OCCURRENCE AND FATE OF SEMIVOLATILE ORGANIC COMPOUNDS (SVOC$_S$) IN THE TROPICAL ATMOSPHERE

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Abstract

Semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), organo-chlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), all of which targeted here are persistent organic pollutants (POPs), are ubiquitous and persistent in the environment. A comprehensive study on these pollutants was conducted in Singapore’s environment to measure their occurrence, and to assess their fate and transfer processes between environmental compartments.

To quantify and characterize SVOCs present in trace levels, an exceptionally effective extraction technique, accelerated solvent extraction (ASE), was developed for the analysis of PAHs, OCPs and PCBs in both gaseous and particulate phases. Systematic optimizations were carried out to study the dependence of the extraction efficiency of SVOCs on ASE operating variable parameters such as the combination of solvents, extraction temperature and static extraction time. The optimal conditions for ASE extraction were established and validated with high procedural recoveries for subsequent field studies.

The levels of a range of PAHs, OCPs, and PCBs in atmospheric particulate and gaseous phases and rainwater samples were studied in Singapore from June 2007 to May 2008. Monthly or seasonal variations were observed. Pearson correlation matrix was constructed to explore the effect of meteorological factors on the concentrations of atmospheric organic contaminants. A single-factor analysis of variance (ANOVA) was performed to determine temporal variations in daily average total concentrations of these compounds in air and rainwater. Diagnostic ratios and principal component analysis

(PCA) with the assistance of air mass backward trajectories were used to identify possible sources of PAHs, OCPs and PCBs in the atmosphere.

Gas- and particle-phase polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were collected at a tropical site in SEA over 12-h periods during November and December 2006 to determine their gas/particle partitioning by analyzing integrated quartz filter and polyurethane foam samples. Gas/particle partitioning coefficients, K_p, were calculated, and their relationship with the subcooled liquid vapor pressure p_L^o for both PAHs and PCBs was investigated. The regressions of log K_p vs. log p_L^o for most of samples gave high correlations for both PAHs and PCBs and the slopes were statistically shallower than -1, but they were relatively steeper than those obtained in temperate zones of the Northern Hemisphere. By comparison, the particle-bound fraction of low molecular weight (LMW) PAHs was underestimated by both Junge-Pankow adsorption and K_{OA} (octanol-air partition coefficient) absorption models, while the predicted values from both ad- and absorption models agree relatively better with those field measured ones for high molecular weight (HMW) PAHs. In addition, the adsorption onto the soot phase (elemental carbon) predicted accurately the gas-particle partitioning of PAHs, especially for LMW compounds. On the other hand, the K_{OA} absorption model (R^2=0.86) using the measured organic matter fraction (f_{OM}) value fitted the PCB data much better than the adsorption model did, indicating the sorption of nonpolar compounds to aerosols might be dominated by absorption into organic matters in this area.

A comprehensive atmospheric scavenging model has been developed with inclusion of major atmospheric deposition processes such as particle scavenging, dissolution (Henry's law) and surface adsorption affecting the total scavenging ratio of SVOCs. This model was subsequently used in this study to calculate precipitation ratios. Particle scavenging, rather than gas scavenging was the dominant removal mechanism, accounting for 86-99% for PAHs and 98-99% for OCPs in terms of the particle contribution to the total scavenging. The variation of both total and particle scavenging ratios over the study period was smaller compared to those reported in the literature, which might be attributed to uniform ambient temperature prevailing throughout the year in this tropical area. The effects of particle fraction, supercooled vapor pressure and rainfall intensity on particle scavenging of SVOCs were assessed. The relationship between gas scavenging ratio and supercooled vapor pressure implied that the domination of gas scavenging might switch from dissolution to adsorption at supercooled vapor pressures around $10^{-3.5}$~10^{-4} Pa, especially for PAHs with five or more aromatic rings.

The external loading of SVOCs onto the sea surface in this tropical environment was investigated. Dry particulate and wet depositions, and air-water diffusive exchange in the Singapore's south coastal area, where most of chemical and oil refinery industries are situated in, were estimated. Based on a yearly dataset, the mean annual dry particulate deposition fluxes and the wet deposition of $\sum_{16}$PAHs and $\sum_{7}$OCPs were calculated, respectively. Seasonal variation of atmospheric depositions was influenced by meteorological conditions. Air-water gas exchange fluxes were shown to be negative values for PAHs, HCHs (hexachlorocyclohexane group) and DDTs (dichlorodiphenyltrichloroethane group), indicating Singapore's south coast as a sink for the above-mentioned SVOCs. The relative contribution of each depositional process to the total atmospheric input was assessed by annual fluxes. The profile of dry particulate deposition, wet deposition and gas exchange fluxes seemed to be correlated with individual pollutant's properties such as molecular weight and Henry's law constant, etc. For the water column partitioning, the organic carbon-normalized partition coefficients between particulate and dissolved phases (K_{OC}) for both PAHs and OCPs were obtained. The relationships between K_{OC} of PAHs and OCPs and their respective octanol-water partition coefficient (K_{OW}) were examined. In addition, both adsorption onto combustion-derived soot carbon and absorption into natural organic matter for PAHs in marine water column were investigated. Enrichment factors in the sea-surface microlayer (SML) of the particulate phase were 1.2~ 7.1 and 3.0 ~ 4.9 for PAHs and OCPs, and those of dissolved phase were 1.1 ~ 4.9 and 1.6 ~ 4.2 for PAHs and OCPs, respectively. These enrichment factors are relatively higher than those reported for nearby coastal areas, which are most likely due to more organic surfactants floating in the south coastal surface of Singapore.

In summary, this study has demonstrated the optimized ASE as a rapid and effective extraction method that can be applied onto both gaseous and particulate (including air and water-filer based) samples. Investigations have revealed that the ambient temperature affected gas/particle partitioning. This partitioning process plays an important role in the distribution of SVOCs in the tropical atmosphere, which can influence the subsequent dry deposition, precipitation scavenging, and liquid-gas diffusive processes. Overall, this study, based on a combination of laboratory experiments, field studies and theoretical models, has provided key insights into our understanding of the fate and distribution of SVOCs in the multi-media environment of SEA.

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List of Symbols

A_{TSP}	Surface area of the TSP
b_r	Y-intercept of gas/particle partitioning relationship
c	Constant parameter, 0.172 Pa·m
C_{DOC}	Concentration of a chemical in colloidal phase (dissolved organic carbon)
C_g	Concentration of a chemical in atmospheric gas
C_m	Equilibrium concentration in phase m
C_n	Equilibrium concentration in phase n
C_p	Concentration of a chemical in atmospheric particle
$C_{R,dissolved}$	Dissolved concentration in water at equilibrium
$C_{R,sorbed}$	Concentration of a chemical sorbed onto the particles
C_{truly}	Truly dissolved concentration of a chemical in water
D	Diffusivity
d_{gm}	Geometric mean diameter of particles
d_R	Diameter of raindrops
$F_{air\text{-}water}$	Diffusive exchange flux of a chemical between air and water
F_{dry}	Dry deposition flux of a chemical
f_{EC}	Elemental carbon fraction
f_{OM}	Organic matter fraction in aersols
H	Henry’s law constant
H’	Dimensionless Henry’s law constant
K_a	Mass transfer coefficient across air layer
$K_{a,comp}$	Mass transfer coefficient for a compound in air
K_{aw}	Water to air equilibrium constant
K_{ia}	Air-water interface adsorption constant
K_{iw}	Interfacial water to bulk water equilibrium constant
K_{mn}	Partition coefficient between phases m and n
K_{OA}	Octanol / air partition coefficient
K_{OL}	Overall mass transfer coefficient between air and water
K_{ow}	Octanol / water partition coefficient
$K_{soot\text{-}air}$	Partition coefficient of a chemical between air and soot carbon
K_P	Gas / particle partition coefficient
K_w	Mass transfer coefficient across water layer
$K_{w,comp}$	Mass transfer coefficient for a compound in water
M	Molar mass of a compound
m_r	Slope of gas/particle partitioning relationship
MW_{OCT}	Molecular weight of octanol
N_s	Surface concentration of sorption sites on particles
p	Vapor pressure
$\overline{P}$	Mean precipitation amount for samples
p_o	Precipitation rate
P^o	Pressure of an ideal gas at 1 molar concentration and 298 K

P_L^o	Subcooled vapor pressure
Q_L	Enthalpy of desorption from the surface
Q_V	Enthalpy of vaporization of the subcooled liquid
R	Universal gas constant
R_a	Aerodynamic resistance
R_b	Quasi laminar layer
S_A	Maximum solubility in air
Sc	Schmidt number
S_m	Maximum solubility in phase m
S_n	Maximum solubility in phase n
S_o	Maximum solubility of a compound in octanol
S_w	Maximum solubility of a compound in water
SEM_w	Standard error of the weighted mean
T	Ambient temperature
u	Wind speed.
V_{comp}	Molar volume of a compound
V_d	Dry deposition velocity
$V_{min,f}$	Volume that can deliver the gas phase mass amount required to achieve gas/filter adsorption equilibrium on filters
$W_{G,ADS}$	Scavenging ratio by adsorption
$W_{G,DISS}$	Scavenging ratio by dissolution
W_G	Scavenging ratio for a chemical in gas
W_P	Scavenging ratio for a chemical in particle
W_T	Total scavenging ratio for a chemical in both gas and particle
Xi	Concentration in sample i
$\overline{X_W}$	Precipitation weighted mean concentration
ϕ	Fraction of a chemical in air which is sorbed to aerosol
θ	Particle surface area per unit volume of air
ζ	Activity coefficient
ρ	Density
α_{soot}	Specific surface area of diesel soot
α_{EC}	Specific surface area of elemental carbon
$\Delta G_S^o(aq)$	Standard-state aqueous free energy of solvation of compounds
ν_s	Gravitational settling velocity
σ_θ	Standard deviation of wind speed
ν_{kin}	Kinematic viscosity
η	Kinematic viscosity of solution

List of Abbreviations

ACE	Acetone
Ace	Acenaphthene
Acy	Acenaphthylene
Ant	Anthracene
ANOVA	Analysis of variance
AOAC	Association of analytical communities
ASE	Accelerated solvent extraction / extractor
B(a)A	Benz[a]anthracene
B(a)P	Benzo[a]pyrene
B(b)F	Benzo[b]fluoranthene
B(ghi)P	Benzo[ghi]perylene
B(k)F	Benzo[k]fluoranthene
Chry	Chrysene
DB(ah)A	Dibenz[a,h]anthracene
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EC	Elemental carbon
EPA	Environmental Protection Agency
Flt	Fluoranthene
Flu	Fluorene
GC-MS	Gas chromatography-mass spectrometry
GDAS	Global Data Assimilation System
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
Ind	Indeno[1,2,3-cd]pyrene
LOD	Limit of detection
Naph	Naphthalene
Phe	Phenanthrene
Pyr	Pyrene
HCHs	Hexachlorocyclohexanes
HEX	n-hexane
HMW	Higher molecular weight
IADN	Integrated Atmospheric Deposition Network
LLE	Liquid liquid extraction
LMW	Lower molecular weight
MAE	Microwave assisted extractor
METH	Methanol
NCEP	National Centers for Environmental Prediction
NEA	National environmental agency, Singapore
NE	Northeast
NOAA	National Oceanic and Atmospheric Administration

NUS	National University of Singapore
OCCs	Organochlorine compounds
OCPs	Organochlorine pesticides
OM	Organic matter
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PLS	Partial Least-Squares Regression method
PM3	Parametric model 3
POA	Primary organic aerosols
ppLEFRs	Polyparameter linear free energy-relationships
PUF	Polyurethane foam
QSPR	Quantitative structure-property relationship
RH	Relative humidity
S.D.	Standard deviations
SE	Soxhlet extractor
SEA	SEA
SFE	Supercritical fluid extraction
SIM	Selective ion monitoring mode
SML	Sea surface microlayer
SOA	Secondary organic aerosols
spLFERs	Single-parameter linear free energy relationships
SRM	Standard reference material
SSW	Sea subsurface water
SVOCs	Semivolatile organic compounds
SW	Southwest
Temp	Temperature
TSM	Total suspended matter
TSP	Total suspended particle
UNEP	United nation environment program
USEPA	Environmental protection agency, USA
VWM	Volume-weighted mean

Chapter 1. Introduction

1.1. Research Background

The atmosphere is stongly coupled with the terrestrial and marine environments especially in tropical areas because of strong vertical movement of air and abundant rainfall. Atmospheric pollution events, such as photochemical smog and acid rain, have major impacts on the terrestrial and water surface. Atmospheric pollution caused by organic chemicals has received increasing attention from the second half of the 20th century. Over 100,000 chemicals were registered in the European Inventory of Existing Commercial Substances (EINECS) in 1981. The latest estimate of marketed chemicals varies from 20,000 to as many as 70,000 (DBT, Danish Board of Technology, 1996), and most of these chemicals in daily use are organic in nature. In addition, a number of potentially hazardous organic chemicals are formed during combustion and industrial processes. Once released into the environment, many such chemicals turn out to be pollutants since they may pose short-term or long-term threats to the environment and human health. In order to assess potential impacts of these pollutants on the natural environment and human health, it is important to gain a comprehensive understanding of the fate and transfer of organic pollutants upon their release into the multi-media environment. The study of the distribution and transport of pollutants in the multi-media environment is based on the concepts of chemo-dynamics where the environment is divided into a number of phases e.g. atmospheric particle, atmospheric gas, rainwater and sea surface, etc. (Tinsley, 1979).

Among the organic chemicals in the atmospheric environment, semivolatile organic compounds (SVOCs) have received considerable attention because of their physic-chemical properties. SVOCs are compounds with high vapor pressures approximately between 10 and 10^{-6} Pa and can therefore easily turn to gases at normal ambient temperatures, but not as readily as volatile organic compounds (Müller, 1997). They are also found in the particulate-phase. The partitioning of SVOCs between gas- and particulate-phases is dependent on a number of factors including their physical-chemical properties such as their volatility/vapor pressure and chemical structures and also prevailing weather conditions, especially ambient temperature, relative humidity, and solar radiation intensity. SVOCs, which include a wide range of priority pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are ubiquitously present in air, water, soil and biota, and even could be found in remote and pristine areas such as the Arctic (Baek et al., 1991; Stern et al., 1997; Yao et al., 2002; Riget et al., 2004). These three groups of SVOCs, namely persistent organic pollutants (POPs), are very resistant to natural breakdown processes and therefore extremely stable and long-lived in the environment. These SVOCs are of concern as they are potentially carcinogenic, mutagenic, and have endocrine-disrupting impacts even onto mammals at the top of the food chain via bioaccumulation in the lipid fraction of biological tissues and biomagnifications in the wildlife and humans (Jones and De Voogt, 1999; Oskam et al., 2004).

PAHs, at least 100 compounds, have been identified in the environment. PAHs are among the most prevalent environmental contaminants, mainly derived from incomplete combustion processes involving carbon fuels and materials such as vehicular traffic, power plants, chemical industries and oil refineries (Headley et al., 2002}. As for OCPs and PCBs, their usage has been banned in most developed countries, but they are still produced and used in some developing countries. OCPs including hexachlorocyclohexanes (HCHs) and DDTs (dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), are still used as pesticides in farming and plantation. These pollutants could exist in the environment for decades due to their resistance to degradation. On the regional scale, cities are the main sources of PCBs, emitted from buildings and PCB-containing materials such as transformers and capicitors, and also revolatilized from earlier contaminated soils, sediments, water reservoirs and even vegetations (Erickson, 1997).

In recent years, a number of studies have been conducted to assess the occurrence of SVOCs in the atmosphere and / or precipitation in various regions including SEA (SEA). In Canada and the United States, the Integrated Atmospheric Deposition Network (IADN) is mandated to measure the deposition of toxic substances to the Great Lakes, and reported the concentrations of SVOCs in precipitation sampled between 1991 and 1997 (Simcik et al., 2000). In addition, the geographic and temporal distributions and trends between 1980 and 2001 were also reported for the atmospheric deposition of PAHs in Atlantic Canada (Brun et al., 2004). In the regional observatory Kosetice, Czech Republic, a central European background station, SVOCs, have been continuously monitored since 1988 with ten years (1996-2005) of air pollution measurement and four years of evaluating the origin of SVOCs which has been reported in the literature (Dvorska et al., 2008). The relationships between concentrations of SVOCs and climatic conditions were investigated at Niigata Plain of Japan based on the concurrent measurements of SVOCs in air and rain over half a year in 2001 (Takase et al., 2003). Panther et al. (1999) and Karthikeyan et al. (2006) have conducted short-term measurement of SVOCs in the urban environment of SEA, but none of them have carried out systematic field studies of SVOCs to examine their seasonal variation in both particulate and gaseous atmospheric phases in SEA.

The region of SEA has been reported to be one of the important sources for SVOCs (Iwata et al., 1993). Once these compounds are emitted into the atmosphere, they would migrate from the tropical to temperate and even to arctic zones through a number of cycles of condensation, deposition and re-evaporation. Semeena and Lammel (2005) found that PAHs and OCPs are transported to both temperate and polar regions through the grass-hopper effect, or global distillation. In addition, from tropical and subtropical regions of Asia, it has been reported that SVOCs could even be transported across the Pacific Oceans to Canadian west coast and arctic regions (Harner et al., 2005; Li et al., 2007). Muir et al. (2004) have also observed atmospheric long-range transport of pesticides into 30 lakes in Canada and the northeastern United States and the half-distance on the order of 560 to 1820 km was estimated by empirical modeling.

An important aspect with regard to the atmospheric fate of SVOCs is their partitioning between the gas and particle phases as mentioned earlier. Once released into the atmosphere, generally SVOCs would be partitioned between these two phases and reach a partitioning equilibrium according to temperature dependences and the vapor pressure of the chemicals (Pankow and Bidleman, 1992; Cotham and Bidleman, 1995). The particles could be transferred from ambient air to other compartments of the environment by dry deposition and wet deposition (particle-sorbed chemicals washed out by rain or snow). The gas concentrations of SVOCs could also be reduced through dissolution in rain droplets or by photo-degradation through exposure to ultraviolet rays. After SVOCs are deposited into the bulk seawater, water-column partitioning can affect the distribution of pollutants between the dissolved aqueous and the solid phases and eventually impact the fate of these compounds in oceans (Luo et al., 2004). Other than the above-mentioned processes, air-sea exchange can make SVOCs diffuse across the air-sea interface. However, the sea surface microlayer (SML), a unique compartment at the air-sea boundary defined operationally as the upper millimeter (1 ~ 1000 μm) of the sea surface, has large storage capacity to delay the transport of SVOCs across the interface. This interfacial effect has been reported as the enrichment of contaminants with different physicochemical properties (Hardy, 1982; Chernyak et al., 1996; Wurl et al., 2006). A schematic overview of some major environmental phases and their interaction is given in Figure 1.1. Although a number of studies as mentioned above have been conducted to assess the SVOCs transport and transfer processes across wide geographical areas, little work has been done to determine the significance of these processes of SVOCs in SEA.

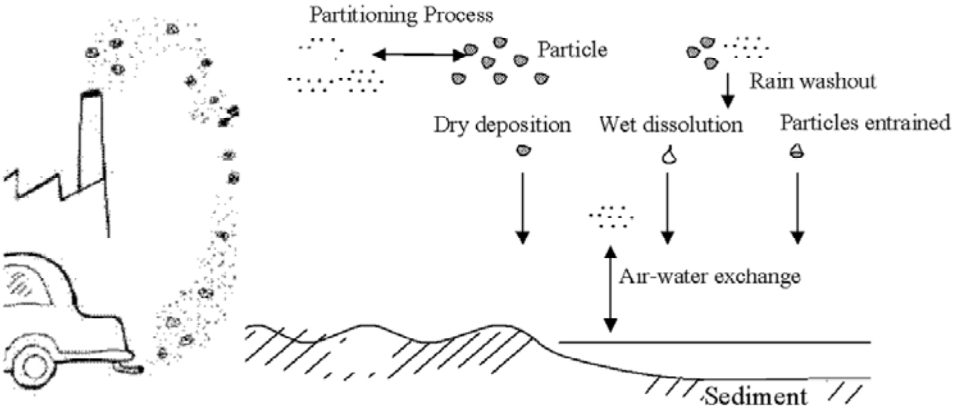


Figure 1.1. Schematic overview of the distribution processes of SVOCs between some major environmental phases

1.2. Research Objectives

SVOCs such as PAHs, PCBs and OCPs are of global concern as they are persistent, ubiquitous and toxic. Atmospheric transport is the primary distribution pathway moving these pollutants from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems. These organic compounds are transboundary pollutants and undergo long range atmospheric transport (LRAT) from sources to remote regions. Indeed, reductions of these persistent organic pollutants (POPs) are now the focus of a coordinated international regulatory framework under the Stockholm Convention. Consequently, environmental data are needed from all regions of the globe to improve the understanding of regional / global sources of POPs and the key processes that control their global distributions. Asia is of global importance economically, yet data of ambient persistent organic pollutant levels are sparse for the region. At present, there is a paucity of reliable environmental data on the levels of SVOCs in SEA from which to assess the effectiveness of pollution control efforts to minimize the release of these chemicals to the environment. The specific research gaps identified in the context of understanding the fate and transfer of SVOCs in SEA are summarized below:

I. Determination of atmospheric SVOCs by means of chemical analyses is often time-consuming due to the high diversity of these compounds present at low concentrations in ambient air. It is an analytical challenge to be able to identify and quantify SVOCs distributed between particulate- and gaseous-phases in atmospheric samples with low detection limits.

II. Several studies have been conducted on short-term measurements of SVOCs in the urban environment of SEA, but their distributions in gas- and particulate phases as well as in rainwater and their seasonal variations remain poorly known in this region.

III. Environmental distribution modeling is an important tool to simulate the exchange and transport processes of chemicals in the environment and to gain insights into their ultimate fate. Gas-particle partitioning, precipitation scavenging, and air-sea exchange models are particularly important in the case of SVOCs, but have never been applied to assess the migration of SVOCs in the multi-media tropical environment.

This doctoral study was conducted to fill these knowledge gaps. The main aim of this study was to provide insights into the distribution of SVOCs in the tropical atmospheric environment and to assess their environmental fate under tropical weather conditions, characterized by deep convection of air and abundant rainfall, using a combination of field experiments and theoretical models. The specific objectives of this research were to:

- develop, optimize, and validate an extraction method for the determination of atmospheric SVOCs distributed in both gas and particle phases under tropical conditions;

- assess the occurrence and distribution of SVOCs in the atmosphere, precipitation (rainwater), and surface seawater in Singapore's coastal area;

- evaluate the partitioning process of SVOCs between vapor- and particle-phases in the atmosphere using partitioning equilibrium models and experimental data obtained under field conditions;

- examine the role of the precipitation scavenging of SVOCs to describe their distributions between gas/particle and aqueous phases under the regional climate conditions;

- use fundamental physical-chemical properties of SVOCs in conjunction with experimental data to provide information on their equilibrium partitioning between the air and surface seawater. .

Overall, this study was designed to gain a better understanding of the distribution of SVOCs among the different compartments in the tropical environment in order to provide more insights into the transport of these selected compounds under various natural conditions. To assess the relative importance of key transport processes, to assess sources, and to validate models, it is important to make simultaneous measurements of prevailing concentrations of SVOCs in different environmental media. Furthermore, knowledge obtained on the fate of toxic organic chemicals in the tropical atmosphere may help develop adequate regulatory guidelines for the protection of the environment and human health on a regional scale.

1.3. Organization of Thesis

The thesis is subdivided into the following chapters.

- **Chapter 2: Literature Review**

  This chapter provides a comprehensive review of the properties of SVOCs targeted in this study and several environmental distribution processes such as gas/particle partitioning, precipitation scavenging and air - sea exchange, as reported by a number of investigators in the literature. This literarure review provides the background information for this doctoral study.

- **Chapter 3: Materials and Method**

  This chapter describes the characteristics of sampling sites where field studies were conducted, the experimental procedures, analytical methods, and materials used in the entire project.

- **Chapter 4: Optimization of Accelerated Solvent Extraction (ASE)**

  This chapter deals with the development and optimization of ASE extraction used for quantifying SVOCs in both gaseous and particulate samples.

- **Chapter 5: Levels, Temporal, and Seasonal Trends of Semi-Volatile Organic Contaminants In Ambient Air and Rainwater In Singapore**

  This chapter reports the concentration and distribution of SVOCs in both gas/particle atmospheric phases and rainwater in this coastal marine environment of Singapore under different weather conditions.

- **Chapter 6: Gas-Particle Partitioning of SVOCs in the Tropical Atmosphere of Southease Asia**

  This chapter discusses the gas / particle partitioning of SVOCs in the tropical atmosphere based on a combination of experimental and theoretical studies.

- **Chapter 7: Precipitation Scavenging of Semi-volatile Organic Compounds (SVOCs) In A Tropical Area**

  This chapter presents data obtained from field studies to explain the role of the precipitation scavenging process as a removal mechanism of SVOCs from the atmosphere.

- **Chapter 8: The Exchange of SVOCs Across The Air-Sea Interface In Singapore's Coastal Environment**

  This chapter discusses the transfer of SVOCs from the atmosphere onto Singapore's coastal area through dry and wet deposition mechanisms and air-sea diffusive exchange processes. Partitioning of SVOCs in the water column and enrichment effect of SML are also discussed.

- **Chapter 9: Conclusions**

  The major findings made in the doctoral study are summarized. The conclusions drawn from the study are also presented in this chapter.

Chapter 2. Literature Review

2.1. Occurrence, Sources and Properties of SVOCs in the Atmospheric Environment

2.1.1. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds with a planar structure of two or more fused aromatic rings interlinked in various arrangements. This means that the number of theoretically possible compounds is large. PAHs occur in oil, coal, and tar deposits, and are produced as byproducts of carbon-based fuel burning (whether fossil fuel or biomass). As PAHs are almost present in mixture, the composition can be complex and tremendous. Thus, only 16 individual compounds were selected for evaluation in this study as follows: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene. These compounds were chosen based on their toxicity, potential for human exposure and frequency of occurrence. Moreover, these 16 PAH compounds have been identified as priority pollutants by US Environmental Protection Agency (EPA). The structure of selected PAHs is shown in Figure 2.1. These PAHs display varying degrees of toxicity, but as a general rule of thumb, the toxicity of PAHs increases with their molecular weight (MW). Higher molecular weight (HMW) PAHs would be more inclined to be adsorbed on particles than exist in the gas phase as compared to lower molecular weight (LMW) PAHs (Fang et al., 2004; Terzi and Samara, 2004) due to lower vapor pressures.

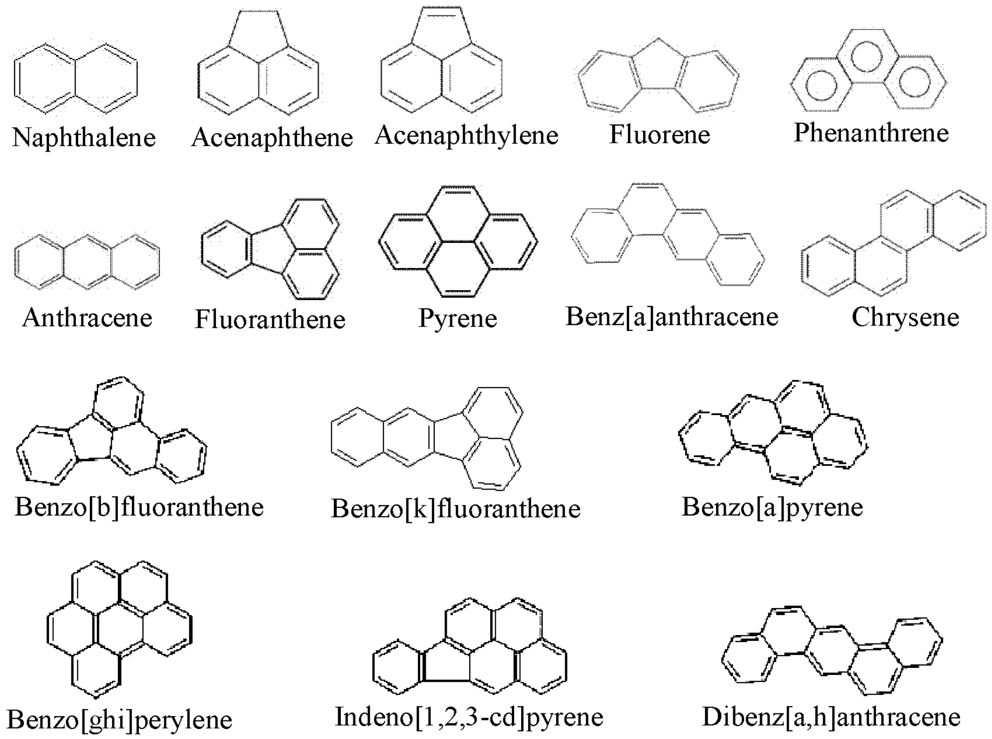


Figure 2.1. Structure of selected PAHs

The main concern regarding PAHs is associated with their toxicity following chronic exposure, although acute toxicity can be induced in feeding experiments with laboratory animals (Osborne and Crosby, 1987). More than 30 parent or unsubstitued compounds plus several hundred derivatives have carcinogenic activities (Bjorseth and Becher, 1986; Straif et al., 2005). In addition, several pollutants among this group are associated with mutagenicity (Durant et al., 1996), genotoxicity (Georgiadis et al., 2001), immunotoxicity (Davila et al., 1995), neurotoxicity (Tang et al., 2003) and toxicity of the reproductive systems (Hoyer, 2005), and mostly those with four to six rings are considered to be very active carcinogens (Müller, 1997).

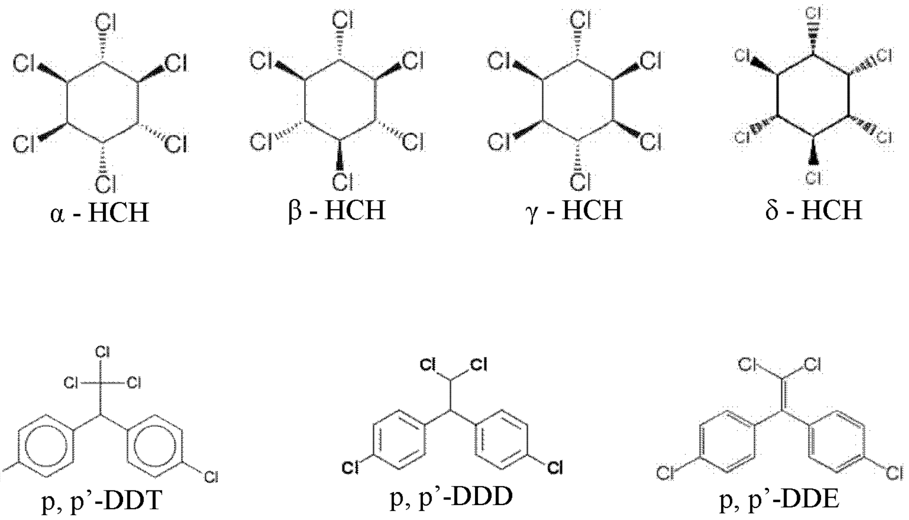
Despite the fact that PAHs can occur naturally in the environment, primarily as a result of fires and volcanic activity, by far the greatest current contributions to the environmental burden arise from human activities (Simcik et al., 1996). PAHs can be formed during any incomplete combustion or high temperature pyrolytic process involving fossil fuels, or more generally, materials containing carbon and hydrogen (Bjorseth and Becher, 1986). On heating, the organic compounds are partially cracked to smaller and unstable fragments (pyrolysis). These fragments, mainly highly reactive free radicals with a very short average lifetime, form more stable PAH formation through recombination reactions (pyrosynthesis) (Bonfanti et al., 1994). Consequently, B(a)P and other PAHs are formed through pyrolysis processes of methane, acetylene, butadiene and other compounds (Mastral and Callén, 2000). PAH formation in combustion can be explained like a waterfall mechanism in which PAH compounds are formed through small radicals to which more radicals add through a series of chain reactions forming compounds of higher molecular weight, soot and fullerenes (Kroto et al., 1991; Mastral and Callén, 2000). The PAH rearrangement and interconversion processes during combustion have also been shown by Visser et al. (1998). Motor vehicles account for the majority of PAH emissions in urban areas (Freeman and Cattel, 1990). In general exhaust emissions of PAH from mobile sources originate by three distinct mechanisms similar to the abovementioned processes: (i) synthesis from simpler molecules in the fuel, particularly from aromatic compounds; (ii) storage in engine deposits and subsequent emission of PAH already in the fuel; and (iii) pyrolysis of lubricants (Baek et al., 1991). The emission rates of PAH from vehicle exhausts depend on a large number of factors including engine type, operating conditions and composition of fuel, additive and lubricating oil (Candeli et al., 1983).

2.1.2. Organochlorine Pesticides (OCPs)

Typically, pesticides refer to substances used for the destruction or control of insects, fungi, vegetation and any microbiological agents. (Smith, 1991). Organochlorine pesticides are potent contact pesticides which do not penetrate plant tissue. These compounds have high chemical stability because they are constructed largely from C-C, C-H and C-Cl bonds that tend to be chemically inactive under normal environmental conditions (Hassal, 1982). Two main families of OCPs were selected in this study: (i) dichlorodiphenyltrichloroethane (DDT) family including p, p’-DDT, p, p’-DDD and p, p’-DDE, characterized by low water solubility and the potential for high bioaccumulation and biomagnifications in birds, mammals and fish; (ii) hexachlorocyclohexane (HCH) family, with γ-HCH being the only isomer with insecticidal properties, characterized by higher water solubility and the potential for wide distribution in the environment (Wilkinson, 2002). The structure of selected OCPs is shown in Figure 2.2.

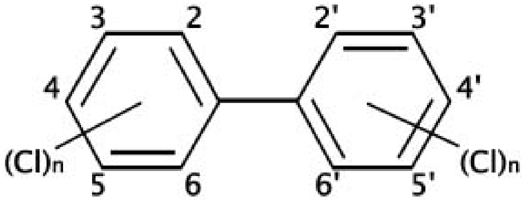
2.1.2.1. HCHs

Hexachlorocyclohexane is a mixture of the eight isomers of compound 1, 2, 3, 4, 5, 6-hexachlorocyclohexane, denoted by α, β, γ, δ, ε, η, θ with the isomer existing in two enantiomeric forms (Willet et al., 1998). HCH was created in 1825, but it was not discovered until 1943 that γ isomer was responsible for the insecticidal activity of technical HCH (Brooks, 1974). Technical HCH is composed of 60 - 70% α-HCH, 5 - 12% β-HCH, 10 - 12% γ-HCH, 6 - 10% δ-HCH and 3 - 4% ε-HCH (Kutz et al., 1991), while lindane consists of more than 99% pure γ-HCH. HCH is produced by chlorinating benzene in the presence of ultraviolet radiation. Subsequent treatment with methanol or acetic acid followed by fractional recrystallization can concentrate the -HCH isomer to 99.9% pure (Wilkinson, 2002).


α - HCH β - HCH γ - HCH δ - HCH

p, p'-DDT p, p'-DDD p, p'-DDE

Figure 2.2. Structure of selected OCPs



PCB

Figure 2.3. Structure of selected PCBs

A significant proportion of technical HCH (~ 88%) is useless as an insecticide and unfortunately needlessly entered the environment where it has persisted for years. Recent total global consumption of technical HCH has been estimated at 6.0 million metric tones (Li et al., 1998). The highest consumption of technical HCH occurred between 0 ~ 30^{o}N latitude, while the highest consumption of γ-HCH occurred between 30^{o}N ~ 60^{o}N latitude (Voldner and Li, 1995). Technical HCH was replaced by lindane in North America and Western Europe in the 1970s and then in China (1983), Russia (1990) and India after 1990 (Li et al., 1998; Willet et al., 1998). Since then, lindane has been reported to be used as an insecticide on fruits, vegetable, rice paddies, as a seed treatment and for the management of forestry products; likewise, it has been applied for the treatment of lice and scabies on humans (Willet et al., 1998). Large quantities of HCHs are still found throughout the environment and are considered to be the most abundant organochlorine compounds in both air and water of arctic and sub-arctic regions (Bidleman et al., 1995).

2.1.2.2. DDTs

DDT synthesis was reported in 1874 and the insecticidal properties of the p, p-DDT isomer was discovered in 1939 (Cremlyn, 1978). DDT is produced by condensation of chloral and chlorobenzene in the presence of an excess of concentrated sulphuric acid. The crude product contains 80% p, p'-DDT, 20% o, p'-DDT and trace amounts of o, o'-DDT. Pure p, p'-DDT can be produced by recrystallization from ethanol at 108^{o}C with more cost (Wilkinson, 2002). DDT began to be used commercially in 1943 and soon became the most widely used insecticide in the world, largely due to its use as a controlling agent against malaria and typhus and also its low toxicity to humans (Brooks, 1974). The adverse environmental effects of DDT started to draw attention after Rachel Carson published "Silent Spring" in 1962. The ability of DDT to persist in the environment and to bioaccumulate and biomagnify in food chains became well known in raptors, bald eagles and peregrine falcons when their populations greatly dropped down due to eggshell thinning and reproductive failure. Consequently, DDT use was banned in the U.S. in 1973, in U.K. in 1984 and restricted in Canada in 1985 (Wilkinson, 2002). Approximately 2.5 billion people in over 90 countries are at risk of contracting malaria (WWF, World Wildlife Fund,1998), therefore DDT is still in use in many of these developing countries (UNEP, 2002).

2.1.3. Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are non-polar, aromatic, chlorinated hydrocarbons (see Figure 2.3). They have a biphenyl nucleus on which one to ten of the hydrogen atoms have been substituted by chlorine. Commercial PCBs were synthesized by chlorination of biphenyl with chlorine gas, in which a mixture of all 209 possible congeners was produced (Erickson, 1997). PCBs were first created in 1881, but these compounds were not produced commercially until 1929 under Aroclor (Monsanto, U.S.) as a response for the electrical industries need for a safer insulator. The thermal stability, resistance to degradation and low dielectric properties of PCBs made them desirable for uses as hydraulic fluids, as a flame retardant in lubricating oils and as a cooling and insulating fluid for industrial transformer and capacitors. In addition, PCBs were also used as plasticizers in sealants, caulkings, synthetic resins, rubbers, paints, waxes and asphalts, and as surface coatings for carbonless copy paper (CCREM, Canadian Council of Resource and Environment Ministers, 1986). The manufacture, processing, distribution and uses of PCBs were banned in 1978 by U.S. congress (Erickson, 1997). Applications were restricted throughout the rest of the world soon after (Wilkinson, 2002).

PCBs are semi-volatile, highly insoluble in water and capable of long-range atmospheric transport in the environment. The lower chlorinated PCBs are more volatile, generally capable of long-range transport in the environment and also more easily excreted by fish and mammals. The higher chlorinated PCBs are less water-soluble. Therefore, they bind more readily to soil and particulate matter and accumulate in lipids to a greater extent (Waid, 1986). The persistence of PCBs coupled with their ability to bioaccumulate in food chains has caused great environmental damage (Erickson, 1997).

2.2. Physicochemical Properties of Selected SVOCs

Simulation of the transport and distribution of selected SVOCs requires knowledge of the physiochemical properties of these compounds; namely, physical-chemical properties have been shown to be important in governing the distribution and fate of atmospheric SVOCs in the environment. The compound saturation vapor pressure, p (Pa), represents a key property. SVOCs generally exhibit relatively low compound saturation vapor pressures, but such compounds may still volatize and transport long distances in the atmosphere (Wania and Mackay, 1993). The compound saturation vapor pressure can be considered to represent equilibrium between the compound in the vapor phase and pure substance itself. The equilibrium distribution of chemicals between two essentially immiscible phases such as air and particle, air and water or water and lipid can be described by an equilibrium concentration ratio or partition coefficient (K) of a compound. Partition coefficients can be approximated from the ratio of the maximum solubilities of the chemicals in each of the phases. That is, for phases m and n, the partition coefficient for a specific compound distributed between m and n is expressed by

$$K_{mn} = \frac{C_m}{C_n} \approx \frac{S_m}{S_n} \tag{2.1}$$

where C_m and C_n are the equilibrium concentrations and S_m and S_n are the maximum solubility of the chemical in the respective phases m and n. Maximum solubilities are temperature dependent, and thus, partition coefficients also have temperature dependence (Müller, 1997).

The primary alcohol 1-octanol has been extensively employed as a surrogate for organic phase; hence octanol / water partition coefficient (K_{OW}) is often regarded as a descriptor for the distribution of a chemical between organic phase and water. The magnitude of K_{OW} is a measure of the hydrophobicity of a chemical and can be calculated by

$$K_{OW} = \frac{S_O}{S_W} \tag{2.2}$$

where S_O and S_W are the maximum solubility of a compound in octanol and water, respectively.

Due to the importance of the organic phase / air partition coefficient in the estimation of organic matter (OM) / air partition coefficients of hydrophobic compounds, the octanol / air partition coefficient (K_{OA}) has been introduced and can be obtained by

$$K_{OA} = \frac{S_O}{S_A} = \frac{S_O RT}{p} \tag{2.3}$$

where R is the universal gas constant (8.3145 Pa m^3 mol^{-1} K^{-1}) and T is the absolute temperature (K).

The Henry's Law constant, H (Pa m^3 mol^{-1}), describes the distribution of a chemical between the aqueous phase and air. A dimensionless partition coefficient between air and water can be computed by

$$K_{AW} = \frac{S_A}{S_W} = \frac{p}{S_W RT} = \frac{H}{RT} \tag{2.4}$$

The properties of vapor pressure, water solubility, octanol-water partition coefficient (K_{OW}), octanol-air partition coefficient (K_{OA}) and the Henry's law constant (H) are listed in Table 2.1.

Table 2.1 Physicochemical properties of selected SVOCs

Compound	Vapor Pressure Pa	Water Solubility mg L^{-1}	Log K_{OW}	Log K_{OA}	k_H Pa m^3 mol^{-1}
PAHs					
Naphthalene	10.4	30.0	3.37	N.A.	48.8
Acenaphthene	3.0	1.9	3.92	6.51	15.7
Acenaphthylene	9×10^{-1}	3.9	4.00	6.33	1.1
Fluorene	9×10^{-2}	1.8	4.18	6.79	6.4
Phenanthrene	2×10^{-2}	1.2	4.57	7.60	2.6
Anthracene	7.6×10^{-4}	7.6×10^{-2}	4.54	7.71	1.8
Fluoranthene	1.2×10^{-3}	2.1×10^{-1}	5.22	8.87	6.6×10^{-1}
Pyrene	6×10^{-4}	1.4×10^{-1}	5.18	8.81	2.5×10^{-1}
Benz[a]anthracene	2.8×10^{-5}	1.0×10^{-2}	5.91	10.28	1.0×10^{-1}
Chrysene	5.7×10^{-7}	2.8×10^{-3}	5.86	10.29	1.1×10^{-1}
Benzo[b]fluoranthene	6.7×10^{-7}	1.2×10^{-3}	5.80	11.33	1.2
Benzo[k]fluoranthene	5.2×10^{-8}	7.6×10^{-4}	6.00	11.36	3.9
Benzo[a]pyrene	7.0×10^{-7}	2.3×10^{-3}	6.04	11.55	4.9×10^{-2}
Benzo[ghi]perylene	6.0×10^{-8}	2.6×10^{-4}	6.50	12.54	1.5×10^{-2}
Indeno[1,2,3-cd]pyrene	7.0×10^{-7}	6.2×10^{-2}	6.58	12.42	7.0×10^{-3}
Dibenz[a,h]anthracene	3.7×10^{-10}	5.0×10^{-4}	6.75	12.58	7.4×10^{-3}
OCPs					
HCHs	$4 \times 10^{-5} \sim 0.08$	$1.0 \sim 30.0$	$3.8 \sim 4.4$	$7.5 \sim 8.7$	$2.0 \times 10^{-3} \sim 0.8$
DDTs	$2 \times 10^{-4} \sim 9 \times 10^{-9}$	$1 \times 10^{-3} \sim 5 \times 10^{-3}$	$5.5 \sim 6.0$	$9.6 \sim 10.1$	$1.2 \sim 6.0$
PCBs					
Mono-CBs	$0.9 \sim 2.5$	$1.2 \sim 5.5$	$4.3 \sim 4.7$	6.80	$58.0 \sim 74.0$
Di-CBs	$1.8 \times 10^{-3} \sim 0.28$	$0.06 \sim 2.0$	$4.9 \sim 5.3$	7.73	$17.0 \sim 92.2$
Tri-CBs	$0.014 \sim 0.14$	$0.015 \sim 0.4$	$5.5 \sim 5.9$	8.01	$24.3 \sim 92.2$
Tetra-CBs	$5.9 \times 10^{-5} \sim 5.4 \times 10^{-3}$	$4.3 \times 10^{-3} \sim 0.1$	$5.6 \sim 6.5$	8.47-9.29	$1.7 \sim 47.6$

Table 2.1 Physicochemical properties of selected SVOCs (cont'd)

Penta-CBs	3.0×10^{-3}~9.0×10^{-3}	4×10^{-3}~0.02	6.2 ~ 6.5	9.14	24.8 ~ 151.4
Hexa-CBs	2×10^{-5}~1.6×10^{-3}	4×10^{-4}~1×10^{-3}	6.7 ~ 7.3	9.80	11.9 ~ 81.8
Hepta-CBs	2.7×10^{-5}	4.5×10^{-4}~2×10^{-3}	6.7 ~ 7.0	9.87	5.4
Octa-CBs	2.7×10^{-5}	2×10^{-4}~3×10^{-4}	7.1	N.A.	38.1
Nona-CBs	6.3×10^{-6}	1.8×10^{-5}~1.1×10^{-4}	7.2 ~ 8.2	N.A.	100.0
Deca-CBs	5.0×10^{-3}	1.2×10^{-6}	8.3	N.A.	20.8

Note: Log K_{OW} (25^{o}C), water solubilities (25^{o}C), vapor pressure (25^{o}C) and Henry's law constant of selected SVOCs adapted from Mackay et al. (1997). Log K_{OA} (25^{o}C) adapted from Harner and Bidleman (1996, 1998), Kömp and McLachlan (1997) and Wania et al. (2002).

K_{OA} has been reported to be an excellent descriptor of gas to particle partitioning of which the extent of gas/particle (g/p) partitioning of SVOCs in the atmosphere affects the rates of dry and wet deposition as well as air-water exchange (Finizio et al., 1997). In addition, subcooled vapor pressure of SVOCs is also preferred to be used to describe g/p partitioning due to its strong relationship with g/p partitioning coefficient, K_P, in the atmosphere (Finizio et al., 1997). For instance, lower chlorinated PCB congeners have lower K_{OA} so that their particle fractions are lower due to higher vapor pressure (Harrad and Mao, 2004; Yeo et al., 2004).

The selected SVOCs are typically hydrophobic and characterized by a low water solubility and relatively high K_{OW} value. Thus, they tend to volatalize from aqueous solution and be associated with organic matter of soil, sediments and suspended particulate matter in water column (Jones and De Voogt, 1999). In general, the less water soluble SVOCs, described by higher K_{OW}, prefer to accumulate on organic matter and in biota to a greater extent. For example, HCHs have relative high water solubilities and low $K_{OW} < 4$, and therefore their bioaccumulation is less significant (Van der Oost et al., 2003). On the contrary, DDTs have higher K_{OW} of 5.6 ~ 6.2 and are expected to have a significant bioaccumulative potential. PCB congeners are known to be variable in physicochemical properties in accordance with their chlorination levels. Water solubility and vapor pressure can vary by up to a magnitude of 10^8, with a decreasing order of these properties with increasing chlorination extent. The vapor pressure and water solubility are the key parameters of SVOCs to transfer into gas phase in the environment and therefore determine the potential to go through long-range transport (Bard, 1999; Wurl, 2006). Physicochemical properties of selected SVOCs certainly depend on prevailing environmental conditions. They are subject to measurement uncertainties (Holmes et al., 1993), and are reported in a wide range, rather than consistent, values (Mackay et al., 1997), which makes it particularly challenging to theoretically simulate the behaviors of SVOCs in the environment.

2.3. Gas-Particle Partitioning

2.3.1. Conventional Simulative Approach

The behavior and fate of SVOCs in the atmosphere greatly depends on the distribution of compounds between different sub-compartments of the atmosphere such as atmospheric gaseous and particulate phases. It has been summarized that gas-particle partitioning is controlling the relative importance of different deposition pathways for SVOCs from the atmosphere to the earth/waterbody surface (Bildleman, 1988).

Pankow (Pankow, 1987) consolidated, and subsequently refined early approaches (Pankow and Bidleman, 1991, 1992) to describe the equilibrium partitioning between gas and particles based on adsorption theory (Junge, 1977; Yamasaki et al., 1982). Much attention has also been paid to the effect of relative humidity (Thibodeaux et al., 1991; Pankow et al., 1993; Storey et al., 1995) and non-exchangeable matter (Pankow, 1988). Pankow (Pankow, 1988) defined the gas-particle partition coefficient, K_P (m^3 μg^{-1}), which can be related to measured fractions or concentrations in both gas (C_g - retained by adsorbent) and particulate phase (C_p – retained by the filter) and the total suspended particulates' concentration (TSP), in $\mu g\,m^{-3}$:

$$K_p = (C_p/TSP)/C_g \qquad (2.5)$$

In case of adsorption, Pankow (1988) derived

$$K_P = \frac{N_s A_{TSP} T e^{(Q_L - Q_V)/RT}}{16 P_L{}^o} \tag{2.6}$$

where N_s is the surface concentration of sorption sites, A_{TSP} is the specific surface area of the TSP, $P_L{}^o$ is the vapor pressure of the subcooled liquid, Q_L is the enthalpy of desorption from the surface and Q_V is the enthalpy of vaporization of the subcooled liquid, respectively.

The dependence of K_P on the subcooled vapor pressure of different compounds has been demonstrated by plotting log K_P vs. log p_L (Pankow, 1987; Pankow and Bidleman, 1991, 1992; Cotham and Bidleman, 1995). The correlation could be shown as

$$\log K_P = m_r \log p_L^o + b_r \tag{2.7}$$

This regression of log K_P against the temperature corrected log $p_L{}^o$ of the compound could potentially yield useful information on the distribution from the slope, m_r and the y-intercept, b_r, of the trendline. For equilibrium distribution, m_r is expected to have a value of near -1 (Pankow and Bidleman, 1992).

Similarly to partitioning in the water column, SVOCs partition through an absorption process in addition to physical adsorption onto the surface of particles. SVOCs would "dissolve" in the amorphous organic matter in the atmosphere, which exists both as primary (POA) and as secondary organic aerosols (SOA) (Lohmann and Lammel, 2004). It has been demonstrated that the experimental data, the observed slopes near -1 of log K_P vs. log $p_L{}^o$, would also be applicable to absorption, e.g. into an organic aerosol fraction (Pankow, 1994a, b). K_P values measured on clean quartz sand at different relative humidities (Goss, 1992) are much lower than measured in urban aerosol (Storey et al., 1995), indicating that absorption to the organic carbon component of urban particulate matter might be more important than adsorption to the available surface area. Some investigations with tobacco smoke (Pankow et al., 1994; Liang and Pankow, 1996) have further strengthened the case for absorption in the organic phase for urban particulate matter, which tends to have a relatively high content of organic material. Accordingly, Finizio et al. (1997) employed the octanol-air partition coefficient (K_{OA}) to describe the partitioning of SVOCs between air and organic films on aerosols. Partitioning between gas-phase and particulate organic matter (OM) phase was empirically related to the partitioning coefficient between octanol and the gas phase, K_{OA}, as in Equations (2.8) and (2.9) for PAHs and OCs, respectively:

$$\log K_P = 0.79 \log K_{OA} - 10.01 \tag{2.8}$$

$$\log K_P = 0.55 \log K_{OA} - 8.23 \tag{2.9}$$

The relationship between log K_P vs. log K_{OA} has been furthered developed with the inclusion of SVOCs' activity coefficients in octanol and OM and their molecular weights proposed by Harner and Bidleman (1998) and simplified to a linear relationship as shown in Equation (2.10) (Pankow, 1994b; Harner and Bidleman, 1998).

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \tag{2.10}$$

For equilibrium partitioning the slope is expected to have a value of near + 1 in log K_P – log K_{OA} correlations. The intercept equals log f_{OM}-11.91, depending on the organic matter content of aerosols which determines the absorptive capacity.

2.3.2. Alternative Approaches

The abovementioned models use single-parameter linear free energy relationships (spLFERs) to describe sorption to aerosol particles. Generally, spLFERs relate the gas-particle partition coefficient to the subcooled liquid vapor pressure, p_L^o, or the octanol-air partition coefficient, K_{OA}, of the chemical. An alternative conceptual model for sorption to aerosol particles has been developed by Goss and co-workers (Goss, 1997; Abraham, 2004; Roth et al., 2005a, b). It has been advocated to describe gas-particle partitioning with polyparameter linear free energy-relationships (ppLEFRs). A ppLEFR describing the gas-particle partition coefficient has the general form

$$\log K_P = w \cdot W + x \cdot X + y \cdot Y + ... + C \qquad (2.11)$$

Each multiplicative group on the right side of the equation describes an interaction between the chemical and the sorbent such as van-der-Waals interactions or hydrogen bonding. The multiplicative groups are composed of a term representing the chemical's ability to participate in an interaction (W, X, Y …). To calculate K_P for a chemical, one needs Abraham salvation parameters for the chemical ($A_{chemical} = \{W,X,Y,...\}$), a set of complementary sorbent parameters (Asorbent = $\{w,x,y,...\}$), and the constant, C. In principal, the ppLFER approach can describe any surface adsorption or bulk phase absorption interactions that are possible between gas molecules and aerosols. In laboratory and field studies, ppLFERs have been developed to describe the distribution of volatile organic compounds between the gas phase and various surfaces and bulk phases (Goss and Eisenreich, 1996; Nguyen et al., 2005; Roth et al., 2005a, b; Arp et al., 2006).

