

Levels and Sources of Personal Inhalation Exposure to Volatile Organic Compounds

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Personal exposures to VOCs of 12 urban dwellers were measured directly via personal monitoring and indirectly via static monitoring combined with personal activity diaries. Over 5–10 days, day-to-day variations in personal exposures of individuals were substantial, with statistically significant ($p < 0.05$) deviation from the normal distribution observed for daily exposures to one or more VOCs for several subjects. Daytime concentrations generally exceeded night time, with day:night mean concentration ratios for each sampling day > 1 for most VOCs, with the maximum (3.85) occurring for 1,3-butadiene. Exposure in the home contributed 50–80% of overall individual exposure to 1,3-butadiene and benzene. For most VOCs, while absolute values of direct and indirect exposure estimates were significantly different ($p < 0.05$), linear regression of direct and indirect exposure estimates revealed statistically significant correlation ($p < 0.01$), confirming previous observations that indirect monitoring can provide satisfactory estimates of personal inhalation exposure to VOCs. ETS, the use of vehicles, and heating (but not cooking) all made appreciable contributions to personal exposure to all target VOCs.

Introduction

As a consequence of their adverse human health effects, Volatile Organic Compounds (VOCs) are the subject of considerable concern. In particular, 1,3-butadiene and benzene have been identified as respectively probable and proven carcinogens by the United States Environmental Protection Agency (USEPA) (1) and specified as toxic air pollutants along with formaldehyde, acetaldehyde, and polycyclic organic materials in the 1990 amendment of the U.S. Clean Air Act (CAA) (2). As a result, considerable efforts have been expended to determine and regulate public exposure to these chemicals.

The U.K. government has set air quality standards for 1,3-butadiene and benzene, of 1 ppb ($2.25 \mu\text{g m}^{-3}$) and 5 ppb ($16.25 \mu\text{g m}^{-3}$) respectively (both expressed as annual running means), with the objective of achieving these standards by December 2003. However, monitoring for compliance with these standards is limited to a relatively small number of stationary outdoor monitoring sites. Given the likely spatial variation in VOC concentrations, it is questionable to what extent such a monitoring strategy represents an accurate reflection of personal exposure. The focus on outdoor

monitoring is also debatable, given that in modern societies, people spend ca. 90% of their time in indoor environments (inter alia 3). Furthermore, there is a growing body of evidence to suggest that indoor concentrations of many VOCs exceed those observed outdoors (inter alia 4). Together, these factors imply that monitoring human exposure to VOCs is inadequately evaluated by the stationary monitoring of ambient air approach currently widely applied.

Even previous studies of personal exposure to VOCs are limited with respect to target compounds and experimental design. For instance, although a considerable body of data exists for benzene, there are comparatively few available for 1,3-butadiene, despite the latter's carcinogenicity and higher unit risk factor. Furthermore, those data that are available for 1,3-butadiene are limited to specific microenvironments such as automobiles, buses, homes, or workplaces (2, 5). Finally, most previous personal exposure studies have been limited to 1 day of sampling per subject (6–8). As a result, daily variations in exposure of individuals to VOCs have not previously been evaluated.

In an earlier paper (4), we reported concentrations of selected VOCs in a wide range of urban microenvironments. In this study, the personal exposure of a number of individual urban dwellers to a range of VOCs—including benzene and for the first time to our knowledge 1,3-butadiene—is measured, both directly by personal monitoring and indirectly via static monitoring of concentrations in representative microenvironments, combined with personal activity diaries. Exposure estimates obtained by the two methods are compared and contrasted. Daily variations in individual exposure are studied by personal monitoring of each subject on a number of different days, diurnal variations in concentrations are evaluated, and the relative contribution of different microenvironments and potential sources such as vehicle use and ETS to overall personal exposure assessed.

It is important to bear in mind, that the air quality standards mentioned above relate to the health impacts of chronic exposure. Unfortunately—in common with other studies of personal exposure—resources did not permit monitoring of exposure over periods consistent with their air quality standards. Hence, care should be taken when extrapolating the short-term exposures reported here to facilitate comparison with such standards.

