

# Large decrease of VOC emissions of Switzerland's car fleet during the past decade: results from a highway tunnel study

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## Abstract

The emissions of 14 C<sub>4</sub>–C<sub>8</sub> VOC species from road traffic have been measured in a highway tunnel (Gubristtunnel) near Zurich, Switzerland in 2002. The investigated traffic situation corresponds to highway driving with an average speed of 90 km h<sup>-1</sup> and hot engine conditions. The comparison with measurements in the same tunnel performed in 1993 indicates that the emission factors of the individual hydrocarbons decreased on average by 80% in the 9 years between both investigations. This improvement can mainly be explained by the nearly complete elimination of non-catalyst gasoline-fuelled cars from the Swiss car fleet in the past decade. The relative emission strengths of the quantified individual VOCs were similar in 1993 and 2002. The emission factors reported in this study are the lowest reported from on-road vehicle emission measurements so far, indicating the efficient technology of modern car fleets with respect to VOC emissions. The emission factors derived from the tunnel study are compared to modelled emission factors based on dynamometric test measurements on Swiss passenger cars. The employed model is the Handbuch für Emissionsfaktoren des Strassenverkehrs; version 1.2 (Umweltbundesamt Berlin and INFRAS AG Bern, 1999). A good agreement between the modelled and measured emissions was found for the investigated traffic situation, indicating that the development of the VOC emissions during the last decade is well understood on the basis of the fleet composition and the dynamometric test measurements. The observed VOC emission reduction corresponds to a traffic situation, where an optimal exhaust gas catalyst performance can be expected. Factors leading to a somewhat less beneficial influence of the catalytic converter technique in other relevant driving situations are therefore additionally discussed.

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## 1. Introduction

Road traffic is a major emission source for many important air pollutants, such as nitrogen oxides, carbon oxides, hydrocarbons or particles. There are two widely used methods to determine vehicular

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emission profiles: dynamometer tests on individual vehicles and outdoor studies nearby busy roads or in road tunnels. The two types of methods have complementary strengths and weaknesses. Tunnel studies allow the determination of the average emissions of large numbers of vehicles, but it is difficult to generalize tunnel measurements to other driving conditions. Dynamometric tests are very suitable to investigate the influence of different driving conditions on the emission of vehicles (Heeb et al., 2000, 2002, 2003). Road traffic emission models are based on extended dynamometric test data, but it is difficult to evaluate their uncertainties because of the many variables incorporated in state-of-the-art emission models. Road tunnel measurements can be used to evaluate road traffic emission models and to assess the achievements of new technologies, particularly if repeated measurements are performed in the same tunnel.

In this study, the emission factors of a selection of 14 important hydrocarbon exhaust components have been investigated in a highway tunnel in Switzerland in September and October 2002. In September 1993, a similar investigation took place at the same site and under very similar conditions (Stahelin et al., 1995, 1997, 1998; John et al., 1999). The results of the present study therefore allow the documentation of the improvements of Switzerland's car fleet with respect to VOC emissions during the last 9 years. This period is sufficiently long for a substantial turnover of the car fleet (in the Swiss registered averaged fleet 70% of the passenger cars and 65% of the delivery vans and trucks are newer than 9 years in September 2002 (BFS, 2003)). This allows assessing the success of new emission reduction technologies and of new emission regulations within the Swiss car fleet.

In Switzerland, new gasoline-powered cars have been equipped with 3-way catalysts since 1986. As a consequence, the fraction of gasoline-fuelled passenger cars that are equipped with a catalyst has increased from 62.1% in 1993 to 93.3% in 2002 (BFS, 2003). In the same period the fraction of diesel-fuelled passenger cars has increased from 2.8 to 5.8% (BFS, 2003). During this period also fuel composition changed. Before 1997, Swiss gasoline had on average a benzene content of about 2.4 vol% and the maximum tolerable level was 5 vol% (BUWAL, 1999; Heeb et al., 2000). The benzene content in gasoline has been gradually reduced, and since 2000 the tolerable level has been set to 1 vol% (BUWAL, 1999). In parallel to technical improvements of the newer car generations, also stricter regulations in respect to emission strengths were introduced in Switzerland. In the mid-1990s these regulations were harmonized with the European directives, leading to the introduction of the EURO-2 and EURO-3 emission norms. These regulations refer only to cars which are set in operation after the respective rules came into force,

and therefore their impact increases corresponding to the turnover ratio of the car fleet.