In 2007, a more general model of gas-particle partitioning has been developed (Götz et al., 2007), which combines existing ppLFERs for sorption to fine aerosols and components of coarse aerosols into a model that is applicable to aerosols with defined size distribution and composition. The new model is applicable to organic non-ionic polar and nonpolar chemicals, and can describe a wide range of aerosol properties. The comparison and contrast was made between the spLFER and ppLFER models by (i) comparing the sorption models for a reference aerosol to identify compound classes where K_P is sensitive to which model is used, and (ii) investigating the variability of K_P among different aerosols. Practical application of the general ppLFER model to a wide range of chemicals is currently still limited by data gaps in measured Abraham salvation parameters and uncertainties in estimation methods.

A different tool depending on quantitative structure-property relationship (QSPR) can be utilized to predict K_P values for SVOCs. QSPR studies have been applied in chemistry, biochemistry and recently for solving environmental problems (Gramatica et al., 1999; Gramatica et al., 2001). The main idea of QSPR is to construct the correlationship by expressing a special physicochemical property of organic compounds in terms of appropriate molecular descriptors (Karelson et al., 1996). Wei et al. (2007) have explored the relationship between molecular descriptors and gas / particle partitioning of PCBs. In their study, overall 14 molecular descriptors of each compound calculated using semi-empirical method parametric model 3 (PM3) were tested against log K_P of selected PCBs to determine the best ones governing partitioning. Eight descriptors molecular weight, molecular volume, total energy, electronic energy, squared atom electron densities on carbon, hydrogen and chlorine atoms in a given molecule and average molecular polarizability were found to be highly correlated with log K_P compared to other molecular descriptors. Using Partial Least-Squares Regression method (PLS), two-, three- and four-descriptor QSPR models with good fitting characters were successfully developed.

2.4. Dry Particle Deposition

Particle-sorbed SVOCs can settle by dry particle deposition, a uni-directional advective transport process from the atmosphere to earth/water surface, which is independent of the fugacities of SVOCs in the receiving medium. In its simplest form, the flux of chemicals to the surface F_{dry} (μg m^{-2} s^{-1}) is expressed as a product of the concentration on particles C_p (μg m^{-3}) and a dry deposition velocity V_d (m s^{-1}) as follows:

$$F_{dry} = C_p \cdot V_d \qquad (2.12)$$

To date there has been no consensus on the appropriate dry deposition velocity to use in the flux estimation. Estimated (Hoff et al., 1996) and experimental (Holsen et al., 1991) dry deposition velocities of SVOCs range over an order of magnitude.

One of the reasons for this discrepancy is that deposition velocity is a function of particle size. Gravitational settling has a significant effect on the deposition of coarse particles, while Brownian motion dominates the deposition of very fine particles (<0.1 μm) (Seinfeld, 1986). As the particle diameter increases, the magnitude of flux increases due to higher deposition velocities. A recent study has shown that a multistep modeling approach, which divides the fine and coarse particle distributions into a number of intervals and assigns an appropriate deposition velocity to each interval, gives a better estimate of dry deposition than the approach shown in Equation (2.12)(Holsen and Noll, 1992). Using this multistep model and other techniques it has been found that coarse particles (>2.5 μm) and compounds associated with them are responsible for the majority of dry deposition (Holsen et al., 1991; Holsen and Noll, 1992; Holsen et al., 1993). However, the information on size distributions combined with size-dependent deposition velocities for SVOCs is still extremely limited and essentially non-existent for the off-shore atmosphere, making it difficult to even estimate applicable mass median diameters.

There have also been many efforts to measure dry deposition directly. However, there is no generally accepted method for collecting particulate dry deposition or gas exchange. Different kinds of surrogate surfaces including Teflon plates, Petri dishes, dry or diol-coated filters, buckets, pans filled with water, oil-coated glass plates, and greased strips have all been used to measure particle dry deposition (Bidleman, 1988). In addition, a moving sheet of water was used to passively trap dry particles and gases to trace organic chemicals (Waite et al., 1999).

2.5. Wet Deposition and Scavenging

SVOCs are scavenged from the atmosphere episodically by precipitation, both as vapors which dissolve in the raindrops, and bound to atmospheric particles, which are incorporated into the rain within or below the clouds. Wet deposition of gases and particles can be described as one bulk process by using a dimensionless total wet scavenging ratio W_T, where W_T is the sum of the effective scavenging ratio for the substance in the gas and particle phases, W_G and W_P, respectively:

$$W_T = W_P\Phi + W_G(1-\Phi) \qquad (2.13)$$

where ϕ is the fraction of chemical in air which is sorbed to aerosol.

It is generally assumed that equilibrium is attained rapidly between the vapor phase and the dissolved phase in a raindrop (Cousins et al., 1999). It has been estimated that equilibrium can be established with the surrounding vapor phase during the time it takes a raindrop to fall a few meters (Ligocki et al., 1985a, b). Therefore, vapor washout ratio, W_G, has been estimated using air-water equilibrium partition coefficients or Henry's Law contant:

$$W_G = \frac{C_{R,dissolved}}{C_g} = \frac{RT}{H} \qquad (2.14)$$

where $C_{R,dissolved}$ is the dissolved concentration in water at equilibrium, and C_g is the vapor concentration in air at equilibrium.

The particle scavenging ratio can be estimated:

$$W_P = \frac{C_{R,sorbed}}{C_P} \qquad (2.15)$$

where $C_{R,sorbed}$ is the concentration of SVOCs sorbed on the particles scavenged by rain and C_P is the concentration of SVOCs in atmospheric particulate phase.

There have been numerous attempts to deduce scavenging ratios for SVOCs by simultaneously measuring rain and ground level air concentrations (Ligocki et al., 1985a, b; Leuenberger et al., 1988; Murray and Andren, 1992; Poster and Baker, 1996b; Franz and Eisenreich, 1998). Washout ratios for SVOCs tend to be much smaller than those reported for trace metals and radio-nuclides (Ligocki et al., 1985a, b; Atlas and Giam, 1988). Vapor scavenging is important especially for SVOCs with low Henry's Law constants; however, deviations from equilibrium partitioning between air and rain have been observed (Cousins et al., 1999). Particle scavenging is not really dependent on the concentration of the compound in the particle and can thus been described as the scavenging of the particles themselves. W_P has been reported to be related to the particle size distribution to which SVOCs are sorbed (Poster and Baker, 1996a). Both particle and vapor scavenging are affected by ambient temperature, which can presumably shift gas-particle partitioning of SVOCs in the atmosphere (Wania et al., 1998).

2.6. Diffusive Air-Sea Exchange

SVOCs can diffuse across the air-water interface; the molecules in the vapor phase in air and the “truly” dissolved molecules in water participate in this diffusive transport which is driven by a deviation from chemical equilibrium between the air and water phase. Chemical equilibrium between two phases does not necessarily mean that the concentrations are equal, rather that the escaping tendency, or fugacity, is equal in both phases. This process is reversible and counteracts any fugacity gradient which may arise from precipitation scavenging, dry particle deposition, air mass changes over a water body, and temperature gradients.

A detailed description of the model formulations commonly used to describe diffusive air - water exchange can be found in the work of Schwarzenbach et al.(2003) (2003). Briefly, the flux across the air - water interface (F in ng m^{-2} d^{-1}) is expressed as the product of a kinetic parameter expressing the resistance to interfacial transfer and a term expressing the deviation from equilibrium as the driving force for interfacial transfer. A classical two-layer model (see Figure 2.4.), which has been previously applied to the air-sea exchange of SVOCs (Achman et al., 1993; Zhang et al., 2007; Li et al., 2009), assumes that the rate of gas transfer is controlled by the pollutant’s ability to diffuse across the air layer and sea surface water on either side of the air-water interface. The molecular diffusivity of the pollutant, dependent on the amount of resistance encountered in the liquid and gas films, describes the rate of transfer while the concentration gradient drives the direction of transfer (Totten et al., 2001). The flux $F_{air\text{-}water}$ (ng m^{-2} day^{-1}) is calculated by

$$F_{air\text{-}water}=K_{OL}(C_{truly}-\frac{C_g}{H'}) \qquad (2.16)$$

where K_{OL} (m day^{-1}) is the overall mass transfer coefficient, and $(C_{truly} - \frac{C_g}{H'})$ describes the concentration gradient (ng m^{-3}) where C_g is the gas-phase concentration of the compound in air that is divided by the dimensionless Henry's law constant (H′) with H′=H/RT where R is the universal gas constant (8.315 Pa m^3 K^{-1} mol^{-1}), H is Henry's law constant (Pa m^3 mol^{-1}) corrected by the temperature and salinity, and T is the temperature at the air-water interface (K). A positive flux indicates net volatilization out of the seawater and a negative flux indicates net absorption into the seawater. The overall mass transfer coefficient (K_{OL}) comprises resistances to mass transfer across the air layer and the water layer.

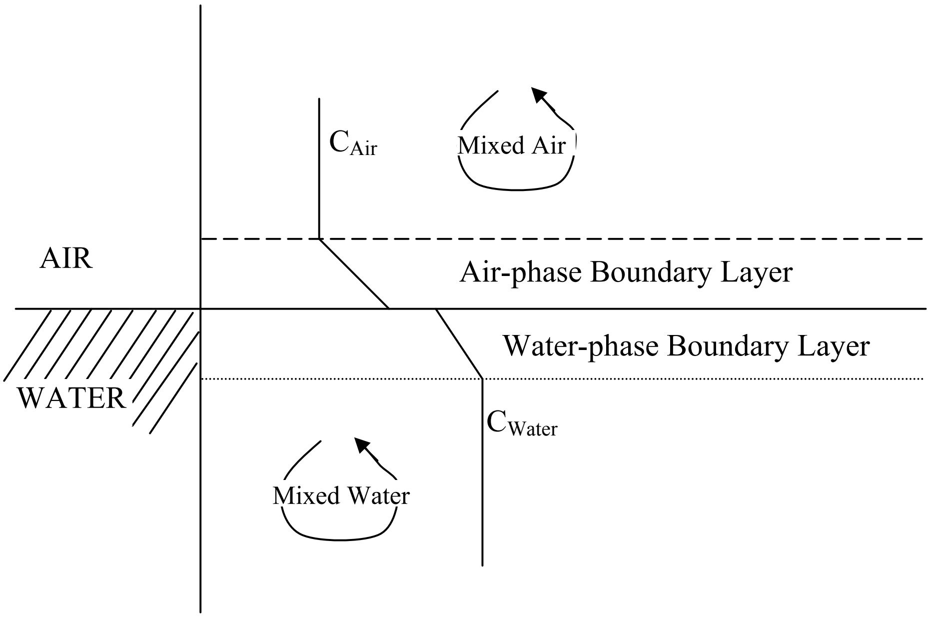


Figure 2.4. Classical two-layer model of a gas-liquid interface

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_a H'} \qquad (2.17)$$

where K_a and K_w (m day^{-1}) are the mass transfer coefficients across the air layer and water layer, respectively, dependent on wind speed, and several empirical relationship exist which relate them to the wind speed measured at a certain height above the water (Liss, 1973; Schwarzenbach et al., 2003). Temperature has an impact on the kinetics of air – sea transfer, i.e. influences the mass transfer coefficients. Molecular diffusivities in both air and water increase with temperature. Using semi-empirical approaches quoted in Schwarzenbach et al. (2003), diffusivities in air and water change by a factor of 1.2 and 2.3 between 0 and 30^{o}C. The main effect of temperature on the kinetics of air – sea exchange, is however, through its effect on Henry's Law constant. The availability of measured temperature-dependent Henry's Law constants for specific SVOCs is still rater limited (Wania et al., 1998).

2.7. Selected SVOCs in the Marine Environment of Singapore

2.7.1. Usage and Emission of Selected SVOCs in Singapore

Singapore is located about 120 km north (1^{o}14′ N, 103^{o}55′E) of the equator with Malaysia to the north and Indonesia to the south. This country is heavily industrialized with chemical industries, major power plants, oil refineries situated in a group of small islands on the west coast of the Singapore Island. Singapore is home to the third largest petroleum refining industry in the world, with a refining capacity in excess of 1 million barrels per day. Strategically located in the South China Sea and Straits of Malacca, this country is also a major port hub, with up to 142,000 ship movements per year (2002 data, Wurl, 2006). Agricultural activities are extensive in the region of SEA, but almost non-existent in Singapore. Due to its high urbanization, PAHs are mainly emitted by the local sources such as vehicles and industrial processes. OCPs and PCBs of concern in this study are officially banned in Singapore, but some of them have been banned quite recently (UNEP, 2002). According to UNEP Chemical's regional report (UNEP, 2002), γ-HCH (lindane) has been banned by most countries in SEA, but the previous reports indicated the use of lindane in Malaysia (Kannan et al., 1995). It has been known that Aroclor 1248 was used most extensively with hydraulic and heat transfer media. Aroclor 1254 was not only used in hydraulic media, but also was the main component in Askarel transformers and capacitors. The import of PCB-containing products was banned in Singapore since 1980, Malaysia in 1995 and in Indonesia in 1994 (UNEP, 2002). All electrical transformers containing PCBs should have been disposed of by end 2002 (UNEP, 2002). Due to its persistence, these pollutants still widely exist in different kinds of media in the environment in this region.

2.7.2. Occurrence of Selected SVOCs in the Environment of Singapore

The concentrations of PAHs in the atmosphere of Singapore have been reported since 1980s (Ang et al., 1986; Chee et al., 1997b; Karthikeyan et al., 2006), all of which are focused on the particulate phase and showed the contributions of 3-4 benzene ring PAHs to the total PAHs have increased considerably with the increasing of the number of on-road in Singapore. Basheer et al. (2003) have characterized PAHs in Singapore's rainwater and northeastern and southwestern coastlines surface seawater (Basheer et al., 2003a, b). Lim et al. (2007) have reported the atmospheric wet deposition of PAHs to the sea-surface microlayer (SML) in Singapore's coastal area by short-term sampling, with the concentration ranges of Σ PAHs 2.6 ~ 46.2 ng L^{-1} and 4.3 ~ 278.0 ng L^{-1} in the SML before rain and after wet deposition, respectively. In the 1990's, DDT residues were detected in human blood serum in Singapore and partially attributed to seafood consumption (Luo et al., 1997). More recently, Bayen et al (2005) reported concentrations of persistent organic pollutants in seafood consumed in Singapore with mean concentrations of 0.95, 3.72, and 3.76 ng g^{-1} for ΣChlordane, ΣDDTs and ΣPCBs, respectively. OCPs and PCBs were analyzed in unfiltered seawater samples collected around Singapore and the prevalence of HCHs (0.02 ~ 18 ng L^{-1}) and PCBs (0.2 ~ 62 ng L^{-1}) were shown, but DDTs appeared to be present in a lower concentration range of 0.02 ~ 1.4 ng L^{-1} (Basheer et al., 2003b). Several recent studies have investigated the occurrence of persistent organic pollutants in atmosphere, sea-surface microlayer and even sediment in Singapore's environment (Wurl and Obbard, 2005a, b; Wurl et al., 2006b), however, all the studies mentioned above have been based on short-term sampling, relatively more extensive dataset has not been set up to observe seasonal variation of selected pollutants and to investigate their systematic distribution and transfer between different matrices in this tropical environment.

Chapter 3. Materials and Method

3.1. Location of Sampling Sites

Singapore, as a representative industrialized country in SEA, is located near the equator (1.5^{o}N and 104^{o}E). Its tropical climate is marked with high humidity and abundant rainfall throughout the year. The ambient temperature and pressure are relatively uniform due to its maritime exposure and geographic location. The average humidity is 84% with maximum 100% during rainy days and temperature ranges from 23-34^{o}C. The climate is governed mainly by Northeast and Southwest monsoons from December to March and June to September, respectively. The seasons caused by respective wind directions. Cloudy conditions exist in December and January with frequent afternoon showers. Spells of widespread moderate to heavy rain occur lasting from 1 to 3 days at a stretch. Drier climate is usually observed during February till early March. The inter-monsoon seasons are influenced by light variable winds and localized weather. During the Southwest Monsoon period, Singapore's air quality is influenced by emissions from biomass burning in the Indonesian province, Sumatra, when dry weather conditions prevail, leading to the occurrence of regional smoke haze in SEA (SEA). The frequency of occurrence of smoke haze events and their intensity might vary from year to year.

In this project, most air and rainwater samples were collected on an event basis at the atmospheric research station in National University of Singapore (NUS). The sampling site was located 67 m above sea level, approximately 1 km away from the open sea. The southern coastal area of Singapore was chosen for the study on sea subsurface water and sea-surface microlayer. The major harbor, one of the busiest harbors in the world, is in the south coastal line of Singapore. Chemical industries as well as oil refineries are situated in a group of small islands on the southwest coast of the Singapore Island. The locations of sampling sites are shown in Figure 3.1.

Figure 3.1. Location of sampling sites: (a) SEA; (b) Singapore (* Sampling sites)

3.2. Sampling Instrumentation

A variety of instruments has been used for field measurements (Table 3.1).

Table 3.1. Summary of field instrumentation used in this study

Instrumentation	Purpose
High Volume PUF Air Sampler	To collect both atmospheric particles and gas samples in the field by using pre-combusted quartz microfiber filters and polyurethane foams (PUF)
Automated Wet-Dry Sampler	To collect wet-only samples (rainwater without interference from dust fall)
Sea Water Sampler and Glass Plate Collector	To collect the SSW and SML samples on the sea surface
Weather Station in National University of Singapore	To record all the relevant meteorological parameters (air temperature, total rainfall, solar incoming radiation, wind speed, etc.) during the sampling period

3.2.1. High Volume PUF Air Sampler

High volume samplers (Model: TE-1000PUF, Tisch Environmental, Inc. USA), equipped with filter holder and glass cartridge, were used for air sampling. The use of correct flow rate is critical to the calculation of particle volume-based concentrations. As per TE-PUF sampler instructions, after every 360 sampling hours, calibration of the high volume sampler was performed by using TE-5040A calibrator (orifice) without a foam plug or filter paper in the sampling module but with the empty glass cartridge remaining in the module. Magnehelic gage readings were taken at the beginning and end of each sampling period to obtain an average standard air flow rate. Pre-combusted quartz filters and polyurethane foams (PUF) were used to capture both ambient particulate and gaseous phases at ca. 250 L min^{-1}. These filters were heated at 450°C for 24 h and conditioned in a desiccator for 24 h prior to use. PUF plugs were pre-cleaned with hexane followed by acetone in 33-ml stainless steel vessels of a Dionex ASE 200 model at 100 atm and 120 °C for 10 min. The same pre-cleaning procedure was conducted six cycles till the targeted PAHs on PUF plugs were in the range of blank values of fresh solvents as above. The samples were collected on an event basis for 24 hr or 48 hr. Prior to and after sampling, quartz filters were conditioned in a dry box under the same condition and then weighed to obtain the particle mass collected. After sampling, both filter and PUF samples were stored at -20°C prior to extraction. The sampling schedule is listed in Table 3.2.

3.2.2. Automated Wet-Dry Sampler

The rainwater samples were collected by an automated wet-dry sampler (Model US-330, Ogasawara Keiki Seisakusho, Tokyo, Japan), which collects only rainwater with no interference from dust fall. All rainwater samples were stored in an internal refrigerator at 4°C by the automated sampler immediately after a rain event. The rainwater samples were collected from the field sites within 24 hours after each rain event. After collection, rainwater samples were filtered with pre-cleaned (heated at 450°C for 24 h) Whatman GF/F filters (0.7 m, 47mm i.d.). The actual volume of each sample collected was measured and recorded after filtration. Before and after filtration, GF/F filters were conditioned in a dry box (maintained at 22°C and 30% RH), and then weighed to calculate the mass of suspended particles.

Table 3.2. Sampling conducted in this study

Sampling Site	Sampling Period & Type	Quantity of Sample	Objective
Atmospheric research station (NUS)	Jul. 2006 (Air sampling)	8 samples (24h sampling)	To apply the optimized ASE technique
Atmospheric research station (NUS)	Nov. 2006 ~ Dec. 2006 (Air Sampling)	14 samples (12h day/night sampling)	To investigate gas / particle partitioning process in Singapore
Atmospheric research station (NUS)	Jun. 2007 ~ May 2008 (Both air and rainwater sampling)	37 atmospheric samples (pairs of PUF (polyurethane foam) and quartz filter samples) and 32 rainwater samples	To obtain a yearly extensive dataset of atmospheric and precipitation concentrations of SVOCs
St Johns Island coastal area	Nov. 2007 ~ Dec. 2008 (Both air, SSW and SML sampling)	8 air samples, 8 SSW samples, and 8 SML samples	To conduct short-term sampling for air-sea exchange study

3.2.3. Sea Surface Water Sampler and Sea Subsurface Microlayer Collector

The SSW samples were collected at the depth of 1 m at a southern coastal area of Singapore with a 2-L glass amber bottle inserted in a stainless-steel sampling device. The SML samples (approximately 1 L) were collected simultaneously using the glass plate technique (Harvey and Burzell, 1972) and stored in an amber glass container. Eight samples were collected for SSW and SML, respectively. After collection, all sea water samples were filtered with pre-cleaned (heated at 450 ^{o}C for 24 h) Whatman GF/F filters (0.7 m, 47mm i.d.). The actual volume of each sample and mass of suspended particles were measured for rainwater samples.

3.2.4. Weather Station in National University of Singapore

The relevant meteorological parameters (air temperature, total rainfall, solar incoming radiation, wind speed, etc.) were obtained from an automated NUS weather station located in the same building where the atmospheric station is housed. This meteorological station has been in operation to provide real-time meteorological data to the NUS community. Ambient temperature, wind speed, incoming solar radiation and rainfall were measured by CS 500 T sensor (Vaisala, Helsinki, Finland), cup anemometer 03001 (R.M.Young, Michigan, USA), LI-200X pyranometer (LI-COR, Nebraska, USA) and CS700 rainguage (Hydrological Services, Sydney, Australia) by mm of rainfall per 5 min, respectively.

3.3. Materials

3.3.1. Reagents

All solvents used for this study were of pesticide grade: n-hexane (HEX), acetone (ACE), dichloromethane (DCM) and methanol (METH) (Tedia, USA). The standard mixture USEPA 610 including 16 priority PAHs (naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (B(a)A), chrysene (Chry), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), benzo[a]pyrene (B(a)P), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DB(ah)A) and benzo[ghi]perylene (B(ghi)P)), in methanol: methylene chloride and the standard mixture of OCPs (α-,β -, γ- and δ-HCH and p, p'-DDD, p, p'-DDE and p, p'-DDT) included in Kit 608-S were purchased from Supelco (USA); standard for PCBs (C-QME-01, 41 congeners) was obtained from AccuStandard (New Haven, USA). Surrogate standards were used as follows: anthracene-d10, fluoranthene-d10 and benzo[e]pyrene-d12 (Sigma-Aldrich, St. Louis, MO, USA) for PAHs; 13C12-PCB 8 and 13C6-Hexachlorobenzene (Cambridge Isotope Laboratories, MA, USA) for OCPs; 13C12-PCBs congeners CB 77, 101, 141, 178 (Cambridge Isotope Laboratories, MA, USA) for PCBs. In addition, internal standards were applied as below: phenanthrene-d10, pyrene-d10 and benzo[a]pyrene-d12 (Sigma-Aldrich, St. Louis, MO, USA) for PAHs; 13C6-Tetrachlorobenzene and 13C12-4,4 DDT (Cambridge Isotope Laboratories, MA, USA) for OCPs; and 13C12- PCBs congeners CB 8 and 206 (Cambridge Isotope Laboratories, MA, USA) for PCBs.

Silica gel and florisil, obtained from Merck (Germany) and used for the column pretreatment of organic samples, were heated at 600°C for 24 h to remove any organic contamination.

3.3.2. Spiked standards

For the preliminary study of ASE optimization, the standard samples were prepared by spiking 20 μL of USEPA 610 PAH mixture (2~20mg L^{-1}), 20 μL of OCPs standard stock solution (500 g L^{-1}) and 20 μL of PCBs standard stock solution (400 g L^{-1}) for recovery evaluation on pre-baked quartz filters and pre-cleaned PUF plugs respectively, wrapped by pre-cleaned aluminum foils, and then followed by approximately 4h drying in a clean hood prior to extraction.

3.4. Sample Preparation and Analysis

A variety of instruments were used for sample preparation and laboratory analysis (Table 3.3).

3.4.1. Accelerated Solvent Extraction (ASE)

For preliminary optimization study, all extractions were conducted using quartz filters and PUF plugs spiked with standards together in 33-ml stainless-steel cells by Dionex (ASE 200). Extractions were performed with 40 ml of solvent at 100 atm pressure by one static cycle. The vessels were rinsed with 10 ml of the same solvent, and the extracted analytes were purged from the sample cells using pressurized nitrogen at 100atm. Varying the pressure in this range did not affect the results significantly (Li et al., 1998a; Saim et al., 1998).

Table 3.3. Summary of instrumentation for sample preparation and laboratory analysis

Instrumentation	Purpose
Accelerated Solvent Extractor (ASE)	To extract both atmospheric particle and gas samples under optimized extraction conditions
Liquid Liquid Extraction (Separatory Funnel)	To extract SVOCs from water samples (rainwater, SSW and SML samples)
Rotary Evaporator	To reduce the volume of organic solvent extracts
Soxhlet Extractor (SE)	To extract the samples spiked with known concentrations of SVOCs standards to investigate the recoveries
Microwave Assisted Extractor (MAE)	To extract the samples spiked with known concentrations of SVOCs standards to investigate the recoveries
Gas Chromatograph-Mass Spectrometer (GC-MS)	To determine the amount of SVOCs in air, rainwater and seawater samples
CHNS/O Analyzer	To determine the amount of carbonaceous particles in ambient particulate samples (elemental and organic carbon)

In the optimization study, the effects of the following parameters on the ASE efficiency were investigated and optimized: the combination of extraction solvents, extraction temperature, and static extraction time. To optimize the extraction solvents, three solvents (DCM, HEX, and METH) and two solvent mixtures (1:1 mixture of HEX and METH, 3:1 mixture of HEX and ACE) were compared for their efficiencies in extracting SVOCs (PAHs, OCPs and PCBs) from the spiked samples. The static ASE extraction was conducted at 100^{o}C for 10 minutes. All extractions were conducted in triplicates. After the selection of the most appropriate solvent for the best extraction, extraction temperature and duration were evaluated by conducting extractions of the prepared samples at 60, 80, 100, 120^{o}C for 10 min and 5, 10, 20, 30, 45, and 60 min at the optimum temperature, respectively.

Based on the outcome of the preliminary experiments described above, the real-world atmospheric samples in PUFs and quartz filters plus filters for water samples were extracted separately under the optimum conditions by two static cycles in order to measure the target compounds.

3.4.2. Liquid-Liquid Extraction (LLE)

All water samples were extracted within the same collection day via liquid-liquid extraction using 3 × 50 ml DCM aliquots in a two liter separatory funnel (EPA method 351^{o}C). The samples were shaken for 10 min and allowed to settle for a further 10 min before the water phase was transferred back to the sample container; and the organic phase was collected in a 500-ml round-bottom flask.

3.4.3. Rotary Evaporator

All extracted analytes were concentrated to 3 ml by rotary evaporator (Inlabo, Italy) and further cleaned using silica gel (for PAHs) or florisil (for OCPs and PCBs) columns. All extracts were finally blown by gentle nitrogen stream and reduced to 50 µL with internal standards for PAHs and organo-chlorine compounds, respectively, and kept in sealed vials at -20^{o}C prior to GC-MS analysis.

3.4.4. Soxhlet Extractor (SE)

In the preliminary optimization study, Soxhlet extraction, as a conventional extraction technique, was used to extract those samples spiked with SVOC standards to investigate the recovery comparison with ASE. The standard-spiked samples were placed in Soxhlet extraction thimbles (Scheider & Schuell GmbH, Dassel, Germany), and extracted with 200 ml n-hexane/acetone (1:1, v/v) for both PUF and filter sample for 8 h in a Soxhlet extractor (4-5 cycles/h), respectively.

3.4.5. Microwave Assisted Extractor (MAE)

A closed vessel microwave digestion system (MLS-1200 mega, Mileston s.r.l, Italy) was used for the extraction of the standard-spiked PUF and filter samples separately to investigate the recovery comparison with ASE as well. The procedure used requires 40 ml mixture of acetone:n-hexane (1:1) for extraction of PAHs at 150 W of microwave energy for 20 min extraction time. The solvents have to be changed manually after each extraction if one more extraction cycle is necessary.

3.4.6. Gas Chromatograph-Mass Spectrometer (GC-MS)

The analysis of target compounds (SVOCs) was performed using a QP2010 GC-MS equipped with a Shimadzu AOC-5000 auto injector and a DB-5 fused silica capillary column (30 m length and 0.25mm I.D; film thickness 0.25 m) with purified helium as carrier gas. Four microlitre sample was injected into the GC-MS in splitless mode with a sampling time of 1.5 min using high-pressure injection mode (pressure 2.47 atm maintained for 2.0 min, initial column flow 3.17 ml min^{-1}), as recommended in the GC-MS manual (Shimadzu). PAHs, OCPs and PCBs standards as well as extracted samples were measured separately in selective ion monitoring mode (SIM) with a detector voltage 700 V. The most abundant ions were selected for quantification. One to four reference ions were used for confirmation of each analyte in SIM mode. Table 3.4 shows the GC temperature program and MS monitoring ions for all target compounds.

3.4.7. CHNS/O Analyzer

Organic carbon (OC) and elemental carbon (EC) were determined by using a laboratory two-step thermal procedure (Zappoli et al., 1999). Carbon contents were obtained by means of the CHNS/O analyzer (2400 series II, Perkin-Elmer Life and Analytical Sciences Inc.), which was operated in CHN mode with acetanilide (71.09% C, 6.71% H, 10.36% N) as a calibration standard and with helium plus 8% oxygen as carrier gas. When the combustion furnace temperature was set at 450°C, the content of OC in a sample aliquot put in a combustion boat could be determined directly. When the combustion temperature was set as high as 950°C, the total of OC and EC was determined. Prior to analysis, carbonates were removed by adding diluted HCl. EC content was then obtained by subtracting OC from the total of OC and EC. The fraction of organic matter (OM) phase on TSP, f_{OM}, was in general obtained by multiplication of the fraction of OC on TSP with factor 1.5 for urban aerosols (Dachs and Eisenreich, 2000; Turpin et al., 2000; Turpin and Lim, 2001).

Table 3.4. GC temperature programs and MS monitoring ions for analysis of SVOCs

	Compounds	Monitoring ions	GC Temperature
PAHs	Naphthalene (Naph)	128[a]	70℃ for 2 min 15℃/min to 200℃ for 4 min 5℃/min to 300℃ for 5 min
	Acenaphthene (Ace)	152[a]	
	Acenaphtylene (Acy)	154[a]	
	Fluorene (Flu)	166[a]	
	Phenanthrene (Phe)	178[a]	
	Anthracene (Ant)	178[a]	
	Fluoranthene (Flt)	202[a]	
	Pyrene (Pyr)	202[a]	
	Benzo[a]anthracene (B(a)A)	228[a]	
	Chrysene (Chr)	228[a]	
	Benzo[b]fluoranthene (B(b)F)	252[a]	
	Benzo[k]fluoranthene (B(k)F)	252[a]	
	Benzo[a]pyrene (B(a)P)	252[a]	
	Indeno[1,2,3-cd]pyrene (Ind)	276[a]	
	Dibenzo[a,h]anthracene (DB(ah)A)	278[a]	
	Benzo[ghi]perylene (B(ghi)P)	278[a]	
OCPs	α-BHC, β-BHC, γ-BHC, δ-BHC	219[a],183,181,217	4°C/min from 125°C to 300°C
	4,4’-DDE	246[a],248	
	4,4’-DDD, 4,4’-DDT	235[a],237	
PCBs	PCB 17+18, 28+31,33	256[a],258	160°C for 10 min 3°C/min to 250°C 8°C/min to 300°C
	PCB 44,49,52,70+95,74	292[a],290	
	PCB 87,99,101,110,110,118	326[a],328	
	PCB 128,149,151,132+153,156,169 183,138+158	360[a],362	
	PCB 170,171,177,180,187,191	394[a],396	
	PCB 194,195,199,205	430[a],428	
	PCB 208	464[a],394	
	PCB 209	498[a],428	

a. Target ions

Chapter 4. Optimization of Accelerated Solvent Extraction (ASE)

4.1. Introduction

The quantification of SVOCs in atmosphere can be achieved through several established methods (Hawthorne et al., 1989; Chee et al., 1997a; Lenicek et al., 2000; Yeo et al., 2003a; Christensen et al., 2005). The USEPA method 3542 (Soxhlet extraction) has been used to extract semi-volatile organic pollutants from air samples such as filters, XAD-2® resin or polyurethane foam (PUF). Sonication is also one of the extraction methods mostly used to prepare air samples for determination of SVOCs. All these traditional procedures require large volumes of solvents, long extraction time and intensive labor due to little or no automation. In order to achieve faster extraction and reduction of solvent volume, some modern extraction techniques such as supercritical fluid extraction (SFE) and microwave-assisted extraction (MAE) have been developed for extraction of SVOCs from various environmental samples (Yang et al., 2003; Cortazar et al., 2005; Sun and Li, 2005). A recent advance in trace environmental analysis is the use of the accelerated solvent extraction (ASE) method, which represents an exceptionally effective extraction technique compared to alternative methods mentioned above such as SE and UAE (Fisher et al., 1997; Shen and Shao, 2005; Sporring et al., 2005; García et al., 2008). This extraction process takes advantage of the increased analyte solubility at temperatures well above the boiling points of common solvents. In addition, the kinetic processes involved for analytes to desorb from the matrix are accelerated, and automated extractions can be carried out. However, despite its significant advantages compared to traditional extraction methods, the effectiveness of ASE has not been sufficiently demonstrated for the extraction of SVOCs from ambient air samples.

In this work, the feasibility of using ASE to extract different groups of SVOCs collected onto quartz filters and PUF plugs was studied. Different parameters affecting the extraction efficiency such as combination of extraction solvents, extraction temperature, and static extraction time were investigated and optimized. The performance of this optimized method, in terms of recovery on PUF and filter samples, was evaluated and compared with that of SE and MAE. Following optimization, a quality assured ASE method was developed and used for the extraction of SVOCs in ambient air samples collected in Singapore. The concentrations of SVOCs in air samples were quantified using GC-MS to demonstrate the practical applications of the ASE method.

4.2. Experimental

4.2.1. Extraction

The ASE method has been optimized in this study as stated in Section 3.4.1. For SE and MAE, the extraction parameters were selected based on previous successful investigations published in the literature (Sporring et al., 2005; Karthikeyan et al., 2006) and conducted as described in Sections 3.4.4 and 3.4.5.

4.2.2. Sampling

For the application of optimized ASE method, short-term field sampling was carried out. Particulate and gaseous air samples were collected using a hi-volume sampler

(Model: TE-1000PUF, Tisch Environmental, Inc., USA) at the atmospheric research station in National University of Singapore for 24 h duration in July 2006. Total suspended particles were collected by a quartz filter of 4'' diameter loaded onto the filter holder followed by an adsorbent cartridge filled with 3 pieces of one-inch PUF plugs in series (each plug of 65 mm diameter and 25 mm length).

4.2.3. Sample Preparation and Analysis

The standard-spiked samples were prepared by the protocols in Section 3.3.2, extracted by ASE, SE or MAE, followed by evaporation, purged by gentle nitrogen stream till 50 μl.

Real-world samples were extracted by the optimum ASE conditions for two cycles and evaporated by rotary evaporator to 3 ~ 5 ml. The concentrated ASE extracts of air samples showed yellow and sticky. As such, it was necessary to clean up the extracts before proceeding further.

PAHs. One portion of the concentrated extract was cleaned up with a chromatographic column (30cm × 10 mm I.D) containing 5 g of silica gel topped with 2 cm of anhydrous sodium sulfate. The column was pre-eluted with 2 × 15 ml of hexane and the eluate was kept just prior to exposure of the sodium sulfate layer to the air. After the sample was transferred onto the column, the silica gel column was first eluted with 25 ml of hexane, and followed by 30 ml of hexane-dichloromethane (3:2, v/v). The first fraction was discarded, and the second contained PAHs.

OCPs and PCBs. A chromatographic column (30 cm×10 mm I.D.) containing 5 g of florisil topped with 2 cm of anhydrous sodium sulfate was washed with 2 × 15 ml of hexane and the eluate was also kept just prior to exposure of the sodium sulfate layer to the air. The other portion of the concentrated extract was then transferred onto the column and eluted with 150 ml hexane-acetone (9:1, v/v).

The extract in each fraction was concentrated to approximately 3 ml at room temperature and further to 50 μl by nitrogen gas stream. Internal standards were added into both standard-spiked and real world sample extracts as described in Section 3.3.1. All extracts were then kept in sealed vials at -20°C prior to analysis. Sample analysis was conducted using a GC-MS (Shimadzu QP2010, Japan), as described in Section 3.4.6.

4.2.4. Quality Control

The analytical quality of the data obtained was determined using limit of detection (LOD), recovery, linearity, and by checking sampling artifacts, etc. During each set of extractions, the field blanks (filter and PUF plugs) were included and the mean blank value was subtracted from the measured levels. Little or no PCBs congeners were detected while trace amount of OCPs was detected in the blanks. Limits of detection (LOD) were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks**.** LODs for SVOCs ranged from 0.05 ± 0.08 to 2.17 ± 0.95 pg m^{-3}.

The reliability of the entire analytical procedure for each sample was evaluated by using surrogate standards. The procedural recoveries of surrogates ranged from 86.7 ± 6.8% (anthracene-d_{10}) to 107.2 ± 6.9% (^{13}C12-PCB141). The linearity of calibration standards was calculated by regression analysis with values ranging from 0.99–1.00 (r^2) for SVOCs. Breakthrough was evaluated under field conditions by connecting three one-inch plugs in series and analyzing them separately. For 24 hr samples, measured SVOCs at the third plug were in the range of blank values. Three one-inch plugs in series used in hi-volume PUF sampler therefore could trap gas-phase target compounds effectively. Control calibration standards spiked with internal standards were measured regularly to check instrument performance during analysis.

4.3. Results and Discussion

4.3.1. Optimization of ASE

A single recovery value is given for each of the four target SVOC compound group (PAHs, HCHs, DDXs, and PCBs). The recovery data discussed as below is based on the average of individual compound recomveries within the same group.

4.3.1.1 Extraction Solvent

Results obtained from the extractions using HEX/METH (1:1), DCM, HEX, HEX/ACE (3:1), and METH are illustrated in Figure 4.1. All of the extractions were performed at 100℃ for 10 min by using one static cycle. The standard deviation values show the reproducibility of the extraction method used. Among the solvent or solvent mixtures studied, the best yield was obtained using a mixture of 3:1 n-hexane and acetone in the range of 81-92% for all SVOCs while those of n-hexane/methanol (1:1), dichloromethane, n-hexane yielded recoveries of 52-83%, 62-81% and 53-88%, respectively. When the methanol alone was used, the recovery was even worse, with a range as low as 32% to a relatively high value of 72%. It has been reported that a combination of different solvent mixtures tends to improve the solvation of the analytes of interest and thus improve overall efficiency of extraction (Hawthorne et al., 2000; Karthikeyan et al., 2006). In addition, the overall low standard deviations obtained for a 3:1 mixture of HEX and ACE solvents are indicative of good reproducibility of experimental data. Based on the results obtained, the mixture of HEX/ACE (3:1) was therefore chosen as the extraction solvents in all subsequent studies.

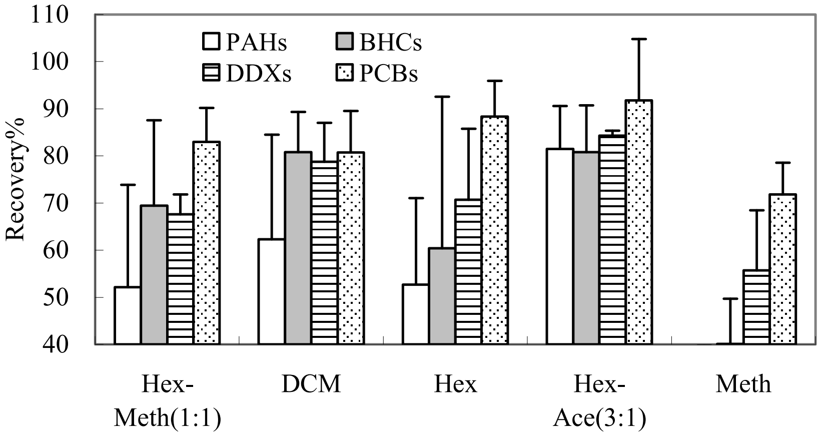


Figure 4.1. Effect of solvent on ASE of SVOCs (PAHs, OCPs and PCBs). OCPs including HCHs, DDTs (recovery data for combined filter and PUF samples)

4.3.1.2 Extraction Temperature

Temperature is one of the most important parameters that affect ASE efficiency. Elevated temperature could increase desorption kinetics of target compounds, and also lower viscosity of solvent. Consequently the analytes could diffuse into the solvent matrix more easily (Hubert et al., 2000). ASE methods generally use temperatures between 60 and 180°C. According to previous reports, the extraction of SVOCs depends on both the level of total pollution and the degree of matrix complexity (Hawthorne et al., 2000; Hubert et al., 2000; Karthikeyan et al., 2006). The compositions of the filters and PUF plugs are significantly different from other matrices such as soil, plants and fishes, etc. It was therefore necessary to determine the response of temperature to extraction efficiency. Figure 4.2 shows the extraction efficiency carried out in the temperature range between 60 and 120°C in 20°C steps using 3:1 HEX/ACE as solvent for 10 min by one static cycle. The highest extraction yields were achieved at 100°C for two groups of pollutants (PAHs and HCHs). For all other compounds, the highest yields were attained at 120°C. The lower extraction efficiency observed at all other temperatures for different groups of compounds can be attributed to the adhesion or fusion of organic matrix containing pollutant fractions (Tao et al., 2002). Within the range of temperatures evaluated, the optimum appears to be somewhere between 100°C and 120°C. PUF is known to decompose around 180°C, and it was found that a high extraction temperature would lead to a relatively high weight loss of PUF of above 7%. After decreasing the extraction temperature to around 100°C, the weight loss could be minimized to 2% which is comparable to that encountered upon soaking PUF in hexane (Braun et al., 1986; Wurl and Obbard, 2005a). Based on the results obtained, the temperature was fixed at 100°C as the optimum for ASE extraction of SVOCs.

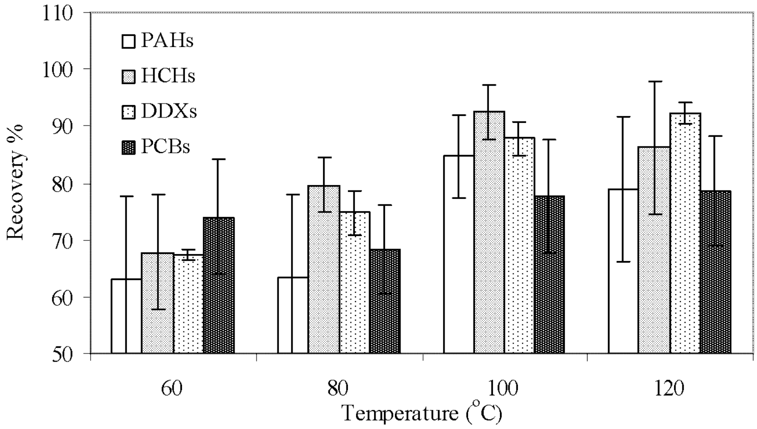


Figure 4.2. Extraction temperature effect on the recoveries of POPs using a 3:1 HEX/ACE as solvent (recovery data for combined filter and PUF samples)

4.3.1.3 Static Extraction Time

Extraction time is the time needed for SVOCs to desorb and dissolve most efficiently from the sample matrix into extraction solvents. In order to determine the optimum extraction time for satisfactory recovery, ASE was performed at 100°C in 40 ml of solvent mixture for 5, 10, 20, 30, 45 and 60 min, respectively. Table 4.1 shows that the recovery reached a maximum between 20 and 30 min. For the time in excess of 30 min, it can be seen that the extraction yield decreased with increasing extraction time, which could be caused by a thermal degradation or the fusion of organic material within the matrix so that the pollutants become too stubborn to be extracted (Tao et al., 2002; PiiTeiro-Iglesias et al., 2004). It was therefore decided to use 25 min as static extraction time in all subsequent studies.

In summary, the optimum ASE extraction conditions were achieved using a 3:1 HEX/ACE combination at 100°C for 25 min.

4.3.2. Recovery Evaluation

Previously, both filters and PUF plugs spiked with standards were extracted and analyzed together. In order to determine whether the above ASE optimized conditions were suitable for filter as well as PUF samples, the ASE extractions were applied by two static cycles to standard-spiked filter/PUF samples, respectively, as described above. All recoveries of SVOCs by ASE are shown in Table 4.2.

With a single extraction step, it can be seen that the recoveries of PAHs, OCPs and PCBs from filters were in the range of 69.2 ~ 93.9%, 71.1~96.9% and 67.6~108.5%, respectively. The recoveries of those from PUF plugs were in the range of 67.8 ~ 92.2%,

Table 4.1. Extraction efficiencies (recovery %) depending on extraction time (recovery data for combined filter and PUF samples)

	Extraction time (min)					
Recovery(SD) (%) Compounds	5	10	20	30	45	60
PAHs	70.1(27.0)	82.3(51.3)	97.7(21.6)	107.0(13.3)	86.7(18.9)	75.0(11.9)
HCHs	74.5(5.8)	74.3(1.9)	90.6(13.1)	84.5(12.6)	75.3(14.5)	59.8(6.1)
DDTs	82.6(6.1)	82.0(8.2)	96.8(5.0)	92.6(8.0)	89.4(5.8)	93.9(12.1)
PCBs	85.2(4.8)	88.2(13.4)	97.8(18.1)	98.8(16.6)	91.9(14.8)	90.4(17.2)

Table 4.2. The recovery (average of duplicates) of POPs by separate analysis of filter/PUF samples spiked with standards

	ASE-Recovery % (Mean ± S.D)					ASE-Recovery % (Mean ± S.D)			
Compounds	1^{st} cycle		1^{st} + 2^{nd} cycle		Compounds	1^{st} cycle		1^{st} + 2^{nd} cycle	
	Filter	PUF	Filter	PUF		Filter	PUF	Filter	PUF
Naph	77.6 ± 13.5	67.8 ± 10.8	90.4 ± 8.6	88.7 ± 6.1	PCB 52	80.5 ± 24.5	62.1 ± 16.0	95.2 ± 12.5	95.3 ± 14.3
Ace	69.2 ± 10.6	74.1 ± 10.6	93.4 ± 12.8	90.1 ± 9.4	PCB 70 + 95	75.8 ± 19.9	63.6 ± 3.1	94.7 ± 10.7	85.2 ± 4.8
Acy	89.4 ± 5.5	92.2 ± 2.9	95.5 ± 6.3	102.8 ± 9.5	PCB 74	78.2 ± 12.6	70.5 ± 1.9	90.8 ± 8.9	91.5 ± 6.9
Flu	93.9 ± 4.2	91.0 ± 0.5	97.3 ± 6.5	93.2 ± 2.3	PCB 87	87.6 ± 12.6	73.9 ± 4.3	96.3 ± 8.6	92.7 ± 8.1
Phe	92.7 ± 4.2	89.3 ± 2.6	95.4 ± 3.8	93.8 ± 5.3	PCB 99	75.7 ± 17.7	68.8 ± 12.3	94.6 ± 12.3	86.6 ± 9.3
Ant	88.3 ± 3.5	84.5 ± 0.1	95.3 ± 5.3	93.7 ± 5.2	PCB 101	86.2 ± 11.8	83.0 ± 15.6	98.9 ± 9.7	96.2 ± 11.3
Flt	92.3 ± 5.2	86.7 ± 4.7	98.4 ± 7.1	97.6 ± 5.6	PCB 110	80.9 ± 10.8	73.7 ± 8.1	95.2 ± 6.5	91.6 ± 6.9
Pyr	86.0 ± 2.6	83.2 ± 0.7	93.7 ± 5.6	96.3 ± 7.1	PCB 118	85.3 ± 13.7	77.0 ± 10.6	93.4 ± 7.8	90.8 ± 11.3
B(a)A	86.9 ± 4.7	87.2 ± 0.5	98.8 ± 6.8	94.6 ± 5.2	PCB 128	77.6 ± 13.5	67.8 ± 10.8	90.4 ± 8.6	88.7 ± 8.1
Chr	87.4 ± 3.6	85.5 ± 0.3	94.7 ± 6.3	93.4 ± 4.3	PCB 149	67.6 ± 10.6	64.1 ± 10.6	93.4 ± 12.8	90.1 ± 9.4
B(b)F	86.8 ± 5.7	82.7 ± 2.6	98.6 ± 5.6	92.5 ± 4.4	PCB 151	89.4 ± 5.5	92.2 ± 2.9	95.5 ± 6.3	102.8 ± 9.5
B(k)F	85.0 ± 3.7	84.1 ± 2.2	94.9 ± 8.2	95.6 ± 5.3	PCB 132 + 153	93.9 ± 4.2	91.0 ± 0.5	97.3 ± 6.5	93.2 ± 2.3
B(a)P	83.5 ± 2.8	84.0 ± 1.8	95.6 ± 6.5	91.3 ± 4.2	PCB 138 + 158	92.7 ± 4.2	89.3 ± 2.6	95.4 ± 3.8	93.8 ± 5.3
Ind	86.0 ± 5.4	82.3 ± 2.4	95.3 ± 6.7	91.2 ± 4.6	PCB 156	88.3 ± 3.5	84.5 ± 0.1	95.3 ± 5.3	93.7 ± 5.2
DB(ah)A	90.3 ± 2.8	87.4 ± 3.0	96.1 ± 7.3	94.6 ± 5.0	PCB 169	92.3 ± 5.2	86.7 ± 4.7	98.4 ± 7.1	97.6 ± 5.6
B(ghi)P	90.2 ± 3.6	81.5 ± 8.3	98.4 ± 6.9	95.5 ± 8.4	PCB 170	86.0 ± 2.6	83.2 ± 0.7	93.7 ± 5.6	96.3 ± 7.1
α-HCH	90.2 ± 7.6	90.6 ± 14.7	92.2 ± 4.1	96.6 ± 6.8	PCB 171	86.9 ± 4.7	87.2 ± 0.5	98.8 ± 6.8	94.6 ± 5.2
β-HCH	89.7 ± 7.8	78.5 ± 18.9	101.3 ± 9.7	94.1 ± 4.5	PCB 177	87.4 ± 3.6	85.5 ± 0.3	94.7 ± 6.3	93.4 ± 4.3
γ-HCH	81.7 ± 7.6	93.1 ± 2.5	93.5 ± 5.9	104.3 ± 8.9	PCB 180	86.8 ± 5.7	82.7 ± 2.6	98.6 ± 5.6	87.5 ± 4.4
δ-HCH	86.7 ± 19.2	73.0 ± 8.5	98.1 ± 9.6	89.0 ± 5.5	PCB 183	85.0 ± 3.7	84.1 ± 2.2	94.9 ± 8.2	95.6 ± 5.3
p, p'-DDE	71.1 ± 4.1	85.4 ± 10.6	93.1 ± 7.3	97.7 ± 8.1	PCB 187	83.5 ± 2.8	84.0 ± 1.8	95.6 ± 6.5	91.3 ± 4.2
p, p'-DDD	96.9 ± 12.5	82.1 ± 13.8	97.4 ± 12.3	98.3 ± 11.5	PCB 191	86.0 ± 5.4	82.3 ± 2.4	95.3 ± 6.7	91.2 ± 4.6
p, p'-DDT	84.3 ± 8.1	77.9 ± 18.2	93.4 ± 6.8	92.7 ± 13.7	PCB 194	90.3 ± 2.8	87.4 ± 3.0	96.1 ± 7.3	94.6 ± 5.0
PCB 17 + 18	83.0 ± 9.3	75.2 ± 3.8	96.2 ± 7.4	88.5 ± 5.4	PCB 195	90.2 ± 3.6	81.5 ± 8.3	98.4 ± 6.9	89.5 ± 6.4
PCB 28 + 31	72.5 ± 11.7	65.0 ± 4.9	87.3 ± 9.2	91.3 ± 7.6	PCB 199	95.0 ± 8.2	91.1 ± 8.7	96.2 ± 7.8	94.5 ± 7.8
PCB 33	74.4 ± 9.8	67.0 ± 8.1	93.6 ± 12.1	89.3 ± 5.9	PCB 205	108.5 ± 1.5	106.0 ± 0.8	110.2 ± 8.6	107.0 ± 1.2
PCB 44	89.7 ± 14.4	78.8 ± 11.5	95.6 ± 8.3	93.6 ± 5.5	PCB 208	86.0 ± 2.9	84.6 ± 2.6	94.5 ± 6.7	96.8 ± 6.5
PCB 49	85.8 ± 9.6	79.7 ± 12.3	91.7 ± 6.5	89.3 ± 9.4	PCB 209	68.0 ± 2.6	66.0 ± 2.3	91.6 ± 8.4	85.9 ± 5.2

73.0 ~ 90.6% and 62.1 ~ 106.0%, respectively. When performing an additional extraction of 25 min with the same solvent mixture, most of the recoveries of SVOCs increased substantially by up to 20% for both PUF and filter media. These types of observations regarding improvement in recovery with additional extraction cycles have been reported for other environmental matrices as well (Björklund et al., 1999; Sporring et al., 2005). Most of the recoveries resulting from two extraction cycles were in the range of AOAC (Association of Analytical Communities) interval (80–115%) (AOAC, 2002).

