VOLATILE HYDROCARBONS IN AMBIENT AIR

Gas Chromatographic Assessment, Emissions and Human Exposure

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ABSTRACT

Hydrocarbons in ambient air constitute a potential health risk for a large number of individuals. The work reported in this thesis focusses on human exposure to volatile hydrocarbons in ambient air. The analytical determinations were made by adsorbent sampling followed by thermal desorption and gas chromatography. The concentrations of about 40 specific volatile alkanes, alkenes, alkadienes, alkynes and arenes from various sources were determined.

The observed hydrocarbon composition with large proportions of alkanes and alkylbenzenes in urban air demonstrates that human exposure in urban areas is caused predominantly by petrol-fuelled cars. Biomass combustion gives rise mainly to unsaturated hydrocarbons. Increasing combustion efficiency causes decreasing emissions but increasing proportions of benzene, ethene and ethyne. Tobacco smoke is characterized by high proportions of isoprene and 1,3-butadiene.

In two short urban road tunnels (500-700 m), the hydrocarbon concentrations were several times higher than in streets with similar traffic. It is concluded that long road tunnels with large numbers of vehicles must be questioned with regard to health hazards.

Observed concentrations of hydrocarbons indicate that typical ratios between roof level, street-side, and car coupés are 1 : 5 : 10. Passenger exposure to traffic emitted volatile hydrocarbons is 2-3 times higher for diesel bus commuters than for train commuters. From these comparisons, it is evident that people's activities, in terms of their time spent close to traffic sources, will strongly influence their hydrocarbon exposure dose.

A comparison of urban air monitoring of benzene, toluene and *p*-xylene by the gas chromatographic technique used in this work and by differential optical absorption spectroscopy (DOAS) demonstrated that DOAS measurements were unreliable at the concentration levels prevailing in a city like Göteborg.

Key words: Hydrocarbons, benzene, ethene, butadiene, gas chromatography, adsorbent sampling, vehicle emissions, biomass burning, tobacco smoke, urban air, human exposure

List of publications

This thesis is based on the following articles, referred to by the Roman numerals I-VII.

I **Volatile hazardous hydrocarbons in a Scandinavian urban road tunnel**
G. Barrefors and G. Petersson (1992)
Chemosphere **25**, 691-696.

II **Assessment of ambient volatile hydrocarbons from tobacco smoke and from vehicle emissions**
G. Barrefors and G. Petersson (1993)
Journal of Chromatography **643**, 71-76.

III **Volatile combustion-formed hydrocarbons in diesel exhaust**
G. Barrefors (1993)
In G. Leslie and R. Perry (Editors), Volatile organic compounds in the Environment, London, pp 199-206.

IV **Exposure to volatile hydrocarbons in commuter trains and diesel buses**
G. Barrefors and G. Petersson (1996)
Environmental Technology (in press).

V **Assessment by gas chromatography and gas chromatography - mass spectrometry of volatile hydrocarbons from biomass burning**
G. Barrefors and G. Petersson (1995)
Journal of Chromatography **710**, 71-77.

VI **Volatile hydrocarbons from domestic wood burning**
G. Barrefors and G. Petersson (1995)
Chemosphere **30**, 1551-1556.

VII **Monitoring of benzene, toluene and p-xylene in urban air with differential optical absorption spectroscopy technique**
G. Barrefors (1996)
The Science of the Total Environment (in press).

In addition to the publications in this thesis, the author has also contributed to the following papers, which are relevant to the work but not included in this thesis.

1. **Ambient solvent hydrocarbons from the gluing of table tennis bats.**
   Ramnäs O., Barrefors G. and Petersson G. (1994)
   Toxicol. Environ. Chem. **47**, 1-6.

2. **Air pollutants in road tunnels**
   Barrefors G. (1996)
   The Science of the Total Environment (in press).

3. **Gas chromatographic assessment of volatile furans from birchwood smoke.**
   Barrefors G., Björkqvist S. and Petersson G. (1996)
   (manuscript submitted for publication).

4. **Volatile hydrocarbons from the burning of grass and straw.**
   Barrefors G. and Petersson G. (1996)
   (manuscript intended for publication).

CONTENTS

Page:

1. INTRODUCTION

The present work was carried out at the department of chemical environmental science during the period 1991 – 1996. The main reason for starting the project was the serious health risks associated with human exposure to potentially carcinogenic volatile hydrocarbons. The detailed characterization of hydrocarbons emitted from road traffic, biomass combustion and tobacco smoke is of great importance for the assessment of human exposure.

In this thesis, results published internationally in seven articles (**I-VII**) are included. Four of the articles (**I-IV**) deal with emissions from road traffic. One of them includes assessment of hydrocarbons in tobacco smoke (**II**). Two articles deal with emissions from biomass combustion (**V,VI**). Ambient air monitoring of benzene, toluene and p-xylene by differential optical absorption spectroscopy (DOAS) is evaluated in one study (**VII**). A revised version of an article dealing with volatile hydrocarbons in long road tunnels is included in this thesis (chapter 5) as a case study of high exposure levels.

The present work is a continuation of earlier work carried out at the department of chemical environmental science on determination of volatile hydrocarbons in urban air (1,2). Related research at the department includes studies of improved, alkylate-based, petrol (3-5). Experience from the assessment of reactive terpene hydrocarbons has been valuable (6).

2. GAS CHROMATOGRAPHIC ASSESSMENT

Adsorbent sampling followed by thermal desorption and gas chromatography has long been a common technique for determinations of volatile hydrocarbons in air. The gas chromatographic system used in this work is outlined in Figure 1. The analytical method used was described in detail for different applications in two articles (**II, IV**).

The use of similar gas chromatographic methods has been reviewed in several studies (7-12).

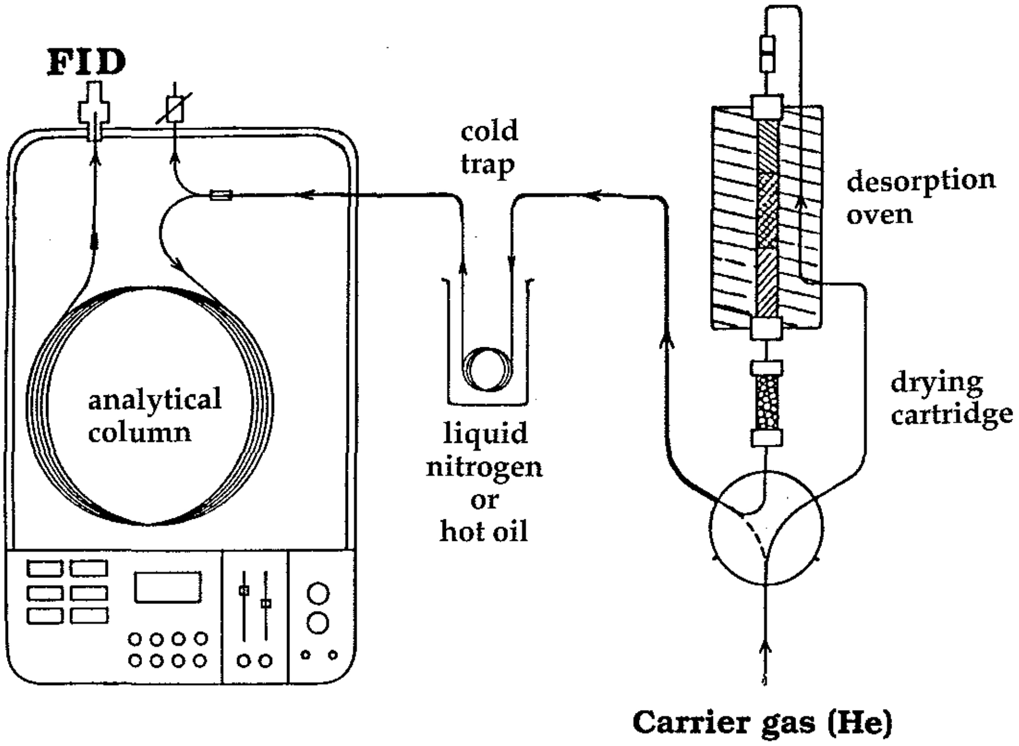


Figure 1. The gas chromatographic system used for assessment of volatile hydrocarbons.

2.1 Sampling

2.1.1 Adsorbent cartridges

For air pollution analysis, the sampling procedure is a key step to reliable measurements. When adsorbent sampling is used, the Tenax porous polymer is usually preferred for sampling of hydrocarbons with more than 5 carbon atoms (12,13). When hydrocarbons with 2 to 5 carbon atoms are to be measured, stronger adsorbents like Carbotrap and Carbosieve S-III are used (13,14).

In this work, adsorbent cartridges were prepared with the following three as adsorbents of increasing strength: Tenax TA, Carbotrap, and Carbosieve S-III. After preparation, the adsorbent cartridges were conditioned in a helium gas flow of 30-40 ml/min at 280°C for more than one hour. Prior to each sampling they were conditioned in a similar way for 10 min.

2.1.2 Sampling with air pumps

A defined volume of air was pumped at a rate of 10 to 50 ml/min through the triple-layer adsorbent cartridges with personal air pumps (active sampling). A low sampling rate has been observed to favour the adsorption efficiency (7). Different sampling rates for duplicate samples were used to check losses by breakthrough and by decomposition of reactive hydrocarbons, as previously described (15).

The preferred sampling pumps (low-flow, Accuhaler 808 Model, MDA, Linconshire, IL, USA) work with constant strike volume and strike counting. The flow rate can easily be adjusted by exchanging a flow restrictor. With this technique, the sampling volume can be determined with high accuracy.

For all other pumps examined, the sampling volume was determined by the flow rate and sampling time. For these pumps the accuracy was found to be poorer since the flow rate can be affected by several parameters such as humidity (enrichment of water on the adsorbent) and temperature.

2.1.3 Other sampling methods

Complementary air sampling in a gastight syringe was used for the characterization of hydrocarbons emitted from biomass burning (**V, VI**). The almost identical results for gas syringe sampling and adsorption sampling confirm that no significant losses occur neither by chemical decomposition of reactive hydrocarbons nor by breakthrough on the triple-layer adsorption cartridges (**VI**). However, aggressive combustion products may give rise to extensive losses of reactive alkenes on the triple-layer adsorption cartridges, as demonstrated for diesel exhaust (**III**).

