Measurement of C₂₄H₁₄ Polycyclic Aromatic Hydrocarbons Associated with a Size-Segregated Urban Aerosol

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Six-ring C₂₄H₁₄ (MW 302) polycyclic aromatic hydrocarbons (PAH), some of which are potent mutagens, are present in urban aerosols. Size-segregated atmospheric aerosol samples from Boston, MA, were analyzed for C₂₄H₁₄ PAH by gas chromatography/mass spectrometry. Eleven peaks were found with mass to charge ratios of 302; of these, eight were identified using authentic standards. Five of the peaks were quantified. For each of these five, the distributions with respect to particle size were bimodal with the majority of the mass associated with accumulation mode particles $(0.3-1.0\,\mu\text{m})$ and a smaller fraction of the mass associated with ultrafine mode particles (0.09–0.14 μ m). These distributions are similar to those observed for PAH of molecular weight 252-278 in the same sample but different from those of benzo[*qhi*]perylene (MW 276) and coronene (MW 300), which were associated to a greater degree with ultrafine particles. The data suggest that C₂₄H₁₄ PAH repartition to larger particles by vaporization and sorption more rapidly than do benzo[ghi]perylene and coronene. The total concentration of C₂₄H₁₄ PAH (1.5 ng/m³) was comparable to that of benzo[a]pyrene in the same sample. Because of their mutagenicities, C24H14 PAH may make a contribution to the genotoxicity of urban aerosols comparable to that of benzo[a]pyrene.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous air pollutants formed as byproducts of combustion. Attention has been focused on PAH because they are believed to play

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a role in the development of cancer, particularly cancer of the lung, in humans (1). Among the most-studied PAH is benzo[a]pyrene (BaP), a five-ring $C_{20}H_{12}$ PAH that has been demonstrated to mutate cells in culture and cause cancer in whole-animal assays (2). While it is recognized that BaP accounts for a significant fraction of the total mutagenic activity of urban aerosol extracts, some investigators have suggested that other PAH may be more important mutagens in urban aerosols.

One group of PAH that has received attention recently is the six-ring C₂₄H₁₄ PAH. Cavalieri et al. found that dibenzo-[a,l]pyrene (DBalP), dibenzo[a,h]pyrene (DBahP), and dibenzo[a,i]pyrene (DBaiP) caused skin tumors in mice and mammary cancers in rats (3). In another study, Cavalieri et al. reported that DBalP was significantly more carcinogenic than BaP (4). In testing $C_{24}H_{14}$ PAH for mutagenicity in human cells, it was found that 16 of the 20 tested C₂₄H₁₄ isomers were mutagenic and that several of the compounds that occur in airborne samples, including dibenzo[*a*,*e*]pyrene (DBaeP), DBahP, DBaiP, naphtho[2,1-a]pyrene (N21aP), and naphtho[2,3-a]pyrene (N23aP), were more mutagenic than BaP (5, 6). These studies suggest that, in urban air where the levels of C₂₄H₁₄ PAH are sufficiently elevated, these compounds could account for a larger fraction of the total genotoxicity of urban aerosol extracts than BaP.

To date, relatively few studies have reported concentrations of C₂₄H₁₄ PAH in atmospheric aerosol samples. The reasons for this lie, at least in part, in the analytical challenges inherent in $C_{24}H_{14}$ PAH measurement: (i) only some of the 65 isomers have been synthesized, and (ii) many of these co-elute from gas and liquid chromatographic columns (7, 8). In addition, C₂₄H₁₄ PAH are not very abundant in air; concentrations of individual compounds in atmospheric aerosol samples are typically in the range $0.01-1.0 \ \mu g/g$ of aerosol mass (9, 10). Despite these challenges, Wise et al. quantified nine C₂₄H₁₄ PAH in two urban atmospheric particulate matter standard reference materials (National Bureau of Standards SRM 1648 and SRM 1649) (9). SRM 1649 was recently analyzed in our laboratory, and additional $C_{24}H_{14}$ PAH were identified (10). Among the $C_{24}H_{14}$ PAH identified in these samples were the human cell mutagens DBaeP, naphtho[1,2-k]fluoranthene (N12kF), dibenzo[b,k]fluoranthene (DBbkF), and naphtho[2,3-b]fluoranthene (N23bF).

