_A	Concentration in the air
CDI	Chronic daily intake averaged over a lifetime
C_G	Concentration in gas-phase
C_H	Concentration in hair based on wet weight
C_{HL}	Concentration in hair lipid
C_{IHG}	Toxicity equivalent concentrations of inhaled gas
C_{IHP}	Toxicity equivalent concentrations of inhaled particles
C_L	Concentration in lipid
C_P	Concentration in particle associated
C_V	Concentration in vegetation
cm	Centimetre
cm^3	Cubic centimetre
C_W	Compound concentration in water
°C	Degree Celsius
DI	Daily intake
DI_{IHG}	Daily intake of inhaled gas
DI_{IHP}	Daily intake of inhaled particles
DI_T	Total daily intake
dt	Time change
DWC	Daily water consumption
ED	Exposure duration
EF	Exposure frequency
f	Fugacity of compound
F	Particle phases concentration of compound
F_L	Fugacity of leaf
FID	Flame ionization detector
f_W	Fugacity of water
g	gram
g-	Gas phase of compound
GC	Gas chromatography
h	Hour
h^{-1}	Per hour
H	Henry's law constant
HPLC	High performance liquid chromatography
J	Joule
$\hat{J}$	Junge's constant
k	kilo
K	Degree kelvin
Kg	kilogram
KR	Kasemraj

k_1	Uptake rate constant
k_2	Clearance rate constant
kPa	Kilo Pascal
K_{AW}	Air-water partition coefficient
K_B	Biota-water partition coefficient
K_{BA}	Blood-air partition coefficient
K_{BL}	Biota lipid-water partition coefficient
K_{FW}	Fish-water partition coefficient
K_{HA}	Hair-air partition coefficient
K_G	Gas-particle partition coefficient
K_{LA}	Leaf-air partition coefficient
K_{LLA}	Leaf lipid-air partition coefficient
K_{LLW}	Leaf lipid-water partition coefficient
K_{LW}	Leaf-water partition coefficient
K_{OA}	Octanol-air partition coefficient
K_{OW}	Octanol-water partition coefficient
K_P	Particle-gas partition coefficient
K_{VA}	Vegetation-air partition coefficient
K_{VLA}	Vegetation lipid-air partition coefficient
K_{WA}	Water-air partition coefficient
L^{-1}	Per litre
L	Length of exposure
m^2	Square metre
m^3	Cubic metre
MFO	Mixed-function monooxydase
min	Minute
mm	Millimetre
mol	Mole
M	Molar
MS	Mass spectrophotometer
MR	Molar refraction
MW	Molecular weight
n	amount of substance in mole
N	Number of sample
na	Not available
ND	Non detectable
nd	No data
ng	Nanogram
P	Pressure of a substance
Pa	Pascal
PP	Pongpetr
PW	Patumwan
P^o	Compound saturation vapour pressure
P^o_L	Vapour pressure for subcooled liquid
ppb	Part per billion
ppm	Part per million
p-	Particle phase
QSAR	Quantitative structure activity relationships
R	Gas constant
Ref	Reference
RP	Relative Potency
r	Fraction of particle retained in the lungs
r^2	Correlation coefficient
RV	Respiratory volume
S	Aqueous solubility
SD	Standard deviation
SK	Sapankwai
SOC	Semivolatile organic compounds

s^{-1}	Per second
S_W	Supercooled liquid aqueous solubility
T	Absolute temperature
t	Exposure time
TEF	Toxic equivalency factor
TEQ	Toxicity equivalent concentration
T_M	Melting point of compound
T_R	Reference temperature
TSP	Total suspended particulates
V	Volume of air
VP	Vapor pressure
VOC	Volatile organic compounds
wt	Weight
W_A	Weight of GFF before use
W_B	Weight of GFF after use
y	Y-axis intercept
Z	Fugacity capacity constants of a compound
Z_L	Fugacity capacity constants in leaf
Z_W	Fugacity capacity constants in the water

GREEK SYMBOLS

μ	Micron
ρ	Density
Θ	Total suspended particulate surface area
Φ	Compound fraction associated with particles

COMPOUND ABBREVIATIONS

ACE	Acenapthene
ACY	Acenapthylene
ANT	Anthracene
ATT	Anthranthene
BaA	Benz(a)anthracene
BACY	Benzacenapthylene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BcPHE	Benzo(c)phenanthrene
BeP	Benzo(e)pyrene
BghiF	Benzo(ghi)fluoranthene
BghiP	Benzo(ghi)perylene
BjbF	Benzo(jb)fluoranthene
BjF	Benzo(j)fluoranthene
BkF	Benzo(k)fluoranthene
CHC	Chlorinated hydrocarbons
CHR	Chrysene
CLA	1-chloroanthracene
COR	Coronene
CPY	Cyclopenta(cd)pyrene
-C13	Thirteen chlorines in the molecule
DbacA	Dibenzo(ac)anthracene
DbahA	Dibenzo(ah)anthracene
DbaeP	Dibenzo(ae)pyrene
DbahP	Dibenzo(ah)pyrene
DbaiP	Dibenzo(ai)pyrene
DbaeF	Dibenzo(ae)fluoranthene
DbahF	Dibenzo(ah)fluoranthene
DbaiF	Dibenzo(ai)fluoranthene

DbalF Dibenzo(al)fluoranthene

DbahP Dibenzo(ah)pyrene

DbaiP Dibenzo(ai)pyrene

DMbaA Dimethylbenz (a) anthracene

DDT Dichlorodiphenyl trichloroethane

FLO Fluorene

FLU Fluoranthene

HCB Hexachlorobenzene

HCH Hexachlorocyclohexane

IP Indeno(1,2,3,-cd)pyrene

MA Methylanthracene

5MC 5-Methylchrysene

MCL 3-Methylcholanthrene

MFLU Methylfluoranthene

1MN 1-Methylnapthalene

2MN 2-Methylnapthalene

1MPHE 1-Methylphenanthrene

NAP Napthalene

PAH Polycyclic aromatic hydrocarbons

PCB Polychlorinated biphenyls

PCDD/F Polychlorinated dibenzodioxin/ furan

PER Perylene

PHE Phenanthrene

PYR Pyrene

2PN 2-Phenylnapthalene

QCB Pentachloro benzene

TCN 1,2,3,4,- tetrachloronapthalene

TRI Triphenylene

ORGANIZATION ABBREVIATIONS

ATSDR Agency for Toxic Substances and Disease Registry

IARC International Agency for Research on Cancer

NRC National Research Council

ONEB Office of National Environment Board

UNEP United Nations Environment Program

USEPA United States Environmental Protection Agency

WHO World Health Organization

Chapter 1
Introduction

1.1 Background

In the atmosphere, polycyclic aromatic hydrocarbons (PAH) can be present as a mixture of thousands of their members at varying concentrations depending on the conditions of combustion. PAH with higher molecular weight (>218) are mostly found adsorbed to particles while those with lower molecular weight are present in the gaseous phase (Jongeneelen, 1997; Westerholm et al., 1988). For example, one study has reported that about 19 PAH are adsorbed in particulate matters in concentrations ranging from 120 to 4000 mg kg^{-1} (Jenkins et al., 1996). A number of researches has indicated that atmospheric conditions (e.g. temperature, humidity, precipitation) and properties of the compound (e.g. volatility) influence on their particle and gaseous partitioning behavior (Lee and Tsay, 1994; Pistikopoulos et al., 1990).

The measurement of atmospheric PAH is often accomplished by using a glass fibre or a Teflon membrane filter followed by an adsorbent such as polyurethane foam (PUF) or Tenax through which the air is drawn by high-volume pumps (e.g. Lee and Tsay, 1994; Davis et al., 1987; Keller and Bidleman, 1984). Such methods require sophisticated equipment, i.e., an air sampler which is costly and would give underestimated results by the presence of oxidants in the air. (e.g. Lodovici et al., 1994). Since vegetation acts as an atmospheric sink of compounds, plants can be considered a promising biomonitoring tool. This accumulation characteristic of the compounds in plants can be described similarly to that occurs in fish from the water which involves the partitioning of the compound between the phases. Several studies dealing with partitioning behavior of organic compounds between vegetation and air were reported. These studies include accumulation patterns between the air and the higher and lower plants under different atmospheric transport and atmospheric conditions (Thomas et al., 1984). In addition, correlations relating concentrations in roots, stem, and foliage to those in the soil and in the air were also developed (Paterson et al., 1991a). Furthermore, many researches were carried out to establish the equilibrium and kinetic characteristics in air-

leaf partitioning of gaseous organic chemicals (Paterson et al., 1991b). Some examples include Lodovici et al. (1994) who used plants as a biomonitor of atmospheric PAH. Mü ller et al. (1994) who developed a multi compartment model to predict the vegetation-air partition coefficients and Simonich et al. (1994) who investigated the vegetation-air partitioning of PAH throughout the growing seasons under natural condition. The results have supported the relationships between concentrations in the terrestrial plants and in the atmosphere. As well as, the potential of terrestrial plants in the prediction of the concentrations in the atmosphere was evidenced. However, information on the behavior of PAH in the vegetation-air system is limited. The risk posed by exposure to these contaminants in Bangkok is also lacking. Thus, this work focuses on evaluation on plant for the potential of biomonitoring airborne organic pollutants and estimation of cancer risk as a consequence of exposure to these PAH mixture.

1.2 Objectives

1.2.1 To evaluate partitioning behavior of airborne PAH in plant leaf and in the air.

1.2.2 To investigate atmospheric concentrations of PAH in four Bangkok roadsides.

1.2.3 To evaluate the potential of plant leaf as a biomonitor

1.2.4 To evaluate cancer risk posed by inhalation of PAH.

1.3 Strategies

1.3.1 Strategy for Objective 1

In order to achieve partitioning behavior of PAH between the plant leaf and the air, plant leaf-water partition coefficient is to determine. The method is based on a fugacity concept describing distribution of a solute between phases. The concept refers to the fugacity (f) in each phase is equal at equilibrium. Thus,

$$f_L = f_W \quad (1.1)$$

where f_L and f_W are fugacity of the leaf and the water respectively. Then,

$$C_L / Z_L = C_W / Z_W \quad (1.2)$$

where C_L, C_W are concentrations in the leaves and in the water and Z_L , Z_W are fugacity constants in the leaves and in the water. Rearrange and substitute $Z_L / Z_W = K_{LW}$, then

$$C_L / C_W = Z_L / Z_W = K_{LW} \quad (1.3)$$

where K_{LW} is leaf-water partition coefficient. Similarly, leaf-air partition coefficient (K_{LA}) can be obtained by introducing a term of C_W / C_W, then

$$C_L / C_W * C_W / C_A = K_{LA}. \quad (1.4)$$

Since C_A / C_W is Henry's law constant (H), therefore

$$K_{LA} = C_L / (C_W * H) \quad (1.5)$$

1.3.2 Strategy for Objective 2

Collecting air samples for 24 h in each study area using high volume air sampler to determine total suspended solids (TSP). The compound gas phase obtained is calculated from the relationship of the particle-gas partition coefficient (K_p), TSP, gas (A) and particle (F) concentrations of the compounds as follows (Pankow, 1998; Pankow, 1987; Yamasaki et al., 1982).

$$K_p = (F/TSP)/A \quad (1.6)$$

Thus, total concentrations, both gas and particle phases of the compounds can be obtained.

1.3.3 Strategy for Objective 3

PAH concentrations in the leaves and in the air at the same site are measured. Atmospheric concentrations of test compounds derived from concentrations in the leaves are plotted against the atmospheric concentrations directly obtained from air sampler to evaluate the relationship.

1.3.4 Strategy for Objective 4

Though, PAH naturally occur in complex mixtures, only 16 PAH are employed in the study. However, risk attributed by individual compounds in the mixtures will be established using toxic equivalency factor approach, which is recommended by the USEPA. Total exposure is quantified first in term of total daily intake taking into account for bioavailability of exposure pathway. Then, excess cancer risk due to exposure to PAH mixtures is estimated using calculated chronic daily intake and the potency factor value in the literature.

Chapter 2
Literature Review

2.1 Characteristics of plant leaves

2.1.1 Leaf Structure

The leaf is one of three basic parts of plants, which comprise the roots, the stems and the leaves. Generally, a complete leaf is composed of the broad thin blade, cylindrical petiole and small appendages of stipule located at the base of the petiole (Parker R. 1998). These parts identify the species of the plant. Its thin and broad structure allows for more light interception useful for photosynthesis and reservoir deposit of atmospheric pollutants. Cross section of leaf can be seen three layers of mesophyll, the upper and the lower layers. The upper layer forms tightly packed elongated palisade cells where photosynthesis occurs mostly. Loosely packed chloroplast containing cells are of the lower layer. The mesophyll is located between an upper and lower epidermis (Figure 2.1) (Mansfield and Michael, 1976). The epidermis forms a continuous layer over the surface except the modified epidermal cells known as stomata, where gas and vapor exchange occurs. Each stoma is surrounded and governed by guard cells to open during daytime. Air in the internal of the leaves is connected to outside air via stomata. The epidermal cells are generally coated with a cuticle, which is resistant to diffusion of gases including carbon dioxide and water and at the same time absorb VOC from the atmosphere. Leaves exhibit variety of form and could be influenced in their development by environmental factors, e.g, light, water content, carbon dioxide content.

2.1.2 Composition

Only relevant compositions are reviewed as following.

Water

Water enters the plant via the root and is transported throughout the plant carrying nutrients and metabolites, which are the products of the chemical reactions or

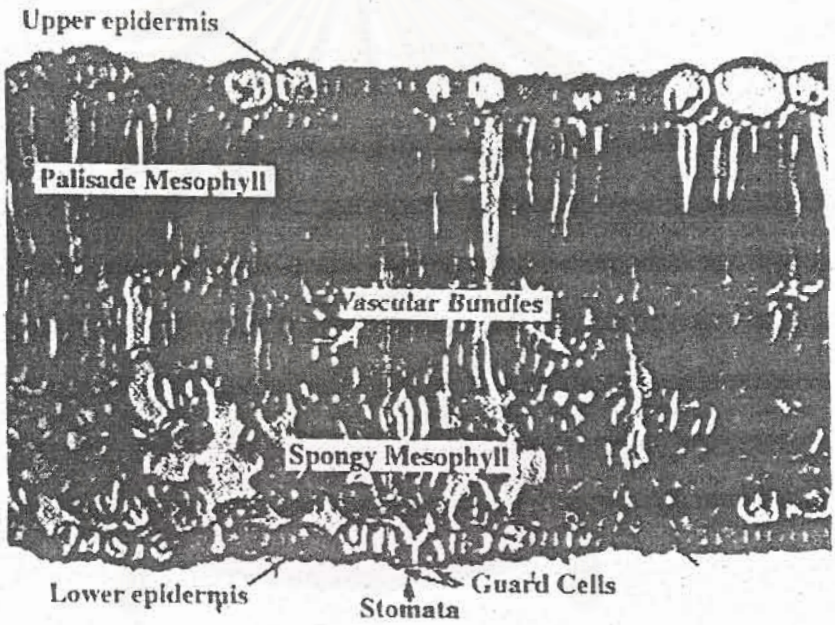


Figure 2.1 A cross section of plant leaf

(source: http/www.umanitoba.ca)

metabolism of the plant, through translocation process. Thus, water is essential to plant since it also transports sugar produced by leaves during photosynthesis to all parts of the plant. On the contrary, water can be lost through all of their parts especially through the stomata of the leaves during transpiration, which can be accounted as major loss (90% loss).

Lipids

Lipids in plant constitute to the structure of membranes known as phospholipids and glycolipids, while another group contributes as a protective coating known as waxes. And the rest of lipids are fats and oils, which are important as reserve food materials (Salisbury and Ross, 1975). Generally lipids have however a major amount of long chains saturated aliphatic component (i.e. alkanes, alcohols, acids, aldehydes, acetals and ketones) and the latter being mainly oleic, linoleic, linolenic, and palmitoleic acisd. The remaining components are the aromatic and phenolic compounds. The phospholipids are phosphate containing lipid comprise both water insoluble fatty acids and water soluble portion, e.g. glycerol, choline, serine. They constitute in various membranes, e.g. chloroplast, mitochondria, nuclear membrane. The glycolipids are hydroxyl group of glycerol attached by glycosidic bond to a sugar, particularly galactose or glucose. They are important for green leaves. Cuticles of the leaves have waxes in major amount. Surface waxes can also be found in the stem, bark and possibly the root surfaces. The surface waxes are normally complex mixtures consisting mainly of a single compound and a wide range of different classes of components. Fats and oils are found in small amounts in leaves about 0.5-2% on the dry weight basis but much higher amounts in seeds (Salisbury and Ross, 1975).

Carbohydrates

Carbohydrates in plant are produced from photosynthesis and constitute about 50-80% on dry weight basis. They are important for plant as food reserves and components of the structure of plant (e.g. cell wall). Carbohydrates comprise carbon, hydrogen and oxygen. They can be classified into monosaccharides, disaccharides and polysaccharides (Parker R, 1998, Salisbury and Ross, 1975).

Proteins

Proteins are essential to life including plants. Proteins comprise sequences of amino acids linked together by peptide bonds. This primary structure is coiled in the form of a helix and stabilized by hydrogen bond to shape into polypeptide. Protein synthesis is carried out in nuclei, mitochondria and chloroplasts, as well as in the cytoplasm surrounding them. Light is known as stimulator for the protein synthesis occurring in chloroplasts. It is believed that all plant tissues could synthesize their own proteins. Plant organs that are growing, i.e. roots, leaves, stems and seeds have very fast synthesis of protein (Salisbury and Ross, 1975). In leaf cells, about 40-50% total protein on a dry weight basis is found inside the chloroplasts.

2.2 Behavior and Accumulation of Semivolatile Organic Compounds in Plants

Uptake of atmospheric lipophilic compounds from the air in most terrestrial plants can be accounted as a major pathway for bioconcentration due to root absorption is far less significant particularly for compounds with log K_{ow} more than 3.5 (Hülster and Marschner, 1993; Ryan et al., 1988; Briggs et al., 1982). These lipophilic compounds present in the soil may be absorbed by the root. However, absorption deep in the root would be limited and so is compound transport to other part of the plant, unlike hydrophilic compounds. Though, there is an exception on roots of dicotyledoneae, e.g. carrot has shown unexpected higher bioconcentration factors of HCB both in the leaves and roots comparable to monocotyledoneae (barley, oat, maize) (Schroll and Scheunert, 1992). Studies of plant uptake have been carried out widely with SOC and VOC and a number of these plants are conclusively evident for their potential biomonitoring capacity. For example, moss for CHC (Bacci et al., 1986), conifer needles for PCDD/F (Reischl et al., 1987), pine needle for CHC (Gaggi et al., 1985), moss for PAH (Thomas et al., 1984) and sugar maple and pine for PAH (Simonich and Hites, 1994). Furthermore, interest of plant uptake is due to its role as an exposure pathway to animals and eventually to humans (Paterson et al., 1991a; Calamari et al., 1987). In most situations, compound gas phase is believed to be responsible for the vegetation-air partitioning process (BÖhme et al., 1999; Reischl et al., 1989; Simonich and Hites, 1994; Tolls and McLachlan, 1994; Bacci et al.,

1990a). The gas phase and that of particle phase which is deposited on plant surface is generally taken up by cuticle wax or lipid layer (cuticular lipid and cellular lipid) on the plant surface through passive diffusion process (Connell, 1990). In rare case, PAH in aerosol or droplet is taken up by additional processes via penetration and deposition in the cuticle. Lately, McLachlan (1999) has suggested that the processes responsible for the bioconcentration in plants from the air depend on the form of compounds in the atmosphere. In his experiment PAH, PCB, PCDD/F with a wide range of log K_{OA} were tested. The study reveals three key mechanisms of bioconcentrating process: equilibrium partitioning with compounds having log K_{OA} < ~9, kinetically limited gaseous deposition of those having 9 < log K_{OA} < 11, and deposition of those particle bound of log K_{OA} >11. Similar results are obtained from Kaupp (1996) who has found that bioconcentration of high MW PAH (>5 rings) in corn from the air is through particle deposition. Parallel results have recently indicated that various high MW PAH, i.e. BbF, BaP, IP, BghiP, DBahA, COR were bioconcentrated in plants via particle bound deposition (BÖhme et al., 1999). Other similar physical chemical property to PAH, e.g. PCDD/F exhibited similar mechanisms (Welsch-Pausch et al., 1995).

Octanol-air partition coefficient property of SOC/VOC influences on the attainment of equilibrium. McLachlan (1991) has demonstrated that compounds with log K_{OA} <9 which were considered to be dominant in the gas phase may not reach equilibrium due to gas phase varied on time and temperature. Higher K_{OA}, which is dominant by limited gas phase, may need several months or years to reach steady state (McLachlan, 1999). An investigation of Simonich and Hites (1994) in the vegetation-air system of sugar maple and pine under natural conditions confirms aforementioned finding and indicated an influence of temperature on the system. McLachlan et al. (1995) have further suggested that since plant lipid-air system is analogy to the octanol-air partitioning which is highly dependent on ambient temperature, temperature dependence of the plant-air system can be expected. At equilibrium, the gas exchange between the plant lipid and the atmosphere can be expressed as

$$K_{VA} = C_V C_A^{-1} \qquad (2.1)$$

where K_{VA} is the vegetation-air partition coefficient, C_V and C_A are the equilibrium concentrations of a chemical in the vegetation and the atmosphere. Similar to bioconcentration in fish, bioconcentration in plant from the air can be alternatively approached using a kinetic model, which is based on uptake, and clearance rate constants assuming a single compartment in plant and first order kinetic occurred in the exchange process between the plant and the air. Thus, rate of concentration changes in the vegetation (C_V) with time is described by

$$dC_V / dt = k_1 C_A - k_2 C_V \quad (2.2)$$

where k_1 and k_2 are the uptake and clearance rate constants (h^{-1}). At equilibrium, $dC_V / dt = 0$. Therefore,

$$k_1 k_2^{-1} = C_V C_A^{-1} = K_{VA} \quad (2.3)$$

An additional entry route for gas phase to transfer between the plant and the air is via stomata which is important particularly during daytime (Riederer, 1990). However, lipid layers on the surface of foliage in most plants are usually considered to be the partitioning site (Paterson et al., 1991a; Connell et al., 1990; Sabljic et al., 1990; Travis et al., 1988). As a general rule, with an increasing lipid content in the vegetation, an increasing concentration of PAH in plant would be expected (Simonich and Hites, 1994). BCF value in plant from the air can be due to the plant lipid which varies on the age of leaves, temperature and radiation intensity (Schneder, 1990). Lower BCF than expected may also be attributed from metabolism in plants once compounds taken up similar to the fish-water system (Riederer, 1990), however this may last for weeks to months leading to less effective on the BCF values (Hauk et al., 1994; Bacci et al., 1990b). Interspecies difference on the BCF values has been recently examined in maize, sunflower leaves and eight grass species using PCB, PCDD/F, chlorobenzene and PAH (BÖhme et al., 1999). The results indicate BCF difference over species is about >30 for VOC with log K_{OA} < 9. For compounds with 9 < log K_{OA} < 11 and log K_{OA} > 11, the difference is reduced to <4. This may be due to their processes dominated by kinetically limited gaseous deposition and

particle bound deposition respectively. Apart from compound specific, the variation can be affected by the horizontal surface area per unit plant volume (BÖhme et al., 1999).

2.3 Human Exposure to Atmospheric PAH

2.3.1 Behavior of Commonly Occurring PAH

Sources

There are two main sources of PAH; natural source and anthropogenic source. The latter is dominant and by far the most important environmental problem of its kind. PAH members can be as high as thousands. They are formed from incomplete combustion of organic materials and different species are produced with temperature being the major factor in determining the mixture of PAH. Natural sources of PAH include petroleum, coal and shale oil. Most of PAH in coals are tightly bound in the structure and hard coal is likely to contain higher concentrations than soft coal, e.g. lignite (WHO, 1998). Bitumen and condensate of bitumen fumes have been reported to contain about 180 PAH including unsubstituted and alkyl-substituted PAH (Östman and Colmjo, 1988). In addition, base oils, aromatic oil, minerals oils, crude oil and coal tars are well known for the presence of PAH (Pullen and Scammells, 1988; Agarwal et al., 1986). In some geological areas, volcanoes and forest fires are major natural sources of PAH. Various PAH are emitted into the atmosphere from fossil-fueled power plants and adsorbed on fly ash (Eiceman and Vandiver, 1983). Coal-fired power plants emitted mainly 2-3 ring PAH, i.e. NAP, PHE and their mono and dimethyl derivatives (WHO, 1998). Industries such as coke production, steel manufacturing, aluminum smelters, refineries and coal liquefaction plants are major anthropogenic sources of PAH in many countries. Estimates of 0.3 ton BghiP and 24 ton NAP have been produced from aluminium smelters in the Netherlands in 1988 (Slooff et al., 1989 in WHO, 1998). Various levels of PAH including BkF, BaP, FLU, PER and BghiP have been measured in the atmosphere which is 3.5 km distant from a steel mill complex (Potvin et al., 1981). Numerous PAH are detected from municipal incinerators. A wide range of PAH, e.g. BghiP, COR, FLO, IPY, PYR, and PER with the concentrations of 0.42, 0.04, 0.58, 0.18, 1.6, 0.18, $\mu g\ m^{-3}$ are formed in the stack gases from British municipal incinerator (Davies, et al., 1976). Incomplete combustion from domestic activities such as

vehicle exhaust, tobacco smoke, refuse burning, residential heating can result in significant concentrations of PAH in the atmosphere. Factors influencing the release of PAH from automobiles include aromaticity of fuel, air/fuel ratio, driving cycles (Westerholm et al., 1991; Stenberg, 1983). PAH emission from vehicles equipped with catalytic converters is reduced by a factor of 40 as compared to that without catalytic converters (Hagemann et al., 1982). PAH profiles in the exhaust gases from petrol and diesel fueled vehicles are still discrepancy. For example, BaP was released at a lower rate from petrol fuelled vehicles with catalysts (2 $\mu g\ km^{-1}$) than diesel fueled vehicles with catalyst (5 $\mu g\ km^{-1}$) which is in contrast to other studies that showed diesel fueled vehicles produce higher PAH than petrol fueled vehicles (WHO, 1998).

Physicochemical Properties

PAH are lipophilic compounds comprising two or more benzene rings interlinked in various arrangements (Hutzinger, 1980). In natural, PAH do not occur as a single compound, on the contrary, they are found in mixtures. They are airborne compounds and in the forms of gas and/or particle. The physicochemical properties of PAH are governed by their sizes and shapes of the molecular structures (Neff, 1979). An increase in ring numbers is generally accompanied by an increase in both boiling point and melting point but a decrease in water solubility. PAH undergo some chemical reactions, i.e. oxidation, reduction, electrophilic substitution. The bay region in the PAH structure is reactive and produces electrophiles. The types and degree of reactions are therefore influenced by angularity and linearity of the compound structure (Lee, 1981). PAH of different molecular weights vary substantially in their behavior and distribution in the environment and their effects on biological systems. The relevant physicochemical properties of PAH are summarized in Table 2.1.

Octanol-Water Partition Coefficient (K_{ow})

K_{ow} describes compound concentrations in the octanol to that in the water. The K_{ow} is dimensionless if the concentrations of the compound in both phases are measured in the same units of mass per unit volume (Connell, 1994). The K_{ow} for a compound is

Table 2.1 Relevant physicochemical properties of test compounds (WHO,1998)

Compounds	Molecular Formula	Molecular Weight (MW)	Boiling Point (BP), ^{o}C	Melting Point, ^{o}C	Vapor Pressure (VP), Pa at 25^{o}C	S_L**at 25^{o}C ($g\ m^{-3}$)	log K_{ow}**	H at 25^{o}C ($Pa\ m^3 mol^{-1}$)
NAP	$C_{10}H_8$	128.2	217.9	81	10.4		3.4	48.9
ACY	$C_{12}H_8$	152.2		92-93	8.9×10^{-1}	18.5	3.55	11.55
ACE	$C_{12}H_{10}$	154.2	279	95	2.9×10^{-1}	15.1	3.92	14.79
FLO	$C_{13}H_{10}$	166.2	295	115-116	9.0×10^{-2}**	3.56	4.18	7.75
ANT	$C_{14}H_{10}$	178.2	342	216.4	0.001**	6.24	4.54	6.59
PHE	$C_{14}H_{10}$	178.2	340	100.5	1.6×10^{-2}	1.70	4.57	3.98
FLU	$C_{16}H_{10}$	202.3	375	108.8	1.2×10^{-3}	2.63	5.22	0.96
PYR	$C_{16}H_{10}$	202.3	393	150.4	6.0×10^{-4}	0.23	5.18	0.52
BaA	$C_{18}H_{12}$	228.3	400	160.7	2.8×10^{-5}	0.37	5.91	0.81
CHR	$C_{18}H_{12}$	228.3	448	253.8	4.0×10^{-6}***	0.038	5.86	0.45
BbFLU	$C_{20}H_{12}$	252.3	481	168.3	5.0×10^{-7}***		5.8	0.051

[1] 20 C * Shiu and Mackay, 1997 ** Mackay et al, 1992 *** Ma et al, 1990. S_L – water solubility of the subcooled liquid, H – Henry's law constant

Table 2.1 (Continued)

Compounds	Molecular Formula	Molecular Weight (MW)	Boiling Point (BP) , °C	Melting Point , °C	Vapor Pressure (VP), (Pa at 25°C)	S_L** at 25°C ($g\ m^{-3}$)	log K_{OW}**	H* at 25°C ($Pa\ m^3\ mol^{-1}$)
BaP	$C_{20}H_{12}$	252.3	496	178.1	7.0×10^{-7}**	0.12	6..04	0.034
BkFLU	$C_{20}H_{12}$	252.3	480	215.7	1.3×10^{-8} [1]	0.063	6.00	0.016
IP	$C_{22}H_{12}$	276.3	536	163.6	1.3×10^{-8} [1]	-	6.58	-
DahA	$C_{22}H_{14}$	278.4	524	266.6	1.3×10^{-8} [1]	0.15	6.50	0.0076
BghiP	$C_{22}H_{12}$	276.3	545	278.3	1.4×10^{-8} [1]	0.081	6.75	0.027

[1] 20 °C * Shiu and Mackay, 1997 ** Mackay et al, 1992 *** Ma et al, 1990

S_L – water solubility of the subcooled liquid, H – Henry's law constant

constant under defined conditions and usually measured at 20° or 25 ° C. However, K_{ow} is slightly temperature dependence with the changed rate of 0.001 to 0.01 log K_{ow} units per degree and can be positive or negative depending on the solute (Connell, 1994; Lyman, 1982; Hutzinger, 1980). K_{ow} is a common property mostly used in the investigation of quantitative structure activity relationships (QSAR) with bioconcentration. The K_{ow} values can be obtained via either measurement or calculation. The experimental measurement methods include traditional shake flask method, chromatographic methods using techniques of paper, thin layer, gas-liquid, high performance liquid chromatography (HPLC). There are various methods available to calculate K_{ow} values with varying reliability (Lyman, 1982; James, 1986). Some methods use molecular characteristics such as molecular surface area or molecular volume or from the relationship between aqueous solubility and the K_{ow} value to calculate K_{ow} value (Connell, 1994; Warne et al., 1990). The K_{ow} plays an important role in determining the partitioning behavior of persistent lipophilic organic compounds (i.e. PAH, biphenyl, PCDD/F) in the environment. It is also a useful measure for the tendency of a compound to sorb in biota lipid or other lipoid substances. PAH have log K_{ow} values lying in the range of about 3.4 (NAP) to 7.3 (DBaiP) (WHO, 1998). Thus, PAH with log K_{ow} < 6.5 would be expected to bioconcentrate to an extent depending on their persistence in the media since a range of log K_{ow} 2 to 6.5 is generally considered to be the range for lipophilic compounds (Chessels et al., 1992; Connell and Hawker, 1988). A decline in bioconcentration would occur in PAH with log K_{ow} > 6.5. As a general rule PAH with lower log K_{ow} values would concentrate in biota lipid or lipoid substances such as humic acid in the soil and sediment to a lesser extent than that of higher log K_{ow} values (Mackay and Shiu, 1981; Means et al.,1980; Banerjee et al.,1980).

