Impact of Road Traffic Emissions on the Ozone Formation in Germany

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by
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To

my parents
&
Shantana

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Abstract

Several measurement campaigns of nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x) were carried out in a road traffic tunnel (the Kiesberg tunnel) and in the city of Wuppertal in order to investigate the road traffic exhaust and their impact on city air. In addition, measurements were carried out in a rural area (Menz) of Germany for comparing and explaining indirectly some aspects of the emission situation of the city of Wuppertal.

The three measurement campaigns during 1997-98 in the Kiesberg tunnel showed similar NMHCs-profiles relative to benzene. They indicated that in spite of the increase of catalyst-equipped passenger cars in the administrative area of Düsseldorf, there were no significant changes in the road traffic exhaust situation in the case of NMHC emissions over this period of time due to the very high contribution of NMHC emissions from the uncontrolled vehicles (so-called super emitters). The NMHC-profile for the road traffic exhaust shows almost equal percental contribution of alkanes, alkenes/alkynes and aromatic compounds. Toluene (1.7±0.5 ppbC/ppbC) among the aromatic compounds, ethene/ethyne (2.5±0.8 ppbC/ppbC) among the alkenes/alkynes, and *iso*-pentane (1.2±0.4 ppbC/ppbC) among the alkanes showed the largest emission ratios relative to benzene. These compounds within their respective emission ratios can thus be considered as markers for road traffic exhaust. A comparison of the fuel's composition with the compostion of the road traffic exhaust in the Kiesberg tunnel indicates an increase of the alkene contribution during the combustion. The NMHC/NO_x ratio in ppbC/ppbv was found to be 0.6–2.0 for weekdays and 4.4±0.4 for weekends, which are in agreement with literature studies. The emission factors (mg/km) and emission indices (g/kg fuel) of NMHCs and NO_x for light duty vehicles (LDV) and heavy duty vehicles (HDV) were calculated by comparing their measured emission ratios relative to CO_2 with the emission value of CO_2 in mg/km (using the German Handbook of Emission Factors for Road Transport) and in g/kg fuel (literature values), respectively, and compared with other studies. The applicability of these factors and indices for estimation of the emissions from LDV in North-Rhine Westfalia is also presented.

The NMHC-profile for the city air of Wuppertal showed that the percental contributions of alkanes, alkenes/alkynes and aromatic hydrocarbons were 57.2±6.5%, 14.5±3.6% and 28.3±5.1%, respectively. Comparison with other literature values shows that the toluene/benzene emission ratio (1.7±0.5) can justifiably be used as a marker for the road traffic sector in a region or an air mass. The calculated NMHC/NO_x values (2.4–4.8) for the city air of Wuppertal agreed well with those of other studies of urban areas. The higher values of this ratio in comparison with that of the Kiesberg tunnel can be explained by the more frequent urban stop-and-go driving situation in the city. It was also confirmed that the limit values for benzene and NO_2 prescribed by the Federal immission control act of Germany (1998) were not exceeded in the city of Wuppertal.

A comparison of the NMHC-profile relative to benzene (ppbC/ppbC) for the city of Wuppertal with that of the tunnel air showed that road traffic still has the largest contribution in the measured NMHC-mix (in the range of C_2-C_9) for the city of Wuppertal, which is in contrast with the report of Federal Environment Agency of Germany (Umweltbundesamt), and this can also be generalized for other German cities. The comparison also showed small effects possibly from other sources, namely solvents and leakage of natural gas. The calculations of percental OH reactivities and the approximate percental MIR and POCP indices for the tunnel air and the city air of Wuppertal showed that only a few NMHCs had major contributions with regard to the ozone formation potential of the measured NMHC-mix and alkenes had the largest percental contribution.

Contents

1 Introduction

1.1 State of knowledge

1.1.1 General

Due to the emissions of trace gases originating from biogenic and in particular anthropogenic activities, the atmospheric environment of the earth is changing dramatically (Hewitt *et al.*, 1999). The emission of radiatively active gases, such as carbon dioxide, methane and nitrous oxide, affects the earth's energy balance, giving rise to an increase in temperature and other changes to the climate. Emissions of ozone depleting substances, including the synthetic chlorofluorocarbons, are causing changes to stratospheric ozone concentrations and hence to the amount of UV light reaching the earth's surface. Emissions of reactive inorganic pollutants, for example, sulfur dioxide and nitrogen oxides are causing acidification of natural waters and soils at the regional scale. Emissions of reactive volatile organic compounds are causing changes to atmospheric chemistry, particularly, the oxidizing capacity of the troposphere, over the whole range of spatial scales, *i.e.* from the local urban scale through the regional scale and ultimately to the global scale. The emissions from the biosphere contribute to the background chemistry of the atmosphere, but in urban areas the composition of air is mostly determined by anthropogenic emissions.

1.1.2 Role of NMVOC and NO_x

Nonmethane volatile organic compounds (NMVOCs) are of major importance in tropospheric chemistry. Together with nitrogen oxides ($NO_x = NO + NO_2$), they contribute to the photochemical production of secondary pollutants such as ozone, peroxyacetylnitrate (PAN), hydrogen peroxide, organic peroxides, organic acids and transient oxidizing species such as hydroxy (OH), hydroperoxy (HO_2) and organic peroxy (RO_2) radicals, which lead to photosmog formation. In the late 1940s and early 1950s it was first observed in Los Angeles (Haagen-Smit *et al.*, 1953). Over the succeeding years, it has been observed in all major and populated centres of the world. In Europe, it was first recognized in the Netherlands in 1965 (Houten, 1966).

VOC (volatile organic compounds) emissions also contribute to particulate matters (PM) via the formation of semi-volatile reaction products that undergo gas-to-particle conversion in the atmosphere. Some VOCs are toxic. For example, benzene, 1,3-butadiene, formaldehyde, acetaldehyde and polycyclic organic matter (POM) are toxic compounds, which are known to cause or suspected of causing cancer or other serious health effects (US EPA, 1994; Claydon *et al.*, 1999). Polycyclic aromatic hydrocarbons (PAHs) are an important component of POM. Some toxic VOCs are emitted directly to the atmosphere (*e.g.*, benzene, 1,3-butadiene and POM), whereas others are also formed *in situ* from other VOCs by chemical reactions.

1.1.3 Formation of ozone, nitrate and other photooxidants

Ozone is an important pollutant in terms of health effects, with clear impacts at all levels of morbidity and an effect on bringing forward death (Ayres, 1998). It has also an adverse affect on vegetation and material.

Figure 1.1 shows a simple scheme of the tropospheric ozone formation including the relevant processes and their relationships with each other. It is known that the formation of tropospheric ozone occurs through the formation of $O(^3P)$ atoms, which are formed through the photolysis of NO_2 by $\lambda<420$ nm:

$NO_2 + h\nu\ (\lambda<420\ \text{nm}) \rightarrow NO + O(^3P)$ (R 1.1)
$O(^3P) + O_2 + M \rightarrow O_3 + M$ (R 1.2)
$O_3 + NO \rightarrow NO_2 + O_2$ (R 1.3).

These three reactions form the so-called photostationary state (Leighton, 1961). Because through this cycle a fast transformation of NO and NO_2 is possible, these compounds are written together as NO_x.

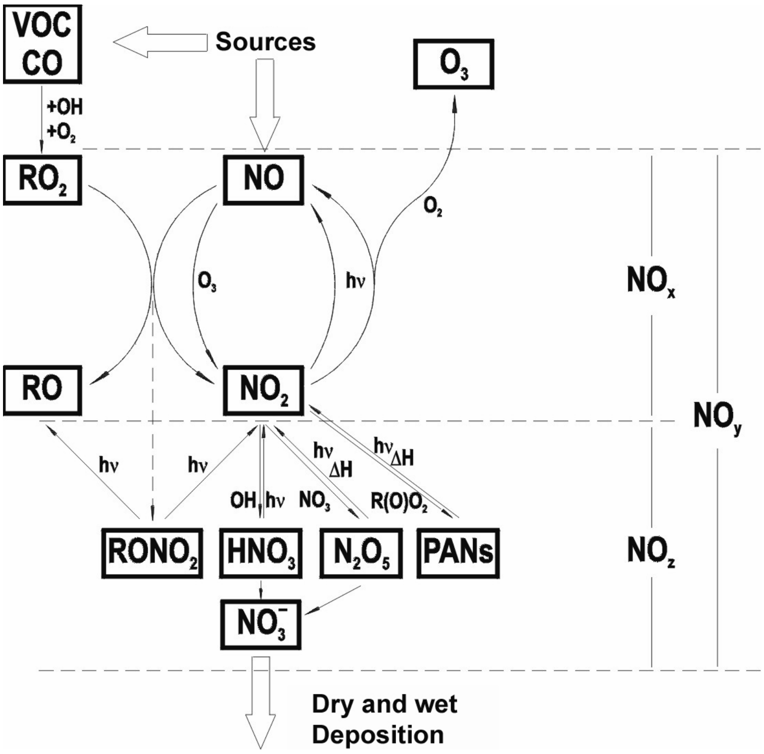


Figure 1.1 Simple scheme of the tropospheric ozone formation and the relevant processes (Source: Volz-Thomas *et al.*, 1992, 1995).

A net ozone production is only possible if NO is oxidized to NO_2 by something other than O_3. This occurs by peroxyradicals (RO_2 and HO_2):

$RO_2 + NO \rightarrow RO + NO_2$ (R 1.4)
$HO_2 + NO \rightarrow OH + NO_2$ (R 1.5).

These peroxy radicals can be formed by the oxidation of hydrocarbons and carbon monoxide, initiated by hydroxyl radicals (Lightfoot *et al.*, 1992):

$RH + OH + O_2 + M \rightarrow RO_2 + H_2O + M$ (R 1.6)
$RH + OH + 2O_2 + NO + M \rightarrow HO_2 + H_2O + RCHO + NO_2 + M$ (R 1.7)
$CO + OH + O_2 + M \rightarrow HO_2 + CO_2 + M$ (R 1.8).

Some sources of hydroxyl radicals are briefly discussed in the following:

$O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D)$ ($\lambda \leq 335$ nm) (R 1.9)
$O(^1D) + H_2O \rightarrow 2OH$ (R 1.10)
$HONO + h\nu \rightarrow OH + NO$ ($\lambda < 400$ nm) (R 1.11)
$H_2O_2 + h\nu \rightarrow 2OH$ ($\lambda < 315$ nm) (R 1.12).

The photolysis of ozone forms $O(^1D)$ atoms, and by reaction with water they form OH radicals.

HONO is one of the substances directly emitted from gasoline and diesel motors (Kurtenbach *et al.*, 2001a). It is also well established that heterogeneous conversion processes of NO_2 on different surfaces lead to the formation of HONO (Lammel and Cape, 1996). As shown in R 1.11, HONO also produces OH radicals at $\lambda < 400$ nm.

H_2O_2 is also one of the sources of OH radicals in the atmosphere as shown in R 1.12. Besides, during the photochemical reactions of hydrocarbons OH radicals are primarily consumed, but in further degradation processes they are reproduced in the form of HO_2 radicals through chemical reactions and photolysis of carbonyl compounds.

The initiating reaction for the ozone formation, as shown in Figure 1.1, is the reaction of OH mainly with VOC.

The oxidation of VOCs is dominated during the night-time by reactions with nitrate radicals and ozonolysis (Paulson *et al.*, 1996; Paulson *et al.*, 1999) forming peroxy radicals. The main source of nitrate radicals in the planetary boundary layer is the reaction of NO_2 with ozone:

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (R 1.13).

During the daytime, the lifetime of NO_3 is limited by the rapid photolysis to NO_2 or NO at $\lambda < 640$ nm, with NO_2 + O being the favourable path (Orlando *et al.*, 1993). On the other hand, NO_3 can react directly with NO and several VOCs or be lost to aerosol surfaces or by dry deposition. It can also be depleted indirectly via sinks of N_2O_5, which is formed by NO_3-NO_2 combination.

Reactive hydrocarbons and photochemical ozone formation are inextricably linked through the set of fast free-radical reactions that occur in the sunlight-irradiated atmospheric boundary layer. These reactions establish steady-state concentrations of a number of highly reactive free-radical species (*e.g.* OH, HO_2, RO_2) that control the formation and destruction of a wide range of major tropospheric trace gases.

1.1.4 Degradation chemistry of NMHC

Since the present work involves the measurement of nonmethane hydrocarbons (NMHC), in the following there is only a brief discussion of only the main features of the degradation processes of these compounds.

1.1.4.1 Alkanes

The principal reaction of alkanes in the troposphere is with the OH radical proceeding by H atom abstraction from C-H bonds. Generally the OH radical will tend to abstract the most weakly bound hydrogen atom in the molecule. The overall OH rate constant reflects the number of available H atoms and the strengths of the C-H bonds for each. By considering the subsequent reaction of HO_2 with NO, the net reaction of the atmospheric oxidation of alkanes (*e.g.* propane) is:

$$CH_3CH_2CH_3 + OH + 2NO \rightarrow 2NO_2 + CH_3C(O)CH_3 + OH \qquad \text{(R 1.14).}$$

The reaction of alkanes with NO_3 radicals is generally of minor (≤10%) importance as an atmospheric loss process under daytime conditions. This reaction proceeds via H-atom abstraction from C-H bonds:

$$RH + NO_3 \rightarrow R + HNO_3 \qquad \text{(R 1.15).}$$

1.1.4.2 Alkenes

The major reaction of alkenes under global tropospheric conditions is with the OH radical. In the case of alkenes, OH adds to the double bond. By considering subsequent reaction of HO_2 solely with NO, the overall result of hydroxyl radical attack on ethene, for example, is:

$$C_2H_4 + OH + 2NO \rightarrow 2NO_2 + 1.44\ HCHO + 0.28\ HOCH_2CHO + OH \qquad \text{(R 1.16).}$$

By comparing R 1.14 with R 1.16, the similarities in the NO to NO_2 conversion and the formation of oxygenated products can be seen.

As expected, the OH reaction mechanisms of the higher alkenes are more complex than that of ethene.

Alkenes will also react with ozone. The reaction with ozone can be an important alkene oxidation path. For some compounds this reaction can be faster than the reaction with OH. It is of great importance that alkene+O_3 reactions also produce OH radicals with a significant yield.

Due to the relatively high concentration of NO_3 during the night, NO_3 can play an important role in the degradation of alkenes in the night time. Geyer (2000) calculated that the relative contribution of NO_3 to the oxidation of the olefenic VOC is about 30% on a 24 h average.

1.1.4.3 Aromatic hydrocarbons

Aromatic hydrocarbons (AHCs) and their degradation products play particularly an important role in urban air pollution (Calvert *et al.*, 2001) and often act as markers reflecting the origin of their sources (McKeen and Lui, 1993; Gelencsér *et al.*, 1997; Christensen *et al.*, 1999; Volz-Thomas *et al.*, 2000).

Aromatic hydrocarbons are an important class of VOCs present in the atmosphere and oxidation through atmospheric reactions is their main removal pathway. The main chemical species that initiates reactions of aromatic compounds in the atmosphere is the hydroxyl radical. For example, benzene produces phenol and other products and similarly, from toluene *ortho*-, *meta*-, *para*-cresol, benzaldehyde and other products are formed. There are mainly two ways for OH to react with aromatic compounds: one is addition of OH to the ring system and another is H-abstraction from the C-H of the ring or the side chain (Andino *et al.*, 1996;. Lay *et al.*, 1996; Klotz *et al.*, 1997, 1998; Kwok *et al.*, 1997). There can be a third pathway of OH addition to >C=C< bond(s) present in the side chain (Smith *et al.*, 1996). However, the reaction of OH radicals with aromatic substituent groups is usually a much less important channel than OH addition to the aromatic ring (Atkinson, 1994). It is already established that the addition path (~90%) predominates over abstraction path (~10%). In short, the mechanism of OH-aromatic reactions remains today one of the least understood area in tropospheric chemistry.

Reactions of the aromatic compounds with ozone under atmospheric conditions are negligible in comparison with reactions with OH radical.

Reaction with the nitrate radical is also significant for aromatic compounds containing alkenic or phenolic groups. Kurtenbach *et al.* (2001b) found that NO_3 radical reactions are important in urban air in the daytime.

The reaction of aromatics with ground state oxygen atoms, $O(^3P)$, is of little importance in the urban atmosphere. Aromatic compounds generally react rapidly with OH, so that the typical atmospheric lifetimes of most aromatic compounds are in the range of hours to days. Consequently, most of them will tend to react in fairly close proximity to where they are emitted. The least reactive aromatic hydrocarbon, benzene, has an atmospheric lifetime on order of ten days, and its transport can occur for hundreds or thousands of km.

1.1.4.4 Overview

Table A1 I (in the Annex-Tables) shows the k-values of reactions of hydrocarbons with OH radical, ozone and NO_3 radical (Atkinson 1991, 1994, 1997, 2000; De More *et al.*, 1997; National Institute of Standard and Technology (NIST) data base, 1998). The life times of the hydrocarbons are also shown in Table A1 II (in the Annex-Tables) using the average values of these reactants (OH, O_3, NO_3) in the atmosphere during the daytime and the night-time (Calvert *et al.*, 2001). The main reaction initiators of nonmethane volatile organic compounds are hydroxyl radicals in the daytime and the calculated lifetime is in the range of hours, whereas nitrate radicals are the main reaction initiators during the night-time and the calculated lifetime is mostly in the range of days. Table 1.1 shows a summary of the qualitative comparison of rate constants of different reaction initiators.

Table 1.1: Qualitative comparison of the rate constants for different reaction initiators (Calvert *et al.*, 2001).

Classes	OH	O_3	NO_3	$O(^3P)$	Photolysis
Alkanes	slow to medium	–	–	–	–
Alkenes	medium to fast	fast	medium to fast	fast	–
Aromatics	slow to fast	none to medium[a]	none to fast [b]	–	–
Oxygenated hydrocarbons	slow to fast	–	slow to medium	–	slow to fast

Blank cells (–) indicate rates which are negligibly slow. a: Reaction with O_3 is only significant for aromatic alkenes. b: Reaction with NO_3 is only significant for aromatic alkenes and phenols.

1.2 Emission Estimate of NMVOC and NO_x

Large quantities of volatile organic compounds (VOC) are emitted into the troposphere from anthropogenic and biogenic sources (Arey *et al.*, 1991; Winer *et al.*, 1992; Guenther *et al.*, 1995, 2000; König *et al.*, 1995; World Meteorological Organization (WMO), 1995; Sawyer *et al.*, 2000; Placet *et al.*, 2000). Emissions of VOCs not only comprise a broad spectrum of species, but also are due to a wide variety of sources (Friedrich *et al.*, 1999). The anthropogenic sources of nonmethane organic compounds (NMOC) include:

- combustion processes (vehicle and fossil-fuelled power plant emissions),
- production, treatment, storage, and distribution of fossil fuels,
- application of volatile organic solvents and solvent-containing products,
- industrial production processes and
- landfills and hazardous waste facilities (Sawyer *et al.*, 2000; Placet *et al.*, 2000).

World-wide anthropogenic emissions of NMOC are estimated at 142 Tg/yr (Middleton, 1995).

Nitrogen oxides are emitted into, or produced in the troposphere. NO is emitted from soils and natural fires and is formed *in situ* in the troposphere from lightning (National Research Council (NRC), 1991; WMO, 1995). It is emitted from combustion processes such as vehicle emissions and fossil-fuelled power plants (NRC, 1991). The estimated world-wide anthropogenic emissions of NO_x are 72 Tg (NO_2)/yr (Müller, 1992). In urban areas, NMOC and NO_x from anthropogenic sources dominate over those from natural sources, while in rural and remote areas NMOC from natural sources dominate (Chameides *et al.*, 1992). For example, isoprene dominates over anthropogenic NMOC in the south-eastern USA (Geron *et al.*, 1994, 1995).

The mass percental contribution of natural and anthropogenic sources to the total emission of VOCs and NO_x for the global and northern hemisphere are shown in Table 1.2.

Table 1.2: Mass% contribution of natural and anthropogenic sources to the total emission of tropospheric ozone precursors in 1990 (CORINAIR, 2001).

Sources		VOCs	NO_x*
Global	Anthropogenic	10%	76%
	Natural	90%	24%
Northern hemisphere	Anthropogenic	16%	84%
	Natural	85%	16%

* NO_x was calculated as NO_2.

In the following, the emission situation of VOC and NO_x in Germany and Europe are briefly discussed.

1.2.1 Germany

Table 1.3 shows the emission of NMVOCs and NO_x in Germany ('Daten zur Umwelt', 1997; Umweltbundesamt (UBA), 2001).

Table 1.3: Emissions of NMVOCs in kt and NO_x in kt (calculated as NO_2) in Germany from 1990 to 1999 ('Daten zur Umwelt', 1997; UBA, 2001).

	Sector of Sources	1990	1992	1994	1996	1997	1998	1999
NMVOC	Solvent	1160	1090	1090	1010	1010	1000	1000
	Industry	156	136	136	127	129	131	138
	Fuel gain and transportation	220	181	88	82	72	63	54
	Other traffic	78	59	65	50	52	54	51
	Road traffic	1404	952	677	541	463	403	336
	Household	103	59	52	66	60	54	53
	Energy and long distance heating works	587	512	488	313	285	272	250
	Small consumer	9	7	8	5	5	5	5
	Industry fire	14	11	11	8	8	8	8
	Energy and long distance heating works	10	9	9	7	6	6	6
	Total in kt	3155	2505	2135	1896	1805	1725	1651
NO_x	Industry	34	23	23	13	13	13	12
	Other traffic	266	228	237	207	214	221	212
	Road traffic	1223	1155	1046	956	897	853	833
	Household	108	109	103	105	97	91	82
	Small enterprises	68	58	59	49	39	38	33
	Industrial fire	354	272	254	234	237	222	215
	Energy and long distance heating works	587	512	488	313	285	272	250
	Total in kt	2640	2357	2211	1877	1781	1709	1637

Table 1.3 shows that the total NMVOC and NO_x emissions are decreasing with time as a consequence of the emission reduction strategy for the ozone precursors in Germany. One can also understand by observing Table 1.3 that the trend of the reduction of NMVOC emission from the road traffic sector was faster than that of NO_x in absolute value. In addition to the road traffic, there is also a moderate contribution from power stations and other traffic (*e.g.* airlines, ship and rail) to the total anthropogenic emission of NO_x.

Table A1 III (in the Annex-Tables) presents a comparison of emissions of NMVOC and NO_x of Germany with those of America and various European countries (Eggleston *et al.*, 2000). According to this Table, it can be seen that the Directive of National Emission Ceilings for Germany will be 924 kt for NMVOC and 1051 kt for NO_x in the year 2010.

It can also be observed from Table 1.3 that according to UBA, although the anthropogenic emissions of NMVOC are decreasing, the contribution from the solvent sector is increasing relatively with the time in comparison with that from the road traffic sector, which can be visualized in Figure 1.2.

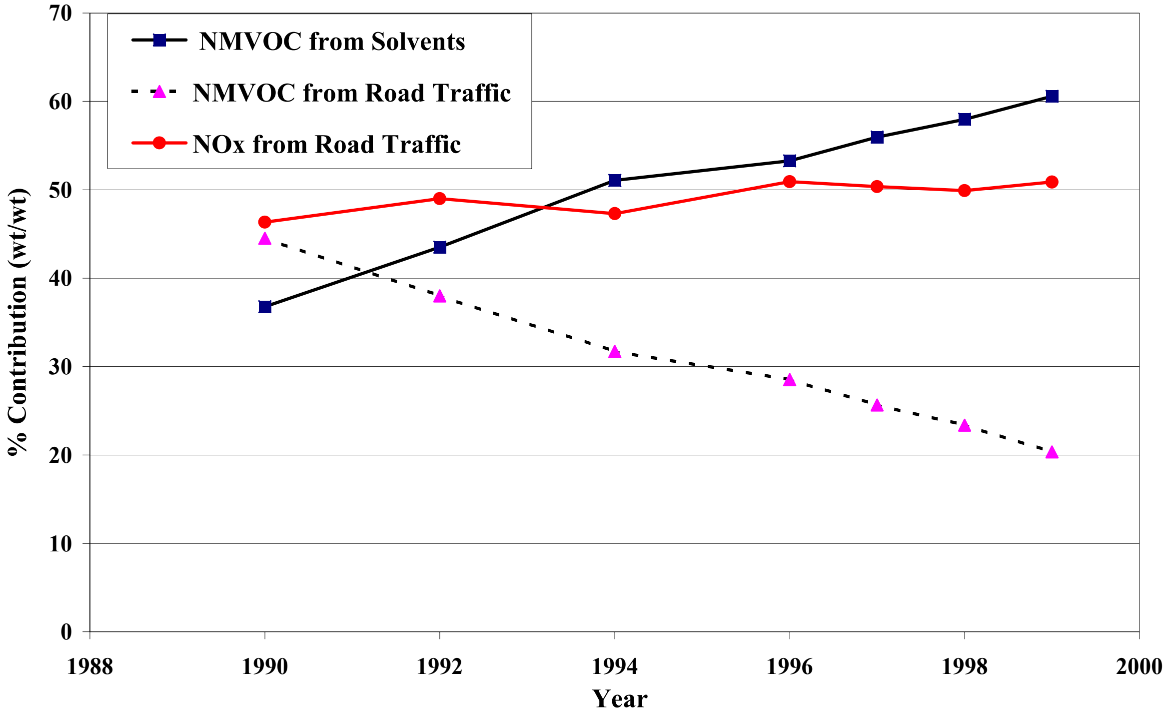


Figure 1.2 Variation of the weight percental contribution (wt%) of NMVOC from the solvent and road traffic sectors and of NO_x from the road traffic sector of Germany from 1990 to 1999 according to UBA (2001).

Figure 1.2 shows that 20% of the total NMVOC emissions and 51% of the total NO_x emissions in Germany were caused by road traffic in 1999 as reported by the Federal Environment Agency of Germany (UBA, 2001). It also shows that the relative contribution of NO_x from the road traffic sector remains almost constant, whereas the relative contribution of NMVOC from the solvent sector seems to be three times as high as that from the road traffic sector. In contrast, Thijsse *et al.* (1999) found that road traffic exhaust contributed to ~80-90% of the non-methane hydrocarbons (NMHC) concentrations in the city of Berlin, Germany.

1.2.2 Europe

According to the CORINAIR report, the EU emission of ozone precursors decreased 15% from 1990 to 1996, while the GDP (gross domestic product) rose showing a decoupling from GDP (Eggleston *et al.*, 2000).

Only 72% of European NMVOC emissions are covered by the top ten sub-sectors as shown in Figure A1 I (in the Annex-Figures). This is due to the fact that emissions of organic compounds occur in many sectors and the sources are therefore widespread. The three most important sub-sectors of the European total of 22 million tonnes are road transport-passenger cars (16%), followed by nature-coniferous forests (11%) and solvent use-paint applications (9%).

Europe emitted 18 million tonnes of NO_x in 1990. Figure A1 II (in the Annex-Figures) shows the contribution of different sources of NO_x for the top ten sub-sectors. From this total amount, road transport-Passenger Cars (PC) contributed 23%, Heavy Duty Vehicles (HDV) 18% and public power and cogeneration plants 20%.

From another report of the European Environment Agency (Ritter, 1998) on 1994 emission estimates in the EU-15 countries, it is also clear that in Europe, the largest contribution of NMVOCs and NO_x is road transport. Therefore, the European situation also contradicts the report of UBA.

1.3 Measurements of NMVOC and NO_x

Up to now, only a few studies have been available in which NMVOC and NO_x emissions from vehicles were determined (Lonneman *et al.*, 1986; Gregori *et al.*, 1989; Hassel *et al.*, 1994, 1995; Staehelin *et al.*, 1995; Kirchstetter *et al.*, 1996; Pierson *et al.*, 1996; Rogak *et al.*, 1998; Fraser *et al.*, 1998b; Keller *et al.*, 1999). There exist some measurements in Germany of the total NMVOC (UMEG, ZIMEN) without the differentiation of the contribution of individual components. However, the information on the emission ratios of individual hydrocarbons is of paramount importance because of their different propensities for ozone formation. There are only a very limited number of studies (Kern *et al.*, 1998; Schmitz, 1997; Mannschreck, 2000) that provide information about the individual hydrocarbons present in a NMHC-mix from the road traffic emissions of Germany. Therefore, it is important to obtain a typical German NMHC-profile and a typical classification of the NMHC/NO_x ratio for the ground level air of Germany differentiating the individual hydrocarbons.

1.3.1 Air pollutant reduction strategy

Despite the fact that hydrocarbons and NO_x have long been identified as the two key precursors of photochemical ozone, the development of an effective strategy for reducing ozone production in photochemical smog by controlling anthropogenic emissions of these precursors has proven to be problematic (Chock and Heuss, 1987; Chameides *et al.*, 1992).

The dependence of ozone production on the initial amounts of VOC and NO_x is frequently represented by means of an ozone isopleth diagram. Such a diagram is a contour plot of maximum ozone concentrations achieved from a large number of simulations with an atmospheric VOC/NO_x chemical mechanism with varying initial concentrations of VOC and NO_x while all other variables are constant.

When hydrocarbon levels are relatively high and NO_x levels are relatively low, the isopleths are oriented horizontally indicating that O_3 production is limited by the availability of NO_x, so that reductions in hydrocarbons have little or no effect on ozone. This is typical of suburban, rural and downwind areas. Under this condition, a further use of catalysts for the reduction of NO_x will efficiently reduce the concentration of ozone.

Conversely, when hydrocarbon levels are low and NO_x levels are high, the isopleths are almost vertical, indicating that ozone production is limited by hydrocarbons and NO_x reductions are ineffective. This is typical of polluted air masses in urban areas.

The behaviour in the VOC limiting region can be used to explain the “weekend effect” of the higher ozone concentrations compared to the weekdays in urban areas. It is due to the lower emissions of NO_x during the weekend which occurs partly due to the smaller contribution of diesel vehicles operating during the weekend (Altshuler *et al.*, 1995; Dreher *et al.*, 1998; Brönnimann *et al.*, 1997).

Thus in order to devise an effective strategy for ozone abatement in a given airshed, it is first necessary to determine where on the ozone isopleth diagram this airshed is located. However, complexities can arise due to natural emissions. Even if an airshed is in the VOC-limited region of the ozone isopleth diagram, hydrocarbon reductions may not be effective, because these natural sources cannot be controlled (Trainer *et al.*, 1987; Chameides *et al.*, 1988; 1992). Therefore, a reliable assessment of the relative contribution of anthropogenic and natural precursors to the airshed is important. Furthermore, important effects on the modelling results also come from the composition of the VOC-mixes, the diurnal variation of the emission and the nature of the transport processes.

Isopleth diagrams serve until now as the graphic illustration of model investigation for the development of air pollutant reduction strategy. Based on the present knowledge about ozone formation, they can be used to explore qualitatively the implications of various control strategy options.

1.4 Reactivity scales

Different types of organic compounds react at different rates to form O_3 and other secondary pollutants in irradiated VOC-NO_x mixtures. VOCs are transformed in the troposphere by photolysis, reaction with the OH radical, reaction with the NO_3 radical (during the night-time) and reaction with O_3 (Atkinson, 2000). Mostly, because of their different tropospheric lifetimes and rates of reaction, VOCs exhibit a range of reactivities with respect to ozone formation.

The rate of ozone production from a given VOC is essentially a function of three factors: the atmospheric concentration of the species, its rate of reaction with OH (and NO_3 and O_3), and the number of ozone molecules produced each time the species is oxidized (Seinfeld and Pandis, 1998). Since some hydrocarbons are more reactive than others, strategies aimed at reducing ozone exposure levels should address the most reactive organic compounds. Thus, a reactivity scale is an ordered list of reactive organic compounds in which the ranking is based on the amount of ozone formed from each reactive hydrocarbon under particular atmospheric conditions. There are mainly five methods of producing reactivity scales for hydrocarbons, namely a) rate coefficient data for OH attack on hydrocarbons, b) smog chamber studies, c) air quality simulation models, d) explicit chemical mechanisms (Derwent *et al.*, 1998; Derwent, 2000) and e) focus on the emissions from motor vehicles.

According to some literature studies (Kern *et al.*, 1998; Thijsse *et al.*, 1997; Calvert *et al.*, 2001), it is possible to find out the components which contribute most to the total ozone forming potential of the hydrocarbon mix by using MIR (maximum incremental reactivity) (Carter, 1994, 1995) and POCP (photochemical ozone creation potential) indices (Derwent *et al.*, 1998). A specific reduction of these compounds should be considered in order to achieve an effective reduction of ozone concentrations in the environment of ozone precursor sources.

1.5 Emission factors

Emission factors and emission inventories have long been fundamental tools for air quality management. The importance of emission estimates is to develop emission control strategies, to determine applicability of permitting and control programmes, to ascertain the effects of sources and appropriate mitigation strategies, and a number of other related applications by an array of users (*e.g.* state, local agencies, industry etc.). Data from source-specific emission tests or continuous emission monitors are usually preferred for estimating a source's emissions because those data provide the best representation of the tested source's emissions (U.S. EPA, 1995). Test data from individual sources, however, are not always available and even when they are, they may not reflect the variability of actual emissions over time. Thus emission factors are frequently the best or only method available for estimating emissions, in spite of their limitations.

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (*e.g.* kilograms of particulate emitted per megagram of coal burnt). Such factors facilitate estimation of emissions from various sources of air pollution. In most cases, these factors are simply averages of all available data of acceptable quality, and they are generally assumed to be representative of long-term averages for all facilities in the source category (*i.e.* a population average).

Emission factors may be appropriate for use in a number of situations such as making source-specific emission estimates for area-wide inventories. The purposes of these inventories include ambient dispersion modelling and analysis, control strategy development and the screening of sources for compliance investigations.

Since in this present work road traffic emissions were studied, in the following the methods for determining EFs from this sector and relevant matters will be briefly discussed.

1.5.1 Road traffic emissions/tunnel studies

Road traffic is one of the most significant sources of primary air pollutants in the industrialized world (John *et al.*, 1999). To describe the amount of emitted air pollutants, emission factors (EF) or emission indices (EI) are used. EFs are defined as the emitted mass of an air pollutant per driven distance of a vehicle. EIs are defined as the emitted mass of an air pollutant per mass of fuel burnt. They are influenced by many factors such as type of engine (gasoline with/without catalytic converter or diesel), driving cycle and composition of the fuel (Staehelin *et al.*, 1997).

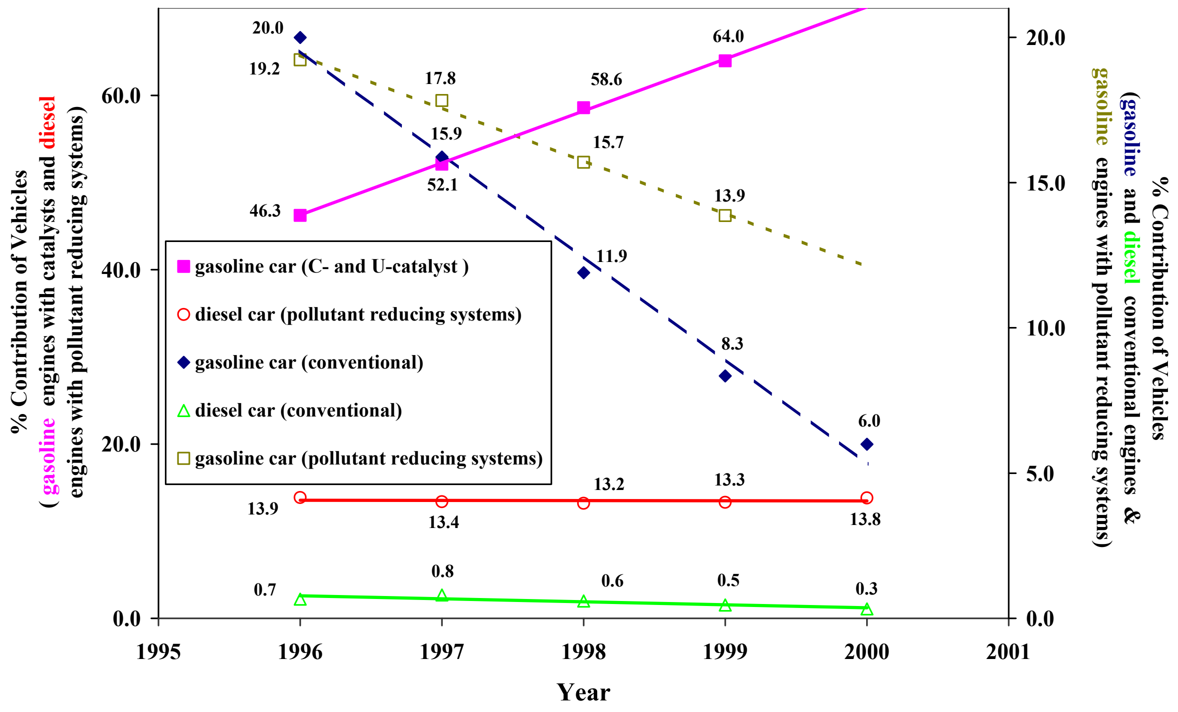
The determined emission factors are useful for a number of reasons: i) they enable an estimation of the relative contribution of vehicle exhaust to the total pollutants in an urban area, ii) they are necessary for determination of the health effects of particularly toxic compounds, and iii) they are essential for the development of realistic models of the formation of photochemical smog and secondary organic aerosols (Duffy *et al.*, 1999).

For a realistic estimation of the emission and the use of the vehicles in road traffic, it is necessary to investigate statistically representative vehicles and conditions. EFs can be obtained from exhaust gas measurements of single vehicles using chassis dynamometric tests (Sigsby *et al.*, 1987; Baily, 1990; Hoekman, 1992; Duffy *et al.*, 1999; Schmitz *et al.*, 1999, 2000; Heeb *et al.*, 2000a, 2000b). But average emission factors for large vehicle fleets can be calculated efficiently under real operating conditions by analysis of the concentration of individual pollutants in the air of road tunnels. Thus several tunnel studies have been performed and the data obtained represent car populations under various velocity and acceleration conditions (Lonneman, 1986; Ingalls, 1989; Pierson *et al.*, 1990, 1996; Staehelin *et al.*, 1997).

In general, from the calculated emission factors attempts have been made to differentiate the contributions from light duty vehicles and heavy duty vehicles (Zielinska *et al.*, 1996).

1.5.1.1 Effects of catalyst-equipped vehicles

It is known from the literature (Patyk, 1995; Keller *et al.*, 1999; Hassel *et al.*, 1994; Schmitz *et al.*, 1999) that the use of catalyst-equipped vehicles reduce drastically the emissions of nonmethane hydrocarbons and nitrogen oxides. It is also reported by the Federal Motor Transport Authority of Germany (Kraftfahrt-Bundesamt (KBA)) that the number of vehicles with catalysts and/or with pollutant-reducing systems is increasing. Figure 1.3 shows the percental distribution of catalyst-equipped and conventional gasoline and diesel powered passenger cars in the surrounding administrative area of Düsseldorf (KBA, 1996-2000).



C: controlled catalyst, U: uncontrolled catalyst.

Figure 1.3: Percental distribution of different types of passenger cars (PCs) in Düsseldorf administrative area, Germany.

From Figure 1.3, it is seen that from 1997 to 1998 the C- and U-catalyst-equipped gasoline driven passenger cars (PC) increased by about 13% and the conventional gasoline powered PCs decreased by 25%. Since the emissions from the conventional cars are much higher than those from the catalyst-equipped cars (Keller *et al.*, 1999; Schmitz *et al.*, 1999), the effect of the increasing number of these catalyst-equipped cars in the presence of conventional cars should be investigated.

1.6 Aim of the present work

There are contradictory reports about the contribution of the road traffic to the total anthropogenic NMVOC emissions in different studies. Accordingly, the main objective of the present study was to clarify the contribution of road traffic emissions to the total anthropogenic NMHC emissions budget, especially for the city air of Wuppertal. For this reason, measurements of NMHC and NO_x were carried out in a road traffic tunnel of Wuppertal (the Kiesberg tunnel) and in the city of Wuppertal. In addition, measurements were also carried out in a rural area of Germany (Menz) to obtain information about the background air quality and at the same time to supply additional information for explaining the emission situation of the city of Wuppertal.

Another objective of this work was to obtain a typical NMHC-profile for Germany from road traffic sector and at the same time to identify the markers from this sector by carrying out several measurement campaigns in the Kiesberg tunnel.

It is known from the statistical data of the Federal Motor Transport Authority of Germany (KBA) that the number of catalyst-equipped vehicles is increasing with time. Therefore, the third objective was to investigate the influence of the increased number of these types of vehicles in the total road traffic situation. It was also intended to calculate the emission factors for different NMHCs and NO_x from the measured values of CO_2 during the Kiesberg tunnel campaigns.

The determination of the typical German NMHC/NO_x ratio for the ground level air was also supposed to be carried out in the present study. Additionally, special consideration would be taken on the contribution of aromatic hydrocarbons to the total NMHC-mix.

It is also known from the literature that only a few NMHCs have major contributions to the total ozone formation potential of a NMHC-mix. Therefore, in this present study, an attempt was also made to determine these components for the city air of Wuppertal using trivial reactivity indices and to compare them with other literature studies.

Until now, the contribution of NMVOC from the solvent sector has been determined only by estimating their yearly consumption. Therefore, it was also planned to estimate indirectly the influence of solvents on the total NMHC-mix in the air composition of the city of Wuppertal by comparing the NMHC-profiles obtained from the tunnel and the city air of this study.

Finally, it was also intended in this work to generalize the influence of road traffic emissions on the city air composition of Germany by considering other literature studies.

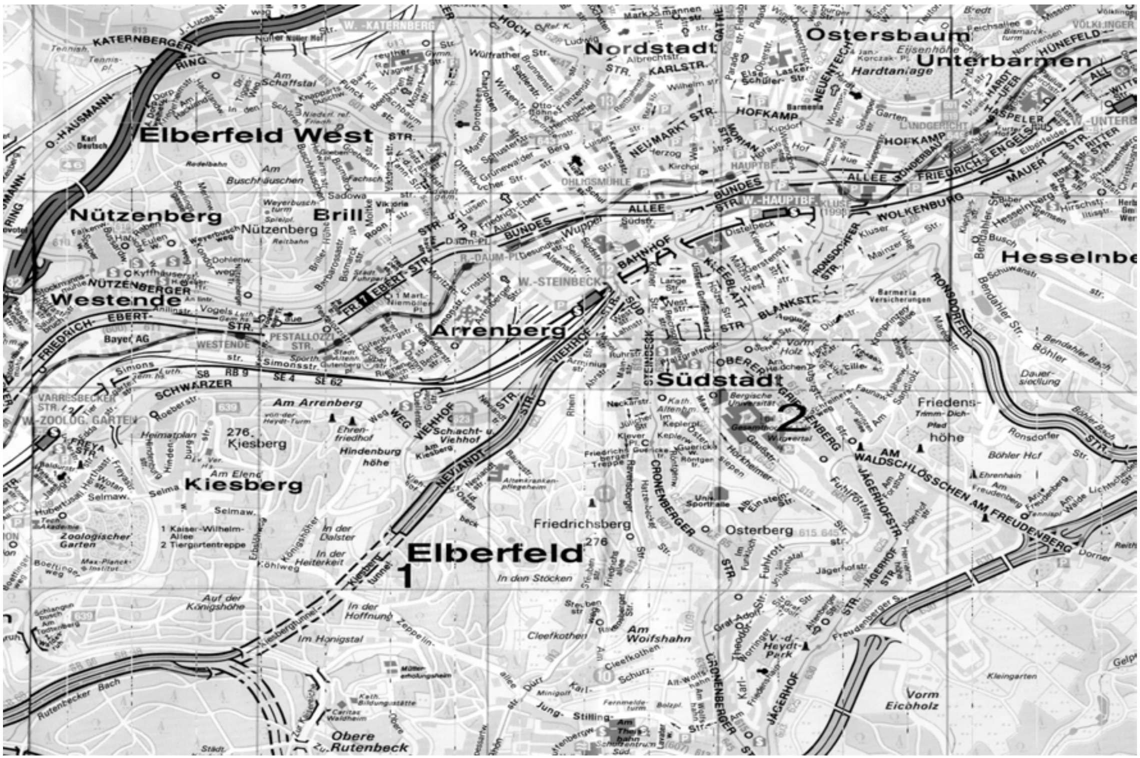
2 Experimental part

2.1 Measurement site

Mixing ratios of ozone precursors (NMHCs and NO_x) and CO_2 were measured in the Kiesberg tunnel of Wuppertal, in the city of Wuppertal and in a rural area (Menz) of Germany. In the following, the position of the measurement sites and related matters are briefly described.

2.1.1 Kiesberg tunnel

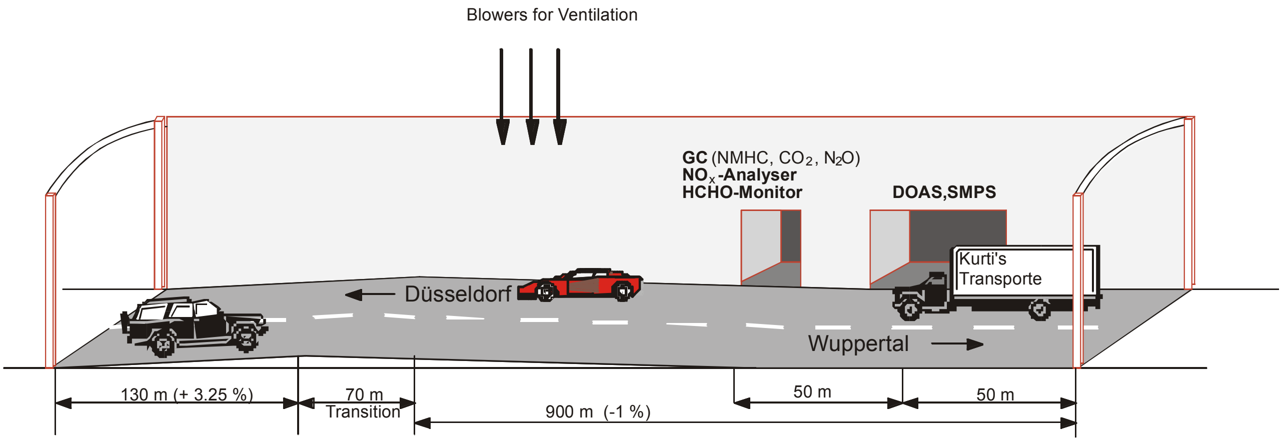
Figure 2.1 shows partially a map of Wuppertal indicating the position of the Kiesberg tunnel and the city air measurement site.



1. Kiesberg tunnel (length: 1.1 km), instruments were installed at the city-bound side, 100 m before exit. 2. Building of the University of Wuppertal.

Figure 2.1: Measurement sites in Wuppertal.

The tunnel has a length of 1.1 km and connects the freeway A46 between Düsseldorf and Wuppertal with the city of Wuppertal-Elberfeld. The tunnel consists of two independent tubes in east-west direction. During the measurement campaign in the tunnel the upper tube was closed for maintenance purposes. Measurements were carried out in the lower (eastbound) tube through which the vehicles passed in both directions. Looking from the western encounter the tunnel has a 3.25% incline for 130 m, which is then reduced over a distance of 70 m to a 1.0% decline that continues for 900 m to the exit. The sampling port was located 1000 m from the western entrance of the tunnel, 100 m before the eastern exit. Due to the position of the federal highway A46 near the tunnel, it is reasonable to assume that the engines of the vehicles which passed the sampling port were under “warm” driving conditions. It is also assumed that the air at the monitoring site was well mixed over the total cross-section of the tunnel by vigorous turbulence caused by the traffic flow. The sampling probe for a quasi-online gas chromatograph (GC) for monitoring nonmethane hydrocarbons (NMHC), chemiluminescence NO analysers, CO_2 monitor (GC) or FTIR (Fourier Transform InfraRed spectroscopy) system for monitoring CO_2 and some selected hydrocarbons were located along the 15 m base length of the DOAS (Differential Optical Absorption Spectrometry) White system. The DOAS system used for monitoring different air pollutants was installed and operated by a group from the University of Heidelberg, and the FTIR system was installed and operated by the 'Fraunhofer-Institut für Atmosphärische Umweltforschung' (IFU) of Garmisch-Partenkirchen. The sampling line consists of a stainless steel tube (length: 15 m, O.D.: 6.25 mm) with one sampling hole in each meter. The diameter of the sampling holes was varied to insure that the sample was collected uniformly from the same gas volume as that of the DOAS system. Figure 2.2 shows a simple sketch of the Kiesberg tunnel and the measurement sites.



1. The above sketch also shows the measurement sites of monitoring N_2O, HCHO and particles (using SMPS) in the tunnel, which were as well measured during different campaigns. 2. The percentage indicates the decline (positive) and incline (negative) grade of the tunnel.

Figure 2.2: A simple sketch of the Kiesberg tunnel, Wuppertal indicating the grade of the tunnel, the direction of the traffic and the measurement sites of different instruments.

As shown in Figure 2.2, there are blowers for ventilation which are connected with a carbon monoxide (CO) sensor. When the value of CO exceeds a certain limit, the blowers start automatically for up to 30 min to bring ambient air into the tunnel and thus diluting the concentrations of gaseous pollutants inside the tunnel.

To provide a comparison with the ambient background air, a sampling line was installed from the instrument site in the tunnel to a site approximately 100 m away from the tunnel exit in a forest, for measuring the ambient air outside the tunnel. The background air was continuously sampled through this line and periodically analysed to provide a comparison of the tunnel air with the outside background air.

2.1.2 City air measurement

In addition to the measurements in the road traffic tunnel, another station was also installed close to the city centre of Wuppertal for measuring air pollutants. It was located at the University of Wuppertal which is nearly 1 km away from the city centre of Wuppertal and about 60 m higher than the ground level of the city centre.

Wuppertal is situated at the south border of the Ruhr region and is about 30 km east of Düsseldorf. The city of Wuppertal is mainly located in a valley which is *ca.* 20 km long and 3 km wide. It is surrounded by small hills at a height of about 250 m above sea-level.

The sampling port for a GC and chemiluminescence NO analysers were located at the University building.

2.1.3 Rural area (Menz, Brandenburg)

In the framework of the Berlioz (Berlin ozone experiment) project, measurements were also carried out in a rural area, Menz, which is situated about 70 km north-west of Berlin (see Figure 2.3). The characterization of the gaseous precursors of ozone was carried out in a mobile monitoring laboratory. It was built in a 7.5 t truck. A simplified sketch of the installation of the instruments in the truck is shown in Figure A2 I (in the Annex-Figures). The truck was placed in a field near a farm-house in Menz. The same mobile laboratory was used for monitoring city air of Wuppertal at the University building.

Figure 2.3: Measurement site in Menz (70 km north-west of Berlin), the measurement was performed in a field near to a farm-house. The map also shows Schönhagen (south-west from Berlin) where the quality assurance for the Berlioz project was carried out.

2.2 Analytical Equipment

In general, non-methane hydrocarbons (NMHCs) and oxides of nitrogen (NO_x) were monitored during tunnel measurements and field campaigns in the city of Wuppertal and Menz. Additionally, CO_2 was monitored only during the tunnel campaigns. Table 2.1 summarized the different instruments used during these campaigns.

Table 2.1 List of analytical instruments (AI) used in the tunnel and field measurements by the Wuppertal group.

Place of the measuring campaigns	Kiesberg tunnel			City of Wuppertal	Menz
Sampling period	Aug., 1997	March, 1998	Nov.-Dec., 1998	Aug.-Sept., 1998	July-Aug., 1998
Components	AI	AI	AI	AI	AI
NMHCs	GC: AIRMOVOC HC2010 (Airmotec)	GC: AIRMOVOC HC2010 (Airmotec)	GC: AIRMOVOC HC2010 (Airmotec)	GC: AIRMOVOC HC2010 (Airmotec)	GC: AIRMOVOC HC2010 (Airmotec)
NO, NO_2	Chemilumin.: 14D/E (Thermoelectron)	–	Chemilumin.: APNA 350 (Horiba)	Chemilumin.: APNA 350 (Horiba), CDL 770AL ppt (Eco-Physics)	Chemilumin.: APNA 350 (Horiba), CDL 770AL ppt
CO_2	GC: A-TCD/ECD Chromato-Sud	GC: A-TCD/ECD (Chromato-Sud)	FTIR*: K300 (Kayser-Threde), M2400C (Midac)	–	–

*Operated by 'Fraunhofer-Institut für Atmosphärische Umweltforschung'. GC: Gas Chromatograph, Chemilumin.: Chemiluminescent analyser, FTIR: Fourier Transform Infrared Spectrometer.

The important characteristics of these instruments were discussed in the following section.

2.2.1 Nonmethane hydrocarbons (NMHCs)

Nonmethane hydrocarbons were monitored using the quasi-online Airmovoc 2010 gas chromatograph with FID detector. In the following, a description of this GC and about the measurement of NMHCs is given.

2.2.1.1 Measuring principle of Airmovoc 2010

Gas chromatograph Airmovoc 2010 is a compact autosampling instrument with a 19 inch format. A simple sketch of the monitor including the typical measurement set-up is shown in Figure 2.4.

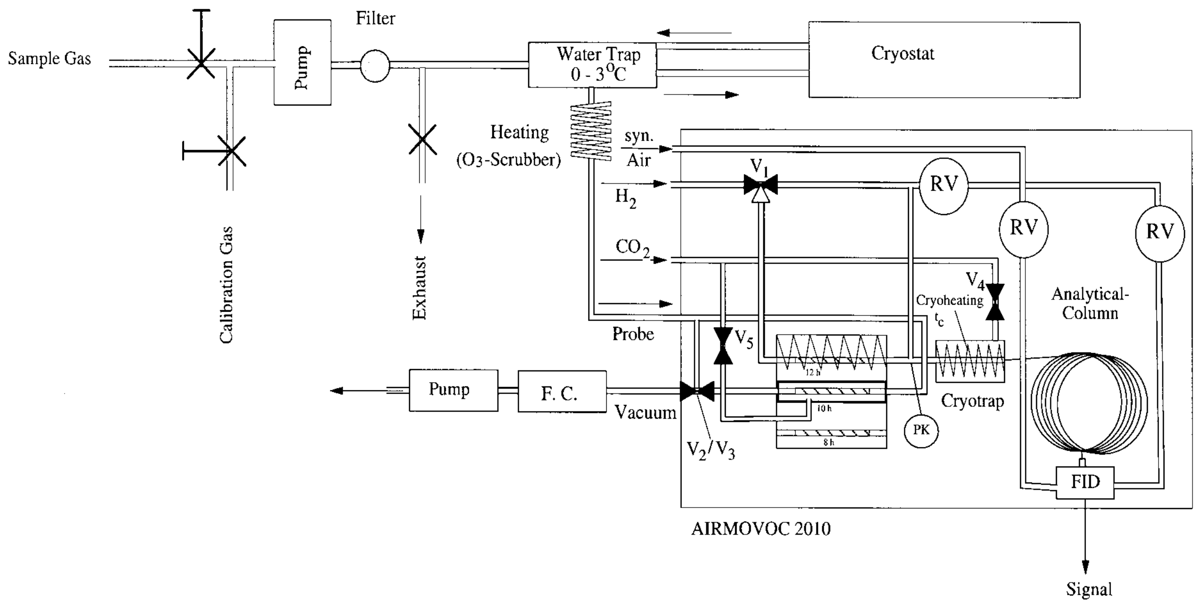


Figure 2.4: Simple sketch of Airmovoc 2010 including the typical measurement set-up (F.C.: flow controller, V: solenoid valve, RV: regulating valve (Piezo)).

As shown in the Figure 2.4, before drawing the gas sample by an external pump through the adsorption tubes of the Airmovoc monitor, it was first passed through a filter (pore-size of the filter paper: 10 μm), then passed through a base-water trap or humidifier having a fixed temperature of 3° C for keeping the gas sample with a constant relative humidity. The reason for this will be discussed in section 2.2.1.3. After that, the gas stream sample was passed through an ozone scrubber, a 50 cm long steel tube heated to ~70° C, for removing ozone present in the sample (Koppmann *et al.*, 1995; Schmitz, 1997).

The gas sample was then drawn through an adsorption tube containing adsorbents, namely Carbotrap and Carbosieve SIII in the ratio of 3:1, which adsorbed mainly C_2-C_9 hydrocarbons present in the sample. The absorption characteristics are listed in Table 2.2.

Table 2.2: Properties of the different absorbents (Source: Cao *et al.*, 1999; Camel *et al.*, 1995; Matisová *et al.*, 1995).

Adsorbent	Carbosieve S-III	Carbotrap	Carbopack B	Envi-Carb X*
Type	Carbon molecular sieve; Mesh: 60-80	Graphitized carbon black; Mesh: 20-40	Graphitized carbon black; Mesh: 60-80	Graphitized carbon black; Mesh: 120-400
Surface area (m^2/g)	820	120	100	250
Adsorption range	C_2-C_3	C_5-C_9	C_4-C_{14}	light hydrocarbons
Stability temperature (°C)	400	400	>400	maximum 500

*Personal communication: Axel Eggemann, After Sales Support, Airmotec GmbH, Essen, Germany; http://www.sigma-aldrich.com/supelco.

The adsorption tube was kept in a cylindrical drum. Six of them were arranged in a circular way on this cylinder having an angular distance of 60° or 2 hours (if the cross section of the cylinder is imagined as a clock) to each other. The cylinder carrying the adsorption tubes was cooled during the adsorption by using the cooling effect of the expanded CO_2 gas (from 60 bar to normal atmospheric pressure).

In an adsorption tube, two kinds of sorption materials were kept in such a way that the gas stream first passed through Carbotrap and then Carbosieve S-III sorbents. Carbotrap can adsorb the hydrocarbons containing higher number of carbon atoms and when the gas stream reaches at Carbosieve S-III adsorbent, it can then adsorb the hydrocarbons containing fewer number of carbon atoms. After collecting the NMHCs in the adsorption tubes, they were desorbed during the next measurement-cycle in the reversed way. The carrier and combustion gas hydrogen was allowed to pass through Carbosieve S-III and then through Carbotrap. The direct flow procedure is carried out in order to get complete adsorption of the hydrocarbons in the respective parts of the adsorbents in the tube and the reverse flow procedure is carried out for the easy desorption of the hydrocarbons from those respective parts of the adsorbents in the tube, according to the convenient sorption capacities (Table 2.2). The adsorption tube was made of glass with two steel endings. Since each adsorption tube has its own characteristic properties, one should consider each tube individually during the data evaluation. Therefore, during most experiments, instead of six, three adsorption tubes (tube number 2, 4 and 6) were used for collecting sample gas for reducing the load of the data-evaluation work.

The sampling time was varied according to the concentration of the NMHCs in the sample gas. Using this instrument, simultaneous adsorption of fresh sample and desorption of the adsorbed sample from last run can be carried out. Thus for a typical method, after adsorption at 10 hour 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 hour position). The tube was then flushed with carrier gas (Hydrogen, 5.0) and heated simultaneously to desorb the sample. It was then concentrated into a very small volume to flow through a micro fused silica capillary tube or cryotrap (cryo focusing temp. −50 °C, obtained by the cooling effect of expansion of CO_2 gas at 60 bar to normal atmospheric pressure) containing adsorbent materials Carbopack B and Envi-Carb X in the ratio of 3:1, for retaining also the light hydrocarbons effectively. After this the condensed sample was subjected to a very rapid rise in temperature (355° C, at a rate of 355° C s^{-1}) to get vaporised. The gaseous sample along with the carrier gas was then flowed into the separating column which was located in an oven whose temperature was increased with a constant rate (*e.g.* 17° C/min up to 160° C), to separate each component in the sample flowing through the column with different rate. The initial temperature of the oven could be decreased near to or below the ambient temperature according to the need by using electric ventilator (or cryostat, cooling fluid: glycol-water mixture). At the end of the column a flame ionisation detector (FID) generated an electrical signal proportional to the quantity of each sample component as it exited the column.

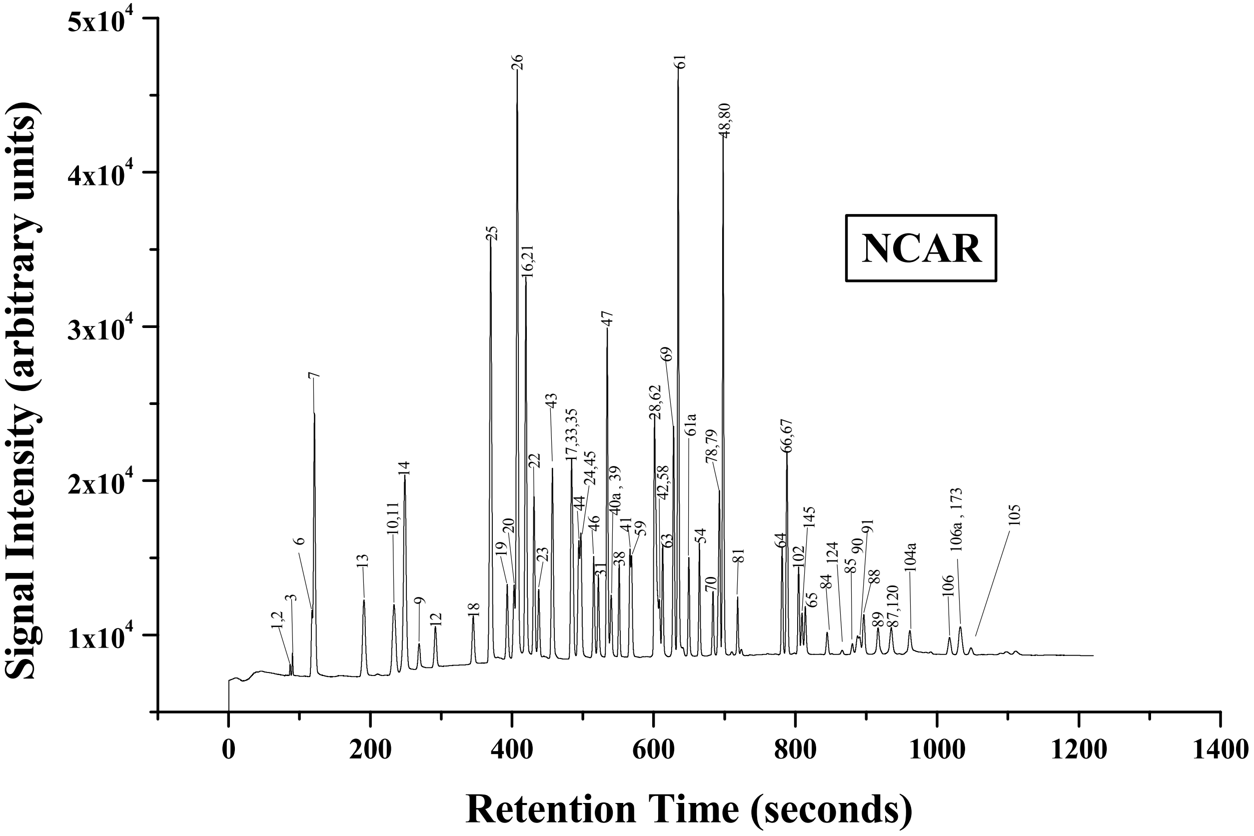
Different operating programmes for this instrument were written in such a way so that the total analytical time could be kept either 20 min or 30 min according to the need. Table A2 I (in the Annex-Tables) shows a typical list of technical parameters of Airmovoc gas chromatograph.

2.2.1.2 Identification

The identification of the NMHCs were mainly performed by comparing the fingerprint chromatograms for the ambient air and those of the standard gas mixtures (*e.g.* NCAR (National Center for Atmospheric Research), NPL (National Physical Laboratory)). Since the capillary column used was nonpolar (BGB 2.5), the specific retention time of most of the components were correlated with their boiling points and chemical structures.

2.2.1.2.1 Chromatograms and retention time

During the Berlioz campaign, the Airmovoc instrument was harmonised with other GC instruments using a NCAR standard gas-mixture containing 71 different NMHCs. Figure 2.5 shows a typical chromatogram of this NCAR standard.



The names of the compounds corresponding to the numbers shown in the figure, are listed in Table 2.3.

Figure 2.5: A typical chromatogram using a NCAR standard gas mixture containing 71 C_2-C_{10} components, supplied and certified by National Center for Atmospheric Research, U.S.A.

