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A Comparison of High Volume and Diffusion Denuder Samplers for Measuring Semivolatile Organic Compounds in the Atmosphere

A. J. P E T E R S , * , † D. A. L A N E , ‡
L. A. G U N D E L , § G. L. N O R T H C O T T , † A N D
K. C. J O N E S †

Department of Environmental Science, Institute for Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, United Kingdom, Environment Canada, Downsview, Ontario, M3H 5T4, Canada, and Lawrence Berkeley National Laboratory, Berkeley, California

A detailed comparison of two inherently different ambient air samplers has been conducted to fully characterize and compare their performance in sampling and measuring the partitioning of a suite of 29 semivolatile organic compounds (SVOCs). A high volume air sampler (hi-vol) utilizing polyurethane foam (PUF) adsorbent for vapor-phase trapping and an annular diffusion denuder sampler were operated concurrently. Sampling artifacts were observed and can be related to the physicochemical properties of the analytes and the designs of the samplers. The results suggest that high volume air samplers equipped with PUF are unsuitable for measuring those organochlorine compounds and 2- and 3-ring PAHs which have subcooled liquid vapor pressures ($p°_L$) greater than ca. 0.2 Pa (log-$[p°_L] = -0.7$), owing to their breakthrough on PUF sampling media at relatively low sample volumes (170 m³) and ambient temperatures typical of temperate regions (mean = 11 °C, max = 18 °C). Theoretical calculations of breakthrough volumes for SVOCs on PUF are presented and in most cases these successfully predict observed behavior. The denuder sampler is more efficient at measuring the relatively volatile SVOCs. For total SVOC measurements the hi-vol and denuder were in good agreement for those compounds which were efficiently sampled, and the denuder yielded total SVOC concentrations which differed by a mean factor of 1.2 relative to those obtained with the hi-vol sampler. The hi-vol sampler provides good agreement with the Junge-Pankow model for partitioning of the relatively less volatile PAHs (log$[p°_L] < -3$), though the fraction of the PCBs in the particle-phase is underestimated. The results from the diffusion denuder indicate that for the more volatile SVOCs (log$[p°_L] > -3$), particulate loadings are overestimated with respect to the Junge-Pankow model, and for less volatile SVOCs, particulate loadings tend to be underestimated. An important observation is that the results from the denuder indicate that PCBs may be adsorbed on atmospheric particulate matter to a similar degree as PAHs.

Introduction

High volume (hi-vol) air samplers equipped with polyure-thane foam (PUF) adsorbent have been a standard method for monitoring semivolatile organic compounds (SVOCs) in air for a number of years. They have been employed extensively to study the occurrence and speciation of SVOCs in the atmosphere (*1–5*) and are recommended by the U.S. EPA for sampling SVOCs such as pesticides, PCBs, and PAHs in ambient air (*6*). In these types of samplers air is drawn through a filter to retain particle-phase SVOCs and then through the PUF adsorbent to retain vapor-phase SVOCs. This sampling geometry has the potential to cause sampling artifacts, most notably "blow-off", whereby SVOCs which are adsorbed on particulate matter in ambient air may be volatilized from the particles after collection on a filter medium, thus enhancing the apparent vapor-phase concentration (*7, 8*). A second effect which may occur is "blow-on", whereby vapor-phase SVOCs in ambient air are adsorbed on the filter media or on accumulated particulate and/or organic matter on the surface of the filter media (*2, 8*). This would result in an apparent increase in the particle-phase loading of the SVOC in question. It is important to note that both of these phenomena can occur simultaneously.

Diffusion denuder systems have been developed to provide an alternative sampling method to minimize potential sampling artifacts (*8–11*). In denuder samplers, vapor-phase SVOCs are removed from the air stream by diffusion onto an adsorbent coating prior to removal of particulate matter by filtration. An adsorbent downstream of the filter then collects any SVOCs which are volatilized from the collected particulate matter. Potential sampling artifacts with diffusion denuders are (i) loss of fine particulate matter to the surface of the denuder tube, which would result in an apparent higher vapor-phase measurement; (ii) desorption of SVOC from particles while in transit through the denuder tube; and (iii) breakthrough of volatile analytes to the downstream adsorbent, resulting in an apparent higher particle-phase measurement.

