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Use of a Versatile High Efficiency Multiparallel Denuder for the Sampling of PAHs in Ambient Air: Gas and Particle Phase Concentrations, Particle Size Distribution and Artifact Formation

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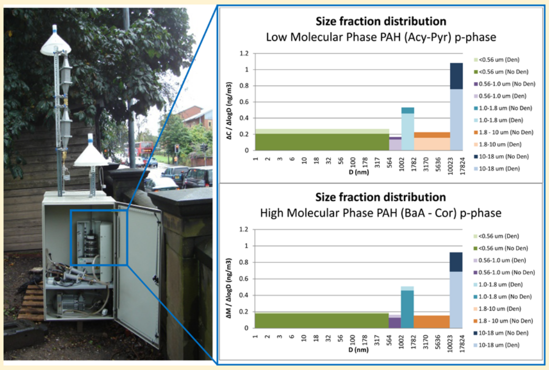
S Supporting Information

ABSTRACT: The design and performance of a multiparallel plate denuder able to operate at low and high-flow (3−30 L/min) for the collection of polycyclic aromatic hydrocarbon (PAH) vapor is described. The denuder, in combination with a micro orifice uniform deposit impactor (MOUDI) was used to assess processes of artifact formation in MOUDIs used with and without an upstream denuder. Duplicate sampling trains with an upstream denuder showed good repeatability of the measured gas and particle-phase concentrations and low break-through in the denuder (3.5−15%). The PAH size distributions within undenuded and denuded MOUDIs were studied. Use of the denuder altered the measured size distribution of PAHs toward smaller sizes, but both denuded and undenuded systems are subject to sampling artifacts.



1. INTRODUCTION

Semivolatile organic compounds (SVOCs) partition between vapor and particle-associated fractions in the atmosphere. Vapor-particle partitioning behavior plays an important role in determining the fate, exposure of wildlife and humans and long-range transport of organic pollutants.[1] In addition deposition rates tend to be greater for the particle-associated fraction, while chemical transformation rates tend to be greater for the vapor fraction. Therefore, sample collection techniques that can accurately separate vapor from particle-associated SVOCs are needed to monitor concentrations and predict behavior of SVOCs in outdoor and indoor environments.[2]

Diffusion denuders have been commonly used to remove trace gases from an aerosol, while allowing the particles to remain suspended in air.[3−6] This has applications for separation of vapor and particulate phases,[7] and has been used for the removal of inorganic oxidants[8] or vapors from organic compounds.[9]

Several designs are available for the collection of gas-phase organic compounds and in particular PAHs. Annular denuders[1,7,9−14] (e.g., IOAGAPs[9]) and denuders consisting of a compilation of sections of capillary gas chromatographic columns[2−4,15] have been extensively used. Denuders exploiting multichannel geometry are scarce, with channelling produced by parallel plates[4,16−19] (e.g., BOSS[16]) or by tubes arranged in a honeycomb style.[15,20] Micro-orifice uniform deposit impactors (MOUDI) operate at 30 L/min, and hence only a few denuders[15,16,19] could potentially be used in combination with the MOUDI. The honeycomb denuder[15] only offers the possibility to eliminate oxidant gases that can potentially introduce sampling artifacts[21] if an additional honeycomb denuder dedicated to oxidant removal is placed upstream in series. As regards the BOSS type denuders,[16,19] these have never been used to analyze organic gas phase extracted from the denuder, but as an organic trapping device instead. The integrity of the denuders, made with carbon impregnated filters, will be compromised if attempts to recover the gas phase were made. Therefore our objective was to develop a new denuder design with high efficiency in trapping organic vapors at a flow rate of 30 L/min, with capabilities to easily introduce oxidant scrubbers, with an extraction protocol that could be performed in any laboratory without destroying the integrity of the denuder.

On the other hand, a variety of sampling artifacts have been reported to affect the measured composition of the collected particle deposit relative to what was actually in the atmosphere. Volatilization of SVOCs (negative artifact) and adsorption into the filter and onto the aerosol collected on the filter (positive artifacts) are known to be significant sources of error in particulate phase sampling.[22] Therefore in order to validate the use of a denuder it is necessary to understand the sampling artifacts that it might introduce in the determination of the particulate phase and size distribution.

This paper presents a versatile design and tests the performance of a multiparallel denuder able to operate at low

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and high flows (3−30 L/min) for the collection of organic compounds in the vapor phase. The denuder also allows extraction of the PAHs to analyze the gas phase concentration. The denuder has been used in different microenvironments in order to test its performance, including the repeatability of the measurements and the breakthrough of the compounds. The denuder has been used in combination with a MOUDI to assess the artifacts produced when sampling the vapor phase upstream of the MOUDI.

2. MATERIALS AND METHODS

2.1. Denuder Design. *2.1.1. Geometry of the Denuder.* A denuder for the collection of organic compounds such as PAHs in ambient air was designed based upon multiparallel plate geometry as described in detail in the Supporting Information (SI) (Figures S1 and S2 and Table S1).

