VEHICLES
BUS
1,3-BUTADIENE
PROPENE
SAMPLING
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BENZENE
ISOPRENE
CHROMATOGRAPHY

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Exposure to volatile hydrocarbons in commuter trains and diesel buses

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EXPOSURE TO VOLATILE HYDROCARBONS IN COMMUTER TRAINS AND DIESEL BUSES

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ABSTRACT

Percentage proportions of 25 C_2-C_7 hydrocarbons were determined inside both diesel buses and commuter trains in regular traffic. The hydrocarbons originate predominantly from petrol-fuelled vehicles. The total proportion of unburnt petrol components (mainly alkanes and arenes) was considerably larger than the proportion of combustion-formed components (mainly ethene, ethyne and propene). The approximate relative proportions 1 : 1 : 0.4 : 0.1 were observed for the genotoxic species benzene, ethene, propene, and 1,3-butadiene. Isoprene from expired air of the passengers constituted a prominent fraction, particularly in the buses. Samples were taken on triple-layer adsorbent cartridges and were analyzed in the laboratory by thermal desorption and gas chromatography on an aluminium oxide column.

Passenger exposure to traffic-emitted volatile hydrocarbons was 2-3 times higher for diesel bus commuters than for train commuters. The presence of road vehicles nearer to the buses explains this difference. Additional pollution in buses from their diesel exhaust strengthens commuter trains as a superior alternative with respect to the exposure of the passengers to hazardous air pollutants.

Key words: Air pollutants, volatile hydrocarbons, benzene, isoprene, exposure in vehicles, adsorbent sampling and gas chromatography.

INTRODUCTION

For investments in public transport, there is often a choice between diesel buses and commuter trains. Electrically powered commuter trains are superior with respect to emissions, but an environmental comparison should also include the little known differences in the exposure of the passengers to air pollutants. The increasing pollutant-related problems with asthma and allergy in Scandinavia [1] and other regions strengthen this aspect. Exposure differences are also important when hazards due to genotoxic volatile hydrocarbons and other traffic-emitted pollutants are considered [2]. The purpose of this study was to determine and compare the presence and origin of non-methane volatile hydrocarbons in diesel buses and commuter trains, using recently described [3] dedicated analytical methods. Earlier studies of hydrocarbons in vehicles have focussed mainly on private cars and C_5-C_{10} exhaust-emitted petrol hydrocarbons [4-6].

EXPERIMENTAL

The vehicles studied were Volvo and Scania diesel buses and ABB X10 commuter trains in regular traffic. Most of the commuter train samples were taken on the line from the town Kungsbacka northwards through the suburb Kållered to Göteborg (Kungsbacka - Göteborg: 25 km, 25 min; Kållered - Göteborg: 12 km, 11 min). From Kållered to Göteborg, the train runs along the motorway (E6), with 50 000 vehicles dayly, and goes underground (3 min) at one station, located by the large amusement park, Liseberg. Corresponding bus samples were taken on the suburban line Kållered - Göteborg (25 min). Samples from the commuter train northwards from Göteborg to Ytterby (20 km, 17 min) were compared with bus samples from the line Ytterby - Göteborg (30 min). The Ytterby railway and bus station is only slightly polluted by traffic. The bus to Göteborg runs partly (13 km) without stops on the motorway. Strictly urban bus samples were taken in Göteborg on local lines with frequent stops. About 50% of the petrol-fuelled cars in the traffic were equipped with catalysts (TWC systems) by the time of the study. Less than 2% of the private cars were diesel-fuelled.

Samples were taken on triple-layer adsorbent cartridges [3] with Tenax TA, Carbotrap and Carbosieve S-III as adsorbents of increasing strength. The sampling pumps and the connected adsorbent tubes were kept among passengers in the vehicle compartments. The sampling volumes were in the range 200-800 ml. Different sampling rates for duplicate samples were used to check losses by breakthrough and by decomposition of reactive hydrocarbons.