To our knowledge, while they are used extensively for inorganic chemical sampling, diffusion denuder samplers are not currently used routinely for SVOC measurements in ambient air. This study was undertaken to fully characterize and compare the sampling of SVOCs by a high volume sampler and a recently designed diffusion denuder sampler. It forms part of an ongoing research project to characterize SVOCs in the U.K. atmosphere and to investigate the processes controlling their distribution in air.

Experimental Section

Sample Collection. Sampling occurred at the Lancaster University experimental field station at Hazelrigg (54°2′N, 2°47′W), a semirural location in northwest England. This site has recently been fully described (*12*). Sampling occurred on six occasions during September and October 1998. Meteorological data for the sampling events were acquired by an automated weather station (Davis Instruments) mounted on a 2 m mast in the vicinity of the air samplers.

The high volume air sampler used was a Graseby-Andersen model PS-1, equipped with two glass fiber filters (GFF), to enable correction to be made for adsorption of vapor-phase SVOC to the filter material, and two polyure-

* Corresponding author phone: +44 1305 213631; fax: +44 1305 213600; e-mail: anpe@ceh.ac.uk. Current address: NERC Centre for Ecology and Hydrology, Winfrith Technology Centre, Dorchester, DT2 8ZD, United Kingdom.
† Lancaster University.
‡ Environment Canada.
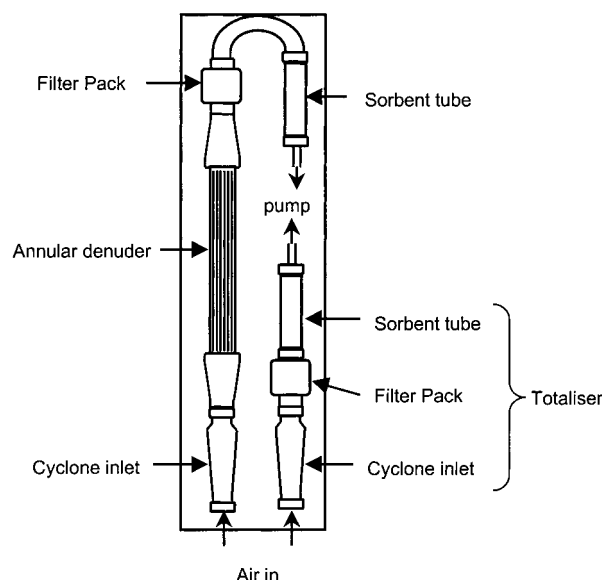§ Lawrence Berkeley National Laboratory.

FIGURE 1. The IOGAPS diffusion denuder sampler.

thane foam (PUF) plugs to provide data on vapor-phase sample breakthrough and retention. The hi-vol was operated at a flow rate of 3.6 m³·h⁻¹, yielding a total volume of 170 m³ over a period of 48 h.

The Integrated Organic Gas and Particle Sampler (IOGAPS) is a diffusion-based air sampler which uses an eight-channel annular denuder. The components of the IOGAPS are illustrated in Figure 1. The totalizer component is provided to supply a measurement of total SVOC concentrations and is not considered further in this work: Lane et al. (*13*) have reported in detail on the performance of the IOGAPS for PAH measurements in air. The denuder tube consists of a 600 mm long, eight channel annular denuder with annuli spacings (from center outward) of 1.0, 1.0, 1.2, 1.0, 1.0, 1.0, 1.4, and 1.2 mm. The surfaces of the annuli are coated with ground XAD-4 (ca. 0.75 μm). Air is drawn through a 2.5 μm cutoff cyclone inlet and through the denuder tube where vapor-phase analytes are adsorbed by the XAD-4 by molecular diffusion out of a laminar flow stream. A filter then removes particles from the air stream and a PUF adsorbent traps any analytes which are volatilized from particulate matter on the GFF. The flow of air through the denuder system was controlled to maintain a constant flow rate of 16.7 L·min⁻¹, yielding 48 m³ over a period of 48 h.

Before use, all PUF adsorbents were washed in hot tap water, rinsed thoroughly with deionized water, dried in a glassware oven overnight at 35 °C, and then Soxhlet extracted with DCM for 24 h. GFFs were cleaned by combusting at 450 °C in a muffle furnace for 12 h in aluminum foil pouches.

