

Digest of Thesis

Atmospheric Partitioning of Polycyclic Aromatic Hydrocarbons (PAH) and Oxygenated PAH

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by

Jonathan O. Allen

Distribution of PAH with Particle Size

Polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH (OPAH) are mutagenic air pollutants formed as by-products of combustion. After formation and emission, these compounds partition between the gas phase and atmospheric aerosols. The environmental fate of PAH and OPAH depends, in part, on their distribution between the gas and particulate phases and among particle size fractions. Particle size affects the removal rate of the associated PAH from the atmosphere by dry and wet deposition. The mechanism and location of particulate phase compounds deposited in the lung are also affected by particle size; large particles tend to impact on the upper regions of the lung and small particles diffuse to the surface of the alveoli. The goal of this work is a better understanding of the atmospheric partitioning of PAH and OPAH necessary to determine the environmental fate of, and human exposure to, these pollutants.

Size-segregated atmospheric aerosols were collected from urban and rural locations in Massachusetts using a micro-orifice inertial impactor [1]. The impaction media were oiled Teflon membranes which have been shown to reduce particle bounce even for high mass loadings [2]. The samples were prepared by size exclusion chromatography and

analyzed for PAH and OPAH using gas chromatography/mass spectrometry (GC/MS) [3]. Very low detection limits, 1.5–5 pg/m³, in samples collected from relatively small volumes of air were achieved using deuterated PAH internal standards and highly concentrated aerosol extracts. This work was the first reported GC/MS analysis of organic species in ultrafine aerosol samples (aerodynamic diameter, D_p , < 0.1 μm). The method can be readily extended to other organic species of interest. This experiment was also ground breaking in the number and variety of species quantified — 20 PAH and 11 OPAH were quantified in the urban sample. This extensive data set was used to test atmospheric partitioning hypotheses for species with a wide range of physical properties.

In the urban samples, PAH were distributed among aerosol size fractions based on their molecular weights; PAH with identical molecular weights had nearly identical distributions [4, 5]. Lower molecular weight PAH were found associated with larger particles (see Figure 1). PAH with molecular weights in the range 178 to 202 were approximately evenly distributed between the fine (D_p < 2 μm) and coarse (D_p > 2 μm) particles; and PAH with molecular weights greater than 228 were associated primarily with the fine aerosol fraction. Because PAH are primarily co-emitted with fine particles by combustors, the most likely explanation for the observed distributions is that low molecular weight, high vapor pressure, PAH redistribute to large particles by vaporization and sorption. High molecular weight, low vapor pressure, PAH do not redistribute in urban aerosols due to slow mass transfer.

In the rural samples, low and high molecular weight PAH were associated with both the fine and coarse aerosols. This finding is consistent with PAH repartitioning to large particles by vaporization and sorption. In the case of rural aerosols, all PAH have had time to redistribution to large particles by either vaporization and condensation or deposition and resuspension.

OPAH were also generally distributed among urban aerosol size fractions based on their molecular weights [6]. OPAH with molecular weights between 168 and 208 were ap-