## 2. Experimental

### 2.1. Description of the tunnel and of the traffic situation

The Gubristtunnel is located on the highway bypassing the town area of Zurich, Switzerland, in the north–west direction. It is located about 9 km from the city centre. The tunnel is a two-bore tunnel with two lanes in each direction and has a length of 3270 m. Each tube has a cross section of 48 m<sup>2</sup>. The traffic speed is limited to 100 km h<sup>-1</sup>. No forced ventilation was in action during the study, and therefore ventilation was caused by the piston effect of the traffic flow. The measured mean air velocity was 5.6 m s<sup>-1</sup> with a variation of 2.2 m s<sup>-1</sup> (1 $\sigma$  of 5 min averages). The investigation was restricted to the slightly ascending tunnel tube, which has a road gradient of 1.3%. The two sampling positions for the VOC analyses were 200 m inside from the entrance portal of the tunnel and about 10 m before the tunnel exit, respectively. The air was sampled about 1.5 m above the road level at both positions. The number of vehicles passing the tunnel, the composition of the fleet and their speeds were measured by automatic loop detectors. On average, about 1800 passenger cars and 140 trucks were passing the tunnel per hour during the measurement period and the measured mean traffic speed was 90  $\pm$  8 km h<sup>-1</sup> (1 $\sigma$  of 5 min averages).

The Environmental Agency of the Kanton Zurich (AWEL) and the regional air quality association 'Ostluft' started measurements in the Gubristtunnel already in 1990 and repeated the measurements of nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO) and total non-methane volatile organic compounds (t-NMVOCs) nine times since then (Zumsteg and Steinemann, 2003). This publication includes more detailed information on the traffic counts, the wind speed measurements and the tunnel design. The results of these measurements will be discussed in forthcoming papers (Colberg et al., 2004a, b). Results of Gubristtunnel measurements of refrigerant losses from mobile air conditioning units (Stemmler et al., 2004) and of particle emissions from road traffic have been reported earlier (Weingartner et al., 1997).

### 2.2. Sampling and analysis

The measurements of organic compounds took place from 17 September to 20 October 2002. During this period the measurement was continuously running for 27 days (17 working days and 10 weekend days).

*Measurements at the tunnel exit:* The analytical setup has been described previously (Stemmler et al., 2004) and is therefore described only briefly. At the exit site, the VOC analyses were performed in situ with an automated gas chromatograph, equipped with a mass-

spectrometer detector (GC–MS, Agilent 5793N). The organic compounds were preconcentrated by an automated adsorption–desorption system (ADS) developed at the University of Bristol (Simmonds et al., 1995). The sampling period for each analysis was 20 min. The

Table 1

Mean mixing ratios of organic exhaust gases in the Gubristtunnel during the experiment in 2002, resulting average emission factors for the vehicle fleet and comparison with results from previous western European tunnel studies

Compound	Mean mixing ratio in the Gubristtunnel 2002		Average emission factors (all vehicles) (mg km <sup>-1</sup> )					
	Entrance <sup>g</sup> (ppb)	Exit <sup>h</sup> (ppb)	Gubrist <sup>a</sup> tunnel Switzerland 2002	Tauern <sup>b,c</sup> tunnel Austria 1997	Thiasis <sup>b,d</sup> tunnel France 1996	Tingstad <sup>c</sup> tunnel Sweden 1994	Gubrist <sup>f</sup> tunnel Switzerland 1993	Tauern <sup>b,c</sup> tunnel Austria 1988
<i>n</i> -Butane	1.68	7.76	2.6±0.4		36±20			
Isobutane	0.68	2.86	0.9±0.1		15±7			
1-Butene	0.77	2.17	0.6±0.1		6.6±4			
<i>trans</i> -Butene	0.17	0.90	0.30±0.04		4.8±4			
<i>cis</i> -Butene	0.14	0.65	0.21±0.04		3.5±3			
<i>n</i> -Pentane	1.04	4.12	1.6±0.3		8±3		10.81	
Isopentane	2.99	14.8	6.2±0.7		95±43			
<i>n</i> -Hexane	0.28	1.22	0.6±0.1	3.6±1.0	3±2		2.94	5.3±1.8
3-Methylpentane	0.42	1.59	0.7±0.1		5.7±4		3.78	
Benzene	1.44	6.65	2.7±0.3	7.9±2.0		52	13.69	101±10
Toluene	3.76	14.5	6.4±0.8	16.9±4.8		120	26.27	173±17
Ethylbenzene <sup>o</sup>	n.a.	2.28	1.4±0.2	3.6±1.0		22	4.29	26.4±1.6
<i>m/p</i> -Xylene <sup>o</sup>	n.a.	5.98	4.0±0.5	12.1±3.6		65	15.49	88±6.6
<i>o</i> -Xylene <sup>o</sup>	n.a.	2.63	1.8±0.2	5.7±1.5		24	7.76	33±1.7
<i>Traffic composition and driving conditions</i>								
Tunnel experiment and date			Gubrist 2002	Tauern 1997	Thiasis 1996	Tingstad 1994	Gubrist 1993	Tauern 1988
Mean traffic speed (km h <sup>-1</sup> )			90±7	74±5	~60	~70	92	63±14
Fraction of non-catalyst gasoline vehicles among the passenger cars (%)			2.7 <sup>i</sup> /6.2 <sup>j</sup>	33 <sup>k</sup>	~95 <sup>l</sup>	~40 <sup>m</sup>	33 <sup>j</sup> /37 <sup>j</sup> /23 <sup>n</sup>	~100 <sup>k</sup>
Average fraction of heavy duty vehicles in the tunnel (%)			7	17.6	6	~10	9	9
Road gradient in the tunnel (%)			1.3	1.5	~0	-4 to +4	1.3	1.5

<sup>a</sup>Error limits are for 95% confidence intervals.