In the laboratory, the hydrocarbons were analyzed by thermal desorption combined with gas chromatography [3]. The separations were performed on an aluminium oxide column (50 m x 0.32 mm i.d., fused silica, PLOT, Chrompack) using temperature-programming and flame ionization detection (Figure 1). The FID response was set equal for all hydrocarbons. Identifications were made from retention data, using different temperature programs, and were confirmed by mass spectrometric studies of selected samples [3].

RESULTS AND DISCUSSION

The proportions of most of the C_2-C_7 hydrocarbons assessed in buses and trains are given in Table 1, and the chromatogram in Figure 1 illustrates the analytical separation of these hydrocarbons. The results given in Table 2 compare passenger exposure during parallel trips in commuter bus and train. In Table 3, potential sources of pollutants inside vehicles are compared with respect to hydrocarbon composition.

Hydrocarbon Assessments

The 25 hydrocarbons reported in Table 1 are ordered according to structural class, number of carbon atoms, and retention on the gas chromatographic column. Results are given for six representative bus samples. Bus samples with analytical deficiencies or non-typical proportions due to incidental contributions from various hydrocarbon sources were excluded. The hydrocarbon proportions in the commuter trains were found to be more uniform, and the results from three single and three duplicate samples are given as average and lowest-highest values. Results from the previously studied major road tunnel in Göteborg [7] are included for comparison.

The hydrocarbon proportions in Table 1 are clearly similar for all the reported samples. They are also similar to the proportions of the tunnel sample which serves as a reference for traffic emissions. It is concluded that hydrocarbons emitted from petrol-fuelled vehicles predominate. Significant contributions from other sources are evident only for isoprene, ethane and propane. Ethene, propene, ethyne and 1,3-butadiene are important combustion-formed species from petrol, whereas the C_4-C_6 alkanes and the arenes are major fuel components emitted in elevated proportions from cold starts and urban slow and irregular traffic [8]. Accordingly, the proportions of fuel hydrocarbons are higher for the first three samples from buses in urban traffic, than for the following three samples from commuter buses partly driving on a motorway. High proportions of benzene (2-4% in Sweden) and alkylbenzenes are typical of reformate-rich European petrol.

Table 1. Hydrocarbon composition (C_2-C_7, % w/w) of selected representative samples taken in diesel buses and commuter trains.

	Local buses			Commuter buses			Commuter trains		Road tunnel
Sampling date 1994	12/4	26/5	26/5	31/5	13/12	14/12	April-Dec (6 trips)		Ref 7
Total C_2-C_7 ($\mu g\ m^{-3}$)	374	129	149	47	193	215	93	44-158	
Alkenes									
C2 Ethene	7.8	6.2	6.0	11.1	11.4	9.7	8.3	6.8 - 11.6	9.6
C3 Propene	2.5	3.5	3.7	4.6	5.6	3.6	3.7	3.3 - 3.9	3.5
C4 *trans*-2-Butene	0.2	0.3	0.3	0.4	0.4	0.5	0.4	0.3 - 0.6	0.4
1-Butene	0.3	0.6	0.6	0.9	1.0	0.9	0.7	0.5 - 1.4	0.7
Methylpropene	1.0	1.4	1.1	1.6	2.2	2.0	1.4	1.2 - 1.7	1.4
cis-2-Butene	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.2 - 0.4	0.3
C5 *trans*-2-Pentene	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1 - 0.2	0.2
2-Methyl-2-butene	0.2	0.2	0.3	0.2	0.2	0.3	0.3	0.2 - 0.3	0.3
1-Pentene	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.1 - 0.2	0.2
2-Methyl-1-butene	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2 - 0.2	0.2
Alkadienes									
C4 1,3-Butadiene	0.4	0.4	0.3	0.7	0.9	0.6	0.5	0.5 - 0.6	0.9
C5 Isoprene	5.0	2.6	3.0	13.0	4.0	6.2	2.7	1.1 - 5.5	0.0
Alkynes									
C2 Ethyne	3.7	2.6	2.4	5.2	4.4	5.4	4.2	3.7 - 4.5	6
Alkanes									
C2 Ethane	1.7	2.5	2.9	3.1	2.6	3.0	5.1	4.1 - 6.9	1.1
C3 Propane	1.3	1.7	2.1	1.5	2.1	1.8	4.0	2.8 - 5.2	0.6
C4 Methylpropane	3.4	3.5	3.4	3.6	3.3	4.4	4.0	3.2 - 5.4	3.5
Butane	7.4	6.7	6.7	9.0	8.3	7.2	8.6	7.4 - 10.3	6.0
C5 Methylbutane	11.4	11.2	11.6	7.9	7.4	8.7	9.8	8.6 - 10.5	8.7
Pentane	3.8	3.7	4.2	2.3	2.5	3.4	3.8	3.2 - 4.7	4.0
C6 Methylcyclopentane	3.5	3.6	3.7	2.2	2.3	2.9	3.5	2.6 - 4.0	2.2
2-Methylpentane	4.7	4.6	4.6	2.5	2.7	3.8	3.7	3.3 - 4.1	3.5
3-Methylpentane	2.8	2.4	2.6	1.2	1.5	2.0	2.0	1.7 - 2.2	3.0
Hexane	2.1	1.8	1.9	1.1	1.1	1.5	1.5	1.4 - 1.6	2.5
Arenes									
C6 Benzene	8.3	10.4	9.0	7.2	8.8	7.0	8.7	7.7 - 9.4	11.2
C7 Methylbenzene	19.5	21.2	20.1	16.3	21.9	17.4	16.8	13.3 - 18.7	21.5

