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Observations of Twelve USEPA Priority Polycyclic Aromatic Hydrocarbons in the Aitken Size Range (10–32 nm D_p)

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Particle size distribution measurements of twelve USEPA priority pollutant polycyclic aromatic hydrocarbons (PAHs)—collected in Riverside, California, down to 10 nm aerodynamic diameter (D_p)—observed on integrated nocturnal samples (7:00 p.m.–6:30 a.m.) revealed that between 46 and 100% of the mass of particles in the Aitken size range was found in the 10–18 nm size bin. Particles in this size range have high alveolar deposition efficiency.

During the last three decades, a great deal of health research interest focused on the mutagenicity and carcinogenicity of PAHs and their oxidation products (Finlayson-Pitts and Pitts, Jr. 1999). More recently, toxicity studies carried out in our center and other centers in North America, Western Europe, and other countries have focused on the ultrafine size fraction component of vehicle exhaust aerosols and ambient air (e.g., Li et al. 2000, 2003; Cho et al. 2004; Oberdorster and Utell 2002; Bastain et al. 2003; Calderon-Garciduenas et al. 2002; Kreyling et al. 2004a, b). Aerosols produced by spark-ignition and diesel engines and by other high-temperature processes contain nanoparticles (NP) in the Aitken ($D_p < 50$ nm), nucleation ($10 < D_p < 50$ nm), and accumulation ($50\ \text{nm} < D_p 1 < \mu\text{m}$) modes, and often fractal-like particles or agglomerates (Xiong and Friedlande 2001). Fuel-and combustion-generated PAHs that accumulate in the engine's lube oil are normally emitted through the exhaust system (Marr et al. 1999). Aitken-size-range PAHs may result from rapid cooling (self-nucleation), while the hot vapors move along the exhaust pipe into ambient air, or, as hypothesized by McMurry (2004, personal communication) they may partition from the vapor phase into oily droplets originated from self-nucleated lube oil. It is still unknown at present which mechanism(s) contribute to the observed mass in the Aitken size range.

Atmospheric particles are of concern due to their adverse effects on human health (e.g., Pope and Dockery 1998; Li et al. 2004), their role in radiative forcing, and their ability to degrade works of art and other cultural materials. NP and ultrafine (UF) particles are of special concern to engine builders because they influence engine performance and wear (Kittelson 1998). Of the perhaps thousands of chemical species found in engine exhaust and in ambient air, polycyclic aromatic hydrocarbons (PAHs)—a class of ubiquitous air toxins of particular interest with respect to chronic and acute toxicity—have been studied widely over several decades. Measurements of the distribution of PAHs with respect to particle size have been conducted in a number of urban and nonurban areas around the world (Kaupp and McLachlan 2000; Schnelle-Kreis et al. 2001). Near vehicular traffic, particulate PAHs are primarily associated with particles with $D_p < 0.2\ \mu$m, with relatively lesser mass found in the accumulation and very little in the coarse mode (Marr et al. 1999). In contrast, at locations downwind of major urban centers a significant fraction of the mass of particulate PAHs may also be found in the accumulation and, depending on season and meteorology, the coarse mode. For instance, as the air parcel is advected from central Los Angeles to downwind areas located to the east some 60 km, a substantial fraction of the PAH mass is found in the accumulation and the coarse modes (Eiguren-Fernandez et al. 2004; Miguel et al. 2004a). Size information on particles that contain PAHs and other air toxins in the Aitken or nucleation size range are needed to improve current estimates of their deposition in the human and animal respiratory system, as well as their atmospheric chemical and physical transformations and

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lifetimes. From a toxicology view point, these data will help improve our current understanding of the processes that govern their transport across the walls of cellular and subcellular targets such as mitochondria, epithelial, dendritic, and other eukaryotic cells (Li et al. 2003).

Whilst PAH particle size distributions have been measured down to 50 nm aerodynamic diameter over the last several decades, we report what are to our knowledge the first measurements of the size distribution of twelve of the sixteen USEPA priority pollutant PAHs down to 10 nm D_p, collected consecutively during nocturnal time periods (7:00 p.m. to 6:30 a.m.). The sampling system consisted of a Nano-MOUDI impactor (10 nm < Dp < 56 nm) behind a MOUDI impactor (56 nm < D_p < 2.5 μm), both running at 10 liters per minute (lpm) by masking two-thirds of the MOUDI orifices. While oiled impaction collection matrices have been used to prevent particle bounce, their use has been shown to cause absorption of semivolatile species from the gas phase, thus artificially increasing the amount of PAHs attributed to the particle phase (Allen et al. 1999). For this reason, samples were collected onto