Sample Extraction and Fractionation. Exposed PUF plugs and GFFs from the hi-vol, and the exposed PUF adsorbents and GFFs from the denuder were Soxhlet extracted with 250 mL of hexane for 12 h. Following extraction, the extracts were spiked with a surrogate mixture solution containing four surrogate OC compounds (tetrabromobenzene, dibromooctafluorobiphenyl, δ-HCH, and mirex) and seven perdeuterated PAHs to monitor analytical efficiency. The denuder tube was manually extracted 3 times with 250 mL of hexane by pouring the solvent into the tube, sealing the ends with PTFE caps, and manually inverting the tube end-on-end while also rotating it along its axis. The first portion of hexane was spiked with the surrogate mixture prior to the extraction and each extract was analyzed separately. All extracts were reduced by vacuum rotary evaporation to ca.

2 mL and subjected to open column (10 mm diameter) chromatography on 3 g of 3% deactivated silica (Merck, Silica Gel 60) and 2 g of 6% deactivated neutral alumina (Merck, Brockman Grade 1). The column was first eluted with 22 mL of hexane to give fraction A containing PCBs and the lower polarity OC-pesticides and then with 20 of mL DCM to give fraction B containing the PAHs and the remaining, more polar OC-pesticides. The solvent was exchanged to isooctane (2,2,4-trimethylpentane) and reduced to ca. 100 μL with a gentle stream of purified N₂. Then tetrachloro-*m*-xylene and PCB-209 were added at a final concentration of 100 pg·μL⁻¹ as internal standards for OC determination, and a further seven perdeuterated PAHs were added at a final concentration of 250 pg·μL⁻¹ as internal standards for PAH determination.

Organochlorine Analysis. Samples (2 μL injected) were analyzed on a Hewlett-Packard 5890 GC with dual electron capture detection (ECD) using HP-5ms and HP-50+ columns (5 and 50%, respectively, phenyl substituted methylsilicone stationary phase). Dimensions for both columns were as follows: length 60 m; internal diameter 0.25 mm; phase thickness 0.25 μm. N₂ was used as the ECD makeup gas at a flow rate of 30 mL·min⁻¹. Electronic pressure control was used to maintain a constant flow of carrier gas (He) at a rate of 1.9 mL·min⁻¹. Temperature conditions were as follows: injector 250 °C; detectors 300 °C; oven initial temperature 100 °C, hold for 2 min, increase at 30 °C·min⁻¹ to 130 °C, increase at 2 °C·min⁻¹ to 250 °C, increase at 4 °C·min⁻¹ to 290 °C, and hold for 10 min. Analytes are considered detected if (i) the two corresponding GC peaks for a particular analyte are each within a retention window of 3 s of the mean expected retention time determined from the calibration analyses; and (ii) the difference between the two quantitated signal responses is less than 25% in the absence of known interferents.

PAH Analysis. GC-MS analysis of the extracts was carried out using an HP 5890 series II gas chromatograph coupled to an HP 5972A MSD. Samples in isooctane (1 μL) were injected by automatic cool-on-column injection using an independent pressure and temperature profile. The GC column was a HP-5ms of dimensions, length 30 m; internal diameter 0.25 mm; phase thickness 0.25 μm, coupled to a deactivated retention gap (length 2 m, ID 0.53 mm). Helium was used as the carrier gas with head pressure controlled by electronic pressure control using the following program: 11 psi, hold for 1 min, then increase at 0.5 psi·min⁻¹ to 30 psi. The on-column injector was held at 60 °C for 0.05 min and then increased at 25 °C·min⁻¹ to 310 °C. The temperature of the GC column was held constant at 60 °C for 1 min, programmed to 130 °C at 20 °C·min⁻¹ and then to 310 °C at 6 °C·min⁻¹, and maintained at this final temperature for 15 min. The temperature of the interface to the MSD was held at 290 °C. The MS was operated in selected ion monitoring (SIM) mode to acquire the signal from the molecular ion of each compound and an additional qualifying ion for confirmation. The MSD was manually tuned with user defined parameters, and PAHs were quantified using perdeuterated internal standards.