Whole air sampling, so-called grab sampling, in stainless steel canisters is a sampling method commonly used (16-20). The introduction of passivated SUMMA polished canisters has been reported to reduce problems with sample stability (21-23).

For passive sampling (diffusion sampling), the sampling process is controlled by the adsorption properties of the adsorbent and by the diffusion processes. The main application of passive samplers is measurements in workplace air and monitoring of urban air pollutants (24). For passive sampling, problems with reliability are different compared to active sampling on adsorbents (25-28).

2.2 Thermal desorption and cryofocusing

The sampled hydrocarbons were released from the adsorbent cartridge by thermal desorption (230 °C, 14 min, 20-30 ml/min).

To prevent peak broadening, the desorbed compounds were cryofocussed in a cryotrap (an empty fused silica column, ~5 m, i.d. 0.32 mm) in liquid nitrogen (-196°C). When the desorption was completed, the trap was manually moved into an oil bath (150°C), transferring the compounds as a narrow band onto the column.

Adsorption of water on Carbosieve S-III may cause plugging of the cryotrap for humid samples. To prevent plugging and to improve the analytical performance, a tube (100 x 4 mm i.d.) filled with a drying agent (magnesium perchlorate) was inserted before the cryotrap. The drying tube was exchanged regularly, and was not found to cause any losses of the determined hydrocarbons, which has also been reported by Matruska et al. (29). A widely used drying device in cryotrapping methods for analysis of gaseous samples is the Naflon membrane dryer, which has been reported to cause losses (30) and contamination (11), however.

2.3 Gas chromatography

2.3.1 Separations

The analytical separations were performed on a fused silica Al_2O_3/5% KCl PLOT column (50 m x 0.32 mm i.d., Chrompack). The major advantages of the this

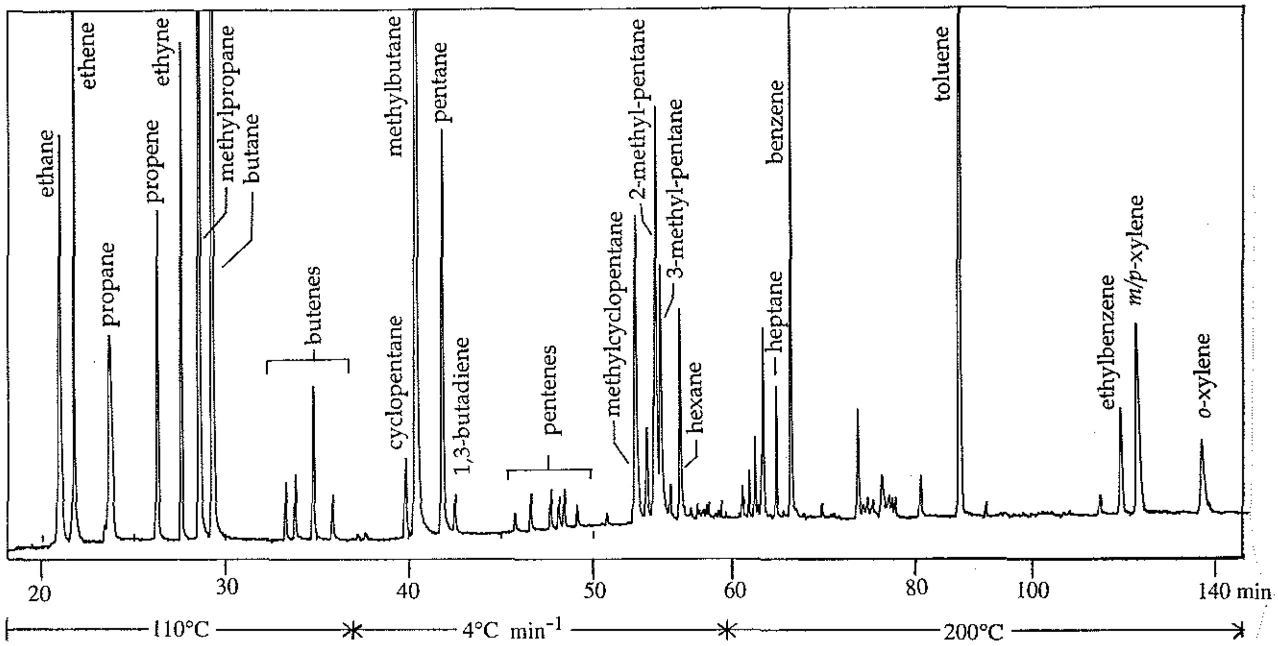


Figure 2. Gas chromatographic separation on the Al_2O_3/5%KCl PLOT column of volatile hydrocarbons sampled in urban air near to road traffic. The temperature program was: 30°C to 110°C with 10°C/min; 14 minutes at 110°C; 110°C to 200°C with 4°C/min; 200°C isothermal.

column were demonstrated as early as 1984 at our department (31). It was then shown to be a very efficient column for the separation of C_1–C_9 hydrocarbons, and it has been used in many projects at the department since then. Aluminium oxide retains polar compounds like alcohols and aldehydes very strongly. These compounds will not elute from the column even at 200°C, which is the maximum temperature recommended.

As described by de Zeeuw et al., there is a wide range of possible applications for the Al_2O_3/KCl PLOT column (32). The main drawback is that water may interfere by decreasing the retention times. Schmidbauer and Oehme reported that water gives rise to a deteriorated peak shape of early eluting compounds (11). However, evaluation of the analytical performance of the Al_2O_3/KCl PLOT column in this work indicated that these problems were caused by methanol. Water was found to interfere with the C_6 and higher hydrocarbons.

A non-linear temperature program further improved the separation of certain hydrocarbons. To ascertain a clear-cut separation of as many hydrocarbons as possible a slow program was chosen (**II, IV, V, VI**). For routine determinations of the major hydrocarbons, the time required can be much decreased by using a rapid linear temperature program (**III**, 33).

The retention times can also be reduced by using a higher carrier gas flow. The optimum velocities are much higher for the Al_2O_3/KCl PLOT column than for liquid-phase coated capillaries. The used helium flow of 30 cm/s can be doubled with only a minor decrease in separation efficiency (32).

The chromatogram in Figure 2 illustrates the separation of hydrocarbons sampled in urban air.

2.3.2 Detection

For the quantitative determinations, the Flame Ionization Detector (FID) was used. The FID is sensitive to practically all organic substances. Since the detector response depends on the number of carbon atoms reaching the detector, it is necessary to use correction factors for compounds with heteroatoms. Traditionally, response factors are given relative to heptane (34,35). The response is almost similar for most volatile hydrocarbons, For benzene, however, the high degree of unsaturation results in a 12% higher response.

The limit of detection in chromatography has been defined as the quantity of analyte that produces a signal equal to three times the standard deviation of the gross blank signal (36). For the GC-FID system with thermal desorption and cryofocusing, this generally corresponds to 5-50 pg of a hydrocarbon. Hence, the lowest detectable concentration should be 5-50 ng/m^3 in an air sample of 1 litre.

The Photo Ionization Detector (PID) is a selective detector with a sensitivity approximately one order of magnitude higher for unsaturated C_3-C_5 hydrocarbons compared to the FID (1). The use of PID and FID in parallel has been reported to be useful for the assesssment of C_3-C_5 alkadienes and alkenes (37,38).

2.3.3 Calibrations

Calibration was performed using gas standards prepared in the laboratory as described by Westberg et al. (39). A mixture (gravimetric quantities) of several liquid hydrocarbons was injected into a known volume of air. Since this method permits injection into the gas chromatograph after sampling on adsorbents, it was regarded as more accurate than calibration using gas standards with direct injection via a gas sampling loop as described by Löfgren et al. (37).

It should be noted that it is extremely difficult to prepare and store hydrocarbon standards at low ppb levels. Furthermore, it is difficult to adjust instrument performance to an undiluted single component gas standard when the gas chromatograph is operated in a mode appropriate for measuring ambient hydrocarbon levels.

2.4 Gas chromatography - Mass spectrometry

Mass spectrometric studies were made on a Varian Saturn II ion trap GC-MS instrument. It proved to be a valuable tool for the identification of a wide range of different hydrocarbons. In several applications, two compounds coelute on the Al_2O_3/5% KCl PLOT column in spite of a slow temperature program. In such cases the mass selective detection of the mass spectrometer was necessary for correct identification and quantitative assessment.

Mass selective detection of sampled environmental air pollutants has been preferred for routine, quantitative assessment of hydrocarbons in some studies (40-42).

2.5 Continuous monitoring

2.5.1 Automatic GC systems

If the gas chromatographic measurements are made with respect to a few selected hydrocarbons, continuous automatic determination has proved to be reliable. Persson and Berg determined C_2–C_4 hydrocarbons in the air by automatic solid sorbent sampling and gas chromatography (46). A system for automatic sampling and analysis of background levels of C_2–C_5 hydrocarbons has been described by Mowrer and Lindskog (47). Automatic systems for contiuous monitoring of speciated C_2–C_{10} hydrocarbons have also been described (48-50). The results from these instruments are less reliable, however (45).

For the purpose of continuous monitoring of concentration trends in ambient air, passive sampling on adsorbents with subsequent GC analysis appears to be a reliable and cost-effective method. The thermal desorption and cryofocusing can then be performed by a commercial automatic instrument (Perkin Elmer ATD 50).

2.5.2 Differential Optical Absorption Spectroscopy (DOAS)

The Differential Optical Absorption Spectroscopy technique (DOAS) is based on the fact that all compounds absorb light at a specific wavelength. Under some circumstances it is possible to calculate the concentration of a compound from the measurement of this absorption (51,52). The DOAS instrument (53) consists of emitter (xenon lamp), receiver and analyzer (spectrometer and computer). In several studies, DOAS measurements of nitrogen dioxide, sulphur dioxide, and ozone have been shown to be in excellent agreement with concurrently operated fixed-point monitoring by other methods (54).