Table 2.3 shows the elution series of different hydrocarbons contained in the NCAR standard and the gross retention time with standard deviation (min).

Table 2.3: List of elution series and retention time of NMHCs contained in NCAR standard gas-mixture.

S/N	ID No.	Components	NCAR (Lab.) Gross retention time in min	NCAR (Lab.) ± (S. D.) in min
1	1,2	Ethene, ethyne	1.28	0.01
2	3	Ethane	1.35	0.01
3	6	Propene	1.96	0.02
4	7	Propane	2.02	0.03
5	13	2-Methylpropane (*iso*-butane)	3.24	0.04
6	10,11	1-Butene, 2-methylpropene (*iso*-butene)	4.02	0.05
7	8,14	1,3-Butadiene, *n*-butane	4.28	0.04
8	9	*trans*-2-butene	4.62	0.04
9	12	*cis*-2-butene	5.06	0.04
10	18,X6	3-Methyl-1-butene, unknown	5.91	0.03
11	25	2-Methylbutane (*iso*-pentane)	6.33	0.04
12	X24,19	Unknown, 1-pentene	6.73	0.04
13	20,26	2-Methyl-1-butene, *n*-pentane	6.93	0.08
14	16,21	2-Methyl-1,3-butadiene (isoprene), *trans*-2-pentene	7.16	0.04
15	22	*cis*-2-pentene	7.33	0.04
16	23	2-Methyl-2-butene (amylene)	7.43	0.04
17	43	2,2-Dimethylbutane (*neo*-hexane)	7.74	0.04
18	17,33,35	Cyclopentene, 3-methyl-1-pentene, 4-methyl-1-pentene	8.19	0.04
19	24,44,45	Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	8.39	0.07
20	46	3-Methylpentane	8.70	0.04
21	31,37	2-Methyl-1-pentene, 1-hexene	8.80	0.04
22	47	*n*-hexane	8.98	0.04
23	40a,39, X11	*cis*-3-Hexene, *trans*-2-hexene, unknown	9.06	0.04
24	38	*cis*-2-hexene	9.24	0.04
25	41,59	Methylcyclopentane, 2,4-dimethylpentane	9.52	0.07
26	28,62	Benzene, 2-methylhexane	10.07	0.05
27	42,58	Cyclohexane, 2,3-Dimethylpentane	10.15	0.05
28	63	3-Methylhexane	10.23	0.05
29	X15, 69	Unknown, 2,2,4-trimethylpentane (*iso*-octane)	10.48	0.05
30	61	*n*-Heptane	10.57	0.05
31	61a	2,3-Dimethyl-2-pentene	10.80	0.05
32	X29, 54	Unknown, methylcyclohexane	11.06	0.05
33	70	2,3,4-Trimethylpentane	11.36	0.05
34	78,79	2-Methylheptane, 3-methylheptane	11.50	0.05
35	48,80	Toluene, 4-methylheptane	11.59	0.05
36	81,X18	*n*-Octane, unknown	11.94	0.06
37	64	Ethylbenzene	12.99	0.06
38	66,67	*m*-/*p*-Xylene	13.11	0.06
39	102	*n*-Nonane	13.38	0.06
40	145	Ethenylbenzene (styrene)	13.47	0.06
41	65	*o*-Xylene	13.55	0.06
42	84	*iso*-Propylbenzene (cumene)	14.08	0.07
43	124	α-Pinene	14.45	0.07

Table 2.3 (continued):

S/N	ID No.	Components	NCAR (Lab.)	
			Gross retention time in min	± (S. D.) in min
44	85	*n*-Propylbenzene	14.69	0.07
45	90,91	1-Ethyl-3-methylbenzene (*m*-ethyltoluene), 1-ethyl-4-methylbenzene (*p*-ethyltoluene)	14.87	0.07
46	88	1,3,5-Trimethylbenzene (mesitylene)	14.97	0.07
47	89	1-Ethyl-2-methylbenzene (*o*-ethyltoluene)	15.32	0.08
48	87,120	1,2,4-Trimethylbenzene, *n*-decane	15.64	0.08
49	104a	*tert*-Butylbenzene	16.10	0.08
50	106	1,3-Diethylbenzene	17.08	0.08
51	106a,173	1,4-Diethylbenzene, *n*-butylbenzene	17.35	0.08
52	105	1,2-Diethylbenzene	17.79	0.40

X: unidentified compounds, S.D.: standard deviation (1 σ), S/N: Serial Number, ID No.: Identification Number.

Table 2.3 also shows the individual identification number (ID) for each component, which will be used occasionally instead of their names in the following sections. Table 2.3 shows that the retention time of different nonmethane hydrocarbons were found to be stable within small deviation in the laboratory with standard gas mixture and also in the tunnel or field measurements (see also Figure A2 II in the Annex-Figures). It is also clear from Table 2.3 that the peaks in the chromatograms were separable and thus easy to be integrated. Therefore, the retention time was used for identification of the components during the field measurements.

2.2.1.2.2 Theoretical hold-up time

The retention time of a substance is dependent on the column material, temperature programme and the flow rate of the carrier gas.

Since in the present study, the hold-up time for the components were not determined, an attempt was taken to calculate the theoretical hold-up time for the Airmovoc system using a GC method translation software (Hewlett Packard, 1995-97, version 2.0a). During a chromatographic run, the column pressure and the oven temperature of the Airmovoc system were changed for optimising the system and for getting better separation and better quality of the elution peaks. That is why, different values of hold-up time were obtained using the above software for the Airmovoc system. Figure 2.6 shows the variation of the theoretical hold-up time, the column pressure and the oven temperature with the gross retention time during a typical chromatographic run.

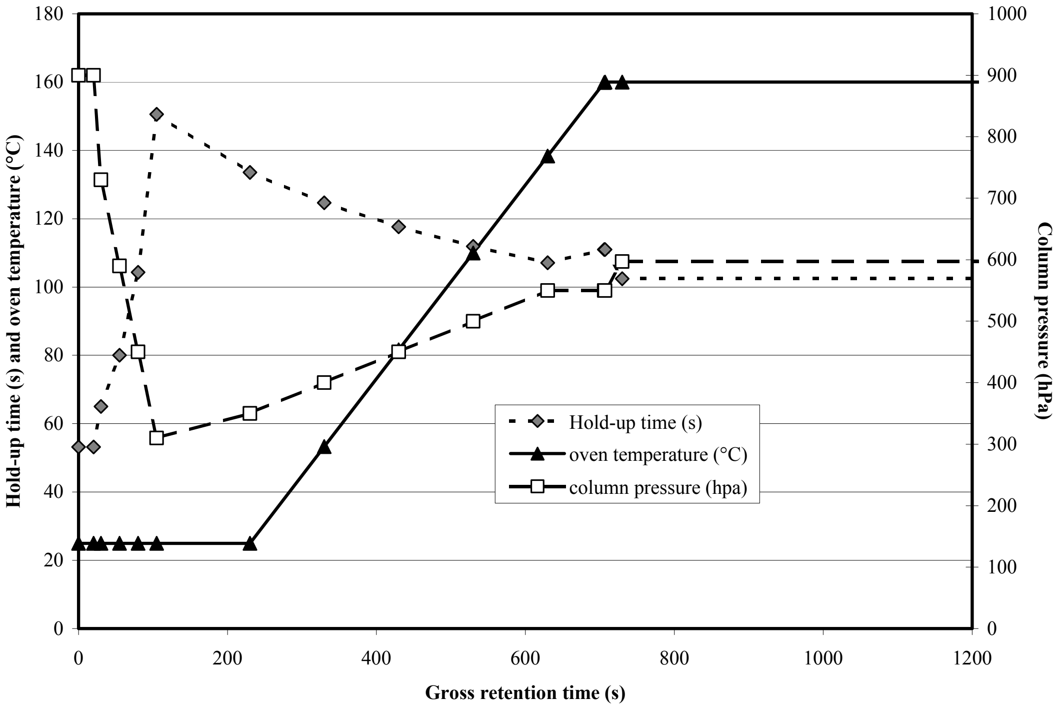


Figure 2.6: Relationship between theoretical hold-up time calculated using GC Method Translation Software (Hewlett Packard, 1995-97, version 2.0a) and gross retention time, obtained for typical conditions using the Airmovoc 2010 quasi-online GC. The variation of the column pressure and the oven temperature is also shown in the Figure.

From Figure 2.6, it is clear that the theoretical hold-up time is inversely proportional to the column pressure and directly proportional to the oven temperature. The theoretical observations can be understood from the fact that when the temperature is increased, the viscosity of the gas inside the column increases leading to the slowing of the atoms and molecules towards the column outlet and the increase of the inlet pressure accelerates the elution of compounds because of a larger pressure gradient between the column inlet (injector) and the column outlet (detector) (Nahir *et al.*, 2000).

Since during a campaign, the measuring conditions were constant and the consecutive chromatograms showed similar pattern, it was not attempted to determine the net retention time for different hydrocarbons.

For the case of the NCAR or NPL standard gas mixture, the identification of the retention time of the substances were rechecked by comparing the response factor (integrated area/mixing ratio (ppbv)/mol. mass/sample volume (ml)) of the components present in the standard gas mixtures. It was also observed that some compounds are coeluted and the identification of these compounds was not clear. That is why, for being certain about the identity of the these compounds, the single compounds were mixed with synthetic air and were measured using the GC system.

Figure 2.7 shows the experimental set-up for the production of the single gas mixture in a 130 *l* gas chamber.

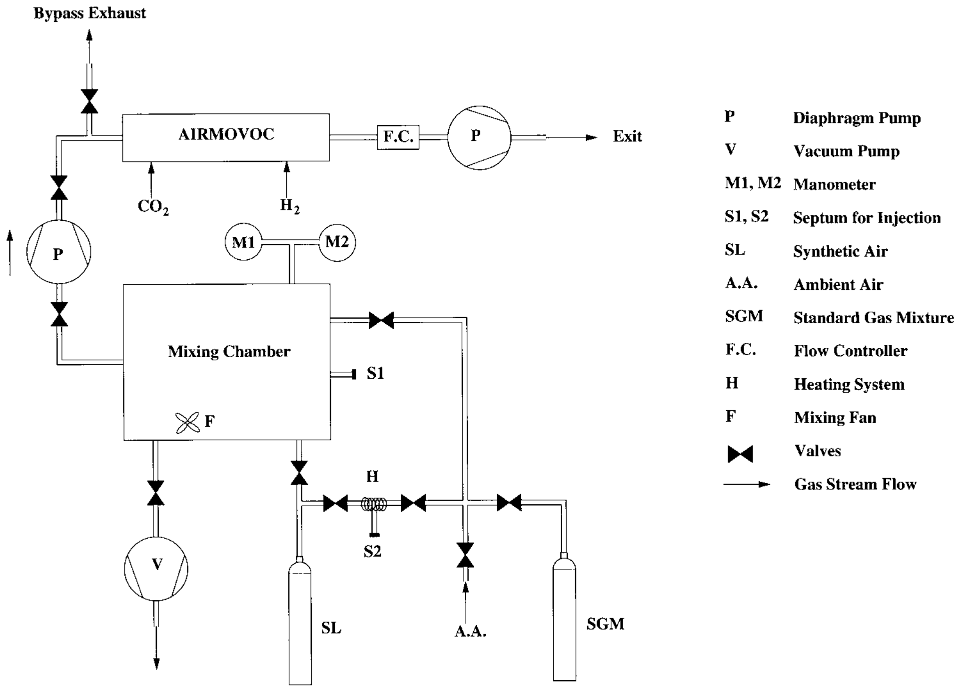


Figure 2.7: Experimental set-up for the identification of non-methane hydrocarbons using a mixing chamber.

The gas chamber consists of an outermost glass cylinder (diameter 45 cm, length 100 cm). Both sides of the cylinder are closed with aluminium metal plates. The manometers, pump-connections, septums etc. are built on the plates. To minimize the wall-effects, the Al-plates are covered with Teflon. An integrated magnetic-coupled fan is built to mix the gases thoroughly. A Rotary vane pump (Leybold-Heraeus-Trivac, Type D40B, pumping capacity 40 m^3h^{-1}, 10^{-3} Torr) and an oil-diffusion pump were used for the evacuation of the chamber. The pressure of the chamber was measured using 10 and 1000 mbar manometers (MKS Instruments INI).

1 µl of the substance was injected in the chamber and diluted with synthetic air up to the sufficient calculated concentration necessary for the GC instrument. The diluted substance was then pumped through the GC instrument for the measurement.

2.2.1.2.3 Integration of peaks

It was observed that the chromatograms obtained from the tunnel/ambient air showed similar pattern and can be treated as finger print chromatograms as shown in Figure A2 III (in the Annex-Figures). Thus by observing every peak shown in the chromatograms and comparing the retention time, the identification was carried out. As discussed in section 2.2.1.2.1, the gross retention time was constant within small deviation, but there were almost always baseline changes. If the baselines of the chromatograms cannot be correctly shown, the integration of the peaks will give erroneous results. Therefore, the automatic integration of the chromatograms using Airmovoc software (Airmovista) could not be used. That is why, every chromatogram was hand-integrated using the Borwin software.

There are in total 49 recognisable peaks in a typical ambient chromatograms, in which 29 peaks are singly eluted and 20 peaks are coeluted. The single peaks and some of the coeluted peaks are integrated by the Borwin software. It was seen that the precision of the hand-integration was for most of the components within 0%-5%. Borwin software uses the longitudinal cut-off of the start and end point of the predefined peak and then integrates the area below it. Therefore, using this integration software for coeluted peaks, there is a possibility of loss or gain of integrated peak area. On the other hand, Origin programme uses the Gauß curves for defining the individual peaks of a coeluted peak and thus minimizes this type of loss or gain of integrated peak area. Figure 2.8 shows a typical example of these Origin separations.

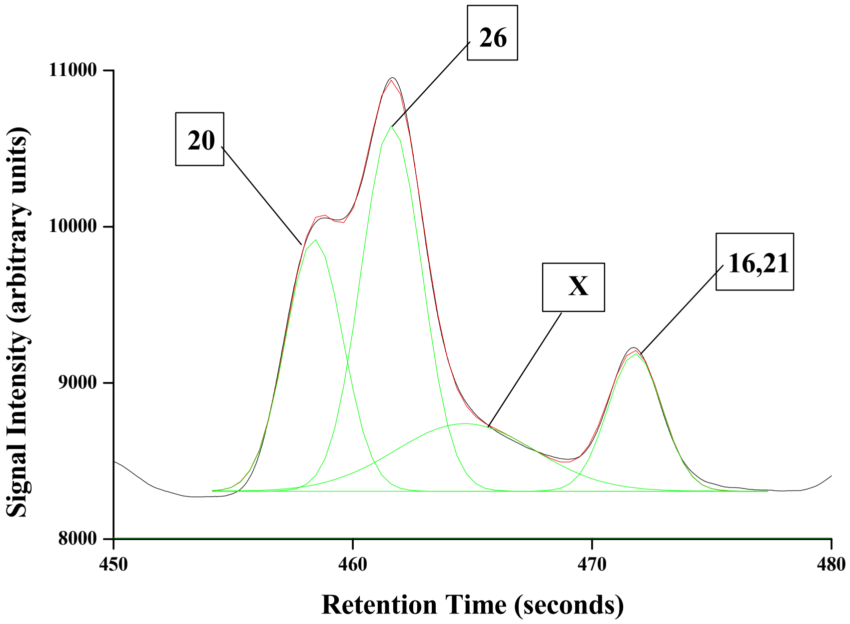


Figure 2.8: Separation of the coeluted peaks using the Origin programme for the compounds 2-methyl-1-butene (20), *n*-pentane (26), X (unknown) and isoprene (16)/*trans*-2-pentene (21).

It can be understood from Figure 2.8 that depending on the shape of the peaks, the Borwin peak integration could give different results than those using the Origin programme. It was also observed that the peak-integration using the Borwin software gives about 10-30% different values for the coeluted peaks than those using the Origin programme. For example, Borwin integration for *n*-pentane gives about 30% higher value than Origin integration. On the other hand, for 2-methyl-1-butene, Borwin integration gives about 8% lower value than Origin integration. Therefore, for the accurate data evaluation, Origin peak-integration method should be used.

For the data evaluation of the tunnel campaigns, the Origin integration method was carried out for the following 6 coeluted peaks, namely for propene/propane, 1,3-butadiene/*n*-butane, 2-

methyl-1-butene/*n*-pentane/X(unknown)/isoprene/*trans*-2-pentene; methylcyclopentane/2,4-dimethylpentane; benzene/2-methylhexane/cyclohexane/2,3-dimethylpentane/3-methylhexane and *n*-nonane/styrene/*o*-xylene.

2.2.1.3 Development of the sampling system

The laboratory test showed that when dry calibration gas was sampled, only 30-50% of the adsorbed aromatic hydrocarbons were desorbed from the cryofocusing material Envi-Carb. It was also observed that due to the change of the water content in the sample, the retention time of the components was drifted. It was known from the literature (Lai *et al.*, 1993; Cao *et al.*, 1994, 1999; Woolfenden, 1997; Harper, 2000) that the air containing moisture plays a role on the adsorption properties and the analytical system. Due to these reasons, a humidifier/watertrap was developed to keep the relative humidity of the air sample at a constant value. In addition, the cryofocusing material (Envi-carb) was changed with a mixed packing of Carbopack B and Envi-Carb X in the ratio of 3:1. After using humid sample and changing the cryofocusing material these memory effects were depressed to about 10% and the drifting of the retention time was minimized (see Table 2.3). No loss of C_2-C_9 nonmethane hydrocarbons within the error limit was observed by using a water trap at a temperature between 0°–16° C.

As mentioned above, the memory effect comes from the incomplete desorption of the adsorbed substances from the adsorption material. An exponential equation can be written for this effect as follows (Schmitz, 1993; Konrad, 2000b):

$$A_n = A_{inf.} + A_0 . e^{-n/k} \qquad \text{Eq. 2.1}$$

where,

n is the no. of measurement cycles of the adsorption tubes indicating the no. of desorption after last standard sampling (*e.g.*, 0: last standard sampling, 1: first zero gas sampling etc.),

k is 1st order time constant (in units of reciprocal n),

A_0 indicates the peak area obtained at the last standard sampling,

A_{inf} indicates the peak area after infinite cycles of zero gas sampling indicating the blank peak area without memory and

A_n indicates the peak area at nth zero gas sampling.

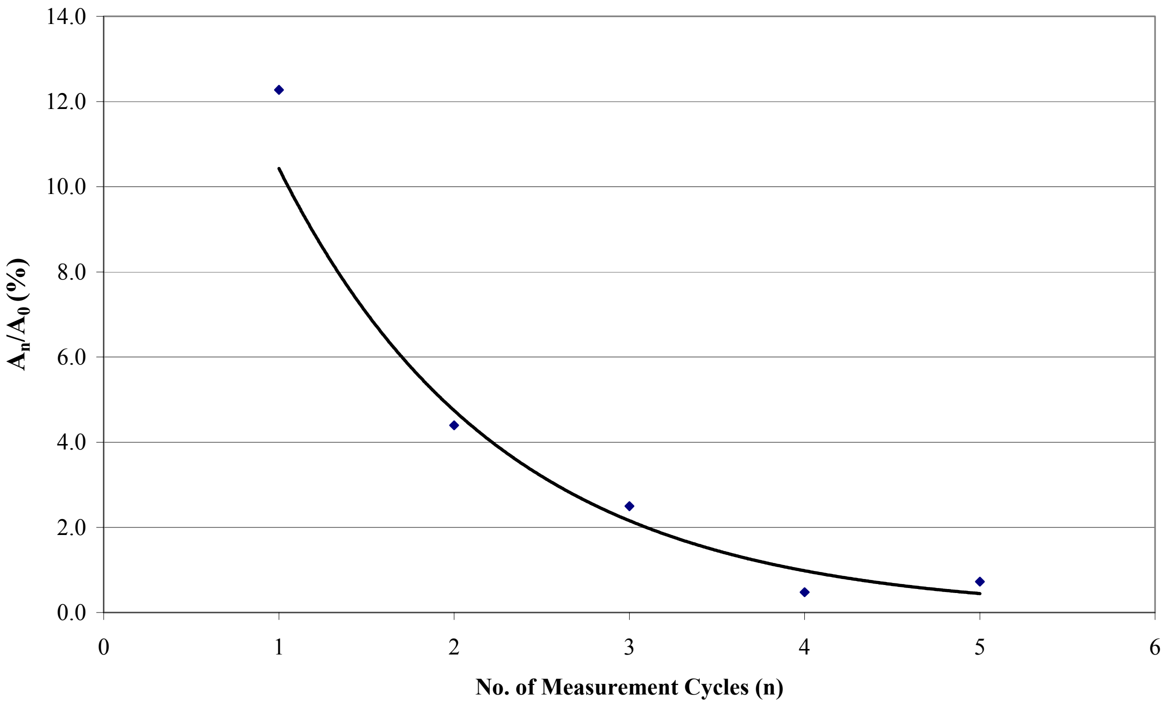
During working at rural areas or with background air where the concentration of NMHCs is small, one should determine the contribution of the memory effect for each component and one should correct the concentrations of them.

Figure 2.9 presents a typical curve showing the exponential decrease of peak area (A_n/A_0) with the increase of the measurement cycles (n). This arbitrary relationship can be described in the following way:

$$A_n/A_0 = C\, e^{-Kn} \qquad \text{Eq. 2.2}$$

where, C designates a constant value for a particular compound and K denotes the arbitrarily determined 1st order time constant in the unit of reciprocal n.

With the help of K- and A_1/A_0-values, it is theoretically possible to make corrections due to the memory effects in the continuous measurements. But, this type of corrections are only needed when there is a great concentration-jump due to the change of the air mass or after the calibration.



A_0: Peak area at the last standard sampling, A_n: Peak area at nth zero gas sampling

Figure 2.9 Typical exponential curve showing the decrease of peak area (A_n/A_0) with the increase of the measurement cycles (n) for propane (tube 2) at nth zero gas sampling.

Table 2.4 shows the list of the average K-values and the percental residue of substances after first zero air sampling (A_1/A_0).

Table 2.4 : List for average K-values for the exponential curves of memory effects for the adsorption tubes of the GC (Airmovoc 2010) and percental residue after 1st zero sampling.

Substances	Memory effects (average)			
	K-values (in units of 1/n)	±	% of residue after 1st zero sampling (A_1/A_0)	±
Ethene/Ethyne	0.12	0.05	23.5	2.3
Ethane	–	–	–	–
Propene	0.57	0.55	11.2	4.1
Propane	0.62	0.57	10.0	1.9
2-Methylpropane (*iso*-butane)	0.41	0.05	35.3	11.4
1-Butene, 2-methylpropene (*iso*-butene)	0.35	0.16	9.1	2.0
1,3-Butadiene, *n*-butane	0.35	0.06	19.8	2.3
trans-2-Butene	1.71	0.68	4.9	2.1
cis-2-Butene	1.81	0.61	4.6	1.3
3-Methyl-1-butene, unknown	0.01	0.06	5.1	3.1
2-Methylbutane (*iso*-pentane)	0.32	0.05	3.3	1.0
1-Pentene	0.12	0.02	6.0	0.5

Table 2.4 (continued):

Substances	Memory effects (average)			
	K-values (in units of 1/n)	±	% of residue after 1st zero sampling (A_1/A_0)	±
n-Pentane	0.32	0.04	2.1	0.2
2-Methyl-1,3-butadiene (isoprene), *trans*-2-pentene	0.35	0.04	0.9	0.2
cis-2-Pentene	0.03	0.03	1.4	0.1
2-Methyl-2-butene (amylene)	1.47	0.31	0.7	0.4
2,2-Dimethylbutane (*neo*-hexane)	0.33	0.03	1.7	0.2
Cyclopentene, 3-/4-methyl-1-pentene	0.31	0.04	0.8	0.2
2,3-Dimethylbutane	0.29	0.05	1.4	0.2
Cyclopentane, 2-methylpentane	0.17	0.02	4.1	0.4
3-Methylpentane	0.35	0.07	1.4	0.2
2-Methyl-1-pentene	0.11	0.04	1.2	0.3
n-Hexane	0.37	0.04	1.5	0.2
cis-3-Hexene, *trans*-2-hexene, unknown	0.60	0.10	1.1	0.3
cis-2-Hexene	0.23	0.05	0.9	0.2
Methylcyclopentane	0.47	0.07	1.3	0.2
2,4-Dimethylpentane	0.49	0.13	1.7	0.2
Benzene, 2-methylhexane	0.17	0.02	4.5	0.1
Cyclohexane, 2,3-dimethylpentane	0.22	0.11	2.3	1.2
3-Methylhexane	0.16	0.02	1.5	0.9
2,2,4-Trimethylpentane (*iso*-octane)	0.38	0.15	1.8	1.1
n-Heptane	0.48	0.18	1.8	1.2
2,3-Dimethyl-2-pentene	0.30	0.16	5.6	2.8
Methylcyclohexane	1.68	0.14	2.2	0.3
2,3,4-Trimethylpentane	1.85	0.13	4.2	1.5
2-/3-Methylheptane	1.28	0.85	8.3	2.7
Toluene, 4-methylheptane	1.18	0.81	5.7	1.6
n-Octane	0.57	0.03	17.1	6.7
Ethylbenzene	0.68	0.07	12.1	3.4
m-/*p*-Xylene	0.77	0.08	17.4	4.1
n-Nonane	0.63	0.07	95.0	29.6
Ethenylbenzene (styrene)	0.62	0.09	21.8	4.3
o-Xylene	0.85	0.05	19.6	3.1
iso-Propylbenzene (cumene)	2.30	0.18	23.7	9.0
α-Pinene	1.20	0.59	3.5	3.1
n-Propylbenzene	0.54	0.24	56.3	42.6
1-Ethyl-3-methylbenzene (*m*-ethyltoluene)	0.64	0.08	51.0	23.8
1-Ethyl-4-methylbenzene (*p*-ethyltoluene)	0.58	0.07	58.4	32.1
1,3,5-Trimethylbenzene (mesitylene)	0.66	0.02	46.3	15.4
o-Ethyltoluene (1-ethyl-2-methylbenzene)	0.31	0.04	90.7	22.7
1,2,4-Trimethylbenzene	0.60	0.06	63.1	35.4
n-Decane	0.69	0.09	57.3	29.5
1,3-Diethylbenzene	0.48	0.27	104.8	48.2
1,4-Diethylbenzene, *n*-butylbenzene, 1,2-diethylbenzene	0.69	0.28	128.0	26.6

According to Table 2.4 most of the recognizable compounds have a memory effect below 5%. Compounds containing higher molecular weight showed higher memory effects, which was mainly due to the strong adsorption in the adsorption tube and/or cryotrap and desorbed slowly in the following desorption runs. Besides, the memory effects for ethyne/ethene, *iso*-butane, 1,3-butadiene/*n*-butane are also high (24%, 35% and 20%, respectively). For compounds containing higher carbon atoms, the memory effects can be more than 100%. This occurred possibly due to the incomplete desorption of these compounds from the cryotrap. From Table 2.4, it can also be seen that on an average the memory after first zero air sampling is about 20%.

One should consider the memory effect of every tube for getting more exact values of mixing ratios of NMHCs in the background air.

2.2.1.4 Calibration

During the tunnel campaigns of August, 1997 and March, 1998, a 26 component C_2-C_9 NMHCs gas mixture was used which was prepared in a 20 *l* steel gas cylinder using the instrumental set-up shown in Figure A2 IV (in the Annex-Figures). This gas mixture was qualified and quantified by HP-GC instrument of Forschung Zentrum Jülich, Germany. The reproducibility of the response factors for C_2-C_5 components was within an error limit of 30% and for C_6-C_9 components within an error limit of 40%.

During the other campaigns a 27 component C_2-C_9 gas mixture, prepared and certified from National Physical Laboratory (NPL), England was used to calibrate the instruments for measuring the mixing ratios of different hydrocarbons. Therefore, in the following, the calibration work with this standard gas mixture was described elaborately. Figure 2.10 shows a typical calibration curve for propene with different concentrations using different adsorption tubes.

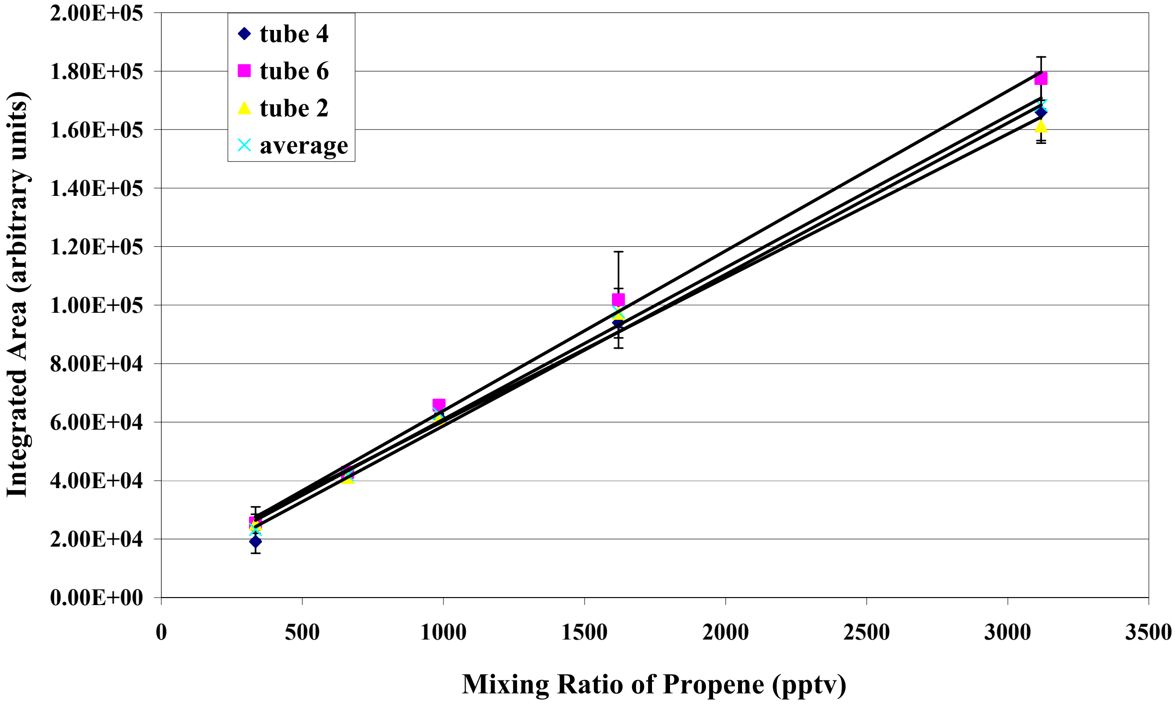


Figure 2.10: Calibration curve for propene.

The above figure shows a good correlation between the integrated peak area and the standard concentrations for different tubes as well as for the average of them. Table 2.5 summarizes the regression parameters obtained for the average.

Table 2.5: List of parameters of linear regression obtained from the average values of the three adsorption tubes, made for calibrating different NMHCs using Airmovoc 2010.

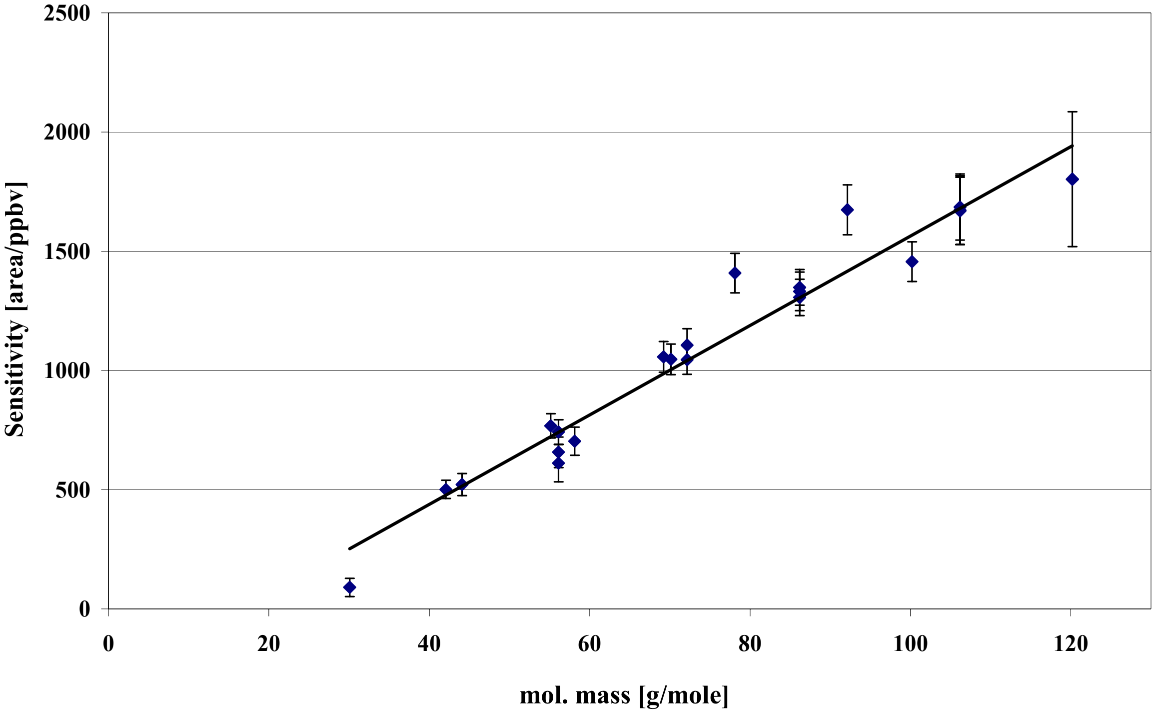
Components	m	±	r^2
	Area/ppbv	Area/ppbv	
Ethene/Ethyne	1846.88	174.53	0.97
Ethane	3832.92	127.81	1.00
Propene	67324.12	2324.28	1.00
Propane	72757.54	2215.88	1.00
iso-Butane	74258.95	4409.70	0.99
iso-/1-Butene	99126.79	5413.75	0.99
1,3-Butadiene	71552.16	5438.05	0.98
n-Butane	72857.09	7006.59	0.97
trans-Butene	115371.40	2073.09	1.00
cis-Butene	99890.85	2598.85	1.00
iso-Pentane	479106.49	9530.41	1.00
n-Pentane	688742.59	17265.54	1.00
Isoprene/*trans*-2-Pentene	656339.45	7831.34	1.00
cis-2-Pentene	564942.05	10688.31	1.00
2-Methylpentane	663487.64	14547.61	1.00
3-Methylpentane	915472.97	18099.66	1.00
n-Hexane	993154.12	18172.15	1.00
Benzene	746257.60	7595.07	1.00
n-Heptane	994540.75	15384.38	1.00
Toluene	862308.84	10946.01	1.00
Ethylbenzene	853790.65	11614.49	1.00
m-Xylene	727842.66	15277.68	1.00
o-Xylene	655446.38	16162.10	1.00
Mesitylene	339787.55	9431.97	1.00
1,2,4-Trimethylbenzene	217479.38	7531.95	1.00

m: slope of the plot of integrated area (arbitrary units) against mixing ratio (ppbv) of the respective component, r^2: correlation coefficient of the calibration plot.

It can be seen that the correlation coefficient (r^2) is 1 for most of the cases. The calculated response factors (Area/ppbv/volume of the sample/mol. mass) of NPL were calculated frequently during measurement campaigns and were used to determine the concentrations of different NMHCs in tunnel/ambient air.

2.2.1.4.1 Sensitivity curve

Since the signal from the FID detector should respond to the number of carbon atoms per unit time, it should also be proportional with the mol. mass of the detected hydrocarbons. Figure 2.11 shows a typical plot of the sensitivity (peak area/ppbv) against the molecular mass.



* Slope of the straight line: 18.76 (peak area∗mol/ppbv/g), intercept: -312.33, correlation coefficient: 0.95

Figure 2.11: Plot of sensitivity (area/ppbv) vs. mol. mass using NPL standard gas-mixture.

The response factor is defined as the integrated peak area per ppbv per mol. mass per sample volume (ml). It is clear from the curve that except for lower carbon containing substances (*e.g.* ethene, acetylene, ethane) and higher carbon containing substances (mesitylene, 1,2,4-trimethylbenzene), there is a good linear relationship between the sensitivity (area/ppbv) with the mol. mass of the hydrocarbons. It is speculated that the low carbon containing substances could not be completely adsorbed by the adsorption materials and the higher carbon containing substances could not be desorbed completely from the adsorbing materials instantaneously and therefore the higher carbon containing substances produced large memory effects as discussed before (see section 2.2.1.3).

The slope value of 18.76 ± 0.93 (peak area∗mol/ppbv∗g) and the intercept of –312.33 ± 75.10 (peak area/ppbv) was used to recalculate the response factor for each substance. Figure 2.12 shows the percental deviation for those substances as a bar diagram.

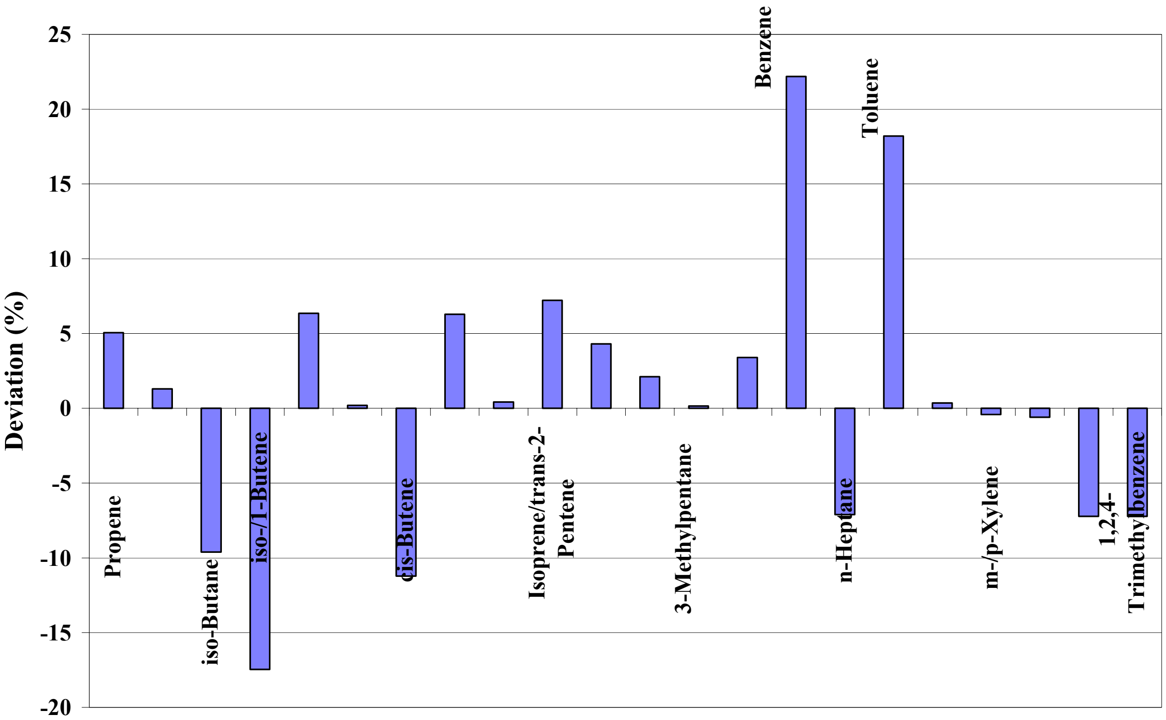


Figure 2.12: Deviation of the individually determined response for the components present in NPL standard gas mixture from the recalculated response using the sensitivity curve (Figure 2.11).

From the diagram, it can be seen that for most of the components, the percental deviations are in between 0 to 10% except *iso*-butane, *iso*-/1-butene, *cis*-butene, benzene and toluene, which have deviation in between 11-22%.

The average value of the sensitivity relative to mol. mass was 15.72 ± 1.14 (peak area mol/ppbv g), which has a negative deviation of 16.2% from the graphically determined value (the slope in Figure 2.11). This indicates that within a certain error limit, the average sensitivity value can also be used to determine the mixing ratio of unknown nonmethane hydrocarbons.

2.2.1.5 Determination of mixing ratios of NMHCs

In reality, the mixing ratios of the individual hydrocarbons were determined by comparing the response factor (peak area/ppbv/mol. mass/ml) of the component of the standard gas mixture and the peak area produced from the sample. Normally, there were several measurements of the standard gas mixture and for every case, the response factors for individual compound were determined. According to the situation, either all these values were averaged for the individual component or the response factors before and after the measurement campaign were compared for obtaining the response factor and thereby the mixing ratio of NMHCs. Figure A2 V (in the Annex-Figures) shows a typical bar diagram presenting the response factors for individual hydrocarbons present in the NPL gas mixtures for the three adsorption tubes used for measurements.

NPL standard gas mixture contained only 27 components. But nearly 68 NMHCs can be observed in the ambient air or tunnel air. The mixing ratios of these compounds were calculated by taking an average response factor of those compounds of the NPL standard mixture, which gave a constant response factor against molecular weight (*e.g.* C_5-C_8). Most of these apparently unknown compounds had carbon numbers in this range. The standard deviation of the average response factor is about 20%.

2.2.1.6 Blank values and detection limit

Like every system, the Airmovoc 2010 instrument has blank values, *i.e.* this system shows values although there is not detectable amount of sample concentrations in the gas stream. This is an inherent property of every instrument. To determine this blank values, the following method was used:

2.2.1.6.1 Blank value determination

Synthetic air was used as zero gas sample. But it is possible that some contributions of NMHCs can come from this zero air due to impurities and some contributions may also come from the sampling line. That is why, to differentiate the blank values and the other contributions, a standard operation procedure (SOP) was carried out during the Berlioz campaign (Konrad *et al.*, 2000a). According to this procedure, each adsorption tube was probed three times each with 100%, 75%, 50%, 25% and 0% of the normal sample volume. The peak areas corresponding to each component were plotted against the volume of synthetic air. A linear relationship between them was obtained. The intercept would give the blank value for the instrument and the slope will give the contribution of that component from the zero air or the inlet line. Figure 2.13 shows a typical plot for toluene for determining the blank values for the instrument. It is also true that every individual adsorption tube gives different value of blank value of the system for different compounds due to their inherent difference of adsorbing/desorbing capacity.

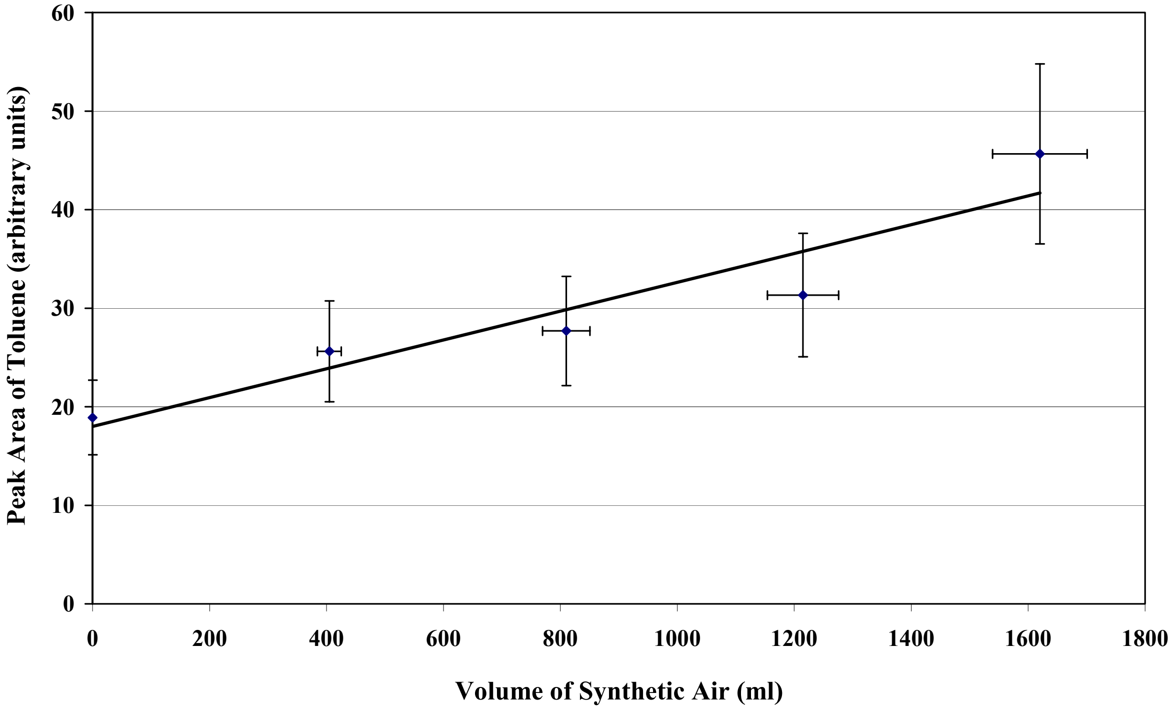


Figure 2.13: Determination of blank value of the system and the contribution from the zero air or inlet line for toluene.

Thus, it is clear from Figure 2.13 that it is very important to determine the blank value of the Airmovoc GC instrument and at the same time the blank value from the sampling line or the zero sample (synthetic air) for getting correct mixing ratios of NMHCs in the ambient air, especially where the mixing ratios of these components are small.

Since the blank value of the system (*e.g.* the intercept of Figure 2.13) and the value for zero sampling agreed within error limit with each other, for simplicity the blank system value could be determined by doing zero sampling for several time.

This value was normally subtracted from the peak area for clean air sample, *i.e.* for ambient air.

Table 2.6 shows some typical blank values.

2.2.1.6.2 Detection limits

According to DIN 32645, the detection limit of a component can be determined by ‘zero’ value method or by calibration method. In the present study, the ‘zero’ value method was used to determine the detection limit of a component. Three times of the standard deviation (3 σ) were first calculated from the average integrated peak areas for each component during zero sampling. Then by using the response factor of each component (integrated area/(molar mass∗volume of sample∗mixing ratio in ppbv)), the detection limit was calculated.

Table 2.6 shows also a list of determined detection limits for different non-methane hydrocarbons.

Table 2.6: Blank values and detection limits of NMHCs determined in the air of a rural area (Menz) using Airmovoc 2010 quasi-online GC instrument for 1620 ml sampling volume.

S/N	ID No	Components	Blank	Detection limit
			pptv	pptv
1	1,2	Ethene/Ethyne	2	15
2	3	Ethane	1	8
3	6	Propene	1	3
4	7	Propane	10	69
5	13	2-Methylpropane (*iso*-butane)	117	548
6	10,11	1-Butene, 2-methylpropene (*iso*-butene)	39	115
7	8,14	1,3-Butadiene, *n*-butane	348	1140
8	9	*trans*-2-Butene	16	28
9	12	*cis*-2-Butene	10	2
10	18,X6	3-Methyl-1-butene, unknown	28	16
11	25	2-Methylbutane (*iso*-pentane)	1	7
12	X24,19	Unknown, 1-Pentene	20	34
13	20,26	2-Methyl-1-butene, *n*-pentane	7	26
14	16,21	2-Methyl-1,3-butadiene (isoprene), *trans*-2-pentene	1	2
15	22	*cis*-2-Pentene	1	1
16	23	2-Methyl-2-butene (amylene)	1	2
17	43	2,2-Dimethylbutane (*neo*-hexane)	1	1
18	17,33,35	Cyclopentene, 3-methyl-1-pentene, 4-methyl-1-pentene	3	3
19	24,44,45	Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	2	6
20	46	3-Methylpentane	2	10
21	31,37	2-Methyl-1-pentene, 1-hexene	2	10
22	47	*n*-Hexane	2	8
23	40a,39,X11	*cis*-3-Hexene, *trans*-2-hexene, unknown	12	22
24	38	*cis*-2-Hexene	1	3
25	41,59	Methylcyclopentane, 2,4-dimethylpentane	2	2
26	28,62	Benzene, 2-methylhexane	31	54
27	42,58	Cyclohexane, 2,3-dimethylpentane	1	1
28	63	3-Methylhexane	5	2
29	X15, 69	2,2,4-Trimethylpentane (*iso*-octane)	1	2
30	61	*n*-Heptane	5	8
31	61a	2,3-Dimethyl-2-pentene	28	11
32	X29, 54	Unknown, methylcyclohexane	1	1
33	70	2,3,4-Trimethylpentane	1	1
34	78,79	2-/3-Methylheptane	1	2
35	48,80	Toluene, 4-methylheptane	5	4
36	81,X18	*n*-Octane, unknown	1	1
37	64	Ethylbenzene	1	1
38	66,67	*m*-/*p*-Xylene	1	1
39	102	*n*-Nonane	1	3
40	145	Ethenylbenzene (styrene)	1	1
41	65	*o*-Xylene	1	1
42	84	*iso*-Propylbenzene (cumene)	1	2
43	124	α-Pinene	3	6
44	85	*n*-Propylbenzene	18	44
45	90,91	*m*-/*p*-Ethyltoluene	1	5
46	88	1,3,5-Trimethylbenzene (mesitylene)	1	1
47	89	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)	28	46
48	87,120	1,2,4-Trimethylbenzene, *n*-decane	1	4
49	104a	*tert*-Butylbenzene	5	6

Total recognizable peaks: 49, Single peaks: 29, Coeluted peaks: 20, Total identifiable substances: 68, S/N: Serial Number, ID No.: Identification Number.

From Table 2.6, it can be seen that the detection limits measured in a rural area were in the pptv range. It should be also noted that since the calculation of the detection limit depends on the sampling volume, for a smaller sampling volume, the value will be correspondingly larger, *e.g.* the detection limit for the city air and tunnel air measurements will be respectively 1.1 and 8.1 time higher than those of the values shown in Table 2.6.

2.2.1.7 Accuracy

To determine the accuracy of this measurement method, an independent calibration gas namely NCAR was used for comparing the standard gas NPL which was normally used for ambient and tunnel air measurements.

Figure 2.14 shows a comparison plot of the accuracy of different components present in NPL in comparison with NCAR for different adsorption tubes and their averages. It was assumed that the values supplied by NCAR were accurate and the relative difference of NPL values from NCAR was taken as a measure for accuracy.

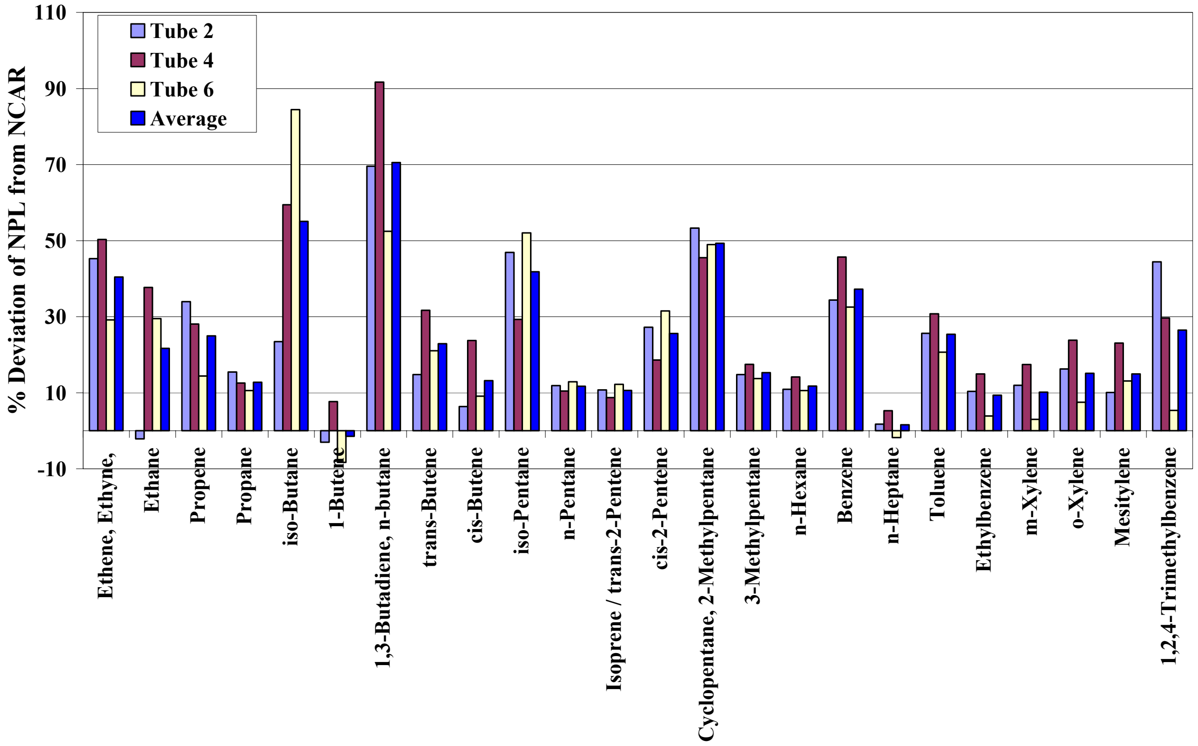


Figure 2.14: Percental deviation of NPL from NCAR standard gas mixtures.

According to the above Figure, it can be concluded that on average alkanes have an accuracy of 26%, similarly alkenes 25% and aromatic compounds 23%. Individually, 1,3-Butadiene/*n*-butane has the largest inaccuracy. The mixing ratios of the components present in the NPL standard gas mixture were validated or corrected according to the deviation from the NCAR standard gas mixture.

2.2.1.8 Precision

Under identical conditions, the standard deviation of the integrated peak areas for the measured hydrocarbons in some gas chromatographic runs can be used to define the precision or reproducibility of the system for the measurement of that respective hydrocarbon. Table A2 II (in the Annex-Tables) shows a list of these values for the substances present in NPL gas mixtures indicating the precision for the adsorption tubes 2, 4, 6 and also the average values. Figure 2.15 shows a bar diagram using the average precision values for the components present in the NPL standard gas mixture.

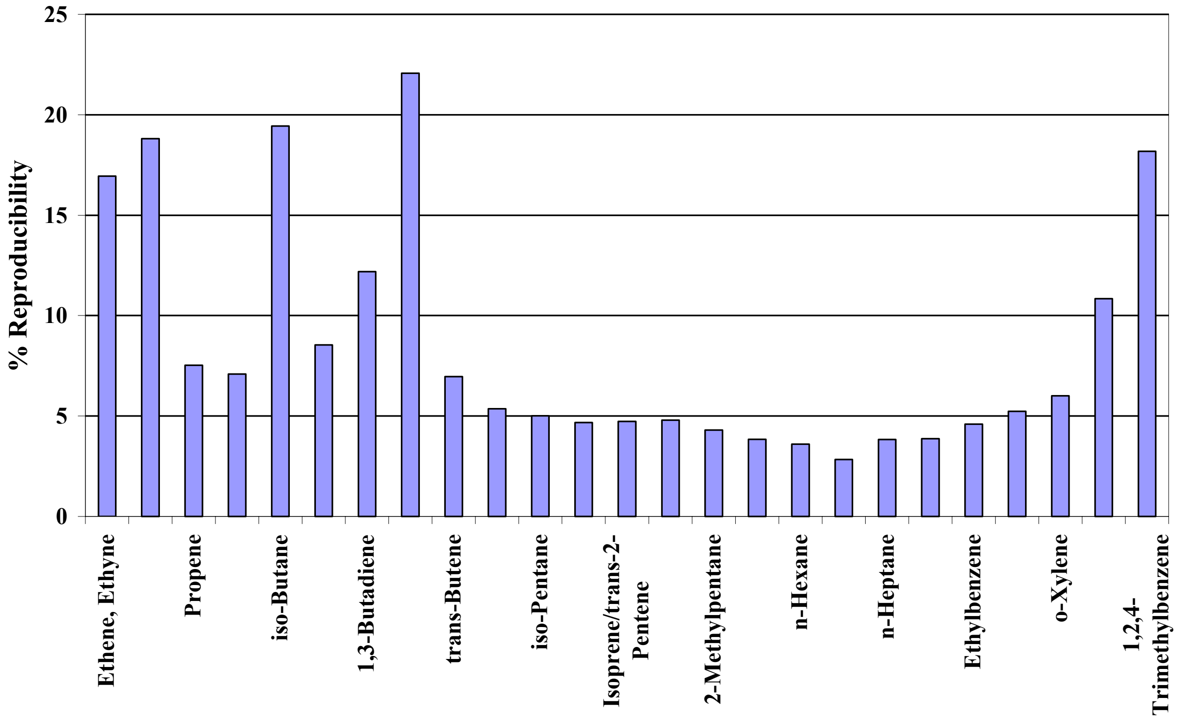


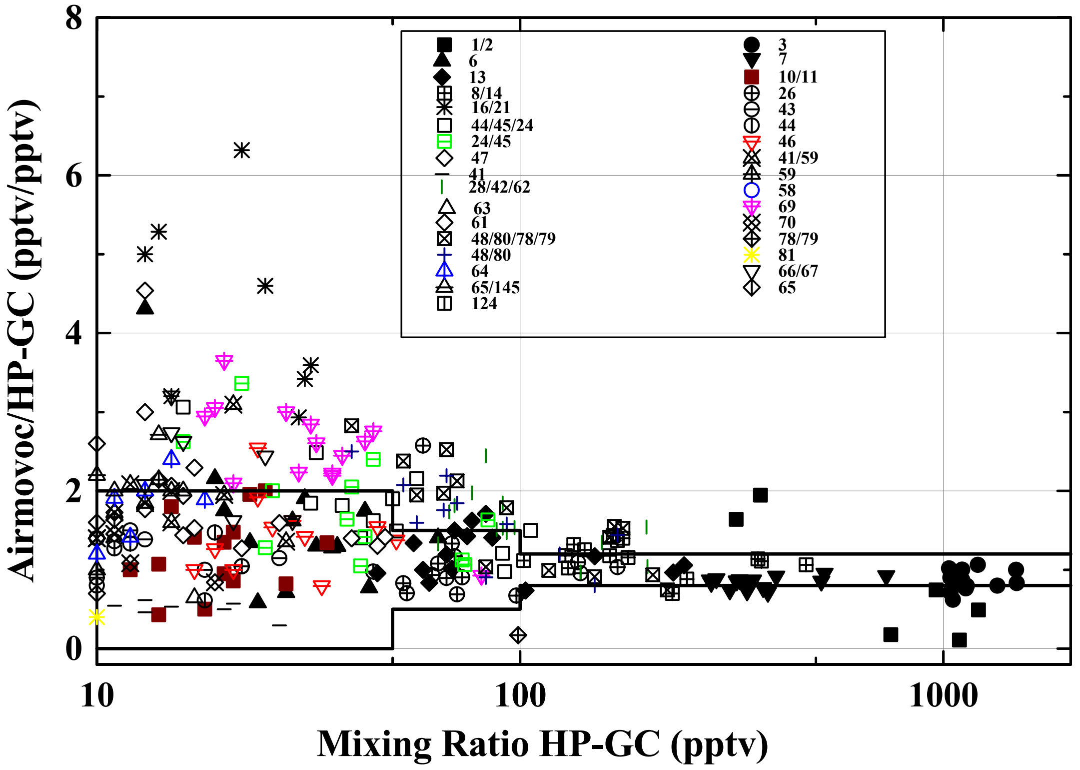
Figure 2.15: Typical description of average reproducibility of response factors calculated from the standard deviation of integrated area for single adsorption tubes (no. 2, 4 and 6).

On an average, the precision for alkanes, alkenes and aromatics are 10%, 9% and 7% respectively. It can be also observed that the different tubes have different precision values. That is why, each tube was individually considered to determine the concentration profile of a substance during the field campaigns.

2.2.1.9 Comparison with other groups

2.2.1.9.1 Berlioz

The Berlioz field campaign gave an opportunity to compare different Airmovoc and other instruments for the quality assurance for the measurements of NMHCs. Thus, in Schönhagen different groups sampled ambient air from the same place and compared the values obtained. The HP-GC instrument was taken as the most correctly measuring system. Figure 2.16 shows a comparison of the ratio of the measured values using the Airmovoc 2010 and those using HP-GC of Forschungszentrum Jülich for different nonmethane hydrocarbons found in the ambient air of Schönhagen.



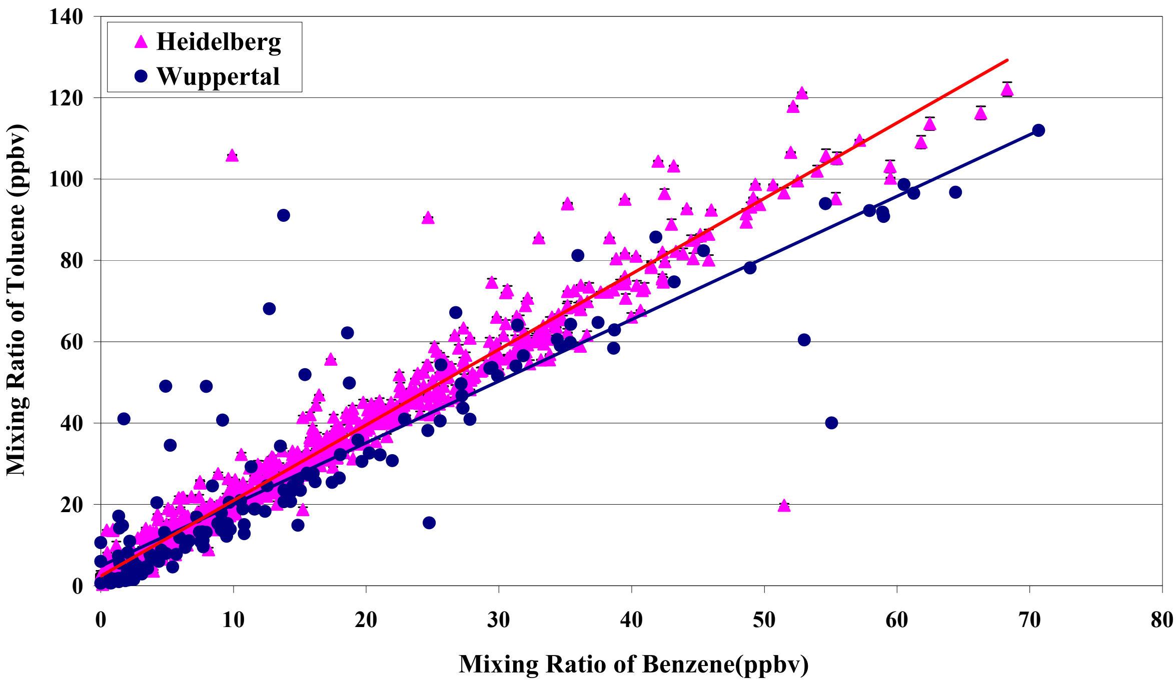
Quality assured: if the deviation of Airmovoc from HP-GC is- a) within 100% in the concentration range of 10-50 pptv, b) within 50% in the concentration range of 50-100 pptv and c) within 20% for the concentration of more than 100 pptv. That is, the data inside the two bold lines shown in the Figure, were taken as quality assured.

Figure 2.16: Comparison of the ratio of the measured values of NMHCs using Airmovoc with those using HP-GC in the pptv-ppbv concentration range. The number indicates the compounds presented in Table 2.3.

Figure 2.16 shows that most of the measured compounds using the Airmovoc instrument were in the quality assurance limits (shown by the two bold lines) in the pptv-ppbv concentration limit.

2.2.1.9.2 DOAS

During the three tunnel measurement campaigns and the city air campaign of Wuppertal, a group from the University of Heidelberg was also involved in the measurements of different air pollutants including aromatic hydrocarbons, namely benzene, toluene, ethylbenzene and *m-/p-/o*-xylene with a DOAS system. Typical correlation plots between the results of the present study and that of the Heidelberg group for toluene relative to benzene are presented in Figure 2.17.



Toluene(ppbv)/Benzene(ppbv) ratio: 1.86 ± 0.01 (DOAS, Heidelberg), 1.52 ± 0.06 (Airmovoc, Wuppertal).

Figure 2.17: Correlation diagrams for toluene against benzene in ppbv/ppbv for a typical Kiesberg tunnel measurement campaign using Airmovoc 2010 and a DOAS system.