Henry's law constant (H)

H describes a ratio of a compound abundant in the gas phase which is expressed as partial pressure in the vapor (Pa or atm or torr) to that in the aqueous phase (mole fraction or mole m^{-3}) at equilibrium (Schwarzenbach et al., 1993; Mackay and Shiu, 1981). It is often convenient to express H as a dimensionless by dividing H values expressed in kPa m^3 mol^{-1} by RT which is normally in the range of 2.2-2.5 kPa m^3 mol^{-1} (Mackay and Shiu,

1981). H is often considered as the air-water partition coefficients (K_{AW}), which is the ratio of concentrations of a compound in the gas phase to that in the water phase. H can be obtained by experimental measure or calculation from vapor pressure and aqueous solubility. The predicted value can be less reliable when vapor pressure and aqueous solubility are not measured under the same conditions since both properties are strongly dependent on temperature (Hulscher et al., 1992; Kollig and Kitchens, 1990). Temperature dependence of H is of importance in assessing the fate of the compounds. Mackay and Shiu (1981) have estimated that H can reach double the value when the temperature changed from 10° to 65°C. Recalculation of H from one temperature to another temperature is usually integrated with van't Hoff equation (Maagd et al., 1998). However, the recalculation may produce an uncertainty since the temperature dependence is compound specific (Maagd et al., 1998; Hulscher et al., 1992). H available in the literature yields a considerable variation (Mackay and Shiu, 1981). Maagd et al. (1998) have shown that at 20 °C, Henry's law constant lied in a range of 37-48 Pa m^3 mol^{-1} for NAP, 48-65 Pa m^3 mol^{-1} for FLO, 2.9-4.6 Pa m^3 mol^{-1} for PHE and 0.9-2.0 Pa m^3 mol^{-1} for PYR. There is an inverse relationship between H and molecular volume of the compound. A linear relationship has been observed by Maagd et al (1998) between H and molecular volume in contrast to other study investigated by Mackay et al. (1992) due to different compounds under the study. Compounds with H < 10^{-7} atm cm mol^{-1} are considered less likely to partition into the gas phase. Unlike those with H>10^{-5} atm cm mol^{-1}, the compounds tend to escape from the water phase to the air phase.

Vapor Pressure (VP)

PAH have relatively low VP for low MW compounds and very low VP for high MW compounds. For example, at 25 °C, NAP which is the lowest MW member (MW=128.2) has vapor pressure of 1.09 x 10^{-2} kPa whereas higher MW, e.g. PHE (MW=178.2) has 2.67 x10^{-5} kPa (see Table 2.1) and BaP (MW=252.3) has 6.67 x 10^{-13} kPa. As a general rule, the vapor pressure decreases with an increasing MW and molecular size. Thus, the vapor pressure can be considered as an influencing factor governing the fate of the compounds in the atmosphere. However, vapor pressure can be double if temperature rose from 10°

to 20 ^{o}C (Mackay and Shiu, 1981). To overcome the temperature dependence of vapor pressure, it is desirable to apply the value of VP at the same experimental temperature.

Aqueous Solubility

PAH are generally characterized as " low to very low" aqueous solubility (Mackay et al., 1992). The aqueous solubility decreases with increasing MW and molecular size. High relationship between aqueous solubility and molecular volume of PAH has been reported (Maagd et al., 1998; Lande and Banerjee, 1981). A thermodynamic analysis of the relationships between molecular size, hydrophobicity, aqueous solubility and octanol-water partition coefficient has suggested that the low aqueous solubility be primarily as a result of unfavorable hydrophobic interaction between the solute and water (Zhang and Gobas, 1995). The accurate data have been recently established due to the advent of gas and liquid chromatography. Aqueous solubility can be obtained from both measurement and calculation. There are a variety of experimental methods measuring the aqueous solubility including mechanical mixing method, optical method, eluting technique.

The aqueous solubility of PAH at 25 ^{o} C are ranged from 2.48 x 10^{-4} mol L^{-1} for NAP to 4.67 x 10^{-10} mol L^{-1} for COR which is the highest MW PAH of environmental interest. The solubility of test compounds is presented in Table 2.1.

2.3.2 Exposure, Absorption, Metabolism and Excretion

Main human exposure to PAH is generally through the lungs by inhalation of PAH-containing aerosol or particles, the gastrointestinal tracts by ingestion of contaminated food or water and the skin by dermal contact of PAH-containing soils. Since a basic structure of cell membrane consists of a lipidbilayer (Klaassen and Rozman, 1991). PAH, which are lipophilic compounds, dissolve readily in and transport through the external and internal of the lipoprotein membranes of mammalian cells. Once inhaled, absorption starts taking place through the pulmonary epithelia. This was evident from experimental results on rats (Vainio et al., 1976). Removal mechanisms could occur particularly an entry of particles. Inside lining of respiratory system contains mucous that entraps particles and cilia that pushes particle-associated mucous down to the mouth where it is eventually

swallowed into the gastrointestinal system. Conclusively, inhaled PAH sorbed particles can either be absorbed or enter the gastrointestinal tract by mucociliary clearance mechanisms. The clearance rate depends on PAH involved and particle size onto which PAH are sorbed (Creasia, et al., 1976; Henry and Kaufman, 1973). Large particles, i.e. diameter of 5 μm may be absorbed through the nasal epithelium or dissolve in the mucous and be carried to the pharynx and ultimately to blood. Particles of 2-5 μm in diameter are mainly deposited in the tracheabronchiolar regions of the lungs where a self-cleaning system occurs through mucous removal or phagocytosis or other processes. However, particles may eventually be swallowed, absorbed into blood and absorbed from the gastrointestinal tract (Klaassen and Rozman, 1991). Fine particles of 1 μm or smaller penetrate to the alveolar sacs of the lungs. They may be absorbed into the blood or alveolar sacs so do the gases and liquid aerosol. It is uncertain that the smaller size of particles fastens the clearance mechanism. Apart from mucous removal, compounds and their metabolites can be reduced or cleared by metabolism. In the studies of dogs and monkeys, BaP can be metabolized by the epithelial lining of nasal cavities (Petridou-Fischer et al., 1988). Similar results have been reported for CHR (Falk et al., 1958). For PAH with high water soluble tend to retain in the nose associated with the mucous. When the compounds absorbed by the lungs, they can be rapidly removed by the blood counting on the VP. Partitioning of inhaled PAH between two media, the air and the blood, consists of absorption stage in the lungs and distribution stage between the blood and tissue. At equilibrium, ratio of concentrations of PAH in the blood and in the air is constant and is known as blood-gas partition coefficient and unique for each PAH (Hee, 1993). Compounds with high blood-gas partition coefficient usually require longer time than those with low ratios to obtain the equilibrium with blood (Klaassen and Rozman,1991). Respiratory rate is a limiting factor for this ratio. Also, compounds with low blood-air partition coefficients are not all absorbed but some are breathed out and those with high blood-air partition coefficients are transferred effectively from alveolar spaces into the blood (Hee, 1993). A gas dissolved in blood is carried to tissues until equilibrium is reached, then a partition coefficient for the tissue-blood is obtained. Time required to reach the blood-air and blood-tissue equilibriums depends on aqueous solubility and

tissue affinity of compounds. Gastrointestinal tract (GI) is the most important site in regard to its major human intake pathway. The GI tract consists of the mouth, esophagus, stomach, intestine and rectum. Absorption can occur along the entire GI but the stomach and the intestine walls are the main absorption sites. This has been evident from tumors developed in rats after intracolonic administration of DMBaA (Huggins et al., 1961 in WHO, 1998). The absorption from GI depends on physicochemical properties of compounds such as lipophilicity. Generally, lipophilic compounds are more rapidly soluble and extensively absorbed by the GI. Particles associated with azo dye can be absorbed by the GI epithelium and taken up by the duodenum, though the diameters are as large as several thousand nanometers (Klaassen and Rozman, 1991). Similar finding with PAH has not been reported. PAH absorbed mucous can diffuse through the intestinal lining (Ree et al., 1971). Experimental results in rats have shown that the absorption rate increase with the presence of bile, however the absorption rate varies on PAH involved (WHO, 1998). The absorption is also influenced by diet components. Oral administrations of 8.7 μg ^{14}C-BaP in rats have shown the influence of food intake. Soya bean oil increases absorption rate while rice flake, potato flake, bread, and lignin suppress (WHO, 1998). The amount of compounds entering the blood stream is closely related to the absorption and biotransformation capacity of the GI cells. Prior entry to the systemic circulation, the compounds can be extracted by the liver and excreted into the bile. This is usually known as a pre-systemic elimination.

The third exposure pathway is through the skin and appendage absorption. This pathway is important particularly for organic compounds, though the total cross sectional areas (sweat glands, sebaceous gland and hair follicles) accounts only 0.1-1 % of the total skin surface. Main absorption is through the stratum corneum, the outermost layer of the epidermis. This layer is composed of densely packed of biological inactive cells served for key barrier of the skin. Non-polar molecules move across the stratum corneum by dissolving and diffusing through the lipid matrix between protein filaments. The diffusion rate is conditional on lipid solubility and MW. However, the absorption alters with the skin location due to thickness difference. Absorption of PAH through skin has been observed in experimental animals and epidemiological reports. Repeated topical application of MCL results in an appearance of tumors in mice (WHO, 1998). Study of human skin *in vitro*, BaP

in soil could be absorbed through percutaneous route (Wester et al., 1990). *In vivo* study, PAH, i.e. PHE, FLU, ANT, and PYR have been detected in peripheral blood samples in humans after topical application of coal tar in petroleum jelly (Storer et al., 1984). Experiments undertaken in mouse skin, human skin and guinea-pig skin shown a range of absorption rates of ^{14}C-BaP in these skins indicate the diffusion and biotransformation difference among species (Kao et al., 1985). Following the absorption, the compounds are distributed to various body tissues, including storage depots and sites of biotransformation (Landis and Yu, 1995). Experimental animals exposed to PAH have shown rapid and wide distribution to the organs. A study of whole-body auto-radiography in mice has suggested that distribution of MCL after intravenous administration is widespread over the organs and across placenta to fetuses. Inhaled and intravenous administration of BaP in mice have shown similar results (WHO, 1998). Distribution to the organs or tissues is through the blood circulatory system and primarily determined by blood flow and by affinity of the compounds to the blood and tissue. Lipophilic compounds are usually found to bind to the lipid fraction in the blood or in the tissue. This is evident from the studies of PAH that the compounds are mainly stored in tissue rich in adipose tissue (WHO, 1998; Takahashi, 1978; Takahashi and Yasushira, 1973). Since a formation of bound form is reversible, equilibrium can be established between the bound and unbound forms (Landis and Yu, 1995). Any concentration change in one compartment alters other compartment concentrations in the body. Discontinued exposure to a toxicant leads to the toxicant concentration in the blood drop and allows the toxicant stored in other compartments to move into the blood toward equilibrium or until a steady state is reached. PAH stored in adipose tissues from which the compounds are gradually released to the blood has been reported (Takahashi, 1978; Takahashi and Yasushira, 1973). Level in individual tissues depends on a number of factors: administration routes, vehicles, availability of enzyme for metabolism, treatment time, and PAH involved. PAH can be found in all tissues at detectable levels. Particularly high levels are in the gastrointestinal tract, no matter the routes of administration. This is partly due to the mucociliary removal mechanism in the respiratory system previously described (WHO, 1998).

Animal organisms develop a number of biochemical processes to increase xenobiotic compounds to be more excretable. These processes are termed biotransformation. The biotransformation of PAH occurs similarly to that of xenobiotic biotransformation, which comprises phases I and II. Phase I involves oxidations of compounds to form epoxides, phenols and dihydrodiols followed by conjugation of these metabolites with either glutathione, sulfate, or glucuronic acid to form phase II metabolites which are much more polar and water soluble than parent compounds (WHO, 1998). Since PAH have been known as carcinogens, it is believed that metabolites of PAH are active carcinogens rather than parent compounds (Lee et al., 1981). The liver is the main biotransformation site due to its location of most enzyme systems used in the biotransformation process. Other tissues, e.g. the lungs, kidneys, intestines have less extent of biotransformation due to limited range and capability of the enzymes. The skin, testis, placenta and adrenals have even more limited biotransformed capacity (Sipes and Gandolfi, 1991). Phase I reactions which are the predominant process generally involve enzyme systems, mixed function oxygenase (MFO) of which the cytochrome P-450 plays an important role (Sipes and Gandolfi, 1991). Experiments on biotransformation of PAH have been undertaken using *in vitro* of which microsomal fractions are prepared from rat liver (or other tissues). The results were not successful due to lack of enzyme necessary for conjugation formation (WHO, 1998). A probable better method to represent the biotransformation of PAH is that of the cell and tissue cultures where complete biodegradation of PAH has taken place in both phases I and II. (Shaw and Connell, 1994). Most of human tissues including bronchus, colon, keratinocytes, lymphocytes have been examined for biodegradation. Particular interest is human pulmonary macrophages which has been suspected to relate to a bronchial cancer in smokers (Harris et al., 1978; Wynder et al., 1970 in WHO, 1998). Study on macrophage mechanism was carried out in isolated perfused lung tissues of rabbits, which were intratracheal administered with BaP with and without ferric oxide. The study has indicated that ferric oxide particles enhanced the uptake and suppressed the mechanism (Schoeny and Warshawsky, 1983 in WHO, 1998). But, *in vitro* administered with BaP-particle associated, hamster alveolar macrophages enhanced both the uptake and biotransformation of BaP (Griefe et al., 1988). The results have demonstrated that particles exerted different toxic effects on rat and hamsters pulmonary macrophages. In

human, a wide range of biotransformation rate could occur depending on individuals (Harris et al., 1976).

Excretion of xenobiotic compounds comprises three principle routes: urinary, feces, and the lungs. Experiments have been performed to identify excretion routes of PAH. The results confirmed that most metabolites of PAH (e.g. 1-hydroxypyrene, 1-hydroxypyrene-glucuronide) were excreted in feces and urine (Elovaara et al., 1995; Strickland et al., 1994). About half of the dose of PYR applied on rat skin has been found in feces six days later (Jongeneelen, 1997). The effect of co-administration on the excretion has been undertaken in rats. No matter whether administered singlely or combined with BaA, there has been no effect on the excretion of CHR in feces (WHO, 1998). The rate of excretion is dependent on dose administration and species. Excretion rates vary on the dose administered in Sprague-Dawley rats, Gunn rats, and guinea-pigs but not that in hamster (WHO, 1998). An increase of human dietary intake of PAH about 100-250 folds can result in an increase of 4-12 folds of 1-hydroxypyrene in the urine (WHO, 1998). There has had no evidence yet that PAH are removed through the body secretions (e.g. sweat, saliva, tears, and breast milk). However, similar lipophilic organic compounds, i.e. PCB, have been detected in cow milk (Travis and Arms, 1988). A study on CHC in hair has indicated a possibility that lipids associated with hair constitute a significant excretory route for CHC (Matthews et al., 1976). Later a study on hair as a matrix for biomonitoring of organic chemicals in mammals have shown the adsorption and desorption between the hair and the atmosphere (Schramm, 1997). It is however, inconclusive whether organic chemicals can be excreted via hair and to what extent. Excretion by the lungs is important for compounds that exist predominantly in gas phase. Simple diffusion is understood to be responsible for the excretion by the lungs (Klaassen and Rozman, 1991). The rate of excretion is approximately inversely proportional to blood-air partition coefficient. High solubility in blood leads to slow excretion by the lungs and the compounds might be present in expired air for a long time.

2.3.3 Toxicity and Carcinogenicity

PAH are claimed as main causative agents and responsible for 70-90% of human and animal cancers (Wynder, 1976). The mechanism of carcinogenicity has long been described (Pullman, 1945) and involved K- and L- regions in the PAH molecule (Lee et al., 1981). According to this theory, the discrete values of ¶—electron delocalization at these two regions are correlated with the carcinogenicity of the compound. However, later experimental work has contradicted the K-region theory and a theory relating to electrophiles has been proposed (Miller and Miller, 1977; WHO, 1998). In the electrophile theory, the proximate and ultimate carcinogens are produced by the activation of microsomal enzymes and these are reacted with nucleophilic sites on macromolecules, i.e. DNA, RNA and protein (WHO, 1998). Other theory describing carcinogenesis has been introduced and described as the bay-region theory (Lee et al., 1981). The bay-region theory indicates that the position of the epoxide ring, which is the initial product of the metabolic degradation of PAH, is highly related to its biological activity. High activity can be expected if the epoxide ring becomes part of the bay region of the original PAH (Lee et al., 1981). This epoxide ring facilitates ring opening to form the carbonium ion. These substances have a capacity to react with different biological molecules such as protein, RNA and DNA. As a consequence, biological malfunctions, mutation and chromosomal damage can result (WHO, 1998). However, these processes can take a considerable period of time and are not well understood yet. The bay-region theory is supported by carcinogenicity data on substituted PAH (Lee et al., 1981). In general, acute toxicity of PAH increases with increasing MW except for those of very high MW which have very low aqueous solubility. Alkyl side chain substitution on the aromatic ring generally increases acute toxicity. The position of alkylation is important in term of its relation to the effect on carcinogenicity of the compounds since attack position of MFO enzyme in PAH molecule alters. The toxic effect is also dependent on target tissue sensitivity, for example, some PAH may be more potent in the lungs than on the skin (Lee et al., 1981). Ultraviolet radiation also has an influencing role on induction of toxicity of PAH (Veith et al., 1995). Apart from this, dietary intake could have an influence on some protective or detoxification mechanisms with PAH, whereas genetic factors, hormones, the endocrine factor, and enzymic systems all play important roles in natural defenses against toxicity (Lee et al.,

1981). Carcinogenicity of PAH is conditional on structure and reactivity of the major metabolites (Neff, 1979). For example, alkylation at the 7-position in BaA where detoxification occurs would result in significant carcinogenic activity (Newman, 1976).

Chronic toxicological effects are also attributed by covalent binding of certain electrophiiic metabolites of PAH to cell molecules (Neff, 1979). Synergistic effects have been demonstrated in animal experiments and epidemiological data. For example, about 10 times higher incidence of lung cancer occurred in smoking workers than non-smoking workers in asbestos and ore industries (Boulos and Smolinski, 1988). Acute toxicity reports for PAH mixtures in animals are rare, however, quite a few investigations are available for some specific compounds. Results from intraperitoneal administration in mice have indicated different degrees of immune suppression effects of PAH, which could pass onto their offspring (Harper et al., 1996). PAH have adverse reproductive effects in rodents administered orally or by injection (ATSDR, 1990). Lung tumors in mice and rats have been induced by many PAH and PAH containing diesel emissions (Nesnow et al., 1995). Experimental results in mice and rats have shown relatively low acute toxicity on oral and dermal exposures but carcinogenicity on prolonged exposure to these animals. WHO (1998) has reported as little as a few micromoles of BaP is sufficient to cause cancer in mice in less than 6 months. In experimental mammals, cancer has been recognized for many years (IARC, 1973). Workers exposed to PAH containing coal tar, coke oven emissions and soot, have shown skin cancer and other cancer sites-esophagus, pancreas and prostate glands in humans (Nadon et al., 1995). Several of high MW PAH, i.e. BaP, BghiP, IPY are known carcinogens and mutagens (Msarvin et al., 1995; Nagpal et al., 1994). Carcinogenicity of PAH classified by IARC is listed in Table 2.2 suggesting 4-6 ring PAH are more carcinogenic than those with rings smaller or larger. In addition, the highly angular configuration is more carcinogenic than those with linear and highly condensed rings (Neff, 1979).

2.4 Relevant Partitioning Model

2.4.1 Background

Distribution of PAH in various phases in the environment (i.e. air, water, soil, sediment, and biota) can be described by their physicochemical properties, for example, aqueous

Table 2.2 Evaluation of carcinogenicity of PAH (WHO, 1998)

Compounds	Evidences for carcinogenicity		IARC (1987)
	Human	Animal	
ANT	inadequate	inadequate	3
BaA	inadequate	sufficient	2A
BaP	inadequate	sufficient	2A
BbF	inadequate	sufficient	2B
BjF	inadequate	sufficient	2B
BkF	inadequate	sufficient	2B
BghiF	inadequate	sufficient	3
BaFLO	inadequate	inadequate	3
BbFLO	inadequate	inadequate	3
BghiP	inadequate	inadequate	3
BeP	inadequate	inadequate	3
CHR	inadequate	limited	3
COR	inadequate	inadequate	3
CPY	inadequate	limited	3
DBahA	inadequate	sufficient	2A
DBaeP	inadequate	sufficient	2B
DBahP	inadequate	sufficient	2B
DBaiP	inadequate	sufficient	2B
FLO	inadequate	inadequate	3
FLU	inadequate	inadequate	3
IP	inadequate	sufficient	2B
PER	inadequate	inadequate	3
PHE	inadequate	inadequate	3
PYR	inadequate	inadequate	3

2A probably carcinogenic to humans, 2B possible carcinogenic to human, 3 is not classifiable

solubility, vapor pressure, partition coefficients and bioconcentration factor (K_B). The transport of these airborne compounds can be influenced by dry and wet depositions, which results in reaching the hydrosphere, geosphere and/or bioconcentrating in biota, e.g. terrestrial biota. The ability to bioconcentrate in biota, which involves closely to the partitioning process, can be expressed as a K_B (Hawker and Connell, 1986). The partitioning between these phases obeys first order kinetic and is controlled by diffusion and related processes. Bioconcentration which is generally referred to the biota-water system, can be quantified by a ratio of concentrations of a chemical in biota (C_B) to that in the water (C_W) at equilibrium. The expression of bioconcentration in other systems, e.g. biota-air system, can also be expected to be similar.

Bioconcentration behavior of PAH is also varied on degree of biodegradation. For example, biota, which exhibits least biodegradation, is likely to have the most comparable bioconcentration behavior (Connell, 1990). The system of aquatic biota-water or fish-water for PCB, PCDD/F has been received most attention followed by terrestrial systems, i.e. vegetation-air system. PAH itself, however, has received little attention and less evidence in partition processes of fish-water, vegetation-air and mammal-air systems

The measurement of partitioning behavior in term of partition coefficient is generally carried out in laboratory, though, costly and time consuming. Alternatively, this characteristic can be achieved through estimation method utilizing quantitative structure activity relationships (QSAR), which has played an increasing important role in the estimation of behavior of new chemicals (e.g. Mackay, 1982). There are quite a number of useful parameters in the QSAR that are in use for prediction, e.g. K_{OW}, K_{OA}, and K_{AW} or H. Other property, e.g. aqueous solubility (S) has also been observed to have satisfactory linear relationships with log K_B in a compound group of NAP, pesticides and other industrial chemicals (Chiou et al., 1977) with MW<290 (Mackay et al., 1980). Thus, it would be expected that S could be a good predictor for K_B.

Within a biota tissue, it is frequently considered to consist of one compartment or more than one compartment with different proportions of volume varying on the tissues considered. The partitioning of the compound among compartments and that of individual compartment with involved abiotic environment generally reach equilibrium to each other if

sufficient time allowed and, thus, the partition coefficients between the biota phase and the abiotic phases can be achieved.

2.4.2 Vegetation-Air System

Multi compartment models of whole plant have been studied with PCB, PCDD and halobenzene using fugacity concept (Paterson et al., 1991a; Trapp et al., 1990; Schramm et al., 1987). In many cases, one compartment model, which is common, is also often used by assuming that leaf compartments are well mixed and that the diffusion transport is faster within the compartments than the transport across the plant-air. Although plant leaves have relatively large surface areas, partitioning mechanism may not distribute evenly over the leaves due to complex composition of plant including intercellular air, water, lipids, structural carbohydrates and proteins. Each plant component and volume fractions have some degree of governing the partitioning process between the vegetation and the air. Umlauf et al. (1994) have evaluated the partitioning behavior of high and low MW SOC in spruce needles. They suggested that one compartment plant model may not be appropriate since high MW SOC are found retained on the leaf surface and lower MW are found in the interior of the needle. Other model using organic compounds (excluding PAH) partitioning in multi compartment vegetation so as to predict the preferential accumulation has been established by Riederer (1990). Factors that are likely to alter the BCF values, i.e. growth dilution, metabolism and degradation have been integrated in the model developed by Trapp and Matthies (1995) using mass-balance approach. Five-compartment plant model (cuticular lipids, cellular lipids, protein, structural carbohydrate and water) has been developed by Müller et al. (1994) to predict the vegetation-air partition coefficients of persistent hydrophobic organic compounds.

Correlation between the BCF value and physicochemical properties of the compound such as MW, S, VP, and K_{OW} usually take a form of linear regression similarly to the fish-water system (Bacci et al., 1990b; Trapp et al., 1990; Reischl et al., 1989). The same correlation can be obtained from K_{OA} which has been suggested to be a key partitioning descriptor for the vegetation-air system of hydrophobic compounds (Paterson and Mackay, 1991b). Linear regression equations have been obtained from the plot between log K_{VA} which have been measured in azalea leaves and *Lolium multiflorum* with log K_{OA}

(Paterson et al., 1991b; Travis and Hattemeyer-Frey, 1988). Tolls and McLachlan (1994) have found that a slope and an intercept for this relationship using HCB, PCB and PAH were 0.91 and 0.68 respectively. K_{VA} is often calculated from lipid plant-water partition coefficient cooperating with K_{AW} or H (Calamari et al., 1987).

2.4.3 Mammal-Air System

There is a limited study on mammal-air system for lipophilic compounds as compared to the fish-water and vegetation-air system. Skin-air systems for VOC (e.g. methanol, benzene) have received much attention (e.g. Batterman et al., 1996, Mattie et al., 1994). Blood-gas systems have been examined to determine the partition coefficients with a large number of compounds. However, the systems are not relevant to the plant-air system in this current study since blood is rather polar as compared to plant leaf. Tissue-gas partition coefficients have also been determined for water-soluble solvents (e.g. acetone, methanol, and ethanol) using muscle, kidneys, lungs, white and gray matter of brain (Fiserova-Bergerova and Maria, 1986). The results can not be applied to PAH due to different physicochemical properties. A system of air-mammal tissue has been investigated using CHC and aromatic hydrocarbons with various mammal tissues, i.e., human blood, rat blood, rat muscle, and rat liver (Connell et al., 1993). However, the partition coefficients obtained cannot be directly applied to PAH due to outside the range from which the model developed.

The relevant hair-air system has been examined by Schramm et al. (1992) using human hair as a monitoring pool of dioxin and found to depend on environmental conditions, i.e. temperature, moisture, and involve dynamic adsorption and desorption on hair. The authors have suggested that compounds with similar VP, lipophilicity and molecular geometry as of PCDD/F such as PAH and PCB would have similar behavior. A hair-air model using controlled gaseous PCB in a closed system has been carried out by Schramm (1997). The measured partition coefficients of PCB (IUPAC No. 28, 31, 52, 101, 138, 153) based on lipid weight were within the range of 4×10^8 to 30×10^8. An air-nasal system developed by Hau et al. (1999) has established the air-nasal partition coefficient using K_{WA} and K_{OW}. The hair-air model (K_{HA}) of 4 PAH has been developed by Karnchanasest (2000) and shown calculated K_{HA} exhibiting good correlation with K_{OW} and

the values lower than vegetation-air partition coefficients observed. This is probably due to different conditions and different biota species involved.