Detection Limits and QA/QC. Nominal method detection limits for the hi-vol and denuder samplers, respectively, are OCs = 0.6 and 2.0 pg·m⁻³, PAHs = 1.5 and 5.0 pg·m⁻³ (based on respective sample sizes of 170 and 48 m³ of air sampled). Separate experiments in which PUF plugs and GFFs were spiked with the suite of analytes and then Soxhlet extracted yielded mean recoveries of OCs and PAHs of 99% and 92%, respectively. Recoveries of the analytical surrogates from the hi-vol samples and the denuder filters and adsorbents were considered acceptable (OC mean: 85%, PAH mean: 92%), and no corrections were made for surrogate recoveries. The denuder tube extractions indicated that 90% of the surrogates

TABLE 1: Calculated and Observed Breakthrough Data for the Hi-Vol Sampler

compd	p°_L (Pa)	log[p°_L]	$V_{g,293}$ (m³·g⁻¹)	V_{PUF} (m³)	$V_B{}^a$ (m³)	obsd B_{HV}
HCB	2.4E−01	−0.61	14	91	140[b]	0.27
a-HCH	1.0E−01	−1.00	35	230	350	0.00
g-HCH	2.7E−02	−1.56	140	920	1400	0.07
PCB-28	2.0E−02	−1.71	200	1300	2000	0.15
PCB-52	2.0E−03	−2.70	2200	15000	23000	0.13
PCB-101	3.5E−03	−2.46	1200	8200	12000	0.06
PCB-118	6.3E−04	−3.20	7400	50000	75000	0.00
PCB-153	7.0E−04	−3.15	6700	45000	68000	0.06
PCB-138	2.7E−04	−3.57	19000	1.2E + 05	1.9E + 05	0.04
PCB-180	6.6E−05	−4.18	81000	5.4E + 05	8.2E + 05	0.06
NAP	3.7E + 01	1.57	0.06	0.41	0.62[b]	0.51[c]
2-mNAP	1.1E + 01	1.05	0.25	1.7	2.6[b]	0.50[c]
1-mNAP	8.8E + 00	0.95	0.33	2.2	3.3[b]	0.49[c]
BIP	3.7E + 00	0.57	0.94	6.3	9.5[b]	0.54[c]
2,6-dimNAP	9.3E +0 0	0.97	0.32	2.1	3.2[b]	0.52[c]
ACE	1.5E + 00	0.18	2.7	18	27[b]	0.21
ACY	4.1E + 00	0.62	0.83	5.5	8.3[b]	0.49[c]
FLR	7.2E−01	−0.15	6.7	45	68[b]	0.30
PHN	1.1E−01	−0.95	61	410	620	0.03
ANT	7.8E−02	−1.11	95	640	960	0.00
FLT	8.7E−03	−2.06	1300	8700	13000	0.03
PYR	1.2E−02	−1.92	900	6000	9000	0.10
BaA	6.1E−04	−3.22	32000	2.1E + 05	3.2E + 05	0.00
CHR	1.1E−04	−3.97	2.5E + 05	1.7E + 06	2.5E + 06	0.01
BkF	4.1E−06	−5.39	1.2E + 07	8.2E + 07	1.2E + 08	0.00
BeP	2.4E−05	−4.62	1.5E + 06	1.0E + 07	1.5E + 07	0.00
BaP	2.1E−05	−4.67	1.7E + 06	1.2E + 07	1.7E + 07	0.00
D(ah)ANT	9.2E−08	−7.04	1.2E + 09	7.8E + 09	1.2E + 10	0.00
B(ghi)PER	2.3E−05	−4.65	1.6E + 06	1.1E + 07	1.6E + 07	0.00

[a] Volume at which B_{HV} is predicted to exceed 0.33. [b] Breakthrough predicted when V_B < sample volume (170 m³). [c] Breakthrough observed (B_{HV} > 0.33).

were extracted in the first extraction, 10% in the second, and none in the third. Field blanks and procedural blanks were used to monitor potential contamination, and all data have been blank corrected where necessary.

Results and Discussion

Hi-Vol Breakthrough. Breakthrough of SVOC analytes is a limiting factor on the application of PUF for air sampling. It can be calculated from

$$B_{HV} = \frac{[PUF]_{back}}{[PUF]_{front} + [PUF]_{back}} \qquad (1)$$

where B_{HV} = specific hi-vol vapor-phase breakthrough and [PUF] = concentration (pg·m⁻³) of a particular analyte on the PUF plug, where the front or back PUF is denoted by subscript (*14*). For this study, a critical value of B_{HV} was taken to be 0.33, i.e., when the concentration of an analyte on the back PUF is ≥50% that of the front PUF, excessive breakthrough was considered to have occurred.

