Air-sea interactions of semi-volatile organic compounds in the tropical environment of Southeast Asia

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Abstract. Major urban and industrial centers increase loadings of semi-volatile organic compounds (SVOCs) to proximate sea waters through riverine transport, atmospheric deposition via dry particle deposition, wet deposition, and air-sea gas exchange. 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. 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. 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. 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 article reports the dry particle deposition and wet deposition of selected SVOCs based on an extensive set of yearly data collected in Singapore. Singapore, a representative country of Southeast Asia (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 acts a sink or source for selected SVOCs via air-sea diffusive exchange as well as to investigate the SML enrichment effect.

1 Introduction

The atmosphere is strongly 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 [1], 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. [2].

Among the organic chemicals in the atmospheric environment, SVOCs have received considerable attention because of their physico-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 [3]. 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 [4–7]. 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 [8,9].

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 [10]. 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 capacitors, and also revolatilized from earlier contaminated soils, sediments, water reservoirs and even vegetations [11].

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. 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 [12]. 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 [13]. 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 [14]. 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 [15]. 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 [16,17].

The region of SEA has been reported to be one of the important sources for SVOCs [18]. 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 [19]. In addition, from tropical and sub-tropical regions of Asia, it has been reported that SVOCs could even be transported across the Pacific Oceans to Canadian west coast and arctic regions [20,21]. 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 [22].

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 [23,24]. 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 [25]. 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 $\sim$ 1000 $\mu$m) 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 [26–28]. A schematic overview of some major environmental phases and their interaction is given in Figure 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.

2 Occurrence, sources and properties of SVOCs in the atmospheric environment

2.1 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 structures of selected PAHs are shown in Figure 2. 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 due to lower vapor pressures [29,30].

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 [31]. More than 30 parent or unsubstituted compounds plus several hundred derivatives have carcinogenic activities [32,33]. In addition, several pollutants among this group are associated with mutagenicity [34], genotoxicity [35], immunotoxicity [36], neurotoxicity [37], and toxicity of the reproductive systems [38], and mostly those with four to six rings are considered to be very active carcinogens [3].

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 [39]. PAHs can be formed during any incomplete combustion or high temperature pyrolytic process involving fossil fuels, or more generally, materials containing carbon and hydrogen [32]. 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) [40]. Consequently, B(a)P and other PAHs are formed through pyrosynthesis processes of methane, acetylene, butadiene and other compounds [41]. 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 [41,42].

The PAH rearrangement and interconversion processes during combustion have also been shown by [43]. Motor vehicles account for the majority of PAH emissions in urban areas [44]. 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

\[ \text{Fig. 2. Structure of selected PAHs.} \]
compounds; (ii) storage in engine deposits and subsequent emission of PAH already in the fuel; and (iii) pyrolysis of lubricants [4]. 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 [45].

2.2 Organochlorine Pesticides (OCPs)

Typically, pesticides refer to substances used for the destruction or control of insects, fungi, vegetation and any microbiological agents [46]. 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 [47]. 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 [48]. The structure of selected OCPs is shown in Figure 3

2.2.1 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 [49]. HCH was created in 1825, but it was not discovered until 1943 that γ isomer was responsible for the insecticidal activity of technical HCH [50]. 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 [51], 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 [48].

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 [52]. The highest consumption of technical HCH occurred between 0 ~ 30°N latitude, while the highest consumption of γ-HCH occurred between 30°N ~ 60°N latitude [53]. 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 [49,52]. 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 [49]. 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 [54].

2.2.2 DDTs

DDT synthesis was reported in 1874 and the insecticidal properties of the p, p-DDT isomer was discovered in 1939 [55]. DDT is produced by condensation of chloral and chlorobenzene in the presence of an excess of concentrated sulfuric 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°C with more cost [48]. 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 [50]. 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 [48]. Approximately 2.5 billion people in over 90 countries are at risk of contracting malaria [56], therefore DDT is still in use in many of these developing countries [57].