<sup>b</sup>Error limits are the standard deviations.

<sup>c</sup>Schmid et al. (2001).

<sup>d</sup>Touaty and Bonsang (2000).

<sup>e</sup>Sjödén et al. (1998).

<sup>f</sup>Stahelin et al. (1995, 1997, 1998).

<sup>g</sup>Canister measurements.

<sup>h</sup>Online GC–MS measurements.

<sup>i</sup>Derived from the Swiss car fleet composition weighted over the annual driving distances of the vehicle subclasses (UBA, 1999).

<sup>j</sup>Derived from the vehicle statistics of Switzerland.

<sup>k</sup>Derived from vehicle statistics.

<sup>l</sup>Estimated by Sallés et al. (1998).

<sup>m</sup>Estimation from a comparable study (see Sjödén et al., 1998).

<sup>n</sup>Based on individual vehicle identification, from license plate decoding, during the tunnel experiment.

<sup>o</sup>For the C<sub>8</sub>-aromatic compounds no measurements at the tunnel entrance are available. For the calculations according to Eq. (1) we assumed entrance concentrations of 23% of the concentrations at the tunnel exit (in analogy with the ratios found for the other compounds).

chromatographic separation is achieved with a  $120 \times 0.32$  mm CP-SIL 5CB capillary column (Chrom-pack) with  $5 \mu\text{m}$  film thickness and the individual compounds are detected by single-ion mass spectrometry of selected characteristic ions. By this analytical method, 14 individual hydrocarbons ( $\text{C}_4$ – $\text{C}_8$ ) are automatically analysed every 2 h (based on 20 min sampling times). Each tunnel air measurement is associated to two-field calibration standard injections performed immediately before and after the measurement. This field air standard was an ambient air mixture collected at Dübendorf, a town in the agglomeration of Zurich, and was stored in a 35 L SUMMA treated canister (Essex). The field standard was calibrated against a 30-component VOC standard containing the individual compounds in the 1–10 ppb range (National Physical Laboratory (NPL), England). The main reason for not using the NPL 30 component mixture as the field standard was the need to calibrate the field standard additionally for automobile air condition refrigerants, which have been measured simultaneously (Stemmler et al., 2004).

*Measurements at the tunnel entrance:* At the entrance no automated analyses of the hydrocarbons were performed. Therefore, air samples have been taken by pumping air at a constant rate through a mass flow controller into air sampling canisters. In total, 16 air samples with individual sampling periods between 20 min and 5.6 days have been taken. The total sampling time of all canisters was 16 days. Nine of these canister samples had a sampling time of 20 min and were taken simultaneously to individual GC–MS measurements at the tunnel exit and seven tanks have been sampled for longer periods (6 h, 10 h, 1.0 d, 2.7 d, 2.9 d, 2.9 d and 5.6 d) to obtain average VOC concentrations at the tunnel entrance. These air samples have been analysed offline by the GC–MS method described above within 3 days after collection. Table 1 gives the observed mean mixing ratios of the VOCs at the tunnel exit and entrance respectively. No measurements for the  $\text{C}_2$ -benzenes were obtained at the tunnel entrance as these compounds were judged to be too unstable in air sampling canisters for reliable measurements (Stahelin et al., 1998; Zielinska et al., 1996).

### 3. Results and discussion

Fig. 1 shows the observed concentrations of a selection of the measured hydrocarbons in the Gubrist-tunnel. During working days the concentrations display the well-known morning and evening rush hours, whereas on weekends the main traffic period starts later and the traffic density is more evenly distributed over the day. As shown in Panel B, the heavy duty vehicles traffic is restricted mainly to working days and takes place

mainly between 5 am and 7 pm. In Switzerland, heavy duty traffic is forbidden during night (22 pm to 5 am) and on Sundays, except with a special permit (e.g. for food transports). Panel A shows that the relative emission strength pattern of the investigated hydrocarbons is not significantly different on weekends, when heavy duty traffic is low compared with weekdays. Fig. 1 Panel B shows additionally the measured wind speed in the tunnel for the selected period. It can be seen that the wind speed is strongly dependent on traffic density in the tunnel. On working days when many trucks travelling through the tunnel, maximal wind speeds of around  $8 \text{ m s}^{-1}$  are measured, whereas on weekends when mainly passenger cars cross the tunnel, the highest wind speeds are around  $6 \text{ m s}^{-1}$ .