The performance of a commercial DOAS system was evaluated for semi-continuous ground-based measurements of benzene, toluene, and p-xylene in Göteborg (**VII**). It was concluded that the concentrations of hydrocarbons prevailing in Göteborg cannot be reliably determined by the instruments used. Similar results are reported from a comprehensive study in London (44).

2.6 Evaluation of measurements

Strong quality control of ambient air hydrocarbon measurements is recommended since erroneous measurements have been demonstrated in several air monitoring programs (**VII**, 43-45).

Normally, a great deal of information is received from environmental measurements using gas chromatography. Every chromatogram has to be studied very carefully to ensure correct identification and integration of each peak. Often each measurement is unique in some respect because the results can be affected by so many evident or unforeseen parameters. To isolate a measurement situation to such an extent that a large number of measurements are comparable in all respects can in many cases be difficult. Common sources of error are contributions from occasional non-typical sources, identification errors due to complicated chromatograms, effects due to meteorological parameters, and analytical deficiencies.

In the present work, the measurements were carefully selected to be well representative of a given situation. In this way, much information was obtained by detailed studies of each chromatogram and errors were avoided by checking against chromatograms from duplicate samples. When results from a large number of measurements are put together in a routine manner, there is a great risk that much information is lost.

3. EMISSIONS

3.1 Source characterization

In this thesis, source profiles consisting of more than 30 volatile hydrocarbons emitted from road traffic, small-scale biomass combustion and tobacco smoking are reported.

Detailed characterization of C_2–C_{10} hydrocarbons measured in a road tunnel (**I**) represents on-road emissions from over 1000 in-use vehicles on each sampling occasion. The proportions of volatile hydrocarbons determined for different kinds of biomass combustion (**V, VI**) demonstrate the major importance of combustion efficiency. The high concentrations of volatile hydrocarbons measured in indoor air polluted by tobacco smoke (**II**) confirm the significant contribution of passive tobacco smoking to human exposure.

In Table 1, source fingerprints consisting of a total of 44 C_2–C_8 volatile hydrocarbons emitted from road traffic, efficient and inefficient wood burning, as well as tobacco smoking are presented. In source reconciliation analysis of air samples, observed differences in hydrocarbon profiles have been used to apportion air pollution to specific sources (55-60).

3.2 Vehicle emissions

3.2.1 Proportions of hydrocarbons

The composition of volatile hydrocarbons emitted from road traffic was studied by measurements in an urban road tunnel (**I**). The determined proportions of volatile non-methane hydrocarbons reflect the composition of exhaust gases from the vehicles passing the tunnel during air sampling (~2000 vehicles, ~10% heavy-duty diesel vehicles). At the time of the study, an estimated proportion of almost 50% of the private cars were equipped with three-way catalytic converters.

The chromatogram in Figure 3 illustrates the source fingerprint of C_2–C_8 hydrocarbons emitted from road traffic. Since approximately 80% of the determined hydrocarbons consisted of unburnt saturated and aromatic fuel hydrocarbons, the proportions of hydrocarbons from urban road traffic reflect the

Table 1. Proportions (% weight) of C_2-C_8 hydrocarbons emitted from road traffic, wood burning and tobacco smoking.

		road traffic emissions	efficient wood burning	inefficient wood burning	tobacco smoke
Alkenes					
C2	Ethene	7.8	30.0	34.7	11.1
C3	Propene	2.8	4.0	11.8	9.6
C4	*trans*-2-Butene	0.3	0.1	0.7	1.0
	1-Butene	0.6	0.7	2.0	2.8
	Methylpropene	1.1	0.2	1.1	2.7
	cis-2-Butene	0.2	0.1	0.5	0.7
C5	Cyclopentene	0.1	0.0	0.2	0.3
	3-Methyl-1-butene	0.1	0.1	0.2	0.7
	trans-2-Pentene	0.2	0.1	0.3	0.4
	2-Methyl-2-butene	0.3	0.0	0.3	2.7
	1-Pentene	0.2	0.2	0.4	1.2
	2-Methyl-1-butene	0.2	0.0	0.3	1.3
	cis-2-Pentene	0.1	0.0	0.2	0.3
C6	1-Hexene	0.1	0.2	0.3	1.3
	2-Methyl-2-pentene	0.1	nd	nd	0.4
C7	1-Heptene	0.0	0.1	0.2	0.6
C8	1-Octene	0.0	0.1	0.3	0.2
Alkadienes					
C3	Propadiene	0.2	0.2	0.4	0.2
C4	1,2-Butadiene	0.0	0.0	0.0	0.1
	1,3-Butadiene	0.7	1.0	2.3	3.2
C5	Isoprene	0.0	0.1	0.3	29.2
	Cyclopentadiene	0.0	0.4	1.3	nd
	cis-1,3-Pentadiene	0.0	0.0	0.0	0.2
	trans-1,3-Pentadiene	0.0	0.1	0.3	0.4
Alkynes					
C2	Ethyne	5	27	7	1
C3	Propyne	nd	1.0	1.5	0.4
C4	2-Butyne	0.0	0.1	0.2	nd
	Butenyne	0.0	0.5	0.4	0.2
	1-Butyne	0.0	0.1	0.1	nd
Alkanes					
C2	Ethane	1	5	14	3
C3	Propane	0.5	0.4	3.0	4.0
C4	Methylpropane	2.8	0.0	0.0	0.5
	Butane	4.8	0.1	0.7	1.7
C5	Methylbutane	7.1	0.1	0.1	0.3
	Pentane	3.2	0.1	0.2	0.5
C6	Methylcyclopentane	1.8	0.0	0.0	0.0
	2-Methylpentane	2.8	0.0	0.0	0.0
	3-Methylpentane	2.4	0.0	0.0	0.0
	Hexane	2.0	0.0	0.1	0.0
Arenes					
C6	Benzene	9.1	20	7.4	3.9
C7	Methylbenzene	17.5	3	3.2	6.4
C8	Ethylbenzene	3.7	0.5	0.4	0.7
	Dimethylbenzenes	14.5	0.7	0.9	2.8
	Styrene	0.0	1.0	0.6	nd

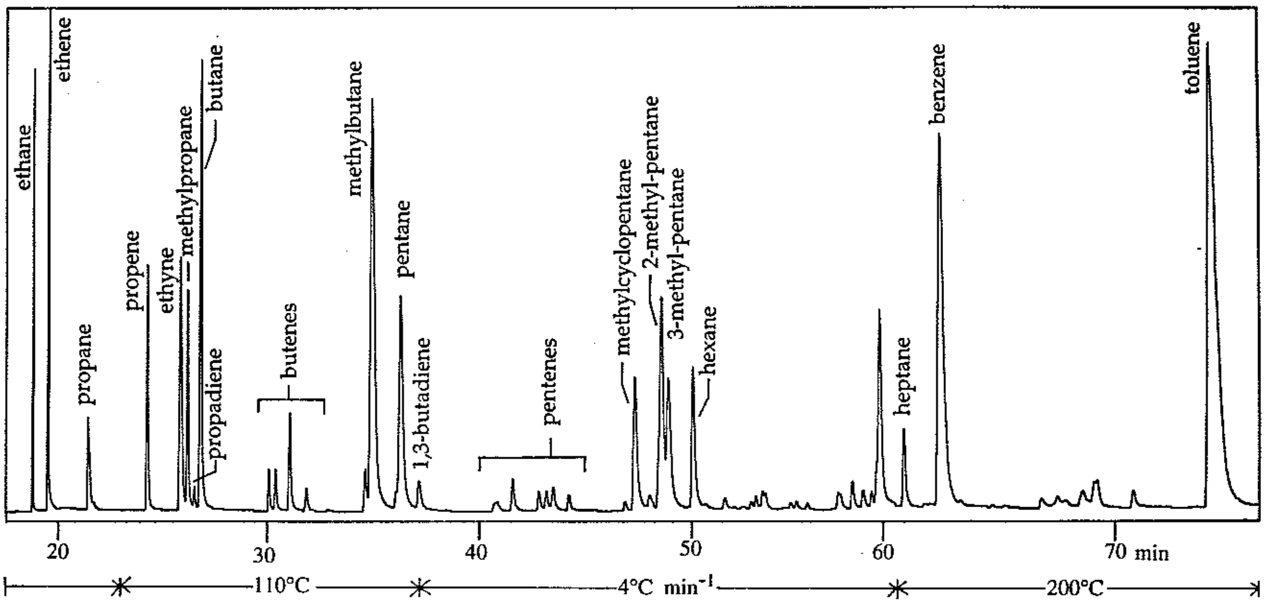


Figure 3. Gas chromatographic separation of volatile hydrocarbons from traffic in an urban road tunnel (Tingstad Tunnel, Göteborg).

composition in the petrol used. The C_2–C_3 hydrocarbons and 1,3-butadiene are products of combustion. In Sweden, petrol is not allowed to contain more than 5% (v/v) benzene. Since benzene is also a combustion product, its proportion is elevated in the exhaust compared to other petrol components.

The C_2–C_8 hydrocarbons given in Table 1 accounted for more than 90% of all C_2–C_8 hydrocarbons measured in the tunnel air and were estimated to constitute ~90% of all emitted C_2–C_{10} hydrocarbons (I). In addition to these C_2–C_{10} hydrocarbons, methane (5-20%), less volatile hydrocarbons (>C_{10}, ~1%), and oxygenates (~1%) contribute to the total hydrocarbon emission (THC) from petrol light duty vehicles (61-63).

3.2.2 Hydrocarbon emission factors

The normal way to determine vehicle emissions is to use scheduled driving cycles on a dynamometer in a laboratory. Ingalls calculated emission factors based on measurements in a road tunnel in Los Angeles, USA (64). This study indicated that dynamometer tests underestimate the real-world emissions by a factor of 2-4.

Table 2. Emission factors (mg/km) estimated from tunnel air measurements[a], and from dynamometer tests for a petrol-fuelled car with and without a catalyst (63) and for a heavy-duty (HD) diesel bus (66).

