



Relationship of personal exposure to volatile organic compounds to home, work and fixed site outdoor concentrations

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ABSTRACT

Personal exposures of 100 adult non-smokers living in the UK, as well as home and workplace microenvironment concentrations of 15 volatile organic compounds were investigated. The strength of the association between personal exposure and indoor home and workplace concentrations as well as with central site ambient air concentrations in medium to low pollution areas was assessed. Home microenvironment concentrations were strongly associated with personal exposures indicating that the home is the driving factor determining personal exposures to VOCs, explaining between 11 and 75% of the total variability. Workplace and central site ambient concentrations were less correlated with the corresponding personal concentrations, explaining up to 11–22% of the variability only at the low exposure end of the concentration range (e.g. benzene concentrations $<2.5 \mu\text{g m}^{-3}$). One of the reasons for the discrepancies between personal exposures and central site data was that the latter does not account for exposure due to personal activities (e.g. commuting, painting). A moderate effect of season on the strength of the association between personal exposure and ambient concentrations was found. This needs to be taken into account when using fixed site measurements to infer exposures.

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1. Introduction

Volatile organic compounds (VOC) are organic compounds whose vapour pressure at 20 °C is less than 760 Torr (101.3 kPa) and greater than 1 Torr (0.13 kPa) (Derwent, 1995). Major anthropogenic sources of VOC in ambient air include industrial processes, fossil fuel combustion in transportation, domestic heating and electricity generation, fuel distribution, solvent use, landfills and waste treatment plants. With regards to indoor air, primary sources of VOC include outdoor air, environmental tobacco smoke (ETS), fuel combustion, building materials, furnishing, furniture and carpet adhesives, paints and solvents, cleaning agents, air fresheners and cosmetics (Jurvelin, 2003). Exposure to VOCs is ubiquitous and can result in a wide range of acute and chronic health effects, such as sensory irritation, nervous system impairment, asthma and cancer (Caprino and Tonga, 1998). EPA classifies some VOCs (e.g. hexane, benzene, toluene, xylenes, 1,3-butadiene) as hazardous air pollutants (EPA, 2008). IARC classify benzene and 1,3-butadiene as known human carcinogens and ethylbenzene, styrene, naphthalene as possibly carcinogenic to humans (IARC, 2006). Therefore, there is an international recognition of the potential health risks associated with exposure to some

VOCs and of the need for action to assess the exposures in the general population and to minimise these risks.

The determination of an individual's exposure to air pollution is dependent on the individual and his/her activity patterns, which is reflected in the time spent in different microenvironments (Harrison et al., 2002). Numerous international studies have reported that people spent 80–93% of their time indoors, 1–7% in enclosed transit and 2–7% outdoors (Jenkins et al., 1992; Thatcher and Layton, 1995). It has been estimated that the home contributes approximately 60–70% of the time spent indoors (Thatcher and Layton, 1995; Hinwood et al., 2003), which suggests that significant exposures may occur in the home. In addition, other indoor microenvironments, and particularly the workplace, are important determinants of overall personal exposure to VOCs (Harrison et al., 2002).

In addition, monitoring for compliance with ambient air quality standards is limited to a relatively small number of stationary ambient monitoring sites. Given the likely spatial variation in VOC concentrations in ambient air, it is questionable to what extent such a monitoring strategy represents an accurate reflection of personal exposure (Kim et al., 2002). Furthermore, since modern societies spend most of their time in indoor environments, focus on fixed monitoring measurements to assess personal exposure risks is of limited value as exposures of individual members of the public may not be well represented. Typically, time-series and cohort epidemiological studies are based on ambient air data from urban air quality monitoring networks. However the harmful health effects of urban air pollutants may not be caused solely by the concentrations of air

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pollutants at those fixed monitoring sites alone. Instead personal exposures will be affected by subjects' daily activities in the indoor and outdoor environment, including commuting (Jantunen et al., 1998).

Some assessments of public exposure to atmospheric pollutants have found that the personal exposures of the urban population to many airborne pollutants are very different from, and often greater than, outdoor air concentrations measured by fixed monitoring stations (Michael et al., 1990; Kim et al., 2002; Payne-Sturges et al., 2004; Serrano-Trespacios et al., 2004; Phillips et al., 2005). Hence, risk estimates based on ambient measurements may under- or overestimate risk, leading to ineffective or inefficient management strategies (Payne-Sturges et al., 2004).

Epidemiological research on air pollution is hence challenged by the ability to accurately assess exposure when studying large populations (Nethery et al., 2008). Zeger et al. (2000) suggested that the generic criticism that measurement errors render the results of time-series epidemiological studies uninterpretable could be avoidable if risk-weighted average personal exposure and ambient concentrations data were collected and compared in order to quantify more precisely the biases due to pollutant measurement errors. Several studies (Serrano-Trespacios et al., 2004; Sexton et al., 2004b; Sax et al., 2006) have performed comparisons of VOC personal exposures to indoor home and outdoor home/neighbourhood ambient air and have found that ambient VOC measured at central monitoring sites can seriously underestimate personal exposures. In the UK, only six ambient monitoring sites measure a comprehensive range of VOC with high time resolution covering a population of 61 million inhabitants and these sites are located ranging between tens to hundreds of kilometres from members of the population. Therefore, from an epidemiological and environmental health management point of view, it is important to assess the magnitude of the error involved in estimating personal exposures to VOCs directly from measurements derived from fixed ambient background monitoring stations in the UK context.

The MATCH (Measurement and Modelling of Air Toxic Concentrations for Health Effect Studies) Project has made a significant contribution to the VOC and PAH personal exposure and micro-environmental database. The study sought to advance understanding of the sources and magnitudes of exposures to VOCs and PAHs (Delgado-Saborit et al., 2009a; Harrison et al., 2009). Another study goal was to establish whether lifestyle information is sufficient for modeling personal exposures reliably compared with exposures measured directly by personal samplers (Delgado-Saborit et al., 2009b). In this paper, the results for personal exposures to VOCs, including 1,3-butadiene, as well as home and workplace concentrations are presented for 100 subjects living in the UK. We also explore the strength of the associations between personal exposures with home, workplace and ambient fixed site concentrations to assess their contribution to personal exposures and their ability to serve as proxies for personal exposures. Multiple ambient sites are correlated with personal exposures to study the variability in ambient contributions to personal exposures and to assess the bias from using fixed site monitors as proxies of personal exposures.

2. Experimental section

2.1. Study design

The MATCH project recruited 100 healthy non-smoker adult volunteer subjects between 2005 and 2007 for non-occupational personal exposure (PE) measurements. Subjects lived in three different areas of the UK, namely London, West Midlands (WM) and rural South Wales, where higher, intermediate and lower exposures were expected (See support information Fig. S1). The exclusion criteria were detailed in Delgado-Saborit et al. (2009a).

Each subject was sampled for VOCs for a total of five consecutive 24-h periods. During the period when personal exposure was measured, VOC samples were concurrently collected also in subjects' homes (two consecutive 12-h samples generally from the living-room) and workplaces (one 8-h sample). Not all the subjects gave their consent to sample at their homes or workplace, hence home and workplace samples were not available for all the subjects. The study collected 500 24-h PE samples, 100 5-day integrated PE samples, 152 12-h home samples, 75 24-h integrated home samples and paired PE/home samples as well as 40 8-h work samples and paired PE/work samples.

The atmospheric sampling was backed up with information collected in questionnaires related to the volunteer subjects, activities performed, journeys carried out, places visited, ventilation patterns, indoor sources and ETS events as described in detail elsewhere (Harrison et al., 2009).

Collection of the samples was spread over two years, from May 2005 to May 2007. London subjects (N = 11) were sampled during the warm season (May–June 2006), Welsh subjects (N = 10) were sampled in winter (October 2006 to February 2007) and West Midlands' subjects (N = 79) were sampled through the four seasons (May 2005 to May 2007, 42% and 58% in the warm (April–September) and cold (October–March) season respectively).