The measured hydrocarbon species represent a selection (see Table 1), which is typical for gasoline-driven vehicle exhaust. These compounds are not only among the most emitted hydrocarbons from gasoline-powered cars, they are also found to be major components in gasoline itself. The strong correlation between exhaust gas and gasoline composition has been shown in many studies (Fraser et al., 1998; Gertler et al., 1996; McLaren et al., 1996; Broderick and Marnane, 2002; Duffy et al., 1999). The selection is however less characteristic for the emission of diesel engines, as none of the  $\text{C}_{10}$ – $\text{C}_{20}$  *n*-alkanes nor  $\text{C}_2$  and  $\text{C}_3$  unsaturated hydrocarbons, which are important diesel exhaust components (Sagebiel et al., 1996; Schauer et al., 1999; Siegl et al., 1999; Schmitz et al., 2000; Zielinska et al., 1996), have been measured in this study.

Average emission factors can be calculated for each sampling period on the basis of the differences in the concentrations at the exit and the entrance of the tunnel, the measured air flow in the tunnel and the traffic density using Eq. (1):

$$\text{EF}_{\text{mass/distance}} = \frac{\Delta C_p V_{\text{air}} t_{\text{sample}} A_{\text{tunnel}}}{n_{\text{vehicles}} l_{\text{tunnel}}}, \quad (1)$$

where  $\text{EF}_{\text{mass/distance}}$  is the mean emission factor per car for a given compound expressed as emitted mass per travelled distance,  $\Delta C_p$  is the difference in concentration of the pollutant (tunnel exit–tunnel entrance),  $V_{\text{air}}$  is the air velocity in the tunnel,  $A_{\text{tunnel}}$  is the tunnel cross-section,  $n_{\text{vehicles}}$  is the number of vehicles crossing the tunnel in the sampling period,  $t_{\text{sample}}$  is the air sampling period for the chemical analyses and  $l_{\text{tunnel}}$  is the length of the tunnel.

Here we use the results from the canister measurements at the entrance of the tunnel (also the canisters with longer sampling times) and the mean values of all online GC–MS measurements performed during the same sampling interval at the exit to calculate the emission factors. The measured mean concentrations and the resulting average emission factors for the whole car fleet are shown in Table 1. In Table 1, the calculated

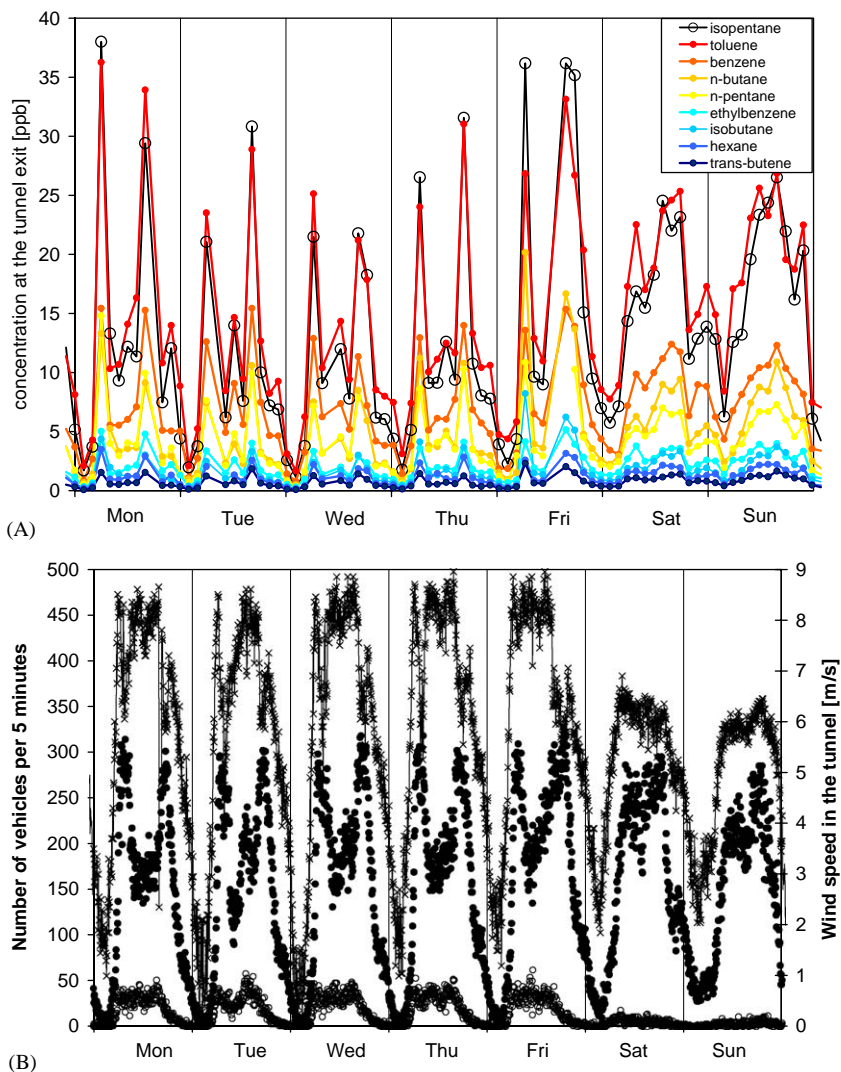


Fig. 1. Panel A: Time series of the mixing ratios of selected VOCs at the Gubristunnel exit for 23–29 September. The legend gives the individual VOCs sorted by decreasing observed concentrations. Panel B: Traffic density and wind speed in the tunnel for the same period. The filled circles (●) represent the number of LDV (length < 6 m), and the open circles (○) represent the number of HDV (length > 6 m) travelling the tunnel per 5 min. The crosses (×) show the course of the wind speed in the tunnel.

