Emissions of Non-Methane Volatile Organic Compounds (NMVOC) from Vehicular Traffic in Europe

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To my husband and our beloved son
and
In loving memory of my parents

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ABSTRACT

Vehicles with combustion engines are significant emitters of air pollutants and therefore have a major influence on the environment. Road and tunnel studies are important tools in evaluating the traffic emission models and in assessing the achievements of new technologies for emission reduction.

During three tunnel measurement campaigns namely: the Lundby Tunnel in Sweden (March, 2001), the Plabutsch Tunnel in Austria (November, 2001), the Kingsway Tunnel in England (March, 2003) and an additional field experiment conducted along a section of the A656 motorway in Germany (May 2001), emissions from a large variety of vehicles were investigated. The measurements covered the standard pollutants CO_2, NO_x and non methane volatile organic compounds (NMVOC).

The data obtained from the measurements carried out in these European locations were analysed with respect to the composition of the NMVOC mixture and the ratio of individual compounds to benzene, CO_2 and NO_x. The NMVOC profiles observed in the tunnel as well as in motorway measurements are in good agreement with the NMVOC profiles observed in other campaigns. Among the aromatic hydrocarbons, toluene showed the highest mixing ratio, whereas iso-pentane and propene had the highest mixing ratios among the alkanes and alkenes, respectively. During the motorway experiment, vertical gradients were observed for several NMVOC downwind of the motorway, in contrast to the upwind measurement site, where NMVOC were constantly distributed. This indicates that the studied NMVOCs are directly emitted by the traffic. The ratio toluene/benzene, which is an indicator of traffic activity, was found in the performed studies to be: 3.09 in the Lundby Tunnel, 2.44 in the Plabutsch Tunnel and 2.87 in the Kingsway Tunnel. During the A656 motorway experiment, the ratio was constantly 2.5 except for stop and go periods when this could increase up to 3.6. These values are higher than the previously measured ratios at traffic sites. This finding can be explained by an over proportional decrease in the benzene emissions compared with the aromatic compounds since the year 2000, when the new European Directive 98/70/EC limiting the benzene content in gasoline to 1% started to be applied.

Within the framework of extensive emission data validation experiments, the emission factors for the Lundby Tunnel, the Plabutsch Tunnel and the A656 motorway have been determined using the local traffic measurements in combination with new emission models. The models provide emission factors with a temporal resolution of 20 min for the tunnel studies and 3 h for the motorway study. The models took as input parameters the emission factors for CO_2 -

model 1; total hydrocarbons (THC) - model 2; and benzene, toluene, xylene (BTX) - model 3 from the Handbook Emission Factors for Road Transport (HBEFA) version 2.1. The input parameters were modified by taking into account the slope gradients for the corresponding measurement sites as well as the fleet composition and the driving pattern. By comparing the direct calculated values of emission factors with the model 1 values, a good correlation of data was obtained for the time intervals characterised by fluent and high traffic density. This proves that the emission factors for CO_2 in the HBFEA 2.1 are a good estimation for the real traffic situation. In the case of the Lundby and the Kingsway Tunnels, for all analysed compounds except benzene, the emission factors calculated through model 1 were higher than those obtained from model 2 and 3. For the Plabutsch Tunnel, the models 2 values were higher. The data analysis of THC emission factors for the given traffic fleets was used in order to clarify the discrepancy between measured and model calculated emission data.

Two hypotheses were verified:

- the THC emission factor of heavy duty vehicles is not correct; and/or
- the percentage of catalyst vehicles determined from the fleet data analysis does not reflect the reality, i.e. cars that are registered with catalyst in fact have a malfunctioning catalyst and should be counted as non-catalyst vehicles with the corresponding emission factor.

The influence on the emission factors of the about 12% malfunctioning catalysts was demonstrated.

From the overall emission factors determined for weekday traffic, in the Plabutsch Tunnel, the emission factors for light duty vehicles (LDV) and heavy duty vehicles (HDV) were calculated by means of a regression analysis. The comparison of the LDV emission factors for benzene and toluene obtained in the Plabutsch Tunnel, to data from a previous study performed in the same tunnel shows a clear decrease of the emission factors in this tunnel.

The A656 motorway experiment, showed for benzene, toluene, ethylbenzene and 1,2,4 trimethylbenzene/decane that within the statistical errors the measured values are in good agreement with the modeled ones.

The results of the present study show that the NMVOC split is influenced by the fleet composition and that the most important contribution to the NMVOC emissions results from poorly maintained vehicles and those with malfunctioning catalysts. The results of the present study reflect the current situation and the improvements of the European car fleet with respect to hydrocarbons emissions after the introduction of the new European legislation in 2000.

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CHAPTER 1

1 INTRODUCTION

1.1 STATE OF THE ART

Air pollution has been recognised as a serious problem throughout the world starting in the Middle Ages when the burning of coal in cities released increasing amounts of smoke and sulphur dioxide to the atmosphere. In the late 18th century, the UK Industrial Revolution led to a significant increase in pollutant emissions, which was mainly caused by the use of coal with high sulphur content by both domestic heating and industry. Also, atmospheric concentrations of several greenhouse gases have increased significantly since pre-industrial times, causing the anthropogenic greenhouse effect (Harries *et al.,* 2001). More recently, pollution from motor vehicles became an air quality issue, which attracted considerable attention. Gasoline and diesel fuelled motor vehicles emit a wide variety of pollutants, principally carbon monoxide (CO), nitrogen oxides (NO_x = NO + NO_2), volatile organic compounds (VOCs) and particulate matter (PM), which all have an important impact on urban air quality.

The revolution in the understanding of atmospheric chemistry began in the late 60-ties, when the OH radicals were identified as the most important oxidizing agent in the troposphere. The discovery resulted in particular from the analysis of the CO budget (Heicklen *et al.,* 1969; Weinstock, 1969; Stedman *et al.,* 1970; Levy, 1971), though the oxidation of CO by OH had already been measured two years earlier (Greiner, 1967). In the early 1970s, Crutzen (1973) and Chameides and Walker (1973) suggested that tropospheric ozone originates mainly from production within the troposphere by photochemical oxidation of CO and hydrocarbons catalyzed by NO_x and HO_x (OH+ HO_2). Radical chemistry, considered to be important only in the stratosphere, was found to be strongly involved in tropospheric chemistry as well, and ozone was identified as the main precursor of the important hydroxyl radical (OH) (Levy, 1971, 1972, 1973). OH is therefore the dominant sink for methane, carbon monoxide and many other organic substances in the atmosphere and is often called the “detergent of the atmosphere".

1.1.1 NMVOC in the atmosphere

The changing composition of the atmosphere is of particular interest since some of the minor constituents (trace gases) can affect the earth's energy balance. The so-called greenhouse gases absorb infrared radiation and can therefore “trap" the outgoing long-wave radiation leading to changes in the climate system (e.g. increasing the surface temperature, changing the hydrological cycle through increased evaporation etc.).

Large quantities of NMVOCs are emitted into the troposphere from anthropogenic and biogenic sources (Guenther *et al*., 1995, 2000; Sawyer *et al.,* 2000; Placet *et al*., 2000). Motor vehicles (Zielinska *et al*., 1996), biomass burning, industrial processes such as chemical production, the production, processing, storage, and distribution of liquid fossil fuels (e.g., crude oil), gaseous products (Friedrich and Obermeier, 1999) and hazardous waste facilities (Placet *et al*., 2000; Sawyer *et al.,* 2000) have all been identified as major sources of NMVOCs.

The emissions of anthropogenic and biogenic NMVOCs have a composition, concentration and reactivity of wide variety. At urban sites, mixing ratios of atmospheric NMVOCs can be in the ppb range, whereas measurements at remote continental or marine sites show levels in the ppt range. The global emission strength from biogenic and anthropogenic sources is estimated to be about 1100 and 180 Tg (Carbon)/yr, respectively (Guenther *et al.,* 1995; Olivier *et al*., 1996). Large uncertainties exist, especially for biogenic emissions. This may be compared to the emission strength of the most abundant hydrocarbon in the atmosphere, methane, which is about 500 Tg (CH_4)/yr (Houweling *et al*., 1999).

Biogenic emissions are of special interest as they could change in the future due to a shifting temperature providing a positive feedback loop through their photochemical impact on ozone and OH radicals. This mechanism has been suggested by Shallcross and Monks (2000) for isoprene, whose emissions are known to depend mainly on temperature and solar irradiance. According to Fuentes *et al.* (2001), the mechanism can be extended to other compounds and provide a general view on biosphere-atmosphere feedbacks.

Typical NMVOCs lifetimes in the Northern hemisphere range from less than one hour to several days depending on a combination of NMVOCs reactivity, atmospheric conditions and solar flux.

NMVOC have important effects on the tropospheric chemistry.

They increase the ozone production efficiency per unit NO_x in the continental boundary layer (Liu *et al.,* 1987), they form organic nitrates such as PAN which provide reservoirs for the long-range transport of anthropogenic NO_x to the remote atmosphere (Singh and Hanst, 1981; Maxim *et al.,* 1996, Jacob, 2000), and provide a sink for OH (Kasting and Singh, 1986) but also provide a source of HOx due to photolysis of NMVOC oxidation products such as formaldehyde and acetone (Sillman *et al*., 1990; Singh *et al*., 1995).

The ozone and photo-oxidants formation is inter-connected in an alternate sequence day/night.

Day time chemistry is controlled by OH radicals whereas night time chemistry is driven by the NO_3 radicals (Finlayson-Pitts and Pitts, 1986, 1997; Kley, 1997). A detailed presentation of the key aspects of the complex interplay of NMHCs and NO_x in the atmosphere can be found in Atkinson, (2000), Atkinson and Arley, (2003), Jenkin and Clemitshaw, (2000), Jenkin *et al.,* (1997) and references therein.

In recent years, the availability of kinetic and mechanistic data relevant to the oxidation of NMVOCs has increased significantly (Becker *et al.,* 1995), and various aspects of the tropospheric chemistry of NMVOCs have been reviewed extensively (e.g. Atkinson, 1997, 2000). Detailed reviews of mechanisms and rate constants of atmospheric reactions of particular groups of compounds can be found in Atkinson (1997, 2000), Atkinson and Arley (2003), Calvert *et al.* (2000), Wayne (2000), and references therein. Because NMVOCs have very diferent chemical reactivities, the speciation of NMVOCs emitted by motor vehicles is therefore very important for estimating their efect on ozone budget.

Studies that have ranked NMVOCs by their ability to generate ozone have involved, therefore, the use of trajectory models of the planetary boundary layer, incorporating detailed chemical schemes describing the degradation of a large variety of organic compounds (Derwent and Jenkin, 1991; Derwent *et al*., 1996). Recalculated historical ozone measurements from 1870s and 1880s in Paris, by using 3D global models have estimated that ozone concentrations may have more than doubled over large parts of the Northern Hemisphere (NH) since pre-industrial times (e.g. Crutzen and Zimmermann, 1991; Lelieveld and Dentener, 2000), which is also supported by older measurements in Paris corrected by Volz and Kley (1988).

1.1.2 Transport air pollution in Europe. Emission trends

Automobile exhaust has been recognized a potential air pollutant since 1915, but only in 1945, in Los Angeles urban pollution was manly attributed to automobiles (Haagen-Smit, 1952). Although the emissions from gasoline–fuelled vehicles have been significantly reduced since 1960, pollution from motor vehicles remains a major problem in many urban areas. As a growing concern for better air quality, legislation was enacted requiring further reduction of vehicle exhaust emissions.

In Europe, the constituents of the vehicle emissions, which are regulated by law are carbon monoxide (CO), nitrogen oxides (NO_x), total hydrocarbons (HC) and particulate material (PM_{10}) (for diesel-powered cars).

However, vehicle exhaust is always associated with the emission of the unregulated species such as CO_2, CH_4, N_2O, NH_3, various organic species (aliphatics, aromatics, PAHs, carbonyls, etc.), primary NO_2, metals (e.g. arsenic, cadmium, mercury, nickel), PM size/number/surface area, some of which such as benzene, 1,3 butadiene are known to be highly carcinogenic and mutagenic.

Benzene levels in car exhaust have attracted considerable attention since this compound is classified by to be carcinogenic (Directive 92/32/EEC). According to EU legislation, the atmospheric threshold (1) level for benzene is 5µg/m3 (Directive 96/62/EEC). Benzene is considered being almost exclusively emitted from road traffic (Doskey *et al.*, 1992; Schmitz *et al.,* 1999; Derwent *et al.,* 2000) because the use of benzene as solvent is forbidden in Western Europe since 1991 (Directive 89/677/EEC; Wickert *et al.*, 1999). The exhaust gas from vehicles includes both burnt and unburnt hydrocarbons. Benzene is formed through the dealkylation of higher molecular weight aromatics (Fraser *et al.,* 1998).

In the framework of the UNECE Convention on Long Range Transboundary Air Pollution the VOC protocol has been developed. The countries that signed the UNECE protocol undertake to reduce emissions of non-methane volatile organic compounds. This specifies reductions of NMVOC emissions per country by 30% relative to the levels the year 1988.

In Germany, the reduction of 50% between 1990 and 2000, according to the German Federal Environmental Agency, as can be observed from Figure 1-1 (http:// www.env-it.de/umweltdaten/) has been achieved possibly by legal regulations on exhaust gases, which brought significant reductions in the emissions from road transport. Under the EU Directive on National Emissions Ceilings, there is a commitment to reduce NMVOC emissions in Germany further to 995 kt by 2010.

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(1) Threshold level represents the level below which no adverse health effects are expected.

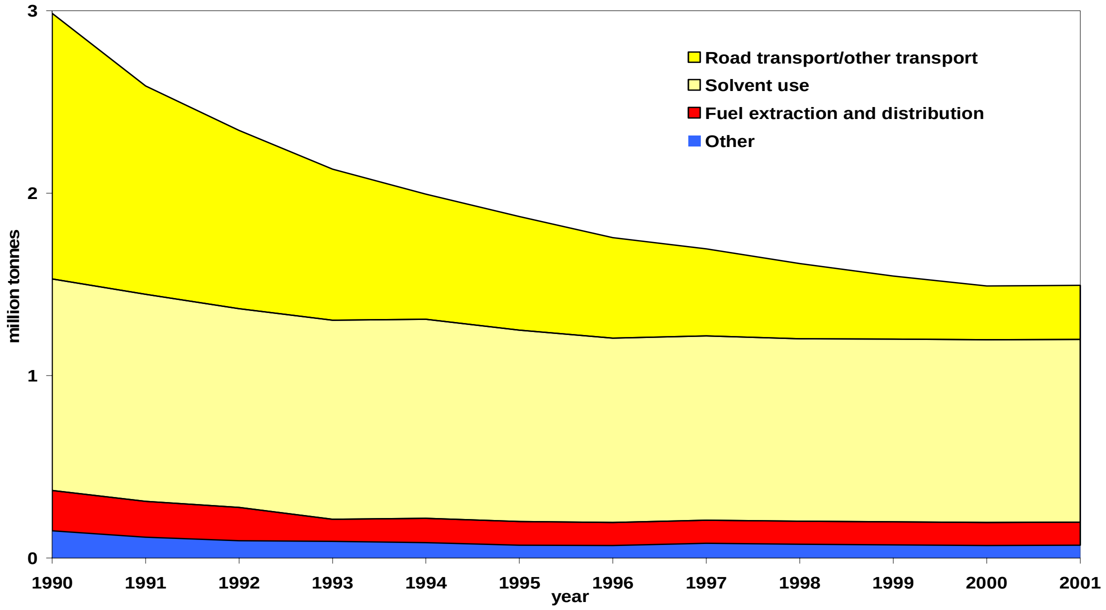

Figure 1-1: NMVOC emissions for the period 1990-2001 in Germany for major source categories, according to to the German Federal Environmental Agency. (source: www.env-it.de/umweltdaten/)

According to the Department for Environment Food and Rural Affairs, DEFRA, U.K., (www.defra.gov.uk/environment/statistics/index.htm) in Figure 1-2, it is obvious that also for the UK road transport, solvent use and fugitive emissions from gas and oil extraction and distribution are the primary sources of NMVOC emissions.

Emissions from road transport peaked in 1989 at 895 kt. Since then they have fallen steadily and in 2003 road transport emissions were 82% lower than in 1989. Emissions from solvent use fell steadily through the 1990s as the UK began modern emission controls in 1992.

Fugitive emissions from the oil and gas industry increased during 1970 - 1990 as industry grew reaching their peak emissions in the mid 1990s. Between the peak year of 1997 and 2002 they fell by 20% (DEFRA, 2005). NMVOC emissions fell by 55% between 1990 and 2003 to a value of 1.1 Mt, which is already slightly below the UK target value for 2010 of 1.2 Mt, according to the UNECE Gothenburg Protocol and the EU National Emissions Ceilings.

Euro 4 emission standards for vehicles became effective in 2003 and the European Commission drafted new Euro 5 and Euro 6 stricter standards in 2005 (Appendix: Table 1).

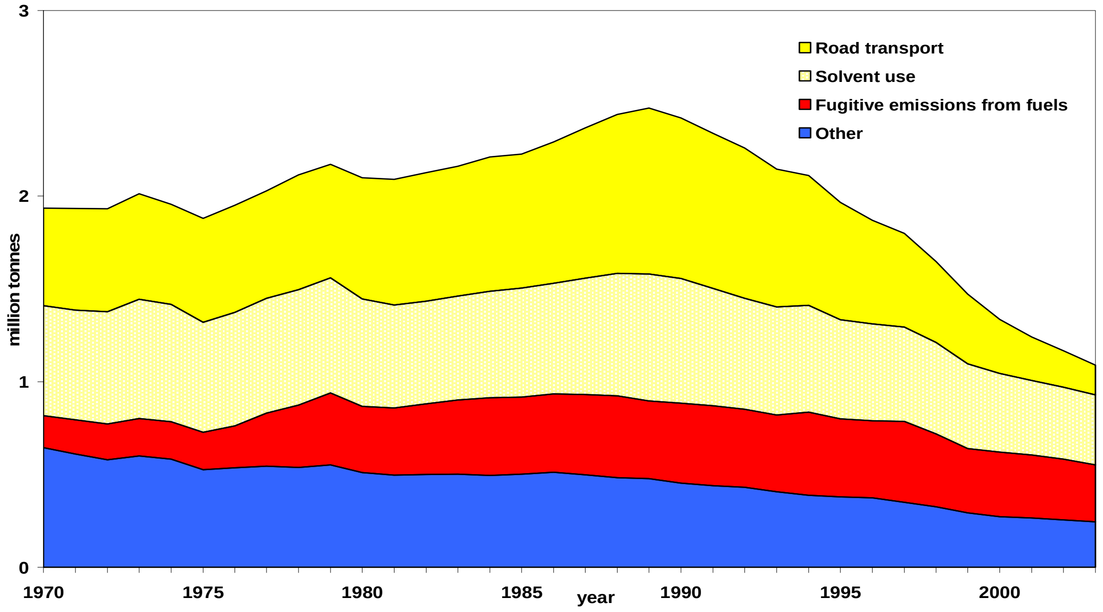

Figure 1-2: NMVOC emissions for the period 1970-2003 in the UK for major source categories, according to DEFRA.
(source: www.defra.gov.uk/environment/statistics/index.htm)

Emission standards for road vehicles have improved significantly since the introduction of the new catalysts. Nevertheless, studies performed in the US and Europe during the last 15 years revealed that several factors may contribute to the emission decreasing, such as improved vehicle technologies, cleaner fuels and also maintenance of the vehicles (Stedmann, 1995; Sjödin *et al*., 2004).

Only few global modeling studies on the impact of road traffic exist. E.g. Granier and Brasseur (2003) investigated the impact of NO_x and CO emissions from road traffic and estimated relative contribution of such emissions to ozone concentrations near the surface in the Northern Hemisphere of between 12 and 15% in industrialized regions and about 9% in remote regions. Current trends indicate that the use of motor vehicles and airplanes will increase continuously in the near future together with the expansion of industrial processes in order to maintain economic growth for both, the developed and developing countries (IPCC, 2000).

1.1.3 Emission models

Emission inventories are an important instrument in air pollution control and atmospheric research. Their data are used as input for dispersion modelling and, thus, are the basis for air pollution reduction scenarios. Chemical modules of computer based dispersion models need, beside others, precise data of the temporally and spatially distributed NO_x and VOC emissions. The basis for emission inventories only partially results from emission measurements but to a large extent from statistical inputs and assumptions (Kühlwein *et al.*, 2005).

Emission factors (EF), which represent a very important tool in developing emission scenarios, are derived from emission measurements. Emission factors have been the fundamental tool for air quality management as they express the emissions as a function of source activity.

As already presented, vehicular emissions are of a special concern for the VOC, NO_x and PM emissions. For a better understanding of the contribution of vehicular emissions to air pollution, their accurate characterisation is required. In order to determine emission factors, different methods are currently being used, namely:

- engine test bed studies (Hausberger *et al.*, 2003),
- chassis-dynamometer studies (Heeb *et al.*, 2000, 2002, 2003; Weilenmann et *al.*, 2001)
- measurements under "real world conditions" (Lonneman et *al.*, 1986; Pierson *et al.*, 1996; Fraser *et al.*, 1998; Kristensson *et al.*, 2004; Stemmler *et al.*, 2005).

The latter studies should ideally be carried out on motorways for a large number of vehicles and include at least the measurement of speciated NMVOCs and NO_x.

Chassis-dynamometer tests are used for the determination of EFs of the whole vehicle according to well-defined boundary conditions such as driving cycles and vehicle load. It is well known that emission factors of vehicles depend on engine design and condition, driving situation, as well as fuel composition (Staehelin *et al.,* 1998).

In order to obtain representative results for real road traffic emissions, the exhaust of a large number of vehicles has to be analysed. These types of studies are usually conducted in road traffic tunnels. However, road traffic tunnel measurements have also some disadvantages, e.g. different emission patterns of the vehicles caused by the so-called piston effect, the resistance caused by tunnel walls, the speed limits inside the tunnels, etc.

Up to now, only a few experimental studies were focused on the comparison of calculated emissions with real world emission measurements (Staehelin *et al.*, 1998; Vogel *et al.*, 2000, Corsmeier, 2005). In addition to "inverse" dispersion modelling of street canyon measurements (e.g. Mannschreck, 2000; Corsmeier *et al.*, 2005; Ketzel *et al.*, 2003) and mass conservation box models of open-road measurements (e.g. Jamriska and Morawska, 2001) such experiments mainly took place in road tunnels (Pierson *et al.*, 1978; Lonneman *et al.*, 1986; Kirchstetter *et al.*, 1996; Zielinska *et al.*, 1996; Weingartner *et al.*, 1997; Fraser *et al.*, 1998; Rogak *et al.*, 1998; Staehelin *et al.*, 1995, 1998; Schmidt *et al.*, 2001; Kean *et al.*, 2001; Sturm *et al.*, 2001; Kurtenbach *et al.*, 2002; Gomes, 2003; Kristensson *et al.*, 2004; McGaughey *et al.*, 2004; Colberg *et al.,* 2005; Stemmler *et al.*, 2005)

Previous studies have observed significant differences between measured and model predicted emissions from on-road vehicles. Tunnel air measurements have been used as a tool for comparing and verifying emission models with "real world emissions" starting in the 1990s.

Instantaneous emissions models (modal modelling) have been developed in Europe since the beginning of the 1990s (Staehelin et al., 1995; Sturm, 1999). Among them, the most commonly used are:

- the German-Austrian-Swiss Handbook for Emission Factors Model (HBEFA) (Hassel, 1995; Keller, 1998). The results of this model can be used at both macro and micro scale (e.g. emission inventories at local, regional or national levels, in the evaluation of strategies to reduce air pollution, environmental impact assessment, etc.). The HBEFA model used instantaneous emission data to generate emission factors for different combinations of vehicle categories, driving cycles, road gradients and vehicle loadings. The basis for the emission matrices was a series of chassis dynamometer tests using the FTP 75 cycle (US-Highway Federal Test Procedure), which includes following segments: cold start, transient phase, hot start phase and the NEDC(2) (New European Driving Cycle), which is an urban driving cycle characterized by low vehicle speed, low engine load and low exhaust temperature. The last version is HBEFA 2.1, released in 2004; this version will be used also in the present study. It showes that instantaneous modelling is no more an available approach for modern vehicles; therefore, for this version new real test bench cycles were developed. Emission factors for Euro 2 and Euro 3 are based on bag data (multiple sets of data) from real world cycles or a linear combination of the results of these cycles. Euro 4 emissions were estimated using reduction factors based on Euro 3 (gasoline) and Euro 2 (diesel) (Haan and Keller, 2004).

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(2) The NEDC represents the typical usage of a car in Europe, and is used to assess the emission levels of car engines.

- The COPERT III (Computer Programme model to calculate Emissions from Road Transport); the development of COPERT (Kouridis *et al.,* 2000) has been financed by the European Environment Agency (EEA) in the framework of the activities of the European Topic Centre on Air Emissions, and it is proposed to be used for road traffic emissions by the EEA(3) member countries. Total emission estimates are calculated by a combination of firm technical vehicle data (e.g. emission factors) and activity data (e.g. total vehicle kilometres) provided by the user.
- In the USA, the EPA's highway vehicles emission-factor model (MOBILE) was released in 1979. MOBILE 6 released in 2000, provides average in-use fleet emission factors for three criteria pollutants, namely NMVOC, CO and NO_x for eight categories of vehicles for the years 1970-2020 and under various conditions affecting in-use emission levels (e.g. ambient temperature, average traffic speed, gasoline volatility) as specified by the model user.
- The EMFAC (Emission Factors) model is developed by the California Air Resources Board (CARB). It is very similar to MOBILE in its concept, but it has been adapted to the Californian car fleet and later on also to the Taiwan car fleet, too.

The performance of the emission models have been verified using data from real-world measurements performed in road traffic tunnels. A summary of the results coming from these studies over the past 30 years is presented in Appendix: Table 2.

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(3)European Environmental Agency (EEA) member countries: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Netherlands, Portugal, Spain, Sweden, United Kingdom, Czech Republic, Cyprus, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovenia, Slovak Republic, Bulgaria, Romania, Turkey, Iceland, Liechtenstein, Norway

1.2 AIM OF THE WORK

This work was performed in the frame of the EU project ARTEMIS (Assessment and Reliability of Transport Emission Models and Inventory Systems) and of the German project BAB II (Bundesautobahn II).

The goal of the road tunnel studies within ARTEMIS was the validation of fleet weighted emission factors, which are based on the ARTEMIS database for vehicle category specific emission factors, which are derived from chassis dynamometer tests (Sturm *et al.*, 2001).

The BAB II project intended to evaluate the quality of emission data, which are deduced from emission models.

As part of these projects, measurements of real world traffic emissions were carried out in four different locations in Europe namely in Sweden, Austria, England and Germany.

Further than a simple identification and apportionment of air pollutants, this work was aimed to present a trend of NMVOC emissions from vehicular traffic in Europe during recent years.

Accordingly, the tasks of the present study were:

- to determine the typical NMVOC profiles from road traffic for the studied locations;
- to estimate the real-world emissions for speciated NMHCs, using different calculation methods;
- to evaluate the relative contributions of light-duty vehicles (LDV) and heavy-duty vehicles (HD) to the NMVOC emissions, and
- to analyse the long term evolution of NMVOC road traffic emissions in Europe.

CHAPTER 2

2 EXPERIMENTAL PART

Road tunnel measurements have been used in the past to define the detailed chemical composition of traffic NMVOC emissions (Pierson *et al.,* 1978, Lonneman *et al.,* 1986, Staehelin *et al.,* 1995, Kirchstetter *et al.,* 1996, Gertler *et al.,* 1997, Rogak *et al.,* 1997, Sagebiel *et al.,* 1996, Zielinska *et al.,* 1996, Kurtenbach *et al*., 2002). From these data emission factors were derived and evaluated.

Motor vehicle emissions of CO_2, NO_x and speciated NMVOCs in the range C_2-C_9 were measured during three campaigns performed in different tunnels, namely:

- the Lundby Tunnel in Sweden (March, 2001),
- the Plabutsch Tunnel in Austria (November, 2001), and
- the Kingsway Tunnel in England (March, 2003).

In addition, a field experiment was conducted along a section of the A656 motorway in Germany (May, 2001).

The set-up of the measurements and the used analytical equipment is presented in detail below.

2.1 SITE DESCRIPTION

2.1.1 Tunnel measurements

For the tunnel experiments the selection of the measurement site was dependent on the tunnel ventilation system. Therefore, the instrument locations were chosen by taking into account:

- the expected concentration in the tunnel air (inlet/outlet),
- the fact that the air flow has to be exactly defined at the measurement point and that
- the measurement site should be ideally not being influenced by changes of engine load due to changes in road gradient (Sturm *et al*., 2001).

It is known that the type of ventilation system is dictated to a large extent by the tunnel length, configuration and ventilation cost. Adequate information on the tunnel ventilation systems is prerequisite for getting reliable measurement data.

For tunnels with uni-directional traffic flow and longitudinal ventilation system, instruments should be placed where the highest concentrations are to be expected and the volume airflow can be defined exactly. This is normally near to the tunnel exit.

For transverse ventilation system, pollutant concentrations are more or less constant over a considered ventilation section. The measurements have to be carried out in this ventilation section and at the entrance of the ventilation system.

In tunnels with more than one ventilation sections, the location of the instruments has to be chosen in such a way that the influence of emissions and air mass transport in or into other sections is minimised. If no measurements inside the bore or at the end of the tunnel are possible, the stack would be an appropriate location.

During the measurement campaigns it was assumed that the air at the sampling site is well mixed over the total cross section of the tunnel by the vigorous turbulence caused by the piston effect of the traffic and that the engines of the vehicles, which passed the sampling port, were under “warm” driving conditions. The relatively well defined dilution and residence time of the exhaust gases in tunnels allowed the absolute determination of the emissions of the observed species.

2.1.1.1 Lundby Tunnel

The Lundby Tunnel is one of the newest tunnels in the area of Gothenburg, Sweden. The tunnel was opened in 1998. It has a length of 2 km and connects the city motorway with the centre of Gothenburg. The tunnel consists of two independent tubes in the east - westerly direction. Each tube is carring traffic on two lanes.

Figure 2-1 shows a sketch of the tunnel and its ventilation. The Lundby Tunnel ventilation system consists of two separate sub-systems: longitudinal ventilation consisting of 40 fans in each tube, placed in the ceilings and an axial ventilator in a vertical shaft mounted 400 m before the tunnel exit. This type of ventilation transports gases down wind to the tunnel exit using the axial ventilator, the fans inside the tunnel and the piston effect of moving vehicles.

During the measurement campaign, the axial ventilator and the fans in the tunnel were not used. Hence, the tunnel could be treated like a longitudinal ventilated tunnel using only the piston effect of moving vehicles.

Accordingly, the analytical instruments were installed 350 m behind the entrance (inlet station-site 1) and 400 m before the city-bound exit (outlet station-site 3) as shown in Figure 2-1.

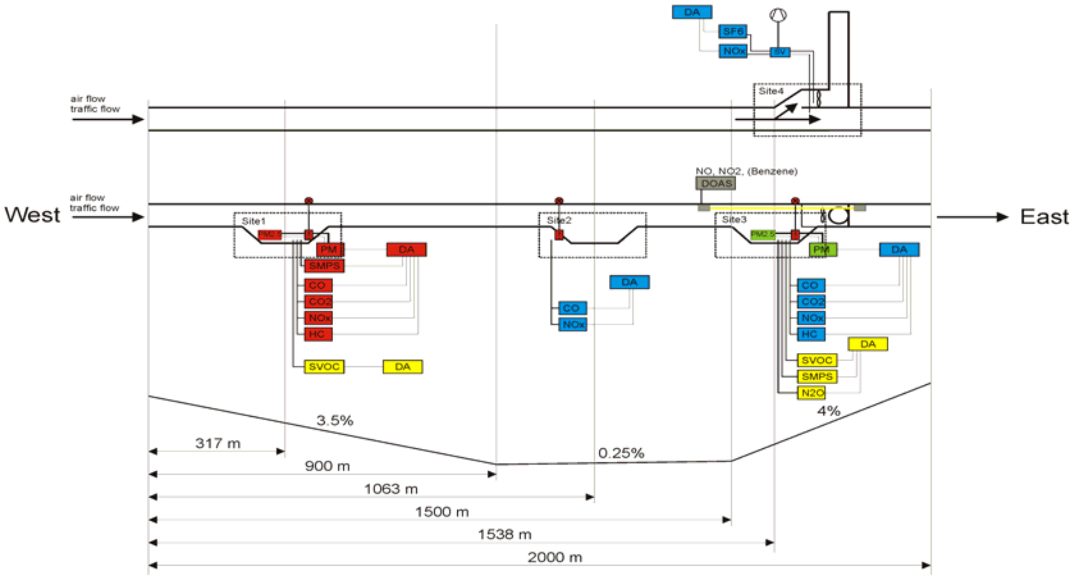

Figure 2-1: View of the Lundby Tunnel with ventilation and measurement sites.

2.1.1.2 Plabutsch Tunnel

The Plabutsch Tunnel has a length of 9755 m and serves as by-pass for the city of Graz, Austria, on the A9 motorway (Pyhrnautobahn).

During the time of the measurements the tunnel consisted of one tube in the south - northerly direction. The traffic was operated in counter flow, i.e. the vehicles passed in both directions.

In Figure 2-2 it is shown that the tunnel is divided into five ventilation sections operating as a transverse ventilation system providing the necessary fresh air supply. Each ventilation section has a length of 2 km.

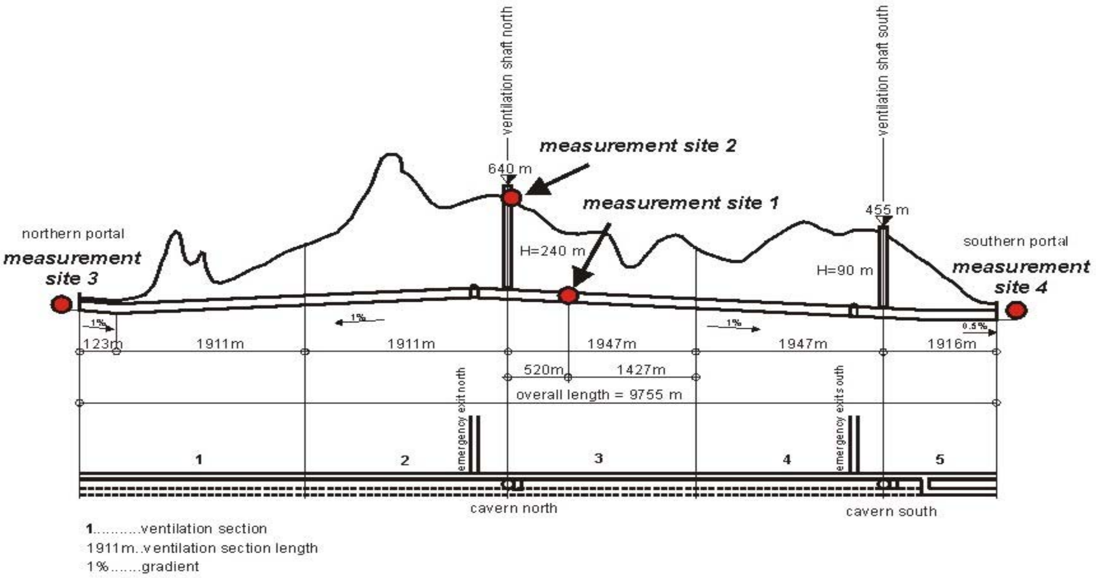

Figure 2-2: View of the Plabutsch Tunnel, ventilation and measurement sites.

The fresh air enters the tunnel's traffic area through fresh air ducts and the exhaust is discharged through exhaust ducts, as can be seen in Figure 2-3.

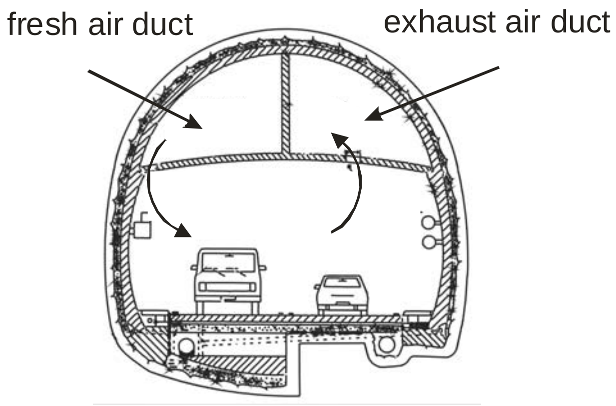

Figure 2-3: Cross section of the Plabutsch Tunnel.

The measurement site 1 inside the tunnel was placed in the middle of the tunnel at a parking bay 4500 m before the southern exit. This location, assured that the emission behaviour of the vehicles was almost constant.

2.1.1.3 Kingsway Tunnel

The Kingsway Tunnel has a length of 2480 m and connects the city of Liverpool, U.K., in the east, with the Wallasey area in the west. The tunnel consists of two tubes, each carrying two lanes with uni-directional traffic.

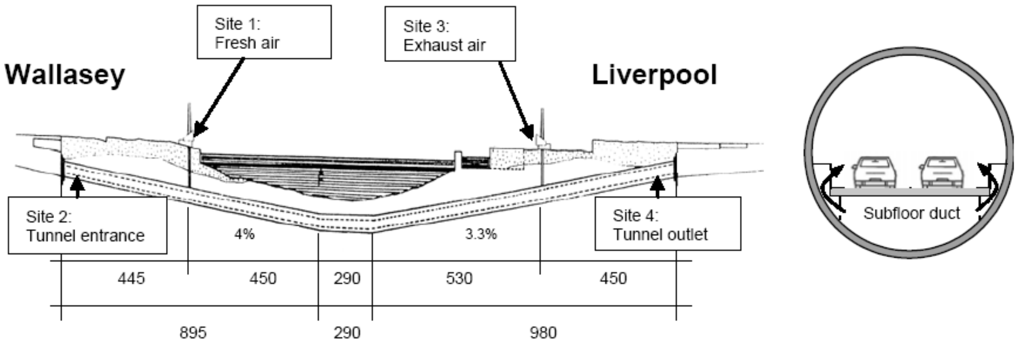

Figure 2-4: View of the Kingsway Tunnel and its ventilation and measurement sites.

The tunnel ventilation is semi-transverse. A longitudinal section of the tunnel is presented in Figure 2-4. Clean air enters the tunnel via the two ventilation shafts and portals. The air from the ventilation shafts is fed into a sub-floor duct and permeates into the tunnels through vents along its length. The vents allow even flow of inlet air along the tunnel length. Exhaust air can also leave via the portals and is removed via two ventilation shafts.

According to the tunnel operators, there is a plug of air that oscillates around the tunnel mid/point, and the air circulation in each half of the tunnel forms a separate system. At times of heavy congested traffic, jet fans mounted in the tunnel crown are activated to force this move the air from its middle-tunnel position to the exit. One of the main problems during the Kingsway Tunnel campaign was to ensure that the ventilation followed a consistent pattern and that tunnel airflow conditions were maintained constantly.

During the experiment, the ventilation was configured in a way, which would encourage the longitudinal flow of air through the northern tube of the tunnel in the traffic direction. At the Promenade ventilation station, site 1, (Figure 2-4) the inlet air fan was switched on and the exhaust fan was switched off. At the Victoria ventilation station, site 3, (Figure 2-4) the exhaust fan was switched on and the inlet fan was switched off as well as the jet fans in the tunnel tube. However, at the portal locations both tunnel tubes lead into two halls used for all four traffic lanes, which could lead to a recirculation of air from one tube into the other. This fact complicated the definition of the volume flow into and out of the tunnel and, hence, the whole measurement set-up. During the measurements, the instruments were located at the Promenade ventilation station (background air) and the Victoria ventilation station (exhaust air). The sampling of the gaseous components required a 6 m sampling line through a hole in the shaft.

Table 2-1 presents a summary of the different tunnel characteristics and the location of the analytical equipment during the experiments.

Table 2-1: Overview of the tunnel characteristics and the location of analytical equipment during the experiments.

Tunnel	**Lundby**	**Plabutsch**	**Kingsway**
Length	2060 m	9755m	2480m
Type of traffic flow	Two tubes one direction, two lanes / tube	One tube two directions, two lanes / tube	Two tubes two directions, two lanes / tube
Ventilation system	longitudinale ventilation system	transverse ventilation system	semi transverse ventilation system
Gradient (Slope)	-3.5% -1217m +0.25% -475m +4% -462m	-1% -3825m +1% -4017m -0.5% -1916m	-4% -895m -0.4% - 290m +3.3% -980m
Vehicle speed	80-120 km/h	80-120 km/h	65 km/h
Equipment location	***inlet*** station: 350m behind entrance ***outlet*** station: 400m before exit	***inlet*** station: in the fresh air shaft ***outlet*** station: 4000 m behind entrance	***inlet*** station: Promenade ***outlet*** station: Victoria vent station

2.1.2 The BAB II - A656 motorway experiment

The measurements took place upwind and downwind of the motorway A656 between Heidelberg and Mannheim near the city of Wieblingen, about 1.5 km west of the Heidelberg motorway intersection of the motorways A5 and A656. The measurements were carried out during four weeks in April and May 2001. The motorway A656 is directed straight from south-east to north-west (135°-315°) and, hence located perpendicular to the expected main wind direction. The motorway runs on a 1.0 to 1.5 m high, grass covered embankment. Corsmeier *et al.,* (2005) give a more detailed description of the field campaign and the experimental set-up.

Figure 2-5 shows the experimental set-up of the upwind and downwind measurements. Quasi on-line NMVOC measurements were performed continuously at the ground level stations, i.e. 3 m above the ground, VOC 1 and VOC 5 at a distance of 60 and 84 m, respectively, from the motorway. Vertical NMVOC profiles were obtained from non-continuous measurements at the two 52 m towers at the following heights above ground level: 5, 17, 27, 37, 47 m (downwind, VOC 6- 10) and 5, 27 and 47 m (upwind, VOC 2- 4). The instruments, which are described in more detail in the following section, were operated during seven so called special observation periods (SOP) during the entire measurement period.

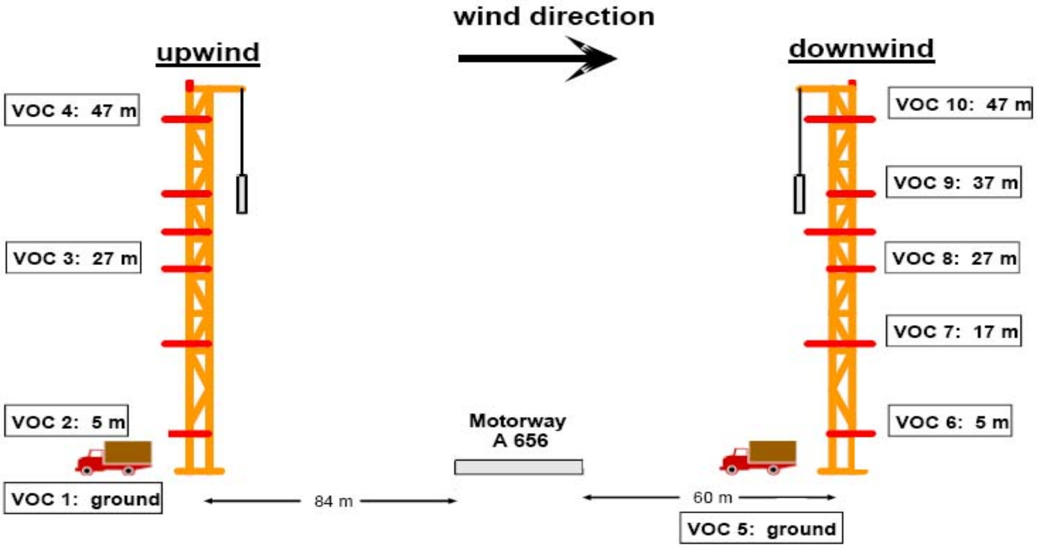

Figure 2-5: Location of the experimental set-up for the NMVOC (VOC) measurements on the A656 highway (sites are numbered as VOC 1-VOC 10).

2.2 ANALYTICAL EQUIPMENT

The analytical equipment used in the tunnel and the A656 motorway campaigns were commercial instruments, optimised and improved in the laboratory for the specific tasks. Table 2-2 presents a summary of the analytical equipment used during the various experiments.

The term NMHC (non-methane hydrocarbons) is introduced to indicate a subset of NMVOC, consisting of compounds containing only carbon and hydrogen.

Table 2-2: Summary of the analytical equipment used during the experiments.

Experiment	Instrument location	Measured compound	Instrument	Measuring method	Sampling Cycle (min)
Lundby Tunnel	Inlet station	NMHC	Airmovoc HC 2010 (NMHC B)	GC-FID	20
	Outlet station	NMHC	Airmovoc HC 2010 (NMHC A)	GC-FID	20
		N_2O/ CO_2	Chromato-Sud	GC-ECD/TCD	5
Plabutsch Tunnel	Outlet station (Site1)	NMHC	Airmovoc HC 2010 (NMHC A)	GC-FID	20
		N_2O/ CO_2	Chromato-Sud	GC-ECD/TCD	5
		NO/NO_2	ML9841	Chemi-luminescence (Mo converter)	1
Kingsway Tunnel	Outlet portal Victoria vent station	NMHC	Airmovoc HC 2010 (NMHC A)	GC- FID	10
		NMHC	Prepared tubes	GC- FID	120-180
		CO_2	Carbondio 1000	NDIR	1
		NO/NO_2	APNA 360	Chemi-luminescence (Mo converter)	1
A656 motorway	Upwind	NMHC	Airmovoc HC 2010 (NMHC B)	GC- FID	20
	Downwind	NMHC	Airmovoc HC 2010 (NMHC A)	GC- FID	20
	Vertical profile (up/down wind)	NMHC	NIOSH charcoal tubes	Tubes + GC-FID	120-160
		NO/NO_2	APNA 360	Chemi-luminescence (Mo converter)	1
		NO/NO_x	CLD AL 770	Photolysis converter	1

2.2.1 Non-methane hydrocarbons (NMHCs)

2.2.1.1 Quasi on-line GC systems Airmovoc 2010

During the various campaigns, the C_2-C_9 aliphatic and aromatic hydrocarbons were monitored using two quasi on-line compact gas chromatographic systems (Airmovoc 2010) with enrichment system (cryotrap) and flame ionisation detector (FID).

The instrument is fully automated and especially designed for field measurements. A more detailed description of the instrument can be found elsewhere (Winkler *et al.*, 2002; Gomes, 2003).

Briefly, the two used Airmovoc systems called NMHC A and NMHC B have the same instrumental design. A simple scheme of the instruments is presented in the Appendix: Figure 1. During sampling, the air was drawn by an external pump into the sampling line at a flow rate of 50-100 ml/min, through a presampling unit. The presampling unit comprised of a filter (10 μm pore-size filter paper) in order to remove particulates from the sampled air and a humidifier at a fixed temperature of 3°C for keeping the sample at constant relative humidity. After that, the gas stream sample passed through an ozone scrubber, i.e. a 50 cm long steel tube heated to ~ 70°C (Schmitz, 1997).

The gas sample was then drawn into the sampling unit represented by an adsorption tube. The adsorption tubes are made of glass with two steel endings. The tubes are packed with the multisorbent materials, Carbotrap and Carbosieve S III (3:1 ratio). The two adsorbent materials were chosen, because they are capable to retain hydrocarbons in the range C_2-C_3 (Carbosieve S III) and C_5-C_9 (Carbotrap), and present good temperature stability up to 400 °C. The tubes are packed in such a way that the compounds with lowest molecular mass go through the initial Carbotrap layer, which is the least active and are trapped in the last Carbosieve S III layer, which is the most tenacious. Six adsorption tubes were kept in a cylindrical drum, arranged in a circular way, having an angular distance of 60° or 2 h (if the cross section of the cylinder is imaged as a clock). The cylinder carrying the adsorption tubes was cooled during the adsorption by using the cooling effect of expanded gaseous CO_2 (from 60 bar to normal atmospheric pressure). Using this instrument, simultaneous adsorption of a fresh sample and desorption of the adsorbed sample from the last run can be carried out. Thus, for a typical method, after adsorption at 10-h position, the drum containing the tube was rotated in such a way that the tube should be inserted into the flow path of the chromatograph at the 12 h position. During desorption the compounds were focused in a small volume, the cryo-focussing unit, at -50^0C. This low temperature was obtained also by the cooling effect of the expansion of gaseous CO_2 from 60 bar to atmospheric pressure. This unit has the role of retaining effectively the light hydrocarbons, and is represented by a micro fused silica capillary tube (18 cm × 0.78 mm × 0.50 mm), packed with Carbopack B and Envi-Carb X (Gomes, 2003; Winkler, 2001). The main characteristics of the employed sorbents are presented in Table 2-3.

Table 2-3: Characteristics of the adsorbent materials used for NMHC sampling (Cao *et al.,* 1994, 1999; Matisova *et al.,* 1995).

