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Polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China: Size distribution characteristics and size-resolved gas-particle partitioning

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ABSTRACT

Size distributions of thirteen polycyclic aromatic hydrocarbons (PAHs), elemental carbon (EC), and organic carbon (OC) in the range of 0.01–18 μm were measured using a nano Micro-Orifice Uniform Deposit Impactor (nano-MOUDI) in an urban location in Guangzhou, China in July 2006. PAH size distributions were fit with five modes and the respective mass median aerodynamic diameters (MMAD) are: Aitken mode (MMAD: ~0.05 μm), three accumulation modes AM_I, AM_{II}, AM_{III} (MMAD: 0.13–0.17 μm, 0.4–0.45 μm, and 0.9–1.2 μm, respectively), and coarse mode (MMAD: 4–6 μm). Seven-ring PAH was mainly in AM_{II} and AM_{III}. Five- and six-ring PAHs were found to be abundant in all the three AM. Three- and four-ring PAHs had a significant presence in the coarse mode in addition to the three AM. Size-resolved gas-particle partition coefficients of PAHs (K_p) were estimated using measured EC and OC data. The K_p values of a given PAH could differ by a factor of up to ~7 on particles in different size modes, with the highest K_p associated with the AM_I particles and the lowest K_p associated with the coarse mode particles. Comparison of calculated overall K_p with measured K_p values in Guangzhou by Yang et al. (2010) shows that adsorption on EC appeared to be the dominant mechanism driving the gas-particle partitioning of three- and four-ring PAHs while absorption in OM played a dominant role for five- and six-ring PAHs. The calculated equilibrium timescales of repartitioning indicate that five- to seven-ring PAHs could not achieve equilibrium partitioning within their typical residence time in urban atmospheres, while three- and four-ring PAHs could readily reach new equilibrium states in particles of all sizes. A partitioning flux is therefore proposed to replace the equilibrium assumption in modeling PAH transport and fate.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are of public concern and research interest mainly due to their carcinogenic potential (Air quality guidelines for Europe, 2000). Knowledge of PAH size distributions in ambient aerosols is important to assess the health effects of PAHs because particles of different sizes deposit on different parts of the human respiratory system. Emissions from vehicles and various industries in urban areas are major PAH sources. Therefore, PAH size distributions in urban ambient aerosols provide important data in regional- and global-scale modeling of PAH transport and fate (Aulinger et al., 2007; Makar, 2007).

Many different sorption mechanisms have been proposed to explain the SVOC partitioning between aerosol particle phase and gas phase. The mechanism is most likely related to the nature of particle composition (e.g. organic material, elemental carbon, salt, and mineral surfaces) and the chemical nature of SVOCs (e.g., polar, non-polar, ionizable molecules). In our understanding, it also depends on the source or generation mechanism of SVOCs, e.g., PAHs and polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) from combustion processes are very possible to have different sorption mechanisms from non-combustion products polychlorinated naphthalenes (PCNs) and polychlorinated biphenyls (PCBs). Even for a single group of compounds, PAHs, there remain many ambiguities on their partitioning mechanisms in the literatures. Allen et al. (1996) hypothesized that slow mass transfer by vaporization and condensation to explain the observed PAH partitioning among aerosol size fractions. Keshtkar and Ashbaugh (2007) speculated that the less volatile five- and six-ring PAHs were predominately on smaller particles where it condensed in the early stages of combustion while the more volatile three- and four-ring PAHs formed on larger particles as the smoke cooled. Venkataraman et al. (1999) proposed that adsorption explained the PAH presence in the nuclei and accumulation modes where the

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aerosol surface area predominated, while absorption explained their predominance in the accumulation mode where absorbing organic matter was available. Arp et al. (2008a) found that the predicted partition coefficient (K_p) values using fitted poly parameter linear free energy relationships (PP-LFERs) based on partitioning to the water insoluble organic matter (WIOM) phase underestimated the literature measurement results of PAHs and suggested that the underestimation by their WIOM model might be attributed to nonexchangeable PAHs from the EC fraction.