emission factors are also compared to emission factors derived from other European tunnel studies. As these emission factors represent emissions from different fleet compositions and under different driving conditions, some aspects of the measurements in the respective tunnel studies are given as well. From Table 1, it is obvious that the emission factors measured in this study are significantly lower than all emission rates found during the earlier VOC measurement campaigns in European tunnels. The earliest study was performed in 1988 in the Tauerntunnel in Austria and was repeated in 1997. The results of these Austrian studies indicate that the emission rates of the individual aromatic compounds

were reduced by 80–90% during this 9-year period. This reduction is in accordance with the reduction of the total NMVOC emission factor by 90% in the same period (Schmid et al., 2001). The authors have related this reduction mainly to a strong increase of catalyst-equipped passenger cars from near zero in 1988 to about 60% of the gasoline-powered cars in 1997. When comparing the results from the Gubristunnel studies in 1993 and in 2002, it can be seen that the emission factors of the aromatic compounds for an average car have lowered by approximately 70–80% during this 9-year period. Interestingly, the relative emission strengths for the five investigated aromatic compounds from road

traffic have varied only little throughout the listed tunnel studies covering a period of 14 years. There appears to be a small downwards trend of the relative fraction of benzene compared to the alkyl substituted aromatics in both the Gubristtunnel and the Tauerntunnel comparisons. Such a trend is, however, not confirmed by dynamometric test on Swiss passenger cars representing the vehicle technology of the last two decades (Heeb et al., 2000, 2003), but continuous ambient air measurements of the aromatic VOCs in the Zurich area (Reimann et al., 2003) do show an over-proportional decrease of the benzene concentrations compared to the concentrations of the alkylated benzenes since the year 2000, which might be related to the new Swiss regulations on the benzene content in gasoline which came into force in 2000. When comparing the emission factors of the light alkanes and alkenes derived in this study with those measured in the Thiasistunnel (France) in 1994 (Touaty and Bonsang, 2000), one observes that all compounds show an approximately 11–17 times lower emission strength in 2002 in Switzerland. Exceptions are *n*-pentane, *n*-hexane and 3-methylpentane, where the results of the Gubristtunnel study are only a factor of 5–8 lower than the results from the Thiasistunnel in 1994. The most obvious explanation for these differences for the light alkanes and alkenes is again the much higher proportions of catalyst-equipped passenger cars in this study (estimated as 93–97% of all gasoline-driven passenger cars; see Table 1) than in the Thiasistunnel study (estimated as about 5%; Touaty and Bonsang, 2000; Sallès et al., 1998). Additionally, the results from the Thiasistunnel are obtained under traffic conditions with a significantly slower average speed, which is expected to lead to higher VOC emissions (UBA, 1999).

In the Gubristtunnel campaign in 1993, additionally a broad range of individual VOCs have been measured from seven 1 h samples. These measurements were reported as separate emission factors for two vehicle classes (light duty vehicles, including passenger cars and delivery vans, mainly gasoline-powered engines and heavy duty vehicles, exclusively diesel powered trucks; for more details see Staehelin et al., 1998). In order to achieve comparable results, the measurements of this study were also attributed to these two vehicle categories by means of a linear regression model according to Eq. (2). The emission factors for the entire fleet ( $EF_{\text{fleet}}$ ) have been split in the two categories ( $EF_{\text{ldv}}$  and  $EF_{\text{hdv}}$ ) for light duty vehicles (LDV) and heavy duty vehicles (HDV) by using the vehicle length specific traffic counts of an induction loop detector. Cars and delivery vans with a total length shorter than 6 m are referred as LDV and vehicles with a length above 6 m are categorized as HDV:

$$EF_{\text{fleet}}(t) = EF_{\text{ldv}} + (EF_{\text{hdv}} - EF_{\text{ldv}})f_{\text{hdv}}(t) + \varepsilon(t), \quad (2)$$