2.1.2. Theoretical Consideration in the Design of the Denuder. The theoretical efficiency of a multiparallel plate denuder according to the equation provided by De Santis[23] (see SI) for parallel plate denuders showed efficiencies of 97−100% for different PAHs and 100% for oxidant gases (SI Table S2). The theoretical efficiencies are better than another mini-parallel plate denuder available (46%) [Calculated using the same De Santis equation] [17] or the BOSS samplers (85−89%) [Calculated using a version of Possanzini equation as defined in Cui et al. (1998)].[16,19]

During passage of ambient air through the denuder, the molecules of vapor diffuse to the wall, while the particles proceed unaffected. Therefore, it is essential to prevent turbulent flows that will lead to particle losses at the walls of the denuder. The values of the Reynolds number calculated for 30 L/min (i.e., the maximum flow capacity of the denuder) in the three distinct sections of the denuder (ranging 25−1882, SI Table S3) show that the flow is laminar throughout the whole denuder.

The theoretical deposition of particles in the denuder was calculated considering impaction and diffusion losses. When the air enters the case containing the plates, it encounters a series of metal plates that collect the gas phase and create the channels that the air passes through. These metal plates act as obstacles forcing air and airborne particles into a curvilinear motion. The Stokes number was calculated for particles of 18 and 10 μm or lower diameter entering the denuder at 30L/min or lower flow rates using both the equations due to de Santis[17] and a version of the Possanzini equation as defined in Cui et al.[19] (SI Table S4). The calculated value confirms that the particles follow the fluid streamlines closely[24] and are not lost by impaction on the plates. The diffusion loss in the denuder calculated for 50−500 nm particles was <1%, with losses of 1−2% for 20−30 nm particles and 9% for 10 nm particles (SI Table S2). The particle losses by diffusion and impaction were not measured in an independent set of experiments. However, the concentrations measured in the denuder for the high molecular weight PAHs—normally present in the particle phase—were negligible (i.e., below limit of detection, see Section 3.2). Therefore, the theoretical calculations showing low particle loss in the denuder are consistent with the true efficiency of the denuder for the particulate phase.

Other particle collection mechanisms include gravitational settling, thermophoresis and electrophoresis. None of them is relevant for the current denuder design as the flow rate is too large to allow gravitational settling; there is no difference of temperature between parts of the denuder as the whole denuder is at ambient temperature in contact with the air; and no voltage is applied to the denuder.

2.1.3. Practical Consideration in the Design of the Denuder. In order to use the denuder case in the laboratory for coating plates and extracting samples, special metallic flat lids were designed, transforming the denuder into an airtight receptacle. The dimensions were optimized to reduce solvent consumption during analytical extraction procedures.

Appropriate materials were selected for the metal plates (stainless steel 316) and the denuder case (aluminum) in order to minimize the impact of corrosion during extraction and to ensure sturdiness of the denuder for transport and handling in the field.

2.1.4. Design of the Collection Plates. Two sizes of denuder plates were designed (see SI Table S1). The larger plates are used to trap the gaseous PAHs. The smaller plates were designed to (a) serve as oxidant scrubbers when coated with the appropriate adsorbent material (e.g., KI[7]) and located upstream of the large plates; or (b) to serve as a backup for sampling gaseous PAHs when placed downstream of the large plates.

XAD-4 (20/60 mesh, Sigma-Aldrich, England) was chosen to collect gaseous PAHs as it has been extensively used for trapping PAHs and other organics in ambient air[9,25−27] and, provides high surface area[9] that facilitates adsorption of the organic vapor onto the resin. XAD-4 was finely ground and cleaned[9] as described in detail in the SI.

To enhance the adherence of the adsorbent material to the collection plates, surface treatments of the metal plates such as chemical etching (SI Table S5) and sandblasting (SI Table S6) were investigated in 1 × 1 cm stainless steel tiles and analyzed using a microscope. The micrographs revealed that the sandblasting treatment with Guyson Honite beads (see SI Table S6 for details) produced a homogeneous smooth surface treatment that allowed the XAD-4 to coat evenly (see SI Figure S3).

The XAD-4 coating was gravimetrically determined showing an average of 2.2 g load, which is greater than the coating in a typical single-channel annular denuder (10−20 mg of XAD-4) or an eight-channel denuder (1 g approximately).[28] This implies that the new denuder has a larger capability to adsorb organic vapor into the surface of the metal plates than the current annular denuders.

2.2. Denuder Performance Evaluation. *2.2.1. Atmospheric Sampling.* A series of experiments was designed to test the repeatability of concentrations measured with the denuders (Experiment A-B), test the breakthrough (Experiment C), test the artifact formation (Experiment D) and test the effect of using an oxidant scrubber (Experiment E). Denuder plates were coated with precleaned XAD-4. The residence time of the air in contact with the denuder plates is 26 and 2.6 s at 3 and 30 LPM respectively. Quartz QMA filters (Millipore AQFA 47 mm diameter reinforced quartz filters) were used in Experiment A. Experiments B−E used PTFE filters (Whatman laminated polypropylene 47 mm diameter 1.0 μm pore size) in two MOUDI 110R impactors with size ranges of (10−18 μm), (1.8−10 μm), (1.0−1.8 μm), (0.56−1.0 μm), and (<0.56 μm) followed by polyurethane foam plugs (PUFs). The tests are briefly described hereunder and further details on the sampling methodology including schematics of the experimental configurations can be found in the Supporting Information.