	THC	benzene	1,3-butadiene	ethene	propene	toluene
Tunnel air study	900[b]	60	6	65	27	123
Petrol car[c]	1460	97	8	89	48	198
Petrol car, cat.[c]	140	21	0.6	8	4	30
Diesel bus (HD)	1300	7	nd[d]	33	8	5

a) The concentration at the tunnel exit (1530 $\mu g/m^3$ C_2–C_{10}, **I**) was assumed to be twice that at the entrance. The air flow has been assessed to 8 m/s (67) under similar conditions (vehicle speed: 70 km/h); Tunnel length: 436 m; Tunnel area: 56 m^2; Number of vehicles/h: 3200. The calculated emission factors are judged to differ from the true emissions by less than a factor of three.
b) The C_2–C_{10} hydrocarbons are estimated to make up 90% of THC.
c) Volvo passenger car, 2.3 litre fuel-injected petrol engine with lambda sensor.
d) nd - not determined

Based on the measurements made in the tunnel air (near the exit) in Göteborg, emission factors of individual hydrocarbons (mg/km) were estimated for the fleet of vehicles passing through the tunnel during air sampling (Table 2). The calculations were performed as described by Pierson et al. (65). Of the tabulated hydrocarbons, ethene, propene and 1,3-butadiene are important combustion-formed hydrocarbons, whereas benzene and toluene are petrol components.

Emission factors of THC, determined in dynamometer tests are reported to be 0.05 – 2.0 g/km for petrol light-duty vehicles equipped with a three-way catalyst (61-82), and 0.5 – 2.5 for vehicles without a catalyst (61-63, 80-83). The estimated road traffic emission of THC, based on the tunnel air measurements in Göteborg, indicates on-road emissions of the same order of magnitude as those observed in dynamometer tests (Table 2).

High emission rates determined in several ”on-road” studies (64,84-88) have been suggested to be caused by high emissions from a small fraction of vehicles with malfunctioning engines (high emitters), as well as from vehicles with cold engines

(65). High proportions of unburnt fuel hydrocarbons in these studies support this conclusion.

High-emitting automobiles

The remote-sensing IR technique offers the ability to trace high-emitting automobiles by continuously measuring real-world on-road automobile THC and carbon monoxide (CO) exhaust emissions (89-95). Measurements with this technique have been made in several regions around the world. A comparison of fleet profiles of THC and CO emissions rate in 22 different cities, indicates higher emissions than in Göteborg for most cities (89). For all the fleets, it was concluded that the average emissions were dominated by a small percentage of high emitters.

Catalyst effects

In order to reduce tail-pipe emissions of regulated pollutants (HC, CO, NO_x and particles), modern automobiles are equipped with a three-way catalyst (TWC). The catalysts also alter the composition of the emitted hydrocarbons significantly, as illustrated by the figures in Table 2. In the catalyst, the order of reactivity for various classes of hydrocarbons (HC) has been observed to be: methane (least reactive) < saturated HC < aromatic HC < unsaturated HC (62, 96-98). Furthermore, the reactivity has been observed to increase with chain length, which is particularly noticeable after ageing of the catalyst (33,63). Deactivation of the catalyst will occur due to high temperatures and catalyst poisons (99).

Cold-start emissions

High emissions of HC and CO are caused by the low combustion efficiency in a cold engine (66,68,100). It has been demonstrated that modern cars prior to catalyst ”light off” (~300°C) generate pollutant emissions comparable to those of pre-catalyst vehicles. The average cold start emission of HC for vehicles with TWC was found to be 2.5 gram at standard test temperature (+20°C) of the urban driving cycle, 17 gram at -7°C and as high as 27 gram at -15°C (100). The cold start emission of older non catalyst cars was found to be 5.4 gram at standard test temperature (+20°C) and 16 gram at -7°C (100).

Fuel composition

Following the increasing efforts reduce emissions of hazardous pollutants, more attention has been given to the relationships between fuel composition and tailpipe emissions. Studies of combustion products from single-component fuels have demonstrated that the total engine out HC emission increased as the average molecular weight of the fuel increased (101-107). The benzene emission increases as aromatic content of the fuel increases, and the emission of 1,3-butadiene seems to increase as the content of alkenes in the fuel increases (71-73,101,108-111). The addition of oxygenated fuel components (such as MTBE and alcohols) has been reported to lower the HC emission (71-73,75,76,81,101).

Since sulphur has been observed to inhibit the oxidation of the hydrocarbons in the catalyst (101), a lowered content of sulphur-containing compounds in the fuel (such as thiophenes) will lower not only the emission of sulphur dioxide, but also the HC emission. A reduction from 450 to 50 ppm of sulphur in the fuel has been reported to lower the HC emission by 15% (101).

Diesel exhaust

Diesel exhaust was demonstrated to be composed of volatile hydrocarbons with a significantly different composition compared to petrol exhaust (**III**). The high proportion of 1-alkenes (especially ethene) in diesel exhaust is explained by the basic combustion chemistry of straight-chain paraffinic diesel fuel hydrocarbons (**III**). In addition to the combustion-formed C_2–C_7 hydrocarbons, heavier diesel fuel hydrocarbons were observed to be released in approximately similar amounts (**III**). An increased occurrence of C_{10}– C_{12} alkanes is a specific indication of an increased contribution of diesel exhaust to urban air pollution (112-114).

The emission factors reported in Table 2, for a heavy-duty diesel bus, were measured on a dynamometer using the bus test cycle developed at the University of Braunschweig, Germany (65). The major importance of engine type, fuel, speed and load should be considered when emission factors for HD diesel vehicles are compared (115,116).

In Sweden, a switch in recent years to improved reformulated diesel fuels has reduced the emissions of regulated pollutants and especially polycyclic aromatic compounds (PAC) (117-123). A further reduction of pollutants from heavy-duty diesel vehicles is gained by the use of an oxidation catalyst and a particulate trap (124,125).

3.2 Biomass combustion

Measurements were performed for the purpose of characterizing the emissions of a wide range of volatile hydrocarbons from incomplete combustion of biomass (**V, VI**). The proportions of volatile hydrocarbons was found to depend highly on the combustion efficiency, as demonstrated in Table 1, and to some extent on the material burned. The combustion efficiency may be defined as the molar emission ratio between carbon dioxide (CO_2) and the sum of CO_2 and CO (126).

3.2.1 Efficient combustion

Efficient biomass burning is characterized by high temperature and a rapid consumption of fuel. The emissions are low for products typical of incomplete combustion, such as hydrocarbons, particulates and CO. The combustion efficiency was found to be higher than 99% when burning dry modified biomass fuels in modern stoves. For flaming combustion in cookstoves, and for open burning, the combustion efficiency has been reported to be 93-98% (127-134). High temperature favours the formation of thermally stable hydrocarbons such as ethyne and benzene. The chromatogram in Figure 4 illustrates the high proportions of ethene, ethyne and benzene from efficient wood burning in a modern stove.

3.2.2 Inefficient combustion

During glowing and smouldering, the combustion is inefficient and incomplete due to low temperature and oxygen deficiency, which causes high emissions of a great number of substances (135-137). In several small-scale experiments with glowing and smouldering biomass, the combustion efficiency was found to be 80-90%. A combustion efficiency as low as ~70% was observed by Sandberg et al. (138).

3.2.3 Natural fires

The demonstrated impact of combustion efficiency on hydrocarbon emissions from biomass burning is confirmed by measurements from large-scale forest and grassland fires (139-146). Ground sampling of hydrocarbons released from natural fires reflects the conditions of smouldering, whereas airborne sampling rather reflects the conditions of flaming combustion. The hotter plumes from flaming combustion rises higher into the atmosphere than those from smouldering fires (129). The proportions of hydrocarbons determined by ground sampling from savanna fires in Africa, reported by Bonsang et al. (147), are remarkably similar to

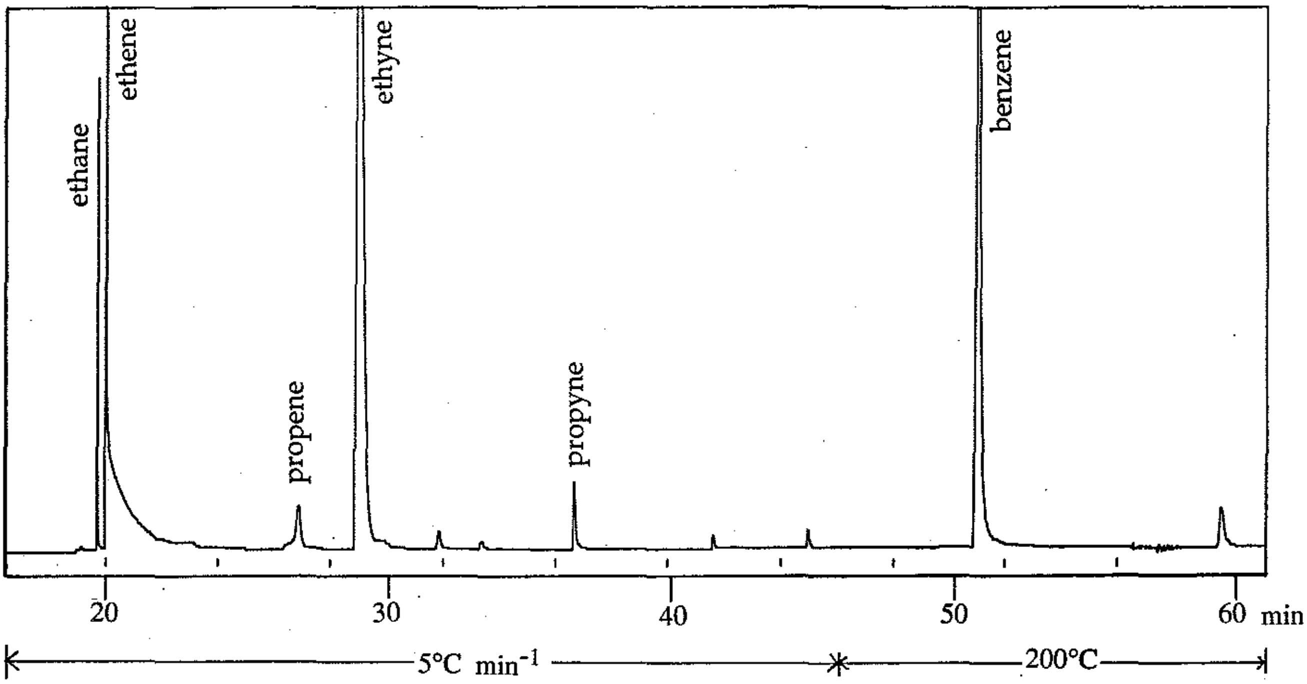


Figure 4. Gas chromatographic separation of chimney-sampled non-methane hydrocarbons from efficient burning of dry birchwood in a modern stove.

the proportions determined from small-scale grass and twig burning (**V**). Similar proportions and remarkably hydrocarbon concentrations were observed in field studies of grass burning in Sweden (148).

