EXPOSURE OF POPULATION AND MICRO-ENVIRONMENTAL DISTRIBUTIONS OF VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN FIVE EUROPEAN CITIES

K Saarela[1*], T Tirkkonen[1], J Laine-Ylijoki[2], J Jurvelin[3], and M Jantunen[4]

[1]Technical Research Centre of Finland, VTT, Building and Transport, Espoo, Finland
[2]Technical Research Centre of Finland, VTT, Processes, Espoo, Finland
[3]Jyvaskyla Polytechnic, School of Engineering and Technology, Jyvaskyla, Finland
[4]Finnish National Institute of Public Health, Department of Environmental Hygiene, KTL, Kuopio

ABSTRACT
Determination of volatile organic compounds, VOCs, formed one part of the EU- EXPOLIS project in which the exposure of European urban population was studied. In the project 201 subjects in Helsinki, 50 in Athens, 50 in Basel, 50 in Milan and 50 in Prague were studied. The micro-environmental and personal exposure in Helsinki and Basel were lowest within all chemical compound groups and remarkable was the complete absence of halogenated compounds in Helsinki. The far highest micro-environmental concentrations of aromatics were in Athens and somewhat lower in Milan. The study was planned in such a way, that the role of micro-environmental concentrations in covering the total exposure could be calculated and their coverage of personal exposure estimated. This comparison suggested that the aromatics and to some extent the alkanes had stronger sources elsewhere than the indoor or residential outdoor environments.

INDEX TERMS
VOCs, Micro-environmental concentrations, Exposure, VOC sources

INTRODUCTION
This study was part of an European project where exposure of the urban European population (M Jantunen et al 1998) for particles of size below 2,5 µm and 10 µm, NO_2 and volatile organic compounds, VOCs, were studied.

The study was performed by monitoring the personal exposure of randomly selected subjects for a period of 48 hours using a, for this study designed special sampling casing with sorbents and pumps. The home indoor, and workplace air were analysed simultaneously at predetermined times when the subjects normally were considered to be present in these microenvironments and the home outdoor simultaneously with the indoor air sampling. In addition, the subjects kept a time activity diary during the 48h study period when carrying the personal exposure monitoring casing, PEM

The fieldwork continued from summer of 1996 to winter of 1997-98.

METHODS
The sampling in each center was done by the national teams using identical sampling equipment, operating procedures, time-microenvironment-activity diaries, questionnaires, database and data entry tools. To assure comparability of the data from the 5 cities in 5

Contact author email: Kristina Saarela@vtt.fi

countries, a strict QA/QC protocol was established and the QA Unit of KTL supervised the fieldwork. Standard operating procedures, SOPs, were prepared for all subjects, laboratory and field procedures, and the *EXPOLIS* field teams were trained in three joint workshops. The SOPs developed for the VOC sampling and analysis are:

-VOC sampling (EXPOLIS/VTT-F-4.0); defines the VOC sampling set-up, flow calibration and other preparation in the laboratory before and after the sampling.

-VOC sample analysis (Expolis/VTT-L-1.0); defines the VOC sampling tube preparation and tube analysis procedures in the analytical laboratory.

-VOC sampling and analysis QA (Expolis/VTT-L-4.0); defining the quality procedures for the VOC sampling and analysis.

The VOC analyses of samples were performed by VTT, except for Basel where the VOC data was produced by a national laboratory. For collecting the VOCs, TENAX TA ® sorbent was selected because of its good all-round properties. In Basel Chrompack ® was used. Both analytical laboratories were inter-calibrated by the European Commission / Joint Research Centre (EC/JRC) Environment Institute in Ispra (J Jurvelin et al. 2001) . Other techniques were inter-calibrated between the teams. In the quantification specific response factors were used.

The VOC compounds were selected on the basis of their environmental and health significance or of the usability of one or group of few compounds as markers of pollution sources. The availability of one single sampling and analysis method for all target compounds was also required. The list of selected VOC target compounds included 30 different compounds and is given in Table 1. Compounds were analyzed with GC/FID/MSD after thermal desorption. The sampling equipment and procedure as well the analytical details are extensively described in (Jurvelin et al. 2001). The single VOCs were identified from the MSD total ion chromatogram by Wiley 275 software library. Compound specific response factors were used to quantify the target compounds.

Table 1. EXPOLIS target VOCs.