From Figure 2.17 it can be observed that on an average, using a DOAS system, one get a factor of 1.2 higher mixing ratios for toluene than those measured by the Airmovoc GC-system. For the case of ethylbenzene and *o*-xylene there were respectively 1.5 (the ratio relative to benzene: 0.45 ± 0.01 using DOAS and 0.30 ± 0.02 using GC system) and 1.7 (the ratio relative to benzene: 0.44 ± 0.01 using DOAS and 0.26 ± 0.02 using GC system) factor higher mixing ratios relative to benzene than those measured by the Airmovoc GC-system. On the other hand, DOAS measured a factor of 1.6 lower mixing ratio for the case of *m*-/*p*-xylene relative to benzene (0.43 ± 0.01) than those measured by GC system (0.69 ± 0.04). If one considers the error limits for the measured values of these compounds using both systems, then it can be seen that the values of these factors of deviation did not change much. Therefore, it can be concluded that there exist similar variations for the measured values of these aromatic hydrocarbons relative to benzene using both of the systems, but the absolute values deviated by a factor of 0.6 to 1.7 according to the compounds. Since the instrument Airmovoc HC 2010 was quality-assured during the Berlioz campaign and the values obtained for the aromatic hydrocarbons were also comparable with other groups participated in that campaign (see Figure 2.16), the mixing ratios obtained by Airmovoc 2010 for these components were taken for the data evaluation of the present study.

2.2.2 NO_x

NO and NO_2 were monitored using Thermoelectron (Model 14D/E) NO_x chemiluminescent analyser with molybdenum converter during the tunnel campaign of August, 1997 in Wuppertal. During the tunnel campaign of March, 1998, no nitrogen oxides were measured because of the unavailibility of the analytical instrument for the measurement. Horiba (APNA 350) chemiluminescent analyser with molybdenum converter was used during the tunnel campaign of November-December, 1998.

The detection limit for both NO and NO_2 using the Thermoelectron instrument was 20 ppbv and the response time was in the range of minutes. A calibration curve for measuring NO using a certified calibration NO gas is shown in Figure 2.18. The response factor of this instrument was calculated as 1.17 ± 0.03 ppmv/Volt.

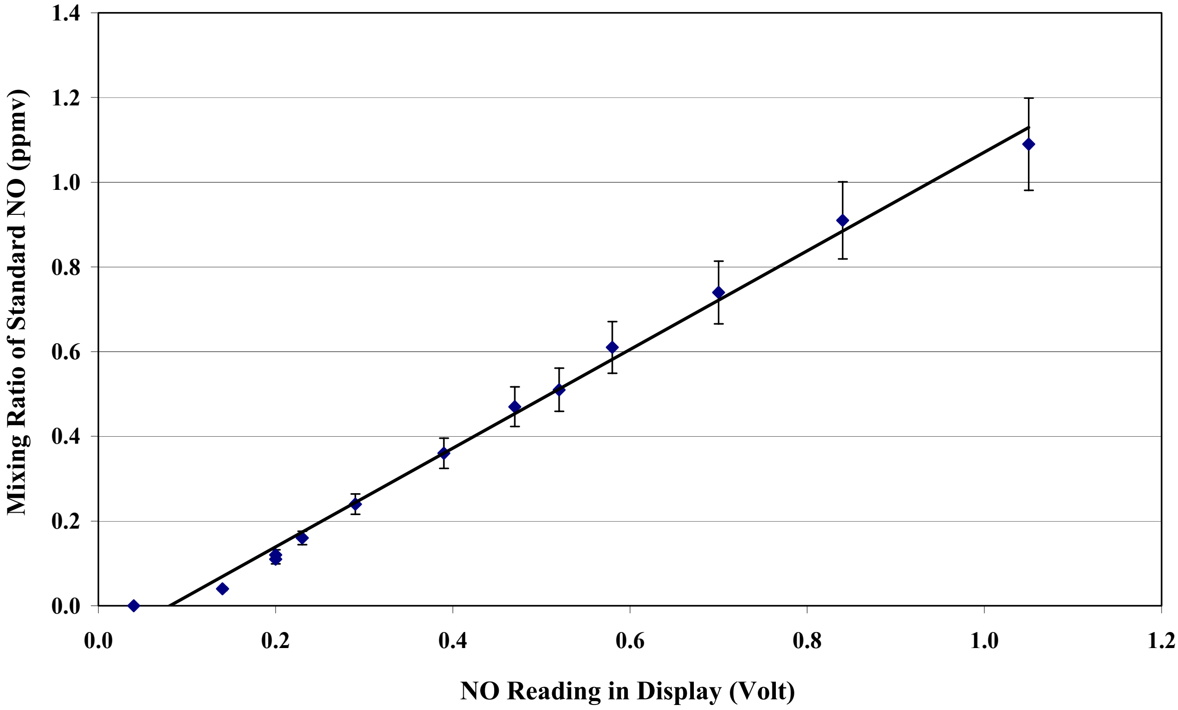
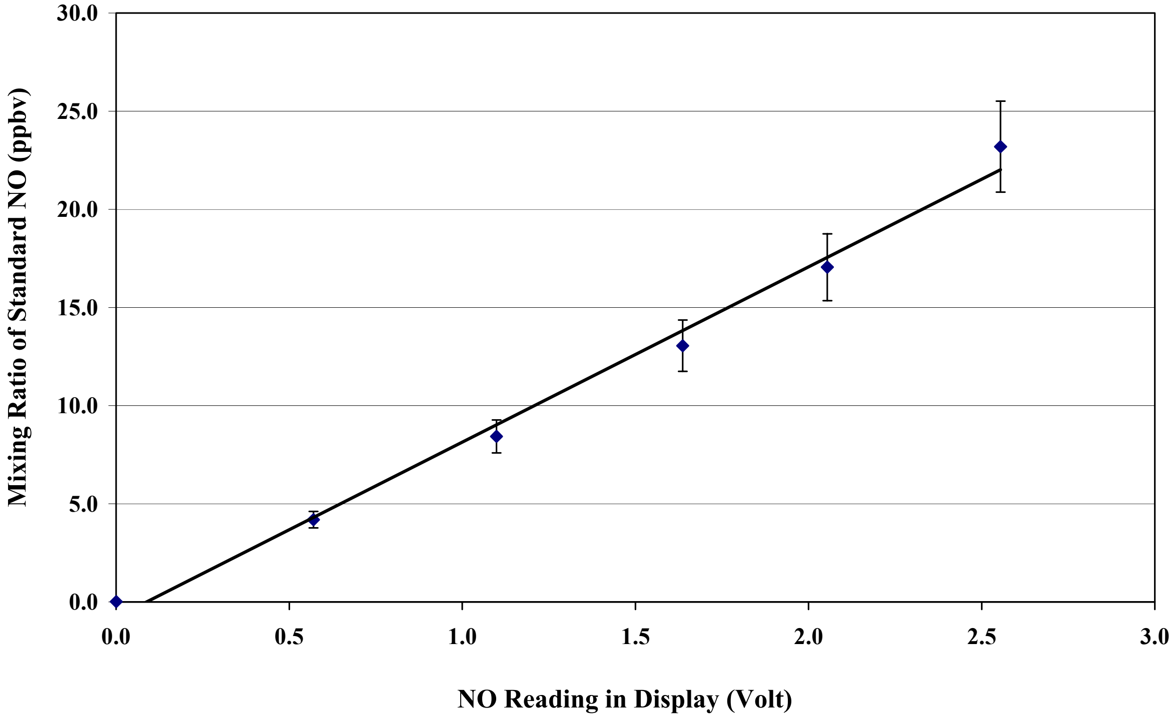
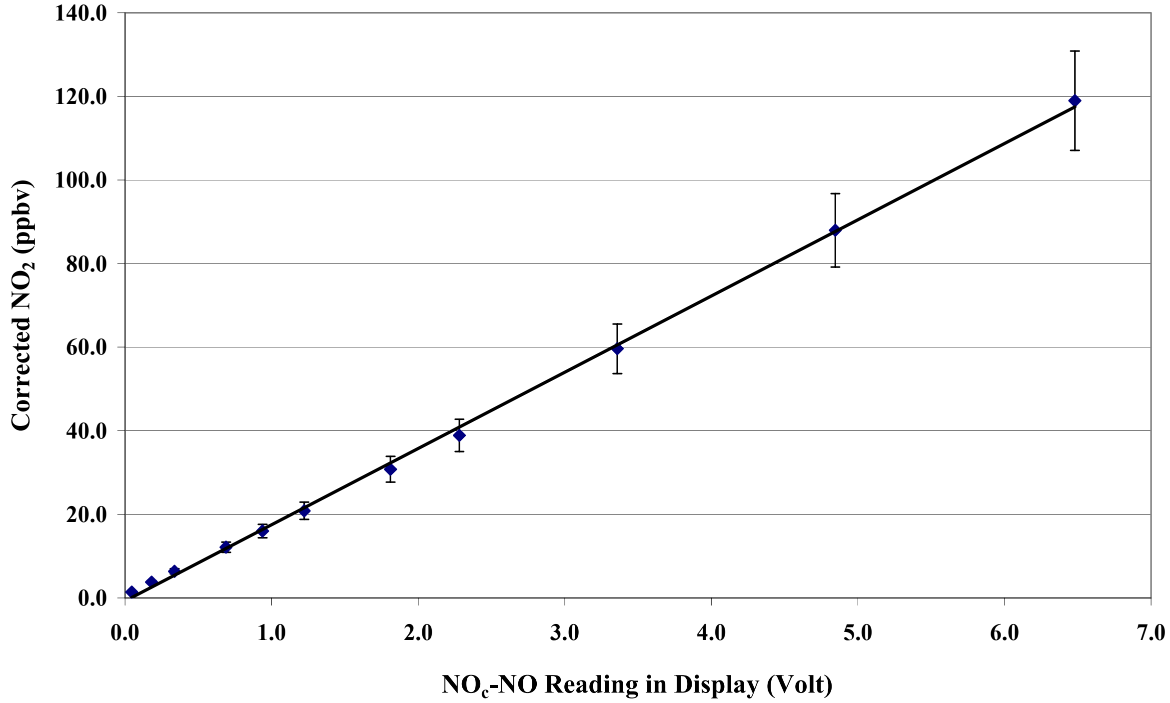


Figure 2.18: Calibration curve for nitrogen monoxide (NO) using Thermoelectron chemiluminescent instrument.

For the campaigns in the city of Wuppertal and in Menz, the chemiluminescent NO analyser with NO_2 converter (using molybdenum, Horiba) and photolytic converter (Eco-Physics, CLD 770 AL ppt) were used for measuring NO and NO_2. The time resolution was 30 s and the detection limit was in the pptv (Eco-Physics) and ppbv range (Horiba), respectively. The calibration of the NO_x system including the sampling system was performed with certified calibration NO and NO_2 gas-mixtures (Messer Griesheim). Figure 2.19 a-b shows typical calibration curves for NO and NO_2 using the Eco-Physics instrument.



(a)



(b)

* NO_c-NO denotes the signal regarding to the fractionally converted NO_2. Corrected NO_2 designates the mixing ratio of the standard NO_2 corrected due to the presence of NO in the gas cylinder or due to the conversion of NO_2 to NO in the sampling system.

Figure 2.19: Typical calibration curve for (a) nitrogen monoxide and (b) nitrogen dioxide using Eco-Physics CDL 770AL ppt.

Eco-Physics NO_x analyser converts NO_2 to NO photolytically. The fractional conversion of NO_2 to NO (Kley and McFarland, 1980) is designated as NO_c-NO. The calibration curves shown in Figure 2.18 and Figure 2.19 a-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 is 8.93 ± 0.42 ppbv/Volt and for NO_2 is 18.25 ± 0.19 ppbv/Volt. These factors were used to calculate the mixing ratios of nitrogen oxides.

2.2.3 Carbon dioxide

As shown in Table 2.1, two instruments were used for monitoring CO_2 in the Kiesberg tunnel of Wuppertal, namely GC (Chromato-Sud) and FTIR (Kayser-Threde K300 and Midac M2400C). In the following, they are discussed briefly.

2.2.3.1 GC

CO_2 was measured using a GC monitor Chromato-Sud (A-TCD/ECD, Saint Antoine France) in the Kiesberg tunnel campaign of August, 1997 and March, 1998 (Becker *et al.*, 1999). It contains multi-port valves with a 2 m column (Porapak Q 80-100 mesh) with a thermal conductivity detector. To avoid contamination by higher hydrocarbons, a 1.3 m precolumn (Porapak Q 80-100 mesh) was used in which the slowly eluting components were backflushed. Tunnel air was pumped at 10 *l*/min to the GC and 150 ml per min through 1 ml sample loops. The analysis time was 6 min and the detection limit is 10 ppmv. Chromatograms were recorded using the GC software BORWIN. The system was calibrated every hour using certified CO_2 calibration gas (Messer Griesheim). The concentrations of the standard gas were chosen in such a way that they were in the same range as in the tunnel air or other ambient air. The mixing ratios of CO_2 in the tunnel air was determined by comparing the peak areas of the sample and standard.

2.2.3.2 FTIR

During the tunnel campaign of November-December, 1998, CO_2 was monitored using two FTIR spectrometers, namely Kayser-Threde K300 and Midac M2400C. In this FTIR system, an open White mirror compartment was used, which had a base length of 491 cm. The mirrors were gold coated with a diameter of 40.6 cm. The open White compartment had an adjustable optical path length between 44 m and 405 m (Sedlmaier *et al.*, 1997). The reference spectra of CO_2 were taken for different concentrations within a wide range and at different wave numbers. Using the absorption values obtained, calibration curves were drawn and by comparing the spectra for the tunnel air, the concentrations of CO_2 were determined. The detection limit was much below ambient concentration and the analysis time was 5 min (Sedlmaier, 2001).

2.2.4 Error calculation

The determination of mixing ratio of NMHCs were carried out using the following equation:

$$\mu_i = PA_i/(RF_i*M_i*V) \qquad \text{Eq. 2.3}$$

where,

μ_i indicates the mixing ratio of i-component,

PA_i symbolizes the integrated peak area for that component,

RF_i indicates the response factor in (integrated peak area)/(mixing ratio (ppbv) ∗molecular mass∗volume of the sample (ml)) for i-component,

M_i means the molecular mass of i-component in g/mole and

V indicates the quantity of sample air in ml.

The statistical error for the determination of the mixing ratio of a component was performed using the Gauß law of propagation of error:

$$(\Delta\mu_i)^2 = (\delta\mu/\delta PA_i)^2*\Delta PA_i^2 + (\delta\mu/\delta RF_i)^2*\Delta RF_i^2 + (\delta\mu/\delta M_i)^2*\Delta M_i^2 + ((\delta\mu/\delta V)^2*\Delta V^2.$$

After some simplification, the relative error (R.E.) becomes as follows:

$$\Delta\mu_i/\mu_i = \sqrt{(\Delta PA_i/PA_i)^2 + (\Delta RF_i/RF_i)^2 + (\Delta M_i/M_i)^2 + (\Delta V/V)^2}\ .$$

Where,

$\Delta PA_i/PA_i$ corresponds to the error during manual integration, which is for most of the case 1%-5%.

$\Delta RF_i/RF_i$ corresponds to the error of calibration, normally the standard deviation value, and for non-NPL compounds, the addition error comes from the average error of the response factor. Depending on the situation , for most of the case, this value can be from 10% to 30%. For a few components, exemplary for *o*-xylene, the relative error of calibration can be 50% or more.

$\Delta M_i/M_i$ plays only a role when there is the case for coelution. In that case, the average error of molecular mass signifies this error. In the case of 1,3-butadiene and *n*-butane, the molecular mass will be written as 56.11 ± 2.02 g/mole.

$\Delta V/V$ corresponds to the error occurred due to the error of flow controller and related equipment involved for the volume measurement. This value is normally within 2%-4%.

Thus for a typical situation the relative error for determining mixing ratio for most of the NMHCs could be up to 35%. For components higher than C_7, *e.g.* *o*-xylene, the relative error could be up to 60%.

Table 2.7 shows in summarized form the relative error for different ozone precursors and carbon dioxide.

Table 2.7: List of relative error for NMHCs, formaldehyde, nitrogen oxides and carbon dioxide.

Components	Relative error (%)
Non-methane hydrocarbons*	20-60%
Nitrogen oxides	10%
Carbon dioxide	10%

*The additional error for NMHCs may come from the contribution of the memory effects, which will make the total error from 40% up to 105% depending on the components.

2.2.5 Meteorological parameter

During the field campaigns in the road traffic tunnel, the city and the rural area, meteorological parameters, for example wind speed, wind direction, temperature, solar light intensity (during the city air campaign), pressure and relative humidity were monitored.

2.3 Statistics of road traffic during tunnel campaigns

In addition to the measurement of compounds in the tunnel air, the number of vehicles passing through the tunnel was counted using contact loops. For weekdays the number of cars passing through the tunnel was about 22,000 vehicles per day, during weekends the traffic decreased to about 13,000 vehicles per day. Video taping conducted during the entire period of the study established an overall average contribution of 6±1% heavy-duty vehicles (HDV), 6±1% of commercial vans, 87±2 % of diesel (12%) and gasoline (75%, 46% with catalyst) powered passenger cars and 1±1% of motorcycles to the traffic volume during the weekdays. During the weekends, the percental contribution of HDV, commercial vans and passenger cars and motor cycles were 1±1, 5±2, 92±10 and 2±1, respectively. All numbers given above refer 100% of the vehicle fleet. The gasoline and diesel fraction of the passenger cars in the tunnel was assumed to reflect the registration of gasoline and diesel powered cars in the surrounding administrative district of Düsseldorf for the corresponding year of 1997 and 1998 (see Figure 1.3).

The speed of the vehicles passing through the tunnel was typically 50-90 km/h, except for congested traffic periods.

3 Results

3.1 Tunnel air

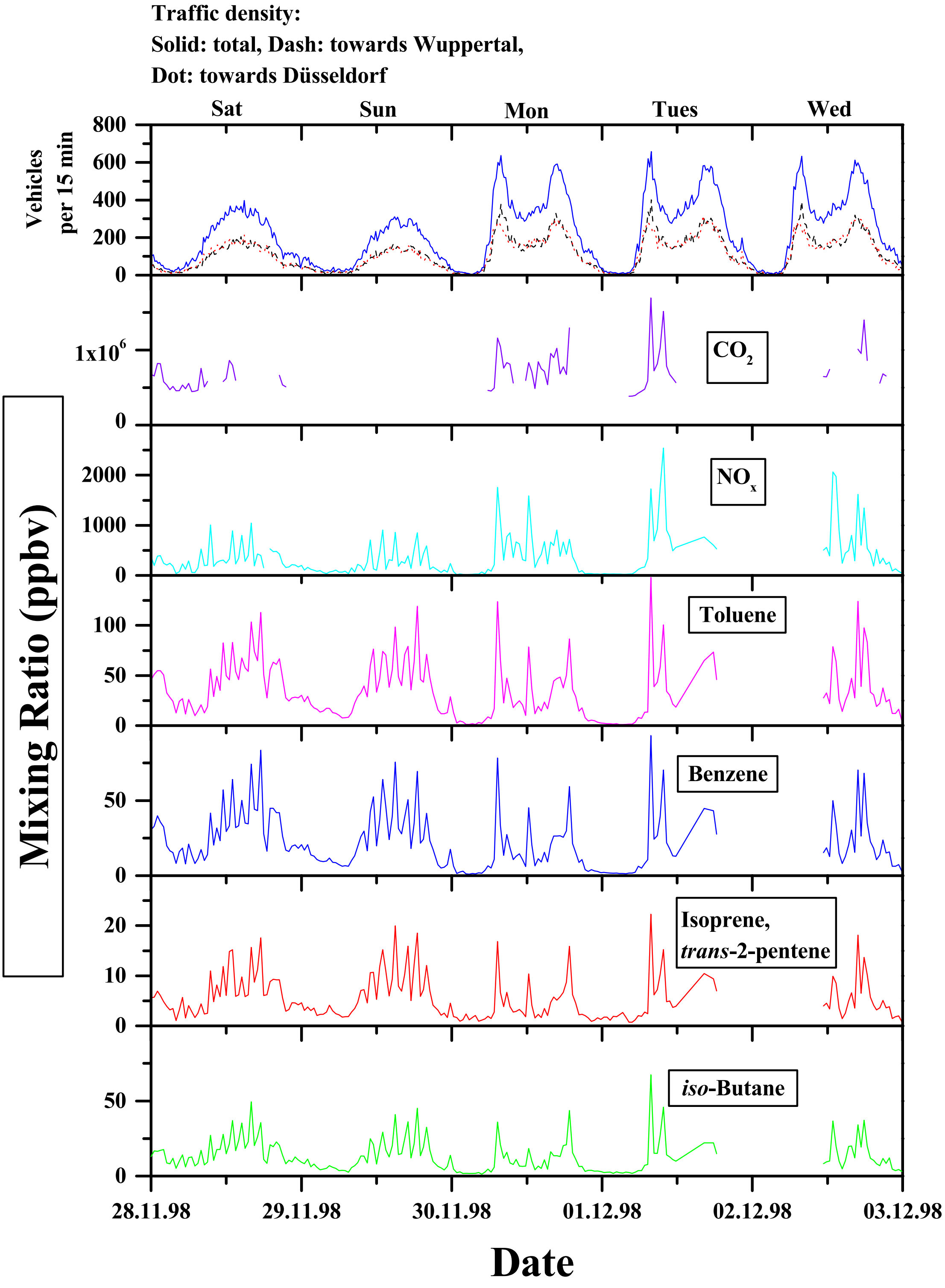
Continuous measurements of NMHCs, NO, NO_2, CO_2, traffic census and meteorological parameters were carried out in the Kiesberg tunnel during several weeks in 1997 and 1998. In the following sections, the results of these campaigns are presented.

3.1.1 Mixing ratios

29 non-methane hydrocarbons were quantified by using a prepared standard gas mixture for calibration during the tunnel campaign of August, 1997. In the tunnel campaigns of March, 1998 and November-December, 1998, due to the information gathered from the Berlioz campaign in 1998 by using standard gas mixtures from NCAR (71 component C_2-C_{10} standard gas mixture) and NPL (27 component C_2-C_9 standard gas mixture), it was possible to identify and quantify 64-66 non-methane hydrocarbons.

Figure 3.1 shows exemplary a typical diurnal variation among the traffic density, CO_2, NO_x, toluene, benzene, isoprene, *trans*-2-pentene and *iso*-butane.

It can be seen from Figure 3.1 that there are good correlations among the NMVOCs compounds, NO_x and CO_2 for high traffic density at daytime. High mixing ratios of up to 199 ppbv toluene (inclusive a small contribution from the coeluted 4-methylheptane), 104 ppbv benzene, 153 ppbv *iso*-pentane, 46 ppbv isoprene/*trans*-2-pentene, 77 ppbv *iso*-butane and 96 ppbv propene were measured.



Analytical instruments used: for NMHCs: Airmovoc HC2010, for NO_x: Horiba, for CO_2: FTIR, for counting no. of vehicles: contact loops.

Figure 3.1: Typical diurnal variation of *iso*-butane, isoprene/*trans*-2-pentene, benzene, toluene, NO_x, CO_2 and traffic density during the Kiesberg tunnel campaign of November-December, 1998 in Wuppertal.

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.

Tables 3.1-3.3 summarize the maximum, minimum, average, standard deviation (S. D.) and median for the three tunnel campaigns. The night values shown in the Tables 3.1-3.3 indicate the values where there passed a very few number of traffic through the Kiesberg tunnel during the night, which can be taken as the background values.

Table 3.1: List of mixing ratios of C_2-C_9 NMHCs, NO and NO_2 measured in the Kiesberg tunnel air during August, 1997.

Components	Tunnel air (ppbv)					Night values (ppbv)		Background air (ppbv)	
	maximum	minimum	average	S. D.	median	average	S. D.	average	S. D.
	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv
Ethene/Ethyne	162.40	2.30	26.20	27.90	17.30	5.00	1.80	3.40	1.80
Ethane	17.30	1.80	5.30	3.70	4.20	2.50	0.20	2.10	0.30
Propene	96.40	0.00	23.70	23.30	16.70	3.20	1.60	2.20	1.30
Propane	4.80	1.20	1.90	1.00	1.60	1.40	0.10	1.10	0.20
iso-Butane	35.10	0.80	9.20	8.80	5.80	1.60	0.50	2.00	1.00
iso-/1-Butene	42.80	0.90	11.20	10.60	7.60	1.50	0.70	1.60	0.70
n-Butane	98.70	0.70	19.90	20.50	11.70	2.60	1.30	2.90	1.70
trans-Butene	24.20	0.80	6.30	5.60	4.30	0.90	0.10	1.00	0.20
cis-Butene	13.70	0.90	4.40	3.20	3.60	<d.l.	–	4.60	4.40
iso-Pentane	153.10	0.80	29.90	34.50	13.70	3.00	1.40	2.00	0.90
1-Pentene	15.60	0.50	6.00	5.10	4.80	<d.l.	–	–	–
n-Pentane	52.30	0.60	10.40	13.90	4.00	0.90	0.20	0.90	0.40
2,2-Dimethylbutane	7.60	0.40	2.70	2.30	2.00	<d.l.	–	0.40	–
Cyclopentane, *iso*-hexane	42.40	0.80	11.00	12.90	4.20	1.30	0.30	1.30	0.40
1-Hexene	7.90	0.40	2.30	2.20	1.30	0.50	0.00	0.60	0.10
n-Hexane	12.10	0.40	3.40	3.50	2.00	0.50	0.10	0.60	0.10
Methylcyclopentane	15.30	0.40	3.90	3.60	2.70	0.70	0.20	0.90	0.50
Benzene	81.30	2.30	21.50	19.60	14.90	4.10	1.50	–	–
Cyclohexane	15.90	0.70	3.30	3.30	2.00	1.00	0.20	1.50	0.60
n-Heptane	11.60	0.30	2.50	2.30	1.70	0.60	0.20	1.30	1.90
Toluene	134.90	1.00	36.80	35.30	24.00	4.00	1.70	3.80	2.40
n-Octane	18.10	0.30	1.90	3.60	0.80	0.30	0.00	0.60	0.30
Ethylbenzene	30.00	0.30	4.70	4.90	3.00	0.60	0.20	1.30	1.30
m-/*p*-Xylene	37.20	0.40	7.90	8.00	4.60	0.60	0.20	2.70	3.60
o-Xylene	15.20	0.30	3.50	3.10	2.70	0.50	0.00	1.80	1.80
NO	8313.9	6.7	1535.1	1807.1	901.9	175.1	141.1	24.2	142.1
NO_2	1939.1	0.5	137.4	162.6	94.3	49.4	31.4	13.3	8.6

S.D.: Standard Deviation, <d.l.: under detection limit, –: values could not be determined, *e.g.*, 1-pentene and benzene could not be measured for this particular case. Analytical instruments: for NMHCs- Airmovoc HC2010, for nitrogen oxides- 14D/E (Thermoelectron).

Table 3.2: List of mixing ratios of C_2-C_9 NMHCs measured in the Kiesberg tunnel air during March, 1998.

Components	Tunnel air					Night values	
	Maximum	Minimum	Average	S.D.	Median	Average	S.D.
	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv
Propene	49.67	0.04	15.14	9.72	12.40	4.01	1.67
Propane	106.32	0.02	7.06	8.93	1.99	1.10	0.19
iso-Butane	27.69	0.07	8.61	6.21	6.42	0.89	0.68
1-/*iso*-Butene	48.79	0.13	10.93	7.90	8.49	1.56	1.11
1,3-Butadiene, *n*-butane	123.83	0.35	28.02	20.57	18.73	3.36	2.46
trans-Butene	18.70	0.06	4.59	3.32	3.41	0.68	0.47
cis-Butene	9.69	0.07	2.46	1.79	1.75	0.37	0.24
3-Methyl-1-butene	2.70	0.03	0.67	0.44	0.54	0.13	0.06
iso-Pentane	110.21	0.45	24.79	17.84	17.56	2.96	2.06
1-Pentene, unknown	7.57	0.13	1.87	1.16	1.63	0.73	0.17
2-Methyl-1-butene	52.48	0.09	3.02	2.40	2.06	0.40	0.23
n-Pentane	38.13	0.52	9.39	6.43	7.00	1.45	0.77
Isoprene, *trans*-2-pentene	16.56	0.12	4.01	2.66	3.29	0.72	0.45
cis-2-Pentene	4.41	0.01	1.07	0.72	0.87	0.18	0.15
2-Methyl-2-butene	14.24	0.11	3.24	2.28	2.48	0.61	0.44
2,2-Dimethylbutane	3.82	0.02	0.78	0.52	0.57	0.16	0.13
Cyclopentene, 3-/4-methyl-1-pentene	6.63	0.10	1.50	1.01	1.13	0.31	0.21
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	52.04	0.18	11.20	7.33	9.08	1.72	1.14
3-Methylpentane	15.81	0.08	3.40	2.17	2.63	0.57	0.37
2-Methyl-1-pentene/1-Hexene	3.25	0.02	0.91	0.53	0.82	0.26	0.14
n-Hexane	12.67	0.19	2.96	1.88	2.50	0.48	0.25
cis-3-Hexene, *trans*-2-hexene, unknown	3.69	0.05	0.72	0.44	0.56	0.16	0.12
cis-2-Hexene	1.60	0.01	0.29	0.21	0.19	0.06	0.04
Methylcyclopentane, 2,4-dimethylpentane	9.76	0.04	2.73	1.89	1.85	0.41	0.37
Methylcyclopentane	13.69	0.06	1.07	0.91	0.66	0.11	0.05
2,4-Dimethylpentane	14.07	0.21	3.32	2.07	2.64	0.51	0.36
Benzene	88.12	0.52	18.24	13.70	12.75	2.64	1.73
Cyclohexane, 2,3-dimethylpentane	7.28	0.10	1.70	1.15	1.21	0.28	0.14
3-Methylhexane	8.19	0.10	1.83	1.23	1.28	0.28	0.13
iso-Octane	12.55	0.11	2.17	1.49	1.43	0.39	0.18
n-Heptane	3.38	0.06	0.83	0.54	0.65	0.14	0.04
2,3-Dimethyl-2-pentene	1.60	0.00	0.25	0.28	0.10	–	–
Methylcyclohexane	5.86	0.11	1.44	0.78	1.17	0.23	0.13
2,3,4-Trimethylpentane	4.56	0.03	0.78	0.58	0.49	0.11	0.07
2-/3-Methylheptane	7.33	0.05	1.43	0.92	1.07	0.29	0.12
Toluene	198.67	1.13	34.26	23.53	24.54	5.39	2.10
Ethylbenzene	36.36	0.45	7.59	4.96	5.98	1.31	0.59
m-/*p*-Xylene	73.53	0.79	16.97	10.79	14.12	2.97	1.67
n-Nonane	0.63	0.02	0.18	0.10	0.14	0.05	0.02
Styrene	10.31	0.08	2.61	1.52	2.27	0.47	0.15
o-Xylene	28.63	0.34	7.00	4.19	5.90	1.35	0.76
n-Octane, unknown	6.47	0.05	1.11	0.72	0.85	0.18	0.09
iso-Propylbenzene	2.39	0.00	0.63	0.42	0.48	0.08	0.06
n-Propylbenzene	4.22	0.03	0.97	0.69	0.69	0.15	0.10
m-/*p*-Ethyltoluene	35.40	0.09	5.73	4.03	4.00	0.74	0.45
Mesitylene	37.47	0.07	4.66	3.47	3.09	0.58	0.38
o-Ethyltoluene	5.41	0.00	1.36	0.92	0.98	0.20	0.14

Analytical instrument used: for NMHCs- Airmovoc HC2010. Ethene/Ethyne and ethane could not be properly measured during this tunnel campaign.

Table 3.3: List of mixing ratios of C_2-C_{10} NMHCs, NO and NO_2 measured in the Kiesberg tunnel air during November-December, 1998.

Components	Tunnel air					Night values	
	Maximum	Minimum	Average	S.D.	Median	Average	S.D.
	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv
Ethene/Ethyne	865.20	7.33	150.40	150.80	101.60	31.34	31.65
Ethane	92.90	3.41	23.00	15.00	19.20	11.32	4.93
Propene	82.40	0.94	18.30	14.90	15.20	5.57	5.64
Propane	28.60	2.33	7.70	3.80	6.50	6.42	3.20
iso-Butane	76.50	1.33	14.40	12.30	11.60	4.16	3.26
iso-/1-Butene	66.50	0.61	13.20	12.10	10.20	2.51	2.44
1,3-Butadiene	47.80	0.09	9.40	9.10	7.10	1.42	1.77
n-Butane	110.50	1.64	21.70	18.90	17.20	5.73	4.34
trans-Butene	29.10	0.03	5.20	5.10	3.80	0.81	1.04
cis-Butene	17.30	0.07	3.10	3.00	2.30	0.54	0.61
3-Methyl-1-butene, unknown	16.30	0.15	4.60	2.50	4.30	3.27	2.11
iso-Pentane	150.00	0.10	30.50	28.90	22.20	5.31	5.62
1-Pentene	9.80	0.17	2.20	1.70	1.80	0.72	0.43
2-Methyl-1-butene	37.00	0.15	9.10	6.20	8.10	3.61	2.89
n-Pentane	17.10	0.13	2.90	2.50	2.00	1.03	0.69
Isoprene, *trans*-2-pentene	45.80	0.20	5.80	5.30	4.20	1.63	1.13
cis-2-Pentene	27.00	0.02	2.50	3.50	1.30	0.83	1.42
2-Methyl-2-butene	23.60	0.03	4.80	4.60	3.40	0.91	1.13
2,2-Dimethylbutane	8.00	0.04	1.40	1.40	1.00	0.25	0.20
Cyclopentene, 3-/4-methyl-1-pentene	42.70	0.05	2.70	3.40	1.90	0.43	0.62
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	79.50	0.60	16.20	14.80	12.40	3.40	3.45
3-Methylpentane	19.10	0.10	3.90	3.70	3.00	0.84	0.96
2-Methyl-1-pentene	8.40	0.01	0.80	0.90	0.60	0.16	0.21
n-Hexane	21.40	0.17	4.30	4.10	3.10	1.10	1.28
cis-3-Hexene, *trans*-2-hexene, unknown	5.80	0.01	1.10	1.00	0.80	0.22	0.25
cis-2-Hexene	2.10	0.00	0.40	0.40	0.30	0.02	0.01
Methylcyclopentane	3.10	0.03	0.40	0.40	0.30	0.07	0.05
2,4-Dimethylpentane	17.50	0.06	2.60	2.80	1.80	0.21	0.15
Benzene	104.30	1.03	23.80	20.90	18.20	5.13	5.09
2-Methylhexane	3.80	0.03	0.80	0.90	0.40	0.08	0.04
Cyclohexane, 2,3-dimethylpentane	8.00	0.20	1.70	1.30	1.50	0.69	0.47
3-Methylhexane	8.90	0.04	1.80	1.50	1.40	0.41	0.40
iso-Octane	16.20	0.05	3.10	3.10	2.20	0.76	1.03
n-Heptane	7.30	0.13	1.70	1.30	1.40	0.60	0.46
2,3-Dimethyl-2-pentene	0.40	0.00	0.10	0.10	0.10	0.04	0.03
Methylcyclohexane	4.30	0.06	1.10	0.90	0.80	0.27	0.22
2,3,4-Trimethylpentane	4.80	0.01	0.80	0.90	0.50	0.20	0.34
2-/3-Methylheptane	4.10	0.03	0.90	0.70	0.90	0.20	0.19
Toluene	163.80	1.04	36.70	31.30	28.90	7.02	7.09
Ethylbenzene	32.20	0.21	8.30	7.70	5.90	2.59	3.14
m-/*p*-Xylene	45.10	0.46	10.60	7.20	10.10	2.75	2.28
n-Nonane	2.10	0.00	0.10	0.10	0.10	0.08	0.03
Styrene	16.30	0.11	3.40	3.10	2.80	1.21	1.55
o-Xylene	22.70	0.21	5.20	3.80	4.50	1.56	1.41
n-Octane	1.70	0.04	0.50	0.40	0.50	0.15	0.09
iso-Propylbenzene	0.80	<d.l.	0.20	0.20	0.20	0.05	0.03
n-Propylbenzene	1.00	0.01	0.40	0.20	0.40	0.13	0.12
m-/*p*-Ethyltoluene	2.80	0.03	1.20	0.70	1.20	0.49	0.39

Table 3.3 (continued):

Components	Tunnel air					Night values	
	Maximum	Minimum	Average	S.D.	Median	Average	S.D.
	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv
Mesitylene	0.70	0.00	0.30	0.20	0.20	0.11	0.10
o-Ethyltoluene	1.30	0.00	0.50	0.30	0.50	0.20	0.18
1,2,4-Trimethylbenzene, *n*-decane	2.90	0.09	1.40	0.70	1.50	0.65	0.38
tert-Butylbenzene	77.00	0.00	0.50	5.80	0.10	0.06	0.03
NO	3309.40	11.70	437.50	516.80	276.80	55.50	2.10
NO_2	228.30	0.00	23.00	33.30	12.20	55.30	3.00

Analytical instruments used: for NMHCs: Airmovoc HC2010, for nitrogen oxides: Horiba. Remark: It can be calculated by considering the average values shown in Table 3.3 and the corresponding unit risk factors (US EPA 1998, 2001; IRIS 1998, 2000) that due to the exposure to fresh vehicular emission in Wuppertal, the relative carcinogenic risk associated with 1,3-butadiene is about 15 times greater than that for benzene (Duffy *et al.*,1996; Calabrese *et al.*, 1991).

From the Tables 3.1-3.3, it can be observed that among alkanes, *iso*-pentane, among alkenes/alkynes, ethene/ethyne and among aromatic hydrocarbons, toluene have the largest mixing ratio.

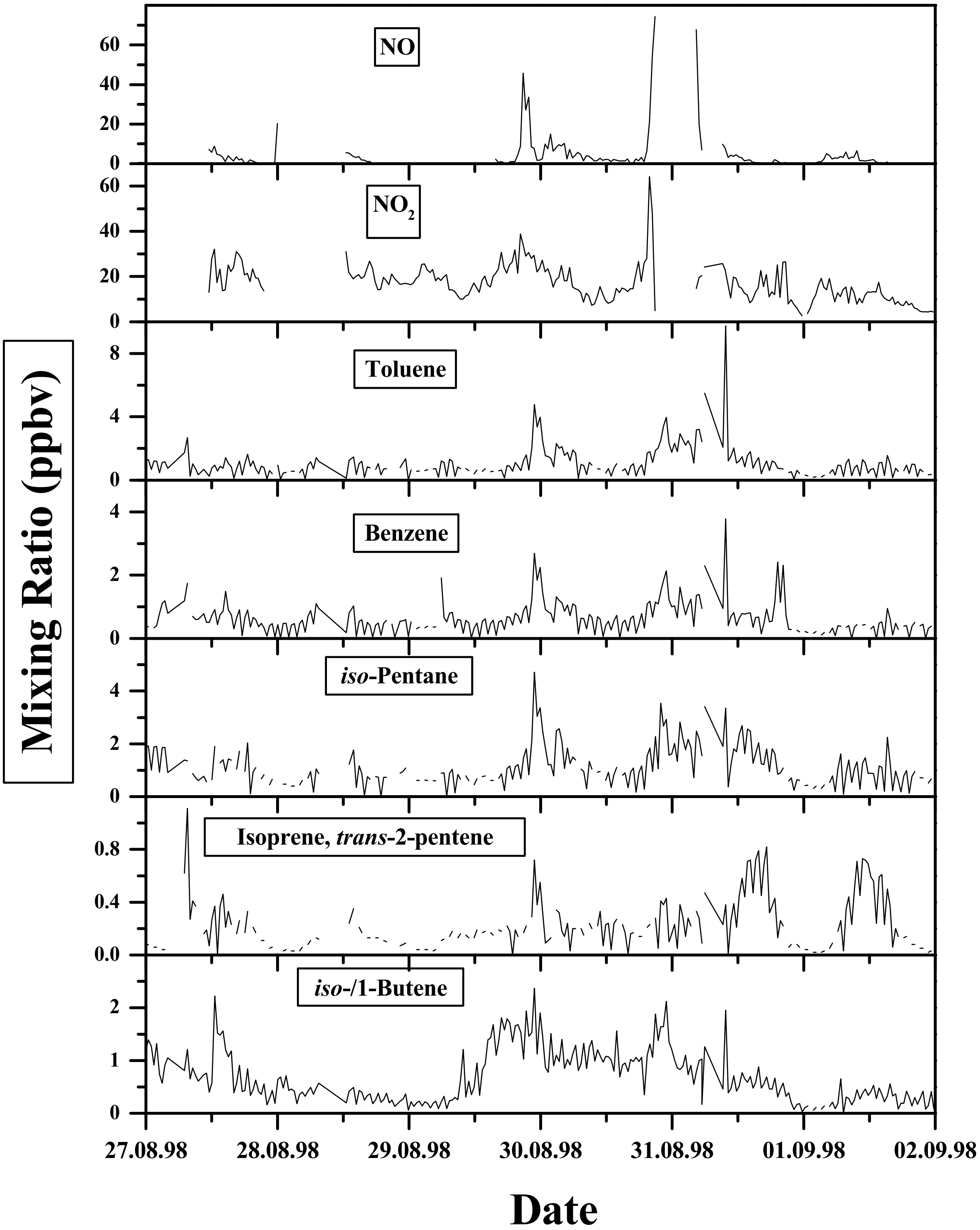
3.2 Ambient air

Continuous measurements of NMHCs, NO, NO_2 and meteorological parameters were carried out at the University of Wuppertal during several weeks in August-September, 1998.
In the framework of the Berlioz project, measurements of NMHCs and NO_x were also performed in a rural area of Germany, Menz in July-August, 1998.

3.2.1 Mixing ratios

3.2.1.1 City air of Wuppertal

Figure 3.2 shows the diurnal variation of NO, NO_2, *iso*-/1-butene, isoprene/*trans*-2-pentene, *iso*-pentane, benzene and toluene during the city air measurement of Wuppertal.



Analytical instruments used: for NMHCs- Airmovoc HC2010, nitrogen oxides- Eco-physics CDL 770AL ppt.

Figure 3.2: Diurnal variation of NO, NO_2, *iso*-/1-butene, isoprene/*trans*-2-pentene, *iso*-pentane, benzene and toluene during the city air measurement of Wuppertal, in August-September, 1998.

From Figure 3.2, one can observe that for 30.08.98 (Sunday) and 31.08.98 (Monday) there was a good correlation among NO, NO_2 and other NMHCs measured in the city of Wuppertal.

Table 3.4 shows an overview of mixing ratios found in the city air of Wuppertal.

Table 3.4: Overview of mixing ratios found in the city of Wuppertal during the measurement campaigns in August-September, 1998.

Components	Maximum	Minimum	average	S.D.	Median
	ppbv	ppbv	ppbv	ppbv	ppbv
Ethene/Ethyne	8.637	1.118	2.608	0.857	2.474
Ethane	15.454	0.346	3.293	2.497	2.618
Propene	3.070	0.004	0.594	0.445	0.512
Propane	1.840	0.006	0.497	0.382	0.408
iso-Butane	4.134	0.005	0.549	0.594	0.399
iso-/1-Butene	2.371	0.000	0.689	0.497	0.554
1,3-Butadiene, *n*-butane	9.885	0.021	1.658	1.293	1.289
trans-Butene	0.915	0.000	0.116	0.130	0.069
cis-Butene	0.700	0.002	0.087	0.085	0.061
3-Methyl-1-butene	0.298	0.001	0.116	0.075	0.112
iso-Pentane	4.709	0.019	1.124	0.741	0.934
1-Pentene	0.130	0.005	0.048	0.029	0.043
2-Methyl-1-butene	0.379	0.058	0.170	0.057	0.166
n-Pentane	1.551	0.022	0.426	0.262	0.387
isoprene, *trans*-2-pentene	1.112	0.002	0.226	0.195	0.175
cis-2-Pentene	0.218	0.000	0.042	0.033	0.034
2-Methyl-2-butene	0.579	0.032	0.148	0.077	0.131
2,2-Dimethylbutane	0.319	0.001	0.055	0.048	0.039
Cyclopentene, 3-/4-methyl-1-pentene	0.130	0.001	0.022	0.021	0.014
Cyclopentane	0.975	0.325	0.513	0.149	0.474
Cyclopentane/2,3-Dimethylbutane/ 2-Methylpentane	5.000	0.032	0.627	0.502	0.510
3-Methylpentane	1.310	0.001	0.150	0.131	0.112
2-Methyl-1-pentene	0.256	0.001	0.028	0.025	0.022
n-Hexane	1.006	0.001	0.170	0.160	0.116
cis-3-Hexene, *trans*-2-hexene	0.283	0.000	0.033	0.043	0.018
cis-2-Hexene	0.068	0.000	0.010	0.007	0.009
Methylcyclopentane	0.104	0.006	0.030	0.020	0.025
2,4-Dimethylpentane	0.411	0.035	0.146	0.081	0.131
Methylcyclopentane, 2,4-dimethylpentane	0.711	0.020	0.145	0.101	0.114
Benzene	3.774	0.001	0.640	0.500	0.531
Cyclohexane, 2,3-dimethylpentane	0.983	0.001	0.141	0.137	0.099
3-Methylhexane	4.525	0.003	0.134	0.343	0.070
iso-Octane	0.805	0.001	0.082	0.083	0.061
n-Heptane	1.748	0.001	0.093	0.188	0.054
iso-Octane, *n*-heptane	4.159	0.003	0.166	0.348	0.104
2,3-Dimethyl-2-pentene	0.034	0.000	0.012	0.013	0.005
Unknown, methylcyclohexane	2.811	0.001	0.107	0.226	0.061
2,3,4-Trimethylpentane	0.229	0.000	0.022	0.023	0.016
2-/3-Methylheptane	0.308	0.000	0.053	0.049	0.039
Toluene	9.749	0.013	1.060	0.976	0.835
n-Octane	0.172	0.000	0.023	0.027	0.015
Ethylbenzene	1.185	0.005	0.144	0.126	0.118
m-/*p*-Xylene	2.361	0.008	0.260	0.245	0.212
n-Nonane	0.089	0.000	0.008	0.011	0.006
Styrene	0.718	0.001	0.129	0.158	0.065
o-Xylene	1.090	0.000	0.118	0.116	0.095
iso-Propylbenzene	0.064	0.000	0.011	0.008	0.009
n-Propylbenzene	0.069	0.000	0.012	0.012	0.010
m-/*p*-Ethyltoluene	0.184	0.000	0.051	0.055	0.025
Mesitylene	0.058	0.000	0.015	0.016	0.007

Table 3.4 (continued):

Components	Maximum	Minimum	average	S.D.	Median
	ppbv	ppbv	ppbv	ppbv	ppbv
o-Ethyltoluene	0.690	0.000	0.029	0.064	0.014
1,2,4-Trimethylbenzene, *n*-decane	0.313	0.000	0.044	0.041	0.038
tert-Butylbenzene	0.022	0.000	0.007	0.007	0.004
NO	75.427	0.007	9.941	21.116	2.118
NO2	64.143	2.681	16.931	8.400	15.430
NO_x	102.254	0.032	24.443	19.901	18.908

S.D.: standard deviation of the average value, analytical instruments used: for NMHCs- Airmovoc HC2010, nitrogen oxides- Eco-physics CDL 770AL ppt.

It can be seen from Table 3.4 that among alkanes, ethane, among alkenes/alkynes, ethene/ethyne and among aromatic hydrocarbons, toluene have the largest mixing ratio.

3.2.1.2 Rural area (Menz)

Table 3.5 shows the average mixing ratios of some selected nonmethane hydrocarbons and nitrogen oxides found in the background air of Menz.

Table 3.5: Mixing ratios of some selected nonmethane hydrocarbons (in pptv) and nitrogen oxides (in ppbv) measured in the background air of Menz.

Components	Maximum	Minimum	average	S. D.	median
	pptv	pptv	pptv	pptv	pptv
Ethene/Ethyne	1338	<d.l.	190	167	95
Ethane	19511	1	1298	1291	561
Propene	1179	<d.l.	174	122	115
Propane	1144	7	315	196	237
iso-Butane	3188	<d.l.	426	313	268
iso/1-Butene	2204	<d.l.	299	247	165
1,3-Butadiene, *n*-butane	9830	<d.l.	1061	789	657
iso-Pentane	1770	2	284	171	215
n-Pentane	1760	1	183	118	133
Isoprene, *trans*-2-pentene	1514	<d.l.	157	145	68
cis-2-Pentene	102	<d.l.	22	13	16
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	555	2	134	66	114
3-Methylpentane	301	<d.l.	74	56	53
n-Hexane	168	<d.l.	45	22	40
Benzene	746	<d.l.	232	95	196
n-Heptane	411	<d.l.	29	19	19
Toluene	1235	<d.l.	216	120	185
Ethylbenzene	291	1	37	21	30
m-/*p*-Xylene	655	1	60	37	50
o-Xylene	192	<d.l.	23	17	15
Mesitylene	17	<d.l.	3	2	2
1,2,4-Trimethylbenzene	563	2	43	31	27
NO (ppbv)	1.009	<d.l.	0.192	0.222	0.104
NO_2 (ppbv)	6.221	<d.l.	2.176	1.225	2.250
NOx (ppbv)	6.985	<d.l.	2.369	1.308	2.479

S.D.: standard deviation, <d.l.: under the detection limit, analytical instruments used: for NMHCs- Airmovoc HC2010, nitrogen oxides- Eco-physics CDL 770AL ppt.

According to Table 3.5, it can be observed that in Menz, among alkanes, ethane, among alkenes/alkynes, isoprene/*trans*-2-pentene and among aromatic hydrocarbons, toluene have the largest mixing ratio.

4 Data evaluation and discussion

4.1 Tunnel studies

In the present study, around 68 different hydrocarbons (NMHCs) were identified and quantified using conventional GC and included about 88 wt% of the totally detected compounds observed in the chromatograms. Fraser *et al.* (1998b) identified more than 200 different C_2-C_{33} NMVOCs by using different analytical techniques, *e.g.* conventional GC, in the exhaust of motor vehicles. Nevertheless, the NMHCs measured in the present study comprised of about 85 wt% of the aromatic hydrocarbons, about 100 wt% of the alkanes and about 100 wt% of the alkenes described in the study mentioned above. Concluding the results of this study, we assume that about 80 wt% of the total NMHC are detected in the present study. On the other hand, Lewis *et al.* (2000) suggest from the results of their studies using an improved method of peak deconvolution from double-column gas chromatography, that the conventional GC technique could only determine around one-third of the total volatile carbon mass. Since there are still questions about the reliability of the results from the double-column GC method and since most of the NMHC-studies found in the literature used conventional GC technique, the present study also utilized this technique for better comparison with other studies.

4.1.1 Emission ratios relative to benzene for different tunnel campaigns

It is well-known that benzene is one of the fingerprint components emitted from road traffic exhaust (Doskey *et al.*, 1992; Schmitz *et al.*, 1999; Derwent *et al.*, 2000) with a life time of a few days (Table A1 II in the Annex-Tables, Seinfeld and Pandis, 1998) during daytime regarding the reaction with OH radicals. Since benzene is officially prohibited from using as solvents in Germany, it is also known that there should be no contribution of benzene from the solvent source sector in Germany (Wickert *et al.*, 1999). Therefore, it can be concluded that principally benzene is emitted from the road traffic exhaust exclusively.

As shown in Tables 3.1-3.3, the mixing ratios of NMHCs were measured in ppbv. For further evaluation, these mixing ratios in ppbv were 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. 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 determined emission ratio in ppbC/ppbC will supply almost the same values of the emission ratios calculated in wt/wt.

Figure 4.1 shows exemplary a correlation curve between toluene (ppbC) and benzene (ppbC) obtained from the measured value for the weekdays of the tunnel campaign of November-December, 1998.

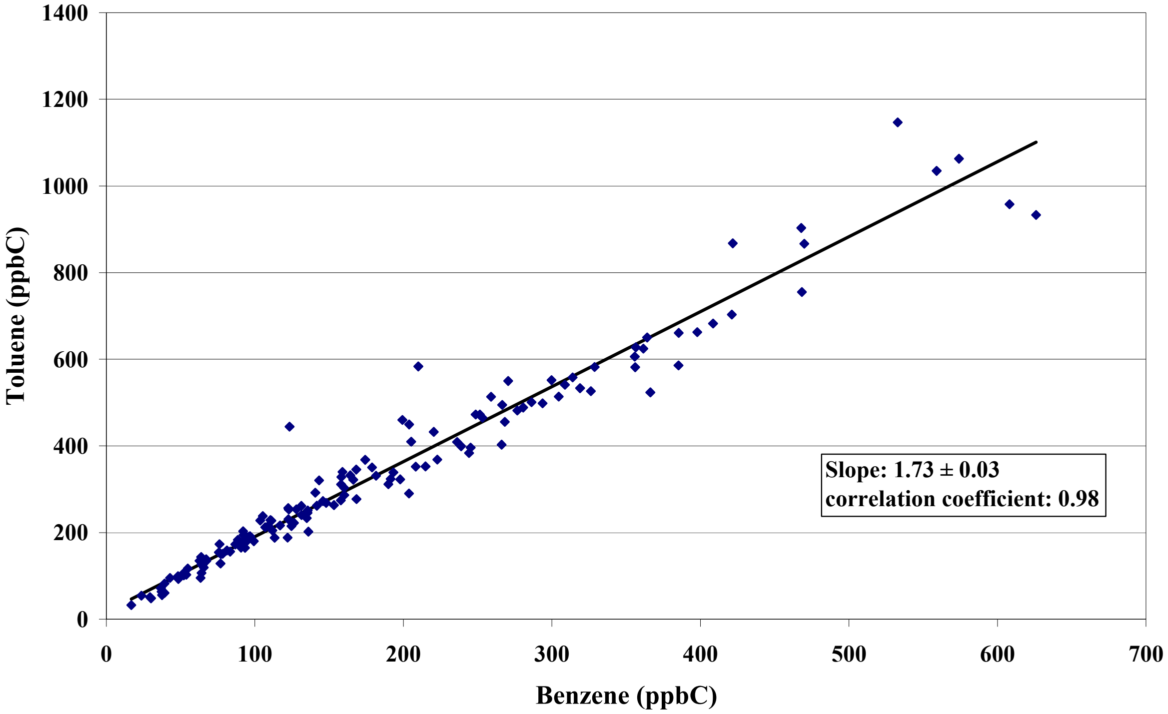


Figure 4.1: Correlation curve between toluene (ppbC) and benzene (ppbC) found for the tunnel campaign of November-December, 1998.

Figure 4.1 shows a good correlation between the values of toluene and benzene. Table A3 I (in the Annex-Tables) presented a list of the emission ratio of other nonmethane hydrocarbons relative to benzene, which also indicate that most of the components correlate with benzene.

For this reason, the mixing ratios of different NMHCs were normalised with respect to benzene, so that a sensible comparison of the mixing ratios of the different NMHCs could be performed with each other for the road traffic exhaust, which would also provide a typical NMHC profile for the road traffic exhaust of Germany. For getting appropriate emission ratios from the road traffic exhaust, only those data points were considered when the traffic density was high in the Kiesberg tunnel, *e.g.* from 6:00 a.m. to 22:00 p.m. Since in the present study, only the emission ratios were further used instead of the absolute values and since the measured mixing ratios of NMHCs in the tunnel were much higher than those of the background air, no subtraction of the mixing ratio of the background air from the measured values were performed.

Figure 4.2 shows the NMHC profile for the different tunnel measurements during weekdays and weekend in ppbC/ppbC. They are also compared with the corresponding values of two European tunnels, namely Gubrist tunnel of Switzerland (Staehelin and Schläpfer, 1994) and Tauern tunnel of Austria (Gregori *et al.*, 1989).

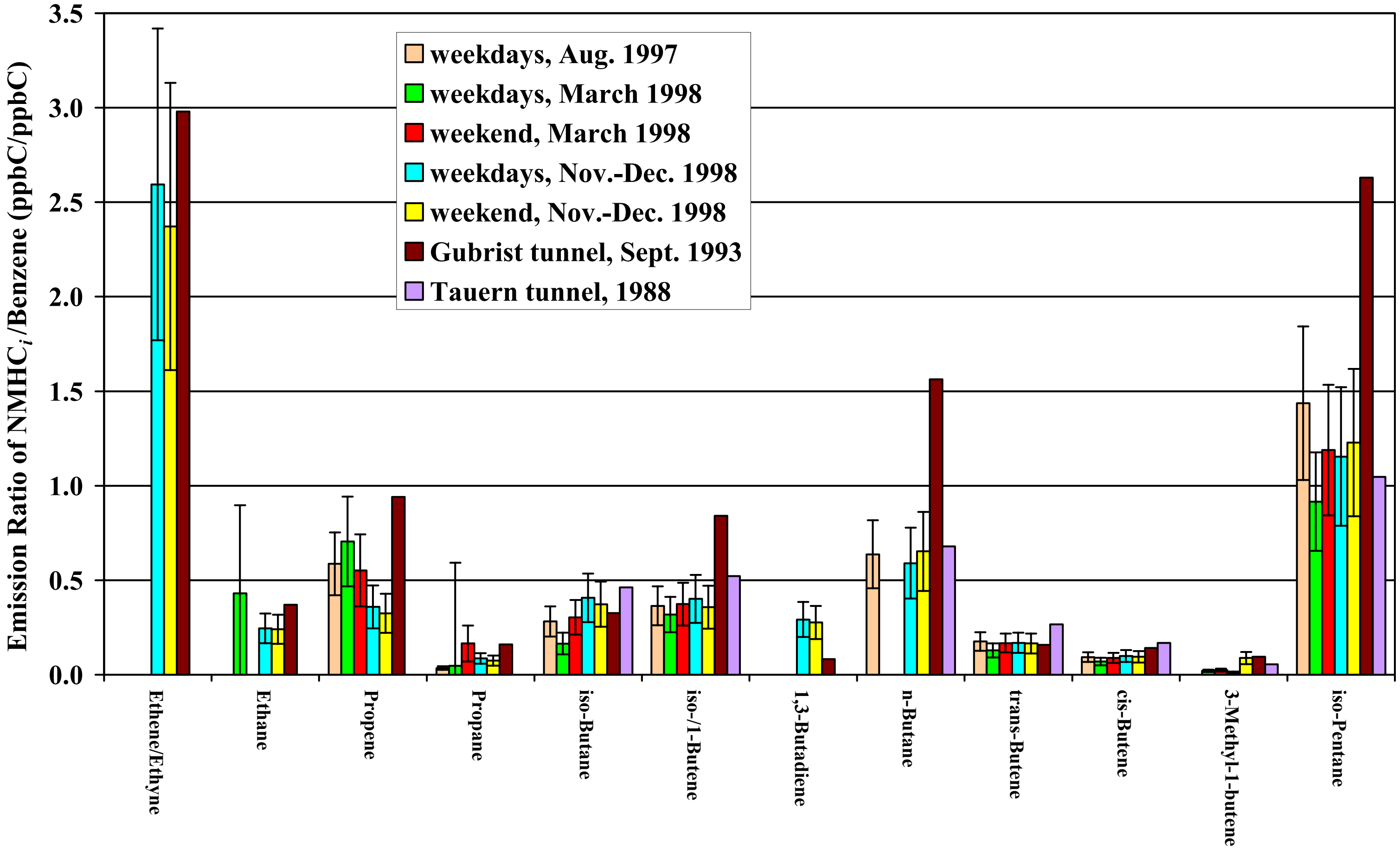


Figure 4.2(a): Comparison of the NMHC-profile for selected components relative to benzene in ppbC/ppbC for the different Kiesberg tunnel campaigns with the Gubrist tunnel (Staehelin and Schläpfer, 1994) and the Tauern tunnel (Gregori *et al.*, 1989).

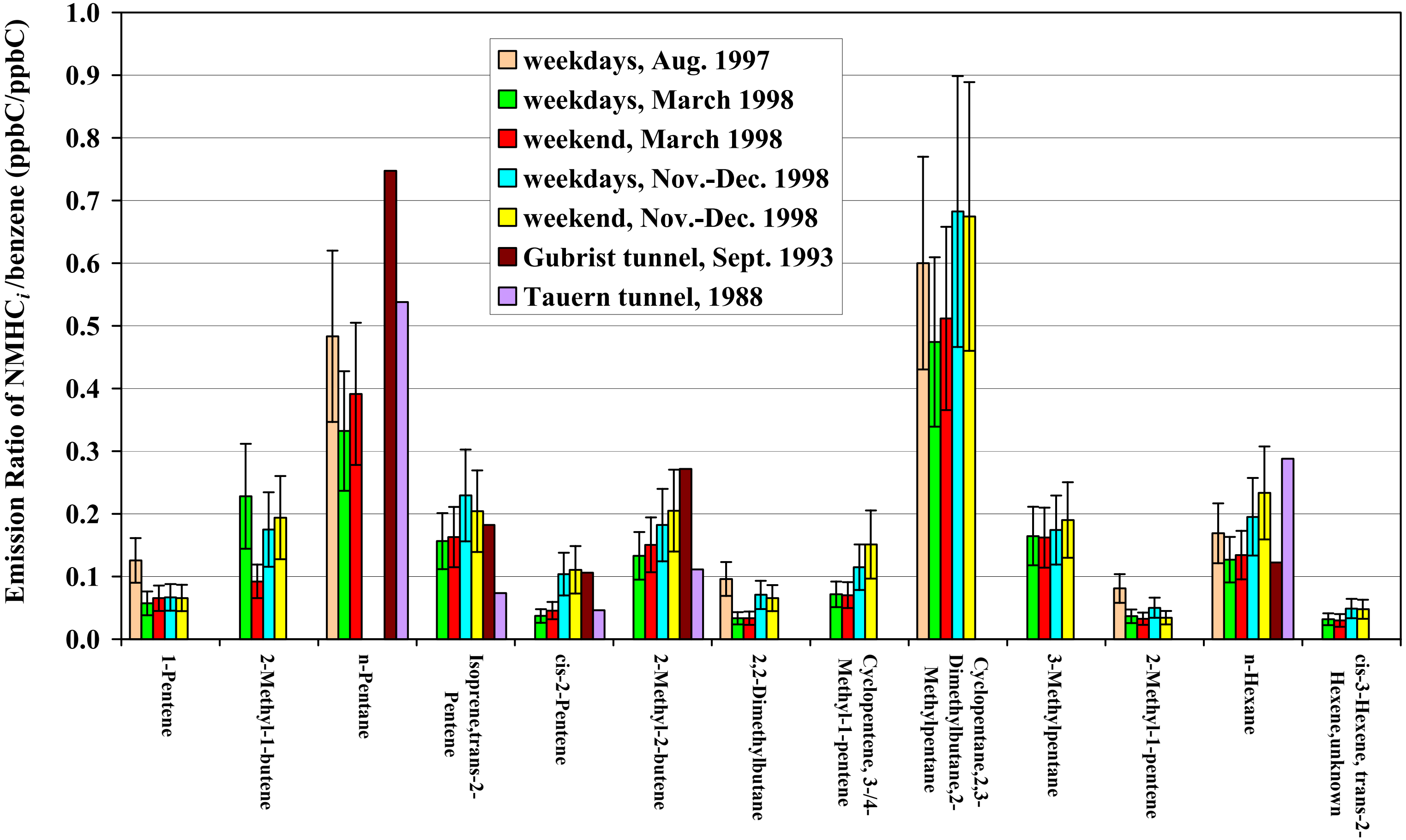


Figure 4.2(b): Comparison of the NMHC-profile for selected components relative to benzene in ppbC/ppbC for the different Kiesberg tunnel campaign with the Gubrist tunnel (Staehelin and Schläpfer, 1994) and the Tauern tunnel (Gregori *et al.*, 1989).