Reproducibility has been tested on the results after two extraction steps under univariate variance-component analysis at 5% significance level by using SPSS 13.0 for Windows (SPSS Inc., Chicago, IL, USA). All P-values are greater than 0.05, indicating that no significant difference between both repetitive samples (inter-sample) and different sampling media (filter and PUF, inter-media) was observed by applying the optimized extraction for two static cycles. Consequently, two extraction cycles were selected for both PUF and filter samples in this study.

4.3.3. Method Comparison

For the comparison of the performance of ASE with commonly used extraction methods such as SE and MAE, standard-spiked PUF and filter samples were processed separately. An overall comparison between the recoveries is shown in Figure 4.3, in which the individual bars represent the average values obtained from triplicate measurements for each target compound. All extraction techniques used the HEX/ACE solvent composition and the optimized extraction time and temperature (for SE and MAE, the optimum conditions are from the literature, see Sections 3.4.4 and 3.4.5). The recoveries of SE even after 8 h extraction were significantly lower than those of MAE (20 min) and ASE (40 min; 2 cycles x 20 min/cycle) for both PUF and filter samples, respectively. Although MAE and ASE-1 cycle achieved similar efficiencies, ASE-2 cycles gave the best recovery for all target compounds. Furthermore, good reproducibility was also obtained for ASE, which is most likely due to the automation of the whole extraction procedure.

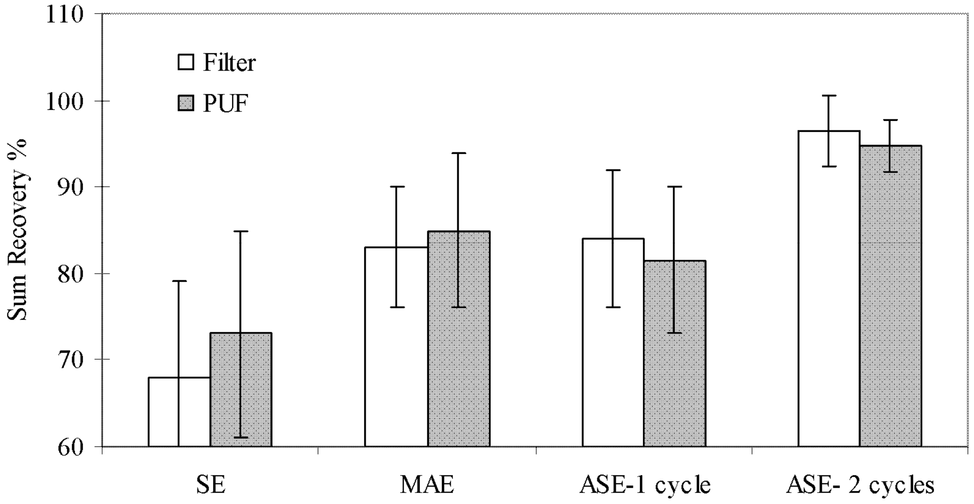


Figure 4.3. Average recovery of target compounds for different extraction techniques

4.3.4. Method Validation

NIST certified reference material SRM 1649a (urban dust-organics) was applied to evaluate ASE method for the determination of selected PAHs, OCPs and PCBs under the optimized extraction conditions. The concentrations, expressed as mass fractions, for 22 PAHs, 35 PCBs (some in combination) and 8 OCPs have been certified in SRM 1649a, of which 12 PAHs, 20 PCBs and 3 OCPs covered by our standards and separated well by the above GC-MS analysis methods were chosen for validation in this study. An accurately weighed 200 mg of SRM 1649a in duplicate was extracted by optimized ASE method, cleaned up according to the procedure as stated above and analyzed by GC-MS. As can be seen from Table 4.3, the recoveries were in the range of 82-126% for PAHs, 73-136% for OCPs and 73-121% for PCBs, respectively. For the group of PAHs, only the recoveries of Phe (119%) and Ant (126%) were out of the range of AOAC (Association of Analytical Communities) recommended interval (80–115%). In the group of OCPs, the concentration of heptachlor provided by NIST is not the certified value but reference concentration, which was in good correlation with the measured value. The measured concentration of p, p'-DDE was relatively higher than the NIST-certified value, even though the samples had been cleaned up through the chromatographic column packed with florisil. This problem might be due to some potential interference from co-eluting compounds. To the best of our knowledge, this is the first study to use SRM 1649a to validate the extraction efficiency of PCBs from air sample using ASE, the measured values of PCB congeners chosen are in good agreement with NIST-certified

Table 4.3. Analysis of NIST SRM 1649a for PAHs, OCPs and PCBs

Compounds	Measured value [1, 2] Mean ± S.D.	Certified value [2] Mean ± S.D.	% Recovery Mean ± S.D.	Compounds	Measured value Mean ± S.D.	Certified value Mean ± S.D.	% Recovery Mean ± S.D.
Phe	4.95±0.64	4.14±0.37	119±15	PCB 52	22.05±2.10	24.65±0.97	89±9
Ant	0.68±0.12	0.43±0.08	126±28	PCB 87	8.18±0.29	10.65±0.62	77±3
Flt	5.20±0.42	6.45±0.18	81±7	PCB 99	8.55±1.20	9.58±0.69	89±13
Pyr	4.59±0.30	5.29±0.25	87±6	PCB 101	40.91±3.45	52.9±1.0	77±6
B(a)A	2.22±0.16	2.21±0.07	100±7	PCB 105	8.90±0.63	8.63±0.80	103±7
Chr	2.92±0.25	3.05±0.060	96±8	PCB 110	23.74±2.47	26.6±1.6	89±9
B(b)F	6.30±0.75	6.45±0.64	98±12	PCB 118	19.52±2.89	25.7±1.5	76±11
B(k)F	1.80±0.11	1.91±0.031	94±6	PCB 128	7.68±0.97	6.35±0.69	121±15
B(a)P	2.18±0.19	2.51±0.09	87±8	PCB 149	74.60±6.54	75.7±1.3	98±9
Ind	3.29±0.38	3.18±0.72	104±12	PCB 151	42±1.81	34.3±3.9	122±5
DB(a,h)A	0.27±0.10	0.288±0.023	94±35	PCB 156	19.35±1.38	16.25±0.77	119±8
B(ghi)P	3.60±0.62	4.01±0.91	90±15	PCB 170	26.27±3.28	30.8±2.2	85±11
p, p'-DDE	54.89±4.72	40.4±1.7	136±12	PCB 180	58.90±4.13	78.70±8.2	75±5
p, p'-DDD	32.39±5.63	34.01±0.48	95±17	PCB 183	18.02±1.70	20.34±0.95	88±8
p, p'-DDT	155.34±30.29	212±15	73±14	PCB 187	36.10±1.72	40.1±2.5	90±4
Heptachlor	15.31±1.78	18.9±0.5 [c]	81±9	PCB 194	26.46±1.53	28.9±3.6	92±5
PCB 44	11.29±1.47	15.4±1.6	73±10	PCB 195	9.13±0.21	9.63±0.37	95±2
PCB 49	9.01±0.82	12.2±1.5	74±7	PCB 209	8.66±1.26	8.04±0.77	108±16

[1] Average of duplicate.

[2] The units of measured and certified value for PAHs are mg Kg^{-1} and for OCPs and PCBs are µg Kg^{-1}.

values. Generally, the concentrations determined in this study correlate well with the NIST-certified and reference concentrations for most of the target compounds in SRM 1649a, which demonstrated that the ASE method is suitable for extraction of SVOCs in air samples at trace levels.

4.3.5. Application of Optimized ASE

The optimized ASE method was applied to the collected filters and PUF plugs in a short-term sampling in July 2006 in Singapore, from which concentrations of SVOCs are discussed briefly as below.

Average total (particle and gas) PAHs concentrations ranged between 13.62 and 52.26 ng m^{-3} with an overall mean concentration of 33.54 ng m^{-3} (see Table 4.4). The concentration of gaseous PAHs varied from 11.90 to 45.74 ng m^{-3} with the mean concentration being 28.82 ng m^{-3} (i.e. 87.5% of the total concentration). The PAH concentration in particles was considerably lower and ranged from 1.93 to 7.53 ng m^{-3} with a mean value of 4.72 ng m^{-3}. The most abundant PAHs in all samples were Pyr (7.28 ng m^{-3}), Phe (7.18 ng m^{-3}), and Flt (5.56 ng m^{-3}). In general, the concentration of heavier PAHs with five or more aromatic rings (B(b)F, B(k)F, B(a)P, Ind, DB(ah)A, and B(ghi)P) was low ranging from 0.07 to 1.24 ng m^{-3}. Average concentrations of the five most abundant PAHs and B(a)P observed in Singapore are compared to those reported in other urban regions. The sum (gas + particle) of mean concentrations of Pyr, Phe, Flt, Flu, Ant, and B(a)P in Singapore were 25.81 ng m^{-3} which are higher than those measured in the suburbs of Athens (14.20 ng m^{-3}) (Mandalakis et al., 2002), while considerably higher levels of these six PAH members were determined in Guangzhou

Table 4.4. Particle and gas phase concentrations of POPs in the air of Singapore (unit: ng m^{-3} for PAHs, pg m^{-3} for OCPs and PCBs)

Compound	Particle Mean ± SD	Gas Mean ± SD	Total Mean ± SD
Naph	0.66 ± 0.31	0.79 ± 0.64	1.45 ± 0.95
Ace	0.04 ± 0.01	0.14 ± 0.06	0.18 ± 0.07
Acy	0.06 ± 0.05	0.25 ± 0.13	0.31 ± 0.18
Flu	0.05 ± 0.04	3.71 ± 0.43	3.76 ± 0.47
Phe	0.25 ± 0.16	6.93 ± 3.58	7.18 ± 3.74
Ant	0.06 ± 0.03	1.97 ± 0.22	2.03 ± 0.25
Flt	0.45 ± 0.27	5.11 ± 3.83	5.56 ± 4.10
Pyr	0.37 ± 0.22	6.91 ± 6.22	7.28 ± 6.44
B(a)A	0.17 ± 0.07	0.30 ± 0.09	0.47 ± 0.16
Chr	0.26 ± 0.22	0.62 ± 0.45	0.88 ± 0.67
B(b)F	0.62 ± 0.40	0.62 ± 0.42	1.24 ± 0.82
B(k)F	0.12 ± 0.07	0.11 ± 0.07	0.23 ± 0.14
B(a)P	0.31 ± 0.18	0.21 ± 0.13	0.52 ± 0.31
Ind	0.67 ± 0.39	0.76 ± 0.45	1.43 ± 0.44
DB(ah)A	0.06 ± 0.09	0.01 ± 0.003	0.07 ± 0.09
B(ghi)P	0.57 ± 0.29	0.38 ± 0.20	0.95 ± 0.49
Σ PAH	4.72 ± 2.80	28.82 ± 16.92	33.54 ± 19.32
α-HCH	1.38 ± 0.86	102.81 ± 16.64	104.17 ± 17.50
β-HCH	0.35 ± 0.54	22.50 ± 18.33	22.85 ± 18.87
γ-HCH	1.36 ± 1.84	84.3 ± 33.03	85.66 ± 34.87
δ-HCH	1.62 ± 0.62	25.93 ± 16.64	27.55 ± 17.26
ΣHCH	4.71 ± 2.26	235.53 ± 84.64	244.95 ± 88.50
4,4'-DDE	0.06 ± 0.08	0.51 ± 0.36	0.57 ± 0.44
4,4'-DDD	0.24 ± 0.30	1.70 ± 1.53	1.94 ± 1.83
4,4'-DDT	0.16 ± 0.14	5.01 ± 2.29	5.17 ± 2.43
ΣDDT	0.46 ± 0.52	7.22 ± 3.59	7.68 ± 4.11
PCB 17+18	0.23 ± 0.08	6.81 ± 2.65	7.04 ± 2.73
PCB 28+31	0.56 ± 0.39	4.94 ± 2.73	5.5 ± 3.12
PCB 44	0.31 ± 0.19	1.92 ± 0.98	2.23 ± 1.17
PCB 52+49	0.20 ± 0.32	2.50 ± 1.42	2.70 ± 1.74
PCB 74+70	0.15 ± 0.23	2.10 ± 0.83	2.25 ± 1.06
PCB 87	0.36 ± 0.61	1.50 ± 1.47	1.86 ± 2.08
PCB 101+99	0.18 ± 0.13	1.25 ± 0.63	1.43 ± 0.76
PCB 110	0.18 ± 0.14	0.83 ± 0.26	1.01 ± 0.40
PCB 118	0.21 ± 0.20	1.19 ± 0.52	1.4 ± 0.72
PCB 128	0.43 ± 0.41	0.82 ± 0.23	1.25 ± 0.64
PCB 132+153	0.22 ± 0.32	0.33 ± 0.41	0.55 ± 0.73
PCB 138+158	0.60 ± 0.49	0.82 ± 0.95	1.42 ± 1.44
PCB 149	0.13 ± 0.14	0.31 ± 0.24	0.44 ± 0.38
PCB 151	0.17 ± 0.10	0.28 ± 0.44	0.45 ± 0.54
PCB 156	0.40 ± 0.15	0.82 ± 0.67	1.22 ± 0.82
PCB 169	0.28 ± 0.09	0.46 ± 0.14	0.74 ± 0.23
ΣPCB	4.61 ± 3.99	26.88 ± 14.58	31.49 ± 18.56

(76.07 ng m^{-3}) (Bi et al., 2003), Hong Kong (71.79 ng m^{-3}) (Lee et al., 2001), and Chicago (171.90 ng m^{-3}) (Simcik et al., 1998).

The concentration levels of ∑HCHs in particulate and gaseous phases were in the range of 2.45~6.97 pg m^{-3} and 150.89~320.17 pg m^{-3}, respectively. Those of ∑DDTs in particulate and gaseous phases were 0.46 ± 0.50 pg m^{-3} and 7.22 ± 3.59 pg m^{-3}, respectively. It can be seen that, in general, the gaseous phase OCPs were dominant over those in the particulate phase. Mean total concentrations of HCHs were: α-HCH = 104.17 ± 17.50 pg m^{-3}; β-HCH = 22.50 ± 18.87 pg m^{-3}; γ-HCH = 85.66 ± 34.87 pg m^{-3}; δ-HCH = 27.55 ± 17.26 pg m^{-3}. During the sampling period, p, p'-DDT, p, p'-DDE, and p, p'-DDD were detected with total concentrations of 0.57 ± 0.44 pg m^{-3}, 1.94 ± 1.83 pg m^{-3}, and 5.17 ± 2.43pg m^{-3}, respectively. These concentrations were almost comparable to the recent data obtained in the Indian Ocean (2.5 ~ 33.2, mean 10.4 pg m^{-3}) (Wurl et al., 2006d), and the coast of Singapore (3.6 ± 0.3 ~ 11.3 ± 1.3 pg m^{-3}).

The mean concentrations of detectable PCB congeners measured during the sampling period were 28.0 ± 15.1 pg m^{-3} in the gas phase and 6.1 ± 4.6 pg m^{-3} in the particle phase, respectively. About 80% (mean) of total PCBs(particle + gas) was distributed in the gas phase, which is in good agreement with the trend reported in previous studies (Bidleman, 1988; Duinker and Bruchertall, 1989; Yeo et al., 2003a) , while the total concentration of PCBs (34.1 ± 19.7 pg m-3) was lower than those reported in other urban areas such as Seoul (Korea), Athens (Greece), Houston (USA), Birmingham (UK) (Park et al., 2001; Mandalakis et al., 2002; Harrad and Mao, 2004; Yeo et al., 2004).

4.4. Conclusion

The prevalence and toxicity of SVOCs present the environment justifies the need to establish their content in atmosphere. An ASE method has been developed for the determination of SVOCs in both atmospheric particulate and gaseous phases. The best extraction solvent used in this study for the ASE is the mixture of HEX/ACE (3:1). The effective extractions should be performed at 100℃ for 25 min. The entire analytical procedure developed in this study proves to be reliable as evident from the analysis of specific surrogate standards with the good recoveries. As compared to SE and MAE, it shows advantages in terms of high efficiency and reproducibility. The optimized method was validated using NIST certified SRM 1649a, of which the results showed good agreement with certified values. The application of the new extraction method was demonstrated by analyzing a set of air samples and the results obtained were compared to the values reported from surrounding areas. Based on our results, the proposed ASE technique appears to be a promising alternative to commonly used extraction techniques, especially when applied to the investigation of a number of air samples due to its complete software-controlled automation.

Chapter 5. Levels, Temporal, and Seasonal Trends of Semi-Volatile Organic Contaminants In Ambient Air and Rainwater In Singapore

5.1. Introduction

Atmospheric semivolatile organic compounds (SVOCs) impact human health, visibility and climate. Temporal, or seasonal trend in atmospheric concentrations are useful for identifying changes in their emission sources and in assessing progress toward regulatory requirements (Yang et al., 2008). The tropical climatic zone is characterized by high ambient temperatures and heavy rainfall, which may probably influence the occurrence and distribution of SVOCs in the environment. According to their physical and chemical characteristics, these substances are either present in the gaseous phase and/or bound to particles (de Souza Pereira et al., 2007) and the removal of these pollutants from the atmosphere and subsequent transfer to other compartments is largely driven by deposition mechanisms (McLachlan, 1997). For instance, wet deposition, an important process, scavenges SVOCs from the atmosphere to the ocean, the magnitude of which is related to the intensity of precipitation and its seasonal variations (Wania et al., 1998).

The objective of this study was to study the concentration and distribution of PAHs, OCPs and PCBs in this coastal marine environment of Singapore under different weather conditions. A 12-month field measurement was carried out in Singapore for selected SVOCs, in both gas/particulate phases and rainwater. The influence of meteorological factors such as air temperature, wind speed, and incoming solar radiation on the occurrence and distribution of local atmospheric SVOCs was examined. In addition, seasonal variation and possible sources of SVOCs were investigated based on air mass backward trajectory analysis, molecular diagnostic ratios and principal component analysis.

5.2. Experimental

5.2.1. Sampling

Atmospheric gaseous, particulate, and precipitation samples were collected simultaneously at the National University of Singapore (NUS) atmospheric research station (1°18'N and 103°46'E). Altogether 37 atmospheric samples (pairs of PUF (polyurethane foam) and quartz filter samples) and 32 rainwater samples were collected and studied under different weather conditions between June 2007 and May 2008 in the tropical environment.

Particulate and gaseous PAHs, OCPs, and PCBs in the atmosphere were collected separately using a high volume sampler (Model: TE-1000PUF, Tisch Environmental, Inc. USA) by drawing air through 4" circular quartz microfiber filters (Whatman, Tisch Environmental, Inc. USA) and polyurethane foam plugs (PUF, TE-1012, Tisch Environmental, Inc. USA) in series at ca.250 L min^{-1} on an event basis for 48 h every week, namely, three to four samples were collected every month. The rainwater samples were collected by an automated wet-dry sampler (Model US-330, Ogasawara Keiki

Seisakusho, Tokyo, Japan), which collects only rainwater with no interference from dust fall. The relevant meteorological parameters (air temperature, total rainfall, etc.) were obtained from an automated NUS weather station located in the same building where the atmospheric station is housed. Monthly meteorological data and TSP concentrations during this sampling period were recorded and are summarized in Table 5.1.

5.2.2. Sample Preparation and Analysis

Prior to extraction, surrogate compounds were added to all samples. Water filters, aerosol filters and PUF samples were extracted separately by Dionex ASE 200 under the following conditions: 3:1 n-hexane and acetone (HEX and ACE) combination at 100^{o}C for 25 min as described in Section 3.4.1 for two cycles. All filtered water samples were extracted on the same day as collection via liquid-liquid extraction using 3 × 50 ml DCM aliquots in a two liter separatory funnel (EPA method 3510C), as described in Section 3.4.2. All extracted analytes were concentrated to 3 ml by rotary evaporator and further cleaned using silica gel (for PAHs) or florisil (for OCPs and PCBs) columns, as described in Section 4.2.3. All extracts were finally blown by gentle nitrogen stream and reduced to 50 μL with internal standards and kept in sealed vials at -20^{o}C prior to analysis. Sample analysis was conducted using a GC-MS (Shimadzu QP2010, Japan), as described in Section 3.4.6.

Table 5.1. Meteorological conditions during June 2007 ~ May 2008 at NUS atmospheric station

Sampling Period	TSP ($\mu g\ m^{-3}$)	Temperature (Temp) (^oC)	Relative Humidity (RH) (%)	Wind Speed (WS) ($m\ s^{-1}$)	Incoming Radiation (IR) ($w\ m^{-2}$)
Jun 07	30.31	27.5	75	2.1	163.9
Jul 07	26.89	27.2	76.2	1.9	126.7
Aug 07	33.16	27.7	72.8	2.4	189.7
Sept 07	25.11	27	75.3	2	161.7
Oct 07	39.92	27	75.4	1.7	155.5
Nov 07	24.44	26.3	77.3	2	122.2
Dec 07	22.34	26.9	76.8	0.7	133.9
Jan 08	25.75	25.9	75.5	3.2	148.5
Feb 08	29.74	25.6	77.8	2.8	135.6
Mar 08	20.44	25.4	81.4	2.3	114.6
Apr 08	19.24	27.6	75.1	1.3	151
May 08	27.07	27.8	72.7	2	141.9

5.2.3. Quality control

The analytical quality of the data obtained was determined using limit of detection (LOD), recovery, linearity, and by checking sampling artifacts, etc. During each set of extractions, the field blanks (filter and PUF plugs) were included and the mean blank value was subtracted from the measured levels. The reliability of the whole analytical procedure was assessed by using surrogate standards for PAHs, OCPs and PCBs. The mean recoveries obtained per sample were greater than 80% and concentrations of all real-world samples were corrected accordingly. The linearity of calibration standards was calculated by regression analysis with values ranging from 0.99–1.00 (r^2) for SVOCs, and breakthrough was evaluated under field conditions by connecting three one- inch plugs in series and analyzing them separately. For 48 hr samples, measured organic compounds at the third plug were in the range of blanks values. Three one-inch plugs used in series with the hi-volume PUF sampler could therefore trap gas-phase target compounds effectively. Control calibration standards spiked with internal standards were measured regularly to check instrument performance during analysis.

5.2.4. Airmass Backward Trajectory Analysis

The latest, updated Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Version 4.9) (Draxler and Rolph, 2003; Rolph, 2003) developed by the National Oceanic and Atmospheric Administration (NOAA), was used to compute backward trajectories for air samples taken from Jun 2007 to May 2008. Meteorological data were obtained from National Centers for Environmental Prediction (NCEP) Global

Data Assimilation System (GDAS, global, 2005-present). Kinematic 3D trajectories were used as they are reported to provide an accurate description of the history of air masses in comparison with all of the other approaches (isentropic, isobaric) (Stohl, 1998; Stohl and Seibert, 1998). Backward air trajectories were generated at eight starting times per sample (every 6 h during each sampling event) for 96 h back in time with 500 m-agl ending level. This level is very frequently used (Lee et al., 2006; Erel, 2007) and ensures that the trajectory starts in the atmospheric boundary layer (ABL) (Dvorská et al., 2009). In addition, cluster analysis was conducted by using HYSPLIT model (version 4.9) as well to classify the trajectory groups of similar length and curvature for monsoon and pre-monsoon seasons (Stohl, 1998).

5.2.5. Data Statistical Analysis

Since atmospheric sampling was conducted in this study for each event in a consistent manner (48 h at 250 L min^{-1}), a median concentration with minimum and maximum values was used for assessing monthly or seasonal concentrations of SVOCs in the atmosphere. However, in the case of rainwater, the rainfall amount for each event varied. Hence, those concentrations were calculated as volume-weighted mean (VWM) values. The standard error of the weighted mean (SEM$_{\mathrm{w}}$) was calculated according to the formula as follows (Offenberg and Baker, 1997):

$$(\mathrm{SEM_W})^2 = \frac{n}{(n-1)(\sum P_i)^2}\Big[\sum(PiXi - \overline{P}\,\overline{X_W})^2 - 2\overline{X_W}\sum(P_i - \overline{P})(P_iX_i - \overline{P}\,\overline{X_W}) + \overline{X_W}^2\sum(P_i - \overline{P})^2\Big] \qquad (5.1)$$

where P_i is the precipitation amount of sample i, X_i is the concentration in sample i, $\overline{P}$ is the mean precipitation amount for samples 1 to n, and $\overline{X_W}$ is the precipitation weighted mean concentration.

Correlation indicates the strength and direction of a linear relationship between two random variables. In this study, Pearson correlation matrix, obtained by dividing the covariance of the two variables by the product, was constructed to explore the effect of meteorological factors and TSP on the occurrence of atmospheric SVOCs in this tropical atmosphere and the confidence level was chosen at 95%. Single factor ANOVA (also known as one-way ANOVA) was performed to assess the seasonal variation of the occurrence of atmospheric SVOCs by using SPSS 13.0 for Windows (SPSS Inc., Chicago, IL, USA).

5.3. Results and discussion

5.3.1. Air Mass Categorization

The 96-h backward trajectories of air masses arriving at the study site during this one-year sampling period were computed and are categorized in Figure 5.1.

(1) SW – a category of continental air masses for southwest monsoon season (Jun-Sept 2007). This category accounts for 86.9% of all the air masses in the examined days during SW monsoon season with high mixing depth and high wind speed. These air masses were partly terrestrial and partly oceanic in origin, passing through islands of southern Indonesia such as Sumba, Lombok and Sumbawa, Java Sea, mass islands of Java and southwestern Sumatra, and even on some cases crossing Kalimantan Island before arriving at Singapore.

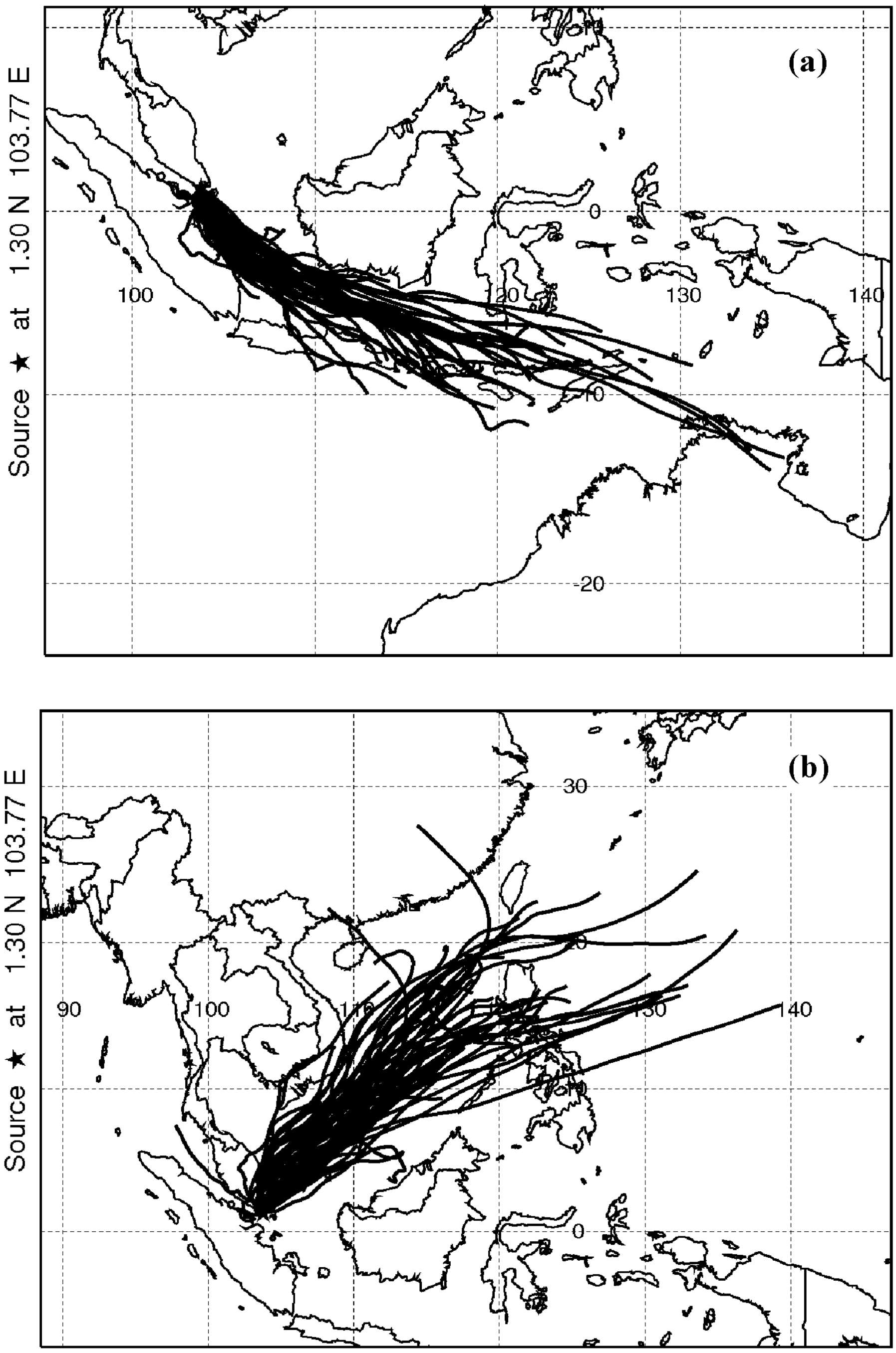


Figure 5.1. Four types of air masses arriving at the study site during Jun 2007-May 2008 ((a) SW; (b)NE; (c) Pre-NE; (d) Pre-SW)

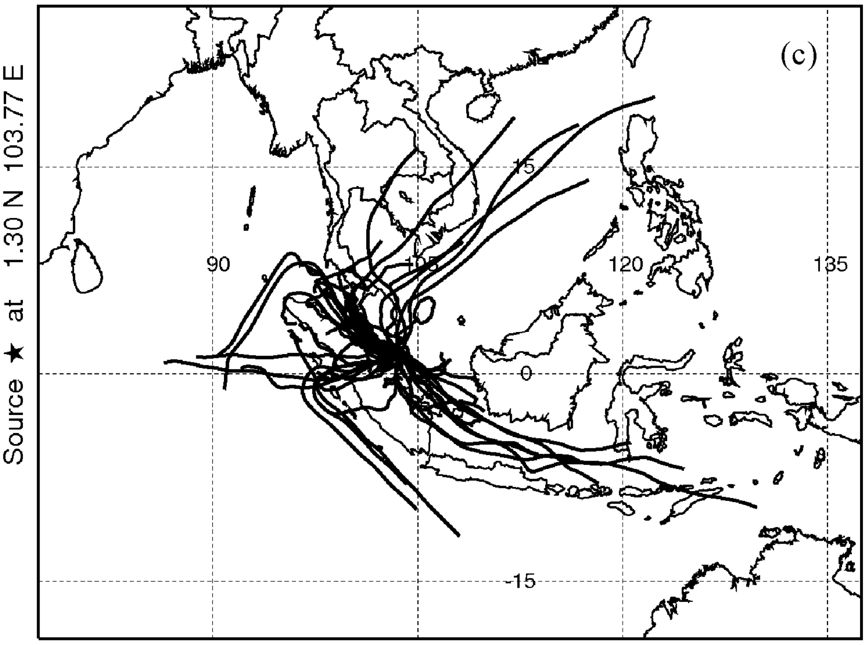
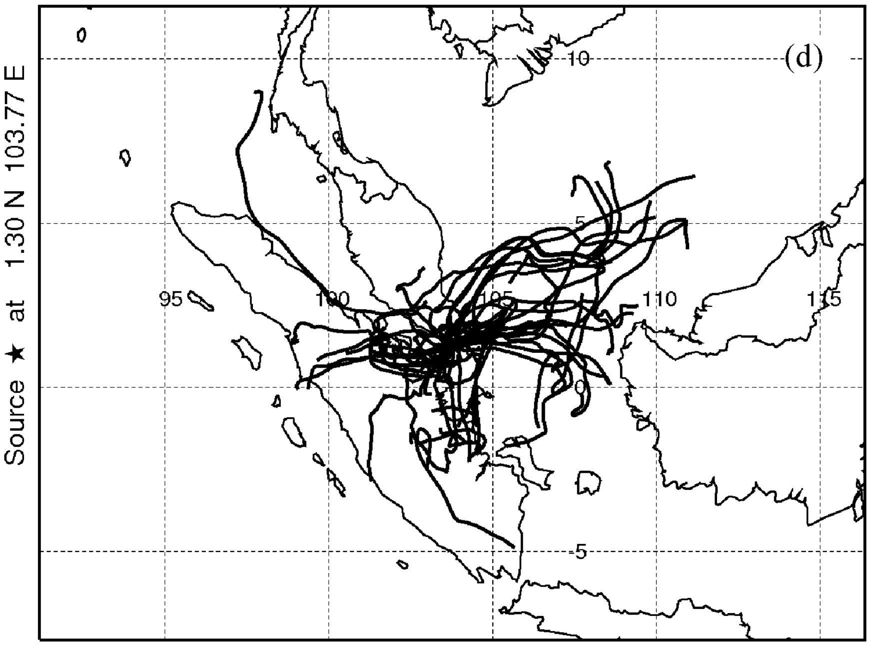


Figure 5.1. Four types of air masses arriving at the study site during Jun 2007-May 2008 ((a) SW; (b)NE; (c) Pre-NE; (d) Pre-SW)



(2) NE – a category of continental air masses for northeast monsoon season (Dec 2007 – Mar 2008) coming from northeast areas with high mixing depth and high wind speed. This category accounts for 93.3% of all the air masses investigated during NE monsoon season. Most of air masses sampled were of oceanic character, travelling over the South China Sea; some originated from the Philippines and some were from Southern China such as Hainan, Canton province or Taiwan Island / strait as well.

(3) Pre-NE and pre-SW – this category of air masses for pre-NE (Oct-Nov 2007) and pre-SW (Apr-May 2008) monsoon seasons with no dominant pathway. For pre-NE, air mass origins were scattered and from various directions such as South China Aea, Java Sea, Indonesia Medan area and even Indian Sea during different events. For pre-SW, air masses were located in low altitude and had a short pathway or with a loop trajectory with most time spending over the sampling point vicinity. Low mixing depth and low wind speed are typical meteorological characteristics during both pre-monsoon seasons.

5.3.2. SVOCs in Air and Rainwater

Table 5.2 shows the median, minimum and maximum concentrations of SVOCs and the frequency of detection among the total 37 samples collected in this study from June 2007 to May 2008. The concentration of gaseous PAHs varied from 5.3 to 277.2 ng m^{-3} with a median value of 98.3 ng m^{-3}. The particulate PAH concentration was considerably lower and ranged from 3.1 to 52.7 ng m^{-3} with a median concentration of 16.2 ng m^{-3}, almost comparable to that reported (24.6 ± 9.6 ng m^{-3}) in an earlier study based on short-term sampling for Singapore (Karthikeyan, 2006) considering variations in the intensity of PAH emissions from different sources during the one year

Table 5.2 Summary of atmospheric SVOCs concentration in Singapore between June 2007 and May 2008 (n = 37)

Compound	Particle-phase			FD*	Gas-phase			FD*
	Median	Min.	Max.		Median	Min.	Max.	
PAHs (concentration in ng m^{-3})								
Naph	1.2	0.10	6.9	100	5.2	0.31	14.1	100
Acy	0.19	0.02	2.7	100	1.3	0.23	3.6	100
Ace	0.18	0.02	2.2	100	0.41	0.03	2.8	100
Flu	0.19	0.03	0.71	100	1.7	0.16	5.4	100
Phe	1.6	0.05	2.9	100	20.7	1.4	48.9	100
Ant	0.19	0.06	0.57	100	3.8	0.51	16.2	100
Flt	1.1	0.04	3.0	100	27.3	4.4	85.2	100
Pyr	1.5	0.05	3.5	100	24.8	0.2	141.3	100
B(a)A	0.50	0.02	2.4	100	3.2	0.91	21.6	100
Chry	1.0	0.08	4.9	100	2.6	0.04	16.6	100
B(b)F	1.6	0.28	4.8	100	0.44	0.09	2.3	100
B(k)F	0.63	0.12	2.3	100	0.10	0.02	1.5	100
B(a)P	0.54	0.04	2.5	100	0.11	0.03	1.9	100
Ind	1.3	0.17	5.9	100	0.12	0.01	1.7	100
DB(ah)A	0.26	0.03	2.5	100	0.03	0.01	0.40	100
B(ghi)P	1.7	0.15	3.8	100	0.08	0.01	0.91	100
Σ PAHs	16.2	3.1	52.7		98.3	5.3	277.2	
OCPs (concentration in pg m^{-3})								
α-HCH	20.4	0.52	86.7	100	277.3	13.2	615.6	100
β-HCH	6.9	0.20	32.3	100	85.5	3.6	480.7	100
γ-HCH	13.9	0.62	65.8	100	194.3	14.0	548.2	100
δ-HCH	8.2	1.7	27.6	100	71.4	10.9	258.1	100
p,p'-DDD	0.31	0.02	4.3	100	4.8	0.45	16.2	100
p,p'-DDE	0.27	0.05	1.4	100	3.2	0.66	12.4	100
p,p'-DDT	5.9	0.24	12.7	100	30.6	5.5	94.3	100
Σ OCPs	53.4	4.8	162.3		614.5	58.5	1529.1	

PCBs (concentration in pg m^{-3})								
17+18	0.49	0.28	1.4	37.0	2.1	0.07	5.9	88.9
28+31	0.13	0.05	0.54	37.0	0.40	0.19	1.4	70.4
33	0.10	0.08	0.12	7.4	0.42	0.08	1.1	25.9
52+49	0.32	0.13	0.85	25.9	0.96	0.15	4.9	70.4
44	0.35	0.10	0.83	29.6	1.7	0.29	6.3	92.6
74	0.34	0.05	0.71	22.2	1.9	0.21	8.7	88.9
70+95	0.16	0.03	0.37	22.2	0.58	0.23	2.1	85.2
101	0.42	0.11	1.6	40.7	0.38	0.06	0.71	85.2
99		<LOD		-	0.16	0.03	0.46	33.3
87	0.23	0.03	0.74	77.8	0.49	0.10	1.2	88.9
110	0.31	0.08	0.85	25.9	0.47	0.14	1.5	25.9
149	1.6	0.10	10.4	70.4	2.5	0.51	8.4	85.2
138+158	1.1	0.06	8.3	74.1	2.6	0.19	5.7	74.1
171	0.53	0.11	4.12	11.1	0.58	0.37	0.80	18.5
177	0.39	0.16	0.92	40.7	1.1	0.41	3.4	59.5
180	0.49	0.03	1.8	44.4	0.13	0.11	0.23	22.2
183	0.64	0.15	3.5	11.1	0.19	0.13	0.42	7.4
Σ PCBs	6.2	0.39	21.4		18.6	5.1	47.5	

* FD: frequency of detection %

period in this study. The gaseous PAHs were dominant in the air as expected and found to be 85.9 % of the total concentration. The most abundant PAHs (particle + gas) in all samples were Flt (28.4 ng m^{-3}), Pyr (25.3 ng m^{-3}) and Phe (22.3 ng m^{-3}), while the occurrence of heavier PAHs with five or more aromatic rings (B(b)F, B(k)F, B(a)P, Ind, DB(ah)A and B(ghi)P) was low ranging from 0.29 to 2.1 ng m^{-3}. Compared with the data obtained in 1994 (Chee, 1997), the composition characteristics of PAHs in recent years have changed significantly since the contributions of 3-4 benzene ring PAHs to the total PAHs have increased considerably. This change in the PAH composition can be attributed to an increase in the number of on-road vehicles in highly industrialized countries such as Singapore.

The total concentrations of ∑HCHs in particulate and gaseous phases were in the range of 3.8 ~ 152.8 pg m^{-3} with a median concentration of 48.4 pg m^{-3} and 14.2 ~ 1441.7 pg m^{-3} with a median of 559.4 pg m^{-3}, respectively. Among HCHs, α- and β-HCH dominated in the present study. The concentrations of HCHs were higher than those observed over Java Sea (75 pg m^{-3}), Celebes Sea (120 pg m^{-3}), but much lower than those in South China Sea (1300 pg m^{-3}) measured more than a decade ago (Iwata et al., 1993). In addition, the current occurrence level of HCHs was comparable to those measured recently in Singapore over short-period sampling (Wurl and Obbard, 2005a; He et al., 2009). It is thus confirmed that no significant decline of HCHs has occurred in this area over the past two decades. The concentrations of ∑DDTs in particulate and gaseous phases were 7.1 (0.36 ~ 15.3) pg m^{-3} and 37.9 (7.3 ~ 115.9) pg m^{-3}, respectively. These concentrations were lower than those measured in surrounding areas of Asia, such as Hong Kong (180 ~970, mean 620 pg m^{-3}) (Jaward et al., 2005), Pearl River Delta of

South China (280 ~ 3700, mean 1300 pg m^{-3}) (Wang et al., 2007), but relatively higher than those reported from short-term sampling over the coast of Singapore (3.6 ± 0.3 ~ 11.3 ± 1.3 pg m^{-3}) (Wurl and Obbard, 2005a) and west area of Singapore (7.7± 4.1 pg m^{-3}) (He et al., 2009). The gaseous OCPs in the air were predominant as the case with PAHs, which was most probably due to their properties of semi-volatility.

The yearly concentrations of 22 PCB congeners measured during the sampling period were 18.6 (5.1 ~ 47.5) pg m^{-3} in the gas phase and 6.2 (0.39 ~ 21.4) pg m^{-3} in the particle phase, respectively, indicating that about 75.0 % of total PCBs (particle + gas) was distributed in the gas phase. The concentrations of PCBs measured in other Asian areas varied from tens to a few hundreds of picograms per cubic meter, with values in the range of 21 ~ 336, 7 ~ 247, and 12 ~ 84 pg m^{-3} for China, Japan and South Korea, respectively (Jaward et al., 2005). Based on the historical data on PCBs reported for Java Sea (36 pg m^{-3}), Celebes Sea (22 pg m^{-3}), and the Strait of Malacca (30 pg m^{-3}) (Iwata et al., 1993), it appears that the current occurrence of PCBs in the region did not undergo appreciable reduction over the years. Higher concentrations in the particle phase appeared in congeners with six to seven chlorine atoms such as PCB 149, PCB138 + 158, PCB 171, PCB 177, PCB 180 and PCB 183 (Table 5.2). Lower chlorinated PCB congeners are known to have higher K_{OA} (octanol-air partition coefficient) while the PCB homologues (> penta-CBs) are more easily condensed onto particles due to lower vapor pressure (Harrad and Mao, 2004; Yeo et al., 2004).

Table 5.3 shows the VWM concentrations with SEM_w and frequency of detection among the total 32 rainwater samples for SVOCs collected in this study from June 2007 to May 2008. In rainwater, the concentrations of PAHs and OCPs in particulate phase were 233.3 ± 182.8 ng L^{-1} and 19.3 ± 14.2 ng L^{-1}, respectively; those in operationally defined (non-filter retained) dissolved phase were 984.8 ± 685.7 ng L^{-1} and 94.9 ± 81.6 ng L^{-1}, respectively. Both PAHs and OCPs were predominantly associated with the operationally defined dissolved phase as compared with those in filter-retained particles. It could be because submicron particles which can not be retained by filters contribute greatly to the operationally defined dissolved phase (Poster and Baker, 1996a; Poster and Baker, 1996b). Poster and Baker (1996a) reported that hydrophobic organic contaminants in precipitation were up to 80% bound to non-filterable particulate material and less than 9% were truly dissolved. In addition, the lower molecular weight (LMW) PAHs were more prominent in rainwater as compared to those higher molecular weight (HMW) PAHs (those with five and six benzene rings) and HCHs was also present in rainwater in relatively larger amounts than DDTs (see Table 5.2). Occurrence patterns in rainwater for PAHs and OCPs were consistent with their corresponding distributions in ambient air, implying that these SVOCs in rain were from the sources similar to those in the atmosphere. Concentrations of PCBs in both operationally defined dissolved and particulate phases of all rainwater samples were below the limits of detection in this study.

Table 5.3 Concentration of SVOCs in rainwater in Singapore between June 2007 and May 2008 (n = 32)

Compound	Particle-associated (VWM ± SEMw)	Frequency of detection %	Dissolved (VWM ± SEMw)	Frequency of detection %
PAHs (concentration in ng L^{-1})				
Naph	48.5 ± 34.2	100	374.9 ± 179.2	100
Acy	9.4 ± 12.1	100	21.9 ± 18.2	100
Ace	12.3 ± 16.5	100	38.8 ± 36.5	100
Flu	5.5 ± 7.5	100	35.6 ± 15.4	100
Phe	38.9 ± 24.2	100	237.0 ± 172.7	100
Ant	5.3 ± 3.9	100	28.6 ± 41.6	100
Flt	28.9 ± 21.5	100	53.5 ± 44.8	100
Pyr	30.1 ± 20.2	100	50.6 ± 57.7	100
B(a)A	10.1 ± 6.5	100	13.4 ± 13.0	100
Chry	13.1 ± 10.9	100	40.8 ± 36.5	100
B(b)F	25.4 ± 16.3	100	45.3 ± 37.3	100
B(k)F	0.77 ± 1.1	100	5.4 ± 6.0	100
B(a)P	0.93 ± 1.2	100	2.9 ± 2.2	100
Ind	0.71 ± 1.9	100	5.2 ± 2.0	100
DB(ah)A	1.4 ± 1.9	100	12.1 ± 6.0	100
B(ghi)P	2.2 ± 3.0	100	18.8 ± 16.6	100
Σ PAHs	233.3 ± 182.8		984.8 ± 685.7	
OCPs (concentration in ng L^{-1})				
α-HCH	0.15 ± 0.11	62.5	45.1 ± 36.5	100
β-HCH	0.31 ± 0.43	87.5	8.3 ± 7.4	100
γ-HCH	4.6 ± 3.3	56.3	19.7 ± 15.7	100
δ-HCH	0.61 ± 0.62	81.3	5.1 ± 3.9	100
4,4'-DDD	0.40 ± 0.40	59.4	4.1 ± 4.1	100
4,4'-DDE	0.42 ± 0.37	90.6	6.6 ± 8.6	100
4,4'-DDT	13.2 ± 9.3	78.1	6.1 ± 5.4	100
Σ OCPs	19.3 ± 14.2		94.9 ± 81.6	
PCBs: non-detectable in rainwater				

5.3.3. Effect of Meteorological Factors and TSP

During the sampling period, TSP concentrations ranged from 1.7 to 39.9 μg m^{-3}; average temperature (Temp), relative humidity (RH), wind speed (WS) and incoming solar radiation (SR) values varied from 24.2 to 28.6℃, 70.9 to 88.2%, 0.7 to 3.8 m s^{-1}, and 65.3 to 199.8 W m^{-2}, respectively.

Positive correlations were observed between most SVOCs concentrations and ambient temperature except for particulate PAHs (Table 5.4). This observation suggested that higher temperatures might fasten the distribution of PAHs from particulate phase into gaseous phase and could also assist in re-emission of both OCPs and PCBs into the atmosphere because these two groups of compounds have been phased out in Singapore for decades and reemission from residual in sediment, soil or vegetations might be the major source. Among the meteorological parameters, SVOCs concentration showed negative correlations with relative humidity and wind speed. In Singapore, the relative humidity is high and uniform throughout the year due to frequent rainfall and marine exposure. The scavenging effects of SVOCs can be caused by wet deposition and water-drop adsorption. As for wind speed, this observation indicated that winds could play an important role in reducing the concentration of SVOCs by increased atmospheric dispersion and dilution (Miguel et al., 2004). Incoming solar radiations showed positive correlations with most of SVOCs levels in the air, but were negatively associated with PAHs. It is known that the reaction of volatile PAHs with active radicals such as ·OH is their most important atmospheric degradation mechanism (Finlayson-Pitts and Pitts, 2000), which could be affected by the energy from incoming solar radiation. However, there were almost no correlations between SR and the occurrence of OCPs and PCBs. Theoretically, the photochemical reactions of organochlorine compounds with atmospheric oxidants are also likely to occur (Muir et al., 2004; Chu et al., 2005), but might be less predominant compared with PAHs due to the complexity of chlorinated benzene and the scarcity of hydrogen atoms needed for photo-reduction processes (Atkinson, 1986). Moreover, TSP showed moderate positive correlations with most of SVOCs in this study, most likely due to their presence in TSP via gas-particle partitioning process.

Table 5.4 Correlation matrix between atmospheric SVOCs and related meteorological factors plus TSP

	p-PAH	g-PAH	p-OCP	g-OCP	p-PCB	g-PCB	TSP	Temp	RH	WS	SR
p-PAH	-	0.56	0.37	-0.17	0.68	-0.10	0.69	-0.18	-0.06	-0.39	-0.23
g-PAH	0.56	-	0.08	0.50	0.14	0.56	0.49	0.35	-0.12	-0.28	-0.09
p-OCP	0.37	0.08	-	0.65	0.55	-0.26	0.72	0.06	-0.26	-0.12	0.34
g-OCP	-0.17	0.50	0.65	-	0.43	0.02	0.42	0.29	-0.18	-0.02	0.33
p-PCB	0.68	0.14	0.55	0.43	-	0.12	0.75	0.23	-0.07	-0.21	0.44
g-PCB	-0.10	0.56	-0.26	0.02	0.12	-	0.08	0.71	-0.16	-0.32	0.26
TSP	0.69	0.49	0.72	0.42	0.75	0.08	-	0.22	-0.41	0.22	0.52
Temp	-0.18	0.35	0.06	0.29	0.23	0.71	0.22	-	-0.83	-0.48	0.59
RH	-0.06	-0.12	-0.26	-0.18	-0.07	-0.16	-0.41	-.83	-	0.05	-0.75
WS	-0.39	-0.28	-0.12	-0.02	-0.21	-0.32	0.22	-0.48	0.05	-	0.11
SR	-0.23	-0.09	0.34	0.33	0.44	0.26	0.52	0.59	-0.75	0.11	-

5.3.4. Seasonal Variation and Source Apportionment

A single-factor analysis of variance (ANOVA) was performed to determine temporal variations in daily average total concentrations of atmospheric PAHs, OCPs and PCBs. The monthly variations of PAHs and PCBs were seen with $p=0.56$ and $F=0.89 < F_{critical}=2.28$ for PAHs, and $p=0.41$ and $F=1.13 < F_{critical}=2.63$ for PCBs, respectively; while the OCPs levels were not statistically different between months with $p=0.03$ and $F=2.45 > F_{critical}=2.23$. Namely, the variations were statistically significant for PAHs and PCBs, but not for OCPs based on both p and F values.