2.4.4 Particle-Gas System

Semivolatile organic compounds (SOC) are compounds with VP range of 10^{-4} to 10^{-8} mm Hg. They exhibit both vapor and particle associated in the atmosphere (Junge, 1977). For PAH, those with two rings are found in gas phase while more than five rings are found primarily in particle phase and those between 3-5 rings are SOC. The knowledge of particle-gas distribution of PAH is important for an understanding of atmospheric transport of these pollutants and also their fates whether atmospheric scavenge or removal would occur. The theoretical explanation for the particle-gas system was first made by Junge (1977) and based on a linear Langmuir isotherm as shown below.

$$\emptyset = C_P (C_G + C_P)^{-1} = \jmath \theta (P^o + \jmath \theta)^{-1} \qquad (2.4)$$

where $\emptyset$ is a fraction of the compound associated with particles (dimensionless), C_P and C_G are particle associated and gas phase concentrations (mol cm^{-3}) respectively, P^o is the saturation vapor pressure of the pure compound (Torr), θ is the surface area concentration of the particle in a given volume of air (cm^2 cm^{-3}) and $\jmath$ is a Junge's constant. The Junge's equation is useful to describe the partitioning which favors particle phase with decreasing VP. The model assumed that the distribution was an equilibrium nonspecific physical adsorption with sufficient particles available for the exchange with the gas phase. Similar approach to examine the temperature dependence of the particle and gas phases of PAH was employed by Yamasaki et al. (1982) using Langmuir isothermal adsorption concept with the assumption that the fraction of sorbate surface area described by the particle associated concentration over the total suspended particulate ($C_P TSP^{-1}$). The particle-gas distribution coefficient derived can be expressed as

$$K_G = \frac{A}{\frac{F}{TSP}} \qquad or \qquad K_P = \frac{F}{A(TSP)} \qquad (2.5)$$

$$\log \frac{A(TSP)}{F} = \frac{m}{T} + b \qquad (2.6)$$

where K_G and K_P are the gas-particle and particle-gas partition coefficients. A and F are the measured gas and particle phase concentrations which may equal to C_G and C_P where artifacts are free (ng m^{-3}), TSP is total suspended particulate ($\mu g\ m^{-3}$), m and b are constants and T is temperature (K).

The Junge's model was re-examined by Pankow (1987). Pankow (1987) has suggested that VP of subcooled liquid (P^o_L, Torr) would give more accurate result than VP of solid phase. This is supported by later investigations indicating that the particle-gas distribution coefficient (K_P, $m^3\ \mu g^{-1}$) is subcooled liquid vapour pressure (P^o_L) dependence, that is, log A(TSP) /F to log P^o_L relationship taken the form of linearity for PAH ranging from low to intermediate volatility (Logocki and Pankow, 1989; Foreman and Bidleman, 1987). The relationship can be described as

$$\log K_P = a \log P^o_L + b \qquad (2.7)$$

where a and b are constants.

Influences of humidity have been examined for the adsorption process of PAH and volatile organics with soot particles (Kamens et al., 1988) and soil particles (Chiou and Shoup, 1985). Influence on the particle-gas phase partitioning for PAH was first investigated in urban atmosphere by Lee and Tsay (1994). Good linear relationship was obtained for log K_P and humidity with the range of 8.2-25.8 (g m^{-3}), which corresponds to 52-93% relative humidity, and taken an inverse form. This indicates significant effect of humidity (over 50 % relative humidity) on the particle-gas partitioning of PAH. Particle-gas partition coefficient (K_P) can be predicted from the relationship with P^o_L as previously described. However, the estimation of P^o_L from VP for the solid phase (P^o_S) by using the relationship with melting point and ambient temperature is likely to cause error (Finizio et al., 1997). Deviations from the linear correlation between log K_P and log P^o_L have been observed with PAH and PCB suggesting P^o_L may not be a good parameter for particle-gas partitioning process (Kaupp and McLachlan, 1999). Since the process of octanol-air partitioning is somewhat similar to that of particle-gas system, these two parameters has

been developed for the relationship and found the relationship taken the form as follows (Kaupp and McLachlan, 1999; Harner and Bidleman. 1998).

$$\log K_P = a \log K_{OA} + b \qquad (2.8)$$

where a, b are constants

Chapter 3
Experimental Procedures

The overall procedures of the experiments (Figure 3.1) were carefully planned to achieve all objectives of the study. The methods for sample preparations, preservation, handling, storage, and transport to the laboratory, as well as analyses available in the literature were reviewed and followed strictly. Various techniques were brought in and applied in order to obtain reliable results, reproducible methods and to avoid any possible artifact. Subsequently, the step-by-step experimental scheme was carried out is detailed below.

3.1 Analytical Materials

3.1.1 Test Compounds

Sixteen PAH (napthalene, acenapthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, crysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene) recommended by the USEPA used as test compounds were purchased from Supelco Company, USA., with 99% purity.

3.1.2 Internal Standard

Though, an isotope labeled internal standard is typically used as a reference and quantitation purpose. However, 1-methyl phenanthrene (MPHE) was chosen as an internal standard in this study due to the difficulty in the radioactive waste treatment in the laboratory. The criteria selection of MPHE is based on its similar physicochemical properties to the test compounds and yields a chromatographic peak separated from the test compounds. Blank analyses were pre-carried out to ensure contamination of MPHE in the analytical procedure for the background leaf and for the water and the air samples. Certain amount of MPHE was added during extraction step in order to quantify mass of the test compounds. The internal standard was prepared in a stock solution. MPHE of 99.5%

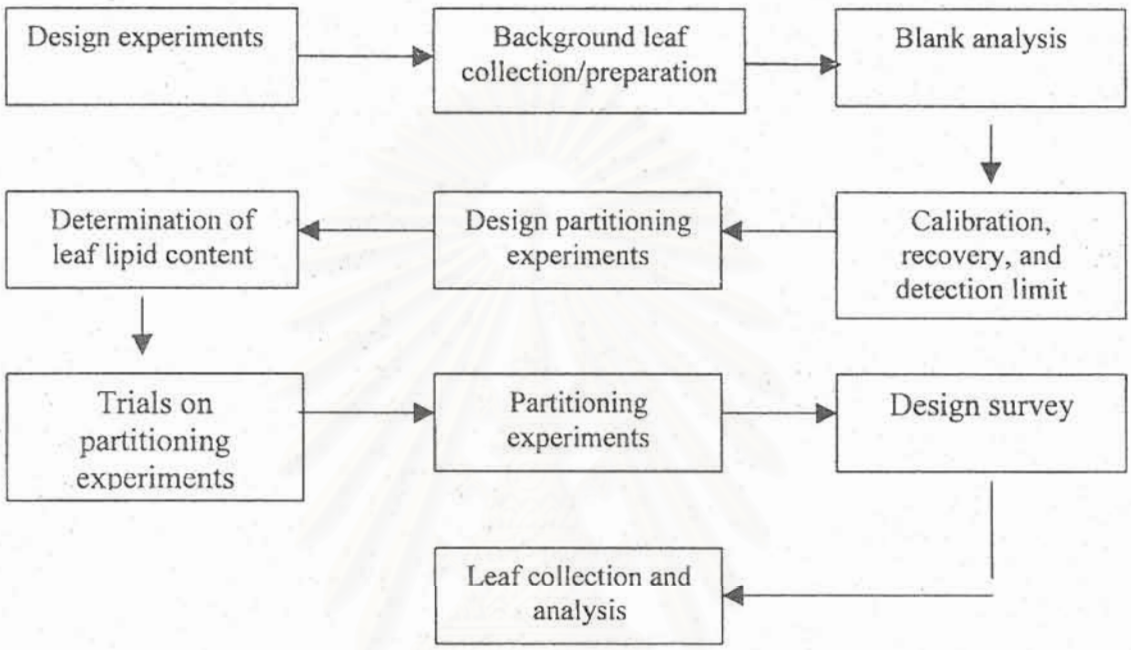


Figure 3.1 Overall scheme for the experiments carried out in this study.

purity was purchased from ChemService Company.

3.1.3 Solvents and Chemicals

Hexane, dichloromethane (DCM), and acetone were used and purchased from Mallinckrodt.

Silica gel (70-230 mesh, analytical grade, Fluka) was pre-activated at 250 °C for 24 h before use. Sodium sulfate (anhydrous, analytical grade, Fischer) was heated at 450°C for 6 h and stored in a desiccator. Glass wool was washed with hexane, air dried and kept in a closed solvent-cleaned glass bottle.

3.1.4 Glassware

All glassware were soaked in 10% Extran-300 detergent overnight, rinsed thoroughly with tap water followed with deionized water and dried in an oven at 105 °C. They were all eventually rinsed with hexane before use. The microwave extractor was cleaned by heating with hexane for 15 min.

3.2 Analytical Methods

The overall analytical scheme is shown in Figure 3.2

3.2.1 Extractions

Extraction of Leaves

Whole leaf samples of 2 g were extracted with 40 ml hexane in a microwave extractor with the power of 500-1000 W for 20 min as instructed by the manual. Known amount of MPHE was also added in this extraction step as an internal standard. The crude extract was filtered out, rinsed with hexane and partially evaporated to 1 ml under a gentle stream of nitrogen. The concentrate was stored at –4°C if subsequent isolation step was not immediately carried out.

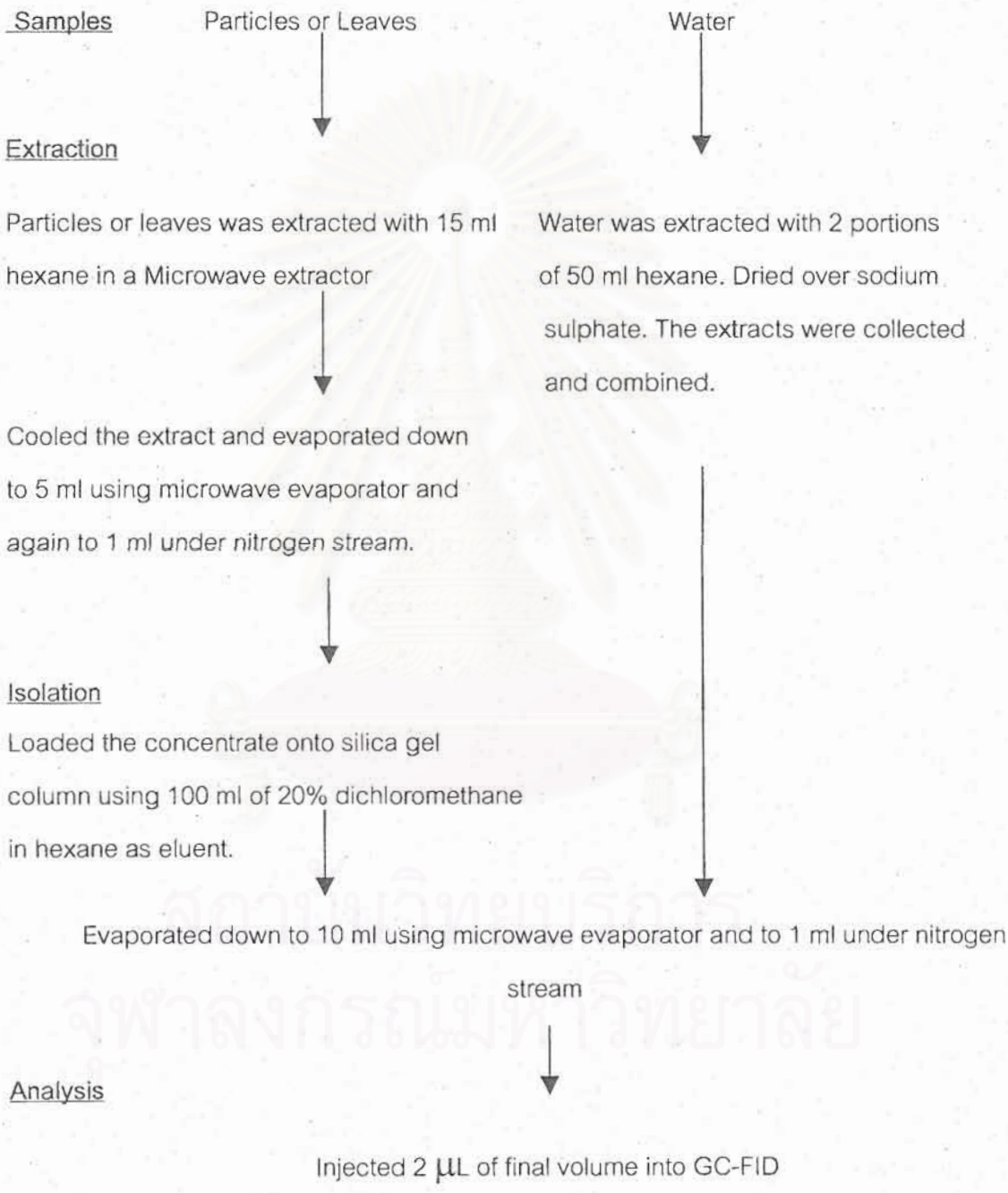


Figure 3.2 Scheme for overall sample analyses employed in this study.

Extraction of Particle

GFF was cut into strips and extracted with the same procedure that applied to leaf.

Extraction of Water

Two litters of water sample and known amount of internal standard were extracted by hand-shaking traditional method using 2 portions of hexane (50 ml each) in a separating funnel. The sample was hand-shaked for about 5-10 min and allowed for layer separation. The extraction of water layer was repeated. The combined hexane extracts were dried over anhydrous sodium sulfate and evaporated down to 1 ml with similar concentrating procedure mentioned above. The concentrate was stored in a sealed vial at −4 °C.

3.2.2 Isolation by Column Chromatography

Isolation step was required for both leaf and particle concentrates. They were loaded on a silica gel column of which on top added with anhydrous sodium sulfate (1 cm thick) and at the bottom lined with glass wool. Prior to the loading, the column was washed with 50 ml 20% DCM in hexane till the solvent level reached the silica gel level again. The analytes were eluted with 100 ml of 20% DCM in hexane and the effluents were evaporated down to 10 ml in a microwave evaporator and again to 1 ml under a gentle stream of nitrogen. The concentrate was stored in a sealed vial at −4 °C.

3.2.3 Gas Chromatographic Analyses

A new Hewlett Packard 6890N equipped with a 30 x 0.25 mm capillary column (DB-5) and fitted with flame ionization detector (FID) was used. The instrument was served by a personal computer installed with ChemStation A0803 Software for peak detection and integration. The condition of GC-FID was preliminary investigated with test compounds and internal standard both in individuals and in mixtures to achieve good resolution of the compounds and within the reasonable retention times. The optimal condition in the study is shown in Table 3.1. Gases used had high purity and fitted with moisture traps and molecular sieves to ensure quality of gas supply. Identification of test compounds and the internal standard were determined by comparison of retention times of the peaks with those of reference chemicals under the same optimal condition of GC-FID. The peaks

Table 3.1 Optimal conditions of GC-FID employed in this study.

Column	Gases
Origin; USA	Nitrogen (carrier); 100 kPa
Phase type; bonded HP-5	Nitrogen (make-up); 45 ml min^{-1}
Dimension; 30 m x 3.2 mm	Air (detector); 450 ml min^{-1}
Film thickness; 0.0025 mm	Helium (detector); 40 ml min^{-1}
Injector	Detector
Type; splitless	Type; FID
Temperature; 280 ^{o}C	Temperature; 250 ^{o}C
Split vent	Temperature program
Turn on time; 1 min	Initial 80 ^{o}C, 1 min.
Injection volume	Rate 1; 25 ^{o}C min^{-1} until 160^{o}C for 3 min
2 μL	Rate 2; 3 ^{o}C min^{-1} until 300^{o}C for 2 min

were later confirmed by GC-MS. The retention times of test compounds and internal standard are shown in Table 3.2.

3.2.4 Determination of Leaf Lipid

Lipid content was determined similarly to the extraction step. An aliquot in a pre-weighed beaker was evaporated to dryness under a gentle stream of nitrogen at room temperature. Calculation of leaf lipid can be obtained from weight difference of beaker with and without residue.

3.2.5 Determination of Total Suspended Solids (TSP)

Airborne particulate matter was collected on a solvent cleaned GFF. The GFF was dried in a desiccator and weighed before and after exposure. TSP can be calculated in according to the equation below.

$$TSP = (W_B - W_A)\, V \qquad (3.1)$$

where W_B = weight of GFF before use (mg), W_A = weight of GFF after use (mg) and V = volume of air (m^3).

3.3 Method Evaluations

3.3.1 Contamination and Procedure Blanks

All chemicals, leaf and water samples were checked for any contamination prior to use. Three replications of a procedure blank were carried out to ensure no contamination in the procedures. The procedure blank was repeated every 15 samples. Deionized water was periodically checked for contamination.

3.3.2 Calibrations, Recoveries and Detection Limits

Calibration curves were determined for water, air and leaf analyses by spiking four concentrations of test compounds and a certain concentration of MPHE on deionized water, the air and leaves. The deionized water was spiked with test compounds prepared

Table 3.2 Mean retention times and standard deviations of test compounds and internal standard obtained under optimal conditions of GC-FID.

Compounds	Mean retention times (min)
NAP	5.17 (N=5, SD=0.08)
ACE	7.89 (N=5, SD=0.09)
ACY	8.43 (N=5, SD=0.11)
FLO	10.12 (N=5, SD=0.08)
PHE	14.38 (N=5, SD=0.10)
ANT	14.50 (N=5, SD=0.06)
MPHE	17.82 (N=5, SD=0.05)
FLU	21.45 (N=5, SD=0.09)
PYR	22.82 (N=5, SD=0.16)
BaA	31.29 (N=5, SD=0.15)
CHR	31.63 (N=5, SD=0.01)
BbFLU	38.68 (N=5, SD=0.12)
BkFLU	39.17 (N=5, SD=0.52)
BaP	41.11 (N=5, SD=0.68)
IP	47.42 (N=5, SD=0.06)
DbahA	47.90 (N=5, SD=0.12)
BghiP	48.66 (N=5, SD=0.10)

N=Numbers of sample, SD=Standard deviation

in acetone whilst the leaf samples were spiked with test compounds prepared in hexane solution. Each spiking experiment was repeated three times. The spiked deionized water and spiked leaves were analyzed by the same procedure as the samples. The detector responses were estimated from calibration curves plotted between relative peak ratio of standard compounds to that of internal standard against compound concentrations. All plots were in linear and presented in Table 3.3.

The detection limits were defined as 3 x SD of the compounds above the blank. This reflected the minimum amount of the compounds that can be detected by the method. In this study, the standard deviation was determined from triplicate analyses of each compound concentration in spiked samples and then plotted against the corresponding concentration for each PAH (Table 3.4). Recoveries of the compounds were determined and repeated three times (Table 3.4).

3.4 Partitioning Experiment

3.4.1 Concentrations of Test Compounds

The concentrations of test compounds in the partitioning experiments were 0.05, 0.12, 0.18, 0.25 of individual PAH aqueous solubility prepared in mixture in acetone. Therefore, each solution contained test compounds of the same concentration in proportion to aqueous solubility.

3.4.2 Conditions of Partitioning Experiments

The condition of partitioning experiments is shown in Table 3.5

3.4.3 Procedures

Deionized water spiked with a mixture solution of test compounds was generally transferred into a screw-cap flask containing a leaf sample (2g). The flasks were tightly closed and shaked until a steady state attained. The partitioning experiments were repeated until achieving four different working concentrations of test compounds. The leaves and the water were separated out by filtering through a solvent-cleaned GFC onto the receiving flask under vacuum. The leaves left over on a GFC were dried with sodium

Table 3.3 Y-intercepts (b), slopes (a), and correlation coefficients (r^2) of calibration curves for quantification of test compounds in the water, leaves and the air.

Compounds	Water			Leaf			Air		
	a	b	r^2	a	b	r^2	a	b	r^2
1.NAP	0.13	90.24	0.90	0.03	-2.72	0.83	177.68	-126.92	0.90
2.ACY	0.13	18.66	0.95	0.09	-0.81	0.95	272.83	-22.76	0.92
3.ACE	0.29	2.71	0.98	0.12	-0.95	0.89	270.68	-22.56	0.93
4.FLO	0.13	10.23	0.96	0.09	0.02	0.93	316.70	-12.85	0.93
5.PHE	0.48	-1.86	0.99	0.12	-1.40	0.89	399.03	-11.73	0.89
6.ANT	0.42	0.08	0.98	0.84	-0.50	0.94	212.06	-0.25	0.80
7.FLU	0.16	0.54	0.97	0.35	-0.58	0.97	534.87	-2.54	0.94
8.PYR	0.25	-0.01	0.97	0.73	-0.75	0.88	344.82	-0.80	0.95
9.BaA	0.20	0.09	0.98	1.01	-0.05	0.80	674.91	-0.11	0.98
10.CHR	0.35	0.02	0.97	3.18	-0.03	0.94	1417.80	-0.05	0.84
11.BbFLU	0.02	0.04	0.74	0.69	-0.37	0.72	294.99	-0.24	0.96
12.BkFLU	0.2	0.03	0.93	10.39	-0.05	0.67	1162	0.0023	0.98

Table 3.3 (Continued)

Compounds	Water			Leaf			Air		
	a	b	r^2	a	b	r^2	a	b	r^2
13.BaP	0.12	0.01	0.84	33.43	-0.22	0.86	3840.70	-0.27	0.66
14.IP	0.10	0.01	0.87	0.30	-0.18	0.85	457.91	-0.51	0.84
15.DbahA	0.41	0.02	0.77	16.07	-0.02	0.90	4598.40	-0.03	0.87
16BghiP	2.96	0.07	0.78	376.97	-0.12	0.91	51223	0.05	0.90

Table 3.4 Detection limit (DL) and recovery for the analytical methods

PAH	Water		Leaf		Air	
	DL ($\mu g\ L^{-1}$)	Recovery (%)	DL ($mg\ kg^{-1}$)	Recovery (%)	DL (μg)	Recovery (%)
NAP	31.1	82	9.15	56	1900	60
ACY	7.7	88	7.9	75	2.0	75
ACE	13.2	87	1.11	72	2.5	77
FLO	0.2	85	1.95	78	2.0	73
PHE	3.5	86	1.0	70	1.9	78
ANT	0.7	88	1.1	72	2.0	79
FLU	0.5	90	0.1	75	1.7	80
PYR	0.05	92	0.01	79	1.5	85
BaA	0.01	88	0.50	78	0.5	82
CHR	0.02	90	0.01	78	0.003	83
BbFLU	0.6	93	0.50	76	0.1	81
BaP	0.01	91	0.01	74	0.1	80
BkFLU	0.04	89	0.01	79	0.01	86
IP	0.6	87	0.60	77	0.1	85
DbahA	0.005	90	0.01	78	0.001	84
BghiP	0.003	85	0.01	79	0.001	80

Table 3.5 Condition of the partitioning experiment.

Weight of leaf	2 g
Volume of water	2 liters
Shaking time	36 h
Number of replications	2
Four concentrations of test compounds	0.25S, 0.18S, 0.12S, 0.05S

sulphate and transferred to the extraction step. Similarly, the water portion was processed to the step of extraction of water.

3.5 Sample Collection and Preparation

3.5.1 Study Area

Field surveys were carried out and four Bangkok roadsides were selected based on different traffic volumes recorded by BMA, availability of plants grown in the area and possibility of running air sampling equipment; i.e. electricity source, safety. The locations were Kasemraj, Patumwan, Pongpetr, and Sapankwai (Figure 3.3). One site served as background was located inside the Asian Institute of Technology.

3.5.2 Collection Strategies

Air Sampling

Due to PAH found at very low concentrations in the atmosphere, a large volume of air was drawn through a high volume air sampler and collected 3 consecutive days for each site. The three air samples were combined in one sample. Particles were trapped on a GFF at an approximate airflow rate of 0.5 m^3min^{-1} for 24 hr. The exposed GFF was folded in half and wrapped in an aluminum foil, kept in a capped plastic bag and stored at −10 °C. The filters were then dried in a desiccator for 24 hours and weighed.

Collections of Leaves

Leaves of *Ixora chinensis Lamk, Ixora spp.* were selected due to availability on the four sites and cut using solvent-cleaned stainless steel scissors and kept in closed solvent-cleaned glass jars wrapped with aluminum foil to prevent possible photo-degradation and stored at -4 °C until analysis. Since Bangkok traffic is usually very busy on the first two weeks of the month, the sampling is designed to carry out during these weeks and after the rainy seasons. Leaf samples were collected 7 consecutive days at each site. All 7 samples were combined into one sample. Background leaf samples were tested for any contamination of test compounds and internal standard before developing calibration curves and partitioning experiments.

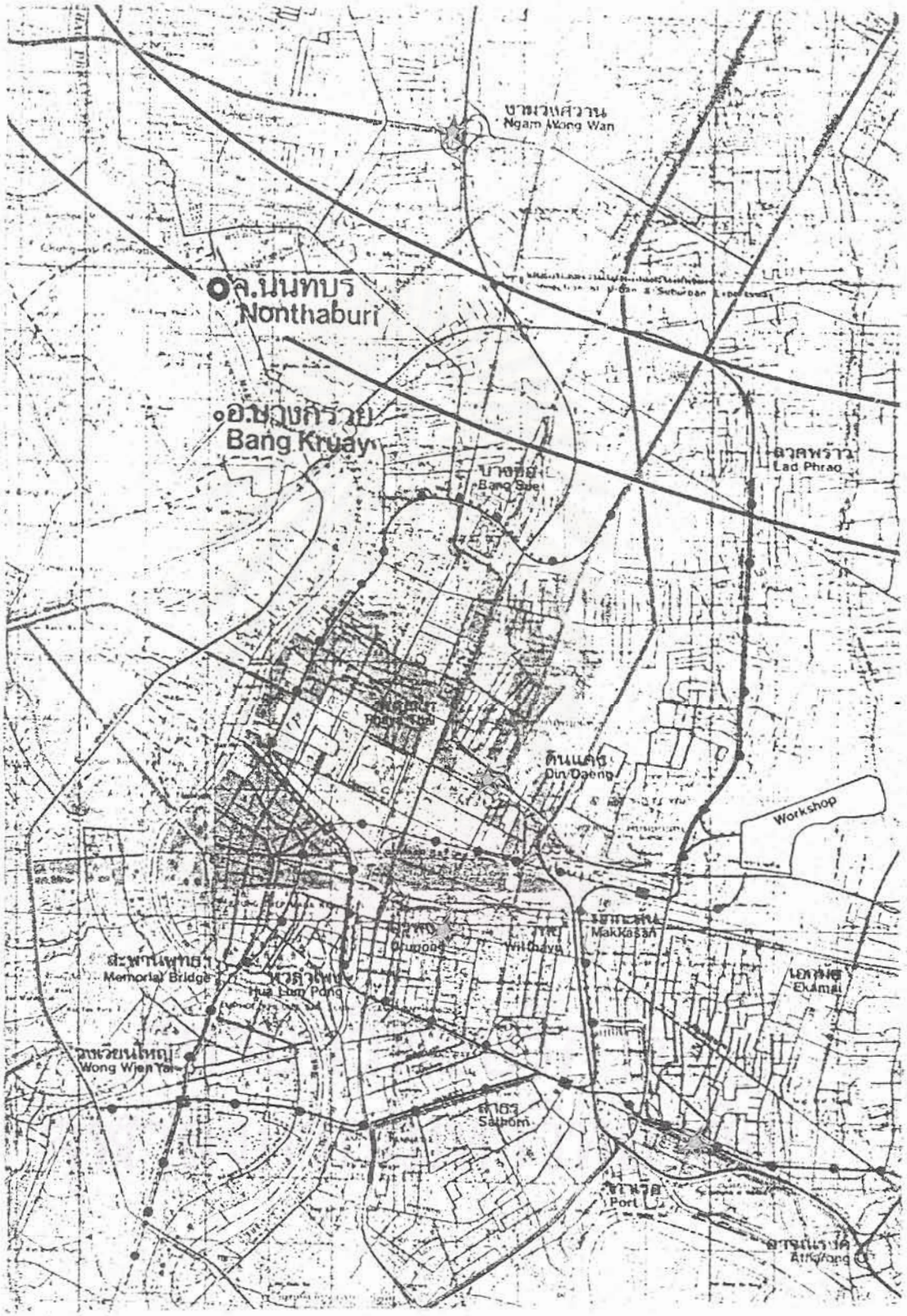


Figure 3.3 Location of the study areas

Chapter 4

Evaluation of Plant Leaf-Air Partitioning Behavior

4.1 Leaf-Air Partitioning Behavior

4.1.1 Leaf-Water Partition Coefficient

Leaf-water partition coefficient (K_{LW}) and leaf lipid-water partition coefficient (K_{LLW}) were calculated using data from leaf-water partitioning experiments (see Table 4.1). The units for the ratios of concentrations in leaf and in leaf lipid to concentrations in water are L kg^{-1}. Multiplication K_{LW} (L kg^{-1}) and K_{LLW} (L kg^{-1}) with a leaf density of 0.87 kg L^{-1} (average of the density of grass and lichen from Tolls and McLachlan, 1994 and Mulr et al, 1993) and a leaf lipid density of 0.92 kg L^{-1} (assume equivalent to hair lipid density), the dimensionless of the coefficients were obtained respectively. To normalize the K_{LW} into lipid leaf basis (K_{LLW}), the values were divided by a leaf lipid fraction of 0.051 (see determination of leaf lipid in Section 3.2.4).