Adsorbent	**Type. Particle size (mesh)**	**Surface m^2/g**	**Adsorption range**	**Max. temp (^{o}C)**
Carbosieve S-III	Carbon molecular sieve; Mesh 60-80	820	C_2-C_3	400
Carbotrap	Graphitized carbon black; Mesh 20-40	120	C_5-C_9	400
Carbopack B	Graphitized carbon black; Mesh 60-80	100	C_4-C_{14}	400
Envi-Carb X	Graphitized carbon black; Mesh 120-400	250	C_2-C_4	maximum 500

The hydrocarbons were afterwards quickly vaporised at 355 ^{o}C and flowed together with the carrier gas (hydrogen, purity >99.999%) into the separation unit. A fused silica capillary column (24m × 0.25 mm), BGB 2.5, with a film thickness of 1 μm represents the separation unit. The relative short column (other systems use columns of 90 m) permits the separation in 20 min of the fraction C_2-C_9 (Schmitz *et al.,* 1997). The stationary phase consists of 2.5% phenyl- and 97.5% methylpolysiloxan. The temperature programme for the chromatographic separation increased with a rate of 17°C /min from a start temperature of 20^{o}C and remains isothermal at 160^{o}C for the next 50 seconds. The effluent from the column is mixed with hydrogen and synthetic air in the FID. The FID responds to the number of carbon atoms entering the detector per unit of time and is a mass sensitive rather than a concentration sensitive device. Consequently, the FID has the advantage that changes in the flow rate of the mobile phase have little effect on the detector response (Skoog, 2000).

The operating conditions of the Airmovoc 2010 system are listed in Table 2-4.

Table 2-4: Operating conditions of the quasi on- line GC system Airmovoc 2010.

Sampling tube	Carbosieve III and Carbotrap in the ratio 1:3
Sampling temperature	Cooling, 0^oC
Sampling flow rate	100 ml/min
Sampling volume	0-1600 ml
Sampling time	0 -960 s
Cryofocusing trap and cooling effect	Micro-packed fused silica capillary tube, adsorbents: Carbopack B and Envi-Carb X in the ratio 3:1 cooling through gaseous CO_2 expanded from 60 bar to atm. pressure
Cryofocusing temperature	-50^oC
Desorbtion temperature	355°C
Column	BGB-2.5 (OV 178) (2.5% phenyl- and 97.5% methylpolysiloxane) 25 m × 0.2 mm, 2 µm
Temperature programme	Isothermal, with ramp (e.g. a constant value of 25°C for first 210 s, then ramp of 17 ^0C/min up to 160^0C)
Pressure programme	from 212 hPa till 900 hPa
Carrier gas	Hydrogen (> 99.999)
Detection	FID

The instrument parameters such as column temperature, start/end of sampling, revolving of the adsorption tubes, start/end of desorption and data acquisition are controlled through the Airmovista software that allows the usage of different controlling programs in order to achieve better performance of the system. The controlling program consists of two parts named concept and method. All instrument settings and the measurement sequences are laid down in a particular method. One or more methods are grouped together in a concept, which describes the methods routine. For both systems, the measuring cycle was 20 min during all measurements. The chromatograms obtained were integrated using the Borwin software. The method for the chomatographic conversion from Airmovista to Borwin is presented in Appendix: Explanation 1.

2.2.1.1.1 Performance of the instrument during the measurement campaigns

Identification

Compounds identification was achieved by matching their retention times with those of an NPL (National Physics Laboratory) (Appendix: Table 3), standard calibration mixture for each compound in reproducible conditions. Identification of the chromatographic peaks in the standard (NPL) chromatogram was realised by correlating the specific retention time of the components with their boiling points and chemical structure.

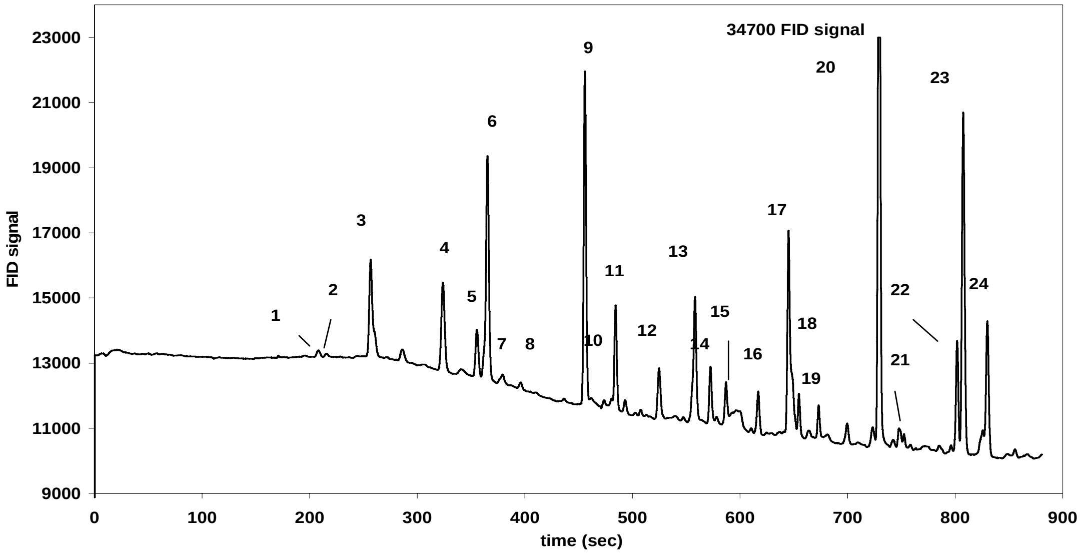

Figure 2-6: A typical chromatogram of air sample registered during the BAB II - A656 experiment using the Airmovoc HC-2010 instrument, namely NMHC A.

1 Ethene/Ethyne; 2 Ethane; 3 Propene/propane; 4 i-Butane; 5 i-Butene; 6 n-Butane/1,3-Butadiene; 7 trans-2-Butene; 8 cis-2-Butene; 9 i-Pentane; 10 1-Pentene; 11 n-Pentane; 12 2,2 Dimethylbutane; 13 Cyclopentane; 14 n-Hexane; 15 Isoprene; 16 trans-2-Pentene; 17 Benzene; 18 Cyclohexane; 19 n-Heptane; 20 Toluene; 21 n-Octane; 22 Ethylbenzene; 23 m-/p-Xylene; 24 o-Xylene.

The retention times of different non-methane hydrocarbons were found to be stable in the laboratory and during the field measurements. The standard deviations of the retention time for the continuous measurements were 4-7% for 24 h runs as can be observed in Appendix: Figure 2.

The following compounds were co-eluted: ethene and ethyne; 1-butene and 2-methylpropene; n-butane and 1,3-butadiene; isoprene and trans-2-pentene; cyclopentane and 2-methylpentane; benzene and cyclohexane as well as m-/p-xylene. In the case of the co-eluted compounds the peak separation was performed by means of the Origin programme. The software fits the Gauss curves in co-eluted peaks and separates them without significant losses or gains of the integrated peak area (Gomes, 2003; Niedojadlo, 2005).

Calibration procedure

The performance of the GC system was checked by periodical calibrations using ppbV levels of standard compounds. During the measurements, the performance of the NMHC GC systems was stable, which is reflected by the response factors. The response factor is defined as the peak area (relative unit) per mixing ratio (ppbV) per molecular mass (g/mol) per sample volume (ml) (Sternberger, 1962). The response factor for the co-eluted peaks was calculated using average molecular masses. This procedure assures small errors due to the similar molar mass of the most co-eluting hydrocarbons present in the NPL standard gas mixture.

In Figure 2-7, for the system NMHC A, the response factors calculated at the beginning and at the end of the Lundby Tunnel experiment are shown as an example.

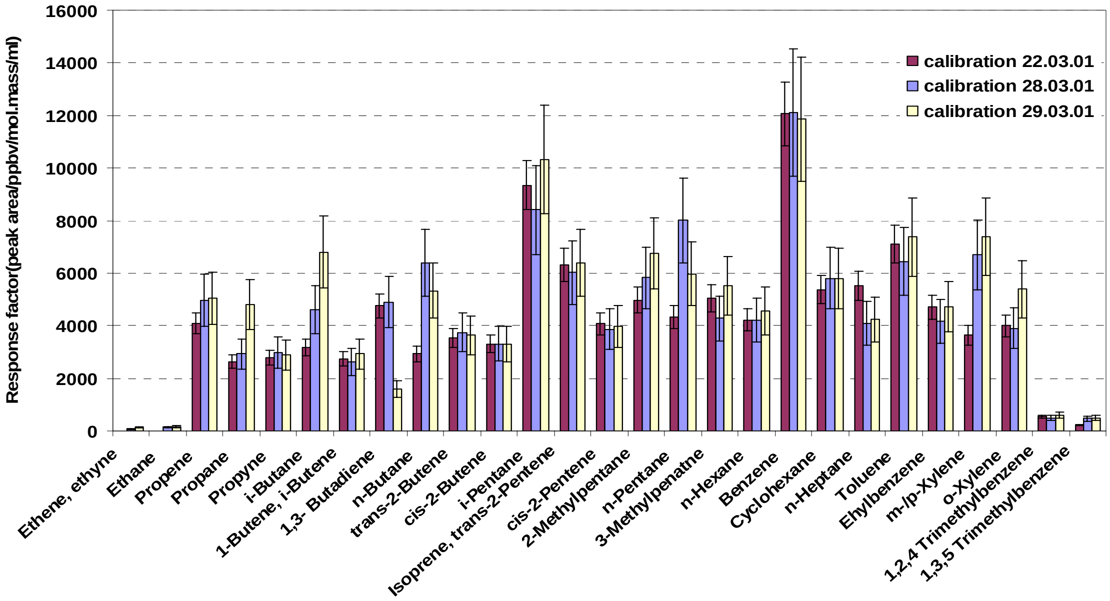

Figure 2-7: Typical bar diagram of the response factors for NMHCs in the NPL standard gas mixture during the Lundby Tunnel experiment. The compounds are shown in the order of their elution.

Similar behaviour has been observed also during the other experiments.

The precision of the NMHC measurement is defined as the agreement (the standard deviation) among the results from repeated measurements of the same concentration under identical conditions. As can be seen from Figure 2-8, the precision ranged from 2 to 16%, i.e. the 1σ standard deviation of the field calibrations using the NPL standard gas mixture. On average, the precision of the NMHCs measurements was 9% for alkanes, 8% for alkenes and 5% for aromatic hydrocarbons.

The comparison between the two GC systems yielded good agreement; the accuracy of the two instruments was about 12%.

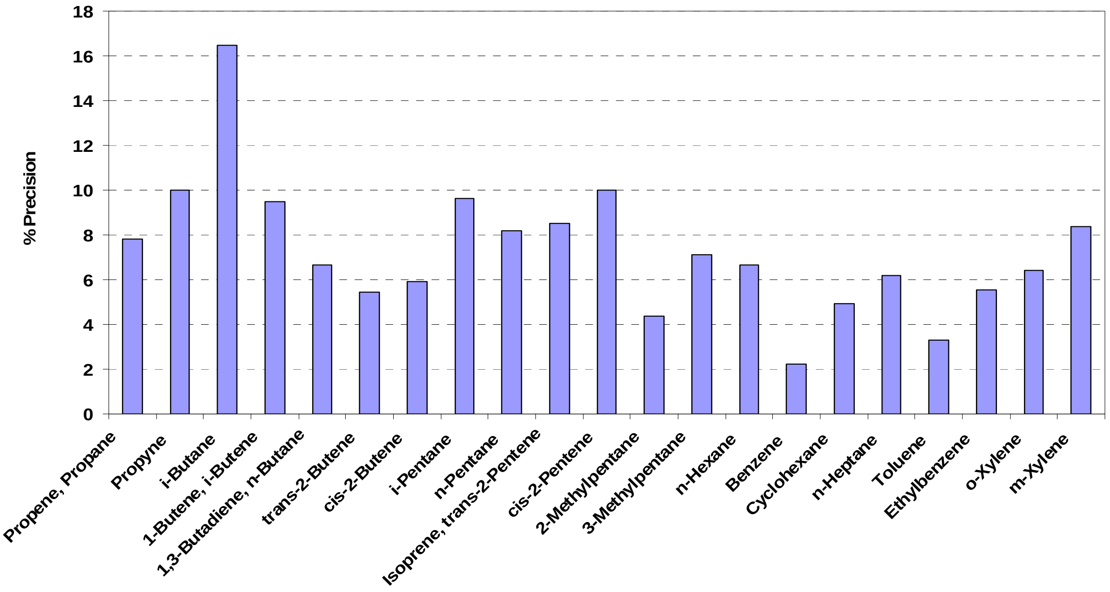

Figure 2-8: The precision of the measurements of different hydrocarbons.

At the beginning of each campaign the adsorption tubes were purged with zero gas (synthetic air), followed by desorption in order to remove impurities. According to earlier investigations (Schmitz, 1999), the memory effect of the adsorption tubes depends on the desorption temperature, which has been found to be optimal at 350°C.

The calibration procedure implied subsequent measurements of zero gas (blanks) in order to insure the absence of impurities. These measurements were performed before and after each calibration.

Mixing ratio determination

The measured individual compounds were quantified by comparing the corresponding response factor of the standard gas mixture and the peak area produced from the sample.

During the experiments, the sampling period was varying according to the expected ambient air concentrations from 5-10 min for tunnel measurements to 16 min for open-air road measurements. The analysis of “clean” air samples with mixing ratios in the lower pptv level afforded a sampling volume of up to 1600 ml in order to achieve a good sensitivity for the quantification of the NMHCs.

2.2.1.2 *Prepared adsorption tubes and off-line GC system*

During the Kingsway Tunnel campaign multi-bed tubes packed with 125 mg Carbotrap graphitized carbon and 150 mg Carbosieve SIII carbon molecular sieve separated by glass wool have been used. The higher molecular weight compounds were retained on the front, on the least retentive material (Carbotrap), the more volatile compounds were retained on the stronger adsobent (Carbosieve S III).

The adsorption tubes (Figure 2-9) are part of a measurement system, which comprises of an enrichment device (Preconcentrator 7100) and gas chromatograph (HP GC 6890) with non-polar column and FID detector. This system is described in more detail elsewhere (Niedojadlo, 2005).

More than 58 compounds including 23 alkanes, 28 alkenes and alkynes as well as 14 aromatic hydrocarbons were identified and quantified.

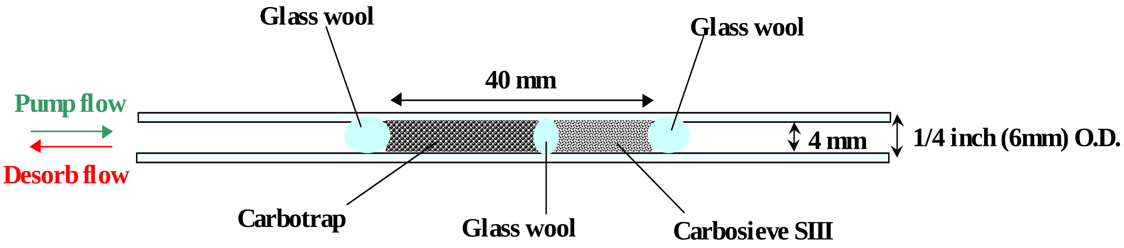

Figure 2-9: Construction of adsorbent tubes used for the sampling of hydrocarbons.

2.2.1.2.1 *Performance of the instrument during measurements campaigns*

During the Kingsway Tunnel measurements the data obtained from the prepared sampling tubes were compared with the data from the quasi on- line GC system, NMHC A. The hydrocarbons were sampled at the same time through a common sampling line. The results exhibit a good correlation for the measured hydrocarbons.

In order to harmonize the data from both systems, a correction factor has been calculated. The average correlation factor for the following compounds: trans-2-butene, cis-2-butene, i-pentane (2-methylbutane), cis-2-pentene, 2-methylpentane, 3-methylpentane, n-hexane, benzene, n-heptane, toluene, ethylbenzene, m-/p- xylene, o-xylene was found to be 0.81 ±

0.08. This factor was applied to the data obtained from the off-line system. This procedure is similar to the application of NIOSH adsorption tubes, which is described below.

2.2.1.3 NIOSH adsorption tubes

During the BAB II experiment the Institut für Verfahrenstechnik und Dampfkesselwesen, University of Stuttgart, (IVD) measured non-continuously the vertical profiles of NMHC. The measurements were performed using special sampling cartridges (NIOSH adsorption cartridges by Draeger). The C_6-C_9 NMHCs were collected on active carbon with a coconut base. After SOP periods, the cartridges were analysed in the laboratory. The collected hydrocarbons were eluted with CS_2 and analysed using a GC-FID system (Fisons 8180) (Glaser, 2001). The NIOSH adsorption tubes have been used during the BERLIOZ field campaign showing excellent results (Volz-Thomas *et al*., 2002).

An intercomparison procedure between the NMHC data obtained from the NIOSH adsorption tubes and the NMHC data obtained from the quasi on- line GC instruments (Airmovoc 2010) has been performed and is discussed in detail in the section below.

2.2.1.4 NMHC data quality assurance (QA)

For each measurement campaign a quality assurance (QA) was performed prior and after the measurements.

A two-stage QA procedure was applied:

- first stage, called *internal quality assurence*, the instruments applied were assured and validated by calibration with synthetic standard gas mixtures (Kanter *et al.*, 2002)
- second stages, called *external quality assurence*, the instruments were inter-compared by sampling and measuring ambient air at the same time and at the same place. From this procedure, the combined uncertainty and relative uncertainties were calculated.

In addition, the instruments were periodically controlled by calibrations.

In the following sections, the QA procedure applied for the NMHC measurement during the BAB II - A656 experiment is presented.

Internal quality assurance

The used calibration gases contained 30 different C_2-C_9 NMHCs in the ppbV range from which the following were measured by all systems: 2-methylpentane, 3-methylpentane, n-hexane, benzene, cyclohexane, n-heptane, toluene, ethylbenzene, m-/p-xylene, o-xylene. According to the expected ambient concentrations, the calibration gas mixtures were diluted with synthetic air and measurements were carried out in the pptV range.

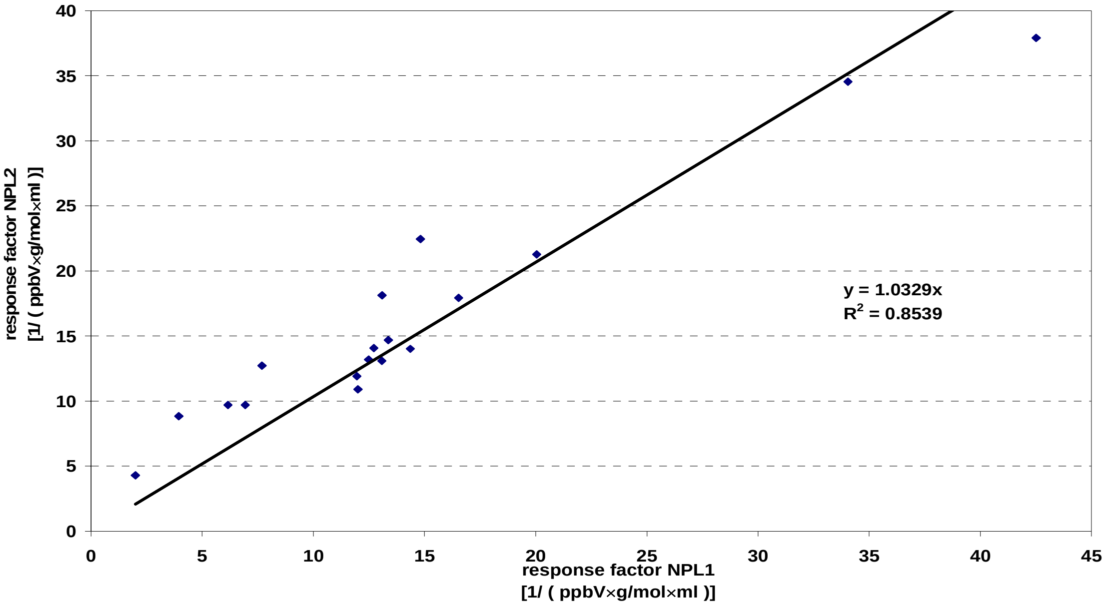

Figure 2-10: Comparison of the calibration gases NPL1 and NPL2 used for the NMHC B system.

Figure 2-10 shows as an example the comparison of the response factors for one of the quasi on-line GC system, namely NMHC B, obtained from the analysis of the NPL1 calibration gas mixture (performed on April 25, 2001) and NPL2 calibration gas (performed on April 27, 2001). It shows that for the NMHC B system the two calibration gases agree within 3%. The off-line system (NIOSH tubes) revealed within the standard deviation the same variation. Accordingly, an average mixing ratio of the two calibrations was used for further calculations. During the campaigns, the on-line systems were calibrated every week. The response factors obtained from different calibrations were averaged and used to calculate the mixing ratios. During a one-month measurement campaign, an average standard deviation of the response factors of 20% was found.

<u>External quality assurance: Comparison of measurements in ambient air</u>

Following the second step of the quality assessment all systems were installed at the same place, sampled and measured ambient air at the same time. The diurnal variation of the toluene mixing ratio, which was calculated by using the corresponding response factors, resulting from the calibration is plotted as an exampled in Figure 2-11.

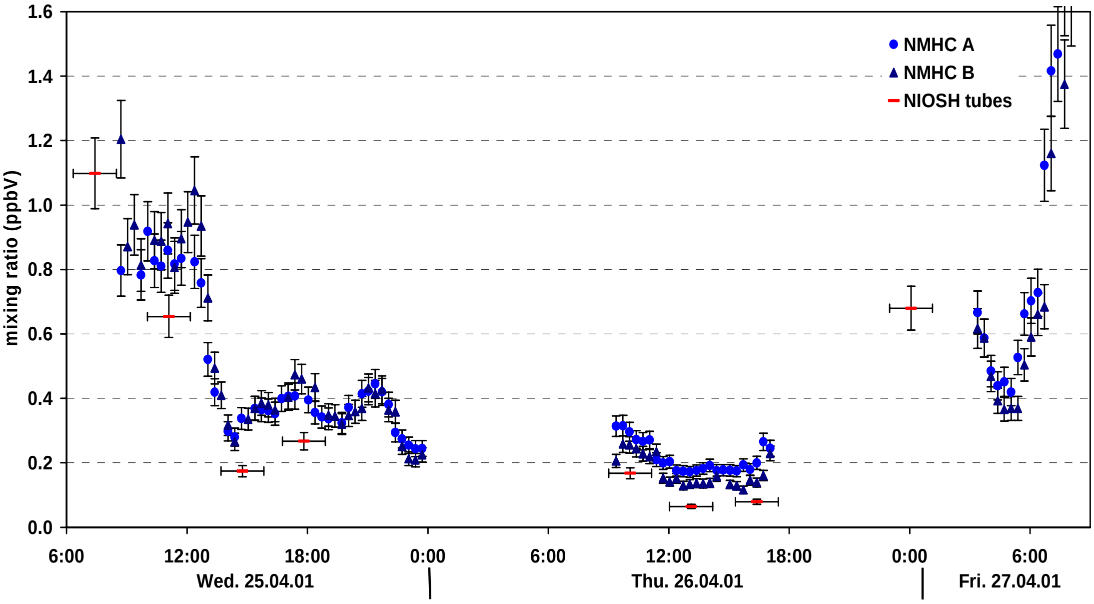

Figure 2-11: Time series of 16 min mean values for the NMHC A and NMHC B systems and of 3 h mean values (NIOSH tubes) for toluene.

The day variation shown in Figure 2-11 is for time series of 16 min time resolution for the on-line systems NMHC A and NMHC B and 3 h mean values for the NIOSH tubes. In order to correlate the data sets, the on-line data were averaged afterwards to the sample interval of the off-line system. For further calculations, the off-line system was used as the reference system since vertical profiles for the C_6-C_9 NMHC were measured only with this system and for some compounds such as 1,2,4 and 1,3,5 trimethylbenzene (TMB) its accuracy was better than that of the on-line systems. Harmonisation of the data: the reduction of the systematic deviation of the on-line analysers data were achieved by applying correction equations, which have been calculated by plotting the off-line data (reference) versus the on-line data, as shown in Figure 2-12.

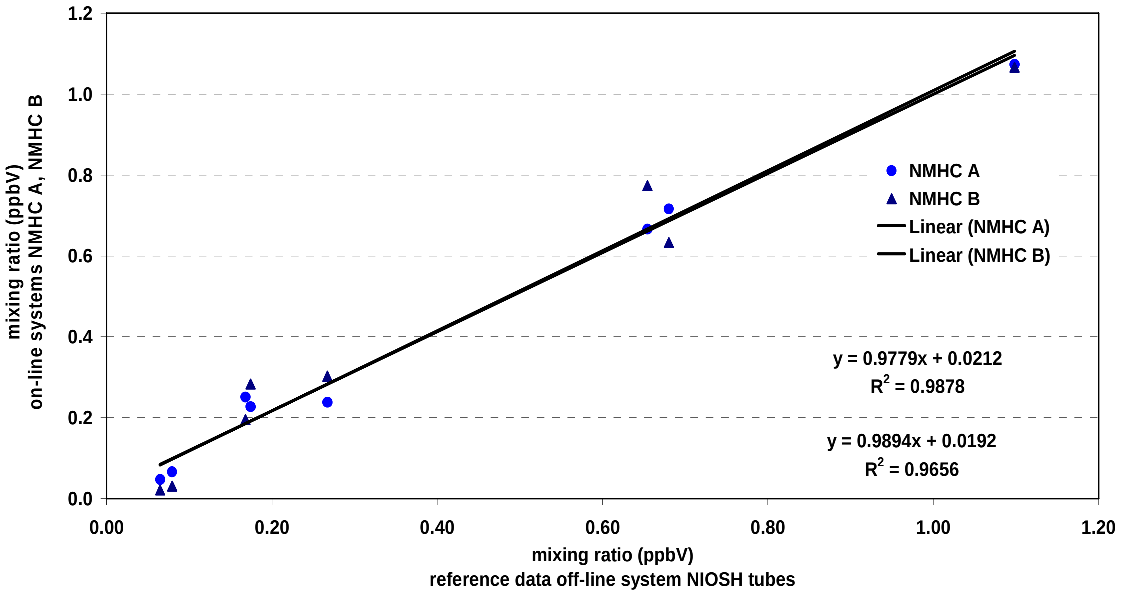

Figure 2-12: Correlation of toluene for the systems NMHC A and NMHC B with the reference systems data (NIOSH tubes)

A good correlation between the on- and off-line systems was found and the obtained correction equations were applied to the on-line data.

Figure 2-13 presents, for toluene as an example, the data after the application of the correction equation.

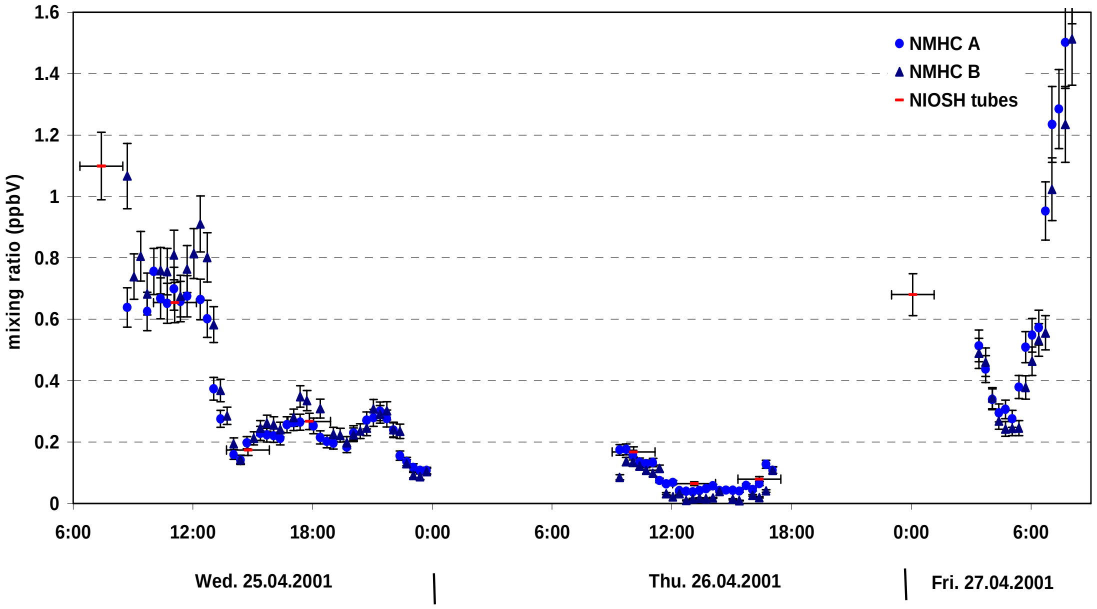

Figure 2-13: Time series of 16 min mean values for the NMHC A and NMHC B systems and of 3 h mean values (NIOSH tubes) for corrected toluene data.

Since C_2-C_6 compounds were measured only by the quasi on-line systems an internal validation procedure was performed. Figure 2-14 shows, for i-pentane as an example, the correlation plot of the mixing ratio obtained for the two quasi on-line GCs. A slope of 1.12 ± 0.026 exhibits good agreement between the two systems. Similar results were obtained for all other compounds.

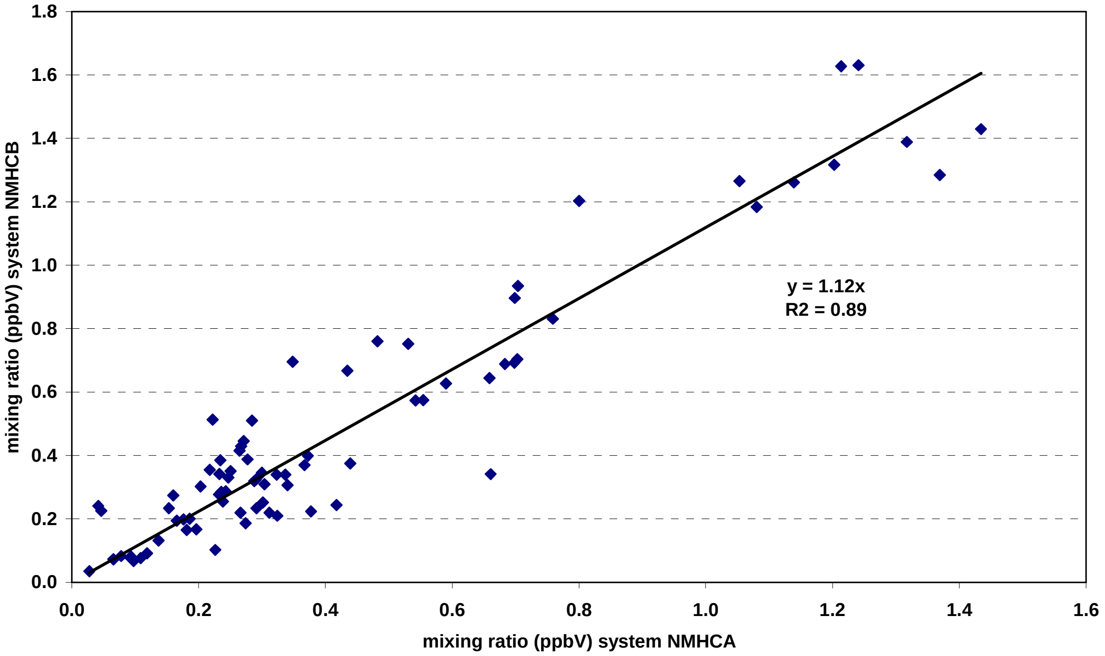

Figure 2-14: Correlation plot of i-pentane mixing ratios, 16 min data, quasi on-line systems.

Assessment of measurement uncertainties

Only recently accepted international guidelines for the calculation of uncertainties have been published. Different guidelines are available for the calculation of measurement uncertainties namely:

- ISO - Guide to the Expression of Uncertainty in Measurements, 1995,
- ISO/IEC Guide 43-1, 1997,
- DIN ISO 13752, 1999.

The German standard DIN ISO 13752 was chosen in the present work, as it was established for the determination of measurement uncertainties under field conditions from results of parallel measurements with different analysers. Contrary to other guidelines, for the DIN ISO 13752 measurement uncertainties depend on the concentration level.

The guideline can be used in case of a linear correlation between the reference values c_{ref} (mean values of all analysers) and the independent measurement values c_a (results of individual analysers). In equations 1-3 b_0 and b_1 are the coefficients of the linear correlation equation, s is the standard deviation, a_0, a_1, a_2 stand for the coefficients of the general variance equation and *u* denotes the measurement uncertainty.

$$c_a = b_0 + b_1 \times c_{ref} \qquad \text{Equation 1}$$

To calculate the standard deviation, the general variance equation was used:

$$s^2 = a_0^2 + a_1^2 \times c_{ref} + a_2^2 \times c_{ref}^2 \qquad \text{Equation 2}$$

The procedure of determining the coefficients, a_0, a_1, a_2, is iterative, using a likelihood function, L[4] for the adaptation of the most probable model function to the data set.

Equation 2 considers the deviation of the analysers' readings from the reference value for low values ($b_0 \rightarrow a_0$), the slope of the correlation equation ($b_1 \rightarrow a_2$) and the general noise of the analysers (a_1). The remaining uncertainty when concentrations of air masses are measured before and after passing an emission source was calculated according to the following equation that results from Equation 2 being extended by the well-known uncertainty propagation equation (ISO, 1995):

$$u = \sqrt{2} \times s = \sqrt{2 \times (a_0^{\,2} + a_1^{\,2} \times c_{ref} + a_2^{\,2} \times c_{ref}^{\,2})} \qquad \text{Equation 3}$$

The measurement uncertainty according to Equation 3 is also called "combined" uncertainty. The uncertainties shown in Table 2-5 are expressed in the form of absolute "combined" uncertainties (ppbV) and relative "combined"uncertainties (%).

The reported uncertainty was given at the concentration level of the sample in question. This is indispensable since the analyses usually encompass wide concentration ranges, while at the

---

[4] A likelihood function L(a) is the probability or probability density for the occurrence of a sample configuration $x_1 \ldots x_n$, given that the probability density f(x, a) with parameter is known:

$L(a) = f(x_1, a) \ldots . f(x_n, a)$ (Harris and Stocker, 1998).

same time the uncertainty is strongly dependent on the concentration. The calculations were performed using the SOLVER program, under Microsoft Excel.

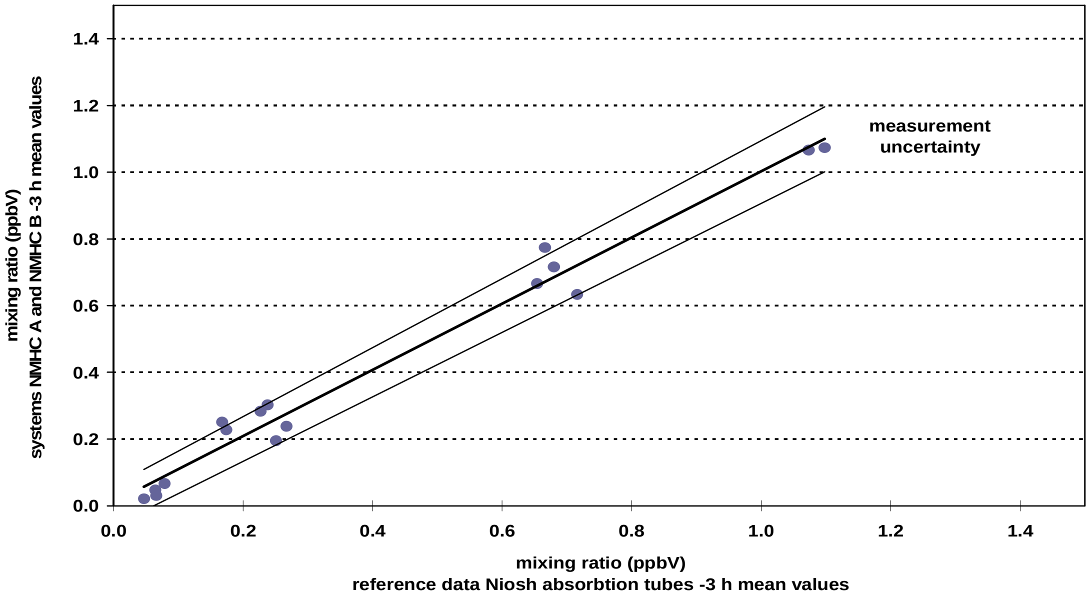

Figure 2-15: Correlation between reference values and mean values from systems NMHC A and NMHC B for toluene (ambient air) and range of measurements uncertainty.

Figure 2-5 and Table 2-5 show that the combined uncertainty is increasing with higher concentrations, whereas the relative uncertainty (%) decreases. In reality, for higher concentrations than those presented in the table, the measured uncertainties would be lower than the presented ones.

Table 2-5: Uncertainties obtained using the Solver program for assessing the C_6-C_9 compounds.

Compound	**Mixing ratios (ppbV)**	**Absolute "combined" uncertainty u (ppbV)**	**Relative "combined" uncertainty u (%)**
2-methylpentane	0.02	0.16	799.30
	0.10	0.16	159.90
	0.15	0.16	106.60
	0.20	0.16	79.90
	0.45	0.16	35.50
3-methylpentane	0.01	0.02	193.20
	0.10	0.02	22.70
	0.15	0.03	17.50
	0.20	0.03	15.30
	0.25	0.04	14.20
n-hexane	0.02	0.02	102.40
	0.04	0.02	56.10
	0.80	0.21	26.60
	0.10	0.03	33.10
	0.15	0.04	29.60
benzene	0.05	0.01	28.70
	0.10	0.03	28.70
	0.30	0.09	28.70
	0.40	0.11	28.70
	0.60	0.17	28.70
cyclohexane	0.01	0.02	183.50
	0.03	0.03	105.90
	0.07	0.05	69.40
	0.09	0.06	61.20
	0.17	0.08	44.50
n-heptane	0.02	0.01	29.50
	0.04	0.01	29.50
	0.06	0.02	29.50
	0.07	0.02	29.50
	0.15	0.04	29.50
toluene	0.05	0.06	121.90
	0.25	0.07	27.60
	0.50	0.08	15.60
	0.75	0.09	11.50
	1.25	0.10	8.00
ethylbenzene	0.02	0.01	63.00
	0.04	0.02	47.90
	0.10	0.04	35.90
	0.20	0.06	30.90
	0.50	0.14	27.40
o-xylene	0.01	0.01	116.20
	0.15	0.04	30.00
	0.20	0.05	26.00

Table 2-5: (continued)

Compound	**Mixing ratios (ppbV)**	**Absolute "combined" uncertainty u (ppbV)**	**Relative "combined" uncertainty u (%)**
o-xylene	0.25	0.06	23.20
	0.30	0.06	21.20
m-/p-xylene	0.03	0.03	93.70
	0.10	0.04	44.00
	0.50	0.12	23.80
	0.60	0.14	22.80
	0.75	0.16	21.80

Similar results were obtained in the case of the NMHC A system in comparison with the prepared tubes. The relative uncertainty in this case range from 3.5 to 20%.

2.2.2 CO_2, NO_x

2.2.2.1 CO_2 Monitor- Chromatosud

Carbon dioxide (CO_2) was measured using an automatic, compact GC system (Chromatosud), which has been described in more detail elsewhere (Becker *et al.,* 1999). The used measuring procedure for this instrument is the one recommended by the US Department of Labor Occupational Safety and Health Administration (OSHA). The air sample is collected using an internal sampling pump through a 1 ml-sample loop and afterwards is injected automatically through a 10-way sampling loop into the GC system. Since this internal sampling pump has only a limited flow rate, a second external pump was used for increasing the pumping capacity. Ambient air was pumped at 10 l/min to the GC and 150 ml per min through 1 ml sample loops. The large flow ensures a small residence time of the sample in the sampling line. The 2 m long separation column has an outside diameter of 0.306 cm and is packed with Porapak Q (80-100 mesh). A thermal conductivity detector (TCD) with helium as carrier gas is used. A computer programme, namely the Borwin software by which the setting parameters of the instrument such as sampling time, sampling volume etc. can be adjusted, automatically controls the instrument. The duration of a typical sampling cycle was 5 min. The same software was used for the integration of the obtained chromatograms. The CO_2 mixing ratios were determinate by comparing the peak areas of the sample chromatogram with the one obtained by using a calibration gas mixture.

2.2.2.1.1 *Performance of the instrument during measurement campaigns*

Calibration procedure

During the Lundby Tunnel experiment the linearity of the instrument's response was verified by a calibration procedure, using two calibration gases namely a calibration gas (BUW) containing 893 ± 18 ppmV and a calibration gas (IVL), containing 967 ± 19.3 ppmV CO_2. According to the expected ambient air concentrations, the calibration gases were diluted with synthetic air and measurements were performed. As can be observed in Figure 2-16 there is a good linear correlation between peak areas and the CO_2 mixing ratio.

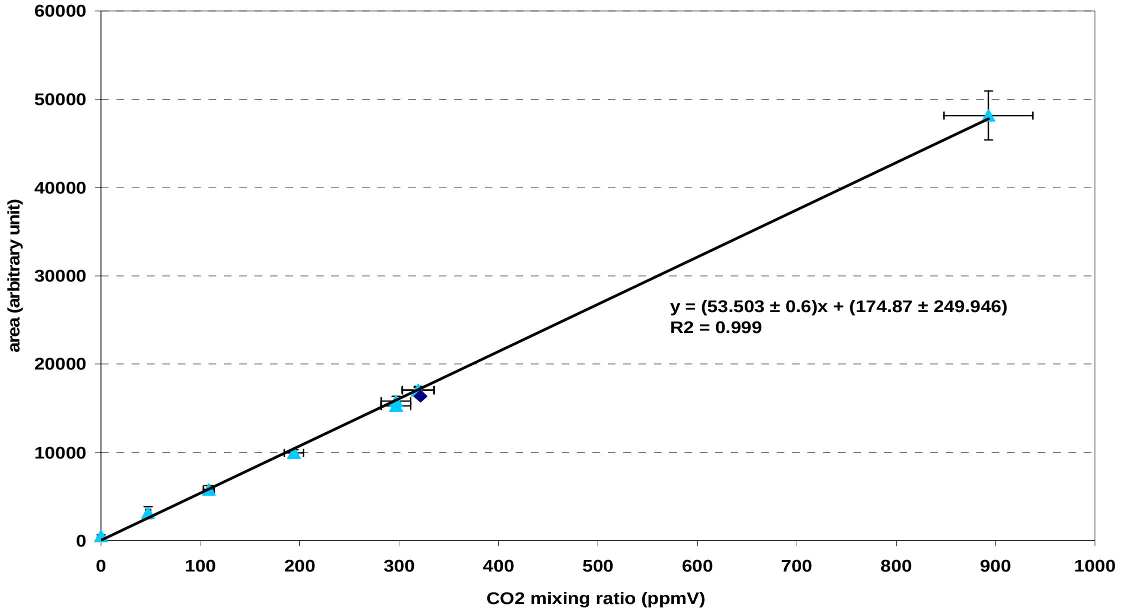

Figure 2-16: Calibration curve for CO_2 using the CO_2 Monitor from Chromatosud.

From the intercept of the straight line in Figure 2-16 a detection limit of 4 ppmV was determined. The slope provided the response factor of the instrument of 53.5 ± 0.6 area/ppmV.

External quality assurence; Intercomparison with other CO_2 monitors

During the different experiments, different working groups were involved in measuring different air pollutants including CO_2, CO, NO and NO_2. Accordingly, the same quality assessment procedure was applied for the CO_2 instruments as for the NMHCs. The CO_2

instruments participating in the quality assessment procedure were inter-compared by sampling and measuring ambient air at the same time and at the same place.

A typical correlation plot of the data obtained from the Chromatosud CO_2 monitor, operated by the BUW group, and the data obtained using the NDIR (API 360) instrument of the Technical University of Graz (TUG) group is presented in Figure 2-17.

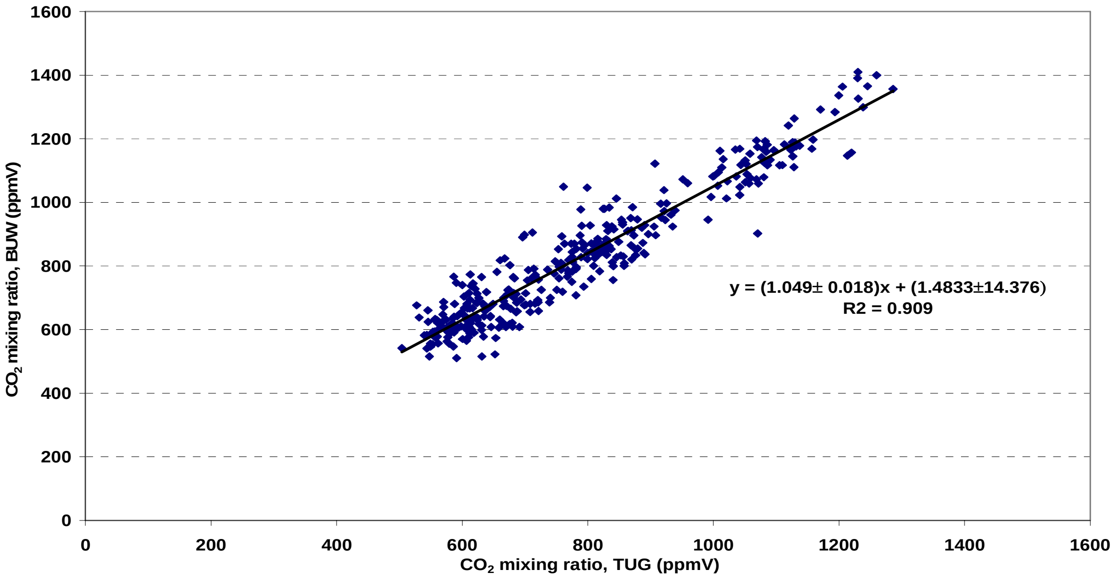

Figure 2-17: Comparison of the CO_2 data (15 min average) from BUW and TUG during the Plabutsch Tunnel campaign.

A good correlation between the two instruments was found, with a correlation factor of 1.05 ± 0.02. Accordingly, the mixing ratios obtained by the BUW instrument were further considered in the data evaluation of the present study.

2.2.2.2 CO_2 Monitor - Carbondio 1000

During the Kingsway Tunnel experiment measurements of CO_2 were performed with the compact automatic Carbondio 1000 analyser from Pewatron AG. The non-dispersive infrared method (NDIR) is used in the instrument to quantify CO_2. As the basis for the concentration measurements, the Lambert-Beer law is applied. The absorption spectra are recorded at 4.26 µm. Calibration of the instrument was performed with a CO_2 standard gas mixture. The system has a measurement range up to 1000 ppmV and a time resolution of 3 s. Figure 2-18 shows a calibration curve for this instrument as an example.

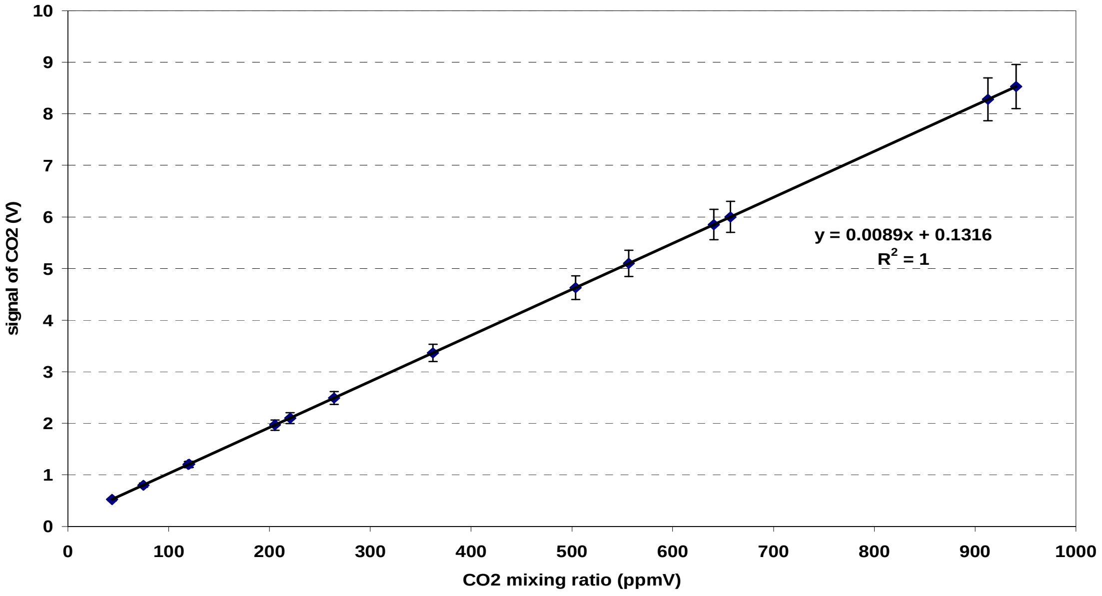

Figure 2-18: Calibration curve for CO_2 using the Carbondio 1000 instrument.

The calibration curve from Figure 2-18 shows an excellent correlation between the standard gas mixture and the instrument readings.

2.2.2.3 NO_x Monitors

NO and NO_2 were measured using different monitors based on the chemiluminescence principle. NO_x measurements were performed during the BAB II - A656 campaign not only at the base of the towers but also at different altitudes. The BUW group operated one analyser, namely: CLD AL 770 ppt (ECO-Physics) with photolysis converter PLC 760. The instruments calibration was performed using standard calibration gas-mixtures (Messer-Griesheim). Figure 2-19 presents typical calibration curves for NO and NO_2 using the Eco-Physics instrument during the A656 measurements.

