Contributions of outdoor, indoor and other sources to personal VOC exposure in five European cities

Vito Ilacqua, Matti Jantunen*

KTL—National Public Health Institute, Department of Environmental Health, Kuopio, Finland

ABSTRACT

Exposure data from the *EXPOLIS* study was used to compare the contributions of indoor and outdoor sources to personal exposure to selected VOCs (TVOC, benzene, xylenes, ethylbenzene, nonane, decane, undecane, alpha-pinene and 3-carene) in Athens, Basel, Helsinki, Oxford and Prague for non-ETS-exposed individuals. Indoor sources were found to be the largest contributors to personal exposure to TVOC, terpenes and alkanes. Their contribution was also important for aromatics, including benzene in Basel and Prague. Workplaces contributed only marginally to the median population exposures. While personal exposures differ between the cities, the relative and absolute contributions of indoor sources differ much less.

INDEX TERMS

VOCs; TVOC; Alkanes; Benzene; Exposure assessment

INTRODUCTION

Personal exposure to VOCs is the result of a variety of different contributions from indoor and outdoor sources. Knowledge of the relative contribution from these environments is helpful in directing regulatory, manufacturing and individual efforts to minimize potential risks. It is also helpful in characterizing VOC sources, whose emissions may differ in terms of risk.

METHODS

The *EXPOLIS* study was a population based study of adult air pollution exposures (Jantunen *et al.*, 1998). Personal exposure and microenvironmental (workplace, residential indoor and outdoor) concentration measurements were performed for selected VOCs—as well as $PM_{2.5}$, CO and NO_2—in six different European cities. Participants were monitored for 48 h and detailed information about their residences, work and habits were collected through a detailed questionnaire.

The approach to separate the different microenvironmental components of exposure was to assume a constant background contribution from the outdoor microenvironment and to consider the indoor levels above that arising from indoor sources (Eqn (1)). The balance between these microenvironmental exposures and personal exposure comprises all contributions from personal activities, including direct traffic exposure. Only non-ETS exposed individuals were included.

$$PE_{48\,\mathrm{h}} = 48\ \mathrm{h} * C_{\mathrm{out}} + (C_{\mathrm{in}} - C_{\mathrm{out}}) * t_{\mathrm{in}} + (C_{\mathrm{work}} - C_{\mathrm{out}}) * t_{\mathrm{work}} + \mathrm{Balance} \quad (1)$$

* Corresponding author. E-mail: matti.jantunen@ktl.fi

Sampling and Analytical Methods

For a detailed description of the sampling and analytical methods, as well as QA/QC measures the reader is referred to already published work (EXPOLIS Study Group, 1999; Jurvelin *et al.*, 2001). In synthesis, active VOC sampling (target volume 2–3 l) was performed onto Tenax adsorbent tubes in all cities but Basel, where active charcoal was used (target volume 30–50 l). Extractions differed accordingly, while in both cases the analytical method used was GC and MSD (as well as FID for Tenax samples).

Data Analysis

Measurements below the LOD were systematically replaced by ½ LOD. Although in some cases a majority of some microenvironmental concentrations were below the LOD, model results were not always adversely impacted and could be interpreted in most cases. The fact would simply reflect a low contribution from that microenvironment, as long as concentrations are well above the LOD in the other microenvironments. A detailed examination of how the percentage of values below the LOD may have affected the reliability of the analysis was performed. In only a few cases, pointed out in the text, the breakdown was considered unreliable. The occurrence of negative balance exposure from Eqn (1) was always connected with a substantial fraction of outdoor concentrations below LOD, indicating overestimation by the LOD/2 value. These situations would lead to underestimation of exposure contributions from indoor environments.

Cluster analysis. Cluster analysis of all VOC personal exposures was performed using (1 – Pearson *r*) as linkage distance and weighted pair-group average as amalgamation rule. Cluster concentrations were expressed as the sum of the compound concentrations. Three groups of compounds with presumably similar sources and/or pathways of personal exposure were identified consistently in all cities: (a) xylenes (all isomers) and ethylbenzene, henceforth simply referred to as *Aromatics*; (b) nonane, decane and undecane (*Alkanes*); (c) alpha-pinene and 3-carene (*Terpenes*). Thus, the present analysis focuses on total VOCs (expressed as toluene), benzene and these three compound groups.