2.3 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are non-polar, aromatic, chlorinated hydrocarbons (see Figure 4). 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 [11]. 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, caulkins, synthetic resins, rubbers, paints, waxes and asphalts, and as surface coatings for carbonless copy paper [58]. The manufacture, processing, distribution and uses of PCBs were banned in 1978 by U.S. congress [11]. Applications were restricted throughout the rest of the world soon after [48].

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 [59]. The persistence of PCBs coupled with their ability to bioaccumulate in food chains has caused great environmental damage [48].
2.4 Physicochemical properties of selected SVOCs

Simulation of the transport and distribution of selected SVOCs requires knowledge of the physicochemical 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 [60]. 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

\[
K_{mn} = \frac{C_m}{C_n} \approx \frac{S_m}{S_n}
\]  

(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 [3].

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

\[
K_{OW} = \frac{S_O}{S_W}
\]  

(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 (KOA) has been introduced and can be obtained by

\[
K_{OA} = \frac{S_O}{S_A} = \frac{S_O RT}{p}
\]  

(2.3)

where \( R \) is the universal gas constant (8.3145 Pa m³ mol⁻¹ K⁻¹) and \( T \) is the absolute temperature (K).

The Henry’s Law constant, \( H \) (Pa m³ 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

\[
K_{AW} = \frac{S_A}{S_W} = \frac{p}{S_{WRT}} = \frac{H}{RT}
\]  

(2.4)

The properties of vapor pressure, water solubility, octanol-water partition coefficient (KOW), octanol-air partition coefficient (KOA) and the Henry’s law constant (H) are listed in Table 1.

KOA 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 [61]. 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 [61]. For instance, lower chlorinated PCB congeners have lower KOA so that their particle fractions are lower due to higher vapor pressure [62,63].

The selected SVOCs are typically hydrophobic and characterized by a low water solubility and relatively high KOW value. Thus, they tend to volatilize from aqueous solution and be associated with organic matter of soil, sediments and suspended particulate matter in water column [8]. In general, the less water soluble SVOCs, described by higher KOW, prefer to accumulate on organic matter and in
Table 1. Physicochemical properties of selected SVOCs.