Experimental Section

Overall Sampling Strategy. All monitoring was conducted at various times between March 1999 and February 2000 in central Birmingham. With a population of 1 million, Birmingham is the second largest city within the U.K. and is part of the West Midlands conurbation that has a population of ca. 2.5 million. The *direct* personal exposure data reported in this study were obtained alongside a previously reported study into measurements of VOC concentrations in different urban microenvironments (4). The results of this earlier study are—in conjunction with personal activity diaries of participating subjects—employed in this paper to derive *indirect* measurements of personal exposure. Twelve subjects were recruited, all were nonsmoking office or laboratory workers between 25 and 30 years old and Birmingham residents. A table (S.1) containing individual subject information listing inter alia potential emission sources that could affect personal exposure of individual subjects to VOCs is included as Supporting Information. In particular, 6 subjects were exposed to Environmental Tobacco Smoke (ETS) by for example sharing accommodation with smokers, with 4 subjects using cars for commuting purposes during this study.

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Personal monitoring was conducted at different times to the microenvironment monitoring described above for between 5 and 10 days for each subject, with sampler inlets attached to the volunteer's lapel ca. 25 cm below the nose. While each individual subject was sampled on consecutive days, different subjects were monitored throughout the period March 1999 to February 2000. Sampling was carried out for 10 h per day (i.e. 5×2 h samples) during daytime between 07:00 and 22:00 (exact times dependent on volunteer preference) and 2 h per day during night time between 00:00 and 02:00. Daily exposures of a given individual on a given sampling day were calculated by summing the exposures recorded for each sample on that day. Indirect exposure estimates in individual microenvironments were calculated by multiplying the mean VOC concentration previously recorded in each microenvironment (4), by the proportion of time spent in that microenvironment on that day (obtained from personal activity diaries). Finally, VOC monitoring for direct estimation of personal exposure was conducted for only 6×2 h periods (12 h total) per day. Thus, it must be acknowledged that our personal exposure estimates are subject to uncertainty when extrapolated to cover 24 h exposure.

Analyte Selection Criteria. VOCs monitored in this study were selected according to the following criteria: (a) adverse human health effects arising from chronic exposure, in particular carcinogenicity (1,3-butadiene, benzene, and styrene), (b) the extent of previous monitoring, and (c) potential utility as a tracer of a specific emission source—e.g. 3-ethenylpyridine for ETS.

Since 1,3-butadiene differs considerably from the other VOCs monitored with respect to adsorption/desorption

characteristics and susceptibility to decomposition/artifact formation, it was monitored using a different protocol to that employed for the other targeted VOCs (benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, styrene, 1,2,4-trimethylbenzene, naphthalene, pyridine, and 3-ethenylpyridine).

Sampling Methodology. Sampling was conducted using two adsorbent tubes fitted to a personal pump operated at a flow rate of ca. 40 mL min^{-1} with tubes changed every ca. 2 h. One adsorbent tube was packed with 1000 mg of Carbpac B (60/80 mesh, Supelco) followed by 150 mg of Carbosieve SIII (60/80 mesh, Supelco) (9) for sampling of 1,3-butadiene, while the other tube was packed with 300 mg of Tenax GR (60/80 mesh, Chrompack) followed by 600 mg of Carbotrap (20/40 mesh, Supelco) (4) for the determination of other target VOCs. Each adsorbent tube was capped with swagelok fittings before and after sampling.

Analytical Methodology. Details of our analytical methods are given elsewhere (4, 9), but a brief summary follows. Analysis of all VOCs was conducted using a thermal desorber (Tekmar 6000/6016) interfaced with a gas chromatograph (HP 5890 series II) and mass selective detector (HP 5971A). Chromatographic separation was achieved using a PLOT capillary column (50 m, 0.32 mm i.d., $5 \mu\text{m}$ film thickness, Chrompack) for 1,3-butadiene, and a Stabil-wax capillary column (50 m, 0.25 mm i.d., Restek) for the other VOCs.