Testing the Repeatability of Concentrations Measured with the Denuders with Concurrent Sampling Trains—Low

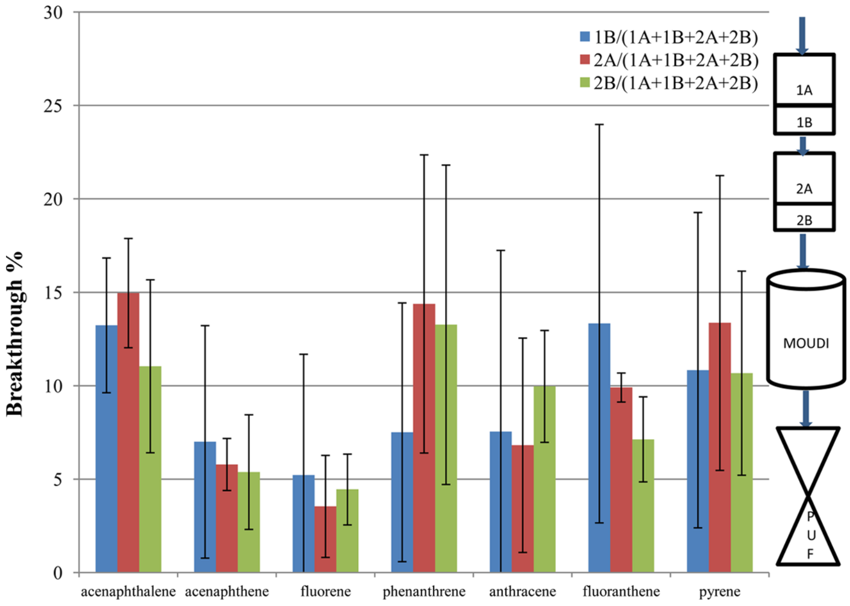

Figure 1. Breakthrough (%) of low molecular weight PAHs collected after the main set of plates (1A) in the subsequent sets of plates (1B, 2A, and 2B) with reference to the total amount collected in all plates (i.e., sum of mass collected in 1A, 1B, 2A, and 2B).

(Experiment A) and High (Experiment B) Flow Rates. In order to test the performance of the designed denuders at low and high flow rates, PAHs in vapor and particle phases were monitored in duplicate in different environments. Two identical sampling trains were deployed concurrently in several microenvironments with expected high and low concentrations. The sampling train consisted of a denuder collecting the gas phase upstream of a microenvironmental sampler[29] (at 3L/min, Exp A) or of a MOUDI 110R (at 30L/min, Exp B). PUF plugs downstream of the MOUDI were used in Experiment B. Six and five 24-h samples were collected in Experiment A and B respectively. See SI for further details on the PUF plugs and the sampling train descriptions.

Testing the Breakthrough of the Denuders—Experiment C. In order to test the breakthrough of the denuder, three extra sets of denuder plates (labeled 1B, 2A, and 2B, see Figure 1) were located downstream of the original plates (labeled 1A), followed by a MOUDI and a PUF holder. Details are found in the SI in Figure S7a, Sampling Train 1- and Figure S7b. Five 24-h samples were collected at a trafficked road site.

The breakthrough of PAH gas from the first set of large plates (1A) was calculated as the ratio of concentration measured in each set of backup plates (1B, 2A, and 2B, see Figure 1 and SI Figure S7b) to the concentration measured in all the plates (1A+1B+2A+ 2B) times 100.

Testing the artifact Formation in a MOUDI Downstream of a Denuder—Experiment D. Five 24-h samples were collected with the aim to study the behavior of the MOUDI performance to collect size fractionated aerosol after removal of the gas-phase. Two different sampling trains (SI Figure S7a), one collecting the vapor phase upstream of the MOUDI using a denuder, and the other collecting it downstream using a PUF holder were deployed concurrently at a trafficked roadside.

Testing the Effect of Using an Oxidant Scrubber—Experiment E. Five 24-h samples were collected with the aim to study the effect of scrubbing oxidants prior to collection of PAHs using 2 multiparallel denuder-MOUDI-PUF sampling trains (SI Figure S8). One of the denuders contained 20 small plates coated with KI, an efficient ozone scrubber,[30] upstream of the collecting plates.

2.2.2. Analytical Methodology. Prior to sampling, the denuder collection plates were coated with ground and cleaned XAD-4; while the PUFs were precleaned in a mixture of solvents. Samples were frozen until analysis. Prior to extraction, all samples were spiked with a mixture of deuterated internal standards covering the whole range of molecular weights and extracted. Details of the analytical protocol are described in the SI.