| Compound                  | Vapor Pressure Pa | Water Solubility mg L\(^{-1}\) | Log KO\(_{\text{OW}}\) | Log KO\(_{\text{OA}}\) | k\(_{\text{H}}\) 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               | \(9 \times 10^{-1}\) | 3.9                             | 4.00                   | 6.33                   | 1.1                              |
| Fluorene                    | \(9 \times 10^{-2}\) | 1.8                             | 4.18                   | 6.79                   | 6.4                              |
| Phenanthrene                | \(2 \times 10^{-2}\) | 1.2                             | 4.57                   | 7.60                   | 2.6                              |
| Anthracene                  | \(7.6 \times 10^{-4}\) | 7.6 \times 10^{-2}             | 4.54                   | 7.71                   | 1.8                              |
| Fluoranthenes               | \(1.2 \times 10^{-4}\) | 2.1 \times 10^{-1}        | 5.22                   | 8.87                   | 6.6 \times 10^{-1}                |
| Pyrene                      | \(6 \times 10^{-5}\) | 1.4 \times 10^{-1}           | 5.18                   | 8.81                   | 2.5 \times 10^{-1}                |
| Benz[a]anthracene           | \(5.7 \times 10^{-7}\) | 2.8 \times 10^{-3}           | 5.86                   | 10.28                  | 1.0 \times 10^{-1}               |
| Chrysene                    | \(6.7 \times 10^{-7}\) | 1.2 \times 10^{-3}           | 5.80                   | 11.33                  | 1.2                              |
| Benzo[b]fluoranthene        | \(5.2 \times 10^{-8}\) | 7.6 \times 10^{-4}           | 6.00                   | 11.36                  | 3.9                              |
| Benzo[k]fluoranthene        | \(7.0 \times 10^{-7}\) | 2.3 \times 10^{-3}           | 6.04                   | 11.55                  | 4.9 \times 10^{-2}               |
| Benzo[a]pyrene              | \(6.0 \times 10^{-8}\) | 2.6 \times 10^{-4}           | 6.50                   | 12.54                  | 1.5 \times 10^{-2}               |
| Indeno[1,2,3-cd]pyrene      | \(7.0 \times 10^{-7}\) | 6.2 \times 10^{-2}           | 6.58                   | 12.42                  | 7.0 \times 10^{-3}               |
| Dibenzo[a]anthracene        | \(3.7 \times 10^{-10}\) | 5.0 \times 10^{-4}           | 6.75                   | 12.58                  | 7.4 \times 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^{-7} \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                    | \(5.9 \times 10^{-3} \sim 5.4 \times 10^{-3}\) | 4.3 \times 10^{-3} \sim 0.1     | 5.6 \sim 6.5           | 8.47 \sim 9.29            | 1.7 \sim 47.6                    |
| Penta-CBs                    | \(3.0 \times 10^{-3} \sim 9.0 \times 10^{-3}\) | 4 \times 10^{-3} \sim 0.02 | 6.2 \sim 6.5           | 9.14                   | 24.8 \sim 151.4                  |
| Hexa-CBs                     | \(2 \times 10^{-3} \sim 1.6 \times 10^{-3}\) | 4 \times 10^{-4} \sim 1 \times 10^{-3} | 6.7 \sim 7.3           | 9.80                   | 11.9 \sim 81.8                   |
| Hepta-CBs                    | \(2.7 \times 10^{-5}\) | 4.5 \times 10^{-4} \sim 2 \times 10^{-3} | 6.7 \sim 7.0           | 9.87                   | 5.4                          |
| Octa-CBs                     | \(2.7 \times 10^{-5}\) | 2 \times 10^{-4} \sim 3 \times 10^{-4} | 7.1                    | N.A.                   | 38.1                          |
| Nonate-CBs                   | \(6.3 \times 10^{-6}\) | 1.8 \times 10^{-3} \sim 1.1 \times 10^{-3} | 7.2 \sim 8.2           | N.A.                   | 100.0                          |
| Deca-CBs                     | \(5.0 \times 10^{-7}\) | 1.2 \times 10^{-6}           | 8.3                    | N.A.                   | 20.8                          |

Note: Log KO\(_{\text{OW}}\)(25°C), water solubilities (25°C), vapor pressure (25°C) and Henry's law constant of selected SVOCs adapted from Mackay et al. (1997). Log KO\(_{\text{OA}}\)(25°C) adapted from Hamer and Bidleman (1996, 1998), Kömp and McLachlan (1997) and Wania et al. (2002).
biota to a greater extent. For example, HCHs have relatively high water solubilities and low $K_{OW} < 4$, and therefore their bioaccumulation is less significant [64]. 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 [28,65]. Physicochemical properties of selected SVOCs certainly depend on prevailing environmental conditions. They are subject to measurement uncertainties [66], and are reported in a wide range, rather than consistent, values [67], which makes it particularly challenging to theoretically simulate the behaviors of SVOCs in the environment.

2.5 Gas-Particle partitioning

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 [68].

Pankow [69] consolidated, and subsequently refined early approaches [23,70] to describe the equilibrium partitioning between gas and particles based on adsorption theory [71,72]. Much attention has also been paid to the effect of relative humidity [73–75], and non-exchangeable matter [76]. Pankow [76] 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 μgm$^{-3}$:

$$K_p = \frac{(C_p/TSP)/C_g}{16P_L^0}$$

(2.5)

In case of adsorption, Pankow (1988) derived

$$K_p = \frac{N_sA_{TSP}Te(Q_d - Q_v)/RT}{16P_L^0}$$

(2.6)

where $N_s$ is the surface concentration of sorption sites, $A_{TSP}$ is the specific surface area of the TSP, $P_L^0$ is the vapor pressure of the subcooled liquid, $Q_d$ 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 $p_L$ [23,24,69,70]. The correlation could be shown as

$$\log K_p = m_r \log p_L^0 + b_r.$$  

(2.7)

This regression of log $K_p$ against the temperature corrected log $p_L^0$ 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 [23].