Method Validation. Extensive validation was conducted of our sampling and analytical methodology. Detailed descriptions of our method validation techniques for VOC analysis and their results are given elsewhere (4, 9).

TABLE 1. Summary of Daytime and Night Time VOC Concentrations Recorded during Direct Personal Exposure Monitoring ($\mu\text{g m}^{-3}$)^a

VOC	daytime concentrations ($n = 473$)					night time concentrations ($n = 99$)					mean D/N ratio ^b	statistical significance level (p value)
	mean	median	σ	min	max	mean	median	σ	min	max		
1,3-butadiene	1.1	0.4	2.4	ND	26.3	0.8	0.4	1.2	ND	7.9	3.85	0.004
benzene	10.6	6.2	19.3	0.9	295.4	9.3	6.2	8.1	1.7	53.3	1.52	0.043
toluene	28.9	15.1	48.6	2.2	525.0	47.0	17.6	103.5	3.9	835.9	1.39	0.187
ethylbenzene	3.0	1.8	5.0	ND	47.4	2.7	1.7	2.3	0.3	12.1	1.73	0.143
<i>p</i> -xylene	7.6	4.0	15.0	0.5	155.6	6.1	4.1	5.9	0.8	37.6	1.92	0.060
<i>m</i> -xylene	2.7	1.4	5.9	ND	67.4	2.2	1.4	2.4	ND	15.8	1.87	0.066
<i>o</i> -xylene	3.1	1.6	6.3	ND	67.2	2.5	1.8	2.6	0.3	19.3	1.80	0.115
1,3,5-TMB	0.7	0.3	1.6	ND	19.3	0.5	0.3	0.7	ND	2.9	2.27	0.014
styrene	0.7	0.5	0.8	ND	7.0	0.8	0.5	0.8	ND	3.6	1.58	0.074
1,2,4-TMB	2.7	1.4	5.8	ND	73.3	2.2	1.4	2.4	ND	11.5	2.18	0.060
3-EP	0.6	0.0	2.0	ND	18.1	0.3	0.0	1.3	ND	8.7	NA	NA
naphthalene	4.4	0.5	24.1	ND	472.4	8.7	0.7	22.2	ND	111.6	0.94	0.099
pyridine	0.5	0.0	1.5	ND	12.8	0.2	0.0	0.8	ND	5.3	NA	NA

^a Note: 1,3,5-TMB = 1,3,5-trimethylbenzene, 1,2,4-TMB = 1,2,4-trimethylbenzene, 3-EP = 3-ethenylpyridine, ND = not detected, NA = insufficient data available to permit calculation. ^b The mean of ratios of mean daytime and night time concentrations.

TABLE 2. Variability of Daily Personal Exposures (Expressed as Relative Standard Deviations, %)

VOC/subject no.	2	4	5	6	7	8	9	10	11	12
1,3-butadiene	58.4 ^a	46.0	35.0	18.4	37.8	46.9	32.9	117.6 ^a	44.7	77.7
benzene	48.2	40.5 ^a	46.6	34.9	26.9	36.3	31.1	38.7	42.3	70.8 ^a
toluene	46.0	26.3	42.0	40.6	25.5	41.5	85.7 ^a	119.8 ^a	55.6	35.9
ethylbenzene	48.4 ^a	31.4	61.3	44.7	53.2 ^a	38.9	50.0 ^a	55.4 ^a	58.1 ^a	57.7
<i>p</i> -xylene	51.1 ^a	33.1	65.5	45.7	71.7 ^a	40.3	42.3 ^a	36.5 ^a	53.3 ^a	61.8 ^a
<i>m</i> -xylene	51.2	32.2	65.8	43.5	70.8 ^a	50.6	48.9 ^a	63.4 ^a	63.9 ^a	61.0
<i>o</i> -xylene	48.4 ^a	30.6	62.3	45.2	80.5 ^a	38.9	36.7 ^a	38.5	71.2 ^a	56.4
1,3,5-trimethylbenzene	56.8 ^a	79.3 ^a	78.3	44.4	39.2	37.5	45.2 ^a	34.6	92.1 ^a	26.7
styrene	45.9	32.0	55.2	43.9	21.3	36.7	33.0	34.0	38.6	24.4
1,2,4-trimethylbenzene	51.6 ^a	67.8 ^a	61.8	37.8	34.6	37.8	45.3	37.4	82.0 ^a	25.0
3-ethenylpyridine	109.8 ^a	179.5 ^a	122.6 ^a	0.0	198.7 ^a	74.1	0.0	0.0	82.1	118.6 ^a
naphthalene	102.1 ^a	29.8	125.2 ^a	24.7	59.1 ^a	65.9	81.3	48.7	37.5	18.6
pyridine	88.2	151.7 ^a	77.9	235.7 ^a	0.0	65.8	0.0	0.0	85.3	216.0 ^a