Figure 2-19 (b) (NOc-NO) represents the signal regarding the fractionally converted NO_2

The calibration curves shown in Figure 2-11 (a and b) showed good correlation between the standard gas mixtures and the readings of the monitors. Using the Eco-Physics instrument, the calculated response factor for NO and NO_2 were used to calculate the mixing ratios of nitrogen oxides. In Figure 2-11(b), NOc-NO denotes the signal regarding to the fractionally converted NO_2. During the campaign, the NO_x monitors participated in the quality assurence procedure. The quality assurence procedure was similar to the one performed for NMHC and is described in more detail by Vogt *et al.,* 2005.

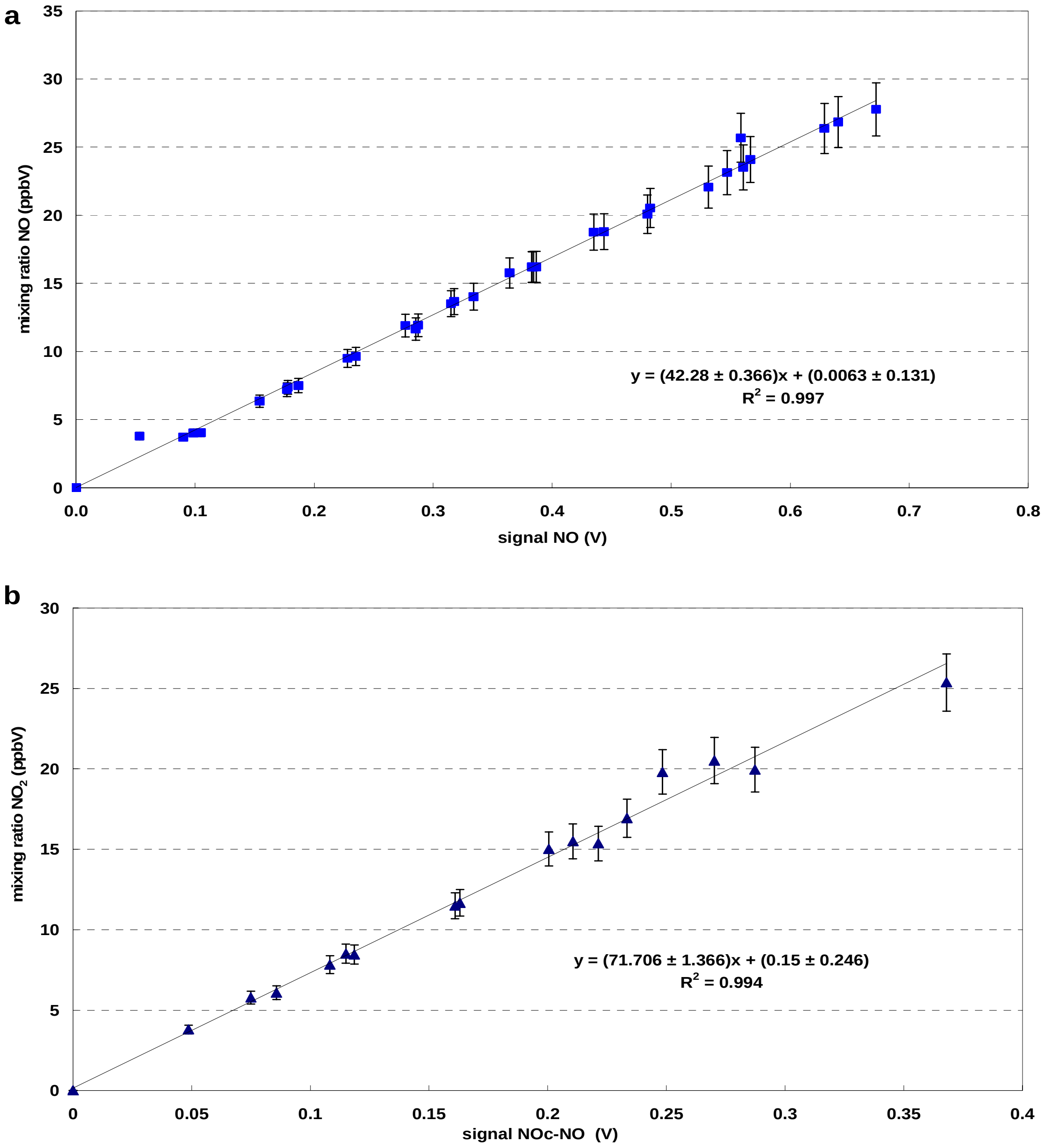

Figure 2-19: Typical calibration curve for nitrogen monoxide (a) and nitrogen dioxide (b).

2.2.3 Meteorological parameters

In order to derive vehicle emission rates from tunnel air measurements it is necessary to know the flow rates of the incoming fresh air and of the outgoing exhaust air.

A large set of instruments were used during the tunnel campaigns. Herewith, information relevant for the discussion of the results of this work will be briefly presented. In the tunnels, the air flow measurements were made using a FLOWSIC 200 ultrasonic device, which measures the mean air flow velocity across the entire width of a tunnel. The device can measure flow velocities of up to 20 m/s with a typical accuracy of ± 0.1 m/s. Sender and receiver units were mounted on both sides of a tunnel at a fixed angle of inclination to the air flow. The units contain piezoelectric ultrasonic transducers which operate alternately as transmitter and receiver. The transit time of the ultrasonic pulses varies according to the flow velocity. The tunnel operators provided data of the performed airflow measurements (Rodler *et al.,* 2005).

During the Lundby Tunnel measurements, wind speed was measured with two instruments at different locations. The tunnel operator provided data of the airflow measurements performed in the middle of the tube. In addition, SF_6 was used as a tracer and measured with a Fourier Transform InfraRed spectrometer (FTIR) at different places. With the measured mixing ratio of SF_6 the wind speed data were validated. A good agreement between the data was found.

Airflow measurements in the Plabutsch Tunnel took place in the third tunnel section; where fresh air was only supplied by the ventilation shaft north, see Figure 2-2. From the airflow measurements, it was concluded that the horizontal air exchange between the section, three and the two adjacent ventilation segments is negligible. An airflow rate typically of 200 m^3/s was applied for the calculation of emission factors.

The airflow in the north bore of the Kingsway Tunnel was recorded continuously during the experiment. The flow rates were calculated from fan settings provided by the tunnel operator (Rodler *et al.,* 2005).

During the BAB II - A656 motorway experiment (Corsmeier *et al.,* 2005) meteorological parameters: temperature, pressure, wind direction, wind speed and relative humidity were recorded (Kohler *et al*., 2005).

2.3 FLEET AND DRIVING CHARACTERISATION

Traffic composition is an important factor for estimating emissions, especially if details of typical vehicle-mixes are available. Although national statistics of fleet composition are available they may not adequately describe the local situation leading to erroneous emission factors. During the performed experiments, traffic data were automatically recorded using loop detectors and/or laser/radar devices from which the fleet composition and vehicle speed was determined with a time resolution of 1 min.

CHAPTER 3

3 MEASUREMENT RESULTS

Continuous measurements of NMHC, NO_x, CO_2, meteorological parameters and traffic census have been carried out during three tunnel measurements i.e. the Lundby Tunnel in Sweden (during March, 2001), the Plabutsch Tunnel in Austria (during November, 2001), the Kingsway Tunnel in England (during March, 2003) and in field experiments conducted along a section of the A656 motorway in Germany (during May, 2001).

Special emphasis was placed on the speciation of the hydrocarbons emissions. From the large number of NMHCs present in the exhaust air, the following groups of hydrocarbons have been analysed:

alkanes: ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, 2-methylpentane, 3-methylpentane, n-hexane, n-heptane

alkenes/alkynes: ethyne, ethane, propene, iso-butene, 1-butene, trans-butene, cis-butene, isoprene, trans-2-pentene, cis-2-pentene, 1,3-butadiene

aromatic hydrocarbons: benzene, toluene, ethylbenzene, m,-p-,o-xylene, 1,2,4 trimethylbenzene, 1,3,5 trimethylbenzene

These compounds are together with the nitrogen oxides important ozone precursor substances recommended for measurements in the European Ozone Directive 2002/3/EC.

The results of these campaigns are presented and discussed in the following sections.

3.1 FLEET AND DRIVING CHARACTERISATION

3.1.1 Tunnel experiments

In order to simplify the traffic data analysis the vehicles were classified into two categories:

- Light duty vehicles (LDV): private cars (PC) and delivery vans (with or without trailer) - light duty commercial vehicles (LDCV)
- Heavy duty vehicles (HDV): trucks with 2 or 3 axes (with or without trailer), urban buses, coaches.

Table 3-1 presents an overview of the road traffic statistics registered during the tunnel experiments.

During the tunnel campaigns for a shorter time period the license plates of the vehicles passing through the tunnels were recorded. These data were used to obtain information about the emission concept of the corresponding vehicles, i.e.conventional, G-cat, EURO 1, EURO 2 etc. For the model calculations, which are described in more detail below, it was assumed that the fleet composition remained constant during the whole measurement campaign.

For the Plabutsch Tunnel, data are presented in comparison with fleet data obtained in a campaign performed in 1998 (Rodler, *2000*). The table shows in addition to an increase of the traffic density an increasing contribution of HDV to the total traffic.

The average vehicle speed was 80 km/h in the Lundby and in the Plabutsch Tunnel and 65 km/h in the Kingsway Tunnel.

Table 3-1: Overview of the road traffic statistics during the performed experiments.

	Lundby Tunnel	**Plabutsch Tunnel**		**Kingsway Tunnel**
	March 2001	November 1998	November 2001	February 2003
LDV(1)	24665	15679	18447	19403
HDV(1)	4011	4156	5410	1702
HDV(4)	14%	21%	22.7%	8%
LDV(2)	7974	12011	13226	15072
HDV(2)	535	1007	1340	470
HDV(5)	6.3%	7.7%	9.2%	3%
LDV+HDV(3)	1194(1) 354(2)	826(1) 542(2)	994(1) 606(2)	880(1) 648(2)

(1)number of vehicles during working days; (2)number of vehicles during weekend, (3) vehicles/h;
(4)contribution of HDV during working days; (5)contribution of HDV during weekend

3.1.2 The BAB II- A656 motorway experiment

During the BAB II - A656 experiment, the traffic measurements allowed the classification of individual passenger cars with respect to the Euro norms they fulfilled. The results showed that in 2001 there were 7.5% more vehicles with low-level catalyst systems, i.e. before EURO 1 standards, on the road than calculated by the HBEFA. Based on HBEFA calculations the prediction for the number of gasoline fuelled cars with high-level catalyst systems (EURO 3) is 29% for the week days, in reality, only 17% have been observed (Kühlwein and Friedrich, 2005).

Table 3-2: Overview of the average road traffic statistics obtained from automatic and manual traffic counts during April 27-May 27, 2001.

A656	**All vehicles**[(1)] Number/day	**HDV**[(1)] %	**All vehicles** [(2)] Number/day	**HDV**[(2)] %	**All vehicles** Vehicles /hour
	60590	5.5	39988	1.5	2524[(1)]/1666[(2)]

[(1)]working days; [(2)]weekend

3.2 TUNNEL AIR MIXING RATIOS

During three-measurement campaigns in the Lundby Tunnel (Sweden), the Plabutsch Tunnel (Austria) and the Kingsway Tunnel (England), 27 C_2-C_9 NMHCs were quasi-continuously measured and quantified by using prepared standard gas mixtures (NPL) for calibration. In Figure 3-1 the average working day profile of NMHC, shown for toluene as an example, follows the diurnal traffic variation.

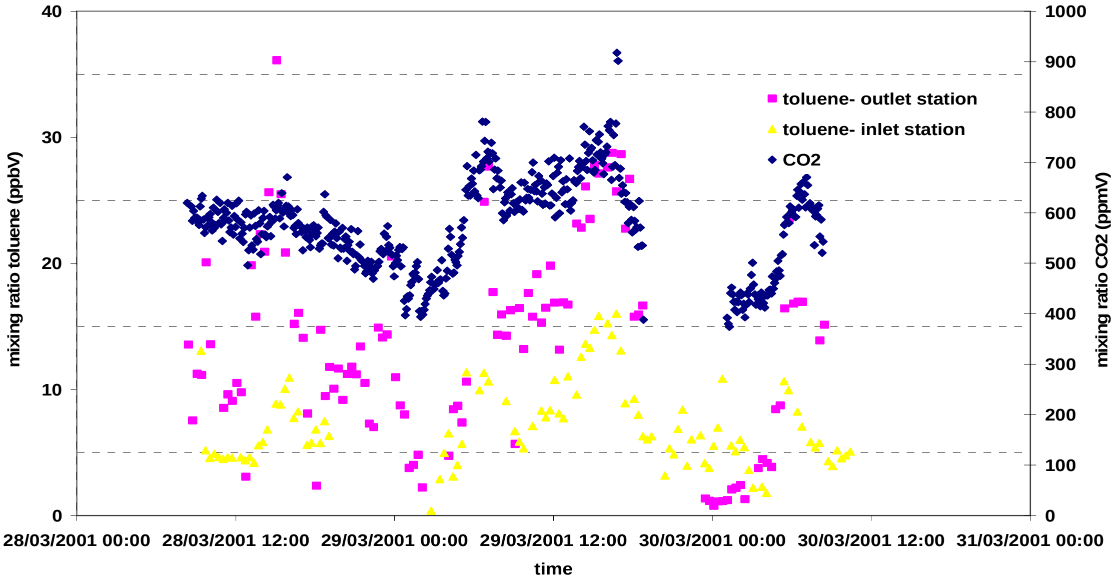

Figure 3-1: Diurnal variation of toluene and CO_2 during a four days period from Tuesday to Friday, March 27-30, 2001 in the Lundby Tunnel.

The higher concentrations of NMHC that were observed at the outlet station during the Lundby Tunnel measurements show in comparison with the results from the inlet station, that these compounds were emitted as primary pollutants from traffic (Lies, 1988; Gregori *et al.*, 1989; Staehelin and Schläpfer, 1995; Fraser *et al.*, 1998; Schmitz *et al.*, 1999; Gomes, 2003).

Since the tunnel is a covered place where no direct sunlight can enter, the tunnel measurements supply the directly emitted values from the road traffic under real world condition without any photochemistry. Accordingly, it was assumed that the increase in the NMHC concentration is proportional to the emission strength of the corresponding species as is presented in Figure 3-2.

Figure 3-3 shows the diurnal variation of traffic density, CO_2, toluene, benzene and i-pentane for one week during the measurement campaign in the Plabutsch Tunnel. The inlet concentration of CO_2 was about 390 ppmV. The diurnal variation observed in the studied tunnels is very similar. However, the CO_2 concentration in the Plabutsch Tunnel was almost a factor of two higher than in the Lundby Tunnel, whereas the NMHC concentrations in the Plabutsch Tunnel were significantly smaller than in the Lundby Tunnel. This difference can be attributed to the different fleet composition in both tunnels, i.e. the Plabutsch Tunnel is passed by more HDV (22.7%) leading to an increase in CO_2 but not in the NMHC concentration. This is confirmed also by the higher values of NO_x in the Plabutsch Tunnel of 4.42 ± 2.11 ppbV.

Figure 3-4 shows the diurnal variation of traffic density, CO_2, toluene, benzene and i-pentane for one day during the measurement campaign in the Kingsway Tunnel. The concentrations start to increase early in the morning and afternoon with a maximum during rush hours. Similar profiles were also obtained for the other NMHC species investigated.

The Appendix: Table 4, Appendix: Table 5 and Appendix: Table 6 summarise the maximum, minimum, average, median and standard deviation (S.D.) mixing ratios (ppbV) of the NMHC, CO_2, and NO_x for the three tunnel campaigns. The presented results show that the largest mixing ratios of the NMHC were found among the alkanes for: ethane, iso-butane, iso-pentane, among the alkenes/alkynes: propene, i-butene/1-butene and among the aromatic hydrocarbons: toluene followed bybenzene, o-xylene and m-/p-xylene.

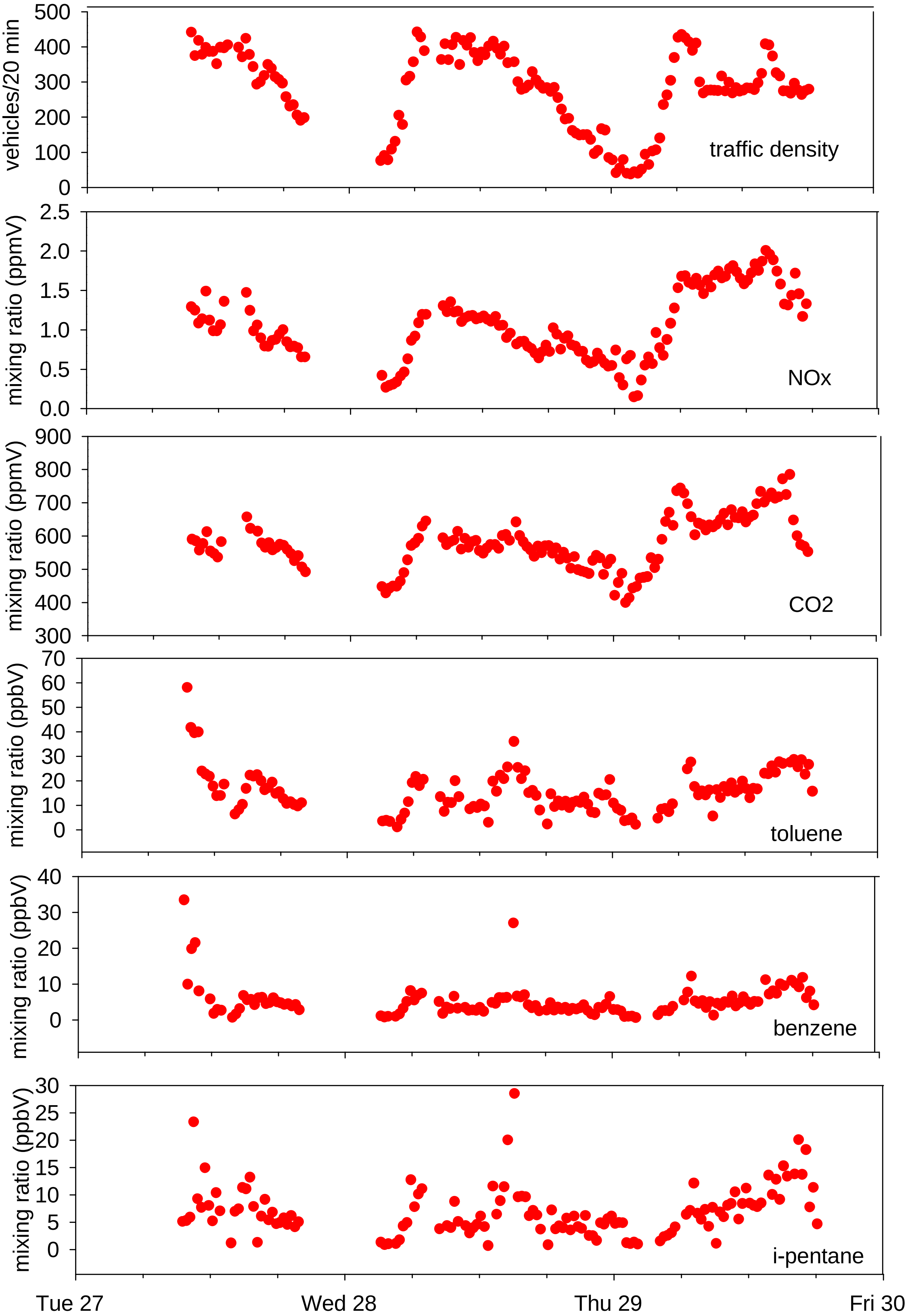

Figure 3-2: Diurnal variation of traffic density, NO_x, CO_2, toluene, benzene and i-pentane during four working days, March 27-30, 2001, in the Lundby Tunnel.

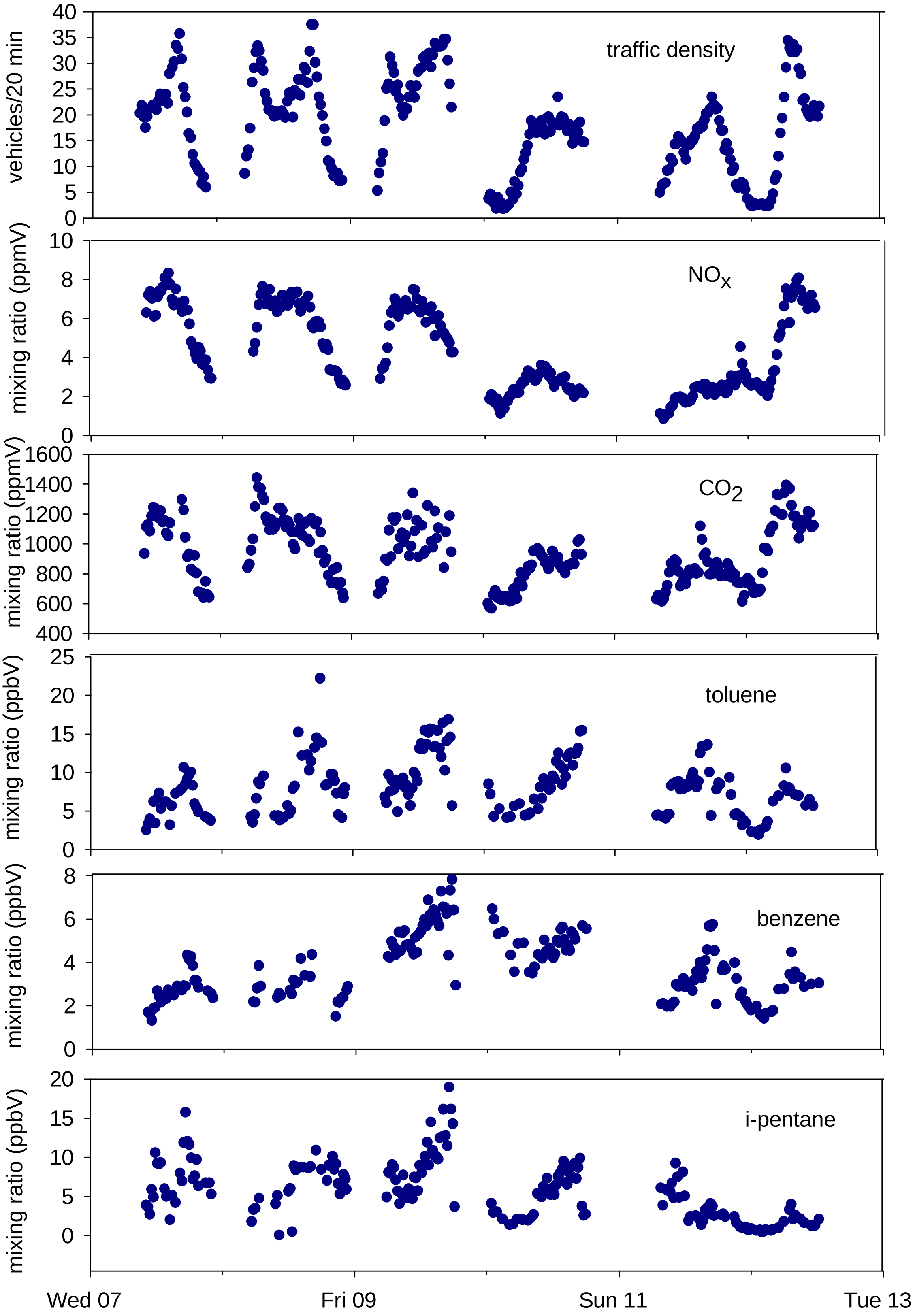

Figure 3-3: Diurnal variation of traffic density, NO_x, CO_2, toluene, benzene and i-pentane during four days, November 7-12, 2001, in the Plabutsch Tunnel.

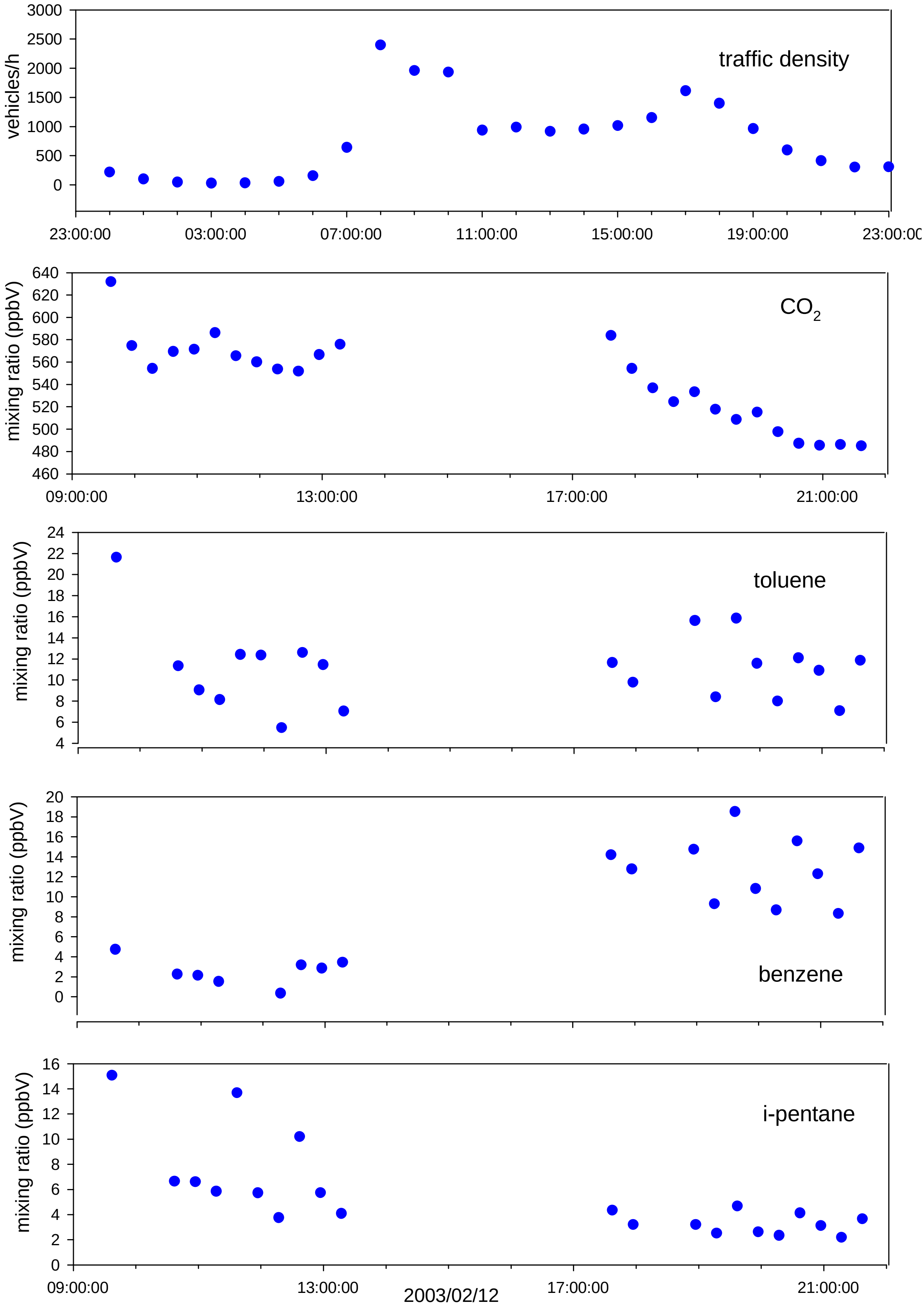

Figure 3-4: Diurnal variation of traffic density, CO_2, toluene, benzene and i-pentane during one day, February 12, 2003, in the Kingsway Tunnel.

A direct comparison of the obtained NMHC mixing ratios in absolute values with results from other studies is difficult to perform because of differences in the tunnel characteristics, traffic volume, and fuel composition. Nevertheless, as it is shown in Table 3-3 the average mixing ratios of some measured species were comparable with results obtained from other studies. The data of the present study agree with studies performed during 2002 in the Gubrist Tunnel, in Switzerland, but are lower compared with the results of the Kiesberg Tunnel, in Germany obtained by measurements performed in 1997-1998.

Table 3-3: Average and mean mixing ratios (ppbV) of some selected compounds from various tunnel studies.

Tunnel	i- butane	i-pentane	benzene	toluene	m-/p -xylene	Traffic density
Lundby (2001)[a,b]	4.9 ± 3.6	6.4 ± 4.61	4.97 ± 4.3	14.69 ± 9.0	NA	14% DV
Plabutsch (2001)[a]	5.3 ± 3.14	5.9 ± 3.6	3.8 ± 1.5	8.2 ± 3.6	5.7 ± 3.0	23% DV
Kingsway(2001)[a]	2.23 ± 1.58	8.72 ± 5.16	5.19 ± 2.76	13.93 ± 6.9	NA	8% HDV
Kiesberg (1998)[c]	14.4 ± 12.3	30.5 ± 28.9	23.8 ± 20.9	36.8 ± 35.3	10.6 ± 8.0	6% HDV
Gubrist (2002)[d]	2.86	14.8	6.65	14.5	5.98	8% HDV

[a] this study; [b]represents the average mixing ratios measured at the outlet station; [c]Gomes, 2003; [d] Stemmler *et al.,* 2004, represent the mean mixing ratios at the outlet station, online GC-MS measurements

3.3 A656 MOTORWAY EXPERIMENT MIXING RATIOS

3.3.1 NMHC emission profiles upwind-downwind

During the one-month measurement campaign, April-May, 2001, the C_2-C_9 NMHCs were continuously measured on both basement sites of the motorway. Only four measurement days, namely May 8, 14, 17 and 18, 2001, were considered having suitable meteorological conditions, such as wind direction perpendicular to the motorway. Accordingly, only data from these days were used for further evaluations. The emission ratios of the C_2- C_9 compounds measured at the north and south towers basement (5 m) are presented, as an example, for May 17, 2001 in the Appendix: Table 7. The observed NMHC distribution is in good agreement with literature data. Among the aromatic hydrocarbons, toluene showed the largest mixing ratio, whereas iso-pentane and propene had the largest mixing ratios among the classes of alkanes and alkenes, respectively.

For further evaluation and data discussion (see paragraph 4.2.4), the NMVOC concentrations were recalculated from the ppbV in μg/m^{3}(5). Typical downwind and upwind concentration differences are up to 1.00 μg/m^3 toluene and 0.35 μg/m^3 benzene, depending on the traffic load.

It should be point out that vertical profiles were measured only for C_6-C_9 NMHC. For computing the vertical distribution of the C_2-C_6 compounds, it was assumed that at the upwind tower the ratio pollutant/toluene at the basement site was equal to the ratio at higher altitude. Toluene was chosen as the reference compound since it was shown to be emitted from road traffic and it has been measured with the on-line and off-line systems. Down-wind vertical concentrations for compounds that were not directly vertically measured, respectively of C_2-C_6 compounds were calculated as a function of altitude starting above the motorway plume, by multiplying the up-wind ratios obtained at ground level (on line measurements), with the toluene concentration at the desired altitude, measured down-wind with the off-line system. As an example, in the Appendix: Table 7 the vertical calculated profiles for May 17, 2001 are presented.

Figure 3-5 shows the vertical variation of toluene on both sides of the motorway for different periods of May 14, 2001, as an example. The figure shows a vertical gradient of the toluene concentration at the north tower (black bullets), which is downwind of the motorway, whereas at the upwind south tower, the toluene concentration is vertically almost constantly distributed (white bullets). The toluene vertical gradient at the downwind north tower is much more pronounced only at the first measurement height of 5 m above ground level (agl). This can be attributed to the motorway as a NMHC emission source. The vertical gradient that was exemplarily shown for toluene has not been observed for all hydrocarbons measured during the campaign. This fact points to the fact that the analysed NMHC compounds are not equally emitted by the traffic and that for the NMHCs, which are characterise by very low emission factors, the difference between downwind and upwind concentrations could not be resolved within the standard deviation of the NMHC measurements. As at the upwind site the NMHC were vertically constant, the existence of a plume of NMHC emitted from road traffic is demonstrated. The difference between downwind and upwind hydrocarbon concentrations is

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(5) concentrations calculated for the normal conditions (273.15 K and 1 atm)

mostly pronounced in the rush hour as this time interval is characterised by the highest traffic density.

The time intervals when emissions of the motorway were moved occasionally to the north tower and occasionally to the south tower as the wind direction turned were not considered in the further calculations.

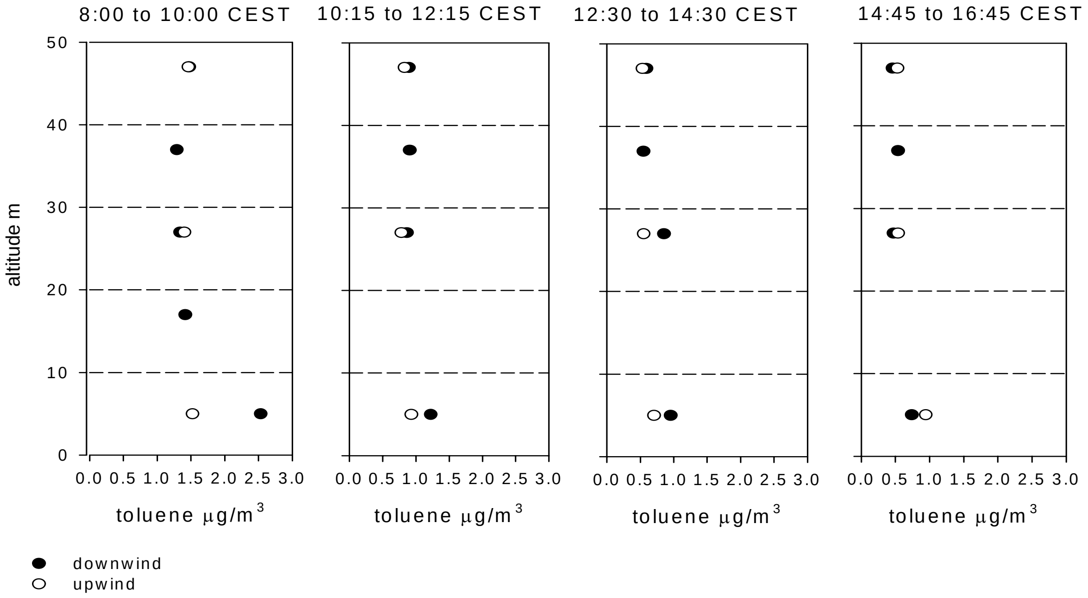

Figure 3-5: Vertical profiles for toluene on May 14, 2001, 08:00-10:00 CEST, 10:15-12:15 CEST, 12:30-14:30 CEST and 14:45-16:45 CEST.

3.4 RELATIONSHIPS BETWEEN HYDROCARBONS AND OTHER POLLUTANTS

Under the assumption of constant background mixing ratios and well-mixed emissions, the emission ratio, E(x)/E(y) is given by the slope of the regression of x and y mixing ratios.

3.4.1 Hydrocarbons versus benzene

In the urban atmosphere, aromatic hydrocarbons are of great interest due to their associated health effects (e.g. benzene) as well as their reactivity with respect to formation of aerosols and ozone.

Since the absolute concentrations measured at different sampling sites cannot be compared directly due to different dilution factors; the normalisation to benzene is commonly used. For further evaluation, these mixing ratios in ppbV were converted into ppbC(6). This unit is related to the moles of carbon and reflects the upper limit of potential reactivity by considering all carbon atoms in a molecule. On the other hand, the evaluation with ppbV could give the lower limit of potential reactivity of carbon atoms in a molecule. In addition, the ratio ppbC/ppbC is related to the moles of carbon in the molecule and will supply almost the same value of the emission ratios calculated in wt/wt.

Figure 3-6 profiles of selected NMHC compounds relative to benzene (ppbC/ppbC) from the Lundby, Plabutsch and Kingsway Tunnel measurements are presented.

For getting an appropriate traffic profile only data points from dense traffic episodes were taken into consideration. The profiles show that propene, propane, i-butane, i-pentane, benzene, toluene, ethylbenzene and the xylenes exhibit the highest mixing ratios and are obviously the most significant constituents of NMHC speciation profiles in the performed studies. The toluene/benzene ratio can be used as a marker of road traffic emissions (Staehelin and Schläpfer, 1994; Schmitz *et al.*, 1999; Rappenglück *et al.,* 2005).

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(6) Mixing ratios in ppbV are converted into ppbC by multiplying them with the number of carbons atoms in the molecule of the particular NMHC, e.g. for propene with 3, for n-butane with 4 etc.

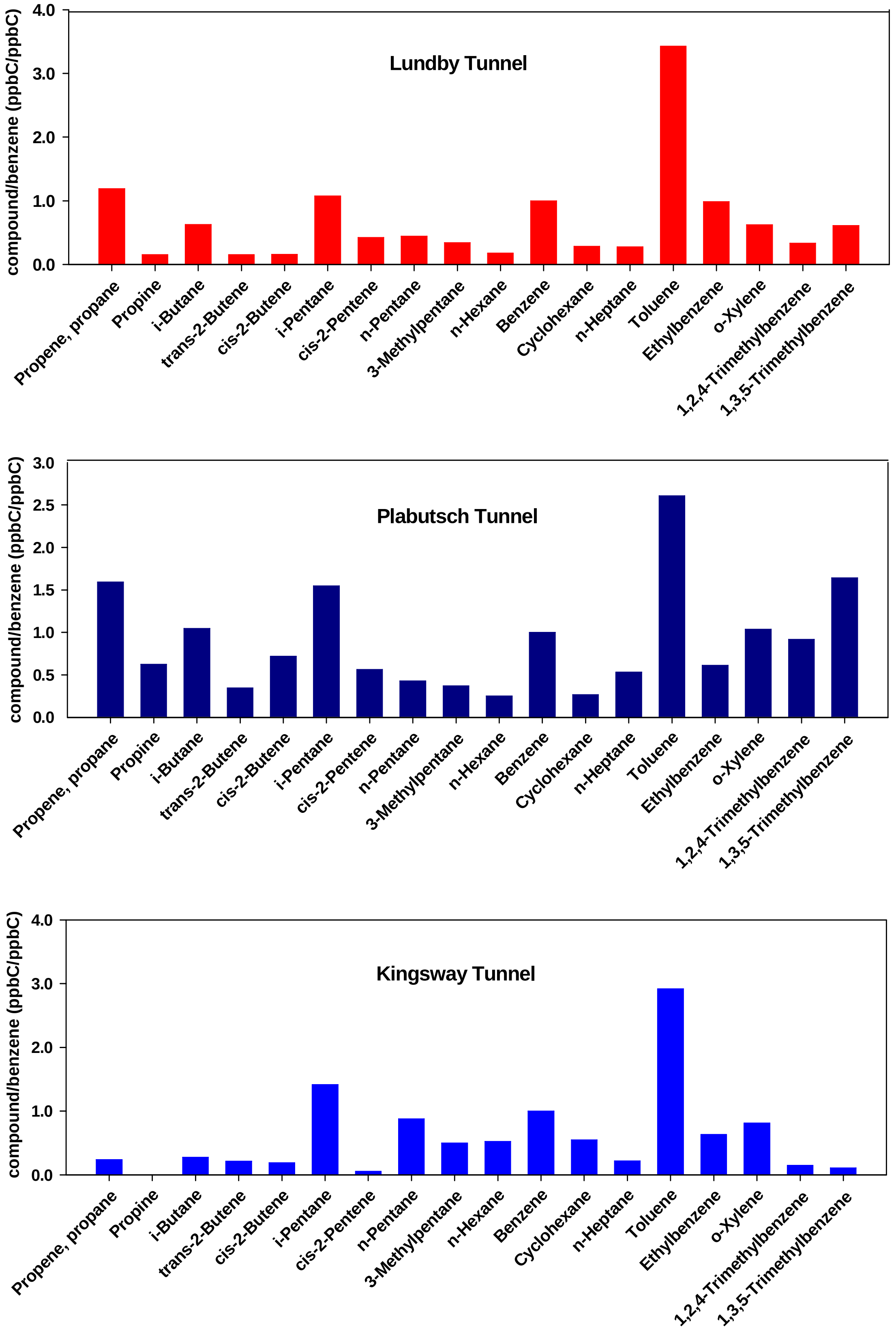


Figure 3-6: Profiles of selected NMHC compounds relative to benzene (ppbC/ppbC) for the Lundby, Plabutsch and Kingsway Tunnel experiments.

Figure 3-7 shows as an example a correlation diagram between toluene (ppbC) and benzene (ppbC) obtained from the measured values for weekdays during the Kingsway Tunnel campaign, February 2003.

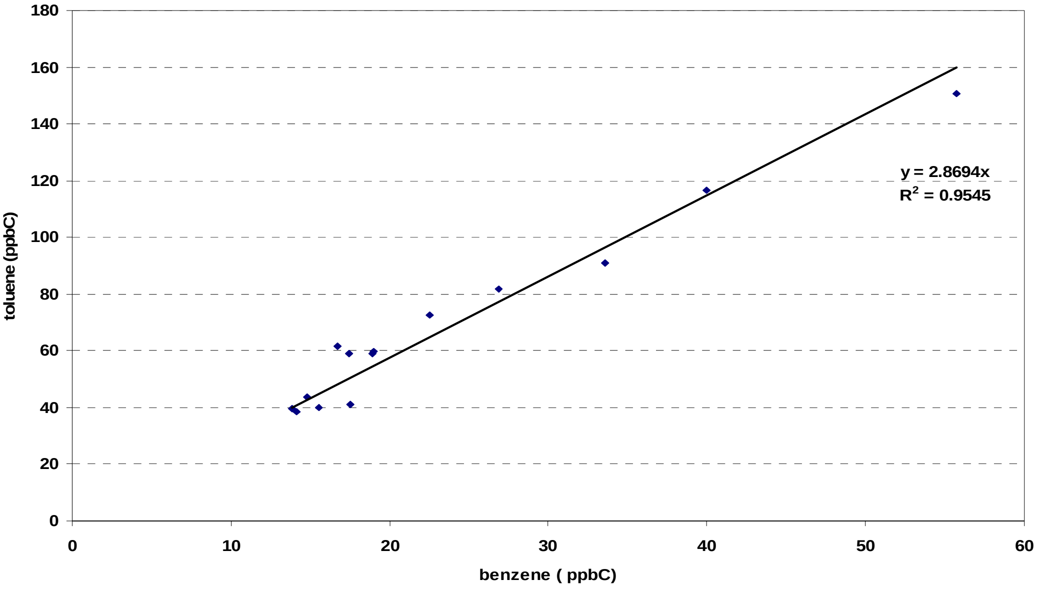


Figure 3-7: Correlation plot between toluene and benzene for the measurements performed in the Kingsway Tunnel, in February, 2003.

Figure 3-7 exhibits a good correlation between the measured values of toluene and benzene. Similar behaviours were found for many other hydrocarbons.

In Table 3-4 emission ratios relative to benzene (ppbC/ppbC) for toluene, ethylbenzene, and the three xylene isomers are compared with literature values. The compounds mentioned above were chosen since they were measured in many traffic emission studies and they are main fuel constituents.

As shown in Table 3-4, similar relations between the ratios to benzene at different sites were found for other hydrocarbons.

The ratio of 3.091 ± 0.06 ppbC/ppbC in the Lundby Tunnel and of 2.89 ± 0.05 ppbC/ppbC in the Kingsway Tunnel are higher than in studies performed earlier than 2000 studies (Brocco *et al.,* 1997; Derwent *et al.,* 1998; Staehelin *et al.,* 1998; Schmitz *et al.,* 2000), when toluene/ benzene ratios of 1.5 up to 2.5 ppbC/ppbC were measured. The obtained ratios were found to be in agreement with the recent studies of Kristensson *et al.*(2004), Niedojadlo, (2005), Stemmler *et al.* (2005).

Table 3-4: Comparison of emission ratios relative to benzene (ppbC/ppbC) during various measurement campaigns.

Location	**Time period**	**Traffic situation**	**Toluene /benzene**	**Ethyl-benzene/ benzene**	**m, p Xylene/benzene**	**o-Xylene/ benzene**	**Reference**
Lundby Tunnel	March 2001	high traffic	3.091	0.81	n.a.	0.45	This study
Plabutsch Tunnel	November 2001	high traffic	2.44	0.57	2.05	0.96	This study
Kingsway Tunnel	February 2003	high traffic	2.87	0.65	2.04	0.8	This study
Gubrist tunnel	2002	High traffic	2.57	0.46	1.20	0.53	Stemmler *et al.,* 2005
A656	2001	traffic	2.48	0.45	1.36	0.51	This study
A656	2001	stop and go	3.6	0.67	1.85	0.61	This study
Wuppertal	2001-2003	high traffic	3.83	0.73	1.28	0.38	Niedojadlo, 2005
Wuppertal	1998	high traffic	2.40	0.49	0.26	0.15	Gomes, 2003
Duesseldorf	1998	traffic	3.00	0.69	1.43	0.52	LUAQS, 1998
Essen	1998	traffic	2.58	0.6	1.20	0.42	LUAQS, 1998

As an example, the toluene/benzene yearly evolution for the city of Gothenburg, according to the Swedish Statistics Central Office (SCB) is shown in Figure 3-8.

In Figure 3-8 the trends show that the yearly mean values for benzene and toluene decreased during 1999/2000 compared to 1998/1999. Possibly, this decrease can be attributed to the increased number of catalyst equipped cars emitting less hydrocarbons, as well as to the lower benzene content in gasoline fuel, which decreased from 5 to 1% since the year 2000 (Directive 98/80/70 /EC). Figure 3-8 shows also that from the years 92/93 to 99/00 the emission ratio between toluene and benzene remained almost constant with a mean value of 2.65 ± 0.43 wt/wt.

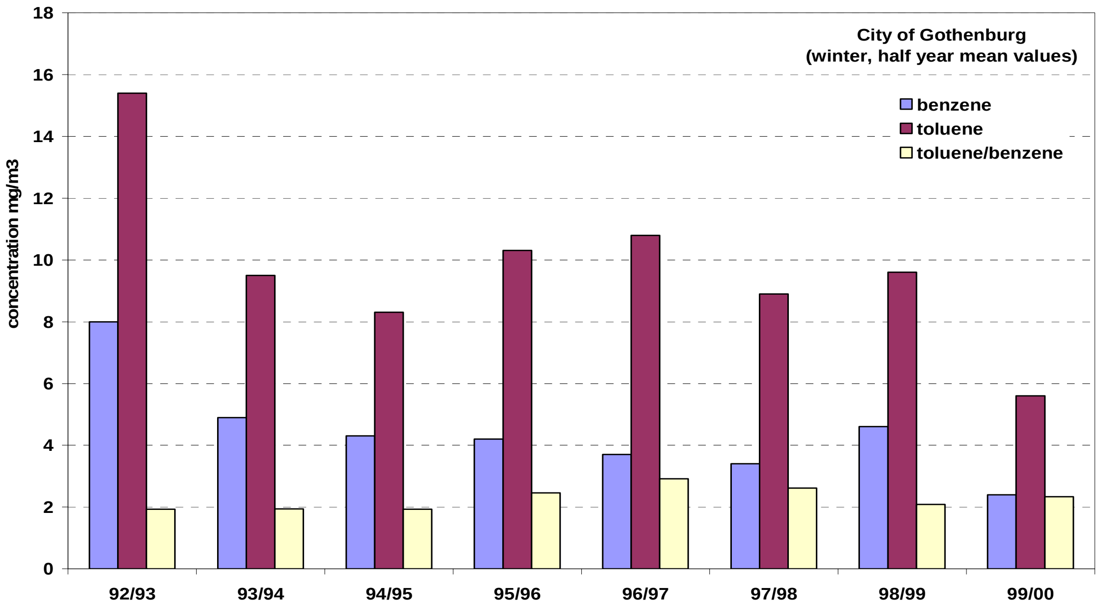


Figure 3-8: Yearly trend of toluene and benzene in the city of Gothenburg according to the Swedish Statistics Central Office (SCB).

3.4.2 Hydrocarbons versus CO_2

From the measured data, emission ratios were calculated for NMHCs relative to CO_2 by plotting the corresponding NMHC mixing ratio vs. CO_2. The emission ratio relative to CO_2 is the slope from the corresponding linear regression. These ratios will be used later to calculate fuel based emission estimates.

Figure 3-9 presents as an example a correlation plot between n-hexane and the CO_2, during the Lundby Tunnel experiment.

Similar results have been obtained for the analysed compounds in the performed experiments. As an example in the Appendix : Table 8 and Appendix: Table 9 the NMHC emission ratios determined in the Lundby Tunnel and in Kingsway tunnel relative to CO_2 are presented.

The Appendix table 9 shows that during Kingsway Tunnel experiment most compounds are well correlated with CO_2, with correlation coefficients exceeding 0.7. For the Lundby Tunnel the correlation coefficients did not exceed 0.5 and for the Plabutsch Tunnel did not exceed 0.6. It is noticeable that for the three campaigns from the present study toluene and iso-pentane showed the largest emission ratios relative to CO_2. This is in agreement also with other tunnel and dynamometer studies reflecting different driving conditions (Duffy *et al.*, 1996; Fraser *et al.*, 1998; Gomes, 2003).