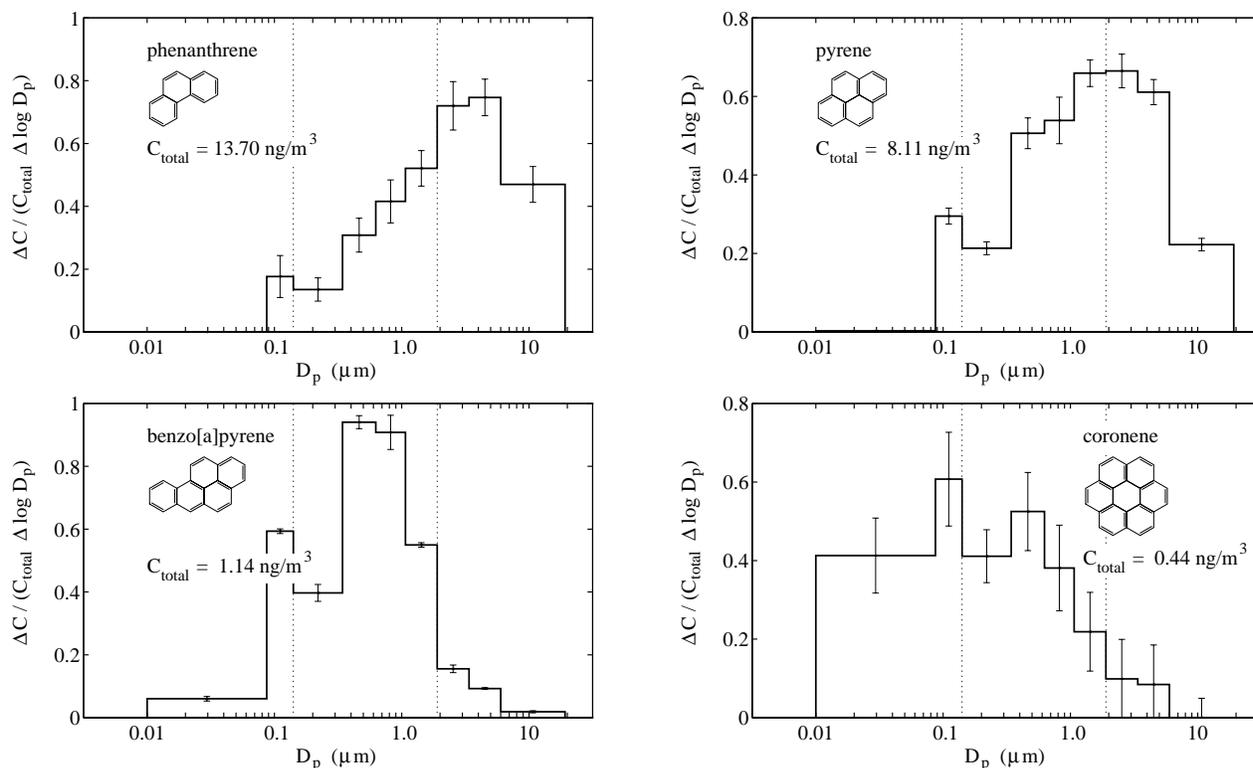


Figure 1: Distribution phenanthrene (MW = 178), pyrene (MW = 202), benzo[*a*]pyrene (MW = 252), and coronene (MW = 300) with particle size in an urban aerosol.

proximately evenly distributed between the fine and coarse particles; compounds with molecular weights of 248 and greater were associated primarily with the fine aerosol fraction. Most OPAH were distributed with particle size in a broad, unimodal hump similar to the the distributions observed for PAH in the same sample. These results indicate that OPAH were initially associated with fine particles following emission by combustors or formation by gas phase photooxidation. OPAH then redistributed from fine particles to larger particles by vaporization and sorption. A few OPAH, including phenanthrene quinone, were distributed in bimodal distributions with peaks at $D_p \approx 0.2 \mu\text{m}$ and $D_p \approx 2.5 \mu\text{m}$. The bimodal distributions suggest that these compounds interact differently with aerosol particles than PAH and other OPAH.

These results have a number of implications for the environmental fate of, and hu-

man exposure to, PAH. Firstly, intermediate molecular weight PAH, for example benzo[*a*]pyrene, are associated with accumulation mode particles which have low lung deposition efficiencies. Therefore the human exposure to these PAH is expected to be lower than for either higher or lower molecular weight PAH. Low molecular weight PAH, for example phenanthrene and pyrene, are associated to a large degree with coarse particles which have substantial deposition velocities. These PAH are expected to have a large flux out of atmosphere by deposition. Finally, the data show that aerosol sampling with an upper cut-off size, for example the proposed PM_{2.5} standard, will bias PAH sampling toward high molecular weight PAH.