2.2.3. QA−QC. QA−QC on sampling consisted of collecting field blanks on 10% of samples and measuring the flow rates before and after each sampling period using calibrated rotameters. The blanks levels (SI Table S7) were recorded and monitored, but were not used in the calculations of the final concentrations.

The GCMS analytical method and limits of detection of PAHs as well as QA−QC procedures are described in detail elsewhere.[31−33] This include extraction of SRM 1649a,[32] lab blanks[32] and recovery levels for denuders, filters and PUFs calculated extracting known concentrations of internal standards spiked onto the substrates. Recovery levels are shown in SI Table S8.

■ RESULTS AND DISCUSSION

This paper presents the design and field evaluation of a multiparallel plate denuder capable of separately collecting vapor and particle associated organic compounds, such as PAHs; and which allows for analysis of both fractions. The design maximizes theoretical collection efficiency (i.e., 97−100%) for a sampling flow of 30 LPM with measured efficiencies ranging 85−96% measured as breakthrough. It provides versatility to sample different gases by coating the plates with appropriate adsorbent material. It allows introduction of a set of small plates coated with KI on top of the collection plates in a single denuder to facilitate the scrubbing of oxidant gases prior to PAHs collection in the sampling train. It allows reuse of the same denuder case with a different set of denuder plates to reduce the cost of sample collection. It can be

Table 1. Slope and Coefficient of Determination R^2 of the Regression Line for the Comparison of Particulate Phase PAHs Measured with Two Collocated MOUDIs in Experiment B and D[a]

size fraction		10−18 μm	1.8−10 μm	1.0−1.8 μm	0.56−1.0 μm	<0.56 μm	∑sizes
				Experiment B			
Acy-Cor	slope	0.899	1.011	0.978	1.115	1.098	0.943
	R^2	0.970	0.970	0.937	0.851	0.708	0.842
Acy-Pyr	slope	0.866	1.068	0.946	1.063	1.061	1.908
	R^2	0.971	0.952	0.917	0.924	0.648	0.864
BaA-Cor	slope	0.998	0.914	0.996	0.908	1.055	0.999
	R^2	0.943	0.858	0.795	0.784	0.916	0.803
				Experiment D[b]			
Acy-Cor	slope	0.547	0.481	0.645	0.683	1.175	0.936
	R^2	0.76	0.82	0.74	0.77	0.9	0.87
Acy-Pyr	slope	0.557	0.515	0.547	0.678	1.2	0.875
	R^2	0.75	0.76	0.51	0.64	0.98	0.87
BaA-Cor	slope	0.45	0.889	1.057	1.216	1.35	1.042
	R^2	0.82	0.77	0.71	0.85	0.97	0.78

[a] Examples of the regression lines are presented in SI Figure S10. [b] In Experiment D the results of the regression line for the comparison of the concentration measured in each of the two MOUDIs follows the equation $\mathrm{PAH}_{\mathrm{particulate}}$ MOUDI (with denuder) = **slope** * $\mathrm{PAH}_{\mathrm{particulate}}$ MOUDI (without denuder) + **b**.

converted into an extraction vessel facilitating sample extraction in the laboratory. These characteristics provide advantages of the current design compared with previous high flow rate denuders; specifically the ability to explore collection artifacts using flexible configurations of denuders, impactors, filters, and sorbent materials.

3.1. Repeatability of Concentrations Measured with Denuders. The difference in concentrations between both denuders, relative difference or bias, modified median absolute deviation (MMAD) and coefficient of variation (CoV) were calculated accordingly with Rowe and Perlinger (2010).[15] Difference in concentrations was normally distributed and a *t* test showed that it was not significantly different from nil ($p > 0.10$, $N = 106$). Relative difference was 0.59%, MMAD was 0.049 ng/m^3 and CoV was 2%.

The regression of vapor phase PAH concentrations measured with the two concurrent denuders in Experiments A and B (SI Figure S9) shows a good correlation both in the whole range of concentrations, and in the smaller range of concentrations (e.g., zoom <3 ng/m^3 − see inset in SI Figure S9). The residual analysis (SI Figure S9b) also shows that the standardized residuals are fairly evenly scattered throughout a horizontal band around 0.0.

Regression parameters for each individual compound in both the vapor and particulate phase in Experiment A indicate R^2 values from 0.84 (i.e., benzo(a)anthracene) to 0.99 (e.g., anthracene) for the vapor phase, and from 0.73 (i.e., dibenz(a,h)anthracene) to 0.99 (e.g., phenanthrene) for the particle phase. For most of the compounds, the slope of the regression is close to unity, ranging from 0.7 (i.e., coronene) to 1.2 (i.e., fluoranthene) for the gas phase measured in the denuder and ranging from 0.65 (i.e., acenaphthalene) to 1.3 (i.e., fluoranthene) for the particulate phase (see SI Table S9).

Similar results were found in Experiment B for high-flow rates. Table 1 shows results for particulate phases collected concurrently in different size fractions in a MOUDI downstream of the denuder. Examples of the regression lines are presented also in SI Figure S10.