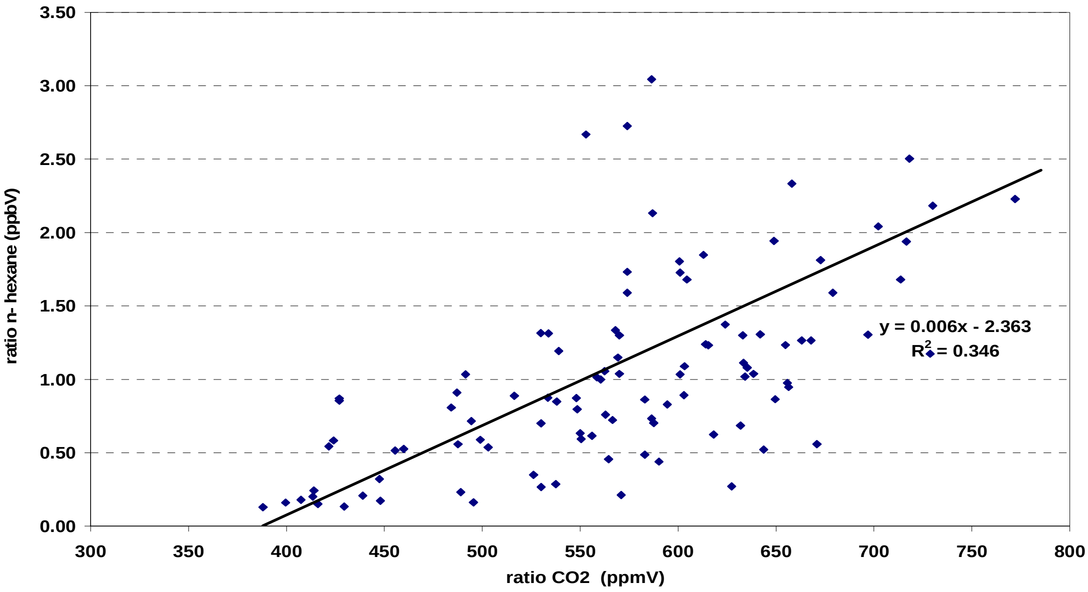


Figure 3-9: Correlation plot between n-hexane and CO_2 mixing ratios for the measurements performed in the Lundby Tunnel, March 2001.

3.4.3 Hydrocarbons versus NO_x

It is known that diesel-powered vehicles, in particular HDVs, emit more NO_x than light-duty vehicles (LDV), in particular, cars powered by gasoline. In contrast, LDVs emit more NMVOC than HDVs (Staehelin *et al.,* 1997; Rogak *et al.,* 1998). NO_2 is directly emitted from transport activities in smaller quantities and is principally formed from secondary reactions of the emitted NO. NO_x is besides particulate matter a critical exhaust component for HDV (Hausberger *et al.,* 2003). The NO_2 fraction in the NO_x traffic exhaust in the investigated tunnels was found to be 15.04 ± 8.77% in the Lundby Tunnel, 7.45 ± 0.98% in the Plabutsch Tunnel and 4.51 ± 1.84% in the Kingsway Tunnel A similar trend of the NO_2/NO_x ratios was reported by Carslaw, 2005 in a study on air quality data from 36 urban monitoring sites in London, UK. Recently, Hueglin *et al.,* 2006, in a study performed in Switzerland during 1992-2004 reported that NO_2 road traffic emissions increased from 92 to 2004 by about 23%. The observed increased NO_2/NO_x ration can partially be explained by the increased fraction of diesel – powered LDV and passenger cars in the vehicular fleet, during the last years. Previous studies (Lies, 1988; Gregori *et al.,* 1989; Staehelin and Schläpfer, 1994; Kirchstetter *et al.,* 1996; Pierson *et al.,* 1996; Becker *et al.,* 1999), reported the NO_2/NO_x ratio to be about 5%.

The ratio NMVOC/ NOx (ppbC/ppbV) plays a very important role in atmospheric chemistry, particulary with regard to the tropospheric ozone production (Carter *et al.,* 1995; Derwent *et al.,* 1996; Jenkin and Hayman, 1999; Andersson-Sköld and Holmberg, 2000).

From the measured data, NMHC/NO_x (ppbC/ppbV) ratios were calculated. Table 3-5 shows the NMHC/NO_x (ppbC/ppbV) ratios obtained from the different tunnel measurements in correlation with the HDV contribution.

Table 3-5: Summary of NMHC/NO_x (ppbC/ppbV) ratios observed in the present study in comparison with literature studies.

Location	**NMHC/NO_x (ppbC/ppbV)**	**HDV contribution**	**Reference**
*Lundby Tunnel (2001)	0.67	14% HDV	This study
*Plabutsch Tunnel (2001)	0.20	23% HDV	This study
*Kingsway Tunnel (2003)	0.55	8% HDV	This study
Gothenburg, 1994-1995	0.68	10%HDV	Sjödin *et al.,* (1998)
**Plabutsch Tunnel (1998)	0.4	21% HDV	Rodler (2000)
**Tauern tunnel (1988)	2.57	Traffic fleet	Gregori *et al.,* (1989)
**Tauern tunnel (1998)	0.05 0.24	17% HDV week-end	Schmidt *et al.,* (2001)
*Kiesberg tunnel (1997)	0.64 – 1.55	6% HDV	Gomes (2003)
*Kiesberg tunnel (2001-2003)	0.56	6% HDV	Niedojadlo (2005)
German traffic	≤1.5	LDV	Hassel *et al.,,* (1994; 1995)

*as sum of the total measured non-methane hydrocarbons (ppbC); **total NMHCs-measured with the THC analyser (FID detector)

Table 3-5 shows that the NMHC/NO_x ratio that was found in the Kingsway Tunnel, corresponding to an 8% HDV load is close to the ratio found in the Lundby Tunnel, which has 14% HDV load. This can be explained by the high fraction of LDV diesel-powered vehicles in the Kingsway Tunnel: 21% among PC, 94% among LDCV. The fraction of LDV diesel powered vehicles in the Lundby Tunnel is 5.1% among PC and 5.05% among LDCV.

It is noteworthy that the results from the present study are consistent with previous studies.

CHAPTER 4

4 VEHICLE EMISSION FACTORS CALCULATIONS

An emission factor or an emission index is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with a source activity associated with the release of that pollutant. By knowing the emission factors or emission indices and the activity rate of the source, it is possible to estimate the emission for a particular emittent.

The emission factors for traffic are being calculated for a specific pollutant and for a particular class of vehicles. Typically, emission factors have been calculated based on dynamometer studies (Weilenmann *et al.* 2001), remote sensing (Kuhns *et al.,* 2004; Chan *et al.,* 2004; Chan and Ning, 2005) or tunnel air measurements coupled with mathematical modelling.

In the literature two different approaches are presented for calculating emissions factors, namely the travel based approach leading to emission factors expressed in g/(km×vehicle) and the fuel based approach leading to emission indices expressed in g/(kg × fuel).

In the present study, the travel based approach calculation was carried out for a better comparison with literature values.

4.1 EMISSION FACTORS CALCULATION - THEORETICAL CONSIDERATIONS

Conservation of mass is the basic principle underlying the development of the emission models. The base assumption is that pollutants are long-lived species with no deposition and no destruction or reaction, and that movement of air and vehicles cause uniform mixing and distribution of pollutants through the tunnel. Additionally, emission rates and wind velocity are assumed being constant.

Measurements of average emission factors (EF) from a road or traffic tunnel may not be representative for different road types and fleet mixes. The disadvantage of the average emission factors is that they do not allow the relative contributions from different individual vehicles to be determined. In this case, an inventory that is based on such emission factors will have limited value as a policy analysis tool. The advantage of the average emission factor is to monitor emission trends over time and to compare the results with emission factors derived from models.

4.1.1 The travel based approach

4.1.1.1 The direct method for emission factors calculation

The different methods for estimating mobile source emissions in tunnels have been previously described in detail (Gertler and Pierson, 1994; Pierson *et al.*, 1996; Bellasio, 1997; El-Fadel *et al.*, 1997).

The direct calculation method produces the EF of a specific pollutant in the tunnel air based on the measured pollutant concentration, tunnel length, tunnel cross section and number of vehicles passing the measurement site.

The mass of a pollutant i emitted by vehicles in a certain time interval j in the tunnel is given by the difference between its concentration at the outlet stations and the inlet stations.

$$\boldsymbol{M_i = \sum_j (C_{out} \times V_{out})_i - \sum_k (C_{in} \times V_{in})_i} \qquad \text{Equation 4}$$

$$EF_{veh} = \frac{M}{n \times d} \qquad \text{Equation 5}$$

where: M = mass of a pollutant emitted by vehicles during time t, [g]

C_i out/in = concentration of a pollutant leaving/entering the tube, [g/m^3]

V_i out/in = volume of air leaving /entering the tube during time t, [m^3]

EF_{veh} = average vehicle emission factor, [g/ (km × vehicle)]

n = number of vehicles, [vehicles]

d = tunnel length [km]

i = index of pollutant,

j, k = number of entrance/exit channels.

For a tunnel with one entrance and one exit air channel, i.e. j, k=1, the emission factors for a given pollutant i, is expressed as:

$$EF_{veh} = \frac{(C_{out} u_{out} - C_{in} u_{in}) \times A \times t}{n \times d} \qquad \text{Equation 6}$$

where: A = tunnel cross sectional area, [m^2]

u = tunnel wind speed, [m/s]

t = time interval, [s]

V = u×A×t, volume of air leaving /entering the tube during time t, [m^3].

In case of negligible differences between entrance and exit air speed, the emission factor is:

$$EF_{veh} = \frac{(C_{out} - C_{in}) \times A \times u \times t}{n \times d} \qquad \text{Equation 7}$$

Otherwise, the airflow at the entrance and exit can be related to the ventilation rate α (s^{-1}) and the tunnel length L [km]:

$$u_{out} = u_{in} + \alpha \times (1000L) \qquad \text{Equation 8}$$

The tunnel length L can be replaced by L_{veh}, i. e. the distance covered by the vehicles travelling through the tunnel at the air speed u_{veh} during the time transit of air over L as presented in Equation 9:

$$L_{veh} = \frac{u_{veh} \times L}{u} \qquad \text{Equation 9}$$

where: u_{veh} = vehicle speed, [m/s]

L_{veh} = distance covered by the vehicles during the time transit of air over L, [km]

Several operational parameters such as variability in the traffic, speed flow and ventilation contribute to the complexity of airflow patterns in a tunnel atmosphere. As a result, significant air speed (or concentration) non-uniformities can be revealed across the tunnel section.

In order to calculate accurately the emission factors, the operational parameters have to be taken into consideration for each tunnel characteristics.

In tunnels with longitudinal ventilation system, pollutant concentrations increase along the length of a tunnel as the emissions from traffic accumulate. In passively ventilated tunnels, the air always moves in the same direction due to the piston effect.

The starting sampling time of the instruments at outlet/inlet stations have to be adjusted according to the average transport times between measuring points. The transport times are calculated from the measured wind speeds.

Steady and transient tracer experiments have been used to estimate the airflow in the tunnels. While in a steady tracer experiment the tracer substance SF_6 is released at one point in the tunnel at a constant rate, in transient tracer experiments SF_6 is released at a constant rate along the tunnel length.

To account for velocity and concentration non-uniformities in the tunnel, the air speed in Equation 8 is multiplied by a correction factor that is determined from SF_6 tracer experiments. The magnitude of the correction factor differs for different tunnels and is considered being inversely proportional to the air velocity inside the tunnel as expressed by Equation 10. The correction factor is the ratio between the measured and the modelled SF_6 concentration at the measurement site.

$$F = \frac{a}{u} + b \qquad \text{Equation 10}$$

where: F = correction factor, dimensionless

a = empirical constant, [m/s]

b = empirical constant, dimensionless

u = vehicles speed, [m/s]

The principle of mass balances at open roadways as is shown in Figure 4-1 considers an imaginary box, which includes the road section on the ground and the total exhaust plume.

There are two vertical measuring lines, one upwind and one downwind of road. The pollutant mass flows entering at one side (x_1) and leaving at the opposite side (x_2) have to be determined. Because of the wind speed perpendicular to the road and pollutant concentrations are not expected to be homogeneous with height z, vertical wind and pollutant concentration profiles have to be measured. More details on the A656 emission factors calculation procedure are given in Corsmeier *et al.* (2005) and Kühlwein and Friedrich (2005). The wind profiles, which were used for the calculation, have been described in more detail elsewhere (Kohler *et al.,* 2005).

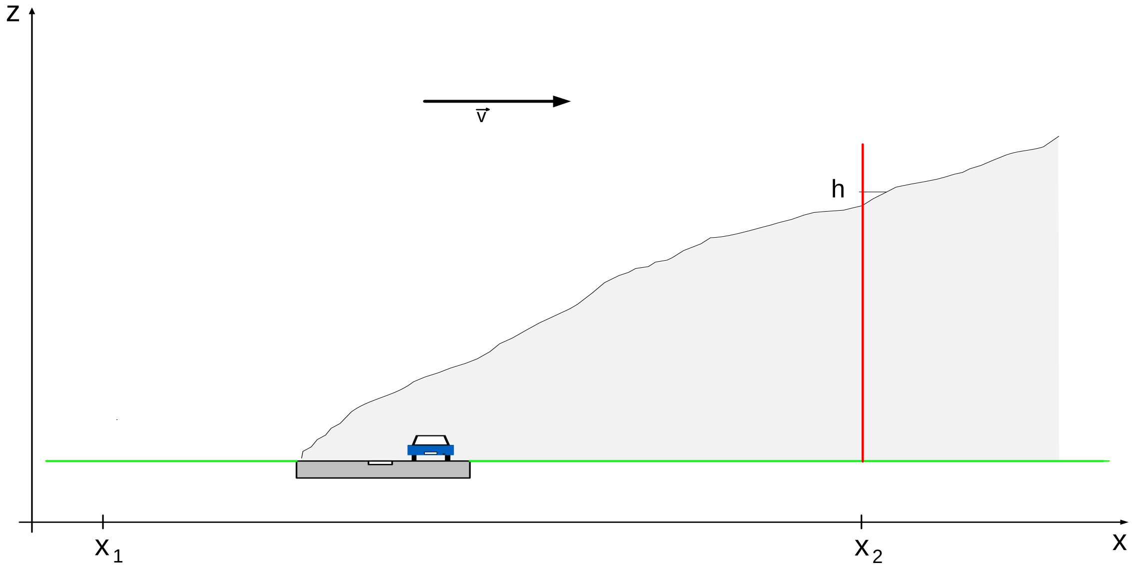


Figure 4-1: Principle of pollutant mass balances from open roadway experiment.

From the results of the profile measurements, the source strength of the motorway traffic emissions was determinate. The method for calculating the source strength in mass per time per driving distance has been described in more detail elsewhere by Vogel *et al.* (2000). The source strength is defined as the mass of the pollutant emitted per unit of time (t) and length (L) and was evaluated by the difference between the downwind and the background concentration multiplied with the wind velocity and integrated over the height of the plume The source strength was calculated from 1 to 51 m with a height resolution Δz of 2 m. From 1 to 5 m, which is the minimum height of NO_x and NHMC measurements, the NO_x as well as the NMHC concentrations were assumed to be constant with height.

The NMHCs source strength was computed by multiplying the corresponding concentration difference measured downwind and upwind the motorway in $\mu g \times m^{-3}$ with the incident wind velocity in m/s, as shown in the following equation:

$$Q_{NMHC_i} = \sum_{n=1}^{25} v_{\perp}(z_n) \times (c_{NMHC_i}(x_{downwind}, z_n) - c_{NMHC_i}(x_{upwind}, z_n))\Delta z \qquad \text{Equation 11}$$

where: Q_{NMHC_i} = the source strength of a selected NMHC component i, $[\mu g \times m^{-1} \times s^{-1}]$

$v_{\perp}(z)$ = incident wind velocity.

Multiplication by 3.6 yields the final desired source strength from µg/(m × s) in g/(km ×h). The calculations were carried out under the assumption that the emissions do not change within the length of 1 km along the motorway during 1 h.

Further, the source strength calculated per time interval divided by the total number of vehicles (n_{total}), which passed the sampling site within this time unit gives the emission factor per vehicle of substance i expressed as [g/(km×veh)].

$$EFi = \frac{Q_{NMHCi}}{n_{total}} \qquad \text{Equation 12}$$

The determination of emission factors of vehicle classes, namely HDV and LDV, is based on statistical modelling, which is required since these vehicles have different emission factors. The approach is based on the linearization of the EF of the entire fleet as function of the proportion of one of the classes, namely LDV or HDV (Staehelin *et al.*, 1997).

The EF_{total} of the entire fleet is a linear combination of the EF_i of the i vehicle class by its fraction n_i/n_t for the different vehicle classes.

$$EF_{total} = \sum_i \frac{n_i}{n_{total}} EF_i \qquad \text{Equation 13}$$

where: EF_i = emission factor for vehicle class i, [g/(km ×veh]

n_i = traffic density of vehicle class i, [veh/min]

n_{total} = total traffic density, [veh/min]

Further, EF is plotted against the fraction of LDV. From the linear regression, the slope yields the EF for LDV and the intercept the EF for HDV.

$$EF_{veh} = \frac{n_{LDV}}{n_{LFV} + n_{HDV}} EF_{LDV} + \frac{n_{HDV}}{n_{LDV} + n_{HDV}} EF_{HDV} \qquad \text{Equation 14}$$

where: EF_{LDV} = emission factor for LDV,

EF_{HDV} = emission factor for HDV.

4.1.2 The fuel based approach - Indirect emission factors calculation

If the exact characterisation of the air flow, and the concentration for the different j, k entrances/exits points are not available, as e.g. for the Kingsway Tunnel experiment, the emission factors for the total fleet can be calculated by using the model calculated emission factor of CO_2 or the vehicle fuel consumption. CO_2 emissions are estimated based on fuel consumption only, assuming that the carbon content of the fuel is fully oxidised into CO_2.

The fuel based approach method for estimating the emission factors obviously does not take into consideration vehicle weight and operating conditions (Singer and Harley, 1996; Kean *et al.,* 2003). The fuel based approach method has also the disadvantage that the CO_2 apportionment between gasoline and diesel engine contribution is not possible.

4.1.2.1 Use of HBEFA 2.1 CO_2 emission factor

During the tunnel campaigns of the present study measurements of the airflow rate and the uniformity of the air mixing inside the tunnels were carried out. Technical problems encountered during the Lundby and Kingsway Tunnel studies for which the airflow inside the tunnels was difficult to characterise. Since CO_2 was always measured during all campaigns, it was possible to calculate the emission factors by using the model-calculated emission value of CO_2 for the vehicles passing through the tunnels.

The emission factors for the entire fleet is in this case calculated by multiplying the model calculated emission factor of CO_2 (mg/km) with the emission ratios of those components relative to CO_2 (mg/mg). In the present study, the modelled emission factor for CO_2 was taken from the HBEFA 2.1. Emissions also vary significantly with the mode of operation, involving factors such as traffic flow, road gradient and vehicle speed. Traffic situations are defined as linear combination of driving patterns. No driving pattern that would describe the tunnel driving (Staehelin and Sturm, 2004)) exists in the literature. Most appropriate for further calculations is the highway driving cycle (HW). As an example for the Plabutsch Tunnel emission factors the HBEFA 2.1 driving cycle 80-AB>80, named HW 80, for traffic smaller than 1400 vehicles/h was used. This driving cycle has an average vehicle velocity of 80 km/h, weighted according to a highway velocity of 70-80 km/h (12%), highway velocity of 80-90 km/h (23%), highway velocity of 90-100 km/h (30%), highway velocity of 100-110 km/h (23%) and highway velocity of 110-120 km/h (12%). This driving pattern is suitable for the driving situation in the Lundby and the Plabutsch tunnels. Table 4-1 presents as an example for the Plabutsch Tunnel experiment the CO_2 emission factors calculated using the HBEFA 2.1 for the driving pattern HW 80 and for different road gradients. Positive road gradients correspond to uphill driving and vice versa. Table 4-1 shows that the model calculated value of CO_2 is strongly influenced by the gradient factor (slope).

Table 4-1: Emission factors for CO_2 (mg/km) for different vehicle categories and road gradients (%) and driving pattern HW-80, in the Plabutsch tunnel.

Road gradient	**Vehicle category**		
	PC	**LDV**	**HDV**
-2	124	201	62
0	169	284	684
2	229	390	1761
-1	149	243	375
0.5	178	310	950
1	200	337	1225

Table 4-2 shows as an example the BTX emission factors for different driving situations.
It is shown that gradient factors have a direct impact on all vehicle emissions as well as on fuel consumption. For example for LDV, BTX emissions do not change significantly for downhill driving, whereas for uphill driving the emission factors can increase up to a factor of 2 compared to the zero gradient driving situation. This behaviour has also been observed during the Gubrist tunnel study (Colberg *et al.,* 2005a).

Table 4-2: Emission factors (g/km) for BTX determined from HBEFA 2.1 for different driving situations, in the Plabutsch tunnel.

Compound	**Vehicle category**	**Road gradient**	**Traffic situation**	
			HW 100	**HW 80**
benzene	PC	-2	0.0045	0.0048
		0	0.0056	0.0049
		+2	0.0151	0.0130
	LDV	-2	0.0058	0.0059
		0	0.0060	0.0052
		+2	0.0107	0.0089
	HDV	-2	0.0049	0.0045
		0	0.0064	0.0063
		+2	0.0058	0.0059

Table 4-2 (continued)

Compound	Vehicle category	Road gradient	Traffic situation	
			HW 100	HW 80
toluene	PC	-2	0.0051	0.0056
		0	0.0059	0.0052
		+2	0.0134	0.0117
	LDV	-2	0.0057	0.0055
		0	0.0061	0.0050
		+2	0.0122	0.0095
	HDV	-2	0.0009	0.0009
		0	0.0012	0.0012
		+2	0.0011	0.0011
xylenes	PC	2	0.0043	0.0046
		0	0.0049	0.0043
		+2	0.0111	0.0096
	LDV	2	0.0048	0.0047
		0	0.0052	0.0043
		+2	0.0101	0.0079
	HDV	2	0.0023	0.0022
		0	0.0031	0.0030
		+2	0.0028	0.0028

4.1.2.2 Use of the emission index

Carbon dioxide is the final C-containing product of fuel combustion and provides a measure of the amount of burned fuel in the engine. Concentrations of NMHC relative to CO_2 provide emissions per quantity of fuel consumed. Using an average emission index of 3.138 g CO_2 per kg burned fuel (Kurtenbach, 2001) the emission indices for NMVOCs can be calculated.

If emissions in g/km are required, obviously averaged fuel consumption per km is required. From the literature it is known that NMHCs, which are emitted especially by gasoline powered passenger cars, depend on driving status as well as vehicle age (affects the tailpipe emissions) and maintenance (Sjödin *et al.,* 1997, 2000). The average age of the vehicles fleet can be used to estimate the fuel consumption per km.

Emission factors can be calculated, by using the emission index corroborated with the fuel consumption and fuel density according to Equation 15:

$$EF = Ei \times f \times \rho \qquad \text{Equation 15}$$

where : Ei = Emission Index ,[g/(kg × fuel)]

f = fuel consumption, [l/km]

ρ = fuel density, [kg/l]

Fuel consumption and hence the CO_2 emission is the variable and can be calculated on the basis of the fleet composition if the driving pattern is accurately described. If the calculated and the measured concentrations have a correlation coefficient close to 1, it can be assumed that boundary conditions such as air flow and vehicle mix fit well to each other.

4.1.3 Models for emission factors

Within the framework of extensive emission data validation experiments, the emission factors for the Lundby Tunnel, the Plabutsch Tunnel, the Kingsway Tunnel and the A656 motorway have been determined using the local traffic measurements in combination with new emission models. The models provide emission factors with a temporal resolution of 20 min for the Lundby and Plabutsch tunnel studies, one hour for the Kingsway Tunnel and 3 h for the motorway study.

The models took as input parameters the fleet composition and the emission factors for THC, CO_2 and BTX from the HBEFA modified by taking into account the slope gradients for the corresponding measurement sites as well as the fleet composition and the driving pattern.

For the model calculation the year 2001 was chosen as base case because the measurements were carried out in the same year. Emission factors were calculated for the following vehicle categories: PC, LDV, HDV, Urban Bus, Coach and Motorcycles. For the calculations the HBEFA 2.1, highway: HW100, 80 and 60 driving patterns with a traffic volume <1400 vehicles/h were chosen. Since vehicles were assumed to reach their maximum working temperature before passing the measurement area “cold running” conditions were not considered in the calculations. The HBEFA 2.1 provides the emission factors for road gradients of 0, ± 2, ± 4, ± 6% from which the desired ones were calculated as discussed in section 4.1.2.

Three emission models were used:

- **Model 1** calculates emissions factors for NMHCs using the HBEFA calculated emission factor for CO_2. The calculation of the emission factors of NMHCs were done by multiplying the estimated emission factor of CO_2 (mg/km) with the emission ratios of those components relative to CO_2 (mg/mg). This method has been described in more detail in section 4.1.2.
- **Model 2** calculates emissions factors for individual compounds by using the total hydrocarbon emission factor calculated from HBEFA and the relative contribution of individual hydrocarbons to the NMHC exhaust according to Schmitz *et al.* (1999). Schmitz *et al.* (1999) analysed on a chassis dynamometer the exhaust of cars equipped with different engine types, i.e. cars with diesel engines, cars with gasoline engines and three-way-catalysts and cars with gasoline engines without catalysts using different driving cycles. For the present calculations the data for the driving cycle “Autobahn Phase 1” (average speed 107 km/h, minimum speed: 90 km/h and maximum speed: 124 km/h, contribution of the stop mode: 0%) was used. Although the speed range of this driving pattern is higher than that in the Lundby and Plabutsch Tunnel, this phase has been considered for comparison because the other driving pattern had an even higher speed range. Since the data from Schmitz *et al.* (1999) did not provide the NMHC speciation for gasoline vehicles with different exhaust after treatments; these data were used in the present calculation for Euro 1, 2, and 3. The data from Schmitz *et al,* (1999) for diesel vehicles were used to calculate the emission factors for all vehicles with diesel engine.

The final emission factor EF of an individual NMHC is represented by the sum of emission factors determined for each vehicle category multiplied with the percental composition of the pollutant in the exhaust mix (according to Schmitz *et al.,* 1999) divided by the number of vehicles passing the measurement site in the chosen time interval:

$$EF_i = \sum_{j=1}^{3} a_{ij} \times EF_{ij} \qquad \text{Equation 16}$$

where: i = compound number

a_1 = percental contribution of the compound i in the hydrocarbon exhaust mix for gasoline engines without catalyst

a_2 = percental contribution of the compound i in the hydrocarbon exhaust mix for gasoline engines with catalyst

a_3 = percental contribution of the compound i in the hydrocarbon exhaust mix for diesel engines without catalyst

EF_j with j from 1 to 3 represent the emission factors for individual vehicles category, as follows:

EF_1 = emission factor of total hydrocarbons for gasoline engines without catalyst for PC, LDV and motorcycles

EF_2 = sum of emission factors of total hydrocarbons for gasoline PC and LDV engines with G-cat, Euro 1, 2 and 3

EF_3 = sum of emission factors of total hydrocarbons for diesel engines without catalyst for HDVs, coaches, urban busses

The emission factor for a specific vehicular category in a time interval was calculated by multiplying the number of vehicles with the percental composition in the fleet for that category and the emission factor for total hydrocarbons from HBEFA calculated for the specific vehicle category and emission concept.

- **Model 3** calculated emission factors for benzene, toluene and xylenes derived from HBEFA by summing the specific vehicular category emission factors.

Since the calculation of the emission factors of NMHCs were carried out by multiplying the estimated emission factor of CO_2 (mg/km) with the emission ratios of those components relative to CO_2 (mg/mg), CO_2 was always measured during the three campaigns of the present study, the model 1 data will be referred as calculated emission factors and the model 2 and 3 values as modelled ones.

4.1.3.1 *Error calculation*

The absolute error of the emission factor $\Delta\overline{EF}$ related to the error of the input parameter x_i results from the multiplication of the sensitivity $\partial EF/\partial x_i$ with calculated or estimated absolute error dx_i or Δx_i. By use of the error propagation law, the mean total error $\Delta\overline{EF}$ of the emission factor EF for any functional relations between the input parameters x_i according to Hartung *et al.* (1995) is:

$$\Delta\overline{EF} = \sqrt{\sum_{i=1}^{n}\left(\frac{\partial EF}{\partial x_i}\Delta x_i\right)^2}$$ Equation 17

where: n = the number of the input parameters

$\frac{\partial EF}{\partial x_i}$ = the sensitivity of the emission factor related to the input parameter x_i

Δx_i = the absolute error of the input parameter x_i (e.g. standard deviation)

More details on the determination of uncertainties of emission factors from road transport models can be found in Kühlwein and Friedrich (2000).

4.2 EMISSION FACTORS CALCULATION FROM MEASUREMENT DATA

4.2.1 Lundby Tunnel

Since in the Lundby Tunnel the wind speed measurements were difficult, SF_6 has been used as a tracer in order to determine the wind speed data. However, the results from the tracer experiments were not reliable enough (Colberg *et al.,* 2005b) and, therefore, in the present study the vehicle emission factors were calculated using the indirect method, namely model 1 and were modelled using model 2 and 3.

4.2.1.1 Calculation of emission factors using HBEFA 2.1

The HBEFA 2.1 emission factors calculated for CO_2, THC and BTX considered according to the tunnel topography, as Figure 2-1 shows, gradients of -3.5%, 0.25% and 4%. The driving pattern HW 80 for traffic smaller than 1400 vehicles/hour is also in agreement with the speed limit in the tunnel, namely 80 km/h and the number of vehicles that transit the tunnel in 1h. As an example the Appendix: Table 10, Table 11, Table 12, Table 13, and Table 14 summarise the results of the emission factors for CO_2, THC, benzene, toluene and xylenes applying HBEFA 2.1 for three driving situations: HW100, HW80 and HW60 and the reference year 2001.

The emission factors of the vehicle fleet in the Lundby Tunnel were calculated as section 4.1.3 presents. The emission factors were calculated with a 20 min time resolution. The model 1 result will be compared with the calculations of model 2 and 3, below.

As an example, Figure 4-2 shows for i-pentane, benzene and toluene the obtained time series from model 1 in comparison with the model 2 results and the corresponding calculated absolute errors. The error calculation included both the possible variation of traffic fleet in the Lundby Tunnel and the contribution of the HW-80 driving situation.

The comparison of the two models shows for i-pentane and toluene that the calculated values are significantly higher than the modelled values for periods with high traffic density. However, it is worth mentioning that for benzene the agreement between the two models is always quite good.

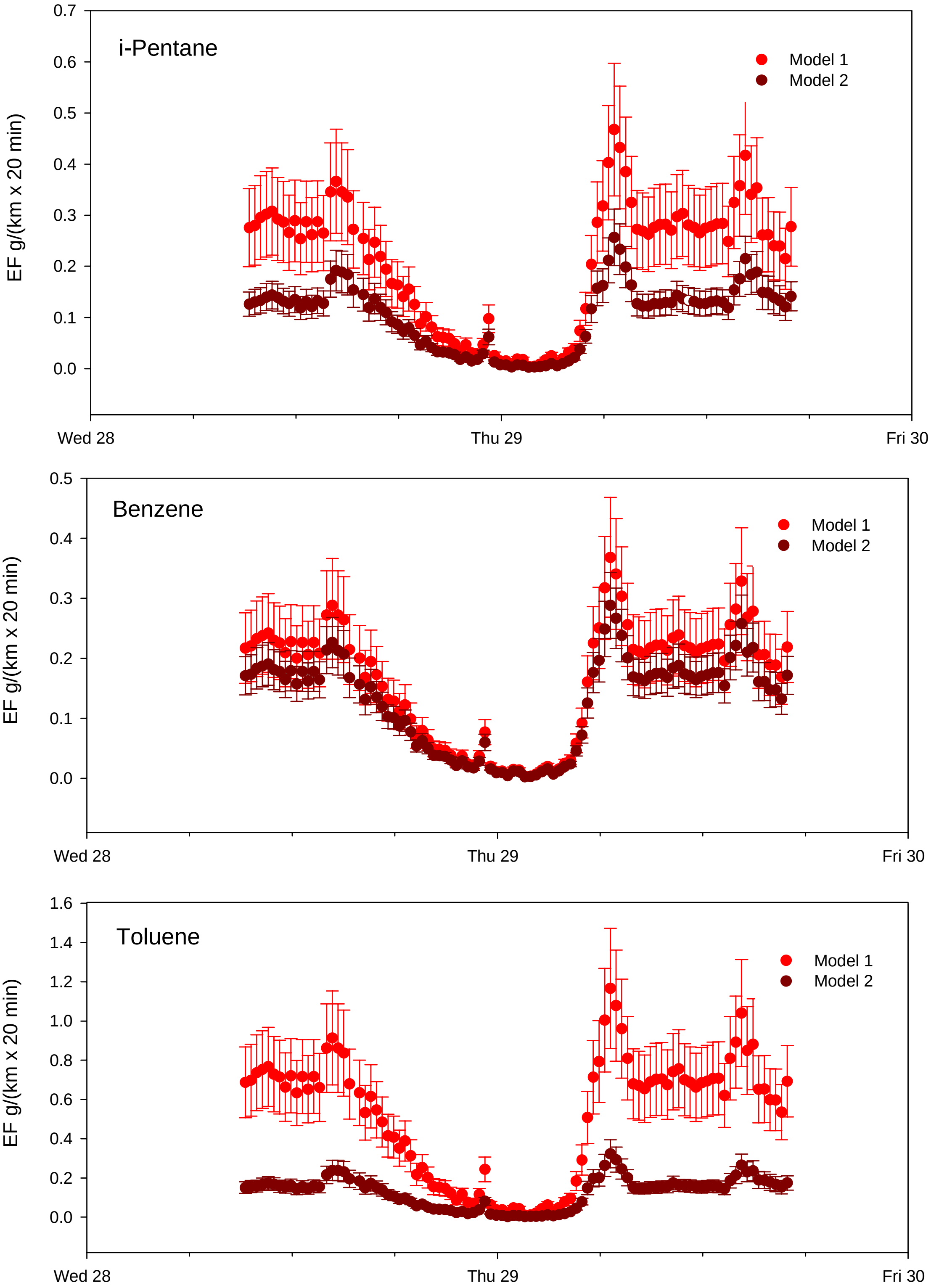


Figure 4-2: Time series for i-pentane, benzene and toluene calculated with model 1 and model 2, in the Lundby tunnel.

Figure 4-3 shows for benzene a good correlation between the different models. This proves that for benzene, the calculated values are within the standard deviation in good agreement with the HBEFA 2.1 model 2 and 3 estimations for the real traffic situation in the Lundby Tunnel.

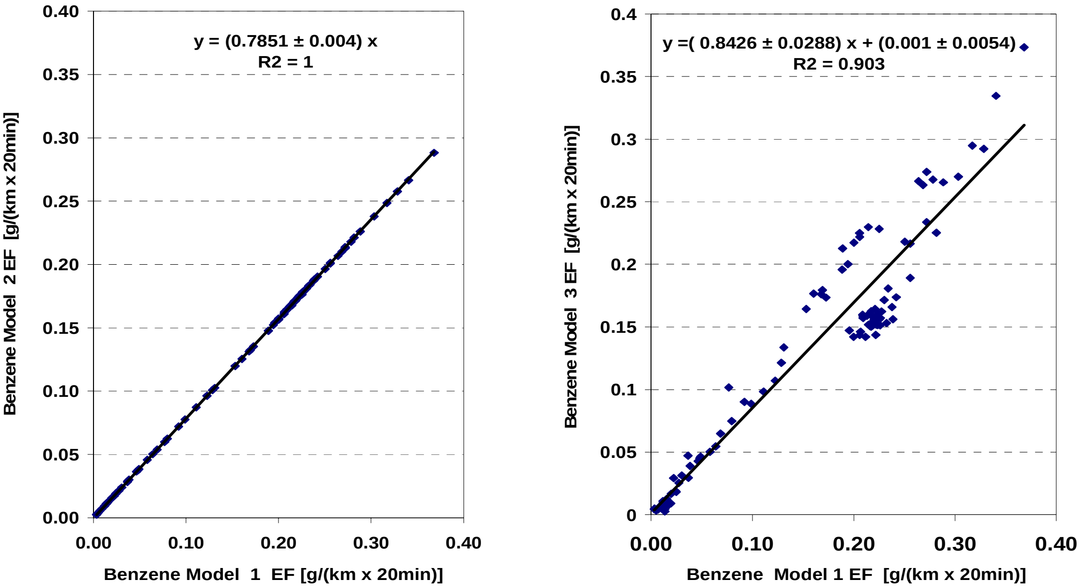


Figure 4-3: Correlation diagrams for benzene: model 2 and model 3 versus benzene model 1 emission factors, respectively.

Figure 4-4 shows a similar correlation plot for toluene. Although the linearity between the different models is quite good as indicated by the R^2 values, the slopes are significantly smaller than the expected 1 to 1 relation.

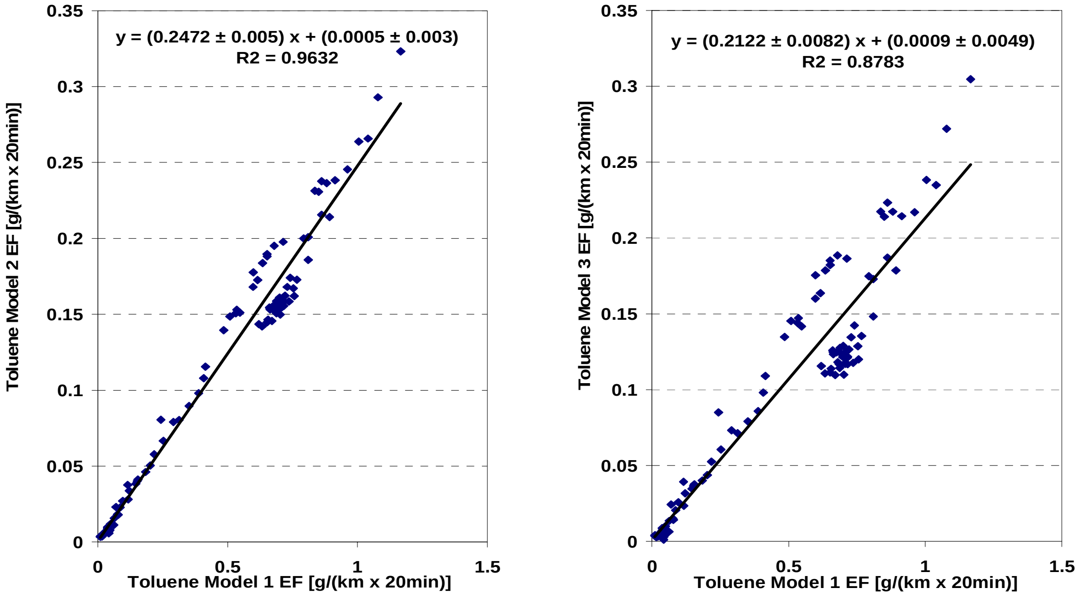


Figure 4-4: Correlation diagrams for toluene: model 2 and model 3 versus model 1 emission factors.

Figure 4-5 shows for a variety of other hydrocarbons the ratio of the emission factors calculated from model 1 and model 2, 3. It is worth mentioning that for model 1 the emission factors are 1.3-8.7 times higher than those obtained from model 2.

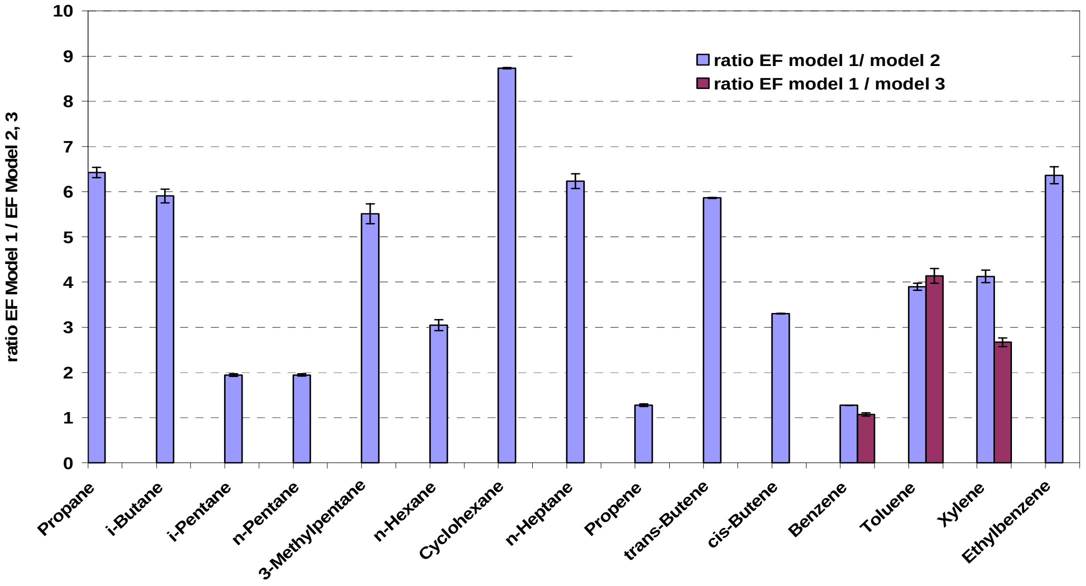


Figure 4-5: Ratio of NMHCs emission factors of model 2 and 3 versus model 1, in Lundby Tunnel.

The data analysis of the THC emission factors for the given traffic fleet in the Lundby Tunnel, PC with catalyst (85%), LDV with catalyst (3%) and HDV (12%), shows that the main contributions result from PC with catalyst (39%), LDV with catalyst (6%) and HDV (52%). The THC emission factors given by the HBEFA 2.1 are higher for HDV than for PC and LDV and though increase the percental contribution to the THC emission factor. The discrepancy between measured and calculated emission data obviously must be found in the emission factors for PC with catalyst, LDV with catalyst and/or HDV.

This leads to two hypotheses:

1. the THC emission factor of HDV is not correct; and/or
2. the percentage contribution of catalyst vehicles resulting from the fleet data analysis does not reflect the reality, i.e. cars that are registered with catalyst in fact have a malfunctioning catalyst and should be counted as non-catalyst vehicles with the corresponding emission factor.

In order to check the HBEFA 2.1 THC emission factor for HDV, it was changed stepwise in 10% increments from 200% to 10%.

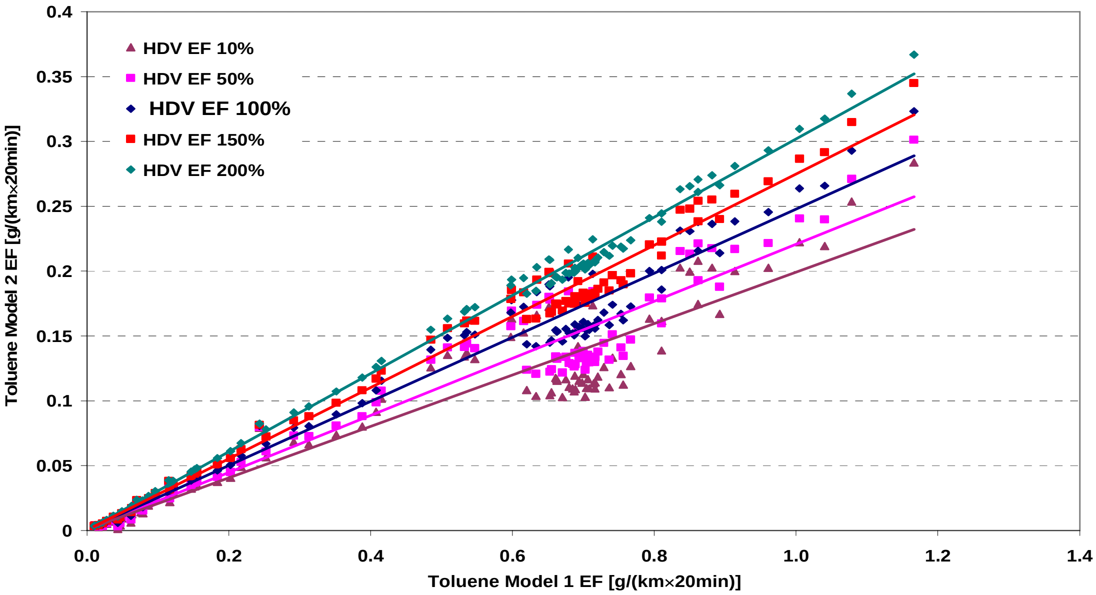


Figure 4-6: Correlation diagrams for toluene (model 2) versus toluene (model 1) with a stepwise change of the THC emission factor for HDV.

Table 4-3: Correlation equations for toluene (model 2) versus toluene (model 1) for a stepwise change of the THC emission factor for HDV.

HDV EF variation	Slope (m)	Intercept (b)	Correlation coefficient (R^2)
10%	0.198 ±0.008	0.0008±0.005	0.88
50%	0.220±0.006	0.0007±0.004	0.93
100%	0.247±0.005	0.0005±0.003	0.96
150%	0.275±0.004	0.0004±0.002	0.98
200%	0.302±0.002	0.0002±0.001	0.99

Figure 4-6 and Table 4-3 show for toluene as an example, only a small variation of the slope when the EF was changed. Accordingly, by a 10% percent decrease of the HDV EF a slope of 0.198 ± 0.008 was obtained, whereas for a 200% increase of the HDV an EF of 0.302 ± 0.002 was determined. The resulting slope variation shows that the HDV EF does not strongly affect the model 2 results.

The European Commission in 2000 and National Environmental Technology Centre, UK (NETCEN) in 2002 reported that about 15% of the PC catalysts have a malfunction leading to a much higher emission of hydrocarbons. In order to test whether this finding could explain the discrepancy observed between model 1 and 2, the emission factors were recalculated considering that 12% of PC and LDV G-cat vehicles have malfunctioning catalysts and, therefore, their emissions have been counted as the ones of conventional cars.

Figure 4-7 shows the modelled values for toluene considering that the PC and LDV G-cat vehicles have conventional exhaust treatment. The slopes change from 0.247 ± 0.005 to 0.745 ± 0.255 for model 2 versus model 1 and from 0.212 ± 0.008 to 0.486 ± 0.02 for model 3 versus model 1, see Figure 4-4 and Figure 4-7. This indicates that the catalyst condition may be the main reason for the discrepancy between measured and modelled emission factors. The same behaviour was observed for the other compounds, although the change is not so significant in all cases.

Table 4-4 presents the correlation equation for NMHC measured compounds, (model 2) versus NMHC (model 1) with and without change in the model assumptions, i.e. PC and LDV G-cat counted as conventional vehicles.

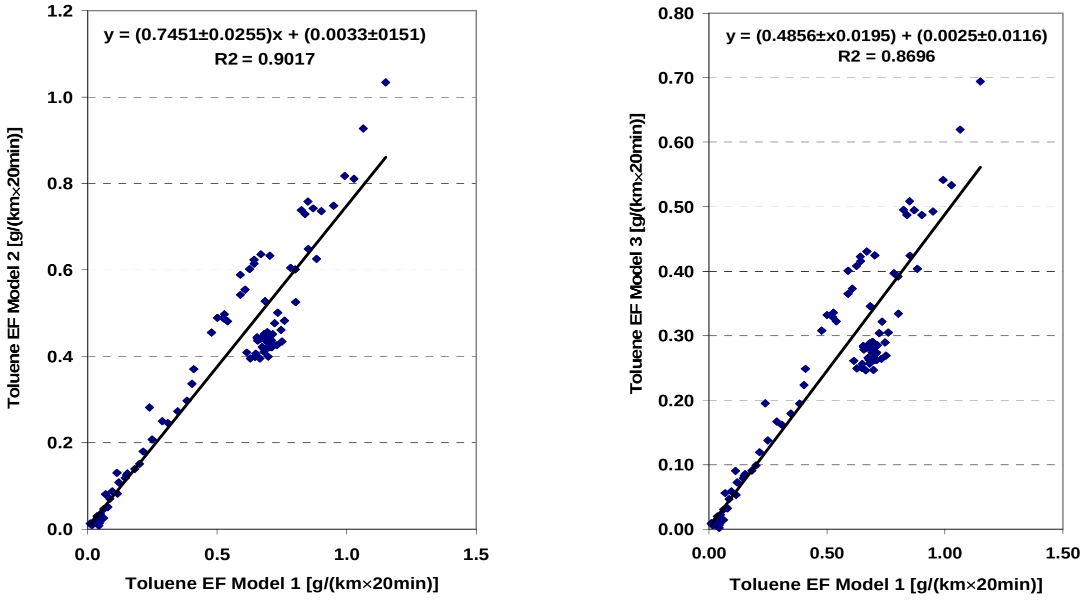


Figure 4-7: Correlation diagram for toluene model 2 and model 3 versus model 1, PC and LDV G-cat counted as conventional vehicles.

Table 4-4: Correlation equation for NMHCs, model 2 versus NMHC model 1 with and without change in the model assumptions, i.e. PC and LDV G-cat counted as conventional vehicles.