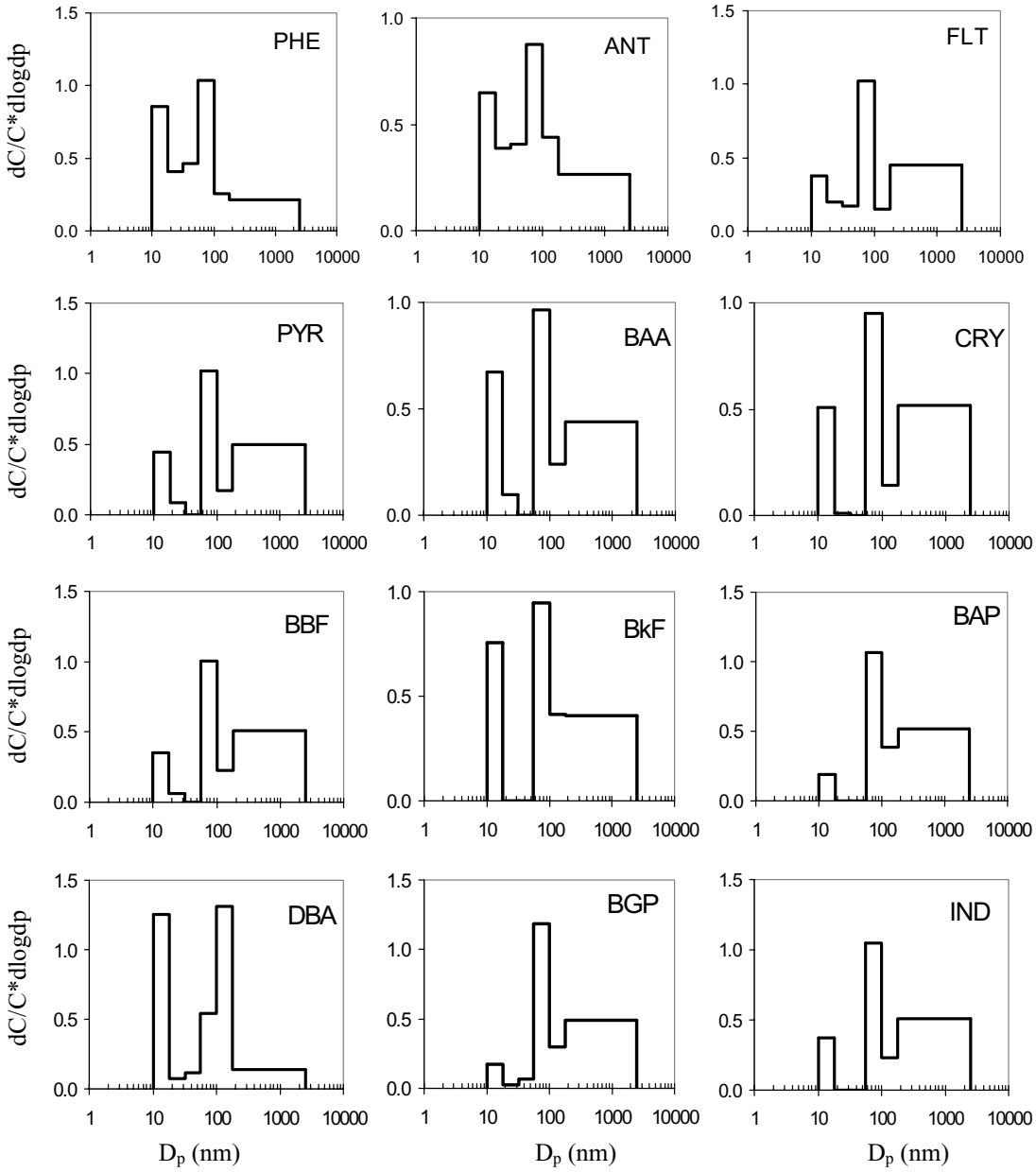

FIG. 1. Nighttime PAH size distributions measured in Riverside, CA. Samples are 5-day, 11.5 h composites taken in 26–30 August 2002. Nighttime temperatures ranged from 13 to 28°C, a variation of 15°C. PHE, phenanthrene; ANT, anthracene; FLT, fluoranthene; PYR, pyrene; BAA, benz[a]anthracene; CRY, chrysene; BBF, benzo[*b*]fluoranthene; BKF, benzo[*k*]fluoranthene; BAP, benzo[*a*]pyrene; IND, indeno[*1,2,3-cd*]pyrene; DBA, dibenz[a,h]anthracene; BGP, benzo[*ghi*]perylene.