The monthly mean atmospheric SVOCs concentrations with possible diagnostic ratios are plotted in Figure 5.2. As for PAHs, there was one clear peak appearing during the pre-NE monsoon (Oct-Nov 07) as shown in Figure 5.2(a). As Singapore is a highly industrialized area (heavy vehicular traffic, chemical industries, major power plants and oil refineries, etc.), local emissions are the major PAH sources. The diagnostic ratios of PAHs have been widely used to evaluate the impact of various sources on the air quality in a specific region (Yunker et al., 1996; See et al., 2007). In order to assess possible differences in sources in this study, a variety of different PAH ratios (Ant/Ant + Phe, Flt/ Flt + Pyr and Ind/ Ind + B(ghi)P) were calculated and are plotted in Figure 5.2(a). The average monthly ratios of Ant/Ant + Phe, Flt/ Flt + Pyr and Ind/ Ind + B(ghi)P were in the ranges of 0.18 ~ 0.31, 0.35 ~ 0.52 and 0.27 ~ 0.45, respectively. These diagnostic ratios demonstrated that liquid-fossil fuel combustion processes rather than unburned fossil fuels or biomass (wood and grass) burning (Yunker et al., 2002) were the predominant origin of PAHs measured at the sampling site. It should be noted that

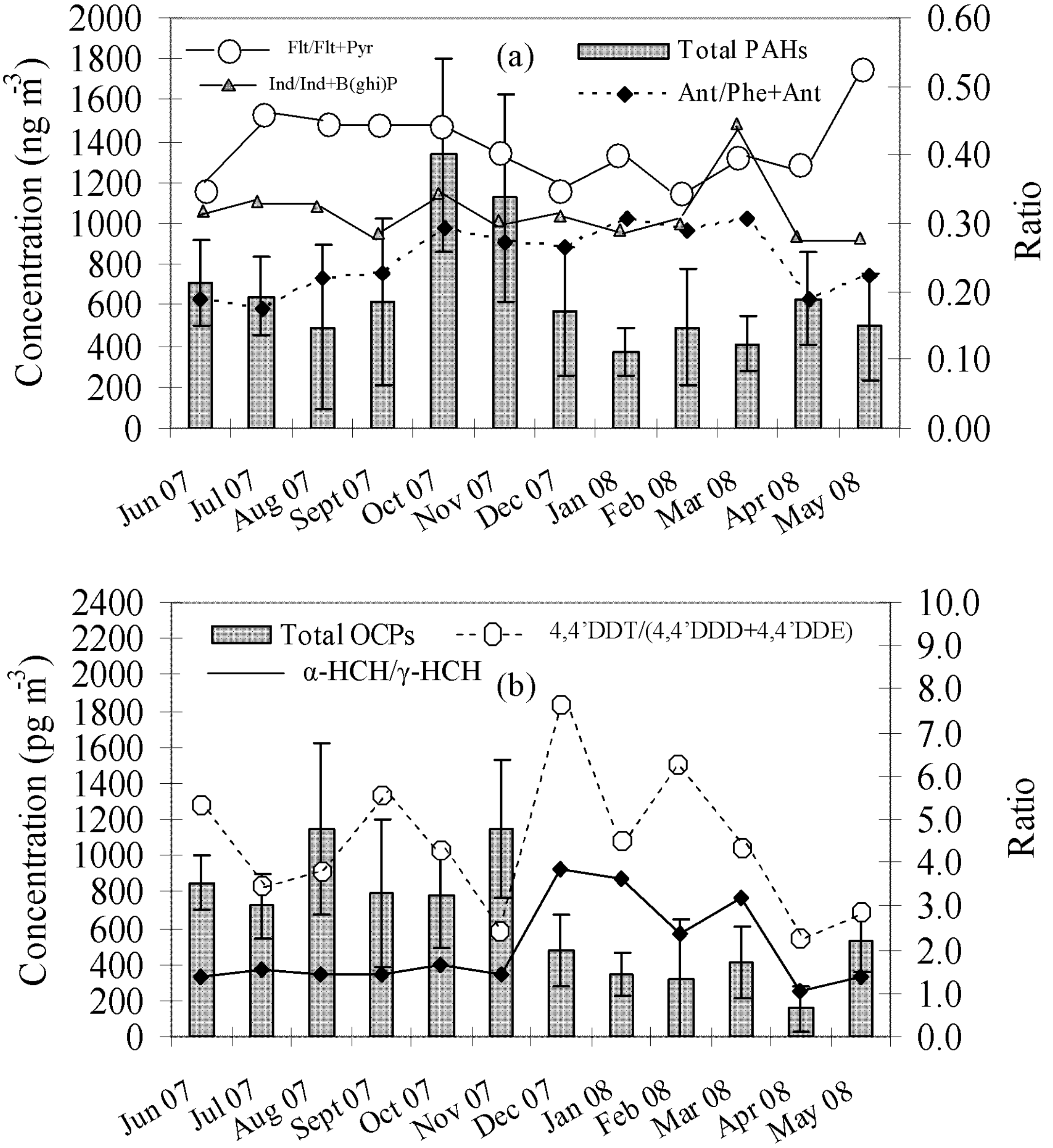


Figure 5.2. Seasonal variation of atmospheric SVOCs and diagnostic ratios (a) PAHs, (b) OCPs, and (c) PCBs

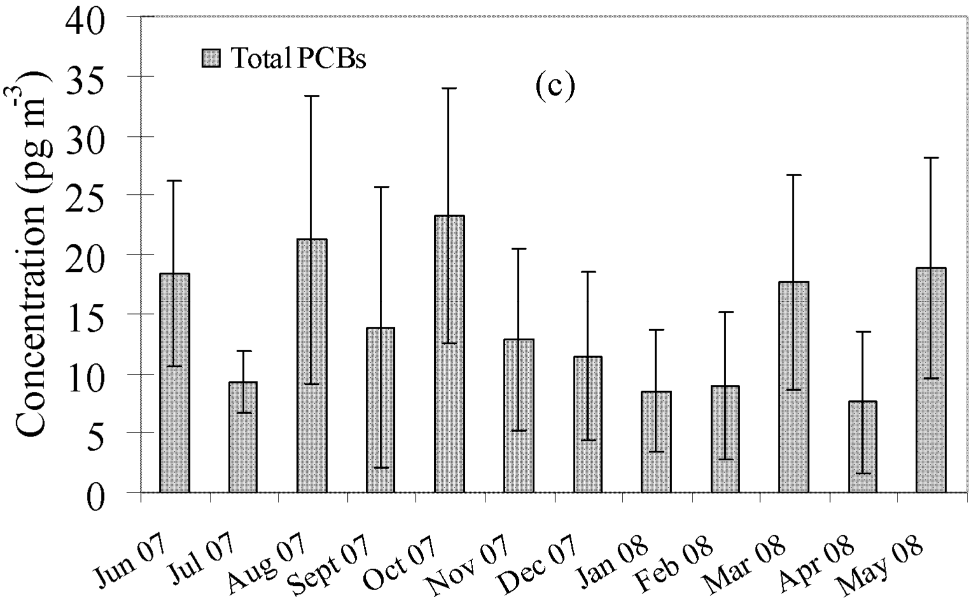


Figure 5.2. Seasonal variation of atmospheric SVOCs and diagnostic ratios (a) PAHs, (b) OCPs, and (c) PCBs

between Jun and Oct 2007 there was no influence of regional biomass burning events over Singapore as evident from Daily Haze Map, NEA Singapore though biomass burning episodes have been a recurring air pollution problem in the Association of Southeast Asian Nations (ASEAN) region in the past few decades. On the other hand, the monthly variations of ratios mentioned above seem to be insignificant, suggesting constant emission sources over the sampling period. It has to be noted that PAH diagnostic ratios have some limitations for source apportionment as stated by Galarneau (2008) such as substantial intrasource variability and intersource similarity of PAH isomer ratios, unconservation of relative PAH concentrations due to particle/gas partitioning, precipitation scavenging, particle deposition, etc. However, considering Singapore is a small but highly industrialized country, the sampling area is mainly influenced by less complex local emissions of PAHs. The existing climate characteristics in Singapore are such that there is little variation in temperature leading to relatively consistent gas/particle partitioning processes. In this study, the gas/partitioning effect has been overcome by calculating diagnostic ratios of total PAH concentrations (gas plus particles). As reported by He and Balasubramanian (2008), organic compounds with more volatility tend to be redistributed onto larger particles while the less volatile compounds remain onto the fine particles with which were directly emitted from their corresponding sources. From this distribution pattern, it is reasonable to hypothesize that the compounds with similar volatility (LMW or HMW) may have similar particle scavenging efficiency by precipitation or dry deposition because the particle size distribution of PAH species is a major factor affecting the efficiency of the above-mentioned two removal processes. Based on these considerations, it is reasonable to conclude the diagnostic ratios used in this study may still provide some insights into source apportionment of PAHs.

Periodical monsoon winds could assist in dispersing aerosol particles during NE and SW monsoon seasons; the lighter winds during the pre-monsoon seasons (Apr-May and Oct-Nov) might strengthen the accumulation of PAHs. In addition, the rainy season (maximum rainfall occurring in Dec and Apr) could cause more PAHs to be washed out from the atmosphere. The occurrence peak of PAHs in Oct and Nov 2007 could likely be due to the typical stagnant atmospheric conditions in pre-monsoon seasons and the relatively less rainfall.

As for the seasonal variations of OCPs (Figure 5.2(b)), no obvious peak was observed over a-year long sampling period in this study. However, the seasonal trends were seen for ratios of α-HCH/γ-HCH and 4,4’DDT /4,4’DDD + 4,4’DDE, which clearly increased between Dec 2007 and Mar 2008. It is known that HCHs are available in two formulations: technical HCH mixture (α-HCH 55-80%, β-HCH 5-14%, γ-HCH 8-15%, δ-HCH 2-16% and ε-HCH 3-%%) and lindane containing >90% of γ-HCH (Yang et al., 2008). The ratio of α-HCH / γ-HCH has been used to identify HCH sources. The ratio mentioned above is close to 1 in areas where the pesticide lindane was used and between 3 and 7 in areas where technical HCH mixtures were used or in remote areas due to possible transformation of γ-HCH to α-HCH (Willet et al., 1998; Lee et al., 2000; Murayanma et al., 2003). The ratios of α-HCH/ γ-HCH were found to be 1.45 ± 0.16 and 3.25 ± 0.65 for SW and NE monsoon seasons, respectively. According to UNEP Chemical's regional report (UNEP, 2002), γ-HCH (lindane) has been banned by most countries in SEA, but the previous reports indicated the use of lindane in Malaysia (Kannan et al., 1995). High percentage of γ-HCH (up to 90%) has also been reported in Singapore and Malaysia (Monirith et al., 2003). During the SW monsoon season, most of air masses were transported from southern Indonesia and western Malaysia and the low ratio of α-HCH / γ-HCH might represent a mixture of sources from local residue re-emissions and regional transport. On the contrary, during the NE monsoon, most air masses arriving at the sampling site originated from China which was one of the largest producers and consumers of technical HCH in the world (Li, 1999). The high concentration of technical HCH mixture in China has also been reported by Monirith et al. (2003). The ratio of 4,4'DDT / 4,4'DDD+4,4'DDE is generally used as an indicator of aging DDTs. A minor value of 4,4'DDT/4,4'DDD+4,4'DDE ratio indicates aged 4,4'-DDT while a value much greater than 1 implies fresh applications (Li et al., 2007). The ratios of 4,4'DDT/4,4'DDD+4,4'DDE were found to be 4.65 ± 1.05 and 5.95 ± 1.61 for

SW and NE monsoon seasons, respectively, indicating fresh input of 4,4'-DDT from external sources through transboundary movement of air masses. In the surrounding areas, the high levels of 4,4' DDT have been reported in China and Vietnam while lower levels of DDTs were observed in mussels from the Phillipines, Cambodia, Indonesia and Malaysia (Minh et al., 2002; Monirith et al., 2003). Furthermore, the usage of DDT possibly still occurs for malaria control in Papua New Guinea (UNEP, 2002), east of Singapore and Indonesia islands. Hence, this study suggests that some DDTs measured in the ambient air of Singapore during SW and NE seasons were likely derived from different regional sources via long-range transport. During the two inter-monsoon periods, the ratios of 4,4'DDT/4,4'DDD+4,4'DDE were 2.81 ± 0.52 and 2.55 ± 0.45, respectively, probably indicating less influence of external air pollution sources within SEA.

From Figure 5.2(c), a clear seasonal trend in PCBs could be observed, with relatively lower levels from Nov 2007 to Feb 2008 (covered by NE monsoon season**).** In this study, penta- and hexa- PCB congeners (Table 5.2) were dominant and the particulate fractions of these compounds were mostly greater than 50%, which are consistent with the composition of the dominant source of Aroclor 1254 (discussion as below) . During the NE monsoon, maximum rainfall occurred in December and January. Also, generally high wind speeds reached 8 ~ 10 m s^{-1} in January and February. These meteorological factors might explain the low concentrations of PCBs during this period due to their washout through rainfall and favorable advective transport of aerosols (Table 5.4). Principal component analysis (PCA) was applied to compare the composition of PCB samples analyzed in this study relative to Aroclor mixtures (Aroclor 1221, 1232, 1016, 1242, 1248, 1254, 1260 and 1262) by using Primer 5 for Windows (Version 5.2.4). PCB composition of each sample was normalized to concentration of total PCBs, and the Aroclor composition that was reported in the literature (Frame et al., 1996) was used (Figure 5.3.). All samples are similar in composition to that of Aroclor 1248 and 1254, but not exactly equivalent, except for few samples being more similar to Aroclor 1260 and 1262. Aroclor 1248 is characterized by tetra-PCBs and Aroclor 1254 is characterized by penta- and hexa-PCBs. It has been known that Aroclor 1248 was used most extensively with hydraulic and heat transfer media. Aroclor 1254 was not only used in hydraulic media, but also in Askarel transformers and capacitors (Lowenbach, 2002). A similar match has also been reported in house dust in Singapore (Tan et al., 2007). Therefore, this analysis might suggest that a mixture of tetra- to hexa-PCBs was introduced into Singapore's atmosphere.

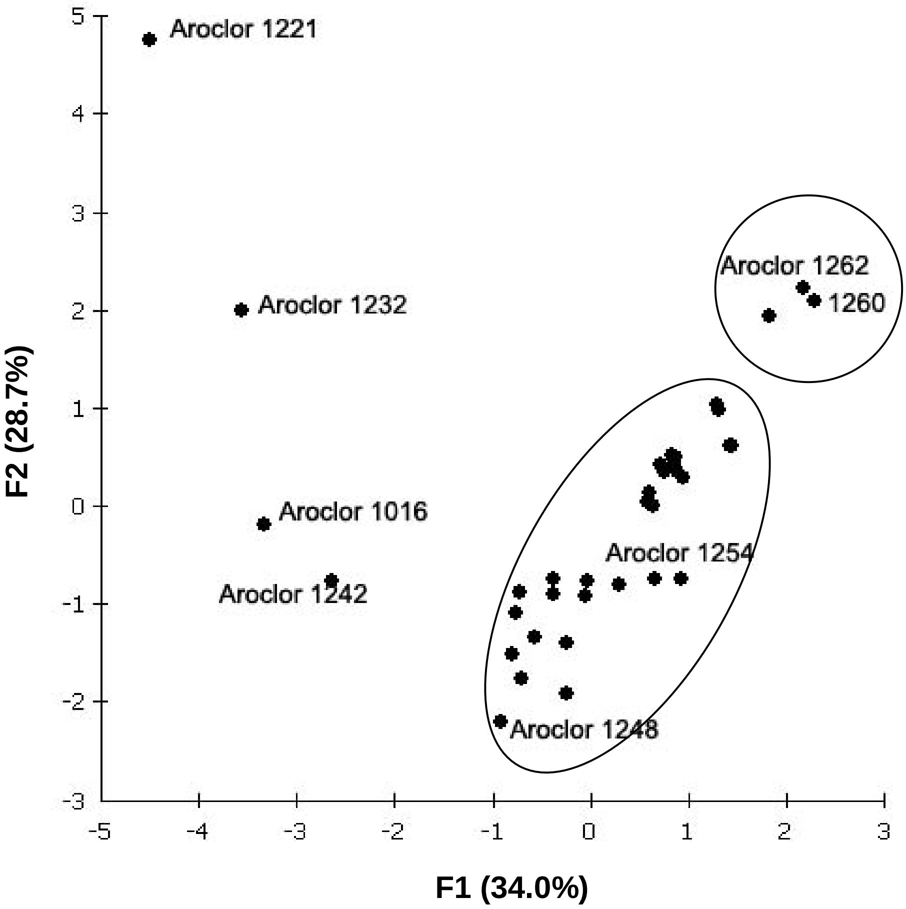


Figure 5.3 PCA score plot for the composition of atmospheric PCB congeners and Aroclor mixtures (the dots not labeled for samples)

A single-factor analysis of variance (ANOVA) was applied to examine temporal variations in daily average total concentrations of PAHs and OCPs in precipitation. The monthly PAHs levels in precipitation were not statistically different with $p=0.04$ and $F=2.57 > F_{critical}=2.49$ while the monthly variations of OCPs were obvious with $p=0.14$ and $F=2.0 < F_{critical}=2.89$. The monthly mean SVOCs concentration in precipitation is plotted in Figure 5.4. As discussed above, more rainfall occurred from December 2007 to February 2008 which could scavenge more aerosols and introduce SVOCs into precipitation. However, VWM concentrations of both PAHs and OCPs in rainwater were still relatively lower during this period. It is known that the washout processes of atmospheric compounds are dependent not only on their aerosol sources and size distributions, but also on rain intensity and duration of rain events (Offenberg and Baker, 1997). From the sequential sampling of rainwater, it has been found that most of the compounds/ions experience an important scavenging process in the first few mm of precipitation, that is, the initial decrease in concentration is much more rapid during the first few mm of precipitation than by the rain samples subsequently collected (Encinas and Casado, 1999). High rain intensity and total precipitation volume are climatic characteristics of Singapore in this marine and tropical area during the abovementioned sampling period. Consequently, the high precipitation volume might cause low pollutant concentrations by dilution effect (He and Balasubramanian, 2008) since all concentrations for precipitation samples were volume-weighted mean values.

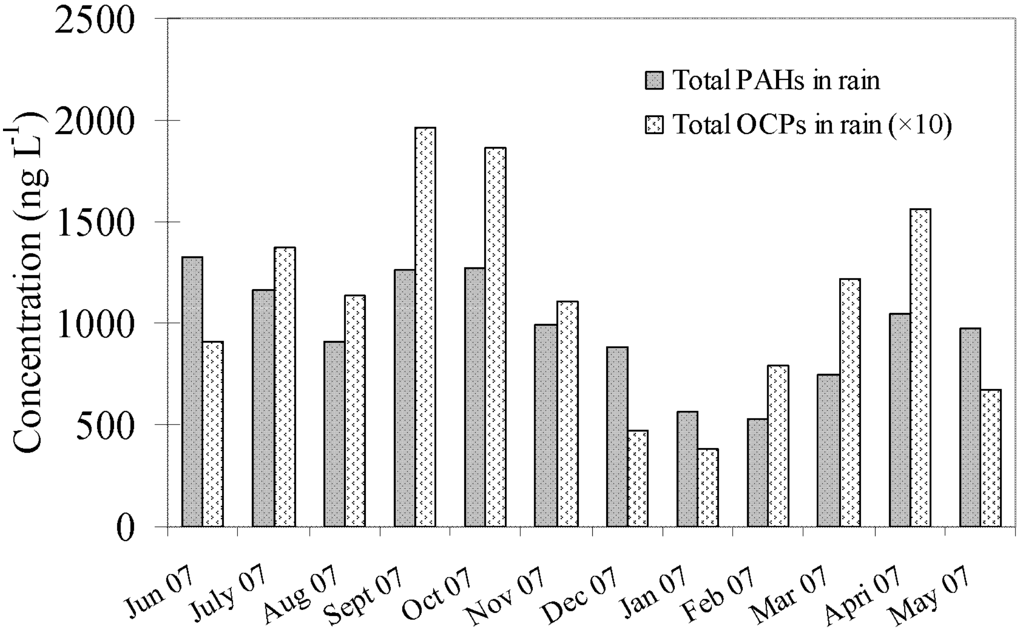


Figure 5.4 Seasonal variation of the total concentration of SVOCs in precipitation samples

5.4. Conclusion

This study investigated the concentrations of SVOCs in particulate and gaseous phases of the atmosphere as well as in particulate and operationally defined dissolved phases of precipitation based on the sampling conducted from June 2007 to May 2008. The atmospheric yearly median concentrations of SVOCs were compared with the historical data in this region. The results indicated that no significant decline of SVOCs in the atmosphere has occurred in this area over the past decade. The observation of a similar occurrence pattern of SVOCs in both air and rainwater implied that SVOCs in rain were from the sources similar to those in the atmosphere. This conclusion is further supported by the air mass backward trajectory analysis and historical usage patterns of SVOCs such as OCPs and PCBs within this region. For air samples, the temporal variations were statistically significant for PAHs and PCBs, but not for OCPs based on both p and F values; for rainwater samples, the monthly PAHs levels in precipitation were not statistically different while the monthly variations of OCPs were obvious. The source apportionment showed that local emissions such as liquid-fossil fuel combustion were the major PAH sources. Most of OCPs such as HCHs and DDTs were transported from external pollution sources within the region. PCBs were identified to be mainly from the commercial mixtures of Aroclors 1248 and 1254.

Chapter 6. Gas-Particle Partitioning of SVOCs in the Tropical Atmosphere of Southease Asia

6.1. Introduction

Partitioning of SVOCs between the gas and particle phases, as mentioned before, can affect their transport and transformation in urban and adjacent coastal atmospheres (Simcik et al., 1998). Once emitted into the atmosphere, generally SVOCs would be partitioned between these two phases and reach a partitioning equilibrium according to their vapor pressure and temperature dependencies (Yamasaki et al., 1982; Pankow and Bidleman, 1992; Cotham and Bidleman, 1995). Several models with the main emphasis on SVOCs gas/particle partitioning have already been proposed (Pankow, 1987, 1994a; Lohmann and Lammel, 2004; Roth et al., 2005b; Götz et al., 2007).

Several field studies have been carried out on the occurrence and distribution of PAHs and chlorinated organic compounds including PCBs in the tropical atmosphere (Ang et al., 1986; Panther et al., 1999; Wurl and Obbard, 2005a; Karthikeyan, 2006), but little is known about their gas/particle partitioning processes under prevailing tropical weather conditions. This partitioning process is an important mechanism affecting the fate and transfer of SVOCs. The present study was carried out to measure gaseous and particulate concentrations of PAHs and PCBs in Singapore urban air. The data were then applied to make an assessment of the Junge-Pankow absorption model (Junge, 1977; Pankow, 1987), the octanol-air partition coefficient (K_{OA}) absorption model (Pankow, 1994) and the combined K_{OA}-$K_{soot\text{-}air}$ (adsorption coefficient to soot) (Lohmann and Lammel, 2004) for gas/particle partitioning of PAHs and PCBs in the tropical and coastal atmosphere of SEA. In this study, the contributions of adsorption and absorption to the gas-particle concentrations of PAHs and PCBs in the tropical atmosphere are discussed.

6.2. Experimental

6.2.1. Sampling

All the air samples were collected between November and December 2006 at the NUS (National University of Singapore) Atmospheric Research Station. Particulate and gaseous SVOCs in air were collected using a high volume sampler (Model: TE-1000PUF, Tisch Environmental, Inc. USA) at ca. 250 L min^{-1} by the same protocol as described in Section 4.2.2.. However, for this study, average sampling time was 12 h periods (successive day time 8.00 am-8.00 pm and night time 8.00 pm-8.00 am) and average sampling volumes were 180 m^3. The filter and PUF samples were stored -20 ^{o}C prior to extraction.

6.2.2. Sample Preparation and Analysis

Prior to extraction, surrogate compounds were added to all samples. Both gaseous and particulate samples were extracted separately by Dionex ASE 200 under the following conditions: 3:1 n-hexane and acetone (HEX and ACE) combination at 100^{o}C for 25 min as described in Section 3.4.1. Extractions were performed with 40 ml of solvent at a high pressure (100 atm) by two static cycles. The extracted analytes were purged from the sample cell using pressurized nitrogen at 100 atm and concentrated to 3 ml by rotary evaporator. All extracts were further cleaned using silica gel (for PAHs) or florisil (for PCBs) columns.

The extract in each fraction was then concentrated to approximately 3 ml at room temperature and further to 50 µl by nitrogen gas stream. Labeled PAHs (Phenanthrene-d_{10}, pyrene-d_{10} and benzo[a]pyrene-d_{12}) and PCBs (13C_6-Tetrachlorobenzene, 13C_{12}- PCBs congeners CB 8, 206) were added to the extracted samples or blanks or calibration standards as internal standards to quantify and account for the loss of these SVOCs during analysis. All extracts were then kept in sealed vials at -20°C prior to GC-MS analysis. Sample analysis was conducted using a GC-MS (Shimadzu QP2010, Japan), as described in Section 3.4.6.

6.2.3. Measurement of OC and EC

Organic carbon (OC) and elemental carbon (EC) were determined as described in Chapter Section. All the OC and EC contents with total suspended particle (TSP) concentrations and ambient temperature (Temp) for this case study are listed in Table 6.1.

Table 6.1 Summary OC, EC, TSP data and f_{OM} for this study (µg m^{-3})

Date	OC	EC	TSP^{-3}	f_{OM} (%)	Temp (K)
17.11.2006	21.8	9.8	42.1	77.8	301.4
17.11.2006	15.6	7.0	40.5	57.9	298.9
19.11.2006	11.3	5.1	33.0	51.2	302.1
19.11.2006	9.5	4.3	29.3	48.6	298.5
23.11.2006	17.0	7.6	40.0	63.6	301.5
23.11.2006	13.9	6.3	36.2	57.7	297.7
04.12.2006	15.7	7.1	34.5	68.4	301.7
04.12.2006	12.7	5.7	30.5	62.5	299.7
06.12.2006	26.6	10.2	46.1	86.7	302.2
06.12.2006	18.4	8.3	37.6	73.6	298.6
11.12.2006	8.0	3.6	29.3	40.9	301.0
11.12.2006	6.2	2.8	24.9	37.5	298.7
13.12.2006	10.6	4.8	28.3	56.4	301.9
13.12.2006	8.9	4.0	25.4	52.8	297.8
15.12.2006	8.6	3.9	23.8	54.1	302.5
15.12.2006	5.4	2.4	19.6	41.3	299.6
20.12.2006	2.3	1.0	14.3	23.8	300.8
20.12.2006	2.5	1.1	18.5	20.4	298.1
22.12.2006	23.9	10.7	45.0	79.6	300.7
22.12.2006	19.6	8.8	41.8	70.4	298.7
Mean	12.9	5.8	32.0	56.3	300.1
S.D.	6.9	3.1	9.2	17.7	1.6

6.2.4. Quality Control

The analytical quality of the data was determined using limit of detection (LOD), recovery, linearity, and by checking sampling artifacts as described before.

Examination of suitability of data set for detailed analyses of gas-particle partitioning is necessary because there are a number of potential sampling artifacts that can lead to over- and under-estimations of SVOCs concentrations in the gas and aerosol phase (such as organochlorine compounds) (Mader and Pankow, 2001). A potential sampling artifact occurs when gaseous SVOCs sorb to filter and particle surfaces, thus leading to an over-estimation of particle-phase SVOCs (Dachs and Eisenreich, 2000). The sampling strategy in this study consisted of 12 h samples (diurnal and nocturnal samples, 180m^3 per sample). Considering the ambient temperature variations were small and relative humidities were uniform and high, backup filters have been used to correct for gas adsorption of SVOCs to a front filter (Hart and Pankow, 1994; Dachs and Eisenreich, 2000; Turpin et al., 2000). According to the method by Mader and Pankow, 2001, the $V_{min,f}$ (the volume that can deliver the gas phase mass amount required to achieve gas/filter adsorption equilibrium on filters) under the climate conditions similar to Singapore was close to 180 m^3. In addition, it was found that less than 5% of mass recovered from the primary filter was sorbed on a secondary filter.

Breakthrough of SVOCs from the PUF can lead to under-estimated SVOCs gas phase concentrations. In this study, breakthrough was evaluated under field conditions by connecting three one-inch plugs in series and analyzing them separately. For 12 h samples, measured SVOCs at the third plug were in the range of blank values. Three one-inch plugs in series used in high-volume PUF sampler therefore could trap gas-phase target compounds effectively.

6.3. Results and Discussion

6.3.1. Atmospheric Levels of SVOCs for This Short-term Study

A statistical summary of the SVOCs measured in this study (Mean SVOCs concentration (Mean)) with their corresponding standard deviations (S.D.), mean particle-bound fraction of SVOCs (Particle Fraction %), the number of samples in which the concentrations were above LOD (Detected Sample No.) is provided in Table 6.2. Mean PAHs (gaseous and particulate) concentrations ranged between 22.1 and 44.6 ng m^{-3} with an overall mean concentration of 33.4 ± 11.2 ng m^{-3}. The most abundant PAHs in all samples were Pyr (7.3 ng m^{-3}), Phe (7.2 ng m^{-3}), and Flt (5.6 ng m^{-3}). In general, the concentration of heavier PAHs with five or more aromatic rings (B(b)F, B(k)F, B(a)P, Ind, DB(ah)A, and B(ghi)P) was low ranging from 0.07 to 1.2 ng m^{-3}, most of which were dominant in particulate phase (>50%). The concentrations of PAHs in this study are comparable to those measured on this island in 2005 (51.6 ± 27.6 ng m^{-3}) (Karthikeyan, 2006), but relatively lower than those in other Asian urban areas such as Guangzhou (134.4 ~ 298.5 ng m^{-3}) (Bi et al., 2003), Hongkong (1083.9 ± 929.7 ng m^{-3}) (Lee et al., 2001).

Table 6.2 Concentrations of measured compounds for this study (PAHs-ng m^{-3}; PCBs- pg m^{-3})

Compounds	Avg Con ± S.D.	Particle Fraction %	Detected Sample No.	Compounds	Avg Con ± S.D.	Particle Fraction %	Detected Sample No.
Naph	1.5 ± 0.3	5.5	20	PCB 17+18	7.0 ± 2.7	3.3	15
Ace	0.7± 0.07	2.9	20	PCB 28+31	5.5 ± 3.1	10.2	15
Acy	0.3 ± 0.2	9.7	20	PCB 44	2.2 ± 1.2	13.9	14
Flu	3.8 ± 0.5	1.3	20	PCB 52+49	2.2 ± 1.1	8.0	15
Phe	7.2 ± 2.7	3.5	20	PCB 74+70	2.7 ± 1.7	6.7	13
Ant	2.0 ± 0.3	3.0	20	PCB 87	1.9 ± 2.1	19.4	13
Flt	5.6 ± 1.1	8.1	20	PCB 101+99	1.0 ± 0.4	14.9	15
Pyr	7.3 ± 3.4	5.1	20	PCB 110	1.4 ± 0.8	14.0	15
B(a)A	0.5 ± 0.2	36.2	20	PCB 118	1.4 ± 0.7	15.0	14
Chr	0.9 ± 0.5	29.5	20	PCB 128	1.5 ± 0.6	22.8	11
B(b)F	1.2 ± 0.6	50.0	20	PCB 132+153	0.6 ± 0.7	40.0	15
B(k)F	0.2 ± 0.1	52.2	20	PCB 138+158	1.4 ± 1.4	42.3	16
B(a)P	0.5 ± 0.3	59.6	20	PCB 149	0.4 ± 0.4	29.5	12
Ind	0.8 ± 0.4	80.7	20	PCB 151	0.5 ± 0.5	37.8	14
DB(ah)A	0.07 ± 0.09	85.7	20	PCB 156	1.2 ± 0.8	32.8	13
B(ghi)P	1.0 ± 0.5	81.1	20	PCB 169	0.7 ± 0.5	37.8	16
ΣPAH	33.4 ± 11.2			ΣPCB	31.7 ± 18.9		

The mean concentrations of PCB congeners measured in this study were 31.7 ± 18.9 pg m^{-3} and about 80% (mean) total PCBs (particle + gas) was distributed in the gas phase. The concentration data obtained from this study are in agreement with those reported recently in Singapore and over Indian Ocean (Wurl and Obbard, 2005a; Wurl et al., 2006d). However, the concentrations of PCBs measured in other parts of Asia were broadly in the range of tens to a few hundreds of picograms per cubic meter, with values in the range of 21 ~ 336, 7 ~ 247, and 12 ~ 84 pg m^{-3} for China, Japan and South Korea, respectively (Jaward et al., 2005).

6.3.2. Gas/particle Partitioning -log Kp versus log p_L^o

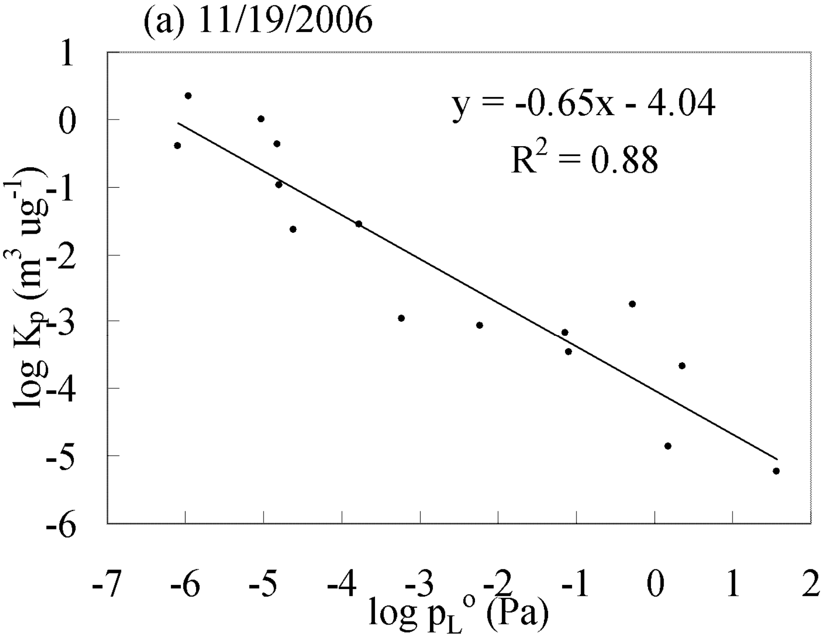
As stated before, SVOCs may occur either in the vapor phase or be associated with atmospheric particles in the natural atmosphere. These partitioning processes are affected by the particle properties such as the particle size distribution, organic carbon content, TSP and the prevailing ambient temperature, etc. (Yeo et al., 2003b). This partitioning process could be parameterized using the gas/particle partition coefficient, K_p (m^3 μg^{-1}), as described in Equation 2.5.

In general, the partitioning of SVOCs between the gas and particulate phases could be described as either surface adsorption (Pankow, 1987), or absorption into organic matter (Pankow, 1994a). Both paradigms relate the total suspended particulate matter (TSP, μg m^{-3}), normalized partition coefficient, K_p, to the subcooled liquid vapor pressure, p_L^o. According to Simcik et al. (1998), from both adsorption and absorption processes, a linear fit between K_p and p_L^o could be derived from Equation 2.7.

At equilibrium, the slope (m_r) for either adsorption or absorption should be close to -1 given the following assumptions: for adsorption, the difference between the enthalpies of desorption and volatilization and the number of available adsorption sites must remain constant over a compound class (Pankow, 1987); for absorption the activity coefficients must remain constant over the same compound class (Pankow, 1994a). However, the slopes, $m_{r,}$ yielded from several field measurements worldwide are largely diverse. While some are close to the theoretical value, significant deviations have also been reported (Cotham and Bidleman, 1995; Gustafson and Dickhut, 1997; Simcik et al., 1998). A number of factors, ranging from the uniformity of ambient temperature during the sampling period to varying activity coefficients in organic matter in a compound class, have been proposed to explain these deviations, and several investigators argue that such deviations do not always indicate disequilibrium (Goss and Schwarzenbach, 1998; Simcik et al., 1998). Moreover, there are a number of sampling limitations, which might lead to shallower slopes than -1 (Pankow and Bidleman, 1992; Simcik et al., 1998).

In this study, the temperature-dependent vapor pressures were corrected using the Clausius-Clapeyron equation (Simcik et al., 1999; Currado and Harrad, 2000) for those compounds which had concentrations well above the detection limit for a given sample based on the enthalpies for PCBs (Falconer and Bidleman, 1994) and for PAHs (Lei et al., 2002; Odabasi et al., 2006). Vapor pressures of co-eluting PCBs were calculated for the dominant PCB in each peak, which is justified by the fact that co-eluting PCBs have very similar vapor pressure. To ensure comparability between the different data sets, all log K_p values measured in this study and those reported in the literature were corrected to the same temperature of 298 K and RH of 70% as done by Lohmann and Lammel (2004).

When log K_p is regressed against the log p_L^o of a group of SVOCs (Equation 2.7), meaningful information about the partitioning of the compounds can be extracted from the slope m_r and the intercept constant of the trend line (Pankow and Bidleman, 1992; Goss and Schwarzenbach, 1998). Figures 6.1 and 6.2 show some representative regressions of log K_p vs log p_L^o for those samples collected in November and December 2006, which gave high correlations for individual samples for both PAHs (r^2=0.80~95) and PCBs (r^2=0.42~0.82), but the slopes and intercepts among samples varied significantly. The regression for high molecular weight (HMW) PAHs (with four and above aromatic rings (Pyr, B(a)A, Chr, B(b)F, B(k)F, B(a)P, Ind and B(ghi)P))) of all samples was plotted separately in Figure 6.1(c) and the slope, $m_{r,}$ was relatively smaller than that for those studied PAHs of all samples, but still greater than -1. Table 6.3 shows the slope and the intercept of log K_p vs log p_L^o obtained for all samples from this study and some other studies reported in the literature (Simcik et al., 1998; Kaupp and McLachlan, 1999; Yeo et al., 2003b). By comparison, it can be seen that the slopes (m_r) of this study in Singapore for both PAHs and PCBs were relatively steeper than those reported for most of the other areas while they were still greater than -1. It has been suggested that at equilibrium, the slope for either adsorption, or absorption should be close to -1 as stated above. Since slopes that deviate from -1 have been determined in field measurements, intense debate has occurred concerning the range of values that slopes can take and the reasons why slopes m_r can deviate from -1 (Pankow and Bidleman, 1991; Pankow et al., 1994; Goss and Schwarzenbach, 1998; Simcik et al., 1998).



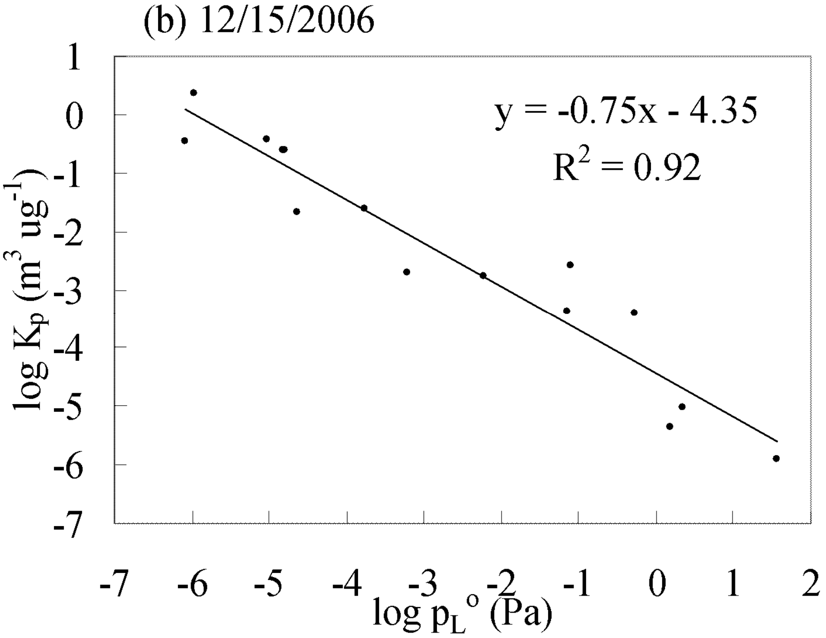
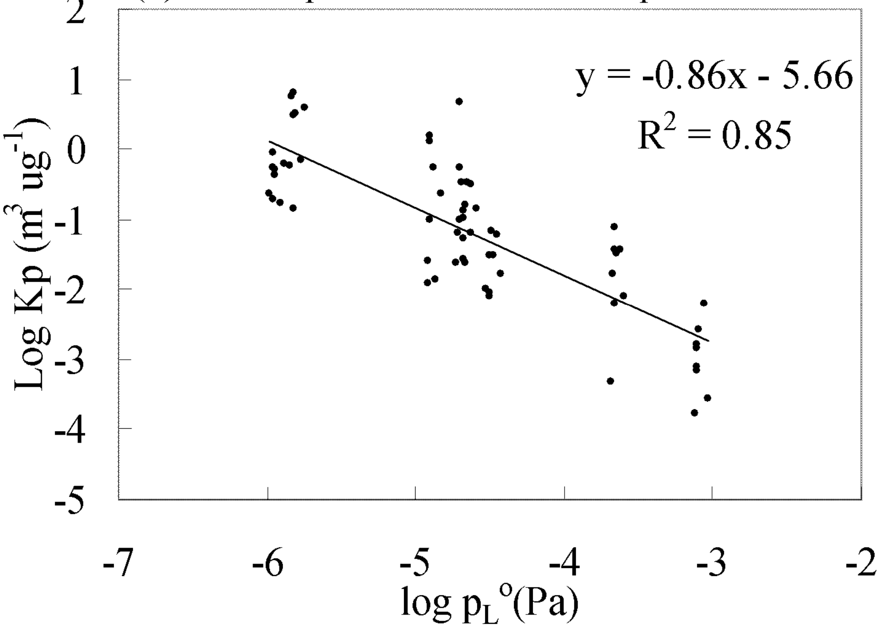


Figure 6.1. Log K_p(m^3 μg^{-1}) (normalized to 298 K and 70% RH) vs log p_L^o (298 K) for PAHs over Singapore (a)11/19/2006, (b) 12/15/2006

(c) All samples for HMW PAHs $p<0.0001$



(d) All samples $p<0.0001$)

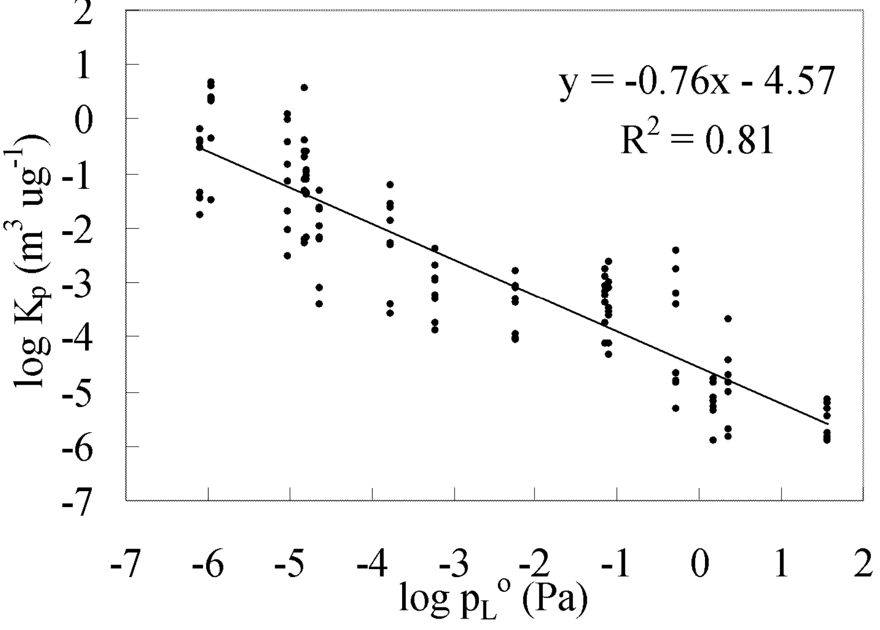
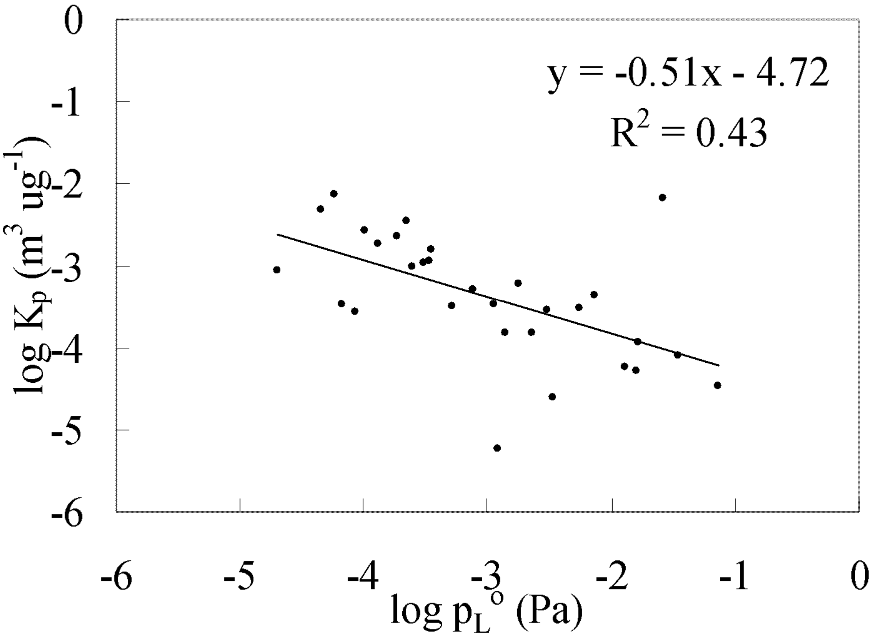


Figure 6.1. Log K_p(m^3 μg^{-1}) (normalized to 298 K and 70% RH) vs log p_L^o (298 K) for PAHs over Singapore (c) all samples for HMW PAHs (n=20), and (d) all samples (n=20)

(a) 11/23/2006



(b) 12/06/2006

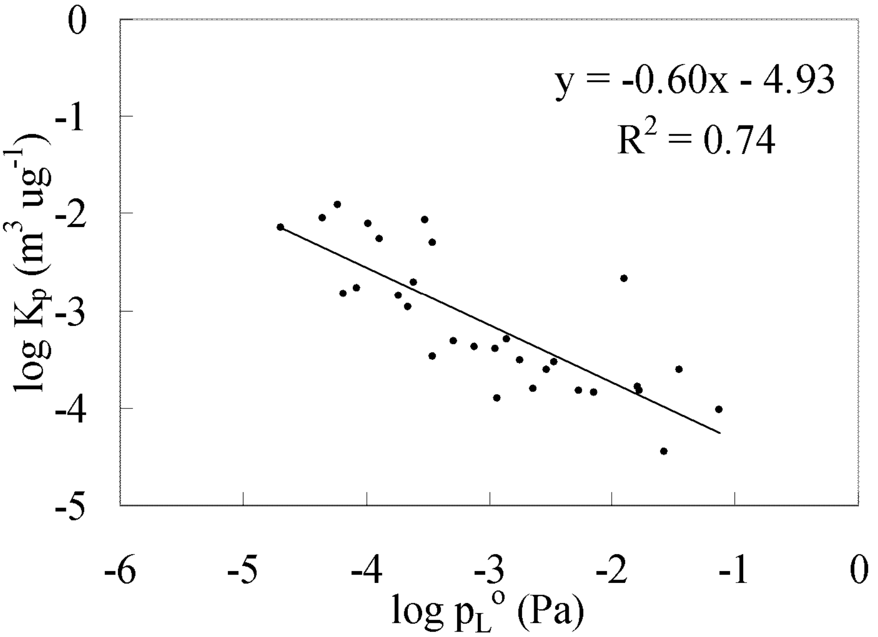
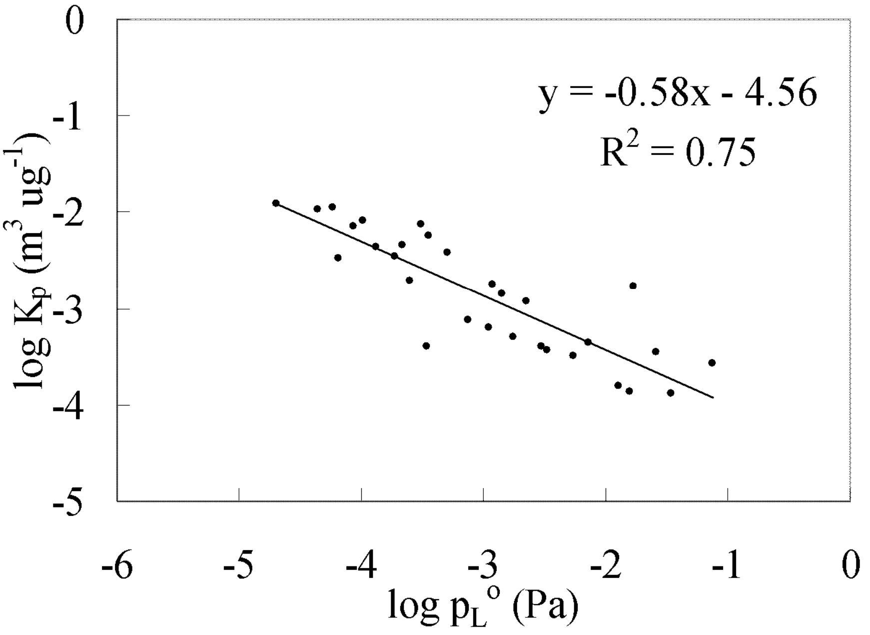


Figure 6.2. Log K_p(m^3 μg^{-1}) (normalized to 298 K and 70% RH) vs log p_L^o (298K) for PCBs over Singapore (a)11/17/2006, (b) 12/6/2006

(c) 12/20/2006



(d) all samples p<0.0001

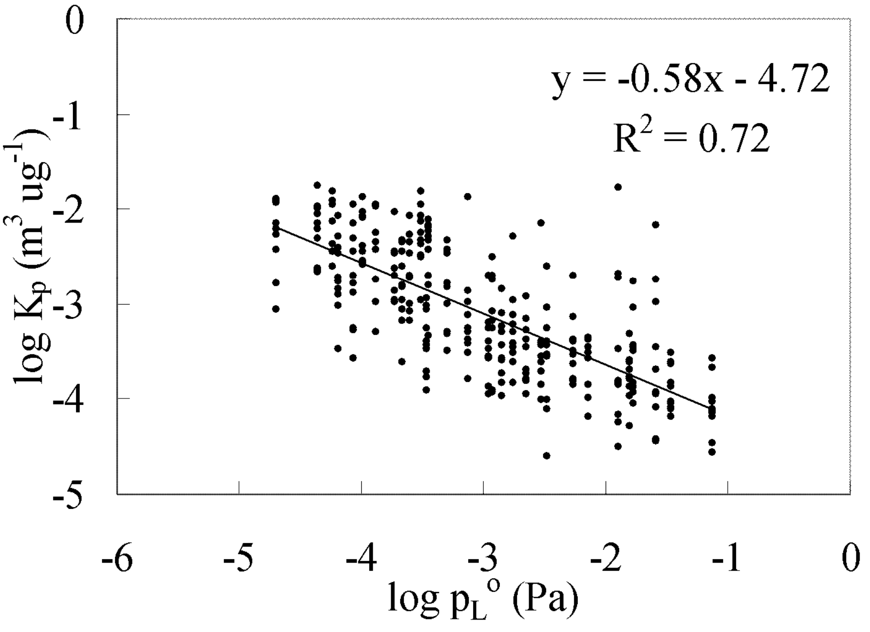


Figure 6.2. Log K_p(m^3 μg^{-1}) (normalized to 298 K and 70% RH) vs log p_L^o (298K) for PCBs over Singapore (c) 12/20/2006, and (d) all samples (n=11, based on samples of which both gaseous and particulate concentrations were above LOD)

Of the possible reasons, variations of ambient temperature during sampling period may not be applicable in this study as the sampling protocol with collection of two 12-h samples per day, one during the day and one at night, minimized the effect of changing temperature and atmospheric concentration during sampling, Furthermore, this tropical area is marked with uniform and high ambient temperature unlike the areas in temperate regions.

According to Simcik et al. (1998), non-exchangeability can occur for PAHs because they are formed in combustion processes; the more volatile species may become trapped inside particles during formation resulting in elevated K_p values (Pankow, 1994a). However, PCBs are emitted into the atmosphere primarily as gases. Hence, their non-exchangeability process is not as important as for PAHs. Consequently, non-exchangeability might be a possible factor for the slopes observed being less than -1 for PAHs, but not PCBs.

The sampling site was located close to major roads with heavy traffic and harbors and oil refining and petrochemical manufacturing industries in Singapore, which is also regularly affected by regional biomass burning events in SEA. Thus, PAHs sources are multiple and complicated, and an important fraction of PAHs may have been only recently introduced in the atmosphere. Sorption and desorption of SVOCs to combustion aerosols may take hours to reach equilibrium (Dachs and Eisenreich, 2000). Furthermore, slower sorption is more likely to happen in the case of those heavier PAHs resulting in slopes smaller than -1 (Cotham and Bidleman, 1995; Terzi and Samara, 2004).

PCB data from the air samples collected in our study provided a shallow slope (-0.58, see Table 6.3). The shallow slopes for PCB gas/particle partitioning were also derived in the urban area of Chicago, Lake Michigan, Kyonggi-do in South Korea and Thisio of Athens in Greece only with values of -0.51, -0.49, -0.56 and -0.44, respectively (Simcik et al., 1998; Mandalakis et al., 2002; Yeo et al., 2003b). In SEA area, most countries have generally banned the import and use of organochlorine pesticides (OCPs) and PCBs and equipment containing PCBs (UNEP, 2002). As for PCBs, due to their long half-lives, the residues in the environment and PCB wastes such as transformers and capacitors can still be the major sources in the urban area. The shallow slopes, determined in this study, for PCBs may be due to slow re-equilibrium of reemitted PCBs from residues locally in the environment to freshly emitted particulate matter in the urban atmosphere (Lohmann et al., 2000).

Other than the non-equilibrium between the aerosols and gas phase, thermodynamically aerosols equilibrate faster with SVOCs under warm conditions than cold conditions and low molecular weight species attain equilibrium more quickly than the heavier compounds (Kamens et al., 1995; Simcik et al., 1998). This might be one of the possible reasons why the slopes of log K_p versus log P_L^o curves for both PAHs and PCBs in this study were greater than most of those obtained in temperate zones of the Northern Hemisphere (see Table 6.3). In addition, the slopes of PAHs in this study were closer to -1 than those for PCBs and a similar observation was made in Manchester, UK (Lohmann et al., 2000).