Compound	**Correlation equation no changes**	**Correlation coefficient R^2**	**Correlation equation Model 2 values, PC and LDV GKat as conventional, HDV 100%**	**Correlation coefficient R^2**
propane	y = 0.156x - 2E-05	0.9784	y = 0.214x - 1E-06	0.999
i-butane	y = 0.159x + 8E-05	0.939	y = 0.318x + 0.0002	0.903
i-pentane	y = 0.159x + 8E-05	0.939	y = 0.935x + 0.0013	0.934
n-pentane	y = 0.509x + 0.0001	0.9822	y = 0.923x + 0.0005	0.941
3-methylpentane	y = 0.157x + 0.0001	0.8701	y = 0.347x + 0.0003	0.865
n-hexane	y = 0.284x + 0.0001	0.8703	y = 0.628x + 0.0003	0.865
cyclohexane	y = 0.116x + 3E-07	0.9997	y = 0.186x + 2E-05	0.980
n-heptane	y = 0.150x + 4E-05	0.9389	y = 0.302x + 0.0001	0.903
propene	y = 0.768x - 0.0004	0.9534	y = 0.963x - 0.0003	0.989
trans-butene	y = 0.173x + 2E-07	0.9996	y = 0.275x + 2E-05	0.981
cis 2 butene	y = 0.308x - 2E-07	0.9995	y = 0.485x + 2E-05	0.982
benzene	y = 0.786x + 0.004	0.9998	y = 1.272x + 0.0008	0.978
o-xylene	y = 0.268x + 0.0001	0.8799	y = 0.583x + 0.0003	0.870
toluene	y = 0.249x + 0.0006	0.9616	y = 0.745x + 0.0033	0.901
ethylbenzene	y = 0.145x + 0.0001	0.9233	y = 0.297x + 0.0004	0.894

This finding emphasizes once more the poor knowledge on NMHC emissions from vehicles, especially from the passenger cars. Accordingly, there is an urgent need for reliable real-world emission factors for most NMHCs compounds, except benzene, which seems to be well described by HBEFA 2.1, taking into account various engine types, exhaust after treatment systems, driving patterns and vehicle age, which are probably the main reasons for the under-prediction of the emissions from model 2 and 3. The influence of 12% malfunctioning catalysts on the emission factors demonstrates not only the importance of modern emission technologies but also that good maintenance of these systems is prerequisite for the reduction of NMHC emissions.

In the new version 2.1 of HBEFA emission factors for PC and LDV Euro 1 (gasoline and Diesel) and Euro 2 (gasoline only) are based on bag data (multiple sets of data) or linear combinations of bag data from real world test bench cycles, and not from instantaneous modelling as in HBEFA 1.1. For other vehicle classes the emission factors for Euro 1 and older vehicles remained unchanged and, hence, still are based on instantaneous modelling, the so-called TÜV method (Haan and Keller, 2004). This is important, as investigations of the past few years have shown that emissions can be significantly higher under real world driving than emission standards suggest (Xie *et al.*, 2005). The Appendix: Table 15 summarises the model 1 calculated emission factors in [g/(km × veh)] for the entire fleet during the Lundby Tunnel experiment.

4.2.2 Plabutsch Tunnel

4.2.2.1 Calculation of emission factors by the direct method

Emission factors [g/(km×vehicle)] have been directly calculated from the Plabutsch Tunnel data for speciated NMHC, NO, NO_2, NO_x using Equation 7 (see section 4.1.1) adapted for a tunnel with transverse ventilation. The Equation 18 was developed by TUG based on the results of two previous tunnel studies in the Plabutsch Tunnel in 1998 and 1999 (Rodler, 2000).

As already mentioned, the Plabutsch Tunnel has a transverse ventilation system, which requires measuring the pollutants in the air entering ventilation system and the air leaving the tunnel ventilation. In tunnels with transverse ventilation systems, pollutant concentrations are more or less constant over a considered ventilation section.

$$EF_{veh} = \frac{c \times u}{t \times L} \times \frac{1}{N} \qquad \text{Equation 18}$$

where: c = concentration of the pollutant, [g/m^3]

u = flow of the supply air, [m^3/s]

t = time period of determination, [s]

L = tunnel length, [km]

N = traffic density, [vehicles/s].

As Figure 4-8 shows, although all pollutants exhibit a strong positive correlation with the traffic count, the flow of the supply air has a far greater impact on emissions. This is particularly visible on Friday, Nov. 9, 2001 when the measured concentrations are low although the traffic is high. It has been observed that minor changes in the flow of the supply air could produce significant changes in the emission factors. As an example, it is shown in the same figure that toluene, i-pentane, i-butane and NO_x exhibited a defined trend consistent with the source strength (traffic count) and the flow of the supply air. This pattern is typical for direct source measurements, when the product peaks mirror the traffic peaks but also diminish with higher wind speed.

As in the studied tunnels the LDV and HDV are not routed through separate tubes, the emissions derived from raw data are representative for the overall fleet and afterwards derived for LDV, HDV. The traffic flow is more or less the same in both directions, as can be observed in the Appendix: Table 3.

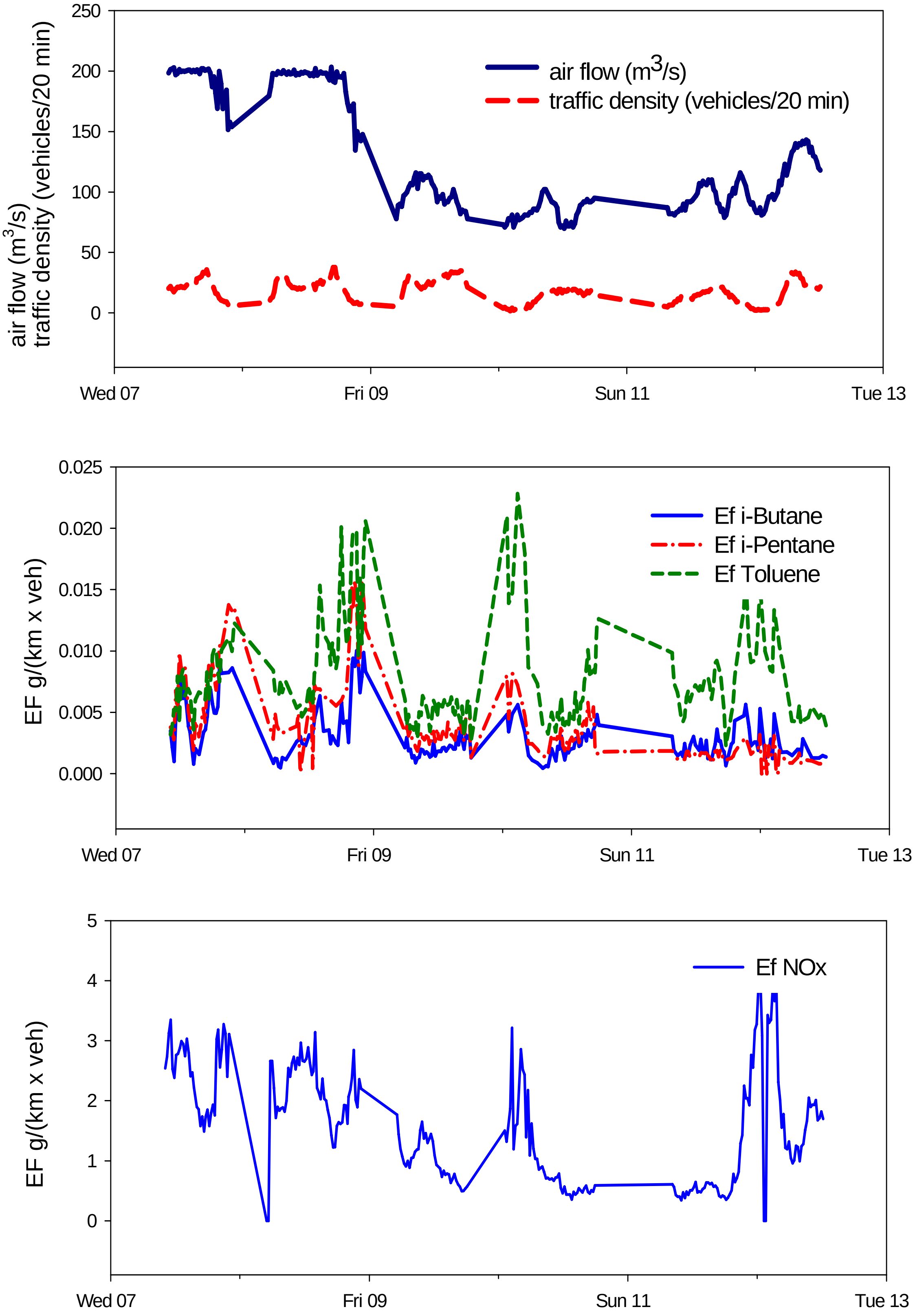


Figure 4-8: Diurnal variation of airflow, traffic density and emission factors for i-butane, i-pentane, toluene and NO_x during the Plabutsch Tunnel measurement, Nov. 2001.

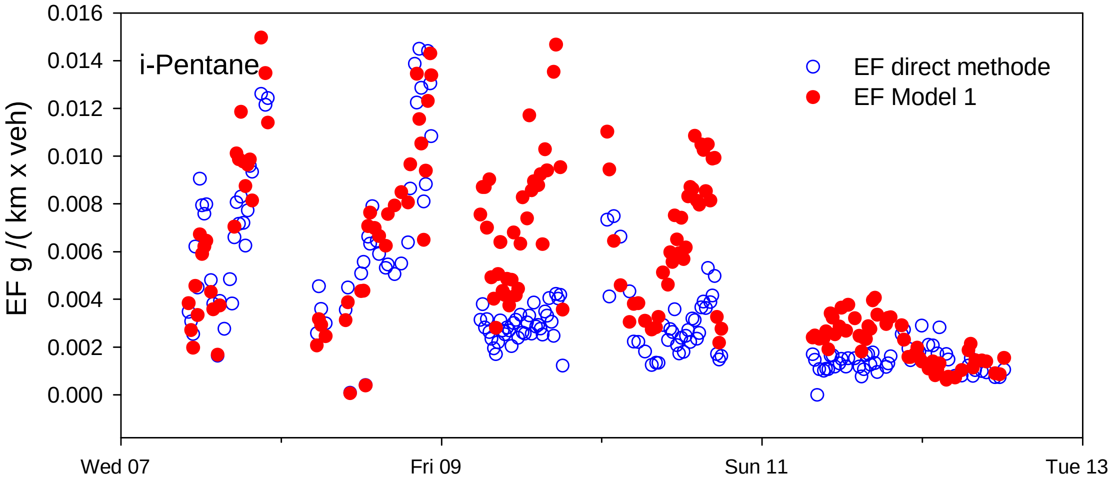
4.2.2.2 Calculation of emission factors using HBEFA 2.1

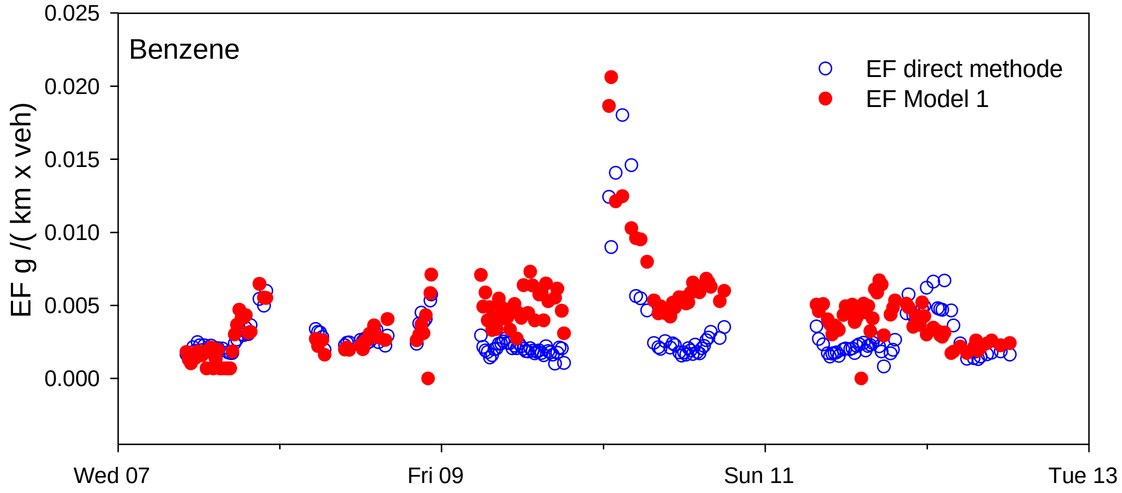
Emission factors for the Plabutsch Tunnel were calculated also using the HBEFA 2.1 model 1, and modelled using model 2 and 3. The HBEFA 2.1 emission factors calculated for CO_2, THC and BTX considered the reference year 2001, a gradient of -1, and +1 and the driving pattern HW 80 for traffic <1400 vehicles/h. The emission factors for road gradients between ± 1%, which were necessary for the Plabutsch Tunnel data evaluation, were obtained from a linear interpolation of emission factors for road gradients of -2, 0 and +2%. The emission factors were calculated with 20 min time resolution. In Appendix Tables, Table 16, 17, 18, 19 and 20 summarise the results of the emission factors for CO_2, THC, benzene, toluene and xylenes applying HBEFA 2.1 for the adequate driving situations.

According to the ARTEMIS Validation Final Report, 2005 (Rodler *et al.,* 2005) there was good agreement between the CO_2 emissions calculated from HBEFA 2.1 and the Plabutsch Tunnel measurements. The regression analysis of emissions factors derived from the HBEFA 2.1 and those derived from the measurements showed a coefficient of determination (R^2) of 0.99 and a regression coefficient (k) of 0.96. This is an important quality check of the used model 1 method.

In order to calculate the emission ratios of different components relative to CO_2, the background value of CO_2 was subtracted punctually for each value for the model 1 calculation.

Figure 4-9 shows the obtained time series from the direct calculated emission factors in comparison with model 1 for i-pentane, benzene and toluene as examples. The comparison shows good agreement for the weekdays November 7-9, 2001. For the weekends, the model 1 values are higher than the emission factors from the direct method, which is probably resulting from the poor ventilation during weekends.





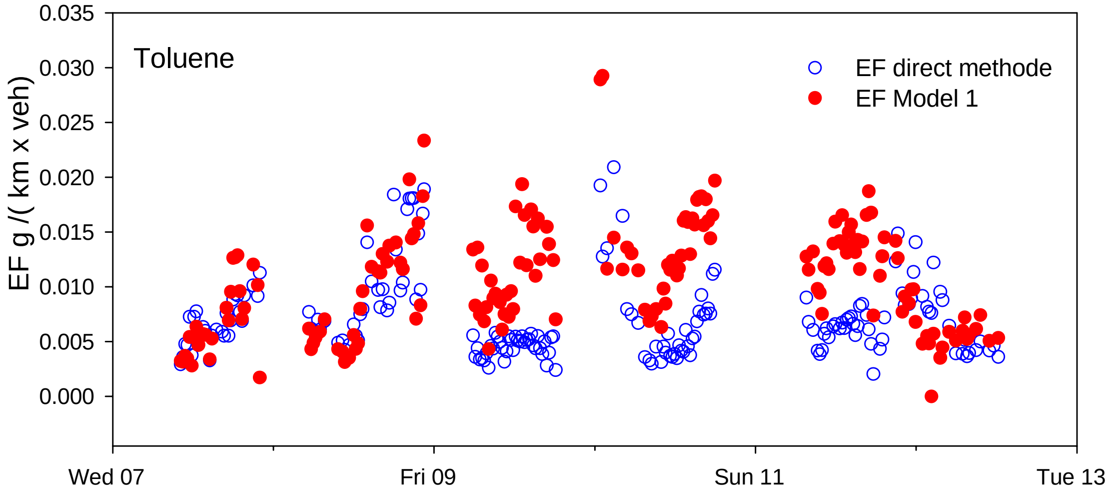


Figure 4-9: Time series for i-pentane, benzene and toluene calculated with the direct method and model 1, in the Plabutsch Tunnel.

Figure 4-10 shows in the red circle that the mechanical ventilation of the tunnel was strongly reduced during weekends, i.e. in our case November 10, 11, and hence the pollutant emission factors could not be accurately determined by using the direct method (Hausberger *et al.*, 2003).

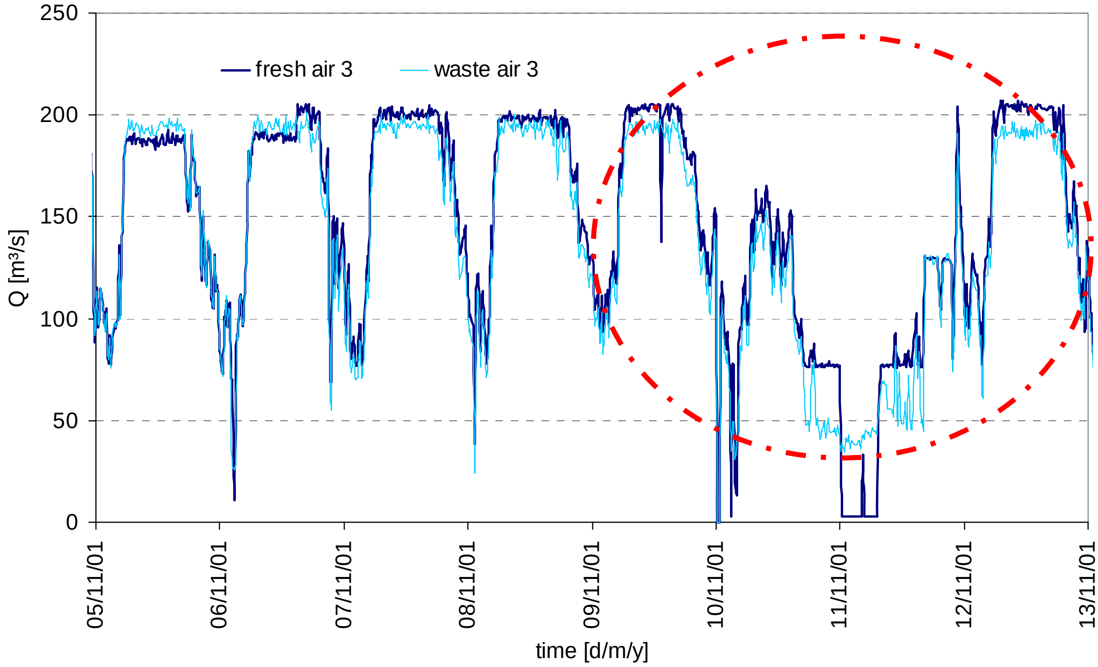


Figure 4-10: Fresh and waste air volume flows (ventilation section 3) for time intervals of 15 minutes.

Figure 4-11 shows for benzene and toluene a good correlation obtained by use of the two calculation methods, namely direct and indirect. The same behaviour was observed for all other compounds. The good agreement between direct and indirect emission factors calculation can be considered as an important “quality check” of the used calculation model because fuel consumption and hence the CO_2 emission is the variable which can be calculated on bases of the fleet composition and description of the driving pattern with the highest accuracy. This proves that the emission factors for CO_2 in the HBFEA 2.1 are a good estimation for the real traffic situation.

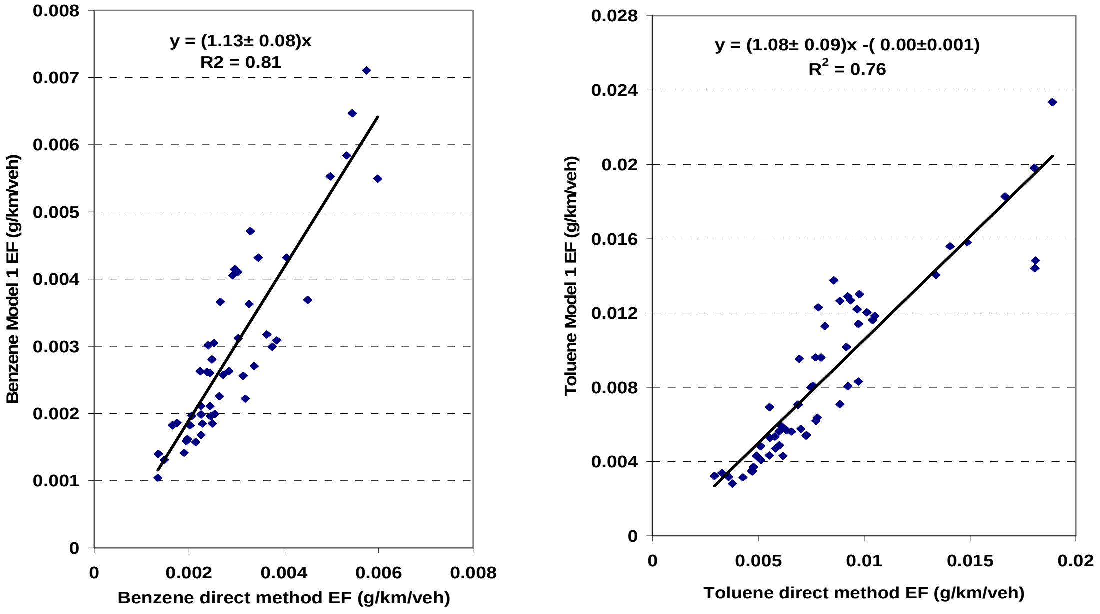


Figure 4-11: Correlation diagram for benzene and toluene (model 1) versus benzene and toluene (direct method).

The model 1 result will be compared with the calculations of model 2 and 3, below.

Appendix: Table 21 and Appendix: Table 22 summarises the direct and the model 1 calculated emission factors [g/(km×vehicle)] for the entire fleet during the Plabutsch Tunnel experiment.

As an example, Figure 4-12 shows for i-pentane, benzene and toluene, the obtained time series from model 1 in comparison with the model 2 results and the corresponding calculated absolute errors. The error calculation included the possible variation of the traffic fleet in the Plabutsch Tunnel and the contribution of the HW 80 driving situation.

The comparison of the two models shows for the selected three compounds that the model 2 values are significantly higher than the model 1 ones for the periods with high traffic density.

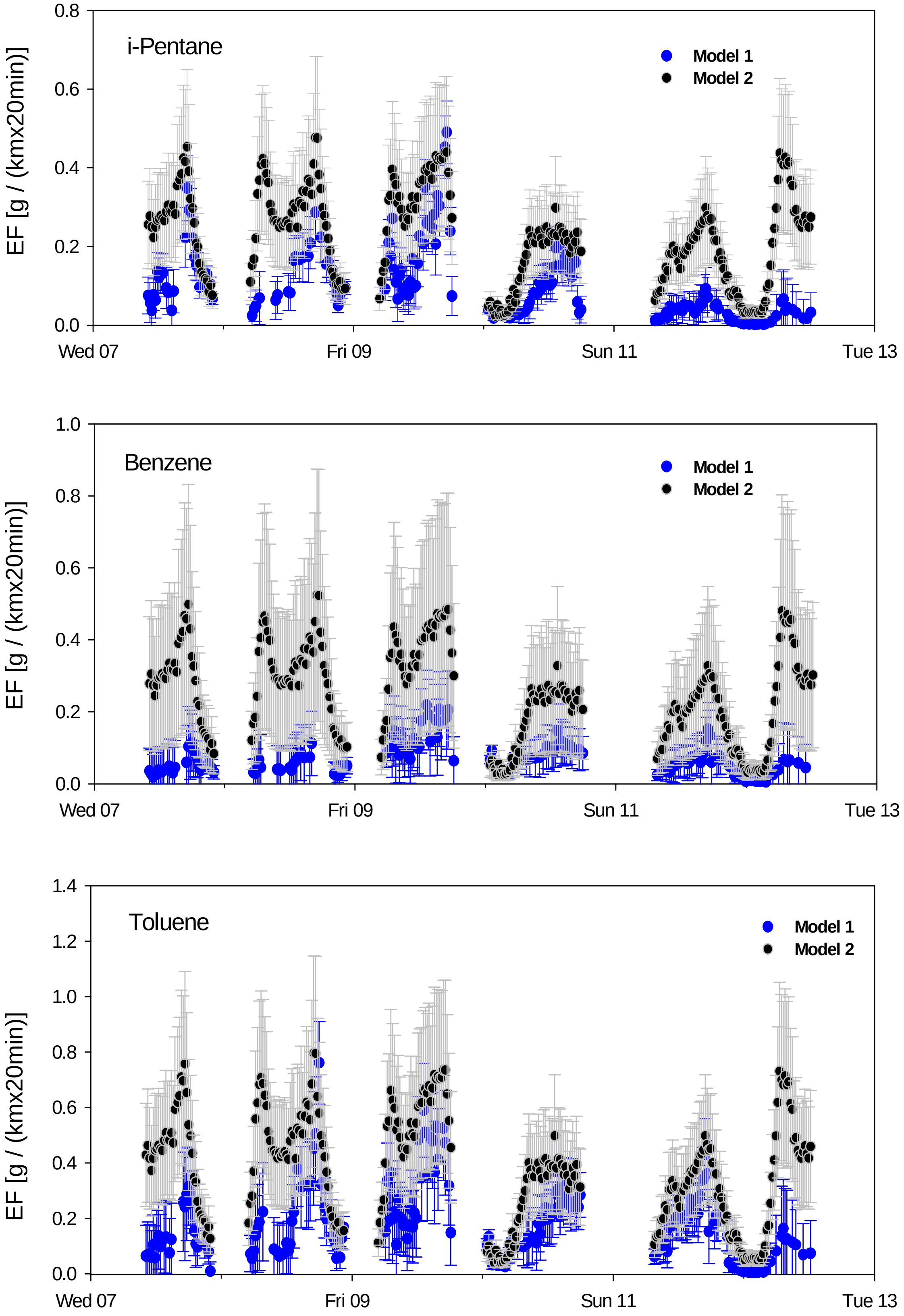


Figure 4-12 Time series for i-pentane, benzene and toluene calculated with model 1 and model 2, in the Plabutsch Tunnel.

The discrepancy between measured and calculated emission data obviously must be found in the emission factors for PC and/or HDV.

As in the previous case, respectively the Lundby Tunnel, the data analysis of the THC emission factors for the given traffic fleet (PC and LDV 75.63% with and without catalyst and HDV 24.37%) was performed. Since the distribution of catalyst and pre-Euro catalyst among the PC gasoline fuelled pre-Euro cars was not available, a sensitivity study of non-catalyst influence was performed for which four different cases were considered:

- all pre-Euro cars were considered as conventional cars,
- all pre-Euro cars were considered as G-catalyst cars,
- from the pre-Euro cars 50% were considered as conventional and 50% as G-catalyst cars,
- from the pre-Euro cars 10% were considered as conventional and 90% as G-catalyst cars.

It is worth mentioning that in the Plabutsch Tunnel among the PC cars 19.27% are pre-Euro, conventional and G-cat, 10.49% are Euro 1, 18.2% Euro 2 and 7.18% Euro 3. Among the LGDV 4.54% are pre-Euro, 2.53% Euro 1 and 4.6% respectively 2.64 are Euro 2 and 3. Among the LDVs, 45.7% are gasoline fuelled and 54.3% are diesel fuelled vehicles.

In order to study the influence of the catalyst, the contribution of pre-Euro PCs was different allocated between conventional and G-cat cars, as presented in Table 4-5.

Table 4-5 shows that the HDVs have the major contribution to the THC emission factors, namely 38-65%. The contribution of PC conventional cars is about 7-43% and of PC G-cat cars about 4-9%.

Table 4-5: THC emission factors percental contribution from different vehicle class categories, for four different cases.

Vehicle category	**Pre-Euro PC vehicles as conventional PC**	**Pre-Euro PC vehicles as G-cat**	**Pre-Euro PC vehicles as 50% conv and 50% G-cat**	**Pre-Euro PC vehicles as 10% conv, and 90% G-cat**
PC /B/without catalyst	42.76	-	26.59	6.56
PC B G-cat	0	9.26	4.09	9.08
PC B Euro 1	1.98	3.40	2.46	3.04
PC B Euro 2	3.05	5.25	3.80	4.68
PC B Euro 3	0.46	0.79	0.57	0.71
PC /D/without catalyst	0.76	-	0.47	0.58
PC G-cat	-	1.00	1.14	1.40
PC D Euro 1	0.62	1.07	-	-
PC D Euro 2	1.20	2.07	1.50	1.84
PC D Euro 3	1.02	1.75	1.27	1.56
LDCV/B/without catalyst	3.65	-	2.27	0.56
LDCV G-cat	-	1.35	-	1.75
LDCV B Euro 1	0.44	0.75	1.03	0.67
LDCV B Euro 2	0.34	0.59	0.42	0.52
LDCV B Euro 3	0.13	0.22	0.16	0.19
LDCV/D/without catalyst	0.81	1.39	1.00	1.24
LDCV D Euro 1	0.62	2.23	0.77	0.95
LDCV D Euro 2	1.30	0.78	1.61	1.99
LDCV D Euro 3	0.45	-	0.56	0.69
Bus	2.23	3.82	2.77	3.41
HDV	38.19	65.59	47.50	58.57

In order to check the HBEFA 2.1 THC emission factor for HDV, it was varied by 10%, 50% and 100%.

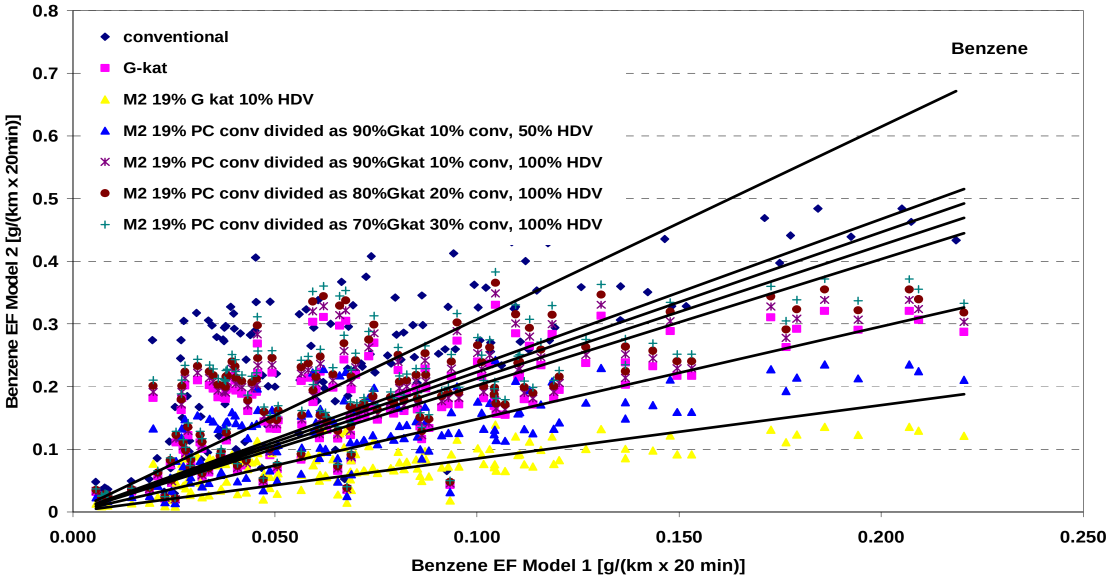


Figure 4-13: Correlation diagram for benzene (model 2) versus benzene (model 1).

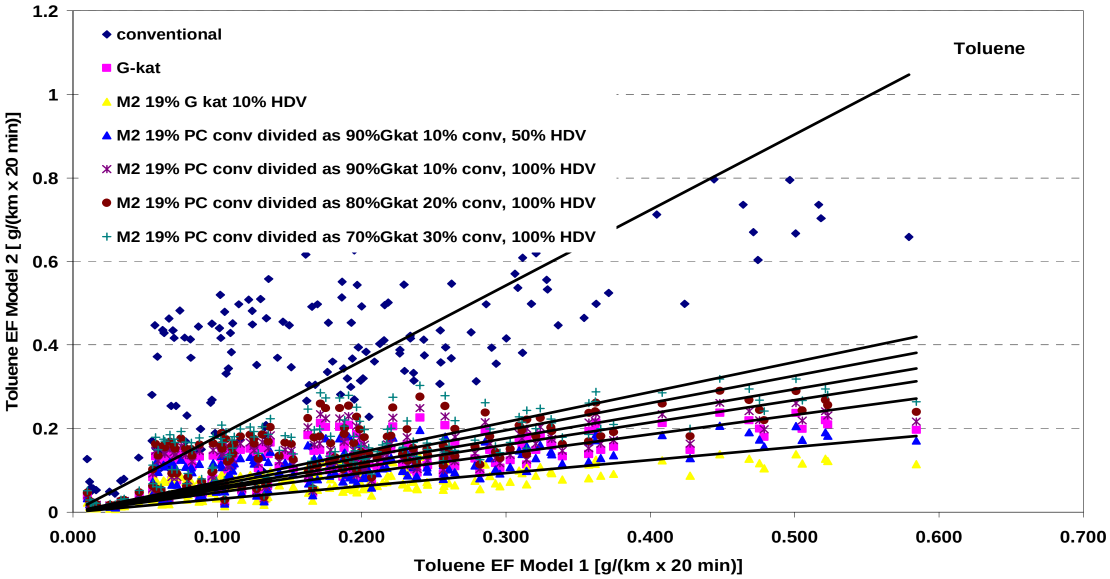


Figure 4-14: Correlation diagram for toluene (model 2) versus toluene (model 1).

Figure 4-13, Figure 4-14 and Table 4-6 show for benzene and toluene small variation of the slope when the HDV EF was changed. Accordingly, by a 10% decrease of the HDV EF, for toluene a slope of 0.304 ± 0.010 was obtained, whereas for a 100% contribution of the HDV EF a slope of 0.575 ± 0.018 was obtained. The slope variation from 3.074 ± 0.112 for benzene and 1.797 ± 0.060 for toluene for non catalyst pre-Euro cars to 2.07 ± 0.07 and 0.575 ± 0.018, respectively, as well as for the other considered situations, as presented in Figure 4-13, Figure 4-14 and Table 4-6 indicate that the catalyst condition may represents the main reason that could explain the discrepancy between measured and modelled emission factors. This emphasizes again the importance of the exact determination of the contribution of non-catalyst or cars with malfunctioning catalyst to the traffic fleet.

Table 4-6: Correlation equations for benzene and toluene, model 2 versus model 1, HDV contribution, conventional and G-cat contribution analysis.

HDV EF contribution	**PC pre-Euro distribution**	**Slope (m)**		**Correlation coefficient (R^2)**	
		Benzene	**Toluene**	**Benzene**	**Toluene**
10%	G-cat	0.829±0.028	0.304±0.010	0.348	0.328
50%	90%Gcat 10% conv	1.439±0.048	0.453±0.014	0.348	0.328
100%	90%Gcat 10% conv	1.962±0.066	0.523±0.017	0.348	0.308
100%	80%Gcat 20% conv	2.145±0.071	0.653±0.022	0.375	0.130
100%	70%Gcat 30% conv	2.338±0.076	0.717±0.022	0.348	0.328
100%	conventional	3.074±0.112	1.797±0.060	0.115	0.265
100%	G-cat	2.070±0.07	0.575±0.018	0.348	0.328

4.2.2.3 Comparison with the literature data

In order to determine the evolution of traffic emissions, the results from the present study have been compared with results from a previous campaign performed in the Plabutsch Tunnel in 1998.

From the direct emission factors determined for weekday, high traffic periods, emission factors for LDV and HDV were calculated by means of regression analysis. Also, has to be specified that although the HDV proportion is increased in the Plabutsch tunnel comparatively to the other tunnels, the percentage of the HDV never exceeds 30%. The obtained LDV and HDV emission factors will be further used in order to compare the trend of emission factors for the Plabutsch Tunnel from 1998 to 2001. Table 4-7 shows the emission factors derived from the Plabutsch Tunnel measurements in 2001, for LDV and HDV [g/(km×vehicle)].

Table 4-7: Emission factors (direct calculation method) for the Plabutsch Tunnel measurements for LDV and HDV [g/(km×vehicle)].

Working day, HDV 10-30%	**LDV**	**SD**	**HDV**	**SD**
propene, propane	0.0163	0.0069	0.0025	0.0013
propine	0.0023	0.0002	0.0005	0.0002
i-butane	0.0092	0.0010	0.0015	0.0009
1-butene, i butene	0.0149	0.0014	0.0028	0.0014
1,3-butadien, n- butanee	0.0183	0.0019	0.0024	0.0018
trans-2-butene	0.0048	0.0008	0.0026	0.0008
cis-2-butene	0.0059	0.0004	0.0005	0.0004
i-pentane	0.0041	0.0008	0.0027	0.0007
isoprene	0.0104	0.0018	0.0017	0.0018
cis-2-pentene	0.0062	0.0005	0.0002	0.0005
2-methylpentane	0.0040	0.0006	0.0019	0.0006
3-methylpentane	0.0018	0.0003	0.0009	0.0003
n-hexane	0.0018	0.0002	0.0005	0.0002
benzene	0.0068	0.0004	0.0011	0.0004
cyclohexane	0.0047	0.0004	-0.0003	0.0004
n-heptane	0.0015	0.0007	0.0015	0.0006
toluene	0.0126	0.0017	0.0053	0.0016
ethylbenzene	0.0024	0.0005	0.0015	0.0004
o-xylene	0.0060	0.0010	0.0019	0.0009
m-/p- xylene	0.0097	0.0017	0.0045	0.0016
1,2,4-trimethylbenzene	0.0090	0.0011	0.0008	0.0010

Table 4-8 shows a clear decrease of the emission factors in the Plabutsch Tunnel from 1998 to 2001 although the traffic density has slightly increased during this period, as Table 3-1 presents.

Table 4-8: Calculated emission factors [g/(km×vehicle)] in the Plabutsch Tunnel in comparison with the previous study performed in 1998 (Rodler, 2000).

Compound, measurement year	**Emission factors for LDV [g/(km×vehicle)]**	**Ratio 1998/2001**
Benzene, 2001	0.0068 ± 0.0041	1.2
Benzene, 1998	0.0079 ± 0.0052	
Toluene, 2001	0.0126 ± 0.0017	1.6
Toluene, 1998	0.0198 ± 0.0016	

The decrease in the emission factors can be attributed to the increased number of catalyst-equipped cars, i.e. 80% LDV and 94% HDV among which more then 60% are Euro 2 and Euro 3.

Similar results have been obtained in Austria during studies performed in the Tauern Tunnel in 1988 and 1997 (Schmidt *et al.,* 2001). The study performed by Schmidt reveals that the emission rates of individual hydrocarbons (aromatics) decrease during 9 years of about 80-90%. The author attributed this reduction mainly to a strong increase of the catalyst equipped passenger cars from 0% in 1988 to 60% in 1997.

4.2.3 Kingsway Tunnel

The complicated situation in defining the flow volume into and out of the tunnel and the whole measurement set-up made the determination of the emission factors by the direct method impossible. Accordingly, the vehicle emission factors were calculated and modelled, as in Lundby Tunnel study.

4.2.3.1 Calculation of emission factors using HBEFA 2.1

The HBEFA 2.1 emission factors calculated for CO_2, THC and BTX considered a gradient of –4% and 3.3% and the driving pattern HW 60, for traffic smaller than 1400 vehicles /hour. This distribution is also in agreement with the speed limit in the tunnel, namely 65 km/h. The emission factors were calculated with 60 minutes time resolution. As an example, in Appendix Tables, Table 23, 24 and 25 summarise the results of the emission factors for $CO_{2,}$ THC and benzene, applying HBEFA 2.1 for the adequate driving situations.

As in the previous tunnel studies reported here, the model 1 results will be compared with the model 2 and 3, below.

Figure 4-15 shows for i-pentane, benzene and toluene, the obtained time series from model 1 in comparison with the model 2 results and the corresponding calculated absolute errors. The error calculation included both, the possible variation of traffic fleet in the Kingsway Tunnel and the contribution of the HW-60 driving situation.

The comparison of the two models shows for i-pentane and toluene that the calculated values are higher than the modelled values for periods with high traffic density. However, it should be pointed out, that for benzene the two models agree quite well.

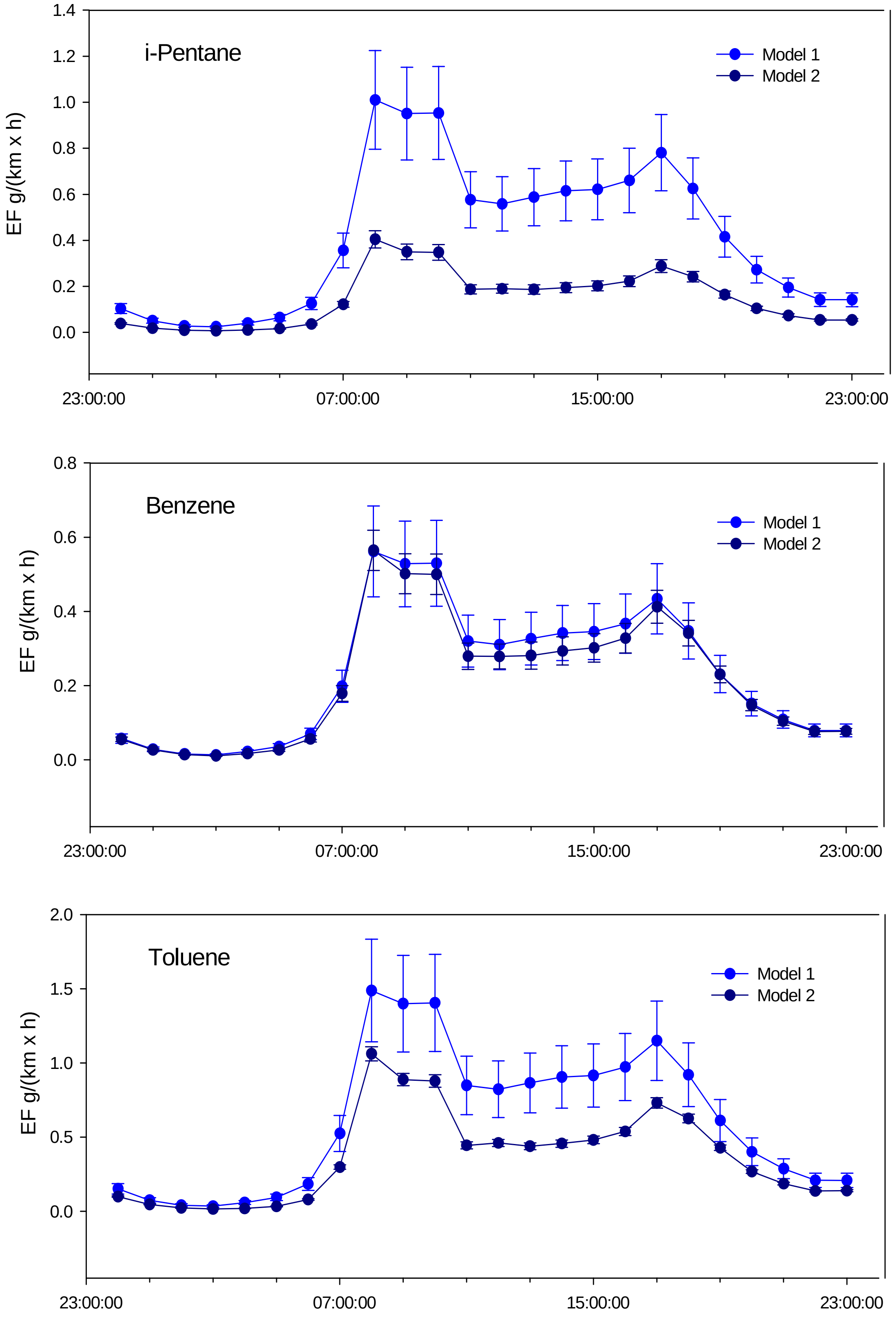


Figure 4-15: Time series for i-pentane, benzene and toluene calculated with model 1 and model 2 during the Kingsway Tunnel campaign.

Figure 4-16 shows for benzene a relatively good correlation between the different models. This proves that the calculated values are within the standard deviation in good agreement with the HBEFA 2.1 model 2 and 3 estimations for the real traffic situation in the Kingsway Tunnel.

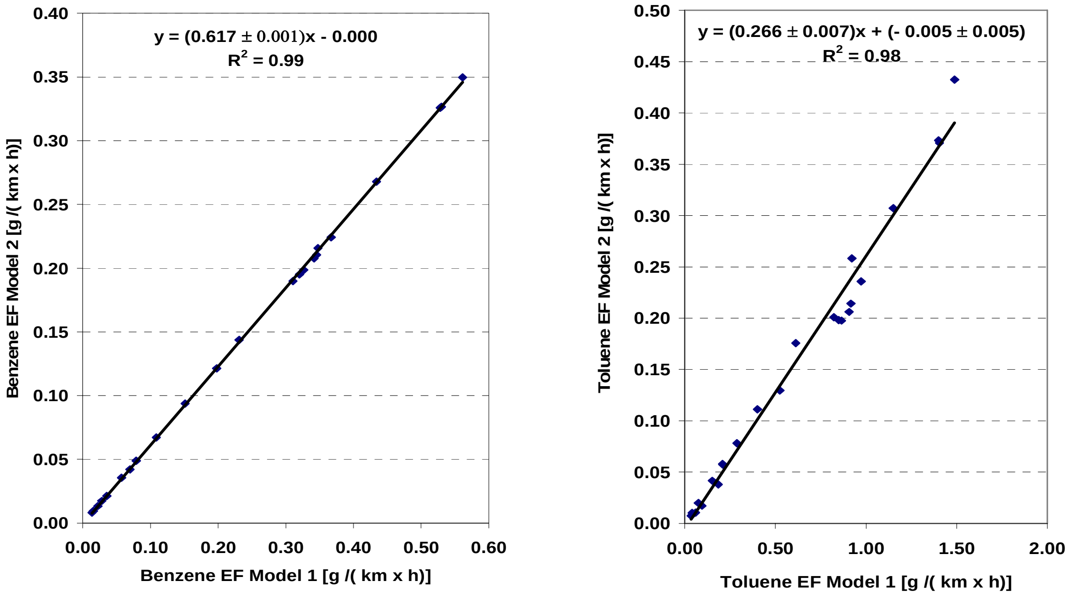


Figure 4-16: Correlation diagrams for benzene and toluene (model 2) versus benzene and toluene (model 1) emission factors.

A similar correlation plot for toluene is presented. Although the linearity between the different models is quite good as indicated by the R^2 values, the slopes are significantly smaller than for the expected 1 to 1 relation.

Figure 4-17 shows for a variety of other hydrocarbons the ratio of the emission factors calculated from model 1, model 2 and model 3. It is worth mentioning that for model 1 the emission factors are from 0.3 (propene) to 8 (cis-2-butene) times higher than those obtained from model 2.

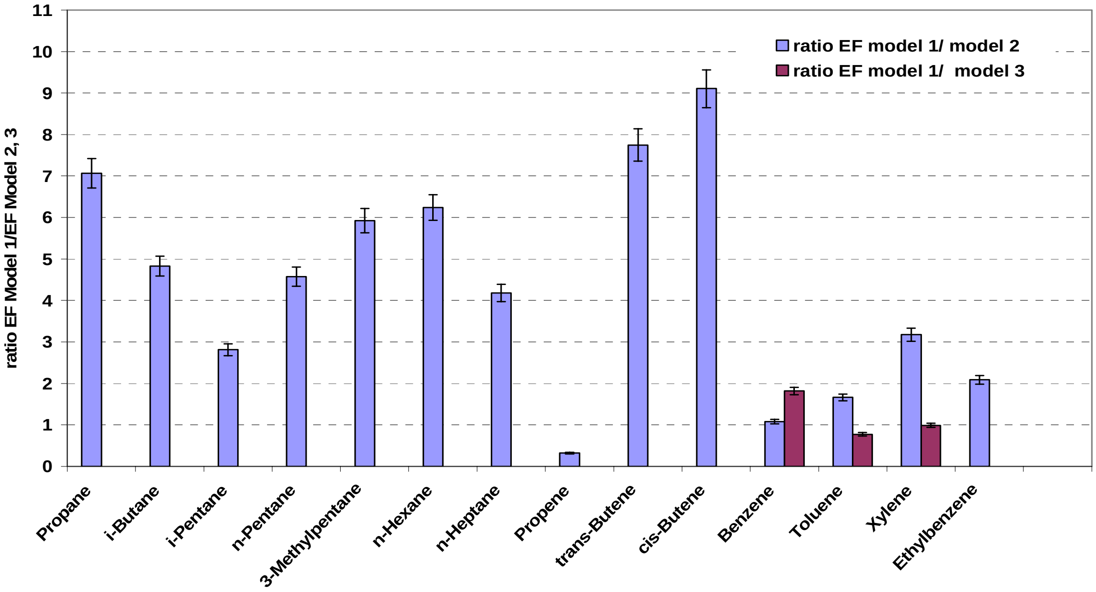


Figure 4-17: Ratio of NMHCs emission factors of model 2 and model 3 versus model 1.

In Figure 4-18, it is shown that for the given traffic fleet of 94.51% LDV and 5.5% HDV, the main contributions is resulting from PC with catalyst (66.97%). HDVs have a contribution of only 8.9%, which is significantly smaller than in the two other studies presented here. From the fleet data analysis, most LDVcars have Euro 2 and Euro 3 catalyst (28.7% and 32.23%, respectively) and only 11.21% are G-cat catalyst cars.

Taking into consideration the small contribution of HDVs, about 5% in the Kingsway Tunnel, the variation of the HDV emission factors was not performed, as has been done in the Lundby and in Plabutsch Tunnel data analysis.

Obviously, the discrepancy between measured and calculated emission data must result from the emission factors for PC and LDV.