Relationship with log K_{OW}

The plots of log K_{LW} and log K_{LLW} values against the log K_{OW} in the range of 3.4 to 5.22 (or MW 128.2 to 202.3) exhibit linear relationships (Equations 4.1 and 4.2).

$$\log K_{LW} = 0.72 \log K_{OW} + 0.15 \qquad (r^2 = 0.75) \qquad (4.1)$$

$$\log K_{LLW} = 0.64 \log K_{OW} + 1.92 \qquad (r^2 = 0.76) \qquad (4.2)$$

According to the theory, such plots, particularly organic compounds with log K_{OW} 3-6, should exhibit a linear relationship, which is reflected by the zero intercept and the slope close to unity. The Equations 4.1-4.2, however, suggest that there are somewhat linear relationships between the leaf or leaf lipid-water partitioning and the octanol, which is a representative for the biota lipid. The slope values (0.72, 0.64) are fairly close to unity and the intercepts (0.15, 1.92) on the log K_{LW} and log K_{LLW} are reasonably reaching zero on the scale of 2 to 6. Although, negative values are expected for the log K_{LW} and the log

Table 4.1 Determination of Average Leaf-Water Partition Coefficients Obtained from Partitioning Experiments

PAH	C_L (mg/Kg)	C_W (ug/L)	K_{LW} (L/Kg)	K_{LW}* (unitless)	log K_{LW}	K_{LLW}** (L/Kg)	K_{LLW}*** (unitless)	log K_{LLW}
NAP	1533.1	2420.1	630	550	2.74	1200	11400	4.06
ACY	245.8	229.4	1100	930	2.97	21000	19300	4.29
ACE	277.1	148.3	1900	1600	3.21	36600	33700	4.53
FLO	229.5	80.9	2800	2400	3.39	55600	51200	4.71
ANT	2.48	1.7	1500	1300	3.10	28500	26200	4.42
PHE	177.9	19.8	9000	7800	3.89	176000	162000	5.21
FLU	14.54	1.2	11900	10300	4.01	233000	214000	5.33
PYR	2.27	0.36	6300	5400	3.74	124000	114000	5.06
BaA	0.84	2.98	280	250	2.39	5500	5100	3.71
CHR	0.07	0.44	170	150	2.17	3300	3100	3.49
BbFLU	0.65	19.11	34	30	1.47	670	600	2.79
BaP	0.01	0.61	16	14	1.15	320	300	2.47
BkFLU	0.01	3.74	2.67	2.30	0.36	52	48	1.68
IP	ND	ND	na	na	na	na	na	na
BghiP	ND	ND	na	na	na	na	na	na
DBahA	ND	ND	na	na	na	na	na	na

*K_{LW} (unitless) = K_{LW}(L/Kg) * ρ (leaf). **K_{LLW} (L/Kg) = K_{LW}(L/Kg) / lipid fraction in leaf

***K_{LLW} (unitless) = K_{LLW} (L/Kg) * ρ (lipid). nd-not detected. na- not available

K_{LLW} against log K_{OW} plots, there is possibility of positive values in some situations (Schüü rmann and Klein, 1988). This is evident from a similar study on chlorinated hydrocarbons in fish, where the relationship based on lipid weight had slopes of 0.89, 0.96 and positive intercepts of 0.61 and 0.25 respectively on the log K_B axis (Chiou, 1985). The fish-water partitioning values were referred due to its similar model used and relatively large information available on a wide range of organic compounds as compared to those on PAH.

On the same plots but covering 13 compounds (from NAP to BkFLU), the second-order polynomial regressions relationships are dominant (Equation 4.3 and Figure 4.1).

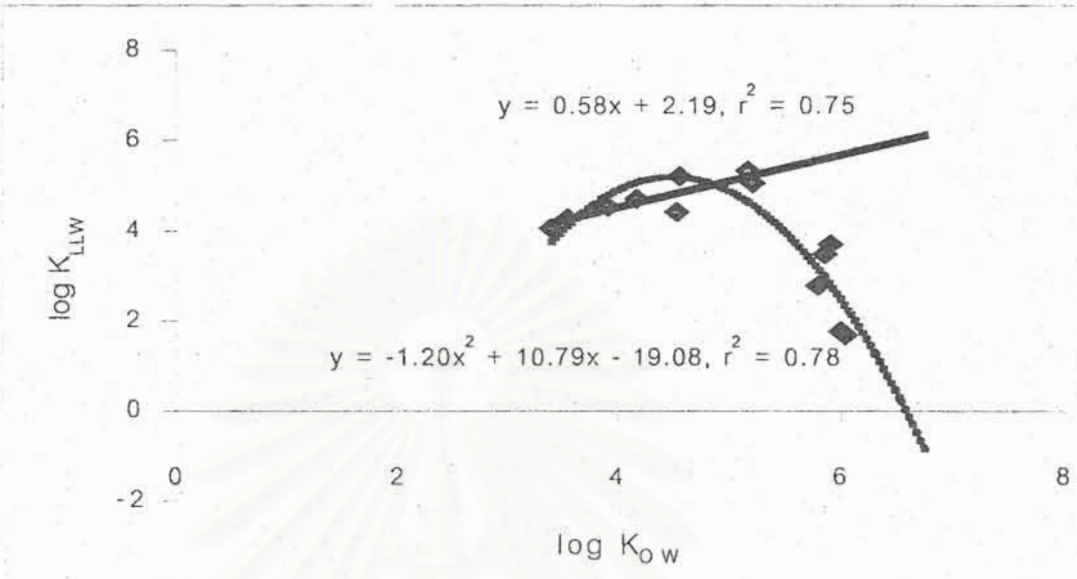
$$\log K_{LLW} = -1.1 (\log K_{OW})^2 + 10. (\log K_{OW}) - 17.4 \qquad (r^2 = 0.77) \qquad (4.3)$$

Such relationship described by the Equation 4.3 and depicted on Figure 4.1 theoretically affords a curvilinear relationship. This is because large molecules with extremely hydrophobic (log K_{OW}>6) do not bioconcentrate as much as predicted by the linear equations as shown on Equations 4.1-4.2 (Connell and Hawker,1988). This can be explained by that larger MW and more hydrophobic hydrocarbons decrease lipid solubility. Therefore, these values are difficult to measure experimentally because of the very low lipid solubility and extremely low aqueous solubility of the compounds.

In considering strictly, the intercepts of such linear relationships exceed zero and calculated lipid fractions are above unity, which are incorrect. In addition, the level off of the parabola shape as shown in Figure 4.1 at log K_{OW} about 5 is somewhat lower than expectation. There are clearly some factors that lead to discrepancies in these relationships between the bioconcentration factor and K_{OW} as following.

Multi-Compartment Partitioning Model.

The study is based on one single compartment model due to lipid is considered to be the main deposit of hydrophobic organic compounds. As a matter of fact, leaf comprises not only cuticular and cellular lipids but also other phases, e.g. water, carbohydrate. When sufficient time available, chemicals partitioning between these compartments are in



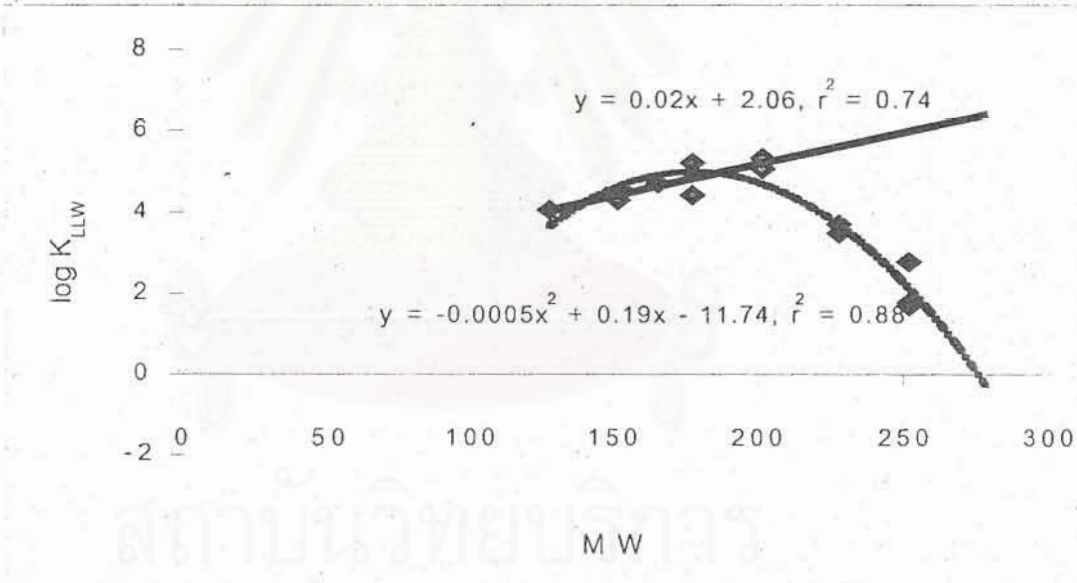


Figure 4.1 Linear and polynomial regressions of the relationships of log K_{LLW} to log K_{ow} and MW

equilibrium to each other and the overall leaf to the ambient water. Clearly, hydrophobic compounds with log K_{ow} 3 to 6 are expected to bioconcentrate in lipid phase. However, non-lipid phase, i.e. structural carbohydrate, water, protein and their volume fractions in the leaf can play more role in the bioconcentration process particularly compounds with relatively high aqueous solubility. The low MW, i.e., NAP, ACE, ACY, FLO which have relatively higher aqueous solubility (small log K_{ow}) possibly partition into the non-lipid phase and consequently affect the correlation between log K_{LW} or log K_{LLW} with log K_{ow} (Chiou, 1985; Mackay 1982). However, recent study noted that a one-compartment model was adequate for the plant-air distribution but only with several days of modeling (Tolls and McLachlan, 1994).

Influence of Compound Degradation

PAH are fairly reactive chemicals and subject to oxidation and photolysis. The degree of reaction is dependent on the phases they reside and the nature of the surrounding environment including sunlight intensity, temperature, presence of reactive radicals, as well as microorganisms (Mackay et al., 1992). In the air, PAH are in general more prone to reaction than in the water where sunlight is less intense. Therefore, PAH in the air are classified generally in the short half-life class than that in the water (Mackay et al., 1992). In the soil, PAH are likely to be preserved by sorption processes and partially screened from sunlight. The latter is likely similar to the situation in the leaf, where PAH are assumed to be absorbed by the lipid in the leaf. However, some of PAH can be lost during the partitioning due to possibility of microorganisms available on the leaves. This is supported by the wilting/aging sign visually observed on the last day of the partitioning experiments. This event probably leads to the unexpected lower partition coefficients, which are clearly seen by abrupt drop of bioconcentration when log K_{ow} reaching about 5.

Relationships with Other Physicochemical Properties

Besides K_{ow}, some other physicochemical properties of the compounds i.e. molecular weight (MW), aqueous solubility and vapour pressure (VP, kPa) (in Table 2.1), were investigated for the relationships to bioconcentration in leaf using the data from the leaf lipid-water partitioning experiments (in Table 4.1). Such correlations are generally good

indicating the potential for the use of these properties to predict the bioconcentration in leaf (in Table 4.2 and Figure 4.1). It is interesting to note that a relatively non-specific parameter such as MW has a reasonably good correlation coefficient. This is presumably due to the close chemical relationships among different members of this group.

4.1.2 Leaf-Air Partition Coefficients

This leaf-air partitioning model is based on one compartment, i.e. lipid. When equilibrium is established, the chemicals partitioning between leaf lipid and the air are constant and can be described by partition coefficients as following.

$$K_{LA} = C_L C_A^{-1} \quad (4.4)$$

where C_L and C_A are the concentrations in the leaf and in the atmosphere respectively at equilibrium and K_{LA} is the leaf-air partition coefficient. Equation 4.4 can be expanded using equilibrium concentration of the chemicals in water ($C_W C_W^{-1}$) as follows

$$K_{LA} = (C_L C_W^{-1}) (C_W C_A^{-1})$$
(4.5)

Universal Gas Law states that PV = n RT, where P the pressure of a substance (kPa), V the volume of gas under investigation (m^3), n the amount of a substance (mole), R the Universal Gas Constant (kPa $m^3 mol^{-1} T^{-1}$), and T the absolute temperature (^oK). Then, $P = n RT V^{-1}$. But, since $n V^{-1} = C_A$ where C_A is concentration in the air. Then, $P = C_A RT$ or $C_A = P (RT)^{-1}$. But

$$K_{AW} = C_A C_W^{-1} \quad (4.6)$$

Substituting for C_A using the expression of $C_A = P (RT)^{-1}$ in Equation 4.6. Then

$$K_{AW} = P (RT C_W)^{-1} \quad (4.7)$$

Table 4.2 Regression Coefficients for the relationships of log K_{LLW} with some physicochemical properties of PAH

Properties	$\log K_{LLW} = a\,(Property) + b$		
	a	b	r^2
log K_{ow}	0.64	1.92	0.75
MW	0.02	2.08	0.74
S	-0.045	5.10	0.60
VP	-0.49	5.04	0.50

Properties	$\log K_{LLW} = a\,(Property)^2 + b\,(Property) + c$			
	a	b	C	r^2
log K_{ow}	-1.23	11.15	-20.23	0.78
MW	-0.0005	0.17	-10.61	0.87
VP	-0.06	0.53	3.76	0.89

But $P\ C_W^{-1} = H$, where H is the Henry's Law constant (kPa $m^3 mol^{-1} T^{-1}$), Substitute H in Equation 4.7 and Equation 4.7 in Equation 4.5 then Equations 4.8-4.9 obtained respectively.

$$K_{AW} = H\ (RT)^{-1} \text{ or } K_{WA} = RT\ H^{-1} \quad (4.8)$$

$$K_{LA} = (C_L\ C_W^{-1})\ (RT\ H^{-1}) \text{ or } K_{LLA} = (C_{LL}\ C_W^{-1})\ (RT\ H^{-1}) \quad (4.9)$$

where C_{LL} is concentration in the leaf lipid. Replace $C_{LL} C_W^{-1} = K_{LLW}$ and RT =2350 Pa $m^3 mol^{-1} T^{-1}$ in Equation 4.9, Equation 4.10 is established and used as a basis for calculating leaf lipid-air partition coefficients in this study (Table 4.3).

$$K_{LLA} = 2350\ K_{LLW}\ H^{-1} \quad (4.10)$$

Comparison with other Vegetation-Air Partitioning Model

A number of vegetation-air partition coefficients are available in the literature but the comparisons are difficult due to some reasons, i.e. units not clearly identified (Polder et al., 1998; Kömp and McLachlan, 1997), lipid fraction in plants not available (McCrady and Maggard, 1993; Reischl, 1989). In addition, different basis of expression (i.e. based on dry weight or wet weight) and moisture content not provided lead to difficulty for inter-comparison. However, these finding mostly concentrated on PCB and few of them can be used. Since there is little data available on the distribution of PAH in the vegetation-air system as described previously, only few studies found appropriate for comparison. One of them was conducted by Simonich and Hites (1994) who measured the partitioning of PAH between vegetation (*Acer saccarum* and *Pinus strobus*: tree bark, seed, needle, leaf) and the atmosphere over growing seasons and under natural conditions. Their vegetation-air partition coefficients (K_{VLA}) in the unit of $m^3 mg^{-1}$, not appropriate for comparison, therefore are converted to Lkg^{-1} and again to dimensionless with factors of 10^9 and 0.92 (leaf lipid density) respectively so as to have the same unit and basis as in our experimental K_{LLA} in this study (see Table 4.4). The adjusted values of K_{VLA} are 0.48×10^8 for PHE and 1.77×10^8 for PYR which are somewhat similar to the experimental K_{LLA} for PHE

Table 4.3 Experimental leaf lipid-air partition coefficient (K_{LLA}) calculated from the leaf lipid-water partition coefficients and Henry's law constant.

Compounds	K_{LLW} ($x10^3$)	H (Pa $m^3 mol^{-1}$) at 25° C	Experimental K_{LLA}	
			$^{**}K_{LLA}$ $x10^5$	log K_{LLA}
NAP	11.4	44.60	6	5.78
ACY	19.3	8.40	54	6.73
ACE	33.7	12.70	62	6.80
FLO	51.2	7.91	152	7.18
ANT	26.2	7.34	84	6.92
PHE	162	7.47	510	7.71
FLU	214	8.60	590	7.77
PYR	114	8.61	300	7.49
BaA	5.1	9.52	13	6.10
CHR	3.1	10.42	7	5.84
BbFLU	0.6	10.17	1.4	5.15
BaP	0.3	10.77	0.7	4.81
BkFLU	0.05	11.18	0.1	4.01
IP	-	na	-	-
BghiP	0.0019*	11.01	0.004	2.61
DbahA	0.0001*	13.91	0.00016	1.22

* Calculated from $\log K_{LLW} = -1.23 (\log K_{OW})^2 + 11.15 \log K_{OW} - 20.23$, ** $K_{LLA} = 2350 K_{LLW} H^{-1}$

na-not available

Table 4.4 Comparison of the experimental partition coefficients on the lipid weight basis obtained in this study with other similar partitioning model and basis.

	log K_{LLA}				log K_{HLA}	
PAH	This work	Ref 1	Ref 2	Ref 3	Ref 4	Ref 5
NAP	5.78		-		-	6.92
ACY	6.73		-		-	-
ACE	6.80		-		-	-
FLO	7.18		-		-	7.99
ANT	6.92	7.59	6.45	7.36	-	-
PHE	7.71	7.68	7.92	7.65	-	8.67
FLU	7.77	8.22	8.30		-	-
PYR	7.49	8.25	8.32		-	10.15
BaA	6.10	9.12	8.40		-	-
CHR	5.84	9.07	8.51		-	-
BbFLU	5.15	9.36	8.81		-	-
BaP	4.81		8.41		-	-
BkFLU	4.01		9.20		-	-
IP			-		-	-
BghiP		9.4	-		-	-
DbahA			-		-	-
PCB-Cl3 #28#31			-		8.6	-
PCB-Cl4 #52			-		8.9	-
PCB-Cl5 #101			-		9.3	-
PCB-Cl6 #138			-		9.6	-
PCB-Cl6 #153			-		9.5	-

IUPAC number. Ref 1: Simonich and Hites (1994); *Acer saccarum* and *Pinus strobus*. Ref 2: Müller et al. (1997); *Malaleuca*. Ref 3: Tolls and McLachlan (1994); *Lolium multiflorum*. Ref 4: Schramm (1997); human head hair. Ref 5: Karnchanasest 2000; human head hair

and PYR respectively. Our results of PAH with log K_{OW} >5.3 are shown apparently having bioconcentration much lower than that studied by Simonich and Hites (1994).

Müller et al. (1994) also measured the vegetation-air partition coefficients (K_{VA}, dimensionless) for PAH in *Melaleuca* leaves over five months and under natural conditions. Their values per vegetation weight were converted to lipid weight basis using a factor of 0.045 as an estimated lipid fraction in the leaves. It is noted that the K_{VA} were averaged from five-month measurements and presented in Table 4.4. Our results have slightly lower bioconcentration than their measurement but a lot more lower is observed when PAH with log K_{OW} > about 5.3, however, some of our data similar to those in *Lolium multiflorum* which were investigated using a solid-phase fugacity meter (Tolls and McLachlan, 1994). In comparing results from Simonich and Hites (1994) and Müller et al. (1994), they are somewhat equivalent but slightly difference is noticeable with PAH of log K_{OW} >about 5.3.

Our results do not all agree well with other investigations probably due to a range of factors, i.e. species difference, accuracy in lipid density and lipid fraction used. Since bioconcentration in leaf from water as expressed by the linear regression relationships with log K_{OW} decline sooner than it should be (log K_{OW} about 6) at log K_{OW} about 5.3 in Figure 4.1, the bioconcentration in leaf from the air calculated from them unavoidably behave accordingly. It is also suspected that the discrepancy may result from the experimental basis since our results derived from the partitioning experiment between the leaf and the water, unlike other previous described experiments, which were carried out on the natural condition of leaf-air partitioning. Particularly, the slight aging sign of leaves in the water was observed and if the experimental basis is a cause, then, a rather persistence biota, e.g. hair, is appropriate to utilize this technique (i.e., derivation of K_{LLA} from K_{LW}), otherwise, a degradation protection should be minimized.

Comparison with Hair-Air Partitioning Model

Since PCB have somewhat similar physicochemical properties to the test compounds, the hair-air partition coefficients (K_{HA}) for PCB measured by exposing hair in a fire experiment (Schramm, 1997) are compared. Conversion of his values (K_{HA}, $m^3 kg^{-1}$) to the same units as our experimental K_{LLA} values was conducted using a factor of 10^3

(conversion from m^3 kg^{-1} units to L kg^{-1} units), 0.023 (lipid fraction) and 0.92 (hair lipid density). Table 4.4 gives K_{HLA} values for PCB in the range 4 $x10^8$ to 30 x 10^8. In this study, the test compounds include PAH within the log K_{OW} range between 3.40-6.75 whilst PCB are in the log K_{OW} 5.75-7.44. Figure 4.2 gives biota-air partition coefficients in relation to log K_{OW}. Clearly, the K_{HLA} values for PCB in the same range of log K_{OW} with K_{LLA} for PAH, have much higher values than our results. This should not partly related to the compound persistence since PCB tend to be more resistance to oxidation and biodegradation than PAH, but the cause might be the aging in leaf during partitioning experiment in this study. However, the work of Schramm likely parallel to the studies of Simonich and Hites (1994) and Müller et al. (1994) are observed, however slightly higher than vegetation-air values. This conforms to the persistence property of the compounds (PCB>PAH) and of the biota (hair>plant). It is also not surprising that our results are lower than K_{HLA} derived from similar hair-water partition experiments for the same compounds as in this study due to compounds in the hair and the hair itself are less likely to be biodegraded than that in the leaf and the leaf itself. This results from the structure of hair, which is keratin-containing appendage (Karnchanasest, 2000).

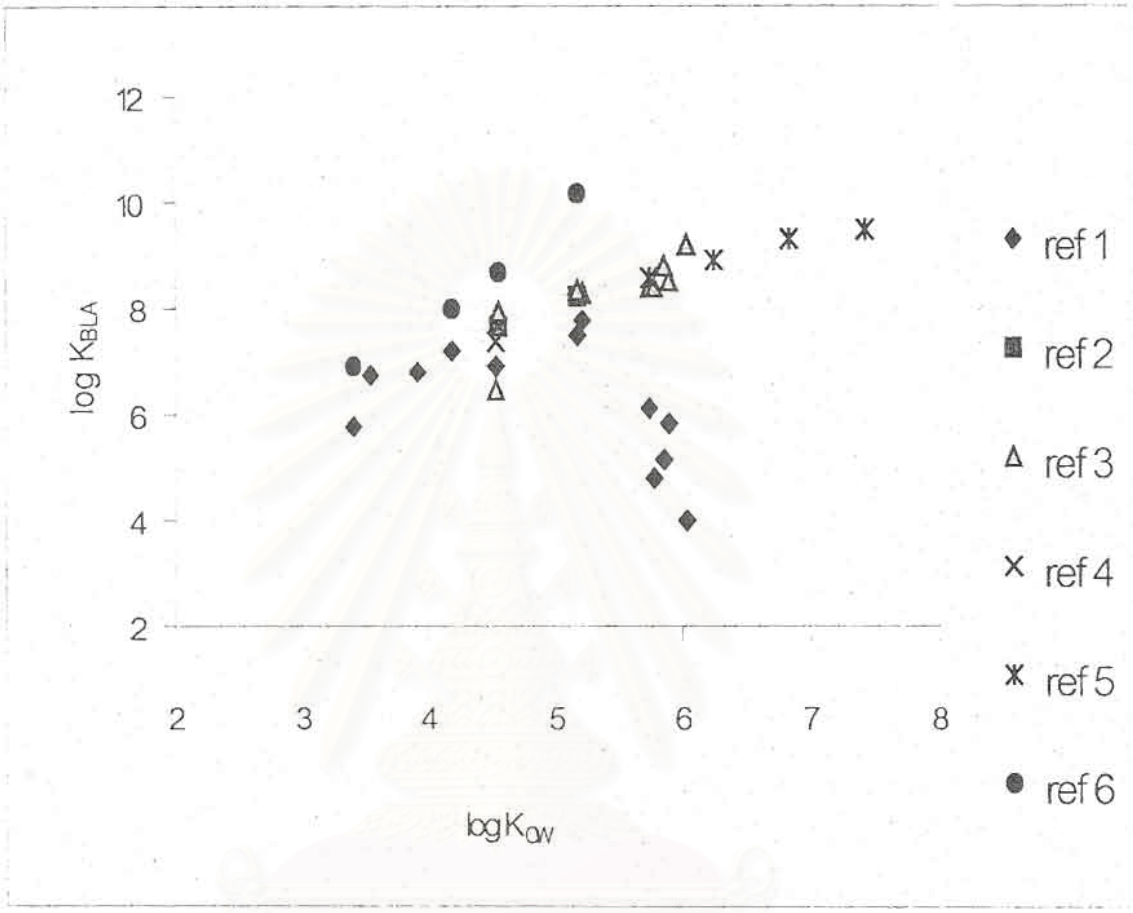
Relationships with Octanol-Air Partition Coefficient (K_{OA})

The octanol-air partition coefficient (K_{OA}) has often been used as a parameter in establishing QSAR (Böhme et al., 1999; McLachlan, 1999; Kömp and McLachlan, 1997; Simonich and Hites, 1994; Tolls and McLachlan, 1994; Paterson and Mackay, 1991a; Bacci et al, 1990a). The K_{OA} values can be defined as follows

$$K_{OA} = C_O C_A^{-1} \qquad (4.11)$$

where C_O concentrations in octanol and C_A concentrations in the air at equilibrium. Introducing the water phase, $C_W C_W^{-1}$, in Equation 4.11, then,

$$K_{OA} = C_O C_W^{-1} C_W C_A^{-1} \qquad (4.12)$$



Ref 1: This study (2003); Ref 2: Simonich and Hites (1994); *Acer saccarum* and *Pinus strobus*. Ref 3: Müller et al. (1997); *Malaleuca*. Ref 4: Tolls and McLachlan (1994); *Lolium multiflorum*. Ref 5: Schramm (1997); human head hair. Ref 6: Karnchanasest 2000; human head hair

Figure 4.2 Biota (plant or hair) -air partition coefficients in relation to log K_{ow}

substituting $K_{OW} = C_O C_W^{-1}$ and $K_{WA} = C_W C_A^{-1}$ in Equation 4.12, the following is then obtained.

$$K_{OA}=K_{OW} K_{WA} \quad (4.13)$$

substituting Equation 4.8 ($K_{WA} = RT H^{-1}$) and RT = 2350 Pa m^3 mol^{-1} T^{-1} in Equation 4.13, then,

$$K_{OA} = 2350 K_{OW} H^{-1} \quad (4.14)$$

This equation can be used to calculate values for K_{OA} from the K_{OW} and H values. The relationship between K_{OA} and K_{HA} can be considered as outlined below.

$$K_{LA} = C_L C_A^{-1} \quad (4.15)$$

where K_{LA} is the leaf-air partition coefficient, C_L and C_A are the concentrations in leaf and air respectively at equilibrium. If lipid is the only medium which accumulates these lipophilic PAH, then

$$K_{LA} = y C_{LL} C_A^{-1} \quad (4.16)$$

where C_{LL} is the concentration of PAH in the leaf lipid. If octanol is a perfect surrogate for the leaf lipid, then

$$K_{LA} = y C_O C_A^{-1} \quad (4.17)$$

$$K_{LLA} = C_O C_A^{-1} \quad (4.18)$$

where K_{LLA} is the leaf lipid-air partition coefficient. Since $C_O C_A^{-1}$ is the octanol-air partition coefficient (K_{OA}), Equations 4.17-4.18 become

$$K_{LA} = y\, K_{OA} \quad (4.19)$$

$$K_{LLA} = K_{OA} \quad (4.20)$$

If logarithms are taken to both sides of these equations, they result in

$$\log K_{LA} = \log K_{OA} + \log y \quad (4.21)$$

$$\log K_{LLA} = \log K_{OA} \quad (4.22)$$

where y is the lipid fraction of the leaf. The relationships between the experimental values of K_{LLA} and log K_{OA} for the PAH is illustrated in Figure 4.3. The solid lines in these figures are in linear regression lines which have a slope = 0.41 and an intercept = 4.28 on a lipid weight basis. The corresponding regression equations are described in Equations 4.23 and below.

$$\log K_{LLA} = 0.41 \log K_{OA} + 4.28 \qquad (r^2 = 0.64) \text{ (lipid weight)} \quad (4.23)$$

This finding is in agreement with expectation suggesting the partitioning between leaf and the atmosphere is governed by the leaf lipid and that K_{OA} is strongly related to K_{LA} and K_{LLA}. The slope and intercept are close to unity and zero respectively. The discrepancy is similar to the relationships between K_{LW} and K_{LLW} with K_{OW}. Related studies on the vegetation gave lower slope of 0.20 (Müller, 1997), 0.35 (Kaupp, 1996 in Müller, 1997), and 0.48 (Simonich and Hites, 1994). However, greater slope for the plots between log vegetation-air partition coefficients and log K_{OA} were obtained from controlled exposure experiments: a slope =0.91 for SOC, i.e. QCB, HCB, HCH, PCB, PAH, CIA and TCN (Tolls and McLachlan, 1994) and a slope=1.09 for PCB (Kömp and McLachlan, 1997). This may result from the experimental conditions: pollutant fluctuation and temperature in the atmosphere as compared to the steady condition of controlled exposure experiments. In the leaf-air partition coefficient calculations, the leaf-water values as well as Henry's law constant values are used. These values measured under controlled laboratory conditions,

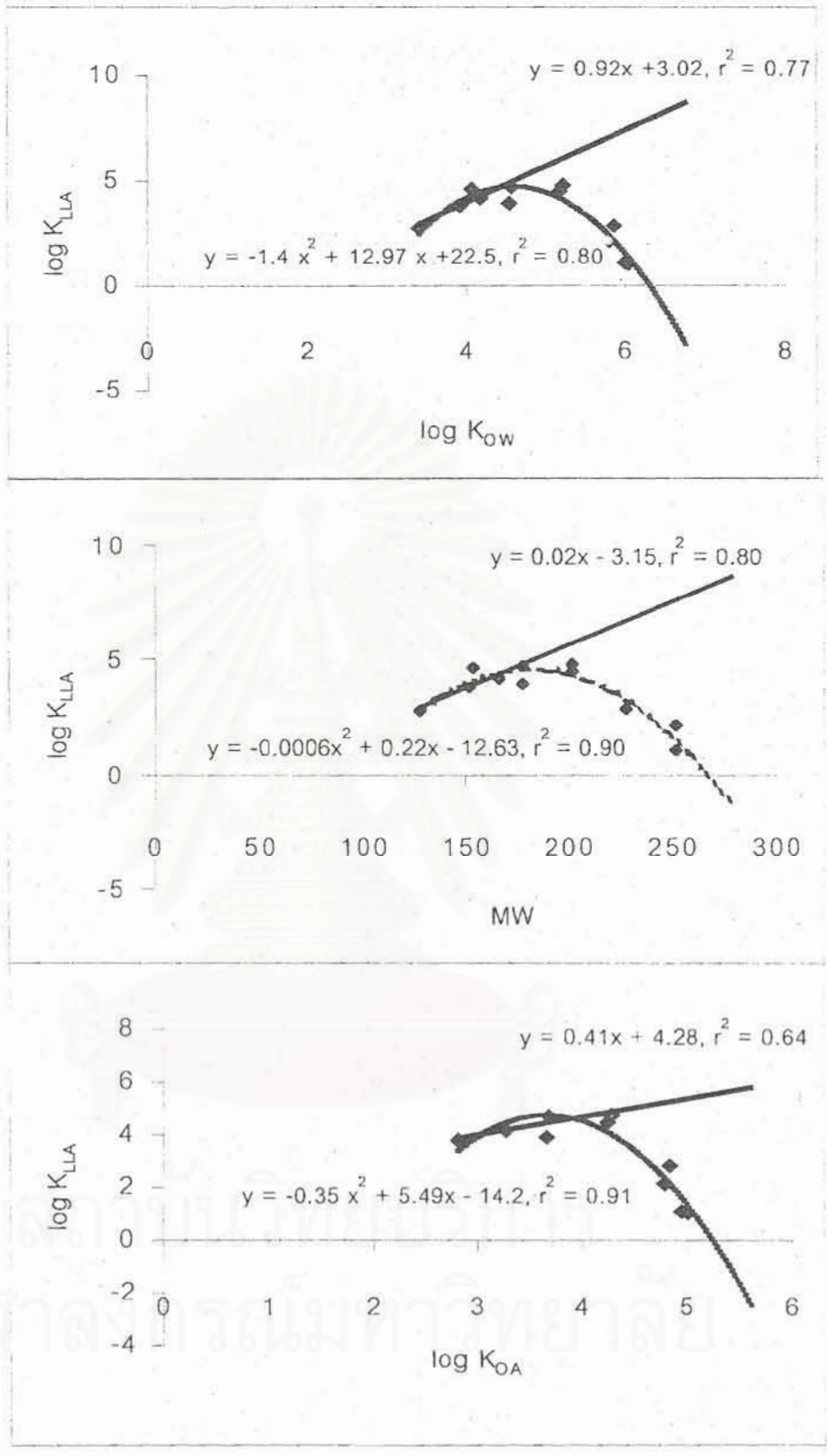


Figure 4.3 Linear and polynomial regression of the relationships of log K_{LLA} to log K_{OW} , MW and log K_{OA}

which would be expected to yield more satisfactory results. The K_{OA} values in this investigation are calculated from K_{OW}, H and the temperature effects are not taken into account. This may account for some of the discrepancies observed (Kömp and McLachlan, 1997; Simonich and Hites, 1995).