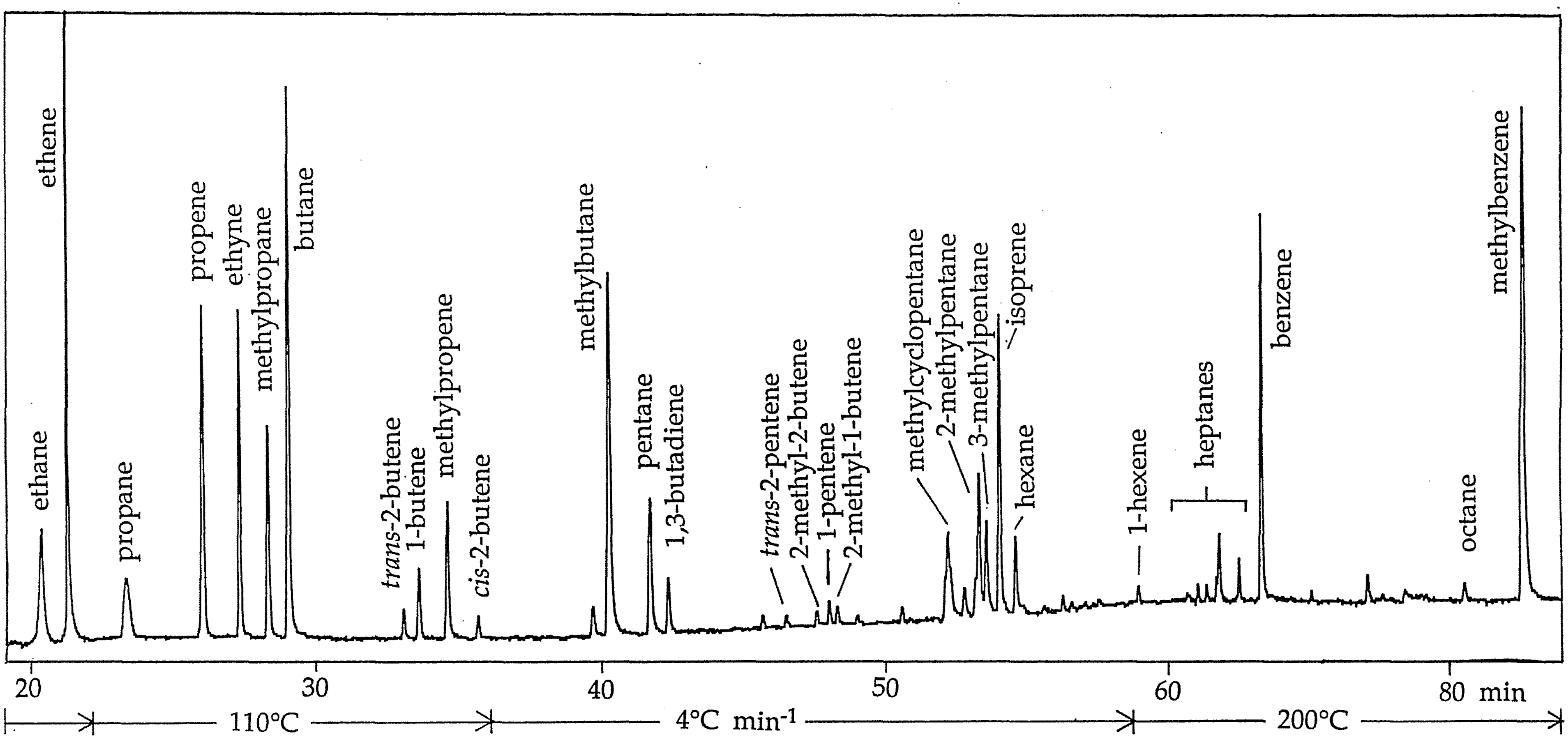

Figure 1. Gas chromatographic separation of C_2-C_7 hydrocarbons sampled inside a commuter diesel bus (13 Dec 1994, cf. Tables 1 and 2, aluminium oxide column, chart speed lowered after 60 min.).

As demonstrated in Figure 1, the aluminium oxide column is very useful for the separation of the C_2-C_7 hydrocarbons. The preceding thermal desorption from the triple-layer adsorbent cartridges is compatible with good resolution. The selected slow temperature program permitted 1,3-butadiene to be separated from pentane, and isoprene from 3-methylpentane. Minor C_2-C_7 hydrocarbons (not reported in Table 1) were found to sum up to 4-8% of the total amount and to include heptanes as well as minor pentenes and hexenes in proportions characteristic of vehicle emissions. The C_8-C_9 alkylbenzenes are eluted late on the aluminium oxide column and were not included. The detailed proportions of alkylbenzenes in commuter vehicles were reported in a previous study [4].

The analytical quality of the results was regularly checked by duplicate samples on different cartridges and with different sampling volumes. Columns two and three in Table 1 illustrate normal deviations for duplicate samples. Breakthrough losses of ethyne on sampling, and partial decomposition of 1,3-butadiene and isoprene were found to be potential sources of error.

Bus versus Train

The results in Table 2 demonstrate markedly higher concentrations of volatile hydrocarbons in diesel buses than in commuter trains. The ratios for specific traffic-emitted hydrocarbons, such as the carcinogenic benzene, were similar to those of total C_2-C_7 hydrocarbons. Several additional samples from less well matching trips or with incidental adjustable contributions from other sources confirmed that concentration ratios of 2-3 between bus and train were typical for traffic-emitted hydrocarbons. The higher concentrations in buses are explained by shorter distances to surrounding cars. The commuter train between Kållered and Göteborg partly runs very near to the motorway, and buses from Kungälv partly through low-traffic areas and on a high-speed motorway. For buses in dense traffic compared with trains without adjacent motor traffic, the ratios may be considerably higher than those reported.

Important parameters influencing the absolute concentrations are distance to surrounding cars, traffic density, and weather conditions. The high levels for the first day in Table 2 are explained by cold weather with a morning inversion, resulting in large cold-start emissions and slow vertical dilution.