Tests of significance. Because of the highly skewed concentration distributions, median, rather than mean, exposure values are used for comparing the contributions of microenvironments. The non-normality of the data, as well as some small sample sizes, required 230 pairwise comparisons using the Mann–Whitney *U*-test. These were interpreted using network graphs, with cities as nodes, and edges representing the lack of differences between cities at the 95% confidence level. Cities could be separated in significantly different groups based on these graphs. In some cases, only 1 or 2 edges were missing on the graphs, while all members were connected. Such situations were interpreted as indicating a substantial homogeneity of the variable across cities. This interpretation is also prudent in light of the fact that a battery of pairwise comparisons tends to overestimate the significance of differences, compared to other post-hoc tests.

RESULTS

There appears to be no relationship between the balance exposure and the time spent out of the microenvironments considered, for any compound in any city. That would suggest that the balance exposure (when meaningful) is due mostly to short exposures at high concentrations, rather than vice versa.

It must be noted that the sum of the median contributions does not—and would not be expected to—add up to the median personal exposure. However, it always comes within 25% of median personal exposures, posing no obstacle to the interpretation of the results.

For *TVOC*, no samples were below the LOD. The median personal, outdoor, residential, workplace and balance exposures are shown in Figure 1(a). Based on personal exposures, a

high and a low group are apparent: {Athens, Prague} and {Helsinki, Oxford}. The high group is exposed to twice as much the low group.

The microenvironmental source apportionment for *benzene* is shown in Figure 1(b). Due to a substantial fraction of measurements (44%) below LOD, Oxford outdoor contribution may be overestimated, which would explain the negative indoor and balance contributions. Based on personal exposures, a high and a low group are apparent: {Athens, Prague} and {Helsinki, Basel, Oxford}. The high group is exposed to three to four times as much the low group.

Outdoor contributions to *Terpenes* exposure, shown in Figure 1(c), are likely to be overestimated in all cities except Basel, due to a large percentage of measurements below the LOD, which explains the observed negative exposure balances. For Athens and Prague, the entire breakdown is only tentative, although the personal exposures are reliable. Overall, indoor contributions are probably even larger than shown. Basel differences from the other cities may well be due to the different sampling technique.

The breakdown of exposures to *Aromatics*, shown in Figure 1(d), is only tentative for the city of Oxford, as the majority (59–78%) of microenvironmental measurements were below the LOD, though the personal exposure figure is reliable. This explains the negative balance. Indoor contributions may also be somewhat larger than shown in Helsinki and Prague.

The exposure apportionment for combined *Alkanes* is reported in Figure 1(e). The exposure contribution breakdown for the city of Oxford is only tentative due to about 60% of measurements below LOD, although personal exposure is reliable. Indoor contributions in Helsinki and Prague may also be larger than shown. Based on personal exposures, a high and a low group are apparent: {Athens, Prague, Oxford} and {Basel, Helsinki}. The high group is exposed to 1.5–2 times as much the low group.

DISCUSSION

Outdoor *benzene* levels appear to determine half or more of personal exposure. This is in agreement with findings by Schneider *et al*. (2001), even in low-traffic areas, but with indoor/outdoor ratios greater than 1. In the present analysis, a variable but positive contribution from indoor sources can be observed. Only in Basel and Prague do these indoor contributions seem to be meaningful, accounting for about 20% of personal exposure. The known list of possible indoor sources include attached garages, smoking guests, hobby materials, gas (Ilgen *et al.*, 2001a), charcoal (Mugica *et al.*, 2001) and wood combustion (Hedberg *et al.*, 2002). No differences in garage presence, coal or wood use for heating between the cities were found, based on questionnaire responses. Direct exposure outside of the indoor microenvironments, most probably traffic, accounts for a rather large fraction (20–30%) of personal exposure in Athens, Basel and Prague.