Relationships with Other Physicochemical Properties.

The relationships between log K_{OW}, MW, VP, S (in Table 2.1) and the leaf lipid-air partition coefficients are explored (see Figure 4.3 and Table 4.5). The plots between these simple properties of compounds and the K_{LLA} values illustrate significant relationships between these parameters and K_{LLA}.

4.2 Influencing Factors of Leaf-Air Partitioning

4.2.1 Lipid Content

The leaf-air partition coefficient values for the same compound and under the same environmental conditions can be varied. This is partly due to the difference in the lipid concentration and is supported by the work of Simonich and Hites (1994). The different values of PAH in the barks, needles, seeds, and leaves of the same plant was observed. The authors also noted there was a positive relationship between lipid content and the PAH concentrations.

4.2.2 Environmental Factors

Degradation

Photodegradation is likely to occur both in the leaf and in the air. However, once compounds sorbed in the leaf, the rate of degradation would be expected to be substantially reduced. This is unlike those in the air, which is subject to direct sunlight. This is supported by the study of photodegradation rate. PAH concentrations in the atmosphere during 10 a.m. to 4 p.m.were found to be reduced by a factor of 2 as compared to the time between 4-10 a.m. and 4-8 p.m. (Freeman and Cattell, 1990). It was estimated that half-life for photo-oxidation of PYR in the air could be as fast as 0.802- 8.02

Table 4.5 Regression coefficients for the relationships of log K_{LLA} with some physicochemical properties of PAH

Properties	log K_{LLA}= a(Property) + b		
	a	b	r^2
log K_{OW}	0.92	-3.02	0.80
MW	0.02	-3.15	0.80
S	-0.05	7.37	0.74
VP	-0.70	7.76	0.90
log K_{OA}	0.41	4.28	0.64

Properties	log K_{LLA} = a(Property)^2 + b(Property) + c			
	a	b	c	r^2
log K_{OW}	-1.40	12.97	-22.50	0.80
MW	-0.0006	0.22	-12.63	0.90
VP	-0.07	0.77	5.22	0.91
log K_{OA}	-0.35	5.49	-14.20	0.91

h^{-1} as compared to NAP of which was 2.96-29.6 h^{-1}. In many situations, oxidation with reactive radicals in the atmosphere could accelerate the process and results in significant degradation of PAH present. Due to PAH in leaf is likely to be preserved by sorption process similarly to the situation in the soil, thus, effects of photodegradation in leaf could be relatively insignificant when compared to that in the air. However, some PAH can be biodegraded or biotransformed by microorganisms in the leaf/ the air (i.e. yeast, fungi, bacteria) (Neilson, 1994; Neff, 1979). The microbial degradation rate constant in air was reported, e.g., for NAP to be as low as 0.23 h^{-1} and biodegradation rate constant in the air for PYR was 0.29 h^{-1} (Mackay et al., 1992; Howard et al., 1991). Degradation of NAP was readily degraded by bacteria while PHE was more readily degraded than ANT (Neilson, 1994).

Growth Dilution

Growth in plants occurs chiefly at meristems where rapid mitosis provides new cells. As these cells differentiate, they provide new plant tissue. Growth rate of plants depends on the stage of development. The growth is low shortly after germination. The growth occurs mainly at vegetative phase until reaching the final stage of maturation and that the growth ends. Thus, inconsistent growth in life cycle of plants can lead to discrepancy in the interpretation of plant uptake. However, the dilution by growth can be calculated from the growth rate constant ((Trapp and Matthies, 1995).

Temperature and Seasonal Variations

Nakajima et al. (1995) and Simonich and Hites (1994) reported that partitioning of PAH between the atmosphere and the vegetation *(Acer saccarum, Pinus strobus*, and *Rhododendron oo-murasaki)* was dependent on ambient temperature (T). A plot of logarithmic of the vegetation-air partition coefficient, K_{VA} for PAH versus the reciprocal of temperature (1/T) exhibited a linear regression line indicating that a decline in temperature resulted in an increase of BCF and vise versa (Simonich and Hites,1994). This finding was in accord with the study of Kömp and McLachlan (1997) for PCB on *Lolium multiflorum* and in agreement with theoretical expectations as expressed in a van't Hoff-type equation, which described the temperature dependence as follows.

$$K_{VA}(T) = K_{VA}(T_R)\exp\left[\left(\frac{1}{T} - \frac{1}{T_R}\right)\frac{\Delta H_{PA}}{R}\right] \quad (4.24)$$

where T is the ambient temperature (K), T_R is a reference temperature (K), R is the gas constant (Pa $mol^{-1}m^3$), and ΔH_{PA} is the enthalpy of phase change between the vegetation and the air (J mol^{-1}). The investigation of Kömp and McLachlan (1997) using PCB under controlled laboratory conditions to validate Equation 4.24 suggested that it was only applicable to SOC with log K_{OA} < 8.1. This is in accord with the finding that K_{OA} was strongly induced by temperature and K_{OA} increased by a factor of 30 with a change of temperature from –10 °C to +20 °C. suggesting a temperature dependence of K_{VA} (Harner and Mackay, 1995). For higher log K_{OA} values, the response of the vegetation-air partition coefficient to temperature change can be negligible. This can be explained by that higher MW PAH are more tightly bound to particles, thus, the effect of temperature is insignificant (Simonich and Hites, 1994). Compounds with log K_{OA} < 8.1 correspond to PAH less than five rings which includes compound group studied in this work.

Influence of seasonal variation on K_{VA} is currently controversal. However, Simonich and Hites (1994) described that levels of PAH concentrations varied accordingly to seasonal changes and were high in spring, decreased in summer and increased again in fall. On the contrary, Kömp and McLachlan (1997) argued this was not related to seasons but the decreased concentrations were as a result of combination affect of growth dilution, leaf surface wash-out, and meteorological driven sources.

Wet and Dry Deposition of Gas and Particle Phases

Mechanism for the uptake of organic pollutant in the leaf from the air is based on dry deposition of gas phase. This is the main pathway for bioconcentration of many lipophilic compounds in plants. However, high MW lipophilic compounds with log K_{OW} > 7 or log K_{OA}> 8.1 are mostly bound to particles particularly in autumn when temperatures become lower (Simonich and Hites, 1995). Fine particles with size of less than 3 μm typically have very low deposition velocity and are poorly scavenged by the rain (Trapp and Matthies, 1995). Thus, it is suggested that the contribution of dry deposition of fine particles to the

concentration in leaf is probably low. Wet or droplet deposition, which usually occurs with large particles, is likely to be effective for low MW lipophilic compounds, which have relatively high aqueous solubility. On the other hand, the lipophilic property of the leaf surface provides a very effective sorption layer for these compounds leading to an uptake of low MW PAH bound to large size of particles by this mechanism.

4.3 Overall evaluation

The results suggest that bioconcentration of PAH in leaves from water increases in similar extent as in fish. This conclusion is indicated by plots of the regression line of log K_{LW} and log K_{LLW} against log K_{OW} corresponding plots developed from fish using chlorinated hydrocarbon and PAH. The trend for bioconcentration capacity is in linear form and parallel to compound having log K_{OW} 3 to about 5, then declines afterwards in second order polynomial shape for all 13 PAH. This is theoretical support that extremely hydrophobic (log K_{OW} >6) do not bioconcentrate as much as those lesser hydrophobic since large compounds decrease in lipid and aqueous solubilities. However, the bioconcentration dropped before log K_{OW}= 6 may result from the biodegradation during partitioning experiments. The similar behavior also occurs on the bioconcentration in leaf from the air since these values calculated from bioconcentration in leaf from water. The behavior of the experimental leaf-air partition coefficients is parallel to the theory and other studies with compounds having log K_{OW} not more than 5.3. For those log K_{OW} >5.3, they do not agree well with other investigation probably as a result of experimental conditions, accuracy of conversion factors used to normalize to the same unit and biodegradation during partitioning experiments. In comparison to similar model of hair-air for PCB, the lower values of our experimental results are shown likely due to higher persistence of PCB, relatively higher persistence in hair and degradation in the leaf-water partitioning. Similar outcome is obtained in comparing results with other hair-air model for PAH derived from hair-water partitioning.

The relationships of log K_{LW} and log K_{LLW} with log K_{OW} indicate the suitability of K_{OW} for the use as a QSAR for bioconcentration of PAH from water in leaf. Similar plots but with log K_{LA} or log K_{LLA} also point out the potential of QSAR approach. In addition, physicochemical properties, i.e. S, MW, BP, VP also have generally good correlation with bioconcentration

in leaf indicating the potential use of these characteristics for prediction of bioconcentration of PAH in leaf.

A number of factors can influence the leaf-air partition coefficient. The lipid fraction has a strong influence on the level of bioconcentration in leaf both from the air and the water. The model is temperature dependence for SOC with log K_{OA} <8.1 since higher MW are tightly bound to particles. The dry deposition of gas phase is responsible for the bioconcentration process. Also, the plant growth tends to effect the dilution in bioconcentration in leaf from the air. In many situations, microbial and photodegradation could substantially reduce PAH concentrations. Particles with size larger than 3μm usually have high deposition rates resulting in a washout of high MW lipophilic compounds bound to these particles. Wet deposition is likely to be effective for low MW lipophilic compounds, which have relatively high aqueous solubility.

Chapter 5

Evaluation of Plant Leaves as a Monitor of PAH

5.1 Observed Values of Atmospheric PAH

5.1.1 Particle Phase Concentrations

The particle phase concentrations of PAH are those associated with suspended particulates in the atmosphere, which is measured in term of total suspended particulates (TSP). TSP were collected using high-volume air samplers to cover 4 Bangkok urban roadsides; Patumwan (PW), Kasemraj (KR), Pongpetr (PP), and Sapankwai (SK), where a range of traffic volume were reported by the BMA. The samples were extracted, analyzed for sixteen PAH and reported in Table 5.1. The temperature at the time of sampling were also recorded (Table 5.2).

Panther et al. (1996) measured the particle phase concentrations of 20 PAH including 16 USEPA priority during 1993-1994 (except Nov 1993 to Jan 1994) at Chulalongkorn University in Bangkok. Since our sampling sites are located on roadsides, the university site can be accounted as off-roadsides. Clearly, individual PAH burden in these two sites confirms the decline of PAH related to the distance from the roadway. These results are in accord with the studies on the relationship between the concentrations on-roadsides and the distance from the roadsides since as a general rule concentrations of PAH in soil and leaf litter decline with the distance from roadways (Pathirana et al., 1994; Yang et al., 1991). The total PAH burden therefore agrees accordingly (off-roadsides; 5-74 ng $m^{-3}$and roadsides; 25-119 ng m^{-3}). In overall, the low MW contribution to the PAH burden outweighs the higher MW. On off-roadside, ACY and ACE were the major low MW PAH present followed with NAP and FLU while BeP was significant for high MW PAH which added up to 10.5% of total PAH. Similar contribution of low MW in four roadside air is observed, i.e. ACY, FLO, and PHE. ACY outweighs at three out of four sites and PHE leads the rest site. This is not in accord with Taiwan urban ambient air that NAP was ruled out (225 $\mu g\ g^{-1}$) and FLO ranked the fifth (36 $\mu g\ g^{-1}$) (Lin Sheu et al, 1997). Other dominant PAH was FLU (15 ng m^{-3}) in Massachusetts urban followed with PHE (13 ng m^{-3}).

Table 5.1 Average TSP ($\mu g\ m^{-3}$), particle phase ($ng\ m^{-3}$) and total concentrations of PAH in the roadside air.

Compounds	Sampling Sites			
	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	ND	ND	ND	ND
ACY	50.29	39.12	ND	59.29
ACE	0.002	ND	0.03	0.002
FLO	24.66	19.25	ND	ND
ANT	1.40	1.25	1.52	1.52
PHE	18.63	15.45	17.27	22.26
FLU	3.07	3.94	2.77	3.60
PYR	ND	1.68	1.30	ND
BaA	ND	15.77	ND	0.44
CHR	0.002	ND	1.30	ND
BbFLU	0.63	8.45	0.52	0.98
BaP	0.09	0.78	0.05	0.24
BkFLU	0.12	2.08	ND	0.011
IP	0.70	11.09	0.64	0.85
DbahA	0.002	ND	ND	0.002
BghiP	0.001	0.03	0.002	0.001
Total PAH	99.60	118.89	25.40	89.20
TSP	172.81	185.77	156.89	217.44
	(168.20-180.11)	(110.60-279.80)	(137.69-166.85)	(198.50-244.50)

Table 5.2 Mean daily atmospheric conditions on the sampling sites

Sampling sites	Temperature (°C)	% Relative humidity	Rainfall (mm)	Total sunshine in a month (h)
Kasemraj	31-32		19 rainy days	
Patumwan	32-33	64-90 (min-max)	37.14 daily	194.7
Pongpetr	27-30	78 (mean)	maximum	
Sapankwai	27-31			

Contribution to PAH burden in the ambient air can be alternately described by the profile, which is defined as the percentage of individual concentrations to that of total PAH. PAH profiles for particle phase are presented in Table 5.3. The profiles are dominated by ACE (33-67%), FLO (16-25%) and PHE (13-25%) at KR, PW and SK. But PHE (68%), FLU (11%) and ANT (6%) are outstanding at PP.

5.1.2 Gas Phase Concentrations

The gas phase concentrations obtained were calculated from the relationship between particle phase concentrations (in Table 5.1), particle-gas partition coefficient (K_p) and K_{OA} values. Firstly, the log K_p values were estimated by their relationship with K_{OA} which were developed by Finizio et al. (1997) from urban particulate matters as shown in Equation 5.1 (see results in Table 5.4). For K_{OA} of 16 PAH, the values were mainly obtained from the finding of Mackay et al. (1992) at 25°C. Those missing data were estimated from K_{OW}/K_{AW}.

$$\log K_p = 0.79 \log K_{OA} - 10.1 \qquad (N=10)\ (r^2 = 0.97) \qquad (5.1)$$

Since K_p values are highly temperature-dependent. Thus, particle-gas partitioning tends to favour particles when the ambient temperature decreases (Yamasaki et al., 1982). However, it should be noted that the log K_{OA} values are based on an ambient temperature of 25°C whereas the average temperatures under investigation of particle phase were 30° C (27-33°C). Since higher temperature favors the gaseous phase, calculated K_p values for Bangkok urban air would be higher than it should be.

In evaluation of the derived K_p values, our estimated K_p fit generally well with those of Finizio et al. (1997) who calculated the average values of K_p from various relationships of K_p and subcooled liquid vapor pressure in the literature, although a slight lower values in this study are observed (Table 5.4). The K_p values derived in this study are lower by a factor of 3-6 as compared to those (Ref 2 in Table 5.4) from field measurement (Kaupp and McLachlan, 1999). Since K_p values are closely correlated with the inverse of ambient temperature (Yamasaki et al., 1982), it is not surprising that the higher values of log K_p

Table 5.3 Particle phase profile* of PAH on the roadsides.

PAH	Roadsides			
	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	-	-	-	-
ACY	50.49	32.90	-	66.47
ACE	0	-	0.10	0
FLO	24.79	16.20	-	-
ANT	1.39	1.05	6.00	1.71
PHE	18.69	13.00	68.0	24.97
FLU	3.10	3.31	10.90	4.03
PYR	-	1.41	5.10	-
BaA	-	13.26	-	0.49
CHR	0	-	5.12	-
BbFLU	0.63	7.11	2.05	1.11
BaP	0.09	0.66	0.20	0.27
BkFLU	0.12	1.75	-	0
IP	0.70	9.33	2.52	0.95
DbahA	0	-	-	0
BghiP	0	0.02	0	0

* (Individual PAH x 100)/Total PAH

Table 5.4 log K_P ($m^3 \mu g^{-1}$) values derived from log K_{OA} as compared to other studies.

Compounds	log K_P					
	1	2	3	4	5	6
	25°C	25°C	25°C	25°C	7°C	20°C
NAP	-6.09					
ACY	-4.27					
ACE	-5.26				4.12	
FLO	-4.84		-4.48		3.36	
ANT	-4.50		-4.27			-4.81
PHE	-4.30	-3.89	-4.20	-3.66	3.02	-4.97
FLU	-3.30	-2.92	-3.37	-2.76	2.20	-3.70
PYR	-3.12	-2.60	-3.27	-2.59	2.09	-3.45
BaA	-	-1.94	-2.13		0.44	
CHR	-2.53	-1.71	-2.16		0.56	
BbFLU	-1.83					
BaP	-1.51					
BkFLU	-1.28					
IP	-					
DBahA	-1.06					
BghiP	-0.43					

[1]This study, [2]Kaupp and McLachlan (1999), [3]Finizio et al. (1997), [4]Pankow et al. (1994), [5]Ligocki and Pankow (1989), [6]Foreman and Bidleman (1987).

measured at a coastal site (ref 5 in Table 5.4) where ambient temperature was relatively low (7°C) are observed (Ligocki and Pankow, 1989). However, the lab measurement of K_p at lower temperature (ref 6 in Table 5.4) exhibited unexpected less than in this study.

The second step to calculate gas phase concentrations (A) is to substitute known concentrations of TSP, particle associated concentrations (F) (in Table 5.1) and K_p into Equation 5.2 results in gas phase values shown in Table 5.5. Equation 5.2 is a useful expression that has been used in characterizing particle-gas partitioning of SOC in the atmosphere (Pankow, 1998; Pankow, 1987; Yamasaki et al., 1982).

$$K_p = (F/\ TSP)/A = C_p/C_G \qquad (5.2)$$

where K_p is in $m^3\ \mu g^{-1}$, F and A are in ng m^{-3}, TSP is $\mu g\ m^{-3}$, C_p is the concentration in/on the particle phase (ng μg^{-1} TSP), and C_G is the concentration in the atmosphere (ng m^{-3}). Assuming artifacts are free, then F and A should be equal to C_p and C_G respectively.

It can be seen that the gas phase exceeds the particle phase for all compounds at Bangkok roadsides. It is possible that at high temperatures the gas phase may increase as a result from volatilization into the atmosphere from particles. Similar profiles for the burden in two sites of KR and PW are FLO (55-56%), ACY (30-31%) and PHE (12-13%). Different profiles are located at PP (85%PHE, 12%ANT, 1%ACE/FLU) and SK (69% ACY, 28%PHE, 3% ANT) (Table 5.6).

5.1.3 Particle and Gas Phase Concentrations

Total particle and gas phases (F+A) concentrations of PAH on roadsides are in the range of 3.61 $\mu g\ m^{-3}$ (PP) to 17.76 $\mu g\ m^{-3}$ (KR) (Table 5.7). FLO is found at highest concentrations (7.16-9.87 $\mu g\ m^{-3}$) at KR and PW but not found in other two sites. ACY is followed with concentrations ranging from 3.93-5.43 $\mu g\ m^{-3}$ in most sites except PP. PHE is abundant at resemble concentrations (1.67-3.21 $\mu g\ m^{-3}$) in all sites. Their contribution in the ambient air is as follows; 55.5% FLO, 30.6% ACY, 12.2% PHE at KR; 54.8% FLO, 30.0% ACY, 12.8% PHE at PW; 89.0% PHE, 8.5% ANT, 1.0% FLU at PP and 68.6% ACY,

Table 5.5 Gas phase concentrations of PAH (ng m^{-3}) in the survey calculated from the relationships of K_p = (F/ TSP)/A (Pankow, 1998).

Compound	Sampling Sites			
	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	-	-	-	-
ACY	5379.17	3892.48	-	5040.17
ACE	2.11	-	34.83	1.68
FLO	9841.38	7146.40	-	-
ANT	256.37	212.94	306.59	221.22
PHE	2151.82	1660.03	3197.15	2043.38
FLU	35.46	42.33	35.24	33.05
PYR	-	11.93	10.93	-
BaA	-	-	-	-
CHR	0.004	-	2.81	-
BbFLU	0.25	3.07	0.22	0.30
BaP	0.02	0.14	0.01	0.036
BkFLU	0.01	0.21	-	0.001
IP	-	-	-	-
DbahA	3.13×10^{-5}	-	-	2.49×10^{-5}
BghiP	6.64×10^{-5}	0.002	0.00015	5.28×10^{-5}
Total PAH	17666.60	12969.53	3587.78	7339.82

Table 5.6 Gas phase profile of PAH in the survey

Compounds	Sampling Sites			
	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	-	-	-	-
ACY	30.45	30.01	-	68.67
ACE	0.01	-	0.97	0.02
FLO	55.71	55.10	-	-
ANT	1.45	1.64	8.55	3.01
PHE	12.18	12.80	89.11	27.84
FLU	0.20	0.33	0.98	0.45
PYR	-	0.10	0.30	-
BaA	-	-	-	-
CHR	0	-	0.08	-
BbFLU	0	0.02	0	0
BaP	0	0	0	0
BkFLU	0	0	-	0
IP	-	-	-	-
DbahA	0	-	-	0
BghiP	0	0	0	0

Table 5.7 Mean atmospheric concentrations of gas and particle phases of PAH on four roadsides.

Compounds	Sampling sites			
(ng m^{-3})	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	-	-	-	-
ACY	5429.46	3931.60	-	5099.46
ACE	2.11	-	34.86	1.68
FLO	9866.04	7165.65	-	-
ANT	257.77	214.19	308.11	222.74
PHE	2170.45	1675.48	3214.42	2065.64
FLU	38.53	46.27	38.01	36.65
PYR	-	13.61	12.23	-
BaA	-	15.77	-	0.44
CHR	0.006	-	4.12	-
BbFLU	0.88	11.52	0.74	1.28
BaP	0.11	0.92	0.06	0.28
BkFLU	0.13	2.29	-	0.012
IP	0.70	11.09	0.64	0.85
DBahA	0.002	-	-	0.002
BghiP	0.001	0.032	0.002	0.001
Total PAH	17766.2	13088.42	3613.19	7429.01

Table 5.8 Gas and particle phases profile of PAH in the survey

Compounds	Sampling sites			
	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	-	-	-	-
ACY	30.56	30.04	-	68.65
ACE	0.01	-	0.97	0.02
FLO	55.53	54.75	-	-
ANT	1.45	1.64	8.53	3.00
PHE	12.22	12.80	88.96	27.8
FLU	0.22	0.35	1.05	0.49
PYR	-	0.10	0.34	-
BaA	-	0.12	-	0
CHR	0	-	0.11	-
BbFLU	0	0.09	0.02	0.02
BaP	0	0	0	0
BkFLU	0	0.02	-	0
IP	0	0.08	0.02	0.01
DbahA	0	-	-	0
BghiP	0	0	0	0

27.8% PHE, 3.0% ANT at SK (Table 5.8). It can be seen that the more volatile PAH are found abundant than those of less volatile compounds in various investigations including this study. Apparently, in Bangkok air, FLO is ruled out accompanied with ACY, PHE, FLU, ANT and PYR. Unlike in British urban air which contained mainly PHE followed with FLO, FLU, ANT, ACY and PYR (Table 5.9). Similar profile as in British air was shown in Brisbane urban air. However, it is difficult to compare these results from different investigations since various factors involved, i.e. different atmospheric conditions, methods, sampling height, land use type, vehicular fuel, etc.

5.1.4 Total PAH Concentrations

Total PAH at Bangkok roadsides have a mean of 83 ngm^{-3} with a range of 25.4-118.9 ng m^{-3} (see Table 5.1). PHE, FLU and PYR found at high concentration at roadsides are in accord with other investigations, which have shown that these PAH are predominant in vehicle emissions (Lowenthal et al., 1994; Westerholm and Li, 1994; Maclet et al., 1986). These values are reasonably higher than the sum of 20 PAH including 16 USEPA priority PAH (25 ng m^{-3}), measured at off-roadsides. The latter measurements had total p-PAH in a range of 5.0-74.0 ng m^{-3}. However, some of these two results may have no difference and that could be influenced by long-range transport by winds (Masclet et al., 1988) from main roads and the loss by photodegradation (Venkataraman and Friedlander, 1994; Arey et al., 1989). Total PAH for both phases obtained in this study and in other investigations is shown on Table 5.9. Due to the complexity of atmospheric reactions, atmospheric concentrations from different sites and different pattern of collections, comparison can be difficult.

5.1.5 Total Suspended Particulates (TSP)

Apart from vehicular traffic which is the main TSP source, combustion of non fossil fuel materials, e.g. bush fires, wood burning, garbage burning and industry emission, can be significant sources for suspended particulates in urban air. Office of National Environment Board in Thailand (ONEB) indicated that about 70-90% of TSP at Bangkok roadsides were from anthropogenic sources (ONEB, 1989) which included diesel-engine exhaust and emission from light industry (WHO/UNEP, 1992). Since there are no major

Table 5.9 Average concentrations of PAH (F+A) in the survey as compared to other studies (ng m^{-3})

	Urban	Brisbane urban[2]			Heavy	British urban[4]			
PAH	Roadsides[1]	Fortitude Valley	Mt Gravatt	Wollongong	industrial[3]	London	Stevenage	Manchester	Cardiff
NAP	-	91	86	94	-	-	-	-	-
ACY	3615.13	23	3.90	35	-	5.78	2.74	2.55	2.86
ACE	9.66	16	2.80	9.90	-	-	-	-	-
FLO	4257.92	25.	3.80	38.11	92	22.50	17.35	20.65	12.55
ANT	250.70	2.63	1.21	4.27	15	5.86	3.65	3.70	2.29
PHE	2281.50	36.40	9.65	35.76	159	79.05	40.95	45.75	34.05
FLU	39.87	4.50	1.73	8.20	56	10.36	6.70	-	-
PYR	6.46	6.03	4.29	14.95	36	9.54	5.61	8.9	6.15
BaA	4.05	0.17	0.11	1.24	21	1.31	1.11	1.68	1.28
CHR	1.03	0.53	0.39	1.98	-	2.27	1.88	2.18	2.09
BbFLU	3.61	0.46	0.14	1.90	-	1.40	1.24	1.30	1.59
BaP	0.34	0.27	0.12	1.50	14	0.81	0.64	1.51	1.15
BkFLU	0.61	0.32	0.25	2.2	-	1.40	1.30	-	-
IP	3.32	0.02	-	0.19	-	-	-	-	-
DbahA	0.001	-	-	-	-	-	-	-	-
BghiP	0.009	1.5	0.31	4.93	11	4.87	3.74	2.14	1.6
Total	10,474.21	207.83	115.7	254.13	404	145.15	86.91	90.36	65.61

[1]This study [2] Muller et al (1996) [3]Cotham and Bidleman (1995) [4] Halsall et al (1994)

sources of PAH on/nearby the four roadsides in the study area, suspended particulates in these areas are presumably from motor vehicle exhaust. The Mean TSP concentrations of 0.18 mgm^{-3}, ranged from 0.16 to 0.22 mgm^{-3}, are within the Thai 24-hour standard (0.33 mgm^{-3}) (see Table 5.1). However, an extreme value of TSP has been reported (0.60 mg m^{-3}) from a location in Bangkok elsewhere in 1989 (WHO/UNEP, 1992). The levels of TSP collected from the study areas are about 1.4 times the off-roadside values. However, TSP concentrations in Sydney are about 4.6 times lower than those observed at Bangkok roadsides reported here (Freeman and Cattell, 1990).