Table 6.3. Slope (m_r), intercept constant, coefficient of determination (R^2) used for the log K_p vs. log p_L^o for this study and other studies

Sample (reference)	Slope m_r	Intercept constant	R^2	Level of ignificance
PAH, Singapore (this study)	-0.76	-4.57	0.81	$p<0.0001$
PAH, Chicago (US) (Simcik et al., 1998)	-0.69	-3.58	0.78	$p<0.001$
PAH, Lake Michigan (US) (Simcik et al., 1998)	-0.70	-3.79	0.83	$p<0.001$
PAH, Athens (Greece) (Mandalakis et al., 2002)	-0.51	-4.75	0.78	$p<0.001$
PCB, Singapore (this study)	-0.58	-4.72	0.72	$p<0.0001$
PCB, Chicago (US) (Simcik et al., 1998)	-0.51	-4.23	0.70	$p<0.001$
PCB, Lake Michigan (US) (Simcik et al., 1998)	-0.49	-4.41	0.70	$p<0.001$
PCB, Kyonggi-do (South Korea) (Yeo et al., 2003)	-0.56	-4.42	0.86	$p<0.001$
PCB, Athens (Greece) (Mandalakis et al., 2002)	-0.44	-4.73	0.79	$P<0.001$

To sum up, factors influencing the observed shallower slopes include non-exchangeability of more volatile SVOCs bound to the particulate phase and non-equilibrium effects caused by fresh emissions of SVOCs (Pankow and Bidleman, 1992; Helm and Bidleman, 2005). The scatter in field gas/particle partitioning data is likely to be caused by minor variations in ambient temperature, atmospheric concentrations and even properties associated with aerosols during the period of sampling (Callén et al., 2008). However, it has also been suggested that shallower slopes may occur even at equilibrium (Simcik et al., 1998). Goss and Schwarzenbach (1998) illustrated this deviation for a number of compound classes due to the fact that the aerosol organic matter differs from that in the model solvent octanol, which would lead to slopes deviating from unity.

6.3.3. Comparison of Adsorption and K_{OA} Absorption Models

*Junge-Pankow Adsorption Model***.** This model was proposed by Junge (1977) and later critically reviewed by Pankow (1987), the Junge-Pankow model (Equation 6.1) is the most common method for estimating adsorption of semi-volatile organic compounds to aerosols.

$$\Phi = c\theta / (p_L^o + c\theta) \qquad (6.1)$$

This model relates the fraction of chemical adsorbed to particles (Φ) to the subcooled liquid vapor pressure of the pure compound (p_L^o, Pa) and the particle surface area per unit volume of air (θ, m^2 of aerosol per m^3 of air). The parameter c (unit, Pa·m) is based on the heat of desorption from the particle surface, the heat of vaporization of the compound, and the moles of adsorption sites on the aerosol. The particle percentage Φ could be calculated by:

$$\Phi = K_p TSP/(1 + K_p TSP) \qquad (6.2)$$

where K_p ($m^3\ \mu g^{-1}$) is the gas/particle partition coefficient and TSP is the concentration of total suspended particles in the air ($\mu g\ m^{-3}$). A value of $c = 0.172$ Pa·m is typically used, although Pankow (1987) suggested that this may vary with the class of SVOC compounds. Values for the surface area parameter, θ, are often assumed to be 1.1×10^{-3} for urban air and $(4.2\text{-}35)\times10^{-5}$ for rural air (Bidleman, 1988).

K_{OA} Absorption Model. It has been proposed by Pankow et al. (1994) that the absorption of gas-phase compounds into an organic film coating surrounding the particle makes an important contribution to the overall gas-particle partitioning process. The octanol-air partitioning coefficient (K_{OA}) can be used to predict K_p with the assumption of predominant distribution process is absorption (Harner and Bidleman, 1998). The relationship between K_p and K_{OA} is

$$K_p = K_{OA}\, f_{OM} MW_{OCT} \zeta_{OCT} / (\rho_{OCT} MW_{OM} \zeta_{OM} 10^{12}) \qquad (6.3)$$

where f_{OM} is the fraction of organic matter (OM) phase on TSP; MW_{OCT}, and MW_{OM} are the mean molecular weights of octanol and the OM phase ($g\ mol^{-1}$), respectively; ρ_{OCT} is the density of octanol ($0.820\ kg\ L^{-1}$); ζ_{OCT} is the activity coefficient of the absorbing compound in octanol; ζ_{OM} is the activity coefficient of the compound in the OM phase. With the assumptions that $\zeta_{OCT} = \zeta_{OM}$ and $MW_{OCT}/MW_{OM}=1$, Eq. (6.3) can be simplified as shown in Equation 2.10.

Table 6.4 Regression parameters of Equation (6.4) for calculation of K_{OA} for SVOCs based on capillary GC data

	Compound	A	B	Range (°C)
PAHs	Flu [a]	-7.74	4332	0~40
	Phe [a]	-5.62	3942	0~40
	Pyr [a]	-4.56	3985	0~40
	Flt [a]	-5.94	4417	20~40
	Acy [b]	-1.97	2476	0~40
	Ace [b]	-2.20	2597	0~40
	Ant [b]	-3.41	3316	0~40
	B(a)A [b]	-5.64	4746	0~40
	Chr [b]	-5.65	4754	0~40
	B(b)F [b]	-6.40	5285	0~40
	B(k)F [b]	-6.42	5301	0~40
	B(a)P [b]	-6.50	5382	0~40
	Ind [b]	-7.00	5791	0~40
	DB(ah)A [b]	-7.17	5887	0~40
	B(ghi)P [b]	-7.03	5834	0~40
PCBs	CB 18 [c]	-6.00	4060	10~43
	CB 28+31 [c]	-6.12	4190	10~43
	CB 44 [c]	-6.20	4340	10~43
	CB 52 [c]	-6.34	4340	10~43
	CB 101 [d]	-3.82	3841	-10~30
	CB 110 [c]	-6.16	4540	10~43
	CB 118 [d]	-5.92	4693	-10~30
	CB 149 [c]	-6.50	4700	10~43
	CB 138 [d]	-5.57	4584	-10~30
	CB 153 [d]	-6.02	4695	-10~30

[a] Harner and Bidleman, 1998; [b] Odabasi, et al., 2006;
[c] Harner and Bidleman, 1996; [d] Kömp and McLachlan, 1997.

In Eq. (2.10), the octanol-air partition coefficient (K_{OA}) is suggested to be an alternative to vapor pressure for describing absorption to aerosols. Values of K_{OA} have been corrected as a function of temperature for several PCB congeners and PAHs using the following equation with the regression parameters (A and B) given by Harner and Bidleman (1996, 1998) and Kömp and McLachlan (1997), which are given in Table 6.4.

$$\log K_{OA} = A + B/T \tag{6.4}$$

Figure 6.3 compares the percent ($\Phi\times100$) on particles as predicted by the Junge-Pankow adsorption model (using $c = 0.172$ Pa·m and $\theta = 1.1\times10^{-3}$) and K_{OA} absorption model with the average experimental values for PAHs and PCBs. The K_{OA} absorption model was applied using the average measured f_{OM} value (0.563). It can be seen that the gas-particle distribution of LMW PAHs with vapor pressure < 10^{-3} Pa or K_{OA} < 10^{8} was under-predicted by both models, while the predicted values agreed better with those observed ones for HMW PAHs (Figures 3(a), (b)). As hypothesized before, this may be related to the possibility that more volatile PAHs easily become bound within the particles during their formation in combustion and non-exchangeable with the atmosphere.

In K_{OA} absorption model, the organic matter fractions in general for urban aerosols between 10% and 20% (Viana et al., 2006; Callén et al., 2008), but the measured average f_{OM} value in this study was much higher than those typically expected. The higher f_{OM} could result from the local heavy traffic emissions and also from oil refinery and petrochemical industries, which are the primary contributors to the organic aerosols. From Figure 3(c), one can see that the Junge-Pankow model over-predicted PCBs

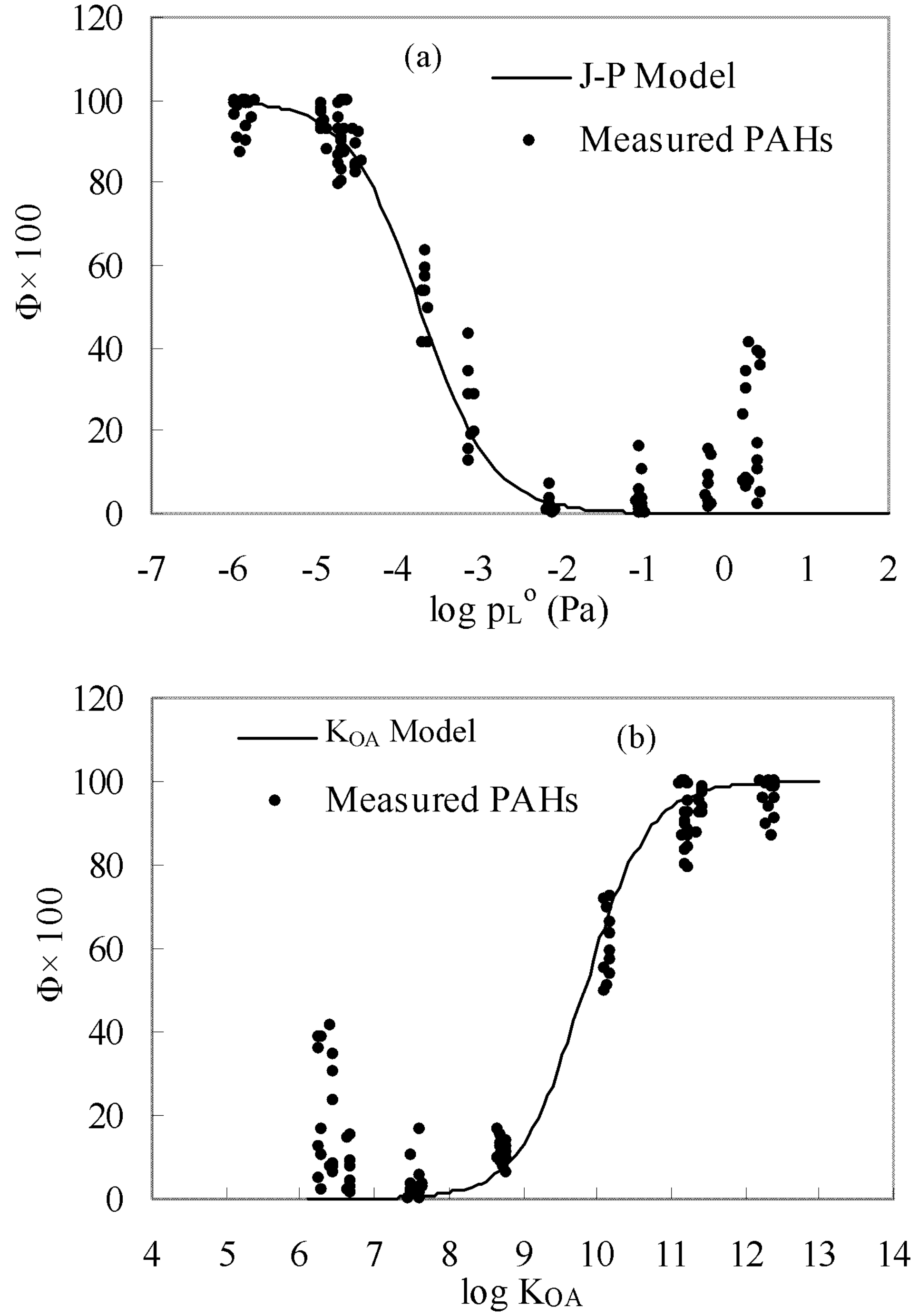


Figure 6.3. Comparison of predicted and measured particle percentage (Φ) for both PAHs and PCBs (a) J-P model for PAHs, (b) K_{OA} model for PAHs, (c) J-P model for PCBs and (d) K_{OA} model for PCBs

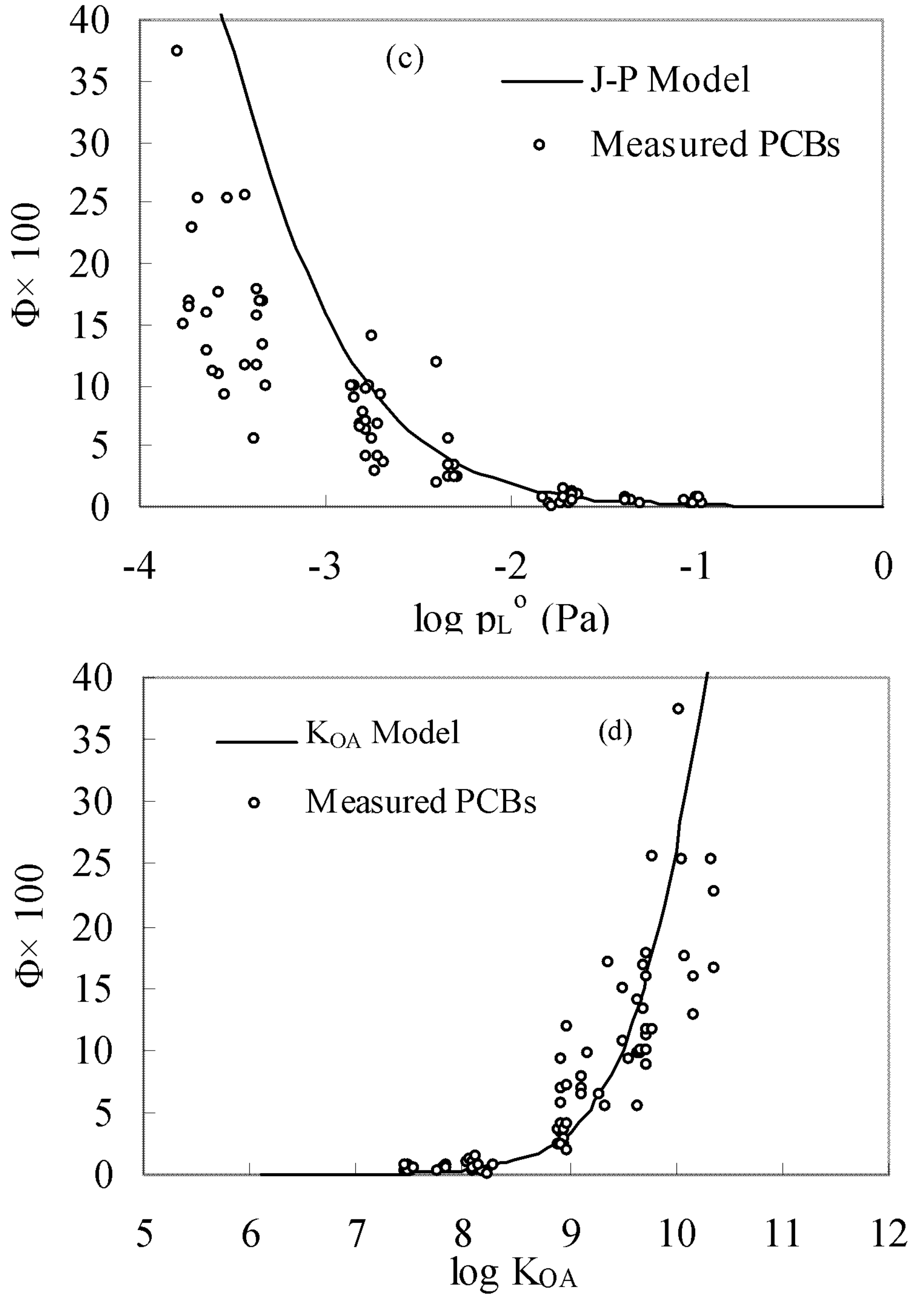


Figure 6.3. Comparison of predicted and measured particle percentage (Φ) for both PAHs and PCBs (a) J-P model for PAHs, (b) K_{OA} model for PAHs, (c) J-P model for PCBs and (d) K_{OA} model for PCBs

Sorption. However, in Figure 3(d), the K_{OA} absorption model using the measured f_{OM} value fits the PCB data much better under tropical climate conditions with uniform ambient temperature and high humidity, indicating the f_{OM} might vary much in different areas. Hence, it is preferable to use the field-measured organic matter fraction, f_{OM}, of urban aerosols instead of the standard values (0.1~0.2) while studying the gas-particle partitioning of SVOCs. In addition, high RH in this coastal area might be another important factor for this absorption predominance since the K_P values of organo-chlorine compounds have been reported to be dominated by OM absorption for RH between 50% and 90% while adsorption to EC becomes the major sorption mechanism under dry conditions (RH<40%) (Götz et al., 2007). Based on the investigations made in this study, it appears that the sorption of nonpolar chemicals, for example, PCBs to "environmental lipids" such as aerosols with high OM content might be dominated by absorption into organic matter under the warm and humid conditions in this highly industrialized area.

In this study, the f_{OM} values were obtained by applying a conversion factor of 1.5 from OC to OM, which was adopted from literature. It is known that this factor varies with organic aerosol chemical composition. Therefore, error analysis has been applied on the sensitivity of calculated K_p corresponding to the uncertainty in this conversion factor. To assess the random errors in the calculation of K_p, a propagation of error analysis (Shoemaker et al., 1996) was performed. Uncertainty in the f_{OM} has been assumed to be 40%, the random error in the K_p was below 1%, ranging between 6.7% - 59%, and below 2% for LMW PAHs, HMW PAHs, and PCBs, respectively. The error analysis showed that the uncertainty of f_{OM} is especially critical to the estimation of K_p by Equation 2.10 for HMW PAHs.

6.3.4. Influence of Soot Carbon

Soot particles are byproducts of the combustion of liquid and gaseous fuels and their production depends strongly on the ratio of carbon to oxygen during combustion (Mader and Pankow, 2001). PAHs are formed concurrently with soot particles and also play an important role in soot formation and particle growth (Seinfeld and Pandis, 1998). It has been found that PAHs have a high affinity for carbonaceous materials as discerned from adsorption experiments with carbon black and activated carbon (Walters and Luthy, 1984). The overall gas-particle partition coefficient that accounts for both the organic matter and the soot phases is given by the following equation (Lohmann and Lammel, 2004):

$$K_P = 10^{-12}(K_{OA} f_{OM} MW_{OCT} \zeta_{OCT} / (\rho_{OCT} MW_{OM} \zeta_{OM}) + f_{EC} a_{EC} / (a_{soot} \rho_{EC}) K_{soot-air}) \qquad (6.5)$$

where f_{EC} is the fraction of atmospheric elemental carbon; α_{EC} is the specific surface area of elemental carbon and α_{soot} is the specific surface area of diesel soot derived from NIST SRM 1650; ρ_{BC} is the density of EC and 1 kg L^{-1} has often been assumed (Dachs and Eisenreich, 2000; Lohmann and Lammel, 2004); as assumed, the EC can be used as a surrogate for the soot carbon (Dachs and Eisenreich, 2000), $\alpha_{EC}/\alpha_{soot}$ is equal to one; $K_{soot\text{-}air}$ is the partitioning coefficient between soot and air. To avoid the controversy surrounding the calculation of $K_{soot\text{-}air}$ from soot-water and air-water partition coefficients, this study employed the approach used by Van Noort (2003) that estimated $K_{soot\text{-}air}$ from the subcooled liquid vapor pressure (p_L^o) and the soot specific area (α_{soot}):

$$\log K_{soot-air} = -0.85 \log p_L{}^o + 8.94 - \log(998 / \alpha_{soot}) \qquad (6.6)$$

100 m^2 g^{-1} was used for α_{soot} (Bucheli and Gustafsson, 2000); the temperature-dependent vapor pressures were corrected as stated above.

The overall K_p values, derived from Equation 6.5, are presented for most of the PAHs characterized in this study and compared with measured K_p values and those predicted from the K_{OA} model (Figure 6.4). As discussed above, the K_{OA}-derived K_p generally under-predicted the observed K_p values; while the combined K_{OA}-$K_{soot\text{-}air}$ model predicted results which more closely matched the observed ones. The gas-particle partitioning coefficients increased by the combined model for LMW PAHs by 0.8~1.8 log units. However, for HMW PAHs, these coefficients increased only by 0.3~0.6 log unit. In this case, the gas-particle partitioning process of lighter PAHs was more affected by soot carbon than their heavier counterparts, indicating the lesser influence of soot sorption on predominantly particle-bound PAHs. A similar result was reported by Prevedouros et al. (2008) for solid-air and solid-water partitioning of PAHs with inclusion of soot sorption. These results differ from those of Helm and Bidleman (2005) who found that the combined K_{OA}-$K_{soot\text{-}air}$ model over-predicted the measured K_p by 0.3-1.4 log units and 1.2-2.2 log units for penta CN-50 and hexa CN-66-67, respectively. However, the partitioning behavior of PAHs in this area is consistent with observations in the literature (Dachs and Eisenreich, 2000; Fernández et al., 2002; Lohmann and Lammel, 2004) that elemental or soot carbon dominates in the partitioning of PAHs to aerosols in some circumstances, especially for LMW compounds.

The f_{EC} (7~24% with average of 17 ± 5 %) used for Equation 6.5 was directly determined from measurements of field samples, and the particulate elemental carbon ranged from 1.0 to 10.2 $\mu g\ m^{-3}$ with an average of 5.8 ± 3.1 $\mu g\ m^{-3}$. The elemental carbon concentrations (f_{EC} values) in this study are relatively higher than those in other urban areas such as Baltimore (1.3 $\mu g\ m^{-3}$, 2.8%) (Brunciak et al., 2001), Chesapeake

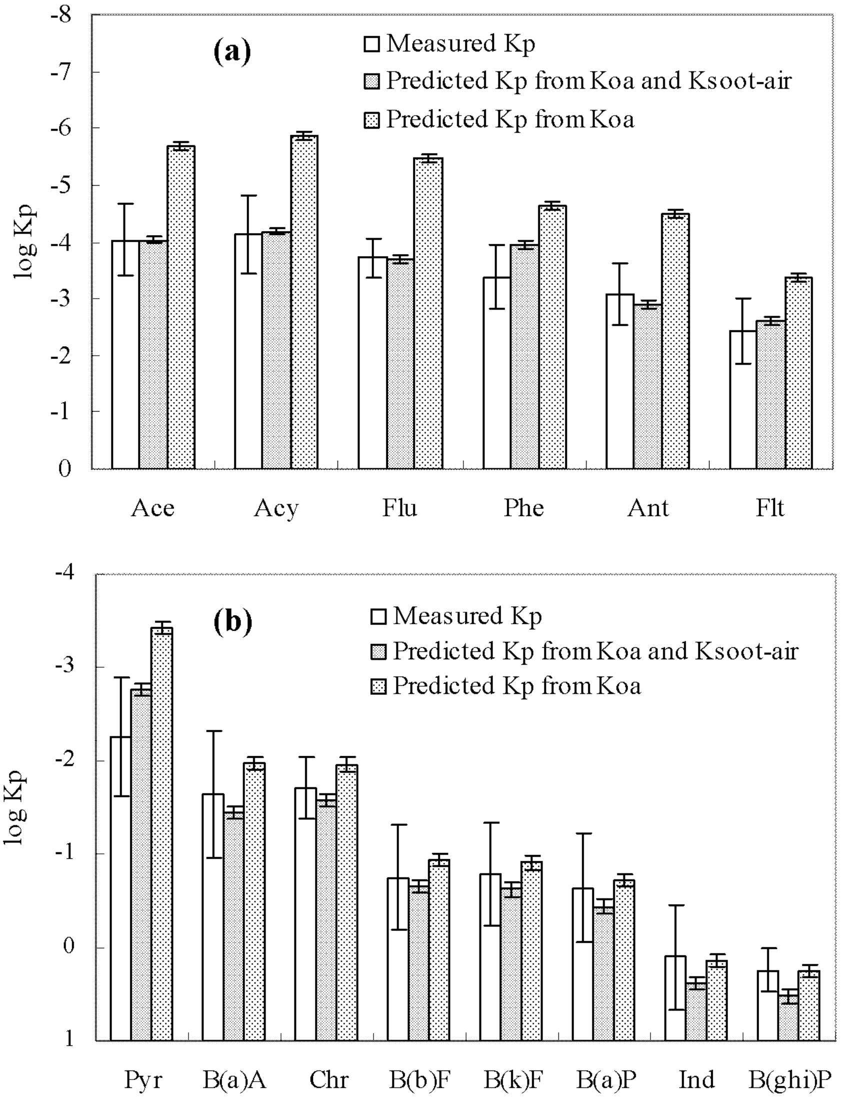


Figure 6.4. Measured and predicted values of K_p (μg m^{-3}) by K_{OA} and the combined K_{OA} + $K_{soot\text{-}air}$ models in Singapore for PAHs (a) LMW PAHs, and (b) HMW PAH

Bay (1.5 µg m^{-3}, 5.1%) (Dachs and Eisenreich, 2000), Washington (2.2 ± 0.1%) and Chur urban aerosols in USA (2.1± 0.1%) (Roth et al., 2005b).

Low OC/EC ratios indicate anthropogenic influences on aerosol composition due to the larger fraction of combustion derived elemental carbon (Kuhlbusch et al., 1998; Brunciak et al., 2001). The mean ratio of OC/EC was 2.2 ± 0.3 in Singapore, much lower than that of 10.3 for rural Meadview, AZ, USA (Turpin et al., 2000). Since OC/EC ratios are source specific (Kadowaki, 1990; Kuhlbusch et al., 1998), the low variability in this study might suggest constant source profiles of both OC and EC, indicative of primary aerosols.

The high content of EC of local aerosol might be associated with the human activities taking place in and around Singapore (heavy traffic emissions, dense oil/gas industries, biomass burning impacts in SEA, etc.). Consequently, once the fresh PAHs have been emitted into atmosphere, diffusion from particles surface coated with thick elemental carbon may be the limiting mass transfer rate for the gas-particle partitioning of PAHs (Strommen and Kamens, 1999; Dachs and Eisenreich, 2000).

6.4. Conclusion

In summary, this research was conducted to study the gas/particle partitioning of PAHs and PCBs in Singapore, a highly industrialized city in SEA. Mean PAHs and PCBs concentrations (gas + particle) were 33.4 ± 11.2 ng m^{-3} and 31.7 ± 18.9 ng m^{-3}, respectively; about 80% of these SVOCs were distributed in the gaseous phase in the urban atmosphere of Singapore. The relationship between log K_p and log p_L^o of SVOCs here shows that the partitioning of SVOCs between particle and gas phases is well correlated with the sub-cooled liquid vapor pressure (p_L^o), but slopes were still statistically shallower than -1 (the theoretical value at equilibrium) under such a tropical climate. K_{OA} is able to explain gas/particle partitioning of PCBs, while the combined K_{OA}-$K_{soot\text{-}air}$ is more suitable to describe that of PAHs, especially for LMW compounds.

Chapter 7. Precipitation Scavenging of Semi-volatile Organic Compounds (SVOCs) In A Tropical Area

7.1. Introduction

Precipitation scavenging represents a significant fraction of the total atmospheric deposition of SVOCs, which has been shown to be an important intermediate transport pathway for the removal of aerosol-bound as well as gaseous SVOCs from the atmosphere via in-cloud and below-cloud scavenging (Offenberg and Baker, 2002; Sahu et al., 2004; Simcik, 2004). In the past decades, several studies have been conducted to investigate the mechanisms of precipitation scavenging through the form of rain, snow and even fog (Ligocki et al., 1985a, b; Offenberg and Baker, 2002; Collett et al., 2008). Previous studies have shown the importance of particulate-bound SVOCs via physical processes controlled by size, number density, aerosol solubility along with meteorological conditions and microphysics, etc (Poster and Baker, 1996b; Sun et al., 2006). Gas-phase SVOCs are washed out by falling rain simultaneously. The transfer of SVOCs into the water droplets of precipitation could be determined by Henry's law under equilibrium condition (Ligocki et al., 1985a, b). However, the measured washout ratio of gaseous SVOCs has often been found to be higher than expected based on Henry's law partitioning for fog, cloud or rain water (Capel et al., 1991; Murray and Andren, 1992; Aneja, 1993). It was concluded that this apparent supersaturation resulted from sub-micron sized particles (< 0.5 μm) that were not filtered out of the rainwater so that concentration of dissolved organic pollutants was over-estimated (Leuenberger et al., 1988; Poster and Baker, 1996a). The deviation of the observational data from the predictions by Henry’s law has also been attributed to the adsorption of gaseous phase SVOCs to the surface of raindrops (Goss, 1994; Simcik, 2004).

Although a considerable number of studies as those mentioned above have been conducted to assess the precipitation scavenging of SVOCs across wide geographical areas, little work has been done to determine the precipitation scavenging of SVOCs in SEA. This region is considered to be an important source of SVOCs, which circulate globally through a process known ‘grasshopper effect’ by which they are transported to both temperate and polar regions, far away from the original sources, via a repeated (and often a seasonal) process of evaporation and deposit (Iwata et al., 1994; Semeena and Lammel, 2005). It is therefore important to determine the precipitation (rain) scavenging of the two classes of semi-volatile organic pollutants in order to make a better assessment of their fate and transfer in a multi-media environment. In this study, a comprehensive mathematical model has been developed by taking into consideration various factors such as particle scavenging, dissolution (Henry’s law), and surface adsorption and used to gain insights into the wet removal of PAHs and OCPs in the tropical environment. The total, particle and gas scavenging ratios by precipitation have been calculated based on the extensive dataset containing the distribution of PAHs and OCPs in gas- and particulate-phases and also in rainwater. Relative contributions of various factors mentioned above to precipitation scavenging were evaluated. In addition, effects of chemical properties of PAHs and OCPs and meteorological conditions on scavenging processes were also investigated.

7.2. Theoretical Basis

The washout ratios of SVOCs can be described by standard equation as described in Equation 2.12. W_T, W_P *and* W_G are unitless total, particle and gas scavenging ratios, respectively. W_P is defined as $C_{R,P}/C_{A,P}$ where $C_{R,P}$ is the particle-associated concentration in rainwater (ng m^{-3} rainwater collected) and $C_{A,P}$ is the particulate concentration of SVOCs in air (ng m^{-3} air collected). Likewise, W_G is defined as $C_{R,D}$ $/C_{A,G}$ where $C_{R,D}$ is the dissolved concentration of SVOCs (ng m^{-3} rain) and $C_{A,G}$ is the gaseous concentration in air (ng m^{-3} air); at equilibrium the gas scavenging ratio W_G equals the dimensionless Henry's law constant H' ($1/H' = RT/H$) where R is the universal gas constant (8.21×10^{-5} m^3 atm K^{-1}mol^{-1}), T is the temperature (K), and H is the Henry's law constant (atm m^{-3} mol^{-1}). Φ, fraction of SVOCs associated with particles, could be obtained through the field measurement or calculated by Junge-Pankow model or $K_{\text{octanol-air}}$ (octanol-air partitioning coefficient) model.

Due to the observational evidence that submicron particles (non-filter retained particles) do exist in the filtrate and influence the partitioning behavior of SVOCs in rainwater (Gschwend and Wu, 1985; Glotfelty et al., 1990), Equation 2.12 was modified considering the scavenging of submicron particles (Poster and Baker, 1996a):

$$W_T = \frac{C_R}{C_A} = W_{P,F}\,\phi_{P,F} + W_{P,NF}\phi_{P,NF} + W_G(1 - \phi_T) \tag{7.1}$$

where $\phi_{P,F}$, $\phi_{P,NF}$, ϕ_T are the fractions of SVOCs bound to filter-retained particles, nonfilter-retained particles, and all particles. Offenberg and Baker (2002) then expanded Equation 7.2 to include a broader range of particle sizes:

$$W_T = \frac{C_R}{C_A} = W_{P,1}\,\phi_{P,1} + W_{P,2}\phi_{P,2} + \ldots + W_{P,X}\phi_{P,X} + W_G(1 - \phi_T) \tag{7.2}$$

where each particle size's washout ratio is exhibited and all sizes are summed to the total aforementioned W_P as in Equation 7.1.

Although the supersaturation could occur when the gaseous SVOCs from the air enter into rainwater partly due to the colloidal association of submicron particles as stated above, an additional mechanism requiring consideration is the adsorption of gaseous phase SVOCs to the surface to raindrops, either to an organic film or pure water (Simcik, 2004). Thus, Simcik (2004) redefined the gas-phase scavenging equation as follows:

$$W_G = W_{G,DISS} + W_{G,ADS} = \frac{1}{H'} + K_{ia}\frac{6\times1000}{d_R} \tag{7.3}$$

where $W_{G,DISS}$ refers to the washout by dissolution involving only Henry's law partitioning to the rainwater, defined as $1/H'$; $W_{G,ADS}$ is the equilibrium adsorption gas-phase scavenging ratio; K_{ia} the air-water interface adsorption constant, used to describe the adsorption of SVOCs to the surface of water, defined as mass of SVOCs per m^2 of water surface / mass of SVOCs per m^3 of air; d_R is the diameter of raindrops (mm) and 1000 converts millimeters to meters.

Therefore, a comprehensive model could be developed with inclusion of all the factors affecting the total scavenging ratio of SVOCs as given below:

$$W_T = \frac{C_R}{C_A} = \sum_{i=1}^{X} W_{P,i}\phi_{P,i} + \frac{(1-\phi_T)}{H'} + K_{ia}\frac{6000}{d_R}(1-\phi_T) \tag{7.4}$$

Offenberg and Baker (2002) explained the difficulty in the application of Equation 7.2 due to the complexities in attributing particles of various sizes to their original atmospheric diameter and inefficiencies in separating small particles in rainwater. As such, Equation 7.4 could be simplified as Equation 7.5 and applied to assess the precipitation scavenging of SVOCs on those samples collected in Singapore.

$$W_T = \frac{C_R}{C_A} = W_P \phi_T + \frac{(1-\phi_T)}{H'} + K_{ia} \frac{6000}{d_R}(1-\phi_T) \quad (7.5)$$

where the parameters such as ϕ_T, H' and K_{ia} can all be correlated to the supercooled liquid saturated vapor pressure, P_L^0 (Pa), of the compound of interest; the diameter of the raindrop, d_R, could be derived from the rain drop size distribution (DSD) described by log-normal distributions (Feingold and Levin, 1986; Mircea et al., 2000), or gamma distributions (Cerro et al., 1998).

In this study, Henry's law constants were corrected to the ambient air temperatures during this sampling period by using published enthalpy and entropy data for PAHs (Hulscher et al., 1992; Bamford et al., 1999b; Monte et al., 2006) and correlation between H and temperature for OCPs (Sahsuvar et al., 2003; Cetin, 2006). Equilibrium gas scavenging ratios ($W_{G,DISS}$) were calculated for PAHs and OCPs using the temperature-corrected Henry's law constants.

For the calculation of $W_{G,ADS}$, rain droplet size distributions have to be considered because they determine the geometric mean diameter d_{gm} (mm) and the total number of raindrops for a rain event by precipitation rate p_o (mm h^{-1}) (Calderón et al., 2008). In this study, the log-normal distribution (Mircea et al., 2000) was chosen to derive d_{gm} which could be used as d_R for Equation 7.3.

$$d_{gm} = 0.72 p_o^{0.23} \ (mm) \quad (7.6)$$

The relationship among water-to-air equilibrium constant K_{aw}, air to interfacial water equilibrium constant K_{ia} and interfacial water to bulk water equilibrium constant K_{iw} is as follows:

$$K_{ia} = K_{iw} / K_{aw} \quad (7.7)$$

where K_{aw} is equal to dimensionless Henry’s law constant, K_{iw} could be calculated by using Equation 7.8 (Kelly et al., 2004):

$$\log K_{iw} = -8.58 - 0.769 \log\left(\frac{P_L^{\,o}}{P^o} \mathrm{e}^{\frac{-\Delta G_S^o(aq)}{RT}} \right) \tag{7.8}$$

where $P_L^{\,o}$ is the supercooled vapor pressure of compounds of interest, corrected to the ambient temperature during this sampling period by using the correlations between $P_L^{\,o}$ and temperature for SVOCs (Hinckley and Bidleman, 1990; Lei et al., 2002; Xiao et al., 2004; Odabasi et al., 2006); P^o is the pressure (24.45 atm) of an ideal gas at 1 molar concentration and 298 K; $\Delta G_S^o(aq)$ is the standard-state aqueous free energy of solvation of compounds of interest, of which the data calculated by Thompson et al. (2003) could be used for SVOCs.

7.3. Experimental

7.3.1. Sampling

Both the atmospheric and precipitation samples were collected simultaneously at the National University of Singapore (NUS) atmospheric research station. Altogether, 37 atmospheric samples (pairs of PUF and filter) and 32 rainwater samples were collected and studied under different weather conditions between June 2007 and May 2008 to get a fundamental understanding of precipitation scavenging processes in the tropical environment; gaseous and particulate-phase distributions of PAHs and OCPs were also measured concurrently. Particulate and gaseous SVOCs in the atmosphere were collected separately using a medium volume sampler (Model: TE-1000PUF, Tisch Environmental, Inc. USA) by drawing air through 4" circular quartz microfiber filters (Whatman, Tisch

Environmental, Inc. USA) and polyurethane foam plugs (PUF, TE-1012, Tisch Environmental, Inc. USA) in series at ca.250 L min^{-1}. The rainwater samples were collected by an automated wet-dry sampler (Model US-330, Ogasawara Keiki Seisakusho, Tokyo, Japan), which collects only rainwater with no interference from dust fall, as described in Section 3.2. All rainwater samples were stored in an internal refrigerator at 4^{o}C by the automated sampler immediately after a rain event. The rainwater samples were collected from the field site within 24 hours after each rain event. After collection, rainwater samples were filtered with pre-cleaned (heated at 450 ^{o}C for 24 h) Whatman GF/F filters (0.7 μm, 47mm i.d.). The actual volume of each sample collected was measured and recorded after filtration. Before and after filtration, GF/F filters were conditioned in a dry box under the same condition as for quartz filters, and then weighed to calculate the mass of suspended particles. The relevant meteorological parameters (air temperature, total rainfall, etc.) were obtained as described in Section 3.2.4.

7.3.2. Sample Preparation and Analysis

Prior to extraction, surrogate compounds were added to all samples. Water filters, aerosol filters, PUF samples and all water samples were extracted separately as described in Section 5.2.2. All extracts were evaporated, cleaned using silica gel (for PAHs) or florisil (for OCPs) columns, then evaporated and finally blown by gentle nitrogen stream, and reduced to 50 μL with internal standards for PAHs and OCPs, respectively, and kept in sealed vials at -20^{o}C prior to GC-MS analysis. All extracts were then kept in sealed vials at -20^{o}C prior to GC-MS analysis. Sample analysis was conducted using a GC-MS (Shimadzu QP2010, Japan), as described in Section 3.4.6.

7.3.3. Quality Control

The analytical quality was guaranteed by the same protocol as described in Section 5.2.3.

7.4. Results and Discussion

7.4.1. SVOCs in Air and Rainwater

Table 7.1 shows the concentration range together with mean concentrations and corresponding standard deviations for the SVOCs measured in this study from June 2007 to May 2008. In ambient air the concentration of total PAHs varied from 15.9 to 484.8 ng m^{-3} with the mean concentration of 128.1 ± 123.6 ng m^{-3} and that of OCPs in the range of 77.7-1655.9 pg m^{-3} with the mean concentration of 692.8 ± 370.2 pg m^{-3}. In rainwater, the mean concentrations of PAHs, BHCs and DDTs were 1185.5 ± 587.9 ng L^{-1}, 72.2 ± 130.9 ng L^{-1} and 13.5 ± 32.8 ng L^{-1}, respectively. The lower molecular weight (LMW) PAHs were more prominent in rainwater as compared to those higher molecular weight (HMW) PAHs (those with five and six benzene rings) and BHCs were also present in rainwater in relatively larger amounts than DDTs. The same dataset was used for precipitation scavenging study as in Chapter 5 and discussion on occurrence of SVOCs in both air and rainwater could be referred in Section 5.3.2.

Table 7.1. Concentration of SVOCs in air (gas + particulate) and rainwater (dissolved + particulate) for precipitation scavenging study

Compound	Air		Rainwater	
	Range	Mean ± S.D.	Range	Mean ± S.D.
PAHs	ng m^{-3}		ng l^{-1}	
Naph	2.6-44.2	6.9 ± 8.8	59.4-780.2	400.1 ± 190.5
Acy	0.8-3.7	1.1 ± 1.1	1.3-71.5	21.9 ± 18.1
Ace	0.7-2.9	0.8 ± 0.7	3.3-759.7	145.7 ± 362.8
Flu	1.2-24.6	2.7 ± 4.5	10.8-72.3	38.5 ± 16.9
Phe	5.3-98.5	27.7 ± 27.9	65.3-262.8	257.2 ± 191.8
Ant	5.1-72.2	4.7 ± 12.2	1.1-181.0	31.4 ± 41.5
Flt	3.2-58.4	37.3 ± 41.6	12.8-237.7	68.4 ± 68.6
Pyr	4.3-41.9	33.8 ± 37.3	9.5-302.5	66.1 ± 82.1
B(a)A	9.0-61.4	4.6 ± 11.9	2.7-56.1	18.6 ± 15.7
Chry	2.1-17.2	4.1 ± 4.9	2.3-132.8	47.6 ± 34.4
B(b)F	1.3-6.6	1.9 ± 1.8	1.1-123.5	58.4 ± 36.7
B(k)F	0.3-1.9	0.4 ± 0.5	0.4-21.2	5.9 ± 5.7
B(a)P	0.4-2.2	0.5 ± 0.5	0.3-19.3	3.1 ± 3.8
Ind	0.2-2.4	0.6 ± 0.7	0.2-9.3	3.6 ± 2.9
DB(ah)A	0.1-1.4	0.2 ± 0.3	0.1-21.1	7.3 ± 7.6
B(ghi)P	0.2-2.5	0.7 ± 0.7	1.6-73.4	11.7 ± 14.2
∑PAHs	15.9-484.8	128.1 ± 123.6	21.5-3122.3	1185.5 ± 587.9
OCPs	pg m^{-3}		ng l^{-1}	
α-BHC	24.3-673.3	278.3 ± 180.5	1.1-21.7	4.0 ± 8.9
β-BHC	16.2-565.0	208.5 ± 162.8	7.1-43.0	17.2 ± 21.0
γ-BHC	14.9-487.9	81.8 ± 96.2	1.1-34.5	7.1 ± 16.0
δ-BHC	12.6-280.8	72.5 ± 62.5	3.1-72.2	43.8 ± 57.2
∑ BHCs	43.8-1564.7	641.0 ± 357.6	14.7-183.2	72.2 ± 130.9
4,4'-DDD	0.5-18.2	6.2 ± 4.9	0.9-12.9	4.4 ± 9.8
4,4'-DDE	0.9-13.5	4.4 ± 3.3	0.2-17.1	6.0 ± 8.3
4,4'-DDT	8.6-101.2	41.2 ± 25	1.5-47.4	12.5 ± 32.6
∑ DDTs	11.4-125.9	51.7 ± 30.6	2.34-75.6	13.5 ± 32.
∑ OCPs	77.7-1655.9	692.8 ± 370.2	15.6-248.8	85.7 ± 141.2

7.4.2. Total Scavenging Ratios of SVOCs

Particle fractions based on the field measurements and total scavenging ratios (particle + gas) for all PAHs and OCPs are summarized in Table 7.2. Total scavenging ratios (W_T based on Equation 7.5) vary among the individual SVOCs ranging from (8.3 ± 5.1) × 10^4 (β-BHC) to (1.2 ± 0.4) × 10^6 (Chry), comparable to those reported from Chesapeake Bay region, USA (W_T: 10^3~10^6 for PAHs) (Dickhut and Gustafson, 1995), Lake Michigan, USA (WT: 10^2~10^7 for PAHs) (Offenberg and Baker, 2002) and Mumbai, India (W_T: 4.43 × 10^3~1.36 × 10^8 for PAHs) (Sahu et al., 2004); however, it has to be noted that the different sampling environments such as rural or urban areas must affect the pollutant compositions and levels of aerosols, which therefore may affect the observed values and could be one of the reasons of variations of scavenging ratios from literatures mentioned above. Generally the total scavenging ratios (W_T) tended to be greater for less volatile compounds i.e., HMW PAHs compared to LMW PAHs; similarly, the W_T of OCPs also increased with the decreasing of volatility of these compounds.

Table 7.2. Particle fraction and scavenging ratios of SVOCs

Compound	$\phi\times100$	W_P	$W_{G,DISS}$	$W_{G,ADS}$	W_T
	Mean (S.D.)[a]		Mean (S.D.)		Mean (S.D.)
Naph	0.6 (0.9)	2.7 (1.5)×10^{7}	24.3 (9.7)	0.2 (1.8)	1.6 (1.2)×10^{5}
Acy	1.2 (1.4)	1.4 (0.5)×10^{7}	1.4 (0.6)×10^{2}	2.2 (2.9)	1.7 (1.9)×10^{5}
Ace	5.0 (2.8)	5.5 (1.1)×10^{6}	1.2 (0.8)×10^{2}	1.6 (3.1)	2.8 (1.7)×10^{5}
Flu	3.4 (2.6)	4.7 (2.4)×10^{6}	2.6 (2.2)×10^{2}	5.3 (6.1)	1.6 (0.6)×10^{5}
Phe	2.8 (2.2)	4.3 (1.3)×10^{6}	7.1 (3.1)×10^{2}	21.4 (10.6)	1.2 (0.5)×10^{5}
Ant	3.5 (2.3)	4.0 (2.7)×10^{6}	8.2 (4.2)×10^{2}	24.7 (10.1)	1.4 (0.4)×10^{5}
Flt	2.7 (3.7)	3.3 (1.6)×10^{6}	1.6 (1.2)×10^{2}	2.6 (3.4)	8.9 (4.3)×10^{4}
Pyr	25.5 (12.7)	2.1 (0.7)×10^{6}	7.2 (1.3)×10^{3}	2.6 (1.2)×10^{3}	5.4 (3.8)×10^{5}
B(a)A	54.2 (9.6)	1.2 (0.3)×10^{6}	9.6 (1.9)×10^{3}	7.7 (2.5)×10^{4}	6.9 (1.6)×10^{5}
Chry	60.4 (11.3)	2.0 (0.9)×10^{6}	1.0 (0.4)×10^{4}	9.2 (1.6)×10^{3}	1.2 (0.4)×10^{6}
B(b)F	85.7 (11.2)	8.9 (3.6)×10^{5}	3.4 (1.4)×10^{3}	1.9 (0.5)×10^{4}	7.7 (2.3)×10^{5}
B(k)F	84.4 (9.2)	7.8 (2.1)×10^{5}	2.2 (0.8)×10^{3}	2.5 (1.6)×10^{4}	6.6 (3.9)×10^{5}
B(a)P	89.3 (6.7)	8.2 (2.7)×10^{5}	2.8 (1.9)×10^{4}	5.6 (1.1)×10^{4}	7.4 (4.8)×10^{5}
Ind	94.6 (7.9)	2.5 (0.6)×10^{5}	2.6 (2.5)×10^{3}	6.9 (2.7)×10^{5}	2.7 (1.5)×10^{5}
B(ghi)P	97.3 (8.3)	1.8 (0.4)×10^{5}	3.3 (1.7)×10^{3}	9.8 (1.0)×10^{5}	2.0 (1.2)×10^{5}
α-BHC	1.7 (1.2)	5.6 (2.6)×10^{6}	4.0 (0.8)×10^{2}	8.8 (6.8)	9.6 (4.3)×10^{4}
β-BHC	2.4 (2.7)	3.4 (1.4)×10^{6}	8.7 (0.6)×10^{2}	29.5 (23.2)	8.3 (5.1)×10^{4}
γ-BHC	4.2 (2.6)	3.7 (0.8)×10^{6}	8.6 (0.9)×10^{2}	28.3 (18.2)	1.6 (0.7)×10^{5}
4,4'-DDD	12.4 (6.9)	3.1 (1.3)×10^{6}	4.1 (2.9)×10^{3}	5.6 (2.9)×10^{2}	3.9 (2.3)×10^{5}
4,4'-DDE	18.5 (13.2)	2.4 (0.5)×10^{6}	5.6 (0.4)×10^{3}	1.6 (1.3)×10^{3}	4.5 (2.2)×10^{5}
4,4'-DDT	26.6 (10.3)	1.8 (0.6)×10^{6}	7.9 (2.0)×10^{3}	2.8 (2.2)×10^{3}	4.9 (1.9)×10^{5}

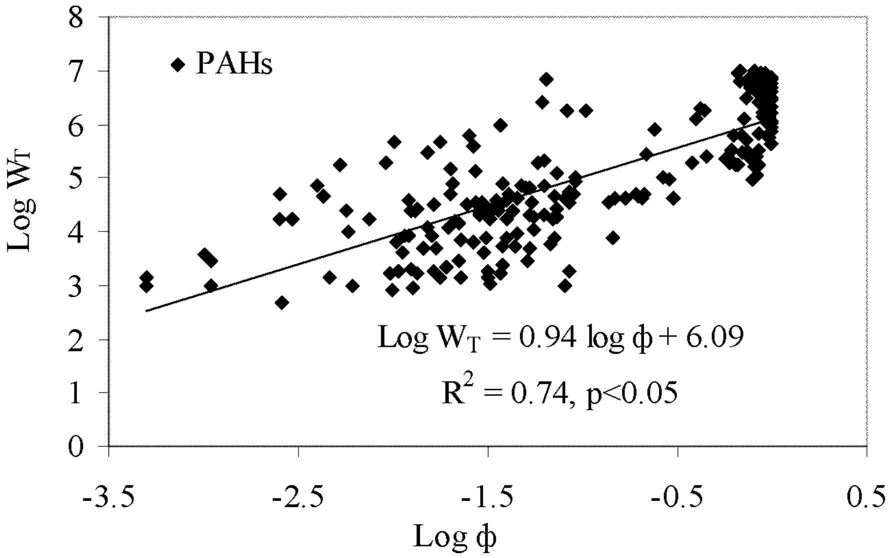
a. Standard deviation (S.D.) in brackets

Equation 7.5 applied in this study illustrates that W_T is highly dependent on the particle fraction (ϕ) of SVOCs in the atmosphere. Therefore, correlations between W_T and ϕ were evaluated and plotted in Figure 7.1. Among all sampling events, moderate correlations were observed between log W_T and log ϕ for both PAHs (R^2=0.74) and OCPs (R^2=0.62). The slope for PAHs (0.94) was relatively higher than that for OCPs (0.82). This observation might be attributed by the HMW PAHs, the precipitation scavenging removal of which was more effective compared to LMW PAHs and OCPs of interest in this study (see W_T in Table 2). Franz and Eisenreich (1998) reported a slope of 0.89 for precipitation scavenging of PAHs. The similarity of these slopes may suggest that the inherent process of scavenging of PAHs from the atmosphere may be reasonably consistent even under different meteorological conditions and concentration gradients (Van Ry et al., 2000).

Scavenging ratios are frequently used to estimate probable SVOCs concentration in rain, especially in the context of mass balance modeling (Blanchard et al., 2006; Van Ry, et al., 2000). From a modeling perspective, it is useful to assess W_T of an atmospheric contaminant from some measurable air parameters such as ϕ. In this article, the following regression equations based on extensive field measurements are recommended to estimate W_T from ϕ for SEA region:

PAHs: $\log W_T = 0.94 \log \phi + 6.09$ ($R^2=0.74$, $p<0.05$) (7.9)

OCPs: $\log W_T = 0.82 \log \phi + 6.34$ ($R^2=0.62$, $p<0.05$) (7.10)



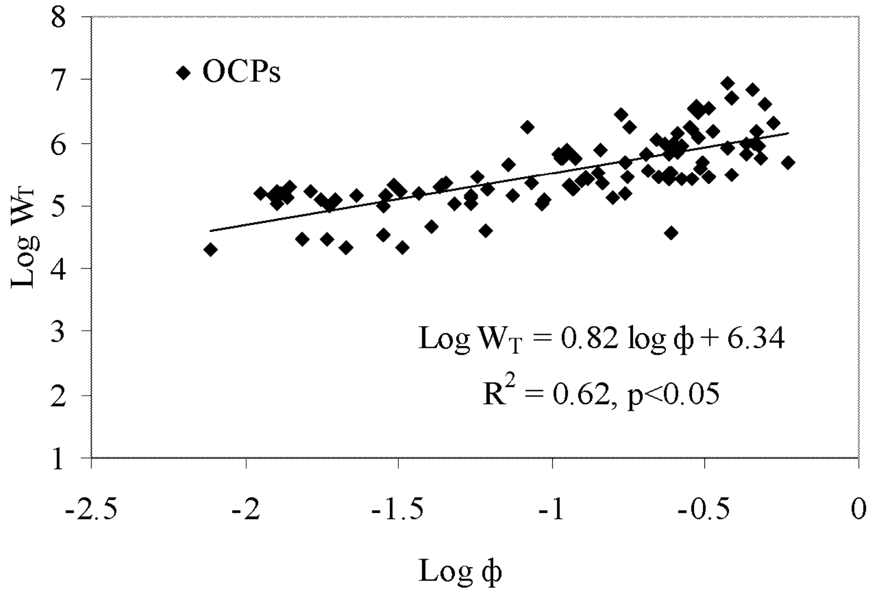


Figure 7.1. Correlations between total scavenging ratios (Log W_T) and the air particle fraction (Log ϕ) (a) PAHs and (b) OCPs

7.4.3. Particle Scavenging vs. Gas Scavenging

Particle scavenging is highly complicated and is determined by several factors such as meteorology, size of particles and rain droplets, etc (Offenberg and Baker, 2002). On the other hand, gas scavenging ratios (W_G) are suggested to be near equilibrium as predicted by temperature-corrected H values ($W_{G,DISS}$, operationally truly dissolved phase), or are supersaturated due to the adsorption of contaminants to the rain droplets ($W_{G,\ ADS}$) or even the presence of nonfilterable submicron particles in the filtrate. Therefore, the relative importance of gas and particle scavenging on the total removal of contaminants from the atmosphere depends on the relative magnitudes of the terms $W_P\phi$, $W_{G,DISS}(1-\phi)$ (equivalent to $(1-\phi)/H'$)and $W_{G,ADS}(1-\phi)$ (equivalent to $K_{ia}\,6000/[d_R(1-\phi)]$) as shown in Table 7.3.