The majority of existing PAH measurements were made on bulk particles. Consequently theories on gas/particle partitioning of PAHs have been formulated to describe the partitioning between gaseous PAHs and bulk particles (Pankow, 1994a,b). Prior to our work, two studies have considered the particle size dependent partitioning of PAHs (Allen, 1997; Venkataraman et al., 1999). They discussed particle size-specific partitioning due to adsorptive and absorptive association of PAHs with particles. A few limitations exist in these two studies: (1) Two major PAH sorbents in particle phase, elemental carbon (EC) and organic material (OM), were not measured in their studies; (2) The effect of initial size distribution of freshly emitted PAHs on atmospheric aging processes was not considered; (3) The non-uniform nature of EC and OM in particles of different sizes was ignored.

In this study, size-segregated atmospheric aerosols were collected using a nano Micro-Orifice Uniform Deposit Impactor (nano-MOUDI) in an urban location of Guangzhou (GZ), China in summer 2006. The abundances and size distributions of thirteen PAHs in GZ were measured and interpreted by linking with EC and OC measurement results. We compared the measured K_p (Yang et al., 2010) with the calculated $K_{p,\mathrm{OM}}$ (considering only absorption mechanism) and $K_{p,\mathrm{EC}+\mathrm{OM}}$ (considering both absorption and adsorption mechanisms), respectively, based on our urban aerosol composition measurement. Such comparisons, together with PAH partitioning equilibrium timescale estimation, help to restrict the sorption mechanisms that resulted in PAHs size distribution characteristics in urban aerosols at our sampling site.

2. Experimental section

Sampling was conducted at an urban location in Guangzhou (GZ) (23°18′03″N, 113°15′50″), a metropolitan city 130 km from the southeast coast of China. We collected size-segregated aerosol samples on the rooftop of a 12-floor building next to a heavily trafficked road in GZ in the size range of 0.01–18 μm using a thirteen stage nano-MOUDI (MSP Corp, Shoreview, MN). Al foil was the sampling substrate. Seven sets of samples were collected from July 03 to July 31, each sample for duration of 2–3 days. One set of field blank samples was obtained at the beginning of the campaign. There was no rain during our sampling period. Daily temperatures ranged from 25.8° to 33.3 °C, with an average of 27.2 °C.

PAHs collected on Al foils were analyzed using in-injection port thermal desorption coupled with GC–MS analysis (TD-GC/MS). PAHs are thermally desorbed in GC liner, followed by separation and quantification by GC–MS. Thirteen PAHs, including PHE, ANT, FLA, PYR, CHR, BbF, BkF, BeP, BaP, PER, IND, BghiP, and COR (see Table 1 for definitions of the abbreviations) were quantified. This TD-GC/MS method is capable of quantifying PAHs at nanogram per sample level collected on quartz/Al foil filter substrates (Ho and Yu, 2004; Ho et al., 2008). The common solvent extraction-GC/MS analytical methods require much more aerosol materials (~500 μg of OC) and therefore require compositing multiple samples or using samplers of coarser particle size-segregation (e.g., Venkataraman et al., 1999; Offenberg and Baker, 1999). The improvement in analytical sensitivity with the TD-GC/MS method allows the determination of PAHs for individual size bins in the nano-MOUDI without sacrificing size resolution. A detailed description of the method can be found in the paper by Ho and Yu (2004). Validation of the TD-GC/MS has been documented in the paper by Ho et al. (2008). EC and OC were measured on the same filters using a thermal/optical transmittance aerosol carbon analyzer (Sunset Laboratory, OR) (Birch and Cary, 1996) and the data have been reported in the paper by Yu and Yu (2009).

Ambient aerosol is a mixture of multiple modes, with each mode commonly assumed to have a lognormal distribution (Seinfeld and Pandis, 2006). Similar to Dong et al. (2004), Dzubay and Hasan (1990) and Howell et al. (1998), we made an inversion algorithm on the basis that ambient aerosol is of multimodal lognormal size distributions. Mass median aerodynamic diameter (MMAD), geometric standard deviation (σ_g) and mass concentration (C_m) of each mode could be retrieved from the measured chemical species (e.g., PAH, EC, OC) on the nano-MOUDI stages and the calibrated kernel function matrix of the nano-MOUDI. The detailed inversion technique was described by Dong et al. (2004).