3.2.4 Methane emissions

Analysis of gaseous samples without enrichment on adsorbents permitts the determination of methane on the aluminium oxide column, as illustrated by the chromatogram in Figure 5 (**VI**). The emission ratio of methane to carbon dioxide was approximately 0.01% for efficient combustion in a modern stove. In the small-scale experiments, the emission ratio was 0.2 to 0.4% for inefficient combustion. In several different experiments, the methane emissions were lower than the total C_2–C_8 hydrocarbon emission (~40%). Lobert et al. report emission ratios of the same order (130), while global estimates indicate a higher proportion of methane (156,157).

Methane is a potent greenhouse gas. In the time horizon of 20 years, one mole of methane absorbs 21 times more radiation than one mole of CO_2 (128). As the most

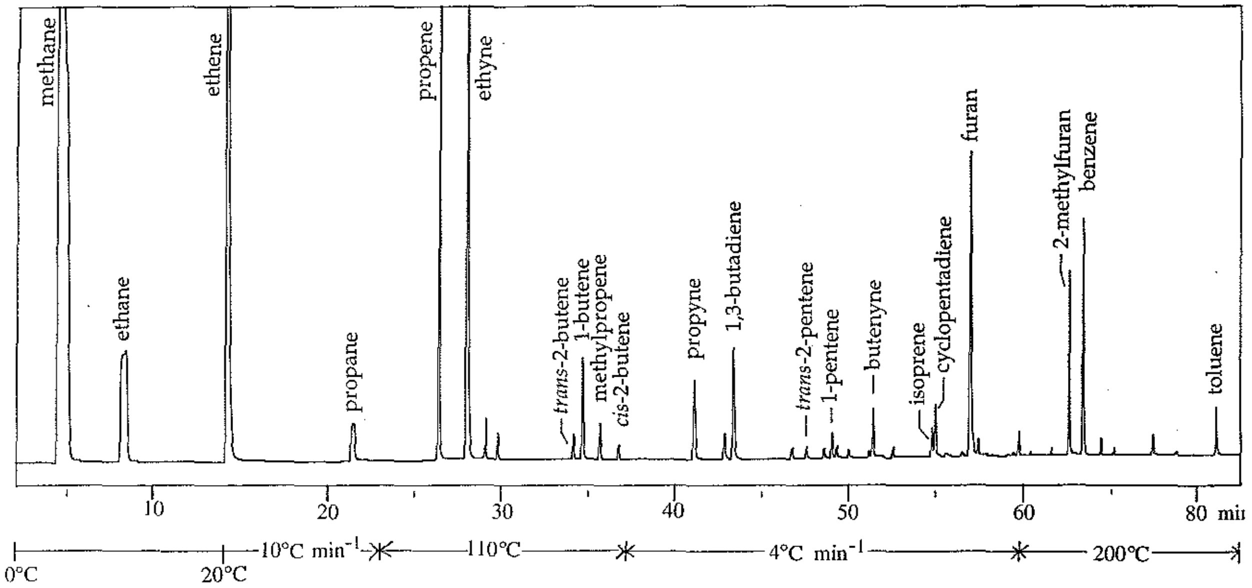


Figure 5. Gas chromatographic separation of hydrocarbons (including methane) from small-scale burning of dry birchwood (gaseous sample, 3.2 ml injected).

abundant hydrocarbon released from biomass combustion, methane has a large impact on the global greenhouse effect (127,128,149).

3.2.5 Furans

Non-hydrocarbon compounds are normally not eluted from the aluminium oxide column, but observed exceptions are furan and methylfurans which appear as prominent peaks among the hydrocarbons in the chromatograms (Figure 5) of biomass smoke samples (**II, V, VI**). Mass spectrometric analysis of samples from different kinds of biomass burning was used to identify the 15 most prominent furans, reported by Barrefors et al. (150). It was found that high emissions of furan and methylfurans are to be expected only from glowing and smouldering combustion.

3.2.6 Carbon dioxide

Optional determination of CO_2 and CO was achieved by gas chromatographic analysis using a thermal conductivity detector (**V, VI**). The concentration ratios of HC to CO_2 and CO to CO_2 were used for assessment of combustion efficiency. The basic changes in relative proportions on a scale from inefficient smouldering to

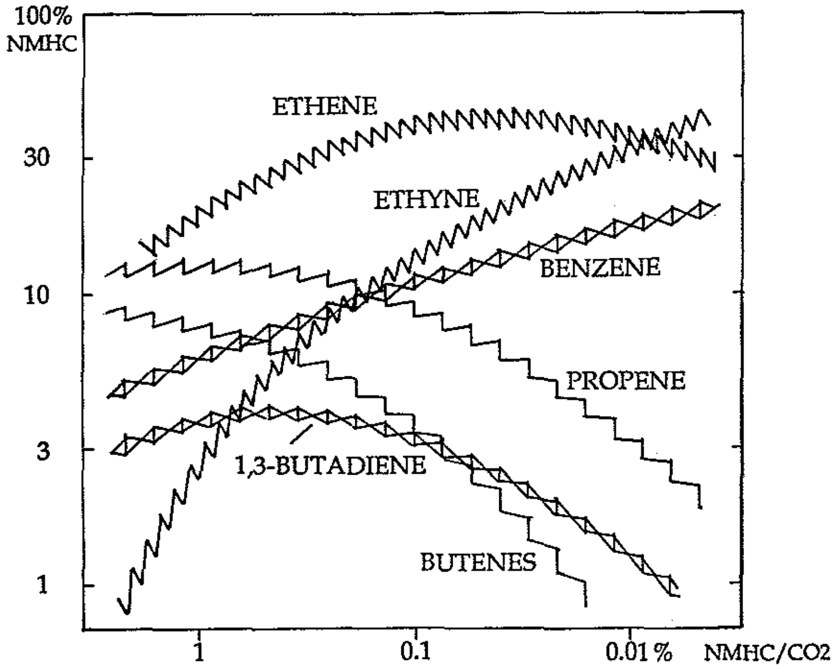


Figure 7. Approximate percentage proportions of prominent specific hydrocarbons relative to total non-methane volatile hydrocarbons from biomass burning. The decrease in hydrocarbon to CO_2 ratio from 1 to 0.01% reflects a shift from smouldering to flaming combustion.

efficient flaming combustion are indicated in Figure 7 for hydrocarbons of particular interest.

3.2.7 Fuel character

In the study of emissions from biomass burning it was found that the hydrocarbon compositions for different kinds of biomass were remarkably similar (**V, VI**). The major exception was the high proportions of isoprene in tobacco smoke, probably linked to a high content of terpenoid components in tobacco (**II**). For major condensible compounds the emissions from biomass combustion have been reported to be much more dependent on the fuel chemistry (151-153).

Determination of specific polycyclic aromatic hydrocarbons and oxygenated organic compounds has been used to distinguish between wood combustion and vehicle emissions, as sources of urban air pollution (154). Wood combustion was found to account for as much as 73% of the extractable organic matter (EOM) as measured during one year in Boise, Idaho, USA (155). However, this fraction only

Table 3. The contribution of biomass burning to global emissions (156,157)

Species	Biomass burning (Tg element/year)	All sources (Tg element/year)	Biomass burning %
CO_2 (gross)	3500	8700	40
CO_2 (net)	1800	7000	26
CO	350	1100	32
Methane	38	380	10
NMHC	24	100	24
Tropospheric ozone	420	1100	38
Total particulate matter	104	1530	7

accounted for about 20% of the estimated life time risk caused by exposure to EOM, since the mutagenicity is over three times more potent for EOM from vehicle emissions than for EOM in woodsmoke (154,155).

3.2.8 Global perspective

Human activities have increased the extent of biomass burning significantly over the past 100 years. Biomass burning is now recognized as a significant global source of emissions, contributing as much as 26% net carbon dioxde (40% gross, i.e. not corrected for compensating biomass growth by photosyntheses) and 38% tropospheric ozone (Table 3). Most of the world's burned biomass consists of natural savanna fires, which contribute the same amount as the combined total combustion of agricultural waste and fuel wood. Considering the greenhouse effect, the need for a reduced use of fossil fuel appears to be even more urgent when the huge emissions of CO_2 and other greenhouse gases from biomass burning are taken in to account (158,161).

Ozone and other photochemical oxidants are formed due to atmospheric reactions involving hydrocarbons and nitrogen oxides (162). High emissions of these ozone forming compounds from biomass burning contribute to an increased background level of ozone (163-165). A build-up of 40-50 ppb above the ambient background ozone concentration in forest burn plumes was reported by Westberg et al. (163).

The determined hydrocarbon to NO_x ratio of 9.9 in the forest burn plumes favours the formation of ozone (163). In addition, high proportions of hydrocarbons with high ozone creation potentials emitted from inefficient biomass burning also favour ozone formation (166-170).

Biomass combustion for the purpose of home heating should be carried out with modern energy-efficient equipment. Today the extensive use of fuel wood in stoves with inefficient combustion gives rise to very high emissions of many air pollutants. Improved equipment for the combustion of biomass fuels has to be a top priority all over the world.

3.3 Tobacco smoke

Tobacco smoking involves the pyrolysis of tobacco, which gives rise to a whole range of compounds in a similar way as inefficient biomass burning. Compared to inefficient wood combustion, the main observed difference in the composition of volatile hydrocarbons is the extensive release of isoprene from tobacco (Table 1). The structurally related carcinogenic 1,3-butadiene is also formed in high proportions. The determined proportions of hydrocarbons in tobacco smoke (**II**) were similar to those reported for a few important hydrocarbons in environmental tobacco smoke (172).