3.2. Breakthrough Experiment. The theoretical collection efficiencies calculated using the de Santis equation[23] (see SI) for all PAH compounds ranged from 97 to 100%, which assumes that the collection surface acts as a perfect sink. Experiment C was designed to test the breakthough of PAHs and results are shown graphically in Figure 1. No data are reported for the higher MW PAHs as the concentrations measured in all four sets of plates are within the field blank levels (SI Table S7).

The measured concentrations varied little between the sets of back up plates (ANOVA $p > 0.10$). If the measured concentrations in the backup stages (1B, 2A, and 2B) were only the consequence of vapor breakthrough, these would be expected to decrease sharply from one set of backup plates to the next, as vapor is trapped in the backup plates. However this was not the case (Figure 1). Therefore, the concentrations measured in the backup plates may be associated with diffusional losses of particles (calculated to range 9−18%) or with vaporization from the particles in transit in the denuder, as discussed in detail in the sampling artifact section. This interpretation is confirmed by SI Figure S11 which shows the huge difference between collection on plate 1A and 1B in comparison to that between 1B and 2A, and 2A and 2B. For use in field measurements, the sampling train used only the first set of plates and hence this artifact was not present.

3.3. Gas and Particle Phase Concentrations. The concentrations measured and analyzed with our designed denuder (SI Table S10) are consistent with the magnitude and profile of gas phase concentrations reported previously in ambient air[29,34−45] (Table S11). The sum of all size fractions measured with the MOUDI is lower than those reported in urban or trafficked areas in some locations,[46,47] although similar to those measured in Canada[48] and Birmingham (UK).[29]

Concentrations measured in the home that burned wood in the fireplace show the highest concentrations, even compared with other combustion sources such as environmental tobacco smoke or traffic. Limited data for PAH vapor concentrations is available from the literature for these indoor environments, but this trend is consistent with published observations of particulate phase PAH concentrations in those specific environments (SI Table S11).

The size fraction distribution of particulate phase collected at our trafficked road site (Figure 2) shows that the highest percentage of mass is collected in the fraction <0.56 μm,