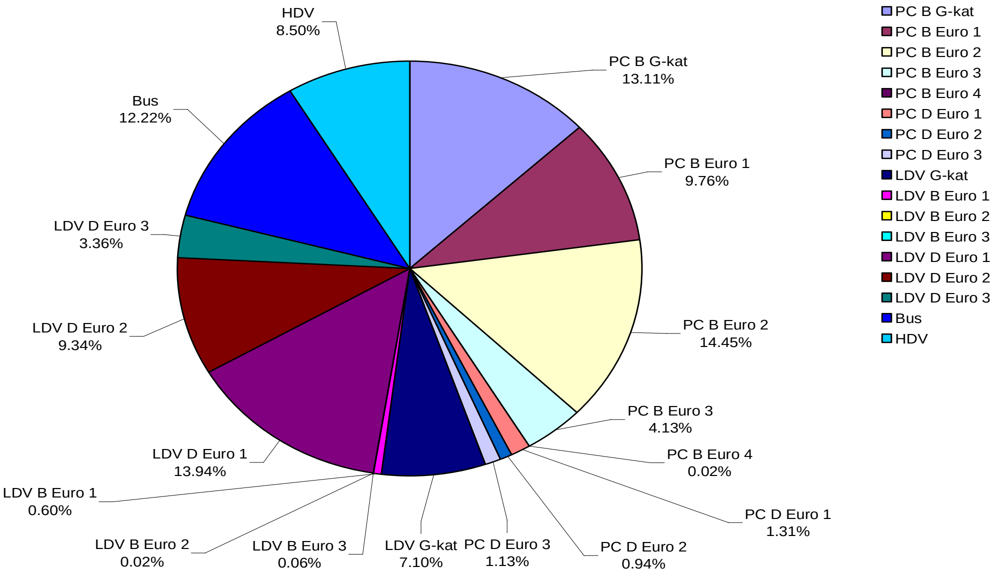


Figure 4-18: THC emission factors percental contribution for the Kingsway Tunnel fleet composition.

In order to test whether the 11.21% G-cat cars have catalysts malfunction the emission factors were recalculated considering their emissions as the ones of conventional cars.

Figure 4-19 shows the correlation diagram for benzene and toluene, model 2 versus model 1, PC and LDV G-cat counted as conventional vehicles

The slopes changes for benzene from 0.615 ± 0.001 to 0.948 ± 0.005, for model 2 versus model 1 and from 0.266 ± 0.008 to 0.632 ± 0.012 for toluene, respectively. The same situation as in Lundby Tunnel is encountered indicating that the catalyst condition represents the main reason that may explain the discrepancy between measured and modelled emission factors.

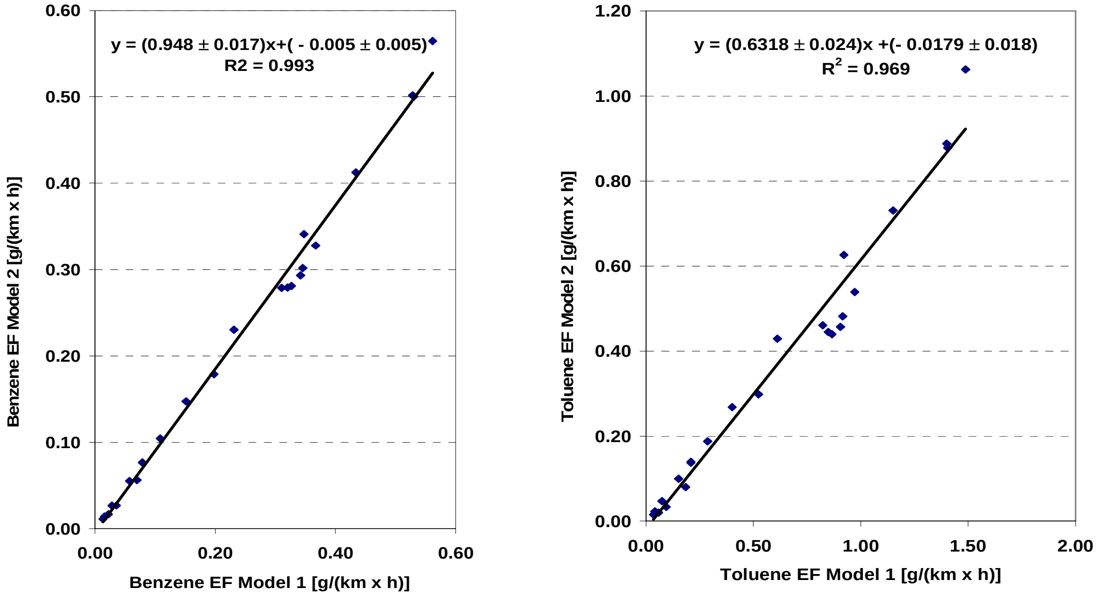


Figure 4-19 Correlation diagram for benzene and toluene (model 2), versus benzene and toluene (model 1), PC and LDV G-cat counted as conventional vehicles.

The Appendix: Table 26 summarises the model 1 calculated emission factors for the entire fleet during Kingsway Tunnel experiment in [g/(km×vehicle)].

4.2.3.2 Comparison with literature data

Figure 4-20 shows the comparison of the NMHCs emission profiles determined in the present study with the estimated road transport emission in Liverpool, for the Mersey area (where the Kingsway Tunnel is located, in 2002. The data were published by DEFRA (source: e-Digest of Environmental Statistics, March 2004).

It is showen that the estimated values for most of the investigated NMHC were higher than the measured ones for most of the compounds, within the statistical error. The differences can be explained by the chosen road profile as well as from the different traffic distribution used by DEFRA model. The DEFRA model is a statistical one, which takes into account the general distribution between urban and rural roads in the whole UK, and not the Kingsway Tunnel traffic conditions. However, the comparison shows the same profile for the measured and modelled NMHCs.

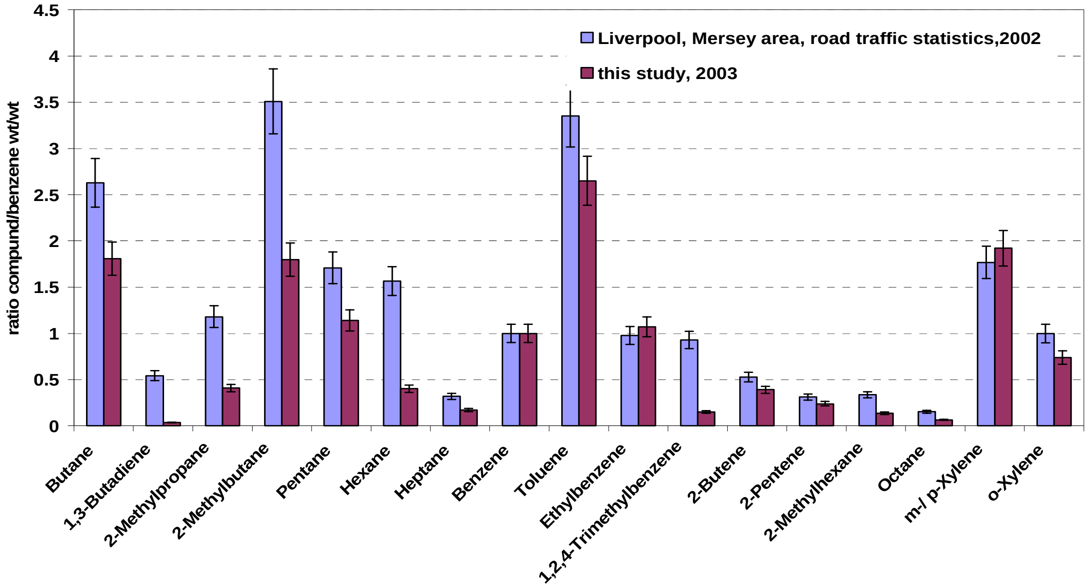


Figure 4-20: Comparison of NMHCs emission profiles relative to benzene determined in the present study with the estimated road transport emission for 2002 published by DEFRA, (source publication: e-Digest of Environmental Statistics, http://www.defra.gov.uk/environment/statistics/index.htm).

4.2.4 A656 Motorway

Calculating the source strength of a compound just by taking the measured vertical profile with its rather low vertical resolution could lead to significant errors in the calculated source strength.

For a more precise calculation of the source strength of a selected compound a quasi-continuous vertical profile (Figure 4-21) of the corresponding compound has to be taken into account as has been measured for NO_x.

Figure 4-21(a), benzene is shown as an example: discontinuous vertical benzene profile (left), quasi-continuous vertical NO_x profile (right). Accordingly, in order to obtain quasi-continuous vertical profiles for the different NMHC the data, which were measured discontinuously at different height, were correlated with the corresponding measured NO_x data, which were obtained with a much better vertical resolution, see Figure 4-21(b). The correlation shown in this figure is strongly dependent on the benzene concentration measured at high NO_x. However, it should be mentioned that the averaging time interval for the concentration shown was 2 hours. Accordingly, e.g. the impact of a single high emitting diesel vehicle on the data would have a neglijable impact on the measured concentrations.

Good correlation was obtained only for the NMHC compounds, for which also in vertical profiles a significant near-surface increase of the concentrations was determined.

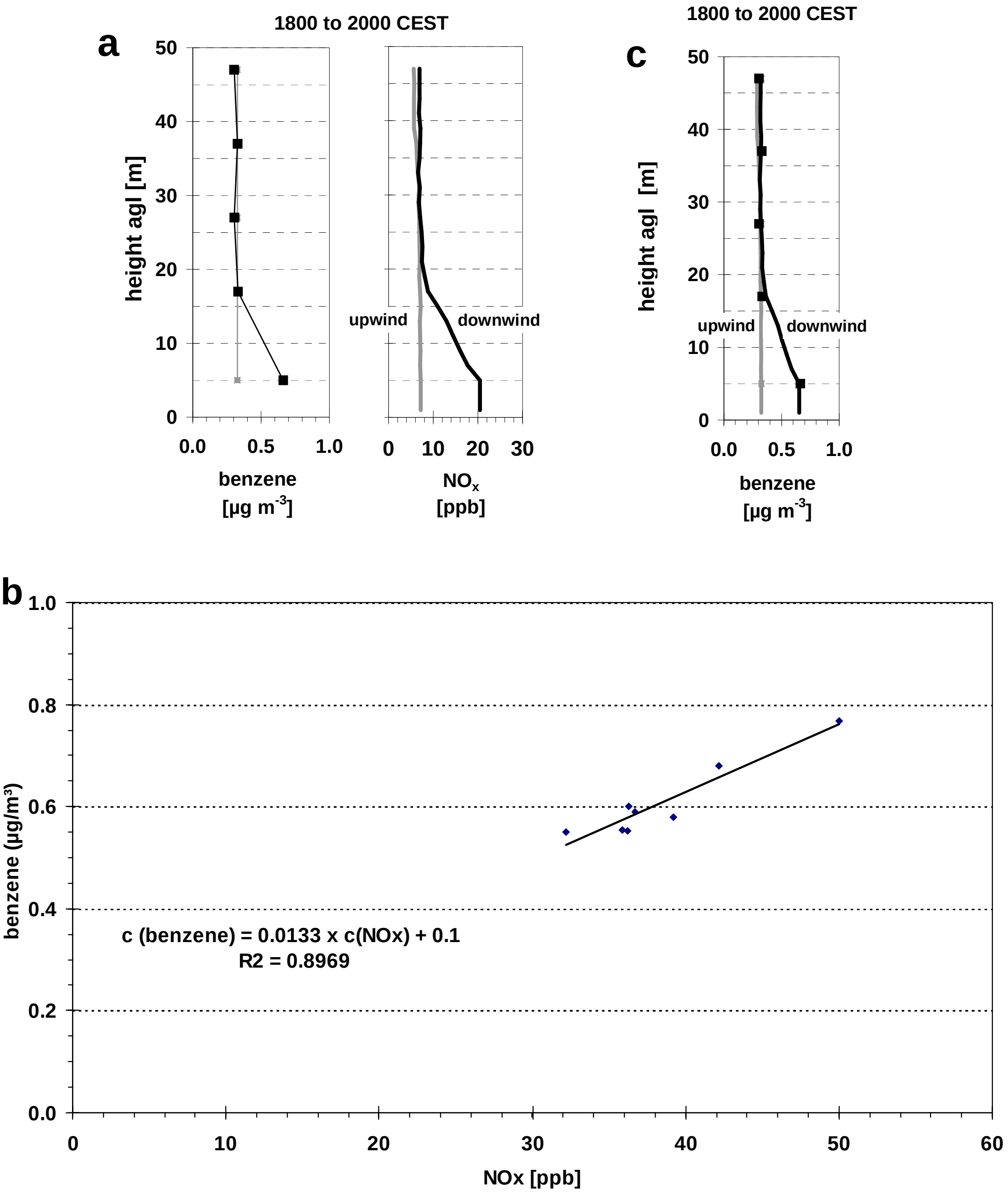


Figure 4-21: Building the quasi-continous vertical NMHC profile from discontinuous profile.

The equations obtained from the linear correlation of the corresponding NMHC and NO_x were used to calculate quasi-continuous profiles for the individual NMHC.

A similar profile structure for NO_x and the individual NMHC components was observed, see Figure 4-21(c). The quasi-continuous vertical profile for benzene after application of the correlation equation to the discontinuous benzene data is shown in Figure 4-21(c).

By use of the Equation 11 the calculated source strengths for the different hydrocarbons, for different time intervals are summarised in the Appendix: Table 27. It shows for increasing traffic density an increase in the source strength. As an example, for toluene, a maximum value of 138.9 ± 41.7 g/(km×h)was obtained for a working day morning rush hour and a minimum of 38.0 ± 11.4 g/(km×h)for a weekend. The same trend was observed for benzene, a maximum of 47.7 ± 14.3 and a minimum of 17.6 ± 5.3 g/(km×h), for i-pentane a maximum of 241.7 ± 72.5 g/(km×h)and a minimum of 53.8 ± 16.4 g/(km×h).

Figure 4-22 shows the source strength for n-butane, i-pentane, benzene and toluene in comparison with the mean course for passenger cars (LDV) and heavy-duty vehicles (HDV) for different time intervals, during a working day, namely May 08, 2001. The source strength variation with the traffic density is shown. Exception is the time interval 0800-1000 CEST, which is characterised by a high traffic volume. Since the reason for this behaviour is unclear, the data obtained during this time interval were not considered for further calculations.

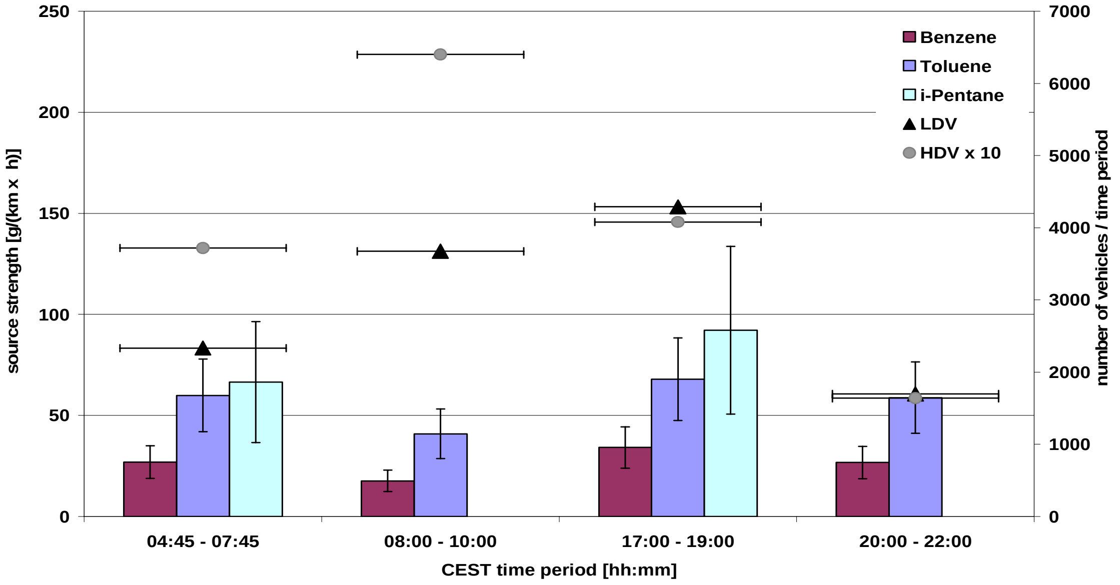


Figure 4-22: Source strength for n-butane, i-pentane, benzene and toluene for different time intervals in comparison with the mean course for passenger cars (LDV) and heavy duty traffic (HDV), during weekday May 08, 2001.

It should be pointed out, that the toluene/benzene mass ratio of 2.5± 1.1 was almost constant during that day, as it is shown in Figure 4-23.

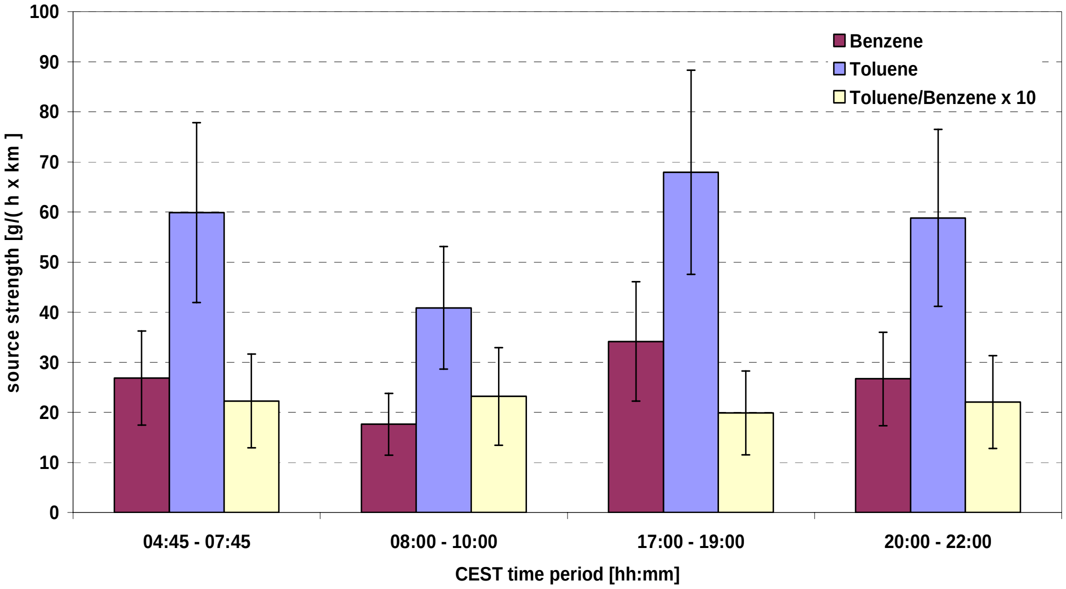


Figure 4-23: Source strength for benzene and toluene in comparison with the toluene/benzene ratio for working day May 08, 2001

From the source strengths, emission factors [g/(km×vehicle)] have been calculated by use of Equation 12.

Table 4-9 presents the calculated emission factor [mg/(km×vehicle)] for the different intervals for four days in May 2001.

The results provide evidence for different emission factors of the fleet for different days of the week, most probably caused by differences in fleet composition, which needs to be considered when comparing the emission factors of tunnel and road studies with road traffic emission models.

Table 4-9: Calculated emission factor [mg/(km×vehicle)] for the different time intervals, in May 2001, BAB II - A656 experiment.

EMISSION FACTOR [mg/(km×veh)]	**08.05.2001 Wednesday**				**14.05.2001 Thursday**			**17.05.2001 Saturday**		**18.05.2001 Sunday**		
	04:45-07:45	**08:00-10:00**	**17:00-19:00**	**20:00-22:00**	**8:00-10:00**	**10:15-12:15**	**12:30-14:30**	**13:00-16:30**	**16:30-20:15**	**12:00-16:00**	**16:00-18:00**	**18:00-20:00**
i-butane	7.5 ± 5.6	4.1 ± 1.5	-	-	1.0 ± 0.4	11.1 ± 3.3	8.3 ± 2.5	3.7 ± 1.3	5.9 ± 2.2	4.6 ± 1.5	5.0 ± 1.5	1.7 ± 0.6
iso-/1-butene	5.6 ± 4.2	1.7 ± 0.6	-	-	-	-	-	1.3 ± 0.5	0.7 ± 0.3	1.2 ± 0.4	-	-
1,3-butadiene/n-butane	19.7 ± 4.8	8.6 ± 3.1	-	-	-	-	-	6.8 ± 2.5	7.2 ± 2.7	9.6 ± 3.1	-	4.9 ± 1.7
i-pentane	18.8 ±13.8	11.6 ± 4.2	-	-	30.3 ± 1.2	54.3 ± 6.3	40.1 ± 2.0	9.0 ± 3.2	11.1 ± 4.1	12.0 ± 3.8	13.0 ± 3.9	16.2 ± 5..5
isoprene/trans-2-pentene	-	-	4.2 ± 1.3	-	7.9 ± 2.9	-	5.4 ± 1.6	-	-	2.1 ± 0.7	3.0 ± 0.9	3.4 ± 1.2
cis-2-pentene	17.3 ± 3.0	12.6 ± 4.5	-	-	3.2 ± 1.2	8.7 ± 2.6	-	-	-	1.0 ± 0.3	-	1.1 ± 0.4
2-methylpentane	5.1 ± 3.9	2.6 ± 0.9	6.4 ± 2.0	-	7.5 ± 2.8	5.7 ± 1.7	3.6 ± 1.1	0.8 ± 0.3	5.6 ± 2.1	-	2.1 ± 0.6	6.9 ± 2.4
3-methylpentane	1.9 ± 1.5	0.7 ± 0.2	1.0 ± 0.3	2.6 ± 1.0	2.6 ± 1.0	-	0.7 ± 0.2	1.3 ± 0.5	1.9 ± 0.7	-	1.9 ± 0.6	-.
n-hexane	2.4 ± 1.8	0.7 ± 0.2	2.0 ± 0.6	5.2 ± 2.0	5.4 ± 2.0	4.2 ± 1.3	2.5 ± 0.8	-	-	4.6 ± 1.5	-	4.0 ± 1.4
benzene	8.4 ± 6.3	4.1 ± 1.5	7.2 ± 2.2	14.2 ± 5.4	8.8 ± 3.3	10.9 ± 3.3	9.3 ± 2.8	4.8 ± 1.7	6.4 ± 2.4	12.4 ± 4.0	10.7 ± 3.2	11.7 ± 4.0
cyclohexane	0.8 ± 0.6	-	0.1 ±0.1	-	0.7 ± 0.3	-	0.7 ± 0.2	-	1.2 ± 0.5	-	0.3 ± 0.1	-
3-methylhexane	1.7 ± 1.3	0.5 ± 0.2	1.6 ± 0.5	2.2 ± 0.8	2.5 ± 0.9	1.0 ± 0.3	2.4 ± 0.7	0.6 ± 0.2	-	2.5 ± 0.8	2.7 ± 0.8	2.1 ± 0.7
2,2,4-trimethylpentane	1.7 ± 1.3	0.3 ± 0.1	1.7 ± 0.5	4.2 ± 1.6	5.0 ± 1.9	7.3 ± 2.2	2.3 ± 0.7	1.8 ± 0.6	2.9 ± 1.1	3.5 ± 1.1	4.3 ± 1.3	3.2 ± 1.1

Table 4-9 (continued)

EMISSION FACTOR [mg/(km×veh)]	**08.05.2001 Wednesday**				**14.05.2001 Thursday**			**17.05.2001 Saturday**		**18.05.2001 Sunday**		
	04:45-07:45	08:00-10:00	17:00-19:00	20:00-22:00	8:00-10:00	10:15-12:15	12:30-14:30	13:00-16:30	16:30-20:15	12:00-16:00	16:00-18:00	18:0-20:0
n-heptane	0.9 ± 0.7	0.4 ± 0.1	0.8 ± 0.3	3.5 ± 1.3	0.5 ± 0.2	1.2 ± 0.4	1.0 ± 0.3	0.1 ± 0.1	1.0 ± 0.4	-	1.7 ± 0.5	1.7 ± 0.6
2,3,4-trimethylpentane	-	-	-	1.0 ± 0.4	1.0 ± 0.4	-	-	-	-	-	-	-
toluene	18.7 ± 4.1	9.4 ± 3.4	14.3 ± 4.4	31.4 ± 11.9	32.0 ± 1.8	19.6 ± 5.9	17.4 ± 5.2	9.0 ± 3.2	16.4 ± 6.1	20.3 ± 6.5	22.3 ± 6.7	21.0 ± 7.2
n-octane	23.9 ± 7.9	7.1 ± 2.6	-	-	4.1 ± 1.5	-	-	-	-	2.5 ± 0.8	-	-
ethylbenzene	3.3 ± 2.5	3.4 ± 1.2	2.0 ± 0.6	10.1 ± 3.8	5.9 ± 2.2	3.6 ± 1.1	3.1 ± 0.9	1.7 ± 0.6	2.8 ± 1.0	4.6 ± 1.5	5.3 ± 1.6	4.4 ± 1.5
m-/p-xylene	9.7 ± 7.3	5.3 ± 1.9	7.5 ± 2.3	20.3 ± 7.7	16.4 ± 6.1	11.8 ± 3.5	9.9 ± 3.0	5.1 ± 1.8	10.0 ± 3.7	12.4 ± 4.0	13.3 ± 4.0	12.8 ± 4.3
o-xylene	2.9 ± 2.2	-	2.6 ± 0.8	5.9 ± 2.2	5.4 ± 2.0	3.9 ± 1.2	-	2.0 ± 0.7	3.9 ± 1.4	4.2 ± 1.3	6.0 ± 1.8	4.1 ± 1.4
1,2,4-TMB/decane	-	-	-	-	10.4 ± 3.8	-	-	1.7 ± 0.6	2.9± 0.9	-	-	-

4.2.4.1 Comparison of measured and modelled-calculated source strength

The measured data from this experiment were used in order to evaluate the quality of a high-performance emission model developed at the Institute of Energy Economics and Rational Use of Energy (IER-University of Stuttgard). The model provides emission rates of individual road section of high temporal resolution and includes measurements of the most important traffic parameters relevant to emissions (Külwein and Friedrich, 2005).

Figure 4-24 gives the comparison of measured and modelled calculated source strength for benzene, for different 12 time intervals between 2 and 4 h duration. As can be observed, the model over and under predicts the measurements, but on average, the measurements are about 26% higher than the modelled calculated values. If the data of May, 8, 20-22 CEST, a period with poorly fulfilled prerequisities for source strength calculations is substracted, the difference between measurements and calculations is reduced to 18%. This result points out relative good emissions factors for benzene from roller test stand investigations compared to most of the other NMHCs compounds.

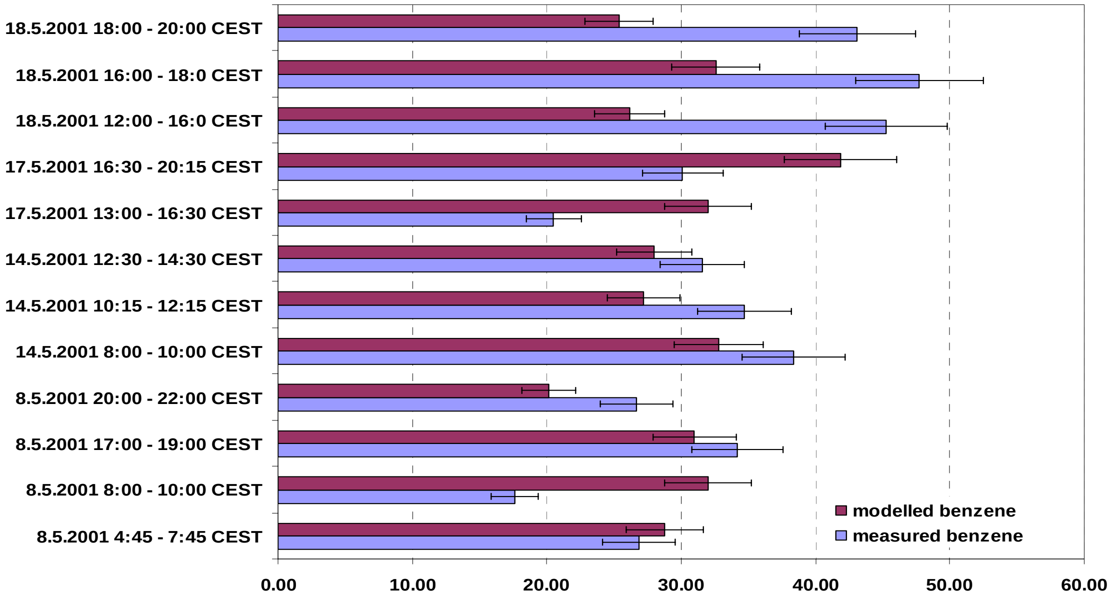


Figure 4-24: Comparison of measured and model-calculated source strength of benzene (error bars- statistic error 1σ).

For benzene, toluene, ethylbenzene and 1, 2, 4 trimethylbenzene/decane the measured values are in good agreement within standard deviation within the modelled ones. For the other hydrocarbons the measured compounds are a factor of 1.3-7 higher, see Figure 4-25 (a).

Exception are: i-butane, 1, 3- butadiene, n-butane, cyclohexane, n-octane for which the measured values are 11-21 higher than the modelled ones, see Figure 4-25 (b).

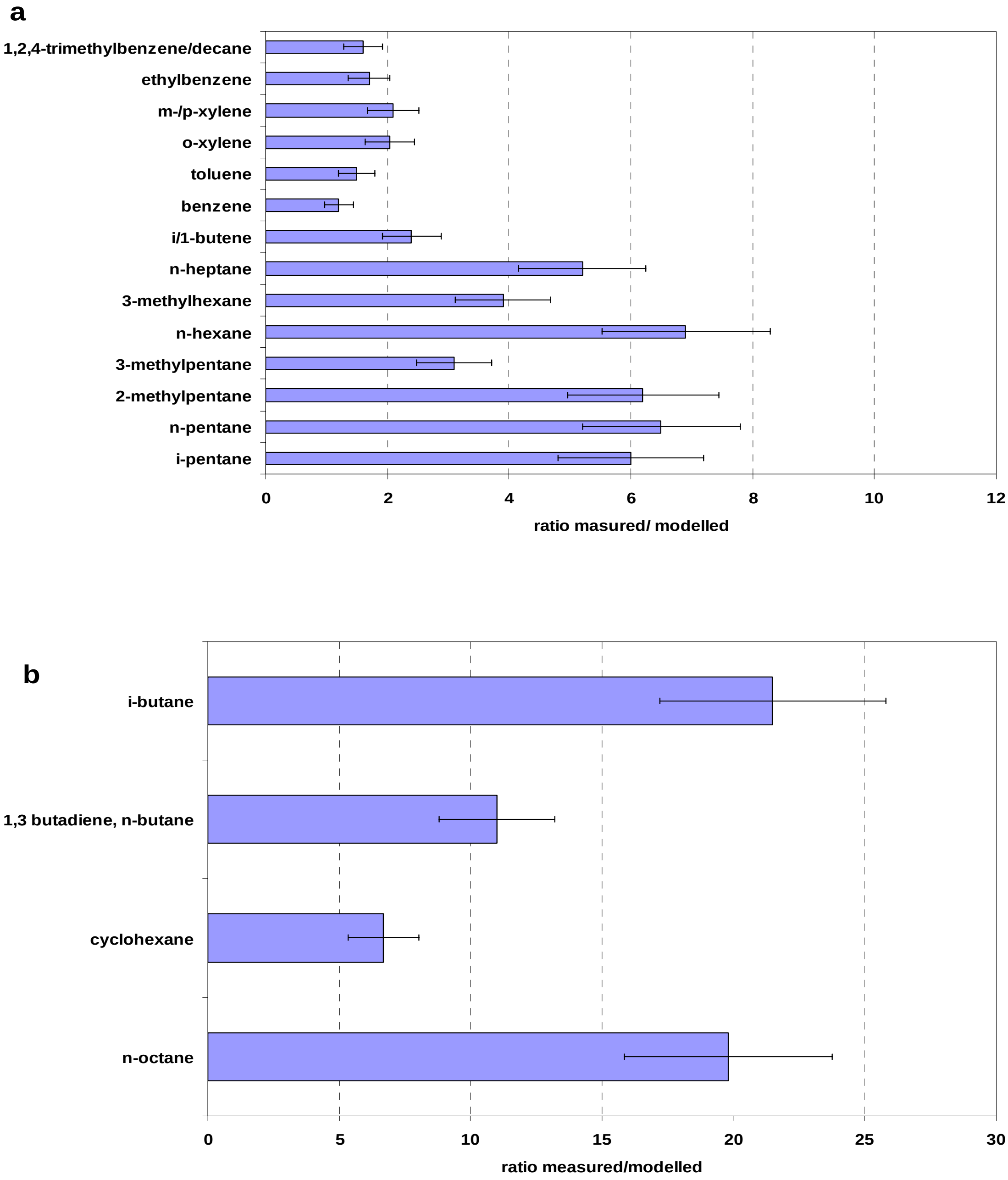


Figure 4-25: Comparison of measured and modelled source strength.

The differences between measured and modelled emissions may have several reasons. Within the EUROTRAC-2 subproject subproject, GENEMIS (Friedrich, 2003) it was shown that an important contribution to NMHCs emissions is made by poorly maintained vehicles and those with defective catalysts. An analysis of measurements of in-use cars in Germany revealed that the exhaust emissions of NMHC from cars with catalysts (current fleet) are about 9% higher due to malfunctioning equipment than the calculated values with actual emission models. From former investigations (Heeb *et al.,* 2000, 2003; Schauer *et al.,* 2002; Clark *et al.,* 2003) it is known that the spectrum of NMHC compounds emitted from the vehicles especially passenger cars differs depending on the actual driving status of individual vehicles and on its age.

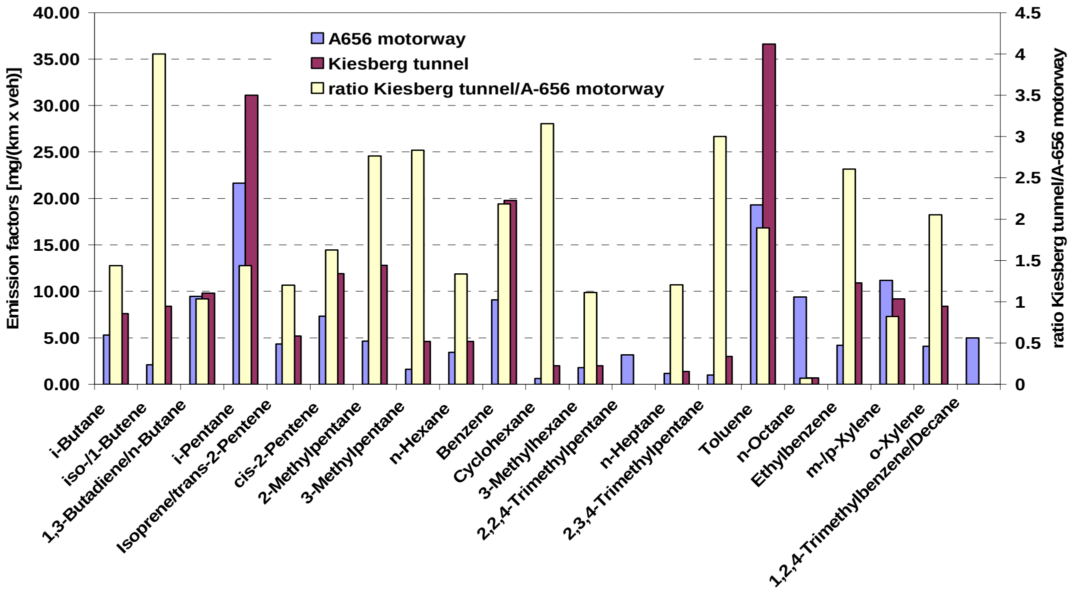


Figure 4-26: Average emission factors for NMHC calculated during the A656 experiment performed in 2001 in comparison with the average emission factors determined from the Kiesberg tunnel campaigns in1997-1998 and ratio between the two measurements.

The comparison of EFs derived from the Kiesberg tunnel and the A656 measurements shown in Figure 4-26 exhibits a clear decrease of emissions for German traffic in the period 1998-2001 for Germany. However large uncertainties of the measurements due to different campaigns cannot be excluded.

4.2.5 Conclusions

The observed NMHC distribution is in a good agreement with literature data. Among the aromatic hydrocarbons, toluene showed the largest mixing ration, whereas iso-pentane had the largest mixing ratio among the class of alkanes.

During the BAB II - A656 motorway experiment, vertical gradients were observed for several NMHC downwind of the motorway, in contrast to the upwind measurement site, where NMHC were constantly distributed. This indicates that these NMHC are directly emitted from traffic.

For the tunnel studies, average road traffic emission factors for the total vehicle fleet were direct calculated and/or modelled using the emission factors for CO_2 (model 1), THC (model 2) and BTX (model 3) from the HBEFA 2.1, adapted for each road traffic fleet composition and highway conditions.

The comparison of the times series from the direct calculated emission factors, in the Plabutsch Tunnel in comparison with model 1 shows good agreement for the weekdays. For the weekends, the model 1 values are higher than the emission factors from the direct method, which is probably resulting from the poor ventilation during weekends. This can be considered as an important “quality check” of the used calculation model because fuel consumption and hence the CO_2 emission is the variable which can be calculated on bases of the fleet composition and description of the driving pattern with the highest accuracy. This proves that the emission factors for CO_2 in the HBFEA 2.1 model are a good estimation for the real traffic situation. Not similar results have been obtained for the other models.

In the case of the Lundby and the Kingsway tunnels the NMHC emission factors calculated from model 1 were higher than those obtained from model 2 and 3. For Plabutsch Tunnel, the models 2 values were higher. For benzene a good correlation between the different models was found. This proves that for benzene, the calculated values are within the standard deviation in good agreement with the HBEFA 2.1 model 2 and 3 estimations for the real traffic situation in the studied tunnels.

The data analysis of THC emission factors for the given traffic fleets seems to clarify the discrepancy between measured and calculated emission data. The influence on the emission factors of about 12% malfunctioning catalysts was demonstrated. The importance of the exact determination of the contribution of non-catalyst cars or of the cars with malfunctioning catalyst to the traffic fleet was revealed. This underlines not only the importance of modern emission technologies but also that good maintenance of these systems is a prerequisite for the reduction of NMHC emissions.

In the case of BAB II – A656 experiment, the measurements exceed the model calculated emissions by factors 1.3-21. This discrepancy may be attributed to the still insufficient knowledge of traffic emissions of NMHC under real-world conditions.

The present work urge the need for reliable real-world emission factors for the NMHCs compounds by taking into account various engine types, fuels, exhaust treatment system, driving patterns and vehicle age.

By comparing the present calculated and modelled emission factors with results obtained from previous studies was found that progress has been achieved over the last years in the area of reduction of NMHCs emissions in Europe.

CHAPTER 5

5 SUMMARY

The objective of this study was to investigate the NMVOC emissions from vehicular traffic in Europe during recent years.

As part of the ARTEMIS – EU project and BAB II project, motor vehicle emissions of CO_2, NO_x and speciated NMHCs in the range C_2-C_9 were measured. The experiments were performed during three campaigns in different tunnels: the Lundby Tunnel in Sweden (March, 2001), the Plabutsch Tunnel in Austria (November, 2001) and the Kingsway Tunnel in England (March, 2003). In addition, a field experiment was conducted along a section of the A656 motorway in Germany (May, 2001). The locations showed different characteristics regarding the traffic flow, the ventilation system, the roadway gradient, the vehicles speed and the vehicle fleet composition.

More than 50 NMHC were detected and 26 of them quantified by using quasi on-line gas chromatography and by using adsorbtion tubes, which were analysed off-line in the laboratory.

The experimental results show that the largest mixing ratios of the NMVOC were found among the alkanes for: ethane, iso-butane, iso-pentane, among the alkenes/alkynes: propene, i-butene/1-butene, and among the aromatic hydrocarbons: toluene followed by o-xylene and m-/p-xylene.

During the A656 experiment, vertical gradients were observed for several NMHCs downwind of the motorway, in contrast to the upwind measurement site, where NMHCs were constantly distributed. This indicates that these NMHC are not equally emitted by the traffic. Accordingly, it was assumed that the increase in the NMHC concentration is proportional to the emission strength of the corresponding species.

As indicator of the traffic emissions, the toluene/benzene (ppbC/ppbC) ratio was calculated. The ratio of 3.091 ± 0.06 ppbC/ppbC in the Lundby Tunnel and of 2.89 ± 0.05 ppbC/ppbC in the Kingsway Tunnel are higher than in studies performed before 2000. The obtained ratios were found to be in agreement with the recent literature. These values can be explained by the over proportional decrease of benzene emissions compared with other aromatic compounds due to the new European regulations on the benzene content in fuel, which became effective in 2000.

With the measured value of CO_2 the emission ratios of NMHCs relative to CO_2 (ppbC/ppbV) were determined. These ratios where further used in the emission factors calculations.

The NMHC/NO_x ratio as ppbC/ppbV was found to be 0.67 in Lundby Tunnel, 0.20 in the Plabutsch Tunnel and 0.55 in Kingsway Tunnel. This variation is explained by the different HDV load in each tunnel. It is noteworthy that the results from the present study are consistent with previous studies. During the A656 experiment the NMHC/NO_x ratio was used in order to obtain quasi-continuous vertical profiles for the different NMHC. Good correlation was obtained only for the NMHC components, for which also in the vertical profiles a significant near-surface increase of the concentrations was determined.

Within the framework of extensive emission data validation experiments, emission factors from the campaigns in the Lundby Tunnel, the Plabutsch Tunnel, the Kingsway Tunnel, and on the A656 motorway have been determined using the local traffic measurements in combination with new emission models.

From the measured data emission factors were calculated by use of different direct and indirect methods. The travel based approach was applied by use of the mass balance equation of pollutant in the tunnel and on the road (direct method). The method was applied in calculating the emission factors in the Plabutsch Tunnel and in the A-656 experiment.

The models took as input parameters the fleet composition and the emission factors for CO_2 (model 1), THC (model 2) and BTX (model 3) from the HBEFA 2.1. The HBEFA 2.1 emission factors were modified by taking into account the slope gradients for the corresponding measurement sites as well as the fleet composition and the driving pattern. The models provide emission factors with a temporal resolution of 20 min for the Lundby and Plabutsch tunnels, 60 min for the Kingsway Tunnel and 3 h for the motorway studies.

The comparison between the direct emission factors calculation and the model 1 during the Plabutsch Tunnel measurements showed a good agreement. This proves that the emission factors for CO_2 in the HBFEA 2.1 model are a good estimation for the real traffic situation.

In the case of the Lundby and the Kingsway Tunnels the emission factors calculated from model 1 were higher than those obtained from model 2 and 3. For Plabutsch Tunnel, the models 2 values were higher. The discrepancy between measured and calculated emission data obviously must be found in the emission factor for PC with catalyst, LDV with catalyst and/or HDV. The data analysis of THC emission factors for the given traffic fleets seems to clarify the discrepancy between measured and calculated emission data.

Two hypotheses were verified:

- the THC emission factor of HDV is not correct; and/or

- the percentage of catalyst vehicles resulting from the fleet data analysis does not reflect the reality, i.e. cars that are registered with catalyst in fact have a malfunctioning catalyst and should be counted as non-catalyst vehicles with the corresponding emission factor.

In order to check the HBEFA 2.1 THC emission factor for HDV, this was changed stepwise in 10% increments from 200% to 10%. The resulting slope variation shows that the HDV EF does not strongly affect the model 2 results in the case of Lundby and Plabutsch tunnels. Publications of European Commission, 2000 and NETCEN, 2002 reported that about 15% of the PC catalysts have a malfunction, leading to a much higher emission of hydrocarbons. In order to test whether this finding could explain also the discrepancy between model 1 and 2, and between model 1 and 3 the emission factors were recalculated considering that the (10-12%) PC and LDV G-cat vehicles have malfunctioning catalysts. Therefore, their emissions have been counted as the ones of conventional cars. The correlation slopes improvement indicates that the catalyst conditions represent the main reason explaining the discrepancy between measured and modelled emission factors. The influence on the emission factors of about 12% malfunctioning catalysts demonstrates not only the importance of modern emission technologies but also that good maintenance of these systems is prerequisite for the reduction of NMHC emissions. The importance of the exact determination of the contribution of non-catalyst cars or of the cars with malfunctioning catalyst to the traffic fleet was demonstrated.

Comparison of measured and modelled emission factors in the BAB II - A656 experiment showed that the measurements exceed the model-calculated emissions by factors 1.3-21. This discrepancy for NMHCs may be attributed to the still insufficient knowledge of traffic emissions of NMHC under real-world conditions.

This work emphasizes once more the poor knowledge on NMHC emissions from vehicles, especially from the passenger car fraction, in real- world conditions. Accordingly, there is an urgent need for reliable real-world emission factors for most NMHCs compounds, except benzene, which seems to be well described by HBEFA 2.1.

By comparing the present calculated and modelled emission factors to results obtained from previous works it was found that a progress has been achieved over the last years in the area of reduction of NMHCs emissions in Europe. Several factors may have contributed to the emissions decrease: stronger emission limits due to EU directives, improved emission-control technology and more rigid quality requirements for fuels.

Appendix: Abbreviations

A656 - Autobahn 656
ARTEMIS - Assessment and Reliability of Transport Emission Models and Inventory Systems
BAB II - Bundesautobahn II
BTX - Benzene, Toluene, Xylenes
BUW - Bergische Universität Wuppertal
BERLIOZ - Berlin Ozone Experiment
CARB - California Air Resources Board
CEST - Central European Summer Time
COPERT - Computer Programme to calculate Emissions from Road Transport
DEFRA - Department for Environment, Food and Rural Affairs, UK
EEA - European Environment Agency
EMFAC - Emission Factors
EPA - U.S. Environmental Protection Agency
FTIR - Fourier Transform InfraRed
FTP 75 - US-Highway Federal Test Procedure
GENEMIS - Generation and Evaluation of Emission data
HBEFA - Handbook Emission Factors for Road Transport
HDV - Heavy Duty Vehicles
IVD - Institut für Verfahrenstechnik und Dampfkesselwesen, University of Stuttgart
IPCC - Intergovernmental Panel on Climate Change
LACTOZ - Laboratory Studies of Chemistry related to Tropospheric Ozone
LDCV - Light Duty Commercial Vehicles
LDV - Light Duty Vehicles
MC - Motorcycles
NAEI - National Atmospheric Emission Inventory
NEDC - New European Driving Cycle
NDIR - Non- Dispersive InfraRed
NETCEN - National Environmental Technology Center, AEA Technology Environment, UK
NMHCs - Non-Methane Hydrocarbons
NMVOCs - Non-Methane Volatile Organic Compounds
NO_x - Oxides of Nitrogen ($NO+NO_2$)

NPL - National Physical Laboratory

MOBILE - Vehicles Emission Factor Model

OSHA - US Department of Labor Ocupational Safety and Health Administration

PAH – Policycle Aromatic Hydrocarbons

PC - Passenger Cars

SOP - Special Observation Periods

THC - Total Hydrocarbons

TUG - Technical University of Graz

U.S.EPA - United States Environmental Protection Agency

UBA - Umbeltbundesamt

UNECE - United Nations Economic Comission for Europe

Appendix: Explanation

Appendix: Explanation 1: Chromatographic Conversion.

The Airmovista software, which was used for the data acquisition, saves the chromatograms in a compressed format. In order to convert these data in a column based ASCII format a new folder has to be created. Here the data will be stored together with the conversion programme: Convert.bat, Deheader.exe, List.exe and Run 386.exe. The conversion programme runs in the MS-DOS modus and saves the chromatograms in the created folder. From this folder the chromatograms can be imported in the Borwin 1.21 programme.

Appendix: Tables

Appendix: Table 1: Progression of Euro norms for passenger cars in Europe (g/km).

Description	**Effective year of implementation**	**CO**	**HC**	**NO$_x$**	**HC and NO$_x$**	**Particulate matter**
Gasoline						
Euro 1	1993	2.72	-	-	0.97	-
Euro 2	1996	2.20	-	-	0.50	-
Euro 3	2000	2.30	0.20	0.15	-	-
Euro 4	2005	1.00	0.10	0.08	-	-
Diesel						
Euro 1	1993	2.72	-	-	0.97	0.14
Euro 2	1996	1.06	-	0.56	0.71	0.080
Euro 3	2000	0.64	-	0.50	0.56	0.050
Euro 4	2005	0.50	-	0.25	0.30	0.025

Appendix: Table 2: Summary of the tunnel studies performed in the last 30 years.