The compound specific retention volume for a specific SVOC on a single PUF plug (V_{PUF}) of density 0.022 g·cm⁻³ at 20 °C is given in Pankow (*15*)

$$V_{PUF} = V_{g,293} \times m_{PUF} \qquad (2)$$

where $V_{g,293}$ = specific gas-phase retention volume (m³·g⁻¹) at 293 K and m_{PUF} = mass of PUF plug (6.7 g). Values of $V_{g,293}$ for PAHs and OCs were calculated from parameters presented in Pankow (*15*) for regression of log[$V_{g,293}$] on log[$p^\circ_{L,293}$], where $p^\circ_{L,293}$ = subcooled liquid vapor pressure at 293 K (note that values were converted between Pa and Torr for these calculations). Calculated values of V_{PUF} are shown in Table 1 and represent the volume of air which can be drawn through a PUF plug of the type used before breakthrough occurs. The data refer to conditions at 20 °C which in this case results
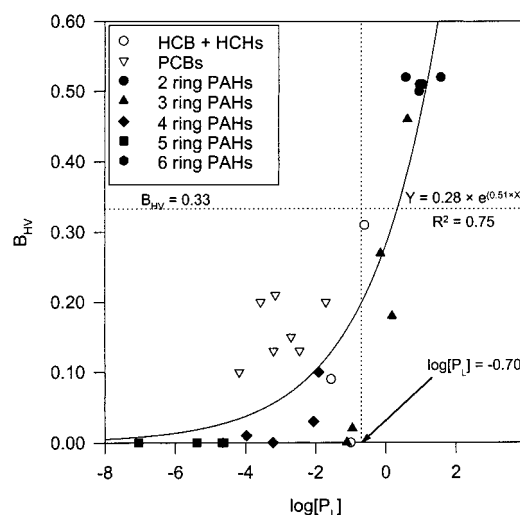

FIGURE 2. Breakthrough of SVOCs on PUF plugs in the hi-vol type sampler (mean of N = 6 measurements). The horizontal dotted line indicates the critical B_{HV} value. Vertical dotted line represents the vapor pressure above which it is calculated that SVOCs will exhibit $B_{HV} \geq 0.33$. Solid line = line of best fit for all data points.

in marginally conservative estimates of V_{PUF} as higher values will pertain at lower temperatures. The mean and maximum air temperatures during the sampling events were 11 and 18 °C, respectively.

The critical value of B_{HV} (eq 1) for a particular compound will be achieved at a volume of $1.5 \times V_{PUF}$ (defined as V_B), and breakthrough is therefore predicted when the value of V_B is less than the sample volume (170 m³). It can be seen from Figure 2 that this approach predicts the breakthrough of the 2-ring PAHs and acenaphthylene. Breakthrough of HCB, acenaphthene, and fluorene is also predicted but not
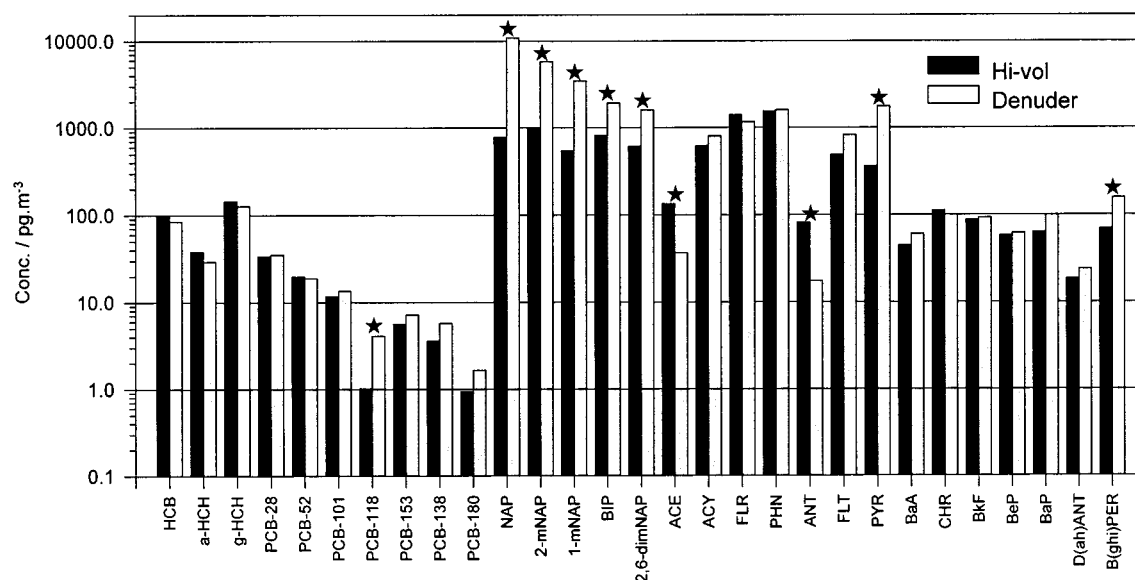
FIGURE 3. Total SVOC concentrations measured by each type of sampler (mean of $N = 6$ measurements). Comparison of paired results where pairs marked with a star differ by more than a factor of 2 (note logarithmic axis).
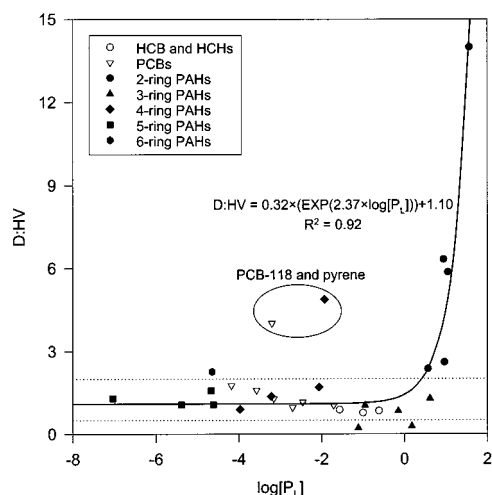