^a Denotes a statistically significant variation from the normal distribution in daily personal exposures ($p < 0.05$).

Possible Influence of Concentrations below Detection Limits. Note that for the purposes of statistical evaluation, concentrations below detection limits were considered to equal MDL/2. While this approach is not perfect, it is our belief that our approach is the least unsatisfactory available and that any of the methods commonly employed to deal with “not detects” have associated problems. Specifically, eliminating all “not detects” from data analyses could potentially lead to a situation where one would fail to detect e.g. differences in concentrations of 3-ethenyl pyridine in smoking and nonsmoking samples as concentrations in the latter were almost always below the detection limit. In contrast, defining “not detect” concentrations as zero will potentially exaggerate differences in such situations; while defining them as equal to the detection limit or as equal to the arithmetic mean of detected values will underestimate differences. In order that the potential influence of this issue on our data analyses may be gauged, we have therefore included a table summarizing the percentage of samples in various categories that displayed undetectable concentrations of different target VOCs as Supporting Information (Table S.2).

Potential Influence of Season on Personal Exposures. Although both microenvironmental and personal sampling was broadly evenly distributed throughout each season, at least some of the variability in VOC concentrations between different microenvironments and between exposures of different subjects will be attributable to seasonal factors. These include the following: microenvironment air exchange rate, indoor air temperature, and proportion of time spent in indoor microenvironments. Data relating to the majority of such variables were not recorded, and therefore we have been unable to systematically investigate the influence of season on personal exposure.

Results and Discussion

Relationship between Daytime and Night Time Concentrations of VOCs during Personal Monitoring. A statistical summary of VOC concentrations ($\mu\text{g m}^{-3}$) detected in samples collected for direct personal exposure estimation purposes during daytime and night time monitoring periods is shown in Table 1. In common with the typical concentration pattern displayed by air pollutants (10), arithmetic means exceed medians and our data do not display a normal distribution. Mean concentrations of 1,3-butadiene and benzene in all personal exposure samples taken during daytime were 1.1 and $10.6 \mu\text{g m}^{-3}$ respectively, while those in all personal exposure samples taken at night time were 0.8 and $9.3 \mu\text{g m}^{-3}$ respectively. The maximum concentrations recorded for an individual 2h personal exposure sample, were 26.3 and $295 \mu\text{g m}^{-3}$ for 1,3-butadiene and benzene respectively. Both average and median VOC concentrations in this study are comparable with these previously published data (6, 8), with the caveat that the sampling duration differed slightly between studies.