These results also have important qualitative implications for the mechanism of PAH partitioning. The observation that a large fraction of some PAH are associated with coarse particles implies that PAH associate with atmospheric particles by absorption into organic material in the aerosol. The observation that low vapor pressure PAH remain associated with the fine particles implies that the redistribution of these species among the aerosol particles has not reached equilibrium. We therefore propose that PAH partitioning in the atmosphere is best explained as non-equilibrium absorptive partitioning.

Non-Equilibrium Absorptive Partitioning of PAH

To test the non-equilibrium absorptive partitioning hypothesis quantitatively, a model of PAH absorption into organic particles was developed. There is a growing body of evidence that atmospheric aerosols contain particles with a large fraction of organic material. Droplets of organic material and organic material associated with soot particles are apparent in transmission electron micrographs of submicron aerosol particles collected as part of this work [3]. Others have found a non-hygroscopic aerosol fraction [7] and single particles composed mainly of organic species [8].

The equilibrium partial pressure of PAH, p , absorbed in an organic particle is

$$p = x\gamma\psi p_L \quad (1)$$

where x is the mole fraction in the absorbent, γ is the activity coefficient of the absorbent, ψ is the partial pressure increase due to the Kelvin effect, and p_L is the vapor pressure of the pure subcooled liquid PAH.

Extensive studies of the chemical composition of major contributors to organic particulate matter reveal that large fractions of it are unidentifiable and that the identifiable fractions are complex mixtures [9, 10, 11, 12]. Mixed with emissions from additional untested sources and products of partial photooxidation, the composition of the organic fraction in atmospheric aerosols can be expected to be even more complex than that from emission sources. Thus, the nature of the organic sorbent in atmospheric aerosols is unknown and as is γ .

The characteristic times for equilibration were estimated by considering the simple case of a spherical particle in stagnant air. The times necessary to establish steady state concentration distributions in the gas phase boundary layer and within the particle are fast for a spherical liquid droplet, with characteristic times of less than one minute. The characteristic time for a particle, in contact with a constant gas phase concentration, to become saturated is

$$\tau_{sat} = \frac{D_p^2 K}{12 \mathcal{D}_G \psi} \quad (2)$$

where K is the equilibrium partition coefficient for a PAH between the gas and organic phases, and \mathcal{D}_G is the gas phase diffusivity of a PAH. The expression for K is

$$K = \frac{\rho_o R T}{M_o \gamma p_L} \quad (3)$$

where ρ_o is the density of the organic sorbent, R is the ideal gas constant, T is the