5.1.6 Relation to Traffic Volume

Investigations of fuel and used lubricant compositions indicated their chemical aromatic components strongly influenced particle bound PAH emissions (BjØrseth and Becher, 1986; Nikolaou et al., 1984). Other studies on the transport of vehicle exhaust to the ambient air confirmed that motor vehicle exhaust was a significant source in many urban areas (Alsberg et al., 1985; MØller et al., 1982; Daisey and Lioy, 1981). In the United States, motor vehicles contributed about 36% of annual load of PAH in the atmosphere (BjØrseth and Ramdahl, 1985). Nielsen (1996) has recently determined the contribution of motor vehicle traffic to PAH in the ambient air of central Copenhagen. It was estimated that the contribution was about 80% and can reach 90% on working days. Panther et al. (1996) reported that the major source of PAH in the urban area of Bangkok was motor vehicle petrol engines (88%) with minor contributions from biomass burning (9%) and oil combustion (3%).

In this study, plots of traffic volumes are made against concentrations of PAH in particle and gas phase separately and also versus TSP. The results, however, exhibit weak correlations (see Figure 5.1). This may suggest that traffic volume alone is not a very good predictor for atmospheric levels of PAH in Bangkok. There may have other contribution. This could be PAH emissions differing from site to site due to vehicle populations and several factors, e.g. fuel to air ratio used for combustion, engine conditions (age, cold start or warm start), fuel type (gasoline or diesel) and driving conditions (e.g. during acceleration, idling) (BjØrseth and Becher, 1986; Nikolauo et al., 1984; Pedersen et al., 1980). Apart from this, traffic stoppages in the morning and

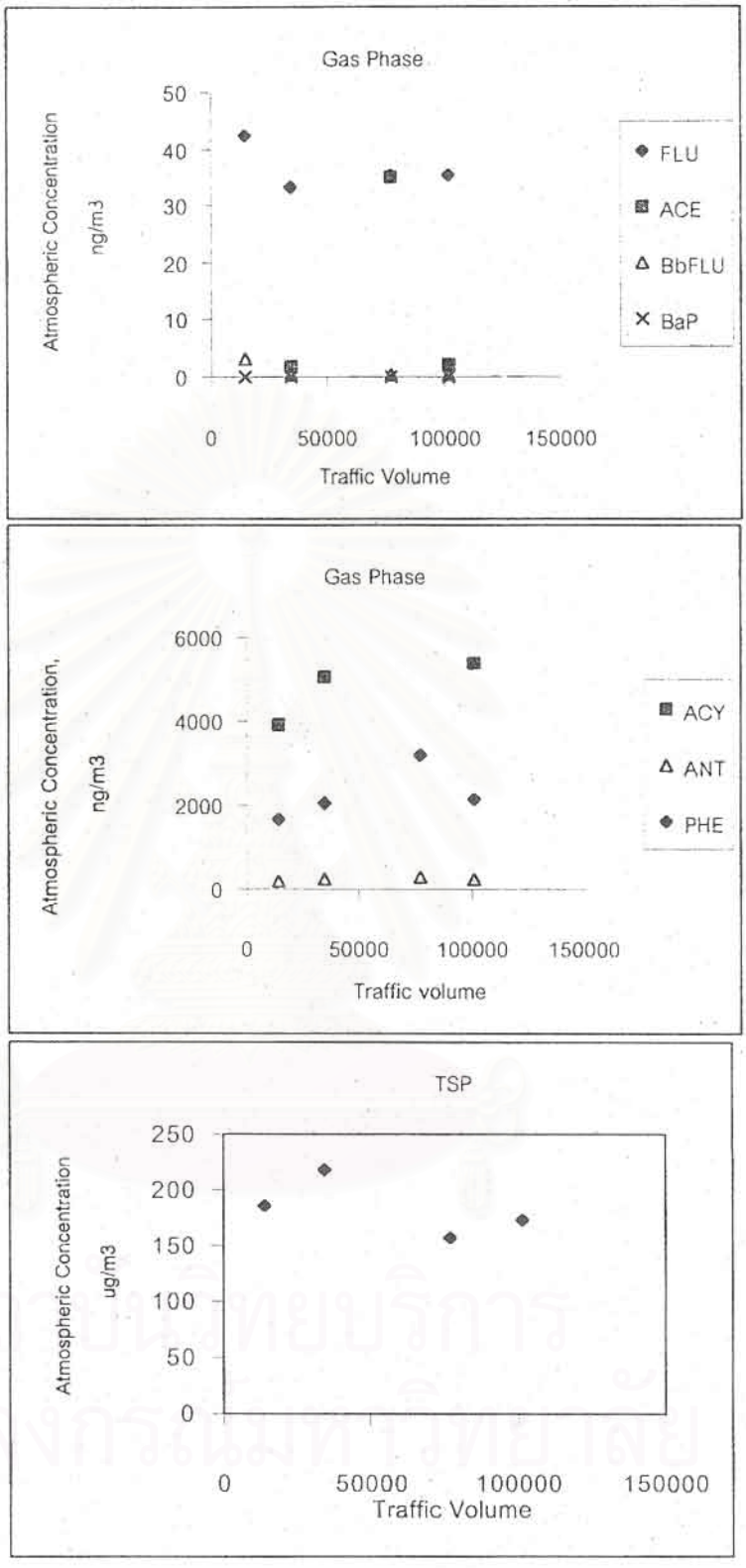


Figure 5.1 Plots of measured atmospheric concentrations versus traffic volume

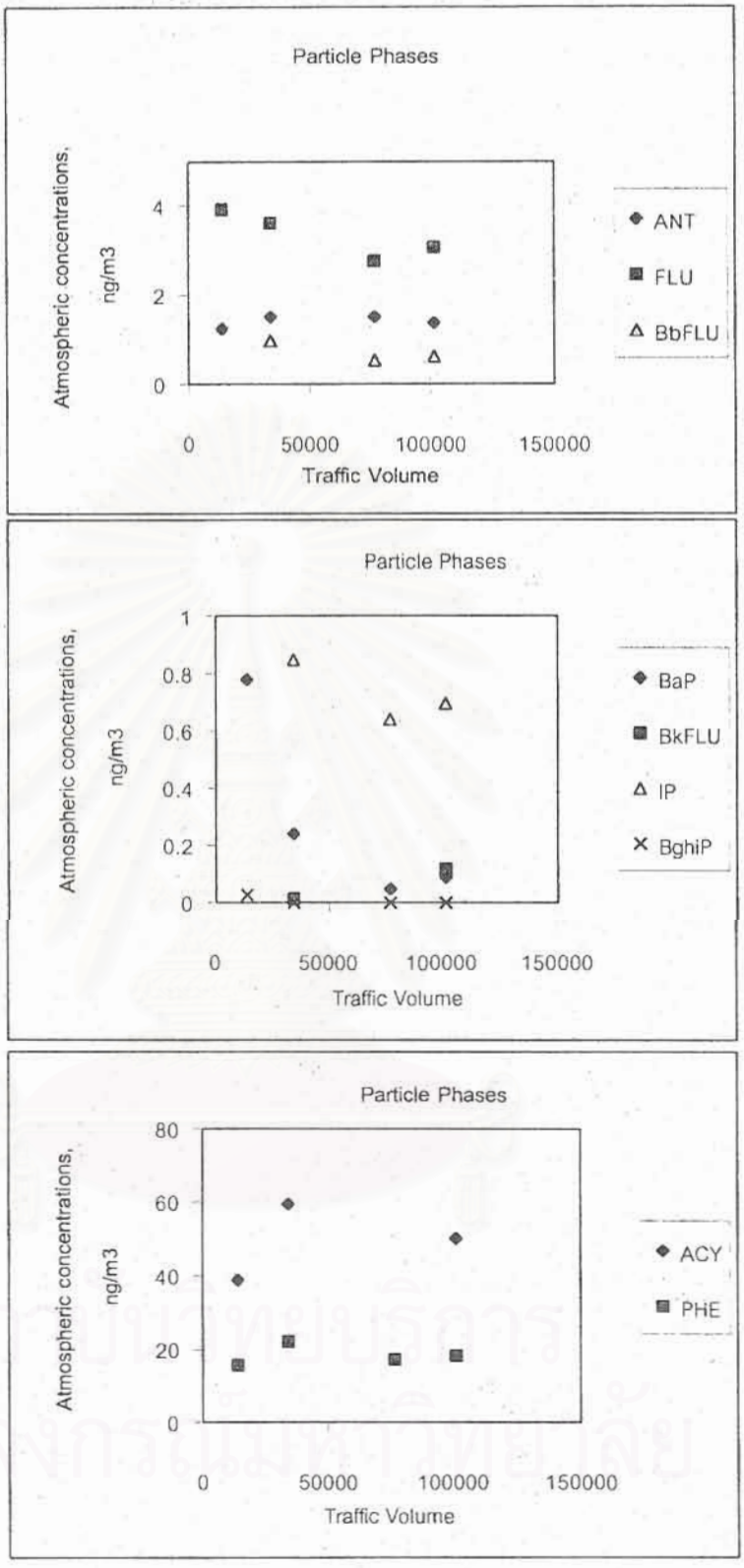


Figure 5.1 continued

afternoon rush hour may play a role causing fluctuating concentrations. Similar traffic problem in central Copenhagen has shown parallel results (Nielsen, 1996).

5.1.7 Seasonal Variations

Seasonal fluctuations of PAH are due to meteorological conditions. For example, precipitation by the rain or snow during particular seasons can remove particle bound PAH from the atmosphere (Leuenberger et al., 1988; Tuominen et al., 1988). Also, loss of PAH by photochemical reactions, decay and various oxidation processes have been observed by many authors (e.g. Pistikopoulos et al., 1990a; Arey et al., 1989; Masclet et al., 1986). Seasonal variation patterns of PAH in tropical cities have been investigated and found to have highest level in wet season and lowest in hot/dry season (Panther et al., 1996). Similar finding was reported in Germany by DÖrr et al., (1996). In considering each phase, plots of total p-PAH in relation to meteorological data including temperature, relative humidity and solar radiation were shown low correlation (Panther et al., 1996). Poor correlation between total PAH and meteorological data was also observed in the UK urban air (Halsall et al., 1994). For the gaseous PAH, g-PHE and g-FLU, were found to remain relatively constant throughout the year in the UK urban air. The relative consistency of these volatile PAH are presumed to result from volatilization of the compounds from the soil and vegetation reservoir adding to the gaseous levels which are usually reduced by photodegradation in summer (Halsall et al., 1994; Nikolaou et al., 1984). This finding is in line with Brown et al. (1996) who observed relatively constant levels of volatile PAH throughout the year in German cities (DÖrr et al., 1996). Higher MW PAH (e.g. PYR) are not added to the atmosphere by the volatilization process due to their low volatility as a result these compounds are reduced significantly in summer by photo-degradation or reaction with oxidants present in the atmosphere or other processes.

5.2 Concentrations of PAH in Leaves

Collection of plant leaf samples is described in section 3.5 and their PAH concentrations are presented in Table 5.10 and Figure 5.2. Apparently, the same profiles across four sites are that of ANT with PHE whereas similar ones are those of FLU with BaA.

Table 5.10 PAH concentrations in leaves (mg kg^{-1})

PAH	Roadsides			
	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	ND	ND	ND	ND
ACY	ND	ND	ND	ND
ACE	8.7	8.37	9	8.25
FLO	2.19	1.71	1.49	1.14
ANT	1.32	1.91	1.04	1.88
PHE	15.92	17.46	14.17	16.21
FLU	2.01	1.79	2.11	2.93
PYR	1.32	1.12	1.44	1.26
BaA	0.43	0.14	0.3	0.37
CHR	0.07	0.06	0.08	0.08
BbFLU	ND	0.55	ND	0.58
BaP	0.15	0.09	0.31	0.07
BkFLU	0.01	ND	0.01	0.1
IP	ND	0.62	ND	ND
DbahA	ND	ND	ND	0.01
BghiP	0.06	ND	ND	0.1
Total PAH	32.18	33.82	29.95	32.98

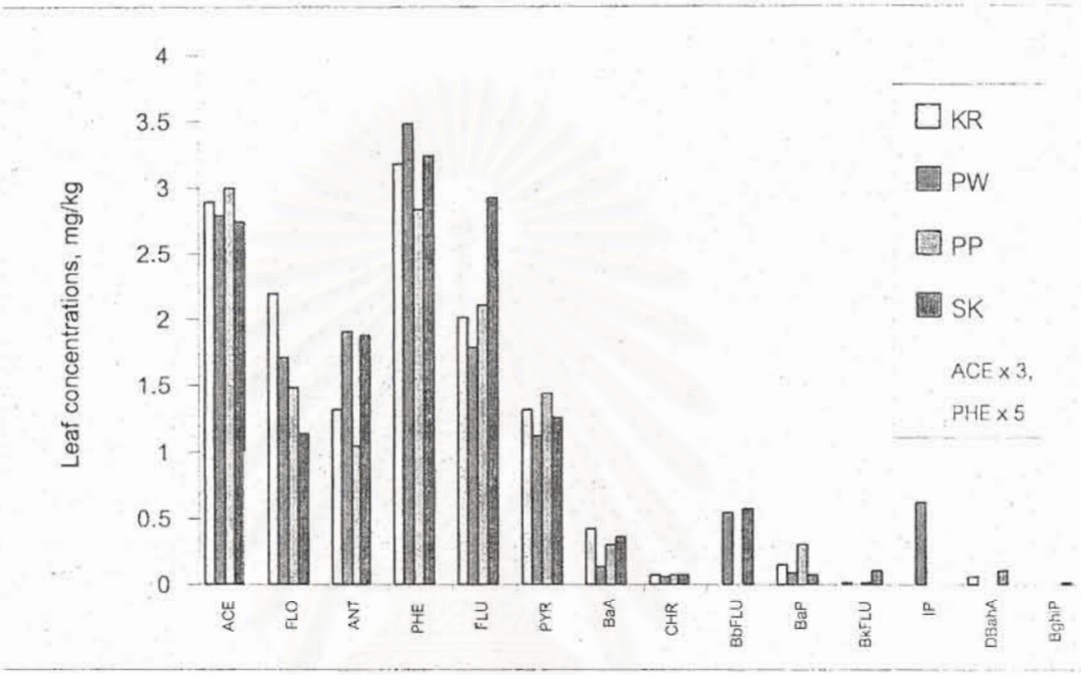


Figure 5.2 PAH concentrations in leaves located on four roadsides

and ACE with PYR (Figure 5.2). The highest level in leaf is PHE (14.17-17.46 mg kg^{-1}) followed with ACE (8.25-9.0 mg kg^{-1}), FLU (1.79 -2.93 mg kg^{-1}), FLO (1.14 -2.19 mg kg^{-1}), ANT (1.04-1.88), PYR (1.12-1.44). The rest of PAH are found less than 1 mg kg^{-1}. The total of PAH found at these sites are in the range of 29.95 to 33.82 mg kg^{-1}. PAH leaf profiles are presented in Table 5.11. PHE has highest contribution in leaf (14.2-17.5 %). The second input in contaminated leaf is ACE (8.3-9.0%) and FLO, ANT, FLU, PYR are following (1.1-2.9%). Other investigations of PAH in plant tissues are presented in Table 5.12. Generally, leaf concentrations in this work are larger than others. It cannot be easily resolved since there is difference in atmospheric conditions, species variation, and emission sources and volume.

5.3 Atmospheric and Leaf Concentration Relationships

5.3.1 Leaf and Measured Air Concentrations

Not all 16 Individual PAH found both in leaves and in the air may be due to high detection limits either in the leaves or in the air, compounds too low to be measurable, and the equilibrium not being reached. Therefore, only successful 5 compounds both in the leaves and in the air can be plotted. The measured atmospheric concentrations of PAH in particle phases plotted against their leaf concentrations are given in Figures 5.3. and clearly shown no relationships between the concentrations in particle phases and in the leaves. This is not in line with the same plots but with measured gas phase instead of particle phases, which exhibits good linear relationships with the corresponding leaf concentrations (Figure 5.4). There is an exception for higher MW (e.g. BaP in Figure 5.4) since the compound mostly bound to particle and that its tiny gas phase concentration do not have any significant role on the leaf concentration. This confirms that gas phase, not particle phase, is mainly responsible for the accumulation in leaf. The result is matched to other similar investigations on plant tissues and atmospheric concentrations (e.g. Lodovici et al, 1998; Nakajima et al., 1995; Umlauf et al., 1994).

5.3.2 Measured and Calculated Air Concentrations

The calculated air concentrations (calculated C_A) are estimated using the observed

Table 5.11 PAH profile* in leaves

PAH	Roadsides			
(%)	Kasemraj	Patumwan	Pongpetr	Sapankwai
NAP	-	-	-	-
ACY	-	-	-	-
ACE	27.03	24.75	30.05	25.02
FLO	6.80	5.05	4.97	3.46
ANT	4.10	5.65	3.47	5.70
PHE	49.47	51.63	47.31	49.15
FLU	6.25	5.29	7.05	8.88
PYR	4.10	3.31	4.81	3.82
BaA	1.33	0.41	1.00	1.12
CHR	0.22	0.18	0.27	0.24
BbFLU	-	1.63	-	1.76
BaP	0.47	0.27	1.04	0.21
BkFLU	0.03	-	0.03	0.30
IP	-	1.83	-	-
DbahA	-	-	-	0.03
BghiP	0.19	-	-	0.30

* (Individual PAH x 100)/Total PAH

Table 5.12 Total PAH in various plant tissues

Plant Tissue	Total PAH ($ng\ g^{-1}$ dry wt)			Sites	Land use type
Kale leaf: *Brassica oleracea*[1]	192-354			1	Town center
	109-124			1	Residential
	65-211			1	Suburban
Grass leaf: *Eragrostis tenuifolia*[2]	91			1	Urban
Pine needle: *Pinus sylvestris*[3]	140-1660			5	Urban
	19-550			13	Suburban
	160-330			4	Remote
	Summer	Autumn	Winter		
Leaf: *Laurus nobilis*[4]	90-433	72-511	113-855	9	Urban
	73-197	109-588	88-880	6	Suburban
Leaf: *Laurus nobilis*[5]	11-354			-	17-477
	Summer and Fall				
Corn Leaf (*Zea mays L.*)[6]	27			30	
Sugar maple leaf (*Acer saccarum*)[6]	220			12	Rural
	510			10	Suburban
	1600			11	Urban
Pine needle (*Pinus strobus*)[6]	370			3	Rural

[1] Franzaring et al, 1992 [2] Yang et al, 1991 [3] Tremolada et al, 1996 [4] Lodovici et al, 1994

[5] Lodovici et al, 1998 [6] Wagrowski and Hites 1997

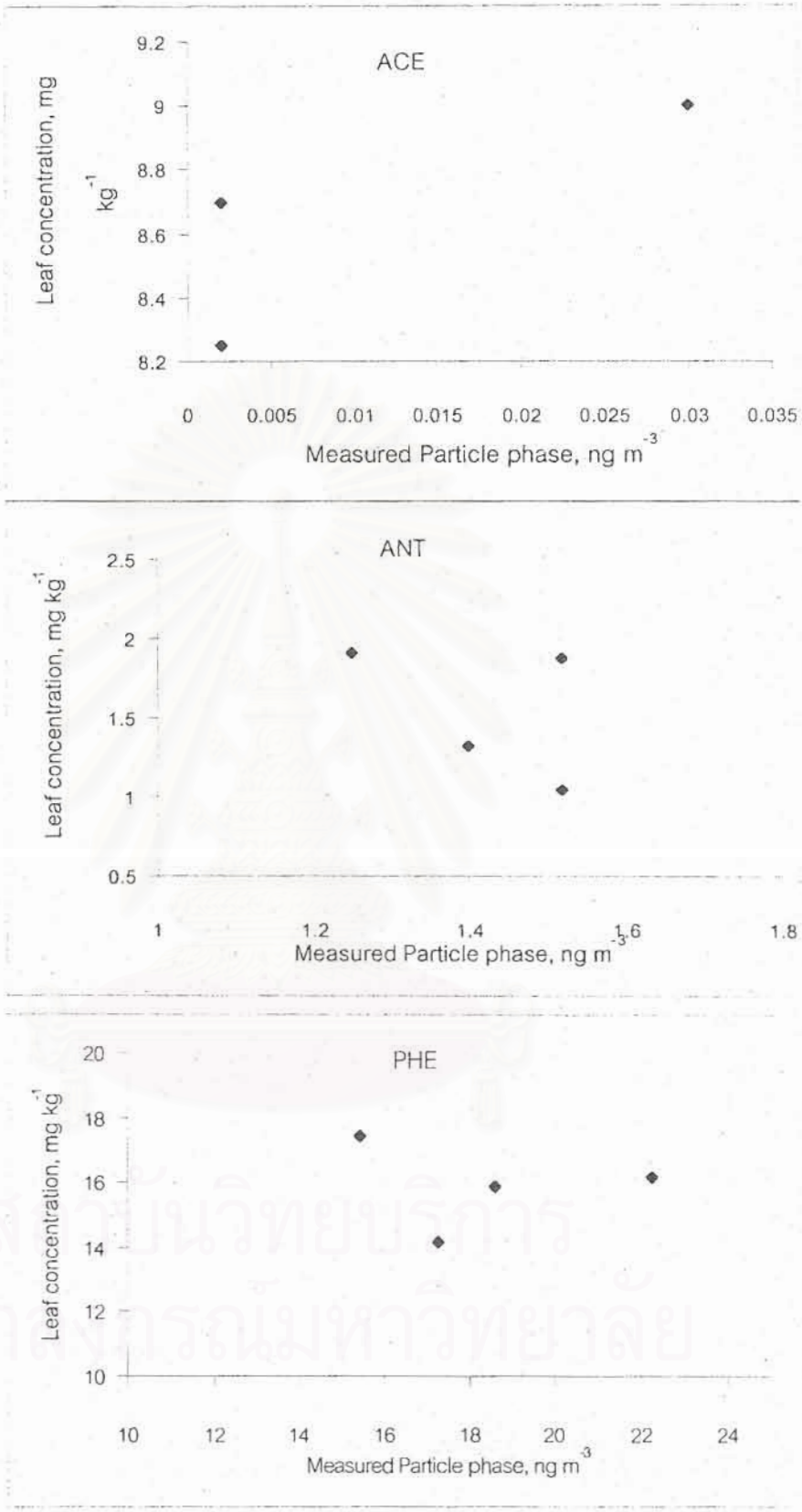


Figure 5.3 Plots of measured particle phase concentrations versus leaf concentrations

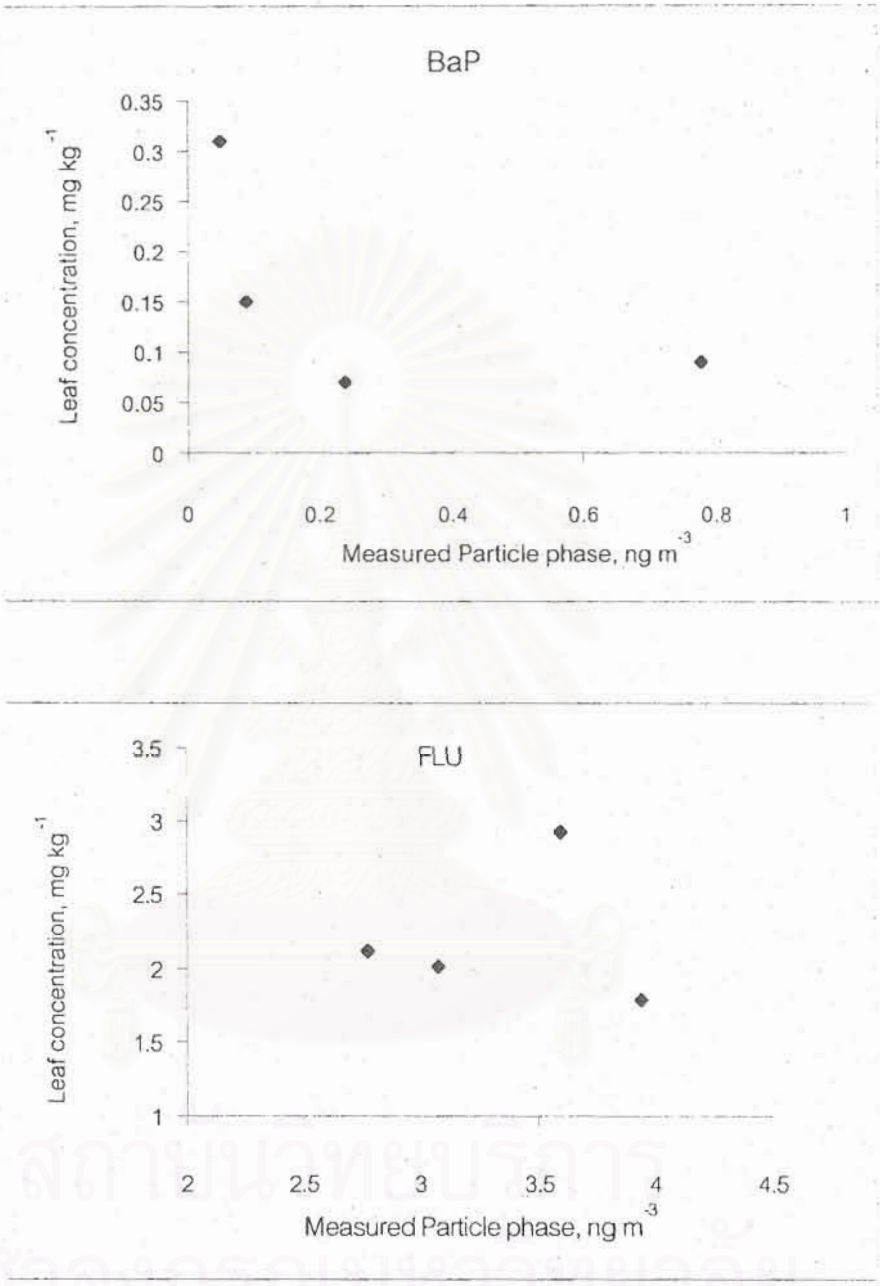


Figure 5.3 continued

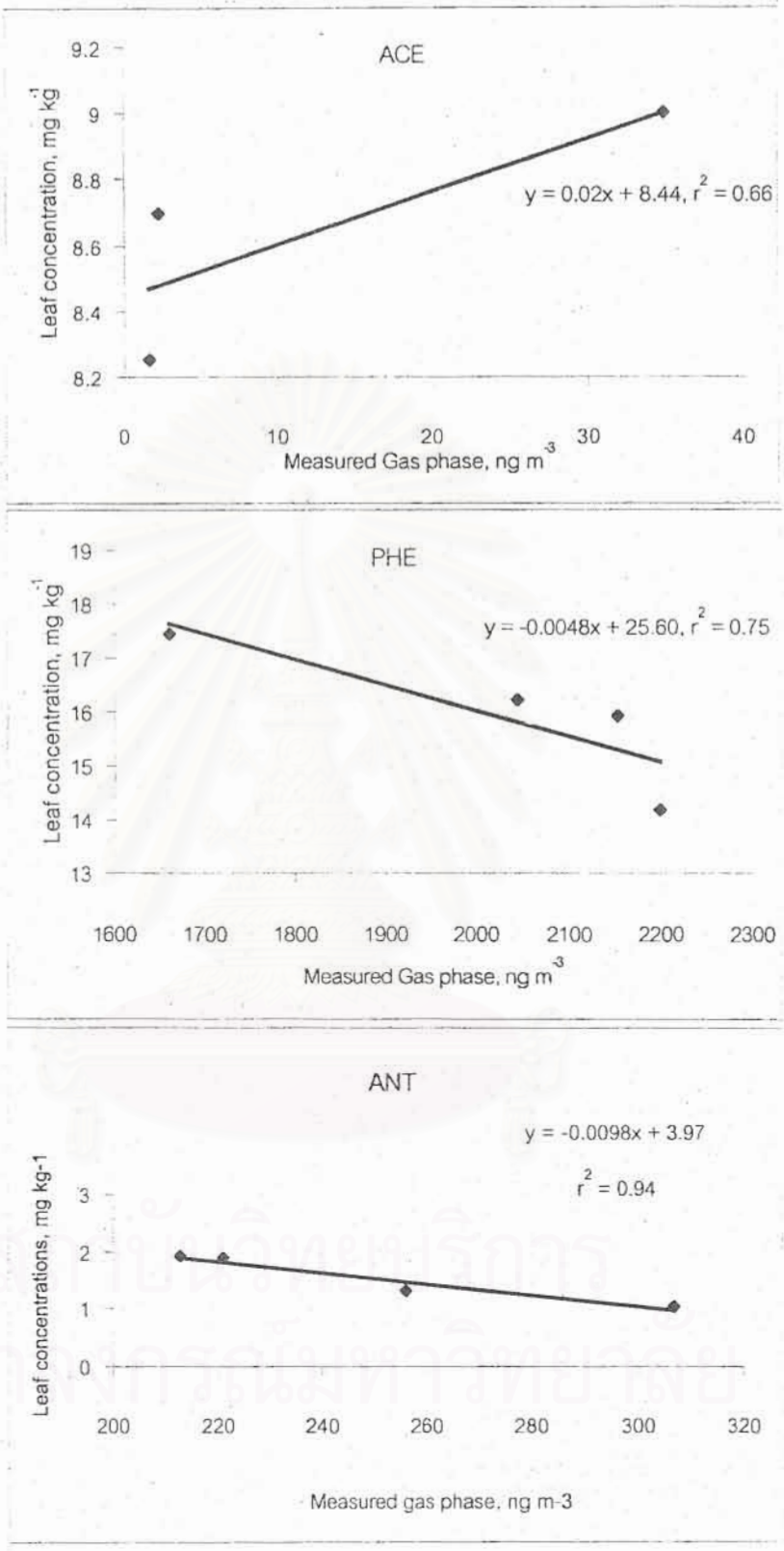


Figure 5.4 Plots of measured gas phase concentrations to that of leaf concentrations