In a previous study [4], exposure to traffic-emitted volatile aromatic hydrocarbons was demonstrated to be at least five times higher for private-car commuters than for train commuters. The higher ratio for cars than for buses does not necessarily imply more serious health hazards for private-car than for bus commuters, however. The reason is that bus passengers are specifically exposed to toxic pollutants such as nitrogen dioxide and non-volatile genotoxic compounds in diesel exhaust. Exposure occurs both at bus stops and inside the bus from exhaust entering the compartment at stops and during driving. The health hazards for bus passengers as compared to train commuters are therefore greater

Table 2. Bus to train hydrocarbon concentration ratios, and absolute inside-bus concentrations (µg/m^3), during four representative sets of matching commuter trips.

	Total C_2-C_7*		Benzene		Isoprene	
	Ratio	Conc.	Ratio	Conc.	Ratio	Conc.
Kållered - Göteborg, 12 April 07 - 09, 0°C, clear sky, weak NW	2.2	300	1.9	27.0	7	16,4
Kållered - Göteborg, 22 April 07 - 09, 10°C, cloudy, SW	3.5	136	3.1	11,7	18	17,4
Kungälv - Göteborg, 13 Dec 08 - 10, 10°C, rain, weak NE	2.5	176	2.3	17.0	5	7.8
Kungälv - Göteborg, 14 Dec 08 - 10, 0°C, cloudy, weak NW	2.0	197	1.8	15.0	11	13.3

*Except isoprene, ethane and propane which originate largely from other sources than motor vehicles. Proportions of other hydrocarbons checked to be representative of vehicle-polluted air.

than the hydrocarbon concentration ratios observed in this study might indicate.

The C_2-C_7 hydrocarbons in diesel exhaust are combustion-formed, with ethene as a major component and 1-alkenes as characteristic alkene isomers [9]. Somewhat increased proportions of ethene and 1-butene were indicated for certain bus samples, and significant contributions are to be expected at bus stations and bus garages. Complementary samples analyzed on a non-polar silicone column demonstrated much higher concentrations of C_{10}-C_{15} diesel oil hydrocarbons in buses than in commuter trains. The quantitative ratios may not be representative of those of the most toxic diesel exhaust components, however, and were therefore not determined.

Sources of Hydrocarbons

Different sources which may contribute significantly to pollutants inside vehicles are characterized in Table 3 with respect to hydrocarbon composition. Non-combusted hydrocarbons from exhaust emissions of petrol-fuelled cars normally constitute the major source quantitatively. Cold-start emissions may further increase the proportion of these hydrocarbons. The combustion-formed hydrocarbons should therefore be better indicators of the concentration levels of non-hydrocarbon

Table 3. Potential sources of non-methane volatile hydrocarbons inside vehicles.

Source	Hydrocarbons constituting >20% **, 5-20% *, and <5% of the total hydrocarbons from the specific source	Ref.
Petrol combustion products	ethene, ethyne ** propene, benzene * 1,3-butadiene, methylpropene	7, 8
Unburnt petrol components	C_4-C_7 alkanes, C_7-C_9 alkylbenzenes ** C_4-C_6 alkenes * benzene	7, 8
Petrol equilibrium vapour	C_3-C_5 alkanes ** benzene, 2-butenes *	10, 11
Diesel combustion products	ethene ** propene, ethyne, benzene * 1-butene	9
Tobacco smoke	isoprene ** propene, ethene * benzene, 1,3-butadiene	3, 12
Human expiration	isoprene **	13
Natural (fossil) gas	ethane **	14

exhaust components such as carbon monoxide.

Isoprene differs from all other reported hydrocarbons by varying percentage proportions (Table 1) and much higher bus to train concentration ratios (Table 2). Isoprene is a major volatile hydrocarbon in human expired air (13) and in tobacco smoke [3, 12], whereas its proportion is typically lower than 0.1% in vehicle-polluted urban air in Scandinavia [3]. Smoking is prohibited in the buses and commuter trains studied. It is therefore concluded that expired air from the passengers is the predominant source of isoprene in these vehicles. The concentrations were found to increase with the number of passengers. Lower compartment volumes and ventilation rates are likely to contribute to the higher levels in buses as compared to trains.