Alkanes	CAS	**Alcohols**	CAS
hexane	110-54-3	2-methyl-1-propanol	78-83-1
nonane	111-84-2	2-ethylhexanol	104-76-7
decane	124-18-5	phenol	108-95-2
undecane	1120-21-4	1-octanol	111-87-5
cyclohexane	110-82-7	1-butanol	71-36-3
Aromatics		**Aldehydes**	
benzene	71-43-2	hexanal	66-25-1
toluene	108-88-3	benzaldehyde	100-52-7
ethylbenzene	100-41-4	octanal	124-13-0
m&p-xylene	108-38-3	**Halogenated**	
o-xylene	95-47-6	trichloroethene	79-01-6
styrene	100-42-5	tetrachloroethene	127-18-4
naphthalene	91-20-3	1,1,2-trichloroethane	79-00-5
propylbenzene	103-65-1	**Miscellaneous**	
trimethylbenzenes	95-63-6	d-limonene	138-86-3
Esters		1-methyl-2-pyrrolidinone	872-50-4
2-buthoxyethanol	111-76-2	Δ^3-carene	13466-78-9
		alpha-pinene	80-56-8

RESULTS

In Table 2 the micro-environmental concentrations of the target VOCs are divided into chemical groups, and are given for the five cities. In addition to the geometric mean, GM, which is the most appropriate statistical measure for characterizing the concentrations in the micro-environments and the exposure of the subjects also arithmetic mean and arithmetic standard deviation (ADS) are given.

Table 2. Micro-environmental VOC concentrations in five European EXPOLIS-cities.

Home in							
	Alkanes	**Aromatics**	**Alcohols**	**Esters**	**Aldehydes**	**Halogenated**	**Miscell.**
Athens							
Mean	42,7	236,7	13,4	10,6	21,1	10,7	91,8
ASD	10,2	43,0	3,6	6,1	9,3	8,0	28,9
GM	25,0	46,0	7,9	16,5	35,7	42,6	78,5
Basel							
Mean	26,5	44,6	2,3	2,9	10,2	2,1	20,8
ASD	12,4	2,5	0,5	1,3	2,5	1,5	5,9
GM	11,0	9,0	1,5	4,5	14,3	16,8	28,2
Helsinki							
Mean	17,8	42,7	27,0	2,5	20,7	2,8	54,2
ASD	7,4	2,9	8,7	4,5	5,4	2,8	20,6
GM	9,3	6,0	15,3	21,8	39,2	44,7	68,6
Milan							
Mean	126,9	462,9	60,0	69,9	63,0	130,4	97,7
ASD	86,7	178,4	40,5	92,1	146,1	147,9	70,9
GM	24,3	42,5	13,2	24,9	50,2	71,5	97,7
Prague							
Mean	35,1	136,3	30,8	3,7	18,0	16,0	43,3
ASD	16,6	3,0	7,8	4,8	5,1	7,2	12,0
GM	14,8	15,8	17,4	25,9	41,3	50,8	75,1
Home out							
	Alkanes	**Aromatics**	**Alcohols**	**Esters**	**Aldehydes**	**Halogenated**	**Miscell.**
Athens							
Mean	8,4	22,2	30,6	30,6	83,5	144,7	289,4
ASD	2,2	1,7	1,9	1,9	1,8	1,9	1,9
GM	6,1	16,6	22,7	22,7	62,0	107,4	214,9
Basel							
Mean	2,2	5,7	7,9	7,9	21,4	37,2	74,3
ASD	0,7	0,6	0,7	0,7	0,7	0,7	0,7
GM	1,5	4,0	5,6	5,6	15,2	26,3	52,6
Helsinki							
Mean	6,4	18,3	24,7	24,7	67,6	117,0	233,9
ASD	3,0	3,3	3,1	3,1	3,2	3,1	3,1
GM	4,8	13,6	18,4	18,4	50,3	87,0	174,0
Milan							
Mean	44,3	110,7	155,0	155,0	420,8	730,9	1461,8
ASD	23,8	19,4	21,6	21,6	20,8	21,3	21,3
GM	11,6	30,7	42,3	42,3	115,3	199,8	399,7
Prague							
Mean	7,1	18,3	25,3	25,3	69,0	119,7	239,3
ASD	1,9	0,9	1,4	1,4	1,3	1,4	1,4