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) [77]. It has been demonstrated that the experimental data, the observed slopes near -1 of log $K_p$ vs. log $p_L^0$, would also be applicable to absorption, e.g. into an organic aerosol fraction [78,79]. $K_p$ values measured on clean quartz sand at different relative humidities [80] are much lower than measured in urban aerosol [75], 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 [78,81] 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 [61]. 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:

$$\log K_P = 0.79 \log K_{OA} - 10.01 \quad (2.8)$$

$$\log K_P = 0.55 \log K_{OA} - 8.23 \quad (2.9)$$

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) [79,82].

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \quad (2.10)$$

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.

### 2.6 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 $F_{dry}(\mu g m^{-2} s^{-1})$ is expressed as a product of the concentration on particles $C_p(\mu g m^{-3})$ and a dry deposition velocity $V_d(m s^{-1})$ as follows:

$$F_{dry} = C_p \cdot V_d \quad (2.11)$$

To date there has been no consensus on the appropriate dry deposition velocity to use in the flux estimation. Estimated [83] and experimental [84] 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 ($<0.1 \mu m$) [85]. 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) [86]. Using this multistep model and other techniques it has been found that coarse particles ($>2.5 \mu m$) and compounds associated with them are responsible for the majority of dry deposition [84,86,87]. 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 [68]. In addition, a moving sheet of water was used to passively trap dry particles and gases to trace organic chemicals [87].

### 2.7 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:

$$W_T = W_P\Phi + W_G(1 - \Phi) \quad (2.12)$$

where $\Phi$ 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 [88]. 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 [89,90]. Therefore, vapor washout ratio, $W_G$, has been estimated using air-water equilibrium partition coefficients or Henry’s Law constant:

$$W_G = \frac{C_{R_{\text{dissolved}}}}{C_g} = \frac{RT}{H} \quad (2.13)$$

where $C_{R_{\text{dissolved}}}$ 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:

$$W_P = \frac{C_{R_{\text{sorbed}}}}{C_P} \quad (2.14)$$

where $C_{R_{\text{sorbed}}}$ 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 [89–94]. Washout ratios for SVOCs tend to be much smaller than those reported for trace metals and radio-nuclides [89,90,95]. 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 [88]. 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 [96]. Both particle and vapor scavenging are affected by ambient temperature, which can presumably shift gas-particle partitioning of SVOCs in the atmosphere [96].

### 2.8 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) [97]. 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 5.), which has been previously applied to the air-sea exchange of SVOCs [98–100], 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 [101]. The flux $F_{\text{air–water}}$ (ng m$^{-2}$ day$^{-1}$) is calculated by

$$F_{\text{air–water}} = K_{OL} \left( C_{\text{truly}} - \frac{C_g}{H'} \right) \quad (2.15)$$
where $K_{OL}$ (m day$^{-1}$) is the overall mass transfer coefficient, and $(C_{\text{g}_{\text{true}}} - C_{g}^\prime)$ 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 ($8.315 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$), $H$ 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.

$$\frac{1}{K_{OL}} = \frac{1}{K_{W}} + \frac{1}{K_{A}H^\prime}$$

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 [97, 102]. 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) [97], diffusivities in air and water change by a factor of 1.2 and 2.3 between 0 and 30°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 [96].