Personal exposure to the other *Aromatics* clearly owes an important contribution to indoor sources. In an analogous study in Germany, I/O ratios of BTEX (which include xylenes and ethylbenzene, but also benzene and toluene) were also found greater than 1 (Schneider *et al.*, 2001), with benzene having the lowest ratio (1.5). The latter figure is consistent with median indoor/outdoor exposure ratios in Basel and Prague. The possible indoor sources include combustion, but also building materials, solvents, air fresheners and pesticide use (Buhamra *et al.*, 1998). Cleaning activity was also identified as a source of benzene and BTEX in Hong Kong homes (Guo *et al.*, 2003). A clearer understanding of these indoor sources still requires further investigation.

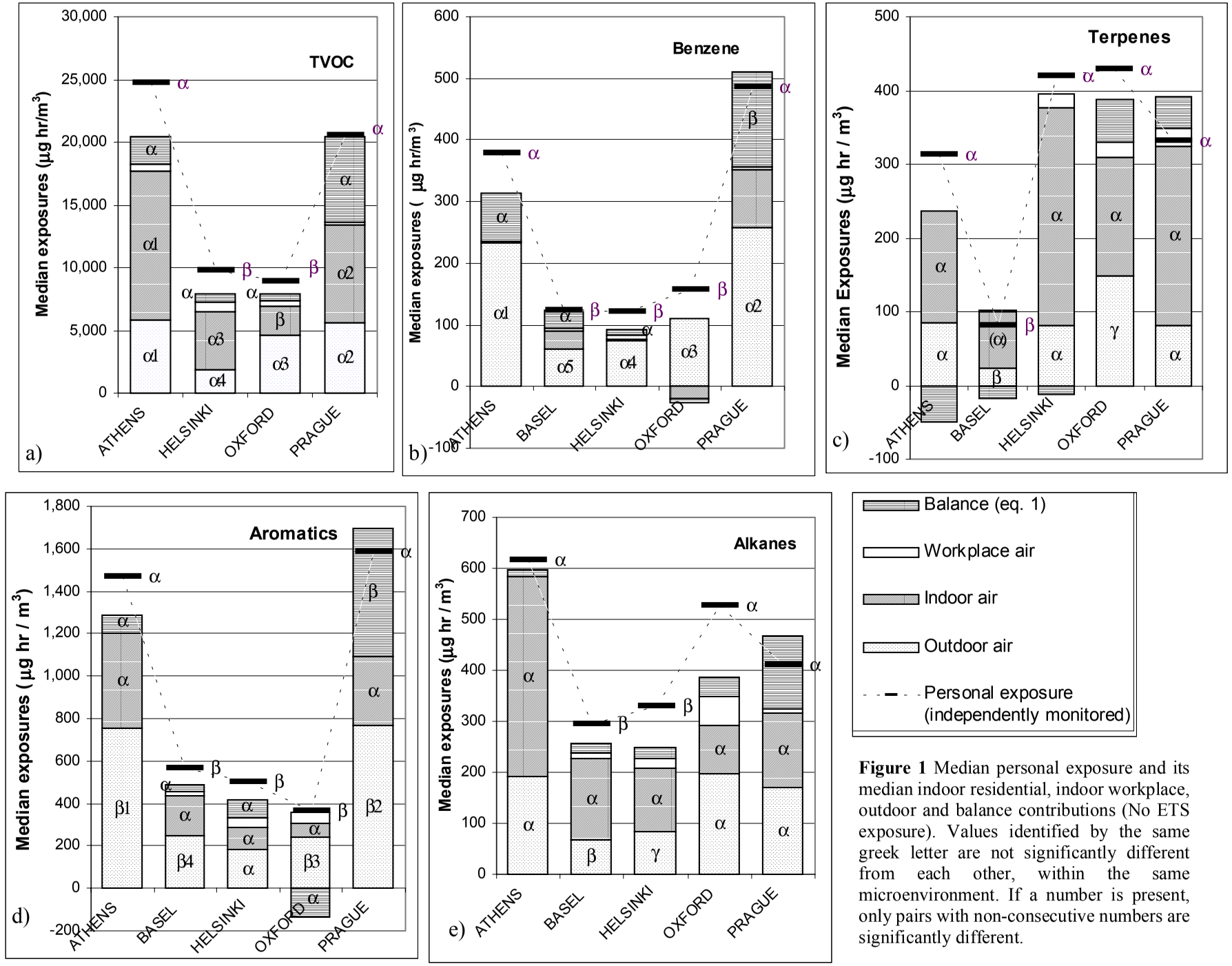

Figure 1 Median personal exposure and its median indoor residential, indoor workplace, outdoor and balance contributions (No ETS exposure). Values identified by the same greek letter are not significantly different from each other, within the same microenvironment. If a number is present, only pairs with non-consecutive numbers are significantly different.

Data on indoor levels of the selected *Alkanes* is sparse, but they seem to be connected with cooking (Srivastava *et al.*, 2000; Mugica *et al.*, 2001). Besides cooking, other indoor sources may be possible, as it is clear that the residential microenvironment is responsible for a large fraction, if not most, of the personal exposure to these compounds.

As for indoor *Terpene* sources, alpha-pinene is a notorious fragrance component in a number of household products and 3-carene is emitted from wood (Manninen *et al.*, 2002), among other sources. From questionnaire responses, there are no clear differences at least in the use of air fresheners between the cities. While high indoor concentrations of these compounds are therefore not surprising, and rather harmless in themselves, terpene reactions with active species (e.g. nitric oxide) in the indoor environment result in carbonyl byproducts that may affect indoor air quality (Sarwar *et al.*, 2002). As for outdoor contributions, acknowledging a possible measurement difference in Basel, Oxford is almost twice as high as Prague and, surprisingly, Helsinki, where the effect of the surrounding large coniferous forests might be expected.