Evidence that C₂₄H₁₄ PAH are both genotoxic and present in urban aerosols raises questions about the health risks that these compounds pose to urban residents. Among the questions that have yet to be addressed are the following: (i) what are the principal sources of $C_{24}H_{14}$ PAH in the urban atosphere; (ii) what are dominant environmental transport and transformation processes for these compounds; and (iii) what are the levels of exposure for urban residents to C24H14 PAH. The distributions of C₂₄H₁₄ PAH among aerosol size fractions provide partial answers to these questions since particle size affects the removal rate of particle-associated PAH from the atmosphere by dry and wet deposition (11, 12). Likewise, the mechanism and location of deposition of particle-associated PAH in the lung are also dependent on particle size. Large particles tend to impact on the upper regions of the lung while small particles tend to diffuse to the surface of the alveoli (13). Thus, measurements of $C_{24}H_{14}$ PAH associated with different aerosol size fractions are important for understanding the environmental fate of and human exposure to these compounds.

The objective of this work was to determine the distribution of $C_{24}H_{14}$ PAH with particle size in an urban aerosol.

TABLE 1. C₂₄H₁₄ PAH Reference Standards

РАН	abbreviation	retention time (min)	retention index	identified in SRM 1649 (10)
naphtho[2,3-j]fluoranthene	N23F	47.40	536.11 ± 0.04	
naphtho[1,2-b]fluoranthene	N12bF	47.29	536.43 ± 0.02	Х
naphtho[1,2-k]fluoranthene	N12kF	46.75	536.71 ± 0.06	Х
dibenzo[a,/]pyrene	DBalP	47.61	538.21 ± 0.20	
naphtho[2,3-b]fluoranthene	N23bF	47.61	538.26 ± 0.08	Х
dibenzo[b,k]fluoranthene	DBbkF	47.68	539.16 ± 0.06	Х
dibenzo[<i>j</i> ,/]fluoranthene	DBjIF	47.53	539.29 ± 0.05	
dibenzo[a,e]fluoranthene	DBaeF	47.69	540.77 ± 0.01	
dibenzo[a,k]fluoranthene	DBakF	47.88	541.12 ± 0.13	
benzo[a]perylene	BaPer	48.01	542.80 ± 0.06	
naphtho[2,3-k]fluoranthene	N23kF	47.32	543.09 ± 0.07	Х
naphtho[2,3-e]pyrene	N23eP	48.46	547.69 ± 0.07	Х
dibenzo[a,f]fluoranthene	DBafF	48.54	550.43 ± 0.08	
dibenzo[a,e]pyrene	DBaeP	48.06	551.53 ± 0.01	Х
naphtho[2,1-a]pyrene	N21aP	48.94	552.92 ± 0.09	Х
dibenzo[<i>e</i> ,/]pyrene	DBeIP	48.95	553.02 ± 0.23	Х
naphtho[2,3-a]pyrene	N23aP	49.18	555.50 ± 0.01	Х
dibenzo[a,i]pyrene	DBaiP	48.49	556.47 ± 0.09	Х
benzo[b]perylene	BbPer	49.30	556.56 ± 0.17	
dibenzo[a,h]pyrene	DBahP	49.60	560.15 ± 0.18	

Particles were collected with a micro-orifice impactor (MOI) from an urban site in Boston. The PAH were identified and quantified by gas chromatography/mass spectrometry (GC/MS). These results are compared with analyses of the same samples for other PAH reported earlier (*14*) to elucidate the formation and partitioning mechanisms of $C_{24}H_{14}$ PAH in the urban atmosphere.

Experimental Methods

The samples used in this work have been analyzed previously for PAH of molecular weights 178 to 300 (14) and oxygenated PAH (15). Since the methods used for sample collection, preparation, and analysis have been described in these earlier works, we will only summarize those methods here and expand upon the portions of the methods that are unique to this effort.

Atmospheric aerosol samples were collected from the roof of the National Ambient Air Quality Standards monitoring station operated by the Massachusetts Department of Environmental Protection at Kenmore Square in Boston. This site is on a traffic island in the center of a divided six-lane street near a major intersection. A bus station is located 170 m away. The sampling inlet was located 4 m above ground level. A total of 188 m³ of air was sampled in five 24-h periods on alternate days in June 1994.