### 3 The exchange of SVOCs across the air-sea interface

#### 3.1 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

\[
F_{\text{dry}}(\mu g \text{ m}^{-2} \text{ yr}^{-1}) = \sum_{i=1}^{12} (C_i \times V_d \times 2592) \tag{3.1}
\]

\[
F_{\text{wet}}(\mu g \text{ m}^{-2} \text{ yr}^{-1}) = \sum_{i=1}^{12} (C_{i\text{WM}} \times P_i \times 10^{-3}) \tag{3.2}
\]

where \(C_i\), \(C_{i\text{WM}}\) 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 \(P_i\) 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 [103] using the following equation.

\[
V_d = \frac{1}{R_a + R_b + R_c v_s + v_s} \tag{3.3}
\]

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 \((R_a = 9/u_s^2)\), which is a function of wind speed, \(u\) and standard deviation of wind speed, \(\sigma_u\) [104] and \(R_b\) is quasi laminar layer resistance, which is a function of particle size, Brownian diffusion, interception and impaction; \(R_c\) on water surface is given by [105]. 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 \(\sigma_\theta\) (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\(\mu m\) by the optical counter was in the fine mode (less than 1\(\mu m\)) [106].

SVOCs in the water column partition into three phases: the truly dissolved phase, the particulate phase and the colloidal organic material [101]. 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 [96]. Based on the empirical estimation of sorption of hydrophobic pollutants onto natural sediments and soils [107] and its application into water-column by Totten et al. (2001) [101], the relationship between partition coefficient \(K_{\text{OC}}\) and \(K_{\text{OW}}\) can be derived as follows:

\[
\log K_{\text{OC}} = \log \left(\frac{K_P}{f_{\text{OC}}}\right) = a \log K_{\text{OW}} + b \tag{3.4}
\]

where \(K_{\text{OC}}\) equals partition coefficient \(K_P\) normalized by organic carbon fraction (\(f_{\text{OC}}\)) in particulate phase. \(K_P\) refers to the partitioning in the water column between the apparent dissolved and particulate phase [101], calculated as \(C_P/(C_{d,a} \times \text{TSM})\) \((C_P\): the concentration of SVOCs associated with the particulate phase; \(C_{d,a}\): the concentration in the apparent dissolved phase; and \(\text{TSM}\): the concentration of total suspended matter). \(K_{\text{OW}}\) (L kg\(^{-1}\)) was obtained from the best available experimental data and predictive models with careful evaluations [108~112]. Since the temperature dependence of \(K_{\text{OW}}\) for selected SVOCs is not significant [113,114] and the temperature of seawater varied by no more than 4°C in this study, \(K_{\text{OW}}\) has not been corrected for temperature.

To accommodate additional sorption to soot phase, Accardi-dey and Gschwend (2002) [115] modified Gustafsson’s model [116] to yield a dual OC/BC model:

\[
K_P = f_{\text{OC}} K_{\text{OC}} + f_{\text{SC}} K_{\text{SC}} C_{d,a}^{n-1} \tag{3.5}
\]

where \(f_{\text{SC}}, K_{\text{SC}}\) 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 [116~118]. Considering the similarity
of distribution between sediment/water and between particulate/water in sea water column, Equation (3.5) can be reasonably applied to the latter process.

The apparent dissolved concentrations of SVOCs \( C_{d,a} \) is the sum of the truly dissolved \( C_{true} \) 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 Wurl et al., 2006) [101,119]

\[
C_{d,a} = C_{true} + C_{DOC} = C_{true}(1 + K_{OW} \times DOC \times 10^{-7}).
\] (3.6)

A classical two-layer model, which has been previously applied to the air-sea exchange of SVOCs [93,99,100], 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 [101]. 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 \( K_{a,i} \) 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 [97]:

\[
K_{a,comp} = K_{a,H_2O} \left( \frac{M_{H_2O}}{M_{comp}} \right)^{0.5 \times 0.67}
\] (3.7)