About 30 chromatograms from samples taken inside trains and diesel buses were carefully scrutinized for deviating proportions of specific hydrocarbons. Regional background contributions were found to be significant only for ethane and propane, as reflected in Table 1 by higher proportions for samples with low total hydrocarbon concentrations. Leakages of natural and light petroleum gas may contribute to the occurrence of ethane and propane. Exceptionally high proportions of butanes and pentanes, typical of petrol equilibrium vapour, were observed for duplicate samples from one bus trip. Service station emissions [10] may cause high concentrations of these hydrocarbons. Specifically increased proportions of methylbenzene in one bus and heptane in another were attributed to incidental contributions from different solvents.

Comparisons with the detailed hydrocarbon proportions of specific sources made it possible to sort out samples with significant contributions from occational non-typical sources. Similar intercomparisons also allowed samples with breakthrough losses of ethyne and samples with other analytical shortcomings to be sorted out. As a result, the bus samples selected for Tables 1 and 2 should reflect prevailing hydrocarbon proportions from traffic emissions better than a conventional statistical representation of all samples. It should be observed, however, that other sources were found to cause incidental additional exposure to hydrocarbons in buses.

REFERENCES

1. Forsberg B., Stjernberg N., Falk M., Lundbäck B. and Wall S., Air pollution levels, meteorological conditions and asthma symptoms. *Eur. Respir. J.*, **6**, 1109-1115 (1993).
2. Törnqvist M. and Ehrenberg L., On cancer risk estimation of urban air pollution. *Environ. Health Perspect.*, **102,** Suppl. 4, 173-182 (1994).
3. Barrefors G. and Petersson G., Assessment of ambient volatile hydrocarbons from tobacco smoke and from vehicle emissions. *J. Chromatogr.*, **643**, 71-76 (1993).
4. Löfgren L., Persson K., Strömvall A.-M. and Petersson G., Exposure of commuters to volatile aromatic hydrocarbons from petrol exhaust. *Sci. Total Environ.*, **108**, 225-233 (1991).
5. Chan C.-C., Spengler J.D., Özkaynak H. and Lefkopoulou M., Commuter exposures to VOCs in Boston, Massachusetts. *J. Air Waste Manage. Assoc.*, **41**, 1594-1600 (1991).
6. Chan C.-C., Özkaynak H., Spengler J.D. and Sheldon L., Driver exposure to volatile organic compounds, CO, and NO_2 under different driving conditions. *Environ. Sci. Technol.*, **25**, 964-972 (1991).
7. Barrefors G. and Petersson G., Volatile hazardous hydrocarbons in a Scandinavian urban road tunnel. *Chemosphere*, **25**, 691-696 (1992).
8. Löfgren L. and Petersson G., Proportions of volatile hazardous hydrocarbons in vehicle-polluted urban air. *Chemosphere*, **24**, 135-140 (1992).
9. Barrefors G., Volatile combustion-formed hydrocarbons in diesel exhaust. In: *Volatile organic compounds in the environment,* Proc. of the Int. Conf. Oct. 1993, London, Leslie G. and Perry R. (Eds), pp. 199-206.

10. Berglund P.M. and Petersson G., Hazardous petrol hydrocarbons from refuelling with and without vapour recovery. *Sci. Total Environ.*, **91**, 49-57 (1990).

11. Östermark U. and Petersson G., Assessment of hydrocarbons in vapours of conventional and alkylate-based petrol. *Chemosphere*, **25**, 763-768 (1992).

12. Löfroth G., Burton R.M., Forehand L., Hammond S.K., Seila R.L., Zweidinger R.B. and Lewtas J., Characterization of environmental tobacco smoke. *Environ. Sci. Technol.*, **23**, 610-614 (1989).

13. Löfroth G., Isoprene - a potential indoor indicator for environmental tobacco smoke. Excerpta Med. Intern. Congr. Ser., **860**, 147-153 (1989).

14. Field R.A., Goldstone M.E., Lester J.N. and Perry R., The variation in volatile organic compound concentrations in central London between 1986 and 1992. *Environ. Technol.* **15**, 801-812 (1994).