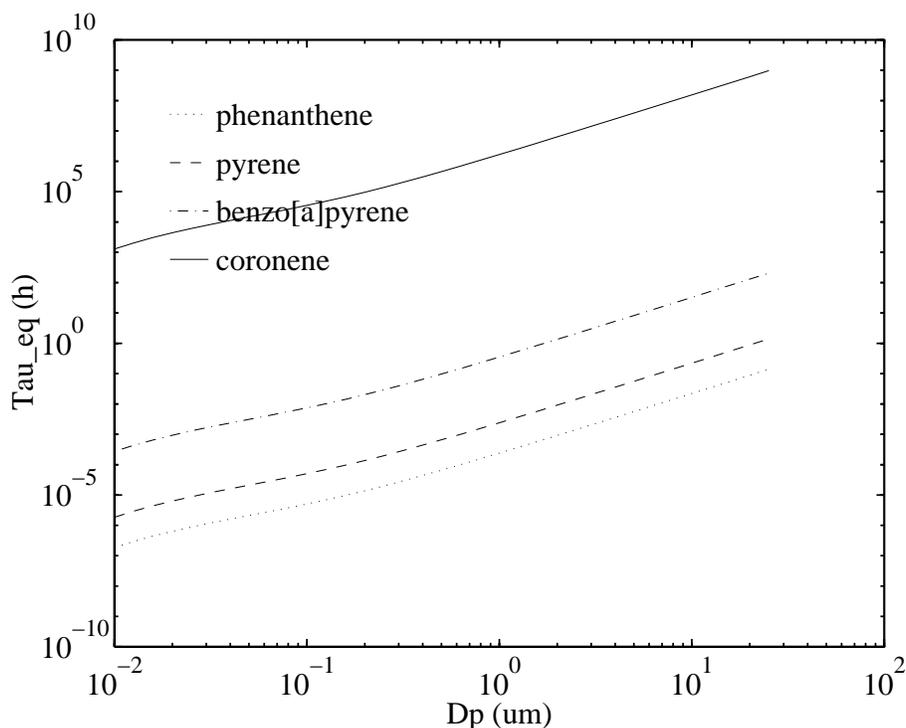


Figure 2: Characteristic times for equilibration between the gas phase and *n*-octanol droplets at 25°C.

temperature, and M_o is the molecular weight of the organic sorbent. The subcooled liquid vapor pressure, p_L , was estimated from literature values for sublimation vapor pressure, enthalpy of fusion, and heat capacities [13]. Thus, all the terms in Equations 2 and 3 except γ can be reliably estimated.

This characteristic time to saturation, τ_{sat} , is representative of particles emitted with high concentrations of PAH, e.g. diesel and auto exhaust, as well as particles emitted with low PAH concentrations, e.g. meat cooking aerosol, into a polluted urban atmosphere. Note that Equation 2 is applicable in the continuum regime, an analogous equation was used to calculate τ_{sat} in the transition regime.

Aerosol particles have a three order of magnitude range in D_p and PAH have a ten order of magnitude range in K for an organic solvent (*n*-octanol), thus values of τ_{sat} extend over 16 orders of magnitude (see Figure 2). The residence time for a Boston

aerosol is approximately 1 h. For low molecular weight PAH, $\tau_{sat} \ll 1$ h; these PAH can be expected to reach an equilibrium distribution among the aerosol particles. For high molecular weight PAH, $\tau_{sat} \gg 1$ h; these PAH are expected to remain with the particles with which they were emitted. For PAH with intermediate values of τ_{sat} , an accurate description of atmospheric partitioning must consider non-equilibrium partitioning.

To test the non-equilibrium absorptive partitioning hypothesis qualitatively, a one dimensional Lagrangian model of aerosol evolution in an urban environment was developed. The air parcel initially contains PAH and organic sorbent at background conditions. Emissions of both PAH and sorbent are added uniformly to the parcel for a residence time, t_{res} , of 100 min. This is representative of an air parcel traveling over an urban area with well distributed sources. For such short residence times, coagulation of particles [14] and photooxidation of PAH [15] can be ignored. The aerosol sorbent evolves due to addition from sources, and PAH evolve by addition from sources and mass transfer between the gas and particle phases.

At equilibrium PAH will distribute among the aerosol size fractions based on the amount and activity coefficient of the sorbent in each size fraction. Because phenanthrene is expected to be in equilibrium with the urban aerosol, the activity-weighted molar distribution of aerosol sorbent is estimated from the distribution of phenanthrene. Similarly, because coronene has large values of τ_{sat} for all particle sizes, the distribution of PAH emissions with particle size is inferred from that of coronene. The evolution of PAH concentration in an aerosol particle size bin, C_i , incorporates both emissions and mass transfer as

$$\frac{\Delta C_i}{\Delta t} = \left(\frac{\Delta C_i}{\Delta t} \right)_{\text{emissions}} - \frac{1}{\tau_{sat}} \left(C_i - \frac{C_G C_{o,i} K}{\psi \rho_o} \right) \quad (4)$$

where t is time, C_G is the gas phase concentration, and $C_{o,i}$ is the concentration of organic sorbent in aerosol size fraction i . The evolution of gas phase PAH is determined from

the mass balance of PAH in the air parcel. The total sorbent mass was assumed to be $10 \mu\text{g}/\text{m}^3$. The model numerically integrates Equation 4 in time for a range of $\log K$ values.