Additionally, ambient air data for VOCs was obtained from the UK National Air Quality Archive (<http://www.airquality.co.uk>). Three stations were selected from the Automatic Hydrocarbon Network. The selected stations were Harwell, Cardiff and London Eltham (See Supporting Information Fig. S1). Harwell is a rural station located in the central southern part of England, whose background data could be compared with PE data for all the subjects. Cardiff is an urban centre station whose ambient concentrations could be compared with Welsh subjects' PE concentrations whilst London Eltham is an urban background station whose ambient data could be compared with all the London subjects' PE.

2.2. Sampling methods

Concentrations of fifteen VOC compounds were collected for compounds selected on the basis of their health effects (e.g. benzene, 1,3-butadiene) or usability as source tracers for environmental tobacco smoke (ETS) (e.g. pyrene, 1,3-pyridine), solvents (e.g. ethylbenzene, xylenes) or traffic (e.g. toluene). The VOC sampled were n-hexane, benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, p-isopropyltoluene, pyridine, 3-ethenylpyridine, 1,3-butadiene and naphthalene. Two methods were used for sampling the main group of VOC compounds and 1,3-butadiene separately as described in detail by Harrison et al. (2009). Briefly, different sorbent tubes connected to pumps collected VOC and 1,3-butadiene in personal exposures, home and workplace microenvironments using different flow rates accordingly to collect the same volume of air. VOCs in ambient air were measured with an automatic gas chromatograph coupled with a thermal desorber. Further details of the sampling methodology for measuring VOC in personal samples, home, work and ambient air can be found in Delgado-Saborit et al. (2009b) and in the Supporting Information.

2.3. Analytical methods

1,3-Butadiene was sampled and analysed separately from the other VOCs due to its high volatility. The VOC and 1,3-butadiene methods briefly comprised the thermal desorption of the compounds and subsequent analysis by Gas Chromatography and Mass Spectrometry detection. Further details of the analytical methodology are available in the Supporting Information.

Table 1
Characterisation of VOC personal exposure, home, workplace and ambient air concentrations ($\mu\text{g m}^{-3}$).

Dates	Personal exposure			Home		
	(20/05/05–03/05/07)			(20/05/05–03/05/07)		
Number of samples	500			155		
Statistic	%BDL	Range	Mean \pm SD	%BDL	Range	Mean \pm SD
n-Hexane	3	0.06–109.6	3.6 \pm 8.26	1.3	0.09–37.15	2.9 \pm 5.09
Benzene	2	0.15–30.2	2.2 \pm 2.48	0	0.32–18.62	1.97 \pm 2.41
Toluene	2	0.06–407.3	19.7 \pm 34.3	0	0.65–177.8	17.53 \pm 24.8
Ethylbenzene	2	0.06–181.9	3.2 \pm 10.62	0	0.12–16.98	1.74 \pm 2.42
p-Xylene (*)	2	n.d.–213.8	3.08 \pm 11.85	0	0.08–17.78	1.7 \pm 2.71
m-Xylene	2	0.01–575.4	7.72 \pm 30.49	0	0.19–38.02	4.14 \pm 6.05
Pyridine	2.4	n.d.–6.92	0.25 \pm 0.36	0	0.01–0.91	0.15 \pm 0.13
o-Xylene	2	0.04–173.7	3.59 \pm 11.22	0	0.1–18.6	2.02 \pm 2.95
1,3,5-Trimethylbenzene	2	0.01–40.74	0.96 \pm 2.07	0	0.03–5.01	0.61 \pm 0.86
Styrene	2.2	0.08–61.66	1.31 \pm 4.58	0	0.09–12.59	0.86 \pm 1.43
p-Isopropyltoluene	2	n.d.–12.88	1.07 \pm 0.94	0	0.12–6.03	1.03 \pm 0.84
1,2,4-Trimethylbenzene	2.2	0.03–102.3	3.5 \pm 8.63	0	0.05–17.78	2.3 \pm 3.36
3-Ethenylpyridine	2.4	n.d.–6.92	0.29 \pm 0.59	0	n.d.–1.45	0.1 \pm 0.2
Naphthalene	2.2	0.02–12.59	0.74 \pm 1.06	0	0.06–12.88	0.79 \pm 1.36
1,3-Butadiene	2.2	n.d.–6.31	0.4 \pm 0.71	10.5	n.d.–2.04	0.24 \pm 0.31

%BDL: percentage of cases below detection limit.

n/a: not applicable, data not measured in the Automatic Hydrocarbon Network.

(*) In London Eltham, Harwell and Cardiff, p-xylene represents p + m-xylene.

n.d.: non detected.

2.4. Quality assurance and quality control (QA-QC)

Quality assurance and quality control (QA-QC) measures implemented in the sampling and analysis procedures as well as blanks, precision and accuracy values are available in the Supporting Material and were described in detail elsewhere (Harrison et al., 2009). The instrument (IDL) and sample (SDL) limits of detection ranged 0.02–0.07 ng (IDL) and 3.7–11 ng/m³ (SDL), except for pyridine (IDL = 0.27 ng, SDL = 47 ng/m³) and 3-ethenylpyridine (IDL = 0.62 ng, SDL = 109 ng/m³) and the majority of the samples were above the limits of detection (Table 1). Precision measured from duplicate samples was 19.5 \pm 6.0%.

2.5. Statistical methods

Data were analysed using SPSS 15.0 for Windows (SPSS Inc. 1989–2006), Excel 2002 (Microsoft Corporation, 1985–2001) and Access 2007 (Microsoft Corporation, 2006). PE and microenvironment concentrations were characterised using descriptive analysis (i.e. arithmetic means, standard deviations, maxima and minima). Measures of the association between PE and home (H), work (W) and ambient air (A) were characterised with a cross-sectional regression of the different microenvironment concentrations with PE. In the case of the relationship between PE and A, a further longitudinal analysis (meaning correlation of repeated observation of the same variables PE vs. A) was performed regressing the PE vs. A for each subject. Ratios of PE/H, PE/W and PE/A were calculated to study the effect of those microenvironments on PE. The values of PE used in the ratios PE/H and PE/W as well as in the PE vs. H and PE vs. W cross-sectional regression analysis were the 5-day integrated average concentrations. On the other hand, the individual 24-h PE concentrations were used for the PE/A and the PE-A regression analysis. The association of PE with concentrations measured at different ambient sites was characterised by the values of the slope (m) and intercept (a), their standard error as well as the coefficients of determination, R². Results were considered significant with p-values less than 0.05 (2-tails). The seasonal effect on the relationship PE vs. H and vs. W was evaluated using a univariate general linear

model, considering season as a fixed value and home or work concentration as covariates. In the case of PE vs. A, the seasonal effect was tested using a linear mixed model, considering each participant as subjects, each day as the repeated factor, season as fixed factor and ambient concentrations as covariates. Seasonal effects were tested in ratios of PE/A, PE/W and PE/A using a t-test of equality of means.

3. Results and discussion

3.1. Subject description

Although there was no intended bias on recruitment, most of the recruited subjects were females (57%), with a predominant average age range between 26 and 35 years old (31%). The main occupation of the subjects was administrative/office worker. Subjects spent 87–91% of their time indoors, with an average of 62% of this time spent indoors at home, 16% indoors at work and 12% in other indoor environments. The average time spent outdoors ranged from 2 to 5% whilst subjects spent between 5 and 7% of their time commuting.

Activities reported with clear implications for the personal exposure were exposure to environmental tobacco smoke, candle/incense burning, fireplace use and DIY activities (Delgado-Saborit et al., 2009a). Further details on the subject demographic characteristics can be found in the Supporting Information and in Harrison et al. (2009).