In the process of smoking, products from incomplete combustion are formed both during the inhalation of puffs (mainstream smoke; MS) and in the interval between the puffs (sidestream smoke; SS). Environmental tobacco smoke (ETS) is the sum of the sidestream smoke and the part of the mainstream smoke which the smoker exhales. Although the temperatures vary between 600°C and 900°C during the pyrolysis of tobacco (171), the compositions of volatile hydrocarbons were found to be similar in MS and SS smoke in this study (**II**). Sidestream smoke from different kinds of cigarettes has been reported to differ less in composition than MS smoke (172). Since the yields of hydrocarbons are 4 to 10 times higher for SS smoke compared to MS (172,173), MS smoke contributes only to a minor extent to ETS. For isoprene the emission has been reported to be 2-5 mg/cigarette in SS smoke, and ~0.5 mg/cigarette in MS smoke (174-177). For benzene the yields have been reported to be ~300 μg/cigarette in SS smoke, and 30-60 μg/cigarette in MS smoke (174-177).

Since the normally used indicator of tobacco smoke, nikotin (175,178,179), requires elaborate sample collection and analysis, isoprene has been suggested as a tracer of tobacco smoke (180). Isoprene occurs, however, in high concentrations (0.5-3 mg/m^3) in exhaled air (180), and is also released from other combustion processes. Therefore, a more comprehensieve analysis of the composition of hydrocarbons appears to be required for the purpose of apportioning pollutants to their source of origin (**IV**).

4. HUMAN EXPOSURE TO VOLATILE HYDROCARBONS

4.1 Exposure assessment

Several species among the large number of pollutants occurring in ambient air have been recognized as severe health hazards. The focus has mostly been on cancer. However, other health effects due to exposure to air pollutants may be as important as cancer. As a consequence, assessment of human exposure to hazardous air pollutants is an issue of great concern (181-186).

From the results presented in this thesis, it is evident that human exposure levels of hydrocarbons vary strongly between different urban microenvironments. Still, many estimations of human exposure to air pollutants rely on fixed-point measurements in urban background locations (181,185,187). This results in a significant underestimation of the average exposure level, since personal activities in microenvironments with high concentration levels are not taken into account (188,189).

In principle, human exposure to air pollutants can be estimated in three different ways:

(1) Direct measurement of the personal exposure dose for an appropriate sample of the population (189,180).

(2) Indirectly, by assessing concentrations in an approprirate selection of micro-environments, and by using general activity patterns for the population (155).

(3) Determining the target dose in humans, for example adducts in blood (191-193), or concentrations in exhaled air (194,195).

Assessment of average exposure levels for a large population is however always an issue involving several estimations with some degree of uncertainty.

4.2 Concentration levels

4.2.1 Outdoor air

In urban air, emissions from road traffic is the major source of hydrocarbons, nitrogen oxides and carbon monoxide (181,196). The concentrations in urban air vary strongly between different microenvironments due to varying emissions and varying dilution. The total amount of hydrocarbons emitted from road traffic depends on the number of vehicles and the driving pattern. How efficiently the emissions are diluted depends on the distance to the emissions, on the climate (wind speed, inversion, temperature), and on the location of vehicle emissions in relation to the surrounding buildings. Due to a normally efficient dilution in urban air, the concentrations of vehicle exhaust compounds decrease rapidly with increasing distance from the stream of vehicles (1,197-200).

In Figure 7, typical concentrations of benzene observed in different urban environments in Göteborg are compared. Typical ratios between roof level, street-side, and car coupés are 1 : 5 : 10. The regional background level is of the order 1 $\mu g/m^3$. From this comparison it is evident that people's activities in terms of their time spent in proximity to traffic sources will strongly influence their average hydrocarbon exposure dose.

The high exposure to hydrocarbons for road commuters was demonstrated for buses in this study (**IV**), as well as in studies of private cars and other vehicles from Boston (199,203), Göteborg (201), Paris (202), New York (204), London (205) and Taipei (206). The results from Taipei differ by higher concentrations for the road commuters (as high as 380 μg benzene per m^3 on motorcycles), compared to the levels determined in the other cities. Benzene exposure during commuting has been estimated to range between 5 and 60% of an individual's daily exposure (188,199,202,204).

As a consequence of the distance to the emissions from road traffic, the exhaust levels are considerably lower in commuter trains and subways. In the present work, the concentrations of hydrocarbons were found to be 2-3 times lower in commuter trains than in diesel buses on the same route (**IV**). For commuter trains with a larger distance to road traffic, higher ratios have been observed relative to private cars (201-203).

An average benzene concentration of 3.9 $\mu g/m^3$ was measured during the winter of 1994/95 at roof level in Göteborg by Sjödin et al. (207). This level is consistent with the concentration reported for background locations in several other European cities (200,208-212). Comparisons of the concentrations measured in different cities have been made in several studies (213-218). However, these kinds of intercomparisons may be misleading due to the major influence of local emissions

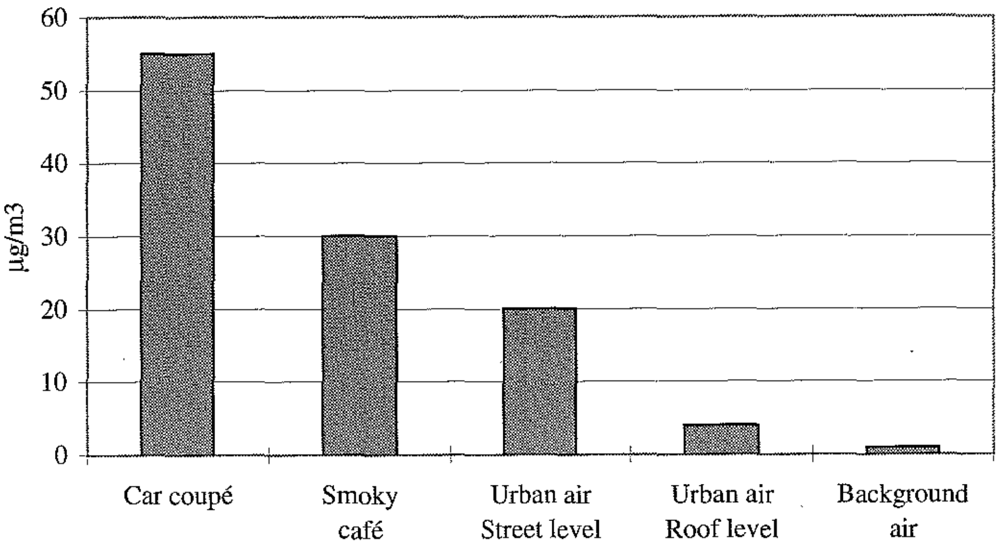


Figure 7. The normal concentration of benzene (µg/m^3) at roof level compared to typical concentrations in other urban environments in Göteborg and in background air by the sea.

and dilution. Lower proportions of benzene in urban air in the USA are explained by a lower content of benzene in the petrol.

In small towns and villages, domestic wood burning during the winter may give rise to high concentrations of hydrocarbons, CO, PAH and black smoke (**VI**,155,181). However, urban traffic emissions at ground level contribute more to human exposure than chimney emissions of the same magnitude from residential wood burning.

Huge emissions of air pollutants from wildland fires give rise to very high concentrations in the plumes. Personal exposure levels for CO have been measured with sampling devices carried by firefighters (126). Based on these measurements, benzene exposure levels of wildland firefighters were estimated to 180 µg/m^3 (corresponding to 40 ppm CO).

4.2.2 Indoor air

Since the Swedish population spends on an average 80 to 90% of the day indoors, the indoor concentrations reflect the average human exposure level for many non-traffic-related hazardous air pollutants (219-222). For pollutants emitted from road traffic, such as benzene, the highest indoor concentrations determined in urban non-smoking apartments appear to be the result of infiltration of polluted outdoor air (223). Environmental tobacco smoke (ETS) is an important source to many hazardous pollutants indoors. In the present work, ETS was found to give rise to high exposure levels of combustion-formed volatile hydrocarbons indoors (**II**).

4.3 Correlations between various air pollutants

Urban air quality is often determined by the continuous monitoring of nitrogen dioxide (NO_2) and carbon monoxide (CO). It is therefore of great interest not only to determine hydrocarbon concentrations but also to relate them to CO and NO_2 concentrations.

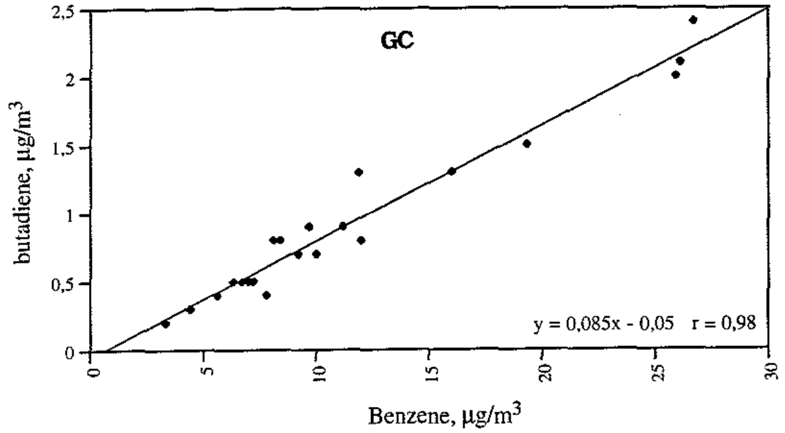
4.3.1 Benzene versus other hydrocarbons

In urban air, the relative concentrations of hydrocarbons have been shown to be similar to the composition of hydrocarbons emitted from road traffic (**I**, **VII**,1,224,225). The ratio between the concentrations of toluene and benzene in urban air was shown to be about 2.1 which is lower than in petrol because benzene is partly formed by combustion.