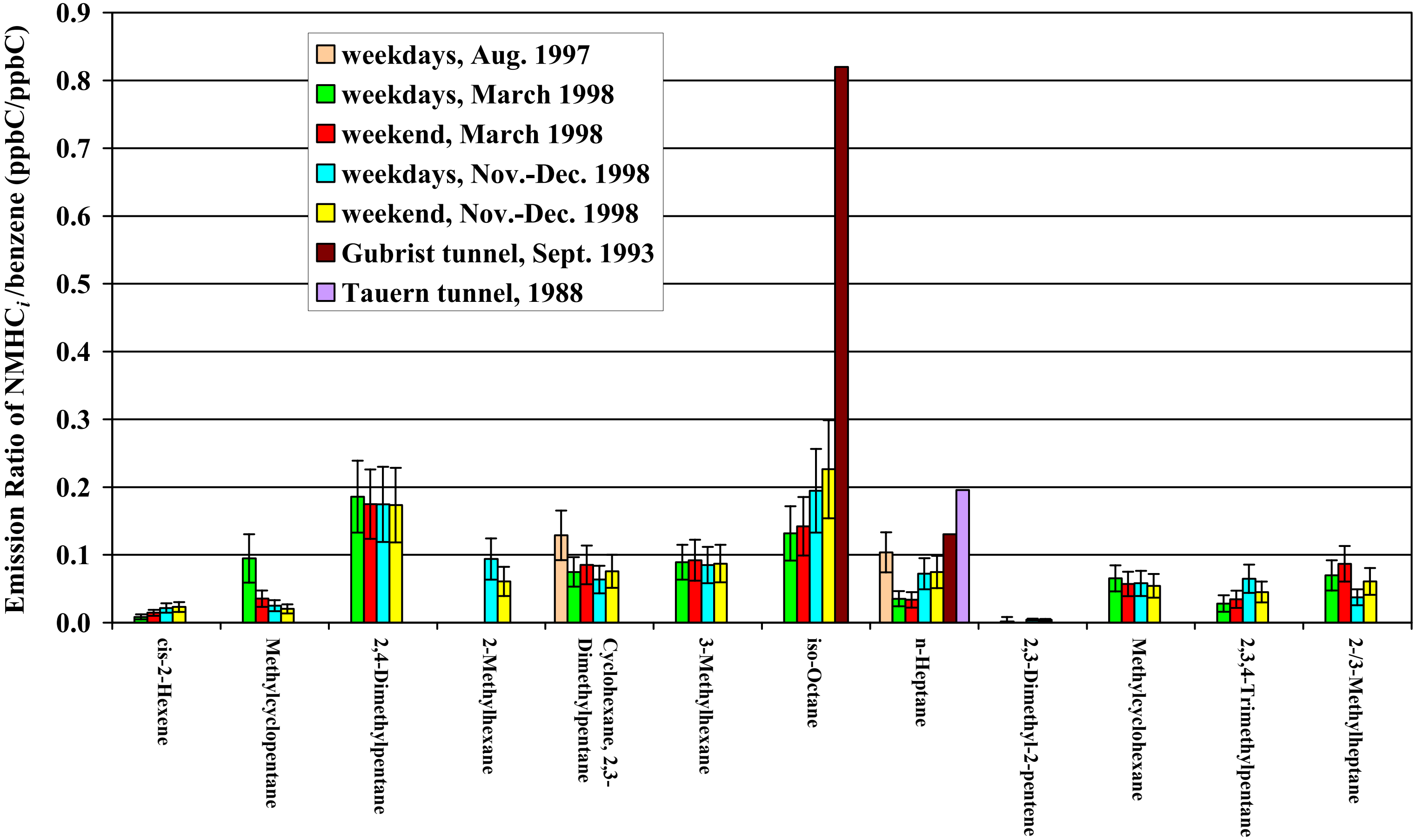


Figure 4.2(c): Comparison of the NMHC-profile for selected components relative to benzene in ppbC/ppbC for the different Kiesberg tunnel campaigns with the Gubrist tunnel (Staehelin and Schläpfer, 1994) and the Tauern tunnel (Gregori *et al.*, 1989).

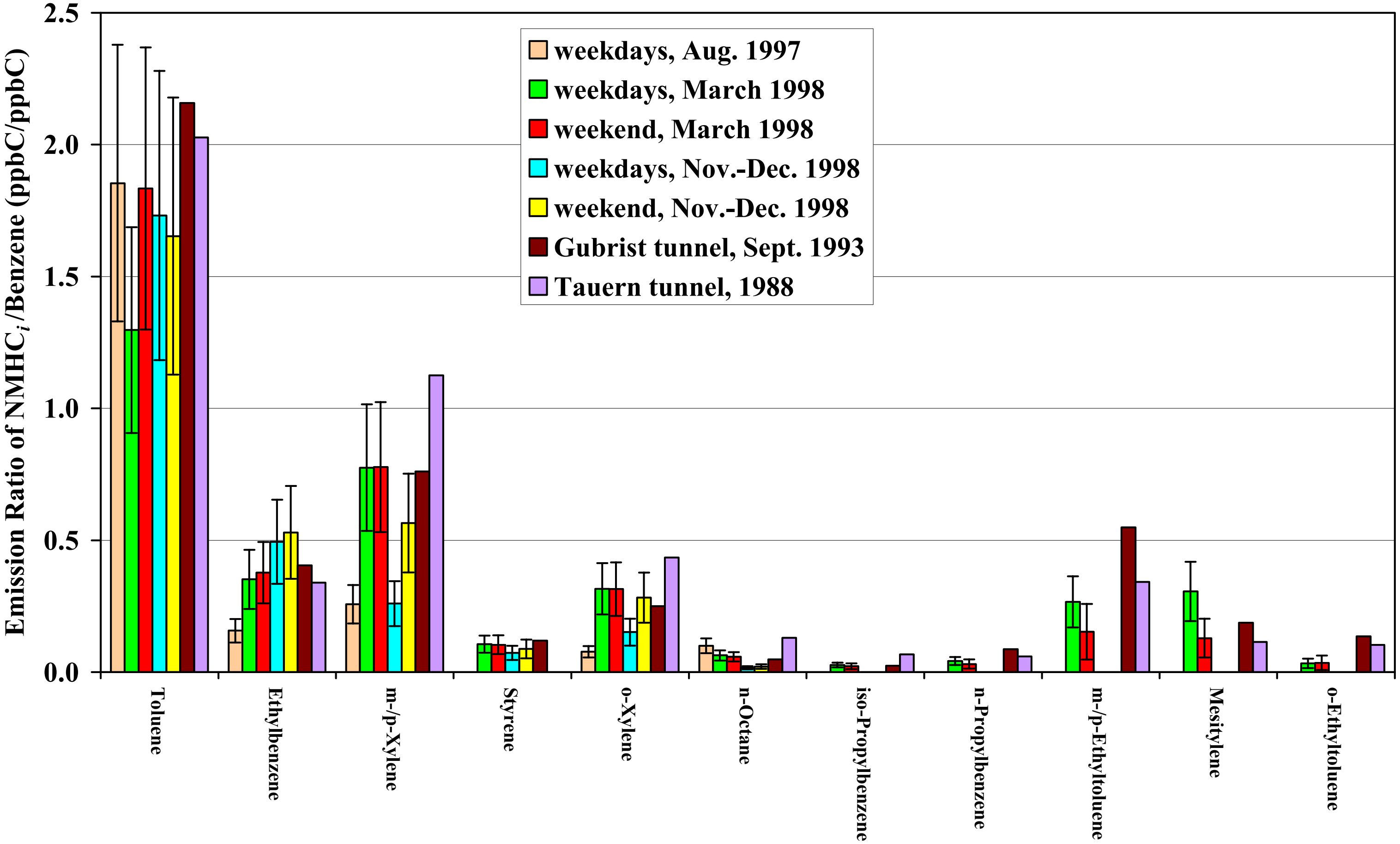


Figure 4.2(d): Comparison of the NMHC-profile for selected components relative to benzene in ppbC/ppbC for the different Kiesberg tunnel campaigns with the Gubrist tunnel (Staehelin and Schläpfer, 1994) and the Tauern tunnel (Gregori *et al.*, 1989).

4.1.1.1 Interpretation of the NMHC-profiles

Figure 4.2 a-d show that for most of the components there were no significant differences within error limits among the NMHC-profiles relative to benzene in ppbC/ppbC for different campaigns in the Kiesberg tunnel, which indicates that during the year 1997 to 1998 there was no significant change of the composition of NMHC-emissions from the road traffic exhaust in the case of Wuppertal Kiesberg tunnel.

According to the statistical picture of the composition of passenger cars for the area of Düsseldorf from the year 1996 to 2000 as shown in Figure 1.3, it is clear that in general, the number of passenger cars with catalyst and other pollutant-reducing systems are increasing and the number of conventional cars are decreasing with time. Specifically, from 1997 to 1998 although the percental number of the gasoline conventional passenger cars in Düsseldorf reduced to three quarters and the gasoline passenger cars with C-and U-catalysts increased by one eighth, there seems to be no influence of this change on the composition of the traffic exhaust. The reason can be explained by the fact that conventional passenger cars (so-called super emitters) emit 10 times more NMVOC than that of a PC with catalyst (Keller *et al.*, 1999). Table 4.1 shows a list of the total emission of NMVOC with catalyst and without catalyst for the year 1996-1998. This data was taken from the Handbook of emission factors for road transport in Germany. The emission factors used in this Handbook, are based essentially on the work which was carried out by the TÜV Rheinland, Cologne, and other institutions (such as the RWTÜV Essen, EMPA Dübendorf, ISB Biel) on behalf of the German Federal Environmental Agency (UBA), Berlin, and the Swiss Federal Office of Environment, Forests and Landscape (FOEFL), Berne. The data for Germany, which are used in this Handbook (such as traffic composition, fuel quality, distribution of trip length, ambient temperature distribution etc.) were collected by IFEU (Institut für Energie- und Umweltforschung, Heidelberg) as part of the research project of the Federal Environmental Agency entitled "Data and Computer Model–Pollutant Emissions Created by Motor Vehicle Traffic in Germany" (UFOPLAN-No. 105 06 057). The data for Switzerland were set up by INFRAS, Berne.

Table 4.1: List of emission factors of total nonmethane hydrocarbons for the vehicles of different categories and engine-systems for the year of 1997 and 1998 in Germany (Keller *et al.*, 1999).

vehicle category	1997				1998			
	gasoline	gasoline	diesel	diesel	gasoline	gasoline	diesel	diesel
	conventional	catalyst-equipped/ pollutant-reducing systems	conventional	pollutant-reducing systems	conventional	catalyst-equipped/ pollutant-reducing systems	conventional	pollutant-reducing systems
	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km
PC	0.704	0.020-0.063	0.052	0.024-0.035	0.680	0.020-0.030	0.053	0.020-0.035
LDV	0.874	0.024-0.038	0.109	0.040-0.054	0.847	0.019-0.039	0.107	0.039-0.054
Truck	–	–	0.967-1.106	0.509-0.707	–	–	0.966-1.106	0.508-0.708

Table 4.1 (continued):

vehicle category	1997				1998			
	gasoline	gasoline	diesel	diesel	gasoline	gasoline	diesel	diesel
	conventional	catalyst-equipped/ pollutant-reducing systems	conventional	pollutant-reducing systems	conventional	catalyst-equipped/ pollutant-reducing systems	conventional	pollutant-reducing systems
	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km
MC	6.160 (2-stroke)	–	–	–	5.908 (2-stroke)	–	–	–
	1.106 (4-stroke)	–	–	–	1.093 (4-stroke)	–	–	–

The above-mentioned values were taken for the driving cycle Highway-60. The characteristics of the driving cycle highway-60: 50% weight for the speed of the vehicles between 70-80 km/h and 50% weight for the speed of the vehicles between 80-90 km/h, the number of vehicles passing per lane- smaller than 1400.

From Table 4.1 it is understandable that for the driving cycle of highway-60, PCs driven by gasoline with conventional engines emit 11-35 times more NMHCs than those with catalyst. Similarly, LDVs operated with gasoline emit 22-45 times more NMHCs with conventional engines than those with catalyst. It can also be noted that the emission of NMHCs from the vehicles driven by diesel for PC and LDV with pollutant-reducing systems is lower by a factor of about 2 than for those without that system.

Schmitz *et al.* (1999) had 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. Figure 4.3a shows a comparison of emission factors of different NMHCs from different car engines for the driving cycle Autobahn Phase 1, which clearly indicates the enormous emissions of different NMHCs from the gasoline engine without catalyst in compared to the emissions from other ones. Figure 4.3b-c also show a comparison of emission ratios of different NMHCs relative to benzene (mg/mg) from the three different car engines with the calculated emission ratios using the traffic fleet composition of LDV in the Kiesberg tunnel. The traffic fleet composition of LDV in the Kiesberg tunnel is as follows: catalyst-equipped cars with gasoline engine: 57%, conventional cars with gasoline engine: 26% and cars with diesel engine: 17%. The data used was 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%). Although the speed range of this phase is higher than that in the Kiesberg tunnel, this phase was considered for comparison because the other phases had higher speed range. The US-75 driving cycle was not considered because it contained some contribution of stop mode and in the Kiesberg tunnel, except the congested period, there is no contribution of stop mode.

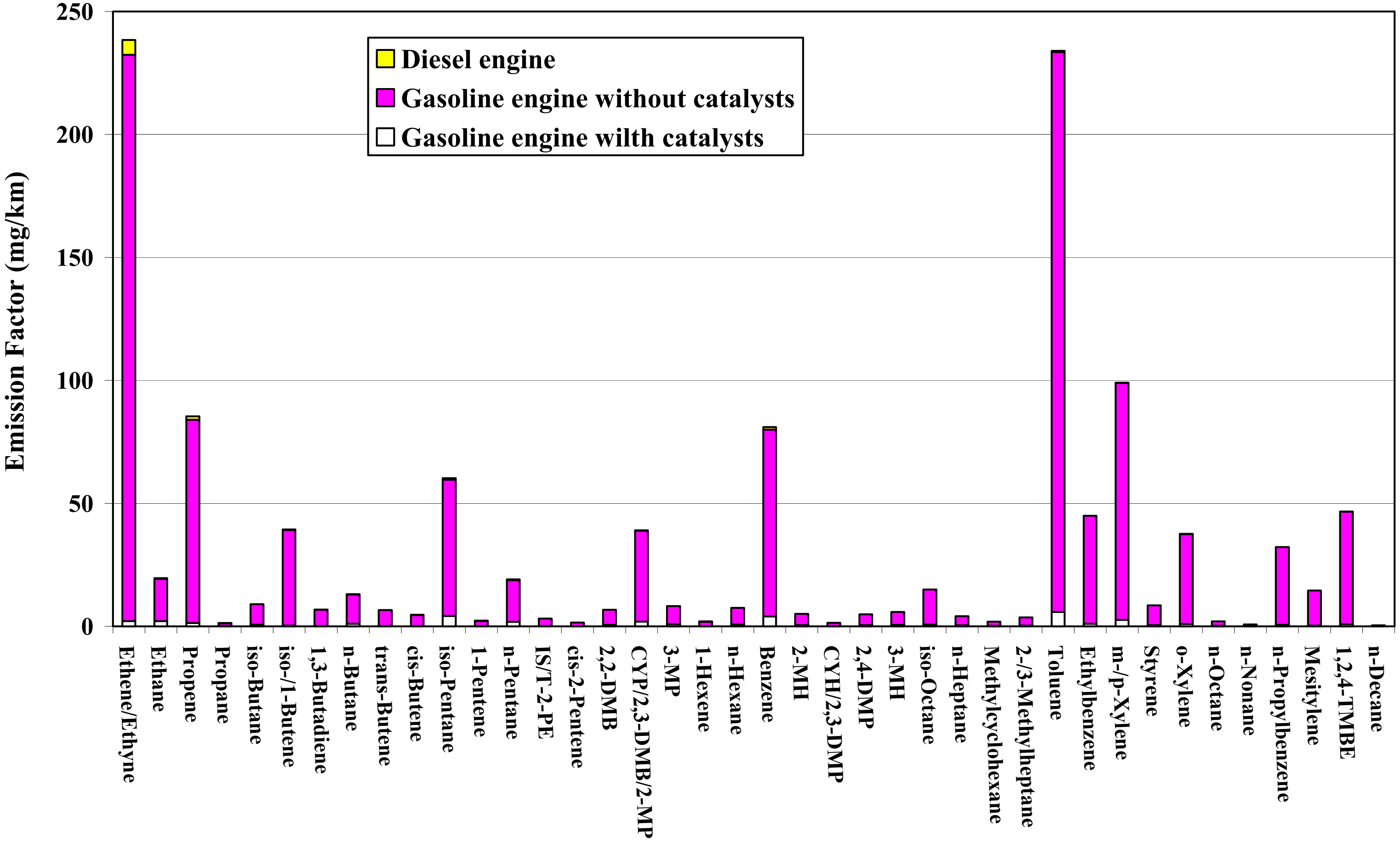


Figure 4.3(a): Comparison of the emission factors of different NMHCs for the driving cycle Autobahn Phase 1, analysed on a chassis dynamometer by Schmitz *et al.* (1999). IS: Isoprene, T-2-PE: *trans*-2-Pentene, DMB: Dimethylbutane, CYP: Cyclopentane, MP: Methylpentane, MH: Methylhexane, CYH: Cyclohexane, DMP: Dimethylpentane, TMBE: Trimethylbenzene.

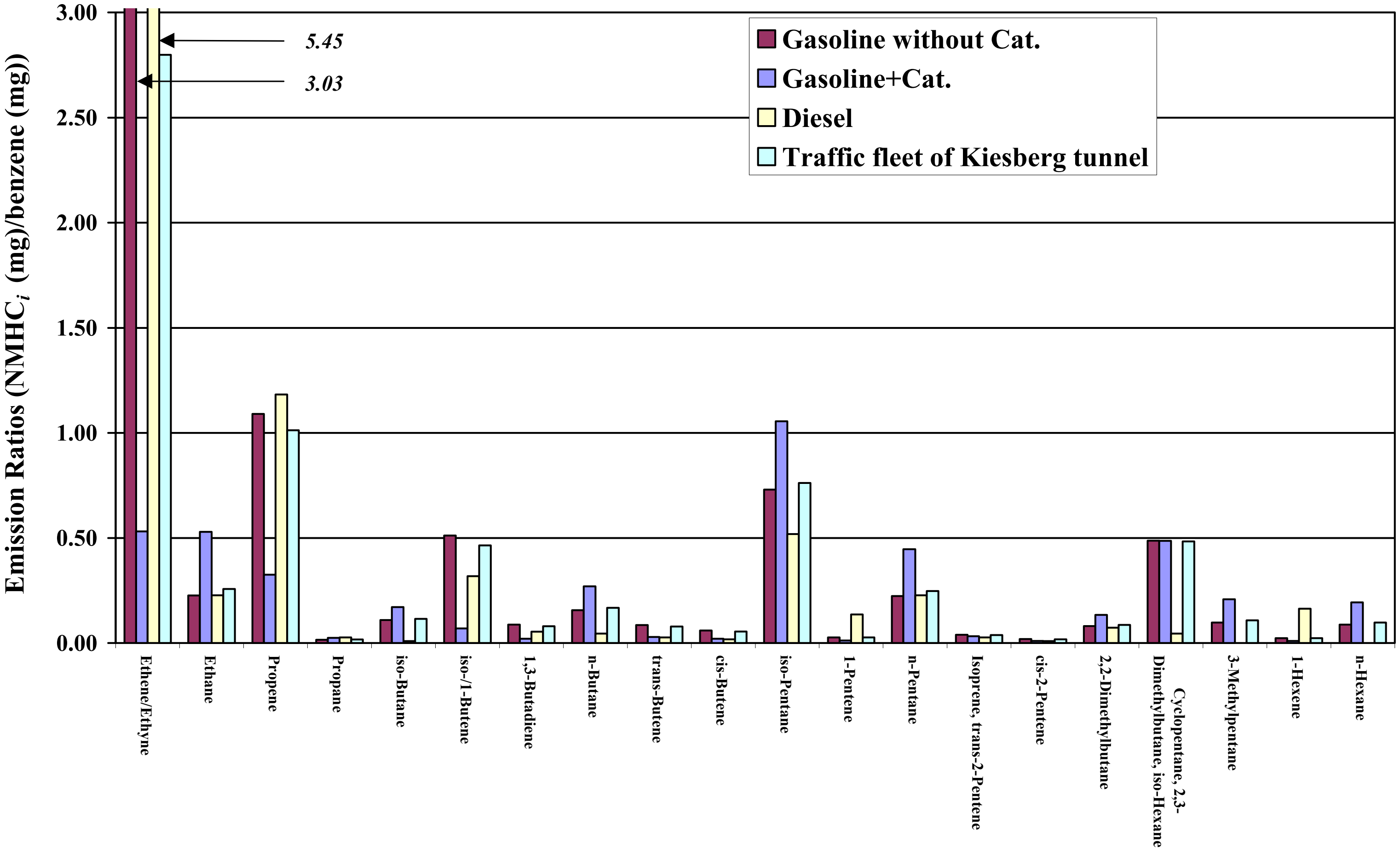


Figure 4.3(b): Comparison of the emission ratios of different NMHCs relative to benzene (mg/mg) for different car engines with the calculated emission ratios according to the traffic fleet composition (PC, LDV and MC) in the Kiesberg tunnel. The calculations were carried out using the data of Schmitz *et al.* (1999) for the driving cycle Autobahn Phase 1.

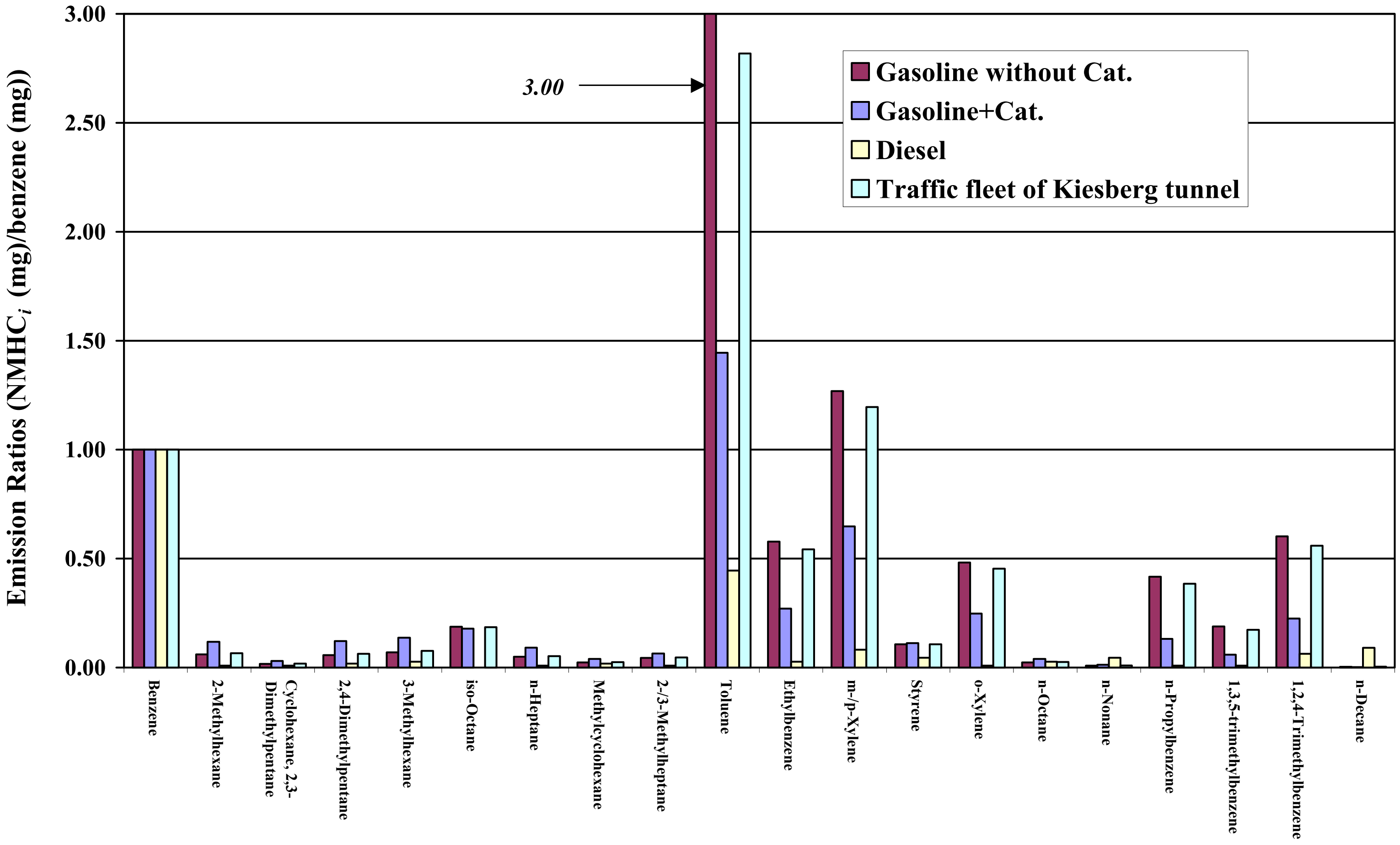


Figure 4.3 (c): Comparison of the emission ratios of different NMHCs relative to benzene (mg/mg) for different car engines with the calculated emission ratios according to the traffic fleet composition (PC, LDV and MC) in the Kiesberg tunnel. The calculations were carried out using the data of Schmitz *et al.* (1999) for the driving cycle Autobahn Phase 1.

According to Figure 4.3b-c, it can also be seen that for almost all the cases, the emissions from the cars without catalysts resemble with the calculated values according to the traffic fleet composition of LDV in the Kiesberg tunnel. It also indicates that the emissions from the uncontrolled vehicles determine the total road traffic emissions of NMHCs.

It can also be seen in Figure 4.2a-d that not all the emission ratios were shown for those compounds measured during the tunnel campaigns of this study. This occurred because some components could not be properly measured for different reasons. For example, *n*-pentane could not be properly quantified in the tunnel campaign of November-December, 1998 due to problems with the calibration of this component. Some impurities produced a very big signal during coelution and thereby covering the peak for *n*-pentane.

It can also be observed from the calculated emission ratios with reference to benzene (ppbC/ppbC) that, among the class of aromatic hydrocarbons, toluene showed the largest emission ratio of 1.7±0.5 ppbC/ppbC. This is in agreement with other tunnel and dynamometer studies reflecting different driving conditions, *e.g.* with a wide range of the speed of the vehicles between 30 to 90 km (Gregori *et al*., 1989; Fujita *et al*., 1992; Staehelin and Schläpfer, 1994; Kirchstetter *et al*., 1996; Fraser *et al*., 1998b; Schmitz *et al*., 1999).

Similarly, among the alkanes, *iso*-pentane and among the alkenes/alkynes, ethene/ethyne showed the largest emission ratio of 1.2±0.4 ppbC/ppbC and 2.5±0.8 ppbC/ppbC, respectively, relative to benzene, which are also in agreement with other tunnel and dynamometer studies (Gregori *et al*., 1989; Fujita *et al*., 1992; Staehelin and Schläpfer, 1994; Kirchstetter *et al*., 1996; Fraser *et al*., 1998b; Schmitz *et al*., 1999).

It can also be observed from Figure 4.2a-d that the normalised NMHC profiles for most of the components of this study showed similarities with those of the two other European tunnel studies, namely for the Gubrist tunnel and for the Tauern tunnel. However, for *n*-butane, *iso*-pentane and *iso*-octane, the values of the Gubrist tunnel study are higher than those of the Kiesberg tunnel study. The reason may be attributed to the differences in the fuel-composition used in the Gubrist tunnel in 1993 and in the Kiesberg tunnel in 1997-98 (Staehelin, 2001, Jäckle, 2001). On the other hand, the values for *n*-butane and *iso*-pentane found in the Kiesberg tunnel and in the Tauern tunnel are comparable with each other. The reason may be attributed to the similar fuel- and road traffic composition in Germany and Austria (Gregori *et al*., 1989; Aral, OMV). Furthermore, it can also be observed that for some of the alkenes, *e.g.* isoprene/*trans*-2-pentene, *cis*-2-pentene and 2-methyl-2-butene, the emission ratios with respect to benzene of the Tauern tunnel are smaller than those of the Kiesberg and the Gubrist tunnel. The probable explanation of this observation may be due to the difference of the fuel composition regarding alkenes in Germany and Austria. For example, there is the difference between the fuel composition of Aral of Germany and OMV Konzern of Austria regarding alkenes, *i.e.* the upper limit of the percentage of alkenes present in the fuel of OMV has lower value than those of Aral (Aral, OMV).

4.1.1.2 Percental composition of the hydrocarbon-mix

Approximately 50% to 75% of the hydrocarbon-mix of the exhaust contains the unchanged fuel components. However, the contribution of the single components in the mix is indeed highly different from that of the fuel. For example, the amount of the higher carbon-containing components is decreased and the amount of the lower carbon containing components is increased in the exhaust. The remaining 25% to 50% of the hydrocarbon-mix of the exhaust partially comes from burning, fragmentation and oxidation of the fuel and slightly also results from recombination products (Patyk *et al.*, 1995). Furthermore, Siegl *et al.* (1999) stated that in the diesel exhaust partial combustion products represent 53%, and unburnt fuel 47% of the NMHC. Therefore, it is expected that the composition of the emitted hydrocarbon-mix will be influenced by the fuel composition.

From the compounds shown in the NMHC-profile (Figure 4.2a-d), the percentage compositions for alkanes, alkenes/alkynes and aromatic compounds were calculated and presented in Figure 4.4(a-c) and in Table 4.2.

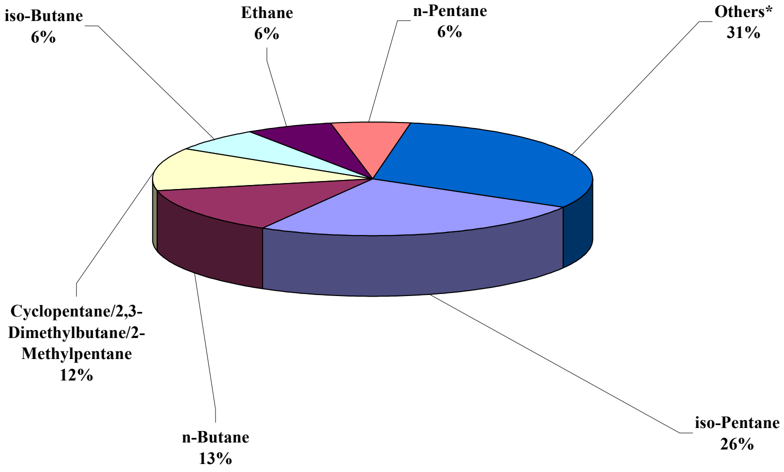


Figure 4.4 (a)

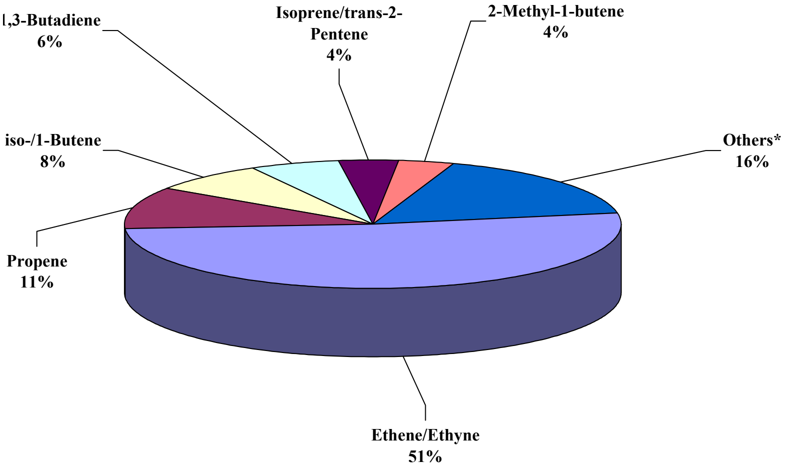


Figure 4.4 (b)

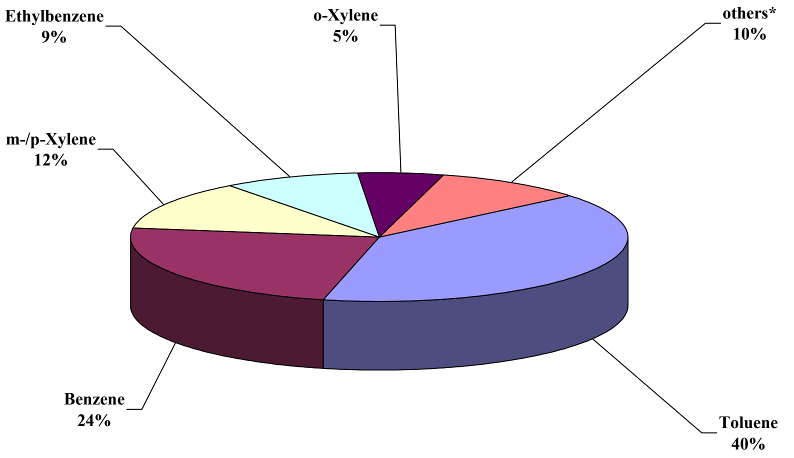


Figure 4.4 (c)

Others*: total of all other components containing individual percental contribution of less than 5%.

Figure 4.4: Percentage composition of (a) alkanes, (b) alkenes/alkynes and (c) aromatic compounds in the hydrocarbon mix relative to benzene in ppbC/ppbC found in the Kiesberg tunnel air in the year 1997-1998.

It can be seen from Figure 4.4 that among the class of aromatic compounds, after toluene (41%), benzene (24%) had the second highest contribution in the hydrocarbon-mix found in the tunnel. Similarly, among alkanes, after *iso*-pentane (25%), *n*-butane (13%) and among alkenes/alkynes, after ethene/ethyne (52%), propene (11%) had the second largest contribution in the hydrocarbon mix of the Kiesberg tunnel air. It can be noted from Table 4.2 that the percentage composition of different classes have within error limits almost equal weight.

Table 4.2 also shows a comparison of the percentage composition of different classes of NMHCs-mix relative to benzene in ppbC/ppbC of the present study in comparison with other tunnel studies. The percental composition for the other tunnel studies were calculated by taking the consideration of the same compounds measured in the present work.

Table 4.2: List of the percentage composition of the different classes of nonmethane hydrocarbon mix of the different tunnel air in ppbC/ppbC.

Tunnels	Sampling Period (year)	% of Alkanes	% of Alkenes	% of Aromatic Compounds	Reference
Kiesberg tunnel, Germany	1997-1998	34.4 ± 5.1	34.9 ± 6.8	30.7 ± 5.7	this study
Gubrist tunnel, Switzerland	1993	41.3	29.7	29.1	Staehelin and Schläpfer,.1994
Harbour tunnel, Australia	1994	37.7	32.4	30.0	Duffy *et al.*, 1996
Lincoln, U.S.A.	1982	33.6	40.3	26.2	Lonneman *et. al.*, 1986
Van Nuys tunnel U.S.A.	1993	40.1	28.7	31.3	Fraser *et al.*, 1998b
Caldecott tunnel, U.S.A.	August, 1994 October, 1994	37.2 37.9	24.8 28.3	38.0 33.9	Kirchstetter *et al.*, 1996
Cassiar tunnel, Canada	1995	45.0	29.6	25.5	Rogak *et al.*, 1998

From Table 4.2, one can observe that in the different tunnel studies, the percentage compositions of different classes of nonmethane hydrocarbon mix are more or less in agreement with the result of this study within the error limit. The small deviation can be attributed to the different fuel composition and also to the different road traffic fleet and driving cycles at different places. Besides, evaporation contribution due to running losses should also be counted.

According to Marschall *et al.* (1995) and CONCAWE (1992), the hydrocarbon (HC) emissions from uncontrolled gasoline motor cars contribute 62% from the exhaust and 25% by evaporation, out of the total HC emissions from the distribution of gasoline and its use in vehicles. The remaining 13% results from the distribution of gasoline from refineries to service stations (8%) and the refuelling of vehicles (5%). Table 4.3 shows the typical composition of gasoline and diesel (Aral) and a comparison with the results of a dynamometric study (Schmitz *et al.*, 1999) regarding exhaust from gasoline (with and without catalyst) and diesel and also the result of this study regarding road traffic exhaust.

Table 4.3: Typical chemical composition of gasoline and diesel (Aral) in mass% and a comparison with a dynamometric study (Schmitz *et al.*, 1999) and this study.

Groups/Company	Type of fuels/engines	% of alkanes	% of alkenes	% of aromatic compounds
Aral (gasoline)	Super Plus	35-55	0-18	25-42
Aral (gasoline)	Super	40-60	0-18	25-42
Aral (gasoline)	Normal	50-65	0-21	25-42
Aral (diesel)		40-70	0.1-5	10-30
Dynamometric Studies (Schmitz *et. al.*, 1999)*	Gasoline engine with catalyst	57.9	11.1	41.6
Dynamometric Studies (Schmitz *et. al.*, 1999)*	Gasoline with conventional engine	25.8	33.4	47.5
Dynamometric Studies (Schmitz *et. al.*, 1999)*	Diesel engine	22.7	71.1	16.0
This Study	Road traffic in Kiesberg tunnel	34.4 ± 5.1	34.9 ± 6.8	30.7 ± 5.7

*These recalculated values of the percental composition were obtained by taking into consideration the compounds shown in Figure 4.2 and by considering the driving cycle 'Autobahn, phase I' which can be taken as representative for the Kiesberg tunnel.

It can be observed from the Table 4.3 that the percental composition of different classes of NMHCs of this study is more similar to those of the dynamometric studies (Schmitz *et al.*, 1999) regarding gasoline with conventional engine than other engines.

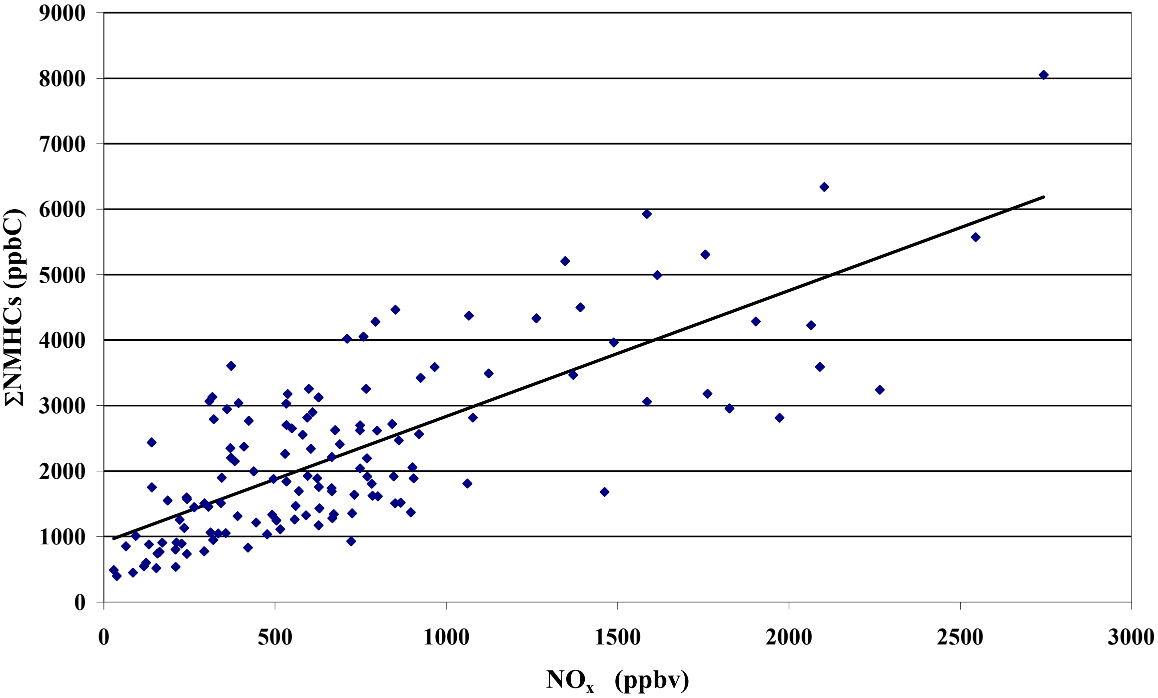
An comparison of the fuel's composition with that of the road traffic exhaust in the Kiesberg tunnel as presented in Table 4.3 indicates an increase of the alkene contribution during the combustion.

4.1.2 NMHC/NO_x

The calculated hydrocarbon emission ratios were normalised to the NO_x emission measured in the tunnel. It was observed that NO accounts for 95% and NO_2 for 5% (averaged values) of the NO_x emission, which is in good agreement with other studies (Lies, 1988; Gregori *et al.*, 1989; Staehelin and Schläpfer, 1994; Kirchstetter *et al.*, 1996; Pierson *et al.*, 1996; Becker *et al.*, 1999).

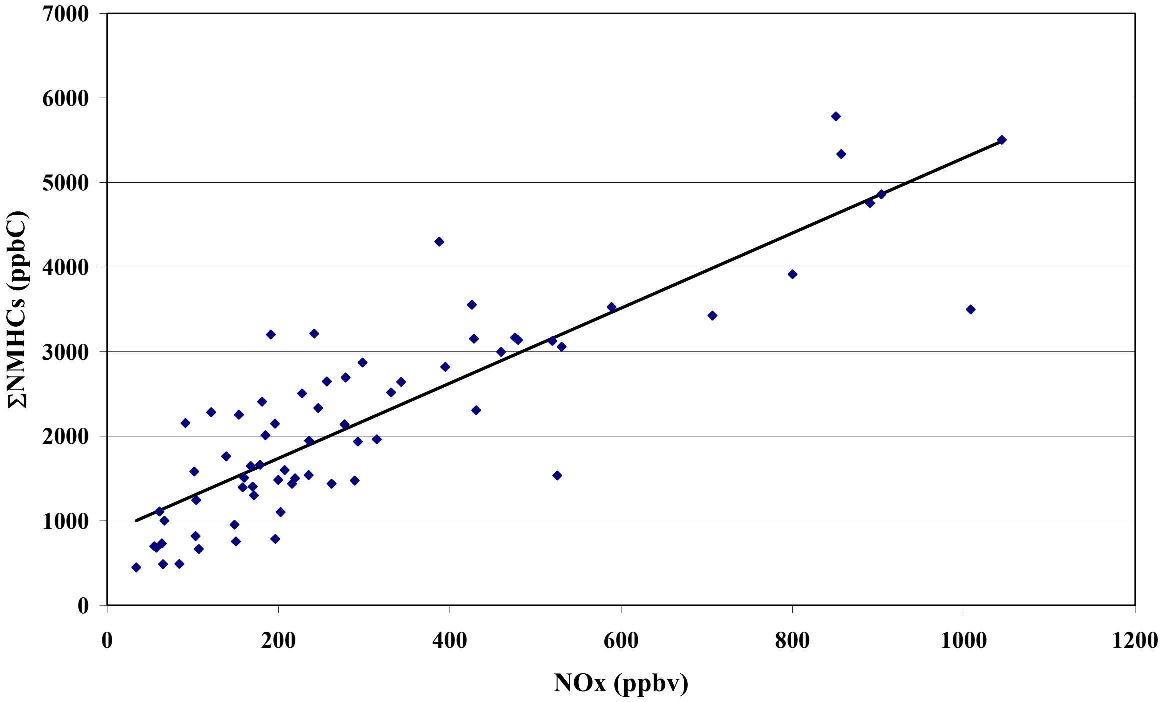
From the measured data, total NMHC/NO_x ratios from 0.64±0.03 up to 1.92±0.14 ppbC/ppbv were calculated for working days with HDVs contributing overall an average of 6% to the total traffic volume in the Kiesberg tunnel. The reason for the factor of 3 between the calculated emission ratios during different campaigns can be attributed to the different numbers of old uncontrolled cars during these campaigns which normally emit a factor of about 5 more NO_x than controlled cars (Keller *et al.*, 1999).

On the other hand, for weekends, when the overall average contribution of HDVs to the total traffic volume was only about 1%, the total NMVOC/NO_x ratio increased up to 4.44 ppbC/ppbv. Figure 4.5 and Figure 4.6 show, for example, the correlation plot between the sum of the total measured nonmethane hydrocarbons (in ppbC) and NO_x (in ppbv) for the weekdays and weekend during the Kiesberg tunnel campaign in November-December, 1998.



Emission ratio of ΣNMHC (ppbC)/NO_x (ppbv) = 1.92 ± 0.14, correlation coefficient: 0.75.

Figure 4.5. Typical correlation plot between the sum of the total measured nonmethane hydrocarbons (ppbC) and nitrogen oxides (ppbv) during weekdays for the Kiesberg tunnel air in November-December, 1998.



Emission ratio of ΣNMHC (ppbC)/NO_x (ppbv) = 4.44 ± 0.31, correlation coefficient: 0.86.

Figure 4.6: Correlation plot between the sum of the total measured nonmethane hydrocarbons (ppbC) and nitrogen oxides (ppbv) during the weekend for the Kiesberg tunnel air of Wuppertal in November-December, 1998.

The calculated NMHC/NO_x ratios from the present study are in good agreement with literature data (Lonneman *et al.*, 1986; Gregori *et al.*, 1989; Staehelin and Schläpfer, 1994; Hassel *et al.*, 1994, 1995; Kirchstetter *et al.*, 1996; Pierson *et al.*, 1996; Rogak *et al.*, 1998). The increase of the total NMHC/NO_x ratio observed with decreasing contribution of HDV to the traffic volume can be explained by literature data of the Handbook emission factors for road transport (Keller *et al.*, 1999). Table 4.4 shows a list of emission factors of NO_x for different vehicles for the year of 1997 and 1998 in Germany.

Table 4.4: List of emission factors* of nitrogen oxides (NO_x) for different vehicle categories and engine-systems for the year 1997 and 1998 in Germany (source: Keller *et. al.*, 1999).

Vehicle category	1997				1998			
	Gasoline	Gasoline	Diesel	Diesel	Gasoline	Gasoline	Diesel	Diesel
	Conventional	Catalyst-equipped/ Pollutant-reducing	Conventional	Pollutant-reducing	Conventional	Catalyst-equipped/ Pollutant-reducing	Conventional	Pollutant-reducing
	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km
PC	1.783	0.057-0.365	0.461	0.361-0.439	1.756	0.060-0.371	0.471	0.266-0.439
LDV	2.904	0.266-0.682	0.993	0.564-0.658	2.880	0.149-0.717	0.987	0.564-0.658
Truck	–	–	5.038-7.419-	3.582-4.103	–	–	5.190-7.419	3.563-4.115

Table 4.4 (continued):

Vehicle category	1997				1998			
	Gasoline	Gasoline	Diesel	Diesel	Gasoline	Gasoline	Diesel	Diesel
	Conventional	Catalyst-equipped/ Pollutant-reducing	Conventional	Pollutant-reducing	Conventional	Catalyst-equipped/ Pollutant-reducing	Conventional	Pollutant-reducing
	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km
MC	0.093 (2-stroke)	–	–	–	0.095 (2-stroke)	–	–	–
	0.265 (4-stroke)	–	–	–	0.268 (4-stroke)	–	–	–

PC: Passenger Car, LDV: Light Duty Vehicles, MC: Motor Cycles. *The values were taken for the driving cycle Highway-60.

By comparing Table 4.1 and Table 4.4, it is clear that diesel-powered vehicles, in particular HDVs, emit more NO_x than light-duty vehicles (LDV), in particular, cars powered by gasoline fuel. In contrast, LDVs emit more NMHC than HDVs (Staehelin *et al.*, 1997; Rogak *et al.*, 1998). Since the percentage of HDV passed through the Kiesberg tunnel during the weekend is only about 1% against 6% during the weekdays, the higher emission ratio of NMHC/NO_x found in this present study during the weekend can be explained.

Table 4.5 summarizes total NMHC/NO_x ratios observed in the present study and in other studies on traffic emissions.

Table 4.5: Comparison of total NMHC/NO_x ratios (ppbC/ppbv) in traffic exhaust from traffic tunnel measurements$^{1)}$, chassis dynamometer test$^{2)}$ and on-road measurements$^{3)}$.

Location	Year	Total NMHC/NO_x ratio (ppbC/ppbv),	Remarks	Reference
°Kiesberg tunnel$^{1)}$	1997-1998	0.64±0.03–1.92±0.14	traffic fleet, 6 % HDV	this study
		4.44±0.31	traffic fleet, 1 % HDV	
*Tauern tunnel$^{1)}$	1988	2. 57	traffic fleet	Gregori *et al.*, 1989
	1997	0.32	traffic fleet (1-17 % HDV)	Schmid *et al.*, 1998
		2.21	LDV	
		0.02	HDV	
$^{\#}$Gubrist tunnel$^{1)}$	1993	0.62	traffic fleet (<1–24 % HDV)	Staehelin *et al.*, 1995, 1997
		1.25±0.15	LDV	
		0.05±0.05	HDV	
*Caldecott tunnel$^{1)}$	1994	1.54±0.18	traffic fleet (0.2 % HDV)	Kirchstetter *et al.*, 1996
		1.81±0.18	(LDV, fuel: 0.3 wt% oxygen),	
		1.49±0.16	(LDV, fuel: 2.0 wt% oxygen)	
°Cassiar tunnel$^{1)}$	1993	1.12±0.68	(LDV)	Rogak *et al.*, 1998
	1995	0.66±0.36	(LDV)	
°Tuscarora tunnel$^{1)}$	1992	2.50±1.74	(LDV)	Pierson *et al.*, 1996
		0.12±0.03	(HDV)	
		0.26	(traffic fleet, 18 % HDV)	
°Ford McHenry tunnel$^{1)}$	1992	2.50±0.46	(LDV)	
		0.35±0.11	(HDV)	
		0.76	(traffic fleet, 9 % HDV)	
°Lincoln tunnel$^{1)}$	1970	2.63	(traffic fleet, mostly LDV)	Lonneman *et al.*, 1986
	1982	1.77	(traffic fleet, mostly LDV)	

Table 4.5 (continued):

Location	Year	Total NMHC/NO_x ratio (ppbC/ppbv),	Remarks	Reference
*Traffic exhaust[2)] (Germany)	1986-1990	≤1.5	(LDV)	Hassel *et al.*, 1994, 1995
*Traffic exhaust[1, 2, 3)]	1999-2000 (Calculated)	0.3–0.9	(LDV)	Keller *et al.*, 1999
		0.3–0.7	(HDV)	
*Theoretical (using the traffic fleet of the Kiesberg tunnel)	1997-1998	0.8–0.9	(weekdays)	this study
		1.2	(weekend)	

°: Sum of all the measured NMHCs, *: total NMHCs, #: total HCs, HDV: heavy-duty vehicle, LDV: light-duty vehicle.

From Table 4.5, it can be observed that the determined NMHC/NO_x values of this study are within the range of those found in other tunnel studies and dynamometric studies. The small deviations of the emission ratios of other studies from the present study may be attributed to the differences of the driving situations, of the traffic fleet, of fuel composition and also in the definition of NMHCs as shown in the remarks and footnotes of Table 4.5. Furthermore, it can also be noted that the theoretical values of NMHC(ppbC)/NO_x(ppbv) were calculated by using the traffic composition of the Kiesberg tunnel and by using the emission factors from the Handbook (Keller *et al.*, 1999). The results show that the theoretically determined emission ratio during the weekend is about 30%-50% higher than those for the weekdays. In contrast, the present study showed that the emission ratio during the weekend is about 200%-700% higher than those for the weekdays. This difference of the result can be understood if one considers the variation of the traffic fleet that was in the Kiesberg tunnel under the real world condition in between 1997 to 1998 and that was used for the theoretical calculation. In addition, according to the Handbook (Keller *et al.*, 1999), NMHCs were considered as total NMHCs, whereas the present study considered the sum of all the measured NMHCs. Since the emission ratio of NMHC(ppbC)/NO_x(ppbv) is dependent on the mixing ratios of the identified nonmethane hydrocarbons and of NO_x, another reason for the difference between the theoretical values and the determined values for the Kiesberg tunnel can be attributed to this point.

4.1.3 Calculations of emission factors and indices

4.1.3.1 NMHC/CO_2

From the measured data, emission ratios were calculated for the nonmethane hydrocarbons relative to CO_2. In Table A3 II (in the Annex-Tables), the observed emission ratios of the C_2–C_{10} NMHCs, NO, NO_2, NO_x relative to CO_2 (in ppbv/ppbv) in the tunnel air during weekdays and weekend are summarized. The correlation coefficients are also shown.

From the emission ratios with reference to CO_2 (ppbv/ppbv), it is noticeable that during both the weekdays and weekend, among the class of aromatic hydrocarbons, toluene, among the alkenes/alkynes, ethene/ethyne and among the alkanes, *iso*-pentane showed the largest emission ratios. This is in agreement with other tunnel and dynamometer studies reflecting different driving conditions (Gregori *et al.*, 1989; Kirchstetter *et al.*, 1996; Fraser *et al.*, 1998b; Baily *et al.*, 1990; Duffy *et al.*, 1999). The correlation coefficients are on an average around 0.6. The smaller values of r^2 signified that a few of the data points did not correlate with other data points. Since in the present study only continuous point-measurements were carried out with certain sampling time (*e.g.* 30 min for the case of nonmethane hydrocarbons) and every data point can exhibit valuable information, all data points are generally retained. During the data evaluation, statistically determined errors were considered (Habram, 1999).

4.1.3.2 Emission factors (EF)

In the literature, two different types of calculations for emission factors can be found, namely emission factors in mg/km and emission indices in g/kg fuel. In the present study, it was attempted to carry out both calculations for the better comparison with the literature values.

During the tunnel campaigns of the present study, no measurements of the air flow rate and the uniformity of the air mixing inside the tunnel were carried out. Furthermore, the exact characterization of every road traffic vehicle passing through the Kiesberg tunnel was not performed. Therefore, it was not possible to calculate directly the emission factors for different types of vehicles (*e.g.* LDV and HDV). But since CO_2 was always measured during the whole campaigns, it was possible to calculate the emission factors by knowing the model-calculated emission value of CO_2 for the driving cycle of the vehicles passed through the Kiesberg tunnel. The emission value of CO_2 was taken from the "Handbook of emission factors for road transport of Germany" (Keller *et al.*, 1999). Since the average driving speed through the tunnel was about 50-90 km/h, CO_2 emission factors (mg/km) were calculated using HW-60 driving situation (speed limit 60, traffic volume less than 1400 per h per lane; equally weighted for highway velocity 70-80 km/h and 80-90 km/h) and the traffic fleet composition of the Kiesberg tunnel. The flat, descent and gradient pattern of the tunnel was also considered.

The calculation of the emission factors of NMHCs and NO_x 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). The traffic composition of Kiesberg tunnel varied within different time periods of a day statistically within a certain range. Table 4.6 shows these variations.

Table 4.6: Statistical variations of traffic composition in the Kiesberg tunnel within different time periods of a day during the tunnel campaigns in 1997-98.

Vehicle category	Weekdays	Weekend
Passenger cars	81%-90%	88%-99%
Commercial vans and other light duty vehicles	5%-8%	0%-7%
Trucks and other heavy duty vehicles	4%-10%	0%-2%
Motor cycles	1%-1%	1%-3%

The calculated emission factors of CO_2 using the above-mentioned variation of traffic fleet changed accordingly for weekdays about 10% and for weekend about 6%. The uncertainty limits of the calculated emission factors included these variations of traffic composition.

It was assumed that the driving situation for the vehicles passing through the Kiesberg tunnel was HW-60, not HW-80 (velocity limit 80, traffic volume less than 1400 vehicles per h per lane, weighted according to highway velocity 70-80 km/h (12%), highway velocity 80-90 km/h (23%), highway velocity 90-100 km/h (30%), highway velocity 100-110 km/h (23%) and highway velocity 110-120 km/h (12%)). The deviation of the estimated EF of CO_2 for HW-60 from that of HW-80 is about 15% for both the weekdays and weekend.

Table 4.7 shows the weighted average of the calculated emission factors of those components for weekdays and weekend of 1997-1998. The error calculation considered both the possible variation of traffic fleet in the Kiesberg tunnel and the probable contribution of the HW-80 driving situation. A comparison with the literature data of the Tauern tunnel study (Schmid *et al*. 2001) is also shown in Table 4.7.

Table 4.7: Emission factors (mg/km/vehicle), calculated using the Handbook value (Keller *et al.*, 1999) of CO_2 and the traffic situation in the Kiesberg tunnel, Wuppertal as discussed in the text and comparison with the literature values.

	Weekdays		Weekend	
	Kiesberg tunnel (average)	Tauern tunnel*	Kiesberg tunnel (average)	Tauern tunnel*
Sampling period	1997-1998 (average)	1997 October	1997-1998 (average)	1997 October
Compounds	mg/km	mg/km	mg/km	mg/km
Ethene/Ethyne	28±5.6	–	57.0±16.2	–
Ethane	2.8±0.5	–	5.9±1.5	–
Propene	5.5±0.8	–	6.1±1.5	–
Propane	0.8±0.1	–	1.6±1.2	–
iso-Butane	4.0±0.6	–	6.9±1.4	–
iso-/1-Butene	4.4±0.6	–	7.3±1.6	–
1,3-Butadiene	3.1±0.6	–	8.7±2.5	–
n-Butane	6.9±1.0	–	15.8±3.0	–
trans-Butene	1.9±0.2	–	3.9±0.8	–
cis-Butene	1.0±0.1	–	1.9±0.4	–
3-Methyl-1-butene	0.3±0.1	–	0.2±0.1	–
iso-Pentane	13.1±1.8	–	27.0±4.7	–
1-Pentene	0.9±0.1	–	0.9±0.2	–
2-Methyl-1-butene	2.6±1.3	–	1.0±0.2	–
n-Pentane	3.1±0.5	–	3.9±0.8	–
Isoprene/*trans*-2-Pentene	2.3±0.3	–	4.5±0.8	–
cis-2-Pentene	1.5±0.2	–	8.1±1.6	–
2-Methyl-2-butene	1.8±0.3	–	3.7±0.7	–
2,2-Dimethylbutane	0.7±0.1	–	1.5±0.3	–
Cyclopentene, 3-methyl-1-pentene, 4-methyl-1-pentene	1.1±0.2	–	0.7±0.2	–
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	6.7±1.0	–	11.0±2.2	–
3-Methylpentane	2.0±0.3	–	4.1±0.8	–
2-Methyl-1-pentene, 1-hexene	0.6±0.1	–	0.7±0.1	–
n-Hexane	2.0±0.2	3.6±1.0	3.5±0.6	5.7±1.2
cis-3-Hexene, *trans*-2-hexene, unknown	0.4±0.1	–	0.8±0.2	–
cis-2-Hexene	0.3±0.1	–	0.18±0.04	–
Methylcyclopentane, 2,4-dimethylpentane	1.9±0.3	–	4.8±1.3	–
Benzene	10.5±1.6	7.9±2.0	15.9±3.4	9.5±1.2

Table 4.7 (continued):

	Weekdays		Weekend	
	Kiesberg tunnel (average)	Tauern tunnel*	Kiesberg tunnel (average)	Tauern tunnel*
Sampling period	1997-1998 (average)	1997 October	1997-1998 (average)	1997 October
Compounds	mg/km	mg/km	mg/km	mg/km
Cyclohexane, 2,3-dimethylpentane	1.0±0.2	–	1.7±0.5	–
3-Methylhexane	1.1±0.2	–	1.8±0.4	–
iso-Octane	2.1±0.3	–	4.0±0.8	–
n-Heptane	0.7±0.1	–	0.9±0.2	–
2,3-Dimethyl-2-pentene	0.1±0.0	–		–
Methylcyclohexane	0.7±0.1	–	1.1±0.2	–
2,3,4-Trimethylpentane	0.6±0.1	–	2.6±0.7	–
2-/3-Methylheptane	0.6±0.1	–	1.0±0.2	–
Toluene	17.0±2.6	16.9±4.8	32.8±8.0	23.0±3.6
Ethylbenzene	3.7±0.5	3.6±1.0	0.020±0.004	4.7±0.8
m-/*p*-Xylene	5.9±0.9	12.1±3.6	9.0±2.3	15.8±2.8
Nonane	0.08±0.03	–	0.03±0.05	–
Styrene	1.2±0.2	–	3.0±0.6	–
o-Xylene	2.5±0.4	5.7±1.5	6.8±2.5	7.0±1.2
n-Octane	0.7±0.1	–	0.7±0.2	–
iso-Propylbenzene	0.5±0.1	–	0.3±0.1	–
n-Propylbenzene	0.8±0.2	–	0.7±0.2	–
m-/*p*-Ethyltoluene	5.0±1.3	–	4.0±1.2	–
Mesitylene	5.1±1.6	–	1.8±0.9	–
o-Ethyltoluene	0.8±0.3	–	0.9±0.3	–
NO	164.4±29.6	3049	162.2±35.8	611
NO_2	17.7±3.7	180	13.1±2.0	91
NO_x	272.8±87.0	3131±383	261.8±112.6	788±107

* Schmid *et al.*, 2001; the average emission factors designate the weighted average of the results of all the tunnel campaigns of this study and the error limits denote the propagated errors.

It can be also observed from Table 4.7 that for most of the components, the values for the weekend are larger than those for the weekdays. This propensity was also found for the measured components in the Tauern tunnel (Schmid *et al.*, 1998). It is also noteworthy that during the weekends, exclusively light duty vehicles (LDV), especially passenger cars (PC) passed through the Kiesberg tunnel and the emission of nonmethane hydrocarbons from the LDV are for some cases larger and for some cases smaller than those from the diesel driven heavy duty vehicles (HDV) (Sagebiel *et al.*, 1996, Hassel *et al.*, 1994, 1995; Keller *et al.*, 1999). It is also seen that the value for *n*-nonane, *iso*-propylbenzene, *n*-propylbenzene, *m*-/*p*-ethyltoluene during the weekend are smaller than those values during the weekdays. This can be explained by HDV emissions. As discussed by Sagebiel *et al.* (1996), HDV emit higher amounts of these compounds than LDV, and in the Kiesberg tunnel exclusively LDV passed during the weekend. It is also noticeable from Table 4.7 that only the calculated weekday emission factors of this study for toluene and ethylbenzene agree within the error limits with those obtained in the Tauern tunnel.

The emission factors (EF) of NO, NO_2 and NO_x of this study during the weekdays are about 10-15 times lower than those of the Tauern tunnel. This discrepancy can be attributed to the much higher contribution of HDV in Tauern tunnel (about 18% during the weekdays) in comparison with that in the Kiesberg tunnel (about 6% during the weekdays, see also Table 4.8).

Since on an average, the traffic contribution during the weekdays and the weekends are different (see section 2.3), it was attempted to differentiate the contribution of the light duty vehicles (LDV, containing PCs, commercial vans and motor cycles) and of heavy duty vehicles (HDV, containing, for example, trucks).

The following simple relationships were used to calculate these values:

$$EF_{weekdays} = EF_{LDV} * C_{weekdays,LDV} + EF_{HDV} * C_{weekdays,HDV} \qquad \text{Eq. 4.1}$$

$$EF_{weekend} = EF_{LDV} * C_{weekend,LDV} + EF_{HDV} * C_{weekend,HDV} \qquad \text{Eq. 4.2}$$

where:

$EF_{weekdays}$ = the calculated emission factor of a component during weekdays,
EF_{LDV} = the calculated emission factors of the component for LDV,
$C_{weekdays,LDV}$ = the contribution of LDV in the traffic fleet during weekdays,
EF_{HDV} = the calculated emission factor of the component for HDV,
$C_{weekdays,HDV}$ = the contribution of HDV in the traffic fleet during weekdays,
$EF_{weekend}$ = the calculated emission factor of the component during weekend,
$C_{weekend,LDV}$ = the contribution of LDV in the traffic fleet during weekend and
$C_{weekend,HDV}$ = the contribution of HDV in the traffic fleet during weekend.

Table 4.8 shows these calculated results for LDV in comparison with other tunnel studies.

Table 4.8: Calculated emission factors for LDV (mg/km) in Kiesberg tunnel, Wuppertal and comparison with literature values.