where  $f_{\text{hdv}}(t)$  is the fraction of HDV passing the tunnel in a given measurement interval and  $\varepsilon(t)$  is the random error. From previous studies at this site (Staehelin et al., 1995, 1997, 1998) and other highway tunnels studies (Schmid et al., 2001; Rogak et al., 1998a, b), it is known that due to the comparatively low maximal proportion of HDV (never exceeding 20% in a sampling period during this study) and their relatively low emissions for the selected hydrocarbons, the information on the latter category is too sparse to obtain firm emission factors. The data given in Table 2 for  $EF_{\text{hdv}}$  are therefore often not significantly differing from zero (95% CI level). We therefore focus more on the emissions of LDV and view the separation in the two categories as a method of making small corrections to the overall fleet emissions in order to obtain better information on the LDV class. In Table 2, the emission factors of the Gubristtunnel studies in 1993 and 2002 are given separately for both vehicle classes. The bold numbers correspond to online gas chromatographic measurements (2002: 315 measurements; 1993: 195 measurements) whereas the italic numbers were derived from the seven 1-h samples in 1993. When considering the compounds for which both online and 1-h measurements have been reported in 1993, it is obvious that it is very delicate to separate the emission factors into the two classes, as although the actual measured concentrations are in good agreement in both methods (Staehelin et al., 1998), the attribution of the emissions to either vehicle class differs strongly. The analysis of the 1-h samples leads to lower emission factors for the LDV and consequently much higher emissions are attributed to the HDV. As the online gas chromatographic measurement exhibits a much better time resolution and consists of more measurements, we prefer these measurements for the comparisons of the data sets. When comparing the emission factors for passenger cars from 1993 and 2002, one finds that all measured VOCs show a distinct emission decrease and on average the emission factors are reduced by a factor of about 4. A more detailed discussion of the specific reduction of individual VOCs seems not possible from these data sets, as (i) the comparison of the online and the 1-h-sample measurements from 1993 show that much of the variation comes from errors and differences in the applied methods and (ii) the relative contributions of the individual compounds are quite similar in 1993 and in 2002.

In the following section (see Table 3 and Fig. 2), we compare the measured VOC emission factors from the Gubrist study with a traffic emission model (UBA, 1999) which is based on dynamometric tests on Swiss cars. The model combines the test stand derived emission functions for different vehicle classes and for different technical stages (according to the emission regulation in charge) with data on the real world driving modes and estimations on the on-road traffic composition. The

Table 2  
Emission factors derived from the Gubristtunnel measurements in 2002 and 1993 assigned to LDV and HDV

Compound	Gubrist 2002 emission factors <sup>a</sup> (mg km <sup>-1</sup> )		Gubrist 1993 emission factors <sup>a</sup> (mg km <sup>-1</sup> )		Ratio of the emission factors for LDV [EF(1993)/EF(2002)]
	LDV	HDV	LDV	HDV	
<i>n</i> -Butane	<b>2.69 ± 0.3</b>	<b>0 ± 3</b>	10 ± 5 <sup>c</sup>	27 ± 27 <sup>c</sup>	3.7
Isobutane	<b>0.96 ± 0.13</b>	<b>0.1 ± 1.1</b>	1.7 ± 1 <sup>c</sup>	5 ± 4 <sup>c</sup>	1.8
1-Butene	<b>0.63 ± 0.04</b>	<b>1.3 ± 0.5</b>	1.9 ± 0.6 <sup>c</sup>	4 ± 3 <sup>c</sup>	2.6
<i>trans</i> -Butene	<b>0.29 ± 0.02</b>	<b>0.1 ± 0.2</b>	1.4 ± 0.6 <sup>c</sup>	3 ± 3 <sup>c</sup>	4.8
<i>cis</i> -Butene	<b>0.23 ± 0.01</b>	<b>0.0 ± 0.2</b>	1.3 ± 0.5 <sup>c</sup>	3 ± 3 <sup>c</sup>	5.6
<i>n</i> -Pentane	<b>1.81 ± 0.12</b>	<b>1 ± 1</b>	<b>13 ± 4<sup>b</sup></b> 6 ± 4 <sup>c</sup>	<b>-2 ± 17<sup>b</sup></b> 16 ± 23 <sup>c</sup>	<b>7.1</b> 3.3
Isopentane	<b>6.4 ± 0.4</b>	<b>-1 ± 4</b>	18 ± 7 <sup>c</sup>	43 ± 37 <sup>c</sup>	2.8
<i>n</i> -Hexane	<b>0.66 ± 0.04</b>	<b>-0.1 ± 0.4</b>	<b>4.2 ± 1.0<sup>b</sup></b> 1.7 ± 0.6 <sup>c</sup>	<b>-1 ± 4<sup>b</sup></b> 3 ± 3 <sup>c</sup>	<b>6.4</b> 2.6
3-Methylpentane	<b>0.96 ± 0.06</b>	<b>-1 ± 1</b>	<b>5.7 ± 1.3<sup>b</sup></b>	<b>-3 ± 5<sup>b</sup></b>	<b>5.9</b>
Benzene	<b>3.3 ± 0.2</b>	<b>0.7 ± 1.6</b>	<b>15 ± 2<sup>b</sup></b> 10 ± 2 <sup>c</sup>	<b>2 ± 10<sup>b</sup></b> 15 ± 12 <sup>c</sup>	<b>4.5</b> 3.0
Toluene	<b>8.7 ± 0.5</b>	<b>1 ± 5</b>	<b>29 ± 5<sup>b</sup></b> 20 ± 7 <sup>c</sup>	<b>-2 ± 20<sup>b</sup></b> 33 ± 35 <sup>c</sup>	<b>3.3</b> 2.3
Ethylbenzene	<b>1.6 ± 0.1</b>	<b>0.4 ± 1.0</b>	<b>4.7 ± 0.8<sup>b</sup></b> 3.6 ± 0.9 <sup>c</sup>	<b>0 ± 3<sup>b</sup></b> 7 ± 5 <sup>c</sup>	<b>2.9</b> 1.9
<i>m/p</i> -Xylene	<b>4.2 ± 0.3</b>	<b>1 ± 3.0</b>	<b>17 ± 3<sup>b</sup></b> 11 ± 3 <sup>c</sup>	<b>-1 ± 13<sup>b</sup></b> 27 ± 15 <sup>c</sup>	<b>4.0</b> 2.5
<i>o</i> -Xylene	<b>1.9 ± 0.1</b>	<b>0 ± 2</b>	<b>8 ± 1<sup>b</sup></b> 4.7 ± 0.6 <sup>c</sup>	<b>1 ± 6<sup>b</sup></b> 6 ± 3 <sup>c</sup>	<b>4.2</b> 2.5