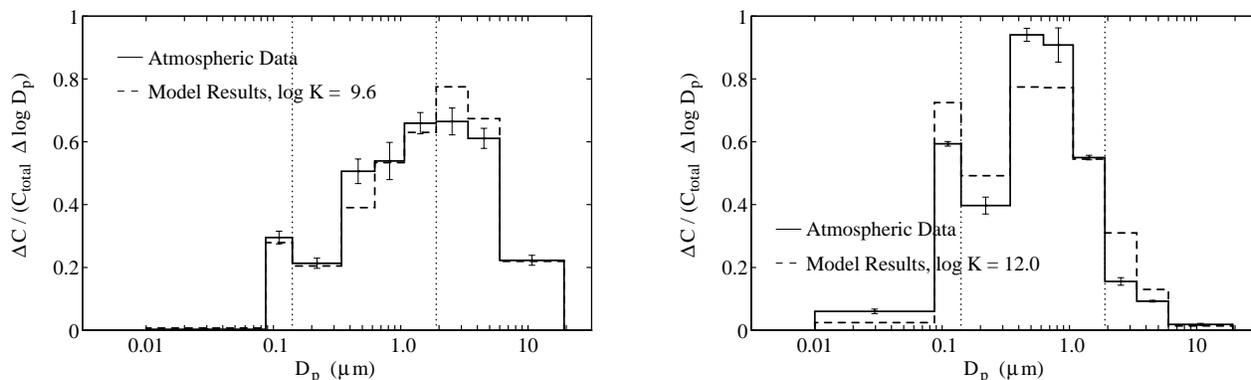


Figure 3: Comparison of the distributions of pyrene (left) and benzo[*a*]pyrene (right) with particle size as measured in an urban aerosol and predicted by the absorptive partitioning model.

The distributions predicted by the model were compared with those measured for PAH in the atmosphere and best fit matches were selected (see Figure 3). Table 1 shows the best-fit values for $\log K$ as well as $\log K$ values for PAH in water, *n*-octanol, and an ideal solvent. Note that data for phenanthrene, anthracene, and coronene were used to develop the model, thus comparisons of $\log K$ for these PAH are not useful. Agreement between the ideal solvent and best-fit values of $\log K$ are good for fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, and benzo[*a*]pyrene. For these PAH, the model of non-equilibrium absorptive partitioning to an ideal sorbent approximately matches the atmospheric data.

For PAH with vapor pressures lower than benzo[*a*]pyrene, the best-fit values of $\log K$ are up to 5 orders of magnitude below that for the ideal solvent. This disagreement may be because the sorbent was assumed to be non-volatile, but may actually redistribute on time scales comparable to, or faster than, these low vapor pressure PAH.

The model results match well the measured distributions of low and intermediate molecular weight PAH ($M < 278$). These results indicate that association of PAH with

Table 1: Equilibrium Gas—Sorbent Partition Coefficients (K).

PAH	$\log K$			
	water	<i>n</i> -octanol	ideal solvent	best-fit
Phenanthrene	3.06	7.63	8.11	9.00
Anthracene	3.11	7.65	8.16	9.00
Fluoranthene	3.42	8.65	9.12	9.40
Pyrene	3.45	8.63	9.26	9.60
Benz[<i>a</i>]anthracene	3.75	9.66	10.51	11.80
Chrysene	4.35	10.21	11.19	11.80
Benzo[<i>e</i>]pyrene	4.77	—	12.31	12.00
Benzo[<i>a</i>]pyrene	4.76	10.80	12.37	12.00
Perylene	6.01	12.26	13.25	11.80
Dibenz[<i>a,h</i>]anthracene	6.51	13.26	13.96	12.00
Benzo[<i>ghi</i>]perylene	10.32	16.82	18.84	13.40
Coronene	12.07	17.47	17.64	18.00

aerosols is by absorption and that, in the urban atmosphere, these compounds do not attain equilibrium partitioning. The Lagrangian model presented here can be extended to predict the distributions with particle size for compounds and environments beyond PAH in urban air, including other combustion generated pollutants, photochemically generated pollutants, and aerosols downwind of urban sources.