FIGURE 4. Ratio of total SVOCs measured by the two samplers (D = denuder, HV = hi-vol) as a function of vapor pressure (mean of $N = 6$ measurements). The dotted lines define the range of agreement within a factor of 2 (i.e. $0.5 < D{:}HV < 2.0$). Solid line = line of best fit (circled outlier points (PCB-118 and pyrene) were excluded from the calculation).

observed, though they do exhibit relatively high degrees of breakthrough close to 0.33 (B_{HV} = 0.27, 0.21, and 0.30, respectively).

For the PUF plugs used in this study, and defining V_B to be equal to the sample volume (170 m³), a critical value for $\log[p°_L]$ of -0.70 ($p°_L = 0.20$ Pa) can be determined for which SVOCs are predicted to be subject to $B_{HV} > 0.33$ when 170 m³ of air is sampled at 20 °C. The relationship between subcooled liquid vapor pressure and hi-vol PUF breakthrough is illustrated in Figure 2. These observations support the findings of Hart et al. (*14*) which suggest that PUF adsorbent is unsuitable for sampling those SVOCs compounds which are more volatile than phenanthrene.

From Figure 2 it can be seen that PCBs exhibit different behavior than PAHs, with PCBs showing higher B_{PUF} than those PAHs which have similar $p°_L$ values. Pankow (*15*) estimates that PAHs are sorbed more strongly to PUF than OCs, which might account for the observed increased migration of PCBs through the PUF plugs.

Adsorption of SVOC to GFFs. Analysis of the second (back-up) GFF in the hi-vol samples shows very similar results to PUF breakthrough and reveals that significant amounts of analyte are detected on the second GFF for PAHs more volatile than phenanthrene and for the OCs. Corrections for this are made in the calculation of the vapor and particle fractions, described below.

Diffusion Denuder Performance. The efficiency (E) of the denuder to quantitatively retain vapor-phase SVOCs is a crucial factor in its performance and for a single denuder annulus can be measured by

$$E(\%) = \left(1 - \frac{C}{C_i}\right) \times 100 \qquad (3)$$

where C = amount of analyte exiting the denuder and C_i = amount of analyte entering the denuder, and from Possanzini et al. (*16*)

$$\frac{C}{C_i} = 0.82 \exp[-22.53\Delta_a] \qquad (4)$$

where

$$\Delta_a = \frac{\pi DL}{4F} \times \frac{d_1 + d_2}{d_2 - d_1} \qquad (5)$$

and where D = gas diffusion coefficient (cm²·s⁻¹); L = length of denuder (cm); F = flow rate (cm³·s⁻¹); d_1 = outer diameter of annulus (cm); and d_2 = inner diameter of annulus (cm).