3.2. Personal exposure, home, workplace and ambient concentrations

Table 1 presents the results of personal exposure, home, work and ambient site concentrations measured at three different sites. The VOC PE concentrations observed in this study (Table 1) were significantly lower than those found in similar studies, conducted in different locations in the USA and Europe and at earlier times, with benzene concentrations ranging 3.9 $\mu\text{g}/\text{m}^3$ (USA, 2002) to 27 $\mu\text{g}/\text{m}^3$ (USA, 1991) and 3.3 $\mu\text{g}/\text{m}^3$ (UK, 1998) to 21.2 $\mu\text{g}/\text{m}^3$ (Italy, 2000) respectively (Wallace, 1986; Carrer et al., 2000; Gonzalez-Flesca et al., 2000; Hoffmann et al., 2000; Fondelli et al., 2008). Higher benzene

Workplace (20/05/05–03/05/07)			London Eltham (08/05/05–23/06/05)		Harwell (20/05/05–03/05/07)		Cardiff (06/11/06–17/02/07)	
%BDL	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
40			26		500		39	
2.5	0.2–2.88	1.03 ± 0.66	0.09–0.79	0.29 ± 0.18	n/a	n/a	n/a	n/a
2.5	0.42–4.07	1.18 ± 0.78	0.32–1.47	0.75 ± 0.31	0.03–1.32	0.37 ± 0.26	0.18–0.88	0.49 ± 0.22
10	0.93–11.48	4.31 ± 2.73	0.71–3.43	1.73 ± 0.75	0.04–5.83	0.68 ± 0.67	0.45–2.28	1.12 ± 0.55
2.5	0.21–6.92	1.23 ± 1.2	0.13–0.59	0.29 ± 0.12	n.d.–1.25	0.11 ± 0.11	0.06–0.41	0.19 ± 0.09
2.5	0.19–6.17	1.2 ± 1.2	0.34–1.72	0.85 ± 0.35	n.d.–2.76	0.31 ± 0.35	0.2–1.44	0.67 ± 0.33
2.5	0.37–19.05	3.2 ± 3.4	n/a	n/a	n/a	n/a	n/a	n/a
5	0.02–0.38	0.11 ± 0.07	n/a	n/a	n/a	n/a	n/a	n/a
2.5	0.17–5.62	1.48 ± 1.26	0.13–0.61	0.3 ± 0.12	n.d.–4.06	0.16 ± 0.33	0.07–1.54	0.4 ± 0.34
5	0.05–0.62	0.26 ± 0.15	0.05–0.23	0.12 ± 0.05	n/a	n/a	n/a	n/a
2.5	0.1–2.69	0.55 ± 0.50	n/a	n/a	n/a	n/a	n/a	n/a
5	0.04–1.48	0.47 ± 0.31	n/a	n/a	n/a	n/a	n/a	n/a
2.5	0.13–13.18	1.33 ± 2.22	0.11–0.55	0.29 ± 0.12	n/a	n/a	n/a	n/a
5	0.01–0.41	0.07 ± 0.08	n/a	n/a	n/a	n/a	n/a	n/a
2.5	0.06–1.66	0.37 ± 0.27	n/a	n/a	n/a	n/a	n/a	n/a
25	0.01–0.39	0.08 ± 0.08	0.04	0.06 ± 0.02	n.d.–0.6	0.01 ± 0.06	n.d.–0.1	0.03 ± 0.03

concentrations were reported in Korea (26.3 $\mu\text{g}/\text{m}^3$, 2001) (Son et al., 2003). Since there were a higher proportion of females, different age ranges and occupations in the MATCH population, VOC concentrations in each of the subgroups were compared with each other. Only occupation had an influence on the VOC concentrations. Retired people had similar VOC concentrations to students and office workers, with the housewives and unemployed population being the subset which presented the highest VOC concentrations (Fig. 1). The high concentrations for the latter group might be a consequence of the greater time spent at home carrying out various activities involving the use of solvents (cleaning agents, DIY, etc).

The concentrations of VOC in homes were also lower compared with other studies in the USA (e.g. benzene concentrations range 3.5 $\mu\text{g}/\text{m}^3$ (2001) to 20 $\mu\text{g}/\text{m}^3$ (1992) (Wallace, 1989a,b; Heavner et al., 1996)), Hong Kong (benzene, 5.3 $\mu\text{g}/\text{m}^3$) (Lee et al., 2002a,b), Korea (benzene, 8.2 $\mu\text{g}/\text{m}^3$) (Baek et al., 1997) and Europe (benzene range between 2.23 $\mu\text{g}/\text{m}^3$ (1996) and 15 (1998) $\mu\text{g}/\text{m}^3$) (Brown and Crump, 1998; Leung and Harrison, 1998; Edwards et al., 2001; Lai et al., 2004). As with personal and home concentrations, VOC concentrations measured in offices in this study were lower than earlier studies in the UK (Brown and Crump, 1998; Leung and Harrison, 1998; Lai et al., 2004), Europe (Carrer et al., 2000; Ilgen et al., 2001), USA (Heavner et al., 1996) and Singapore (Zuraimi et al., 2006), with values of benzene ranging between 2.4 $\mu\text{g}/\text{m}^3$ (USA, 1996) and 87 $\mu\text{g}/\text{m}^3$ (Singapore, 2006). A similar study performed in West Midlands (UK) offices in the late 1990s, showed similar concentration for the xylenes, trimethylbenzenes, styrene and p-isopropyltoluene, but recorded higher concentrations for benzene, toluene, ethylbenzene, n-hexane, naphthalene and 1,3-butadiene (Kim et al., 2001), all of which are compounds heavily associated with road traffic emissions. As regards the ambient concentrations (Table 1), the lowest values were recorded as expected at the rural site, Harwell, whilst the highest were measured in London Eltham (urban background). These values were considerably lower than previously reported in the UK, which ranged between 9.4 and 27 $\mu\text{g}/\text{m}^3$ (Leung and Harrison, 1998; Kim et al., 2001; Lai et al., 2004), which was consistent with the downward trend in emissions and airborne concentrations occurring over the last decade (Dollard et al., 2007).

Personal exposures show the highest concentrations (Table 1), followed closely by VOC concentrations measured at home, then in

the workplace and lastly in ambient air, where the lowest concentrations were generally measured. This pattern was reflected in the values of ratios higher than unity, with PE/H ratio (ranging from 1.2 to 5.3), PE/W (ranging from 1.7 to 8.7) as shown in Table 2 and PE/A measured at different monitoring stations (ranging from 2.6 to 153, Table 3). The values of PE/H were consistent with previously reported data (Turpin et al., 2007), whilst the values of PE/A are higher than those previously reported (Adgate et al., 2004; Pekey and Arslanbas, 2008). The ratio of PE/A was also affected by distance to the central site. For instance, PE/A for benzene was 2.6 ± 2.7 using data for London subjects and the urban background station of London Eltham (distance 18.7 ± 8.3 km) and was 10.2 ± 12.4 (Table 3) using the rural station Harwell (distance 88 ± 5.3 km) respectively.

On the contrary, season did not have a clear effect on the ratios. In the case of PE/A for subjects living in the West Midlands, which were sampled across all stations, winter ratios were similar to summer ones, except for toluene, whose ratios were higher in winter ($p < 0.01$). For PE/H and PE/W ratios, most of the compounds had higher ratios in summer; however, this difference was not statistically significant ($p > 0.05$) (Tables S8 and S9, Supplementary Information). These results were similar to those reported by Pekey and Arslanbas (2008), where higher ratios were found in summer for most of the compounds, except for benzene for PE/H and higher concentrations were found in winter for the PE/A ratios (Pekey and Arslanbas, 2008). This lack of a clear-cut effect of season in PE to microenvironment ratios might reflect the effect of indoor sources or activities that affect PE concentrations (Delgado-Saborit et al., 2009b), which were independent of seasonal patterns.