The observed relationship between the concentrations of benzene, 1,3-butadiene and ethene given in Figure 8 is based on the results from more than twenty measurements near road traffic in Göteborg (**VII**). The concentration of 1,3-butadiene was found to be 8% (w/w) of the benzene concentration, whereas the concentrations of ethene and benzene were found to be similar. These results support the conclusion that petrol exhaust is the dominating source of hydrocarbons in urban air. The contributions of volatile hydrocarbons from diesel exhaust and from petrol vapours to urban air pollution appear to be of minor importance in Sweden.

4.3.2 Hydrocarbons versus CO

Carbon monoxide (CO) is emitted from vehicles due to incomplete fuel combustion. In urban air, CO originates almost exclusively from vehicle exhaust. In a comprehensive study caried out in Stockholm during 1986 and 87, a clear relationship between the concentrations of ethene and CO was demonstrated (226). The measurements showed that 1 mg/m^3 CO corresponded to 6 μg/m^3



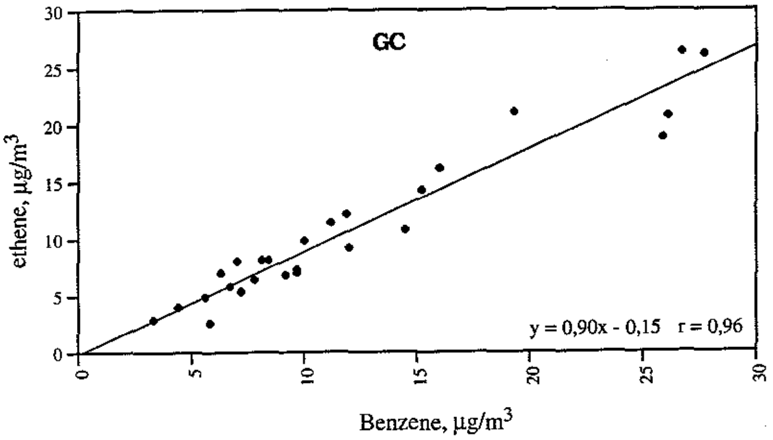


Figure 8. The relationship of the benzene, 1,3-butadiene and ethene concentrations measured along streets in Göteborg (r = correlation coefficient).

ethene. Because the concentrations of ethene and benzene are similar in urban air, a CO concentration of 1 mg/m^3 also normally corresponds to 6 µg/m^3 of benzene. Similar results have been reported from both urban air and vehicle exhaust measurements (79,211,227,228).

4.3.3 Hydrocarbons versus NO_2

Boström et al. reported the assessment of human exposure to nitrogen dioxide for the Swedish population based on measurements made in sixty Swedish cities (181). By using the characteristic relationship between different substances in vehicle-polluted air, average exposure levels for several other substances were also estimated.

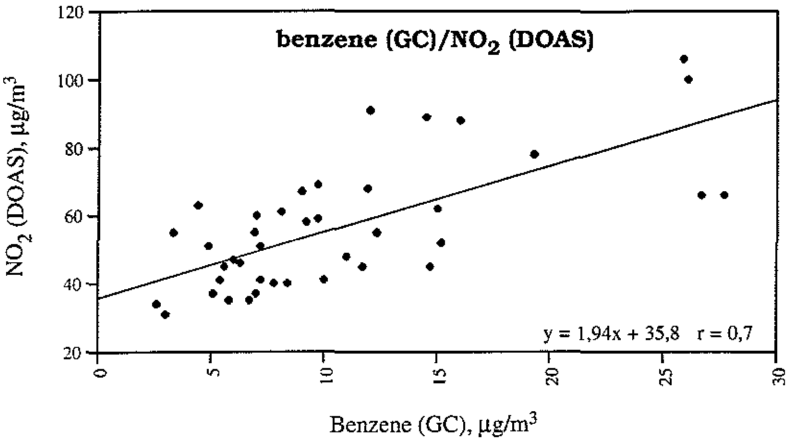


Figure 9. Relationship of the nitrogen dioxide (NO_2) concentration, measured by DOAS, and the benzene concentration, simultaneously measured by gas chromatography (r = correlation coefficient).

In Swedish cities, 80 to 90% of nitrogen oxides (NO_x) are generated by traffic (181). In vehicle exhaust, nitrogen monoxide (NO) is the major compound (80 to 97%) and nitrogen dioxide (NO_2) the minor one (3-20%). In urban air, the relative concentration of NO_2 is higher, especially in the summer when regional ozone (O_3) levels are elevated and cause oxidation of NO to NO_2.

In Göteborg, the observed correlation between benzene and NO_2 (Figure 9) was fair ($r = 0.7$) for measurements performed near to traffic (**VII**). The incomplete correlation is explained by a rather high background concentration of NO_2 and by a varying concentration of ozone. High emissions of hydrocarbons from ”high emitters” and ”cold starts” also affect the relationship between NO_2 and hydrocarbons in urban air.

During episodes of inversion, very high concentrations of air pollutants occur in urban areas. Due to depletion of ozone during these episodes, the concentration of NO_2 does not increase to the same extent as other exhaust-emitted substances. This phenomenon was observed twice in Göteborg in November 1994 (Figure 9), and should be considered in studies of annoyance and health effects due to urban air pollution.

4.4 Health effects

Public exposure to urban air pollution is of great concern due to several possible health effects. Most attention has been payed on cancer. Other health effects of possible concern are central nervous system effects, heritable genetic effects, liver and kidney toxicity, cardiovascular toxicity and asthma (183,229-232). An inreased incidence of colds, allergies and other respiratory ailments may also be linked to air pollution (183,187,230,231).

4.4.1 Hydrocarbons

Unsaturated hydrocarbons are metabolized to reactive epoxides to a varying degree (233). Some of these epoxides have been recognized as possible carcinogens (234). For humans, about 5% of inhaled ethene at low doses is metabolized to the carcinogenic ethylene oxide (235-239). Propene is metabolized to propylene oxide, but to a lesser extent (235). 1,3-Butadiene is more hazardous due to the biotransformation to a reactive diepoxide. 1,3-Butadiene has been reported to be carcinogenic in experimental animal studies (240-247). Benzene is one of nine air pollutants identified as carcinogenic to humans (183). Epidemiological studies of benzene toxicity are normally made for leukemia (248-250), but other forms of cancer are also of concern (251-255). Certain alkanes have been linked to specific neurotoxic and metabolic effects (256-259).

4.4.2 Secondary pollutants

In the presence of sunlight, volatile hydrocarbons and oxides of nitrogen react to form ozone and a myriad of other photochemical products, including mutagenic compounds (260-264). Measurements of the products of hydrocarbon photooxidation in smog chambers have identified peroxy acetyl nitrate (PAN) as a major organic secondary pollutant (265-267). PAN has been shown to be mutagenic, contributing up to approximately one-third of the total mutagenic activity measured in chamber experiments with irradiation of simulated urban atmospheres (268).

4.4.3 Risk estimation

Risk estimations for individual toxic substances are normally based on data from epidemiological studies or animal exposure in chamber experiments. The exposure levels in ambient air are much lower compared to the prevailing concentrations in these studies. The calculation of cancer risks due to low doses, assuming a linear dose-response relationship is an issue associated with considerable discussion and controversy (269-277). However, the hypothesis of low-dose linearity for chemical carcinogens is supported by theoretical arguments (269,277) as well as some empirical data (191,278).

If a linear dose-response relationship is assumed (no threshold dose), a unit risk factor can be calculated. This factor is usually given as the risk of cancer resulting from lifetime inhalation of 1 μg/m^3 of the substance. The collective cancer risk is proportional to the long-term total exposure for all affected people (279-281). Unit risk factors have also been used to determine recommended guideline values for certain volatile hydrocarbons (282). The concentration values given in Table 4 are regularly exceeded in traffic-polluted urban air. For toluene and xylene, guideline values in the range of 40 - 400 μg/m^3 are recommended, based on effects on the central nervous system (282).

With a substantial formation of secondary pollutants with unknown effects, there is a great potential for interactive effects between different substances (268, 283,284). Therefore, a future comprehensive assessment of the health effects due to hydrocarbon emissions should also consider atmospheric transformation processes.

Table 4. Recommended guideline values for specific volatile hydrocarbons (282).

	Benzene	1,3-Butadiene	Ethene	Propene
μg/m^3	1.3	0.02-0.08	1.2	3-20

5. AIR POLLUTANTS IN ROAD TUNNELS

Efforts to support the present road transportation system and to find space for the rapidly growing fleet of vehicles have led to extensive plans for new road tunnels in Scandinavia and Europe. A major concern associated with road tunnels is the elevated level of human exposure to air pollutants when driving through them. Specific inorganic and organic pollutants have been studied in tunnels in Sweden (**I**,285), Austria (286), Belgium (87,287), Germany (288), Switzerland (88) and USA (289,290). American tunnel studies demonstrate that three-way catalysts do not reduce private car emissions and air pollution levels as efficiently as anticipated (65).

The increased knowledge, in recent years, of human health hazards due to air pollutants (291) necessitates a lowered human exposure. Today, non-smokers get a large proportion of their dose of air pollutants in environments polluted by traffic. This article discusses road tunnels in terms of air pollutants and health hazards.

5.1 Road tunnels planned in Sweden

At present, billion-dollar investments in new transportation systems are being considered for the Stockholm region, for the Göteborg region, and for a road link across the Öresund channel between Sweden and Denmark.

In Stockholm, a planned circumferential route would include about 13 km of road tunnels. An external transversal road with about 9 km in tunnels is also considered. In Göteborg, three tunnels of 8 km total length are planned. The planned 20 km combined road and railway connection over the Öresund channel also includes a 4 km long tunnel.

5.2 Air pollutants in road tunnels

5.2.1 Different types of tunnels

Tunnel ventilation can be either transverse or longitudinal. Longitudinal ventilation is normally preferred due to lower costs for construction and service. Longitudinal ventilation is caused mainly by the piston action of the traffic in one-way tubes.

Additional mechanical ventilation is necessary, especially during traffic congestion.

Vehicle emissions accumulate along a road tunnel, giving rise to the highest levels of air pollutants at the tunnel exit. With the same traffic intensity, the maximum concentrations increase with the length of the tunnel. A method to avoid extremely high concentrations in long road tunnels is to construct ventilation towers, with fans for supply air and vented air. The idea is to partially replace the air in the tunnel and to dilute the remaining polluted air. Techniques to clean the polluted tunnel air from particles exist, while removal of gaseous pollutants does not seem to be realistic today.