Hence for the largest annulus and considering benz[*a*]-anthracene with a value of $D = 0.072$ cm²·s⁻¹ at 10 °C (*17*) yields values of $C/C_i = 1.4 \times 10^{-8}$ and a corresponding $E = 99.999999\%$, i.e., a potential loss of 10 ppb of the original ambient concentration. Higher temperatures and higher diffusion coefficients yield even lower values of C/C_i and hence higher trapping efficiencies, and so corrections for denuder efficiency are not considered appropriate. The fact that naphthalene exhibits no significant particle-phase ($\Phi < 0.01$) suggests that the denuder is not susceptible to vapor-phase breakthrough of SVOCs creating a positive particle-phase artifact. We are therefore confident that the denuder is efficiently sampling vapor-phase SVOCs. It is not expected that denuder efficiency would be reduced by competitive adsorption by water vapor at high relative humidity levels as

the XAD-4 used to coat the surfaces of the annuli is extremely hydrophobic.

Total SVOC Measurements. Figure 3 shows fairly good agreement between the two samplers for the total (vapor + particulate) amounts of each analyte measured. Excluding those analytes which exhibit differences greater than a factor of 2, the mean denuder:hi-vol ratio (D:HV) is 1.2. When the difference between the samplers is analyzed as a function of vapor pressure (Figure 4), it can be seen that this is an important factor, with an exponential relationship between the measured difference and vapor pressure for each analyte. A constant difference of ca. 1.1 is observed for the majority of compounds with $p°_L$ up to about 0.1 Pa, after which nonlinear deviation occurs. This is most likely a result of breakthrough of the more volatile SVOCs occurring on the hi-vol, as described above. The difference cannot be attributed to losses of SVOCs during Soxhlet extraction of the hi-vol sampling media, owing to the high analyte recoveries detailed above.

The relatively constant values of D:HV for those compounds with $p°_L$ values < 0.1 Pa suggests that the denuder systematically records air concentrations 20% higher than the hi-vol. It is difficult from these data to suggest a reason for this difference. It cannot be attributed to differences in analytical efficiency or blank levels between the two types of sampler, as these were comparable. It is also difficult to attribute the difference to the different particle size range that may be sampled by the two samplers. As the denuder is equipped with a 2.5 cyclone inlet it is excluding larger particles which may be collected by the hi-vol. If these particles contributed significantly to the atmospheric loading of SVOCs it would be expected that the hi-vol would record higher SVOC concentrations, but this is not the case.

Vapor/Particle Partitioning. Partitioning of SVOCs in the atmosphere between the vapor and particle-phase is an important factor in determining their behavior and fate in the environment. This study is a comparison of two methods for measuring SVOC partitioning and is not intended to be a study of partitioning phenomena per se, for which there exists a wealth of literature (*4, 18, 19*, and references therein).

The particulate fraction (Φ) of each SVOC analyte in the atmosphere is calculated from

$$\Phi = \frac{P}{P + V} \qquad (6)$$

where P = concentration in particulate fraction (pg·m^{-3}) and V = concentration in vapor fraction (pg·m^{-3}). Values of P and V for each sampler are calculated from the following:

Hi-vol:

$$P_{\text{hi-vol}} = [\text{GFF}]_{\text{front}} - [\text{GFF}]_{\text{back}} \qquad (7)$$

and

$$V_{\text{hi-vol}} = [\text{PUF}]_{\text{front}} - [\text{PUF}]_{\text{back}} + (2 \times [\text{GFF}]_{\text{back}}) \quad (8)$$

Thus the back GFF is used to correct for vapor-phase adsorption of SVOCs onto the filter medium.

For the diffusion denuder

$$P_{\text{DD}} = [\text{filter}] + [\text{adorbent}] \qquad (9)$$

where [filter] and [adsorbent] are the air concentrations in pg·m^{-3} determined from the filter and back-up adsorbent and
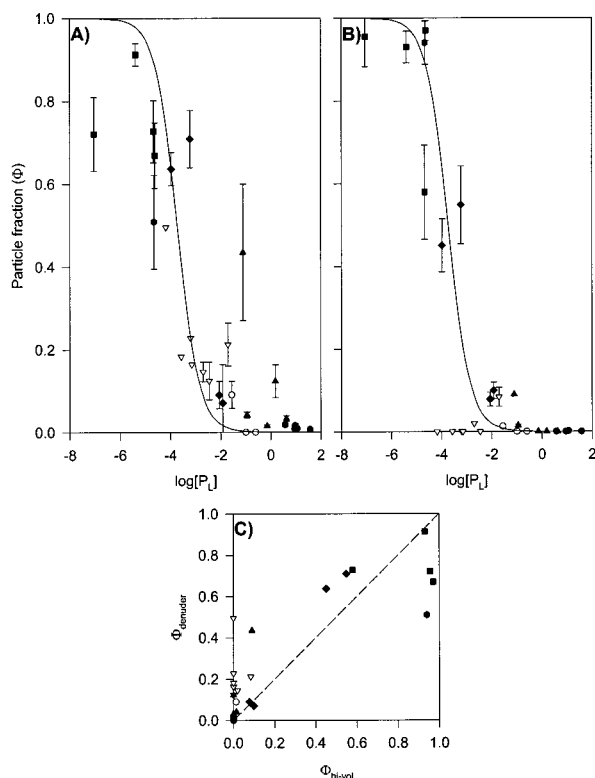
$$V_{\text{DD}} = [\text{denuder}] \qquad (10)$$