The close relationship between PE concentrations and home concentrations was due to the fact that the subjects spent between 58 and 67% of their time in their own house. Therefore, PE concentrations seemed to be controlled by home sources (including infiltration of outdoor air) and modified according to the activities carried out and places visited during the normal routine of the day (e.g. workplace, vehicles, streets, etc). Consequently, personal exposure concentrations although similar, were greater than home concentrations (i.e. PE/H > 1) due to exposure of the subjects to elevated VOC concentrations originating from personal activities, e.g. photocopying, use of cleaning products, exposure to ETS or commuting (Delgado-Saborit et al., 2009b). This was consistent

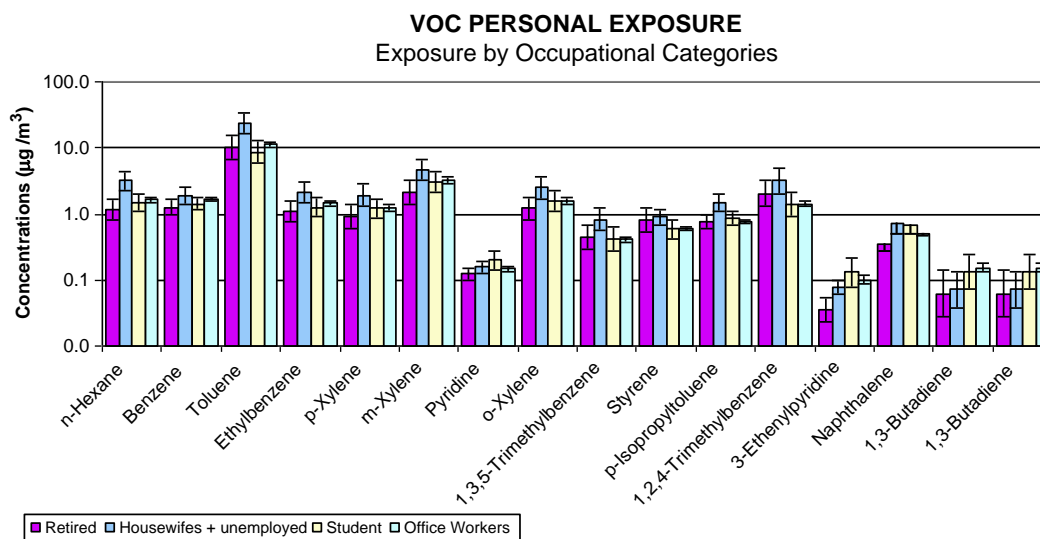


Fig. 1. Average VOC personal exposures according to occupational category. ($N_{\text{Retired}} = 35$, $N_{\text{Housewife + Unemployed}} = 24$, $N_{\text{Student}} = 46$, $N_{\text{Office Workers}} = 372$).

with previous studies in which researchers reported PE concentrations of VOC to be on average higher than concentrations measured in the home or workplace, and much higher than the concentration in outdoor air in low traffic areas (Wallace, 1996; Gonzalez-Flesca et al., 2000; Edwards et al., 2001; Ilgen et al., 2001). In contrast, other researchers have shown home concentrations higher than PE concentrations for children, who spent longer time periods outdoors (Adgate et al., 2004), whilst Lai et al. (2004) reported higher aromatic compound concentrations measured in the workplace, followed by PE, residential indoor and residential outdoor concentrations (Lai et al., 2004). Nevertheless, all the studies coincided to report that the distribution of outdoor concentrations fell well below the distribution of indoor concentrations (Phillips et al., 2005).

3.3. Personal exposure vs. home and workplace concentrations

Personal exposure concentrations (5-day average) were regressed against the concentrations measured at the subjects' homes (24-h) and workplaces (8-h). The values of the regression parameters slope (m), intercept (a) with standard error and coefficient of determination (R^2) with p -value of the ANOVA tests are shown in Table 2. The regression of PE, H and W for benzene is shown in Fig. 2. The information extracted from the regression of PE with home and workplace gives valuable insights into the influence on PE of the two microenvironments where people spent most of their time. Comparing the coefficients of determination for home and work (Table 2), it can be inferred that home concentrations had a greater impact on PE concentrations, as the coefficients of determination for the regression PE vs. home were in the range 0.04–0.75 for home, all significant at the 0.05 level (2-tails) and were considerably greater than those for the regression between PE vs. workplace, which ranged between 0 and 0.17 and none of which was significant at the 0.05 level. It should be borne in mind that one of our criteria for selection of subjects was the absence of occupational exposure to VOC. Clearly, higher correlation between PE and workplace concentrations might be expected for occupationally exposed subjects (Jo and Song, 2001; Jo and Yu, 2001). Our results of PE vs. H and PE vs. W were similar to those reported in the literature. Adgate et al. (2004) reported coefficients of determination between PE and home indoors for BTEX, with values of R^2 ranging between 0.2 and 0.6. Sexton et al. (2004a) obtained R^2 for matched indoor residential and PE with values in the range of 0.2–0.8, whilst Lai et al. (2004) reported the

lowest R^2 values for TVOC (R^2 for home = 0.05 and work = 0.10) (Adgate et al., 2004; Lai et al., 2004; Sexton et al., 2004a).

Personal exposure was hence most influenced by the contribution from the residential environment for all compounds as found by Kim et al. (2002) and Adgate et al. (2004). The results suggested that for most of the compounds, home concentration contributed between 50 and 70% to the variance in concentrations of PE (e.g. 75% for benzene). VOCs in indoor air can originate from outdoor air (e.g. traffic source) and also from sources located indoors such as building materials and furniture, attached garages, heating and cooking systems, storage of solvents and various human activities (Harrison et al., 2009). However for other compounds such as 1,3-butadiene, although 11% of the variance in personal exposures might be explained from home concentrations, additional sources such as commuting might contribute to the total burden of 1,3-butadiene in personal exposures. Personal exposures to 1,3-butadiene indoors were likely associated with exposure to ETS, parking vehicles in garages connected to the main house, space heating and use of solvents (Delgado-Saborit et al., 2009b), whilst traffic and gas and petrol distribution are likely sources outdoors (Curren et al., 2006).

In this context, the significant regression coefficients observed in the regression between home (24-h) and PE concentration (5-day average) for most of the VOCs suggested that home contribution will impact greatly on the PE. This was especially relevant for those situations where subjects spent great amount of time at home, there was little ventilation, or there were additional indoor sources (e.g. heating systems or use of cleaning products, ETS at home or recent redecoration) as supported by information provided by the participants through questionnaires. Hence home concentrations were mostly a good predictor of personal exposures, even when considering different integration periods (i.e. 24-h home concentration and 5-day personal exposure).

The relationship between PE (5-day average) and W (8-h average) as shown in Table 2 was not significant ($p > 0.10$). However, in the case of benzene ($R^2 = 0.12$, Fig. 2b), several cases can be considered as outliers. Those cases were two subjects that had benzene concentrations at the workplace higher than $2.5 \mu\text{g}/\text{m}^3$ and two subjects that had personal exposures higher than $5 \mu\text{g}/\text{m}^3$. Further investigation of these cases showed that the first two cases corresponded with two subjects whose microenvironment work samples due to space constraints were taken in a general office which had photocopiers and fax machines nearby, different from the subjects' usual working space. Hence, these work samples did not truly relate to the workplace

Table 2

Personal exposure (PE) vs. home (H) and work (W) concentrations. Arithmetic mean and standard deviations of the ratio, slope (m) and intercept (a) with standard errors and determination coefficients (R²) with ANOVA p-values for the regression between personal exposures and home and workplace concentrations.