Sampling was done with a micro-orifice cascade impactor manufactured by MSP Corporation (Minneapolis, MN) (*16*). Size-segregated aerosols were collected on nine stages with aerodynamic cutoff diameters of 19.2, 6.00, 3.38, 1.90, 1.07, 0.626, 0.343, 0.141, and 0.087 μ m. The impaction medium consisted of a polytetrafluoroethylene (PTFE) membrane with an aluminum foil underlay. The PTFE membranes were coated with dibutyl phthalate, which has been shown to reduce particle bounce (*17*). A quartz afterfilter downstream of the impactor was used to collect particles smaller than 0.087 μ m.

Samples from the five collection days were composited for analysis. The composited sampling media were spiked with known amounts of deuterated PAH standards dissolved in CH_2Cl_2 . The media were then immersed in approximately 20 mL of CH_2Cl_2 and sonicated for 30 min. To test the efficacy of the extraction protocol, the impactor stage 7 sample was extracted twice. No $C_{24}H_{14}$ PAH were present in quantifiable amounts in this sample, indicating that the initial extraction was complete. The volume of the extract was reduced by evaporation under a stream of N_2 to approximately 1 mL. To facilitate chemical analysis, the PAH fraction of the extract was separated from the dibutyl phthalate and other sample constituents by size exclusion chromatography (18). The PAH eluent fraction was then evaporated under N_2 to approximately 5 μ L.

Analysis for C₂₄H₁₄ PAH was done using gas chromatography with mass selective detection (GC/MS). The GC/MS system consisted of a Hewlett Packard (HP) 5890 series II Plus GC and an HP 5972 MS operated in the electron impact mode (70 eV). The GC column was a capillary column coated with 5% cross-linked phenyl methyl siloxane stationary phase. Selected ions were monitored at integral mass units including the molecular ions and single ¹³C isotope ions of PAH and the deuterated PAH standards. Three 1.0- μ L injections of each sample were analyzed. One blank sample was carried to the field, and three additional method blanks were prepared in the laboratory. No C₂₄H₁₄ PAH were detected in any of the blank samples.

Identification of the C24H14 PAH isomers was based on three criteria: (i) a positive match between the GC retention index of the C₂₄H₁₄ PAH isomer and authentic standards; (ii) a positive match of the 303-302 ion mass ratios for the isomer and authentic standards; and (iii) agreement with analyses of C₂₄H₁₄ PAH in an airborne particle standard reference mixture (SRM 1649; National Institute of Standards and Technology; Gaithersburg, MD). Eleven C₂₄H₁₄ PAH have been identified in SRM 1649 in our laboratory by both GC/ MS and HPLC separation coupled with diode array UV absorption detection (10). GC/MS chromatograms of SRM 1649 and the present sample were very similar, thus it was assumed that only those C24H14 PAH identified in SRM 1649 would be present in the Boston sample. Table 1 shows the C24H14 PAH reference standards that were available. The retention times were normalized by assigning retention indices relative to the deuterated PAH internal standards. Retention indices of 494.21 and 549.71 were assigned to dibenzo[a,h]anthracene- d_{14} and coronene- d_{12} respectively; these indices are comparable to the retention indices assigned by Lee et al. (19). Authentic standards for C₂₄H₁₄ PAH were acquired from the Aldrich Chemical Co. (Milwaukee, WI), the Commission of the European Communities Bureau of Reference (Brussels, Belgium), and the PAH Research Institute (Greifenberg, Germany).

Quantification was done by comparing the peak areas of molecular ions (m/z 302) to the peak area for the molecular ion of coronene- d_{12} (m/z = 312). The average reponses of coronene and dibenzo[a,l]pyrene relative to coronene- d_{12} were measured for solutions containing equal amounts of



FIGURE 1. Selected ion mass chromatogram (m/z 302) for the impactor stage 5 sample.

TABLE 2. C₂₄H₁₄ PAH Identified in Kenmore Square Samples

		concn in	fraction with aerosol modes		
PAH	peak ^a	(ng/m ³)	ultrafine	accumulation	coarse
PAH-302a	а	identified			
PAH-302b	b	identified			
N12kF/N12bF	С	0.474 ± 0.022	0.151	0.783	0.066
N23bF/DBbkF	d	0.352 ± 0.019	0.146	0.791	0.063
PAH-302e	е	0.305 ± 0.020	0.164	0.778	0.058
N23kF	f	identified			
N23eP	g	0.052 ± 0.007	0.095	0.905	0.000
DBaeP	ň	0.133 ± 0.021	0.172	0.787	0.041
N21aP/DBelP	i	0.202 ± 0.019	0.136	0.800	0.064
N23aP	i	identified			
DBaiP	k	identified			
^a Designation in Figure 1.					