Tunnel	**Year**	**Emission model**	**Toluene/ Benzene**	**NMHC: Model/ Calc.**	**References**
Unites States					
Allegheny	1979 1981	MOBILE 1 MOBILE 2	-	-1.4 LDV <2 HDV	Gorse *et al.*, 1981, 1984 Pierson *et al.*, 1983
Van Nuys	1987 1995	EMFAC 7C slow speed EMFAC 7F high speed	-	1.9 ± 0.6 4.0 ± 1.4 1.2 ± 0.6	Inghalls *et al.*, 1989 Gertler *et al.*, 1996 Gofa *et al.*,1998
Ford Mc Henry	1992	MOBILE 4.1 MOBILE 5	1.9 (LDV) 1.4 (HDV)		Robinson *et al.*, 1996 Sagebiel *et al.*, 1996 Pierson *et al.*, 1996
Tuscaora	1992	MOBILE 4.1 MOBILE 5	1.5 LDV, 1.6 HDV 1.5 LDV 1.6 HDV		Robinson *et al.*, 1996 Pierson *et al.*, 1996 Gertler *et al.*, 1996
Sepulveda	1995	MOBILE 5 C		1.8 ± 0.4	Gertler *et al.*1997
Lincoln	1995	MOBILE 5a		0.83 ± 0.24	Gertler *et al.*, 1997
Callahan	1995	MOBILE 5a		0.64 ± 0.23	Gertler *et al.*, 1997
Deck Park	1995	MOBILE 5a		0.91± 0.50	Gertler *et al.*, 1997
Washburn					McGaughey *et al.*, 2004
Canada					
Cassiar	1993	MOBILE 4.1 MOBILE 5 C		1.35 ± 0.53 0.77 ± 0.30	Gertler *et al.*, 1994, 1997 ; McLaren *et al.*, 1996 ; Rogak *et al.*, 1998
EUROPE					
Craeybeckx	1991	CORINAIR			De Fré *et al.*, 1992
Tingstads	1994	EVA	2.3	0.86	Sjödin *et al.*, 1997
Gubrist,	1993 1998 2002	UBA	2 LDV 1.6 HDV	1.69 ± 0.47 LDV 0.64 HDV	John *et al.*, 1999 Staehelin *et al.* 1995 Stemmler *et al.*, 2005
Söderleds	1995/ 1996	EVA	3.7 3.9	- -	Johansson *et al.*, 1996
Stockholm,	1998/1999				Kristenson *et al.*, 2004

Appendix: Table 2 (continued)

EUROPE					
Lundby	2001	HBEFA 2.1	3.09		This study, Colberg *et al.*, 2005
Thiais	1996	EF in g/km C1-C5			Tuaty and Bonsang, 2000
Tauern	1989 1997	-	 2.1	-	Gregory *et al.*, 1989; Schmid *et al.*, 2001
Plabutsch	1998/1999 2001	HBEFA 1.1 HBEFA 2.1	 2.4	-	Rodler, 2000 This study
Kiesberg,	1998/1999	HBEFA 2.1	-	1.73	Gomes, 2003
Kingsway	2003	HBEFA 2.1	2.9		This study
AUSTRALIA					
Sydney Harbour	1995			-	Duffy *et al.* 1996
ASIA					
Chung-Cheng,	1997	MOBILE Taiwan (5)		-	Hsu *et al.* 2001
Taipei	2000	MOBILE Taiwan (5)		1.6	Hwa *et al.* (2002)
Seul	2000				Na *et al.* (2002)
Japan					Sakurai *et al.*, 2002
Salim –Slam,	1998	EMFAC7F1.1			El-Fadel *et al.* 2000

Appendix: Table 3: NPL standard gas mixture (ppbV), delivered by National Physical Laboratory.

Compound	**Id.**	**NPL1**	**S.D.**	**NPL2**	**S.D.**
ethane	3	6.79	0.15	7.30	0.15
ethene	2	10.63	0.20	11.50	0.20
ethyne	1	8.86	0.20	9.60	0.20
propane	7	2.57	0.05	2.77	0.05
propene	6	6.70	0.15	7.20	0.15
propyne	5	2.89	0.05	3.12	0.05
n-butane	14	2.59	0.05	2.80	0.05
iso-butane	13	3.00	0.05	3.24	0.05
iso-butene	11	2.84	0.05	3.07	0.05
but-1-ene	10	3.33	0.05	3.59	0.05
trans-2-butene	9	2.22	0.05	2.40	0.05
cis-2-butene	12	2.38	0.05	2.57	0.05
1,3-butadiene	8	5.32	0.10	5.75	0.10
n-pentane	26	2.65	0.05	2.86	0.05
i-pentane	25	1.18	0.02	1.28	0.02
trans-2-pentene	21	4.04	0.10	4.35	0.10
cis-2-pentene	22	1.54	0.03	1.66	0.03
isoprene	16	1.84	0.04	1.99	0.04
2-methylpentane	45	3.18	0.05	3.43	0.05
3-methylpentane	46	3.64	0.05	3.93	0.05
cyclohexane	42	3.33	0.05	3.60	0.05
n-hexane	47	1.77	0.04	1.91	0.04
benzene	28	3.42	0.05	3.70	0.05
n-heptane	61	2.77	0.05	2.99	0.05
toluene	48	3.22	0.05	3.48	0.05
ethylbenzene	64	1.77	0.04	1.91	0.04
o-xylene	65	1.00	0.02	1.06	0.02
m-xylene	66	1.40	0.03	1.51	0.03
1,2,4-tmb	87	1.13	0.02	1.22	0.02
1,3,5-tmb	88	0.93	0.02	1.00	0.02

S.D.: standard deviation

Appendix: Table 4: Summary of the volume mixing ratios (ppbV) measured at the inlet/outlet station during the Lundby Tunnel experiment, March, 2001.

Compund (ppbV)	**OUTLET STATION**					**INLET STATION**				
	Max	**Min**	**Median**	**Average**	**SD**	**Max**	**Min**	**Median**	**Average**	**SD**
ethane	62.33	3.80	8.0	12.49	11.85	11.6	1.52	3.66	4.05	1.75
propene	30.34	0.63	8.27	8.44	4.55	9.90	0.17	3.44	3.59	2.04
propane	17.03	0.06	2.46	3.36	3.02	8.93	0.3	1.84	2.27	1.50
propine	4.35	0.15	1.41	1.53	0.79	2.03	0.16	0.51	0.65	0.52
i-butane	33.04	0.36	4.35	4.85	3.60	13.42	0.48	2.28	3.01	2.22
i-butene, i-butene	12.85	0.38	4.26	4.33	2.58	4.38	0.19	1.34	1.51	0.86
1.3 butadiene, n-butane	36.51	0.27	13.32	13.50	7.93	7.00	0.94	3.81	3.79	1.68
trans-2-butene	45.14	0.07	0.52	1.15	5.06	0.73	0.08	0.16	0.22	0.17
cis-2-butene	55.04	0.09	0.47	1.17	6.14	0.35	0.08	0.16	0.18	0.07
i-pentane	28.54	0.01	5.74	6.41	4.61	13	0.15	3.42	4.04	2.48
n-pentane	18.6	0.26	2.15	2.65	2.14	4.85	0.1	1.38	1.6	0,87
isoprene, trans-2-penten	13.90	0.04	0.34	1.56	2.52	1.09	0.04	0.34	0.36	0.19
cis-2-penten	9.85	0.08	0.94	2.51	2.79	4.15	0.03	0.97	1.12	0.8
3-methylpentane	13.01	0.14	1.68	2.04	1.57	2.58	0.12	0.77	0.89	0.47
n-hexane	5.7	0.13	0.89	1.08	0.84	1.78	0.05	0.5	0.58	0.31
benzene	33.47	0.46	4.27	4.97	4.31	6.6	1.23	3.01	3.21	1.06
cyclohexane	23.69	0.11	0.98	1.41	2.21	2.31	0.08	0.59	0.7	0.42
n-heptane	6.53	0.12	1.09	1.19	0.77	1.4	0.05	0.36	0.44	0.24
toluene	58.13	0.76	14.19	14.59	9.02	16	0.36	6.15	7.13	3.9
ethylbenzene	19.87	0.08	3.58	3.68	2.72	4.37	0.04	1.25	1.55	0.89
o-xylene	11.31	0.01	2.08	2.33	1.65	4.53	0.07	1.46	1.66	0.81
1,3,5-trimethylbenzene	5.09	0.25	1.72	2.02	1.07	3.29		0.58	0.92	0.81
1,2,4-trimethylbenzene	2.77	0.13	0.92	1.11	0.72	2.6	0.23	0.94	1.01	0.54

Appendix: Table 5: Summary of the volume mixing ratios (ppbV) measured at the middle point station during the Plabutsch Tunnel experiment, November, 2001.

Compound	**Max**	**Min**	**Median**	**Average**	**SD**
CO_2*	1443.615	568.279	915.195	941.393	206.174
NO*	7.631	0.774	3.618	4.082	1.936
NO_2*	0.703	0.088	0.257	0.340	0.176
NO_x *	8.332	0.866	3.877	4.428	2.110
propene, propane	25.557	0.872	11.203	10.980	6.267
propine	7.016	0.619	3.368	3.774	1.790
i-butane	16.702	0.461	5.115	5.319	3.139
1-butene,i-butene	22.671	1.848	8.163	9.133	5.169
1,3-butadiene, n-butane	27.307	1.355	8.064	8.704	5.320
trans-2-butene	4.549	0.245	1.508	1.637	0.887
cis-2-butene	7.713	0.545	2.717	2.962	1.393
i-pentane	18.965	0.089	5.666	5.933	3.658
n-pentane	15.311	0.013	0.695	1.661	2.001
isoprene, trans 2- pentene	18.950	0.422	3.245	4.291	3.268
cis-2-pentene	14.808	0.137	1.443	2.389	2.648
2-methylpentane	8.232	0.270	2.675	2.755	1.236
3-methylpentane	3.780	0.190	1.125	1.297	0.771
n-hexane	2.017	0.176	0.893	0.886	0.357
benzene	7.833	1.329	3.569	3.788	1.464
cyclohexane	2.559	0.127	0.687	0.764	0.439
n-heptane	8.594	0.187	1.335	1.840	1.449
toluene	22.229	1.957	8.095	8.224	3.628
ethylbenzene	4.365	0.226	1.607	1.629	0.804
o-xylene	8.469	0.094	2.743	2.744	1.477
m-/p-xylene	19.188	0.700	5.663	5.697	3.037
1,3,5-trimethylbenzene	12.677	0.318	3.918	4.139	2.369
1,2,4-trimethylbenzene	13.264	0.159	2.140	2.411	1.531

* ppmV

Appendix: Table 6: Summary of the volume mixing ratios (ppbV) measured at the Victoria vent station during the Kingsway Tunnel experiment, February, 2003.

Compound	Background air		Tunnel air				
	Average	SD	Max	Min	Median	Average	SD
ethene	0.22	0.15	1.31	0.31	0.64	0.69	0.40
ethine	0.25	0.17	3.38	0.54	0.85	1.10	0.94
ethane	0.20	0.15	0.88	0.26	0.41	0.48	0.32
propene	0.20	0.15	5.83	0.32	0.87	1.43	1.71
propane	0.23	0.17	4.46	0.24	0.86	1.28	1.40
propadiene	0.14	0.14	0.20	0.14	0.15	0.16	0.16
propine	0.14	0.14	0.49	0.14	0.16	0.20	0.24
i-butane	0.19	0.16	5.82	0.84	1.63	2.23	1.58
1-butene, i-butene	0.60	0.37	6.35	1.14	2.26	2.62	1.65
1,3-butadiene,n-butane	0.61	0.37	6.89	1.22	2.40	2.82	1.78
trans-2-butene	0.19	0.16	5.76	0.45	1.31	1.78	1.69
cis-2-butene	0.16	0.16	4.92	0.39	1.28	1.57	1.48
3-methyl-1-butene	0.15	0.15	0.71	0.23	0.35	0.39	0.28
i-pentane	0.23	0.17	20.97	3.99	6.95	8.72	5.16
1-pentene	0.17	0.15	2.98	0.63	0.97	1.22	0.82
n-pentane, 2-methyl-1-butene	0.35	0.21	14.55	2.15	4.02	5.47	3.48
isoprene	0.17	0.15	1.69	0.36	0.51	0.66	0.50
trans-2-pentene	0.16	0.15	2.98	0.47	0.75	1.09	0.85
cis-2-pentene	0.15	0.15	1.17	0.26	0.38	0.49	0.39
2,2-dimethylbutane	0.21	0.15	3.97	0.76	1.51	1.75	1.01
cyclopentene	0.15	0.15	0.50	0.16	0.23	0.26	0.24
2-methylpentane	0.39	0.18	8.45	2.33	3.85	4.17	1.90
3-methylpentane	0.31	0.16	5.27	1.51	2.52	2.67	1.22
n-hexane, 2-ethyl-1-butene	0.36	0.17	5.37	1.57	2.78	2.79	1.23
2,3-dimethyl-1,3-butadiene	0.15	0.14	1.02	0.15	0.25	0.42	0.45
methylcyclopentane, 1-methyl-1-cyclopentene	0.26	0.16	4.57	1.36	2.19	2.24	1.04
2,3-dimethyl-2-butene	0.16	0.15	0.79	0.26	0.43	0.46	0.30
benzene	0.48	0.21	12.21	3.14	4.09	5.19	2.76
cyclohexene	0.15	0.15	0.41	0.24	0.29	0.31	0.20
1-heptene	0.19	0.16	1.07	0.47	0.65	0.69	0.33
n-heptane	0.23	0.15	1.85	0.61	1.01	1.09	0.51
toluene	0.656	0.195	30.541	7.778	12.358	13.939	6.689
n-octan	0.033	0.008	0.461	0.145	0.222	0.247	0.096
ethylbenzene	0.114	0.026	4.378	0.816	1.646	1.855	0.964
m-/ p-xylene	0.386	0.081	14.077	2.147	5.565	6.021	3.293
o-xylene	0.178	0.011	5.438	0.684	2.146	2.374	1.300

Appendix: Table 7: Summary of concentrations measured at ground level (N/S – 05 m) (µg/m^3)* measured during the A656 experiment (May 17, 2001) and calculated resolved on vertical profile (N/S- 17, 27, 37, 47 m) for the compounds C_4-C_5.

Time interval of measurements		**13:00- 16:30**							**16:30- 20:15**						
Altitude on N/S tower	**N-05**	**N-17**	**N-27**	**N-37**	**N-47**	**S-05**	**S-27**	**S47**	**N-05**	**N-17**	**N-27**	**N-37**	**S-05**	**S-27**	**S47**
i-butane	0.267	0.022	0.019	0.020	0.017	0.020	0.020	0.020	0.347	0.021	0.021	0.019	0.020	0.022	0.011
i-butene, 1-butene	0.323	0.346	0.303	0.325	0.275	0.316	0.314	0.325	0.451	0.319	0.322	0.287	0.297	0.324	0.171
1,3-butadiene, n-butane	0.483	0.312	0.273	0.293	0.248	0.285	0.283	0.293	0.523	0.342	0.342	0.342	0.318	0.347	0.183
trans-2-butene	0.026	0.047	0.041	0.044	0.038	0.043	0.043	0.044	0.043	0.047	0.048	0.042	0.044	0.048	0.025
cis-2-butene	0.028	0.060	0.052	0.056	0.048	0.055	0.054	0.056	0.046	0.044	0.045	0.040	0.041	0.045	0.024
i-pentane	0.904	0.120	0.105	0.113	0.096	0.110	0.109	0.113	1.067	0.080	0.081	0.072	0.074	0.081	0.043
n-pentane	0.443	0.399	0.349	0.374	0.317	0.364	0.362	0.375	0.368	0.668	0.675	0.600	0.621	0.678	0.357
isoprene, trans-2 pentene	0.128	0.051	0.045	0.048	0.041	0.047	0.047	0.048	0.196	0.190	0.192	0.171	0.177	0.193	0.102
cis-2-pentene	0.012	0.054	0.048	0.051	0.043	0.050	0.049	0.051	0.074	0.127	0.128	0.114	0.118	0.129	0.068
2-methylpentane	0.095	0.049	0.042	0.046	0.039	0.044	0.044	0.046	0.118	0.044	0.045	0.040	0.041	0.045	0.024
3-methylpentane	0.119	0.275	0.240	0.258	0.219	0.251	0.249	0.258	0.136	0.286	0.289	0.257	0.266	0.290	0.153
benzene	0.320	0.195	0.170	0.183	0.155	0.222	0.221	0.229	0.382	0.213	0.215	0.191	0.198	0.216	0.114
cyclohexane	0.087	0.053	0.047	0.050	0.042	0.081	0.081	0.084	0.113	0.096	0.097	0.086	0.090	0.098	0.051
toluene	0.688	0.420	0.367	0.394	0.334	0.383	0.381	0.394	0.893	0.450	0.455	0.405	0.419	0.457	0.241
ethylbenzene	0.135	0.124	0.108	0.116	0.099	0.113	0.112	0.116	0.191	0.130	0.131	0.116	0.121	0.131	0.148
o-xylene	0.131	0.080	0.070	0.075	0.064	0.057	0.057	0.059	0.173	0.074	0.075	0.067	0.069	0.075	0.040
m-, p-xylene	0.349	0.213	0.186	0.200	0.169	0.166	0.166	0.171	0.476	0.240	0.242	0.216	0.187	0.204	0.108

*concentrations calculated for the normal conditions (273.15 K and 1 atm)

Appendix : Table 8: Emission ratios of NMHC/CO_2 (ppbV/ppmV) determined using the measured data in Lundby Tunnel, March, 2001.

Compound	**Slope(m)**	**± (Δm)**	**R^2**
ethane	0.033	0.028	0.039
propene	0.030	0.005	0.276
propane	0.008	0.005	0.030
1,3-butadiene, n-butane	0.045	0.007	0.415
trans-2-butene	0.004	0.001	0.558
cis-2-butene	0.002	0.000	0.310
i-pentane (2-methylbutane)	0.032	0.004	0.343
cis-2-pentene	0.021	0.003	0.515
n-pentane	0.015	0.002	0.299
3-methylpentane	0.012	0.002	0.332
n-hexane	0.006	0.001	0.347
benzene	0.023	0.003	0.340
cyclohexane	0.005	0.001	0.242
n-heptane	0.005	0.001	0.289
toluene	0.062	0.007	0.473
ethylbenzene	0.014	0.003	0.243
o-xylene	0.006	0.002	0.107

Appendix: Table 9: Emission ratios of NMHC to CO_2 (ppbV/ppmV) determined using the measured data in Kingswaytunnel, February, 2003.

Compound	**Slope(m)**	**± (Δm)**	**R^2**
propene, propane	0.023	0.005	0.67
propine	0.001	0.000	0.61
i-butane (2-methylpropane)	0.014	0.001	0.91
1-butene, i-butene (2-methylpropene)	0.013	0.002	0.72
1,3-butadiene	0.001	0.000	0.91
n-butane	0.061	0.009	0.79
trans-2-butene	0.014	0.002	0.77
cis-2-butene	0.012	0.002	0.74
3-methyl-1-butene	0.001	0.000	0.68
i-pentane (2-methylbutane)	0.049	0.003	0.94
1-pentene	0.007	0.001	0.93
n-pentane, 2-methyl-1-butene	0.032	0.003	0.9
isoprene	0.003	0.000	0.88
trans-2-pentene	0.007	0.001	0.88
cis-2-pentene	0.002	0.000	0.89
2-methylpentane	0.016	0.002	0.79
3-methylpentane	0.010	0.001	0.78
n-hexane, 2-ethyl-1-butene	0.009	0.002	0.73
methylcyclopentane, 1-methyl-1-cyclopentene	0.008	0.001	0.75
benzene	0.025	0.002	0.91
cyclohexane, 2,3-dimethylpentane, 1,3 cyclohexadiene	0.011	0.001	0.84
2-methylhexane	0.003	0.000	0.8
cyclohexene	0.001	0.000	0.81
2,2,4-trimethylpentane (i-octane)	0.013	0.002	0.79
n-heptane	0.003	0.000	0.81
toluene	0.057	0.007	0.85
2-methylheptane	0.016	0.002	0.85
3-methylheptane	0.001	0.000	0.62
n-octane	0.001	0.000	0.8
ethylbenzene	0.011	0.002	0.75
m- and p-xylene	0.036	0.007	0.68
ortho-xylene	0.014	0.003	0.65
1,3,5-trimethylbenzene	0.002	0.000	0.61

Appendix: Table 10: CO_2 emission factors (g/km) alculated from the HBEFA 2.1.e for the Lundby Tunnel.

Vehicle class	**Fuel**	**Emission concept**	**EF HW 100**	**EF HW 80**	**EF HW 60**
PC	Gasoline	PC/gas/conv.	181.316	99.231	87.334
		PC/gas/cl.l.cat.<91	194.562	106.766	95.214
		PC/gas/Euro1	151.127	78.322	65.580
		PC/gas/Euro2	181.211	99.885	86.134
		PC/gas/Euro3	175.777	96.881	83.526
		PC/gas/Euro4	180.625	99.583	85.863
	Diesel	PC/dies./conv.	194.396	103.454	89.266
		PC/dies./XXIII/EEA1	186.220	98.906	85.321
		PC/dies./Euro2	165.480	87.624	74.163
		PC/dies./Euro3	160.379	84.926	71.886
LDV	Gasoline	LDV/gas/conv.	267.389	223.625	180.437
		LDV/gas/cl.l.cat.<91	278.563	282.227	277.769
		LDV/gas/Euro2	262.846	267.027	258.412
		LDV/gas/Euro3	269.611	274.821	266.142
		LDV/gas/Euro4	271.705	277.293	268.818
	Diesel	LDV/dies./conv.	273.708	272.543	265.775
		LDV/dies./Euro1	262.062	262.765	258.383
		LDV/dies./Euro2	256.594	259.298	256.257
		LDV/dies./Euro3	261.339	264.698	262.227
COACH	Diesel	HDV/80ies	769.876	747.820	730.595
		HDV/Euro1	698.782	683.330	671.287
		HDV/Euro2	682.148	675.232	659.393
		HDV/Euro3	728.395	715.361	703.652
URBAN BUS	Diesel	HDV/80ies	733.515	733.515	733.515
		HDV/Euro1	636.923	636.923	636.923
		HDV/Euro2	633.777	633.777	633.777
		HDV/Euro3	669.855	669.855	669.855
HDV	Diesel	HDV/80ies	694.654	685.212	685.717
		HDV/Euro1	693.217	681.238	729.313
		HDV/Euro2	746.421	739.920	776.428
		HDV/Euro3	807.147	797.189	683.996
MC	Diesel		104.776	98.625	94.998

Appendix: Table 11: THC emission factors (g/km) calculated from the HBEFA 2.1.e for the Lundby Tunnel .

Vehicle category	**Fuel**	**Emission concept**	**EF HW 100**	**EF HW 80**	**EF HW 60**
PC	Gasoline	PC/gas/conv.	0.863	0.916	1.054
		PC/gas/cl.l.cat.<91	0.132	0.142	0.213
		PC/gas/Euro1	0.100	0.095	0.100
		PC/gas/Euro2	0.085	0.085	0.092
		PC/gas/Euro3	0.032	0.032	0.036
		PC/gas/Euro4	0.021	0.021	0.023
	Diesel	PC/dies./conv.	0.062	0.070	0.082
		PC/dies./XXIII/EEA1	0.042	0.044	0.054
		PC/dies./Euro2	0.035	0.033	0.033
		PC/dies./Euro3	0.030	0.028	0.028
LDV	Gasoline	LDV/gas/conv.	1.175	1.215	1.356
		LDV/gas/cl.l.cat.<91	0.371	0.329	0.271
		LDV/gas/Euro2	0.195	0.163	0.116
		LDV/gas/Euro3	0.150	0.118	0.066
		LDV/gas/Euro4	0.110	0.086	0.047
	Diesel	LDV/dies./conv.	0.054	0.075	0.101
		LDV/dies./Euro1	0.032	0.056	0.079
		LDV/dies./Euro2	0.022	0.043	0.061
		LDV/dies./Euro3	0.027	0.025	0.035
COACH	Diesel	HDV/80ies	0.346	0.356	0.417
		HDV/Euro1	0.394	0.402	0.341
		HDV/Euro2	0.236	0.251	0.249
		HDV/Euro3	0.234	0.244	0.287
URBAN BUS	Diesel	HDV/80ies	1.389	1.389	1.389
		HDV/Euro1	0.486	0.486	0.486
		HDV/Euro2	0.306	0.306	0.306
		HDV/Euro3	0.290	0.290	0.290
HDV	Diesel	HDV/80ies	0.501	0.452	0.431
		HDV/Euro1	0.425	0.389	0.368
		HDV/Euro2	0.296	0.272	0.258
		HDV/Euro3	0.291	0.263	0.246
MC	Diesel		0.838	0.829	0.830

Appendix: Table 12: Benzene emission factors (g/km) calculated from the HBEFA 2.1.e for the Lundby Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**EF HW 100**	**EF HW 80**	**EF HW 60**
PC	Gasoline	PC/gas/conv.	0.0378	0.0360	0.0462
		PC/gas/cl.l.cat.<91	0.0171	0.0194	0.0275
		PC/gas/Euro1	0.0129	0.0102	0.0129
		PC/gas/Euro2	0.0110	0.0090	0.0119
		PC/gas/Euro3	0.0041	0.0070	0.0046
		PC/gas/Euro4	0.0028	0.0050	0.0030
	Diesel	PC/dies./conv.	0.0010	0.0016	0.0014
		PC/dies./XXIII/EEA1	0.0007	0.0011	0.0009
		PC/dies./Euro2	0.0006	0.0005	0.0005
		PC/dies./Euro3	0.0005	0.0004	0.0005
LDV	Gasoline	LDV/gas/conv.	0.1372	0.1412	0.1570
		LDV/gas/cl.l.cat.<91	0.0162	0.0144	0.0119
		LDV/gas/Euro2	0.0160	0.0153	0.0150
		LDV/gas/Euro3	0.0051	0.0111	0.0086
		LDV/gas/Euro4	0.0008	0.0012	0.0061
	Diesel	LDV/dies./conv.	0.0009	0.0010	0.0017
		LDV/dies./Euro1	0.0006	0.0008	0.0013
		LDV/dies./Euro2	0.0005	0.0005	0.0010
		LDV/dies./Euro3	0.0003	0.0001	0.0006
COACH	Diesel	HDV/80ies	0.0058	0.0059	0.0061
		HDV/Euro1	0.0066	0.0067	0.0069
		HDV/Euro2	0.0039	0.0042	0.0043
		HDV/Euro3	0.0039	0.0041	0.0043
URBAN BUS	Diesel	HDV/80ies	0.0232	0.0232	0.0232
		HDV/Euro1	0.0081	0.0081	0.0081
		HDV/Euro2	0.0051	0.0051	0.0051
		HDV/Euro3	0.0048	0.0048	0.0048
HDV	Diesel	HDV/80ies	0.0084	0.0076	0.0072
		HDV/Euro1	0.0071	0.0065	0.0061
		HDV/Euro2	0.0049	0.0046	0.0043
		HDV/Euro3	0.0049	0.0044	0.0041

Appendix: Table 13: Toluene emission factors (g/km) calculated from the HBEFA 2.1.e for the Lundby Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**EF HW 100**	**EF HW 80**	**EF HW 60**
PC	Gasoline	PC/gas/conv.	0.0906	0.0962	0.1107
		PC/gas/cl.l.cat.<91	0.0123	0.0132	0.0198
		PC/gas/Euro1	0.0093	0.0089	0.0093
		PC/gas/Euro2	0.0079	0.0079	0.0086
		PC/gas/Euro3	0.0030	0.0030	0.0033
		PC/gas/Euro4	0.0020	0.0020	0.0021
	Diesel	PC/dies./conv.	0.0002	0.0002	0.0003
		PC/dies./XXIII/EEA1	0.0001	0.0006	0.0002
		PC/dies./Euro2	0.0001	0.0015	0.0001
		PC/dies./Euro3	0.0001	0.0001	0.0001
LDV	Gasoline	LDV/gas/conv.	0.1114	0.1152	0.1287
		LDV/gas/cl.l.cat.<91	0.0389	0.0345	0.0284
		LDV/gas/Euro2	0.0181	0.0151	0.0108
		LDV/gas/Euro3	0.0140	0.0110	0.0062
		LDV/gas/Euro4	0.0102	0.0080	0.0044
	Diesel	LDV/dies./conv.	0.0002	0.0002	0.0003
		LDV/dies./Euro1	0.0001	0.0002	0.0003
		LDV/dies./Euro2	0.0001	0.0001	0.0002
		LDV/dies./Euro3	0.0001	0.0001	0.0001
		HDV/80ies	0.0011	0.0011	0.0012
COACH	Diesel	HDV/Euro1	0.0013	0.0013	0.0013
		HDV/Euro2	0.0008	0.0008	0.0008
		HDV/Euro3	0.0007	0.0008	0.0008
URBAN BUS	Diesel	HDV/80ies	0.0012	0.0044	0.0044
		HDV/Euro1	0.0013	0.0016	0.0016
		HDV/Euro2	0.0008	0.0010	0.0010
		HDV/Euro3	0.0008	0.0009	0.0009
		HDV/80ies	0.0016	0.0014	0.0014
HDV	Diesel	HDV/Euro1	0.0014	0.0012	0.0012
		HDV/Euro2	0.0009	0.0009	0.0008
		HDV/Euro3	0.0009	0.0008	0.0008
MC	Diesel		0.0880	0.0871	0.0872

Appendix: Table 14: Xylene emission factors (g/km) calculated from the HBEFA 2.1.e for the Lundby Tunnel.

Vehicle category	Fuel	Emission concept	EF HW 100	EF HW 80	EF HW 60
PC	Gasoline	PC/gas/conv.	0.073	0.078	0.090
		PC/gas/cl.l.cat.<91	0.010	0.011	0.016
		PC/gas/Euro1	0.008	0.007	0.008
		PC/gas/Euro2	0.007	0.007	0.007
		PC/gas/Euro3	0.002	0.002	0.003
		PC/gas/Euro4	0.002	0.002	0.002
	Diesel	PC/dies./conv.	0.000	0.001	0.001
		PC/dies./XXIII/EEA1	0.000	0.000	0.000
		PC/dies./Euro2	0.000	0.000	0.000
		PC/dies./Euro3	0.000	0.000	0.000
LDV	Gasoline	LDV/gas/conv.	0.092	0.095	0.106
		LDV/gas/cl.l.cat.<91	0.032	0.028	0.023
		LDV/gas/Euro2	0.015	0.009	0.005
		LDV/gas/Euro3	0.012	0.007	0.004
		LDV/gas/Euro4	0.008	0.001	0.001
	Diesel	LDV/dies./konv	0.000	0.001	0.001
		LDV/dies./Euro1	0.000	0.000	0.001
		LDV/dies./Euro2	0.000	0.000	0.000
		LDV/dies./Euro3	0.000	0.000	0.000
COACH	Diesel	HDV/80ies	0.003	0.003	0.003
		HDV/Euro1	0.003	0.003	0.003
		HDV/Euro2	0.002	0.002	0.002
		HDV/Euro3	0.002	0.002	0.002
URBAN BUS	Diesel	HDV/80ies	0.011	0.011	0.011
		HDV/Euro1	0.004	0.004	0.004
		HDV/Euro2	0.002	0.002	0.002
		HDV/Euro3	0.002	0.002	0.002
HDV	Diesel	HDV/80ies	0.004	0.004	0.003
		HDV/Euro1	0.003	0.003	0.003
		HDV/Euro2	0.002	0.002	0.002
		HDV/Euro3	0.002	0.002	0.002
MC	Diesel		0.071	0.070	0.071

Appendix: Table 15: Emission factors [g(km×veh)] calculated for the entire fleet using model 1 for the Lundby Tunnel measurements in March, 2001.

Compund	**Emission factors**	**SD**
propane	0.002	0.001
i-butane	0.006	0.001
i-pentane	0.013	0.003
n-pentane	0.006	0.001
3-methylpentane	0.006	0.001
n-hexane	0.004	0.006
cyclohexane	0.002	0.001
n-heptane	0.003	0.001
propene	0.008	0.002
trans-butene	0.001	0
cis-butene	0.001	0
benzene	0.01	0.003
toluene	0.033	0.008
o-xylene	0.004	0.001
m/p-xylene	0.014	0.003
ethylbenzene	0.009	0.002

Appendix: Table 16: CO_2 emission factors (g/km) calculated from the HBEFA 2.1.e for the Plabutsch Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**Emission factors**
PC	gasoline	PC/gas/conv.	158.81
		PC/gas/cl.l.cat.<91	178.58
		PC/gas/Euro1	124.68
		PC/gas/Euro2	164.51
		PC/gas/Euro3	159.54
		PC/gas/Euro4	163.99
	diesel	PC/dies./conv.	175.03
		PC/dies./XXIII/EEA1	167.3
		PC/dies./Euro2	146.53
		PC/dies./Euro3	142.02
LDV	gasoline	LDV/gas/conv.	210.06
		LDV/gas/cl.l.cat.<91	320.54
		LDV/gas/Euro2	300.65
		LDV/gas/Euro3	310.28
		LDV/gas/Euro4	313.46
	diesel	LDV/dies./konv	314.57
		LDV/dies./Euro1	306.14
		LDV/dies./Euro2	303.85
		LDV/dies./Euro3	311
URBAN BUS	diesel	HDV/80ies	785.57
		HDV/Euro1	674.45
		HDV/Euro2	668.57
		HDV/Euro3	710.17
HDV	diesel	HDV/80ies	674.79
		HDV/Euro1	659.88
		HDV/Euro2	701.73
		HDV/Euro3	755.79

Appendix:Table 17: THC emission factors (g/km) calculated from the HBEFA 2.1.e for the Plabutsch Tunnel.

Vehicle category	Fuel	Emission concept	Emission factors
PC	gasoline	PC/gas/conv.	0.780
		PC/gas/cl.l.cat.<91	0.120
		PC/gas/Euro1	0.066
		PC/gas/Euro2	0.059
		PC/gas/Euro3	0.023
		PC/gas/Euro4	0.015
	diesel	PC/dies./conv.	0.049
		PC/dies./XXIII/EEA1	0.037
		PC/dies./Euro2	0.025
		PC/dies./Euro3	0.021
LDV	gasoline	LDV/gas/conv.	1.004
		LDV/gas/cl.l.cat.<91	0.215
		LDV/gas/Euro2	0.092
		LDV/gas/Euro3	0.059
		LDV/gas/Euro4	0.043
	diesel	LDV/dies./konv	0.072
		LDV/dies./Euro1	0.057
		LDV/dies./Euro2	0.044
		LDV/dies./Euro3	0.025
URBAN BUS	diesel	HDV/80ies	1.593
		HDV/Euro1	0.532
		HDV/Euro2	0.329
		HDV/Euro3	0.317
HDV	diesel	HDV/80ies	0.529
		HDV/Euro1	0.408
		HDV/Euro2	0.270
		HDV/Euro3	0.264

Appendix: Table 18: Benzene emission factors (g/km) calculated from the HBEFA 2.1.e for the Plabutsch Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**Emission factors**
PC	gasoline	PC/gas/conv.	0.033
		PC/gas/cl.l.cat.<91	0.015
		PC/gas/Euro1	0.008
		PC/gas/Euro2	0.007
		PC/gas/Euro3	0.002
		PC/gas/Euro4	0.001
	diesel	PC/dies./conv.	0.001
		PC/dies./XXIII/EEA1	0.0006
		PC/dies./Euro2	0.0004
		PC/dies./Euro3	0.0004
LDV	gasoline	LDV/gas/conv.	0.116
		LDV/gas/cl.l.cat.<91	0.0094
		LDV/gas/Euro2	0.011
		LDV/gas/Euro3	0.007
		LDV/gas/Euro4	0.005
	diesel	LDV/dies./konv	0.001
		LDV/dies./Euro1	0.001
		LDV/dies./Euro2	0.0007
		LDV/dies./Euro3	0.0005
URBAN BUS	diesel	HDV/80ies	0.026
		HDV/Euro1	0.009
		HDV/Euro2	0.005
		HDV/Euro3	0.005
HDV	diesel	HDV/80ies	0.009
		HDV/Euro1	0.007
		HDV/Euro2	0.005
		HDV/Euro3	0.004

Appendix: Table 19: Toluene emission factors (g/km) calculated from the HBEFA 2.1.e for the Plabutsch Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**Emission factors**
PC	gasoline	PC/gas/conv.	0.081
		PC/gas/cl.l.cat.<91	0.011
		PC/gas/Euro1	0.006
		PC/gas/Euro2	0.006
		PC/gas/Euro3	0.005
		PC/gas/Euro4	0.004
	diesel	PC/dies./conv.	0.004
		PC/dies./XXIII/EEA1	0.0001
		PC/dies./Euro2	0.00008
		PC/dies./Euro3	0.00007
LDV	gasoline	LDV/gas/conv.	0.09
		LDV/gas/cl.l.cat.<91	0.023
		LDV/gas/Euro2	0.008
		LDV/gas/Euro3	0.005
		LDV/gas/Euro4	0.004
	diesel	LDV/dies./konv	0.0002
		LDV/dies./Euro1	0.0002
		LDV/dies./Euro2	0.0001
		LDV/dies./Euro3	0.00008
URBAN BUS	diesel	HDV/80ies	0.005
		HDV/Euro1	0.002
		HDV/Euro2	0.001
		HDV/Euro3	0.0009
HDV	diesel	HDV/80ies	0.002
		HDV/Euro1	0.001
		HDV/Euro2	0.0008
		HDV/Euro3	0.0008

Appendix:Table 20: Xilenes emission factors (g/km) calculated from the HBEFA 2.1.e for the Plabutsch Tunnel.

Vehicle category	Fuel	Emission concept	Emission factors
PC	gasoline	PC/gas/conv.	0.071
		PC/gas/cl.l.cat.<91	0.011
		PC/gas/Euro1	0.005
		PC/gas/Euro2	0.004
		PC/gas/Euro3	0.002
		PC/gas/Euro4	0.001
	diesel	PC/dies./conv.	0.0005
		PC/dies./XXIII/EEA1	0.0002
		PC/dies./Euro2	0.0002
		PC/dies./Euro3	0.0001
LDV	gasoline	LDV/gas/conv.	0.078
		LDV/gas/cl.l.cat.<91	0.018
		LDV/gas/Euro2	0.007
		LDV/gas/Euro3	0.004
		LDV/gas/Euro4	0.003
	diesel	LDV/dies./konv	0.0006
		LDV/dies./Euro1	0.0005
		LDV/dies./Euro2	0.0004
		LDV/dies./Euro3	0.0002
URBAN BUS	diesel	HDV/80ies	0.012
		HDV/Euro1	0.004
		HDV/Euro2	0.003
		HDV/Euro3	0.002
HDV	diesel	HDV/80ies	0.004
		HDV/Euro1	0.003
		HDV/Euro2	0.002
		HDV/Euro3	0.002

Appendix: Table 21: Emission factors [g/(km×veh)] calculated for the entire fleet using the direct method for the Plabutsch Tunnel measurements in November, 2001.

Compound	**Emission factors**	**SD**
CO2*	495.387	320.039
NO*	1.349	0.802
NO2*	0.162	0.087
NO_x*	1.377	0.810
propene,propane	0.006	0.004
propyne	0.001	0.000
i-butane	0.003	0.002
1-butene	0.006	0.003
1,3-butadiene	0.005	0.004
trans-2-butene	0.004	0.003
cis-2-butene	0.002	0.001
i-pentane	0.004	0.003
n-pentane	0.001	0.001
isoprene	0.003	0.004
cis-2-pentene	0.002	0.004
2-methylpentane	0.002	0.002
3-methylpentane	0.001	0.001
n-hexane	0.001	0.001
benzene	0.003	0.002
cyclohexane	0.001	0.001
n-heptane	0.002	0.002
toluene	0.008	0.004
ethylbenzene	0.002	0.001
o-xylene	0.003	0.002
m-/p- xylene	0.006	0.004
1,3,5-trimethylbenzene	0.006	0.005
1,2,4-trimethylbenzene	0.004	0.005

Appendix: Table 22: Emission factors [g/(km×veh)] calculated for the entire fleet using model 1 for the Plabutsch Tunnel measurements in November, 2001.

Compound	**Emission factors**	**SD**
propane	0.007	0.004
i-butane	0.004	0.003
i-pentane	0.006	0.004
n-pentane	0.002	0.002
3-methylpentane	0.001	0.001
n-hexane	0.001	0.001
cyclohexane	0.001	0.001
n-heptane	0.002	0.002
propene	0.006	0.004
trans-butene	0.001	0.001
cis-butene	0.003	0.005
cis-2-pentene	0.000	0.001
benzene	0.004	0.003
toluene	0.011	0.005
o-xylene	0.004	0.002
m/p-xylene	0.009	0.005
ethylbenzene	0.002	0.001

Appendix: Table 23: CO_2 emission factors (g/km) calculated from the HBEFA 2.1 for the Kingsway Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**Emission factors**
PC	gasoline	PC/gas/conv.	148.789
		PC/gas/cl.l.cat.<91	178.368
		PC/gas/Euro1	122.108
		PC/gas/Euro2	158.529
		PC/gas/Euro3	153.749
		PC/gas/Euro4	153.810
	diesel	PC/dies./conv.	168.712
		PC/dies./XXIII/EEA1	161.507
		PC/dies./Euro2	137.965
		PC/dies./Euro3	132.408
		PC/dies./Euro4	132.359
LDV	gasoline	LDV/gas/conv.	192.874
		LDV/gas/cl.l.cat.<91	306.214
		LDV/gas/Euro2	284.890
		LDV/gas/Euro3	292.978
		LDV/gas/Euro4	292.699
	diesel	LDV/dies./konv	192.163
		LDV/dies./Euro1	285.466
		LDV/dies./Euro2	283.680
		LDV/dies./Euro3	286.547
		LDV/dies./Euro4	285.035
COACH	diesel	HDV/80ies	886.455
		HDV/Euro1	163.477
		HDV/Euro2	813.389
		HDV/Euro3	890.498
		HDV/Euro4	909.069
HDV	diesel	HDV/80ies	824.031
		HDV/Euro1	831.933
		HDV/Euro2	946.456
		HDV/Euro3	1011.042

Appendix: Table 24: THC emission factors (g/km) calculated from the HBEFA 2.1 for the Kingsway Tunnel.

Vehicle category	**Fuel**	**Emission concept**	**Emission factors**
PC	gasoline	PC/gas/conv.	1.176
		PC/gas/cl.l.cat.<91	0.284
		PC/gas/Euro1	0.129
		PC/gas/Euro2	0.126
		PC/gas/Euro3	0.047
		PC/gas/Euro4	0.031
	diesel	PC/dies./conv.	0.089
		PC/dies./XXIII/EEA1	0.059
		PC/dies./Euro2	0.034
		PC/dies./Euro3	0.029
		PC/dies./Euro4	0.028
LDV	gasoline	LDV/gas/conv.	1.526
		LDV/gas/cl.l.cat.<91	0.362
		LDV/gas/Euro2	0.156
		LDV/gas/Euro3	0.088
		LDV/gas/Euro4	0.061
	diesel	LDV/dies./konv	0.102
		LDV/dies./Euro1	0.085
		LDV/dies./Euro2	0.065
		LDV/dies./Euro3	0.038
		LDV/dies./Euro4	0.032
COACH	diesel	HDV/80ies	0.344
		HDV/Euro1	0.575
		HDV/Euro2	0.353
		HDV/Euro3	0.348
		HDV/Euro4	0.468
HDV	diesel	HDV/80ies	0.379
		HDV/Euro1	0.489
		HDV/Euro2	0.254
		HDV/Euro3	0.232

Appendix: Table 25: Benzene emission factors (g/km) calculated from the HBEFA 2.1 for the Kingsway Tunnel.

Vehicle category	Fuel	Emission concept	Emission factors
PC	gasoline	PC/gas/conv.	0.052
		PC/gas/cl.l.cat.<91	0.037
		PC/gas/Euro1	0.017
		PC/gas/Euro2	0.016
		PC/gas/Euro3	0.006
		PC/gas/Euro4	0.004
	diesel	PC/dies./conv.	0.001
		PC/dies./XXIII/EEA1	0.001
		PC/dies./Euro2	0.001
		PC/dies./Euro3	0.001
		PC/dies./Euro4	0.000
LDV	gasoline	LDV/gas/conv.	0.176
		LDV/gas/cl.l.cat.<91	0.016
		LDV/gas/Euro2	0.020
		LDV/gas/Euro3	0.011
		LDV/gas/Euro4	0.008
	diesel	LDV/dies./konv	0.002
		LDV/dies./Euro1	0.001
		LDV/dies./Euro2	0.001
		LDV/dies./Euro3	0.001
		LDV/dies./Euro4	0.001
COACH	diesel	HDV/80ies	0.006
		HDV/Euro1	0.007
		HDV/Euro2	0.004
		HDV/Euro3	0.004
HDV	diesel	HDV/80ies	0.007
		HDV/Euro1	0.006
		HDV/Euro2	0.004
		HDV/Euro3	0.004
		HDV/Euro4	0.006

Appendix: Table 26: Emission factors [g/(km×veh)] calculated for the entire fleet using the model 1 for the Kingsway Tunnel measurements, February, 2003.

Compound	**Emission factors**	**SD**
propane	0.0013	0.0003
i-butane	0.0024	0.0005
i-pentane	0.0107	0.0024
n-pentane	0.0068	0.0015
3-methylpentane	0.0025	0.0006
n-hexane	0.0024	0.0005
cyclohexane	0.0027	0.0006
n-heptane	0.0010	0.0002
propene	0.0018	0.0004
trans-butene	0.0023	0.0005
cis-butene	0.0020	0.0004
cis-2-pentene	0.0003	0.0001
benzene	0.0059	0.0013
toluene	0.0158	0.0035
o-xylene	0.0044	0.0010
m/p-xylene	0.0114	0.0025
ethylbenzene	0.0035	0.0008

Appendix: Table 27: Calculated NMHC source strength [g/(km×h)], mean total traffic density (MTTD) (vehicle h^{-1}) and % HDV contribution for different time intervals for four days in May, 2001.