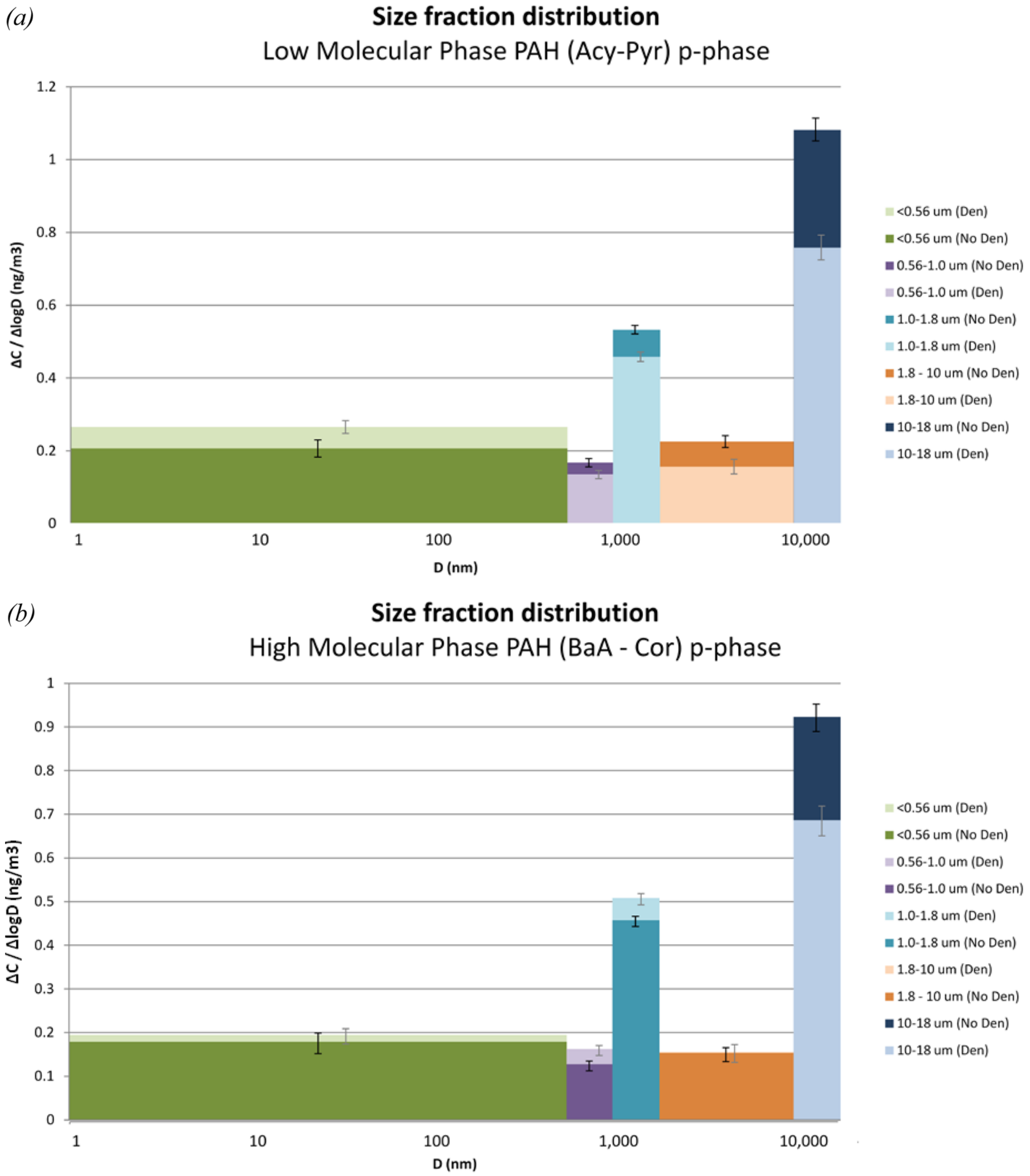

Figure 2. Comparison of size fraction distribution of (a) low (∑Acy-Pyr) and (b) high (∑BaA-Cor) molecular weight PAHs - MOUDI without denuder (dark color scheme) and MOUDI with denuder (light color scheme).

consistent with concentrations reported in the Sepulveda tunnel and in an urban area in Central Los Angeles,[49,50] which is indicative of fresh vehicular emissions.

3.4. Sampling Artifacts in the Characterization of Size Segregated Particulate Phase Downstream of a Denuder and Vapor Measurement. Two sampling trains, with and without a denuder upstream of a MOUDI followed by a PUF, were located concurrently at a trafficked roadside. The results of the size fraction distribution for the sum of the low (Acy-Pyr) and high (BaA−Cor) MW PAHs in the regular and denuded MOUDIs are presented in Figure 2, while the fraction of particulate phase mass collected in each size fraction for each MOUDI is presented in SI Figure S13. Figure 3 presents the concentrations measured downstream of the MOUDI in each of the sampling trains (the denuded MOUDI and the regular undenuded MOUDI).

Ambient temperature is a factor affecting the vapor/particle partitioning. Higher ambient temperatures will shift the vapor/particle equilibrium toward the vapor phase. The temperature range was 12−21 °C during the sampling campaign. The temperature effect is more important in the low MW PAHs, as they are more volatile compared to higher MW PAHs. Although this fluctuation might have had some effect on the vapor/particle partitioning of the lower MW PAHs, it is not expected to greatly affect one sampling train more than the other. Likewise, water vapor content is another factor to consider, as increasing relative humidity can suppress the adsorption of gas phase organic species onto particle surfaces[60] shifting the partitioning toward the vapor phase. However, the

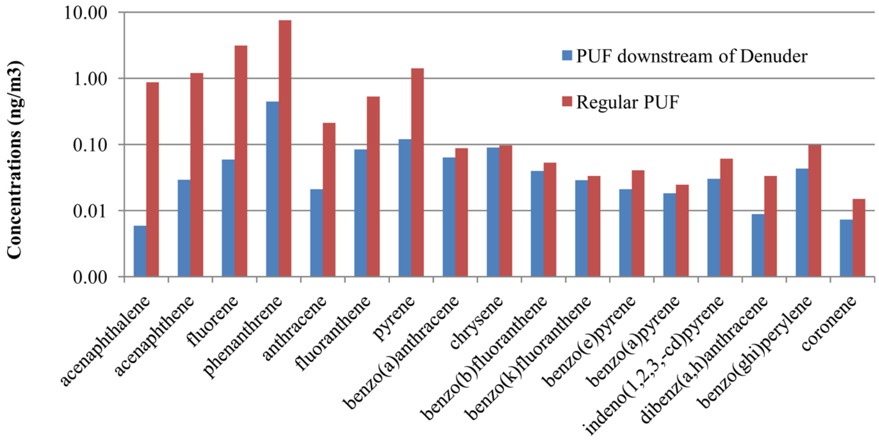

Figure 3. Gas-phase concentrations measured on the PUFs downstream of the denuded MOUDI (blue) and the regular undenuded MOUDI (red). Limits of detection can be found in SI Table S7.

changes in relative humidity during the study period (68−92%) will affect both sampling trains in a similar manner.

The concentrations measured in each size fraction for the regular and denuded MOUDI were compared and the results of the regression line are shown in Table 1, Experiment D. The information portrayed in Figure 2, SI Figure S13 and Table 1, Experiment D shows that the undenuded MOUDI tends to measure higher concentrations than the denuded MOUDI for the low MW PAHs in all size fractions, with the exception of the last stage (<0.56 μm) where it shows lower concentrations. For the high MW PAHs, the undenuded MOUDI measures higher concentrations for the largest fraction (>10 μm), similar concentrations in the size fraction 1−10 μm and lower concentrations in the size fractions below 1 μm compared with the denuded MOUDI.