While the presence of Aitken mode in <100 nm size range and coarse mode in >2 μm size range is more obvious and straightforward, we tried from 1 to 3 modes in the accumulation mode size range (0.07 μm–1.2 μm) for all of our data (13 PAHs, EC, OC, sulfate, nitrate, and ammonium). Because we collected samples at a heavily polluted urban site during a one-month intensive campaign, it is reasonable to assume that 1) a certain individual PAH has consistent mode characteristics in all sets of samples, 2) different PAHs may have different mode numbers due to their volatility variations, but

Table 1
Mean modal concentrations of thirteen PAHs in Guangzhou urban samples ($n = 7$) and correlation coefficients of PAHs with EC and OC in all size modes ($n = 35$). ND: not detected.

	Abbr.	*MW*	Vapor pressure at 25 °C (Pa)	Modal concentrations and percentage contributions											Correlation coeff (R^2) $n = 35$	
				Nuclei mode		AM_I		AM_{II}		AM_{III}		Coarse mode		Total		
				ng m^{-3}	%	ng m^{-3}	%	ng m^{-3}	%	ng m^{-3}	%	ng m^{-3}	%	ng m^{-3}	with EC	with OC
phenanthrene	PHE	178	2×10^{-2}	0.021	1.4%	0.406	26.7%	0.45	29.5%	0.29	19.3%	0.35	23.1%	1.5	0.69	0.24
Anthracene	ANT	178	1×10^{-3}	0.015	3.3%	0.09	19.4%	0.16	33.6%	0.10	22.3%	0.10	21.4%	0.5	0.65	0.32
fluoranthene	FLU	202	1.23×10^{-3}	0.009	0.7%	0.242	19.8%	0.40	32.7%	0.32	25.9%	0.26	20.9%	1.2	0.75	0.37
Pyrene	PYR	202	6.0×10^{-4}	0.028	1.9%	0.342	23.0%	0.50	33.4%	0.37	24.9%	0.25	16.9%	1.5	0.72	0.23
Chrysene	CHR	228	5.7×10^{-7}	0.013	0.4%	0.556	18.4%	0.95	31.4%	1.03	34.1%	0.48	15.7%	3.0	0.69	0.22
benzo[b]fluoranthene	BbF	252	5.0×10^{-7}	0.011	0.1%	2.023	15.6%	5.79	44.6%	4.56	35.1%	0.62	4.7%	13.1	0.55	0.04
benzo[k]fluoranthene	BkF	252	5.2×10^{-8}	0.032	1.6%	0.368	18.5%	0.95	47.6%	0.56	28.3%	0.08	4.1%	2.0	0.52	0.10
benzo[e]pyrene	BeP	252	7.4×10^{-7}	0.053	0.6%	1.632	18.2%	3.88	43.2%	3.04	33.9%	0.38	4.2%	9.0	0.48	0.02
benzo[a]pyrene	BaP	252	7.0×10^{-7}	0.119	1.2%	1.28	12.4%	5.56	54.1%	3.11	30.3%	0.21	2.0%	10.3	0.49	0.02
Perylene	PER	252	1.4×10^{-8}	0.047	3.0%	0.331	21.0%	0.63	40.1%	0.51	32.1%	0.06	3.8%	1.6	0.25	0.02
indeno[1,2,3-cd]pyrene	IND	276	1.33×10^{-7}	0.128	1.4%	1.242	13.4%	4.35	47.1%	3.12	33.7%	0.41	4.4%	9.3	0.52	0.05
benzo[ghi]perylene	BghiP	276	6×10^{-8}	0.097	0.9%	1.737	16.4%	5.00	47.1%	3.39	31.9%	0.39	3.7%	10.6	0.46	0.03
Coronene	COR	300	2.0×10^{-10}	ND		ND		3.74	61.3%	2.36	38.7%	ND		6.1	0.004	0.004