From Table 7.3 it can be seen that particle scavenging is an extremely efficient mechanism of removal of SVOCs from the atmosphere based on the thorough investigation conducted in this study; gas scavenging ($W_{G,DISS}(1-\phi)+W_{G,ADS}(1-\phi)$) has much less relative importance as a scavenging mechanism for all individual compounds of interest. The particle scavenging contribution to the total scavenging accounts for 86-99% for PAHs and 98-99% for OCPs. This observation that the efficiencies of washouts from the atmosphere by precipitation are much higher in the particulate phase than in the gas phase is also supported by those reported by Ogura et al. (2001), Offenberg and Baker (2002) and Sahu et al. (2004).

Table 7.3.Relative contributions of particulate, gaseous (Henry's law) and adsorbed individual SVOCs scavenging to the total scavenging process

Fraction % Compound	$W_P\Phi/W_T$	$W_{G,DISS}(1-\Phi)/W_T$	$W_{G,ADS}(1-\Phi)/W_T$
Naph	99.99	0.01	0.00
Acy	99.92	0.08	0.00
Ace	99.96	0.04	0.00
Flu	99.84	0.16	0.00
Phe	99.41	0.57	0.02
Ant	99.42	0.56	0.02
Flt	99.82	0.17	0.00
Pyr	98.65	0.99	0.36
B(a)A	94.25	0.64	5.11
Chry	99.37	0.33	0.30
B(b)F	99.58	0.06	0.35
B(k)F	99.36	0.05	0.59
B(a)P	98.79	0.40	0.81
Ind	86.35	0.05	13.60
B(ghi)P	86.84	0.04	13.12
α-BHC	99.58	0.41	0.01
β-BHC	98.94	1.03	0.03
γ-BHC	99.46	0.53	0.02
4,4'-DDD	98.95	0.92	0.13
4,4'-DDE	98.70	1.01	0.29
4,4'-DDT	98.39	1.19	0.42

From Table 7.2, it can also be seen that particle scavenging ratios W_P for the more volatile compounds were generally larger than those for less volatile ones. For PAHs, W_P range from 1.8×10^5 to 2.7×10^7, relatively more scattered compared to those for OCPs which vary only within the same magnitude. The reason might be because the group of PAHs has more variability in volatility than that of OCPs of interest does (see Φ in Table 7.2). On the other hand, the variation of both W_T and W_P is smaller compared to those mentioned above (Dickhut and Gustafson, 1995; Offenberg and Baker, 2002; Sahu et al., 2004). The particle fraction, Φ, of SVOCs in the atmosphere described by Junge-Pankow adsorption model or $K_{\text{octanol-air}}$ absorption model which is a function of P_L^o as affected by meteorological condition such as ambient temperature (Pankow, 1987; Harner and Bidleman, 1998). Since the particle scavenging by rain dominates wet deposition, the effect of the yearly uniform ambient temperature in this tropical area on gas/particle partitioning might reduce the variability of precipitation scavenging ratios. The larger W_T and W_P values found for more volatile compounds may be due to their preference to larger particles, that is, more volatile compounds exhibit a broader distribution and can redistribute onto larger particles via gas-particle partitioning, while the less volatile compounds tend to stay on the particles on which they were emitted (Poster and Baker, 1996b; Sahu et al., 2004); the below-cloud scavenging rates increase with particle size because the collision efficiency of particle-droplet encounter increase with increasing particle diameters (Sahu et al., 2004; Calderón et al., 2008). These observations indicated the consistency of the increase in W_T and W_P for compounds associated with larger particles with the particle scavenging mechanism.

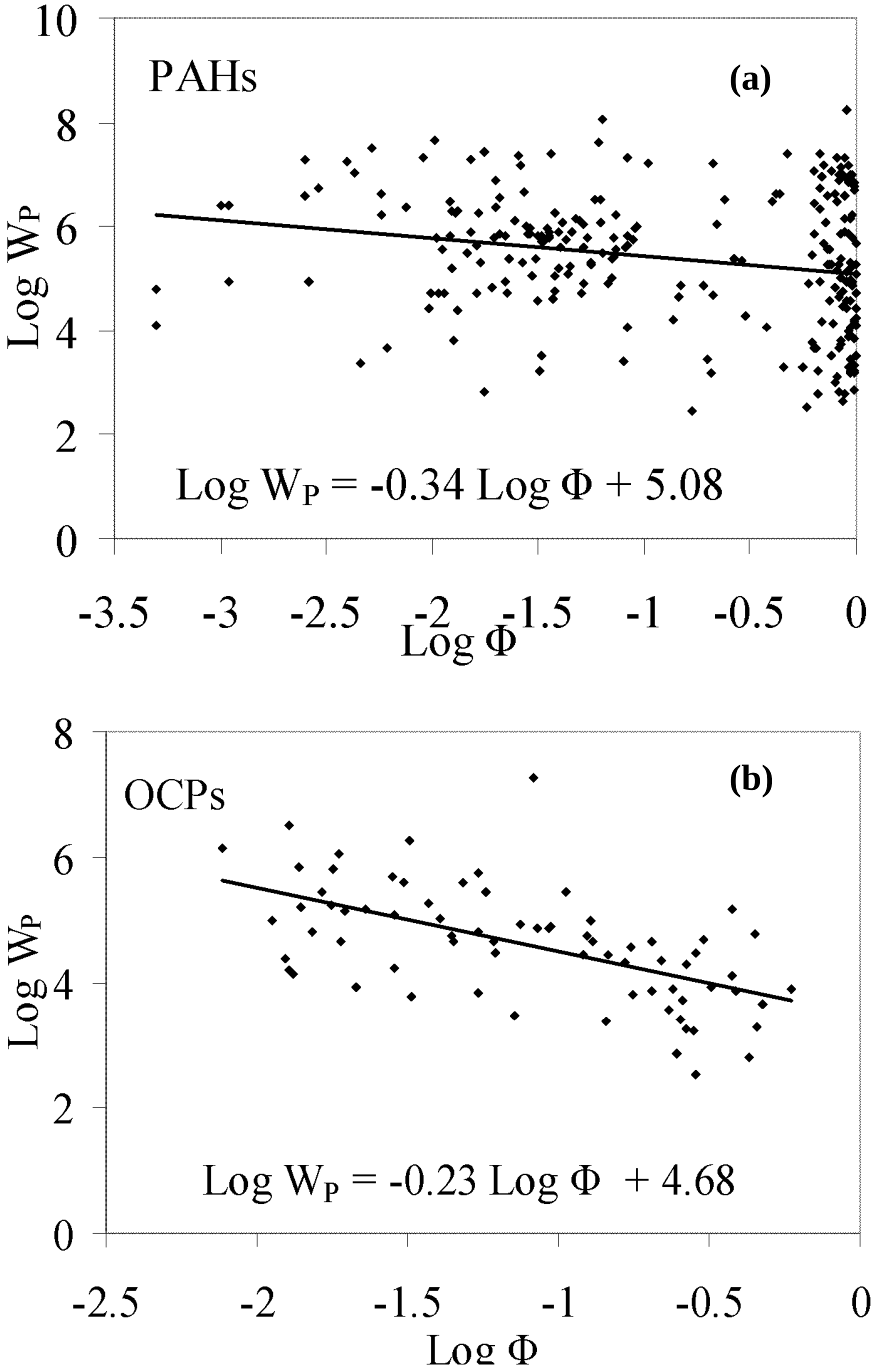


Figure 7.2. Relationship between particle scavenging ratio W_P and particle fraction Φ, supercooled vapor pressure P_L^o and rainfall intensity p_o (a) PAHs: $\log W_P$ vs. $\log\Phi$ (b) PCBs: $\log W_P$ vs. $\log\Phi$ (c) PAHs: $\log W_P$ vs. $\log P_L^o$ (d) PCBs: $\log W_P$ vs. $\log P_L^o$ (e) PAHs: $\log W_P$ vs. $\log p_o$, and (f) PCBs: $\log W_P$ vs. $\log p_o$

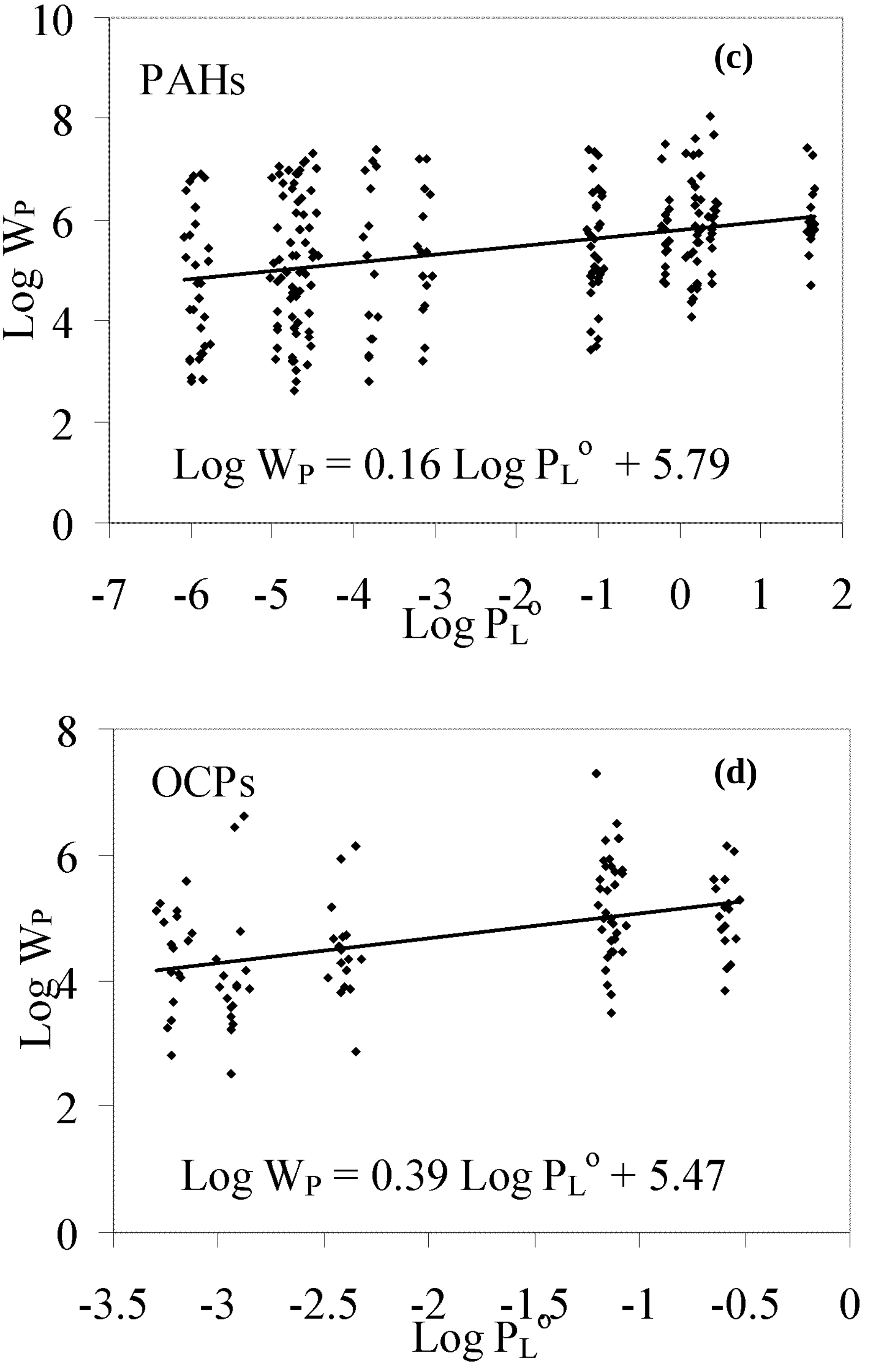


Figure 7.2. Relationship between particle scavenging ratio W_P and particle fraction Φ, supercooled vapor pressure P_L^o and rainfall intensity p_o (a) PAHs: logW_P vs.logΦ (b) PCBs: logW_P vs.logΦ (c) PAHs: logW_P vs.log P_L^o (d) PCBs: logW_P vs.log P_L^o (e) PAHs: logW_P vs.log p_o, and (f) PCBs: logW_P vs.log p_o

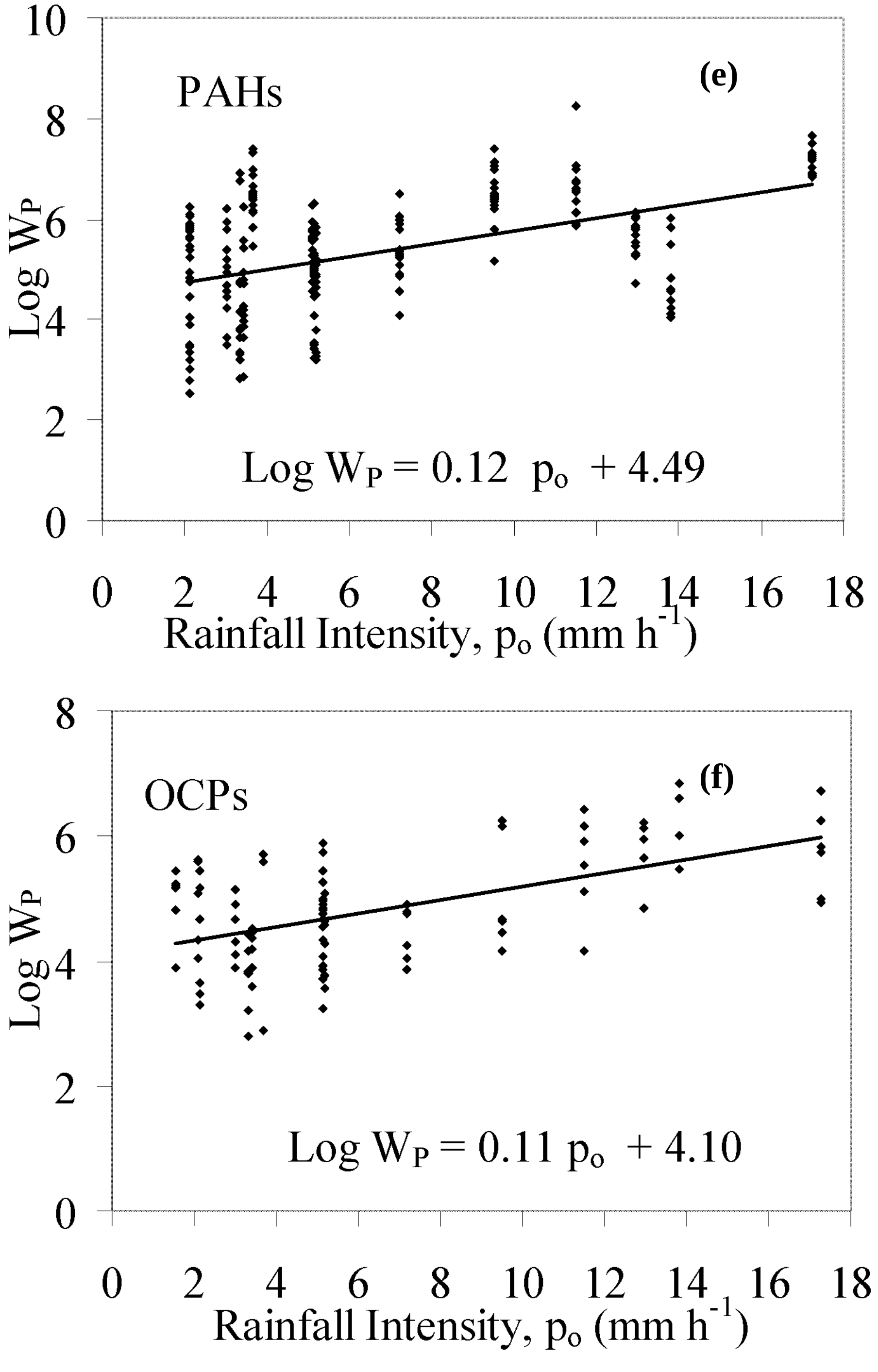


Figure 7.2. Relationship between particle scavenging ratio W_P and particle fraction Φ, supercooled vapor pressure P_L^o and rainfall intensity p_o (a) PAHs: $\log W_P$ vs.$\log\Phi$ (b) PCBs: $\log W_P$ vs.$\log\Phi$ (c) PAHs: $\log W_P$ vs.$\log P_L^o$ (d) PCBs: $\log W_P$ vs.$\log P_L^o$ (e) PAHs: $\log W_P$ vs.$\log p_o$, and (f) PCBs: $\log W_P$ vs.$\log p_o$

Relationships between particle fraction (Φ), supercooled vapor pressure (P_L^o), rainfall intensity Φ, and W_P have been investigated as shown in Figure 7.2 and the correlations for all data were of significance ($p<0.05$). It can be observed that particle scavenging decreased with particle fraction because the relationships for both PAHs and OCPs were with shallow negative slopes. The latter suggests that the particle scavenging by rain is less efficient for higher molecular weight SVOCs, which in the ambient atmosphere prefer to distribute into submicron particles. This observation is supported by the reports published by Poster and Baker (1996b) and Franz and Eisenreich (1998). A similar behavior was shown by the relationship between log W_P and log P_L^o. Although the slopes were slightly positive, particle scavenging increased with P_L^o, implying that lower molecular weight SVOCs with more volatility may have been associated with larger particles that were scavenged more efficiently as stated above. In addition, W_P and p_o were positively correlated, signifying an increased efficiency for particle scavenging from the atmosphere with rainfall intensity. The role of other factors such as rain droplet size distributions and collision efficiency between particles and rain droplets for particle scavenging can not be disregarded (Seinfeld and Pandis, 1998). Theoretical analysis of the Marshall-Palmer rain droplet size distribution shows that the number of rain-droplets increases with increasing rain intensity (Marshal and Palmer, 1948), which might lead to more removal of particles through more collision interaction between rain droplets and particles.

Besides the abovementioned factors, some other factors might contribute to particle scavenging as well. Nucleation scavenging has been reported to be one of the dominant mechanisms by which particles, especially fine particles containing ammonium, sulphate and nitrate, can be incorporated as cloud condensation nuclei (CNN) into cloud droplets (Sievering et al., 1984; Perry and Hobbs, 1994). The capability of an aerosol to be CCN depends on the particle number concentration and size distribution of the particles as well as chemical composition and the mixing state (Martinsson et al., 1999). There is little information on the scavenging of organic compounds within cloud by nucleation but it cannot be ignored. The organic compounds, in particular, have to be investigated further in terms of the effects of surface active compounds, effect on the droplet nucleation process and possible contribution to their total particle scavenging. In-cloud scavenging collection mechanisms also include Brownian diffusion, directional interception, inertial impaction and electrical charge effects, all of which generally are affected by particle size distribution (Chate, 2005). Brownian diffusion is the main removal process for 0.01 ~ 0.5 μm particles while the particles in 0.5 ~ 2.0 μm are too large to have sufficient Brownian diffusivity and too small to get effectively collected by inertial impaction or directional interception (Laakso et al., 2003; Ma et al., 2004); in addition, the electrical force is one of the major effects for particles smaller than 1 μm (Jaward et al., 2005). In addition, the aerosol vertical profiles are quite important to rainwater concentrations by below-cloud scavenging (Gonçalves et al., 2000). The vertical distribution of aerosols partly depends on the position and strength of their sources. In general, the concentrations of aerosols (e.g. $PM_{2.5}$) decrease with height because most sources are at or close to ground level (Qi et al., 2000; Xu et al., 2006). The vertical profile is also strongly affected by the extent of the atmospheric boundary layer and meteorological conditions (Tao et al., 2007). Unfortunately, evolutions of aerosol particle size distribution as well as the vertical profile of aerosols at various heights were not investigated before and after rain events in this study. However, the contributions of electrical effects in collision efficiency combined with the Brownian diffusion, directional interception and inertial impaction have to be considered on in-cloud particle scavenging ratios and the below-cloud modeling coupled with different aerosol vertical profiles need to be explored in future research.

In Equation 7.5, the gas scavenging is modified to include SVOCs dissolution into bulk rainwater and adsorption to the surface of raindrops, both of which are strong functions of particle fraction Φ. Since Φ is highly dependent on supercooled vapor pressure and ambient temperature, a relationship between dissolution ($W_{G,DISS}$) or adsorption ($W_{G,ADS}$) might be expected as plotted in Figure 7.3. As supercooled vapor pressure decreased, the gas scavenging ratios for both adsorption and dissolution increased. From Table 7.2, it can be seen that $W_{G,DISS}$ ranges from ~20 to as high as 10^4, and the $W_{G,ADS}$ ranges from <1 to as high as 10^5. Since the slopes of log $W_{G,DISS}$ vs. log P_L^o and log $W_{G,ADS}$ vs. log P_L^o are different, both trends intersect as shown in Figure 7.3. At a supercooled vapor pressure of approximately $10^{-3.5}$~10^{-4} Pa, the relative importance shifted from dissolution dominated scavenging to adsorption dominated scavenging with decreasing of P_L^o. This observation was supported by the theoretical simulation of adsorption and dissolution scavenging for PAHs at assumed rainfall intensity (10 mm h^{-1}) and full range of particle fraction (Φ: 0~100%) (Simcik, 2004). SVOCs of interest with supercooled vapor pressures between $10^{-3.5}$ and 10^{-4} Pa used in this study mainly include PAHs with five or more aromatic rings. From Table 7.3, it can be observed that for B(b)F, B(k)F, B(a)P, Ind and B(ghi)P, the relative contributions of $W_{G,ADS}$ to W_T were more dominant than those of $W_{G,DISS}$ to W_T. In the case of Ind and B(ghi)P, their $W_{G,ADS}$

contribution to the total scavenging can account for ~13%. As mentioned above, this study cannot distinguish the contribution of nonfilterable submicron particles to the gas scavenging. Particle size distribution analysis might need to be considered in the future study.

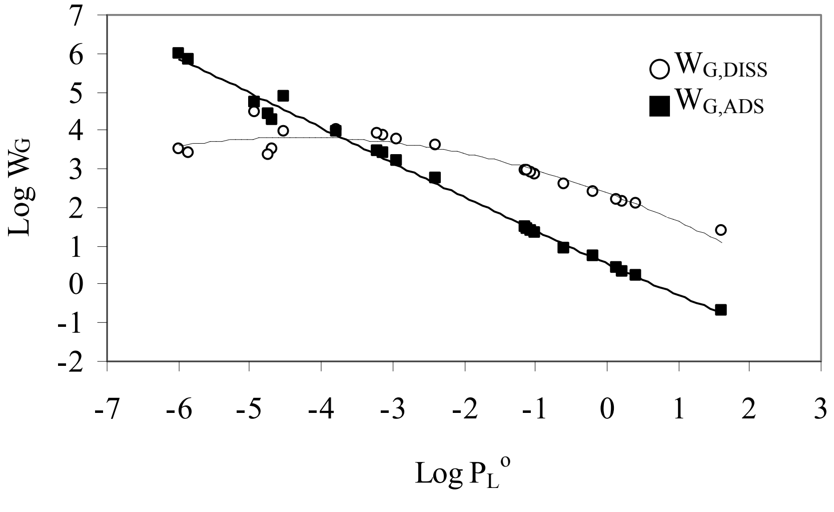


Figure 7.3. Relationship between $W_{G,DISS}$, $W_{G,ADS}$ and P_L^o

7.5. Conclusion

This research was conducted to study the precipitation scavenging of PAHs and OCPs in Singapore, a country representing SEA in this study. Particle scavenging was the dominant contributor to the total scavenging in precipitation. Both W_T and W_P tended to be greater for less volatile SVOCs, but the values were more invariant as compared to those reported in the literature, which was most likely due to the uniform ambient temperature prevailing throughout the year in Singapore. Relationships between particle fraction (Φ), supercooled vapor pressure (P_L^o), rainfall intensity, and W_P were investigated. Particle scavenging decreased with particle fraction Φ, but increased with supercooled vapor pressure. This observation suggests that the particle scavenging by rain is less efficient for higher molecular weight SVOCs, while lower molecular weight SVOCs with more volatility may have been associated with larger particles that were scavenged more efficiently. In addition, the meteorological factors such as rain droplet size distributions and collision efficiency between particles and rain droplets also have to be considered since W_P and rainfall intensity were positively correlated with significance of $p<0.05$. Other than the contribution from dissolved SVOCs in rainwater, the adsorption of SVOCs onto the surface of rain droplets might be dominant for those with suitable supercooled vapor pressure. For HMW PAHs such as Ind and B(ghi)P, their $W_{G,ADS}$ contribution to the total scavenging could be up to ~13%.

Chapter 8. The Exchange of SVOCs Across The Air-Sea Interface In Singapore's Coastal Environment

8.1. Introduction

Major urban and industrial centers increase loadings of SVOCs to proximate sea waters through riverine transport, atmospheric deposition via dry particle deposition, wet deposition, and air-sea gas exchange (McVeety and Hites, 1988; Bidleman et al., 1995; Park et al., 2002; Fang et al., 2008). In addition to acting as sinks for SVOCs, oceans can act as sources of SVOCs to coastal atmospheres and play important roles in the global biogeochemistry of SVOCs (Hinckley et al., 1991; Dachs et al., 1999; Dachs et al., 2002). Particle-sorbed SVOCs can settle to the ocean surface by dry particle deposition, a uni-directional advective transport process from the atmosphere to the water, the removal rate by which is a function of the physical and chemical properties of the aerosols and bound pollutants, meteorological conditions and surface characteristics (Wania et al., 1998; Odabasi et al., 1999). In addition, SVOCs are removed from the atmosphere and transported to the waters by precipitation scavenging of atmospheric vapors and particles, which are incorporated into the rain within or below the clouds. After SVOCs are deposited into the bulk seawater, water-column partitioning can affect the distribution of pollutants between the dissolved aqueous and the solid phases and eventually impact the fate of these compounds in oceans (Luo et al., 2004). Other than the abovementioned processes, air-sea exchange can make SVOCs diffuse across the air-sea interface; however, the sea surface microlayer (SML), a unique compartment at the air-sea boundary defined operationally as the upper millimeter (1 ~ 1000 μm) of the sea surface, has large storage capacity to delay the transport of SVOCs across the interface. This interfacial effect has been reported to be responsible for the enrichment of contaminants in the SML (Hardy, 1982; Chernyak et al., 1996; Wurl et al., 2006b).

Although a considerable number of studies as mentioned above have been conducted to assess the SVOCs exchange between air-sea interface across wide geographical areas, little work has been done to determine the significance of these fate and transfer processes of SVOCs in SEA. The tropical regions of Asia are considered to be an important source of many SVOCs (Iwata et al., 1994) as stated before. Those SVOCs with a log K_{OA} of around 8 and a log K_{OW} of around -2 such as PCBs and OCPs can be classified as "multi-hoppers", which can volatilize effectively after deposition to either soils and waters and thus undergo "multiple hops" to migrate from tropical to temperate and even polar regions (Wania, 2003). In SEA, Basheer et al. (2003) (Basheer et al., 2003b) have characterized persistent organic pollutants (PAHs, OCPs and PCBs) in Singapore's northeastern and southwestern coastlines surface seawater, but have not investigated any air-sea exchange processes mentioned above. Wurl et al. (Wurl et al., 2006c) have studied the distribution of organochlorine compounds (OCCs, including OCPs and PCBs) in the SML and subsurface water (SSW) in Hong Kong. Wurl and Obbard (Wurl et al., 2006b) have also determined the occurrence of OCs in the water column of shallow Johor Strait, between Malaysia and northeastern Singapore, by short-term measurements; in addition, Wurl et al. (2006a) have investigated the role of the SML in air-sea gas exchange of OCs by snapshot sampling in the same sites of Johor Straits. However, the latter work by Wurl et al. (2006a) was just focused on diffusive exchange, one of the air-sea exchange processes only.

In this study, dry particle deposition and wet deposition of selected SVOCs were investigated based on an extensive set of yearly data. In addition to receiving riverine inflows and direct emissions, coastal areas tend to experience higher atmospheric deposition than the rest of the oceans due to the proximity to the sources which are predominantly land-based. Singapore, a representative country of SEA, is a small but highly developed island with dense industrial parks in the Southwestern part, where the terrestrial sources affect the surrounding coasts. In this study, Singapore's Southern coastline was chosen during the Northeast monsoon season to evaluate if this coastal area is a sink or source for selected SVOCs via air-sea diffusive exchange as well as to investigate the SML enrichment effect. Furthermore, the water-column partitioning was assessed by a short-term measurement on different aquatic particulate matrices in the ocean.

8.2. Theoretical Approach

Atmospheric sampling was conducted in this study for each event in a consistent manner (24 ~ 48 h at 250 L min^{-1}); weekly concentrations of SVOCs in the atmosphere were computed as arithmetic mean values. In the case of rainwater, the rainfall amount for each event varied. Hence, those concentrations were calculated as volume-weighted mean (VWM) values.

Dry particulate and wet deposition flux can be calculated according to

$$F_{\text{dry}}(\mu\text{g m}^{-2}\text{ yr}^{-1}) = \sum_{i=1}^{12}(C_A^i \times V_d \times 2592) \qquad (8.1)$$

$$F_{\text{wet}}(\mu\text{g m}^{-2}\text{ yr}^{-1}) = \sum_{i=1}^{12}(C_{VWM}^i \times P_W^i \times 10^{-3}) \qquad (8.2)$$

where C_A^i, C_{VWM}^i are the monthly particulate concentration of pollutant in air (ng m^{-3}) and monthly total (dissolved plus particulate) concentration of pollutant in rain (ng L^{-1}), respectively; V_d is the deposition velocity (ms^{-1}) and P_W^i is the rainfall (mm) for sampling month (i). V_d at a particular vertical height is calculated as the inverse of the sum of a number of resistances (Seinfeld and Pandis, 2006) using the following equation.

$$V_d = \frac{1}{R_a + R_b + R_a R_b v_s} + v_s \tag{8.3}$$

where v_s is the gravitational settling velocity (a function of particle size, density, and viscosity), R_a is aerodynamic resistance refers to turbulent transport from the free atmosphere down to the receptor surface ($R_a = 9/[u\sigma_\theta^2]$, which is a function of wind speed, u and standard deviation of wind speed, σ_θ (Turner, 1986) and R_b is quasi laminar layer resistance, which is a function of particle size, Brownian diffusion, interception and impaction; R_b on water surface is given by van den Berg et al.(2000). Each R_a and R_b is site specific and determined to a large extent by atmospheric properties. Meteorological parameters such as ambient temperature (K) of 299.6 ~ 303.2, wind speed (m s^{-1}) of 1.1 ~ 3.6, and standard deviation of wind direction σ_θ (rad) of 0.13 ~ 0.78 were observed during the sampling period. In SEA air, a majority of aerosols observed in the size range of 0.1–20 μm by the optical counter was in the fine mode (less than 1 μm) (Kondo et al., 2004).

SVOCs in the water column partition into three phases: the truly dissolved phase, the particulate phase and the colloidal organic material (Totten et al., 2001). The truly dissolved and colloidal phases can be categorized as apparent dissolved phase, which refers to the non-filter retained fraction. The partitioning of SVOCs onto particulate and colloidal phases results in the removal of SVOCs from surface layers via gravitational settling and consequently reduces their volatilization rates (Wania et al., 1998). Based on the empirical estimation of sorption of hydrophobic pollutants onto natural sediments and soils (Karickhoff, 1981) and its application into water-column by Totten et al. (2001), the relationship between partition coefficient K_{OC} and K_{OW} can be derived as follows:

$$\log K_{OC} = \log(\frac{K_P}{f_{OC}}) = a \log K_{OW} + b \tag{8.4}$$

where K_{OC} equals partition coefficient K_P normalized by organic carbon fraction (f_{OC}) in particulate phase. K_P refers to the partitioning in the water column between the apparent dissolved and particulate phase (Totten et al., 2001), calculated as $C_P/(C_{d,a} \times \mathrm{TSM})$ (C_P: the concentration of SVOCs associated with the particulate phase; $C_{d,a}$: the concentration in the apparent dissolved phase; and TSM: the concentration of total suspended matter). K_{OW} (L kg^{-1}) was obtained from the best available experimental data and predictive models with careful evaluations (de Lima Ribeiro and Ferreira, 2003; Xiao et al., 2004; Shen and Wania, 2005; Zhou and Zhu, 2005; Lü et al., 2007). Since the temperature dependence of K_{OW} for selected SVOCs is not significant (Bahadur et al., 1997; Lei et al., 2000) and the temperature of seawater varied by no more than 4^{o}C in this study, K_{OW} has not been corrected for temperature.

To accommodate additional sorption to soot phase, Accardi-dey and Gschwend (2002) modified Gustafsson's model (Gustafsson et al., 1997) to yield a dual OC/BC model:

$$K_P = f_{OC} K_{OC} + f_{SC} K_{SC} C_{d,a}^{n-1} \tag{8.5}$$

where f_{SC}, K_{SC} are soot carbon fraction in particulate phase of seawater and soot-water partition coefficient, respectively, and n is Freundlich constant. If n = 1, this model assumes that soot-water partition was a linear isotherm, otherwise it is a nonlinear process. This model has been applied to multi media and especially the sediment-water (porewater) partitioning (Gustafsson et al., 1997; Cornelissen and Gustafsson, 2005; Prevedouros et al., 2008). Considering the similarity of distribution between sediment / water and between particulate/water in sea water column, Equation (8.5) can be reasonably applied to the latter process.

The apparent dissolved concentrations of SVOCs ($C_{d,a}$) is the sum of the truly dissolved (C_{truly}) and colloidal(C_{DOC}, DOC-dissolved organic carbon, mg L^{-1}) phases, onto both of which the fractions of SVOCs partitioned can be estimated as described in equation (8.5) by Totten et al.(2001) and 0Wurl et al., 2006a)

$$C_{d,a} = C_{truly} + C_{DOC} = C_{truly}(1 + K_{OW} \times DOC \times 10^{-7}) \quad (8.6)$$

A classical two-layer model, which has been previously applied to the air-sea exchange of SVOCs (Achman et al., 1993; Zhang et al., 2007; Li et al., 2009), assumes that the rate of gas transfer is controlled by the pollutant's ability to diffuse across the air layer and sea surface water on either side of the air-water interface. The molecular diffusivity of the pollutant, dependent on the amount of resistance encountered in the liquid and gas films, describes the rate of transfer while the concentration gradient drives the direction of transfer (Totten et al., 2001). The flux, F (ng m^{-2} day^{-1}), is calculated by Equation 2.15. A positive flux indicates net volatilization out of the seawater and a negative flux indicates net absorption into the seawater. The overall mass transfer coefficient (K_{OL}) comprises resistances to mass transfer across the air layer and the water layer, estimated by Equation 2.16.

The mass transfer coefficient $K_{a,comp}$ (cm s^{-1}) for a compound in air was calculated using the following equation (Schwarzenbach et al., 2003):

$$K_{a,comp} = K_{a,H_2O}(\frac{M_{H_2O}}{M_{comp}})^{-0.5\times 0.67} \tag{8.7}$$

where $K_{a,H_2O} = 0.2\times u_{10} + 0.3$ and M (g mol^{-1}) is molar mass of the compound. Wanninkhoff's quadratic equation (Wanninkhof, 1992) for the mass transfer coefficient K_w has been applied in a number of studies (Totten et al., 2001; Wanninkhof et al., 2004; Wurl et al., 2006a), but this relationship was a semi-empirical estimation with low correlation ($r^2 = 0.66$) only at steady winds. A more robust model was thus used in this study to calculate $K_{w,comp}$ (cm s^{-1}) for compounds of interest (Schwarzenbach et al., 2003):

$$K_{w,comp} = \begin{cases} 0.65\times 10^{-3}(\frac{Sc_{comp}}{600})^{-0.67} \text{ for } u_{10} \le 4.2\text{ms}^{-1}\text{(smooth surface regime)} \\ (0.79u_{10} - 2.68)\times 10^{-3}(\frac{Sc_{comp}}{600})^{-0.5} \text{ for } 4.2<u_{10} \le 13\text{ms}^{-1}\text{(rough surface regime)} \\ (1.64u_{10} - 13.69)\times 10^{-3}(\frac{Sc_{comp}}{600})^{-0.5} \text{ for } u_{10} > 13\text{ms}^{-1}\text{(breaking wave regime)} \end{cases} \tag{8.8}$$

where the Schmidt number, S_c, is the ratio of kinematic viscosity ν_{kin} (cm^2 s^{-1}) and diffusivity D (cm^2 s^{-1}) by $S_c = \nu_{\text{kin}}/D$. The kinematic viscosity of seawater is obtained using the method recommended by Chen et al. (1973). The diffusivities of compounds of interest in seawater were calculated using Equation (8.9) developed by Wilke and Chang (1955).

$$D = 7.4\times 10^{-8}\frac{(2.6M_{comp})^{0.5}T}{\eta V_{comp}^{0.6}} \tag{8.9}$$

where T is the average temperature during each sampling event, V_{comp} is the molar volume of compound investigated (Mackay et al., 1992, 1996) and η is equal to the kinematic viscosity of solution (in this case referring to seawater). The important parameters involved in the abovementioned equations are listed in Table 8.1.

Table 8.1. Relevant parameters used in this study (source indicated in the text)

Compound	log K_{OW}	$H'(\times 10^{-4})$	$K_{a,comp}$ (cm s^{-1})	D ($\times 10^{-5}$ cm^2 s^{-1})	$Sc_{comp}(\times 10^{-4})$	V_{comp} (cm^3 mol^{-1})	$K_{w,comp}(\times 10^{-5}$cm s$^{-1})$
Naph	3.37	1.28 ~ 1.48	0.99 ~ 1.96	1.95 ~ 2.00	4.46 ~ 4.72	169.8	3.49 ~ 3.62
Ace	3.92	79.5 ~ 88.8	1.06 ~ 2.08	2.12 ~ 2.17	4.12 ~ 4.36	173.0	3.68 ~ 3.82
Flu	4.18	45.4 ~ 50.4	1.09 ~ 2.13	2.09 ~ 2.14	4.17 ~ 4.42	188.0	3.65 ~ 3.79
Phe	4.57	19.7 ~ 21.7	1.11 ~ 2.19	2.09 ~ 2.14	4.17 ~ 4.41	199.0	3.65 ~ 3.79
Ant	4.54	23.9 ~ 26.5	1.11 ~ 2.19	2.10 ~ 2.16	4.14 ~ 4.39	197.0	3.67 ~ 3.81
Flt	5.22	8.17 ~ 8.84	1.16 ~ 2.28	2.11 ~ 2.17	4.12 ~ 4.37	217.3	3.68 ~ 3.82
Pyr	5.18	8.12 ~ 8.90	1.16 ~ 2.28	2.13 ~ 2.19	4.09 ~ 4.33	214.0	3.70 ~ 3.84
B(a)A	5.91	5.42 ~ 6.20	1.21 ~ 2.37	2.07 ~ 2.13	4.20 ~ 4.45	248.0	3.63 ~ 3.77
Chry	5.86	2.58 ~ 3.20	1.21 ~ 2.37	2.06 ~ 2.11	4.23 ~ 4.48	251.0	3.61 ~ 3.75
B(b)F	5.75	0.29 ~ 0.32	1.25 ~ 2.46	2.08 ~ 2.13	4.19 ~ 4.44	268.9	3.63 ~ 3.78
B(k)F	6.00	0.26 ~ 0.29	1.25 ~ 2.46	2.08 ~ 2.13	4.19 ~ 4.44	268.9	3.63 ~ 3.78
B(a)P	6.04	0.20 ~ 0.22	1.25 ~ 2.46	2.11 ~ 2.16	4.14 ~ 4.38	263.0	3.67 ~ 3.81
Ind	6.54	0.15 ~ 0.16	1.29 ~ 2.53	2.14 ~ 2.19	4.08 ~ 4.32	277.0 [a]	3.70 ~ 3.85
B(ghi)P	6.50	0.14 ~ 0.15	1.29 ~ 2.53	2.14 ~ 2.19	4.08 ~ 4.32	277.0	3.70 ~ 3.85
α-HCH	3.82	1.47 ~ 1.61	1.31 ~ 2.57	2.37 ~ 2.43	3.68 ~ 3.90	243.6	3.97 ~ 4.12
β-HCH	3.80	0.17 ~ 0.19	1.31 ~ 2.57	2.37 ~ 2.43	3.68 ~ 3.90	243.6	3.97 ~ 4.12
γ-HCH	3.72	1.10 ~ 1.15	1.31 ~ 2.57	2.37 ~ 2.43	3.68 ~ 3.90	243.6	3.97 ~ 4.12
4,4'-DDD	6.33	4.80 ~ 5.22	1.35 ~ 2.66	2.14 ~ 2.19	4.08 ~ 4.32	312.6	3.70 ~ 3.85
4,4'-DDE	6.93	29.0 ~ 33.1	1.35 ~ 2.65	2.16 ~ 2.22	4.03 ~ 4.27	305.2	3.73 ~ 3.88
4,4'-DDT	6.39	5.05 ~ 5.73	1.40 ~ 2.75	2.16 ~ 2.22	4.03 ~ 4.26	333.5	3.73 ~ 3.88

a. The molar volume of Ind is not available yet to the best of our knowledge. Due to its similarity of molecular structure and weight to B(ghi)P, it is reasonably presumed that the molar volume of B(ghi)P could be used for Ind.

8.3. Experimental

8.3.1. Sampling

Dry and Wet Deposition Sampling. For the study of depositional fluxes of selected SVOCs, both the atmospheric and precipitation samples were collected simultaneously at the National University of Singapore (NUS) atmospheric research station. Altogether, 37 atmospheric particulate samples and 32 rainwater samples were collected under different weather conditions between June 2007 and May 2008. More details are shown in Section 5.2.1. The SSW and SML samples were collected as described in Section 3.2. The relevant meteorological parameters (air temperature, rainfall, wind speed, etc.) were obtained from an automated NUS weather station located in the same building where the atmospheric station is located. This meteorological station has been in operation to provide real-time meteorological data to the NUS community. After collection, all water samples were filtered with pre-cleaned (heated at 450 ^{o}C for 24 h) Whatman GF/F filters (0.7 µm, 47mm i.d.). The actual volume of each sample collected was measured and recorded after filtration. Before and after filtration, GF/F filters were conditioned in a dry box (maintained at 22^{o}C and 30% RH), and then weighed to calculate the mass of suspended particles.

8.3.2. Sample Preparation and Analysis

Prior to extraction, surrogate compounds were added to all samples. Water filters, aerosol filters and PUF samples were extracted separately by Dionex ASE 200 All filtered water samples were extracted on the same day as collection via liquid-liquid extraction using 3 × 50 ml DCM aliquots in a two liter separatory funnel (EPA method 3510C). Details of extraction for both air and water samples are shown in Section 5.2.2. After purification by the protocol in Section 4.2.3, all extracts were finally blown by gentle nitrogen stream and reduced to 50 µL with internal standards, and kept in sealed vials at -20°C prior to GC-MS analysis. Chemical analysis was performed using a GC-MS (Shimadzu QP2010, Japan) equipped with an auto injector (Shimadzu AOC-5000 , Japan) and a DB-5 fused silica capillary column (30m length and 0.25mm I.D; film thickness 0.25µm) with purified helium as carrier gas. Organic carbon (OC) and elemental carbon (EC) were determined as described in Section 3.4.7.

8.3.3. Quality Control

The analytical quality was guaranteed by the same protocol as described in Section 5.2.3.

8.4. Results and Discussion

8.4.1. Dry and Wet Depositions of SVOCs

Both dry and wet depositions were estimated on an annual basis based on the monthly concentrations of SVOCs as shown in Figure 8.1 using Equations (8.1) and (8.2), respectively. V_d (0.003 m s^{-1}) was not derived from sampling with dry deposition plates in this study but calculated using Equation (8.3), which is also in the range of 0.001-0.01 m s^{-1} for PAHs, OCPs and PCBs as reported in the literature (Eisenreich et al., 1981; McVeety and Hites, 1988; Hoff et al., 1996). Concentrations of PCBs in both dissolved and particulate phases of all rainwater samples were below the limits of detection in this study.

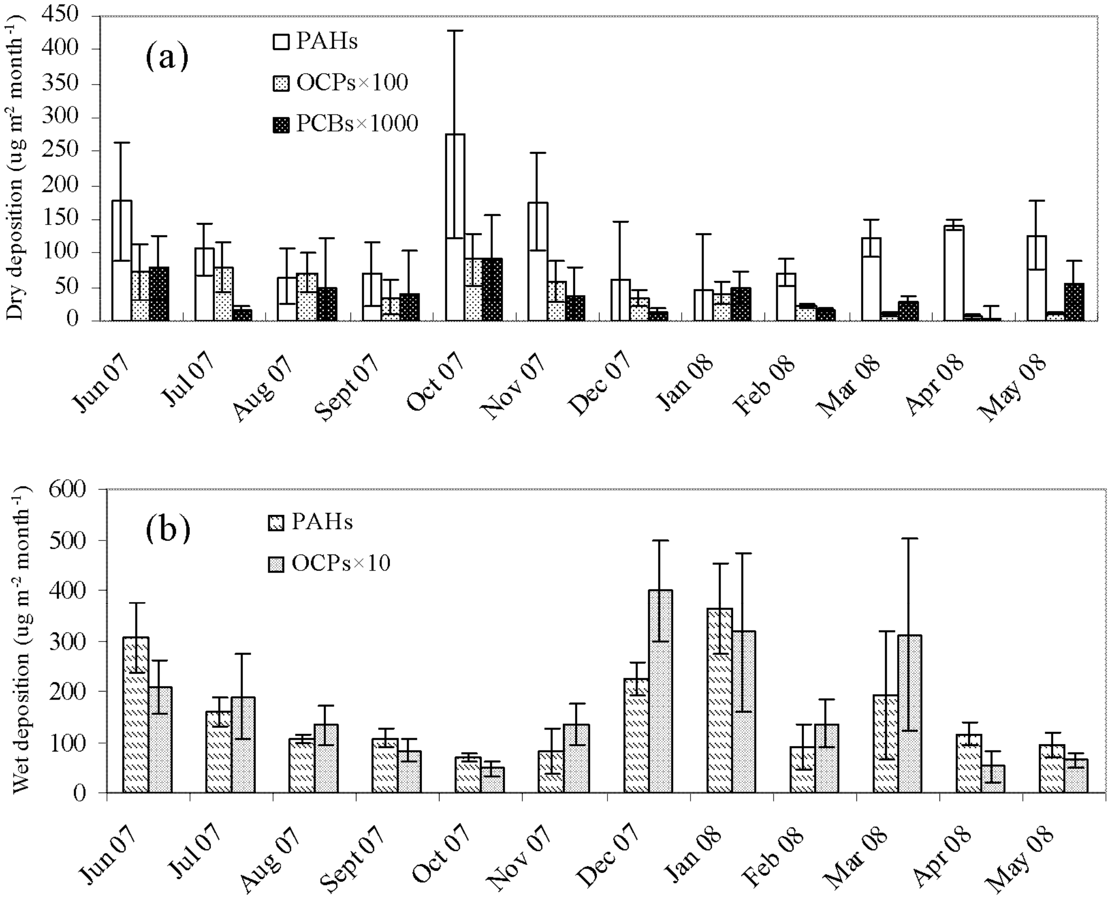


Figure 8.1. Seasonal variation in both dry and wet depositions of selected SVOCs between Jun 2007 and May 2008 (a) dry deposition and (b) wet deposition

In Singapore's coastal area, the monthly dry deposition fluxes for PAHs, OCPs and PCBs were in the range of 46.0 ~ 275.6 μg m^{-2} $month^{-1}$, 60.7 ~ 906.1 ng m^{-2} $month^{-1}$ and 3.1 ~ 93.1 ng m^{-2} $month^{-1}$, respectively. A significant increase in the dry deposition fluxes of most investigated pollutants was observed during the pre-NE monsoon (Oct-Nov 2007) as shown in Figure 8.1(a), especially for PAHs. In this area, periodical monsoon winds could assist in dispersing aerosol particles during NE and SW monsoon seasons; the lighter winds during the pre-monsoon seasons (Apr-May and Oct-Nov) might strengthen the accumulation of particulate SVOCs. The monthly wet deposition flux for PAHs and OCPs ranged from 70.0 ~ 363.5 μg m^{-2} $month^{-1}$ and 4.7 ~ 39.9 μg m^{-2} $month^{-1}$, respectively. High wet deposition fluxes were observed from Dec 2007 to Mar 2008 for both PAHs and OCPs (Figure 8.1(a) in sharp contrast to the low dry deposition fluxes during the same period (Figure 8.1(b)). The rainy season during the period from Dec 2007 to Mar 2008 might have contributed to pronounced wet scavenging of aerosols containing SVOCs from the atmosphere. On the other hand, the peak in the dry deposition flux observed during Oct and Nov 2007 was likely be due to the typical low wind speeds during pre-monsoon seasons and the relatively less rainfall.

Table 8.2. Annual Mean Atmospheric Fluxes of selected SVOCs

Compound	Dry deposition flux (Mean ± S.D.)	Wet deposition flux (Mean ± S.D.)	Air-sea exchange (Mean ± S.D.)
PAHs	μg m^{-2} y^{-1}	μg m^{-2} y^{-1}	ng m^{-2} day^{-1}
Naph	65.3 ± 56.0	850.7 ± 428.8	-1608.4 ± 869.6
Acy	28.0 ± 13.1	62.9 ± 60.9	-
Ace	32.7 ± 20.5	102.7 ± 106.5	-36.5 ± 8.0
Flu	19.6 ± 10.3	82.6 ± 46.0	-27.3 ± 22.0
Phe	130.6 ± 78.4	554.4 ± 395.6	-457.7 ± 489.7
Ant	19.6 ± 14.0	68.1 ± 91.4	-210.6 ± 53.9
Flt	112.0 ± 88.6	165.6 ± 133.2	-394.5 ± 283.5
Pyr	140.0 ± 13.1	162.2 ± 156.5	-674.4 ± 359.3
B(a)A	62.5 ± 52.3	47.2 ± 39.2	-192.2 ± 137.4
Chry	121.3 ± 102.6	108.3 ± 95.2	-825.1 ± 669.0
B(b)F	102.6 ± 78.4	142.1 ± 107.7	-383.1 ± 131.7
B(k)F	62.5 ± 72.8	12.4 ± 14.3	-405.6 ± 386.8
B(a)P	75.6 ± 89.6	7.7 ± 6.8	-630.0 ± 563.0
Ind	149.3 ± 168.0	11.9 ± 7.8	-21.7 ± 20.2
DB(ah)A	39.2 ± 67.2	27.1 ± 15.9	-
B(ghi)P	168.0 ± 121.3	42.2 ± 39.4	-17.0 ± 6.6
Σ PAHs	1328.8 ± 961.1	6,667.1 ± 1,745.2	-5884.0 ± 4040.7
OCPs	ng m^{-2} y^{-1}	μg m^{-2} y^{-1}	ng m^{-2} day^{-1}
α-HCH	1847.6 ± 1136.8	45.5 ± 36.8	-73.7 ± 31.3
β-HCH	625.2 ± 439.8	8.7 ± 8.8	-44.4 ± 37.8
γ-HCH	1390.3 ± 711.5	24.4 ± 19.1	-48.4 ± 30.4
δ-HCH	933.1 ± 765.2	5.8 ± 4.6	-
4,4'-DDD	54.1 ± 74.6	0.45 ± 0.44	-2.9 ± 1.8
4,4'-DDE	41.1 ± 35.5	0.71 ± 0.89	-0.74 ± 0.67
4,4'-DDT	531.9 ± 261.3	1.9 ± 1.4	-1.1 ± 0.85
Σ OCPs	5421.4 ± 3426.7	87.5 ± 72.1	-171.3 ± 102.8
PCBs	ng m^{-2} y^{-1}		
CB 17+18	58.8 ± 34.5	-	-
CB 28+31	14.9 ± 10.9	-	-
CB 33	9.3 ± 2.8	-	-
CB 52+49	34.5 ± 22.4	-	-
CB 44	31.7 ± 22.4	-	-
CB 74	29.9 ± 23.3	-	-
CB 70+95	17.7 ± 13.1	-	-
CB 101	39.2 ± 46.7	-	-
CB 99	24.3 ± 16.8	-	-
CB 110	34.5 ± 28.0	-	-
CB 149	168.0 ± 105.3	-	-
CB 138+158	121.3 ± 79.3	-	-
CB 171	63.5 ± 9.3	-	-
CB 177	43.9 ± 21.5	-	-
CB 180	51.3 ± 49.5	-	-
CB 183	72.8 ± 9.3	-	-
Σ PCBs	811.8 ± 578.3	-	-

The mean annual atmospheric fluxes of selected SVOCs are summarized in Table 8.2. Particulate dry deposition fluxes of $\sum_{16}$PAHs, $\sum_7$ OCPs and $\sum_{21}$ PCBs were 1328.8 ± 961.1 μg m^{-2} y^{-1}, 5421.4 ± 3426.7 ng m^{-2} y^{-1} and 811.8 ± 578.3 ng m^{-2} y^{-1}, respectively. The dry particulate deposition fluxes of $\sum_7$OCPs and $\sum_{21}$ PCBs were much lower than that of $\sum_{16}$-PAHs. This is most likely due to the local heavy PAH emissions into the atmosphere. In addition, the wet deposition fluxes of $\sum_{16}$PAHs and $\sum_7$ OCPs were 6,667.1 ± 1,745.2 and 87.5 ± 72.1 μg m^{-2} y^{-1}, respectively, which were much more dominant over their dry particulate deposition fluxes. However, it has to be noted that only particles were considered for dry deposition, but both particulate and dissolved phases were included for wet deposition in this study.