FIGURE 5. Particulate fraction measured by each type of sampler (mean of $N = 6$ measurements). (A) Denuder particulate fraction $\pm$ 1 s.e. (B) Hi-vol particulate fraction $\pm$ 1 s.e. Symbols as defined for Figures 2 and 4. The curve shown in A and B is the Junge-Pankow model fit for partitioning of SVOCs in a typical urban atmosphere (*17*). (C) Scatter plot of denuder v. hi-vol particulate fractions.

where [denuder] = the air concentration (pg·m^{-3}) determined from the sum of the three denuder tube extractions.

Figure 5 illustrates the measured particulate fraction of SVOCs by each method and relates these to the Junge-Pankow model for SVOC partitioning in a typical urban atmosphere (*19*). It is important to note that neither the results of the two sampling methods or the Junge-Pankow model are necessarily the "correct" representation of SVOC partitioning in the atmosphere: the model is being used as a reference for comparative purposes between the two methods.

The hi-vol sampler appears to provide good agreement with the Junge-Pankow model for partitioning of the relatively less volatile PAHs (log[$p°_L$] < −3), though the fraction of the PCBs in the particle-phase is underestimated. Conversely, the results derived from the diffusion denuder show that for the more volatile SVOCs (log[$p°_L$] > −3), particulate loadings are overestimated with respect to the Junge-Pankow model, and for less volatile SVOCs, particulate loadings tend to be underestimated. An important observation is that the results from the denuder indicate that PCBs may be associated with atmospheric particulate matter to a similar degree as PAHs, in contrast to the observations made using the hi-vol sampler by ourselves and others (e.g. ref *18*). PAHs may be sorbed to atmospheric particles to a greater degree than PCBs (*18*) and so PCBs are therefore more available for vapor exchange, i.e., they are susceptible to higher degrees of volatilisation during hi-vol sampling and thus higher apparent vapor-phase concentrations will be observed using this method.

The observation that the denuder sampler may underestimate the particle-phase relative to the Junge-Pankow

model for some of the less volatile SVOCs may be attributable to the aerosol size distribution at the sampling site. Owing to the location of the site being less than 1 km from a major highway, it is feasible that the aerosol could contain a significant amount of particles derived from diesel combustion which would be in the size range < 5 μm. The compounds in question, being predominantly high molecular weight PAHs, may therefore be present adsorbed on to particles of size < 5 μm, and it has been estimated that for particles of size 0.1−0.05 μm there is a potential 10% loss by adsorption to the denuder tube surfaces (*13*). However, if there was a highly significant loss of particles to the denuder surface, then this would cause a strong positive vapor-phase artifact, and the denuder would produce results more like the hi-vol's. The fact that the denuder shows a higher particle fraction (and a significantly higher particle fraction in the case of the four ring PAHs) suggests that this loss is not significant.

Our data suggest that hi-vol samplers equipped with PUF are suitable for measuring atmospheric burdens of SVOCs with $p°_L$ values < 0.2 Pa but will underestimate more volatile SVOCs owing to breakthrough. The diffusion denuder does not appear to suffer from this limitation and appears to efficiently sample SVOCs with relatively high vapor pressures, such as naphthalene ($p°_L$ = 37 Pa). Differences in the measured partitioning of SVOCs in air using the two samplers are seen to be a function of vapor pressures and sampler geometry. It is important to state that differences between the two sampler designs remain: i.e., differences in particle size range collected, differences in sample volume and flow rates, and the fact that both samplers operationally define the particulate and vapor fractions. Hi-vol samplers will continue to be used owing to their robustness and ease of field application, but we believe that further characterization of diffusion denuder performance will result in their increased use in studies of SVOC partitioning in the atmosphere.

Acknowledgments

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