5.2.2 Concentration levels

Concentrations of a wide range of traffic-emitted volatile hydrocarbons were recently reported for the Tingstad tunnel in Göteborg with one-way tubes (**I**). Samples were taken on adsorbent cartridges and analyzed in the laboratory using thermal desorption and gas chromatography (**II**).

In Table 5, representative concentration levels for ethene, propene, 1,3-butadiene, benzene and toluene (methylbenzene) are given for four different, heavily polluted urban environments. In road tunnels, cars and outdoor urban air, these hydrocarbons normally originate predominantly from emissions of petrol-fuelled vehicles. Their concentrations are then also indicative of the level of other traffic-emitted air pollutants in urban air.

The first two samples give rush hour levels in two different urban road tunnels in Göteborg. The 500 m long Tingstad tunnel consists of two one-way tubes. The 700 m long Gnistäng tunnel carries two-way traffic. The next two samples represent high indoor levels of cigarette smoke, and rush-hour levels of vehicle-emitted pollutants inside a car during urban driving. The last column gives background pollution levels.

Although the tunnels studied are short, 500 respectively 700 m, the pollution levels are several times higher than inside a car during urban driving. The concentrations of hydrocarbons from cigarette smoke in the café are similar to those inside the car from traffic emissions. Compared with the background levels in rural air, the concentrations in the road tunnels are more than five hundred times higher.

Table 5. Concentrations ($\mu g/m^3$) of hazardous hydrocarbons in road tunnels as compared with a smoky café and a private car.

	Tingstad Tunnel[a]	Gnistäng Tunnel[b]	Smoky Café[c]	Car Coupé[d]	Rural air Göteborg
CH_x (C_2-C_8)	**3600**	**2250**	**570**	**630**	
Ethene	280	160	42	30	0.5
Propene	100	65	37	15	0.2
1,3-Butadiene	25	17	12	1.3	0.0
Benzene	330	194	38	55	0.9
Toluene	630	365	40	110	0.6

a) Sampling near tunnel exit, 19 Feb-92; 8.10-8.40; -4°C, 3200 vehicles per hour; 0-70 km/h; 10% heavy-duty trucks (**I**).
b) 5 March-92; 8.00-8.20; +4°C; 3200 vehicles/h; 50-70 km/h; 10% heavy-duty trucks.
c) 15 April-92; 13.25-13.55; Junggrens Café, Göteborg (**II**).
d) 24 Sept-92; 7.50-8.10; +14°C; Central Göteborg; 0-60 km/hour (**II**).

The flow of air through the two tunnels studied is governed by the piston action of the traffic in different ways. In spite of poorer ventilation because of two-way traffic and the same amount of vehicles, the top concentrations of hydrocarbons were often lower in the Gnistäng than in the Tingstad tunnel. This may be due to the much larger air volume in the wider and higher Gnistäng tunnel. Pulsating traffic, due to traffic lights, also improves the ventilation in the Gnistäng tunnel.

In vehicle exhaust, the proportion of nitrogen dioxide (NO_2) is only 3 - 25% as compared with nitric oxide (NO). In urban air, NO_2 is formed by the reaction of NO with ozone (O_3). In road tunnels with high NO concentrations, O_3 is depleted without causing significant conversion of NO to NO_2. An additional problem during congestion, and in long road tunnels, is the elevated proportion of NO_2, due to thermal oxidation of NO. At normal urban atmospheric conditions this reaction is of minor importance, while the formation rate of NO_2 is as high as approximately 1 ppm h^{-1} at an NO concentration of 5 ppm (292). Since the reaction rate is exponentially dependent on the NO concentration, the NO_2 formation increases fast in road tunnels during congestion with NO concentrations much higher than 5 ppm.

5.2.3 Human exposure

Traffic exhaust is rapidly diluted by horizontal as well as vertical mixing. Consequently, concentrations decrease rapidly with distance from the exhaust pipes. This is the reason why the time spent in vehicles is very important for public exposure to air pollutants. The high exposure of road commuters has been demonstrated in studies from Boston (199) as well as from Göteborg (201). It is concluded that the concentration ratios in Göteborg are approximately 1:10:50 between commuter trains, commuter cars on roadways, and air in road tunnels. The exposure of professional drivers should be specifically considered because of their long average exposure times.

The air pollution problem is particularly serious in long tunnels because of higher pollution levels and a longer time of exposure. Reported concentrations of hydrocarbons in a 3 km long road tunnel in Brussels (286) indicate about twice as high levels as in the 0.5 km long Tingstad tunnel. This is so in spite of mechanical ventilation and fewer vehicles per hour in the Brussels tunnel.

5.2.4 Health hazards

With respect to short-time effects, nitrogen dioxide is commonly regarded as the most critical urban air pollutant. In Sweden, the WHO limit for one-hour exposure (400 $\mu g/m^3$) is presently considered as a 98-percentile limit for road tunnels. The limit to be permitted heavily influences the investments in mechanical ventilation. Nitrogen dioxide affects respiratory organs (231), and asthmatics and children are particularly susceptible. Synergistic effects with other irritating compounds such as aldehydes reduce the acceptable maximum concentration of nitrogen dioxide. The potential connection between the increasing number of allergic persons and exposure to irritating air pollutants, such as nitrogen dioxide, should also be considered (231).

Exposure in tunnels also contributes to long-term effects among which cancer and other genotoxic effects are regarded as particularly important. Air pollutants from traffic include a great many carcinogenic compounds. Among the hydrocarbons in Table 1, benzene is a feared human carcinogen (253) whereas 1,3-butadiene, ethene and propene have been put forward as important cancer risks more recently (279).

In Sweden, ambient air hygienic threshold values (low-risk levels) are proposed for

Table 6. Estimated individual cancer risk from exposure to volatile hydrocarbons, when driving through a 13 km long road tunnel (as presently planned in Stockholm)[a].

	Unit risk factor[a] per µg/m^3 x 10^6	Unit risk[b] factor per µg x 10^{11}	Dose (15 min)[c] [µg]	Risk of cancer x 10^9	Risk of cancer/year[d] x 10^6
Ethene	125	25	63	16	8
Propene	20	4	22	1	1
1,3-Butadiene	600	120	6	7	4
Benzene	16	3	74	2	1

a) Calculations based on these lifetime unit risk factors (279).
b) The conversion from lifetime unit risk factors (µg/m^3) is made assuming an average inhalation of 20 m^3/day during 70 years.
c) Inhaled dose during 15 min (15 l of air/min) in a tunnel assuming the concentrations measured in the Tingstad tunnel (column one of Table 1).
d) Based on the assumptions of two tunnel passages a day, five days a week, during a year. Considering theoretical and statistical errors, the figures given are judged to be uncertain by a factor of three (279).

benzene (1.3 µg/m^3), 1,3-butadiene (0.05-0.2 µg/m^3), ethene (1.2 µg/m^3) and propene (1.7-17 µg/m^3) (282). These low-risk levels theoretically result in one cancer case per 100000 exposed individuals during life-time inhalation. For toluene, a low-risk level of 38 µg/m^3 is proposed with reference to effects on the central nervous system.

Human exposure to benzene, butadiene, ethene and propene has recently been estimated to cause approximately 100 cases of cancer per year in Sweden, as calculated from lifetime unit risk factors (279). In Table 6, the same approach is used to calculate the cancer risk due to the exposure levels when driving through a 13 km long road tunnel. The estimations indicate 14 cases of cancer disease per year among one million individuals driving regularly through the tunnel. Considering the presence of a great number of other genotoxic compounds in the tunnel air, the cancer risk of driving through a long road tunnel appears to be unacceptable, especially during rush hours and congestions.

5.3 Discussion

The high concentrations of traffic-emitted air pollutants found in short road tunnels in Göteborg emphasize that hazardous effects are to be expected due to the still higher exposure levels anticipated in the long urban road tunnels planned in Scandinavia and Europe.

Road tunnels can relieve certain urban areas which are affected by high levels of vehicle exhaust. However, if motorists are taken into consideration, not only rural but also urban new road tunnels normally increase the total population dose of air pollutants. Moreover, the tunnels give rise to problems with short-time health effects.

Private motorists as well as the more heavily exposed professional drivers have strong reasons to oppose new road tunnels with respect to health hazards. Asthmatics, children and pregnant women are particularly vulnerable. Large investments in circumferential roadways in tunnels cannot be justified with respect to health effects.

Sustainable mobility requires investments favouring rail rather than road alternatives. The rail tunnel between England and France stands out as a good example, whereas a bridge and tunnel road link across the Öresund channel presents a bad example for a future Europe.

6. CONCLUSIONS

The composition of hydrocarbons from road traffic, biomass combustion and tobacco smoking has been determined. Sampling on adsorption cartridges and subsequent analysis by gas chromatography has been shown to be a versatile, reliable and very useful method for determination of volatile hydrocarbons.

The determined almost uniform proportions of volatile hydrocarbons in urban air are in good agreement with those of the present urban road traffic emissions. In the near future, the proportions of hydrocarbons in urban air will probably change somewhat due to an increased number of vehicles equipped with a catalyst (both petrol and diesel vehicles) and due to the introduction of improved fuels.

High amounts of hydrocarbons were found to be released during the combustion of several different biomass fuels. Domestic wood burning may be an important source of human exposure to volatile hydrocarbons in winter time in areas where residential wood combustion is common. By using appropriate equipment with more efficient combustion, the hydrocarbon emissions may be lowered by one order of magnitude. Indoors, tobacco smoke may give rise to high hydrocarbon concentrations.

Observed concentrations of hydrocarbons indicate that typical ratios between roof level, street-side, and car coupés are 1 : 5 : 10. From this comparison, it is evident that people's activities in terms of their time spent close to traffic sources will strongly influence their average hydrocarbon exposure dose.

At present, quantitative estimates of risks of hydrocarbon-induced health effects are difficult to make with a high degree of confidence. Available information leaves little doubt, however, that repeated exposure to high concentrations of volatile hydrocarbons is hazardous and should be minimized.

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