The profile of particulate $\sum_{16}$PAHs fluxes was dominated by B(ghi)P (12.8%), Ind (11.4%), Pyr (10.7%), Phe (10.0%) and Chry (9.3%) on an annual basis; and in wet precipitation, the dominant pollutants were Naph, Phe, Flt and Pyr, accounting for 12.8%, 8.3%, 2.5% and 2.4% of the $\sum_{16}$PAHs fluxes, respectively. Previous studies indicated that volatile organic compounds could be redistributed onto larger particles via gas-particle partitioning, while the less volatile compounds tend to stay on the particles on which they were emitted (Sahu et al., 2004; He and Balasubramanian, 2009). One can see in Table 8.2 that the dry deposition fluxes of high molecular weight (HMW) PAHs are comparable to those of low molecular weight (LMW) PAHs. HMW PAHs have been reported to contribute more to the dry deposition (Gigliotti et al., 2002), this anomaly in present study may be because the particulate fractions of LMW PAHs in aerosols which prefer to be in coarse-mode readily settled. Table 8.2 clearly shows that the contribution of the LMW PAH pollutants in wet deposition was increased as compared to those in dry deposition. The main processes contributing to wet deposition fluxes of SVOCs are precipitation scavenging of particle-sorbed and gaseous chemicals, but particle scavenging, rather than the gas scavenging, is the dominant removal mechanism (Offenberg and Baker, 2002; Sahu et al., 2004). The below-cloud scavenging rates increase with particle size because the collision efficiency of particle-droplet encounter increases with increasing particle diameters (Calderón et al., 2008). In this study, it is understandable that the washout of those volatile pollutants attached with coarse particles dominated the wet depositional flux of SVOCs such as LMW PAHs and HCHs, considering the high rainfall amount and precipitation intensities in Singapore. However, scavenging of fine particles needs to be considered and could contribute as well via nucleation, Brownian diffusion, etc (Perry and Hobbs, 1994; Chate, 2005).

8.4.2. Water Column Partitioning

In sea subsurface water (SSW), the apparent dissolved and particulate occurrence levels of SVOCs are reported in Table 8.3. The mean concentrations of PAHs were 43.9 ± 35.8 and 131.4 ± 101.8 ng L^{-1} for both phases, respectively, showing a 3-fold enrichment of PAHs in the suspended particulate-phase in this marine environment. For HCHs and DDTs, the total mean concentrations were 1147.8 ± 898.5 and 361.9 ± 271.8 pg L^{-1} in the dissolved phase, and 728.9 ± 622.0 and 560.3 ± 501.5 pg L^{-1} in the particulate phase, respectively. The levels of both HCHs and DDTs were comparable to those reported for Straits of Johor located between Singapore and Malaysia previously reported by Wurl et al. (2006b).

Table 8.3. Concentrations of SVOCs in SSW, SML and atmospheric gas phases during Nov to Dec 2007 in Singapore's coastal area

Compound	SSW			SML		Gas
	$C_{d,a}$	C_p	$F_{DOC,C}$ (%)	$C_{d,a}$	C_p	C_a
PAHs	ng L^{-1}			ng L^{-1}		ng m^{-3}
Naph	18.4 ± 10.6	33.5 ± 23.8	0.10 ± 0.13	19.6 ± 16.1	43.2 ± 22.2	8.7 ± 6.0
Ace	0.58 ± 0.39	3.1 ± 1.8	0.32 ± 0.47	1.4 ± 1.5	2.7 ± 1.6	0.98 ± 0.84
Flu	2.3 ± 3.6	6.1 ± 4.6	0.58 ± 0.44	4.7 ± 3.5	11.0 ± 10.2	3.7 ± 3.2
Phe	6.2 ± 2.0	17.7 ± 8.4	1.4 ± 1.2	16.9 ± 12.1	60.6 ± 20.5	34.8 ± 22.4
Ant	0.38 ± 0.25	1.5 ± 2.6	1.3 ± 0.92	2.1 ± 3.0	6.8 ± 4.4	3.4 ± 1.8
Flt	5.8 ± 9.1	6.5 ± 8.6	5.5 ± 3.2	3.8 ± 2.6	17.2 ± 3.3	51.8 ± 38.7
Pyr	1.1 ± 0.43	3.9 ± 2.5	5.1 ± 5.7	7.4 ± 5.9	19.6 ± 4.5	56.3 ± 44.1
B(a)A	1.3 ± 1.2	9.2 ± 5.9	18.7 ± 14.8	2.5 ± 2.1	20.0 ± 8.5	15.1 ± 25.9
Chry	1.5 ± 1.4	6.8 ± 4.1	17.3 ± 12.0	3.2 ± 2.1	26.5 ± 14.7	8.0 ± 5.9
B(b)F	0.74 ± 0.50	5.6 ± 5.2	14.5 ± 13.2	4.2 ± 2.2	25.1 ± 15.3	1.9 ± 0.96
B(k)F	0.58 ± 0.36	8.4 ± 6.1	21.4 ± 19.1	1.7 ± 1.3	27.9 ± 18.5	0.61 ± 0.56
B(a)P	1.2 ± 0.72	15.7 ± 11.0	22.7 ± 16.3	4.5 ± 4.2	47.6 ± 27.9	0.85 ± 0.74
Ind	0.91 ± 1.6	5.1 ± 8.4	42.5 ± 23.9	3.1 ± 1.5	12.7 ± 8.7	0.026 ± 0.014
DB(ah)A	2.1 ± 2.8	0.97 ± 0.72	51.9 ± 24.7	1.9 ± 1.3	3.0 ± 2.7	0.010 ± 0.007
B(ghi)P	0.87 ± 0.79	7.3 ± 8.1	40.7 ± 23.8	3.8 ± 2.0	26.3 ± 12.5	0.028 ± 0.025
∑PAHs	43.9 ± 35.8	131.4 ± 101.8		80.8 ± 61.3	365.3 ± 209.1	187.5 ± 138.3

OCPs	pg L^{-1}			pg L^{-1}		pg m^{-3}
α-HCH	403.3 ± 206.7	230.0 ± 186.9	0.26 ± 0.37	509.7 ± 194.4	465.5 ± 249.9	415.5 ± 135.7
β-HCH	306.5 ± 280.2	326.6 ± 258.9	0.25 ± 0.36	835.3 ± 533.9	506.7 ± 314.4	238.6 ± 143.1
γ-HCH	257.4 ± 181.2	112.7 ± 131.4	0.20 ± 0.30	232.2 ± 240.2	230.5 ± 145.9	195.9 ± 193.6
δ-HCH	180.6 ± 230.4	59.6 ± 44.8	-	310.5 ± 319.5	208.9 ± 219.2	109.1 ± 101.3
∑HCHs	1147.8 ± 898.5	728.9 ± 622.0		1887.8 ± 1288.1	1411.7 ± 929.5	958.9 ± 336.7
4,4'-DDD	28.6 ± 22.4	8.7 ± 7.9	33.4 ± 22.7	39.3 ± 36.9	26.3 ± 32.5	7.5 ± 5.9
4,4'-DDE	91.2 ± 50.5	10.3 ± 16.1	40.1 ± 33.9	165.9 ± 50.6	34.6 ± 20.3	3.3 ± 2.4
4,4'-DDT	242.1 ± 198.9	541.3 ± 477.5	35.9 ± 23.1	290.6 ± 130.2	1179.8 ± 872.4	28.7 ± 11.5
∑DDTs	361.9 ± 271.8	560.3 ± 501.5		493.4 ± 214.1	1240.7 ± 925.1	39.5 ± 7.7

* $C_{d,a}$: concentration in apparent dissolved phase; C_P, concentration in suspended particulate phase in seawater; $F_{DOC,C}$: the fraction of SVOCs sorbed onto DOC; C_a, concentration in atmospheric gas

8.4.2.1. Relationship between K_{OC} and K_{OW}

The organic carbon-normalized partition coefficients between particulate and dissolved phases (K_{OC}) for both PAHs and OCPs were obtained based on the data obtained from field measurements. The relationships between K_{OC} of PAHs and OCPs and their respective K_{OW} were investigated with the inclusion of predicted K_{OC} values by Karickhoff's model (Karickhoff, 1981) as in Figure 8.2. In Figure 8.2(a), the observed K_{OC} values, especially for those PAHs with smaller K_{OW}, are much larger than predictions and the log K_{OC} is poorly correlated with log K_{OW} with low slope value of 0.13 only. It has been suggested that the slope of log K_{OC}/log K_{OW} relation should be equal to 1 when partitioning is in equilibrium (Chiou et al., 1983; Gschwend and Wu, 1985). Researchers initially hypothesized that the significant deviation from 1 may mainly be due to the non-equilibrium or the sorption of compounds to colloids but not particulate phase (Gschwend and Wu, 1985). Till now, a number of studies have reported that the field measured K_{OC} values were higher than the theoretically predicted ones in many different settings such as lake, sediments, and rain water (Baker et al., 1991; Poster and Baker, 1996a; Accardi-dey and Gschwend, 2002). These results suggest the presence of particulate phase like soot (black carbon), to which the parent PAHs are more strongly associated than with natural organic matter/carbon. In contrast, field-obtained K_{OC} values for OCPs are correlated better with K_{OW} with a slope of 0.79 closer to theoretical value and greater R^2 = 0.66 (Figure 2(b)). In addition, these K_{OC} for OCPs are typically lower, but agree better with the model simulations, indicating the dominant influence of organic-carbon on water column partitioning for OCPs. Similar observations for hydrophobic polychlorinated biphenyls (PCBs) have been widely reported as well (Baker et al., 1991; McGroddy et al., 1996; Poster and Baker, 1996a).

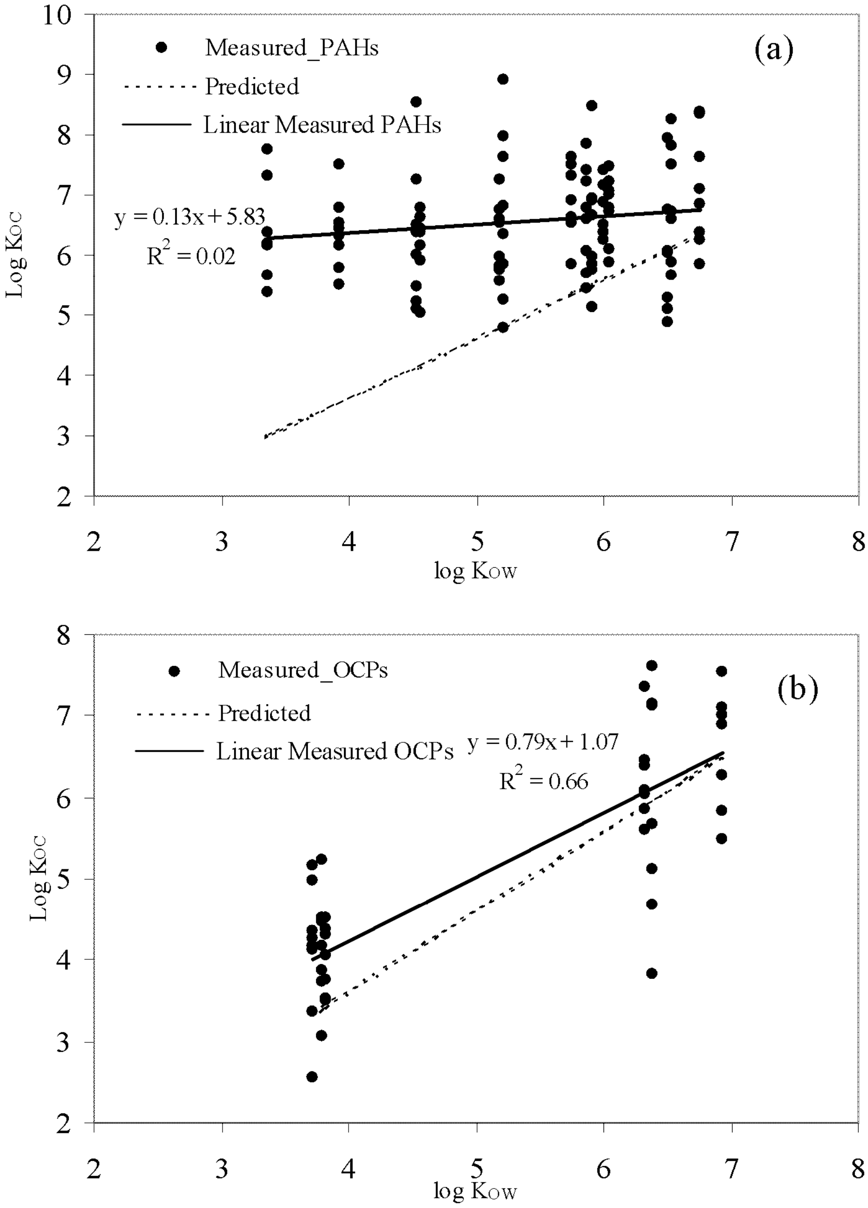


Figure 8.2. Relationship between log K_{OC} (measured and predicted) and log K_{OW} (a) PAHs and (b) OCPs

8.4.2.2. Sorption of PAHs to Soot Carbon

The observed partition coefficients (K_P) between particulate and dissolved phases are compared with predicted values by Equation 8.5 as shown in Figure 8.3 for lower molecular weight (LMW) PAHs such as Flu, Phe, Ant, and Pyr and higher molecular weight (HMW) PAHs such as B(a)A, Chry, B(b)F, B(k)F, B(a)P, and B(ghi)P. The use of Freundlich exponent $n = 0.62$, which was derived for pyrene in sediment by Accardi-dey and Gschwend (2002), over-estimates the sorption of both LMW (Figure 8.3(a)) and HMW (the predicted line not shown in Figure 8.3(b)) to the particulates in Singapore's coastal sub-surface seawater using the measured f_{OC} and f_{SC} values, indicating the sorption dynamics may be different due to variations in specific surface areas and surface chemistries of soot carbons of various origins. Freundlich exponent, n, was varied to achieve the best fit at $n = 0.80$ for LMW PAHs and at $n = 1.2$ for HMW compounds. Both optimized Freundlich exponents are not equal to one, implying that K_{BC} is dependent on sorbate levels and the sorption of PAHs to soot carbon is a nonlinear process. For LMW PAHs such as Phe, Ant, Pyr, $n<1$ has been reported (Cornelissen and Gustafsson, 2005; Prevedouros et al., 2008), but for HMW compounds such as B(a)P, K_P was over-predicted by a factor of 2 ~ 5 by using $n<1$ (Prevedouros et al., 2008). At the optimum Freundlich exponents, K_P values increased by 1.4 ~ 1.6 log units and 0.7 ~ 1.3 log units for LMW and HMW PAHs, respectively. Soot carbon was the dominant sorbent here since its sorption contributed ~ 90% of the total partition coefficients, while the OC fraction was still an important sorbent and contributed to ~ 10% of the overall K_P values. It is hypothesized that sorptions onto both combustion-derived soot carbon and natural organic matter act in parallel to bind PAHs to particulate phase in marine water column.

Additionally, it can be seen that the inclusion of soot carbon sorption reduced the dissolved water concentrations and increase the particulate enrichment of PAHs. The soot carbon fraction would lower the chemical availability of PAHs as compared to that expected from $f_{OC}K_{OC}$ alone so that the bioavailability may be reduced accordingly.

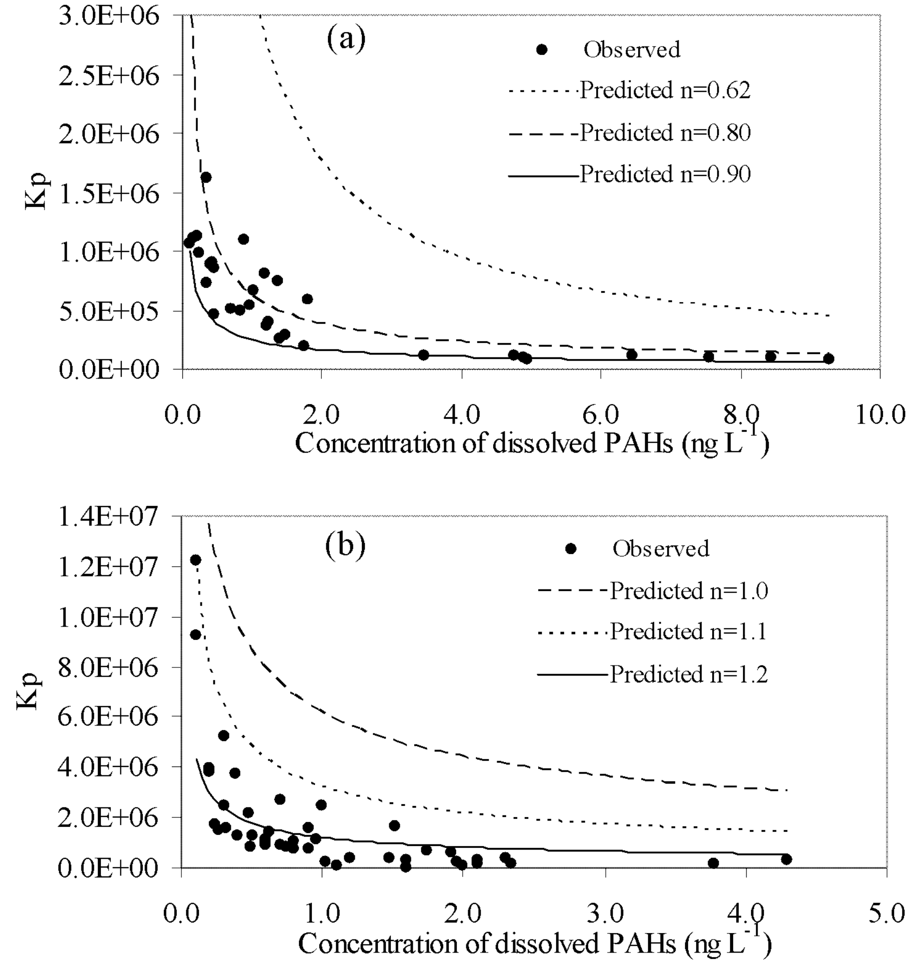


Figure 8.3. Comparison of predicted and observed K_P (a) Flu, Phe, Ant, and Pyr; (b) B(a)A, Chry, B(b)F, B(k)F, B(a)P, and B(ghi)P

8.4.3. Air-Water Diffusive Exchange

8.4.3.1. Truly dissolved SVOCs

Those SVOCs sorbed onto colloidal matter (DOC) are not available for air-water exchange. The partitioning between truly dissolved and colloidal phases has to be investigated in order to obtain the truly dissolved concentrations of SVOCs. In this study, DOC concentrations are in the range of 0.6 ~ 7.8 mg L^{-1}. The predicted mean fractions adsorbed to DOC for individual PAH varied in the range of 0.1 ~ 40% as can be seen from Table 8.3. It clearly showed that HMW PAHs are more readily adsorbed to DOC (10 ~ 50%) than those LMW compounds (below 10%). α-, β-, and γ-HCH were adsorbed to DOC at a mean fraction of 0.26, 0.25 and 0.20 %, respectively. These values are consistent with the values (~ 0.4%) reported by Wurl et al. (2006b), while $F_{DOC,C}$ (%) for DDTs was much higher in the range of 30 ~ 40%. This distribution pattern suggests that the sorption of SVOCs onto DOC in the seawater is correlated with the chemical's K_{OW}, namely, pollutants with higher K_{OW} are more easily sorbed onto DOC.

8.4.3.2. Air-water gas exchange flux

Atmospheric gas-phase mean concentrations of ∑PAHs, ∑HCHs and ∑DDTs during Nov and Dec of 2007 (Table 8.3) were 187.5 ± 138.3 ng m^{-3}, 958.9 ± 336.7 pg m^{-3} and 39.5 ± 7.7 pg m^{-3}, respectively, which were in the range of levels reported previously (He et al., 2009). The mean annual fluxes of SVOCs across the air-water interface were estimated and are summarized in Table 8.2.

The fluxes of the individual PAH compound were in the range of -21.7 ± 20.2 ~ -1608.4 ± 869.6 ng m^{-2} day^{-1} and ∑PAH flux reached up to -5884.0 ± 4040.7 ng m^{-2} day^{-1}.

All PAHs showed negative fluxes indicating the tendency to transfer these contaminants from air to water (net absorption). The magnitude and direction of PAH fluxes varied widely on temporal and spatial scales all over the world. In Chesapeake Bay, individual fluxes ranged from 14200 ng m^{-2} y^{-1} net volatilization of Flu to 11400 ng m^{-2} day^{-1} net absorption of Phe on different sampling events (Bamford et al., 1999a). Both New York harbor and Raritan Bay systems exhibited net volatilization fluxes for the majority of PAHs (Gigliotti et al., 2002), while LMW PAHs showed positive fluxes and HMW PAHs showed negative values in Mumbai harbor of India (Pandit et al., 2006). The magnitudes of net PAH fluxes are comparable to the reported values (-0.01 ~ -21.2 μg m^{-2} day^{-1}) in an urban lake in Guangzhou, China (Li et al., 2009). The large net absorption fluxes in this island were likely a result of high gaseous concentrations of PAHs, attributed to the highly uniform ambient temperature and the strong terrestrial sources such as island-wide vehicular traffic, chemical industries, major power plants and oil refineries.

Air-water gas exchange fluxes were estimated in the range of -44.4 ± 37.8 ~ -73.7 ± 31.3 ng m^{-2} day^{-1} and -0.74 ± 0.67 ~ -2.9 ± 1.8 ng m^{-2} day^{-1} for HCHs and DDTs, respectively (Table 8.2), indicating Singapore's south coastal line as a sink for both HCHs and DDTs. The fluxes estimated here were comparable to those for the Johor strait located between Singapore and Malaysia with -8.2 ~ -66.8 ng m^{-2} day^{-1} (Wurl et al., 2006b). It has been reported that air-water gas exchange of SVOCs is a dynamic process that is especially sensitive to fluctuations in concentrations of both air and water phases (Wilkinson et al., 2005). Even though the Henry's law constants of DDTs are larger than those of HCHs, their net absorption was still much lower than that of HCHs, most likely due to much higher occurrence levels of gaseous HCHs, driving more HCHs transferred across the air-sea interface.

Annual air-sea gas exchange fluxes were calculated by multiplying the average daily fluxes by 365 days and the relative contribution of each depositional process to the total atmospheric deposition is shown in Figure 8.4. For OCPs, most contribution to total OCP inputs was from wet deposition and air-sea exchange gas fluxes, while the dry particulate deposition dominated the total PAH inputs for Ind and B(ghi)P with ~ 80% of contribution. As molecular weight increases from the low- to medium-molecular weight PAHs, dry deposition fluxes contribution generally increased, reflecting more fractions on particles. Wet deposition dominated the total PAH inputs for LMW compounds from Naph to Phe, and the profile of wet deposition contribution to total PAH inputs (Figure 8.4) was similar to that of wet deposition fluxes for individual PAH compounds (Table 8. 2). The contribution of air-sea gas absorption has been reported to decrease with the increasing of molecular weight (Gigliotti et al., 2002). However, in this study, it mostly prevailed for medium molecular weight compounds from Ant to B(a)A, but not for LMW PAHs. This may be because the volatile degassing of these LMW compounds from the seawater to air under this tropical climate offsets their transfer from gas to seawater and led to the low net absorption fluxes observed here.

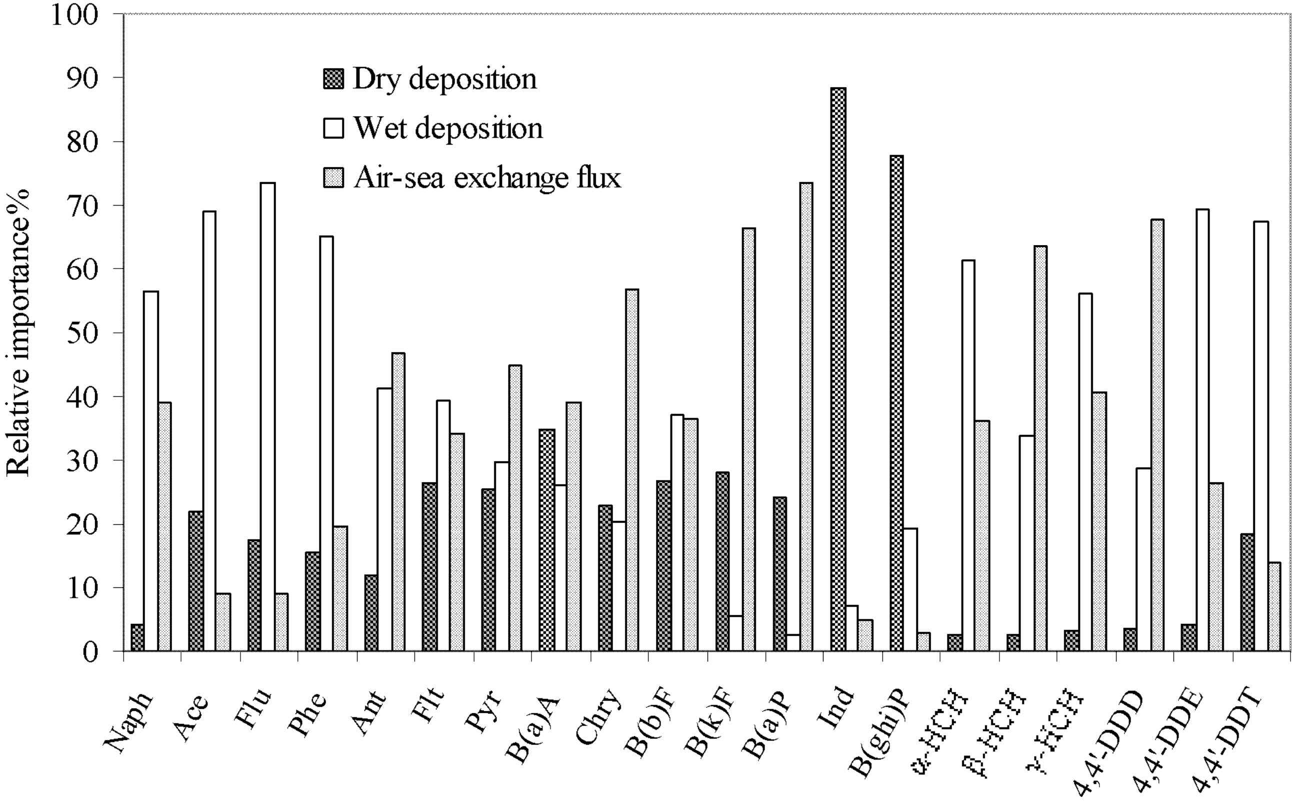


Figure 8.4. The relative importance of dry particulate deposition, wet deposition, and air-sea gas exchange flux to total atmospheric deposition in the Singapore's south coastal area

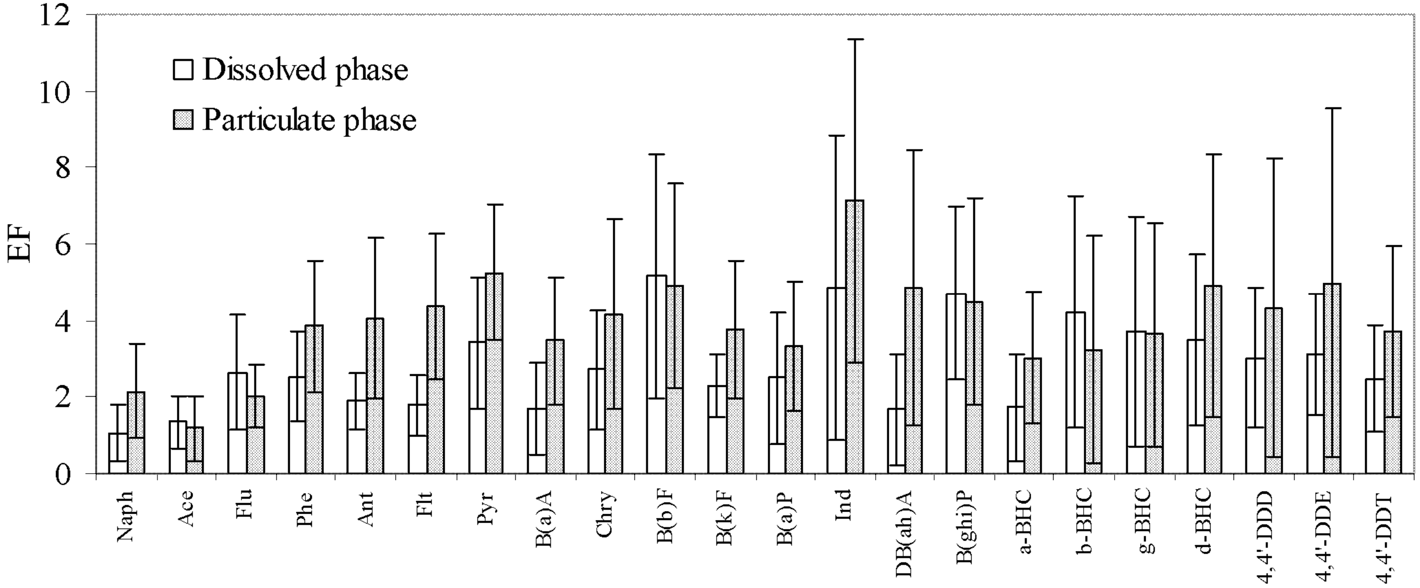


Figure 8.5. Enrichment factors (EF) of PAHs and OCPs in the sea-surface microlayer of Singapore's coastal line

8.4.4. Sea-Surface Microlayer Enrichment

SML has an enrichment effect of SVOCs, most likely due to their hydrophobic character and high affinity for surfactants collected at the air-water interface (Hardy, 1982; Chernyak et al., 1996; Wurl et al., 2006a). This effect can be quantified by the enrichment factor EF, calculated as the ratio between SML and SSW concentrations (Manodori et al., 2006) as shown in Figure 8.5. EFs in the SML of particulate phase were 1.2~ 7.1 and 3.0 ~ 4.9 for PAHs and OCPs, and those of dissolved phase were 1.1 ~ 4.9 and 1.6 ~ 4.2 for PAHs and OCPs, respectively. EFs in the SML for HCHs found in this study were relatively higher than those reported for the Johor Strait between Malaysia and Singapore (EF = 1.1 ~ 1.4 for particulate phase and EF = 3.3 ~ 4.4 for dissolved phase) by Wurl et al. (2006b). Similar profiles were found in the SML that EFs generally increased with an increase in molecular weight for both particulate and dissolved phases. In addition, the individual components exhibited similar trends in both phases, with relatively higher enrichments for particulate than for dissolved SVOCs. It is known that the major harbor, one of the busiest harbors in the world, is in the south coastal line of Singapore, and chemical industries as well as oil refineries situated in a group of small islands on the southwest coast of the Singapore Island. It is understandable that more organic film floats in the south coastal surface than in the north area (Johor Strait), resulting in more SVOCs enriched in the SML of the south coastal area. It also indicated that SML really has larger storage capacity (per volume) and may be able to delay the transport of SVOCs across the interface to SSW. In addition, the SML is a relatively dynamic compartment, highly influenced by changes of the meteorological and hydrographical conditions (Guitart et al., 2007). This may be the reason for high variation of EFs obtained in this study.

8.5. Conclusion

Both dry and wet depositions were estimated on the basis of the monthly concentrations of SVOCs. The dry particulate deposition showed lower fluxes during the monsoon seasons but a significant increase within the pre-NE monsoon. It was also observed that the high wet deposition fluxes took place during the rainy season (Dec 2007 ~ Mar 2008) in sharp contrast to the low dry deposition fluxes during the same period. It has to be noted that the deposition profile was significantly influenced by meteorological/atmospheric conditions in this study. In SSW, the observed organic carbon-normalized partition coefficients between particulate and dissolved phases (K_{OC}) values for PAHs were much larger than predictions and the log K_{OC} is poorly correlated with log K_{OW}, while the field-obtained K_{OC} values for OCPs are correlated better with K_{OW}. The study of sorption of PAHs to soot carbon showed that soot carbon was the dominant sorbent for PAHs since its sorption contributed ~ 90% of the total partition coefficients, indicating soot carbon sorption reduced the dissolved water concentrations and possibly lowered the bio-availability of these pollutants in the sea water column. Other than the soot sorbent, colloidal matter (DOC) also played an important role in the partitioning of SVOCs in the water column, and reduced the availability of SVOCs for air-water exchange. In the air-water exchange study, all mean negative gas exchange fluxes showed net absorption of SVOCs onto the Singapore's south coastal sea-surface. The contribution of this process mostly prevailed for medium molecular weight compounds from Ant to B(a)A, but not for LMW PAHs as compared to dry particulate and wet depositions. Lastly, in the investigation of SML enrichment, a similar increasing trend of EFs for both particulate and dissolved phases was found with an increase in molecular weight and the individual components had relatively higher enrichments for particulate than for dissolved SVOCs. In addition, this study also implied that SML may have the large storage capacity to delay the transport of SVOCs across the interface to SSW.

Coastal areas are vulnerable to the accumulation of semivolatile organic compounds, such as PAHs, OCPs and PCBs from atmospheric inputs. From this study, dry particulate and wet depositions were estimated to contribute around 510 kg of the abovementioned pollutants per month onto Singapore's territorial sea surface. Monthly or seasonal variation was dry and wet deposition was observed to be affected by meteorological conditions. Negative gas diffusive exchange fluxes showed net absorption of SVOCs, indicating the Singapore's south coastal area is a pure sink for PAHs and OCPs. In SSW, the study showed that the organic carbon can dominate the sorption of OCPs while the black carbon was the dominant sorbent for the sorption of PAHs in the water column, indicating organic / black carbon might be able to reduce the bio-availablity of these pollutants in the aqueous environment. The large storage capacity of SVOCs in SML, where the particulate phase had EF 1.2~ 7.1 and 3.0 ~ 4.9 for PAHs and OCPs, dissolved phase had 1.1 ~ 4.9 and 1.6 ~ 4.2 for PAHs and OCPs, respectively, demonstrated that SML may delay the transport of these pollutants across the interface.

Chapter 9. Conclusions

9.1. Summary and Major Conclusions

In general, the targeted SVOCs, including PAHs, OCPs and PCBs, could be partitioned between the gaseous and particulate phases and reach a partitioning equilibrium according to temperature dependences and the vapor pressure of the individual chemicals. Airborne particles can also naturally fall out onto ground/water surface, which is affected by gravitational force, Brownian diffusion, atmospheric disturbance, etc. In addition, both the particles and gas could undergo natural precipitation scavenging processes. Furthermore, the gaseous compounds could diffuse between the interfaces of air and water / seawater surface. In order to assess potential risks of these pollutants for the natural environment and human health, it is important to understand their fate once they are introduced into the environment. This thesis represents one of the first studies that systematically investigated the fate and transfer of PAHs, PCB, and OCPs in the tropical atmosphere and the factors that affect their distributions in the multi-media environment.

The major conclusions drawn from each segment of the study are presented below i n the same order as in the Results & Discussion chapters.

To determine the atmospheric concentrations of PAHs, PCBs, and OCPs present in trace levels, an accelerated solvent extraction (ASE) method was developed for the extraction of semi-volatile organic compounds (SVOCs) distributed in both atmospheric particulate and gaseous phase. Conclusions :

(a) Optimal extraction conditions determined for SVOCs were as follows: a mixture of n-hexane and acetone (3:1) at 100 ^{o}C for 25 min by two static cycles.

(b) The proposed extraction method is very simple, fast, and effective and appears to be a promising alternative to commonly used extraction techniques such as Soxhlet extraction, ultra-sonication and microwave solvent assisted extraction, especially when applied to the investigation of a number of air samples due to its software-controlled automation.

The levels of SVOCs in particulate and gaseous phases of the atmosphere as well as those in particulate and operationally defined dissolved phases of precipitation were evaluated based on the field sampling conducted from June 2007 to May 2008. Conclusions :

(a) The yearly average concentrations of SVOCs indicated no significant decline in their atmospheric levels in this area over the past decade as compared with the historical data in this region. The air mass backward trajectories showed that most air masses were partly terrestrial and partly oceanic, originating from Southern Indonesia during the southwest (SW) monsoon season, while during the northeast (NE) monsoon season, they were mainly derived from China, travelling over the South China Sea to Singapore.

(b) For air samples, the monthly variations were statistically significant for PAHs and PCBs but not for OCPs; for rainwater samples, the monthly PAHs levels in precipitation were not statistically different unlike those of OCPs. This difference in occurrence patterns seems to be influenced by the regional meteorological conditions.

(c) Diagnostic ratios and PCA analysis showed that local emissions such as liquid-fossil fuel combustion, air mass transport and commercial mixtures of Arocolors 1248 and 1254 are the likely sources of PAHs, OCPs and PCBs, respectively. All these observations were consistent with the air mass origins analyzed here and historical usage records in this region.

In order to examine the distribution patterns of SVOCs between vapor and particulate phases in this region, the gas/particle partitioning for PAHs and PCBs was studied on the basis of characterization and quantification of SVOCs in the atmosphere. Conclusions :

(a) The non-exchangeability of more volatile SVOCs bound to particles and non-equilibrium (slower sorption than expected) appear to be the major reasons for the deviation of the observed quantitative relationships between between log K_p and log p_L^o from theoretical predictions (slope < -1).

(b) However, the slopes of log K_p versus log P_L^o (small or capital P- be consistent, see the above (a)) curves for both PAHs and PCBs in this study are smaller than those obtained in temperate zones of the Northern Hemisphere. This discrepancy is most likely due to tthat aerosols, thermodynamically, equilibrate faster with SVOCs under warm conditions than cold conditions and low molecular weight species attain equilibrium more quickly than the heavier compounds.

(c) The simulative results showed that the combined K_{OA}-$K_{soot-air}$ is more suitable to describe PAHs behavior, especially for low molecular weight (LMW) compounds. It is obvious that PAHs have a high affinity for carbonaceous materials, especially the black carbon, because these compounds are formed concurrently with soot particles and also play an important role in soot formation and particle growth. In addition, although the soot-inclusive method for estimating K_P provided considerably better estimates of empirical K_P values for LMW PAHs, it still over-predicted K_P for high molecular weight

(HMW) PAH compounds, which demonstrates the need to better constrain the parameter values in the modified models.

Rain samples were collected concurrently with gas-phase and particulate samples from June 2007 to May 2008 in Singapore and processed to investigate precipitation scavenging of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). Conclusions :

(a) Particle scavenging, dissolution (Henry's law) and surface adsorption are major factors affecting the total scavenging ratio of SVOCs. In this study, particle scavenging was the dominant contributor to the total scavenging in precipitation.

(b) Both W_T (total scavenging)and W_P (particulate scavenging) tended to be greater for less volatile SVOCs, most likely due to the uniform ambient temperature prevailing throughout the year in Singapore.

(c) In addition, the equations used to estimate total scavenging based on the particle fraction (Φ) can be summarized as: $\log W_T = 0.94 \log \phi + 6.09$ ($R^2=0.74$) for PAHs and $\log W_T = 0.82 \log \phi + 6.34$ ($R^2=0.62$) for OCPs.

Coastal areas are vulnerable to the accumulation of SVOCs such as PAHs, OCPs and PCBs from atmospheric inputs. The external loadings from dry particulates and wet deposition and air-sea exchange were summarized as below:

(a) Dry particulates and wet deposition were estimated to contribute around 510 kg of the above-mentioned SVOCs per month onto Singapore's territorial sea surface. Monthly or seasonal variations of dry and wet deposition were observed to be affected by meteorological conditions.

(c) Negative gas diffusive exchange fluxes showed net absorption of SVOCs, indicating that Singapore's south coastal area is a pure sink for PAHs and OCPs.

(d) In SSW, the study showed that the organic carbon can dominate the sorption of OCPs while the black carbon was the dominant sorbent for the sorption of PAHs in the water column, indicating organic/black carbon might be able to reduce the bio-availablity of these pollutants in the aquatic environment.

(e) In SML, the particulate phase had enrichment factors 1.2~ 7.1 and 3.0 ~ 4.9 for PAHs and OCPs, and the dissolved phase had 1.1 ~ 4.9 and 1.6 ~ 4.2 for PAHs and OCPs, respectively. This suggests that the SML has a large storage capacity of SVOCs and may therefore delay the transport of these pollutants across the interface.

In conclusion, this work has fulfilled its objectives and provides new insights into the fate and distribution of targeted SVOCs in Singapore's tropical and coastal environment. These studies serve as a solid knowledge-base for further work to advance our understanding of the regional and global distribution of SVOCs, particularly in the tropical regions of SEA.

9.2. Suggestions for Further Studies

Specific recommendations for future studies include:

(i) The assumptions made in the use of diagnostic ratios, namely, source specificity and species conservation, do not generally hold for PAHs as a class due to their emissions from a variety of sources and changes in source intensities and atmospheric removal/transformation processes over the study period (Galarneau, 2008). As Galarneau (2008) recommended, the regional-scale air quality modeling based on regional emission inventories may represent a better approach to source apportionment of PAHs in ambient air as it would overcome the above-mentioned drawbacks of conventional source apportionment methods. A larger number of ambient air (gas and particulate phases) and rainwater samples obtained from a network of strategic sampling locations are needed to gain a better understanding of the fate and transport of SVOCs on a regional scale, such as in SEA.

(ii) Studies on the bioaccumulation of targeted SVOCs in the tropical marine biota and environmental degradation processes are sparse and comprehensive investigations are therefore necessary to serve as inputs to environmental fate models.

(iii) Considering the present global distributions of persistent organic pollutants and the role of the ocean on their transport and fate, more systematic studies may need to be conducted to investigate how the atmospheric behavior of such chemicals as PBDEs released would be controlled by their physico-chemical properties and the meteorological conditions and how those compounds would affect the quality of adjacent water bodies.

Reference

Abraham, M.H., 2004. Determination of sets of solute descriptors from chromatorgaphic measurements. J. Chromatogr., A 1037, 29-47.

Accardi-dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. Environ. Sci. Technol. 36, 21-29.

Achman, D.R., Hornbuckle, K.C., Eisenreich, S.J., 1993. Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. Environ. Sci. Technol. 27, 75-87.

Aneja, V.P., 1993. Organic compounds in cloud water and their deposition at a remote continental site. J. Air Waste Manage. Assoc. 43, 1239-1244.

Ang, K.P., Gunasingham, H., Tay, B.T., 1986. The distribution of polynuclear aromatic hydrocarbons in ambient air particulates in Singapore. Environ. Monit. Assess. 6, 171-180.

AOAC, 2002. Association of Analytical Communities (AOAC) Guidelines for Single Laboratory Validation of Chemical Methods.

Arp, H.P., Goss, K.U., Schwarzenbach, R.P., 2006. Evaluation of a predictive model for air/surface adsorption equilibrium constans and enthalpies. Environ. Toxicol. Chem. 25, 45-51.

Atkinson, R., 1986. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chem. Rev. 86, 69-201.

Atlas, E., Giam, C.S., 1988. Ambient concentration and precipitation scavenging of atmospheric organic pollutants. Water, Air, Soil Pollut. 38, 19-36.

Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. Water. Air. Soil Pollut. 60, 279-300.

Bahadur, N.P., Shiu, W.Y., Boocock, D.G.B., Mackay, D., 1997. Temperature dependence of octanol-water partition coefficient for selected chlorobenzenes. J. Chem. Eng. Data 42, 685-688.

Baker, J.E., Eisenreich, S.J., Eadie, B.J., 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. Environ. Sci. Technol. 25, 500-509.

Bamford, H.A., Offenberg, J.H., Larsen, R.K., Ko, F.C., Baker, J.E., 1999a. Diffusive exchange of polychclic aromatic hydrocarbons across the air-water interface of the Patapsco river, an urbanized subestuary of the Chesapeake Bay. Environ.Sci. Technol. 33, 2138-2144.

Bamford, H.A., Poster, D.L., Baker, J.E., 1999b. Temperature dependence of henry's law constants of thirteen PAHs between 4 C degree and 31 C degree. Environ. Toxicol. Chem. 18, 1905-1912.

Bard, S.M., 1999. Global transport of anthropogenic contaminants and the consequences for the Arctic marine ecosystem. Mar. Pollut. Bull. 38, 356-379.

Basheer, C., Balasubramanian, R., Lee, H.K., 2003a. Determination of organic micropollutants in rainwater using hollow fiber membrane/liquid-phase microextraction combined with gas chromatography-mass spectrometry. J. Chromatogr. A 1016, 11-20.

Basheer, C., Obbard, J.P., Lee, H.K., 2003b. Persistent organic pollutants in Singapore's coastal marine environment: part I, seawater. Water, Air, Soil Pollut. 149, 295-313.

Bayen, S., Koroleva, E., Lee, H.K., Obbard, J.P., 2005. Persistent organic pollutants and heavy metals in typical seafoods consumed in Singapore. J. Toxicol. Environ. Health 68, 151-166.

Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J., 2003. Distribution of particulate- and vapor- phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. Atmos. Environ. 37, 289-298.

Bidleman, T.F., 1988. Atmospheric process wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Technol. 22, 361-367.

Bidleman, T.F., Falconer, R.L., Walla, M.D., 1995. Toxaphene and other organochlorine compounds in air and water at Resolute Bay, N.W.T., Canada. Sci. Total Environ. 160-161, 55-63.

Björklund, E., Bøwadt, S., Nilsson, T., Mathiasson, L., 1999. Pressurized fluid extraction of polychlorinated biphenyls in solid environmental samples. J. Chromatogr. A 836, 285-293.

Bjorseth, A., Becher, G., 1986. PAH in work atmosphere: Occurrence and Determiantion. CRC Press, Boca Raton, Fl., USA.

Bonfanti, L., DeMichele, G., Riccardi, J., Lopez-Doriga, E., 1994. Influence of coal type and operating conditions on the formation of incomplete combustion products. Pilot plant experiments. Comb. Sci. Technol. 101, 505-525.

Braun, T., Navratil, J.D., Farag, A.B., 1986. Polyurethane Foam Sorbents in Separation Science. CRC Press, Boca Raton, FL., USA

Brooks, G.T., 1974. Chlorinated Insecticides, Volume I: Technology and Application. CRC Press, Cleveland, Ohio, USA, p. 249.

Brun, G.L., Vaidya, O.C., Léger, M.G., 2004. Atmospheric deposition of polycyclic aromatic hydrocarbons to Atlantic Canda: geographic and temporal distributions and trends 1980-1921. Environ. Sci. Technol. 38, 1941-1948.

Brunciak, P.A., Dachs, J., Franz, T.P., Gigliotti, C.L., Nelson, E.D., Turpin, B.J., Eisenreich, S.J., 2001. Polychlorinated biphenyls and particulate organic/elemental carbon in the atmosphere of Chesapeake Bay, USA. Atmos. Environ. 35, 5663-5677.

Bucheli, T.D., Gustafsson, Ö., 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. . Environ. Sci. Technol. 34, 5144-5151.

Calderón, S.M., Poor, N.D., Campbell, S.W., Hartsell, B., 2008. Rainfall scavenging coefficients for atmospheric nitric acid and nitrate in a subtropical coastal environment. Atmos. Environ. 42, 7757-7767.

Callén, M.S., de la Cruz, M.T., López, J.M., Murillo, R., Navarro, M.V., Mastral, A.M., 2008. Some inferences on the mechanism of atmospheric gas/particle partitioning of polycyclic aromatic hydrocarbons (PAH) at Zaragoza (Spain). Chemosphere 73, 1357-1365.

Candeli, A., Morozzi, G., Shapiro, M.A., 1983. Mobile source emissions including polycylic organic species. In: Rondia, D., Cooke, M., Haroz, R.K. (Eds.). D. Reidel Pub. Co., Dordrecht, Netherlands, pp. 29-47.

Capel, P.D., Leuenberger, C., Giger, W., 1991. Hydrophobic organic chemicals in urban fog. Atmos. Environ. A: General Topics 25, 1335-1346.

CCREM, Canadian Council of Resource and Environment Ministers, 1986. The PCB Story. Joint publication by federal, provincial and territorial governments in Canada, Toronto, Ontario, Canada.

Cerro, C., Bech, J., Codina, B., Lorente, J., 1998. Modeling rain erosivity using disdrometric techniques. Soil Sci. Soc. Am. J. 62, 731-735.

Cetin, B., Ozer, S, Sofuoglu, A, Odabasi, M., 2006. Determination of Henry's law constants of organochlorine pesticides in deionized and saline water as a function of temperature. Atmos. Environ. 40, 4538-4546.
Chate, D.M., 2005. Study of scavenging of submicron-sized aerosol particles by thunderstorm rain events. Atmos. Environ. 39, 6608-6619.

Chee, K.K., Wong, M.K., Lee, H.K., 1997a. Microwave-assisted solvent extraction of air particulates for the determination of PAHs. Environ. Monit. Assess 44, 391-408.

Chee, K.K., Wong, M.K., Lee, H.K., 1997b. Microwave-assisted solvent extraction of air particulates for the determination of PAHs. Environ. Monit. Assess. 44, 391-403.

Chee, K.K., Wong, M.K., Lee, H.K., 1997. Microwave-assisted solvent extraction of air particulates for the determination of PAHs. Environ.Monit.Assess. 44, 391-408.

Chen, S.F., Chan, R.C., Read, S.M., Bromley, L.A., 1973. Viscosity of sea water solutions. Desalination 13, 37-51.

Chernyak, S.M., Rice, C.P., McConnell, L.L., 1996. Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Seas. Mar. Pollut. Bull. 32, 410-419.

Chiou, C.T., Porter, P.E., Schmedding, D.W., 1983. Partition equilibria of non-ionic organic-compounds between soil organic-matter and water. Envrion. Sci. Technol. 17, 227-231.

Christensen, A., Ostman, C., Westerholm, R., 2005. Ultrasound-assisted extraction and on-line LC-GC-MS for determination of polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. Anal. Bioana. Chem. 381, 1206-1216.

Chu, W., Chan, K.H., Kwan, C.Y., Jafvert, C.T., 2005. Acceleration and quenching of the photolysis of PCB in the presence of surfactant and humic materials. Environ. Sci. Technol. 39, 9211-9216.

Collett, J.L., PHerckes, P., Youngster, S., Lee, T., 2008. Processing of atmospheric organic matter by California radiation fogs. Atmos. Res. 87, 232-241.

Cornelissen, G., Gustafsson, Ö., 2005. Prediction of large variation in biota to sediment accumulation factors due to concentration-dependent black carbon adsorption of planar hydrophobic organic compounds. Environ. Toxicol. Chem. 24, 495-498.

Cortazar, E., Bartolome, L., Delgado, A., Etxebarria, N., Fernandez, L.A., Usobiaga, A., Zuloaga, O., 2005. Optimisation of microwave-assisted extraction for the determination of nonylphenols and phthalate esters in sediment samples and comparison with pressurised solvent extraction. Anal.Chim.Acta 534, 247-254.

Cotham, W., Bidleman, T., 1995. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan. Environ.Sci.Technol. 29, 2782-2789.

Cousins, I.T., Beck, A.J., Jone, K.C., 1999. A review of the processes involved in the exchange of semi-volatile organic compounds (SVOC) across the air-soil interface. Sci. Total Environ. 228, 5-24.

Cremlyn, R., 1978. Pesticides. John Wiley and Sons, Ltd., Chichester, U.K., p. 240.

Currado, G.M., Harrad, S., 2000. Factors influencing atmospheric concentrations of polychlorinated biphenyls in Birmingham, U.K. Environ. Sci. Technol. 34, 78-82.

Dachs, J., Eisenreich, S.J., 2000. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 34, 3690-3697.

Dachs, J., Lohmann, R., Ockenden, W.A., Mejanelle, L., Eisenreich, S.J., Jones, K.C., 2002. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. Environ. Sci. Technol. 36, 4229-4237.

Dachs, J., Van Ry, D.A., Eisenreich, S.J., 1999. Occurrence of estrogenic nonylphenols in the urban and coastal atmosphere of the lower Hudson River estuary. Environ. Sci. Technol. 33, 2676-2679.

Davila, D.R., Davis, D.P., Campbell, K., Cambier, J.C., Zigmond, L.A., Burchiel, S.W., 1995. Role of alterations in Ca_2^+-associated signaling pathways in the immunotoxicity of polycyclic aromatic hydrocarbons. J. Toxicol. Environ. Health 45, 101-126.