The attachment of the denuder to the inlet of the MOUDI will change the inlet cutoff for very large particles. Since theoretical calculations of loss of large particles in the denuder due to impaction or diffusion has shown to be negligible (see Section 2.1.1), because no breakthrough is reported for high MW PAHs, which are mainly in the particulate phase,, and because the >10 μm particles are not respirable, this is not a matter of concern.

The difference between the regular and the denuded MOUDI size fraction distribution was assessed using the statistical methods described by Allan et al. (2004).[51] A one sample *t* test performed in the log database of the differences between the regular and denuded concentrations measured in each stage confirmed that the differences were significantly different from zero ($p < 0.05$ level), with the exception of high MW PAHs in the 1.8−10 μm and <0.56 μm region.

This behavior can be explained by a combination of processes occurring in the MOUDI. The airstream entering the regular undenuded MOUDI still contains the vapor phase PAHs. Therefore, for the lower molecular PAHs which tend to be mainly in the vapor phase (Table 2), there is an increase in concentrations in the undenuded MOUDI associated with the adsorption of vapor onto the impaction substrate (positive artifact), as displayed in the slope values in Table 1, which is consistent with previous studies.[10,52−54] The gas adsorption artifact would have been higher if quartz rather than Teflon filters had been used.[55]

Table 2. PAH Vapour Concentrations (Arithmetic Mean and Standard Deviation, $N = 5$) Measured in the First of the Two Denuders Used in Sampling Train 1 (Sampling Train 1, Experiment D) and in the PUF Downstream of the Undenuded MOUDI (Sampling Train 2, Experiment D)

	denuder		PUF	
compounds	average (ng/m^3)	std dev (ng/m^3)	average (ng/m^3)	std dev (ng/m^3)
acenaphthalene	0.20	0.06	0.17	0.14
acenaphthene	3.3	0.23	1.20	0.15
fluorene	4.19	1.22	3.14	0.36
phenanthrene	12.8	3.38	7.53	1.60
anthracene	0.33	0.22	0.21	0.20
fluoranthene	1.45	0.39	0.53	0.23
pyrene	5.10	3.43	1.41	0.25
benzo(a) anthracene	0.03	0.01	0.09	0.06
chrysene	0.10	0.02	0.10	0.12
benzo(b) fluoranthene	0.025	0.008	0.05	0.08
benzo(k) fluoranthene	0.008	0.003	0.03	0.05
benzo(e)pyrene	0.009	0.004	0.04	0.07
benzo(a)pyrene	0.009	0.002	0.02	0.04
indeno(1,2,3,-cd) pyrene	0.003	0.005	0.06	0.04
dibenz(a,h) anthracene	0.002	0.006	0.03	0.04
benzo(ghi) perylene	0.019	0.009	0.10	0.09
coronene	0.005	0.012	0.02	0.03

The second process results from the fact that in the denuded MOUDI, the air stream entering the MOUDI is no longer in thermodynamic equilibrium as it does not contain vapor in equilibrium with the particle phase. Because the vapor/particle equilibrium is shifted, part of the particle phase is volatilized to restore the equilibrium.[10,56] For particles deposited on the first stage the vapor-particle equilibrium is never achieved as the vapor enters the air stream traveling to subsequent impactor stages. This results in a constant process of volatilization of vapor from particles to restore the equilibrium (negative artifact) on the first stage −shown by the highest difference in concentrations in the first stage (10−18 μm) in Figure 2. The airstream entering the subsequent stages, however, contains the vapor volatilized from the first stage, and hence in the subsequent stages the vapor/particle partitioning will be closer to equilibrium (Figure 2).

The absolute pressure within the impactor sampler reduces as a consequence of the restricting orifices and the backup filter. This pressure drop within the MOUDI sampler is greatest for smaller size fractions and causes evaporative loss of volatile compounds from particles, which can be substantial (i.e., 10% or more) when the ratio of gas to particle concentration of the evaporating species is higher than one.[56] This is the case for the low MW PAHs (acenaphthalene to pyrene), whose predicted volatilisation losses are within 5−15% in the undenuded MOUDI and up to 60% in the denuded MOUDI according to Zhang and McMurry (1991).[57] Consistent with this, our results show a greater fractional contribution by mass in the size fraction <0.56 μm for the denuded MOUDI for the low MW PAHs (Figure S13).

It is worth noting that in the denuded impactor, the air flows over the surface of the impaction substrates at high velocity, reducing the potential for equilibration by volatilization of previously collected particles, which are not homogenously deposited in the filter. On the other hand, in the backup stage, where most of the combustion related aerosols will be collected, particles have a high surface to volume ratio and the air has a more intimate contact with the collected particles. This contact, in addition to the pressure drop on the last stage would facilitate the volatilisation of the final (back-up) stage particles to reach equilibrium in both regular and denuded MOUDIs (Figure 2). This emphasizes the importance of using a vapor trap downstream of a MOUDI, which is of greatest importance when a denuder is used to collect the vapor upstream of the MOUDI.