As a whole, indoor residential sources are responsible for the largest fraction of total VOC exposures. Of the specific compound classes analysed, terpenes and alkanes also show the same heavy weighting of indoor sources. A substantial fraction (20–30%) of the aromatic compounds, including benzene in Basel and Prague, is also attributable to indoor sources. The pattern of inter-city variability for indoor contributions is complex. In general differences are not significant across the cities for each compound class. Only for TVOC differences are significant moving from high (Athens) to low levels (Helsinki and Oxford). That seems to indicate that sources and patterns of indoor emissions for these VOC groups are consistent across these European cities.

The amount of outdoor contributions to aromatics, benzene, alkanes and even TVOC exposures decreases in the same consistent fashion moving across cities, indicating that vehicular traffic is the main source of the outdoor contributions to exposure for the above compounds.

The balance of the exposure is generally not significantly different across cities, with the exception of high values in Prague for both benzene and aromatics (32 and 38%), as well as TVOC and Alkanes (33 and 35%), though not significantly. This difference suggests a higher direct traffic exposure. Indeed, the homes in Prague are reported by study participants to be on average closer to heavy traffic than in the other cities. It should be noted, though, that Prague microenvironmental apportionment results are based on only 8 individuals.

In general, workplace contributions to exposure are small. However this is a population-based analysis, which includes non working people, whose workplace exposure is zero by definition. The situation appears drastically different, however, if the extreme exposures, rather than central tendencies, are considered. Workplace environments provide the highest peak exposures for alkanes and aromatics in Basel and Helsinki, for terpenes in Helsinki and Oxford and for benzene in Basel. While indoor workplace environments have little influence on the median general population exposures, they may be the dominant sources of total personal exposure for some individuals.

CONCLUSION AND IMPLICATIONS

The above discussion, based on samples form five European cities, clearly confirmed the role of indoor residential sources as the largest contributors to personal exposure to TVOC, as well as several VOCs classes. Outdoor sources were most important only for benzene. Workplaces contributed only marginally to the median exposures. While personal exposures differ between the cities, the relative and absolute contributions of indoor sources differ much less. The identification of some of these apparently common sources requires further efforts, in order to better assess the possible impact on residential air quality.