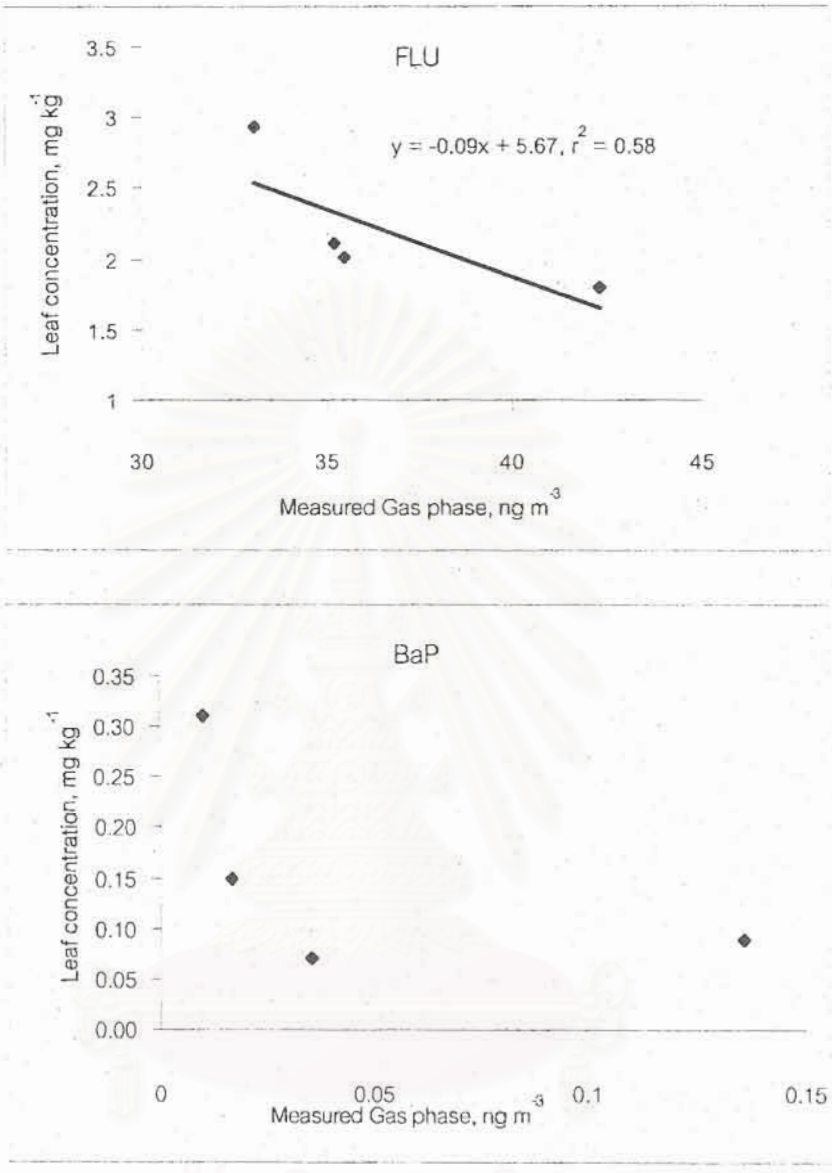


Figure 5.4 continued

leaf concentrations and the experimental values of the leaf-air partition coefficients using $C_A = C_L K_{LA}^{-1}$. It is appeared that only 5 PAH both in calculated gas and measured gas concentrations from field measurements (measured C_A) can be matched and plotted (Figure 5.5). The regression analysis of these plots produces promising relationships between concentrations in the leaves and in the air. Therefore, the regression equations in Figure 5.4 can be used to predict the atmospheric concentrations from leaf concentrations except those PAH of high MW (i.e., BaP) which exhibit mostly on particle bound and do not accumulate well in the leaves as shown in Figure 5.3. However, additional experimental work should be carried out over the sites of more than four sites to obtain better relationships (the more sites, the more points on the plots).

5.4 Overall Evaluation

There is potential for plant leaf being an indicator of atmospheric PAH and other SOC that have similar physicochemical properties, e.g. PCDD/F. This is indicated by the regression equations of the calculated and measured atmospheric concentrations and their reasonable correlation coefficients. Thus, atmospheric PAH concentrations can be obtained from leaf concentrations and the available leaf-air partition coefficients of individual PAH as expressed by $C_A = C_L K_{LA}^{-1}$. Plots of atmospheric concentrations against leaf concentrations point out that gas phase plays an important role in the accumulation in leaves throughout the year due to an addition to summer loss by photo-degradation occurred via volatilization of the compounds from the soil and vegetation. FLO and PHE are dominant in four Bangkok roadside atmospheres in both gas phase whereas PHE and ACE are dominated in the leaf concentrations over the sites. This may be influenced by the partitioning capacity of the leaves between FLO and ACE. The difference in atmospheric concentrations of PAH across the sites is independent on traffic volume but involves the traffic stoppage, driving and vehicle conditions, type of fuel, engine conditions, seasonal variation, etc. Similar profiles of PAH in leaves across the sites are those of FLU with BaA and ACE with PYR are observed but the same profile is of ANT and PHE. Factors influencing the accumulation in leaves involve the meteorological conditions, seasons, leaf lipid, leaf surface, PAH emission, etc.

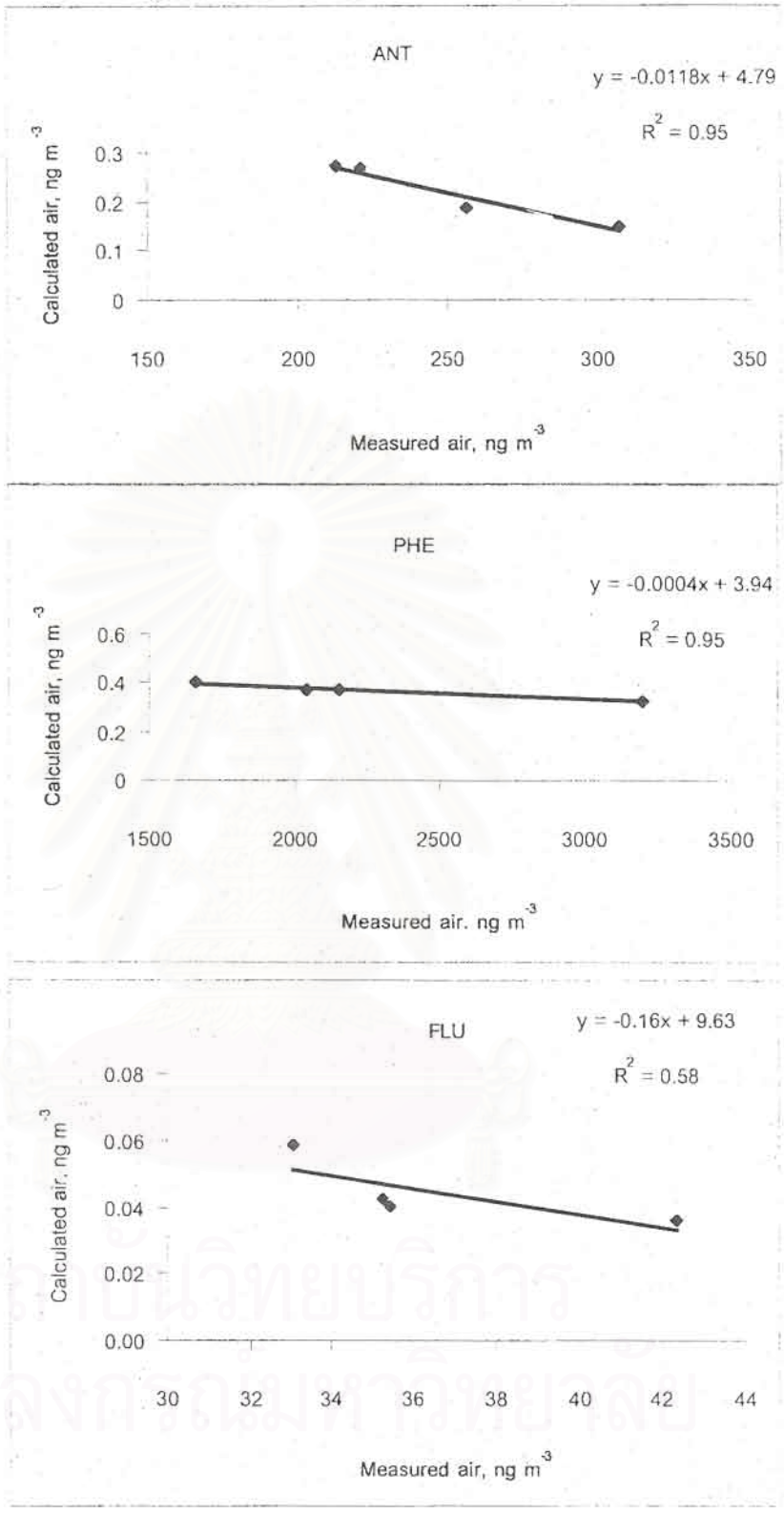


Figure 5.5 Relationships of calculated and measured atmospheric concentrations

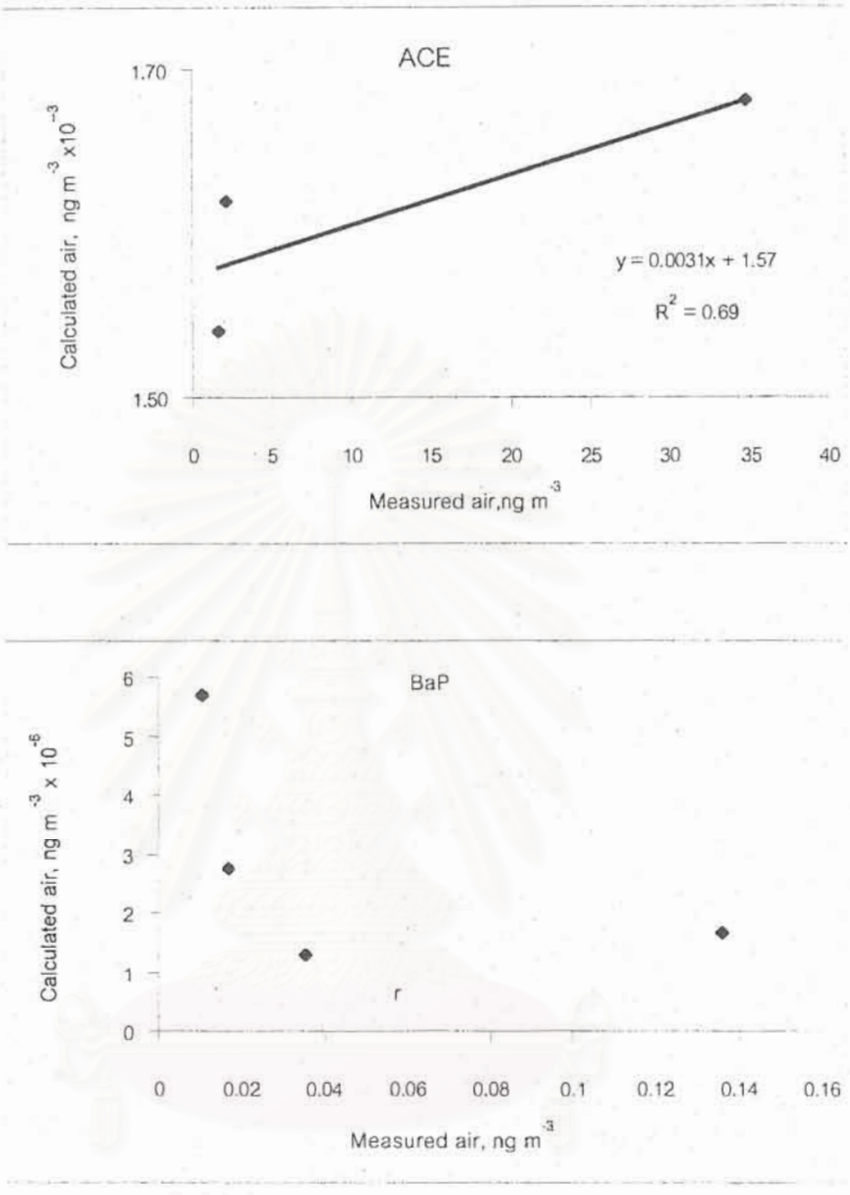


Figure 5.5 continued

Chapter 6

Evaluation of Cancer Risk

6.1 Background

Health risk assessment is a scientific process to predict the likelihood of any adverse effect that would be seen in expected human population by using toxicological data collected from animal studies and human epidemiology combined with degree of exposure (Leeuwen and Hermens, 1995; Batt and Peterson, 1988). The US National Research Council (NRC) has described a four-step process of risk assessment, which comprises hazard identification, dose/response relationship, exposure assessment, and risk characterization (Connell et al., 1997; Covello and Merkhofer, 1993). The health hazard identification involves a collection and an evaluation of health injury or diseases that may be produced from that interested chemicals. Such Informative sources are obtained from human epidemiological studies or animal studies (Hall, 1997; Batt and Peterson, 1998). The dose/response relationships are generally and currently extrapolated from high doses in animal studies to low doses in human exposure. The exposure assessment requires an identification of exposure pathways. This allows level of exposure from each pathway to be determined by direct measurement of chemical concentration in environmental media or pathways (e.g. air, water, food, dust). In many studies, the concentrations can be alternatively measured from biological samples. The last step is the characterization of risk, which can be attained by integration of the first three steps to develop a level of risk.

In general, chemicals can pass into human body by three exposure routes; inhalation, ingestion and dermal contact. Since this study emphasizes on inhalation, only atmospheric sources are considered. Traffic police, bus/taxi drivers, vendors, and pedestrians are described as road users, target population in this study. In previous Chapters, the studies indicate a good relationship between the leaf and the air concentrations (r^2 =0.95). However, PAH found in leaf concentrations may not be all available in the measured air and vise versa probably due to low concentration in the air, photo-degradation, biodegradation, high detection limit of the method, etc. To achieve the goal of the study,

the measured atmospheric concentrations of PAH in urban air are evaluated for the risk level. Since BaP is usually the dominant PAH and is classified by the IARC as probable human carcinogen (IARC, 1987), all pathway exposure concentrations of PAH family are converted to the toxicity equivalent concentrations of BaP_{equi} Therefore, the total daily intakes of the road users are estimated based on Teq_{BaP}. Health hazard of BaP and its dose-response relationships are then reviewed to select the relevant potency factors used to estimate the increased risk.

6.2 Possible Sources of Exposure

Since the study emphasizes on inhalation pathway, its possible sources are under careful consideration. Clearly, contaminated air on the roadsides is the main exposure for road users. Besides the vehicular emission, tobacco smoke and cooking stoves are another interesting sources. It was estimated that tobacco smoke emission consisted of more than 4500 compounds including PAH both in particle and gas forms. Several hundreds of PAH were identified in both mainstream and side stream smoking with BaP as a major component (Gold and Naugle, 1993). Particularly in the case of poor ventilation, a room of 40 m^3 could contained higher than 2-4 $\mu g\ m^{-3}$ of BaP emitted from three smokers (Nikolaou et al., 1984). Nevertheless, a passive smoker 50 cm distant from a cigarette may inhale >10 times the amount taken up by the smoker (Maroni et al., 1995). As mentioned previously, cooking such as gas-cooking stove, electric stove, wood burning, coal-burning, which are currently in general use by Thais and of course by roadside vendors in Bangkok, are another contribution of PAH in outdoor air. Particle bound PAH are usually emitted from coal, oil, and wood fired stoves and these are high MW compounds mostly sorbed onto particles. It can be concluded that emission of both tobacco smoke and cooking from either indoor or outdoor air eventually enter the air and are accounted by the concentration in the leaf since the relation between the air and the leaf concentration has been evident.

In the study areas, exposure to PAH by inhalation of contaminated soil and dust can be minimal. This is due to soil contamination often important only in particular area such as land dumping sites or building sites, where large amount of soil particles in the

atmosphere is often caused by wind action. However, there is no major soil area to act as a source in this manner in the study areas. For particle exposure originated from traffic, they are accounted both in the air and in leaf concentrations. In this study, contaminated soil dermal contact is considered negligible.

6.3 Evaluation of Exposure

6.3.1 Toxicity Equivalent Concentrations

Due to lack of toxicological data on individual compound, a toxic equivalency factor (TEF) was developed to be able to estimate risk associated with exposure to a complex mixture, i.e. PCDD/F (Olson et al., 1989; Eadon et al., 1986; Lipsky, 1989). The method relates individual compound toxic potency to a compound, often the most toxic compound in the mixture. The derived exposure is then expressed as toxicity equivalent concentration (TEQ) which is obtained by multiplying exposure concentration with a reference compound relative potency known as the most potent as described earlier. This approach has been officially adopted in many countries, e.g. Canada, the Netherlands, the United Kingdom, and the United States of America (USEPA, 1989).

In considering PAH, BaP was believed the most potent, however, has been well characterized toxicologically, and often used as an indicator of human exposure. Recent studies indicate DbahA has the same potent or even more potent than BaP. Since BaP has been recognized as an indicator of PAH and its potency is 1, TEF for individual PAH which is based on relation to that of BaP, is expressed as BaP_{equi} (WHO, 1998). It should be noted that TEF approach might be over- or under-estimated since synergistic and antagonistic effects could occur (Larsen and Larsen, 1998; Krewski et al., 1989). It is also not clear that the application of relative potency derived from experimental studies administered by one route can be valid for other exposure routes. However, WHO has recommended this method using BaP as an index for the carcinogenic potential of PAH mixture with recognition of its limitations (Larsen and Larsen, 1998; USEPA, 1993). It is noteworthy that the TEF approach accounts only for carcinogenic activity of PAH, but not for other carcinogenic or co-carcinogenic substances present in the same environmental

media, for example, tobacco smoke, vehicle exhaust, smoked foods (WHO, 1998; Petry et al., 1996).

Relative Potency of PAH to BaP

TEF approach for PAH first developed by US EPA was initially applied a potency value of 1.0 for all classified carcinogenic PAH and zero for non-carcinogenic compounds (USEPA, 1984a). Other TEF model derived from epidemiological investigations of coke oven workers was established by Nisbet and LaGoy (1992). Derivation from various routes of exposure, including skin painting, intraperitoneal, subcutaneous and lung plantations was later initiated by USEPA in 1993. Other strategy was based on oral, pulmonary, and skin application of PAH in experimental animals given a range of relative potencies of PAH (Larsen and Larsen, 1998). A compilation of above mentioned relative potency is given in Table 6.1 Noticably, DbahA has appeared to be equipotent or somewhat more potent than BaP in most cases whereas NAP, FLO, PHE, and PYR, as well as ACE and ACY, are about three orders of magnitude less potent than BaP.

Calculation of Toxicity Equivalent Concentrations

Table 6.1 gives different potency of the same PAH. In order to safe guard human health, the most potency available for individual PAH is selected for the estimation of TEQ as shown in Equation 6.1

$$TEQ=Cx\ RP \qquad (6.1)$$

where TEQ and C are toxicity equivalent concentration and environmental media concentration which varies with the media involved whereas RP is the relative potency of the compound.

The individual PAH concentrations in the air listed in Table 5.1 and Table 5.5 are converted to toxicity equivalent concentrations (BaP_{equi}) using Equation 6.1, Summation of all these BaP_{equi} yield the total toxicity equivalent concentrations (total BaP_{equi}) and are given in Tables 6.2-6.5. The results show that total BaP_{equi} in four roadside air are high at KR and PW (71.25 and 71 ng m^{-3} respectively) and lowest at PP with the range of 8-71.25

Table 6.1 Relative potency of individual PAH to BaP (unity) from various investigations.

Compounds	Relative potency to BaP					
	(1)	(2)	(3)	(4)	(5)	(6)
ACE		0	0.32			0.001
ACY		0				0.001
ANT		0				0.01
ATT				0.32		
BaA	0.013	1	0.145	0.145	0.145	0.1
BaP	1	1	1	1	1	1
BbFLU				0.141		
BeP				0.004		
BghiP		0	0.022	0.022	0.021	0.01
BjbFLU	0.08	1	0.14		0.12	0.1
BkFLU	0.004	1	0.066	0.061	0.052	0.1
CHR	0.001	1	0.0044	0.0044	0.0044	0.01
CPY				0.023		
DbahA	0.69	1	1.1	1.11	1.11	1
FLU		0				0.001
FLO		0				0.001
IP	0.017	1	0.232	0.232	0.278	0.1
NAP		0				0.001
PHE		0				0.001
PYR		0	0.081	0.81		0.001

(1) Chu and Chen, 1984. (2) EPA, 1984. (3) Clemens, 1986. (4) Krewski et al., 1989. (5) Thorslund, 1990. (6) Nisbet and LaGoy, 1992.

Table 6.1 continued

Compounds	Relative potency to BaP					
	(7)	(8)	(9)	(10)	(11)	(12)
ACE	0	0.001	0.001			
ACY		0.001	0.01			
ANT		0.01	0.01			0.0005
ATT					0.28	0.3
BaA	0.1	0.1	0.1	0.1	0.014	0.005
BaP	1	1	1	1	1	1
BbFLU	0.1	0.1	0.1	0.1	0.11	0.1
BeP		0.01			0	0.002
BghiFLI						0.01
BghiP		0.01	0.01		0.012	0.02
BjFLU			0.1	0.1	0.045	0.05
BkFLU	0.01	0.1	0.1	0.1	0.037	0.05
CHR	0.001	0.01	0.01	0.1	0.026	0.03
COR		0.001				0.01
CPY		0.1		0.1	0.012	0.02
DBaeP				1		0.2
DBacA		0.1				
DBahA	1	1	1	1	0.89	1.1
DBalP				100	100	1
DBaeF					1	
DBahP				1	1.2	1
DBaiP				0.1		0.1
FLU		0.001	0.01			0.05
FLO		0.001	0			0.0005
IP	0.1	0.1	0.1	0.1	0.067	0.1
NAP		0.001				
PER		0.001				

Table 6.1 continued.

Compounds	Relative potency to BaP					
	(7)	(8)	(9)	(10	(11)	(12)
PHE		0.001	0		0.00064	0.0005
PYR		0.001	0.001		0	0.001

(7) EPA, 1993. (8) Malcolm and Dobson, 1994. (9) Kalberlah et al., 1995. (10) McClure and Schoeny, 1995. (11) Muller et al., 1995a,b, 1996. (12) Larsen and Larsen, 1998.

Table 6.2 Calculation of toxicity equivalent concentrations of PAH (BaP_{equi}) at KR site.

Compounds	Relative potency	Phase	Concentration. (ng m^{-3}).	Toxicity equivalent concentrations (BaP_{equi}) (ng.m^{-3}).
NAP	0.001	Gas	-	
		Particle	-	
ACY	0.01	Gas	5379.17	53.79
		Particle	50.29	0.503
ACE	0.001	Gas	2.11	0.002
		Particle	0.002	0.000002
FLO	0.001	Gas	9841.38	9.84
		Particle	24.66	0.025
ANT	0.01	Gas	256.37	2.56
		Particle	1.4	0.014
PHE	0.001	Gas	2151.82	2.15
		Particle	18.63	0.019
FLU	0.05	Gas	35.46	1.773
		Particle	3.07	0.154
PYR	0.001	Gas	-	-
		Particle	-	-
BaA	0.15	Gas	-	-
		Particle	-	-
CHR	0.1	Gas	0.004	0.0004
		Particle	0.002	0.0002
BbFLU	0.14	Gas	0.25	0.035
		Particle	0.63	0.088
BaP	1	Gas	0.017	0.017
		Particle	0.09	0.090
BkFLU	0.1	Gas	0.013	0.0013
		Particle	0.12	0.012
IP	0.28	Gas	-	-
		Particle	0.7	0.196
BghiP	0.02	Gas	3.13×10^{-5}	0.0000006
		Particle	0.001	0.00002
DBahA	1.11	Gas	6.64×10^{-5}	0.00007
		Particle	0.002	0.0022
BaP_{equi} (Gas)				70.17
BaP_{equi} (Particle)				1.10
Total BaP_{equi}				71.27

Table 6.3 Calculation of toxicity equivalent concentrations of PAH (BaP_{equi}) at PW site.

Compounds	Relative potency	Phase	Concentration. ($ng\ m^{-3}$).	Toxicity equivalent concentrations (BaP_{equi}) ($ng\ m^{-3}$).
NAP	0.001	Gas	-	-
		Particle	-	-
ACY	0.01	Gas	3892.48	38.93
		Particle	39.12	0.39
ACE	0.001	Gas	-	-
		Particle	-	-
FLO	0.001	Gas	7146.40	7.15
		Particle	19.25	0.019
ANT	0.01	Gas	212.93	2.13
		Particle	1.25	0.125
PHE	0.001	Gas	1660.03	1.66
		Particle	15.45	0.016
FLU	0.05	Gas	42.33	2.12
		Particle	3.94	0.20
PYR	0.001	Gas	11.93	0.012
		Particle	1.68	0.002
BaA	0.15	Gas	-	-
		Particle	15.77	2.37
CHR	0.1	Gas	-	-
		Particle	-	-
BbFLU	0.14	Gas	3.07	0.43
		Particle	8.45	1.18
BaP	1	Gas	0.14	0.14
		Particle	0.78	0.78
BkFLU	0.1	Gas	0.21	0.021
		Particle	2.08	0.208
IP	0.28	Gas	-	-
		Particle	11.09	3.11
BghiP	0.02	Gas	-	-
		Particle	0.03	0.0006
DBahA	1.11	Gas	-	-
		Particle	-	-
BaP_{equi} (Gas)				52.59
BaP_{equi} (Particle)				8.41
Total BaP_{equi}				71.00

Table 6.4 Calculation of toxicity equivalent concentrations of PAH (BaP_{equi}) at PP site.

Compounds	Relative potency	Phase	Concentration. ($ng\ m^{-3}$).	Toxicity equivalent concentrations (BaP_{equi}) ($ng\ m^{-3}$).
NAP	0.001	Gas	-	-
		Particle	-	-
ACY	0.01	Gas	-	-
		Particle	-	-
ACE	0.001	Gas	34.83	0.0348
		Particle	0.03	0.00003
FLO	0.001	Gas	-	-
		Particle	-	-
ANT	0.01	Gas	306.59	3.066
		Particle	1.52	0.0152
PHE	0.001	Gas	2197.15	2.197
		Particle	17.27	0.0173
FLU	0.05	Gas	35.24	1.762
		Particle	2.77	0.139
PYR	0.001	Gas	10.93	0.011
		Particle	1.36	0.0014
BaA	0.15	Gas	-	-
		Particle	-	-
CHR	0.1	Gas	2.81	0.281
		Particle	1.3	0.130
BbFLU	0.14	Gas	0.22	0.031
		Particle	0.52	0.073
BaP	1	Gas	0.01	0.010
		Particle	0.05	0.050
BkFLU	0.1	Gas	-	-
		Particle	-	-
IP	0.28	Gas	-	-
		Particle	0.64	0.179
BghiP	0.02	Gas	-	-
		Particle	0.002	0.00004
DBahA	1.11	Gas	-	-
		Particle	-	-
BaP_{equi} (Gas)				7.39
BaP_{equi} (Particle)				0.61
Total BaP_{equi}				8.00

Table 6.5 Calculation of toxicity equivalent concentrations of PAH (BaP_{equi}) at SK site.

Compounds	Relative potency	Phase	Concentration. (ng m^{-3}).	Toxicity equivalent concentrations (BaP_{equi}) (ng m^{-3}).
NAP	0.001	Gas	-	-
		Particle	-	-
ACY	0.01	Gas	5040.17	50.40
		Particle	59.29	0.59
ACE	0.001	Gas	1.68	0.0017
		Particle	0.002	0.000002
FLO	0.001	Gas	-	-
		Particle	-	-
ANT	0.01	Gas	221.22	2.21
		Particle	1.52	0.152
PHE	0.001	Gas	2043.38	2.04
		Particle	22.26	0.022
FLU	0.05	Gas	33.05	1.65
		Particle	3.6	0.18
PYR	0.001	Gas	-	-
		Particle	-	-
BaA	0.15	Gas	-	-
		Particle	0.44	0.066
CHR	0.1	Gas	-	-
		Particle	-	-
BbFLU	0.14	Gas	0.30	0.042
		Particle	0.98	0.137
BaP	1	Gas	0.04	0.04
		Particle	0.24	0.24
BkFLU	0.1	Gas	0.001	0.0001
		Particle	0.011	0.0011
IP	0.28	Gas	-	-
		Particle	0.85	0.238
BghiP	0.02	Gas	2.49×10^{-5}	-
		Particle	0.001	0.0000005
DahA	1.11	Gas	5.28×10^{-5}	0.0000586
		Particle	0.002	0.0022
BaP_{equi} (Gas)				56.38
BaP_{equi} (Particle)				1.63
Total BaP_{equi}				58.01

(ng m^{-3}). Apparently, the gas phase of total BaP_{equi} dominates the particle phase. The outstanding compounds in gas phase that contribute the atmospheric concentrations are those of low MW of ACY, ANT, FLO, PHE, and FLU. Specially, ACY and ANT are found at 3 out of 4 sites with ACY the highest concentration followed with FLO, PHE and FLU detected at 2 out of 4 sites. For particle phase BaP_{equi}, IP, ACY, FLU, BaA, BbFLU, BkFlu, CHR are discovered at most sites.