Compound	Personal exposure vs. Home				Personal exposure vs. Workplace			
	PE/H ratio Mean	m ± Std Error	a ± Std Error	R ² (a) (p-values)	PE/W ratio Mean	m ± Std Error	a ± Std Error	R ² (a) (p-values)
	No samples = 77				No samples = 40			
Hexane	2.66 ± 6.62	0.23 ± 0.089	2.22 ± 0.437	0.146 (0.014)	6.19 ± 12.8	0.09 ± 0.09	3.46 ± 0.85	0.097 (0.359)
Benzene	1.30 ± 0.56	0.63 ± 0.04	0.83 ± 0.12	0.745 (<0.001)	2.32 ± 2.69	0.52 ± 0.51	1.63 ± 0.69	0.131 (0.3250)
Toluene	1.62 ± 1.34	0.67 ± 0.04	6.01 ± 1.11	0.656 (<0.001)	3.79 ± 3.82	0.27 ± 0.18	15.04 ± 4.37	0.166 (0.135)
Ethylbenzene	2.36 ± 3.77	0.77 ± 0.08	0.81 ± 0.19	0.581 (<0.001)	3.9 ± 8.1	0.06 ± 0.21	3.55 ± 0.81	0.048 (0.562)
p-Xylene	2.40 ± 3.51	0.74 ± 0.07	0.8 ± 0.19	0.593 (<0.001)	4.04 ± 9.55	0.35 ± 0.62	3.5 ± 1.18	0.078 (0.356)
m-Xylene	2.51 ± 3.84	0.76 ± 0.08	2.07 ± 0.51	0.549 (<0.001)	4.21 ± 11.15	0.06 ± 0.22	9.47 ± 2.03	0.06 (0.453)
Pyridine	1.88 ± 2.01	1.68 ± 0.27	0.005 ± 0.05	0.389 (<0.001)	2.31 ± 3.07	0.01 ± 0.09	0.2 ± 0.28	0.001 (0.889)
o-Xylene	2.38 ± 3.89	0.89 ± 0.09	0.79 ± 0.29	0.557 (<0.001)	3.66 ± 7.41	0.51 ± 0.63	3.31 ± 1.33	0.069 (0.221)
1,3,5-Trimethylbenzene	1.66 ± 1.14	1.62 ± 0.18	-0.08 ± 0.18	0.486 (<0.001)	3.48 ± 7.2	2.82 ± 0.38	0.75 ± 0.29	0.014 (0.459)
Styrene	2.42 ± 10.5	0.71 ± 0.08	0.28 ± 0.13	0.046 (<0.001)	1.67 ± 1.28	0.08 ± 0.10	0.59 ± 0.077	0.01 (0.579)
p-Isopropyltoluene	1.23 ± 0.78	0.48 ± 0.09	0.55 ± 0.13	0.295 (<0.001)	4.07 ± 9.6	0.29 ± 0.24	0.76 ± 0.14	0.051 (0.264)
1,2,4-Trimethylbenzene	1.65 ± 1.08	1.36 ± 0.13	0.1 ± 0.51	0.542 (<0.001)	3.41 ± 7.00	0.44 ± 0.48	2.46 ± 1.18	0.005 (0.362)
3-Ethenylpyridine	5.30 ± 20.4	0.24 ± 0.25	0.04 ± 0.05	0.615 (<0.001)	8.73 ± 27.5	0.4 ± 0.63	0.18 ± 0.07	0.013 (0.563)
Naphthalene	1.40 ± 1.61	0.24 ± 0.15	-0.04 ± 0.24	0.203 (<0.001)	2.05 ± 2.23	0.56 ± 0.48	0.47 ± 0.22	0.036 (0.228)
1,3-Butadiene	2.75 ± 4.44	0.45 ± 0.48	0.19 ± 0.22	0.111 (0.008)	5.66 ± 9.24	0.26 ± 0.39	0.19 ± 0.05	0.048 (0.224)

(a) Bold values represent significant correlation at 0.05 level.

environment where the subject was performing his/her job. The second set of outliers corresponded to two subjects that had been carrying out activities in the out-of-work hours such as painting and printing at home, which had considerably increased their PE

concentrations. If these four cases were excluded from the comparison, then PE benzene concentrations showed an association with workplace concentrations significant at the 0.01 level (R² = 0.21). Given the very different averaging times for PE and workplace

Table 3

Cross-sectional analysis of personal exposure (PE) vs. ambient (A) concentrations. (a). Arithmetic mean and standard deviations of the ratio, slope (m) and intercept (a) with standard errors and determination coefficients (R²) with ANOVA p-values for the regression between personal exposures and ambient air concentrations.

Statistics		Benzene	Toluene	Ethylbenzene	m + p-Xylene	o-Xylene	1,3-Butadiene
Harwell	PE/A ratio						
	Mean ± Std dev	7.82 ± 10.9	44.7 ± 83.8	44.6 ± 123	83.6 ± 279	53.3 ± 160	98.3 ± 272
All subjects	m ± std error	1.29 ± 0.44	4.61 ± 2.44	1.39 ± 5.36	-3.50 ± 6.68	-0.60 ± -1.91	0.66 ± 0.58
N = 500	a ± std error	1.69 ± 0.20	16.6 ± 2.35	2.93 ± 0.82	11.33 ± 3.09	3.83 ± 0.702	0.37 ± 0.03
	R ² /R ² _{adj}	0.020/0.017	0.008/0.004	0.000/-0.02	0.001/-0.002	0.000/-0.002	0.002/0.001
	(p-value) (b)	(0.003)	(0.086)	(0.794)	(0.601)	(0.755)	(0.237)
Harwell	PE/A ratio						
	Mean ± Std dev	10.2 ± 12.4	41.1 ± 61.1	26.2 ± 46.5	34.7 ± 71.4	52.3 ± 113.9	29.1 ± 33.5
London subjects	m ± std error	-2.13 ± 1.71	2.48 ± 7.44	-2.79 ± 7.41	-4.54 ± 10.2	-8.12 ± 10.0	-3.05 ± 5.02
N = 55	a ± std error	2.58 ± 0.52	18.39 ± 6.21	2.74 ± 1.12	9.21 ± 4.41	4.66 ± 1.85	0.13 ± 0.03
	R ² /R ² _{adj}	0.039/0.14	0.003/-0.023	0.004/-0.23	0.004/-0.17	0.017/-0.009	0.008/-0.14
	(p-value) (b)	(0.221)	(0.741)	(0.709)	(0.658)	(0.420)	(0.546)
Harwell	PE/A ratio						
	Mean ± Std dev	8.40 ± 13.6	59.5 ± 80.4	43.3 ± 39.7	147 ± 184	66.1 ± 84.6	55.8 ± 116
Welsh subjects	m ± std error	3.53 ± 2.49	1.61 ± 8.33	-3.19 ± 3.33	-11.59 ± 6.57	-4.99 ± 2.68	-0.99 ± 3.19
N = 50	a ± std error	1.44 ± 1.02	16.45 ± 4.31	1.99 ± 0.33	8.30 ± 1.26	2.71 ± 0.42	0.23 ± 0.05
	R ² /R ² _{adj}	0.042/0.021	0.001/-0.021	0.020/-0.002	0.065/0.044	0.080/0.057	0.002/-0.20
	(p-value) (b)	(0.163)	(0.847)	(0.344)	(0.085)	(0.070)	(0.757)
Harwell	PE/A ratio						
	Mean ± Std dev	7.63 ± 10.5	44.4 ± 87.6	47.5 ± 136	78.9 ± 293	52.2 ± 171	109 ± 295
WM subjects	m ± std error	1.29 ± 0.46	4.19 ± 2.75	1.35 ± 6.29	-4.04 ± 7.84	-0.55 ± 2.12	0.54 ± 0.64
N = 395	a ± std error	1.61 ± 0.22	17.44 ± 2.80	3.34 ± 1.00	13.03 ± 3.85	4.03 ± 0.85	0.42 ± 0.04
	R ² /R ² _{adj}	0.021/0.018	0.006/0.004	0.000/-0.003	0.001/-0.002	0.000/-0.003	0.002/0.000
	(p-value) (b)	(0.006)	(0.128)	(0.831)	(0.607)	(0.796)	(0.401)
London Eltham	PE/A ratio						
	Mean ± Std dev	2.55 ± 2.68	8.31 ± 9.77	4.98 ± 3.96	6.12 ± 6.00	6.44 ± 6.54	1.66 ± 1.98
London subjects	m ± std error	-0.495 ± 0.573	5.48 ± 3.17	3.53 ± 1.30	5.29 ± 1.99	5.79 ± 2.54	0.177 ± 0.920
N = 56	a ± std error	2.22 ± 0.488	5.20 ± 5.99	0.512 ± 0.418	0.649 ± 1.82	0.360 ± 0.828	0.086 ± 0.060
	R ² /R ² _{adj}	0.020/-0.007	0.075/0.050	0.166/0.143	0.147/0.126	0.123/0.100	0.001/-0.023
	(p-value) (b)	(0.393)	(0.092)	(0.010)	(0.011)	(0.028)	(0.848)
Cardiff	PE/A ratio						
	Mean ± Std dev	6.50 ± 8.82	19.2 ± 22.8	13.2 ± 15.1	15.9 ± 20.7	10.8 ± 14.6	17.2 ± 43.7
Welsh subjects	m ± std error	-0.79 ± 1.36	3.44 ± 4.96	1.63 ± 2.90	0.824 ± 3.43	-0.24 ± 1.07	-4.18 ± 4.34
N = 50	a ± std error	2.67 ± 0.716	13.6 ± 6.07	1.64 ± 0.614	6.85 ± 2.52	2.49 ± 0.556	0.462 ± 0.172
	R ² /R ² _{adj}	0.009/-0.18	0.013/-0.14	0.008/-0.18	0.002/-0.025	0.001/-0.026	0.024/-0.002
	(p-value) (b)	(0.564)	(0.492)	(0.578)	(0.812)	(0.824)	(0.342)