	Tunnel studies					Chassis dynamometer studies			
	Kiesberg (Germany)	Tauern[1] (Austria)	°Gubrist[2,3] (Switzerland)	McHenry [4,5] (U.S.A.)	Tuscarora[4,5] (U.S.A.)	°VW Study [6]	Duffy *et al.*[7]	°Schmitz *et al.*[8]	°Heeb *et al.*[9]
Sampling period	1997-98	1997	1993	1992	1992	1979-86	1994-95	1997	1995
	Average		September	June	September	(for gas. PC)	Average (per ADR Test*)	(calculated)	
Components	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
Ethene/Ethyne	62.8±21.8	–	41.3±10.2	29.4±2.4	18.3±1.2	36.5±5.6	59.0±62.2	61.5±9.4	–
Ethane	6.5±2.0	–	4.1±1.3	5.4±0.5	3.5±0.3	4.7±0.7	9.5±5.0	5.7±0.9	–
Propene	6.6±2.1	–	15.5±5.1	8.3±0.7	5.8±0.7	–	18.0±20.0	22.2±3.4	–
Propane	1.8±1.5	–	1.2±1.4	0.4±0.8	0.6±0.4	–	1.1±0.8	0.4±0.1	–
iso-Butane	7.6±1.9	–	2.3±1.2	0.8±0.2	1.0±0.2	–	5.2±3.5	2.5±0.4	–
iso-/1-Butene	8.4±2.3	–	11.0±3.6	5.6±0.6	5.2±0.7	–	8.4±8.8	10.2±1.6	–
1,3-Butadiene	9.8±3.4	–	1.0±0.4	1.8±0.3	1.3±0.4	–	3.5±4.9	1.8±0.3	–
n-Butane, 1,3-butadiene	17.9±4.3	–	12.8±6.7	6.5±1.1	5.0±1.1	–	12.0±8.0	3.7±0.6	–
trans-Butene	4.3±1.1	–	1.7±0.7	1.3±0.3	0.5±0.1	–	1.8±1.7	1.7±0.3	–
cis-Butene	2.4±0.6	–	1.5±0.7	0.9±0.1	0.8±0.2	–	1.5±1.3	1.2±0.2	–
3-Methyl-1-butene	0.2±0.1	–	0.9±0.4	0.6±0.1	0.3±0.1	–			–
iso-Pentane	31.1±7.0	–	22.7±9.4	31.9±2.5	14.4±3.5	–	39.0±26.0	16.7±2.6	–
1-Pentene	1.0±0.3	–	1.1±0.5	1.1±0.2	0.5±0.2	–		0.6±0.1	–
2-Methyl-1-butene	0.7±0.5	–	2.0±1.1	2.2±0.2	1.0±0.3	–			–
n-Pentane	3.9±1.0	–	7.9±5.5	9.7±0.9	5.4±1.4	–	21.0±14.0	5.4±0.8	–
Isoprene/*trans*-2-Pentene	5.2±1.2	–	1.6±0.9	3.2±0.4	1.7±0.4	–	0.7±1.2	0.9±0.1	–
cis-2-Pentene	11.9±3.1	–	1.0±0.6	1.3±0.1	0.7±0.2	–		0.4±0.1	–
2-Methyl-2-butene	4.1±1.0	–	2.5±1.7	3.4±0.3	1.9±0.5	–			–
2,2-Dimethylbutane	1.9±0.5	–	–	2.8±0.7	1.5±0.6	–		1.9±0.3	–
Cyclopentene, 3-/4-methyl-1-pentene	0.7±0.3	–	–	0.8±0.1	0.3±0.1	–	0.5±0.4		–
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	12.8±3.2	–	–	15.3±0.9	6.7±1.5	–	1.2±0.9	6.5±1.0	–
3-Methylpentane	4.6±1.1	–	–	5.8±0.5	3.0±0.9	–	11.0±8.0	2.4±0.4	–
2-Methyl-1-pentene, 1-hexene	0.7±0.2	–	–	0.7±0.2	0.4±0.3	–			–
n-Hexane	4.6±1.0	6.0±3.3	1.9±0.8	4.7±0.4	2.4±0.7	–	10.0±8.0	2.2±0.3	–

Table 4.8 (continued):

	Tunnel studies					Chassis dynamometer studies			
	Kiesberg (Germany)	Tauern[1] (Austria)	°Gubrist[2,3] (Switzerland)	McHenry [4,5] (U.S.A.)	Tuscarora[4,5] (U.S.A.)	°VW Study [6]	Duffy *et al.*[7]	°Schmitz *et al.*[8]	°Heeb *et al.*[9]
Sampling period	1997-98	1997	1993	1992	1992	1979-86	1994-95	1997	1995
	Average		September	June	September	(for gas. PC)	Average (per ADR Test*)	(calculated)	
Components	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
cis-3-Hexene, *trans*-2-hexene, unknown	1.0±0.2	–	–	1.5±0.1	0.8±0.2	–	–	–	–
cis-2-Hexene	0.2±0.1	–	–	0.5±0.1	0.4±0.1	–	–	–	–
Methylcyclopentane/ 2,4-Dimethylpentane	5.3±1.7	–	–	6.0±0.4	2.9±0.6	–	4.1±3.0	–	–
Benzene	19.9±5.8	9.8±3.0	11.7±4.5	14.8±1.1	9.2±0.9	17.8±2.7	42.0±35.0	22.0±3.4	14.4±7.0
Cyclohexane, 2,3-dimethylpentane	2.0±0.6	–	4.8±2.7	3.6±0.3	1.7±0.3	–	0.5±0.4	0.4±0.1	–
3-Methylhexane	2.0±0.6	–	–	4.9±0.9	1.5±0.4	–	5.0±4.5	1.7±0.3	–
iso-Octane	4.6±1.1	–	8.0±4.7	11.5±0.9	3.9±0.7	–	1.8±1.2	4.1±0.6	–
n-Heptane	1.4±0.4	–	1.5±0.6	2.4±0.2	1.0±0.3	–	3.6±3.0	1.2±0.2	–
Methylcyclohexane	1.1±0.3	–	–	1.5±0.2	0.8±0.3	–	1.0±0.8	0.6±0.1	–
2,3,4-Trimethylpentane	3.0±0.9	–	–	4.1±0.3	1.3±0.3	–	–	–	–
2-/3-Methylheptane	1.1±0.3	–	–	3.1±0.2	1.5±0.6	–	–	1.0±0.2	–
Toluene	36.6±10.7	23.8±7.9	19.8±5.9	29.0±2.6	14.6±2.3	42.0±6.4	62.0±66.0	61.9±9.4	42.3±30.9
Ethylbenzene	10.9±3.0	4.8±1.6	4.2±1.3	7.0±1.4	2.8±0.5	–	9.0±9.9	11.9±1.8	67.3±72.0*
m-/*p*-Xylene	9.2±3.1	16.2±5.5	13.7±4.1	23.9±4.9	10.5±2.2	–	35.0±38.0	26.3±4.0	–
n-Nonane	0.0±0.1	–	0.6±3.2	0.8±0.3	0.1±0.1	–	0.7±0.7	0.20±0.03	–
Styrene	3.9±1.0	–	–	3.1±0.5	1.6±0.2	–	1.0±0.9	2.3±0.4	–
o-Xylene	8.4±2.2	7.1±2.4	5.0±1.0	8.8±1.6	4.0±0.9	–	12.0±12.0	10.0±1.5	–
n-Octane	0.7±0.2	–	0.4±1.0	1.1±0.1	0.4±0.1	–	1.3±1.2	0.6±0.1	–
iso-Propyl-benzene	0.3±0.2	–	0.2±0.1	0.6±0.1	0.5±0.3	–	–	–	–
n-Propyl-benzene	0.7±0.3	–	0.9±0.4	2.2±0.5	0.8±0.2	–	1.4±2.7	8.5±1.3	–
m-/*p*-Ethyltoluene	3.8±1.6	–	5.3±1.2	12.2±2.1	4.4±0.8	–	5.7±6.4	–	–
Mesitylene	1.2±1.4	–	1.4±0.4	4.1±0.8	1.7±0.4	–	3.2±3.9	3.8±0.6	–
o-Ethyltoluene	1.0±0.4	–	1.7±0.5	3.5±0.8	1.4±0.4	–	1.4±1.7	–	–

Table 4.8 (continued):

	Tunnel studies					Chassis dynamometer studies			
	Kiesberg (Germany)	Tauern[1] (Austria)	°Gubrist[2,3] (Switzerland)	McHenry [4,5] (U.S.A.)	Tuscarora[4,5] (U.S.A.)	°VW Study [6]	Duffy *et al.*[7]	°Schmitz *et al.*[8]	°Heeb *et al.*[9]
Sampling period	1997-98	1997	1993	1992	1992	1979-86	1994-95	1997	1995
	Average		September	June	September	(for gas. PC)	Average (per ADR Test*)	(calculated)	
Components	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km	mg/km
NO_x	274±140	359±61	1053±92	506±56	244±163	843±129	1300±800	–	516±720

° Recalculated for LDV according to the traffic fleet in the Kiesberg tunnel, *all C-2 benzenes; ** Australian Design Rules (ADR 37/00): Emission Control for Light Vehicles; gas. PC: gasoline driven passenger cars. (1) Schmid *et al.*, 1998, 2001; (2) Staehelin *et al.*, 1998; (3) John *et al.*, 1999; (4) Pierson *et al.*, 1996; (5) Sagebiel *et al.*, 1996; (6) Lies *et al.*, 1988; (7) Duffy *et al.*, 1999; (8) Schmitz *et al.*, 1999; (9) Heeb *et al.*, 2000a.

A comparison of the estimated emission factors (EF) for LDV is also presented in Table 4.8 with the recalculated emission factors according to the traffic contribution of the Kiesberg tunnel in the case of the Gubrist tunnel study (Staehelin *et al.*, 1998; John *et al.*, 1999), the VW study (Lies *et al.*, 1988) and dynamometric studies by Schmitz *et al.* (1999) and Heeb *et al.* (2000a). The recalculation for the Gubrist tunnel was done from the GAV (gasoline powered vehicles) and DIV (diesel powered vehicles) values. Using the chassis dynamometer values measured by Schmitz *et al.* (1999) for both gasoline and diesel powered vehicles and for the driving situation Autobahn phase 1 (average speed 107 km/h, zero contribution for the stop mode) the emission factors for LDV were recalculated and also shown in Table 4.8. Besides, a comparison with the Tauern tunnel (Schmid *et al.*, 1998, 2001), the McHenry tunnel and the Tuscarora tunnel (Sagebiel *et al.*, 1996) was also carried out. It can be observed that the values of the Kiesberg tunnel study have better agreement with those of the Tuscarora tunnel than those of the McHenry tunnel. The reason can be possibly due to the effect of the grade. About 80% part of the Kiesberg tunnel has 1% down/up grade and the Tuscarora tunnel has 0.3% grades towards the middle from either end (Pierson *et al.*, 1996). On the other hand, the McHenry tunnel has 3.76% down/upgrade with no significant level portion. The Gubrist tunnel has a gradient of 1.3% (Staehelin *et al.*, 1995) and the measurement was done only the direction towards uphill. The Tauern tunnel has a gradient of 1.5% for up/down grade. Table 4.9 shows the effect of the grade on the calculation of CO_2 using the Handbook (Keller *et al.*, 1999), the traffic fleet and the driving situation of the Kiesberg tunnel.

Table 4.9: Effect of the grade on the calculated value of CO_2 using the Handbook (Keller *et al.*, 1999) and the traffic fleet and the driving situation of the Kiesberg tunnel.

Grade	-4%	-2%	0%	+2%	+4%
Calculated CO_2 in mg/km	60.7	98.7	144.7	206.2	269.8
% Deviation of the calculated value from that of the Kiesberg tunnel	-59.4	-34.0	-3.2	+37.9	+80.4

Positive grade values indicate the decline of the tunnels and vice versa.

From Table 4.9 it can be observed that depending on the grade of the tunnel, the model-calculated value of CO_2 can widely vary. Since the calculated value of CO_2 according to the grades of the Kiesberg tunnel was used to calculate the EFs of the present study, there is the possibility that due to the different grade of the tunnels, the calculated EFs for nonmethane hydrocarbons will be different. For example, using the calculated CO_2 values shown in Table 4.9 for two extreme grades of +4 and -4%, it can be seen that the calculated EFs for toluene can vary from +69% to –57% from that of the calculated value using the grade of the Kiesberg tunnel (Table 4.8, Figure 2.2). This can also be one of the reasons for the existing differences between the values of Kiesberg tunnel and the Gubrist tunnel.

The LDV contribution for only toluene, *o*-xylene and NO_x of the Tauern tunnel study agreed within the error limits with those of the Kiesberg tunnel study. There was another study in Berlin Tegeler tunnel (Isräel *et al.*, 1996), where the EF of benzene for LDV was calculated as 23.2 ± 0.6 mg/km, which is comparable with the present study. On the other hand, the determined EF of NO_x (871 ± 16) for LDV was more than 2 factor higher than that of the present study. It is to be noted that the study carried out by Isräel *et al.* (1996), was done in February-March 1994 and that there existed a decline of *ca.* 4% at the beginning and the traffic composition for LDV is slightly different from the present study (*e.g.* the percentage composition of commercial vans was 3%). In addition, the contribution of C and U-catalyst equipped passenger cars in the Berlin Tegler tunnel was about 1.4 time smaller than that in the Kiesberg tunnel and the contribution of the conventional passenger cars in the Tegler tunnel was about 3.5 time higher than that in the Kiesberg tunnel. According to Hassel et al. (1994), the emission of NO_x from conventional PCs is 2.6 time higher that from catalyst-equipped PCs.

Good agreement is also observed within the error limits among the values for some components of the Kiesberg tunnel and the dynamometric studies. The discrepancy occurred for the case of propene, *m*-/*p*-xylene and *o*-xylene.

In conclusion, there existed agreements and at the same time disagreements among the results of the present study and the other tunnel studies and dynamometric studies. The reasons for the discrepancy can only be partially explained. The calculated emission factors of this study can only be taken as the range of the EF values.

Table 4.10 shows the calculated emission factors for HDV of this study with an comparison with other tunnel studies.

Table 4.10: Calculated emission factors for HDV (mg/km) in Kiesberg tunnel, Wuppertal and comparison with literature values.

	Kiesberg tunnel	Gubrist tunnel[1,2]	McHenry tunnel[3,4]	Tuscarora tunnel[3,4]
	Germany	Switzerland	USA	USA
Sampling period	1998	1993	1992	1992
	HDV	DIV (HDV)	HD	HD
Components	mg/km	mg/km	mg/km	mg/km
Ethene/Ethyne	-517.3±348.1	61.0±35.1	46.8±12.4	25.6±4.0
Ethane	-54.1±32.9	3.2±4.5	4.4±2.6	1.0±1.0
Propene	35.3±20.8	22.4±19.4	15.0±3.5	10.0±2.1
Propane	-13.2±25.1	5.7±5.9	8.4±3.9	1.9±1.2
iso-Butane	-83.5±55.2	5.2±4.8	1.0±1.1	1.9±0.8
iso-/1-Butene	-63.8±31.6	16.0±13.4	11.1±2.9	7.2±2.4
1,3-Butadiene	-101.1±51.5	-1.6±1.1	1.2±1.5	2.5±1.2
n-Butane	-290.9±132.1	27.3±27.1	2.4±6.0	5.8±3.5
trans-Butene	-58.6±26.9	2.9±2.9	0.9±1.7	-0.02±0.43
cis-Butene	-30.5±14.2	2.5±2.7	1.1±0.4	0.9±0.5
3-Methyl-1-butene	1.3±2.2	1.9±1.5	1.1±0.3	0.8±0.2
iso-Pentane	-666.0±291.5	43.4±37.0	4.9±12.9	18.9±11.7
1-Pentene	-6.5±5.1	3.4±2.0	3.3±0.8	1.9±0.7
2-Methyl-1-butene	31.7±26.7	4.0±4.2	2.1±1.1	1.6±0.9
n-Pentane	-39.0±21.0	15.8±22.6	5.7±4.8	5.7±4.7
Isoprene/*trans*-2-Pentene	-77.7±33.6	3.5±3.8	1.0±1.8	2.8±1.2
cis-2-Pentene	-323.8±120.0	2.1±2.4	1.1±0.7	0.7±0.7
2-Methyl-2-butene	-81.1±39.8	4.6±6.8	2.4±1.8	1.1±1.7
2,2-Dimethylbutane	-36.1±17.1	–	9.9±3.7	7.5±2.1
Cyclopentene, 3-/4-methyl-1-pentene	4.2±5.9	–	0.2±0.7	0.6±0.4
Cyclopentane/2,3-Dimethylbutane/ 2-Methylpentane	-217.2±124.3	–	9.8±4.8	8.6±4.9
3-Methylpentane	-91.3±42.9	–	3.4±2.6	3.8±2.9
2-Methyl-1-pentene/1-Hexene	-1.5±0.9	–	3.7±1.0	4.3±1.1
n-Hexane	-105.5±47.7	2.9±3.1	3.6±2.3	3.8±2.3

Table 4.10 (continued):

	Kiesberg tunnel	Gubrist tunnel^{1,2}	McHenry tunnel^{3,4}	Tuscarora tunnel^{3,4}
	Germany	Switzerland	USA	USA
Sampling period	1998	1993	1992	1992
	HDV	DIV (HDV)	HD	HD
Components	mg/km	mg/km	mg/km	mg/km
cis-3-Hexene/ trans-2-Hexene, unknown	-16.7±9.0	–	2.2±0.7	0.5±0.8
cis-2-Hexene	-1.0±1.4	–	-0.04±0.36	0.1±0.4
Methylcyclopentane/2,4-Dimethylpentane	-71.2±37.9	–	3.7±2.1	3.0±2.1
Benzene	-164.0±77.7	18.2±18.1	12.0±5.7	8.5±3.1
Cyclohexane/2,3-Dimethylpentane	-20.7±9.4	6.1±10.9	4.3±35.5	2.0±1.1
3-Methylhexane	-27.9±15.1	–	8.7±4.9	2.5±1.2
iso-Octane	-94.8±46.7	13.2±18.8	5.6±4.8	4.1±2.2
n-Heptane	-10.3±5.0	3.8±2.5	2.2±1.1	1.9±1.0
Methylcyclohexane	-3.5±7.6	–	1.7±1.0	1.0±0.8
2,3,4-Trimethylpentane	-51.0±20.5	–	1.2±1.7	1.1±0.9
2-/3-Methylheptane	-11.2±9.3	–	1.4±1.2	2.7±2.1
Toluene	-527.7±326.9	27.2±21.4	17.6±13.7	14.8±7.7
Ethylbenzene	-194.4±89.3	7.2±4.6	10.7±7.5	2.5±1.7
m-/*p*-Xylene	-88.9±53.8	27.2±15.3	41.4±25.8	10.7±7.2
n-Nonane	1.0±1.1	1.7±11.4	4.2±1.3	1.3±0.2
Styrene	-87.9±31.4	–	7.0±2.7	2.8±0.7
o-Xylene	-208.1±83.3	6.3±2.9	14.1±8.6	4.3±2.9
n-Octane	3.4±5.8	0.6±4.1	1.2±0.6	1.5±0.5
iso-Propylbenzene	3.1±3.1	0.3±0.4	1.2±0.6	0.7±0.8
n-Propylbenzene	2.2±5.6	1.9±1.5	4.0±2.6	1.0±0.7
m-/*p*-Ethyltoluene	23.2±35.2	8.0±3.7	20.9±11.2	5.6±2.5
Mesitylene	66.3±35.7	2.7±2.0	7.9±4.1	2.2±1.3
o-Ethyltoluene	-1.3±8.3	1.6±1.6	7.5±4.2	3.1±1.2
NO$_x$	-901±2704	15589±786	9019±281	12163±531

(1) Staehelin *et al.*, 1998; (2) John *et al.*, 1999; (3) Pierson *et al.*, 1996; (4) Sagebiel *et al.*, 1996.

The negative values for EFs of HDV shown in Table 4.10 were the consequences of the calculation of the LDV and HDV contributions using Eq. 3.1 and 3.2. This is also perceivable because of the small contribution from the heavy duty vehicles in the Traffic fleet of the Kiesberg tunnel, namely 6% in the weekdays and 1% in the weekends. It can also be observed that although generally there were disagreements among the calculated values of HDV contribution of this study and other tunnel studies, there are a few components which agreed within the large error limits of this study with other tunnel studies as shown in Table 4.10, *e.g.*, propane, 3-methyl-1-butene, cyclopentene/3-/4-methyl-1-pentene, *cis*-2-hexane, methylcyclohexane and *n*-octane. There are also agreement within error limits for the components mentioned beforehand as mostly HDV-emittants, *i.e.*, *iso*-propylbenzene, *n*-propylbenzene and *m*-/*p*-ethyltoluene and *o*-ethyltoluene. In addition, the HDV contribution calculated in this study for propene, 2-methyl-1-butene and *n*-nonane are also comparable within the error limits with those of the Gubrist tunnel. The HDV contribution of propene within the error limit of this study agreed as well with that of the McHenry tunnel and *n*-nonane with that of Tuscarora tunnel.

It should be noted that the determined emission factors for HDV contained large error limits and less precise as also for other tunnel studies (Staehelin *et al.*, 1998, Sagebiel *et al.*, 1996). For practical purposes, the negative emission factors can be interpreted as non-detectable.

4.1.3.3 Emission indices (EI)

Using the emission indices of 3.162 g CO_2 per kg of diesel fuel and 3.134 g CO_2 per kg of gasoline fuel (Marland and Rotty, 1984; Kurtenbach *et al.*, 2001a; Kleffmann *et al.*, 2001) and the emission ratios of components against CO_2 (ppbv/ppbv) shown in Table A3 II (in the Annex-Tables), emission indices of the components were calculated and are summarized in Table A3 III (in the Annex-Tables).

Equations 4.1 and 4.2 were also used to estimate the LDV and HDV contributions of the emission indices (EI) and they were presented in Table 4.11. A comparison with the Van Nuys tunnel study (Fraser *et al.*, 1998b) and the Caldecott tunnel study (Kirchtetter *et al.*, 1996) were also presented in Table 4.11.

Table 4.11: Emission indices in g/kg fuel for LDV and HDV, calculated from the measured values of the Kiesberg tunnel in comparison with literature.

	Germany		USA		
	Kiesberg tunnel		Van Nuys tunnel[1]	Caldecott tunnel[2]	
	LDV	HDV	LDV	LDV	
Sampling period	1998	1998	Sept. 1993	August, 1994	October, 1994
Compounds	g/kg fuel	g/kg fuel	g/kg fuel	g/kg fuel	g/kg fuel
Ethene/Ethyne	4.19±0.92	-28.83±11.26	1.49	0.59±0.08	0.44±0.04
Ethane	0.17±0.05	-1.57±0.67	0.16	0.07±0.01	0.05±0.01
Propene	0.17±0.04	-0.56±0.28	0.39	0.19±0.03	0.15±0.01
Propane	0.05±0.04	-0.40±0.60	0.06	0.014±0.002	0.010±0.007
iso-Butane	0.20±0.04	-2.34±1.02	0.02	0.027±0.004	0.015±0.003
iso-/1-Butene	0.21±0.05	-2.65±1.08	0.25	0.10±0.02	0.14±0.01
1,3-Butadiene	0.25±0.08	-2.79±1.10	–	0.02±0.01	0.02±0.01
n-Butane	0.44±0.09	-7.46±2.59	0.19	0.10±0.02	0.09±0.02
trans-Butene	0.10±0.02	-1.84±0.69	0.04	0.02±0.01	0.02±0.01
cis-Butene	0.06±0.01	-0.99±0.37	0.05	0.01±0.00	0.02±0.01
3-Methyl-1-butene	0.01±0.00	0.01±0.04	0.01	–	–
iso-Pentane	0.71±0.13	-16.91±5.81	0.75	0.44±0.05	0.31±0.04
1-Pentene	0.03±0.01	-0.30±0.19	0.04	0.009±0.004	0.009±0.002
2-Methyl-1-butene	0.02±0.01	0.59±0.53	0.05	0.01±0.01	0.015±0.002
n-Pentane	0.10±0.02	-1.08±0.50	0.31	0.12±0.02	0.11±0.02
Isoprene,*trans*-2-Pentene	0.13±0.02	-2.28±0.73	0.05	0.01±0.01	0.02±0.01
cis-2-Pentene	0.30±0.07	-8.08±2.55	0.03	0.006±0.002	0.008±0.003
2-Methyl-2-butene	0.10±0.02	-2.14±0.83	0.07	0.024±0.004	0.022±0.003
2,2-Dimethylbutane	0.04±0.01	-0.99±0.38	–	0.03±0.01	0.02±0.01
Cyclopentene, 3-/4-Methyl-1-pentene	0.02±0.01	0.03±0.11	0.01	0.008±0.003	0.007±0.002
Cyclopentane/ 2,3-Dimethylbutane/2-Methylpentane	0.29±0.06	-6.48±3.05	0.43	0.19±0.03	0.13±0.01
3-Methylpentane	0.10±0.02	-2.33±0.86	0.20	0.07±0.01	0.05±0.01
2-Methyl-1-pentene /1-Hexene	0.020±0.005	-0.17±0.09	0.02	0.006±0.003	0.007±0.002
n-Hexane	0.09±0.02	-2.95±1.11	0.18	0.07±0.03	0.06±0.01

Table 4.11 (continued):

	Germany		USA		
	Kiesberg tunnel		Van Nuys tunnel[1]	Caldecott tunnel[2]	
	LDV	HDV	LDV	LDV	
Sampling period	1998	1998	Sept. 1993	August, 1994	October, 1994
Compounds	g/kg fuel	g/kg fuel	g/kg fuel	g/kg fuel	g/kg fuel
cis-3-Hexene/*trans*-2-Hexene	0.03±0.01	-0.43±0.18	–	–	–
cis-2-Hexene	0.005±0.001	-0.03±0.03	–	–	–
Methylcyclopentane/2,4-Dimethylpentane	0.14±0.04	-1.90±0.81	0.11	0.08±0.02	0.06±0.01
Benzene	0.50±0.13	-7.27±3.21	0.66	0.37±0.05	0.28±0.02
Cyclohexane/ 2,3-Dimethylpentane	0.05±0.01	-0.68±0.26	0.18	0.02±0.01	0.016±0.002
3-Methylhexane	0.05±0.01	-0.87±0.40	0.16	0.05±0.01	0.04±0.01
iso-Octane	0.10±0.02	-2.63±1.07	0.28	0.07±0.01	0.05±0.01
n-Heptane	0.03±0.01	-0.43±0.19	0.01	0.03±0.01	0.03±0.01
Methylcyclohexane	0.03±0.01	-0.16±0.14	0.03	0.020±0.004	0.03±0.01
2,3,4-Trimethylpentane	0.08±0.02	-1.31±0.44	0.10	0.019±0.003	0.01±0.01
2-/3-Methylheptane	0.03±0.01	-0.26±0.16	0.14	0.02±0.01	0.013±0.004
Toluene	0.92±0.24	-13.78±6.66	0.99	0.49±0.06	0.33±0.03
Ethylbenzene	0.26±0.06	-5.71±2.33	0.19	0.08±0.01	0.050±0.004
m-/*p*-Xylene	0.23±0.07	-3.34±2.06	0.74	0.32±0.04	0.20±0.02
n-Nonane	0.001±0.001	0.02±0.03	0.003	–	–
Styrene	0.09±0.02	-2.46±0.79	–	0.02±0.01	0.014±0.002
o-Xylene	0.18±0.04	-5.92±2.25	0.27	0.13±0.02	0.08±0.01
n-Octane	0.017±0.004	0.02±0.11	0.004	0.01±0.01	0.005±0.003
iso-Propylbenzene	0.008±0.003	0.04±0.06	0.02	–	–
n-Propylbenzene	0.02±0.01	-0.01±0.11	0.05	0.014±0.004	0.010±0.001
m-/*p*-Ethyltoluene	0.10±0.03	0.18±0.66	0.29	0.14±0.02	0.09±0.01
Mesitylene	0.03±0.03	1.26±0.69	0.10	–	–
o-Ethyltoluene	0.03±0.01	-0.10±0.18	0.07	0.030±0.003	0.019±0.002
NO_x	7.04±3.33	-39.03±59.76	–	–	–

(1) Fraser *et al.*, 1998b; (2) Kirchtetter *et al.*, 1996.

Table 4.11 exhibits that, within the error limits, the LDV contributions of the calculated emission indices of the present study for ethane, propane, *iso*-/1-butene, *cis*-butene, 3-methyl-1-butene, *iso*-pentane, 1-pentene, cyclopentene/3-/4-methyl-1-pentene, 2-methyl-1-pentene/1-hexene, methylcyclopentane/2,4-dimethylpentane, methylcyclohexane, 2,3,4-trimethylpentane and toluene agreed with those of the measured values of Van Nuys tunnel (Fraser *et al.*, 1998b), where about 97% of the traffic fleet (Fraser *et al.*, 1998a) were LDV.

It can also be observed from Table 4.11 that the LDV contributions of the calculated emission indices of the present study for propene, 2-methyl-1-butene, *n*-pentane, 2,2-dimethylbutane, cyclopentene/3-/4-methyl-1-pentene, *n*-hexane, methylcyclopentane/2,4-dimethylpentane, benzene, 3-methylhexane, *iso*-octane, *n*-heptane, methylcyclohexane, 2-/3-methylheptane, *m*-/*p*-xylene, *o*-xylene, *n*-octane, *m*-/*p*-ethyltoluene and *o*-ethyltoluene are comparable with the values of the Caldecott tunnel (either the values of October, 1994 or both). There exist for some components of the Van Nuys tunnel a factor of 2-5 higher values in comparison with this study. The values of the Van Nuys tunnel were actually also found higher than represented by governmental emissions inventories (*e.g.* EMFAC 7G, 1998; Fraser *et al.*, 1998b). The percentage contributions of passenger cars and light duty vehicles of the Van

Nuys and the Caldecott tunnel are *ca.* 70% and 30%, respectively, whereas in the Kiesberg tunnel, they are *ca*. 90% and 6%, respectively. Thus, one of the reason of these discrepancies of the calculated values could be attributed to these differences in the traffic contribution in the different tunnels. Since the fuel composition differs slightly from places to places (Aral, OMV, Main *et al.*, 1998), the emission of different amount of unburnt fuel or running loss of fuel from the road traffic vehicles passed through the different tunnels could be another reason for the discrepancies of the calculated values.

Table 4.11 shows also the HDV contributions of the components. Most of them show negative values. As discussed in Section 4.1.3.2, these negative values are the consequence of the Eqs. 4.1 and 4.2, used for calculating the LDV and HDV contributions which arise due to the small difference of the percental contribution of HDV between weekdays and weekends.

4.1.3.4 Emission estimate (EE)

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 an 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 emittant for a particular situation. The general equation for emission estimation is (OAQPS, 1999):

$$E = A \times EF \times (1 - ER/100) \qquad \text{Eq. 4.3}$$

Where:

E = emissions,
A = activity rate,
EF = emission factor, and
ER = overall emission reduction efficiency, %.

For simplicity, if the overall emission reduction efficiency term is ignored in Eq. 4.3, the emission estimate can be calculated by multiplying the activity rate (*e.g.* driving performance in vehicle km per year or fuel consumption per year) with the emission factors or emission indices for a particular component (ERG 2001). Since in the present study, the emission factors (mg/km) and emission indices (g/kg fuel) were calculated for LDV, using the value of total driven km per year or the value indicating the total consumption of gasoline and diesel per year, it is possible to calculate approximately the total emission per year for a particular region for LDV. The emission estimate for HDV will not be carried out since the emission factors and emission indices of most of the NMHCs and of NO_x calculated by this study for HDV were found negative and the emission estimation with them may lead to erroneous results.

For an example, using the values of the driving performance for NRW in 1997 (million vehicle km) found in the emission report ‘Luft 1996/1997’ of the State Environment Agency of North-Rhine Westfalia (‘Landesumweltamt Nordrhein-Westfalen’ (LUA NRW, 1999)) and the calculated average emission factors of this study, an emission estimation for LDV was carried out for NMHCs and NO_x as shown in Table A3 IV (in the Annex-Tables). A summary of the results including a comparison with the literature values of LUA NRW (1999) is presented in Table 4.12.

Table 4.12: Emission estimate for NRW for the year 1997 using the calculated average emission factors (mg/km) of the present study for LDV and the literature value (LUA NRW, 1999) of the average driving performance between 'Bundesautobahnen' (BAB) and 'Bundesstraßen' (BS) in million vehicle-km. A comparison of the literature values from the road traffic source sector (LUA NRW, 1999) is also shown.

	Average between BAB and BS			
	This study		North-Rhine Westfalia (NRW)	
	Light duty vehicles (LDV)		Road traffic	
Components	t/a	Standard deviation	t/a	Standard deviation
Benzene	632	159	656	33
Total NMHCs	12159	3241	12479	76
NO_x	9052	3917	57970	42028

In the above estimation, an average value of driving performance of federal highways ('Bundesautobahnen', BAB) and federal streets ('Bundesstraßen', BS) were taken because of the possibility that the traffic composition through the Kiesberg tunnel consists of vehicles from both of the federal highways (BAB) and federal streets (BS).

The similarity of the estimated emission of benzene and total NMHCs for LDV from the sector of road traffic of this study with those of LUA may indicate that the emission of these components from HDV should be smaller than LDV. It can be only pointed out that the contribution of driving performance (million km/a) of HDV in the total driving performance of road traffic in NRW for BAB is about 13% and for BS is about 6%. Similarly, the results shown in Table 4.12 also indicate that the contribution of NO_x from HDV should be higher than LDV which can also be found in literature (Pierson *et al.* 1996, Schmid *et al.* 2001).

Table A3 V (in the Annex-Tables) shows another emission estimation using the values of fuel-consumption in NRW in 1997 (LUA NRW, 1999) for LDV. The summary of the calculated average emission indices of the present study in comparison with the literature data (LUA NRW 1999) is presented in Table 4.13.

Table 4.13: Estimation of road traffic emissions in NRW in the year 1997 using the calculated average emission indices of the present study and the literature values (LUA NRW, 1999) of fuel consumption in ton/year (t/a) for LDV. A comparison with the literature values (LUA NRW, 1999) is also shown.

	Using fuel consumption in NRW			
	Using emission indices of this study		NRW	
	Light duty vehicles (LDV)		LDV	HDV
Components	t/a	S. D. (t/a)	t/a	t/a
Benzene	3806	3405	4545	215
Total NMHCs	64554	51184	77174	11052
NO_x	54686	25867	103241	83306

HDV: Heavy Duty Vehicles. S. D.: Standard Deviation (1 σ).

The estimated average values for benzene and total NMHC emitted from LDV from the present study agree within the error limits with the literature values (LUA NRW, 1999). The calculated emissions for NO_x from LDV had a negative discrepancy of about 50% from those of LUA. As it is postulated above, it can be observed from Table 4.13 that the emission estimate for benzene and NMHCs for HDV in NRW are much lower than those of LDV. On the other hand, the emission estimate for NO_x for HDV in NRW is higher than that of LDV.

It is also noteworthy that the estimated benzene, total NMHCs and NO_x for LDV in NRW using the average driving performance of BAB and BS were about one sixth less than those estimation using the fuel consumption for LDV in NRW. It possibly indicates that the emissions of these components from BAB and BS are about one fifth lower than those emission from other parts of NRW.

4.1.4 Conclusion

To improve the air quality regarding nonmethane hydrocarbons, it is possibly not enough only to increase the number of PC with catalysts, but it may be recommendable to remove all conventional passenger cars without exhaust after treatment.
Among aromatic compounds, toluene, among alkenes/alkynes, ethene/ethyne and among alkanes, *iso*-pentane showed the largest emission ratios relative to benzene from the road traffic exhaust, which can also be considered as fingerprint components from this source sector.
The percental composition of these classes in the total measured NMHC-mix in the Kiesberg tunnel showed almost equal distribution among each other with a slight higher value for the alkanes. A comparison of the fuel's composition with the compostion of the road traffic exhaust indicates an increase of the alkene contribution during the combustion.
The toluene/benzene ratio (1.7 ± 0.5 ppbC/ppbC) can be used as a marker of road traffic emissions.
The NMHC/NO_x ratio in ppbC/ppbv was found to be 0.6-2.0 for weekdays and 4.4 ± 0.4 for the weekend. Since HDVs emit higher amount of NO_x than that of LDVs, the increased value of this emission ratio during the weekend can be justified due to the decrease of the contribution of HDV from 6% during the weekdays to 1% during the weekend, which is in agreement with literature studies.
The determined emission factors and emission indices of LDV for NMHCs and NO_x can be considered as the range values from the road traffic exhaust which may be used for developing the emission inventory from this source sector.

4.2 City air of Wuppertal

The city air consists of not only emissions from different sources, but it indicates the total situation of emissions, transport, dilution and photodegradation of pollutants (in German 'Immission'). Since one of the objectives of this work was to investigate the contribution of road traffic emissions to city air pollution, therefore, the data evaluation was carried out by considering the meteorological data, *i.e.* wind direction and wind speed, which would indicate the direct transport of the air from the city centre without photochemical degradation.

4.2.1 Meteorological data and NMHC/NO_x ratio

Figure 4.7 shows a wind rose for Monday, 31.08.98.

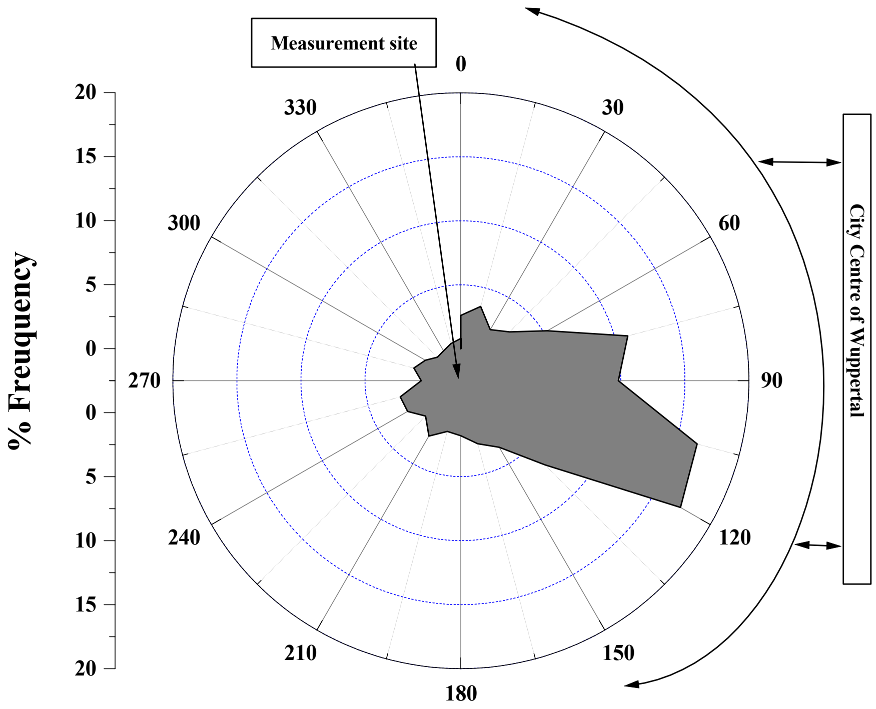
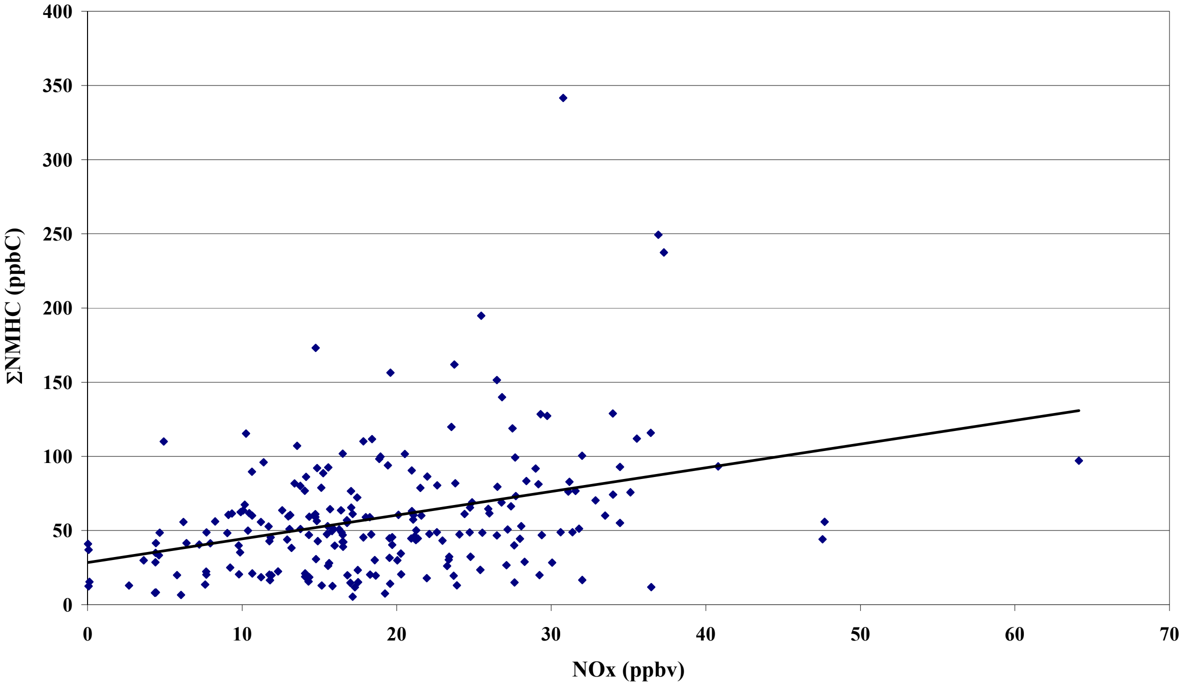


Figure 4.7: Wind rose for Monday (31.08.98) indicating qualitatively the main flow of air from the city centre to the measurement centre. The sector 11°-151° indicates the city centre part of Wuppertal.

Figure 4.7 clearly indicates that the air parcel investigated came directly to the measurement centre from the city centre containing traffic exhaust on Monday 31.08.98. Similar situation was also observed on Sunday, 30.08.98.

Figure 4.8 shows the plot of the emission ratios between total nonmethane hydrocarbons and nitrogen oxides (NO_x) in ppbC/ppbv for all days.



Emission ratio of ΣNMHC (ppbC)/NO_x (ppbv) = 1.6 ± 0.3, corr. Coeff. 0.1.

Figure 4.8: Correlation plot between total nonmethane hydrocarbons (ppbC) and NO_x (ppbv) measured for all the days of the field measurement campaign in the city of Wuppertal in August-September, 1998.

As shown in Figure 4.8, the NMHC/NO_x emission ratio in ppbC/ppbv is 1.6 ± 0.3. But due to the diffuse character of the correlation plot, the correlation coefficient is only 0.1. If all the weekdays and weekends are considered irrespective of the wind direction and meteorological parameters, the emission ratios between NMHC and NO_x were found to be 2.0 ± 0.4 (corr. coeff. = 0.2) and 1.3 ± 0.4 (corr. coeff. = 0.1), respectively. These low correlation and the emission ratio values can be explained by the fact that on an average, the air can reach the measurement station of this study from any direction, *e.g.* from the forests or countryside containing different NMHC-mixes qualitatively and quantitatively. Similarly, the mixing ratio of NO_x can be different for different wind direction and meteorological parameters.

That is why, it was attempted for getting more appropriate emission ratio of NMHCs against NO_x by considering only those days, when a good correlation between some selected hydrocarbons and NO_x can be observed, which can be seen in the diurnal variations of these compounds (see Figure 4.8) and by considering the meteorological data.

Therefore, to derive the influence of the traffic exhaust in the city air of Wuppertal, Sunday (30.08.98) and Monday (31.08.98) were considered for further calculation. Figure 4.12 and Figure 4.13 show the correlation plot of NMHCs against NO_x for a weekend (Sunday) and for a weekday (Monday), respectively.

4.2.2 OH degradation

It was also observed that the average wind speed was in between 3-9 km per hour.

Using this wind speed value, the average distance from the city centre of Wuppertal (1-2 km) and k_{OH} values of the nonmethane hydrocarbons found in the tunnel air, it was attempted to evaluate the approximate percental degradation of the NMHCs using the probable transport time of 10-40 min from the city centre to the measuring station at the University of Wuppertal. Table 4.14 shows the summary of the percental degradation for the transport time of 10 and 40 min for the measured NMHCs in this study.

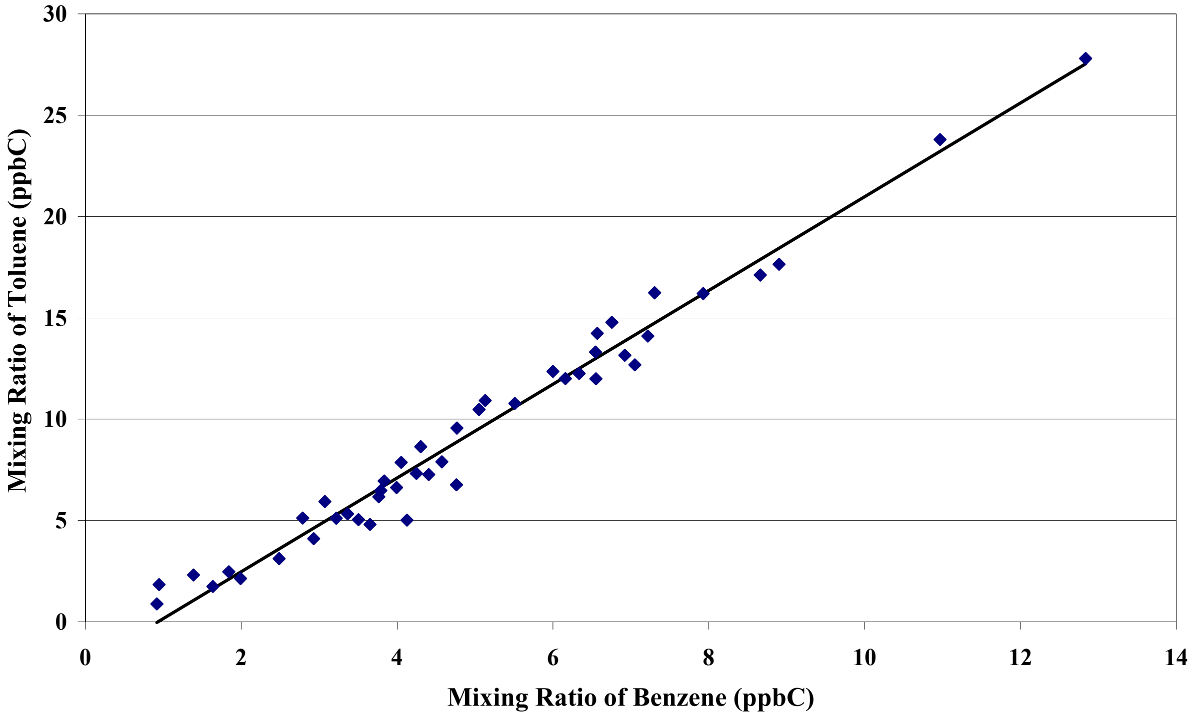
Table 4.14: Summary of the percental degradation of the measured NMHCs using k_{OH} values for the probable transport time from the city centre to the measuring station in the University of Wuppertal.

Range of the percental degradation	No. of the degraded NMHCs relative to total NMHCs (%)	
	Transport time: 10 min	Transport time: 40 min
<1%	62	27
1%- 5%	35	37
5%-10%	3	12
10%-15%	–	19
15%-22%	–	5

According to Table 4.14, for the transport time of 10 min, 37 NMHCs (62%) degrade scarcely more than 1% and 58 NMHCs (97%) degrade only less than 5% from their initial concentrations. Similarly, for the transport time of 40 min, 95% of the measured NMHCs degrade within 15% of the initial concentrations. Only for isoprene, 2-methyl-1-butene and 2,3-dimethyl-2-pentene, for 10 min transport time, the pencental degradation are within 5%-6% and for the 40 min transport time, they are within 19%-21% of their initial mixing ratios. All the calculations were carried out using the k_{OH} values shown in Table A1 I (in the Annex-Tables). Since the error limits for the measurement of NMHCs is *ca.* 30%, the percental degradation of the NMHCs transported from the city centre to the measurement station is negligible.

4.2.3 Emission ratios relative to benzene

Since benzene is mainly emitted from the road traffic and its contribution from other sources, *e.g.* solvent use, is decreasing with time, as the use of benzene as solvent is forbidden, emission ratios of different nonmethane hydrocarbons for the city air of Wuppertal were determined by normalizing them against benzene. Figure 4.9 shows as an example, the correlation plot of toluene against benzene in ppbC/ppbC for the weekend.



Emission ratio of toluene/benzene (ppbC/ppbC) = 2.21 ± 0.07, correlation coefficient = 0.99.

Figure 4.9: A correlation plot between the mixing ratio of toluene and benzene in ppbC/ppbC for the weekend (30.08.98) during the measurement campaign in the city of Wuppertal.

Figure 4.9 shows a good correlation between the mixing ratio of toluene with that of benzene in ppbC/ppbC for the city air of Wuppertal during the weekend. Table A3 VI (in the Annex-Tables) presents a list of the emission ratios of NMHC relative to benzene (in ppbC/ppbC) for the city of Wuppertal during the weekend, which also indicates good correlations between different NMHCs and benzene.

4.2.3.1 NMHC Profile

The transport time from the city centre to the measurement station at the University of Wuppertal was on average about 10-40 min. During this time the degradation of the hydrocarbons by the reaction with OH radicals can change scarcely (see section 4.2.2) the emission ratio of the hydrocarbons to benzene. It is well known that in an aged background air mass the relative toluene to benzene ratio can be decreased due to the longer lifetime of benzene. However, due to the dilution during the transport the mixing ratios of benzene and toluene in the aged background air mass decreased strongly and cannot influence those of the city air, if aged upwind air would mix with freshly emitted polluted city air. In the present study an average mixing ratio of 1.1 ±0.98 ppbv toluene in the city air was observed, whereas a typical average mixing ratio of 216±120 pptv toluene was observed in a background air mass of Menz (see Table 3.5).

A NMHC-profile, normalized to benzene (in ppbC/ppbC), for the city air was derived from the measured data. Figure 4.10 shows the NMHC profile of the city air during the weekday and the weekend.

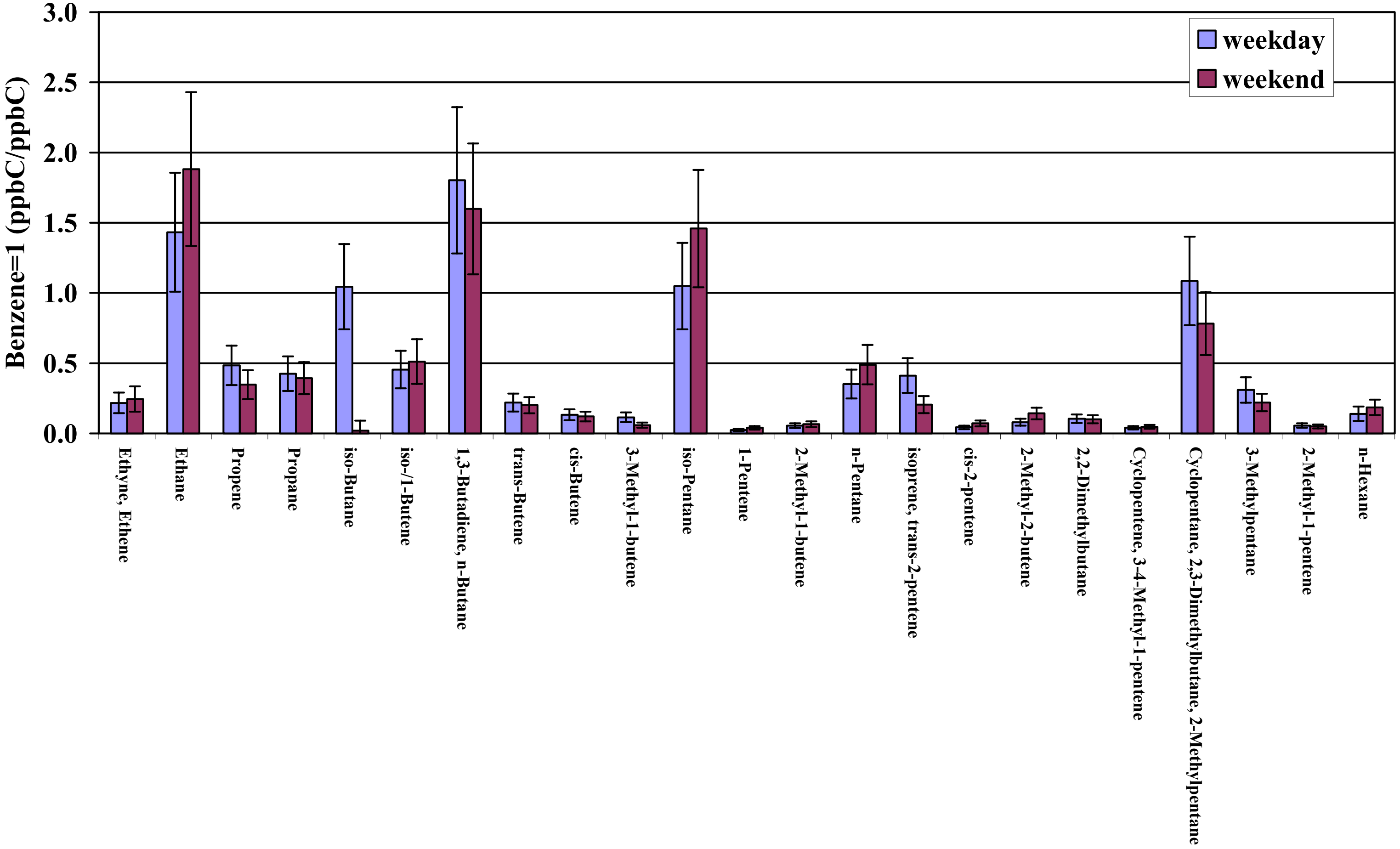
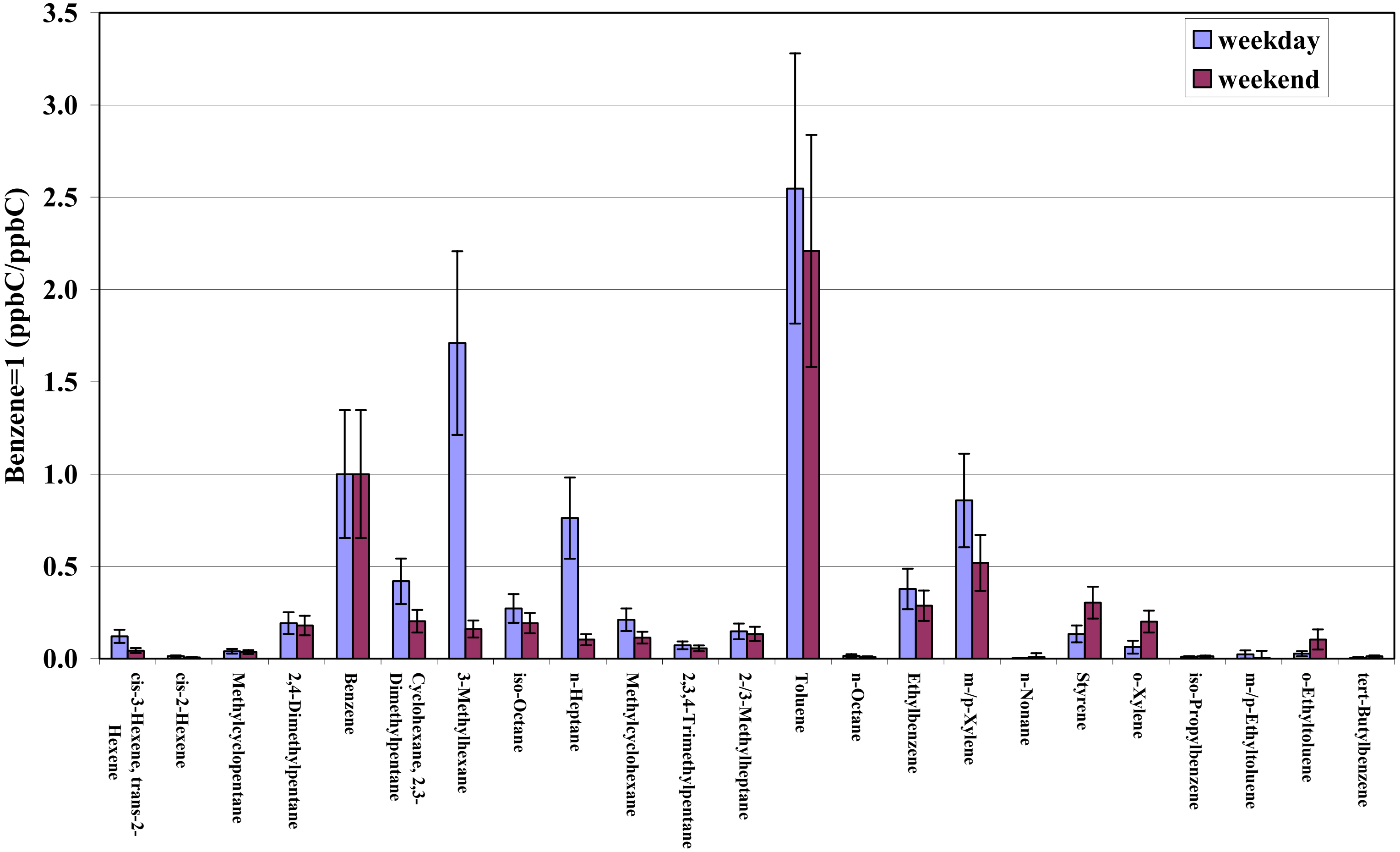

Benzene=1 (ppbC/ppbC)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
weekday
weekend
Ethyne, Ethene
Ethane
Propene
Propane
iso-Butane
iso-/1-Butene
1,3-Butadiene, n-Butane
trans-Butene
cis-Butene
3-Methyl-1-butene
iso-Pentane
1-Pentene
2-Methyl-1-butene
n-Pentane
isoprene, trans-2-pentene
cis-2-pentene
2-Methyl-2-butene
2,2-Dimethylbutane
Cyclopentene, 3-4-Methyl-1-pentene
Cyclopentane, 2,3-Dimethylbutane, 2-Methylpentane
3-Methylpentane
2-Methyl-1-pentene
n-Hexane

Figure 4.10 (a)



(b)

Figure 4.10 (a-b): NMHC-Profile relative to benzene in ppbC/ppbC during the weekday and the weekend in the city of Wuppertal in August-September, 1998.

It can be seen from Figure 4.10 that the NMHC profile relative to benzene in ppbC/ppbC during the weekday and the weekend are almost similar within the error limits except for cyclohexane/2,3-dimethylpentane, 3-methylhexane and *n*-heptane, which are during the weekday greater than those during the weekend. Since some alkanes are used as solvents, the high emission ratios for these components could be due to the partial contribution from solvent use (see section 4.3.1).

4.2.3.2 Percentage composition

From the NMHC profile shown in Figure 4.10, the average percentage composition of the different classes of nonmethane hydrocarbons was calculated and the result is presented in Table 4.15. It also shows a comparison with a study by Schmitz *et al.* (1997), which was carried out in the city of Wuppertal in 1995.

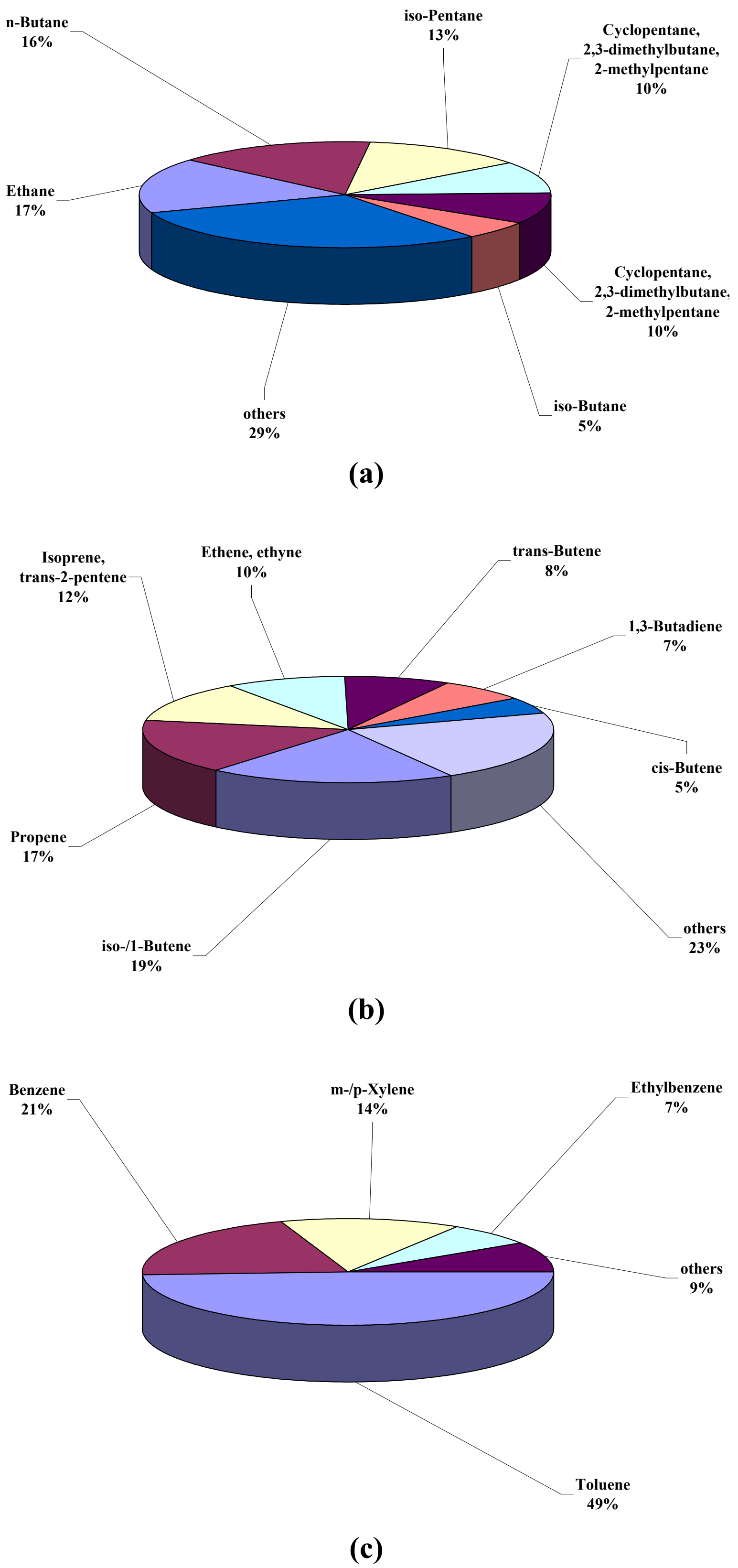
Table 4.15: Percentage composition of NMHC-mix of the city air of Wuppertal relative to benzene in ppbC/ppbC using the same compounds.

	Year	Alkanes	±	Alkenes/Alkynes	±	Aromatic Hydrocarbons	±	References
Weekday	1998	59.7	6.5	13.9	1.8	26.4	4.8	This study
	1995	62.5	24.0	10.8	6.0	26.7	14.9	Schmitz *et al.*, 1999
Weekend	1998	52.8	7.4	15.0	4.4	32.2	5.9	This study
	1995	61.4	17.7	11.6	7.3	27.0	10.5	Schmitz *et al.*, 1999
Average	1998	57.2	6.5	14.5	3.6	28.3	5.1	This study
	1995	61.9	20.1	11.3	8.7	26.9	12.5	Schmitz *et al.*, 1999

Comments: 1. The above calculation was done using the same nonmethane hydrocarbons. 2. Both studies were carried out in the month of August and/or September. 3. The average percental distribution was calculated by averaging the values of the individual components during the weekdays and the weekend. 4. The values of the coeluted peak 1,3-butadiene/*n*-butane were separated by assuming 10±7% contribution from 1,3-butadiene and 90±7% contribution from *n*-butane as reported by other studies for German cities (Schmitz *et al.*, 1997; Mannschreck, 2000).

According to Table 4.15, during the weekday and the weekend, the highest contribution is from alkanes and the second highest contribution is from the aromatic compounds. The percental contribution of the different classes determined by this study agreed with the work of Schmitz *et al.* (1999).

Figure 4.11 a-c show the distribution of different compounds in the three main classes of hydrocarbons, namely alkanes, alkenes and aromatic compounds.



Others: total of all other components containing percental contribution of less than 5%.

Figure 4.11 (a-c): Percental distribution of the nonmethane hydrocarbons among (a) alkanes, (b) alkenes/alkynes and (c) aromatic compounds relative to benzene (in ppbC/ppbC) for the city air of Wuppertal during August-September, 1998.