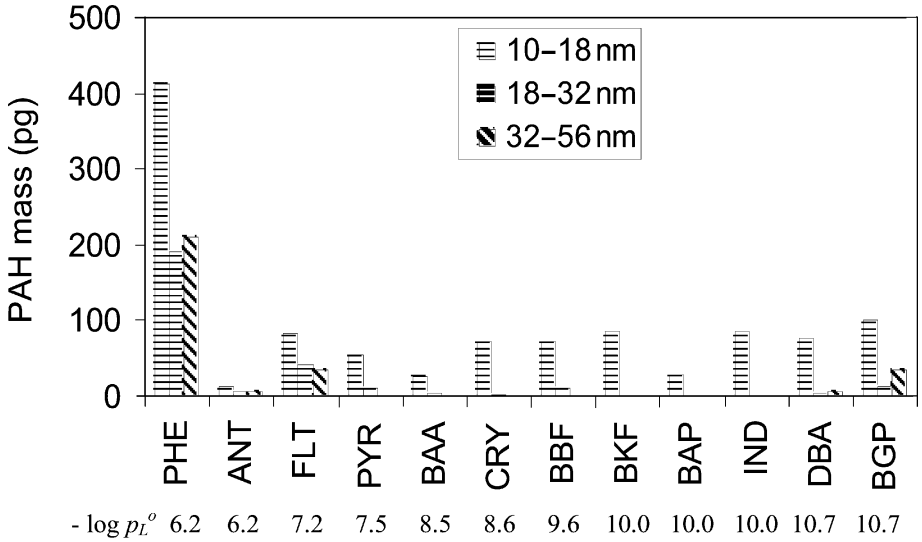

FIG. 2. Distribution of individual PAH masses in each of the differential fractions in the 10–18 nm, 10–32 nm, and 1–56 nm size bins, collected during the entire sampling period. Subcooled liquid vapor pressures (log p_L°) are in atm at 25°C (compiled by Calvert et al. 2002).

prebaked, uncoated aluminum foils in six size intervals: 10–18 nm, 18–32 nm, 32–56 nm, 56–100 nm, 100–180 nm, and 0.18–2.5 μm. An uncoated 47 mm diameter quartz fiber filter (Pallflex Corp., Putnam, CT, USA) placed ahead of the 2.5 μm cutpoint stage was used as an impaction substrate to minimize particle bounce. Sampling occurred in the fall of 2002 during nighttime and daytime periods in Riverside, located ~70 km downwind from central Los Angeles. Daytime samples (not reported here) showed very little mass for phenanthrene and anthracene in the Aitken size range. For this reason, in this communication we report only the nighttime measurements. Samples from the five nightly collection periods allowed sufficient PAH mass on each size bin for accurate polycyclic aromatic hydrocarbons (PAHs) quantification by HPLC with selective fluorescence detection (Eiguren-Fernandez and Miguel 2003). Although denuders were not used in this study, aerosol dynamic considerations indicate that the use of denuders—commonly used to remove vapor-phase species to minimize sampling artifacts—may actually promote sampling artifacts for particles between 10–30 nm D_p. Particles in this size range approach the behavior of vapor-phase molecules, which diffuse to the denuder walls. An assessment of the losses of $10 < D_p < 30$ nm particles to the walls of commonly used denuders suggest that substantial losses may occur when they are operated under the sampling conditions used in the study reported here (Miguel et al. 2004b).

The observed size distributions of the twelve target PAHs in the 10 nm $< D_p <$ 2.5 μm size range, plotted in order of decreasing subcooled liquid vapor pressure, are shown in Figure 1. For all PAHs, regardless of vapor pressure, the masses in each of the differential fractions (10–18 nm, 18–32 nm, and 32–56 nm) are larger in the smallest fraction (10–18 nm) than that in the two larger fractions (Figure 2). The masses in the 10–18 nm size bin ranged from 100% (BKF, BAP, and IND) to 46% (ANT) of the masses collected in the $D_p < 56$ nm size range. Park et al. (2003) observed a small particle mass peak around ~20 nm (using a similar Micro-Orifice Uniform Deposit Impactor (MOUDI) impactor) but not with an SMPS. They hypothesized that, for some but not all measurements this peak might have resulted from particle bounce from upper stages or some unidentified artifact formation in the low-pressure stages. Particles that bounce in the upper stages do so because of their large impact velocities. In the stages that are designed to capture the smaller particles impact velocities will be even larger, so the probability of bounce may be expected to increase with decreasing cut size. Our observation that the PAH masses collected increase with decreasing cut size suggests that, although bounce or artifact formation cannot be discounted as a possible source, it is unlikely to dominate.

CONCLUSIONS

We conclude that PAHs found in the Aitken size range represent a previously unreported particle size range, adding a fourth mode to the typical PAH size distributions found in ambient air in the nucleation, accumulation, and coarse size modes. In terms of health significance, this finding is important because of the increased deposition efficiency in the alveolar area of the human respiratory tract of particles in the 10–32 nm diameter range. Particles in this size range may enter cellular and subcellular walls of target eukariotes. Finally, our results will be compared with those obtained using an electrostatic sampler (McMurry 2004, personal communication) operated side by side with a nano-MOUDI under similar ambient circumstances to further validate our nano-MOUDI measurements.

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