(a) For ambient air there is only data available for benzene, toluene, ethylbenzene, m + p-xylene, o-xylene and 1,3-butadiene.

(b) Bold values represent significant correlation at 0.05 level.

WM refers to West Midlands.

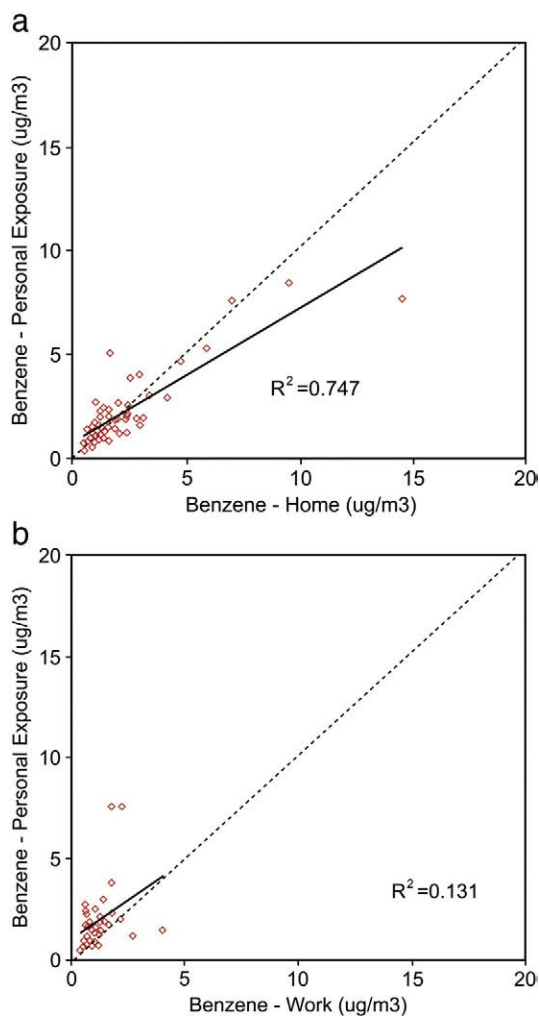


Fig. 2. Benzene personal exposure concentrations ($\mu\text{g m}^{-3}$) vs. concentration measured at (a) home ($N = 155$) and at (b) work ($N = 40$).

concentration, this suggests a potentially important influence of the workplace upon overall PE.

Analysing the effect of season upon the contribution of home or workplace concentrations to PE there was a mixed pattern of effect in the regression analysis, similar to what happened with the ratios (Table 2). For some compounds such as benzene, toluene, pyridine, and 3-ethenylpyridine, the regression was stronger in summer than in winter. However, for other compounds such as ethylbenzene and the xylenes, the regression was stronger in winter. This might be a consequence of different sources for these compounds. For example, benzene and toluene were mainly emitted by traffic, and hence traffic sources might have had greater impact on home and work concentrations in summer than in winter due to higher ventilation. On the other hand, ethylbenzene and the xylenes were previously associated with indoor sources such as paints and printers (Watson et al., 2001; Song et al., 2007; Harrison et al., 2009), which will have a greater impact in winter when ventilation with outdoor air is lower, as reported by the subjects through questionnaires. 3-Ethenylpyridine and pyridine are tracers of ETS (Bi et al., 2005), which has an important indoor source. The fact that the PE vs. H was stronger in summer may be a consequence of the higher concentrations measured at home for 3-ethenylpyridine (summer = 0.11 ± 0.21 vs. winter = $0.08 \pm 0.10 \mu\text{g/m}^3$) and pyridine (summer = 0.18 ± 0.13 vs. winter = $0.12 \pm 0.07 \mu\text{g/m}^3$). Additional analysis using univariate general linear models did not identify season as a variable

accounting for the variability of personal exposures ($p > 0.05$) for any compound.

3.4. Personal exposure vs. outdoor air concentrations: longitudinal and cross-sectional analysis

In order to assess the representativeness of ambient air concentrations as a surrogate for personal exposure, simultaneous daily ambient concentrations measured at the rural Harwell site were regressed with PE concentrations measured in this study for all the subjects (London, West Midlands and Wales). In addition, ambient concentrations in Cardiff were regressed against PE concentrations of Welsh subjects and London Eltham concentrations against PE concentrations of London subjects. The results of the cross-sectional regression analysis (i.e. m , a , R^2 , R^2_{adj} and ANOVA p -value) are presented in Table 3, whilst Table 4 shows the arithmetic mean and standard deviation for the same regression parameters corresponding to the longitudinal analysis.

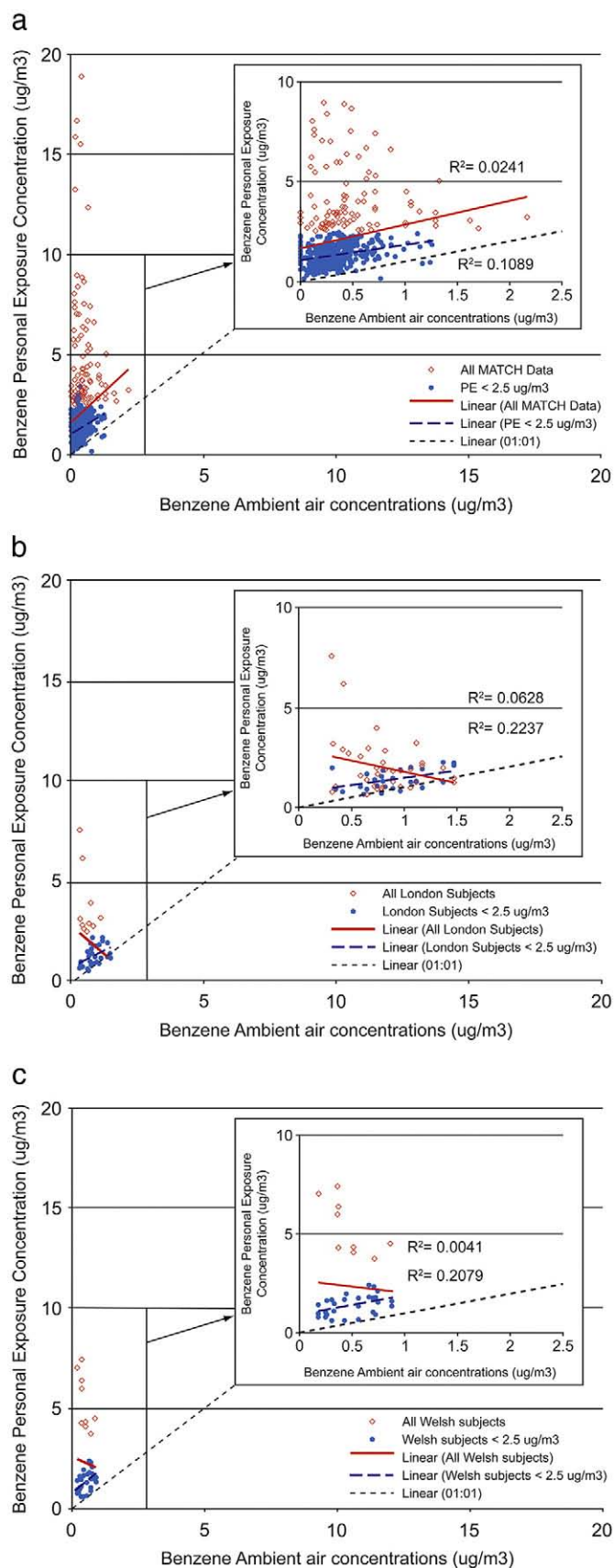
Table 3 shows weaker associations between PE and ambient air concentrations (R^2 range from 0 to 0.02) compared to regressions between PE vs. H and W. This might be a consequence of the higher limit of detection of the equipment sampling ambient air (e.g. benzene $\text{SDL} = 0.32 \mu\text{g/m}^3$; 0.1 ppb) compared with the PE methodology ($\text{SDL} = 8 \text{ ng/m}^3$) or to the low ambient concentrations, both causes leading to greater noise, thus reducing associations. These results were similar to those reported by Lai et al. (2004) for TVOC ($R^2 = 0.02$) although in that case the relationship was PE to outdoor residential air rather than to central site air.