GM	5,1	14,2	19,4	19,4	53,0	91,7	183,3
Workplace							
	Alkanes	**Aromatics**	**Alcohols**	**Esters**	**Aldehydes**	**Halogenated**	**Miscell.**
Athens							
Mean	21,2	98,5	6,4	1,7	10,8	19,1	8,4
ASD	3,6	10,2	1,1	1,4	2,6	23,0	2,2
GM	14,3	66,1	5,4	1,4	9,2	3,7	6,1
Basel							
Mean	4,4	16,2	0,5	0,5	1,9	1,2	2,2
ASD	1,3	0,9	0,1	0,2	1,0	0,3	0,7
GM	3,0	14,0	0,4	0,5	1,3	0,9	1,5
Helsinki							
Mean	9,5	16,7	7,4	1,5	7,3	2,6	6,4
ASD	10,0	2,9	5,1	2,5	3,1	1,5	3,0
GM	4,6	12,0	5,0	1,3	6,0	2,2	4,8
Milan							
Mean	117,1	413,2	26,9	49,8	65,8	39,6	44,3
ASD	71,6	105,1	10,3	235,7	62,1	27,9	23,8
GM	19,5	127,9	10,1	3,2	18,6	13,0	11,6
Prague							
Mean	14,0	50,5	6,4	1,4	8,3	12,3	7,1
ASD	3,5	3,9	0,7	0,3	1,2	9,2	1,9
GM	8,7	35,8	5,7	1,3	7,2	5,0	5,1

Figure 1 illustrates the actual personal exposure during the 48h study period in four cities.

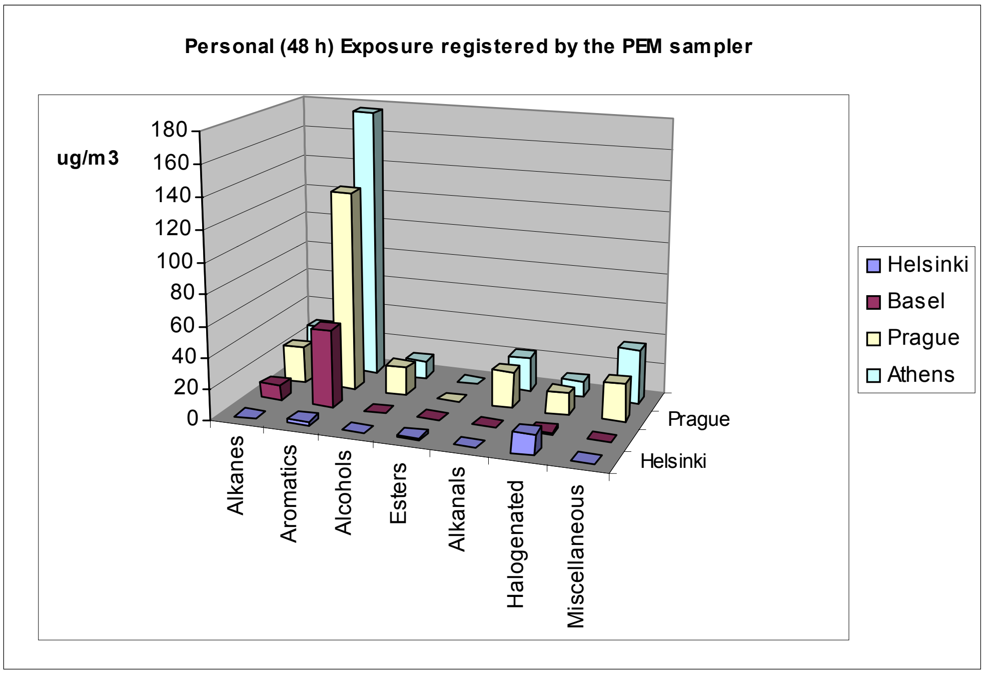

Figure 1. Personal exposure to VOCs in EXPOLIS-cities.

In order to get information of the impact and coverage of the micro-environmental sources the total exposure attained by personal sampling (PEM), and shown in Figure 1, an approximation was made, that the subjects spend seven hours of the day in the workplace, two hours outdoors and 15 hours in the home. The micro-environmental values were treated according to this simplified time distribution, and the relation to the measured PEM values is shown in Figure 2.