Consistent with other studies, although mean VOC concentrations in daytime samples are slightly higher than those in night time samples, no significant difference is discernible. However, such simple comparison of daytime and night time mean and/or median VOC concentrations may fail to detect real differences due to the disproportionate influence on mean/median values of a few extremely high concentration values. As a result, daily mean daytime VOC concentrations (i.e. the mean of concentrations recorded for all daytime samples for an individual subject on a given day) were compared with daily night time VOC concentrations for each sampling day. Day:night (D/N) mean concentration ratios were calculated for each sampling day, with the mean of these ratios shown in Table 1. These mean D/N ratios exceed 1 for all VOCs except naphthalene, with the

TABLE 3. Comparison of Direct and Indirect Estimates of VOC Exposure^d

VOC	mean percentage difference ^a	statistical significance level ^b	correlation coefficient values ^c
1,3-butadiene	-9.9	+	0.67*
benzene	-62.3	+	0.88*
toluene	-140	+	0.37*
ethylbenzene	-55.0	+	0.53*
<i>p</i> -xylene	-55.8	+	0.44*
<i>m</i> -xylene	-64.3	+	0.45*
<i>o</i> -xylene	-56.3	+	0.44*
1,3,5-TMB	-93.7	+	0.45*
styrene	-36.6	-	0.63*
1,2,4-TMB	-43.9	+	0.43*
naphthalene	-126	-	-0.14

^a Mean percentage difference between direct and indirect exposure estimates calculated thus: [(direct estimate - indirect estimate)/direct estimate] \times 100. ^b + denotes a statistically significant difference ($p < 0.05$) between absolute values of direct and indirect exposure estimates; - denotes no statistically significant difference ($p > 0.05$). ^c * denotes a statistically significant correlation ($p < 0.01$) between direct and indirect exposure estimates. ^d Note: 1,3,5-TMB = 1,3,5-trimethylbenzene, 1,2,4-TMB = 1,2,4-trimethylbenzene.

highest value of 3.85 observed for 1,3-butadiene. In addition to the calculation of ratios, the wilcoxon sum rank test was used to evaluate whether there were significant differences between absolute values of daily mean daytime and daily mean night time VOC concentrations recorded in this study. This test is appropriate in this context, as it is a nonparametric test designed for the evaluation of data sets that do not display normal distribution. The results of this test are given in Table 1. In summary, mean day time concentrations of 1,3-butadiene, benzene, and 1,3,5-trimethylbenzene are significantly greater than night time concentrations at the 95% significance level, while those of *p*-xylene, *m*-xylene, styrene, and 1,2,4-trimethylbenzene are significantly greater at the 90% significance level.

Contribution of Each Microenvironment to Exposure to VOCs. If personal exposure to VOCs is to be minimized, it is important to identify those microenvironments exerting the greatest influence on personal exposure. In this study, the contribution to overall exposure made by each of 11 different microenvironments was evaluated.

The contribution of each microenvironment depends on two factors: (a) VOC concentrations in that microenvironment and (b) the period of time spent in the microenvironment. In this study, homes, offices, and laboratories are the 3 dominant microenvironments with respect to time occupied.

The mean concentrations of VOCs in specific microenvironments used to indirectly estimate personal exposure have been reported previously—see Table 3 in ref 4—and are therefore not repeated here.

The contribution of each microenvironment to indirect estimates of personal exposure to VOCs of a given individual was then calculated by multiplying the proportion of time spent by that individual in a given microenvironment (from personal activity diary) by the mean VOC concentration recorded for that microenvironment. To illustrate, the contribution of the home to overall personal exposure level to 1,3-butadiene for a given subject was calculated thus

$$\text{mean contribution of home} = \frac{P_H \times C_H}{\sum_1^x (P_x \times C_x)} \times 100$$

where P_H = the fraction of time spent in the home by a subject,

C_H = the mean concentration of 1,3-butadiene in homes (either nonsmoking or smoking dependent on the subject), P_X = the fraction of time spent in microenvironment X by the subject, and C_X = the mean concentration of 1,3-butadiene in microenvironment X.

Tables showing the percentage of time spent in different microenvironments for each subject recorded over the period they were monitored (S.3) and the mean contribution of each microenvironment to overall indirectly estimated personal exposure to 1,3-butadiene and benzene (S.4) are included as Supporting Information. Homes are the most influential microenvironment with respect to 1,3-butadiene (51–87%) and benzene (52–85%). A similar pattern was observed for all other VOCs. Other influential microenvironments were workplaces such as offices and laboratories, automobiles, and trafficked roads. Although as previously reported, the highest concentrations of VOCs were detected in automobiles (4), the contribution of this microenvironment to overall personal exposure was for most subjects substantially less than that of homes, due to the small fraction of time spent in automobiles. A similar observation applies to pubs, where although concentrations of 1,3-butadiene were high (4), the contribution of this microenvironment to overall personal exposure was 5% or less, owing to the small fraction of time spent in pubs.