The results of the cross-sectional analysis for benzene appear in Fig. 3, which exhibits two differentiated groups of points. The first group, which correspond to the low personal exposures (Fig. 3 solid dots) showed a fair association of ambient air with PE concentrations. In the second group (Fig. 3 hollow diamonds), which mainly represents high personal exposures, no association was seen with ambient benzene concentrations. These high PE values may be attributed to indoor sources such as building materials and furniture (Hodgson and Levin, 2003) common to homes and offices, attached garages (Batterman et al., 2007), heating and cooking systems, exposure to ETS (Heavner et al., 1995), storage of solvents and various human activities that the subjects perform during the day (e.g. commuting, DIY, incense burning, photocopying- specially in offices), which would be superimposed on the background ambient concentrations. Although none of the subjects had reported strong outdoor sources (e.g. proximity to industries), this might be also a factor increasing PE concentrations above the background ambient concentrations in other cases. Overall, when regressing PE with ambient concentrations, the coefficients of determination for each site were not statistically significant (Table 3) with the exception of benzene. It was decided to apply a virtual filter to the personal exposures concentrations in order to eliminate the high values of PE attributed mainly to indoor sources. The filters applied would be the expected maxima PE concentrations attributable to outdoor concentrations. These concentrations can be extracted applying the average slope and intercept obtained in the cross-sectional analysis for each compound as shown in Table 3 to the maximum ambient concentrations measured in the study. For instance, the benzene filter will be circa $3 \mu\text{g/m}^3$ applying the values of $m = 1.29$, $a = 1.69$, extracted from the cross-sectional regression of all subject data in Harwell station, and maximum ambient air concentration of $1.32 \mu\text{g/m}^3$ measured at Harwell. Applying this virtual filter into PE so as to consider only values of PE lower than $3 \mu\text{g/m}^3$, the coefficient of determination R^2 of the regression of PE vs. ambient concentrations increased for the three sites (e.g. from 0.0091 to 0.225 in Cardiff for Welsh subjects, Fig. 3). Hence, for the low exposure population (benzene $< 3 \mu\text{g/m}^3$), ambient concentrations measured at a central site correlated with PE concentrations explaining up to 11–22% of the variability of personal

Table 4
 Longitudinal analysis of personal exposure levels (PE) vs. ambient air concentrations (A) for each subject. All data report the regression parameters for the all subjects' database. Positive slope data reports the statistics only for those subjects where slopes are positive. All R² have p-values < 0.05.

Ambient Site	Strata	Stats	1,3-Butadiene			Benzene			Ethylbenzene			Toluene			m + p-Xylene			o-Xylene		
			m	a	R ²	m	a	R ²	m	a	R ²	m	a	R ²	m	a	R ²	m	a	R ²
			Harwell	All data	Mean	9.71	0.45	0.29	-0.8	2.55	0.29	42	7.31	0.31	0.69	25.9	0.28	3.87	15.9	0.29
	N=100	SD	99.9	0.71	0.26	10.5	3.61	0.28	333	35.6	0.29	76.1	46.2	0.27	162	51.8	0.29	127	13.1	0.24
	Summer	Mean	9	0.27	0.27	-3	2.89	0.26	98	13.2	0.36	-8	25.6	0.28	24	25.8	0.33	43	2.67	0.28
	N=45	SD	83	0.35	0.23	14	4.53	0.27	506	53.9	0.29	48	50	0.25	237	76.9	0.3	188	18.9	0.27
	Winter	Mean	10	0.55	0.32	1	2.33	0.32	7	2.92	0.29	7	26.8	0.3	-11	8.4	0.28	-9	3.33	0.27
	N=55	SD	111	0.85	0.28	6	2.82	0.3	49	5.41	0.28	94	44.7	0.28	64	15.1	0.28	38	6.88	0.22
	London	Mean	-13	0.05	0.37	-4	2.61	0.36	-3	2.01	0.39	-12	26.8	0.35	7.1	0.39	14	1.94	0.3	
	N=9	SD	24	0.03	0.28	11	3.25	0.36	21	3.66	0.36	33	40.8	0.29	32	12.5	0.38	14	2.24	0.32
	WM	Mean	15	0.49	0.28	2.39	0.29	52	8.42	0.31	5	26.1	0.27	10	17.6	0.3	17	3.22	0.27	
	N=82	SD	106	0.76	0.25	11	3.58	0.29	368	39.3	0.28	81	48.8	0.26	176	57.2	0.29	141	14.6	0.24
	Wales	Mean	-17	0.31	0.33	-2	3.8	0.19	-5	2.98	0.3	-24	23.7	0.32	-39	9.9	0.19	2	2.7	0.22
	N=10	SD	64	0.31	0.36	8	4.25	0.13	95	3.06	0.3	58	28	0.31	92	7.7	0.25	24	1.68	0.23
Harwell positive slope data	All DATA	N	52			77			76			75			100			99		
		Mean	40.6	0.4	0.31	0.3	2.18	0.29	60	8.67	0.33	5.9	26.6	0.31	3.9	15.9	0.29	13.8	3.1	0.27
		SD	112	0.5	0.3	11.5	3.72	0.29	383	40.9	0.3	86	51.8	0.28	162	51.8	0.29	127	13.1	0.24
	Summer	N	19			31			37			33			43			42		
		Mean	31.5	0.31	0.28	4.35	1.08	0.28	117	14.6	0.37	16.2	9.07	0.41	23.9	25.8	0.33	43.3	2.7	0.28
		SD	94	0.4	0.26	5.27	1.11	0.27	544	58.1	0.29	23.7	12.1	0.28	237	76.9	0.3	187	18.7	0.27
	Winter	N	30			43			37			39			55			54		
		Mean	49.8	0.47	0.36	1.97	1.87	0.31	6	2.98	0.31	18	26.5	0.33	18.3	10.7	0.27	7.53	1.27	0.29
		SD	128	0.58	0.32	6.19	2.55	0.3	57.3	6.41	0.3	108	51	0.3	15.8	25.6	0.32	8.28	1.21	0.25
	London	N	1			7			8			7			9			9		
		Mean	6.45	0.04	0.77	5.15	0.29	0.15	5.52	0.41	0.18	5.79	3.62	0.35	4.83	2.08	0.10	0.92	1.14	0.01
		SD	-	-	-	12.0	3.66	0.36	7.66	0.57	0.26	6.56	4.06	0.50	31.5	12.5	0.38	0.99	0.33	0.00
	WM	N	46			61			61			60			82			80		
		Mean	44	0.44	0.28	0.82	2.03	0.29	75	10.2	0.32	10	28.0	0.31	10	17.6	0.3	17	3.22	0.27
		SD	119	0.53	0.28	12.1	3.8	0.29	425	45.6	0.29	94	55.8	0.28	176	57.2	0.29	141	14.6	0.24
	Wales	N	5			9			7			8			10			10		
		Mean	33.9	0.11	0.57	1.10	0.99	0.07	67.2	1.45	0.34	25.0	0.54	0.56	18.1	1.78	0.03	12.0	1.82	0.05
		SD	29.4	0.06	0.46	0.14	0.16	0.04	87.3	1.61	0.52	36.9	12.9	0.26	91.9	7.69	0.25	13.3	1.49	0.05
London Eltham	All data	Mean	-1.5	-0.1	0.32	-0.4	3.12	0.28	8.16	-1.0	0.28	7.81	2.32	0.35	4.1	2.21	0.27	4.91	1.42	0.3
	N=10	SD	6.48	1.08	0.37	7.9	4.28	0.19	21.2	8.47	0.33	23.5	47.6	0.26	14.1	14.8	0.36	13.6	3.81	0.35
	Positive slope data	N	5			3			4			5			4			4		
		Mean	1.42	-0.6	0.38	6.31	-0.7	0.22	20.8	-5.3	0.41	17.9	-18	0.44	16.2	-6.5	0.47	14.5	-0.7	0.44
		SD	1.74	1.39	0.43	8.47	2.31	0.07	24.1	10.3	0.42	22.6	38.9	0.26	14.6	17.4	0.51	12.3	3.28	0.45
Cardiff	All data	Mean	7.49	0.07	0.24	-2.1	3.18	0.45	-1.9	2.28	0.4	-4.9	22.6	0.32	-3.9	9.51	0.38	-1.3	2.76	0.37
	N=8	SD	11.9	0.15	0.29	4.41	3.38	0.28	8.53	2.2	0.3	12.1	22.1	0.31	8.49	8.89	0.31	5.19	2.56	0.31
	Positive slope data	N	7			5			5			5			4			5		
		Mean	8.56	0.07	0.28	1.04	0.83	0.35	3.5	1.03	0.3	1.93	13.3	0.38	2.57	4.69	0.3	1.76	1.42	0.32
		SD	12.4	0.17	0.3	0.7	0.58	0.26	2.21	1.37	0.29	1.65	16.3	0.38	1.96	6.62	0.35	1.69	2.06	0.37