the PAH and deuterated PAH and found to be 1.53 and 0.72, respectively. Because sufficient quantities of many $C_{24}H_{14}$ PAH were not available to determine their quantitative responses, the response factors for all $C_{24}H_{14}$ PAH relative to coronene- d_{12} were assumed to be 1.0. Confidence intervals for quantitation were based on a comparison of replicate GC/MS runs and do not include an estimate of uncertainties due to the assumed response factor. Thus, the confidence intervals presented below accurately reflect the relative uncertainty among the particle size fractions. A comparison of the relative responses for coronene and DBalP indicates that absolute quantification has an additional uncertainty of approximately a factor of 2.

The minimum quantifiable amount of $C_{24}H_{14}$ PAH was approximately 30 pg in a 1- μ L injection; the limit of quantitation for $C_{24}H_{14}$ PAH in the sample was therefore approximately 3 pg/m³. The minimum quantifiable amount was the amount that generated peaks with a signal to noise ratio of approximately 20. Compounds were considered identified in the whole aerosol sample if they were present in at least one size fraction sample in a quantifiable amount.

Results

Figure 1 shows the m/z 302 selected ion chromatogram for the impactor stage 5 sample (0.34 < aerodynamic diameter, $D_{\rm p}$, < 0.63 μ m). This sample had the largest amounts of C₂₄H₁₄ PAH; other samples showed similar peaks for the prominent species. Eleven peaks were found with m/z 302 and identified as C₂₄H₁₄ PAH (see Table 2). Compounds listed in Table 1 but not in Table 2 were not identified in the samples.



FIGURE 2. Distribution of naphtho[1,2-*k*]fluoranthene/naphtho[1,2-*b*]fluoranthene with particle size in an urban aerosol.



FIGURE 3. Distribution of naphtho[2,3-*b*]fluoranthene/dibenzo[*b*,*k*]-fluoranthene with particle size in an urban aerosol.

Peaks that matched no $C_{24}H_{14}$ PAH reference standard are designated PAH-302*x*, where *x* is the letter designating the GC/MS peak in Figure 1. In some cases, the retention indices of two authentic standards matched that of a peak within one retention index unit. In these cases, the coeluting isomers could not be distinguished and were quantified together.

Six of the *m*/*z* 302 peaks, identified as N12kF/naphtho-[1,2-*b*]fluoranthene (N12bF), N23bF/DBbkF, PAH-302e, naphtho[2,3-*e*]pyrene (N23eP), DBaeP, and naphtho[2,1-*a*]pyrene (N21aP)/dibenzo[*e*,*l*]pyrene (DBelP), were quantified. A summary of the C₂₄H₁₄ PAH quantification results is given in Table 2. The fraction of C₂₄H₁₄ PAH collected on stage 8 and the afterfilter ($D_p < 0.14 \ \mu$ m) is referred to as the ultrafine fraction in Table 2. PAH collected on impactor stages 4–7 (0.14 < $D_p < 1.9 \ \mu$ m) is the accumulation fraction. The sum of ultrafine and accumulation fractions is referred to as the fine fraction. PAH collected on stages 1–3 (1.9 < $D_p < 19 \ \mu$ m) is the coarse fraction.

Figures 2 and 3 show the normalized distributions with particle size of N12kF/N12bF and N23bF/DBbkF. (Similar figures for the other C₂₄H₁₄ PAH present in quantifiable amounts are available as Supporting Information). Dashed lines at $D_{\rm p} = 0.14$ and 1.9 μ m show the ultrafine—accumulation and accumulation—coarse fraction divisions. The error bars show one standard deviation from the mean analysis results. The lower limit of particle size collected on the afterfilter, $D_{\rm p} = 0.01 \ \mu$ m, has been arbitrarily selected. Within the experimental uncertainty, all of the C₂₄H₁₄ PAH have identical distributions with particle size. The major peaks are in the accumulation mode size range, $0.3 < D_{\rm p} < 1.0 \ \mu$ m. Additional minor peaks in the ultrafine mode at $D_{\rm p} \approx 0.1 \ \mu$ m are suggested by the data.



FIGURE 4. Distribution of benzo[*a*]pyrene and coronene with particle size in an urban aerosol (*14*).