Pankow (1987)[58] defined the vapor/particle partitioning coefficient as the ratio of the compound's thermodynamic activity in/on the particulate matter (ratio of the particle concentration of a given compound respective to the total suspended particulate matter (TSP)) to that in the gas phase. Therefore, for any given species, the partition between phases is dependent on the vapor/particle distribution of all the other species, as this will affect the TSP variable. For a given temperature and relative humidity, the partitioning coefficient will be constant. In the denuded MOUDI, the vapor phase is negligible (SI Figure S11), and hence there will be volatilization of particles trying to reach equilibrium. The volatilization of one species will reduce the total TSP concentration, therefore affecting the thermodynamic activity of the particulate matter (i.e., F/TSP) for the other species. This will further facilitate the volatilisation of the other species in the airborne mixture, specially the lower MW PAHs. This will produce a shift of the size-fraction distribution toward smaller particles (as seen in Figure 2, size fraction <560 nm). In the undenuded MOUDI, the airstream entering the sampler is normally close to equilibrium, and hence no change in the vapor/particle partitioning of any one species is expected to affect the partitioning of other species in the mixture. This effect, although of minor magnitude, is also consistent with the observed behavior.

The combination of these processes explains the observation of higher concentrations of the lower MW PAHs in all the stages (Figure 2a), especially the first stage of the undenuded (regular) MOUDI due to adsorption of vapor on the substrates in the undenuded MOUDI; volatilisation of the particles deposited in the denuded MOUDI to restore equilibrium; enhanced volatilisation losses in the denuded MOUDI due to the pressure drop;[57] and volatilisation of particulate species in the denuded MOUDI due to the loss of particulate material as a substrate for absorption/adsorption processes.

For the higher MW PAHs (Figure 2b), absorption of vapor onto the filter is less important as most of these compounds are predominantly in the particle phase. Therefore a large increase of the concentrations due to vapor adsorption on the filters collected with the undenuded MOUDI is not expected. On the other hand, in the denuded MOUDI volatilization of particles to restore the vapor-particle equilibrium will still be active, since the system will try to reach equilibrium and the airstream entering the MOUDI has been stripped of the gas phase. This explains why for the high MW PAHs, the first stage of the denuded MOUDI collects lower particle concentrations than the undenuded MOUDI; the concentrations collected in the middle stages are very similar in both sampling trains consistent with previous results,[10,59] while the latter two stages in the denuded MOUDI collect larger concentrations.

The effect of desorption of PAHs from particles during their residence time in the denuder (3s at 30L/min) can result in an underestimation of the particle phase for these compounds of up to 23% for phenanthrene according to Kamens and Coe (1997).[61] This process will also contribute to an underestimation of the concentration of the low MW PAHs by the denuded MOUDI, consistent with the results reported in this study.

Figure 3 shows that the PUF located downstream of the denuded MOUDI collects lower low MW vapor concentrations, which are attributed to the evaporative loss of particles, than the PUF located downstream of the undenuded MOUDI. This difference is significant for the low MW PAHs ($p < 0.05$). On the other hand, the regression of the sum of the concentrations measured in the denuded sampling train, that is, denuder+MOUDI+PUF concentrations vs the concentrations measured in the regular sampling train, that is, MOUDI +PUF concentrations is very similar (slope = 0.98; $R^2 = 0.92$, SI Figure S15). Therefore the denuder is collecting most of the vapor phase, the impactor collects the majority of the breakthrough gas, while the PUF downstream of the denuded MOUDI collects the volatilized particle phase from the MOUDI. Likewise, in the regular sampling train (without denuder) the vapor phase is partially absorbed into the impactor and backup filters, but the majority, corresponding with the initial gas phase and a small percentage of volatilisation losses, is collected in the PUF downstream of the MOUDI. The outcome is a surprisingly small but statistically significant shift in the size distribution (Figure 2) caused by the denuder relative to the undenuded system. However, as discussed below, neither can be regarded as artifact-free.

It is informative to compare the vapor concentrations measured by the denuder and that from the PUF in the nondenuder configuration. These appear in Table 2, and show decreased ($p < 0.05$) collection of the low MW species by the PUF downstream the nondenuded impactor due to artifactual losses of the vapor absorbed in the impactor filters of the nondenuder system. The reverse is seen for the high MW compounds (Table 2) with the PUF showing markedly higher concentrations than the denuder due to vaporisation of particulate PAHs, although not statistically significant. These data indicate that the nondenuder system can substantially underestimate low MW PAHs vapor concentrations.

Similarly, higher concentrations (i.e., sum of the total PAHs across the sampling train) were found in a sampling train which contained an oxidant scrubber compared with a regular sampling train (SI Figure S16). The extent to which this, that is, the effect of collecting the gas phase before or after particle collection or using oxidant scrubbers, applies to the more usual high volume sampling systems is not known, but requires investigation.

Overall, the use of the denuder altered the measured size distribution of PAHs toward smaller sizes, but both denuded and undenuded systems are subject to sampling artifacts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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