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 [120] for the mass transfer coefficient \( K_{a} \) has been applied in a number of studies [101,119,121], 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 [97]:

\[
K_{w,comp} = \begin{cases} 
0.65 \times 10^{-3} \left( \frac{Sc_{comp}}{600} \right)^{-0.67} & \text{for } u_{10} \leq 4.2 \text{ m s}^{-1} \text{ (smooth surface regime)} \\
(0.79u_{10} - 2.68) \times 10^{-3} \left( \frac{Sc_{comp}}{600} \right)^{-0.5} & \text{for } 4.2 < u_{10} \leq 13 \text{ m s}^{-1} \text{ (rough surface regime)} \\
(1.64u_{10} - 13.69) \times 10^{-3} \left( \frac{Sc_{comp}}{600} \right)^{-0.5} & \text{for } u_{10} > 13 \text{ m s}^{-1} \text{ (breaking wave regime)}
\end{cases}
\] (3.8)

where the Schmidt number, \( Sc_{e} \), is the ratio of kinematic viscosity \( \nu_{kin}(cm^2 s^{-1}) \) and diffusivity \( D \) (cm\(^2\) s\(^{-1}\)) by \( Sc_{e} = \nu_{kin}/D \). 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 (3.9) developed by Wilke and Chang (1955) [122],

\[
D = 7.4 \times 10^{-8} \left( \frac{2.6M_{comp}^{0.5}T}{\eta V_{comp}^{0.6}} \right)
\] (3.9)

where \( T \) is the average temperature during each sampling event, \( V_{comp} \) is the molar volume of compound investigated [123,124] and \( \eta \) 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 2.

### 3.2 Experimental

#### 3.2.1 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
Table 2. 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$^3$ s$^{-1}$) | $S_C$ (cm$^3$ mol$^{-1}$) | $V_{comp}$ ($\times 10^{-5}$ cm$^3$ s$^{-1}$) | $K_{a,comp}$ ($\times 10^{-3}$ 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                               | 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.
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. 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°C for 24 h) Whatman GF/F filters (0.7 μm, 47 mm 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.

3.2.2 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 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 (30 m length and 0.25 mm i.d.; film thickness 0.25 μm) with purified helium as carrier gas. Organic carbon (OC) and elemental carbon (EC) were determined as described in Section 3.4.7.

3.3 Results and discussion

3.3.1 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 6 using Equations (3.1) and (3.2), respectively. $V_d$ (0.003 m s$^{-1}$) was not derived from sampling with dry deposition plates in this study but calculated using Equation (3.3), which is also in the range of 0.001–0.01 m s$^{-1}$ for PAHs, OCPs and PCBs as reported in the literature [83,125,126]. Concentrations of PCBs in both dissolved and particulate phases of all rainwater samples were below the limits of detection in this study.

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 6(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 6(a)) in sharp contrast to the low dry deposition fluxes during the same period (Figure 6(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.

The mean annual atmospheric fluxes of selected SVOCs are summarized in Table 3. Particulate dry deposition fluxes of $\Sigma_{16}$PAHs, $\Sigma_2$OCPs and $\Sigma_{21}$ PCBs were 1328.8 ± 961.1 μg m$^{-2}$ year$^{-1}$, 5421.4 ± 3426.7 ng m$^{-2}$ year$^{-1}$ and 811.8 ± 578.3 ng m$^{-2}$ year$^{-1}$, respectively. The dry particulate deposition fluxes of $\Sigma_2$OCPs and $\Sigma_{21}$ PCBs were much lower than that of $\Sigma_{16}$-PAHs. This is most likely due to the
Seasonal variation in both dry and wet depositions of selected SVOCs between Jun 2007 and May 2008.

(a) dry deposition and (b) wet deposition.