Absorption Artifact

Size-segregated atmospheric aerosols were collected on oiled impaction media in this work to prevent particle bounce during sampling [2]. The use of the oiled impaction media, however, may have introduced another sampling artifact — the absorption of species from the gas phase. Such absorption would artificially increase the amount of PAH attributed to the aerosol and possibly distort the measured size distributions. Absorption of pyrene from the gas phase to the oiled impaction media was measured in the laboratory at three exposure times (see Figure 4) [16]. These data fit well to a first order mass transfer model which accounts for the saturation of pyrene in the oil

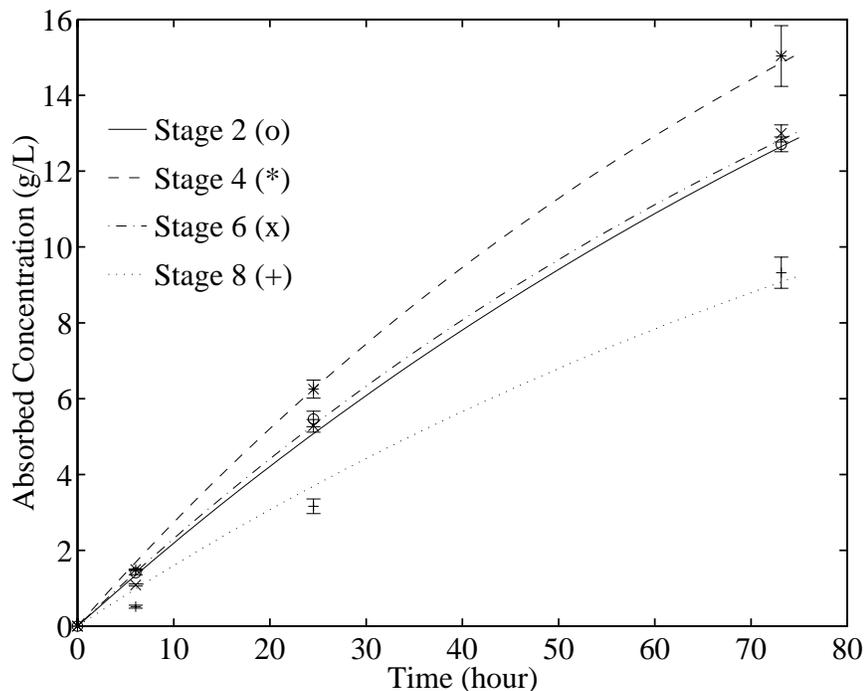


Figure 4: Pyrene absorption into oiled impaction medium on stages 2, 4, 6 and 8 of the micro-orifice impactor.

(shown by the lines in Figure 4). The measured overall mass transfer coefficients were in the range 7 to 13 cm/s. The amounts absorbed on each stage during atmospheric sampling were estimated from these coefficients. Because the overall mass transfer coefficients were in a narrow range, the amounts absorbed were approximately equal for all the impactor stages. In contrast, all PAH had distributions with a distinct peak (see Figure 1). This comparison indicates that the absorption artifact results in a small increase in the amount of PAH collected and no qualitatively significant distortion in the measured distributions.

The experimental measurements of the absorption artifact are valid for the impactor design and impaction media used in this work. A model of the absorption artifact, based on the laminar impinging jet mass transfer literature, was developed to predict the absorption artifact for other impactor designs and impaction media. The model predictions compared well to experimental measurements for the first four impactor

stages. The model overpredicted absorption on the last four stages, probably due to the interference of tightly packed impinging jets on these stages. A lower estimate of absorption on these stages was made by considering the mass transfer from a single jet. The experimental results were bracketed by the array of jets and single jet models.

With the results of this work one can estimate the absorption artifact for all popular impactor designs and design sampling methods which minimize this artifact.

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