ACKNOWLEDGEMENTS

This work formed part of a European Union 4th Framework RTD Program funded multi-centre study. Support by EU Contracts ENV4-CT96-0202 (DG12–DTEE) and ERBIC20CT96-0061, Academy of Finland Contracts N36586, N42610 and intramural funding by KTL.

REFERENCES

Buhamra, S.S., Buhamra, W.S. and Elkilani, A.S. (1998). Assessment of air quality in ninety-nine residences of Kuwait. *Environmental Technology* **19**, 357–368.

EXPOLIS Study Group (1999). *EXPOLIS Final Report*. Kuopio, Finland: National Public Health Institute, ISBN 951-740-143-4.

Guo, H., Lee, S.C., Li, W.M. and Cao, J.J. (2003). Source characterization of BTEX in indoor microenvironments in Hong Kong. *Atmospheric Environment* **37** (1), 73–82.

Hedberg, E., Kristensson, A., Ohlsson, M., Johansson, C., Johansson, P.-Å., Swietlicki, E., Vesely, V., Wideqvist, U. and Westerholm, R. (2002). Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmospheric Environment* **36** (30), 4823–4837.

Ilgen, E., Karfich, N., Levsen, K., Angerer, J., Schneider, P., Heinrich, J., Wichmann, H.-E., Dunemann, L. and Begerow, J. (2001a). Aromatic hydrocarbons in the atmospheric environment: Part I. Indoor versus outdoor sources, the influence of traffic. *Atmospheric Environment* **35** (7), 1235–1252.

Jantunen, M.J., Hanninen, O., Katsouyanni, K., Knoppel, H., Kuenzli, N., Lebret, E., Maroni, M., Saarela, K., Sram, R. and Zmirou, D. (1998). Air pollution exposure in European cities: the 'EXPOLIS' study. *Journal of Exposure Analysis and Environmental Epidemiology* **8** (4), 495–518.

Jurvelin, J., Edwards, R., Saarela, K., Laine-Ylijoki, J., De Bortoli, M., Oglesby, L., Schlapfer, K., Georgoulis, L., Tischerova, E., Hanninen, O. and Jantunen, M. (2001). Evaluation of VOC measurements in the EXPOLIS study. *Journal of Environmental Monitoring* **3** (1), 159–165.

Kousa, A., Monn, C., Rotko, T., Alm, S., Oglesby, L. and Jantunen, M.J. (2001). Personal exposures to NO_2 in the EXPOLIS-study: relation to residential indoor, outdoor and workplace concentrations in Basel, Helsinki and Prague. *Atmospheric Environment* **35** (20), 3405–3412.

Manninen, A.M., Pasanen, P. and Holopainen, J.K. (2002). Comparing the VOC emissions between air-dried and heat-treated Scots pine wood. *Atmospheric Environment* **36** (11), 1763–1768.

Mugica, V., Vega, E., Chow, J., Reyes, E., Sanchez, G., Arriaga, J., Egami, R. and Watson, J. (2001). Speciated non-methane organic compounds emissions from food cooking in Mexico. *Atmospheric Environment* **35** (10), 1729–1734.

Sarwar, G., Corsi, R., Kimura, Y., Allen, D. and Weschler, C.J. (2002). Hydroxyl radicals in indoor environments. *Atmospheric Environment* **36** (24), 3973–3988.

Schneider, P., Gebefugi, I., Richter, K., Wolke, G., Schnelle, J., Wichmann, H.-E. and Heinrich, J. (2001). Indoor and outdoor BTX levels in German cities. *The Science of the Total Environment* **267** (1–3), 41–51.

Srivastava, P.K., Pandit, G.G., Sharma, S. and Mohan Rao, A.M. (2000). Volatile organic compounds in indoor environments in Mumbai, India. *The Science of the Total Environment* **255** (1–3), 161–168.