Daily Variation in Direct Personal Exposures for Individual Subjects. In most previous studies of personal exposure to VOCs, exposure levels were based on a single day's monitoring per subject, thus ignoring potential daily variations that could exert a marked influence on exposures over prolonged periods. In this study, daily variations of exposure levels to VOCs, were evaluated over the full period during which monitoring was conducted for individual subjects. The purpose of this was to evaluate the validity of estimating long-term exposure from a single day's monitoring data.

Variations in daily exposures to VOCs for individual subjects were statistically evaluated by the Kolmogorov-Smirnov test (a goodness of fit test). Application of this test (see Table 2) reveals that for several subjects, there is statistically significant ($p < 0.05$) variation from a normal distribution in daily exposures to one or more VOCs during the period that they were monitored.

These data demonstrate the existence of significant daily variations in personal exposure to VOCs, implying that estimates of long-term exposure obtained via extrapolation from a single day's personal exposure monitoring must be treated with caution. The cause of such daily variations in exposure is a combination of the following factors: (a) daily variations in the relative proportion of time spent in different microenvironments and (b) the daily variations in VOC concentrations in a given microenvironment. This study was unable to distinguish the relative impact of these factors, and more detailed study of this issue appears warranted.

Comparison of Direct and Indirect Measurements of Personal Exposure. Direct measurement of human exposure to VOCs via personal monitoring is the most accurate exposure assessment method currently available. However, its wide-scale application to evaluating exposures at the population level is prohibitive both in terms of cost and time. Consequently, indirect measurements via a combination of microenvironment monitoring and personal activity diaries represent a potentially useful alternative. If indirect exposure estimates are to be routinely employed, then it is important that they are evaluated by comparison with direct measurements. Such a comparison was conducted by Leung and Harrison (8), with the authors concluding that with some exceptions—largely associated with individual smoking habits—"there is good agreement between the two methods". We conducted a similar comparison for our data.

The presence of significant differences between direct and indirect exposure estimates was evaluated by means of a Wilcoxon signed rank test, together with calculation of the mean percentage difference between each pair of exposure estimates obtained via the different methods. However, although absolute exposure estimates obtained by the 2 methods can be significantly different, they can still be linearly related. We therefore calculated the correlation coefficients (R) for plots of direct versus indirect exposure estimates.

Table 3 summarizes the results of this data analysis. Mean percentage difference values were negative for all target VOCs. This denotes that indirect estimates exceeded direct estimates. The most likely difference for this is the limited nature of our data set, with the result that the mean microenvironment concentrations used to derive indirect estimates are unlikely to be representative of those encountered by individual subjects during personal monitoring. In our study, this has resulted in an overestimation of personal exposure, but as shown in earlier work in Birmingham (8), direct exposure estimates can also exceed indirect estimates. Furthermore, the Wilcoxon signed rank test revealed significant differences ($p < 0.05$) between absolute exposure values derived via the two estimation techniques for all VOCs, except styrene and naphthalene. However, direct and indirect exposure estimates were significantly linearly correlated ($p < 0.01$) for all VOCs except naphthalene. To summarize, our data are not inconsistent with previous findings for Birmingham residents (8), that while the absolute values of direct and indirectly derived exposure estimates may differ significantly for most VOCs, they do so in a linearly predictable fashion, suggesting that indirect monitoring methods may provide satisfactory estimates of personal exposures. An important caveat to this, is in cross-sectional studies, where the accuracy of exposure estimates is paramount, and more work must be conducted if indirect exposure estimates are to be used with confidence under such circumstances. Also worthy of comment is the potential influence of our choice of the arithmetic mean of concentrations in a given microenvironment as the basis for our indirect exposure estimates—which we used for consistency with previous work by our group (8). Given the distribution of the concentration data, the use of the arithmetic mean in this study could at least partly account for the fact that indirect exposure estimates exceed direct estimates, although previous work (8) found the opposite. Use of the median or geometric mean would reduce indirect personal exposure estimates to bring them closer to direct estimates, while the use of minimum and maximum concentrations would provide lower and upper bound exposure estimates, both of which would be highly unlikely to be experienced by any of our subjects.