Local heavy PAH emissions into the atmosphere. In addition, the wet deposition fluxes of \( \sum_{16}^{\text{PAHs}} \) and \( \sum_{7}^{\text{OCPs}} \) 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 \( \sum_{16}^{\text{PAHs}} \) 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 \( \sum_{16}^{\text{PAHs}} \) 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 [127,128]. One can see in Table 3 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 [129], 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 3 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 particlesorbed and gaseous chemicals, but particle scavenging, rather than the gas scavenging, is the dominant removal mechanism [127,130]. The below-cloud scavenging rates increase with particle size because the collision efficiency of particle-droplet encounter increases with increasing particle diameters [131]. 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 [132,133].
Table 3. 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     | $\mu g \text{ m}^{-2} \text{ y}^{-1}$ | $\mu g \text{ m}^{-2} \text{ y}^{-1}$ | ng m$^{-2}$ day$^{-1}$      |
| Naph     | 65.3 ± 56.0                        | 850.7 ± 428.8                     | −1608.4 ± 869.6              |
| Ace      | 28.0 ± 13.1                        | 62.9 ± 60.9                       | −                         |
| Flu      | 32.7 ± 20.5                        | 102.7 ± 106.5                     | −36.5 ± 8.0                  |
| Phe      | 19.6 ± 10.3                        | 82.6 ± 46.0                       | −27.3 ± 22.0                 |
| Ant      | 130.6 ± 78.4                       | 554.4 ± 395.6                     | −457.7 ± 489.7               |
| 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(g)hIP  | 168.0 ± 121.3                      | 42.2 ± 39.4                       | −17.0 ± 6.6                  |
| ΣPAHs    | 1328.8 ± 961.1                     | 6677.1 ± 1745.2                   | −5884.0 ± 4040.7             |
| OCPs     | ng m$^{-2}$ y$^{-1}$               | $\mu g \text{ m}^{-2} \text{ y}^{-1}$ | 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 ± 1.85                  |
| 4,4'-DDE | 41.1 ± 35.5                        | 0.71 ± 0.89                      | −0.74 ± 0.67                 |
| ΣOCPs    | 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                         | −                                  | −                        |
| ΣPCBs    | 811.8 ± 578.3                      | −                                  | −                        |

3.3.2 Water column partitioning

In sea subsurface water (SSW), the apparent dissolved and particulate occurrence levels of SVOCs are reported in Table 4. 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
Table 4. Concentrations of SVOCs in SSW, SML and atmospheric gas phases during Nov to Dec 2007 in Singapore’s coastal area.

| Compound | SSW $C_{\text{d}}$ | SSM $C_p$ | FDOC C (%) | SML $C_{\text{d}}$ | SML $C_p$ | Gas $C_{\text{a}}$ |
|----------|-------------------|-----------|------------|-------------------|-----------|-----------------|
| 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(ab)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   |
| $\sum$PAHs | 43.9 ± 35.8    | 131.4 ± 101.8| 80.8 ± 61.3| 365.3 ± 209.1     | 187.5 ± 138.3| 36.5 ± 20.1     |
| $\alpha$-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   |
| $\beta$-HCH | 306.5 ± 280.2 | 326.0 ± 258.9| 0.25 ± 0.36| 835.3 ± 533.9     | 506.7 ± 314.4| 238.6 ± 143.1   |
| $\gamma$-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   |
| $\delta$-HCH | 180.6 ± 230.4 | 59.6 ± 44.8| 310.5 ± 319.5| 208.9 ± 219.2     | 109.1 ± 101.3| 95.8 ± 36.7     |
| $\Sigma$HCHs | 1147.8 ± 898.5 | 728.9 ± 622.0| 1887.8 ± 1288.1| 1411.7 ± 929.5 | 958.9 ± 336.7 | 38.7 ± 11.5 |
| 4,4'-DDT | 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     |
| $\Sigma$DDTs | 361.9 ± 271.8 | 560.3 ± 501.5| 493.4 ± 214.1| 1240.7 ± 925.1 | 39.7 ± 7.7 |
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. (2006) [134].

### 3.3.2.1 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 [107] as in Figure 7. In Figure 7(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 [135,136]. 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 [136]. 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 [115,137]. 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 [137,138].

