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A study of gas/particle partitioning of SVOCs in the tropical atmosphere of Southeast Asia

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ABSTRACT

Gas- and particle-phase polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were collected at a tropical site in Southeast Asia over 12-h periods during November and December 2006 to determine their gas/particle distributions 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 agree relatively better with those observed 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 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.

1. Introduction

Semivolatile organic compounds (SVOCs) as defined by the U.S. EPA Terminology Reference System are those compounds that volatilize relatively slowly at standard temperature (20 °C) and pressure (1 atm). SVOCs comprise many priority pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) which are toxic and persistent. SVOCs may pose a threat to environmental and human health once released into the environment. In addition, they are also transported by atmospheric pathways over the Earth's surface and be found far from any source in different environmental media such as waters, soils, biota or even ice-cores (Kawamura et al., 1994; Muir et al., 1996). In order to assess potential risks of these pollutants for the natural environment and human health, it is important to understand the fate of pollutants once they are introduced into the environment.

An important aspect with regard to the atmospheric fate of SVOCs is their partitioning between the gas and particle phases which could 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, 1994; Lohmann and Lammel, 2004; Roth et al., 2005; 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, 2005; Karthikeyan et al., 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

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the tropical and coastal atmosphere of Southeast Asia. In this manuscript, the contributions of ad- and absorption to the gas/particle concentrations of PAHs and PCBs in the tropical atmosphere are discussed.

2. Experimental

2.1. Sampling

All the air samples were collected between November and December 2006 at the NUS (National University of Singapore) Atmospheric Research Station which is located 67 m above sea level and in the vicinity of a highway and traffic intersection. The site is approximately 1 km away from the open sea, influenced by emissions from urban vehicular traffic, chemical industries, major power plants, oil refineries situated in a group of small islands on the west coast of the Singapore Island and as well as by advection of biomass burning-impacted air masses from the nearby provinces of Indonesia (Sumatra and Kalimantan).

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}. Particles were collected by a pre-combusted (at 450 °C for 24 h) circular quartz filter of 4 inches diameter loaded onto the filter holder; an adsorbent cartridge filled with 3 pieces of one-inch PUF plugs in series (7.62 cm) were used to trap gas phase compounds. PUF plugs were pre-cleaned with hexane followed by acetone in 33 mL stainless steel vessels of a Dionex ASE 200 under optimized conditions described below. Average sampling time was 12 h periods (successive daytime 8.00 am–8.00 pm and nighttime 8.00 pm–8.00 am) and average sampling volumes were 180 m^3. The filter and PUF samples were stored −20 °C prior to extraction.

2.2. Material

The standard mixture USEPA 610 includes 16 native PAHs (naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (B(a)A), chrysene (Chr), 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. The standard mixture of PCBs (C-QME-01) was obtained from AccuStandard (New Haven, USA). 13C$_{12}$-PCBs congeners CB 77, 101, 141, 178 (Cambridge Isotope Laboratories, MA, USA) and anthracene-d$_{10}$, fluoranthene-d$_{10}$ and benzo[e]pyrene-d$_{12}$ (Sigma–Aldrich, St. Louis, MO, USA) were used as surrogates; 13C$_6$-Tetrachlorobenzene and 13C$_{12}$-PCBs congeners CB 8 and 206 (Cambridge Isotope Laboratories, MA, USA) and phenanthrene-d$_{10}$, pyrene-d$_{10}$ and benzo[a]pyrene-d$_{12}$ (Sigma–Aldrich, St. Louis, MO, USA) were used as internal standards. Silica gel, florisil and anhydrous sodium sulfate were of GR analysis grade (Merck, Germany), heated at 600 °C for 24 h to remove any organic contamination.

2.3. Sample preparation and analysis

Both gaseous and particulate samples were extracted by Dionex ASE 200 under the following conditions developed in our lab: 3:1 (HEX and ACE) n-hexane and acetone combination at 100 °C for 30 min. 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 as well 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.

GC–MS Analysis. Chemical analysis 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 0.25 mm I.D; film thickness 0.25 μm) with purified helium as carrier gas. 4 μL of the 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 and PCBs standards as well as extracted samples were analyzed separately in selective ion monitoring mode (SIM) with a detector voltage 700 V. For PAHs, GC temperature program was as follows: 70 °C for 2 min; 15 °C min^{-1} to 200 °C, held for 4 min; 5 °C min^{-1} to 300 °C, held for 5 min; for PCBs, GC temperature program was as below: 170 °C for 11 min; 3 °C min^{-1} to 250 °C; 10 °C min^{-1} to 300 °C, held for 5 min.

Measurement of OC and EC. 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 2400 series II CHNS/O analyzer (Perkin–Elmer Life and Analytical Sciences Inc.), which was operated in CHN mode with acetanilide (71.09%C, 6.71% H, 10.36% H) 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 is set as high as 950 °C, the total of OC and EC was determined. Prior to analysis, carbonates are removed by adding diluted HCl. EC content can then be obtained by subtracting OC from the total of OC and EC. All the OC and EC contents with total suspended particle (TSP) concentrations and ambient temperature (Temp) are listed in Table 1. 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 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