WM refers to West Midlands.



exposure in this subpopulation. In the case of 1,3-butadiene, no significant association ($p > 0.10$) was observed between PE concentrations and ambient air concentrations in any of the studied monitoring stations (Table 3). The small variance of personal exposure accounted by ambient concentrations suggested that the association between ambient concentration and PE to 1,3-butadiene is complex and warrants further research. This may be a consequence of the relatively high reactivity of this gas.

Table 4 shows the results of the longitudinal analysis, i.e. average data for the slope, intercept and R^2 extracted from the individual regression of PE vs. ambient air for each subject (as shown in Table S8). When considering all the results from the longitudinal analysis, R^2 values ranged from 0.27 to 0.31, whilst some of the slopes had negative values (Table S8). However, having a negative slope is not consistent with the fact that ambient air is a source of PE concentrations, and hence both values should be positively correlated. After analysing the information provided by the subjects regarding activity patterns and description questionnaires, the cases with negative slopes could be linked with participants that on some days had high personal exposures due to personal activities (e.g. use of solvents) or indoor sources (e.g. ETS exposure). Therefore, a summary of regression parameters only considering those cases where the slope is positive, i.e. those subjects that do not have strong indoor or personal sources, is presented also in Table 4. From this table it was clear that between 50 and 100% of the cases have a positive slope, suggesting that increases in personal exposures were associated with increases in ambient air concentrations.

Further information can be extracted from the regression of VOC PE concentrations with ambient concentrations. In both the cross-sectional (Table 3) and the longitudinal analysis (Table 4), PE concentrations were described by equations that have an intercept greater than zero. This suggested that in the absence of outdoor VOC, there was generally a background exposure which corresponds to indoor or personal activity sources (e.g. benzene $1.7\text{--}3.2 \mu\text{g}/\text{m}^3$). Therefore, it is likely that the use of ambient air as a surrogate for personal exposure would underestimate the personal exposure concentrations and hence would underestimate the pollution effects, as predicted by Zeger et al. (2000) and Sexton et al. (2004a). The presence of this background exposure, likely associated with indoor or personal activities, should be considered when designing strategies to reduce human exposures to VOCs. In this case, not only outdoor sources should be targeted, but also indoor ones.

With reference to the effect that season had in the longitudinal regression PE-A (Table 4), 1,3-butadiene showed a stronger PE-A relationship in winter, whilst for ethylbenzene it was stronger in summer which might be attributed to different prevalent outdoor and indoor sources for the compounds as explained in the previous section, or to lower chemical reactivity affecting winter concentrations. A similar trend for benzene was observed in the cross-sectional analysis for West Midlands subjects, as this area was the only one sampled through several seasons. The association was significant at the 0.01 level for subjects sampled in winter ($R^2 = 0.02$, $N = 235$), whereas for summer the strength decreased ($R^2 = 0.003$, $N = 160$). These seasonal effects were consistent with results reported for other pollutants (Adgate et al., 2007; Brown et al., 2008). Additional analysis of the effect of season on the association between ambient and PE was performed using a linear mixed model. Only 1,3-butadiene showed a significant effect of season on the relationship between PE-A, with an estimate, std error and p-value of -0.172 (summer), 0.050 and 0.001 respectively. For the rest of the compounds, season did not show any

Fig. 3. Benzene personal exposure concentrations ($\mu\text{g m}^{-3}$) all data (red hollow rhomboids) and less than $4.5 \mu\text{g m}^{-3}$ (blue solid squares) vs. ambient air concentration measured at (a) Harwell rural site ($N_{\text{all}} = 483$, $N_{<2.51} = 336$), (b) London Eltham urban background site ($N_{\text{all}} = 41$, $N_{<2.51} = 30$, London subjects) and (c) Cardiff urban centre site ($N_{\text{all}} = 39$, $N_{<2.51} = 30$, Welsh subjects).

effect in the linear mixed model. The influence of seasonal effects on the relationship between personal and ambient air detected in the longitudinal, cross-sectional and linear mixed models suggests that seasonal effects are a factor that should be considered when using central site data for epidemiological studies.

4. Conclusions

The strong association of personal exposures to several VOCs, including benzene, with home concentrations indicates that home concentrations were the largest driving factor determining exposures to VOCs, explaining between 11 and 75% of the total variability of personal exposures. Workplace and central site ambient concentrations were less well correlated with the corresponding personal concentrations explaining up to 11–22% of the variance in the low exposure data. These associations were only relevant provided that samples influenced by strong indoor sources or personal activity VOC sources were eliminated.

The relationship between personal exposure and VOC ambient concentrations not only showed PE/A ratios greater than unity but also intercepts greater than zero. The existence of the intercepts was attributed to the presence of a background concentration due to indoor or personal activity sources of VOC. It is likely that not only would the use of ambient air as a surrogate for personal exposure not correctly represent personal exposures due to the low correlation but also would generally underestimate these exposures. One of the reasons for the discrepancies between personal exposures with central site data was that central site data did not account for exposure due to personal activities (e.g. commuting). It was observed that season had a small effect on PE-to-microenvironment ratios and PE-to-microenvironment associations in home, work and ambient air. This could reflect seasonal differences attributed to the strength of indoor sources, reactivity of some compounds, personal activities and air exchange rates. Therefore, it is advisable that influences of season upon exposure estimates should be considered in epidemiological studies of VOCs in order to minimise the error in estimated exposure.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2010.10.014.

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