Significant differences between the absolute values of directly and indirectly obtained exposure estimates are not unexpected. In essence, this is because the dynamic nature of the source-receptor relationship means that sampling air at stationary monitoring locations may not accurately reflect the contaminant composition of the air inhaled by individuals, except where the level of a contaminant is spatially uniform and/or where subjects are relatively static (8, 11, 12). Viewed in this context, and bearing in mind that the influence of subject mobility will be equal for all VOCs monitored, the absence of correlation between direct and indirect exposure estimates for naphthalene suggests that concentrations of this compound are subject to far greater spatial variability than other VOCs studied. This is supported by examination of Table 1, that reveals the relative standard deviation of daytime (i.e. 83% of the samples analyzed) naphthalene concentrations to be 550%—i.e. well in excess of that for any of the other VOCs monitored. However, this does not explain the lack of any significant difference between the absolute values of direct and indirect exposure estimates

TABLE 4. Results of Factor Analysis of Samples Associated with ETS, Vehicle Use, and Heating^c

factor 1 (52.2% ^a)	factor 2 (20.0% ^a)	factor 3 (8.3% ^a)	
(a) Samples Associated with ETS (<i>n</i> = 71)			
1,2,4-TMB (0.963 ^b)	3-EP (0.941)	benzene (0.808)	
1,3,5-TMB (0.954)	pyridine (0.936)	toluene (0.707)	
<i>m</i> -xylene (0.950)	1,3-butadiene (0.857)		
<i>o</i> -xylene (0.944)	styrene (0.732)		
ethylbenzene (0.931)			
<i>p</i> -xylene (0.927)			
factor 1 (62.2% ^a)	factor 2 (16.2% ^a)	factor 3 (8.4% ^a)	
(b) Samples Associated with Vehicle Use (<i>n</i> = 69)			
<i>p</i> -xylene (0.983)	3-EP (0.953)	1,3-butadiene (0.759)	
<i>m</i> -xylene (0.982)	pyridine (0.894)	toluene (0.575)	
1,2,4-TMB (0.981)	naphthalene (0.558)		
1,3,5-TMB (0.980)			
<i>o</i> -xylene (0.976)			
ethylbenzene (0.970)			
benzene (0.945)			
styrene (0.901)			
factor 1 (38.8% ^a)	factor 2 (17.0% ^a)	factor 3 (15.0% ^a)	factor 4 (10.8% ^a)
(c) Samples Associated with Heating (<i>n</i> = 60)			
ethylbenzene (0.944)	1,2,4-TMB (0.961)	naphthalene (0.803)	3-EP (0.861)
<i>m</i> -xylene (0.931)	1,3,5-TMB (0.955)	toluene (0.732)	1,3-butadiene (0.684)
<i>o</i> -xylene (0.930)		styrene (0.618)	
<i>p</i> -xylene (0.850)			
benzene (0.828)			
styrene (0.663)			

^a Variance explained by each factor. ^b Factor loading. ^c Note: 1,3,5-TMB (1,3,5-trimethylbenzene); 1,2,4-TMB (1,2,4-trimethylbenzene); 3-EP (3-ethenylpyridine).