<sup>a</sup>Error limits are for 95% confidence intervals.

<sup>b</sup>Continuous GC-FID measurements (time resolution of 15 min, 195 measurements).

<sup>c</sup>Results from 7 canister or adsorbent trap samples with a sampling period of 1 h.

Table 3  
Comparison of measured emission factors from the Gubristtunnel studies in 2002 and 1993 with modelled emission factors based on dynamometric test data

Compound, model year	Emission factors for LDV from tunnel measurement (mg km <sup>-1</sup> )	Emission factors (mg km <sup>-1</sup> ) for LDV from emission model derived from dynamometric tests (UBA, 1999). The individual case studies are characterized by variation of the following input parameters: vehicle speed (S), road gradient (G), fraction of delivery vans included (F).			
		S: 87 km h <sup>-1</sup> G: 0% F: 0%	S: 103 km h <sup>-1</sup> G: 0% F: 0%	S: 87 km h <sup>-1</sup> G: 1% F: 0%	S: 87 km h <sup>-1</sup> G: 0% F: 8%
Benzene, 2002	3.3 ± 0.2	3.15	3.51	5.64	3.5
Benzene, 1993	15 ± 2	19.1	20.2	26.9	20.3
Toluene, 2002	8.7 ± 0.5	5.34	5.87	9.08	5.5
Toluene, 1993	29 ± 5	34.0	35.7	46.5	34.4
Xylenes, 2002	6.1 ± 0.4	4.38	4.82	7.47	4.53
Xylenes, 1993	25 ± 3	27.6	29	37.8	27.9

model allows the selection of distinct traffic conditions, which differ in respect of measures such as traffic speed, road slope, road type, fraction of foreign vehicles, and distinguishes different types of emissions like cold start

emissions or evaporative emissions. The emission factors for benzene, toluene and the group of the xylenes are incorporated in this model and are represented as vehicle class-dependent split-ratios of the total VOC emission

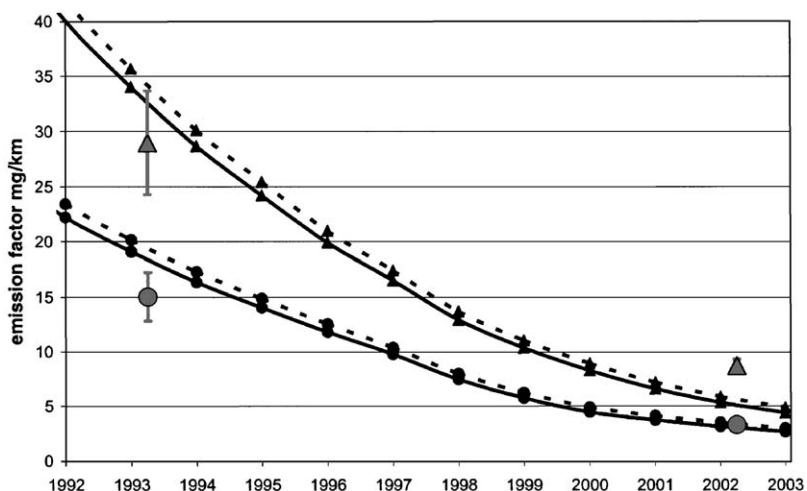


Fig. 2. Measured emission factors of LDV for benzene (grey circles) and toluene (grey triangles) in the Gubristunnel 1993 and 2002 compared to emission factor calculations for benzene (black circles) and toluene (black triangles) based on an emission model derived from dynamometric tests (UBA, 1999). The black bold lines represent model calculations for passenger cars at a speed of  $87 \text{ km h}^{-1}$ , and the dotted lines represent calculations for passenger cars at a speed of  $103 \text{ km h}^{-1}$ .