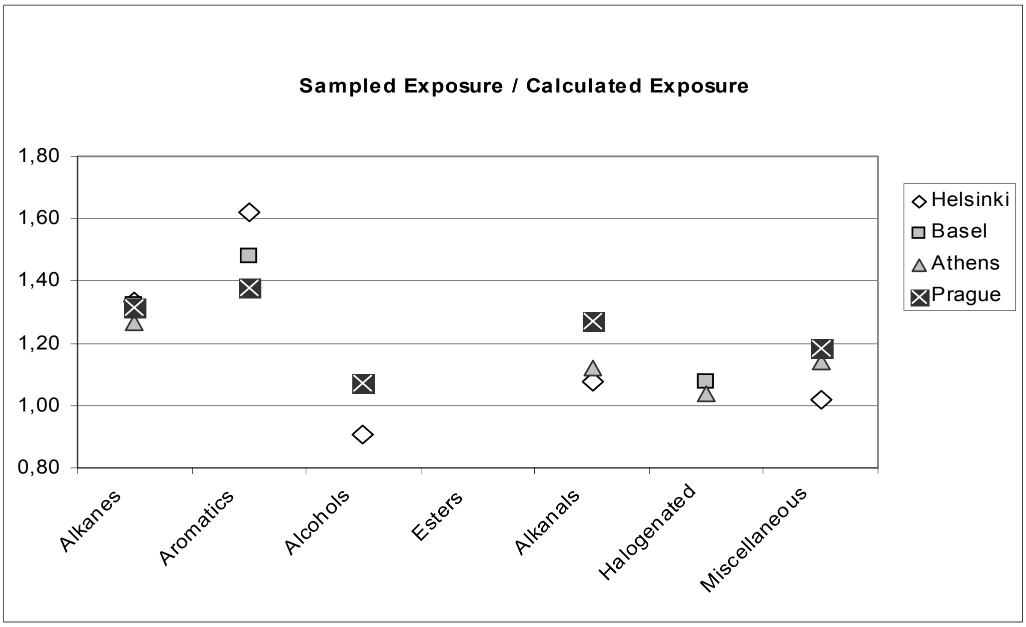

Figure 2. Relationship between sampled exposure (PEM) and exposure derived from approximated hourly exposure to the sampled microenvironments.