TABLE 5. Results of Factor Analysis of All Samples (*n* = 572)^c

factor 1 (33.0% ^a)	factor 2 (22.1% ^a)	factor 3 (16.5% ^a)
<i>p</i> -xylene (0.959 ^b)	3-ethenylpyridine (0.954)	1,3,5-TMB (0.938)
<i>o</i> -xylene (0.946)	pyridine (0.953)	1,2,4-TMB (0.936)
<i>m</i> -xylene (0.943)	1,3-butadiene (0.702)	
ethylbenzene (0.930)	styrene (0.664)	
benzene (0.470)		

^a Variance explained by each factor. ^b Factor loading. ^c Note: 1,3,5-TMB (1,3,5-trimethylbenzene); 1,2,4-TMB (1,2,4-trimethylbenzene).

for naphthalene. Again, examination of Table 1 provides a potential explanation as the 9-fold excess of the average over the median shows the data set to be exceptionally influenced by a small number of very high concentrations. As a result, while the majority of direct and indirect exposure estimates for naphthalene may be similar in absolute terms, the presence of a few cases where these parameters are very different means that no linear correlation is apparent for the data set as a whole.

The Contribution of ETS and Other Sources to Personal Exposure to VOCs. A variety of potential sources of VOCs was recorded in the personal activity diaries of subjects during this study, namely the following: ETS, vehicle use, space heating, cooking, moth balls, hair sprays, cleaning, and painting. Out of these, the first 4 were selected for detailed evaluation, with the others excluded because the number of samples associated with such sources that were collected (<10 per source) was insufficient to permit meaningful statistical analysis. In contrast, out of the 572 samples collected in this study, at least 60 were attributable to each of the first 4 source categories. A table (S.1) summarizing the relevant data with respect to exposure to these sources for each subject is included as Supporting Information.

To evaluate the relative contribution of each potential source to personal exposure, we first compared concentra-

tions recorded for each group of samples associated with a specific source with all other samples—e.g. all ETS-related samples were compared with all other non-ETS-related samples. A table (S.5) summarizing these data is included as Supporting Information. For samples related with ETS, vehicle use, and heating; mean concentrations of VOCs exceeded those recorded in nonrelated samples, and the Wilcoxon sum rank test revealed concentrations of most VOCs in samples related with each of these sources, to be statistically significantly different from those in nonrelated samples at the 95% level. However, no significant differences were discernible between samples associated with cooking (either gas or electricity) and nonrelated samples. As a result, the 3 principal sources of personal exposure to VOCs for the small number of subjects studied were indicated to be the following: ETS, vehicle use, and heating devices.

To examine the relative contribution of each of these sources to personal exposure, we first conducted factor analysis of concentration data recorded for samples associated with each group of samples associated with exposure to ETS, vehicle use, and heating. Factor analysis incorporating Varimax rotation was performed using SPSS for Windows Version 10.0. The results of this analysis—which was designed to reveal “signature” factors for each source—are shown in Table 4. The key factor for ETS is factor 2 which groups 1,3-

butadiene, pyridine, and styrene with the ETS "marker" 3-ethenylpyridine; while for vehicle use, it is factor 1 which features high factor loadings for the monoaromatic hydrocarbons found in gasoline. For heating, although factor 2—that groups together the trimethyl benzenes—may constitute a "signature" factor for this source; we are unaware of any previous reports associating heating with elevated emissions of these compounds.

Factor analysis was then repeated on the full data set—i.e. all 572 samples collected in this study, with the results shown in Table 5. Based on the "signature" factors described above, the 3 main factors identified may be attributed thus to the following: factor 1 to vehicle use (33% of the variance in the data set), factor 2 to ETS (22%), and factor 3 to heating (17%). Although analysis of the data set as a whole inevitably masks variations in personal exposure of individuals to specific VOCs, these data suggest that for the limited number of subjects studied; ETS, vehicle use, and heating all make appreciable contributions to personal exposure to our target VOCs.

Acknowledgments

The authors are grateful to the Department of the Environment, Transport and the Regions for financial support of this research (Contract No. EPG 1/5/72).

Supporting Information Available

Tables of data relating to various aspects of this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review May 30, 2001. Revised manuscript received September 9, 2002. Accepted September 17, 2002.

ES010148Y