factors. In Fig. 2 and Table 3, the measured emission factors for LDV from the Gubristunnel studies are compared to the modelled development of the emission factors from 1992 to 2003. For the comparison in Fig. 2, a simple scenario was used as the model input: highway driving with average speeds of  $87$  and  $103 \text{ km h}^{-1}$ , respectively; no road gradient; all vehicles running under warm engine conditions; and no delivery vans incorporated in the group of LDV. This scenario is clearly a simplification of the real situation in the Gubristunnel because effects from the tail wind situation (John et al., 1999) or a potentially smoother driving mode in tunnels are not taken into consideration. In order to show the sensitivity of the modelled emission factors on the exact model input, Table 3 gives the emission factors for aromatic compounds under slightly varying conditions. It can be seen that the variation of the average speed between  $86$  and  $103 \text{ km h}^{-1}$  and the inclusion of delivery vans in the model are not critical, but the model is very sensitive on the road gradient.

Thus, an absolute agreement of the model with the observations should not be expected and we focus therefore more on the relative decrease of the emission factors between 1993 and 2002. The model predicts a decrease by  $80$ – $85\%$  for benzene, toluene and the xylenes and the two measurement campaigns showed a decrease by  $70$ – $80\%$ . From this good agreement we conclude that the factors leading to the decrease of the average vehicle emissions in the model are likely also valid for the on-road situation in the Gubristunnel. The model suggests the following reasons for the decreasing emission factors: the on-road fraction of the non-catalyst-equipped fraction of the passenger cars de-

creased from  $33\%$  to  $2.6\%$  between 1993 and 2002. This leads to an overall reduction of the average benzene emission factor by  $80\%$ . The fraction of diesel-fuelled passenger cars increased from  $6.2\%$  to  $8.5\%$  (these are the model assumptions for the on-road fraction of the diesel passenger cars). Due to this small change the effect on the average emission is marginal. Among the catalyst equipped passenger cars, a substantial technical improvement leads to a decrease of about  $50\%$  of the emission factors within this class. However, the average absolute emission factors of the catalyst passenger cars modelled for benzene are with  $4.8 \text{ mg km}^{-1}$  in 1993 and  $2.5 \text{ mg km}^{-1}$  in 2002 very low and therefore contribute only little to the overall emission reduction in the investigated time period.

#### 4. Conclusions

This study documents a large decrease of the VOC emission factors of Switzerland's passenger car fleet during the last decade. The main reason for the observed emission reduction is the increasing spread of the exhaust catalyst technique for gasoline-powered vehicles. It has to be emphasized that the present results are obtained under conditions where exhaust catalysts have an optimal effectiveness, as under the investigated driving conditions most vehicles are operated at hot stabilized engine conditions and the traffic flow is generally much steadier than for example during urban driving. Dynamometric tests on passenger cars using more diverse driving cycles and investigations of the cold start behaviour (Heeb et al., 2003) show that the VOC

reduction efficiency of catalytic converters is reduced after cold starts. These investigations showed that the VOC emissions of catalyst-equipped vehicles are reduced by only 80–90% during cold starts compared to the emissions of non-catalyst cars, whereas under hot engine conditions reductions of 97–99% were achieved. Based on such dynamometric tests, Swiss traffic emission models (BUWAL, 1999) indicate that during the 1990s the traffic VOC emissions of the passenger car fleet driving under hot stabilized conditions could be reduced by about 80%, whereas only a reduction of about 50% was achieved for the cold start emissions of passenger cars in Switzerland. All in all, these models predict an overall VOC emission reduction from Swiss passenger vehicles (this number includes additionally losses by evaporation of fuel from the tank and losses occurring when the motor is stopped) of about 75% during the 1990s. Resulting from this development, it is estimated (BUWAL, 1999) that the cold start emissions of Swiss passenger cars represent a larger VOC emission source, than their emissions under hot engine conditions since the year 2000. Ongoing distinct improvements of the VOC emissions of passenger vehicles are therefore only possible when the cold start emissions can be reduced by additional technical measures.

Another important finding of the dynamometric test is that certain aromatic compounds (like benzene, toluene) might even be produced in catalytic converters under situations with high engine loads or driving with excessive speeds ( $<120 \text{ km h}^{-1}$ ) (Heeb et al., 2003, 2002). In the investigated road tunnel the speed limit is  $100 \text{ km h}^{-1}$ , whereas the general speed limit on Switzerland's highways is  $120 \text{ km h}^{-1}$ . Therefore, such additional emissions of aromatics are hardly represented in this study. Therefore, the generalization of the strong reduction of the VOC emissions observed for the investigated highway situation to other traffic conditions, as urban driving, can be problematic, due to lower catalyst efficiencies after cold starts.

One main result of the present study is the comparison of modelled VOC emission strengths of vehicles (UBA, 1999) with measured emissions under real-world conditions. This is important as Swiss national traffic emission inventories (BUWAL, 1995, 1999) are based on such traffic models.

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