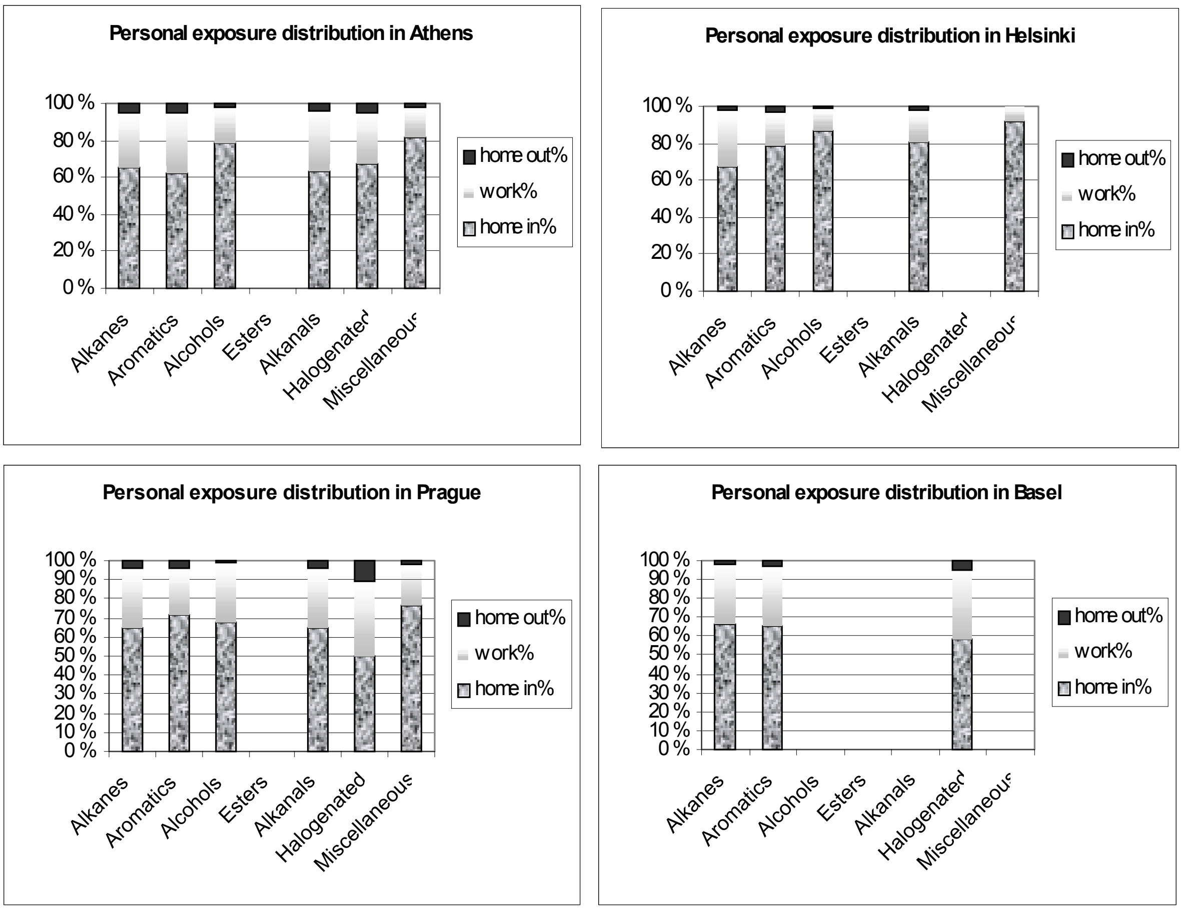

Figure 3. Personal exposure distribution of the total exposure between microenvironments in four cities.

DISCUSSION

The micro-environmental concentrations are highest in Milan and Athens, and lowest in Helsinki and Basel. However, the comparison between Basel and the other cities is not straightforward as Basel used another sorbent in sampling of the VOCs.

The normalized personal exposure distributions in Figure 3 show clearly that the difference is in the exposure distribution can be noticed between cities in that the exposure in Helsinki home indoor air is more prevailing than in the other cities even if it is very low as absolute concentrations. One of the home indoor air sources is the outdoor air. The role of outdoor air and smoking is discussed for Helsinki by R D Edwards et al (R D Edwards 2001). Indoor materials and activities are prominent sources. The effect of materials in the Helsinki indoor air is discussed by T Tirkkonen (T Tirkkonen et al 2002). In the paper of H Jarnstrom (H Jarnstrom et al 2002) the role of inhabitants is studied and seems to be remarkable.

Figure 2 shows, that the measured real exposure for some chemical groups is higher (the relationship measured exposure/calculated exposure >1) than the calculated. This is true especially for aromatics with the PEM sampler/calculated ratio 1,38 to 1,62 being biggest in Helsinki indicating a pronounced exposure in other microenvironments than the measured, e.g. traffic and free time activities. In Athens and Prague this effect was more subdued. For alcohols the most typical sources are indoor related such as paints and glues and this hypothesis is supported by the relationship being near one.

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REFERENCES

R D Edwards, J Jurvelin, K Saarela, M Jantunen. 2001, VOC concentrations measured in personal samples and residential indoor, outdoor and workplace microenvironments in EXPOLIS-Helsinki, Finland, in *Atmospheric Environment,* Vol 35 (2001) 4531 – 4543.

M Jantunen , O Hanninen, K Katsouyanni, H Knoppel, N Kunzli, E Lebret, M Maroni, K Saarela, R Sram, D Zmirou, 1998, Air Pollution Exposure in European Cities, the Expolis Study. *Journal of Exposure Analysis and Environmental Epidemiology,* Vol 8 (4), 495-518.

H Jarnstrom, K Saarela, The apportionment of volatile organic compounds and the effect of remedial action at two indoor air problem sites, *Proceedings of the 9th International Conference on Indoor Air Quality and Climate-Indoor Air 2002, Santa Cruz: Indoor Air 2002.*

J Jurvelin, R d Edwards, K Saarela, M de Bortoli, J Laine-Ylijoki, L Oglesby, K Schlapfer, L Georgoulis, E Ticherova, L Lovato, M J Jantunen, 2001. Evaluation of VOC Measurements in the Expolis study. *Journal of Environmental Monitoring* Vol 3(1), 159-165.

T Tirkkonen, K Saarela, K. Villberg, J Jurvelin and M Jantunen, Building realated factors and inhabitant exposure to indoor air volatile compounds in the Expolis Helsinki study, *Proceedings of the 9th International Conference on Indoor Air Quality and Climate-Indoor Air 2002, Santa Cruz: Indoor Air 2002.*

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