Discussion

Analyses of the same aerosol samples for PAH of molecular weights 178-300 found higher molecular weight compounds to be associated with smaller particles (14). This observation held for all these PAH and was explained as mass transferlimited partitioning, i.e., PAH are emitted in the gas phase or associated with fine particles and then associate with large particles in the atmosphere by vaporization followed by sorption to large particles. The flux from fine to coarse particles is directly related to the fraction of PAH in the gas phase relative to that in the particulate phase. It has been shown that the gas-particle distribution of PAH measured in the atmosphere correlates with their subcooled liquid vapor pressures (20, 21). Therefore, higher molecular weight PAH, which have much lower vapor pressures, are expected to require much longer times to partition to coarse particles than lower molecular weight PAH. For very low vapor pressure PAH, the characteristic times for this repartitioning process are on the order of months (22). Thus, high molecular weight PAH tend to remain with the fine particles with which they were initially associated while lower molecular weight PAH partition to other particles.

All PAH with MW ≥ 252 , including the $C_{24}H_{14}$ PAH had, within experimental error, the same fraction associated with coarse particles. This suggests that all the high molecular weight PAH associate with coarse particles by the same mechanism. The small amounts associated with the coarse particles may be the result of condensation onto coarse particles, coagulation of fine and coarse particles, or resuspension of PAH deposited on surfaces. In any case, these data are consistent with the hypothesis that the partitioning of PAH to coarse particles is mainly by vaporization and sorption and that this process is slow for high molecular weight PAH.

Within the fine particle fraction, however, the $C_{24}H_{14}$ PAH tend to be associated with larger particles than is the case for benzo[*ghi*]perylene (MW 276) and coronene (MW 300) (see Figure 4), contrary to the general trend that higher molecular weight PAH were associated with smaller particles. Instead, the $C_{24}H_{14}$ PAH have distributions like those of benzofluoranthenes (MW 252), benzopyrenes (MW 252) (see Figure 4), perylene (MW 252), and dibenzanthracenes (MW 278).

PAH can migrate to larger particles by vaporization and sorption or by coagulation. Wexler et al. have shown that the time scale for coagulation of particles in an urban aerosol is greater than 1 h (23). The site from which these samples were collected was located on a traffic island in a busy city street; therefore, the samples are expected to have been strongly influenced by the nearby vehicle emissions. Because the time scale for coagulation is long as compared to the

TABLE 3. Vapor Pressures for Subcooled Liquid PAH

	log[<i>p</i> _ (Pa)(298 K)]			
РАН	estd from exptl data (25)	calcld from group contribution method (24)		
benzo[<i>e</i>]pyrene benzo[<i>a</i>]pyrene perylene dibenz[<i>a</i> , <i>h</i>]anthracene benzo[<i>gh</i>]perylene coronene dibenzopyrenes dibenzofluoranthenes	-5.5 -5.5 -6.4 -7.1 -12.0 -12.8	-6.0 -6.0 -7.7 -7.0 -8.1 -8.7 -9.4		

time between emission and sampling of the vehicle exhaust, coagulation can be neglected.

The rate of repartitioning by vaporization and sorption is directly proportional to the gas-particle phase distribution. For absorptive partitioning, the gas phase concentration is proportional to the product of the vapor pressure and the activity coefficient. Because the molecular structures of all PAH are similar, the activity coefficients are expected to be approximately equal. Therefore, to evaluate the observed size distributions within the context of repartitioning by vaporization and sorption, one must know the vapor pressures of the compounds of interest. For $C_{24}H_{14}$ PAH, vapor pressure data are not available and must be estimated.

Macknick and Prausnitz have developed a group contribution method to estimate the vapor pressures of heavy liquid hydrocarbons (24). These estimates agree reasonably well with estimates made directly from experimental data (25) for most PAH including the benzofluoranthenes, benzopyrenes, and dibenzanthracenes (see Table 3). In contrast, the estimates from the group contribution method and from experimental data do not agree well for benzo[*ghi*]perylene and coronene. These large differences, of 5 orders of magnitude, may be due to the highly condensed structures of benzo[*ghi*]perylene and coronene, compounds that were not included in the development of the group contribution method.

The vapor pressures of $C_{24}H_{14}$ PAH containing pyrene and fluoranthene subunits at 298 K were estimated to be 1.8 × 10^{-9} and 4.2 × 10^{-10} Pa, respectively, by the group contribution method. If these estimates are close to the actual vapor pressures of these compounds, then the $C_{24}H_{14}$ PAH have vapor pressures 3–4 orders of magnitude greater than benzo-[*ghi*]perylene and coronene. In this case, the rate of repartitioning of the $C_{24}H_{14}$ PAH by vaporization and sorption will be much faster than that of benzo[*ghi*]perylene and coronene. In fact, the repartitioning rates will be comparable to that of the the dibenzanthracenes and the observed distributions of $C_{24}H_{14}$ PAH are then explained by repartitioning by vaporization and sorption.