It is noticeable that among the alkanes, ethane, *n*-butane and *iso*-pentane, among the alkenes, *iso*-/1-butene, propene and isoprene/*trans*-2-pentene, and among the aromatic compounds, toluene, benzene and *m*-/*p*-xylene have the 1st, 2nd and 3rd highest percental distributions, respectively. In the hydrocarbon-mix of the Kiesberg tunnel air, the highest percental distribution of the alkanes, alkenes/alkynes and aromatic compounds were namely *iso*-pentane, ethene/ethyne and toluene, respectively. Thus it seems that the city air of Wuppertal contains the same finger-print compounds as found in the Kiesberg tunnel air. The percental contribution of alkenes/alkynes of the city air, which have in general very high k_{OH} values, is smaller than that of the Kiesberg tunnel.

4.2.4 Aromatic hydrocarbons

Aromatic hydrocarbons are of great interest in the chemistry of the urban atmosphere because of their abundance in motor vehicle emissions and because of their high reactivity with respect to ozone formation and secondary organic aerosol formation (Seinfeld and Pandis, 1998; Becker, 2000). One can find in literature various measurements of benzene, toluene and other aromatic compounds in ambient air. Whether these compounds are emitted from road traffic or not, the contribution of these compounds to road traffic exhaust can only be understood by knowing the correlation of these compounds with respect to a marker for road traffic exhaust, *e.g.* benzene. Table 4.16 shows a comparison of the emission ratios of some selected aromatic compounds relative to benzene in ppbC/ppbC of this present study with other studies of the world.

Table 4.16: List of emission ratios of some selected aromatic compounds relative to benzene in ppbC/ppbC for Wuppertal and other places of the world.

Place	Year	Toluene/Benzene	Ethylbenzene /Benzene	*m*-/*p*-Xylene /Benzene	*o*-Xylene/ Benzene	References
Urban area						
City air of Wuppertal	August-September, 1998	2.4±0.7	0.3±0.1	0.7±0.2	0.13±0.05	This study
Kiesberg tunnel, Wuppertal	1997-1998	1.7±0.5	0.4±0.1	0.5±0.2	0.2±0.1	This study
Düsseldorf (road traffic)	1998	3.0	0.7	1.5	0.5	LUQS, 1999
Essen (road traffic)	1998	2.6	0.6	1.2	0.4	LUQS, 1999
Bonn	1998	3.0	0.7	1.2	0.4	LUQS, 1999
Duisburg	January, 2001	1.6	0.4	0.8	0.4	LUQS, 2001
City of Augsburg (down wind)	March, 1998	1.0	0.2	0.4	0.2	Mannschreck, 2000
City of Augsburg (down wind)	October, 1998	1.1	0.1	0.3	0.1	Mannschreck, 2000
Freiburg	August, 1998	2.1		1.2	0.5	UMEG, 1998
Heidelberg	August, 1998	3.2		1.4	0.5	UMEG, 1998
Karlsruhe	August, 1998	2.1		1.4	0.5	UMEG, 1998
Pforzheim	August, 1998	2.0		1.3	0.5	UMEG, 1998
Stuttgart	August, 1998	2.1		1.5	0.5	UMEG, 1998
Tübingen	August, 1998	1.8		1.3	0.5	UMEG, 1998
Ulm	August, 1998	2.1		1.7	0.6	UMEG, 1998
Rheinland-Pfalz	1998	2.9±0.4				ZIMEN, 1999
Budapest (tunnel)	1990	2.4	0.5	1.5	0.6	Haszpra, 1994
City of Yokohama, Japan	1997	4.8±0.7	0.7±0.2	1.0±0.4	0.15±0.03	Yamamoto *et al.*, 2000
City of Changchun, China (Road side)	1997-1998	2.1±1.8	0.5±0.4	0.6±0.6*		Liu *et al.*, 2000
City of Changchun, China (down town)	1997-1998	1.9±1.2	0.3±0.2	0.4±0.3		Liu *et al.*, 2000
Copenhagen, Denmark	December, 1997	3.7	0.8	2.2	1.1	Christensen *et al.*, 1999
London	1991-1992	1.8-2.0	0.3	0.9–1.1	0.4	Derwent *et al.*, 1995
Caracas, Venezuela	1999-2000	2.7		3.3*		Holzinger *et al.*, 2001
Algiers (road side)	1997-1998	1.4±0.8	0.2±0.2	0.7±0.4	0.3±0.2	Kerbachi *et al.*, 1999
Algiers (urban)	August, 1998	1.6±0.9	0.1	0.3±0.3		Kerbachi *et al.*, 1999
Rome	1992-93	2.8	0.5	1.5	0.7	Brocco *et al.*, 1997
Suburban area						
Altos de Pipe, Venezuela	1999-2000	2.3		2.4*		Holzinger *et al.*, 2001

Table 4.16 (continued):

Place	Year	Toluene/Benzene	Ethylbenzene /Benzene	*m*-/*p*-Xylene /Benzene	*o*-Xylene/ Benzene	References
Rural area						
Menz (Plume)	July, 1998	1.5±0.4	0.3±0.1	0.5±0.2	1.3±0.4	This study
Menz (background)	July, 1998	0.8 ± 0.2	0.14 ± 0 04	0.2 ± 0.1	0.4 ± 0.1	This study
Rothaargebirge (background)	1997	1.5	0.4	1.0	0.3	LUQS, 1999
Eifel (background)	1998	1.8	0.5	1.1	0.3	LUQS, 1999
Calabozo, Venezuela	1999-2000	0.6-1.3		0.2-1.2*		Holzinger *et al.*, 2001
Changchun, China		3.9 ± 2.7	0.8 ± 0.7	1.3 ± 1.0*		Liu *et al.*, 2000
Algiers (rural area)	August, 1998	2.1 ± 0.5	0.1 ± .01	0.7 ± 0.4		Kerbachi *et al.*, 1999
Remote area						
Parupa, Venezuela	1999-2000	0.6		0.5*		Holzinger *et al.*, 2001
Central Amazonia (canopy forest)		0.5				Kesselmeier *et al.*, 2000
Bermuda (in-sector)	April, 1996	0.6	0.2			Milne *et al.*, 2000
Bermuda(marine boundary layer, 500 m)	April, 1996	0.6	0.1			Milne *et al.*, 2000
Bermuda(marine boundary layer, 1500 m)	April, 1996	2.2	0.4			Milne *et al.*, 2000

* all xylenes, ** At off-shore marine boundary layer (1500 m), the presence of anthropogenically influenced signatures of continentally derived air incurred the high value of toluene to benzene ratio (Milne *et al.*, 2000).

From the Table 4.16, it can be seen that the measured toluene/benzene ratio of the present study is in agreement with other urban and tunnel measurements. Since the result obtained from the tunnel studies implies the road traffic exhaust, accordingly, the similarity of this ratio with those of other places will also indicate the influence of road traffic in those places. Therefore, the fact that, the toluene/benzene ratio acts as source marker for road traffic emission, is ascertained. As expected, the toluene/benzene ratios for the rural and remote areas are smaller than those of urban areas.

Table 4.17 shows the percentage contribution of aromatic compounds in wt% from the present study in comparison with literature values.

Table 4.17: Percental contribution of aromatic compounds in wt% from the present study compared with literature values.

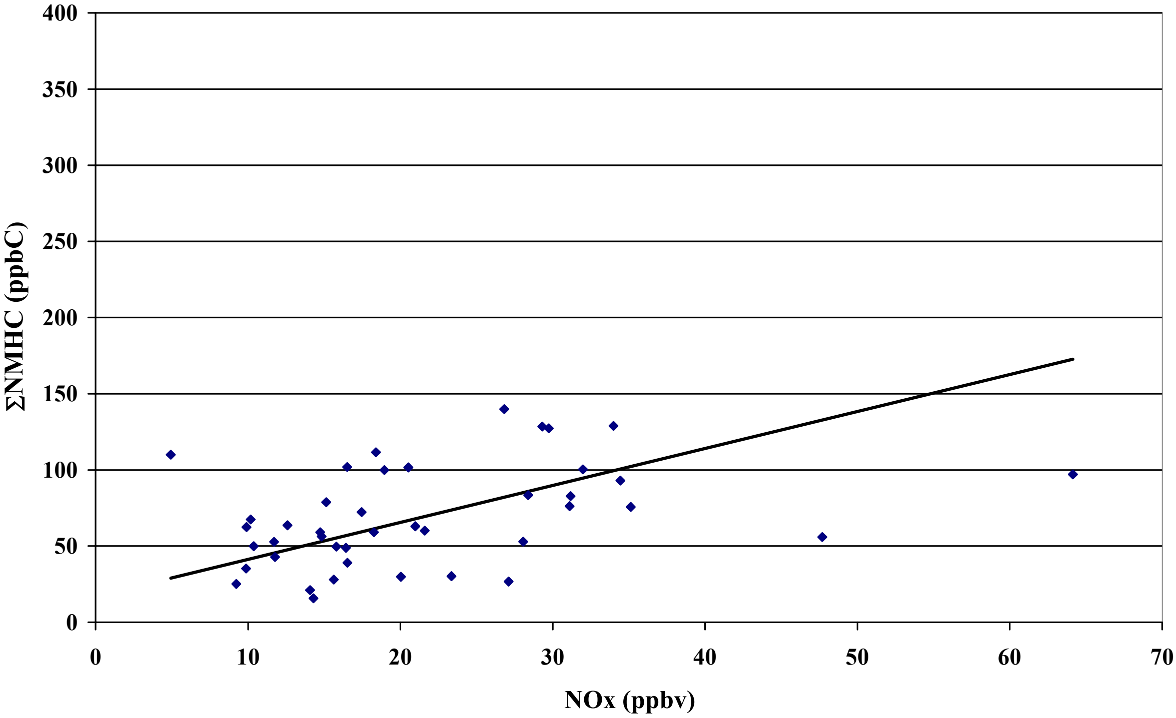
Location	Characterisation	Country	% Aromatic compounds	References
Wuppertal	Urban	Germany	28.3 ± 5.2	This study
Wuppertal	Traffic tunnel	Germany	30.7 ± 5.7	This study
Menz	Rural, Berlin plume	Germany	28	This study
Menz	Rural, background	Germany	19.0	This study
Frohnau	Suburban	Germany	18.0	Thijsse *et al.*,1999
Nansenstrasse	Urban, roadside	Germany	29.0	Thijsse *et al.*,1999
Frankfurter Allee	Urban, roadside	Germany	35.0	Thijsse *et al.*,1999
Munich	Mean values (all days)	Germany	34.0	Kern *et al.*, 1998
Storkow	Pine-forest	Germany	25.8*	Ciccioli *et al.*, 1999
Madrid	Suburban	Spain	34.5*	Ciccioli *et al.*, 1999
Milan	Urban	Italy	43.7*	Ciccioli *et al.*, 1999
Rome	Urban	Italy	32.9*	Ciccioli *et al.*, 1999
Taranto	Urban	Italy	34.1*	Ciccioli *et al.*, 1999
Montelibretti	Suburban/rural	Italy	6.0*	Ciccioli *et al.*, 1999
Castelporzio	Forest/rural	Italy	2.6*	Ciccioli *et al.*, 1999
Castelporzio	Pine-oak forest	Italy	3.9*	Ciccioli *et al.*, 1999
Apenini Mountains	Forest-rural	Italy	1.6*	Ciccioli *et al.*, 1999
Monti Crimini	Pine-forest	Italy	8.7*	Ciccioli *et al.*, 1999
Viols en Laval	Forest maquis	France	6.0*	Ciccioli *et al.*, 1999
Burriana	Orange-field	Spain	5.0*	Ciccioli *et al.*, 1999
Svalbard Islands	Remote arctic	Norway	5.2*	Ciccioli *et al.*, 1999

*: calculations included oxygenated volatile organic compounds.

From Table 4.17 it can be seen that the measured percentage of aromatic compounds from the present study is in agreement with other cities, although the measured percentage composition of aromatic compounds for the background air of Menz does not agree with other background air studies. It can also be seen that the literature values about the percental composition of aromatic compounds widely vary with each other. The reason can be attributed to the different hydrocarbon-mix in different rural locations. Besides, due to different sources for hydrocarbons, the percentage composition of aromatic compounds can be different. It is also dependent on the number of the measured/identified hydrocarbons forming the sum of hydrocarbons or volatile organic compounds.

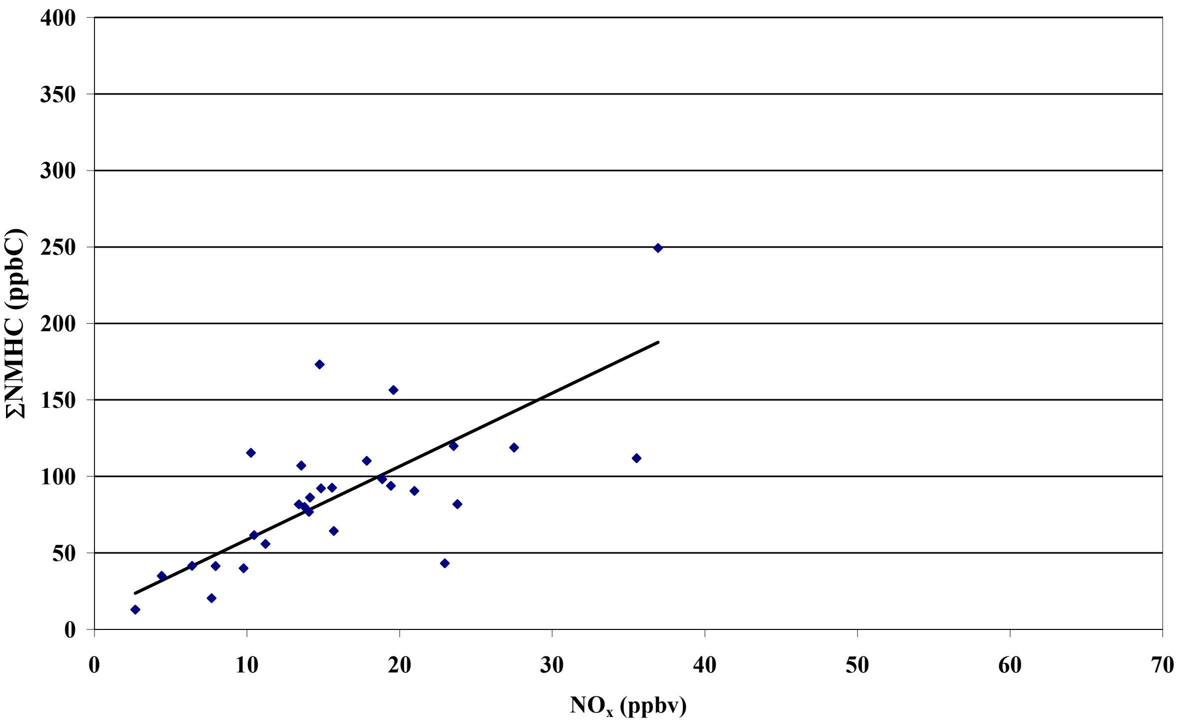
4.2.5 NMHC/NO_x

By considering only the data for Sunday (30.08.98) and for Monday (31.08.98), when the air from the city centre was transported to the measuring station, the following plots regarding ΣNMHC/NO_x (in ppbC/ppbv) were obtained.



Emission ratio of ΣNMHC (ppbC)/NO_x (ppbv) = 2.4 ±0.5, corr. coeff.: 0.4

Figure 4.12: Correlation plot of the sum of the total measured nonmethane hydrocarbons in ppbC against NO_x in ppbv for Sunday 30.08.1998 for the city air of Wuppertal.



Emission ratio of ΣNMHC (ppbC)/NO$_x$ (ppbv) = 4.8 ± 0.8, corr. coeff.: 0.7.

Figure 4.13: Correlation plot of the sum of the total measured nonmethane hydrocarbons in ppbC against NO$_x$ in ppbv for Monday 31.08.1998 for the city air of Wuppertal.

For the weekday, the determined NMHC/NO$_x$ ratio of the present study (4.8 ± 0.8) is comparable with the value (5.4 ± 0.4) by Schmitz *et al.* (1997) for the city of Wuppertal in August, 1995. Schmitz *et al.* (1997) studied the city air in a nearby place of the measurement station of the present study. But the obtained value of the present study for the weekend (2.4 ± 0.5) is 3 times smaller than the value (7.5 ± 0.7) of Schmitz *et al.* (1997). The discrepancy between the two measurements can be occurred due to the difference in emissions and sources of NMHCs and NO$_x$ and possibly they were not the same during these two measurement campaigns.

The reason for the smaller value found during the weekend in compared with that during the weekday by the present study can be attributed to the fact that the city air consists not only of the traffic exhaust of the city, but it denoted the total emission situation of the city. Furthermore, during the weekend the amount of road traffic running in the city, mostly consisted of passenger cars, is smaller than that during the weekdays which will lead to less amount of NMHC emissions in compared to the emissions of NO$_x$ from road traffic or other sources. Altogether, it may result smaller value of NMHC/NO$_x$ during the weekend.

Table 4.18 shows a comparison of the NMHC/NO$_x$ ratio of the present study with literature values.

Table 4.18: Comparison of ΣNMHC/NO_x (in ppbC/ppbv) values found in the present study and in literature.

Location	Characterisation	Country	Ratio	Year	References
Wuppertal-Elberfeld*	Urban	Germany	2.4-4.8	1998	This study
Wuppertal-Elberfeld*	Urban	Germany	5.4-7.5	1995	Schmitz *et al.*, 1997
Kiesberg tunnel, Wuppertal*	Road traffic tunnel	Germany	0.6-4.4	1997-1998	this study
München**	Urban	Germany	4.4	1996	Kern *et al.*, 1998
Koblenz**	Roadside	Germany	1.6-2.0	1998-99	ZIMEN, 1999
Rheinland-Pfalz**	Urban	Germany	1.6-4.0	1998-99	ZIMEN, 1999
Jülich-Mersch*	Access road	Germany	3.3-3.9	1995	Schmitz *et al.*, 1997
°Eschweiler*	Access road	Germany	1.1-1.4	1995	Schmitz *et al.*,1997
Menz *	Berlin plume	Germany	3.8	1998	This study
Baden-Württemberg**	Urban	Germany	1.4-4.4	1999	UMEG, 1999
Southern California**	Ambient	U.S.A.	5.3-9.1	1987	Fujita *et al.*, 1992
Baden-Württemberg**	Industrial/Residential	Germany	1.8-4.4	1999	UMEG, 1999
Rheinland-Pfalz**	Industrial/Residential	Germany	2.0-4.0	1998-1999	ZIMEN, 1999
Menz*	Rural area	Germany	12	1998	This study
Schwarzwald-Süd**	Forest	Germany	8.0	1999	UMEG, 1999

* Sum of the identified NMHCs, ** Total NMHCs, °The value of Eschweiler is smaller compared to other values because of higher contribution of HDV which emits higher NO_x than LDV.

From Table 4.18, it can be seen that the values obtained in the present study are comparable with other cities of Germany. Bruckmann *et al.* (1980) and Klemp *et al.* (1997) also reported similar emission ratios in Germany. For example, Bruckmann *et al.* (1980) reported the VOC/NO_x ratio of 3.5 ppbC/ppbv for the city of Essen and Klemp *et al.* (1997) estimated the mean anthropogenic source ratio of VOC/NO_x at Schauinsland (Black Forest) as 5.0 ppbC/ppbv.

In comparison with tunnel values (see Table 4.5), there is an increase of NMHC/NO_x ratios in the city air or rural areas. This is caused by the following facts:

- Firstly the city air contains not only the traffic emissions, but it represents the total emission of the city.
- Secondly, in the atmosphere, during the transportation of traffic exhaust containing air, photochemical degradation processes may occur. Not only NMHCs will degrade, but nitrogen oxides can also react with OH radicals as a sink:

$NO_2 + OH + M \rightarrow HNO_3 + M$ Eq. 4.4
(k_{OH}: $1.4*10^{-11}$ cm^3s^{-1} (Atkinson *et al.*, 1992)).

The rate constant of NO_x with OH indicates that it can react with OH radical faster than some of the NMHCs (*e.g.* ethene). This fact can also explain, why the NMHC/NO_x ratio is larger than those from road tunnels.

- Thirdly, this value can be higher than in road traffic emissions because of the mixing of aged air containing photodegraded or diluted nonmethane hydrocarbons (Klemp *et al.*, 1997).
- In addition, in the city the road traffic does not have always a smooth moving, instead, there are traffic-jams, which increase the amount of stop and go exhausts.

Table 4.19 shows the Handbook data for the emission of NMHC and NO_x according to Keller *et al.* (1999).

Table 4.19: Handbook data for the emission of total NMHCs and NO_x for different driving cycles for the year of 1998 (Keller *et al.*, 1999).

Types of vehicles	LDV		PC		Truck		MC	
Components	NMHC	NO_x	NMHC	NO_x	NMHC	NO_x	NMHC	NO_x
Traffic situation	(g/km)	(g/km)	(g/km)	(g/km)	(g/km)	(g/km)	(g/km)	(g/km)
Urban stop+go	0.99	1.51	1.16	0.57	8.53	19.18	4.34	0.12
Highway stop+go	0.50	0.96	0.47	0.36	8.55	21.86	4.34	0.12
Urban average	0.33	1.01	0.35	0.49	2.16	6.61	2.78	0.14
Rural average	0.15	0.96	0.18	0.54	0.81	4.38	1.74	0.24
Highway average	0.12	1.15	0.12	0.71	0.78	5.19	1.77	0.47
Highway>120	0.12	1.19	0.13	0.82	0.65	4.93	1.74	0.54
Highway 100	0.11	1.16	0.10	0.58	0.65	4.93	1.73	0.39
Highway 60	0.11	0.86	0.08	0.33	0.79	4.63	1.72	0.25
Highway 80	0.11	1.04	0.09	0.45	0.70	4.81	1.72	0.30

LDV: light Duty Vehicles, PC: Passenger Car, MC: Motor Cycle.

Table 4.19 shows that urban stop+go driving situation emits the highest amount of NMHC and NO_x. Thus the higher value of this emission ratio in the city air is plausible.

4.2.6 Verification of the limit value according to BImSchG for benzene and NO_2

According to the Federal Immission control act (23. Bundesimmisssionsschutzverordnung, §40 Abs. 2 Bundesimmissionsschutzgesetz [BImSchG]), from 01.07.98 the following values have been prescribed: for benzene, 10 $\mu g/m^3$ (2.9 ppbv) as a yearly average value and for NO_2 160 $\mu g/m^3$ (78.4 ppbv) as 98 percentile of the half-hourly average value during one year.

In the city of Wuppertal, since both of the components were monitored for weeks, it was possible to check these limit values. In this present work, the average value of benzene at STP (Standard Temperature and Pressure) was found to be 2.2 ±1.7 $\mu g/m^3$ or 0.64 ±0.50 ppbv. The 98 percentile value of NO_2 at STP was found for the city of Wuppertal as 56.7 $\mu g/m^3$ or 27.7 ppbv. This shows that the limit values prescribed by the German Immission control act for benzene and NO_2 were not exceeded in the city air of Wuppertal during the measurement campaign in August-September, 1998.

4.2.7 Contribution of solvents: literature studies

4.2.7.1 UBA

Different nonmethane volatile organic compounds can be used as solvents. Figure 4.14 shows a plot regarding the percental contribution of different volatile nonmethane organic compounds found in Germany according to UBA 2000 (Theloke *et al.*, 2000).

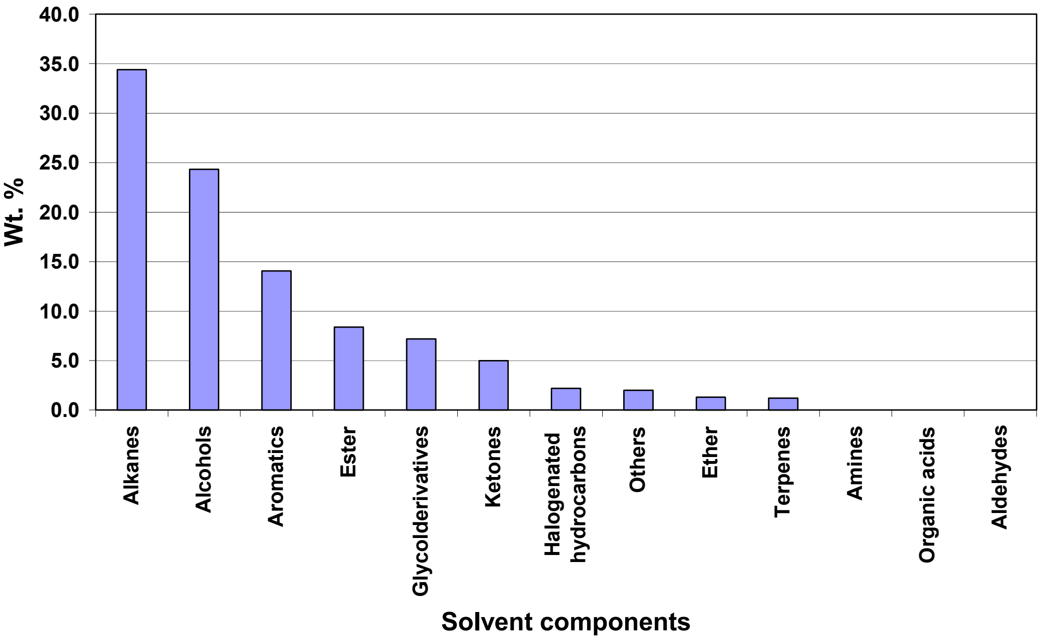


Figure 4.14: Differentiation of solvent components in Germany according to UBA, 2000.

According to Figure 4.14, the contribution of alkanes and aromatic compounds in solvents is about 50%.

Recently a report of the institute for energy economics and rational use of energy, IER (Institut für Energiewirtschaft und rationelle Energieanwendung, Universität Stuttgart) was published, where the estimation of the contribution from the different sources regarding the total NMVOC and also regarding the single NMHC component were calculated for the city of Augsburg (TFS data bank). IER normally calculated emissions of different air pollutants in Germany for UBA. Figure 4.15 shows the percental contribution of the total emission from different anthropogenic sources.

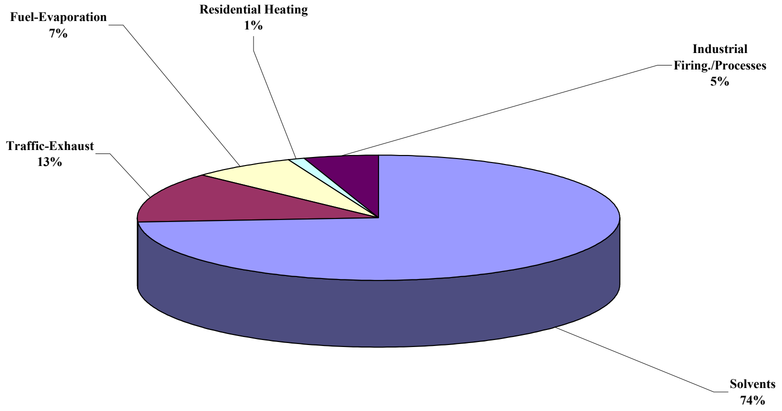


Figure 4.15: Contribution of different sources to the total anthropogenic emission of the city of Augsburg, calculated by IER.

From Figure 4.15, one can observe that the contribution from the solvent sector was estimated to be about 74% regarding only the statistical data of the yearly solvent-consumption. If the total calculated anthropogenic emission of NMVOC for Augsburg are classified, one can obtain a diagram as shown in Figure 4.16.

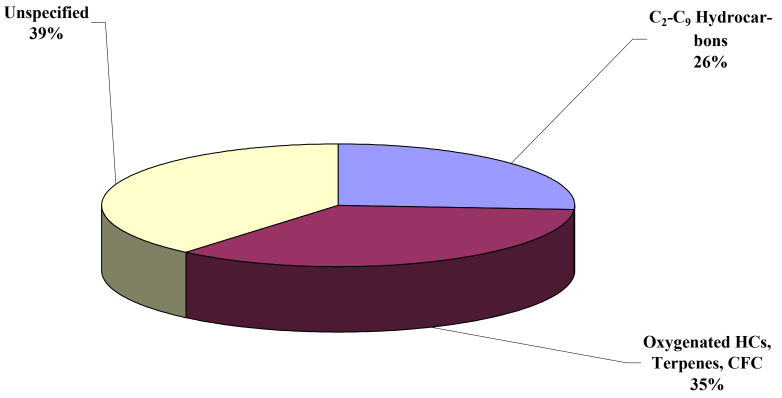


Figure 4.16 Classification of the NMVOC according to IER for the city of Augsburg.

Since in the present study, the measurement was performed only for the group of C_2-C_9 hydrocarbons, *i.e.* only for 26% as shown in Figure 4.16, the statements coming out from this study should be limited to this number. However, one should also remember that the percental contribution of 39% for unspecified hydrocarbons (containing solvent naptha (3%), high boiling solvents (2%), special and test petrol (19%) and other unspecified hydrocarbons (15%)) originated only from the calculations. Among 35% of the oxygenated hydrocarbons, terpenes and chlorofluorohydrocarbons, only up to formaldehyde were measured.

According to Mannschreck (2000), among this 26% of C_2-C_9 hydrocarbons, the contribution from the road traffic is 48% (calculated in ppbv) and the contribution from solvent is 12% (calculated in ppbv). It is also stated by Mannschreck (2000), although the HP-GC (Hewlett Packard GC, HP 5890) can measure hydrocarbons up to C_{13}, the measured contribution of these higher hydrocarbons was negligible.

Figure 4.17 shows a comparison of the emission ratios relative to benzene obtained by the present study with the estimated emission ratios for different compounds relative to total benzene for different source sectors of Augsburg prepared by IER.

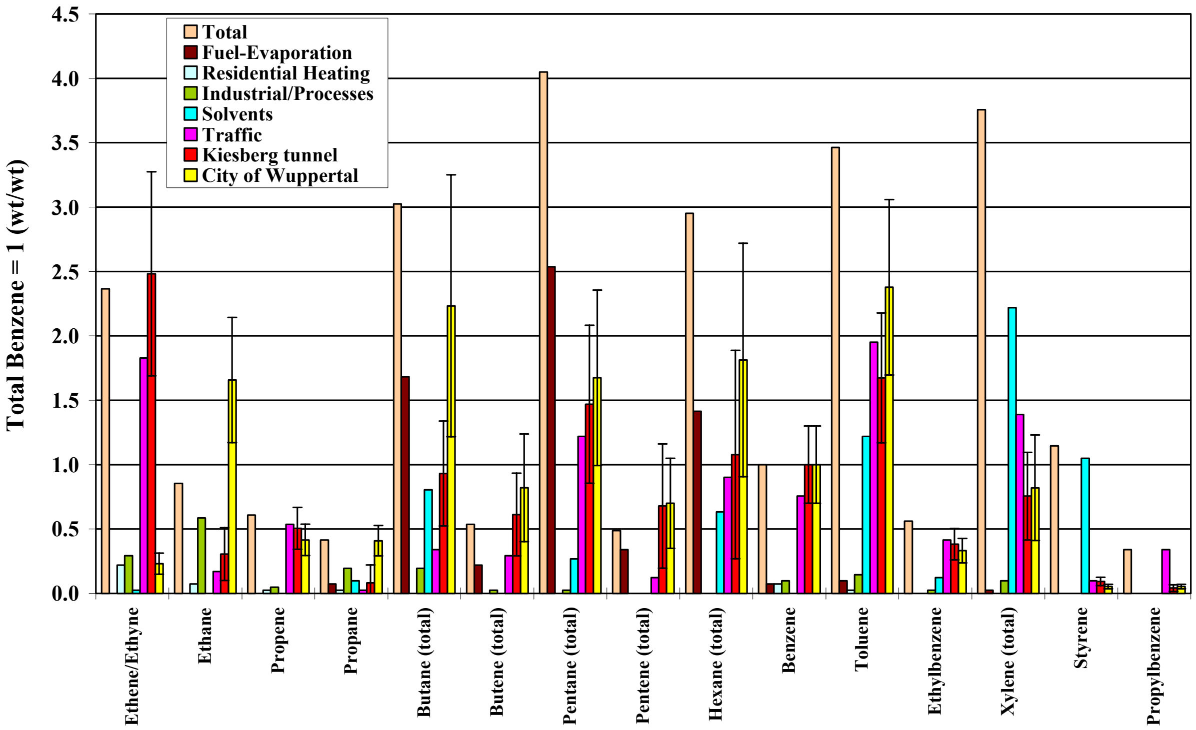


Figure 4.17: Differentiation of emission of C_2-C_9 Hydrocarbons from different sources for the city of Augsburg and comparison with the measured values with the city of Wuppertal relative to total benzene (wt/wt).

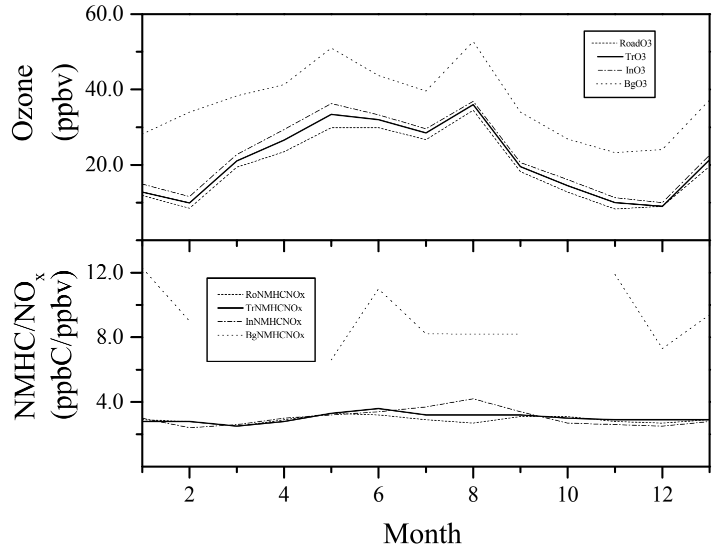
According to Figure 4.17, one can understand that if the contribution estimated by IER was correct, then one should get higher emission ratios than obtained for the city of Wuppertal of the present study. For example, one should get emission ratio for toluene 3.27 instead of 2.38 which was obtained in this study.

In this present study, the total emission of the city of Wuppertal was measured. But it can be seen from Figure 4.17 that the calculated ratios of IER for different hydrocarbons are higher than those found for the city of Wuppertal. Another observation is that the calculated emission ratios for the traffic sector is in agreement with this study for most of the cases. This is happened because the calculation for this source sector was done by using the literature values, which were derived from measurements.

It can also be noted that the calculation of IER was actually done for Augsburg, which should be a typical German city. It may be assumed that the similar type of estimation of emission for Wuppertal regarding solvents would give a similar contribution. Therefore, it can be concluded that the result calculated by IER is an overestimation of the emission from solvent use.

4.2.7.2 Baden-Württemberg

Using the average values of NMHCs and NO_x published in the reports of UMEG ('Gesellschaft für Umweltmessungen und Umwelterhebungen') for the year 1998, the ratios of NMHC/NO_x in ppbC/ppbv for different situations were calculated for different categories, namely roadside, traffic influenced, residential/industrial region and background air as shown in Figure 4.18 from January to December. Similarly, the monthly variations of ozone (UMEG 1998) are also shown in Figure 4.18 for comparison.



The number 13 in the x-axis indicates the yearly average value, Ro: Roadside, Tr: Traffic-influenced, In: Industrial/residential area, Bg: Background.

Figure 4.18: Yearly variation of average ozone concentration (ppbv) and NMHC/NO$_X$ ratio (ppbC/ppbv) in Baden-Württemberg (UMEG, 1998).

According to Figure 4.18, it can be seen that the average values of NMHC/NO$_X$ had almost the same range (2-4) for the different city parts of Baden-Württemberg. These values are in the same range found in Wuppertal during weekdays and the weekend (2-5).

The background ratios of NMHC/NO$_X$ (7-12) of Baden-Württemberg are comparable with that of the measured background ratio (12) found in Menz.

The higher average ozone concentration during July and August of 1998 (40-53 ppbv) of the background area of Baden-Württemberg is also comparable with the measured ozone concentration (39 ± 9 ppbv) in Menz in July-August of 1998 by Kurtenbach *et al.* (1999). Overall the NMHC/NO$_X$ ratios remained more or less constant within a limited range during the year (Figure 4.18). However, a decrease of this ratio in February and an increase in August in the industrial/residential areas led to a decrease and an increase of ozone, respectively, in the same areas. For the background air of Baden-Württemberg, not for all months of 1998, NMHCs were measured. Thus, the monthly variations of the ratios of NMHC/NO$_X$ for background air (forest) were incomplete.

Figure 4.19 shows the calculated distribution of NMVOC in Baden-Württemberg for 1998, which was prepared by IER using the emission model developed by them (Wickert *et al.*, 1999).

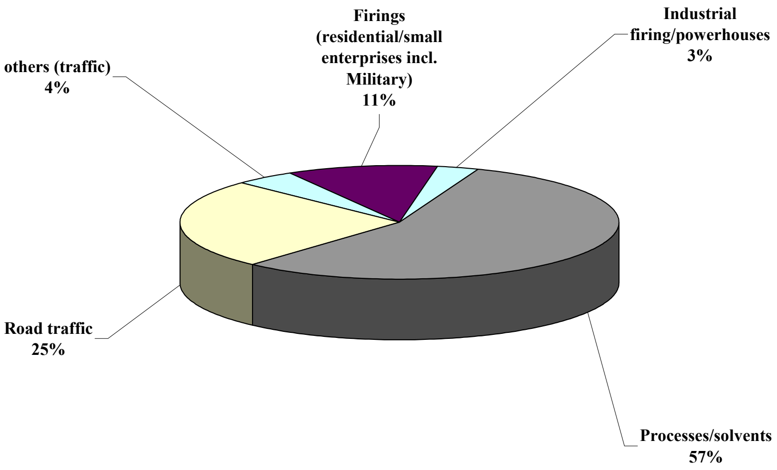
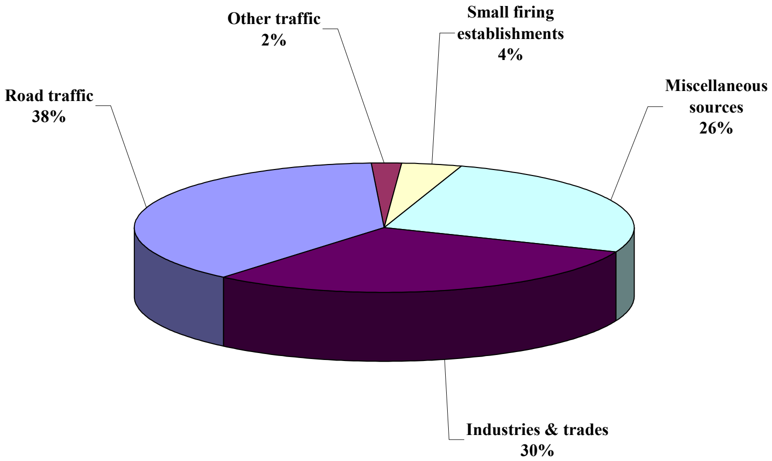


Figure 4.19: Percental distribution of NMVOC emission of 1998 in Baden-Württemberg, calculated by IER.

Although, according to Figure 4.19, it is shown that the contribution from solvents is more than 50% in Baden-Württemberg for 1998, Wickert *et al.* (1999) also pointed out that the knowledge about the sources of solvents is still incomplete. Therefore, the question arises about the reliability of the estimation from the solvent sector. This emission report consisted of the whole of Baden-Württemberg and 13% area of this region is used for traffic, 48% for agricultural use and 38% for forests (Statistisches Landesamt Baden-Württemberg, 2001). It can also be seen in Figure 4.19 that the contribution of NMVOC from the road traffic is 25%. On the other hand, there is another report published by 'Ministerium für Umwelt und Verkehr', Baden-Württemberg (2000), where emission of NMVOC of Baden-Württemberg was calculated by UMEG. According to this report, 40% of the anthropogenic NMVOC emissions in Baden-Württemberg in the year 1998 comes from traffic and 30% from industry and trade. Figure 4.20 shows the percental distribution of NMVOC emission of Baden-Württemberg in the year of 1998, which was calculated by UMEG.



Comments: 1. Industries: the explanation-obligatory establishments according to 11th BimSchV, 2. Trades: the non-explanation-obligatory establishments according to 11. BimSchV. 3. Miscellaneous sources indicated the anthropogenically influenced emittants, which correlate directly with the population and the sources which can not be directly classified to any other groups, *e.g.* loss of natural gas during distribution and leakage, product use, combustion machines used in sport, military, agriculture etc.

Figure 4.20: Percental distribution of NMVOC emission of 1998 in Baden-Württemberg, calculated by UMEG.

A report on emissions of NMVOC for the year 1998 from a part of Baden-Württemberg, namely Friedrichshafen/Ravensburg was also published by 'Ministerium für Umwelt und Verkehr', Baden-Württemberg (2000). According to this report, about 17% of the investigated area is used for traffic and buildings and 23% for forests and 57% for agricultural use. It was also reported that 69% of the total organic gases and vapours (VOC) was originated from road traffic as shown in Figure 4.21.

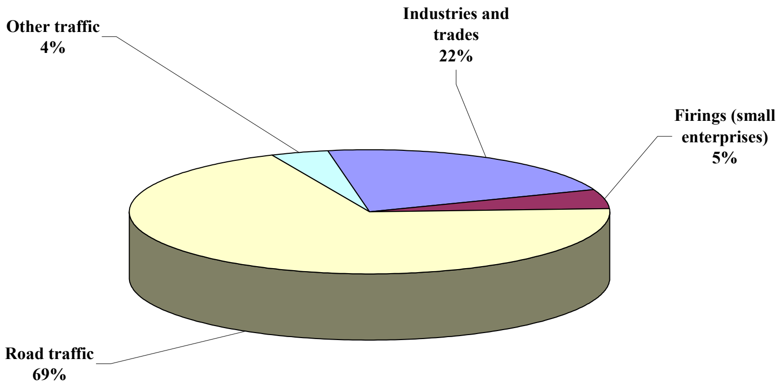


Figure 4.21: Percental distribution of organic gases and vapours (VOC) found in Friedrichshafen/Ravensburg in 1998 (Ministerium für Umwelt und Verkehr, Baden-Württemberg 2000).

It can be noted that the land area of Friedrichshafen/Ravensburg is only about 1% in comparison with the area of Baden-Württemberg. The annual driving performance pro vehicle for Fiedrichshafen/Ravensburg is10340 km and for Baden-Württemberg 12440 km. The fuel consumption by road traffic and the emissions from industries and small firing establishments for both of the regions are also comparable when their land area are considered. Therefore, the contribution from the road traffic should be also similar for both the cases if unspecified emissions are ignored.

It can be seen from Figure 4.19-Figure 4.21 that the estimated emission of NMVOC from the processes/solvents sector by IER is a factor of 2 higher than that estimated by UMEG in Baden-Württemberg. Similarly, it is a factor of 3 higher than the percental estimation of VOC from the sector of industry and trades in Friedrichshafen/Ravensburg.

As deductions from the above mentioned literature and comparison studies, one finds the following facts:

There is an over-estimation of emission of solvents prepared by IER.

The calculated emission ratio of NMHC/NO_x (ppbC/ppbv) from the present study for the city of Wuppertal has the same order of magnitude as found in Baden-Württemberg in the year of 1998.

As reported for the Friedrichshafen and Ravensburg area of Baden-Württemberg in 1998 ('Ministerium für Umwelt und Verkehr', Baden-Württemberg, 2000) and for the city of Augsburg (Mannschreck, 2000), the influence of road traffic can be the largest in the composition of the city air in Germany.

4.2.8 Conclusion

Among aromatic compounds, toluene and among alkanes, ethane have the largest contribution and among alkenes/alkynes, 1-/*iso*-butene showed the largest emission ratios in the city air of Wuppertal.

In general, emission ratios of NMHCs relative to benzene are similar within error limits both weekdays and the weekend except cyclohexane/2,3-dimethylpentane, 3-methylhexane and *n*-heptane, which had higher emission ratios relative to benzene during the weekdays than those during the weekend, indicating small contribution from other source sectors during weekdays in the city air of Wuppertal.

The somewhat higher NMHC/NO_x ratio found in the city of Wuppertal than that of the Kiesberg tunnel can be explained by considering the urban stop+go driving situations.

It was verified that the toluene to benzene ratio can be used as a marker for the road traffic emission by comparing literature studies for urban areas. The contribution of aromatic compounds was also found, on an average, to be about one-third of the total nonmethane hydrocarbons for the European urban areas.

It was also confirmed that the limit values for benzene and NO_2 prescribed by Federal immission control act of Germany (1998) were not exceeded in the city of Wuppertal.

The estimation of the contribution of solvent use in total anthropogenic emission prepared by IER for UBA seems to be an overestimation.

4.3 Impact of road traffic on the city air of Wuppertal

One of the objectives of this work was to find out the sources and their impact on the city air of Wuppertal. Since Wuppertal is a model city of Germany with about 375 thousands inhabitants (Stadtverwaltung Wuppertal, 2001) and a moderate number of small industries, there are existing different sources which might influence the hydrocarbon-mix of the city air of Wuppertal, for example, road traffic, solvents, biogenic emission etc. Before drawing any conclusion, the following point will be first discussed.

4.3.1 Comparison of the NMHC-profiles

In sections 4.1.1 and 4.2.3, the NMHC-profile of the Kiesberg tunnel air and of the city air of Wuppertal relative to benzene in ppbC/ppbC were discussed. Figure 4.22 shows a comparison between the NMHC-profile relative to benzene in ppbC/ppbC obtained in the Kiesberg tunnel and in the city of Wuppertal using the average values of the different campaigns in 1997-1998.

It can be seen from Figure 4.22 that for most of the components measured in the Kiesberg tunnel air and in the city air of Wuppertal, the NMHC-profiles are almost identical within the error limits except for ethene/ethyne, ethane, propane, 1,3-butadiene/*n*-butane, cyclohexane/2,3-dimethylpentane, 3-methylhexane, methylcyclohexane, *n*-heptane, 2-/3-methylheptane and styrene.

In the present study, the emission profile was calculated by measuring the air parcel composition coming directly from the city centre. It was already discussed in section 4.2.1 that during the estimated transport time of 10-40 min, no significant degradation with respect to OH or O_3 (see Table A1 II in the Annex-Tables) could occur. But it should be remembered that in reality, this emission situation is a total emission situation. That means, although it represents principally the road traffic exhaust, but at the same time it includes some contribution from other sources and also from the aged air mass.

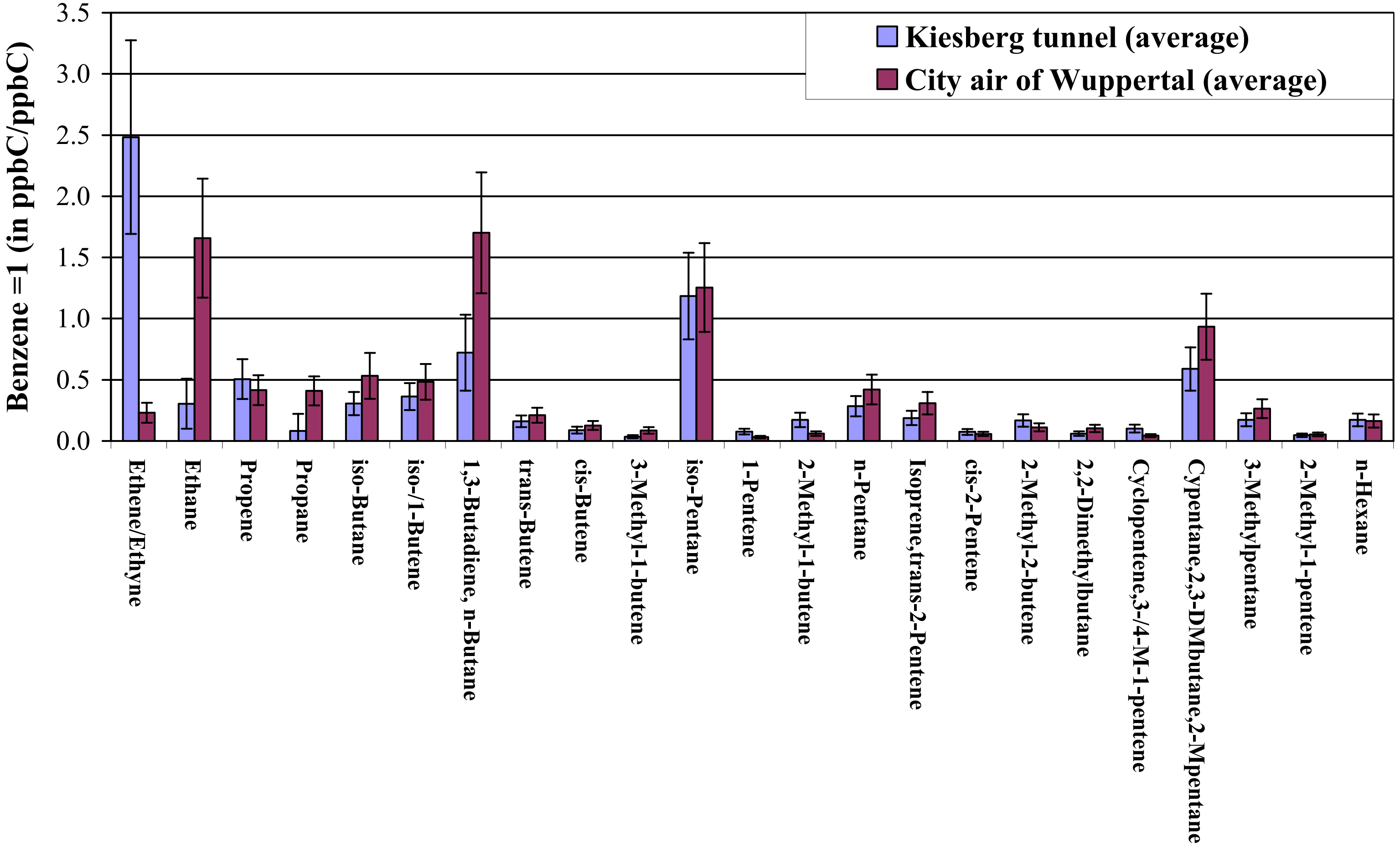
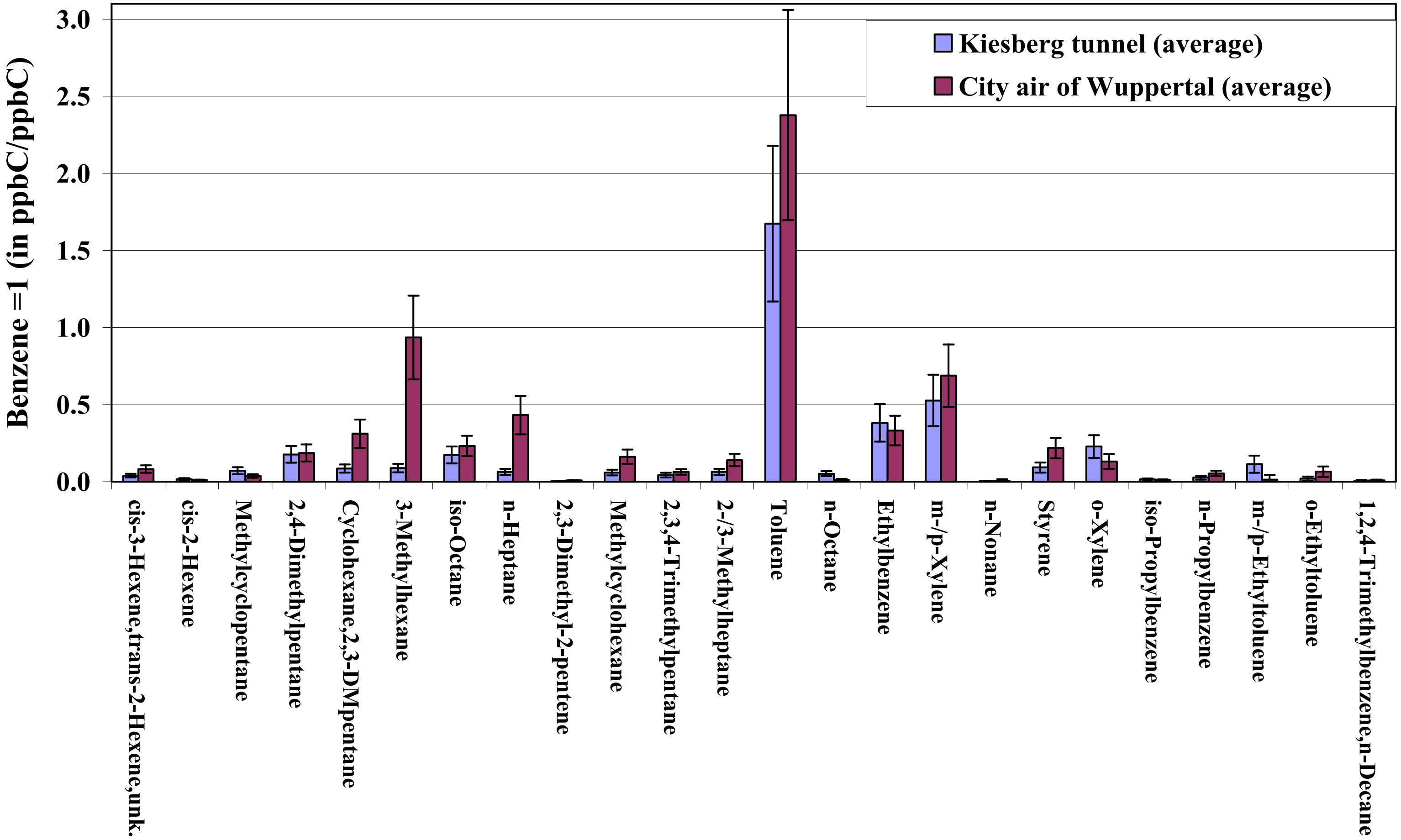

Benzene =1 (in ppbC/ppbC)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Kiesberg tunnel (average)
City air of Wuppertal (average)
Ethene/Ethyne
Ethane
Propene
Propane
iso-Butane
iso-/1-Butene
1,3-Butadiene, n-Butane
trans-Butene
cis-Butene
3-Methyl-1-butene
iso-Pentane
1-Pentene
2-Methyl-1-butene
n-Pentane
Isoprene,trans-2-Pentene
cis-2-Pentene
2-Methyl-2-butene
2,2-Dimethylbutane
Cyclopentene,3-/4-M-1-pentene
Cypentane,2,3-DMbutane,2-Mpentane
3-Methylpentane
2-Methyl-1-pentene
n-Hexane

Figure 4.22 (a)

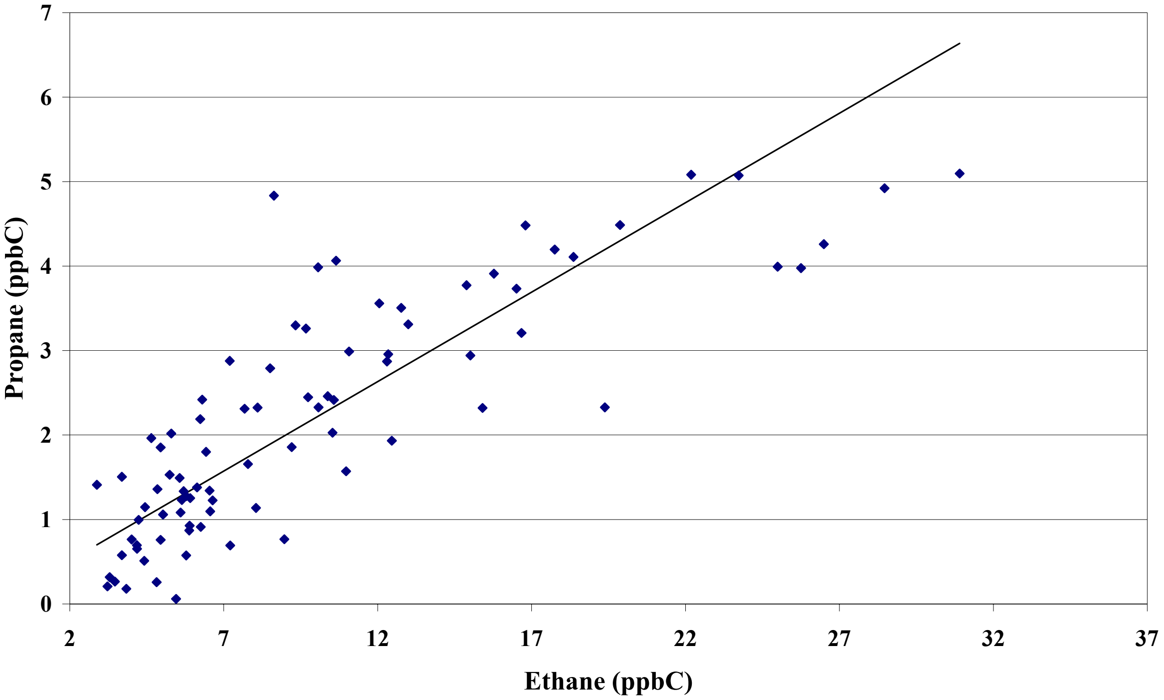


(b)

Figure 4.22(a-b): Comparison of the NMHC-profiles relative to benzene in ppbC/ppbC for the average values of the Kiesberg tunnel air and of the city of Wuppertal.

It can be seen from Figure 4.22 that the emission ratio between ethene/ethyne and benzene (ppbC/ppbC) found in the tunnel is 11 times higher than that of the city. This lower ratio of the city air for ethene/ethyne cannot be explained.

Since there exists a considerable amount of background air concentration of >1 ppbv as found also in the rural area, Menz (see Table 3.20), the higher normalized value of ethane for the city air of Wuppertal in comparison with the road traffic tunnel may be attributed to this background concentration. Schmitz *et al.* (1997) also found a higher emission ratio (2.2) of ethane relative to benzene in Wuppertal in 1995. Another possible reason for the higher emission ratios of ethane and propane may be attributed to the leakage of natural gas, which was also found in Berlin (Thijsse *et al.*, 1997). There exists a good correlation between ethane and propane for 30.08.98 and 31.08.98 (as used also for preparing the NMHC-profile of Figure 4.22) as shown in Figure 4.23.



Emission ratio of propane (ppbC)/ethane (ppbC) = 0.21 ± 0.01, corr. coeff. 0.83.

Figure 4.23: Correlation plot between propane and ethane in ppbC measured during 30.08.98 and 31.08.98 in the city air of Wuppertal.

According to the National Toxic Inventory (US EPA, 2001a), mobile sources account for approximately 60% of the total 1,3-butadiene emissions. Other sources of it include industrial processes. It is also known that propane and butane are used for residential purposes. Therefore, it can only be postulated that the 5 times higher value of propane and 2 times higher value for 1,3-butadiene/*n*-butane in the city air may be due to the contribution of these sources beside the road traffic exhaust. Schmitz *et al.* (1997) also found about 2 times higher value for propane and 1,3-butadiene/*n*-butane in the city air of Wuppertal.

Although the k_{OH} values for cyclohexane, 3-methylhexane and *n*-heptane are higher in comparison to other NMHCs ($\sim 6\text{-}7*10^{-12}$ cm^3 s^{-1}), the higher normalized values found for the city air can only be understood by considering other sources. It is also noteworthy that during the weekend, these values for cyclophexane/2,3-dimethylpentane, 3-methylhexane and *n*-

heptane are, respectively, about 2 times, 10 times and 7 times smaller than those values found in the city air of Wuppertal during the weekdays. It is also known from the literature studies that in addition to cyclohexane, methylhexane, methylcyclohexane and *n*-heptane, 2-methylheptane and styrene are also used as solvents (Wickert *et al.*, 1999; Barton, 1991; Tennant, Ullmann, Theloke *et al.*, 2000). Roughly, if it is assumed that the excess portion of the emission ratio profile of these compounds for the city air relative to the tunnel air is exclusively from the solvent sector, then the contribution from the solvent sector will be 10.2 ± 1.9% relative to the total measured NMHC-mix. If the excess emission ratios of propane and 1,3-butadiene/n-butane are also taken from other sources in addition of road traffic exhaust, it will comprise of altogether 17.8 ± 4.0%.

4.3.2 Deduction

The above mentioned reasons clearly show that the road traffic emissions in Wuppertal have still the largest impact on the air composition in the city. A small contribution from solvent use to the monitored NMHC (C_2-C_9) distribution has been postulated, which is in agreement with Thijsse *et al.*, (1999) but in contrast to the German emission inventory (Umweltbundesamt, 1999). During the EVA experiment in Augsburg (Mannschreck, 2000), it was also clearly observed that the city air of Augsburg is mainly influenced by road traffic exhaust. The same conclusion was also drawn by Thijsse *et al.* (1997) for the city of Berlin, where it was stated that about 90-95% of the total NMHCs came from traffic exhaust and evaporative losses of fuel. Therefore, it can be concluded that the road traffic emission still determine the air composition of German cities.

4.3.3 Conclusion

Road traffic emission has the largest impact on the air composition of the city of Wuppertal in the total measured NMHC-mix (C_2-C_9).

The indirect estimation of the contribution of emissions from the solvent sector was 10.2±1.9% relative to the total measured NMHC-mix (C_2-C_9) in the city air of Wuppertal.

Leakage of natural gas may also have a small contribution in the total measured NMHC-mix (C_2-C_9) in the city air of Wuppertal.

By comparing other literature studies, it can be generalized that road traffic is still the dominant source sector for the total anthropogenic emission of NMHCs.

4.4 Calculations of percental reactivities

4.4.1 Tunnel studies

It is well-known that most NMHCs mainly react with OH radicals during daytime. Therefore, for having the first simplified impression about the ozone formation potential of these directly emitted hydrocarbons from road traffic, the percental OH-reactivities using the respective k_{OH} values for the hydrocarbon-mix found in the Kiesberg tunnel, were determined. Since no photochemistry occurs in the tunnel, these values will give an idea about the upper limit of the OH-reactivities from this source sector. These calculations may also allow to find out those reactive hydrocarbons whose contributions are largest with respect to the ozone formation potential in comparison with the remaining hydrocarbons.

Since these simplified calculations only deliver, first of all, ideas about the rate of degradation of NMHCs regarding the attack by OH radical and secondly, they do not include the other reactions of these components and their reaction-intermediates/products in the atmosphere leading to ozone formation, calculations using maximum incremental reactivity (MIR) and photochemical ozone creation potential (POCP) indices were also carried out for having an approximate more general idea about the ozone formation potentials of the measured NMHCs. Since the MIR (Carter, 1994) and POCP (Derwent *et al.*, 1998) indices were taken from the literature and the conditions of the calculations in the literature were only an approximation of this study, the calculated percental reactivities of this work should be taken as rough values, which were carried out only for estimation by considering further aspects of the reactions of NMHCs leading to ozone formation, for comparing the results with those of the OH-reactivities. For producing more exact values, one should engage oneself for modelling, which was not undertaken in the framework of this study.

In the following, the results of these calculations are presented.

4.4.1.1 OH reactivities

The values of the average mixing ratios of nonmethane hydrocarbons relative to benzene in ppbC/ppbC were recalculated as percentage composition relative to total detected nonmethane hydrocarbon-mix. Here, 12% contribution for the unknown hydrocarbons were also considered as discussed in section 3.1.1. These values were then multiplied with the k_{OH} values of the respective nonmethane hydrocarbons and presented in Table 4.20. Since the k_{OH} values of some coeluted components differ tremendously with each other, the percental contributions of these components were separated according to the literature data. For example, the value of the coeluted peak ethene/ethyne was separated by assuming 70±6% contribution from ethene and 30±6% contribution from ethyne as reported by tunnel studies (Zielinska *et al.*, 1996, Staehelin *et al.*, 1998) and a dynamometric study (Schmitz *et al.*, 1999). Similarly, the value of the coeluted peak 1,2,4-trimethylbenzene/*n*-decane was separated assuming 98±2% contribution from 1,2,4-trimethylbenzene and 2±2% contribution from *n*-decane as reported by a tunnel study (Zielinska et al., 1996) and a dynamometric study (Schmitz *et al.*, 1999).

Table 4.20: List of compounds containing the simple description of reactivity (% of $NMHC_i * k_i^{OH}$) found for the Kiesberg tunnel air, Wuppertal.