DBT, Danish Board of Technology, 1996. The non-assessed chemicals in the EU. Report and recommendations from an interdisciplinary group of Danish experts. Report No. 5/96. Copenhagen

de Lima Ribeiro, F.A., Ferreira, M.M.C., 2003. QSPR models of boiling point, octanol–water partition coefficient and retention time index of polycyclic aromatic hydrocarbons. J. Mol. Struct. 663, 109-126.

de Souza Pereira, M., Heitmann, D., Reifenhauser, W., Meire, R.O., Santos, L.S., Torres, J.P.M., Malm, O., Korner, W., 2007. Persistent organic pollutants in atmospheric deposition and biomonitoring with Tillandsia usneoides (L.) in an industralized area in Rio de Janeiro state, southeast Brazil - Part II: PCB and PAH. Chemosphere 67, 1736-1745.

Dickhut, R.M., Gustafson, K.E., 1995. Atmospheric washout of polycyclic aromatic hydrocarbons in the Southern Chesapeake Bya region. Environ. Sci. Technol. 29, 1518-1525.

Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Springs, M.D., USA. .

Duinker, J.C., Bruchertall, F., 1989. On the distribution of atmospheric polychlorinated congeners between vapor, aerosols, and rain. Environ. Sci. Technol. 23, 57-62.

Durant, J.L., Busby, W.F., Lafleur, A.L., Penman, B.W., Crespi, C.L., 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutat. Res. 371, 123-157.

Dvorská, A., Lammel, G., Holoubek, I., 2009. Recent trends of persistent organic pollutants in air in central Europe-Air monitoring in combination with air mass trajectory statistics as a tool to study the effectivity of regional chemical policy. Atmos. Environ. 43, 1280-1287.

Dvorska, A., G., L., Klanova, J., Holouobek, I., 2008. Kosetice, Czech Republic-ten years of air pollution monitoring and four years of evaluating the origin of persistent organic pollutants. Environ. Pollut. 156, 403-408.

Eisenreich, S.J., Looney, B.B., Thornton, J.D., 1981. Airborne organic contaminants in the Great Lakes ecosystem. Environ.Sci. Technol. 15, 30-38.
Encinas, D., Casado, H., 1999. Rain-aerosol coupling in a rural area in Basque country (Spain): Scavenging Ratios. Aerosol Sci. Technol. 30, 411-419.

Erel, Y., Kalderon-Asael, B., Dayan, U., Sandler, A., 41, 5198-5203., 2007. European atmospheric pollution imported by cooler air masses to the Eastern Mediterranean during the summer. Environ. Sci. Technol. 41, 5198-5203.

Erickson, M.D., 1997. Analytical Chemistry of PCBs (2nd ed). CRC Lewis Publishers, Boca Raton, FL. pp. 17-25

Falconer, R.L., Bidleman, T.F., 1994. Vapor pressures and predicted particle/gas distributions of polychlorinated biphenyl congeners as functions of temperature and ortho-chlorine substitution. Atmos. Environ. 28, 547-554.

Fang, G.C., Wu, Y.S., Fu, P.P.C., Lin, I.L., Chen, M.H., 2004. Polycyclic aromatic hydrocarbons in the ambient air of suburban and industrial regions of central Taiwan. Chemosphere 54, 443-452.

Fang, M., Ko, F., Baker, J.E., Lee, C., 2008. Seasonality of diffusive exchange of polychlorinated biphenyls and hexachlorobenzene across the air-sea interface of Kaohsung Harbor, Taiwan. Sci. Total Environ. 407, 548-565.

Feingold, G., Levin, Z., 1986. The lognormal fit to raindrop spectra from frontal convective clouds in Israel. J. Clim. Appl. Meteor. 25, 1346-1363.

Fernández, P., Grimalt, J.O., Vilanova, R.M., 2002. Atmospheric gas-particle partitioning of polycyclic aromatic hydrocarbons in high mountain regions of Europe. Environ. Sci. Technol. 36, 1162-1168.

Finizio, A., Mackay, D., Bidleman, T., Harner, T., 1997. Octanol-air partition coefficient as a predictor of partitioning of semivolatile organic chemicals to aerosols. Atmo.Environ. 31, 2289-2296.

Finlayson-Pitts, B.J., Pitts, J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego, CA.

Fisher, J.A., Scarlett, M.J., Stott, A.D., 1997. Accelerated solvent extraction: an evaluation for screening of soils for selected U.S.EPA semivolatile organic priority pollutants. Environ. Sci. Technol. 31, 1120-1127.

Frame, G.M., Wagner, R.E., Carnahan, J.C., Brown, J.F., May, R.J., Smullen, L.A., Bedard, D.L., 1996. Comprehensive, quantitative, congener-specific analyses of eight aroclors and complete PCB congener assignments on DE-1 capillary GC columns. Chemosphere 33, 603-623.

Franz, T.P., Eisenreich, S.J., 1998. Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota. Environ. Sci. Technol. 32, 1771-1778.
Freeman, D.J., Cattel, F.C.R., 1990. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 24, 1581.

Götz, C.W., Scheringer, M., Macleod, M., Roth, C.M., Hungerbühler, K., 2007. Alternative approaches for modeling gas-particle partitioning of semivolativle organic chemicals: model development and comparison. Environ. Sci. Technol. 41, 1272-1278.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment. Atmos. Environ. 42, 8139-8149.

García, I., Ignacio, M., Mouteira, A., Cobas, J., Carro, N., 2008. Assisted solvent extraction and ion-trap tandem mass spectrometry for the determination of polychlorinated biphenyls in mussels. Comparison with other extraction techniques. Anal. Bioanal. Chem. 390, 729-737.

Georgiadis, P., Topinka, J., Stoikidou, M., Kaila, S., Gioka, M., Katsouyanni, K., Sram, R., Autrup, H., Kyrtopoulos, S.A., 2001. Biomarkers of genotoxicity of air pollution (the AULIS project): bulky DNA adducts in subjects with moderate to low exposures to airborne polycyclic aromatic hydrocarbons and their relationship to environmental tobacco smoke and other parameters. Carcinogenesis, 1447-1457.

Gigliotti, C.L., Brunciak, P.A., Dachs, J., Glenn, T.R., Nelson, E.D., 2002. Air-water exchange of polycyclic aromatic hydrocarbons in the New York-New Jersey, USA, harbor estuary. Environ. Toxicol. Chem. 21, 235-244.

Glotfelty, D.E., Majewski, M.S., Seiber, J.N., 1990. Distribution of several organophosphorus insecticides and their oxygen analogs in a foggy atmosphere. Environ. Sci. Technol. 24, 353-357.

Gonçalves, F.L.T., Massambani, O., Beheng, K.D., Vautz, W., Schilling, M., Solci, M.C., Rocha, V., Klockow, D., 2000. Modeling and measurements of below cloud scavenging processes in the highly industrialized region of Cubatao-Brazil. Atmos. Environ. 34, 4113-4120.

Goss, K.-U., 1994. Predicting the enrichment of organic compounds in fog caused by adsorption on the water surface. Atmos. Environ. 28, 3513-3517.

Goss, K.U., 1992. Effects of temperature and relative humidity on the sorption of organic vapors on quartz sand. Environ. Sci. Technol. 26, 2287-2294.

Goss, K.U., 1997. Conceptual model for the adsorption of organic compounds from the gas phase to liquid and solid surfaces. Environ. Sci. Technol. 31, 3600-3605.

Goss, K.U., Eisenreich, S.J., 1996. Adsorption of VOCs from the gas phase to different minerals and a mineral mixture. Environ. Sci. Technol. 30, 2135-2142.

Goss, K.U., Schwarzenbach, R.P., 1998. Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants. Environ. Sci. Technol. 32, 2025-2032.

Gramatica, P., Consolaro, F., Pozzi, S., 2001. QSAR approach to POPs screening for atmospheric persistence. Chemosphere 43, 655-664.

Gramatica, P., Consonni, V., Todeschini, R., 1999. QSAR study on the tropospheric degradation of organic compounds. Chemosphere 38, 1371-1378.

Gschwend, P.M., Wu, S.C., 1985. On the constancy of sediment water partition-coefficients of hydrophobic organic pollutants. Environ.Sci. Technol. 19, 90-96.

Guitart, C., García-Flor, N., Bayona, J.M., Albaigés, J., 2007. Occurrence and fate of polycyclic aromatic hydrocarbons in the coastal surface microlayer. Mar. Pollut. Bull. 54, 186-194.

Gustafson, K.E., Dickhut, R.M., 1997. Particle/gas concentrations and distributions of PAHs in the atmosphere of southern Chesapeake Bay. Environ. Sci. Technol. 31, 140-147.

Gustafsson, Ö., Haghseta, F., Chan, C.H., MacFarlane, J., Gschwend, P.M., 1997. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. Environ. Sci. Technol. 31, 3341-3347.

Hardy, J.T., 1982. The sea surface microlayer: biology, chemistry and anthropogenic enrichment. Progr. Oceanogr. 11, 307-328.

Harner, T., Bidleman, T.F., 1996. Measurements of octanol-air partition coefficients for polychlorinated biphenyls. J. Chem. Eng. Data 41, 895-899.

Harner, T., Bidleman, T.F., 1998. Octanol-air partition coefficient for describing particle / gas partitioning of aromatic compounds in urban air. Environ. Sci. Technol. 32, 1494-1502.

Harner, T., Shoeib, M., Kozma, M., Gobas, F., Li, S.M., 2005. Hexachlorocyclohexanes and endosulfans in urban, rural, and high altitude air samples in the Fraser Valley, British Columbia: evidence for trans-Pacific transport. Environ. Sci. Technol. 39, 724-731.

Harrad, S., Mao, H., 2004. Atmospheric PCBs and organochlorines pesticides in Birmingham, UK: concentrations, sources, temporal and seasonal trends. Atmos. Environ. 38, 1437-1445.

Hart, K.M., Pankow, J.F., 1994. High-Volume Air Sampler for Particle and Gas Sampling 2.Use of Backup Filters To Correct for the Adsorption of Gas-Phase Polycyclic Aromatic Hydrocarbons to the Front Filter. Environ. Sci. Technol. 28, 655-661.

Harvey, G.W., Burzell, L.A., 1972. A simple microlayer method for small samples. Limnology and Oceanography 17, 156-157.

Hassal, K.A., 1982. The Chemistry of Pesticides: Their Metabolism, Mode of Action and Uses in Crop Protection. The Macmillan Press Ltd., London, U.K. pp. 372

Hawthorne, S.B., Krieger, M.S., Miller, D.J., 1989. Supercritical carbon dioxide extraction of polychlorinated biphenyls, polycyclic aromatic hydrocarbons, heteroatom-containing polycyclic aromatic hydrocarbons, and n-alkanes from polyurethane foam sorbents. Anal.Chem. 61, 736-740.

Hawthorne, S.B., Trembley, S., Moniot, C.L., Grabanski, C.B., Miller, D.J., 2000. Static subcritical water extraction with simultaneous solid-phase extraction for determining polycyclic aromatic hydrocarbons on environmentals solids. J.Chromatogr.A 886, 237-244.

He, J., Balasubramanian, R., 2008. Rain-aerosol coupling in the tropical atmosphere of SEA: distribution and scavenging ratios of major ionic species. J. Atmos. Chem. 60, 205-220.

He, J., Balasubramanian, R., 2009. A study of precipitation scavenging of semi-volatile organic compounds (SVOCs) in a tropical area. J. Geophys. Res. 114. 10.1029/2008JD011685.

He, J., Balasubramanian, R., Karthikeyan, S., Joshi, U.M., 2009. Determination of semi-volatile organochlorine compounds in the atmosphere of Singapore using accelerlated solvent extraction. Chemosphere. 75, 640-648.

Headley, J.V., Marsh, P., Akre, C.J., Peru, K.M., Lesack, L., 2002. Origin of polycyclic aromatic hydrocarbons in lake sediments of the Mackenzie Delta. J. Environ. Sci. Health A, 37, 1159-1180.

Helm, P.A., Bidleman, T.F., 2005. Gas-particle partitioning of polychlorinated naphthalenes and non- and mono-orgho-substituted polychlorinated biphenyls in arctic air. Sci. Total Environ. 342, 161-173.

Hinckley, D.A., Bidleman, T.f., 1990. Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data. J. Chem. Eng. Data 35, 232-237.

Hinckley, D.A., Bidleman, T.F., Rice, C.P., 1991. Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexane in the Bering and Chukchi Seas. J. Geophys. Res. 96, 7201-7213.

Hoff, R.M., Strachan, W.M.J., Sweet, C.W., Chan, C.H., Shackleton, M., Bidleman, T.F., Brice, K.A., Burniston, D.A., Cussion, S., Gatz, D.F., Harlin, K., Schroeder, W.H., 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: a review of data through 1994. Atmos. Environ. 30, 3505-3527.

Holmes, D.A., Harrison, B.K., Dolfing, J., 1993. Estimation of gibbs free energies of formation for polychlorinated biphenyls. Environ. Sci. Technol. 27, 725-731.

Holsen, T.M., Noll, K.E., 1992. Dry deposition of atmospheric particles: application of current models to ambient data. Environ. Sci. Technol. 26, 1807-1815.

Holsen, T.M., Noll, K.E., Fang, G.-C., Lee, W.J., Lin, J.-M., Keeler, G.J., 1993. Dry deposition and particle size distributions measured during the Lake Michigan Urban Air Toxics study. Environ. Sci. Technol. 27, 1327-1333.

Holsen, T.M., Noll, K.E., Liu, S.-P., Lee, W.J., 1991. Dry deposition of polychlorinated biphenyls in urban areas. Environ. Sci. Technol. 25, 1075-1081.

Hoyer, P.B., 2005. Damage to ovarian development and function. Cell Tissue Res. 322, 99-106.

Hubert, A., Wenzel, K.D., Manz, M., Weissflog, L., Engewald, W., Schueuermann, G., 2000. High extraction efficiency for POPs in real contaminated soil samples using accelerated solvent extraction. Anal. Chem. 72, 1294-1300.

Hulscher, T.T., Velde, L.E., Bruggeman, W.A., 1992. Temperature dependence of henry's law constants for selected chlorobenzenes, PCBs and PAHs. Environ. Toxicol. Chem. 11, 1595-1603.

Iwata, H., Tanabe, S., Sakai, N., Nishimura, A., Tatsukawa, R., 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. Environ. Pollut. 85, 15-33.

Iwata, H., Tanabe, S., Sakai, N., Tatsukawa, R., 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Envrion. Sci. Technol. 27, 1080-1098.

Jaward, T.M., Zhang, G., Nam, J.J., Sweetman, A.J., Obbard, J.P., Kobara, Y., Jones, K.C., 2005. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. Environ. Sci. Technol. 39, 8638-8645.

Jones, K.C., De Voogt, P., 1999. Persistent organic pollutants (POPs): state of science. Environ. Pollut. 100, 209-221.

Junge, C.E., 1977. Fate of Pollutants in the Air and Water Environments, Part I. Wiley, New York.

Kömp, P., McLachlan, M.S., 1997. Octanol/air partitioning of polychlorinated biphenyls. Environ. Toxicol. Chem. 16, 2433-2437.

Kadowaki, S., 1990. Characterization of carbonaceous aerosols in the Nagoya urban area. 1. Elemental and organic carbon concentrations and the origin of organic aerosols. . Atmos. Environ. 24, 741-744.

Kamens, R., Odum, J., Fan, Z.H., 1995. Some observations on times to equilibrium for semivolatile polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 29, 43-50.

Kannan, K., Tanabe, S., Tatsukawa, R., 1995. Geographical distribution and accumulation features of organochlorine residues in fish in Tropical Asia and Oceania. Environ. Sci. Technol. 29, 2673-2683.

Karelson, M., Lobanov, V.S., Katritzky, A.R., 1996. Quantum-chemical descriptors in QSAR/QSPR studies. Chem. Rev. 96, 1027-1043.

Karickhoff, S.W., 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10, 833-846.

Karthikeyan, S., Balasubramanian, R., See, S.W., 2006. Optimization and validation of a low temperature microwave-assisted extraction method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter. Talanta 69, 79-86.

Kaupp, H., McLachlan, M.S., 1999. Gas/particle partitioning of PCDD/Fs, PCBs, PCNs and PAHs. Chemosphere 38, 3411-3421.

Kelly, C.P., Cramer, C.J., Truhlar, D.G., 2004. Predicting adsorption coefficients at air-water interfaces using universal solvation and surface area models. J. Phys. Chem. B 108, 12882-12897.

Kondo, Y., Morino, Y., Takegawa, N., et al., 2004. Impacts of biomass burning in SEA on ozone and reactive nitrogen over the western Pacific in spring. J. Geophys. Res. 109. doi:10.1029/2003JD004203.

Kroto, H.W., Allaf, A.W., Balm, S.P., 1991. C60-Buckminsterfullerene. Chem. Rev. 91, 1213-1235.

Kuhlbusch, T.A.J., Hertlein, A.-M., Schütz, L.W., 1998. Sources, determination, monitoring and transport of carbonaceous aerosols in Mainz, Germany. Atmos. Environ. 32, 1097-1110.

Kutz, F.W., Wood, P.H., Bottimore, D.P., 1991. Organochlorine pesticides and polychlorinated biphenyls in human adipose tissue. Rev. Environ. Contam. Toxicol. 120, 1-82.

Lü, W., Chen, Y., Liu, M., Chen, X., Hu, Z., 2007. OSPR prediction of n-octanol/water partition coefficient for polychlorinated biphenyls. Chemosphere 69, 469-478.

Laakso, L., Gronholm, T., Rannik, U., Kosmale, M., Fiedler, V., Vehkamaki, H., Kulmala, M., 2003. Ultra fine particlescavenging coefficients calculated from 6 years field measurements. Atmos. Environ. 37, 3605-3613.

Lee, K.H., Kim, Y.J., Kim, J.J., 2006. Characteristics of aerosol observed during two severe haze events over Korea in June and October 2004. Atmos. Environ. 40, 5146-5155.

Lee, R.G.M., Burnett, V., harner, T., Jones, K.C., 2000. Short term temperature dependent naphthalenes and organochlorine pesticides. Environ. Sci. Technol. 34, 269-288

.

Lee, S.C., Ho, K.F., Chan, L.Y., Zielinska, B., Chow, C.J., 2001. Polycyclic aromatic hydrocarbons (PAHs) and carbonyl compounds in urban atmosphere of Hong Kong. Atmos. Environ. 35, 5949-5960.

Lei, Y.D., Chankalal, R., Chan, A., Wania, F., 2002. Supercooled liquid vapor pressures of the polycyclic aromatic hydrocarbons. J. Chem. Eng. Data 47, 801-806.

Lei, Y.D., Wania, F., Shiu, W.Y., Boocock, D.G.B., 2000. HPLC-based method for estimating the temperature dependence of n-octanol-water partition coefficient. J. Chem. Eng. Data 45, 738-742.

Lenicek, J., Sekyra, M., Bednarkova, K., Benes, I., Sipek, F., 2000. Short term temperature dependent air–surface exchange and atmospheric concentrations of polychlorinated naphthalenes and organochlorine pesticides. Environ.Sci.Technol. 34, 393-398.

Leuenberger, C., Czuczwa, J., Heyerdahl, E., Giger, W., 1988. Aliphatic and polycyclic aromatic hydrocarbons in urban rain, snow and fog. Atmos. Environ. 22, 695-705.

Li, J., Cheng, H., Zhang, G., Qi, S., Li, X., 2009. Polycyclic aromatic hydrocarbon (PAH) deposition to and exchange at the air-water interface of Luhu, an urban lake in Guangzhou, China. Environ. Pollut. 157, 273-279.

Li, J., Zhang, G., Guo, L.L., Xu, W.H., Li, X.D., Lee, C.S.L., Ding, A.J., Wang, T., 2007. Organochlorine pesticides in the atmosphere of Guangzhou and Hongkong: regional sources and long-range atmospheric transport. Atmo.Environ. 41, 3889-3903.

Li, K., Landriault, M., Fingas, M., Llompart, M., 1998a. Pressurised solvent extraction of environmental organic compounds in soils using a supercritical fluid extractor. Analusis 26, 365-369.

Li, Y.F., 1999. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1994 to 1997. Sci. Total Environ. 232, 121-158.

Li, Y.F., Bidleman, T.F., Barrie, L.A., 1998. Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. Geophys. Res. Lett. 25, 39-41.

Liang, C., Pankow, J.F., 1996. Gas/particle partitioning of organic compounds to environmental tobacco smoke (ETS): partition coefficient measurements by desorption, and comparison to urban particulate material. Environ. Sci. Technol. 30, 2800-2805.

Ligocki, M.P., Leuenberger, C., Pankow, J.F., 1985a. Trace Organic-Compounds in Rain.2. Gas Scavenging of Neutral Organic-Compounds. Atmos. Environ. 19, 1609-1617.

Ligocki, M.P., Leuenberger, C., Pankow, J.F., 1985b. Trace Organic-Compounds in Rain.3. Particle Scavenging of Neutral Organic-Compounds. Atmos. Environ. 19, 1619-1626.

Lim, L., Wurl, O., Karuppiah, S., Obbard, J.P., 2007. Atmospheric wet deposition of PAHs to the sea-surface microlayer. Mar. Pollut. Bull. 54, 1212-1219.

Liss, P.S., 1973. Processes of gas exchange across an air-water interface. Deep-Sea Research 20, 221-238.

Lohmann, R., Harner, T., Thomas, G.O., Jones, K.G., 2000. Comparative study of the gas-particle partitioning of PCDD/Fs, PCBs, and PAHs. Environ. Sci. Technol. 34, 4943-4951.

Lohmann, R., Lammel, G., 2004. Adsorptive and absorptive contributions to the gas-particle partitioning of polycyclic aromatic hydro-carbons: state of knowledge and recommended parametrization for modeling. Environ. Sci. Technol. 38, 3793-3804.

Lowenbach, W.A., 2002. Allocation of PCB Sources at a scrap metal yard. Science and Technology Committee Newsletter Archive, 3 (available online).

Luo, X., Mai, B., Yang, Q., Fu, J., Sheng, G., Wang, Z., 2004. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China. Mar. Pollut. Bull. 48, 1102-1115.

Luo, X.W., Foo, S.C., Ong, H.Y., 1997. Serum DDT and DDE levels in Singapore general population. Sci. Total Environ. 208, 97-104.

Müller, J.F., 1997. Occurrence and Distribution Processes of Semivolatile Organic Chemicals in the Atmosphere and Leaves. Doctor of Philosophy. Faculty of Environmental Sciences. Griffith University, Brisbane, Australia.

Ma, C.J., Tohna, S., Kasahara, M., Hayyakawa, S., 2004. The nature of individual solid particles retained in size-resolved raindrops fallen in Asian dust storm event during ACEAsia,. Atmos. Environ. 38, 2951-2964.

Mackay, D., Shiu, W.Y., Ma, K.C. (Eds.), 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Lewis Publisher, Boca Raton, FL.

Mackay, D., Shiu, W.Y., Ma, K.C. (Eds.), 1996. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Lewis Publishers, Boca Raton, FL.

Mackay, D., Shiu, W.Y., Ma, K.C., 1997. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Lewis Publishers, Chelsea, MI, U.S.A.

Mader, B.T., Pankow, J.F., 2001. Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters. 3. An analysis of gas adsorption artifacts in measurements of atmospheric SOCs and organic carbon (OC) when using Teflon membrane filters and quartz fiber filters. Environ. Sci. Technol. 35, 3422-3432.

Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G., 2002. Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). Atmos. Environ. 36, 4023-4035.

Marshal, J.S., Palmer, W.M., 1948. The distribution of rain-drops with size. J. Atmos. Sci. 5, 165-166.

Martinsson, B.G., Frank, G., Cederfelt, S.-I., Swietlicki, E., Berg, O.H., Zhou, J.C., Bower, K.N., Bradbury, C., Birmili, W., Stratmann, F., Wendisch, M., Wiedensohler, A., Yuskiewicz, B.A., 1999. Droplet nucleation and growth in orographic clouds in relation to the aerosol population. Atmos. Res. 50, 289-315.

Mastral, A.M., Callén, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. Environ. Sci. Technol. 34, 3051-3057.

McGroddy, S.E., farrington, J.W., Gschwend, P.M., 1996. Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls Environ.Sci. Technol. 30, 172-177.

McLachlan, M., 1997. A simple model to predict accumulation of PCDD/Fs in an agricultural food chain. Chemsophere 34, 1263-1276.

McVeety, B.D., Hites, R.A., 1988. Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. Atmos. Environ. 22, 511-536.

Miguel, A.H., Eiguren-Fernandez, A., Jaques, P.A., Froines, J.R., Grant, B.L., Mayo, P.R., Sioutas, C., 2004. Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California. Atmos. Environ. 38, 3241-3251.

Minh, T.B., Kunisue, T., Yen, T.H., Watanabe, M., Tanabe, S., Hue, N.D., Qui, V., 2002. Persistent organochlorine residues and their bioaccumulation profile in resident and migatory birds from Norht Vietnam. Environ. Toxicol. Chem. 21, 2108-2118.

Mircea, M., Stefan, S., Fuzzi, S., 2000. Precipitation scavenging coefficient: influence of measured aerosol and raindrop size distributions. Atmos. Environ. 34, 5169-5174.

Monirith, I., Ueno, D., Takahashi, S., Nakata, H., Sudaryanto, A., Subramanian, A., Karuppiah, S., Ismail, A., Muchtar, M., Zheng, J.S., Richardson, B.J., Prudente, M., Hue, N.D., Tana, T.S., Tkalin, A.V., Tanabe, S., 2003. Asia-Pacific mussel watch: monitoring contamination of persistent organochlorine compounds in coastal waters of Asian countries. Mar. Pollut. Bull. 46, 281-300.

Monte, M.J.S., Santos, L.M.N.B.F., Fulem, M., Fonseca, J.M.S., Sousa, C.A.D., 2006. New static apparatus and vapor pressure of reference materials: Naphthalene, benzoic acid, benzophenone, and ferrocene. J. Chem. Eng. Data 51, 757-766.

Muir, D.C.G., Teixeira, C., Wania, F., 2004. Empirical and modeling evidence of regional atmospheric transport of current-use pesticide. Environ. Toxicol. Chem. 23, 2421-2432.

Murayanma, H., Takase, Y., Mitobe, H., Mukai, H., Ohzeki, T., Shimizu, K., Kitayama, Y., 2003. Seasonal change of persistent organic pollutant concentrations in air at Niigata Area, Japan. Chemosphere 52, 683-694.

Murray, M.W., Andren, A.W., 1992. Precipitation scavenging of polychlorinated biphenyl congeners in the great lakes region. Atmos. Environ. A: General Topics 26, 883-897.

NEA, National Environmental Agency of Singapore.Climatology of Singapore. http://app.nea.gov.sg/cms/htdocs/article.asp?pid=1088

Nguyen, T.H., Goss, K.U., Ball, W.P., 2005. Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. Environ. Sci. Technol. 39, 913-924.

Odabasi, M., Cetin, E., Sofuoglu, A., 2006. Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: Application to gas-particle partitioning in an urban atmosphere. Atmos. Environ. 40, 6615-6625.

Odabasi, M., Sofuoglu, A., Tasdemir, Y., Holsen, T.M., 1999. Measurment of dry deposition and air-water exchange of polycyclic aromatic hydrocarbons with the water surface sampler. Environ. Sci. Technol. 33, 426-434.

Offenberg, J.H., Baker, J.E., 1997. Polychlorinated biphenyls in Chicago precipitation: enhanced wet deposition to near-shore lake Michigan. Environ. Sci. Technol. 31, 1534-1538.

Offenberg, J.H., Baker, J.E., 2002. Precipitation scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons along an urban to over-water transect. Environ. Sci. Technol. 36, 3763-3771.

Ogura, I., Masunaga, S., Nakanishi, J., 2001. Parameters characterizing atmospheric behavior of PCDDs/PCDFs. Organohalogen Compd. 52, 483-486.

Osborne, M., Crosby, N., 1987. Benzopyrenes. Cambridge University Press, Cambridge, U.K.

Oskam, I.C., Ropstad, E., Lie, E., Derocher, A.E., Wiig, Ø., Dahl, E., Larsen, S., Skaare, J.U., 2004. Organochlorines affect the steroid hormone cortisol in free-ranging polar bears (ursus Maritimus) at Svalbard, Norway. J. Toxicol. Environ. Health 67, 959-977.

Pandit, G.G., Sahu, S.K., Puranik, V.D., Venkat Raj, V., 2006. Exchange of polycyclic aromatic hydrocarbons across the air-water interface at the creek adjoining Mumbai harbour, India. Environ. Int'l. 32, 259-264.

Pankow, J.F., 1987. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmos. Environ. 21, 2275-2283.

Pankow, J.F., 1988. The calculated effect of non-exchangeable material on the gas particle distribution of organic compounds. Atmos.Environ. 22, 1405-1409.

Pankow, J.F., 1994a. An absorption model of gas/aerosol partitioning involved in the formation of secondary organic aerosol. Atmos.Environ. 28, 189-193.

Pankow, J.F., 1994b. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. Atmos. Environ. 28, 185-188.

Pankow, J.F., Bidleman, T.F., 1991. Effects of temperature, TSP and percent non-exchangeable material in determining the gas-particle partitioning of organic compounds. Atmos. Environ. 25A, 2241-2249.

Pankow, J.F., Bidleman, T.F., 1992. Interdependence of the slopes and intercepts from log-log correlations of measured gas-particle partitioning and vapor pressure-I. Theory and analysis of available data. Atmos.Environ. 26A, 1071-1080.

Pankow, J.F., Isabelle, L.M., Buchholz, D.A., Luo, W., Reeves, B.D., 1994. Gas/particle partitioning of polycyclic aromatic hydrocarbons and alkanes to environmental tobacco smoke. Envrion. Sci. Technol. 28, 363-365.

Pankow, J.F., Storey, J.M., Yamasaki, H., 1993. Effects of relative humidity on gas/particle partitioning of semivolatile organic compounds to urban particulate matter. Environ. Sci. Technol. 27, 2220-2226.

Panther, B.C., Hooper, M.A., Tapper, N.J., 1999. A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments. Atmos.Environ. 33, 4087-4099.

Park, J.S., Wade, T.L., Sweet, S., 2001. Atmospheric deposition of organochlorine contaminants to Galveston Bay, Texas. Atmos. Environ. 35, 3315-3324.

Park, J.S., Wade, T.L., Sweet, S.T., 2002. Atmospheric deposition of PAHs, PCBs and organochlorine pesticides to Corpus Christi Bay, Texas. Atmos. Environ. 36, 1707-1720.

Perry, K.D., Hobbs, F.V., 1994. Further evidence for particle nucleation in clear air adjacent to marine cumulus clouds. J. Geophys. Res. 99, 22803-22818.

PiiTeiro-Iglesias, M., Grueiro-Noche, G., Lopez-Mahy'a, P., Muniategui-Lorenzob, S., Prada-Rodry'guez, D., 2004. Assessment of methodologies for airborne BaP analysis. Sci.Total Environ., 334–335, 377-384.

Poster, D.L., Baker, J.E., 1996a. Influence of submicron particles on hydrophobic organic contaminants and distributions of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in rain water. Environ.Sci. Technol. 30, 341-348.

Poster, D.L., Baker, J.E., 1996b. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. scavenging of polycyclic aromatic hydrocarbons by rain. Environ. Sci. Technol. 30, 349-354.

Prevedouros, K., Palm-Cousins, A., Gustafsson, Ö., Cousins, I.T., 2008. Development of a black carbon-inclusive multi-media model: Application for PAHs in Stockholm. Chemosphere 70, 607-615.

Qi, S.H., Sheng, G.Y., Fu, J.M., Min, Y.S., Wu, J.X., Jian, Y.T., Ye, Z.X., 2000. Study on distributions of polycyclic aromatic hydrocarbons (PAHs) in aerosols at different levels. Acta Scientiae Circumstantiae 20, 308-311.

Riget, F., Dietz, R., Vorkamp, K., Johansen, P., Muir, D., 2004. Levels and spatial and temporal trends of contaminants in Greenland biota: an updated review. Sci. Total Environ. 331, 29-52.

Rolph, G.D., 2003. Real-time Environmental Applications and Display sYstem (READY) Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD, USA.

Roth, C.M., Goss, K.U., Schwarzenbach, R.P., 2005a. Sorption of a diverse set of organic vapors to diesel soot and road tunnel aerosols. Environ. Sci. Technol. 39, 6632-6637.

Roth, C.M., Goss, K.U., Schwarzenbach, R.P., 2005b. Sorption of a diverse set of organic vapors to urban aerosols. Environ. Sci. Technol. 39, 6638-6643.

Sahsuvar, L., Helm, P.A., Jantunen, L.M., Bidleman, T.F., 2003. Henry's law constants for alpha-, beta- and gamma-HCHs as a function of temperature and revised estimates of gas exchange in Arctic regions. Atmos. Environ. 37, 983-992.

Sahu, S.K., Pandit, G.G., Sadasivan, S., 2004. Precipitation scavenging of polycyclic aromatic hydrocarbons in Mumbai, India,. Sci. Total Environ. 318, 245-249.

Saim, N., Dean, J.R., Abdullah, M.P., Zakaria, Z., 1998. An experimental design approach for the determination of polycyclic aromatic hydrocarbons from highly contaminated soil using accelerated solvent extraction. Anal. Chem. 70, 520-424.

Schwarzenbach, R.P., Geschwend, P.M., Imboden, D.M. (Eds.), 2003. Environmental Organic Chemistry. Wiley-Interscience, New York.

See, S.W., Balasubramanian, R., Rianawati, E., Karthikeyan, S., Streets, D.G., 2007. Characterization and source apportionment of particulate matter ≤ 2.5 μ m in Sumatra, Indonesia, during a recent peat fire episode. Environ. Sci. Technol. 41, 3488-3494.

Seinfeld, J.H., 1986. Atmospheric Chemistry and Physics of Air Pollution. John Wiley and Sons, New York.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics:From Air Pollution to Climate Change. Wiley, New York.

Seinfeld, J.H., Pandis, S.N. (Eds.), 2006. Atmospheric Chemistry and Physics: from Air Pollution to Climate Change (2nd ed). John Wiley, New York.

Semeena, V.S., Lammel, G., 2005. The significance of the grasshopper effect on the atmospheric distribution of persistent organic substances. Geophys. Res. Lett. 32, L07804, doi:07810.01029/02004GL022229.

Shen, J., Shao, X., 2005. A comparison of accelerated solvent extraction, Soxhlet extraction, and ultrasonic-assisted extraction for analysis of terpenoids and sterols in tobacco. Anal. Bioanal. Chem. 383, 1003-1008.

Shen, L., Wania, F., 2005. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. J. Chem. Eng. Data 50, 742-768.

Sievering, H., Van Valin, C.C., Barrett, E.W., Pueschel, R.F., 1984. Cloud scavenging of aerosol sulfur: two cases studies. Atmos. Environ. 18, 2685-2690.

Simcik, M.F., 2004. The importance of surface adsorption on the washout of semivolatile organic compounds by rain. Atmos. Environ. 38, 491-501.

Simcik, M.F., Basu, I., Sweet, C.W., Hites, R.A., 1999. Temperature dependence and temporal trends of polychlorinated biphenyl congeners in the Great Lakes atmosphere. Environ. Sci. Technol. 33, 1991-1995.

Simcik, M.F., Eisenreich, S.J., Golden, K.A., Liu, S.-P., Lipiatou, E., Swackhammer, D.L., Long, D.T., 1996. Atmospheric loading of polycyclic aromatic hydrocabons to Lake Michigan as recorded in the sediments. Envrion. Sci. Technol. 30.

Simcik, M.F., Franz, T.P., Zhang, H.X., Eisenreich, S.J., 1998. Gas-particle partitioning of PCBs and PAHs in the Chicago urban and adjacent coastal atmosphere: states of equilibrium. Environ. Sci. Technol. 32, 215-257.

Simcik, M.F., Hoff, R.M., Strachan, W.M.J., Sweet, C.W., Basu, I., Hites, R.A., 2000. Temporal trends of semivolatile organic contaminants in Great Lakes precipitation. Environ. Sci. Technol. 34, 361-367.

Smith, A.G., 1991. Chlorinated Hydrocarbon Insecticides. In: Hayes, W.J., Laws, E.r. (Eds.). Handbook of Pesticide Toxicology: Volume II, Classes of Pesticides. Academic Press, Inc., Toronto, Canada.

Sporring, S., Bøwadt, S., Svensmark, B., Björklund, E., 2005. Comprehensive comparison of classic Soxhlet extraction with Soxtec extraction, ultrasonication extraction, supercritical fluid extraction, microwave assisted extraction and accelerated solvent extraction for the determination of polychlorinated biphenyls in soil. J. Chromatogr. A 1090, 1-9.

Stern, G.A., Halsall, C.J., Barrie, L.A., 1997. Polychlorinated biphenyls in Arctic air. 1. Temporal and spatial trends: 1992-1994. Environ. Sci. Technol. 31, 3619-3628.

Stohl, A., 1998. Computation, accuracy and applications of trajectories-A review and bibliography. Atmos. Environ. 32, 947-966.

Stohl, A., Seibert, P., 1998. Accuracy of trajectories as determined from the conservation of meteorological tracers. Quart. J. Roy. Meteor. Soc. 124, 1465-1484.

Storey, J.M., Luo, W., Isabelle, L.M., Pankow, J.F., 1995. Gas/solid partitioning of semivolatile organic compounds to model atmospheric solid surfaces as a function of relative humidity. 1. Clean quartz. Environ. Sci. Technol. 29, 2420-2428.

Straif, K., Baan, R., Grosse, Y., Secretan, B., El Ghissassi, F., Cogliano, V., 2005. Carcinogenicity of polycyclic aromatic hydrocarbons. Lancet Oncol. 6, 931-932.

Strommen, M.R., Kamens, R.M., 1999. Simulation of Semivolatile Organic Compound Microtransport at Different Time Scales in Airborne Diesel Soot Particles. Environ. Sci. Technol., 1738-1746.

Sun, H.W., Li, J.G., 2005. Availability of pyrene in unaged and aged soils to earthworm uptake, butanol extraction and SFE. Water, Air, Soil Pollut. 166, 353-365.

Sun, P., Backus, S., Blanchard, P., Hites, R.A., 2006. Temporal and spatial trends of organochlorine pesticides in great lakes precipitation. Environ. Sci. Technol. 40, 2135-2141. http://dx.doi.org/10.1021/es051861g

Takase, Y., Murayama, H., Mitobe, H., Aoki, T., Yagoh, H., Shibuya, N., Shimizu, K., Kitayama, Y., 2003. Persistent organic pollutants in rain at Niigata, Japan. Atmo.Environ. 37, 4077-4085.

Tan, J., Cheng, S.M., Loganath, A., Chong, Y.S., Obbard, J.P., 2007. Selected organochlorine pesticide and polychlorinated biphenyl residues in house dust in Singapore. Chemosphere 68, 1675-1682.

Tang, Y., Donnelly, K.C., Tiffany-Castiglioni, E., Mumtaz, M.M., 2003. Neurotoxicity of polycyclic aromatic hydrocarbons and simple chemical mixtures. J. Toxicol. Environ. Health 66, 919-940.

Tao, S., Cui, Y.H., Cao, J., Xu, F.L., Dawson, R., Li, B.G., 2002. Determination of PAHs in wastewater irrigated agricultural soil using accelerated solvent extraction. J. Environ. Sci. Health B37, 141-150.

Tao, S., Yang, Y., Wu, S.M., Liu, S.Z., Dou, H., Liu, Y.N., Lang, C., Hu, F., Xingh, B.S., 2007. Vertical distribution of polycyclic aromatic hydrocarbons in atmospheric boundary layer of Beijing in winter. Atmos. Environ. 41, 9594-9602.

Terzi, E., Samara, C., 2004. Gas-particle partitioning of polycyclic aromatic hydrocarbons in urban, adjacent coastal, and continental background sites of western Greece. Environ. Sci. Technol. 38, 4973-4978.

Thibodeaux, L.J., Nadler, K.C., Valsaraj, K.T., Reible, R.R., 1991. The effect of moisture on volatile organic chemical gas-to-particle partitioning with atmospheric aerosols-competitive adsorption theory predictions. Atmo.Environ. 25A, 1649-1656.

Thompson, J.D., Cramer, C.J., Truhlar, D.G., 2003. Predicting aqueous solubilities from aqueous free energies of solvation and experimental or calculated vapor pressures of pure substances. J. Chem. Phys. 19, 1661-1670.

Tinsley, I., 1979. Chemical concepts in pollutant behaviour. John Wiley and Sons, New York, USA.

Totten, L.A., Brunciak, P.A., Gigliotti, C.L., Dachs, J., Glenn, T.R., Nelson, E.D., Eisenreich, S.J., 2001. Dynamic air-water exchange of polychlorinated biphenyls in the New York-New Jersey harbor estuary. Environ. Sci. Technol. 35, 3834-3840.

Turner, D.B., 1986. Comparison of Three Methods for Calculating the Standard Deviation of the Wind Direction. J. Climate Appl. Meteor. 25, 703-707.

Turpin, B.J., Lim, H.J., 2001. Species contribtuions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci. Technol. 35, 602-610.

Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos. Environ. 34, 2983-3013.

UNEP, U.N.E.P., 2002. Regionally based assessment of persistent toxic substances. South East Asia and South Pacific. UNEP Chemicals 11-13, chemin des Anémones, CH-1219 Châtelaine, GE, Switzerland.

van den Berg, A., Dentener, F., Lelieveld, J., 2000. Modelling the chemistry of the marine boundary layer: Sulfate formation and the role of sea-salt aerosol particles. J. Geophys. Res. 105, 11671-11698.

Van der Oost, R., Beyer, J., Vermeulen, N.P.E., 2003. Fish bioaccumulation and biomarkers in environmental risk assessment: a review. Environ. Toxicol. Pharmacol. 13, 57-149.

Van Noort, P.C.M., 2003. A thermodynamics-based estimation model for adsorption of organic compounds by carbonaceous materials in environmental sorbents. Environ. Toxicol. Chem. 22, 1179-1188.

Viana, M., Chi, X., Maenhaut, W., Querol, X., Alastuey, A., Mikuškac, P., Večeřa, Z., 2006. Organic and elemental carbon concentrations in carbonaceous aerosols during summer and winter sampling campaigns in Barcelona, Spain. Atmos. Environ. 40, 2180-2193.

Visser, T., Sarobe, M., Jenneskens, L.W., Wesseling, J.W., 1998. Identification of isomeric polycyclic aromatic hydrocarbons (PAH) in pyrolysates from ethynylated PAH by gas chromatography-fourier infrared spectorscopy. Their relevance for the understanding of PAH rearrangement and interconversion processes during combusion. Fuel 77, 913-920.

Voldner, E.C., Li, Y.F., 1995. Global usage of selected persistent organochlorines. Sci. Total Environ. 160-161, 201-210.

Waid, J.S., 1986. PCBs and the Environment, Volume I. CRC Press, Inc., Boca Raton, Florida, U.S.A.

Waite, D.T., Cessna, A.J., Gurprasad, N.P., Banner, J., 1999. A new sampler for collecting separate dry and wet atmospheric depositions of trace organic chemicals. Atmos. Environ. 33, 1513-1523.

Walters, R.W., Luthy, R.G., 1984. Equilibrium adsorption of polycyclic aromatic hydrocarbons from water onto activated carbon. Environ. Sci. Technol. 18, 395-403.

Wang, J., Guo, L., Li, J., Zhang, G., Lee, C.S.C., Li, X., Jone, K.C., Xiang, Y., Zhong, L., 2007. Passive air sampling of DDT, chlordane and HCB in the Pearl River Delta, South China: implications to regional sources. J. Environ. Monit. 9, 582-588.

Wania, F., 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in Polar regions. Environ. Sci. Technol. 37, 1344-1351.

Wania, F., Axelman, J., Broman, D., 1998. A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface. Environ. Pollut. 102, 3-23.

Wania, F., Mackay, d., 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio 22, 10-18.

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. 97, 7373-7382.

Wanninkhof, R., Sullivan, K.F., Top, Z., 2004. Air-sea gas transfer in the Southern Ocean. J. Geophys. Res. 109, C08S19.01-C08S19.12.

Wei, B.N., Xie, S.D., Yu, M., Wu, L., 2007. QSPR-based prediction of gas/particle partitioning of polychlorinated biphenyls in the atmosphere. Chemosphere 66, 1807-1820.

Wilke, C.R., Chang, P., 1955. Correlation of diffusion coefficients in dilute solutions. AIChE Journal 1, 264-270.

Wilkinson, A.C., 2002. The dynamics of persistent organic pollutants in air and in selected lakes of the Canadian Rocky Mountains. Ottawa-Carleton Institute of Biology. University of Ottawa, Ottawa, Ontario Canada.

Wilkinson, A.C., Kimpe, L.E., Blais, J.M., 2005. Air-water gas exchange of chlorinated pesticides in four lakes spanning. Environ. Toxicol. Chem. 24, 61-69.

Willet, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ. Sci. Technol. 32, 2197-2207.

Wurl, O., Obbard, J.P., 2005a. Organochlorine compounds in the marine atmosphere of Singapore. Atmos.Environ. 39, 7207-7216.

Wurl, O., Obbard, J.P., 2005b. Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. Chemosphere 58, 925-933.

Wurl, O., 2006. Persistent Organic Pollutants in Asia: Fate and Distribution in the Ocean and Atmosphere. Doctor of Philosophy. Department of Chemical and Biomolecular Engineering. National University of Singapore, Singapore.

Wurl, O., Karuppiah, S., Obbard, J.P., 2006. The role of the sea-surface microlayer in the air-sea gas exchange of organochlorine compounds. Sci. Total Environ. 369, 333-343.

Wurl, O., Obbard, J.P., Lam, P.K.S., 2006a. Distribution of organochlorine compounds in the sea-surface microlayer, water column and sediment of Singapore's coastal environment. Chemosphere 62, 1105-1115.

Wurl, O., Obbard, J.P., Lam, P.K.S., 2006b. Distribution of organochlorines in the dissolved and suspended phase of the sea-surface microlayer and seawater in Hong Kong, China. Mar. Pollut. Bull. 52, 768-777.

Wurl, O., Potter, J.R., Obbard, J.P., Durville, C., 2006c. Persistent organic pollutants in the equatorial atmosphere over the open Indian Ocean. Environ. Sci. Technol. 40, 1454-1461.

WWF, World Wildlife Fund,1998. Resolving the DDT Dilemma: Protecting biodiversity and human health. Canada

Xiao, H., Li, N.Q., Wania, F., 2004. Compilation, Evaluation, and Selection of Physical-Chemical Property Data for α-, β-, and γ-Hexachlorocyclohexane. J. Chem. Eng. Data 49, 173-185.

Xu, S.S., Liu, W.X., Tao, S., 2006. Emission of polycyclic aromatic hydrocarbons in China. Environ. Sci. Technol. 40, 702-708.

Yamasaki, H., Kuwata, K., Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 25, 189-194.

Yang, J.S., Lee, D.W., Lim, H., 2003. Microwave-assisted extraction (MAE) of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins from fly ash and sea sediments: Effect of water and removal of interferences. J.Liq.Chromatogr.Related Technol. 26, 803-818.

Yang, Y.Y., Li, D.L., Mu, D.H., 2008. Levels, seasonal variations and sources of organochlorine pesticides in ambient air of Guangzhou, China. Atmo.Environ. 42, 677-687.

Yao, Z.W., Jiang, G.B., Xu, H.Z., 2002. Distribution of organochlorine pesticides in seawater of the Bering and Chukchi Sea. Environ. Pollut. 116, 49-56.

Yeo, H.G., Choi, M., Chun, M.Y., Kim, T.W., Cho, K.C., Sunwoo, Y., 2004. Concentration characteristics of atmospheric PCBs for urban and rural area, Korea. Sci. Total Environ. 324, 261-270.

Yeo, H.G., Choi, M., Chun, M.Y., Sunwoo, Y., 2003a. Concentration distribution of polychlorinated biphenyls and organochlorine pesticides and their relationship with temperature in rural air of Korea. Atmos. Environ. 37, 3831-3839.

Yeo, H.G., Choi, M., Chun, M.Y., Sunwoo, Y., 2003b. Gas/particle concentration and partitioning of PCBs in the atmosphere of Korea. Atmos. Environ. 37, 3561-3570.

Yunker, M.B., Macdonald, R.W., Brewer, R., Mitchell, R.H., Goyette, D., Sylvester, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489-515.

Yunker, M.B., Snowdon, L.R., Macdonald, R.W., Smith, J.N., Fowler, M.G., Skibo, D.N., McLaughlin, F.A., Danyushevskaya, A.I., Petrova, V.I., Ivanov, G.I., 1996. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. Environ. Sci. Technol. 30, 1310-1320.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencsér, A., Kiss, G., Krivácsy, Z., Molnár, Á., Mészáros, E., Hansson, H.-C., Rosman, K., Zebühr, Y., 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. Atmos. Environ. 33, 2733-2743.

Zhang, G., Li, J., Cheng, H., Li, X., Xu, W., Jones, K.C., 2007. Distribution of organochlorine pesticides in the Northern South China Sea: Implications for land outflow and air-sea exchange. Environ. Sci. Technol. 41, 3884-3890.

Zhou, W., Zhu, L., 2005. Distribution of polycyclic aromatic hydrocarbons in soil-water system containing a nonionic surfactant. Chemosphere 60, 1237-1245.

Appendix A: List of Publications

International journal articles

He, J., Balasubramanian, R. 2010. The exchange of SVOCs across the air-sea interface in Singapore's coastal environment. Atmospheric Chemistry and Physics, 10, 1837-1852.

He, J., Balasubramanian, R. 2010. A comparative evaluation of passive and active samplers for measurements of gaseous semi-volatile organic compounds in the tropical atmosphere. Atmospheric Environment, 44, 884-891

He, J., Balasubramanian, R. 2010. Semi-volatile organic compounds (SVOCs) in ambient air and rainwater in a tropical environment: Concentrations and temporal and seasonal trends. Chemosphere, 78, 742-751

He, J., Balasubramanian, R. 2009. A study of precipitation scavenging of semi-volatile organic compounds (SVOCs) in a tropical area. Journal of Geophysical Research, 114, D12201, doi:10.1029/2008JD011685

He, J., Balasubramanian, R., Karthikeyan, S., Joshi, U.M. 2009. Determination of semi-volatile organo-chlorine compounds in the atmosphere using acclerated solvent extraction. Chemosphere, 75(5), 640-648

He, J., Balasubramanian, R. 2009. A study of gas-particle partitioning of SVOCs in the tropical atmosphere of Southeast Asia. Atmospheric Environment, 43(29), 4375-4383

He, J., Balasubramanian, R. 2009. Determination of atmospheric polycyclic aromatic hydrocarbons using accelerated solvent extraction. Analytical Letters, 42(11), 1603-1619

Karthikeyan, S., He, J., Palani, S., Balasubramanian, R., Burger, D. 2009. Determination of total nitrogen in atmospheric wet and dry deposition samples. Talanta 77, 979-984.

Karthikeyan, S. He, J., Joshi, U.M., Balasubramanian, R. 2009. Determination of total nitrogen in environmental samples: validation by comparison of techniques and interlaboratory studies. Analytical Letters, 42, 1-10.

Karthikeyan, S., Balasubramanian, R., He, J. 2009. Inter-laboratory study to improve the quality of the analysis of nutrients in rainwater chemistry. Atmospheric Environment , 43(21), 3424-3430

He, J., Balasubramanian, R. 2008. Rain-aerosol coupling in the tropical atmosphere of southeast Asia: distribution and scavenging ratios of major ionic species. Journal of Atmospheric Chemistry, 60(3), 205-220

Peer-reviewed conference publications

1) He, J; Balasubramanian, R. The exchange of SVOCs across the air-sea interface in a tropical environment. Poster at American Association for Aerosol Research (AAAR) 2009 Annual Conference (28^{th}), Minneapolis, MN, USA, October 26-30, 2009.

2) He, J; Balasubramanian, R. The exchange of SVOCs across the air-sea interface in Singapore's coastal environment. Presented at the Young Water Talents Symposium, Suntec Singapore, 22 June 2009

3) He, J; Balasubramanian, R. Rain-aerosol coupling in the tropical atmosphere of SEA. Poster at American Association for Aerosol Research (AAAR) 2008 Annual Conference (27th), Orlando, Florida, USA, October 20-24, 2008

4) He, J; Zielinska, B; Balasubramanian, R. The organic composition of ambient atmosphere in SEA during the 2006 haze episode. Presented at American Geophysical Union (AGU) 2007 Meeting, San Francisco, California, USA, Decemeber 10-14, 2007

Technical Report

He, J., Karthikeyan, S., Balasubramanian, R. Project report on passive sampler inter-comparison under Malé Declaration, United Nations Environmental Programme (UNEP).

Book Chapter

Balasubramanian, R. and He, J. Characterization of Persistent Organic Pollutants in the Atmosphere. Accepted for book publication "Urban Airborne Particulate Matter. Origin, Chemistry, Fate Health" (in press)

Balasubramanian, R. and He, J. Fate and Transfer of Persistent Organic Pollutants in a Multi-Media Environment. Accepted for book publication "Urban Airborne Particulate Matter. Origin, Chemistry, Fate Health" (in press)