### 3.3.2.2 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 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(a)) and HMW (the predicted line not shown in Figure 8(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 [117,118], but for HMW compounds such as B(a)P, $K_P$ was over-predicted by a
factor of 2 $\sim$ 5 by using $n_{11}$ [118]. At the optimum Freundlich exponents, $K_P$ values increased by 1.4 $\sim$ 1.6 log units and 0.7 $\sim$ 1.3 log units for LMW and HMW PAHs, respectively. Soot carbon was the dominant sorbent here since its sorption contributed $\sim$90% of the total partition coefficients, while the OC fraction was still an important sorbent and contributed to $\sim$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.

3.3.3 Air-water diffusive exchange

3.3.3.1 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 $\sim$ 7.8 mg L$^{-1}$. The predicted mean fractions adsorbed to DOC for individual PAH varied in the range of 0.1 $\sim$ 40% as can be seen from Table 4. It clearly showed that HMW PAHs are more readily adsorbed to DOC (10 $\sim$ 50%) than those LMW compounds (below 10%). $\alpha$-, $\beta$-, and $\gamma$-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 ($\sim$0.4%) reported by Wurl et al. (2006) [134], while $F_{\text{DOC,C}}$ (%) for DDTs was much higher in the range of 30 $\sim$ 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.

3.3.3.2 Air-water gas exchange flux. Atmospheric gas-phase mean concentrations of $\Sigma$PAHs, $\Sigma$HCHs and $\Sigma$DDTs during Nov and Dec of 2007 (Table 4) were 187.5 $\pm$ 138.3 ng m$^{-3}$, 958.9 $\pm$ 336.7 pg m$^{-3}$ and 39.5 $\pm$ 7.7 pg m$^{-3}$, respectively, which were in the range of levels reported previously [139]. The mean annual fluxes of SVOCs across the air-water interface were estimated and are summarized in Table 3.

The fluxes of the individual PAH compound were in the range of $\sim$21.7 $\pm$ 20.2 $\sim$ 1608.4 $\pm$ 869.6 ng m$^{-2}$ day$^{-1}$ and $\Sigma$PAH flux reached up to $\sim$5884.0 $\pm$ 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 [140]. Both New York harbor and Raritan Bay systems exhibited net volatilization fluxes for the majority of PAHs [129], while LMW PAHs showed positive fluxes and HMW PAHs showed negative values in Mumbai harbor of India [141]. The magnitudes of net PAH fluxes are comparable to the reported values ($\sim$0.01 $\sim$ 21.2 $\mu$g m$^{-2}$ day$^{-1}$) in an urban lake in Guangzhou, China [99]. 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 $-44.4 \pm 37.8 \sim -73.7 \pm 31.3$ ng m$^{-2}$ day$^{-1}$ and $-0.74 \pm 0.67 \sim -2.9 \pm 1.8$ ng m$^{-2}$ day$^{-1}$ for HCHs and DDTs, respectively (Table 3), 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 $-8.2 \sim -66.8$ ng m$^{-2}$ day$^{-1}$ [134]. 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 [142]. 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 9. 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 $\sim 80\%$ 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 9) was similar to that of wet deposition fluxes for individual PAH compounds (Table 3). The contribution of air-sea gas absorption has been reported to decrease with the increasing of molecular weight [129]. 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.

### 3.3.4 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 [26, 27, 119]. This effect can be quantified by the enrichment factor EF, calculated as the ratio between SML and SSW concentrations as shown in Figure 10. EFs in the SML of particulate phase were 1.2 $\sim$ 7.1 and 3.0 $\sim$ 4.9 for PAHs and OCPs, and those of dissolved phase were 1.1 $\sim$ 4.9 and 1.6 $\sim$ 4.2 for PAHs and OCPs, respectively. EFs
Fig. 10. Enrichment factors (EF) of PAHs and OCPs in the sea-surface microlayer of Singapore’s coastal line.

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. (2006) [134]. 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 [142]. This may be the reason for high variation of EFs obtained in this study.

4 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 (KOC) values for PAHs were much larger than predictions and the log KOC is poorly correlated with log KOW, while the field-obtained KOC values for OCPs are correlated better with KOW. 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-availability 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.

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