Compounds	% of OH-reactivity	Error of propagation
Ethene[#]	5.9	2.4
Ethyne[#]	0.2	0.1
Ethane	0.0	0.0
Propene	5.3	2.1
Propane	0.0	0.1
iso-Butane	0.3	0.1
iso-/1-Butene	4.6	1.7
1,3-Butadiene	7.6	3.0
n-Butane	0.6	0.2
trans-Butene	4.3	1.6
cis-Butene	2.0	0.8
3-Methyl-1-butene, unknown	0.4	0.2
iso-Pentane	1.8	0.7
1-Pentene	1.0	0.4
2-Methyl-1-butene	4.2	1.7
n-Pentane	0.5	0.2
Isoprene, *trans*-2-pentene	6.4	2.7
cis-2-Pentene	1.7	0.7
2-Methyl-2-butene	5.9	2.2
2,2-Dimethylbutane	0.1	0.0
Cyclopentene, 3-/4-methyl-1-pentene	2.1	1.0
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	1.3	0.5
3-Methylpentane	0.4	0.2
2-Methyl-1-pentene	0.9	0.4
n-Hexane	0.4	0.1
cis-3-Hexene, *trans*-2-hexene, unknown	1.0	0.4
cis-2-Hexene	0.4	0.2
Methylcyclopentane	0.1	0.1
2,4-Dimethylpentane	0.4	0.1
Benzene	0.5	0.2
2-Methylhexane	0.2	0.1
Cyclohexane, 2,3-dimethylpentane	0.2	0.1
3-Methylhexane	0.3	0.1
iso-Octane	0.2	0.1
n-Heptane	0.2	0.1
2,3-Dimethyl-2-pentene	0.1	0.1
Methylcyclohexane	0.2	0.1
2,3,4-Trimethylpentane	0.1	0.1
2-/3-Methylheptane	0.2	0.1
Toluene	4.0	1.5
Ethylbenzene	1.1	0.4
m-/*p*-Xylene	4.0	1.5
n-Nonane	0.0	0.0
Styrene	4.0	1.7
o-Xylene	1.3	0.5
n-Octane	0.2	0.1
iso-Propylbenzene	0.0	0.0
n-Propylbenzene	0.1	0.0
m-/*p*-Ethyltoluene	0.7	0.4
Mesitylene	3.4	1.6
o-Ethyltoluene	0.1	0.1
1,2,4-Trimethylbenzene[##]	0.0	0.1

Table 4.20 (continued):

Compounds	% of OH-reactivity	Error of propagation
n-Decane##	0.0	0.0
Unknown	19.1	22.3
Total	100.0	32.1

* The k_{OH} value for the coeluted compounds were taken as the average value of the individual compounds. k_i^{OH}: rate constant for the reaction of i component with OH. #: The value of the coeluted peak ethene/ethyne was separated by assuming 70±6% contribution from ethene and 30±6% contribution from ethyne as reported by tunnel studies (Zielinska et al. 1996, Staehelin et al., 1998) and a dynamometric study (Schmitz *et al.*, 1999). ##: The value of the coeluted peak 1,2,4-trimethylbenzene/n-decane was separated assuming 98±2% contribution from 1,2,4-trimethylbenzene and 2±2% contribution from n-decane as reported by a tunnel study (Zielinska et al., 1996) and a dynamometric study (Schmitz *et al.*, 1999).

From Table 4.20 one can observe that the percental contribution regarding OH-reactivity for 1,3-butadiene is the highest, then isoprene/*trans*-2-pentene (coeluted), 2-methyl-2-butene and other alkenes. Among aromatic compounds, toluene and among alkanes, *iso*-pentane have the highest percental contribution regarding the OH-reactivity.

4.4.1.2 Specific reactivity using MIR values

There has been extensive work on quantitatively assigning reactivities to individual organic compounds in auto exhaust based on their ozone potential (Croes *et al.*, 1992; Carter, 1994; Ho *et al.*, 1998; Calvert *et al.*, 1993). California Air Resources Board (CARB) adopted regulations, which limits mass emission rates from vehicles based on the reactivity of the exhaust for the generation of photochemical smog.

The reactivity (R) of the exhaust is determined by the product of the total mass (M) of the organic emissions and the specific reactivity (SR) of the exhaust:

$$R = M * SR \qquad \text{Eq. 4.5}$$

The SR is defined in terms of the grams of ozone formed by photochemical reaction in the atmosphere per gram of organic species emitted by a vehicle. The reactivity of each hydrocarbon species is defined in terms of its maximum incremental reactivity (MIR) factor (Carter *et al.*, 1989; Tsuchida *et al.*, 1993). The peak of incremental reactivity (IR) of a VOC is known as its maximum incremental reactivity (MIR). IR is defined as the number of molecules of ozone formed per VOC carbon atom added to an initial „surrogate“ atmospheric reaction mixture of VOC and NO_x (Finlayson-Pitts and Pitts, 2000). The IR values peak at a ratio of VOC/NO_x of *ca.* 6 and drop off significantly at higher values. Incomplete mechanistic understanding may lead to large uncertainties to the MIR values, in particular with respect to unknown interference with NO_x, the oxidation mechanism and unknown photolysis processes of the degradation products.

The specific reactivity can be calculated using the following equation (Duffy *et al.*, 1996):

$$SR = \Sigma (M_i * MIR_i) / \Sigma M_i \qquad \text{Eq. 4.6}$$

where, M_i is the mass of individual NMHC species.

Since in the tunnel, the absolute concentration of a substance will vary with the number and art of vehicles passing through the tunnel, therefore for getting more sensible results the emission ratios of different NMHCs relative to benzene in ppbC/ppbC were used for calculations instead of the absolute concentrations. These values were recalculated in percentage by considering the 12% contribution for the unknown substances. These percentage values were used for obtaining the specific reactivity and finally the percentage of total specific reactivity (Duffy *et al.*, 1996). Table A3 VII (in the Annex-Tables) shows the result.

According to Table A3 VII (in the Annex-Tables), ethene/ethyne has the highest contribution to the specific reactivity in comparison with the total specific reactivity, then propene and the third position is for toluene and the second one among aromatics is for *m*-/*p*-xylene. Among the alkanes, *iso*-pentane has the highest percental contribution to the total specific reactivity, which was also found in OH-reactivity calculation (see Table 4.20) and by Duffy *et al.* (1996).

4.4.1.3 Photochemical Ozone Creation Potential (POCP)

The POCP values are the results of model calculations applying a trajectory model and using the master chemical mechanism, which includes 2400 chemical species and over 7100 reactions (Derwent *et al.*, 1996, 1998) and modelled air masses moving over Europe with respect to ozone formation. The results, however, depend on the reliability of the calculations. The derived POCPs for the alkanes fall in the range of 30-54, the alkenes in the range of 62-115 and the aromatic hydrocarbons in the range of 50-138. 1,3,5-Trimethylbenzene shows the highest POCP value among all the 120 organic compounds studied by Derwent *et al.* (1998). According to Andersson-Sköld *et al.* (2000), POCP values for VOCs should be presented as ranges instead of single values. For many VOCs, the ranges overlap, but if their ranking stays intact through the individual environments, the species can still be considered fully separated on the ranking scale.

Table A3 VIII (in the Annex-Tables) shows the list containing the POCP values for the compounds found in the Kiesberg tunnel. These values were taken from the literature of Derwent *et al.* (1996, 1998) and Heslinga *et al.* (1992). Calculations of the percental POCP values for these NMHCs were performed for a comparison with other methods used in section 4.4.1.1 and section 4.4.1.2 and presented in Table A3 VIII (in the Annex-Tables). Since some of the nonmethane hydrocarbons were not listed by Derwent *et al.* (1998), the surrogate compounds were written by comparing the compounds closest in chemical reactivity.

It can be seen from Table A3 VIII (in the Annex-Tables) that like the MIR reactivity (Table A3 VII (in the Annex-Tables)), ethene/ethyne shows the highest contribution among all the estimated POCPs. Among aromatic compounds toluene and among alkanes, *iso*-pentane show the highest percental contribution of the estimated POCPs.

4.4.2 Percental reactivity calculations for the city air of Wuppertal

As discussed in section 4.4.1, for finding out those NMHCs which contribute largest to the ozone formation potential, similar types of reactivity calculations were carried out for the city of Wuppertal. Instead of using the emission ratios of the individual NMHC relative to benzene in ppbC/ppbC, average concentrations of individual NMHC during the campaign were used for getting an idea on the real situation regarding ozone formation potential in the city air of Wuppertal. To get an representative average value for the measured compounds, firstly, the concentrations of each component were converted to percentage of total NMHCs (mass percent), secondly, the weight percentages were averaged over all samples; thirdly, the average mass percentage for each species was multiplied by the average NMHC mixing ratio

(Calvert *et al.*, 2001). For some sampling periods, not all the NMHCs could be integrated and sometime, there were some highly deviated values, which were rejected during the final calculation. Still, since the calculation using this average method considered all the days irrespective of meteorology, it may reflect the real situation of the city of Wuppertal.

The percental reactivity of the individual NMHC relative to the total NMHC-mix were determined for the city air of Wuppertal in the following way:

4.4.2.1 OH reactivity

Table 4.21 shows the calculated percental reactivity using the average concentrations of the measured NMHCs and k_{OH} values of the respective components. The relative NMHCs values were recalculated as percental composition from the total NMHCs by considering 12% unknown components. As discussed in section 4.4.1.1, the percental contributions of some coeluted components with highly different k_{OH} values were separated according to the literature data. For example, the value of the coeluted peak ethene/ethyne was separated by assuming 40±15% contribution from ethene and 60±15% contribution from ethyne as reported by other studies for German cities (Schmitz *et al.*, 1997; Mannschreck, 2000). The values of the coeluted peak 1,3-butadiene/*n*-butane were separated by assuming 10±7% contribution from 1,3-butadiene and 90±7% contribution from *n*-butane as reported by other studies for German cities (Schmitz *et al.*, 1997; Mannschreck, 2000). The values of the coeluted peak benzene/2-methylhexane were separated by assuming 90±3% contribution from benzene and 10±3% contribution from 2-methylhexane as reported by other studies for German cities (Schmitz *et al.*, 1997; Mannschreck, 2000; Winkler *et al.*; 2001). The values of the coeluted peak 1,2,4-trimethylbenzene/*n*-decane were separated by assuming 67±11% contribution from 1,2,4-trimethylbenzene and 33±11% contribution from *n*-decane as reported by Mannschreck (2000) for a German city.

Table 4.21: Percental contribution of OH reactivities of the measured NMHCs using average method.

Components	% OH contribution using average concentration of NMHC	Error of propagation
Ethene$^{\Diamond}$	2.2	1.3
Ethyne$^{\Diamond}$	0.3	0.2
Ethane	0.2	0.1
Propene	4.2	1.7
Propane	0.1	0.1
iso-Butane	0.3	0.1
iso-/1-Butene	8.5	3.6
1,3-Butadiene°	3.6	2.9
n-Butane°	1.2	0.5
trans-Butene	2.3	1.0
cis-Butene	1.7	0.7
3-Methyl-1-butene	2.1	0.9
iso-Pentane	1.6	0.7
1-Pentene	1.6	0.7
2-Methyl-1-butene	6.3	2.7
n-Pentane	0.7	0.3
Isoprene, *trans*-2-pentene *	7.7	3.6

Table 4.21 (continued):

Components	% OH contribution using average concentration of NMHC	Error of propagation
cis-2-pentene	1.2	0.5
2-Methyl-2-butene	7.5	3.1
2,2-Dimethylbutane	0.1	0.0
Cyclopentene, 3-/4-methyl-1-pentene*	0.6	0.3
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane *	1.6	0.7
3-Methylpentane	0.4	0.2
2-Methyl-1-pentene	0.7	0.3
n-Hexane	0.4	0.2
cis-3-Hexene, *trans*-2-Hexene	0.9	0.4
cis-2-Hexene	0.4	0.2
Methylcyclopentane, 2,4-dimethylpentane	0.4	0.2
Benzene[#]	0.4	0.2
2-Methylhexane[#]	0.2	0.1
Cyclohexane, 2,3-dimethylpentane	0.5	0.2
3-Methylhexane	0.5	0.2
iso-Octane	0.2	0.1
n-Heptane	0.3	0.1
2,3-Dimethyl-2-pentene	0.7	0.3
Methylcyclohexane	0.5	0.2
2,3,4-Trimethylpentane	0.1	0.0
2-/3-Methylheptane	0.2	0.1
Toluene	3.5	1.5
Ethylbenzene	0.6	0.2
m-/*p*-Xylene	2.9	1.2
n-Nonane	0.1	0.0
Styrene	7.8	3.3
o-Xylene	1.0	0.4
n-Octane	0.1	0.0
iso-Propylbenzene	0.1	0.0
n-Propylbenzene	0.0	0.0
m-/*p*-Ethyltoluene	0.6	0.3
Mesitylene	0.6	0.3
o-Ethyltoluene	0.2	0.1
1,2,4-Trimethylbenzene**	1.0	0.7
n-Decane**	0.2	0.1
tert-Butylbenzene	0.1	0.1
unknown contribution	18.7	22.6
Total	100.0	33.1

*The k_{OH} values for these components were averaged. ◊: The value of the coeluted peak ethene/ethyne was separated by assuming 40±15% contribution from ethene and 60±15% contribution from ethyne as reported by other studies for German cities (Schmitz *et al*., 1997; Mannschreck, 2000). °: The values of the coeluted peak 1,3-butadiene/*n*-butane were separated by assuming 10±7% contribution from 1,3-butadiene and 90±7% contribution from *n*-butane as reported by other studies for German cities (Schmitz *et al*., 1997; Mannschreck, 2000). #: The values of the coeluted peak benzene/2-methylhexane were separated by assuming 90±3% contribution from benzene and 10±3% contribution from 2-methylhexane as reported by other studies for German cities (Schmitz *et al*., 1997; Mannschreck, 2000; Winkler *et al*.; 2001). ** The values of the coeluted peak 1,2,4-trimethylbenzene/*n*-decane were separated by assuming 67±11% contribution from 1,2,4-trimethylbenzene and 33±11% contribution from *n*-decane as reported by Mannschreck (2000) for a German city.

According to Table 4.21, the first three positions among alkenes are namely, *iso*/1-butene, isoprene/*trans*-2-pentene and 2-methyl-2-butene; among aromatic compounds: namely styrene, toluene and *m*-/*p*-xylene and among alkanes: namely *iso*-pentane, cyclopentane/2,3-dimethylbutane/2-methylpentane and *n*-butane. The total contribution for the different classes are as follows: alkenes: 52.5%, alkanes: 9.9%, aromatic compounds: 18.9% and unknown components: 18.7%. The calculated OH-reactivities were averaged using the average mixing ratio of the total known NMHCs and the determined value of $(1.06\pm0.5)*10^{-11}$ cm^3 s^{-1} was in agreement with $(1.03\pm0.12)*10^{-11}$ cm^3 s^{-1} of Schmitz (1997).

4.4.2.2 MIR and POCP

Using the maximum incremental reactivity (MIR) scale, it was attempted to approximate the potential of NMHC-mix found in the city air of Wuppertal for forming ozone under conditions where the availability of NO_x does not limit ozone formation. Table A3 IX (in the Annex-Tables) shows the percental specific reactivities which were calculated using the equation as discussed in section 4.4.1.2.

According to the calculated result as presented in Table A3 IX (in the Annex-Tables), the total contribution from alkanes was 14.7±2.7%, from alkenes 48.3±9.8% and from aromatic compounds 22.5±5.5%. *iso*-Pentane, ethene and toluene were found as the largest contributors from alkanes, alkenes and aromatic compounds respectively. The comparison with the Los Angeles morning air of October 1995 (Calvert *et al.*, 2001) shows that 50% of the MIR values contained only 7 NMHCs in Los Angeles and 12 NMHCs in Wuppertal. These 7 components for Los Angeles were *iso*-pentane, *m*-/*p*-xylene, ethene, 1,2,4-trimethylbenzene, toluene and propene, whereas for Wuppertal, they were ethene, *iso*-/1-butene, toluene, propene, *m*-/*p*-xylene, isoprene/*trans*-2-pentene, 1,3-butadiene, *iso*-pentane and 2-methyl-2-butene.

In Table A3 IX (in the Annex-Tables), the result of the similar types of calculations using POCP values (Derwent *et al.*, 1998) are also presented. The POCP indices used were taken from Derwent *et al.* (1996, 1998) and Heslinga *et al.* (1992). An estimate of the missing POCP indices was made by comparison with NMHC of similar chemical structures.

According to Table A3 IX (in the Annex-Tables), the largest contributions came from toluene among aromatic compounds, *iso*-pentane among alkanes and ethene among alkenes. Alkenes have the highest total contributors. It can be seen that 14 NMHCs contained more than 50% of the total POCP reactivities using the average concentration. These compounds are toluene, ethene, *iso*-/1-butene, propene, *iso*-pentane, *n*-butane, *m*-/*p*-xylene, cyclopentane/2,3-dimtheylbutane/2-methylpentane and isoprene/*trans*-2-pentene. These compounds comprised about 60-90% of the VOC having over 50% POCP in Nansenstrasze and Frankfurter Allee in Berlin (Thijsse *et al.*, 1997).

From Table 4.21 and Table A3 IX (in the Annex-Tables), it can be seen that due to different index-values for different NMHCs, the percental contribution for individual NMHC is different for MIR, OH and POCP scales, but the tendency of ascending serials is similar. By comparing the results regarding different reactivity scales, it is also clear that the city air of Wuppertal has the largest reactivity with respect to ozone formation from the contribution of alkenes.

4.4.3 Comparison between the tunnel and the city of Wuppertal

The reactivities calculated for the tunnel air and the city air were summarized according to the different classes of NMHCs and are presented in Figure 4.24.

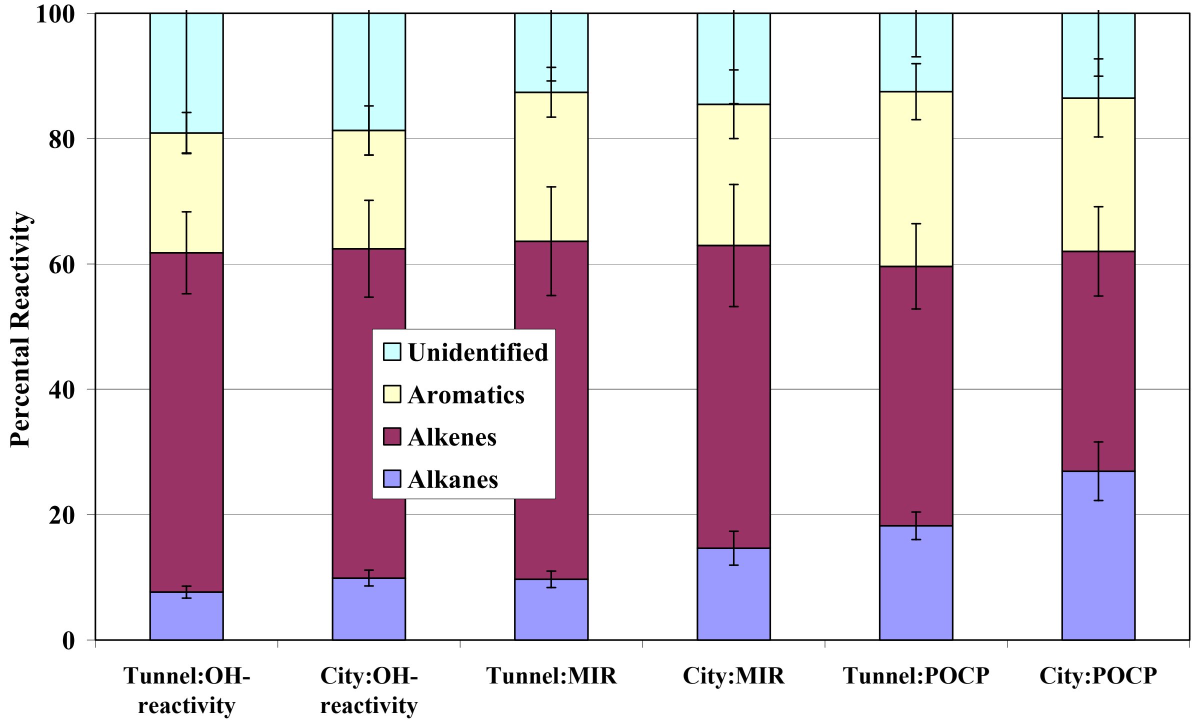


Figure 4.24: An overview of the calculated percental reactivities for the tunnel and the city air of Wuppertal regarding different classes of NMHCs. The unidentified percental composition were calculated by considering 12% unidentified contribution to the total measured NMHC-mix.

According to Figure 4.24, one can observe that there is a very good similarity among the calculated OH-, MIR- and POCP reactivities within the error limits for the NMHC-mix in the Kiesberg tunnel and in the city air of Wuppertal and the alkenes had the largest percental contribution.

By observing the results of the calculation of different reactivities presented in Table 4.20-4.21 and Table A3 VII-IX (in the Annex-Tables), it is noticed that only some few components have major contribution to the ozone formation potential of the total NMHC-mix. For most of the cases, same compounds appeared as the highest contributors in different classes calculated for different reactivity scales. Table A3 X (in the Annex-Tables) presents an overview of the calculated percental reactivities for the tunnel air and the city air of Wuppertal with error limits. Figure 4.25 shows a comparison of different percental reactivities for some selected NMHCs.

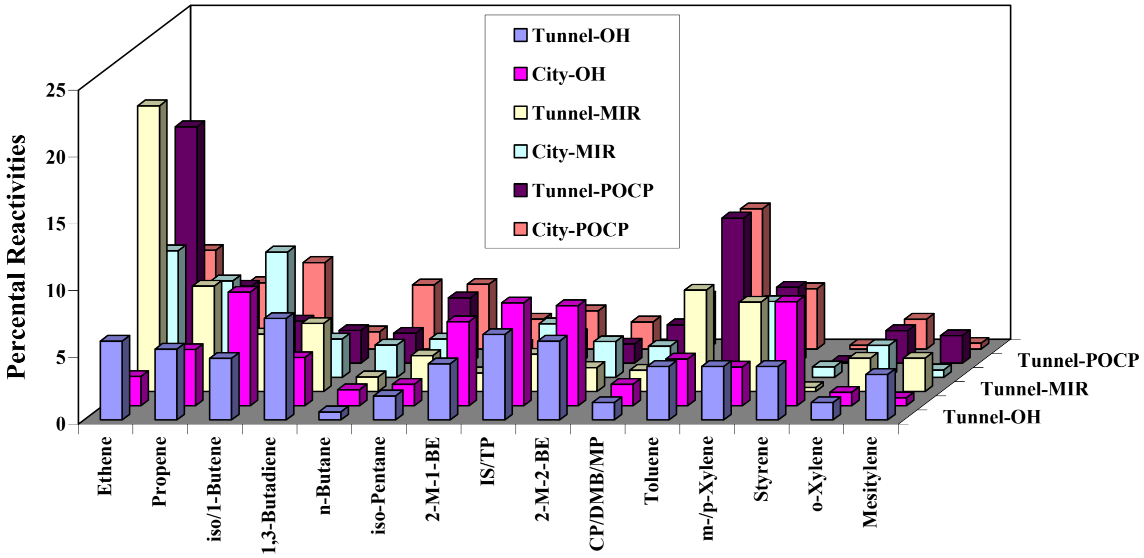


Figure 4.25: Comparison of the different percental reactivities for some selected NMHCs measured in the Kiesberg tunnel and the city air of Wuppertal. IS: Isoprene, TP: *trans*-2-Pentene; 2-M-2-BE: 2-Methyl-2-butene, CP: Cyclopentane, DMB: 2,3-Dimethylbutane, MP: 2-Methylpentane.

According to Figure 4.25, it can been seen that only a few compounds comprise more than 50% percental reactivities, namely *iso*/1-butene, styrene, isoprene/*trans*-2-pentene, propene, toluene, *m*-/*p*-xylene, ethene, 1,3-butadiene and *o*-xylene. Some of them are also comparable with other literature studies (Kern *et al.*, 1998; Calvert *et al.*, 2001). It can also be noticed that styrene shows the highest OH-reactivity in city air among aromatics. It results due to the high emission found in the city air of Wuppertal, justifying the existence of some other sources for this compound other than the road traffic, *e.g.* solvent use (Wickert *et al.*, 1999).

During taking decisions regarding the strategy for the effective reduction of the ozone concentration, one should consider these components containing the high ozone formation potentials.

4.4.4 Conclusion

In general, the calculated reactivities for different components of NMHC for the Kiesberg tunnel and the city of Wuppertal showed similar tendencies and for both cases, alkenes supplied the highest percental contribution.

It can also be concluded that in the city air composition of Wuppertal, there existed only a few compounds, namely styrene, xylenes, ethylbenzene and toluene among aromatic hydrocarbons, *iso*/1-butene, ethene, propene, 1,3-butadiene and isoprene/*trans*-2-pentene among alkenes/alkynes and *iso*-pentane, cyclopentane/2,3-dimethylbutane/2-methylpentane and *n*-butane among alkanes, which have largest contributions to the total ozone formation potential. One should consider these components when making decisions about the strategy for the effective reduction of the ozone concentration.

5 Summary

The main objective of the present study was to investigate the road traffic exhaust and at the same time to determine its impact on the city air of Wuppertal. For these purposes, several measurement-campaigns of nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x) were carried out in a road traffic tunnel (Kiesberg tunnel) and in the city of Wuppertal. In addition, measurements of NMHCs and NO_x were also carried out in a rural area (Menz) of Germany within the framework of the Berlioz campaign, for comparing and explaining indirectly some aspects of the emission situation of the city of Wuppertal. The main findings of the present study can be summarized as follows:

Instrumental:

The sampling system of the quasi-online Gas Chromatograph Airmovoc HC2010 was improved and integration methods were developed for improving the data quality of the measured NMHCs during field measurements.

Tunnel campaigns:

The three measurement campaigns during 1997-98 in the Kiesberg tunnel showed similar NMHCs-profiles relative to benzene, which indicates that there were no significant changes in the road traffic exhaust over this period of time. The study also supplied a fingerprint NMHC-profile for road traffic exhaust. Among the aromatic compounds, toluene (1.7±0.5 ppbC/ppbC), among the alkenes/alkynes, ethene/ethyne (2.5±0.8 ppbC/ppbC) and among the alkanes, *iso*-pentane (1.2±0.4 ppbC/ppbC) had the highest emission ratios relative to benzene and can also be considered as markers for road traffic exhaust. The percental contribution of these classes in the measured NMHC-mix was almost equal with a slightly higher value for the alkanes. A comparison of the fuel's composition with the compostion of the road traffic exhaust in the Kiesberg tunnel indicates an increase of the alkene contribution during the combustion.

Although there was a decrease in the number of the conventional passenger cars (PCs) of about 25% and an increase of the PCs with catalysts of about 13% in 1998 compared to 1997 in the administrative area of Düsseldorf, the similar NMHC profiles and the comparison with the literature data indicate that the emissions are mainly caused by uncontrolled cars (so-called super emitters). It is therefore not sufficient merely to increase the number of PCs with catalysts, but it is necessary to remove all conventional PCs without exhaust after treatment in order to improve the air quality.

The NMHC/NO_x ratio in ppbC/ppbv was found to be 0.6-2.0 for weekdays and 4.4±0.4 for the weekend. As heavy duty vehicles (HDV) emit more NO_x than light duty vehicles (LDV), the increased value of this emission ratio during the weekend can be attributed to the decrease of the contribution of HDV to the traffic composition from 6% to 1% in this period of time, which is in agreement with literature studies.

With the measured value of CO_2, the emission ratios of NMHCs relative to ppbv/ppbv were determined. Here, it was also found that the emission ratios of toluene, ethene/ethyne and iso-pentane relative to CO_2 were the largest among the classes of aromatic compounds, alkenes/alkynes and alkanes, respectively, which is also comparable with other studies.

By comparing the Handbook value for the emission of CO_2 in mg/km, the emission factors of NMHCs and NO_x in mg/km were calculated. The contribution from light duty vehicles (LDV) and heavy duty vehicles (HDV) were also calculated by using the values during weekdays and the weekend, the traffic composition of the tunnel and the statistical vehicle distribution in the Düsseldorf administrative area. From the standard value of CO_2 emitted by the combustion of fuels, the emission indices in g/kg fuel of NMHCs and NO_x were calculated for weekdays and the weekend. In addition, the LDV and HDV contributions of these emission indices were also calculated. These values agreed with literature values only for a limited number of compounds. From these emission factors and emission indices, an estimate of the total NMHCs and NO_x emissions was also carried out for North-Rhine Westfalia (NRW) for LDV. These values were comparable within large error limits with the values calculated by the State Environment Agency (Landesumweltamt) of NRW.

The OH reactivities of the NMHC-mix found in the Kiesberg tunnel were calculated from the emission ratios relative to benzene in ppbC/ppbC. This gave an idea of the upper limit of the ozone formation potential of the mix. Additionally, the percental contributions of MIR and POCP indices were also calculated for the measured NMHCs using the literature values.

City air of Wuppertal:

From the measured values in the city of Wuppertal, the individual NMHC-profiles relative to benzene in ppbC/ppbC were determined. In this manner, the fingerprint for the air composition of a typical German city was established.

The percental contribution of alkanes, alkenes/alkynes and aromatic hydrocarbons for the city of Wuppertal were found to be 57.2 ± 6.5%, 14.5 ± 3.6% and 28.3 ± 5.1%, respectively. The average mixing ratios and at the same time the emission values of NMHCs relative to benzene showed that among aromatic compounds, toluene, among alkanes, ethane and among alkenes/alkynes, 1-/iso-butene have the largest contribution. Considering the k_{OH} values for ethene and some other NMHCs and the aged mixing ratios compared to the measured mixing ratios in background air (*e.g.* Menz), it can be seen that the tunnel profile showed a similar hydrocarbon-mix as the air composition of the city of Wuppertal. A comparison with other literature values shows that the toluene/benzene emission ratio (1.7 ± 0.5) can justifiably be used as a marker from the sector of source road traffic in a region or an air mass.

The calculated NMHC/NO_x values (2.4-4.8) for the city air of Wuppertal agreed well with other studies of urban areas. The high values of this ratio in comparison with that of the Kiesberg tunnel can be explained by considering the increase of the urban stop+go driving situation in the city.

It was also confirmed that the limit values for benzene and NO_2 prescribed by the Federal immission control act (1998) were not exceeded in the city of Wuppertal.

The OH reactivities, percental contribution of MIR and POCP indices were also calculated for the city air of Wuppertal. These values showed for most of the cases good agreement with those for the tunnel studies and in general alkenes had the largest percental contribution in the total calculated reactivities for both cases. The following components have the largest contribution to the ozone formation potential: styrene, xylenes, ethylbenzene and toluene among aromatic hydrocarbons, *iso*-/1-butene, ethene, propene, 1,3-butadiene and isoprene/*trans*-2-pentene among alkenes/alkynes and iso-pentane, cyclopentane/2,3-dimethylbutane/2-methylpentane and *n*-butane among alkanes in the NMHC-mix of the city

of Wuppertal. This indicates that when formulating ozone reduction strategy one should consider these emittants with larger ozone formation potential.
The NMHCs-profile also showed a small effect from other sources. For example, the components cyclohexane, 2,3-dimethylpentane, 3-methylhexane, methylcyclohexane, 2-/3-mehtylheptane, *n*-heptane and styrene may have contributed to the emission from the solvent source sector, which altogether constituted about 10± 2% of the total NMHC-mix. In addition, part of the contribution of ethane and propane may be attributed to the leakage of natural gas.

Impact on city air of Wuppertal:

A comparison of the NMHC-profile relative to benzene (ppbC/ppbC) for the city of Wuppertal with that of the tunnel air showed that road traffic has until now the largest contribution in the measured NMHC-mix (in the range of C_2-C_9) for the city of Wuppertal, which is in contrast with the report of Federal Environment Agency of Germany (Umweltbundesamt). By considering the facts of the similar NMHC-profiles (in the range of C_2-C_9) relative to benzene, NMHC/NO_x ratios, reactivity indices and finally by comparing some recent literature studies, *e.g.* in Augsburg and Friedrichshafen/Ravenburg, it can be stated that until now road traffic exhaust has in general the largest impact on the air composition of German cities.

In the future, the measurements of oxygenated hydrocarbons and higher carbon containing hydrocarbons can be stressed in making the emission estimate of these compounds more realistic. Another prospect can be implied for the continuation of the data analysis produced by this study using mathematical calculations or modelling which may show new views regarding the ozone formation and the emission situation of Germany.

6 Abbreviations

AI	Analytical Instrument
BERLIOZ	Berlin Ozone Experiment
BImSchG	Bundesimmissionsschutzgesetz (Federal Immission Control Act of Germany
CARB	California Air Resources Board
CFC	Chlorofluorocarbons
CORINAIR	CO-ordination of INformation on AIR emission (the European air emission inventory system)
DIN	Deutsches Institut für Normung e.V.
DOAS	Differential Optical Absorption Spectrometry
EE	Emission Estimate
EF	Emission Factors
EI	Emission Indices
EMFAC	Emission Factor
ERG	Eastern Research Group, Inc. (Morrisville, North Carolina, USA)
EU-15	Germany, United Kingdom, France, Italy, Spain, Netherlands, Greece, Belgium, Portugal, Sweden, Austria, Denmark, Finland, Ireland and Luxembourg
FID	Flame Ionisation Detector
FTIR	Fourier Transform InfraRed spectroscopy
GC	Gas Chromatograph
GDP	Gross Domestic Product
HC	Hydrocarbon
HDV	Heavy Duty Vehicles
HP-GC	Hewlett-Packard Gas Chromatograph
ID No.	Identification Number
IER	Institut für Energiewirtschaft und rationelle Energieanwendung (Institute for Energy Economics and Rational Use of Energy), Universität Stuttgart
IFU	Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen, Germany
KBA	Kraftfahrt-Bundesamt (Federal Motor Transport Authority of Germany)
LDV	Light Duty Vehicles
LUA	Landesumweltamt (North-Rhine Westfalia, Germany)
LUQS	Luftqualitäts-Überwachungs-System
MC	Motor Cycles
MIR	Maximum Incremental Reactivity
NCAR	National Center for Atmospheric Research (Boulder, Colorado, USA)
NIST	National Institute of Standard and Technology (Washington, USA)
NMHC	Nonmethane Hydrocarbon
NO_x	Oxides of nitrogen
NPL	National Physical Laboratory (U.K.)
NRC	National Research Council
NRW	Nordrhein-Westfalen
NVOC	Nonmethane Volatile Organic Compound
OAQPS	Office of Air Quality Planning and Standards (US EPA)
PAN	Peroxyacetyl nitrate
PC	Passenger Cars

PCP	Percental Contribution of POCP index relative to total values
POCP	Photochemical Ozone Creation Potential
PSR	Percental contribution of Specific Reactivity relative to total values
RF	Response Factor
SMPS	Scanning Mobility Particle Sizer
S/N	Serial Number
SOP	Standard Operating Procedure
STP	Standard Temperature and Pressure (0°C and 101.325 kPa)
TFS	Troposphärenforschungsschwerpunkt (Main Focus of the Tropospheric Research)
VOC	Volatile Organic Compound
UBA	Umweltbundesamt (Federal Environmental Agency of Germany)
UMEG	Gesellschaft für Umweltmessungen und Umwelterhebungen, Germany
US EPA	United States Environmental Protection Agency
UV	Ultra-Violet
WMO	World Meteorological Organization
ZIMEN	Zentrales Immissionsmessnetz, Germany

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8 Annex-Tables

Table A1 I: Rate constants at 298 K for reactions of VOCs with NO_3, OH and ozone (Atkinson, 1991, 1994, 1997, 2000; De More *et al.*, 1997, National Institute of Standard and Technology (NIST) data base, 1998).

Compounds	k_{OH}	k_{NO3}	k_{O3}
	$(10^{-12}\ cm^3s^{-1})$	$(10^{-17}\ cm^3s^{-1})$	$(10^{-18}\ cm^3s^{-1})$
Ethyne	0.82	5.1	0.0078
Ethene	8.52	20.5	1.59
Ethane	0.254	0.14	$<10^{-5}$
Propene	26.3	949	10.1
Propane	1.12	1.7	$<10^{-5}$
iso-Butane	2.19	10.6	$<10^{-5}$
1-/*iso*-Butene	31.4	1350	9.64
1,3-Butadiene	66.6	10000	6.3
n-Butane	2.44	4.59	$<10^{-5}$
trans-Butene	67	37000	160
cis-Butene	56.4	35000	125
3-Methyl-1-butene	31.8	17000	9.51
iso-Pentane	3.7	16.2	$<10^{-5}$
Acetone	0.226	<0.85	–
1-Pentene	31.4	19000	10
2-Methyl-1-butene	61	33000	16
n-Pentane	4	8.7	$<10^{-5}$
Isoprene	101	67800	12.8
trans-2-Pentene	67	37000	160
cis-2-Pentene	57	28200	209
2-Methyl-2-butene	86.9	937000	403
2,2-Dimethylbutane	2.34	–	$<10^{-5}$
Cyclopentene	67	46000	655
3-Methyl-1-pentene	–	–	–
4-Methyl-1-pentene	38	4270	10.6
Cyclopentane	5.02	–	$<10^{-5}$
2,3-Dimethylbutane	5.78	40.6	$<10^{-5}$
2-Methylpentane	5.6	–	$<10^{-5}$
3-Methylpentane	5.7	20.4	$<10^{-5}$
2-Methyl-1-pentene	55	23500	17
1-Hexene	37	1200	11
n-Hexane	5.45	11	$<10^{-5}$
cis-3-Hexene	60	37000	150
trans-2-Hexene	60	37000	160
cis-2-Hexene	62	38900	–
Methylcyclopentane	–	–	$<10^{-5}$
2,4-Dimethylpentane	5	15	$<10^{-5}$
Benzene	1.23	3	$<10^{-2}$
Cyclohexane	7.21	14	$<10^{-5}$
2-Methylhexane	6.79	–	$<10^{-5}$
2,3-Dimethylpentane	6.1	–	$<10^{-5}$
3-Methylhexane	7.16	–	$<10^{-5}$
iso-Octane	3.57	9	$<10^{-5}$
n-Heptane	7.02	15	$<10^{-5}$
2,3-Dimethyl-2-pentene	101	–	–
Methylcyclohexane	10	–	$<10^{-5}$

Table A1 I (continued):

Compounds	k_{OH}	k_{NO3}	k_{O3}
	$(10^{-12}\ cm^3s^{-1})$	$(10^{-17}\ cm^3s^{-1})$	$(10^{-18}\ cm^3s^{-1})$
2,3,4-Trimethylpentane	7.1	–	$<10^{-5}$
2-Methylheptane	–	–	$<10^{-5}$
3-Methylheptane	–	–	$<10^{-5}$
Toluene	5.96	6.8	$<10^{-2}$
4-Methylheptane	–	–	–
n-Octane	8.71	19	$<10^{-5}$
Ethylbenzene	7.1	70	$<10^{-2}$
m-/*p*-Xylene	18.8	40	$<10^{-2}$
n-Nonane	10	23	$<10^{-5}$
Styrene	106	468000	17
o-Xylene	13.7	37	$<10^{-2}$
iso-Propylbenzene	6.5	70	$<10^{-2}$
α-Pinene	53.7	616000	86.6
n-Propylbenzene	6.08	70	$<10^{-2}$
m-Ethyltoluene	19.2	70	$<10^{-2}$
p-Ethyltoluene	12.1	70	$<10^{-2}$
Mesitylene	57.3	80	0.0029
o-Ethyltoluene	12.3	–	–
1,2,4-Trimethylbenzene	32.5	180	$<10^{-2}$
n-Decane	11.2	28	$<10^{-5}$

Table A1 II: Calculated lifetimes of different NMVOCs for daytime and night-time using the average values of OH, NO_3 and O_3 (Calvert *et al.*, 2001) and the k-values of Table A1 I (Atkinson, 1991, 1994,1997, 2000; De More *et al.*, 1997; NIST data base 1998).

	day-time			night-time		
Average Concentration	OH	NO_3	O_3	OH	NO_3	O_3
molecules cm^{-3}	3.90E+06	7.00E+07	2.70E+12	1.70E+04	2.50E+09	2.00E+12
Compounds	τ_{OH}	τ_{NO3}	τ_{O3}	τ_{OH}	τ_{NO3}	τ_{O3}
Ethyne	3.6 days	8.9 yrs	1.5 yrs	2.3 yrs	90.8 days	2.0 yrs
Ethene	8.4 hrs	2.2 yrs	2.7 days	79.9 days	22.6 days	3.6 days
Ethane	11.7 days	323.6 yrs	>1174.4 yrs	7.3 yrs	9.1 yrs	>1585.5
Propene	2.7 hrs	17.4 days	10.2 hrs	25.9 days	11.7 hrs	13.8 hrs
Propane	2.6 days	26.6 yrs	>1174.4 yrs	1.7 yrs	272.3 days	>1585.5
iso-Butane	1.4 days	4.3 yrs	>1174.4 yrs	310.9 days	43.7 days	>1585.5
1-/*iso*-Butene	2.3 hrs	12.2 days	10.7 hrs	21.7 days	8.2 hrs	14.4 hrs
1,3-Butadiene	1.1 hrs	1.7 days	16.3 hrs	10.2 days	1.1 hrs	22.0 hrs
n-Butane	1.2 days	9.9 yrs	>1174.4 yrs	279.0 days	100.9 days	>1585.5
trans-Butene	1.1 hrs	10.7 hrs	38.6 min	10.2 days	18.0 min	52.1 min
cis-Butene	1.3 hrs	11.3 hrs	49.4 min	12.1 days	19.0 min	1.1 hrs
3-Methyl-1-butene	2.2 hrs	23.3 hrs	10.8 hrs	21.4 days	39.2 min	14.6 hrs
iso-Pentane	19.3 hrs	2.8 yrs	>1174.4 yrs	184.0 days	28.6 days	>1585.5
Acetone	13.1 days	>53.3 yrs	–	8.3 yrs	1.5 yrs	–
1-Pentene	2.3 hrs	20.9 hrs	10.3 hrs	21.7 days	35.1 min	13.9 hrs
2-Methyl-1-butene	1.2 hrs	12.0 hrs	6.4 hrs	11.2 days	20.2 min	8.7 hrs
n-Pentane	17.8 hrs	5.2 yrs	>1174.4 yrs	170.2 days	53.2 days	>1585.5

Table A1 II (continued):

	day-time			night-time		
Average Concentration	OH	NO_3	O_3	OH	NO_3	O_3
molecules cm^{-3}	3.90E+06	7.00E+07	2.70E+12	1.70E+04	2.50E+09	2.00E+12
Compounds	τ_{OH}	τ_{NO3}	τ_{O3}	τ_{OH}	τ_{NO3}	τ_{O3}
Isoprene	42.3 min	5.9 hrs	8.0 hrs	6.7 days	9.8 min	10.9 hrs
trans-2-Pentene	1.1 hrs	10.7 hrs	38.6 min	10.2 days	18.0 min	52.1 min
cis-2-Pentene	1.2 hrs	14.1 hrs	29.5 min	11.9 days	23.6 min	39.9 min
2-Methyl-2-butene	49.2 min	25.4 min	15.3 min	7.8 days	42.7 s	20.7 min
2,2-Dimethylbutane	1.3 days	–	>1174.4 yrs	291.0 days	–	>1585.5
Cyclopentene	1.1 hrs	8.6 hrs	15.4 min	10.2 days	14.5 min	12.8 min
3-Methyl-1-pentene	–	–	–	–	–	–
4-Methyl-1-pentene	1.9 hrs	3.9 days	9.7 hrs	17.9 days	2.6 hrs	13.1 hrs
Cyclopentane	14.2 hrs	–	>1174.4 yrs	135.6 days	–	>1585.5
2,3-Dimethylbutane	12.3 hrs	1.1 yrs	>1174.4 yrs	117.8 days	11.4 days	>1585.5
2-Methylpentane	12.7 hrs	–	>1174.4 yrs	121.6 days	–	>1585.5
3-Methylpentane	12.5 hrs	2.2 yrs	>1174.4 yrs	119.4 days	22.7 days	>1585.5
2-Methyl-1-pentene	1.3 hrs	16.9 hrs	6.1 hrs	12.4 days	28.4 min	8.2 hrs
1-Hexene	1.9 hrs	13.8 days	9.4 hrs	18.4 days	9.3 hrs	12.6 hrs
n-Hexane	13.1 hrs	4.1 yrs	>1174.4 yrs	124.9 days	42.1 days	>1585.5
cis-3-Hexene	1.2 hrs	10.7 hrs	41.2 min	11.3 days	18.0 min	55.6 min
trans-2-Hexene	1.2 hrs	10.7 hrs	38.6 min	11.3 days	18.0 min	52.1 min
cis-2-Hexene	1.1 hrs	10.2 hrs	–	11.0 days	17.1 min	–
Methylcyclopentane	–	–	>1174.4 yrs	–	–	>1585.5
2,4-Dimethylpentane	14.2 hrs	3.0 yrs	>1174.4 yrs	136.2 days	30.9 days	>1585.5
Benzene	2.4 days	15.1 yrs	>1.2 yrs	1.5 yrs	154.3 days	>1.6 yrs
Cyclohexane	9.9 hrs	3.2 yrs	>1174.4 yrs	94.4 days	33.1 days	>1585.5
2-Methylhexane	10.5 hrs	–	>1174.4 yrs	100.3 days	–	>1585.5
2,3-Dimethylpentane	11.7 hrs	–	>1174.4 yrs	111.6 days	–	>1585.5
3-Methylhexane	9.9 hrs	–	>1174.4 yrs	95.1 days	–	>1585.5
iso-Octane	20.0 hrs	5.0 yrs	>1174.4 yrs	190.7 days	51.4 days	>1585.5
n-Heptane	10.1 hrs	3.0 yrs	>1174.4 yrs	97.0 days	30.9 days	>1585.5
2,3-Dimethyl-2-pentene	42.3 min	–	–	6.7 days	–	–
Methylcyclohexane	7.1 hrs	–	>1174.4 yrs	68.1 days	–	>1585.5
2,3,4-Trimethylpentane	10.0 hrs	–	>1174.4 yrs	95.9 days	–	>1585.5
2-Methylheptane	–	–	>1174.4 yrs	–	–	>1585.5
3-Methylheptane	–	–	>1174.4 yrs	–	–	>1585.5
Toluene	12.0 hrs	6.7 yrs	>1.2 yrs	114.2 days	68.1 days	>1.6 yrs
4-Methylheptane	–	–	–	–	–	–
n-Octane	8.2 hrs	2.4 yrs	>1174.4 yrs	78.2 days	24.4 days	>1585.5
Ethylbenzene	10.0 hrs	236.2 days	>1.2 yrs	95.9 days	6.6 days	>1.6 yrs
m-/p-Xylene	3.8 hrs	1.1 yrs	>1.2 yrs	36.2 days	11.6 days	>1.6 yrs
n-Nonane	7.1 hrs	2.0 yrs	>1174.4 yrs	68.1 days	20.1 days	>1585.5
Styrene	40.3 min	50.9 min	6.1 hrs	6.4 days	1.4 min	8.2 hrs
o-Xylene	5.2 hrs	1.2 yrs	>1.2 yrs	49.7 days	12.5 days	>1.6 yrs
iso-Propylbenzene	11.0 hrs	236.2 days	>1.2 yrs	104.7 days	6.6 days	>1.6 yrs
α-Pinene	1.3 hrs	38.7 min	1.2 hrs	12.7 days	1.1 min	1.6 hrs

Table A1 II (continued):

	day-time			night-time		
Average Concentration	OH	NO_3	O_3	OH	NO_3	O_3
molecules cm^{-3}	3.90E+06	7.00E+07	2.70E+12	1.70E+04	2.50E+09	2.00E+12
Compounds	τ_{OH}	τ_{NO3}	τ_{O3}	τ_{OH}	τ_{NO3}	τ_{O3}
n-Propylbenzene	11.7 hrs	236.2 days	>1.2 yrs	112.0 days	6.6 days	>1.6 yrs
m-Ethyltoluene	3.7 hrs	236.2 days	>1.2 yrs	35.5 days	6.6 days	>1.6 yrs
p-Ethyltoluene	5.9 hrs	236.2 days	>1.2 yrs	56.3 days	6.6 days	>1.6 yrs
Mesitylene	1.2 hrs	206.7 days	4.0 yrs	11.9 days	5.8 days	5.5 yrs
o-Ethyltoluene	5.8 hrs	–	–	55.4 days	–	–
1,2,4-Trimethylbenzene	2.2 hrs	91.9 days	>1.2 yrs	20.9 days	2.6 days	>1.6 yrs
n-Decane	6.4 hrs	1.6 yrs	>1174.4 yrs	60.8 days	16.5 days	>1585.5

Table A1 III: National emission of NMVOC and NO_x in kt for the year of 1993 (source: 'Daten zur Umwelt' (UBA), 1997; Eggleston *et al.*, 2000).

Country	NMVOCs (kt)			NOx (kt)		
	1993	1996	2010 (Draft NECD/ Target)	1993	1996	2010 (Draft NECD/ Target)
Austria	388	260	129	182	161	91
Belgium	359	324	102	340	330	127
Bulgaria	199	147	185	238	259	266
Germany	2289	1877	924	2274	1887	1051
Denmark	161	139	85	267	291	127
Finland	195	173	110	280	267	152
France	2197	2075	932	1544	1695	679
Greece	343	371	173	349	374	264
Great Britain	2110	2221	964	2339	2018	1181
Ireland	202	103	55	122	121	59
Liechtenstein	1	1		1	1	
Iceland	14	12		23	30	
Italy	2344	2368	962	1997	1768	869
Croatia	68			53		
Luxembourg	19	17	6	25	22	8
Holland	401	359	156	552	486	238
Norway	283	368		229	222	
Poland	756	766	800	1120	1154	879
Portugal	672	691	102	371	407	144
Romania	502	505	523	318	319	437
Russia	2979			2269		
Sweden	502	458	219	398	301	152
Switzerland	239		–	145	–	–
Slovak Republic	107			184	130	130
Slovenia	122	104	140	61	70	45
Spain	1970	1911	662	1227	1203	781
Czech Republic	438	284	220	574	432	286
Estonia	42	50	–	38	44	–
Turkey	–	–	–	1	–	–
Ukraine	972	–	–	700	–	–
Hungary	143	189	137	173	196	198
Latvia	98	42	136	46	35	84
Lithuania	54	79	92	78	65	110
Belarus	372	–	–	207	–	–

Table A1 III (continued):

Country	NMVOCs (kt)			NOx (kt)		
	1993	1996	2010 (Draft NECD/ Target)	1993	1996	2010 (Draft NECD/ Target)
Canada	2763	–	–	2006	–	–
USA	20604	–	–	21229	–	–

NECD: Directive on National Emission Ceilings.

Table A2 I: Technical parameters of Airmovoc 2010 used in different measurement sites.

Subject	Airmovoc HC 2010
Column	BGB-2.5 (OV 178) (2.5% phenyl- and 97.5% methyl polysiloxane)
Length	25 m
Inner diameter	0.2 mm
Film thickness	2 µm
Sorbent	Carbosieve III & carbotrap in the ratio 1:3
Cryofocusing trap and cooling effect	Micro-packed fused silica capillary tube, cooling through CO_2 gas expanded from 60 bar to atm. pressure, adsorbents: Carbopack B and Envi-Carb X in the ratio 3:1
Temperature programme	Isothermal and with ramp (*e.g.* a constant value of 25° C for first 210 s, and then ramp of 17 °C/min up to 160 °C)
Pressure programme	from 212 hp till 900 hp
Sampling time	0 s-1500 s
Sampling volume	0 ml-2250 ml
Measurement period	1200 s-1800 s

Table A2 II: List of percental reproducibility of integrated area for different adsorption tubes.

		tube 4	tube 6	tube 2
Components	Average (%)	average (%)	average (%)	average (%)
Ethene/Ethyne	16.9	19.0	17.6	14.3
Ethane	18.8	27.5	13.4	15.5
Propene	7.5	6.9	9.3	6.4
Propane	7.1	7.2	9.1	5.0
iso-Butane	19.4	20.3	17.3	20.7
iso/1-Butene	8.5	8.9	10.6	6.1
1,3-Butadiene	12.2	10.7	14.2	11.7
n-Butane	22.1	28.8	16.2	21.2
trans-Butene	7.0	3.8	9.9	7.2
cis-Butene	5.4	3.9	7.2	5.0
iso-Pentane	5.0	3.2	8.4	3.4
n-Pentane	4.7	2.7	7.3	4.0
Isoprene/ *trans*-2-Pentene	4.7	3.2	7.9	3.1
cis-2-Pentene	4.8	3.2	8.0	3.1
2-Methylpentane	4.3	2.6	5.9	4.4
3-Methylpentane	3.8	2.6	6.1	2.7
n-Hexane	3.6	2.7	5.8	2.3
Benzene	2.8	1.9	5.4	1.3
n-Heptane	3.8	3.3	6.0	2.2
Toluene	3.9	3.2	6.3	2.1

Table A2 II (continued):

		tube 4	tube 6	tube 2
Components	Average (%)	average (%)	average (%)	average (%)
Ethylbenzene	4.6	3.9	6.8	3.1
m-Xylene	5.2	4.3	7.5	3.9
o-Xylene	6.0	5.5	7.4	5.1
Mesitylene	10.8	12.7	10.7	9.1
1,2,4-Trimethylbenzene	18.2	20.8	15.2	18.5

Table A3 I: List of emission ratios and correlation coefficients for the measured NMHCs normalized against benzene in ppbC/ppbC for the tunnel campaign of November-December, 1998.

Components	Slope (m)	± (Δm)	corr. coeff.
Ethene/Ethyne	2.59	0.09	0.92
Ethane	0.24	0.01	0.94
Propene	0.36	0.01	0.98
Propane	0.09	0.00	0.84
iso-Butane	0.41	0.01	0.95
iso-/1-Butene	0.40	0.01	0.97
n-Butane, 1,3-butadiene	0.97	0.02	0.95
1,3-Butadiene	0.29	0.01	0.95
n-Butane	0.59	0.02	0.94
trans-Butene	0.17	0.00	0.96
cis-Butene	0.10	0.00	0.96
iso-Pentane	1.15	0.03	0.94
1-Pentene	0.07	0.00	0.96
2-Methyl-1-butene	0.18	0.02	0.34
n-Pentane	0.08	0.00	0.84
Isoprene/*trans*-2-Pentene	0.23	0.01	0.87
cis-2-Pentene	0.10	0.01	0.47
2-Methyl-2-butene	0.18	0.00	0.96
2,2-Dimethylbutane	0.07	0.00	0.91
Cyclopentene, 3-/4-methyl-1-pentene	0.11	0.00	0.95
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	0.68	0.01	0.97
3-Methylpentane	0.17	0.00	0.98
2-Methyl-1-pentene	0.05	0.00	0.78
n-Hexane	0.20	0.01	0.94
cis-3-Hexene, *trans*-2-hexene, unknown	0.05	0.00	0.92
cis-2-Hexene	0.02	0.00	0.96
Methylcyclopentane, 2,4-dimethylpentane	0.17	0.00	0.97
Methylcyclopentane	0.03	0.00	0.71
2,4-Dimethylpentane	0.17	0.01	0.96
2-Methylhexane	0.09	0.01	0.97
Cyclohexane, 2,3-dimethylpentane	0.06	0.00	0.94
3-Methylhexane	0.09	0.00	0.97
iso-Octane	0.19	0.01	0.93
n-Heptane	0.07	0.00	0.96
2,3-Dimethyl-2-pentene	0.00	0.00	0.87
Methylcyclohexane	0.06	0.00	0.89
Unknown, methylcyclohexane	0.07	0.00	0.94
2,3,4-Trimethylpentane	0.07	0.00	0.84
2-/3-Methylheptane	0.04	0.00	0.92
Toluene	1.73	0.03	0.98

Table A3 I (continued):

Components	Slope (m)	± (Δm)	corr. coeff.
Ethylbenzene	0.49	0.03	0.73
m-/*p*-Xylene	0.26	0.02	0.64
Styrene	0.04	0.01	0.47
o-Xylene	0.15	0.02	0.42
n-Octane	0.02	0.00	0.39

Table A3 II: Emission ratios of NMHC(ppbv)/CO_2(ppbv) determined using the measured data in the Kiesberg tunnel, Wuppertal (Nov.-Dec. 1998).

Compounds	Weekdays (ppbv/ppbv)	±	Corrected correlation (r^2)	Weekend (ppbv/ppbv)	±	Corrected correlation (r^2)
Ethene/Ethyne	3.05E-04	2.64E-05	0.69	7.41E-04	1.75E-04	0.66
Ethane	2.62E-05	2.70E-06	0.66	6.66E-05	1.45E-05	0.75
Propene	2.79E-05	2.40E-06	0.71	5.41E-05	1.28E-05	0.72
Propane	6.70E-06	7.00E-07	0.67	–	–	–
iso-Butane	2.58E-05	1.90E-06	0.77	6.03E-05	1.34E-05	0.71
iso-/1-Butene	2.42E-05	2.00E-06	0.73	6.58E-05	1.55E-05	0.66
1,3-Butadiene	1.71E-05	1.50E-06	0.70	5.64E-05	1.33E-05	0.64
n-Butane	3.65E-05	2.90E-06	0.75	1.43E-04	3.42E-05	0.62
trans-Butene	1.02E-05	8.00E-07	0.72	3.55E-05	8.30E-06	0.63
cis-Butene	6.00E-06	5.00E-07	0.73	1.98E-05	4.60E-06	0.65
iso-Pentane	5.35E-05	5.00E-06	0.67	2.40E-04	5.72E-05	0.60
1-Pentene	3.10E-06	3.00E-07	0.71	6.60E-06	2.00E-06	0.58
2-Methyl-1-butene	–	–	–	7.20E-06	7.70E-06	0.22
n-Pentane	3.40E-06	3.00E-07	0.67	1.48E-05	4.90E-06	0.46
Isoprene, trans-2-pentene	1.09E-05	1.00E-06	0.65	3.60E-05	6.40E-06	0.79
cis-2-Pentene	8.60E-06	9.00E-07	0.44	9.71E-05	2.52E-05	0.36
2-Methyl-2-butene	8.50E-06	8.00E-07	0.68	3.24E-05	8.30E-06	0.56
2,2-Dimethylbutane	2.90E-06	3.00E-07	0.67	1.15E-05	2.90E-06	0.52
Cyclopentene, 3-/4-methyl-1pentene, 4-methyl-1-pentene	4.90E-06	4.00E-07	0.70	–	–	–
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	2.81E-05	2.50E-06	0.69	8.92E-05	2.39E-05	0.56
3-Methylpentane	7.00E-06	6.00E-07	0.71	2.86E-05	7.20E-06	0.57
2-Methyl-1-pentene	2.10E-06	2.00E-07	0.70	4.20E-06	1.10E-06	0.57
n-Hexane	7.80E-06	6.00E-07	0.71	3.37E-05	8.60E-06	0.56
cis-3-Hexene, *trans*-2-hexene	1.80E-06	2.00E-07	0.62	6.00E-06	1.60E-06	0.55
cis-2-Hexene	1.00E-06	1.00E-07	0.64	–	–	–
Methylcyclopentane, 2,4-dimethylpentane	6.10E-06	6.00E-07	0.68	2.21E-05	5.80E-06	0.55
Benzene	3.89E-05	3.88E-06	0.71	1.26E-04	3.26E-05	0.59
Cyclohexane, 2,3-dimethylpentane	2.20E-06	2.00E-07	0.67	8.20E-06	2.00E-06	0.67
3-Methylhexane	2.80E-06	3.00E-07	0.66	9.40E-06	2.70E-06	0.52
iso-Octane	5.80E-06	5.00E-07	0.71	2.33E-05	6.40E-06	0.51
n-Heptane	2.30E-06	2.00E-07	0.65	7.00E-06	2.20E-06	0.46
2,3-Dimethyl-2-pentene	2.00E-07	0.00E+00	0.60	–	–	–
Methylcyclohexane	2.00E-06	2.00E-07	0.63	–	–	–
2,3,4-Trimethylpentane	1.70E-06	2.00E-07	0.60	1.05E-05	2.60E-06	0.52
2-/3-Methylheptane	1.00E-06	1.00E-07	0.62	3.10E-06	1.40E-06	0.31
Toluene	5.49E-05	5.30E-06	0.67	1.77E-04	5.05E-05	0.53

Table A3 II (continued):

Compounds	Weekdays (ppbv/ppbv)	±	Corrected correlation (r^2)	Weekend (ppbv/ppbv)	±	Corrected correlation (r^2)
Ethylbenzene	1.04E-05	1.30E-06	0.53	5.14E-05	1.52E-05	0.48
m-/*p*-Xylene	5.20E-06	1.10E-06	0.40	3.13E-05	1.61E-05	0.24
Styrene	1.80E-06	6.00E-07	0.22	1.99E-05	5.20E-06	0.56
o-Xylene	3.10E-06	7.00E-07	0.34	4.63E-05	1.55E-05	0.13
n-Octane	3.00E-07	1.00E-07	0.30	–	–	–
NO	1.40E-03	1.00E-04	0.67	1.90E-03	3.00E-04	0.79
NO_2	1.00E-04	1.41E-05	0.55	1.00E-04	1.41E-05	0.64
NO_x	1.30E-03	1.00E-04	0.67	2.00E-03	4.00E-04	0.78

Table A3 III: Calculated emission indices (g/kg fuel) in Kiesberg tunnel, Wuppertal.

	Kiesberg tunnel, Wuppertal			
	Weekdays		Weekend	
Sampling period	1997-1998		1998	
	g/kg fuel	g/kg fuel	g/kg fuel	g/kg fuel
Compounds	Average	±	Average	±
Ethene/Ethyne	0.590	0.118	1.433	0.343
Ethane	0.050	0.005	0.148	0.031
Propene	0.099	0.007	0.155	0.034
Propane	0.020	0.002	0.041	0.030
iso-Butane	0.098	0.007	0.179	0.031
iso-/1-Butene	0.097	0.006	0.185	0.032
1,3-Butadiene	0.066	0.006	0.218	0.051
n-Butane	0.149	0.011	0.391	0.061
trans-Butene	0.041	0.002	0.095	0.016
cis-Butene	0.023	0.002	0.051	0.008
3-Methyl-1-butene	0.006	0.001	0.006	0.002
iso-Pentane	0.275	0.021	0.610	0.080
1-Pentene	0.018	0.002	0.023	0.005
2-Methyl-1-butene	0.054	0.026	0.026	0.004
n-Pentane	0.047	0.004	0.100	0.016
Isoprene/*trans*-2-Pentene	0.050	0.004	0.115	0.015
cis-2-Pentene	0.036	0.004	0.262	0.049
2-Methyl-2-butene	0.041	0.003	0.079	0.011
2,2-Dimethylbutane	0.017	0.002	0.037	0.006
Cyclopentene, 3-/4-methyl-1-pentene	0.024	0.003	0.018	0.004
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	0.147	0.015	0.251	0.038
3-Methylpentane	0.042	0.004	0.093	0.013
2-Methyl-1-pentene /1-Hexene	0.013	0.001	0.015	0.003
n-Hexane	0.044	0.003	0.083	0.011
cis-3-Hexene, *trans*-2-hexene	0.011	0.001	0.020	0.003
cis-2-Hexene	0.005	0.001	0.004	0.001
Methylcyclopentane/2,4-Dimethylpentane	0.039	0.003	0.123	0.029
Benzene	0.218	0.026	0.415	0.081
Cyclohexane/2,3-Dimethylpentane	0.019	0.002	0.044	0.010
3-Methylhexane	0.022	0.002	0.042	0.008
iso-Octane	0.045	0.004	0.085	0.013
n-Heptane	0.016	0.001	0.021	0.004
2,3-Dimethyl-2-pentene	0.001	0.000	–	–
Methylcyclohexane	0.014	0.001	0.027	0.004

Table A3 III (continued):

	Kiesberg tunnel, Wuppertal			
	Weekdays		Weekend	
Sampling period	1997-1998		1998	
	g/kg fuel	g/kg fuel	g/kg fuel	g/kg fuel
Compounds	Average	±	Average	±
2,3,4-Trimethylpentane	0.013	0.002	0.068	0.015
2-/3-Methylheptane	0.011	0.001	0.025	0.004
Toluene	0.359	0.040	0.822	0.179
Ethylbenzene	0.080	0.007	0.221	0.042
m-/*p*-Xylene	0.142	0.015	0.224	0.051
n-Nonane	0.002	0.001	0.001	0.001
Styrene	0.031	0.003	0.071	0.011
o-Xylene	0.061	0.006	0.147	0.023
n-Octane	0.017	0.002	0.017	0.003
iso-Propylbenzene	0.010	0.001	0.008	0.003
n-Propylbenzene	0.016	0.003	0.017	0.004
m-/*p*-Ethyltoluene	0.105	0.021	0.101	0.026
Mesitylene	0.107	0.027	0.046	0.022
o-Ethyltoluene	0.017	0.004	0.023	0.008
NOx	7.786	2.021	6.582	2.641

Table A3 IV: Emission estimate for LDV in NRW for the year of 1997 using the calculated average emission factors (mg/km) of this present study for LDV and the literature value (LUA NRW, 1999) of the average driving performance between 'Bundesautobahnen' (BAB) and 'Bundesstraßen' (BS) in million vehicle-km.