An alternative possibility is that the vapor pressures of C₂₄H₁₄ PAH are comparable to benzo[*ghi*]perylene and coronene. In this case, the group contribution method is deemed to provide poor estimates of vapor pressures for the C₂₄H₁₄ PAH and the more simplistic correlation of vapor pressure with molecular weight is accepted. The repartitioning rates of C24H14 PAH would then be expected to be as slow as those for benzo[ghi]perylene and coronene, and the observation that C₂₄H₁₄ PAH are associated with larger particles in the fine fraction cannot be explained by differential rates of vaporization and sorption. The differences between the distributions of the C24H14 PAH and those of benzo[ghi]perylene and coronene could then be explained by hypothesizing that C₂₄H₁₄ PAH are emitted by sources different from those that emit benzo[ghi]perylene and coronene. An example of such a hypothesis is that C₂₄H₁₄ PAH might be emitted upwind of the sampling site whereas

benzo[*ghi*]perylene and coronene are emitted by vehicles near the site. In this case, transformations of the particles themselves, by coagulation or growth by condensation, would explain the observed association of $C_{24}H_{14}$ PAH with accumulation mode particles. Such remotely emitted $C_{24}H_{14}$ PAH might also have had time to repartition by vaporization and condensation to the accumulation mode particles. In this explanation, the $C_{24}H_{14}$ PAH may be emitted mainly by regional scale sources, e.g., industrial and power plants.

Without experimental data on the vapor pressures and emission sources of C24H14 PAH, we cannot determine whether the differences in the observed distributions relative to benzo[ghi]perylene and coronene are due to differences in relative volatilities or emission sources. Estimates of the group contribution method support the hypothesis that the C24H14 PAH have faster rates of repartitioning by vaporization and sorption than benzo[ghi]perylene and coronene. In contrast, there is no evidence that C24H14 PAH have different emission sources from benzo[ghi]perylene and coronene. Indeed, as stated earlier, we believe that the sampled aerosols were dominated by emissions from nearby vehicles. Therefore, we suggest that C₂₄H₁₄ PAH have higher vapor pressures than benzo[ghi]perylene and coronene and that their observed distributions are explained by their rates of vaporization and sorption.

Regardless of the cause of the distributions of $C_{24}H_{14}$ PAH among aerosol size fractions, the observed distributions of these species have implications for human exposure. The concentrations of these individual compounds were 3–30 times lower than that of BaP in the same sample, 1.14 ng/m³. However, five $C_{24}H_{14}$ PAH were identified that are at least as mutagenic as BaP: DBbkF, DBaeP, DBaiP, N21aP, and N23aP. The sum of the concentrations of peaks which include these $C_{24}H_{14}$ PAH was 0.9 ng/m³, comparable to the total concentration of BaP. This suggests that the $C_{24}H_{14}$ PAH together may significantly contribute to the genotoxicity of aerosol samples and that this contribution is similar to that of BaP.

A second implication concerns the extent to which particles containing $C_{24}H_{14}$ PAH are deposited in the lung. We have shown that $C_{24}H_{14}$ PAH were primarily associated with accumulation mode particles ($0.14 < D_p < 1.9 \ \mu$ m). Since these particles neither readily impact on nor diffuse to the surface of the lung, they have low deposition efficiencies of approximately 15% (*13*). Thus, for the urban aerosol sampled here, human exposure to $C_{24}H_{14}$ PAH may be as much 5 times lower than for PAH associated with either larger or smaller particles. The same lower exposure is expected for BaP and other compounds associated mainly with accumulation mode particles.

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Supporting Information Available

Four figures and their captions showing the distribution of PAH-302e, naphtho[2,3-*e*]pyrene, dibenzo[*a*,*e*]pyrene, and naphtho[2,1-*a*]pyrene/dibenzo[*e*,*l*]pyrene with particle size in an urban aerosol (5 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche ($105 \times 148 \text{ mm}, 24 \times \text{reduction}, \text{negatives})$ may be obtained from Microforms Office, American Chemical

Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$15.00 for photocopy (\$17.00 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL http://www.chemcenter.org. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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