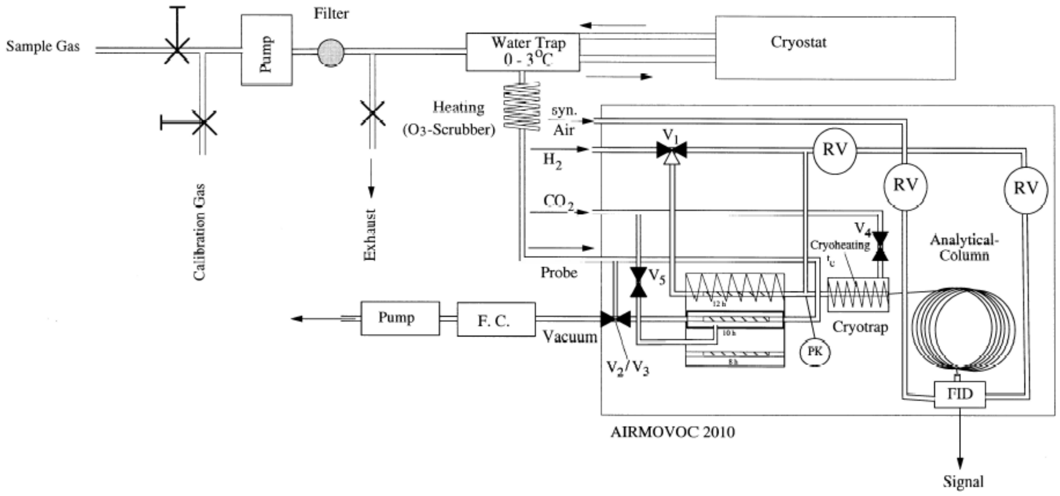
SOURCE STRENGTH (g h^{-1} km^{-1}) per time interval	**08.05.2001 Wednesday / Weekdays**				**14.05.2001 Thursday / Weekdays**			**17.05.2001 Saturday / Weekend**		**18.05.2001 Sunday / Weekend**		
	04:45-07:45 HDV: 6.8 ± 2.0	**08:00-10:00 HDV: 7.6 ± 1.0**	**17:00-19:00 HDV: 2.9 ± 0.3**	**20:00-22:00 HDV: 2.9 ± 0.4**	**8:00-10:00 HDV: 6.7 ± 0.8**	**10:15-12:15 HDV: 10.6 ± 1.1**	**12:30-14:30 HDV: 8.7 ± 0.5**	**13:00-16:30 HDV: 7.7 ± 2.3**	**16:30-20:15 HDV: 3.3 ± 0.6**	**12:00-16:00 HDV: 7.1 ± 1.3**	**16:00-18:00 HDV: 3.8 ± 1.3**	**18:00-20:00 HDV: 2.0 ± 0.2**
i-butane	23.96 ± 7.19	17.84 ± 5.35	-	-	4.46 ± 1.34	35.39 ± 0.62	28.02 ± 8.41	15.58 ± 4.67	27.62 ± 8.29	16.90 ± 5.07	22.26 ± 6.68	6.24 ± 1.87
iso-/1-butene	17.79 ± 5.37	7.30 ± 2.19	-	-	-	-	-	5.45 ± 1.64	3.12 ± 0.94	4.20 ± 1.26	-	-
1,3-butadiene/ n-butane	63.04 ± 8.91	37.30 ± 1.19	-	-	-	-	-	28.79 ± 8.64	33.75 ± 0.13	34.96 ± 0.49	-	18.09 ± 5.43
i-pentane	58.82 ± 17.65	50.11 ± 15.03	-	-	131.74 ± 39.52	172.76 ± 51.83	135.68 ± 40.70	38.26 ± 11.48	51.80 ± 15.54	43.68 ± 13.10	58.39 ± 17.52	59.80 ± 17.94
isoprene/trans-2-pentene	-	-	20.06 ± 6.02	-	34.29 ± 0.29	-	18.26 ± 5.48	-	-	7.69 ± 2.31	13.63 ± 4.09	12.49 ± 3.75
cis-2-pentene	55.38 ± 6.61	54.54 ± 6.36	-	-	13.76 ± 4.13	27.65 ± 8.30	-	-	-	3.78 ± 1.13	-	4.04 ± 1.21
2-methylpentane	16.40 ± 4.92	11.25 ± 3.38	30.36 ± 9.11	-	32.52 ± 9.76	18.23 ± 5.47	12.18 ± 3.65	3.30 ± 0.99	26.36 ± 7.91	-	9.36 ± 2.81	25.45 ± 7.64
3-methylpentane	6.18 ± 1.85	2.92 ± 0.88	4.86 ± 1.46	4.89 ± 1.47	11.32 ± 3.39	-	2.23 ± 0.67	5.47 ± 1.64	8.82 ± 2.65	-	8.30 ± 2.49	-

Appendix: Table 27 (continued)

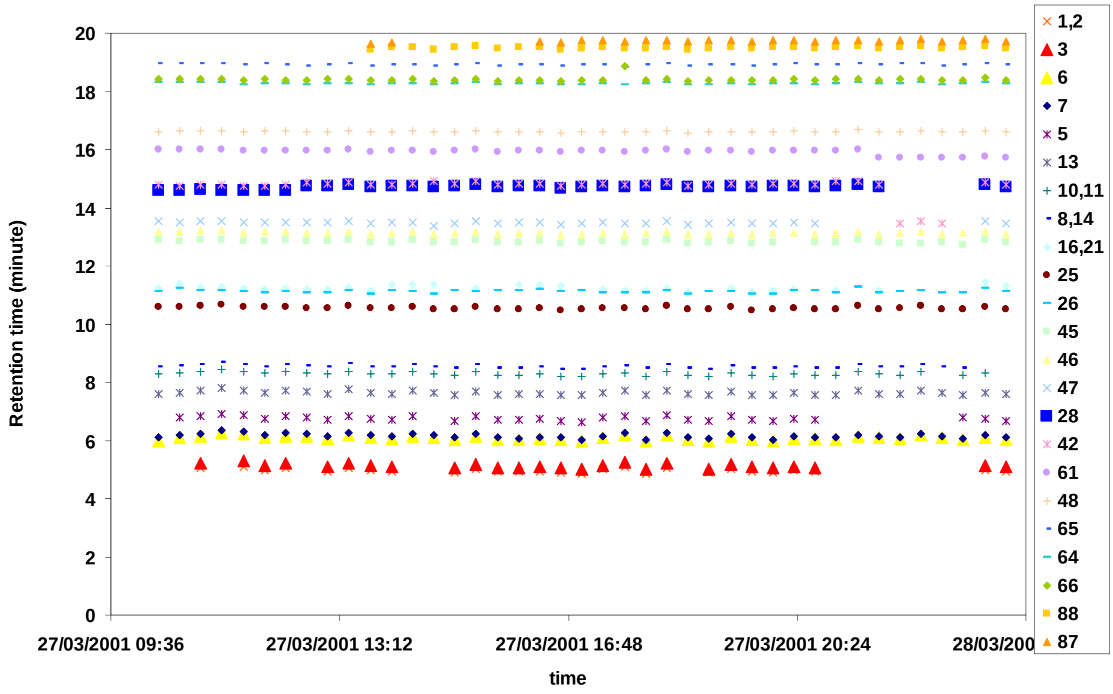
SOURCE STRENGTH ($g\ h^{-1}\ km^{-1}$) per time interval	**08.05.2001 Wednesday / Weekdays**				**14.05.2001 Thursday / Weekdays**			**17.05.2001 Saturday / Weekend**		**18.05.2001 Sunday / Weekend**		
benzene	26.86 ± 8.06	17.63 ± 5.29	34.17 ± 0.25	26.69 ± 8.01	38.35 ± 1.50	34.74 ± 0.72	31.57 ± 9.47	20.50 ± 6.15	30.11 ± 9.03	45.24 ± 3.57	47.73 ± 4.32	43.11 ± 2.93
cyclohexane	2.48 ± 0.74	-	0.63 ± 0.19	-	2.90 ± 0.87	-	2.32 ± 0.70	-	5.70 ± 1.71	-	1.37 ± 0.41	-
3-methylhexane	5.54 ± 1.66	2.17 ± 0.65	7.55 ± 2.27	4.14 ± 1.24	10.77 ± 3.23	3.17 ± 0.95	8.23 ± .47	2.62 ± 0.79	-	8.95 ± 2.68	12.16 ± 3.65	7.74 ± 2.32
2,2,4-trimethylpentane	5.53 ± 1.66	1.28 ± 0.38	7.90 ± 2.37	7.82 ± 2.35	21.84 ± 6.55	23.12 ± 6.94	7.73 ± .32	7.55 ± 2.27	13.68 ± 4.10	12.63 ± 3.79	19.32 ± 5.79	11.85 ± 3.55
n-heptane	2.78 ± 0.83	1.50 ± 0.45	3.94 ± 1.18	6.56 ± 1.97	2.07 ± 0.62	3.94 ± 1.18	3.24 ± 0.97	0.52 ± 0.16	4.63 ± 1.39	-	7.40 ± 2.22	6.12 ± 1.84
2,3,4-trimethylpentane	-	-	-	1.94 ± 0.58	4.30 ± 1.29	-	-	-	-	-	-	-
toluene	59.86 ± 7.96	40.86 ± 2.26	67.90 ± 0.37	58.83 ±17.65	138.92 ± 1.68	62.18 ± 8.65	58.79 ± 7.64	38.14 ± 1.44	76.55 ± 2.96	74.20 ± 2.26	100.08 ± 0.02	77.58 ± 3.27
n-octane	76.28 ± 2.88	30.93 ± 9.30	-	-	17. 80 ± 5.34	-	-	-	-	9.21 ± 2.76	-	-
ethylbenzene	10.48 ± 3.14	14.61 ± 4.38	9.67 ± 2.90	18.90 ± 5.67	25.65 ± 7.70	11.29 ± 3.39	10.54 ± 3.16	7.19 ± 2.16	12.84 ± 3.85	16.95 ± 5.09	23.70 ± 7.11	16.35 ± 4.91
m-/p-xylene	31.05 ± 9.3	22.92 ± 6.88	35.53 ± 10.6	38.02 ± 1.41	71.10 ± 1.33	37.53 ± 1.26	33.52 ± 0.06	21.71 ± 6.51	46.98 ± 4.09	45.14 ± 3.54	59.76 ± 7.93	47.10 ± 4.13
o-xylene	9.16 ± 2.75	-	12.20 ± 3.66	10.97 ± 3.29	23.55 ± 7.07	12.29 ± 3.69	-	8.69 ± 2.61	17.98 ± 5.39	15.28 ± 4.58	26.83 ± 8.05	15.26 ± 4.58
1,2,4-tmb/decane	-	-	-	-	44.94 ±13.48	-	-	7.28 ± 2.18	13.32 ± 4.00	-	-	-

Appendix: Figures

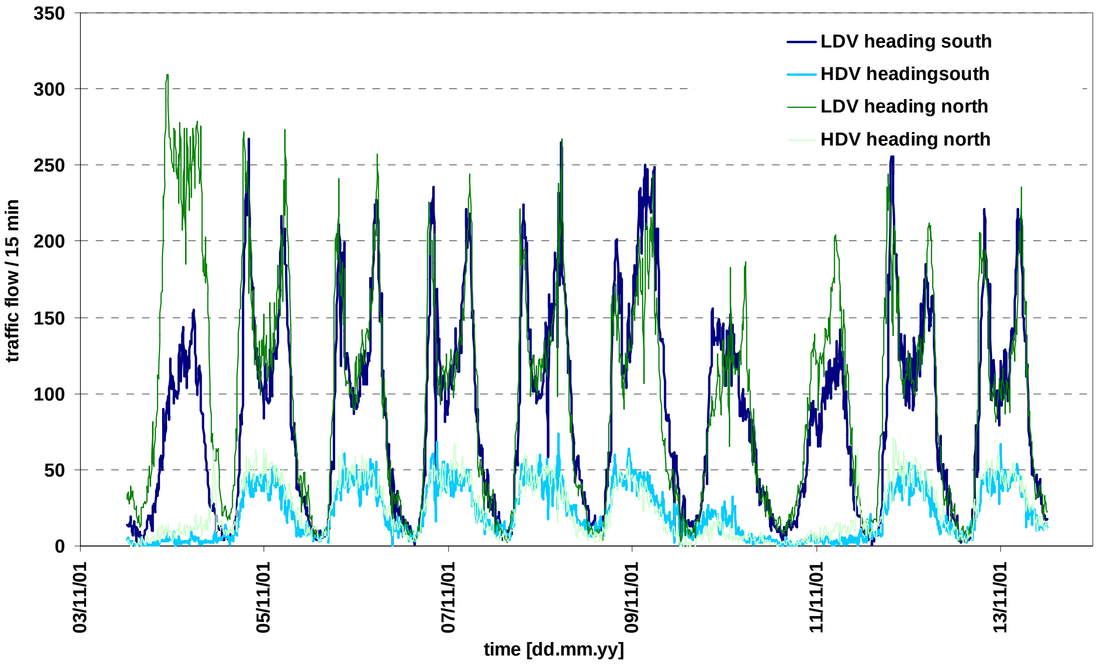
Appendix: Figure 1: Simple sketch of the Airmovoc 2010.



Appendix: Figure 2: Variation of the gross retention time of NMHCs detected by the quasi on-line GC system Airmovoc 2010 in the Lundby Tunnel air. The numbers in the table represent the identification number of the hydrocarbons as specified in Appendix - Table 3.



Appendix: Figure 3: Traffic count with loop detectors in the Plabutsch Tunnel over the whole measurement period for time intervals of 15 minutes.



REFERENCES

Andersson-Sköld, Y., Holmberg, L.: Photochemical Ozone Creation Potential (POCP) and Replacement of Solvents in Europe, Atmospheric Environment, 34, 3159-3169, **2000**

Atkinson, R., Arley, A.: Atmospheric degradation of Volatile Organic Compounds, *Chemical Reviews*, 103, 4605-4638, **2003**

Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmospheric Environment*, 34, 2063-2101, **2000**

Atkinson, R.: Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes, *Journal of Physical and Chemical Reference Data*, 26, 215-290, **1997**

Becker, K. H., Barnes, I. Bierbach, A., Brockmann, K. J., Kirchner, F., Klotz, B. ,Libuda, H. G., Mayer-Figge, A, Mönninghoff, S., Ruppert, L. , Thomas, W., Wiesen, E., Wirtz, K., Zabel F.: OH-Initiated Oxidation of VOC Under Variable NO_X Conditions, A contribution to the EUROTRAC subproject LACTOZ**, 1995**

Becker, K. H., Lörzer, J. C., Kurtenbach, R., Wiesen, P., Jensen, T., Wallington, T. J.: Nitrous oxide (N_2O) emissions from vehicles, *Environmental Science and Technology,* 33, 4134-4139, **1999**

Bellasio, R.: Modelling traffic air pollution in road tunnels, *Atmospheric Environment*, 31, 1539-1551, **1997**

Brocco, D., Fratarcangeli, R., Lepore, L., Petricca, M., Ventrone, I.: Determination of Aromatic Hydrocarbons in Urban Air of Rome, *Atmospheric Environment*, 31, 557-566, **1997**

Bruehlmann, S., Forss, A.-M., Steffen, D., Heeb, N.: Benzene A Secondary Pollutant Formed in the Three-Way Catalyst, *Environmental Science and Technology*, 39, 331-338, **2005**

Burgard, D. A., Bishop, G. A, Williams, M. J., Stedman, D.H.: On-Road Remote Sensing of Automobile Emissions in the Denver Area: Year 4, Final Report prepared for *Coordinating Research Council (CRC),* No E-23-4, **2003** http://www.feat.biochem.du.edu.

Cao, X. L., Hewitt, C. N.: Build-up of artifacts on adsorbents during storage and its effects on passive sampling and gas chromatography-flame ionization detection of low concentrations of volatile organic compounds in air, *Journal of Chromatography A*, 688, 368-374, **1994**

Cao, X. L., Hewitt, N.: The Sampling and Analysis of Volatile Organic Compounds in the Atmosphere, in Hewitt, C.N. (ed): Reactive Hydrocarbons in the Atmosphere, *Academic Press,* San Diego, **1999**

Carslaw, D.C.: Evidence of an increasing NO_2/NO_x emission ratio from road traffic emissions, *Atmospheric Environment*, 39, 4793-4802, **2005**

Carslaw, D.C., Beevers, S.D.: Investigating the potential importance of primary NO_2 emissions in a street canyon, *Atmospheric Environment*, 38, 3585-3594, **2004**

Carter, W. P. L., Pierce, J. A., Luo, D., Malkina, I.: Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds, Atmospheric Environment, 29, 2499-2511, **1995**

Chameides, W. L., Walker, J. C. G.: A photochemical theory of tropospheric ozone, *Journal of Geophysical Research*, 78, 8751-8760, **1973**

Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D. R., Rasmussen, R. A., Zimmerman, P., Greenberg, J., Middleton, P., and Wang, T.: Ozone precursor relationships in the ambient air, *Journal of Geophysical Research*, 97, 6037-6055, **1992**

Chan, T.L., Ning, Z., Leung, C.W., Cheung, C.S., Hung, W.T., Dong, G.: On road remote sensing of petrol vehicle emissions measurement and emission factors estimation in Hong Kong, *Atmospheric Environment,* 38, 2055-2066, **2004**

Chan, T.L., Ning, Z.: On road remote sensing of diesel vehicle emissions measurement and emission factors estimation in Hong Kong, *Atmospheric Environment,* 39, 6843-6856, **2005**

Clark, N.N., Gajendran, P., Kern, J.M.: A predictive tool from heavy-duty diesel vehicles, *Environmental Science and Technology*, 37, 7-15, **2003**

Colberg, C. A., Tona, B., Stahel, W. A., Meier, M. and Staehelin, J.: Comparison of a road traffic emission model (HBEFA) with emissions derived from measurements in the Gubrist road tunnel, Switzerland, *Atmospheric Environment*, 39, 4703-4714, **2005 a**

Colberg, C.A., Tona, B., Catone, G., Sangiorgio, C., Stahel, W. A, Sturm, P., Staehelin, J.: Statistical analysis of the vehicle pollutant emissions derived from several European road tunnel studies, *Atmospheric Environment*, 39, 2499-2511, **2005 b**

Corsmeier, U., Kohler, M., Vogel, B., Vogel, H., and Fiedler, F.: BAB II: a project to evaluate the accuracy of real-world traffic emissions for a motorway, *Atmospheric Environment*, 39, 5627-5641, **2005a**

Corsmeier, U.: The Karlsruher Autobahn-campaign BAB II: Validation of emission data, *Atmospheric Environment*, 39, 5625-5626, **2005b**

Crutzen, P. J., A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, *Pure and Applied Geophysics*, 106-108, 1385-1399, **1973**

Crutzen, P., Zimmermann, P. H.: The changing photochemistry of the troposphere, *Tellus*, 43 AB, 136-151, **1991**

DEFRA- Department for Environment, Food and Rural Affairs, UK http://www.defra.gov.uk/environment/statistics/index.htm, published March, **2005**

De Fré, R., Bruynseraede, P., Kretzchmar, J.G.,: Air pollution measurements in traffic tunnels, *Environmental Health Perspectives*, 102, 31-37, **1992**

Derwent, R. G., Jenkin, M.E., Saunders, S. M., Pilling, M.J., Simmonds, P.G., Passant, N.R., Dollard, G.J., Dumitrean, P., Kent, A.: Photochemical ozone formation in north west Europe and its control, *Atmospheric Environment*, 37, 1983-1991, **2003**

Derwent R.G., Davies, T., Delany, M., Dollard, G.J., Field, R.A., Dumitrean, P., Nason, P.D., Jones, B.M.R., Pepler, S.A., Analysis and interpretation of the continuous hourly monitoring data for 26 C_2-C_8 Hydrocarbons at 12 United Kingdom sites during 1996, *Atmospheric Environment*, 34, 297-312, **2000**.

Derwent, R. G., Jenkin, M.E., Saunders, S. M., Pilling, M.J.: Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism, *Atmospheric Environment*, 32, 2429-2441, **1998**

Derwent, R.G., Jenkin, M.E., Saunders, S.M.: Photochemical Ozone Creation Potentials for a Large Number of Reactive Hydrocarbons under European Conditions, *Atmospheric Environment*, 30, 181-199, **1996**

Derwent, R.G., Jenkin, M.E.: Hydrocarbons and the Long Range Transport of Ozone and PAN across Europe, *Atmospheric Environment*, 25A, 1661-1678, **1991**

DIN ISO 13752: Luftbeschaffenheit. Ermittlung der Unsicherheit eines Messverfahrens unter Feldbedingungen mit Hilfe eines als Referenz benutzten zweiten Messverfahrens, *Deutsches Institut für Normung. Berlin*, Beuth Verlag, **1999**

Directive 2002/3/EEC: Directive 2002/3/EEC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air, Official Journal of the European Communities, 14-30, L67/ 09.03, **2002**

Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of the petrol and diesel fuels and amending Council Directive 93/12/EEC, Official Journal of the European Communities, L350/ 28.12., **1998**

Directive 96/62/EEC: Directive 96/62/EEC on ambient air quality assessment and management, 27.09. **1996**

Directive 92/32/EEC: Directive 92/32/EEC amending Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances, 30.04., **1992**

Directive 89/677/EEC: Directive 89/677/EEC of 21 December 1989 amending for the eight time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the member states relating to restrictions on the marketing and use of certain dangerous substances and preparations, L398/ 30.12., **1989**

Doskey, P.V., Porter, J.A., Scheff, P.A.: Source Fingerprints for Volatile Non-Methane Hydrocarbons, *Journal of the Air & Waste Management Association*, 42, 1437-1445, **1992**

Duffy, B.L., Nelson, P.F.: Non-methane Exhaust Composition in the Sydney Harbour Tunnel: A Focus on Benzene and 1,3-Butadiene, *Atmospheric Environment*, 30, 2759-2768, **1996**

EEA (European Environmnetal Agency) Report No 3/2004: Ten key transport and environment issues for policy-makers; TERM: Indicators tracking transport and environment integration in the European Union, **2004**

El-Fadel, M., Hashisho, Z.: Vehicular Emissions in Roadway Tunnels: A Critical Review, *Environmental Science and Technologie*, 31, 125-174, **2001**

EMFAC 7G (Emission Factor), Air Resources, Board´s computer model for estimating calendar year specific on road motor vehicle emission factors, California, http://www.arb.ca.gov, updated October, **1998**

EPA- Latest Findings on National Air Quality: 1999 Status and Trends, EPA-454/F-00-002, www.epa.gov/airtrends, **2000**

EPA- National Air Quality Emissions Trends, United States Environmental Protection Agency, Research Triangle Park, NC, EPA-454/R-00-003, **2000**

EPA-U.S. Environmental Protection Agency., Federal and California Exhaust and Evaporative Emission Standards for Light-Duty Vehicles and Light-Duty Trucks; EPA Publication 420-B-00-001; http://www.epa.gov/otaq/stds-ld.htm**, 2000**

European Commission: Review of the Auto-Oil II Programme, COM (2000) 626 final. Brussels, Belgium, October **2000**

Finlayson-Pitts, B.J., Pitts, J.N. Jr.: Chemistry of the Upper and Lower Atmosphere, *Academic Press*, New York, **2000**

Finlayson-Pitts, B. J. and Pitts, J.N. Jr.: Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles, *Science*, 276, 1045-1051, **1997**

Finlayson-Pitts, B.J. and Pitts, J.N. Jr.: Atmospheric Chemistry: Fundamentals and Experimental Techniques, Wiley, New York, **1986**

Fraser, M.P., Cass, G.R., Simoneit, B.R.T.: Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel, *Environmental Science and Technology,* 32, 2051-2060, **1998**

Friedrich, R.: Overview of Subproject GENEMIS, Chapter 7: Generation and Evaluation of Emission Data, www.gsf.de/eurotrac/publications/ et2_fin_rep/fr_7_genemis.pdf , **2003**

Friedrich, R., Obermeier, A.: Antropogenic emissions of Volatile Organic Compounds, in Hewitt, C.N (ed.) Reactive Hydrocarbons in the Atmosphere, *Academic Press*, San Diego, **1999**

Fuentes, J.D., Hayden, B.P., Garstang, M., Lerdau, M., Fitzjarrald, D., Baldochi, D.D., Monson, R., Lamb, B., Geron, C.: New Directions: VOCs and biosphere-atmosphere feedbacks, *Atmospheric Environment*, 35, 189-191, **2001**

Gajendran, P., Clark, N.: Effect of Truck Operating Weight on Heavy-Duty Diesel Emissions, *Environmental Science and Technology,* 37, 4309-4317, **2003**

Gertler, A.W., Fujita, E.M., Pierson, W.R., Wittorff, D.N.: Apportionment of NMHC tailpipe and non-tailpipe emissions in the Fort McHenry and Tuscarora Mountain tunnels, *Atmospheric Environment* 30, 2297-2305, **1996**

Gertler, A.W., Pierson, W.R.: Recent measurements of mobile source emission factors in North American tunnels, *Science of the Total Environment*, 189/190, 107-113, **1996**

Gertler, A. W. and Pierson W. R.: Motor vehicle emission modeling issues, *Science of the Total Environment*, 146-147, 333-338, **1994**

Gorse, Jr, R.A., Norbeck, J.M.: CO emission rates for in-use gasoline and diesel vehicles, *Journal of Air Poluttion Control Association*, 31, 1094-1096, **1981**

Gorse, Jr, R.A.: On road emission rates of carbon monoxide, nitrogen oxides and gaseous hydrocarbons, *Environmental Science and Technology*, 18, 500-507, **1984**

Glaser, K.: Methoden der Qualitätssicherung bei der Messung von Luftverunreinigungen bei Feldexperimenten, Ph.D. Thesis, *Institut für Verfahrenstechnik und Dampfkesselwesen, Universität Stuttgart*, Germany, **2001**

Gomes, J.A.G.: The Impact of road traffic emissions on the ozone formation in Germany, Ph.D. Thesis, *Physikalische Chemie*, *University of Wuppertal*, Bericht. 61, ISSN: 1436-2198, **2003**

Granier, C., Brasseur, G.: The impact of road traffic on global tropospheric ozone, Geophys. Res. Letter, 30, 1086, **2003**

Gregory, M., Lanzerstorfer, CH., Oberlinninger, H., Puxbaum, H., Biebl, P., Gläser, O., Villinger, J.: Tauerntunnel-Luftschadstoffuntersuchung 1988, Bericht 4/89, Abteilung für Umweltanalytik, *Institut für Analitische Chemie, Technische Universität Wien*, **1989**

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley P., Fall, R.: Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, *Atmospheric Environment*, 34, 2205-2230, **2000**

Guenther, A., Hewitt,C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P.: A global model of natural volatile organic compound emissions, *Journal of Geophysical Research*, 100, 8873-8892, **1995**

Haagen-Smit, A.J.: Chemistry and Physiology of Los Angeles, Indian Engineering Chemistry, 44, 1342-1346, **1952**

Haan, P., Keller, M.: Emission factors for passenger cars and light duty vehicles; handbook emission factors for road transport (HBEFA) version 2.1; *INFRAS*, www.infras.ch, **2004**

Harries, J. E., Brindley, H.E.P.J. Sagoo, B.R.J.: Increases in greenhouse forcing inferred from the outgoing long wave radiation spectra of the Earth in 1970 and 1997, *Nature*, 410, 355-357, **2001**

Harris, J.W., Stocker, H.: Handbook of Mathematics and Computational Science, New York: *Springer-Verlag*, **1998**.

Hartung, J., Elpelt, B., Klösener, K.-H.: Statistik-Lehr und Handbuch der angewandten Statistik, 10. Auflage, *R. Oldenbourg Verlag*, München, **1995**

Hassel, D., Jost, P., Weber, F. J., Dursbeck, F., Sonnborn, K. S., Plettau, D.: Abgas-Emissionsfaktoren von Nutzfahrzeugen in der Bundesrepublik Deutschland für das Bezugsjahr 1990, Final Report, No. 104 05 151/02, *Umweltbundesamt*, Berlin, **1995**

Hassel, D., Jost, P., Weber, F.J., Dursbeck, F., Sonnborn, K.S., Plettau, D.: Abgas-Emissionsfaktoren von Pkw in der Bundesrepublik Deutschland; Abgasemissionen von Fahrzeugen der Baujahre 1986 bis 1990, Abschlußbericht zum Vorhaben UFO-PLAN-Nr.: 104 05 152 und 104 05 509, *Umweltbundesamt*, Berlin, **1994**

Hausberger, St., Rodler, J., Sturm, P., Rexeis, M.: Emission factors for heavy-duty vehicles and validation by tunnel measurements, *Atmospheric Environment,* 37, 5237–5245, **2003**

Heincklen, J., Westberg, K., Cohen, N., Report, center for Air Environmental Studies, 115-169, **1969**

Hueglin, C., Buchmann, B., Weber, O. R.: Long-term observations of real-world road traffic emission factors on a motorway in Switzerland, *Atmospheric Environment,* 40, 3696-3709, **2006**

HBEFA 2.1.: Handbuch Emissionsfaktoren des Straßenverkehrs (HBEFA), (Handbook of Emission Factors for Road Traffic), Version 2.1, Umweltbundesamt Berlin, Bundesamt für Umwelt, Wald und Landschaft Bern, Umweltbundesamt Wien, published as software on CD-ROM, *Infras AG*, Bern, **2004**

HBEFA 1.1.: Handbuch Emissionsfaktoren des Straßenverkehrs (HBEFA), (Handbook of Emission Factors for Road Traffic), Version 1.2, Umweltbundesamt Berlin, Bundesamt für Umwelt, Wald und Landschaft Bern, Umweltbundesamt Wien, published as software on CD-ROM, *Infras AG, Bern*, **1999**

Heeb, N.V., Forss, A.-M., Saxer, C.J., Wilhelm, P.: Methane, benzene and alkyl benzene cold start emission data of gasoline-driven passenger cars representing the vehicle technology of the last two decades, *Atmospheric Environment*, 37, 5185–5195, **2003**

Heeb, N.V., Forss, A.-M., Wielenmann, M.: Pre- and post-catalyst- fuel-, velocity- and acceleration-dependent benzene emission data of gasoline-driven EURO-2 passenger cars and light duty vehicles, *Atmospheric Environment*, 34, 3103–3116, **2002**

Heeb, N.V., Forss, A.-M., Bach, C., Reimann, S., Herzog, A., Jäsckle, H.W.: A comparison of benzene, toluene and C_2-benzenes mixing ratios in automotive exhaust and in the suburban atmosphere during the introduction of catalytic converter technology to the Swiss car fleet, *Atmospheric Environment*, 34, 3103–3116, **2000**

Houweling, S., Kaminski, T., Dentener, F., Lelieveld, J., Heimann, M.: Inverse modeling of methane sources and sinks using the adjoint of a global transport model, *Journal of Geophysical Research*, 104, 137-160, **1999**

Hsu, Y.C., Tsai, J.H., Chen, H.W., Lin, W.Y.: Tunnel study of on-road vehicle emissions and photochemical potential in Taiwan, *Chemosphere,* 42, 227-234, **2001**

Hwa, M-Y., Hsieh, C-C., Wu, T-C, Chang, L-F.W.: Real-world vehicle emissions and VOCs profile in the Taipei tunnel located at Taiwan Taipei area, *Atmospheric Environment*, 36, 1993-2002, **2002**

Ingalls, M.N., On-Road Vehicle Emission Factors from Measurements in a Los Angeles Area Tunnel, *Journal of Air & Waste Manage. Assoc.*, 82nd Annual Meeting & Exhibition, Anaheim, California, 1-25, **1989**

IPCC: Special Report Emission Scenarios, Tech, rep., Intergovernmental Panel on Climate Change, *Cambridge University Press*, NY, USA, **2000**

ISO/IEC Guide 43-1: Proficiency testing by interlaboratory comparisons. Part 1: development and operation of proficiency testing schemes. 2nd Ed. International Organisation for Standardisation, Geneva, Switzerland, **1997**

ISO- Guide to the Expression of Uncertainty in Measurement, 1st edition, ISBN 92-67-10188-9, **1995**

Jacob, D.J.: Heterogeneous chemistry and tropospheric ozone, NARSTO Critical Review Papers, **2000**

Jamriska, M., Morawska, l.: A model for determination of motor vehicle emission factors from on-road measurements with a focus on sub micrometer particles, *The Science of the Total Environmen*t 19, 1110-1115, **2001**

Jenkin, M., Saunders, S. M., Pilling, M. J.: The Tropospheric Degradation of volatile organic compounds: A protocol for mechanism development, *Atmospheric Environment*, 31, 81-104, **1997**

Jenkin, M. E., Hayman, G. D.: Photochemical Ozone Creation Potentials for Oxygenated Volatile Organic Compounds: Sensitivity to Variations in Kinetic and Mechanistic Parameters, *Atmospheric Environment*, 33, 1275-1293, **1999**

Jenkin, M. E., Clemitshaw, K. C.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, *Atmospheric Environment*, 34, 2499-2527, **2000**

Johansson, C., Romero, R., Vesely, V.: Report no 61, in Swedish (English Summary), ITM, SE- 106-91, *Institute of applied Environmental Research, Stockholm University*, Sweden, **1997**

John, C., Friedrich, R., Staehelin, J., Schläpfer, K., Stahel, W.A.: Comparison of emission factors for road traffic from a tunnel study (Gubrist tunnel, Switzerland) and from emission modelling, *Atmospheric Environment,* 33, 3367-3376, **1999**

Junge, C. E.: Global ozone budget and exchange between stratosphere and troposphere, *Tellus*, 14, 363-377, **1962**

Kanter, H.-J., Mohnen, V.A., Volz-Thomas, A., Junkermann, W., Glaser, K., Weitkamp, C., Slemr, F.: Quality assurance in TFS for inorganic compounds, *Journal of Atmospheric Chemistry*, 42, 235-253, **2002**

Kasting, J.F., Singh, H.B.: Nonmethane hydrocarbons in the troposphere: Impact on the old hydrogen and odd nitrogen chemistry, *Journal of Geophysical Research*, 91, 239-256, **1986**

Kean, A., Harley R., Kendall, G.: Effects of Vehicle Speed and Engine Load on Motor Vehicle Emissions*, Environmental Science and Technology*, 37, 3739-3746, **2003**

Keller, M., Hausberger, S., DeHaan, P.: Handbuch Emissionsfaktoren für den Strassenverkehr in Österreich . im Auftrag von BMUJF und UBA, Österreich, Wien, **1998**

Ketzel, M., Wåhlin, P., Berkowicz, R.: Particle and trace gas emission factors under urban driving conditions in Copenhagen based on street and roof level observations, *Atmospheric Environment*, 37, 2735-2749, **2003**

Kirchsteter, T.W., Singer, B.C., Harley, R.A., Kendall, G.R., Chan, W.: Impact of oxygenated gasoline use on California light-duty vehicles emissions, *Environmental Science and Technology*, 30, 661-670, **1996**

Kley, D.: Tropospheric Chemistry and Transport, *Science*, 276, 1043-1044, **1997**

Kohler, M., Corsmeier, U., Vogt, U., Vogel, B.: Estimation of gaseous real world traffic emissions downstream a motorway, *Atmospheric Environment*, 39, 5665-5684, **2005**

Kouridis, C., Ntziachristos, L., Samaras Z.: COPERT III, Computer programme to calculate emissions from road transport User manual (Version 2.1), http://www.eea.eu.int, **2000**

Kristensson, A., Johansson, C., Westerholm, R., Swietlicki, E., Gidhagen, L., Wideqvist, U., Vesely, V.: Real-world traffic emission factors of gases and particles measured in a raod tunnel in Stockholm, Sweden, *Atmospheric Environment*, 38, 657-673, **2004**

Kühlwein, J., Friedrich, R.: Traffic measurements and high performance modelling of motorway emission rates, *Atmospheric Environment*, 39, 1659-1660, **2005**

Kuhns, H.D., Mazzoleni, C., Moosmüller, H., Nikolic, D., Keislar, R.E., Barber, P.W., Li, Z., Etyemezian, V., Watson, J.G.: Remote sensing of PM, NO, CO, and HC emission factors for on-road gasoline and diesel engine vehicles in Las Vegas, NV, *Science of the Total Environment*, 322, 123-137, **2004**

Kurtenbach, R., Ackermann, R., Becker, K.H., Geyer, A., Gomes, J.A.G., Lörzer, J.C., Platt, U., Wiesen, P.: Verification of the contribution of vehicular traffic to the total NMVOC emission in Germany and the importance of the NO_3 chemistry in the city air, *Journal of Atmospheric Chemistry*, 42, 395-411, **2002**

Kurtenbach, R., Ackermann, R., Becker, K.H., Geyer, A., Gomez, J.A.G, Lörzer, J.C, Platt, U, Wiesen, P.: Investigation of Emissions and Heterogeneous Formation of HONO in a Road traffic Tunnel, *Atmospheric Environment*, 35 (20) 3385-3394, **2001**

Leighton, P. A.: Photochemistry of air pollution, *Academic Press*, **1961**

Lelieveld, J., Dentener, F.J.: What controls tropospheric ozone, *Journal of Geophysical Research*, 105, 3531-3551, **2000**

Levy, H.: Photochemistry of minor constituents in the troposphere, *Planetary and Space Science*, 21, 575-591, **1973**

Levy, H.: Photochemistry of the lower troposphere, *Planetary and Space Science*, 20, 919-935, **1972**

Levy, H.: Normal Atmosphere: Large radical and formaldehyde concentrations predicted. *Science*, 173, 141-143, **1971**

Lies, K. H., (ed.): Nicht limitierte Automobil-Abgaskomponent, Volkswagen AG, Wolfsburg, **1988**

Liu, S., Trainer, M., Fehsenfeld, F., Parrish, D., Williams, E., Fahey, D., Hübler, G., Murphy, P.: Ozone production in the rural troposphere and the implication for the regional and global ozone distribution, *Journal of Geophysical Research*, 92, 4191-4207, **1987**

Lonneman, W. A., Sella, R.L., Meeks, S.A.: Non-methane organic composition in the Lincoln Tunnel*, Environmental Science and Technology,* 20, 790-796, **1986**

LUQS, 1998- Luftqualität in Nordrhein-Westfalen, Jahresbericht 1998, Essen, **1999**

Mannschreck, K.: Experimentelle Bestimmung von städtischen Emissionen anhand von Konzentrationsmessungen im Lee einer Stadt - Untersuchungen zum Beitrag verschiedener Quelltypen und Vergleich mit einem Emissionsberechnungsmodell, Disertation of the Bergische Universität Wuppertal, **2000**

Maxim, W.J., Levy, H., Kasibhatla, P.S.: Simulated globaltropospheric PANIts transport and impact on NO_x, *Journal of Geophysical Research*, 101, 621-638, **1996**

Matisová, E. and Skrabakova, S.: Carbon sorbents and their utilization for the preconcentration of organic pollutants in environmental samples, *Journal of Chromatography A*, 707, 145-179, **1995**

McLaren, R., Gertler, A.W., Wittorff, D.N., Belzer, W., Dann T., Singleton D. L.: Real-World Measurements of Exhaust and Evaporative Emissions in the Cassiar Tunnel Predicted by Chemical Mass Balance Modeling, Environmental Science and Technology, 30, 3001-3009, **1996**

McGaughey, Gary R., Nimish R. Desai, David T. Allen, Robert L. Seila, William A. Lonneman, Matthew P. Fraser, Robert A. Harley, Alison K. Pollack, Jason M. Ivy and James H. Pric, Analysis of motor vehicle emissions in a Houston tunnel during the Texas Air Quality Study 2000, *Atmospheric Environment*, 38, 20, 3363-3372, **2004**

Method no. ID-172-US Department of Labor Ocupational Safety and Health Administration, CO_2 in workplace atmosphere, **www.osha.gov**

Metz, N, Road transportation trend in Germany and Europe (EU15), US-EPA/Germany-BMU-UBA workshop, Bad-Breisig, Oct.11, **2002**

Na, K., Yong, P. K., Kil, Ch. M.: Seasonal variation of the C_2–C_9 hydrocarbons concentrations and compositions emitted from motor vehicles in a Seoul tunnel, *Atmospheric Environment*, 36, 12, 1969-1978, **2002**

NAEI : National Atmospheric Emission Inventory**, www.airquality.co.uk, 2005**

NETCEN: UK fleet projections from 1996-2025, Fractions of Traffic Flows by Vehicle type on Different Roads, **2002**

Niedojadlo, A., The impact of NMVOC emissions from Traffic and Solvent use on Urban Air in Wuppertal- an experimental study, Ph.D. Thesis, *Bergische Universität- Wuppertal,* **2005**

Olivier, J. G. J., Bouwman, A. F.,. van der Maas, C. W. M, Berdowski, J. J. M., Veldt, C., Bloos, J. P. J.,. Visschedijk, A. J. J., Zandveld, P. Y. J., Haverlag, J. L.: Description of EDGAR Version 2.0: A set of global inventories of greenhouse gases and ozone-depleting substances for all anthropogenic and most natural sources on a per country 1o×1o grid. RIVM rep. 771060002, *Rijksinstituut, Bilthoven*, Netherlands, **1996**

Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger. R.B., Ray, W.D.: Real-world automotive emissions - Summary of studies in the Fort McHenry and Tuscarora mountain tunnels. *Atmospheric Environment*, 30, 2233-2256, **1996**

Pierson, W.R.,: Automotive CO emission trends derived from measurements in highway tunnels, *Journal of Air Waste Management Association*, 45, 831-832, **1995**

Pierson, W.R., Gorse, R.A., Szkarlat, Jr., A.C., Brachaczek, W. W., Japar, S.M., Lee, F. S.C., Zweidinger, R.B., Claxton, L.D.: Mutagenicity and Chemical Characteristics of Carbonaceous Particulate Matter from Vehicles on the Road, *Environmental Science & Technology,* 17, 31-44, **1983**

Placet, M., Mann, C.O., Gilbert, R.O., Niefer, M.J., Emissions of ozone precursors from stationary sources: a critical review, *Atmospheric Environment,* 34, 2183-2204, **2000**

Rappenglück, B., Schmitz, R., Bauerfeind, M., Cereda-Balic, F., von Baer, D., Jorquera, H., Silva, Y., Oyola, P.: An urban photochemistry study in Santiago de Chile, *Atmospheric Environment*, 39, 2913-2931, **2005**

Robinson, N.F., Pierson, W.R., Gertler, A.W., Sagebiel, J.C.: Comparison of MOBILE 4.1 and MOBILE 5 predictions with measurements of vehicle emission factors in Fort Mc Henry and Tuscarora Mountain tunnels, Atmospheric Environment, 30, 2257-2267, **1996**

Rodler, J., Sturm P., Bacher M., Sjödin A., Ekström M, McCrae, I.,, Boulter, P., Kurtenbach, R., J- Lörzer, Petrea, M., Imhof, D., Prevot, A.S.H., Staehelin, J., Sangiorgo, C., Tona, B., Colberg, C.A.: ARTEMIS Assessment and Reliability of Transport Emission Models and Inventory Systems, Validation Final Report, 15.12., DGTREN Contract 1999-RD.10429 WP1200, **2005**

Rodler, J.: Luftschadstoffuntersuchungen mit unterschiedlichen Messsystemen zur Validierung von Emissions und Aubreitungsmodellen, Ph.D. Thesis, *Technische Universität Graz*, **2000**

Rogak, S. N., Pott, U., Dann, T., Wang, D.,: Gaseous Emissions from Vehicles in a Traffic Tunnel in Vancouver, British Columbia, *Journal of the Air and Waste Management Association*, 48, 604-615, **1998**

Sagebiel, J.C., Zielinska, B., Pierson, W.R., Gertler, A.W.: Real-World Emissions and Calculated Reactivities of Organic Species from Motor Vehicles, *Atmospheric Environment*, 12, 2287-2296, **1996**

Sakurai, T., Tanabe, K., Moriguchi, Y., Wakamatsu, S., Hoshi, J., Ishii, K., Nakamura, K., Izumikawa, S.: Volatile Organic Compunds Emission Factors from Road Traffic in a Highway Tunnel in the Tokyo Metropolitan Area in Japan, *Journal of Japan Society of Air Pollution*, 37, 47-74 (in Japanese with English abstract), **2002**

Sawyer, R.F., Harley, R.A., Cadle, S.H., Norbeck, J.M., Slott, R., Bravo, H.A.: Mobile sources critical review: NARSTO assessment, *Atmospheric Environment,* 34, 2161-2181, **2000**

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T.: Measurements of emissions from air pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles, *Environmental Science & Technology*, 36, 4337-4346, **2002**

Schmidt, H., Pucher, E., Reinhard, E., Biebl, P., Puxbaum, H.: Decadal reductions of traffic emissions on a transit route in Austria- results of the Tauerntunnel experiment 1997, *Atmospheric Environment* 35, 3585–3593, **2001**

Schmitz, T., Hassel, D., Weber, F.-J.: Determination of VOC-Components in the exhaust of gasoline and diesel passenger cars, *Atmospheric Environment,* 34, 4639-4647, **2000**

Schmitz, T., Hassel, D., Weber, F.-J.: Zusammensetzung der Kohlenwasserstoffe im Abgas unterschiedlicher Fahrzeugkonzepte, Research Report Jül-3646, *Forschungszentrum Jülich*, **1999**

Schmitz, T.: Messungen der Immissionskonzentrationen verschiedener Ozonvorläufer-substanzen in Ballungsgebieten und an Autobahnen, Ph.D. Thesis, *Bergische Universität Gesamthochschule Wuppertal,* **1997**

Shallcross, D. E., Monks, P. S.: New Directions: A role for isoprene in biosphere-climate-chemistry feedbacks, *Atmospheric Environment,* 34, 1659-1660, **2000**

Sillman, S., Logan, J.A., Wofsy, S.C.: The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes, *Journal of Geophysical Research*, 95, 1817-1851, **1990**

Singer, B.C., Harley, R.A.: A fuel –based motor vehicle emission inventory. *Journal of the Air and Waste Management Association,* 46, 581-593, **1996**

Singh, H.B., Kanakidou, M., Crutzen, P.J., Jacob, D. J.: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature*, 378, 50-54, **1995**

Singh, H.B., Hanst, P.L.: Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides, *Geophysical Research Letter*, 8, 941-944, **1981**

Sjödin, Å.: VOC emissions from high-emitting gasoline passenger cars, in Friedrich , R., Reis, S. (ed), Emission of Air Pollutants, Measurements, Calculations and Uncertainties, *Springer-Verlag*, Berlin, **2004**

Sjödin, Å., Andréasson, K., Ekström, M., Potter, A., Sternbeck, J., Wingfors, H., Hammarström, U., Cedersund, H.A.: Influence of maintenance and driving behaviour on real-world road vehicles emissions, *Genemis Annual Repport*, **2000**

Sjödin, Å., Persson, K., Andreason, K., Arlander, B., Galle, B.: On road emission factors derived from measurements in a traffic tunnel (special issue), *International Journal of Vehicle Design*, 20, 147-158, **1998**

Sjödin, Å., Andréasson K., Wallin, M., Lenner, M., Wilhelmsson, H.: Identification of high emitting catalyst cars on the road by means of remote sensing, *International Journal of Vehicle Design*, 18, 326-339, **1997**

Skoog, A.D., Leary, J.J.: Priniciples of Instrumental Analysis. Fourth Ed., Saunders College Publishing, **2000**

Staehelin, J., Sturm, P. : Tunnel Studies, in Emissions of Air pollutants – Measurements, Calculations and Uncertainties, GENEMIS, EUROTRAC-2 Subproject Final Report, R. Friedrich and S. Reis (Eds.), 187-191,Springer, Berlin, Heidelberg, New York, **2004**

Staehelin, J., Locher, R., Mönkeberg, S., Stahel, W.A.: Contribution of road traffic emissions to ambient air concentrations of hydrocarbons: the interpretation of monitoring measurements in Switzerland by Principal Component Analysis and road tunnel measurements, *International Journal of Vehicle Design*, 27, 161 – 172, **2001**

Staehelin, J., Keller, C., Stahel, W.A., Schläpfer, K., Wunderli, S.: Emission factors from road traffic from a tunnel study (Gubrist tunnel, Switzerland). Part III: results of organic compounds, SO_2 and speciation of organic exhaust emission, *Atmospheric Environment*, 32, 999-1009, **1998**

Staehelin, J., Keller, C., Stahel, W.A., Schläpfer, K., Steinemann, U., Bürgin, T., and Schneider, S.: Modelling emission factors of road traffic from a tunnel study, *Environmetrics,* 8, 219-239, **1997**

Staehelin, J., Schläpfer, K., Bürgin, T., Steinemann, U., Schneider, S., Brunner, D., Bäumle, M., Meier, M., Zahner, C., Keiser, S., Stahel, W., Keller, C.: Emission factors from road traffic from a tunnel study (Gubrist tunnel, Switzerland). Part I: concept and first results, *Science of the Total Environment*, 169, 141-147, **1995**

Staehelin, J., Schläpfer, K.: Erfassung von Emissionen des Kraftfahrzeugverkehrs mittels Messungen im Gubrist tunnel; Project within the EUROTRAC-Subproject GENEMIS, Final Report, Carbotech AG, Basel, **1994**

Stedman, D.H.: Playing with fire: Science and Politics of Air Pollution from Cars, http://www.feat.biochem.du.edu/assets/reports/Univ_Lecture/index.html, **1995**

Stemmler K., Bugmann, S., Buchmann, B., Reimann, S., Staehelin, J.: Large decrease of VOC emissions of Switzerland's car fleet during the past decade: results from a highway tunnel study, *Atmospheric Environment*, 39, 1009-1018, **2005**

Sternberger, J.C., Gallaway, W.S., Jones, D.T.L.: *Gas Chromatography*, 231, Academic Press, New York, **1962**

Sturm P., Staehelin, J., Kurtenbach, R., McCrane, I., Prevot, A.: Measurements and validation protocol for gaseous pollutants and particular matters, *VKM-THD Report I-*01/2001 Stu-612, TU Gratz, **2001**

Sturm P.J., Rodler, J., Almbauer, R.A.: Validation of emission factors for road vehicles based on street tunnel measurements, *International Journal of Vehicle Design*, 27, **2001**

Sturm, P.: Instantaneous vehicle emissions, in Jourmard, R. (ed.) Methods of Estimations of Atmospheric Emissions from transport, action COST 319 final report, LTE 9901 report, **1999**

Swedish Statistics (Statistiska centralbyran) **(SCB)**: Emission to air in Sweden: carbon dioxide, methane, nitrous oxide, nitrogen oxides, carbon monoxide, volatile organic compounds and sulphur dioxide 1990-2000, www.scb.se, **2003**

Touaty, M., Bonsang, B.: Hydrocarbon emissions in a highway tunnel in the Paris area, *Atmospheric Environment*, 34, 985-996, **2000**

Vogel, B., Corsmeier, U., Vogel, H., Fiedler, F., Kühlwein, J., Friedrich, R., Obermeier, A., Weppner, J., Kalthoff, N., Bäumer, D., Bitzer, A., Jay, K., Comparison of measured and calculated motorway emission data, *Atmospheric Environment,* 34, 2437-2450, **2000**

Vogt, U., Dreiseidler, A., Baumbach, G., Kurtenbach, R., Petrea, M., Kohler, M., Corsmeier, U.: Quality assurance for gaseous components and particulate matter within BAB II field experiment, *Atmospheric Environment*, 39, 5642-5664, **2005**

Volz, A., Kley, D.: Evaluation of the Montsouris series of ozone measurements made in the 19th-century, *Nature*, 332, 240-242, **1988**

Volz-Thomas, A., Slemr, J., Konrad, S., Schmitz, Th., Apel, E.C., Mohnen, V.A.: Quality assurance of hydrocarbon measurements for the German tropospheric research focus (TFS), *Journal of Atmospheric Chemistry,* 42, 255–279, **2002**

Wayne R.P.: Chemistry of Atmospheres, Oxford University Press, New York, **2000**

Weilenmann, M., Bach, C., Rudy, C.: Aspects of instantaneous emission measurement, *International Journal of Vehicle Design* 27, 94-104, **2001**

Weingartner, E., Keller, C., Stahel, W.A., Burtscher, H.: Aerosol emission in a road tunnel. *Environmental Science and Technology*, 31, 451-462, **1997**

Weinstock, B.: Carbon Monoxide: Residence Time in the Atmosphere, *Science*, 166, 224-225, **1969**

Wickert, B., Pregger, T., Theloke, J., Friedrich, R.: Emissionen Gesundheitsschadlicher Stoffe bei Produktionsprozessen, im Verkher und im Privaten Bereich, Arbeitsgruppe Luftreinhaltung der Universitat Stuttgard ALS, 25-35, **1999**

Winkler, J., Blank, P., Glaser, K., Gomes, J.A.G., Habram, M., Jambert, C., Jaeschke, W., Konrad, S., Kurtenbach, R., Lenschow, P., Lörzer, J.C., Perros, P.E., Pesch, M., Prümke, H.J., Rappenglück, B., Schmitz, Th., Slemr, F., Volz-Thomas, A., Wickert, B.: Ground-based and airborne measurements of nonmethane hydrocarbons in BERLIOZ: analysis and selected results, *Journal of Atmospheric Chemistry*, 42, 465-492, **2002**

Winkler, J.: Atmosphärische Nichtmethan-Kohlenwasserstoffe im Grossraum Berlin/ Branderburg: Messtechnik, Bestandsaufnahme und Beiträge zur lokalen Photooxidantienbildung, Ph.D. Thesis, *Johann Wolfgang Goethe Universität, Frankfurt am Main*, **2001**

Xie, S., Bluett, J.G., Fischer, G.W., Kuschel, G.I., Stedman, D.H.: On-road remote sensing of vehicle exhaust emissions in Auckland, New Zealand, *Clean Air and Environmental Quality*, 39 , **2005**

Zielinska, B., Sagabiel, J. C., Harshfield, G., Gertler, A. W., Pierson, W.R.: Volatile Organic Compounds up to C_{20} Emitted from Motor Vehicles, Measurements Methods; *Atmospheric Environment*, 30, 2269-2286, **1996**