	Average between BAB and BS			
	This study		North-Rhine Westfalia	
	Light Duty Vehicles (LDV)		Road traffic	
Components	t/a	s. d. (t/a)	t/a	s. d. (t/a)
Ethene/Ethyne	2078	899	–	–
Ethane	237	123	–	–
Propene	173	11	–	–
Propane	60	26	–	–
iso-Butane	232	39	–	–
iso-/1-Butene	246	43	–	–
1,3-Butadiene	324	140	–	–
n-Butane	610	43	–	–
trans-Butene	132	28	–	–
cis-Butene	72	18	–	–
3-Methyl-1-butene	7	3	–	–
iso-Pentane	1159	254	–	–
1-Pentene	33	1	–	–
2-Methyl-1-butene	23	10	–	–
n-Pentane	127	63	–	–
Isoprene, *trans*-2-pentene	158	44	–	–
cis-2-Pentene	385	221	–	–
2-Methyl-2-butene	148	37	–	–
2,2-Dimethylbutane	60	25	–	–
Cyclopentene, 3-/4-methyl-1-pentene	22	10	–	–
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	474	103	–	–

Table A3 IV (continued):

	Average between BAB and BS			
	This study		North-Rhine Westfalia	
	Light Duty Vehicles (LDV)		Road traffic	
Components	t/a	s.d. (t/a)	t/a	s.d. (t/a)
3-Methylpentane	167	33	–	–
2-Methyl-1-pentene, 1-hexene	23	3	–	–
n-Hexane	182	59	–	–
cis-3-Hexene, *trans*-2-hexene	33	8	–	–
cis-2-Hexene	6	3	–	–
Methylcyclopentane, 2,4-dimethylpentane	141	20	–	–
Benzene	632	159	656	33
Cyclohexane, 2,3-dimethylpentane	50	11	–	–
3-Methylhexane	67	8	–	–
iso-Octane	168	53	–	–
n-Heptane	43	14	–	–
2,3-Dimethyl-2-pentene			–	–
Methylcyclohexane	37	16	–	–
2,3,4-Trimethylpentane	72	31	–	–
2-/3-Methylheptane	36	13	–	–
Toluene	1192	61	–	–
Ethylbenzene	363	86	–	–
m-/*p*-Xylene	318	82	–	–
n-Nonane	1	0	–	–
Styrene	135	43	–	–
o-Xylene	331	87	–	–
n-Octane	22	9	–	–
iso-Propylbenzene	10	4	–	–
n-Propylbenzene	22	9	–	–
m-/*p*-Ethyltoluene	126	55	–	–
Mesitylene	38	17	–	–
o-Ethyltoluene	32	14	–	–
unidentified (12%)	1152	202	–	–
Total	12159	3241	12479	76
NO_x	9052	3917	57970	42028

LDV: Light duty vehicles, HDV: Heavy duty vehicles, NRW: North-Rhine Westfalia, s.d.: standard deviation.

Table A3 V: Estimation of emission of NMHCs and NO_x from LDV in NRW in the year of 1997 using the calculated average emission indices of this present study and the literature values (LUA NRW, 1999) of fuel consumption in ton/year (t/a) for LDV.

	This study		North-Rhine Westfalia	
	LDV	s.d.	LDV	HDV
Components	t/a	t/a	t/a	t/a
Ethene/Ethyne	12429	3806	–	–
Ethane	1423	255	–	–
Propene	1067	469	–	–
Propane	357	288	–	–
iso-Butane	1396	1102	–	–
iso-/1-Butene	1494	1183	–	–
1,3-Butadiene	1942	621	–	–
n-Butane	3624	2344	–	–
trans-Butene	781	653	–	–

Table A3 V (continued):

	This study		North-Rhine Westfalia	
	LDV	s.d.	LDV	HDV
Components	t/a	t/a	t/a	t/a
cis-Butene	430	380	–	–
3-Methyl-1-butene	45	16	–	–
iso-Pentane	6923	5919	–	–
1-Pentene	213	138	–	–
2-Methyl-1-butene	155	79	–	–
n-Pentane	773	105	–	–
Isoprene, *trans*-2-pentene	935	875	–	–
cis-2-Pentene	2298	3122	–	–
2-Methyl-2-butene	900	815	–	–
2,2-Dimethylbutane	347	388	–	–
Cyclopentene, 3-/4-methyl-1-pentene	137	41	–	–
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	2855	2443	–	–
3-Methylpentane	983	806	–	–
2-Methyl-1-pentene /1-Hexene	150	118	–	–
n-Hexane	1090	1095	–	–
cis-3-Hexene, *trans*-2-hexene	193	166	–	–
cis-2-Hexene	38	9	–	–
Methylcyclopentane, 2,4-dimethylpentane	859	653	–	–
Benzene	3806	3405	4545	215
Cyclohexane, 2,3-dimethylpentane	293	244	–	–
3-Methylhexane	411	297	–	–
iso-Octane	1005	996	–	–
n-Heptane	270	278	–	–
2,3-Dimethyl-2-pentene			–	–
Methylcyclohexane	226	51	–	–
2,3,4-Trimethylpentane	427	495	–	–
2-/3-Methylheptane	220	19	–	–
Toluene	7132	4415	–	–
Ethylbenzene	2163	1885	–	–
m-/*p*-Xylene	1932	344	–	–
n-Nonane	4	11	–	–
Styrene	820	818	–	–
o-Xylene	1984	1809	–	–
n-Octane	132	33	–	–
iso-Propylbenzene	61	26	–	–
n-Propylbenzene	134	41	–	–
m-/*p*-Ethyltoluene	775	259	–	–
Mesitylene	259	243	–	–
o-Ethyltoluene	191	76	–	–
unidentified (12%)	6916	5484	–	–
total	64554	51184	77174	11052
NO_x	54686	25867	103241	83306

s.d.: standard deviation

Table A3 VI: List of emission ratios and correlation coefficients for the measured NMHCs normalised against benzene in ppbC/ppbC for the city of Wuppertal during the weekend.

components	emission ratio (m)	± m	corr. coeff. r
Ethene/Ethyne	0.24	0.06	0.35
Ethane	1.88	0.13	0.79
Propene	0.35	0.03	0.62
Propane	0.39	0.03	0.82
iso-Butane	0.02	0.07	0.00
iso-/1-Butene	0.51	0.07	0.48
1,3-Butadiene/*n*-Butane	1.60	0.11	0.79
trans-Butene	0.20	0.01	0.87
cis-Butene	0.12	0.01	0.88
3-Methyl-1-butene	0.06	0.01	0.54
iso-Pentane	1.46	0.07	0.91
1-Pentene	0.04	0.005	0.76
2-Methyl-1-butene	0.07	0.01	0.70
n-Pentane	0.49	0.02	0.89
isoprene/*trans*-2-Pentene	0.21	0.02	0.78
cis-2-pentene	0.07	0.01	0.84
2-Methyl-2-butene	0.14	0.01	0.84
2,2-Dimethylbutane	0.10	0.01	0.88
Cyclopentene, 3-/4-methyl-1-pentene	0.05	0.003	0.87
Cyclopentane/2,3-Dimethylbutane/2-Methylpentane	0.78	0.03	0.94
3-Methylpentane	0.22	0.01	0.94
2-Methyl-1-pentene	0.05	0.001	0.97
n-Hexane	0.19	0.01	0.83
cis-3-Hexene, *trans*-2-hexene	0.04	0.01	0.68
cis-2-Hexene	0.01	0.002	0.16
Methylcyclopentane	0.04	0.002	0.90
2,4-Dimethylpentane	0.18	0.01	0.86
Methylcyclopentane/2,4-Dimethylpentane	0.24	0.01	0.87
Cyclohexane/2,3-Dimethylpentane	0.20	0.02	0.56
3-Methylhexane	0.16	0.004	0.97
iso-Octane	0.19	0.01	0.94
n-Heptane	0.10	0.01	0.90
iso-Octane/*n*-Heptane	0.26	0.01	0.94
2,3-Dimethyl-2-pentene	0.01	0.001	0.99
Methylcyclohexane	0.11	0.005	0.92
Unknown, methylcyclohexane	0.14	0.01	0.93
2,3,4-Trimethylpentane	0.06	0.002	0.95
2-/3-Methylheptane	0.13	0.005	0.94
Toluene	2.21	0.07	0.99
n-Octane	0.01	0.001	0.92
Ethylbenzene	0.29	0.01	0.93
m-/*p*-Xylene	0.52	0.04	0.85
Styrene	0.30	0.01	0.95
o-Xylene	0.20	0.02	0.81
iso-Propylbenzene	0.01	0.001	0.68
n-Propylbenzene	0.05	0.01	0.67
o-Ethyltoluene	0.10	0.05	0.12
1,2,4-Tmbenzene, n-decane	0.09	0.06	0.17
tert-Butylbenzene	0.01	0.004	0.64

Table A3 VII: Relative ozone formation potentials of the average exhaust emission ratios of nonmethane hydrocarbons relative to benzene in (ppbC/ppbC) found in the Kiesberg tunnel, Wuppertal.

Components	% wt/wt	MIR* (g O3/g NMHC)	Specific reactivity (MIR*%wt/wt)	PSR (% of specific reactivity relative to total values)	Error of propag-ation for PSR
Ethene	11.10	7.4	82.17	21.4	7.7
Ethyne	4.75	0.5	2.38	0.6	0.2
Ethane	1.95	0.25	0.49	0.1	0.1
Propene	3.23	9.4	30.34	7.9	2.8
Propane	0.52	0.48	0.25	0.1	0.1
iso-Butane	1.95	1.21	2.36	0.6	0.2
iso-/1-Butene	2.32	7.11	16.48	4.3	1.5
1,3-Butadiene	1.81	10.9	19.78	5.1	1.8
n-Butane	4.00	1.02	4.08	1.1	0.4
trans-Butene	1.03	9.94	10.21	2.7	0.9
cis-Butene	0.57	9.94	5.65	1.5	0.5
3-Methyl-1-butene	0.22	6.2	1.38	0.4	0.2
iso-Pentane	7.57	1.38	10.44	2.7	0.9
1-Pentene	0.49	6.2	3.02	0.8	0.3
2-Methyl-1-butene	1.10	4.9	5.40	1.4	0.5
n-Pentane	1.82	1.04	1.89	0.5	0.2
Isoprene, *trans*-2-pentene	1.20	8.95	10.76	2.8	1.0
cis-2-Pentene	0.47	8.8	4.17	1.1	0.4
2-Methyl-2-butene	1.07	6.4	6.86	1.8	0.6
2,2-Dimethylbutane	0.38	0.82	0.31	0.1	0.0
Cyclopentene, 3-/4-methyl-1-pentene	0.65	7.7	5.01	1.3	0.5
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	3.76	1.66	6.24	1.6	0.7
3-Methylpentane	1.10	1.53	1.69	0.4	0.1
2-Methyl-1-pentene	0.30	4.4	1.32	0.3	0.1
n-Hexane	1.10	0.98	1.08	0.3	0.1
cis-3-Hexene, *trans*-2-hexene	0.25	6.7	1.70	0.4	0.2
cis-2-Hexene	0.11	6.7	0.73	0.2	0.1
Methylcyclopentane	0.46	2.82	1.29	0.3	0.1
2,4-Dimethylpentane	1.13	1.78	2.02	0.5	0.2
Benzene	6.39	0.42	2.68	0.7	0.2
2-Methylhexane	0.49	1.08	0.53	0.1	0.1
Cyclohexane, 2,3-dimethylpentane	0.55	1.30	0.71	0.2	0.1
3-Methylhexane	0.56	1.4	0.79	0.2	0.1
iso-Octane	1.11	0.93	1.03	0.3	0.1
n-Heptane	0.41	0.81	0.33	0.1	0.0
2,3-Dimethyl-2-pentene	0.02	5.5	0.12	0.0	0.0
Methylcyclohexane	0.38	1.85	0.69	0.2	0.1
2,3,4-Trimethylpentane	0.28	1.6	0.44	0.1	0.0
2-/3-Methylheptane	0.41	0.98	0.40	0.1	0.0
Toluene	10.69	2.73	29.20	7.6	2.6
Ethylbenzene	2.44	2.7	6.59	1.7	0.6
m-/*p*-Xylene	3.37	7.69	25.90	6.7	2.5
n-Nonane	0.02	0.54	0.01	0.0	0.0
Styrene	0.59	2.2	1.30	0.3	0.1
o-Xylene	1.46	6.46	9.43	2.5	0.9
n-Octane	0.33	0.61	0.20	0.1	0.0
iso-Propylbenzene	0.09	2.2	0.21	0.1	0.0

Table A3 VII (continued):

Components	% wt/wt	MIR* (g O3/g NMHC)	Specific reactivity (MIR*%wt/wt)	PSR (% of specific reactivity relative to total values)	Error of propag-ation for PSR
n-Propylbenzene	0.17	2.1	0.36	0.1	0.0
m-/*p*-Ethyltoluene	0.72	7.2	5.22	1.4	0.7
Mesitylene	0.94	10.12	9.52	2.5	1.1
o-Ethyltoluene	0.13	7.2	0.90	0.2	0.2
1,2,4-Trimethylbenzene	0.02	8.80	0.17	0.0	0.1
n-Decane	0.00	0.46	0.00	0.0	0.0
unknown components	12.00	4.04	48.45	12.6	10.8
Total	100.00		384.67	100.0	19.6

*Incremental reactivities in units of grams ozone formed per gram VOC emitted for the ozone yield reactivity scale for the MIR scale (Carter 1994). The ROG /NOx ratios in the base case scenarios were within 3.9-11.6, which were considered for calculating MIR incremental reactivities by Carter (1994). ROG: reactive organic compounds.

Table A3 VIII: Percental contribution of POCP values (Derwent *et al.*, 1998) for the nonmethane hydrocarbons found in the Kiesberg tunnel, Wuppertal.

Compounds	% wt/wt	POCP*	Surrogat-es	POCP*% wt/wt	PCP (% of POCP index relative to total values)	Error of propaga-tion for PCP
Ethene	11.10	100.0	–	1110.41	17.71	6.15
Ethyne	4.75	8.5	–	40.41	0.64	0.22
Ethane	1.95	12.3	–	23.97	0.38	0.26
Propene	3.23	112.3	–	362.47	5.78	1.99
Propane	0.52	17.6	–	9.15	0.15	0.25
iso-Butane	1.95	30.7	–	59.95	0.96	0.32
iso-/1-Butene	2.32	85.3	–	197.70	3.15	1.33
1,3-Butadiene	1.81	85.1	–	154.42	2.46	0.84
n-Butane	4.00	35.2	–	140.84	2.25	0.74
trans-Butene	1.03	113.2	–	116.28	1.85	0.61
cis-Butene	0.57	114.6	–	65.09	1.04	0.34
3-Methyl-1-butene, unknown	0.22	67.1	–	14.97	0.24	0.10
iso-Pentane	7.57	40.5	–	306.52	4.89	1.58
1-Pentene	0.49	97.7	–	47.55	0.76	0.25
2-Methyl-1-butene	1.10	77.1	–	84.89	1.35	0.49
n-Pentane	1.82	39.5	–	71.86	1.15	0.36
Isoprene, *trans*-2-pentene	1.20	110.45	–	132.84	2.12	0.70
cis-2-Pentene	0.47	112.1	–	53.14	0.85	0.29
2-Methyl-2-butene	1.07	84.2	–	90.20	1.44	0.47
2,2-Dimethylbutane	0.38	24.1	–	9.20	0.15	0.05
Cyclopentene, 3-/4-methyl-1-pentene	0.65	87.4	1-Hexene	56.90	0.91	0.31
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	3.76	48.05	–	180.71	2.88	1.00
3-Methylpentane	1.10	47.9	–	52.85	0.84	0.28
2-Methyl-1-pentene	0.30	87.4	1-Hexene	26.18	0.42	0.14
n-Hexane	1.10	48.2	–	52.88	0.84	0.28
cis-3-Hexene, *trans*-2-hexene,unknown	0.25	107.3	–	27.15	0.43	0.15
cis-2-Hexene	0.11	106.9	–	11.60	0.19	0.07
Methylcyclopentane	0.46	29	Cyclo-hexane	13.22	0.21	0.07

Table A3 VIII (continued):

Compounds	% wt/wt	POCP*	Surrogat-es	POCP*% wt/wt	PCP (% of POCP index relative to total values)	Error of propaga-tion for PCP
2,4-Dimethylpentane	1.13	36.4	3-Methyl-hexane	41.23	0.66	0.22
Benzene	6.39	21.8	–	139.28	2.22	0.72
2-Methylhexane	0.49	41.1	–	20.34	0.32	0.12
Cyclohexane, 2,3-dimethylpentane	0.55	29	–	15.89	0.25	0.08
3-Methylhexane	0.56	36.4	–	20.56	0.33	0.11
iso-Octane	1.11	41.1	2-Methyl-hexane	45.63	0.73	0.26
n-Heptane	0.41	49.4	–	20.19	0.32	0.11
2,3-Dimethyl-2-pentene	0.02	107.3	*trans*-Hex-2-ene	2.36	0.04	0.04
Methylcyclohexane	0.38	29.9	Cyclohexane	11.23	0.18	0.06
2,3,4-Trimethylpentane	0.28	45.3	n-Octane	12.52	0.20	0.07
2-/3-Methylheptane	0.41	45.3	n-Octane	18.46	0.29	0.10
Toluene	10.69	63.7	–	681.25	10.87	3.55
Ethylbenzene	2.44	73	–	178.16	2.84	0.97
m-/*p*-Xylene	3.37	105.9	–	356.68	5.69	1.95
n-Nonane	0.02	41.4	–	0.66	0.01	0.00
Styrene	0.59	14.2	–	8.42	0.13	0.05
o-Xylene	1.46	105.3	–	153.74	2.45	0.84
n-Octane	0.33	45.3	–	14.99	0.24	0.08
iso-Propylbenzene	0.09	50	–	4.66	0.07	0.03
n-Propylbenzene	0.17	63.6	–	10.88	0.17	0.08
m-/*p*-Ethyltoluene	0.72	96.25	–	69.72	1.11	0.56
Mesitylene	0.94	138.1	–	129.90	2.07	0.93
o-Ethyltoluene	0.13	89.8	–	11.27	0.18	0.12
1,2,4-Trimethylbenzene	0.02	127.8	–	2.40	0.04	0.12
n-Decane	0.00	38.40	–	0.01	0.00	0.00
unknown components	12.00	65.6	average	784.63	12.52	6.94
Total	100.00		–	6268.44	100.00	14.87

* The POCPs calculated for standard, halved and doubled NO_x were generally similar (Derwent *et al.*, 1998).

Table A3 IX: List of the calculated percental MIR and POCP reactivities for the NMHC-mix in the city air of Wuppertal using the relative ratio of the average mixing ratio of individual NMHC to total NMHCs.

Components	Mean composition (%wt/wt relative to total NMHC)	MIR[1] (g O3/g NMHC)	% of total specific reactivity (PSR)*	Error of propagation for PSR	POCP[2]	PCP* (% of POCP index relative to total values)	Error of propagation for PCP
Ethene	4.27	7.4	9.49	6.14	100.0	7.39	4.71
Ethyne	6.40	0.5	0.96	0.56	8.5	0.94	0.54
Ethane	10.84	0.25	0.81	0.43	12.3	2.31	1.19
Propene	2.56	9.4	7.23	3.81	112.3	4.98	2.56
Propane	1.96	0.48	0.28	0.15	17.6	0.60	0.31
iso-Butane	2.55	1.21	0.93	0.49	30.7	1.36	0.70
iso-/1-Butene	4.40	7.11	9.39	4.94	85.3	6.49	3.76
1,3-Butadiene	0.88	10.9	2.87	2.50	85.1	1.29	1.11
n-Butane	7.88	1.02	2.42	1.35	35.2	4.81	2.64
trans-Butene	0.56	9.94	1.66	0.88	113.2	1.09	0.56
cis-Butene	0.49	9.94	1.47	0.77	114.6	0.98	0.50
3-Methyl-1-butene	1.08	6.2	2.00	1.06	67.1	1.25	0.64
iso-Pentane	6.91	1.38	2.87	1.51	40.5	4.85	2.50
1-Pentene	0.80	6.2	1.50	0.79	97.7	1.36	0.70
2-Methyl-1-butene	1.68	4.9	2.48	1.31	77.1	2.25	1.16
n-Pentane	2.98	1.04	0.93	0.49	39.5	2.04	1.05
Isoprene, *trans*-2-pentene	1.50	8.95	4.02	2.12	110.45	2.86	1.47
cis-2-Pentene	0.33	8.8	0.88	0.46	112.1	0.64	0.33
2-Methyl-2-butene	1.39	6.4	2.68	1.41	84.2	2.03	1.05
2,2-Dimethylbutane	0.43	0.82	0.11	0.06	24.1	0.18	0.09
Cyclopentene, 3-/4-methyl-1-pentene	0.17	7.7	0.40	0.21	87.4	0.26	0.13
Cyclopentane, 2,3-dimethylbutane, 2-methylpentane	4.68	1.66	2.33	1.41	48.05	3.89	2.06
3-Methylpentane	1.06	1.53	0.49	0.26	47.9	0.88	0.45
2-Methyl-1-pentene	0.24	4.4	0.32	0.17	87.4	0.37	0.19
n-Hexane	1.30	0.98	0.38	0.20	48.2	1.09	0.56
cis-3-Hexene, *trans*-2-hexene	0.24	6.7	0.48	0.25	107.3	0.44	0.23
cis-2-Hexene	0.11	6.7	0.23	0.12	106.9	0.21	0.11
Methylcyclopentane, 2,4-dimethylpentane	1.20	2.16	0.78	0.47	29	0.60	0.31
Benzene	4.77	0.42	0.60	0.33	21.8	1.80	0.98
2-Methylhexane	0.52	1.08	0.17	0.09	41.1	0.37	0.19
Cyclohexane/ 2,3-Dimethylpentane	1.18	1.30	0.46	0.24	29	0.59	0.30
3-Methylhexane	1.17	1.4	0.49	0.26	36.4	0.74	0.38
iso-Octane	0.78	0.93	0.22	0.11	41.1	0.56	0.29
n-Heptane	0.79	0.81	0.19	0.10	49.4	0.67	0.35
2,3-Dimethyl-2-pentene	0.12	5.5	0.19	0.10	107.3	0.22	0.11
Methylcyclohexane	0.82	1.85	0.46	0.24	29.9	0.43	0.22
2,3,4-Trimethylpentane	0.22	1.6	0.11	0.06	45.3	0.17	0.09
2-/3-Methylheptane	0.53	0.98	0.15	0.08	45.3	0.41	0.21
Toluene	9.52	2.73	7.82	4.11	63.7	10.51	5.41
Ethylbenzene	1.30	2.7	1.06	0.56	73	1.65	0.85
m-/*p*-Xylene	2.46	7.69	5.69	3.05	105.9	4.52	2.34

Table A3 IX (continued):

Components	Mean compo-sition (%wt/wt relative to total NMHC)	MIR[1] (g O3/g NMHC)	% of total specific reactivi-ty (PSR)*	Error of propagation for PSR	POCP[2]	PCP* (% of POCP index relative to total values)	Error of propagation for PCP
n-Nonane	0.10	0.54	0.02	0.01	41.4	0.07	0.04
Styrene	1.20	2.2	0.79	0.42	14.2	0.29	0.15
o-Xylene	1.23	6.46	2.39	1.26	105.3	2.24	1.15
n-Octane	0.19	0.61	0.03	0.02	45.3	0.15	0.08
iso-Propylbenzene	0.20	2.2	0.13	0.07	50	0.17	0.09
n-Propylbenzene	0.12	2.1	0.07	0.04	63.6	0.13	0.07
m-/*p*-Ethyltoluene	0.64	7.2	1.39	0.73	96.25	1.07	0.55
Mesitylene	0.18	10.12	0.56	0.29	138.1	0.44	0.23
o-Ethyltoluene	0.33	7.2	0.71	0.37	89.8	0.51	0.26
1,2,4-Trimethylbenzene	0.48	8.80	1.27	0.90	127.8	1.07	0.74
n-Decane	0.24	0.46	0.03	0.02	38.40	0.16	0.10
tert-Butylbenzene	0.09	1.9	0.05	0.03	50	0.08	0.04
unknown components	12.00	4.03	14.53	14.42	65.31	13.53	10.02
Total	100.00	–	100.00	25.30	–	100.00	20.03

(1):Incremental reactivities in units of grams ozone formed per gram VOC emitted for the ozone yield reactivity scale for the MIR scale (Carter, 1994), (2): The POCPs calculated for standard, halved and doubled NOx were generally similar (Derwent *et al.*, 1998). * PSR and PCP were determined using similar procedures as shown in Table A3 VII and Table A3 VIII respectively.

Table A3 X: An overview of the calculated percental reactivities for the tunnel air and the city air of Wuppertal.

Scales	Tunnel air of Wuppertal					City air of Wuppertal (average values)			
	Classes	position 1	position 2	position 3	% contribution	position 1	position 2	position 3	% contribution
OH-reactivity	alkanes	*iso*-Pentane	Cyclopentane/*	*n*-Butane	7.65±0.95	*iso*-Pentane	Cyclopentane/*	*n*-Butane$^{\#}$	9.89±1.26
	%	1.76±0.66	1.28±0.49	0.61±0.23		1.58±0.66	1.56±0.66	1.19±0.55	
	alkenes	1,3-Butadiene	Isoprene/*	Ethene	54.12±6.53	*iso*-/1-Butene	Isoprene/*	2-Methyl-2-butene	52.53±7.72
	%	7.60±2.97	6.35±2.74	5.95±2.35		8.51±3.59	7.75±3.62	7.47±3.15	
	aromatics	Toluene	*m*-/*p*-Xylene	Styrene	19.12±3.28	Styrene	Toluene	*m*-/*p*-Xylene	18.88±3.92
	%	4.01±1.51	3.98±1.55	3.95±1.65		7.82±3.29	3.50±1.47	2.86±1.20	
	unidentified				19.11±22.31				18.70±22.63
MIR	alkanes	*iso*-Pentane	Cyclopentane/*	*n*-Butane	9.69±1.30	*iso*-Pentane	*n*-Butane$^{\#}$	Cyclopentane/*	14.66±2.71
	%	2.72±0.91	1.62±0.73	1.06±0.36		2.87±1.51	2.42±1.35	2.33±1.41	
	alkenes	Ethene	Propene	1,3-Butadiene	53.93±8.68	Ethene	*iso*-/1-Butene	Propene	48.28±9.74
	%	21.36±7.66	7.89±2.81	5.14±1.82		9.49±6.14	9.39±4.94	7.23±3.81	
	aromatics	Toluene	*m*-/*p*-Xylene	Mesitylene	23.78±3.96	Toluene	*m*-/*p*-Xylene	*o*-Xylene	22.53±5.48
	%	7.59±2.57	6.73±2.47	2.47±1.13		7.82±4.11	5.69±3.05	2.39±1.26	
	unidentified				12.59±10.78				14.53±14.42
POCP	alkanes	*iso*-Pentane	Cyclopentane/*	*n*-Butane	18.23±2.19	*iso*-Pentane	*n*-Butane$^{\#}$	Cyclopentane/*	26.93±4.67
	%	4.89±1.58	2.88±1.00	2.25±0.74		4.85±2.50	4.81±2.64	3.89±2.06	
	alkenes	Ethene	Propene	*iso*-/1-Butene	41.39±6.79	Ethene	*iso*-/1-Butene	Propene	35.07±7.12
	%	17.71±6.15	5.78±1.99	3.15±1.33		7.39±4.71	6.49±3.76	4.98±2.56	
	aromatics	Toluene	*m*-/*p*-Xylene	Ethylbenzene	27.86±4.45	Toluene	*m*-/*p*-Xylene	*o*-Xylene	24.47±6.22
	%	10.87±3.55	5.69±1.95	2.84±0.97		10.51±5.41	4.52±2.34	2.24±1.15	
	unidentified				12.52±6.94				13.53±10.02

Cyclopentane/*: coeluted peak containing cyclopentane, 2,3-dimethylbutane, 2-methylpentane; isoprene/*: coeluted peak inclusive *trans*-2-pentene. Positions: indicate the descending orders of components within a class of NMHCs, *e.g.* position 1 denotes the highest percental contribution within the respective class of NMHCs and so on. The percental numbers indicate the contribution relative to the total NMHCs; #:coeluted with 1,3-butadiene, but separated by assuming 10±7% contribution from 1,3-butadiene and 90±7% contribution from *n*-butane as reported by other studies for German cities (Schmitz *et al.*, 1997; Mannschreck, 2000).

9 Annex-Figures

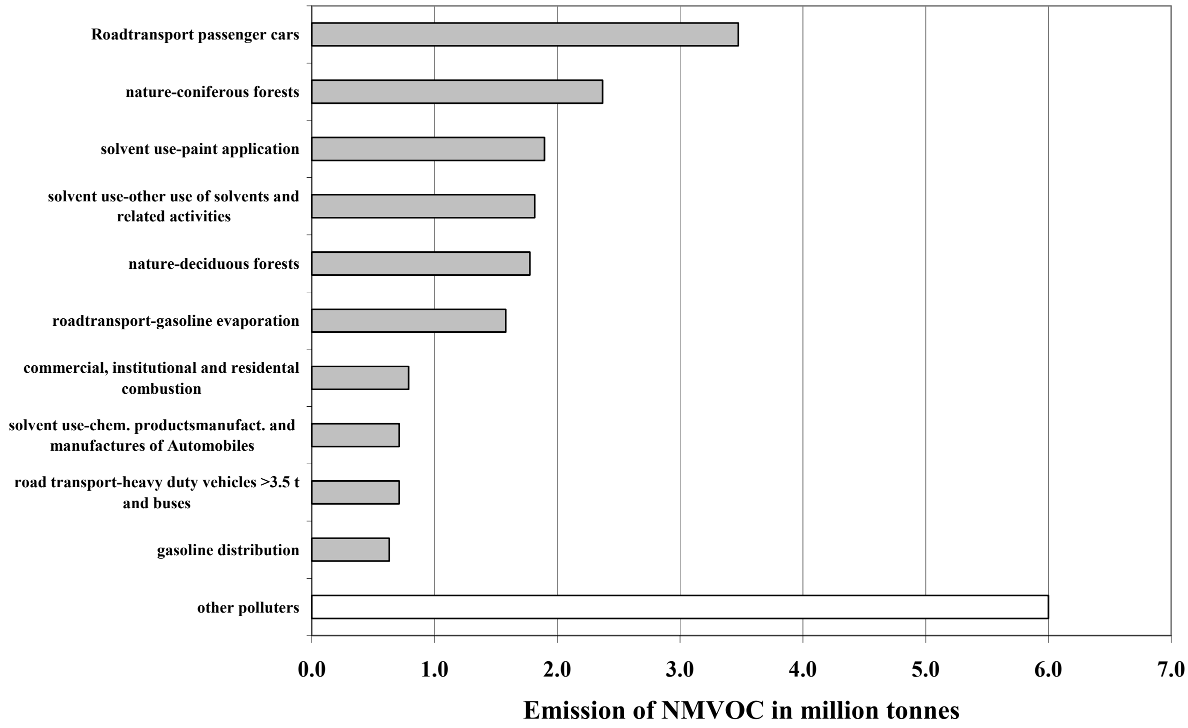


Figure A1 I: The graphic presentation of the different sources of NMVOCs in Europe (Grösslinger *et al.*, 1996).

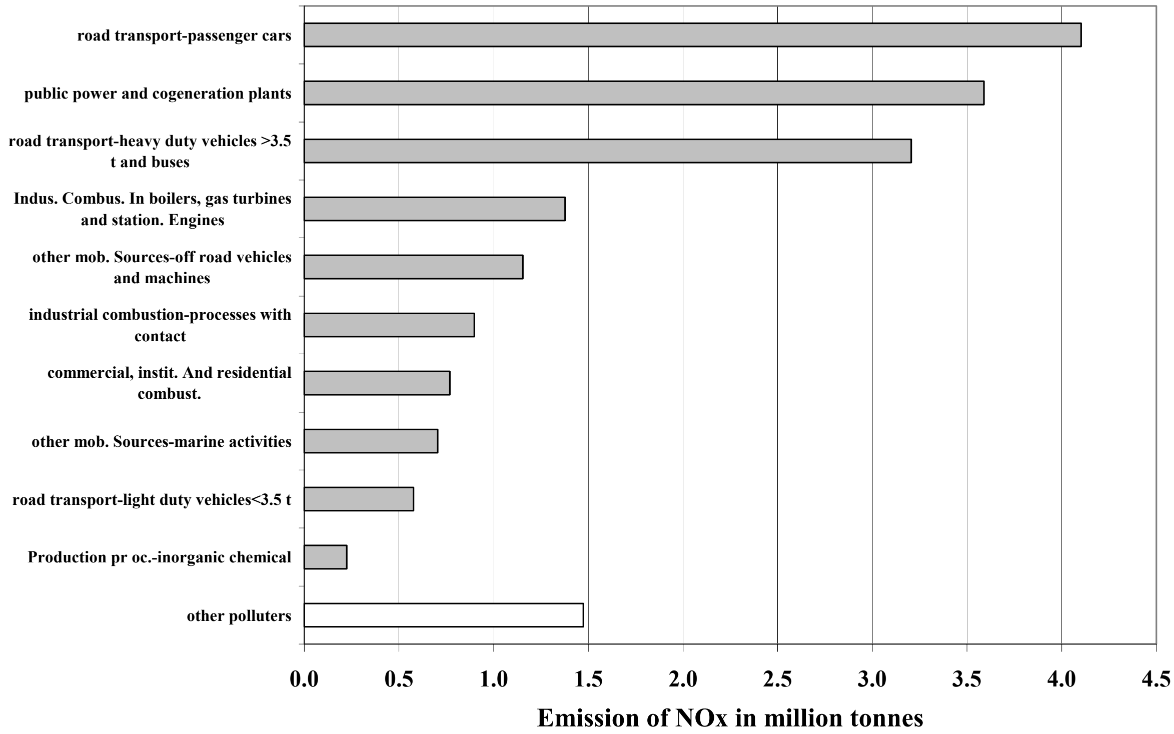
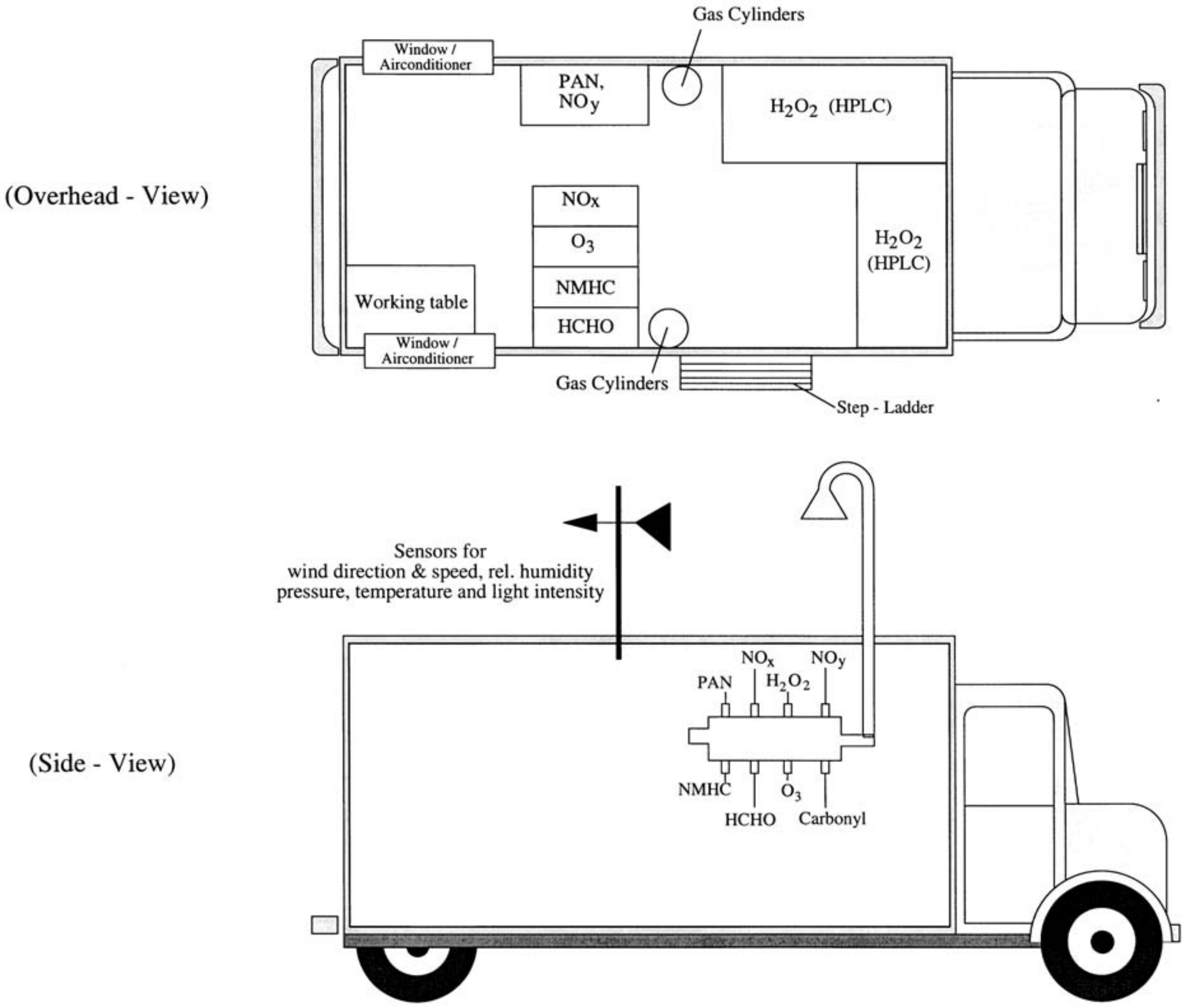
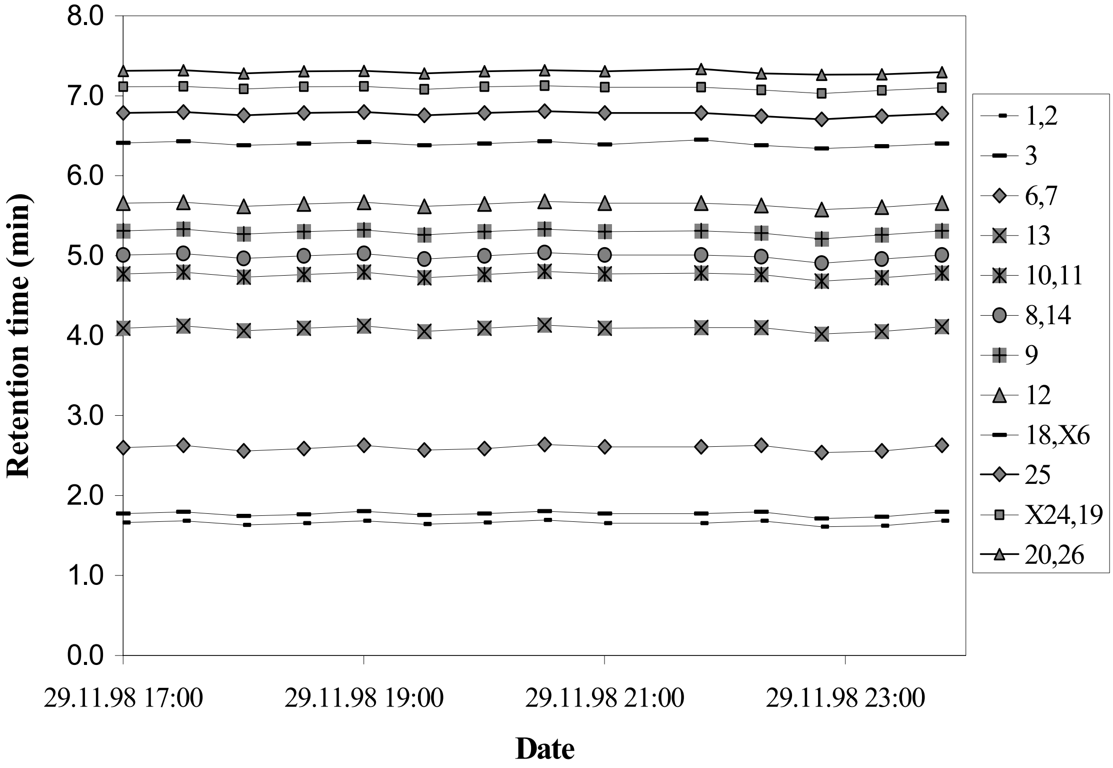


Figure A1 II: Graphic presentation of the different sources of NO_x in Europe (Source: Grösslinger *et al.*, 1996).



* H_2O_2 and carbonyl compounds were measured by other groups

Figure A2 I: Overhead-view and the side-view of the mobile laboratory used for ambient air measurements for the city of Wuppertal and Menz.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5.0
4.0
3.0
2.0
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Retention time (min)
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29.11.98 19:00
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29.11.98 23:00
Date
1,2
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10,11
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12
18,X6
25
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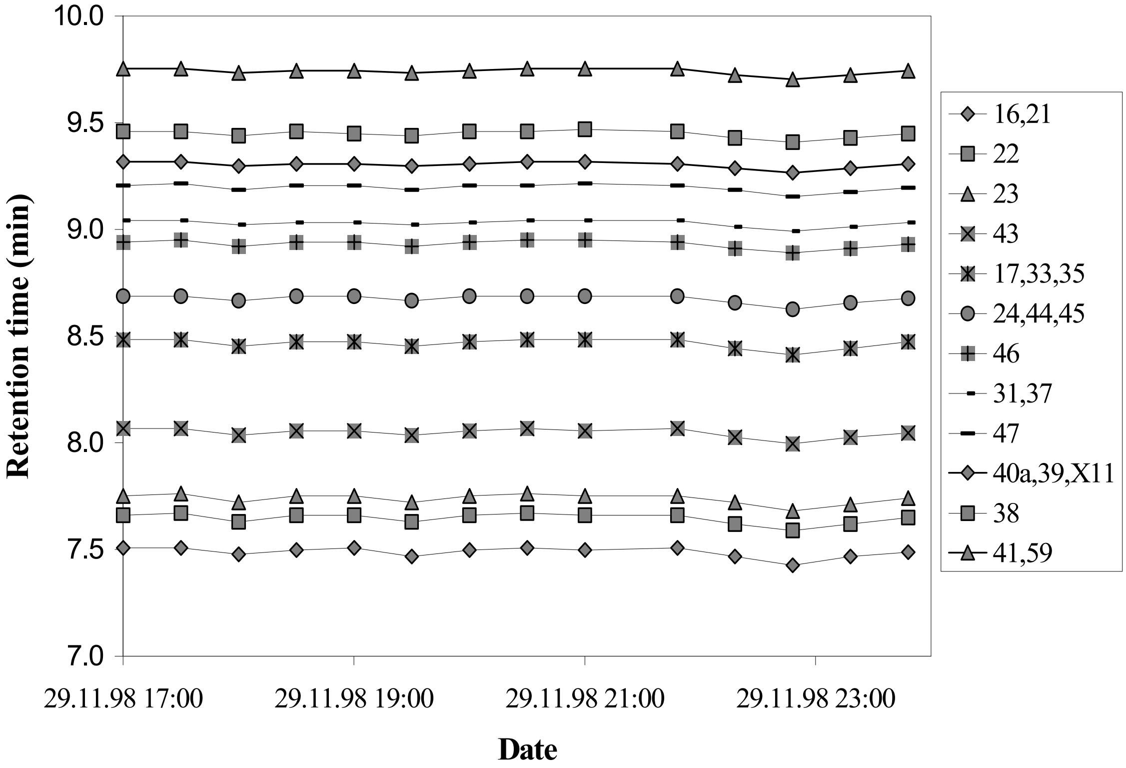
20,26

A2 II (a)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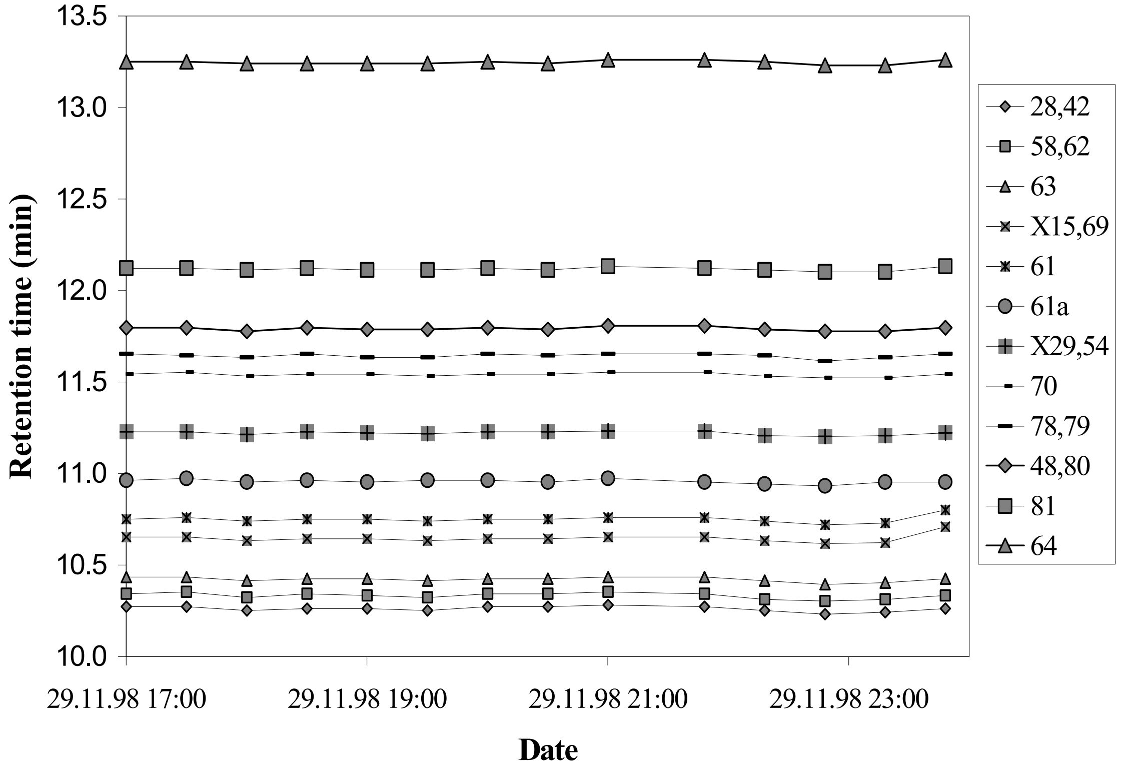
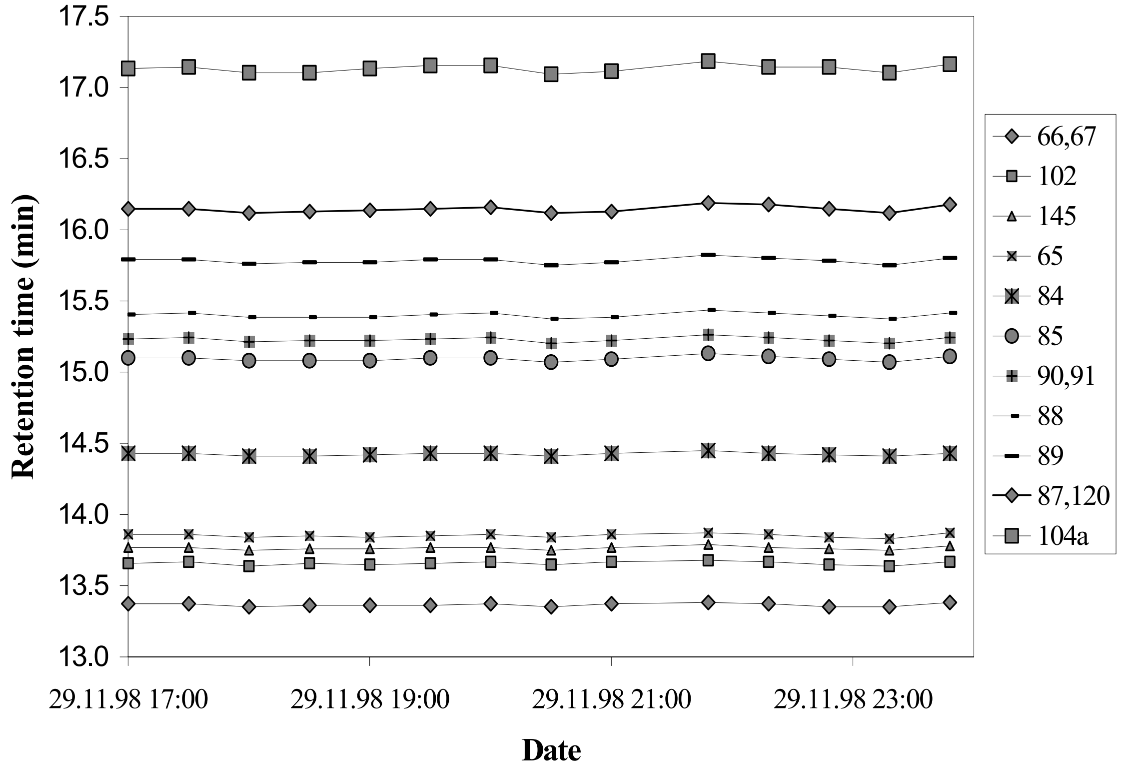
A2 II (b)

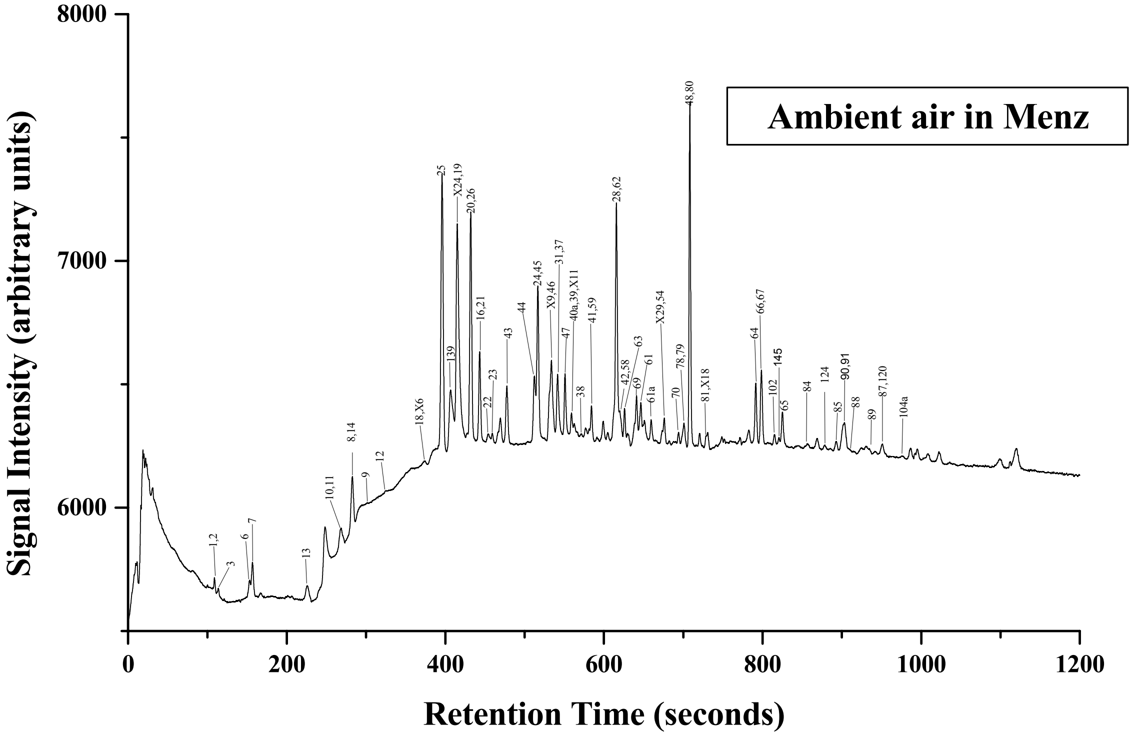


A2 II (c)

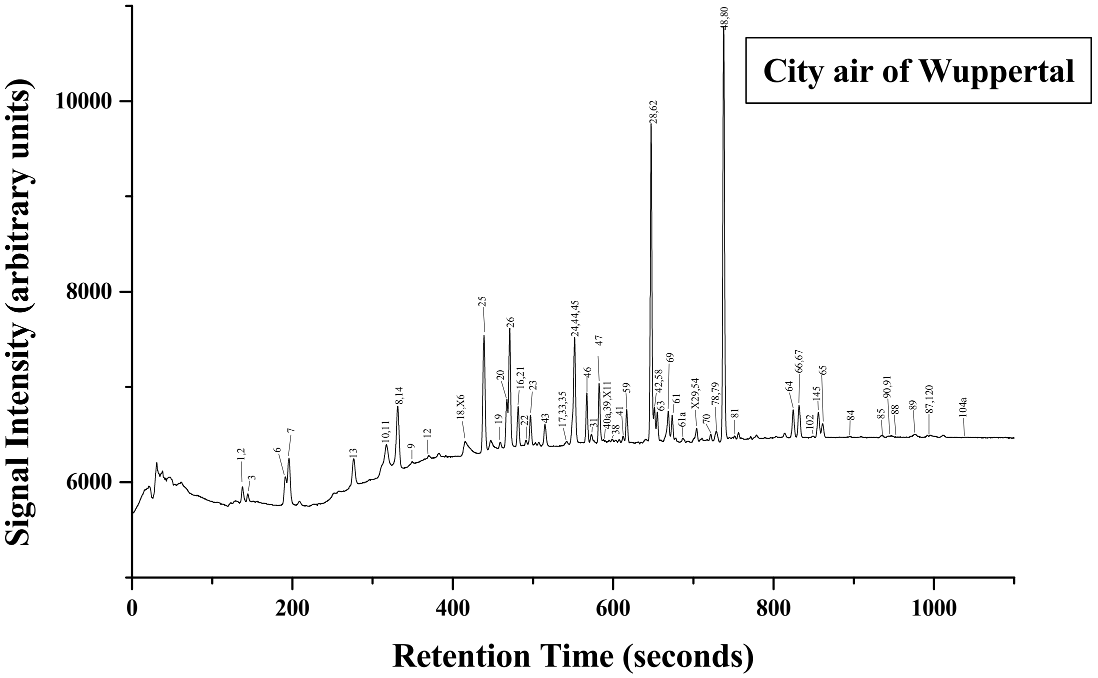


A2 II (d)

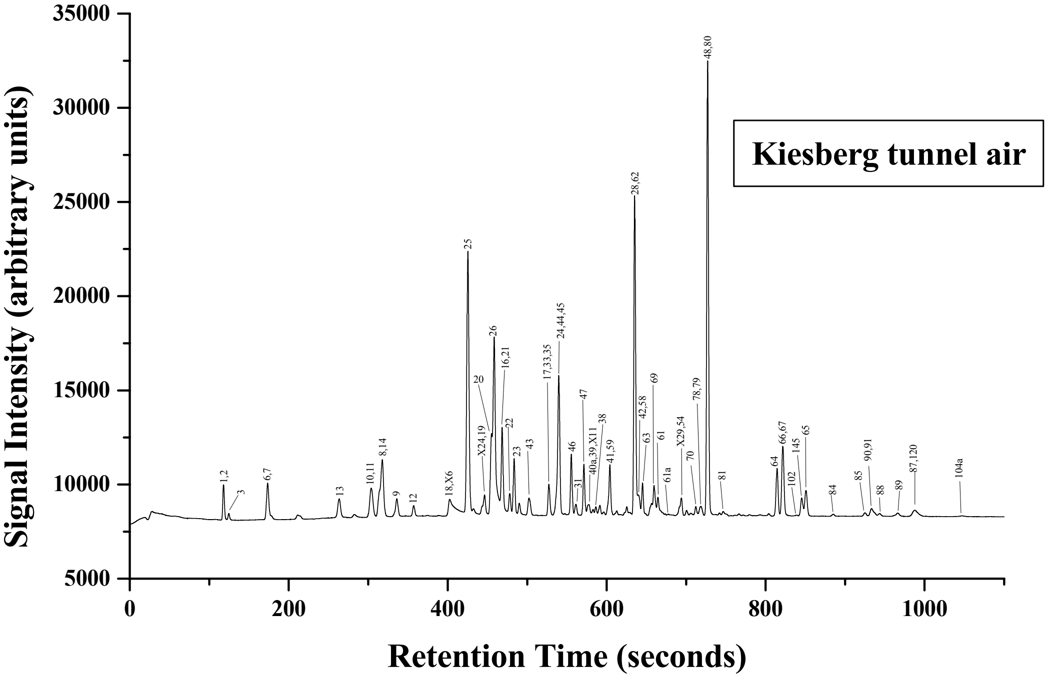
Figure A2 II (a-d): Variation of the gross retention time of NMHCs detected by the Airmovoc 2010 gas chromatograph in tunnel air. The numbers in the legend indicate the nonmethane hydrocarbons as shown in **Table 2.3**.



A2 III (a)



A2 III (b)



A2 III (c)

Figure A2 III: Typical chromatograms obtained for the air of (a) Menz, (b) the city of Wuppertal and (c) Kiesberg tunnel. The numbers indicate the components as described in **Table 2.3**.

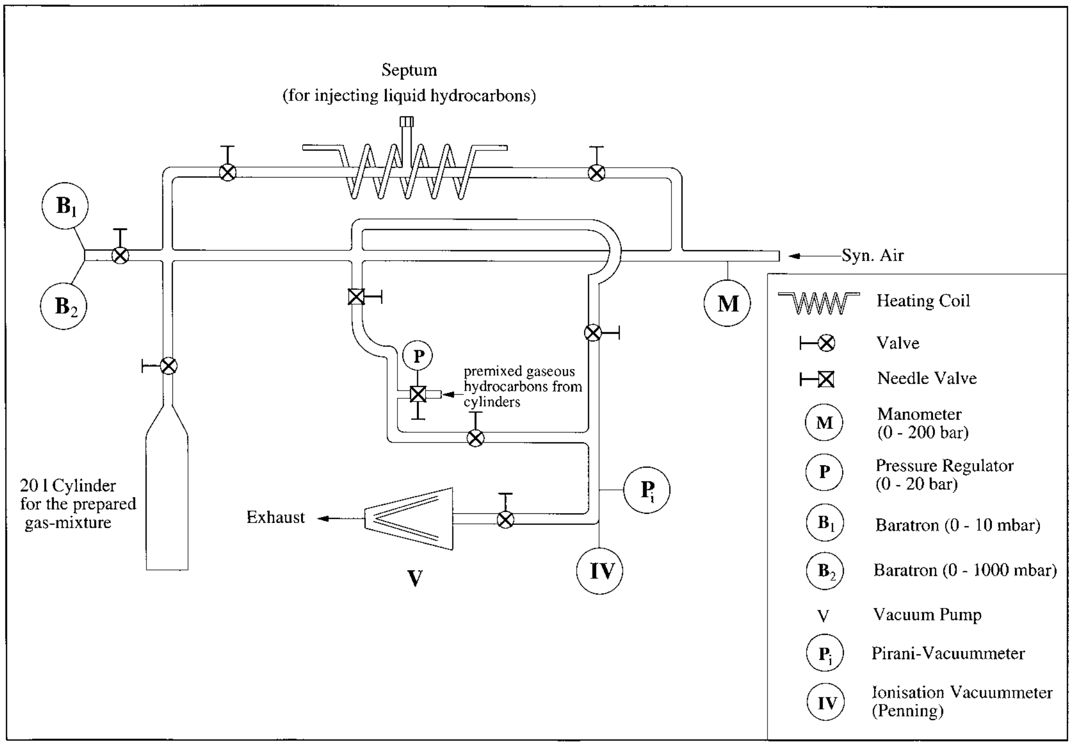
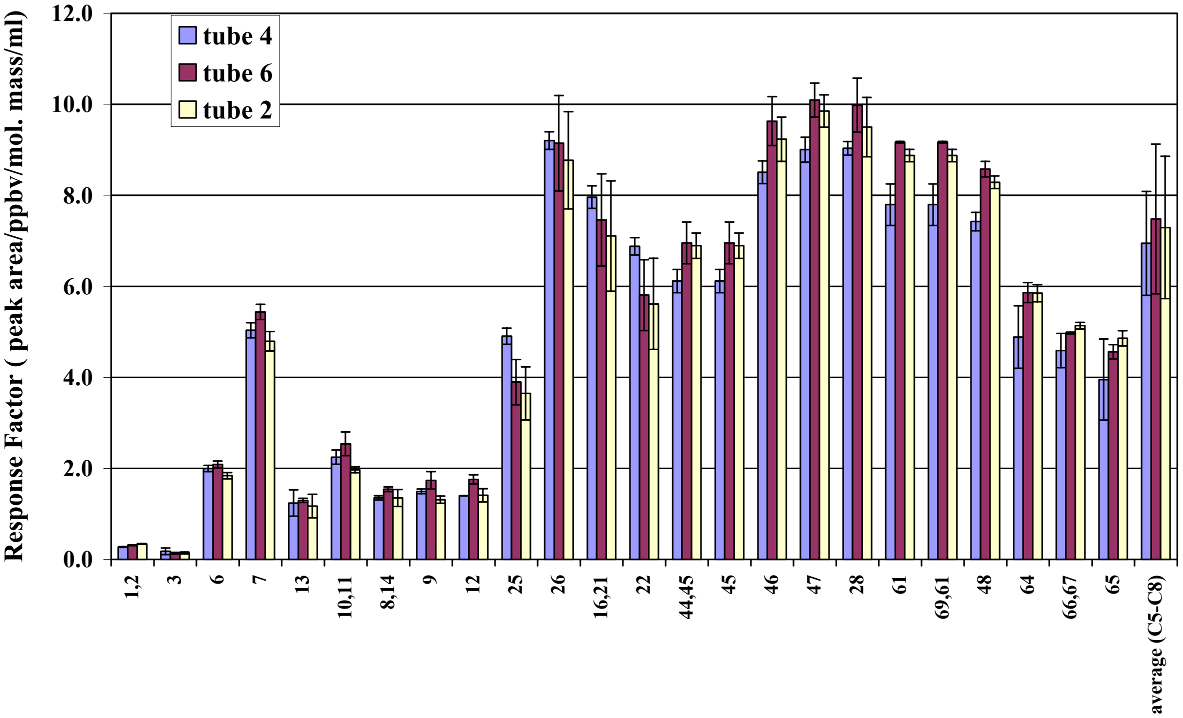


Figure A2 IV: Instrumental set-up for the preparation of the standard gas mixture used for the tunnel measurement campaigns, occurred in August 1997 and in March 1998.



The average response factor of the components having carbon number in between C_5-C_8 gave an average error of 20%.

Figure A2 V: A typical bar diagram showing the response factors (peak area/ppbv/mol. mass/ml) for the nonmethane hydrocarbons present in the NPL standard gas mixture for the three adsorption tubes used during measurements in the city air of Wuppertal.