6.3.2 Daily Intake

In calculating the daily intake, exposure expressed in terms of the internal concentrations at the site in the body where the actual toxic effect occurs is preferred. Realistically this data is not available/ difficult to obtain. The exposure assessment based on external concentrations in the environmental media taken into account for the bioavailability is therefore mostly in practice. As a result, an uncertainty for risk assessment can be reduced. In this current work, total exposure is quantified in term of total daily intake expressed as mg compound kg^{-1} body weight day^{-1}.

Exposure Scenarios

Since inhalation is the relevant exposure for the road users, the scenario is designed to cover the likely activity hours they spent on the streets. Most hours the traffic police on duty on the street are in the range of 6-8 hour with the possibility of 12 hours at high peak depending on the job they are responsible for. Vendors selling foods/goods along the footpath are present on the roadsides ranged from 6 to 12 hours. Vendors who own/rent the premise are subject to operate 6-12 hr. On the contrary, those who cannot afford usually carry their foods/goods around in the area and are subject to higher hour of expsoure. Pedestrains could be those on the way for work/business during the rush hour taken approximate an hour or two for one way and 2-4 h on both ways. Clearly, the more hour they spend the higher risk they would have. Thus, choices of exposure scenarios for all target population are categorized based on minimum and maximum hours spent as follows.

Scenario 1: 2 h day^{-1}, 5 days a week exposure

Scenario 2: 4 h day^{-1}, 5 days a week exposure

Scenario 3: 6 h day^{-1}, 5 days a week exposure

Scenario 4: 12 h day^{-1}, 5 days a week exposure

Estimation of Daily Intake

As previously described (Section 6.2) the dermal intake would be expected to be negligible and the ingestion intake is out of the scope of the study, thus daily intake for road users can be calculated as shown in Equation 6.2

$$DI_T = DI_{IHG} + DI_{IHP} \quad (6.2)$$

where DI_T is the total daily intake, DI_{IHG} is daily intake of inhaled gas, DI_{IHP} is daily intake of inhaled particle. Equation 6.2 can be expanded as follows (Di Macro, 1993; Kofi Asante-Duah, 1993; Lipsky, 1989).

$$DI_T = \left\{ (C_{IHG}\, RV\, t\, BA_{IHG} x10^{-6}) + (C_{IHP}\, RV\, t\, BA_{IHP}\, r\, x10^{-6}) \right\} / bw \quad (6.3)$$

where C_{IHG}, C_{IHP}, are the toxicity equivalent concentrations of inhaled gas, inhaled particles in the unit of ng m^{-3}.

RV is the respiratory volume (m^3 h^{-1}).

t is the exposure time (h day^{-1}).

r is the fraction of particles retained in the lungs.

10^{-6} is the conversion factor (mg ng^{-1}).

bw is the body weight (kg)

BA_{IHG} is the bioavailability factor of BaP for inhaled gas (unitless).

BA_{IHP} is the bioavailability factor of BaP for inhaled particle (unitless).

Although human absorption of BaP through inhalatory exposure has been studied and quantitative values are available but not in good agreement with one another. Intratracheal administration of BaP with animals has shown variable bioavailability factors; rats (0.57-0.78), guinea pig (0.55-0.68) and hamster (0.74). Similar administration but with diesel carboneceous particles with rats gave a bioavailability of 0.20 (Hrudey et al., 1996; Bevan

and Ruggio, 1991; Weyand and Bevan, 1986,1987). Thus, the averages of the values available are 0.68 and 0.20 and these are assumed to be the Bioavailability Factor in humans due to inhalation of gaseous BaP and particle bound BaP respectively.

A portion of the inhaled particles retains in the lungs related to particle sizes. The USEPA has estimated that about 0.75 of PCDD/F bound to particles retained in the lungs (USEPA, 1981). Since there is no data available for PAH retention and its similarity in physicochemical properties to the PCDD/F, a value of 0.75 has been applied to particle bounded BaP in this work.

It is estimated that an adult body weight is 70 kg (Paustenbach, 1992) and respiratory volume for an adult is 0.83 m^3 h (Lipsky, 1989). Gas and particle PAH concentrations are calculated separately due to a difference in absorption capacity between these two phases and in accordance to Equation 6.3. The results of daily intake on different exposure hour are given in Table 6.6.

6.4 Dose Response Relationships

Dose/response assessment is to characterize the relationship between dose of BaP and incidences of cancer. For example, single subcutaneous injection of 0.05, 0.1, 0.5, and 1 mg of BaP in olive oil has produced tumors in 1/7, 4/31, 9/17, and 64/69 rats, respectively while 10 intratracheal administrations of BaP with total doses of 25.0, 2.5, 0.5, and 0.1 mg given 42.5, 30.7, 15.6 and 0% malignant broncheogenic tumors, respectively (Griciute, 1979). Carcinogenic potency factors, generally required in health risk assessment particularly for carcinogenic compounds, can be derived from dose-response relationships and expressed as "unit risk" or "slope factor". Unit risk or unit risk factor is normally applied to respiratory exposure and expressed as $(\mu g\ m^{-3})^{-1}$. Slope factor is generally a measure for all routes of exposure and expressed as $(mg\ kg^{-1} day^{-1})^{-1}$ (Kofi Asante-Duah, 1993; Patrick, 1994). A number of unit risk estimates have been measured. Generally, the USEPA uses the linearized multistage model to develop unit risk or slope factor. Unit risk values for BaP assessed and compiled by USEPA based on extrapolation from studies in rodents exposed by respiration are in the range of 7.0×10^{-9} to 4.7×10^{-6} $(ng\ m^{-3})^{-1}$ which is a range of about three orders of magnitude (WHO, 1998). Other unit risks have been investigated by the Netherlands Institute of Public Health and Environment

Table 6.6 Daily intake (mg kg^{-1} day^{-1}) based on exposure time at four sites

BaP_{equi} (ng m^{-3})			Daily intake based on Exposure time (h day^{-1})			
Sites	Gas phase	Particle phase	2	4	6	12
KR	70.17	1.10	1.14×10^{-6}	2.27×10^{-6}	3.41×10^{-6}	6.81×10^{-6}
PW	52.59	8.41	8.78×10^{-7}	1.76×10^{-6}	2.63×10^{-6}	5.27×10^{-6}
PP	8.39	0.61	1.37×10^{-7}	2.75×10^{-7}	4.12×10^{-7}	8.25×10^{-7}
SK	56.38	1.63	9.15×10^{-7}	1.83×10^{-6}	2.74×10^{-6}	5.49×10^{-6}

Protection. As a result, a unit risk of 6.58×10^{-5} $(ng\ m^{-3})^{-1}$ for human exposure to smoky coal is adopted. Also unit risks of 2.3×10^{-7} and 1.1×10^{-7} $(ng\ m^{-3})^{-1}$ estimated from human exposure to diesel and gasoline vehicles respectively are used (Larsen and Larsen, 1998; Lewtas, 1993). The slope factor can be derived for respiratory route. For example, a study of Golden Syrian hamsters inhaling 0, 2.2, 9.5, and 46.5 mg m^{-3} BaP for 10-96.4 weeks has been investigated (Thyssen et al., 1981). The incidence of respiratory tumors has been used in the linearized multistage model adopted by the USEPA and the carcinogenic potency or slope factor obtained for human is 6.1 $(mg\ kg^{-1}\ day^{-1})^{-1}$ (USEPA, 1984b).

6.5 Risk due to inhalation of PAH

Risk is characterized on the assumption that individual risks are additive or approximately additive particularly at low environmental doses. This approach is recommended by the USEPA (1989), the most common risk measure, which involves the combination of the exposure and potency. Cancer risk indicates the probability of an excess cancer over a lifetime. The estimation follows the Equation 6.4

$$\text{Excess Cancer Risk} = \text{CDI} \times \text{Slope Factor} \qquad (6.4)$$

where CDI is Chronic Daily Intake averaged over a lifetime $(mg\ kg^{-1}day^{-1})$ via inhalation. CDI can be obtained from Equation 6.5 as following.

$$\text{CDI} = (\text{DI} \times \text{ED} \times \text{EF} \times \text{L}) / \text{AT} \qquad (6.5)$$

where DI is the daily intake via inhalation $(mg\ kg^{-1}day^{-1})$, ED is exposure duration (5 day $week^{-1}$), EF is exposure frequency (52 week $year^{-1}$), L is length of exposure (10, 20, 30 years), AT is period over which exposure is averaged, usually 365 x70 day lifetime.

Table 6.7 is given for excess cancer risk calculated in accordance with Equation 6.4 using a slope factor of 6.1 $(mg\ kg^{-1}day^{-1})^{-1}$ for BaP on inhalation exposure (USEPA, 1984b). Table 6.7 provides an estimate of increased cancer incidences per 10^6 human populations exposed to the corresponding chronic daily intake. Since 1×10^{-6} is generally an exceptional risk describing one excess cancer case would occur out of one million

Table 6.7 Excess cancer risk sorted by sites (cases per 10^6)

Scenarios	Roadsides											
	KR			PW			PP			SK		
	10 **	20 **	30 **	10	20	30	10	20	30	10	20	30
1	0.12	0.23	0.35	0.09	0.18	0.27	0.014	0.028	0.042	0.09	0.19	0.28
2	0.23	0.46	0.69	0.18	0.36	0.54	0.028	0.056	0.084	0.19	0.37	0.56
3	0.35	0.69	1.0	0.27	0.53	0.80	0.042	0.084	0.13	0.28	0.56	0.84
4	0.70	1.4	2.1	0.54	1.1	1.6	0.084	0.17	0.25	0.56	1.1	1.7

Scenario 1; 2 h day^{-1} 5 days $week^{-1}$ exposure

Scenario 2; 4 h day^{-1} 5 days $week^{-1}$ exposure

Scenario 3; 6 h day^{-1} 5 days $week^{-1}$ exposure

Scenario 4; 12 h day^{-1} 5 days $week^{-1}$ exposure

** Years of exposure

population, it is clearly seen that the 10-year exposure at all sites and under the exposure hour scenarios would have least cases of cancer suffering; a chance of one cancer case would occur out of two million people at the peak (0.01-0.56 x 10^{-6}). Longer exposure to 20 years via inhalation at 12 h day^{-1}, the increased risk would happen at all sites except PP site with the chance of 1 x10^{-6} to 1.4 x10^{-6}. Similar occurrence of risk is that of 12 h day^{-1} and 30 year-exposure but found the incidents of cancer higher (1.6 x10^{-6} to 2.1 x10^{-6}). Among all sites, risk is low at PP site but the highest level is as a result from exposure at the rate of 12 h day^{-1} for 30 years (0.25 x10^{-6}). Similar risk levels would be obtained at PW and SK. Considering risk sorted by road users, pedestrians walking on the street for the hour <12 h day^{-1} and the year <30 years would have cancers at the chance of 0.03-0.7 x 10^{-6} (Table 6.8). Traffic police and vendors who have similar exposure (6-12 h day^{-1} for 20-30 years) would encounter higher cancer incidents as much as 0.5 x10^{-6} to 2.1 x10^{-6}. Within this risk range, the police/vendors at KR site would have highest cancer cases (2.1 x10^{-6}) under the determined situation of exposure (12 h day^{-1} for 30 years) whereas risk as low as 0.5x10^{-6} resulted from inhalation 6 h day^{-1} for 20 years at PW. Although taxi drivers is unlikely driving within the sites, however, the risk levels indicate the likely chance of cancer if inhalation in such concentrations and exposure time would result. Taxi drivers would only suffer the health effect of cancer if they work 12 h day^{-1} for 20 years or more and under the concentrations of PAH in the air at KR, PW and SK sites (in Chapter 5).

6.6 Overall Evaluation

Sources of exposure via inhalation pathway are discharged mainly from vehicular emissions and small amount of wood/charcoal burning and tobacco smoke. The inhalation of contaminated soil is considered negligible. Assessment of risk on road users identified as traffic police, vendors and pedestrians who works on the adjacent areas of four Bangkok sites is based on 4 scenarios; a range of hour per day (2, 4, 6, 12 h), 5 days per week and 10, 20, and 30 year exposure. Also the risks are evaluated using TEF approach to cover all individual PAH potency in the mixture. The bioavailability of PAH in humans including the absorption capacity of the gas and particle phases (e.g. particle

Table 6.8 Excess cancer risk sorted by occupation (cases per 10^6) *

Occupation	Roadsides											
	KR			PW			PP			SK		
	10**	20**	30**	10	20	30	10	20	30	10	20	30
Traffic Police	0.4-0.7	0.7-1.4	1.0-2.1	0.3-0.5	0.5-1.1	0.8-1.6	0.04-0.08	0.08-0.2	0.1-0.3	0.3-0.6	0.6-1.1	0.8-1.7
Vendors	0.4-0.7	0.7-1.4	1.0-2.1	0.3-0.5	0.5-1.1	0.8-1.6	0.04-0.08	0.08-0.2	0.1-0.3	0.3-0.6	0.6-1.1	0.8-1.7
Taxi drivers	0.2-0.7	0.5-1.4	0.7-2.1	0.2-0.5	0.4-1.1	0.5-1.6	0.03-0.08	0.06-0.2	0.08-0.3	0.2-0.6	0.4-1.1	0.6-1.7
Pedestrians	0.1-0.2	0.2-0.5	0.4-0.7	0.1-0.2	0.2-0.4	0.3-0.5	0.01-0.03	0.03-0.06	0.04-0.08	0.1-0.2	0.2-0.4	0.3-0.6

*based on individual minimum and maximum hour per day and 5 days $week^{-1}$

** Years of exposure

retention in the lungs) has been taken into account. Among all sites, PP would be dominant for least cases of cancer of less than 1 $x10^{-6}$, which is the general acceptance of risk. Similar but higher levels of cancer incidents would occur at PW and SK and thus the KR would have the highest cases of cancer. The highest incidents of cancer found across scenarios could be as high as $2.1x10^{-6}$ which is located at KR and posed on those who inhale PAH contaminated air containing gas and particle phases of 17,666.6 and 99.6 ng m^{-3} for a length of 30 years at the rate of 12 h day^{-1}, 5 days a week. In considering exposure sorted by occupation, all occupation under this study would have least chance to have cancer at PP sites as compared to the other three sites (0.01×10^{-6} to 0.2×10^{-6}). The traffic police and vendors likely have serious health effect since the calculated risk could be as high as 2.1×10^{-6}. This is as a result of inhalation of contaminated air at the rate and times of 12 h day^{-1}, 5 days a week and for 30 years particularly at KR site whereas other sites would cause lesser risk; 0.8×10^{-6} to 1.7×10^{-6} at SK and 0.5×10^{-6} to 1.1×10^{-6} at PW. Pedestrians seem to have fewer problems since their risks would be at the range of $0.01\text{-}0.7 \times 10^{-6}$. Taxi drivers under the same exposure scenario as police and vendors would have highest chance of cancer at the range of $0.7\text{-}2.1 \times 10^{-6}$ at KR. Lower events of cancer would be in taxi drivers at PW and SK which are in the range of 0.5×10^{-6} -1.6×10^{-6} and 0.6×10^{-6} -1.7×10^{-6} respectively.

Chapter 7
Conclusions

Determination of leaf-air model from leaf-water partitioning is appropriate and the model developed in this study to PAH can be applicable to other SOC within the range of log K_{OW} between 3 to 6.5. Bioconcentration both from the air and the water are in linear regression equations with PAH having log K_{OW} in the range of 3 to <5.3. Such relationships become polynomial regression equations if taken PAH longer range of log K_{OW} 3-6.75. However there are discrepancies for higher log K_{OW} since the bioconcentration both from the water and the air in leaves for PAH with log K_{OW} about 5.3 and more are lower than expected. This probably results from biodegradation capacity across species and a single compartment model used in this study. However, there has been a controversial on which appropriate compartment model is. QSAR approach is promising as shown by reasonable regression equations between properties (log K_{OA}, MW, S, VP) and the leaf lipid –air (or water) partition coefficients indicating the potential use of these characteristics in predicting bioconcentration. There are a number of factors influencing the leaf-air partition coefficients including leaf lipid fraction, wet/dry deposition, growth dilution, biodegradation and seasonal variation. However the observed leaf-air partition coefficients are generally lower than those comparable results reported for vegetation. This is probably due to different conditions and the different biota species involved. The approach in this study is appropriate but precaution should be taken to avoid leaf aging during partitioning experiments, e.g. shaking more vigorously to reach a constant as soon as possible.

Plant leaf can be an indicator of SOC as indicated by the linear regression equations of the measured air from the field survey and the calculated air concentrations estimated from leaf concentrations. A lot higher measured air than calculated air is observed and it is likely due to the leaf-air system does not reach or never reaches an equilibrium but the steady state in the leaf-water system is suitable. The model developed in this study is however based on the assumption that the atmospheric concentrations are constant prior to the time of sampling. In addition, the model does not take account for factors, e.g.

growth dilution, biodegradation, photo-degradation and temperature variation. The model if further developed should include more sites under the study and carry out over seasons to give better satisfactory regression equations. This would strengthen the more reliable use of plant leaf concentrations to predict the atmospheric concentrations.

The procedure developed for the assessment of risk posed by a complex mixture of PAH in Bangkok roadside air follows a four-step process. The TEF approach applied in this current approach is useful and can be applied to other compound groups, which occur in a complex mixture where individual toxicity data is unknown. The reliability of the results depends largely on how close the pathway concentrations are to actual human uptake and how well dose/response relationships and bioavailability factors from experimental animal data represent human beings. Similarly, inputs in the estimation of daily intake, chronic daily intake and cancer risk can differ from the actual human situation.

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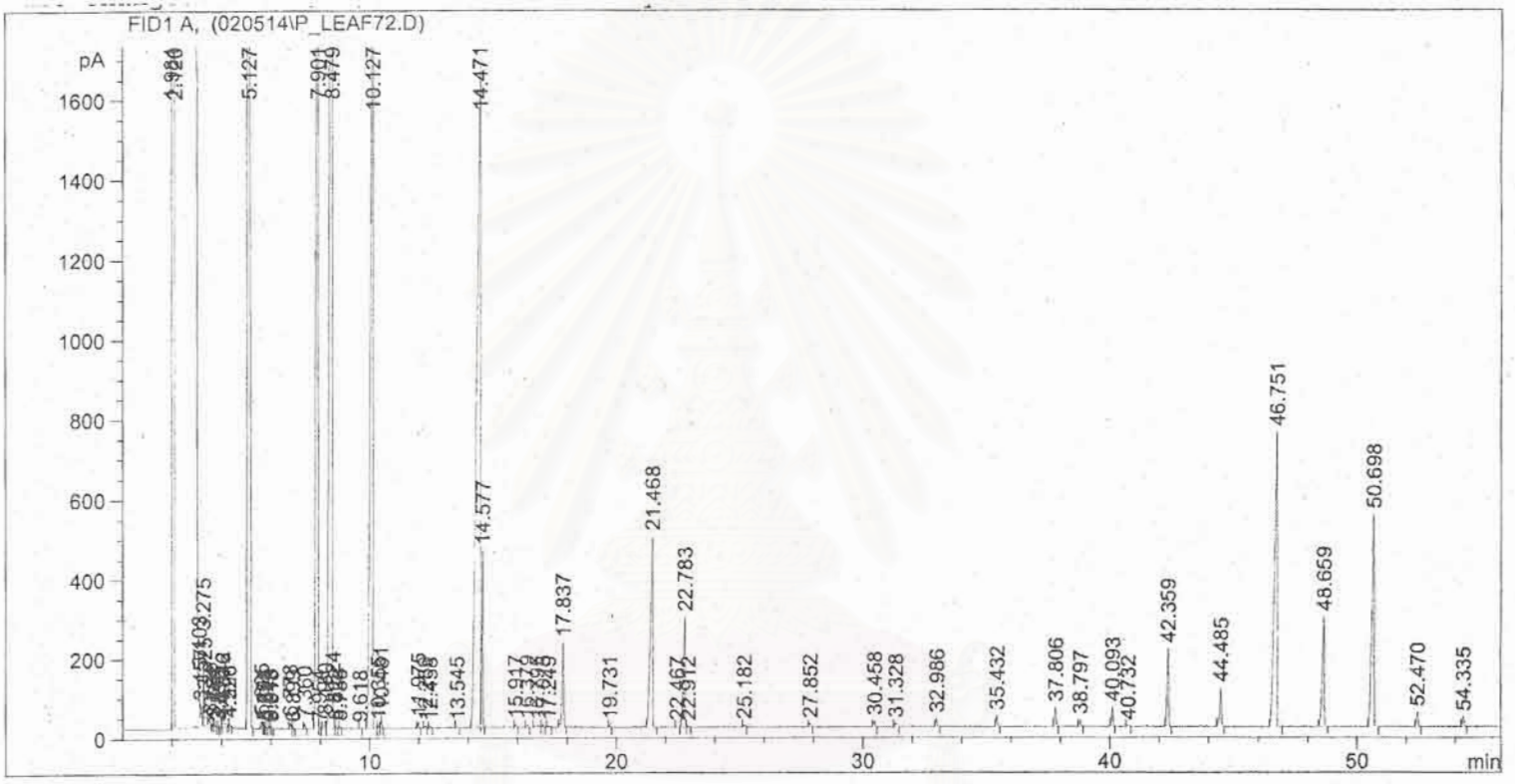
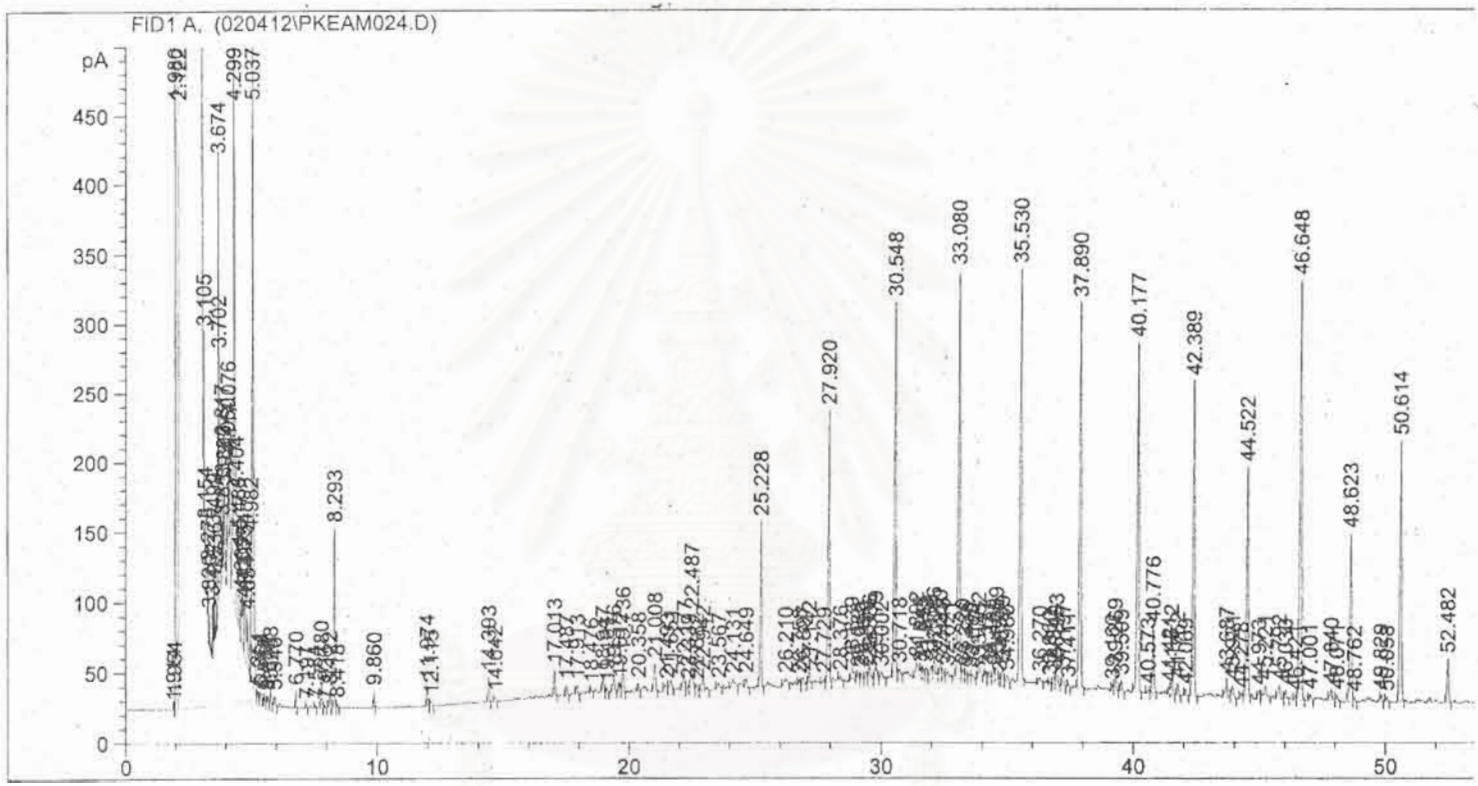
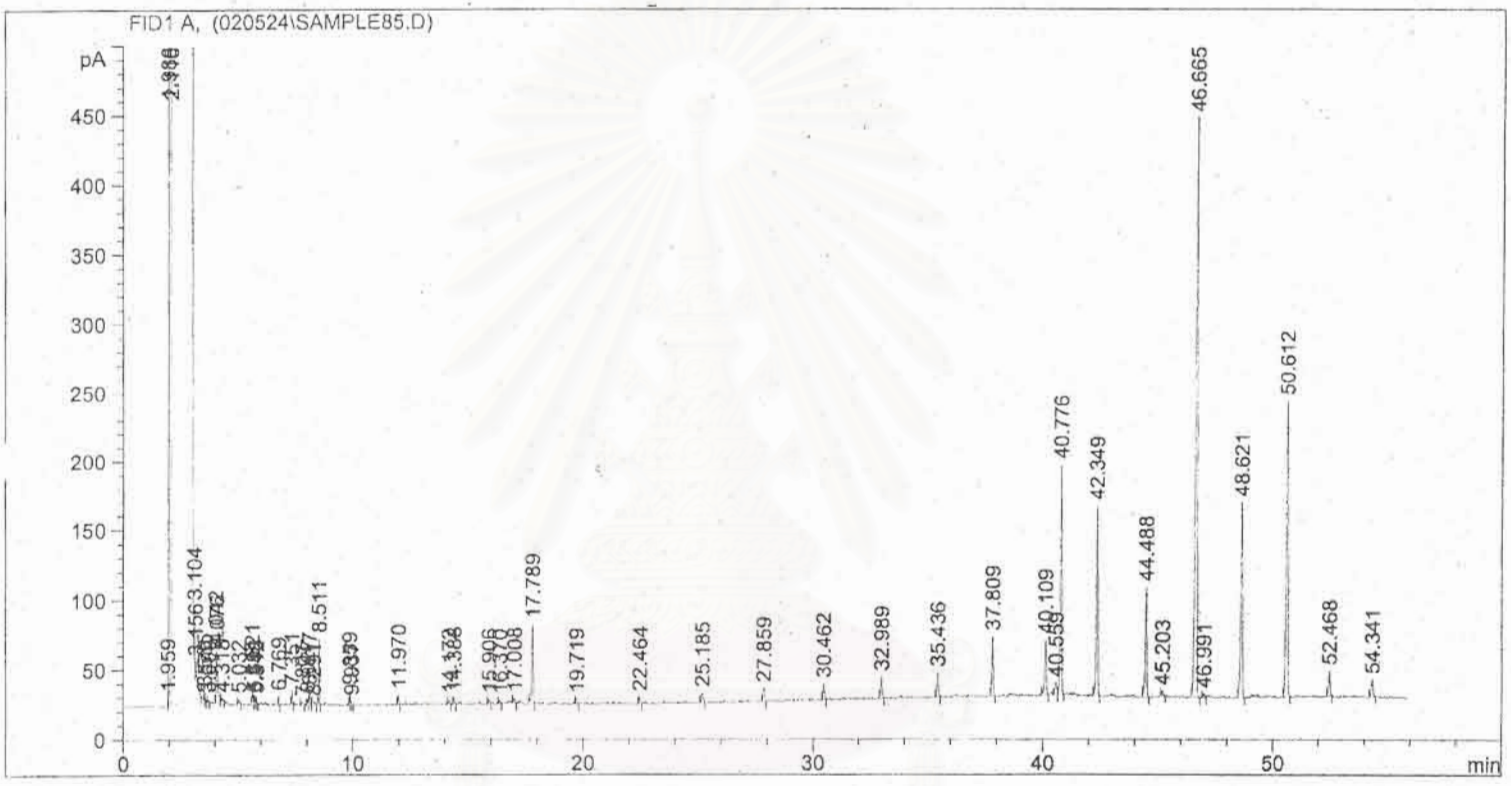
Appendix 1 A chromatogram of spiked water



Appendix 2 A chromatogram of spiked leaves



Appendix 3 A chromatogram of partitioning leaves



Appendix 4 A chromatogram of leaf samples collected from SK