

'Measurements of OVOCs and NMHCs in a Swiss Highway Tunnel for Estimation of Road Transport Emissions

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Eighteen oxygenated volatile organic compounds (OVOCs) and eight nonmethane hydrocarbons (NMHCs) were measured continuously during a two-week campaign in 2004 in the Gubrist highway tunnel (Switzerland). The study aimed to estimate selected OVOC and NMHC emissions of the current vehicle fleet under highway conditions. For the measured OVOCs the highest EFs were found for ethanol (9.7 mg/km), isopropanol (3.2 mg/km), and acetaldehyde (2.5 mg/km), followed by acetone, benzaldehyde, and acrolein. Formaldehyde, the most abundant OVOC measured in other studies, was not measured by the method applied. Relative emissions of the measured OVOCs were estimated to contribute approximately 6 and 4% to the total road traffic VOC emissions from Switzerland and Europe, respectively. Results are compared with those from previous studies from the same tunnel performed in 1993 and 2002, and from campaigns in other tunnels. A continuous reduction in the emission factors (EFs) was determined for all measured compounds from 1993 until 2004. The relative contributions of light-duty vehicles (LDV) and heavy-duty vehicles (HDV) to the total emissions indicated that OVOCs were mainly produced by the HDVs, whereas LDVs dominated the production of the NMHCs.

Introduction

Road transportation is a major source of anthropogenic volatile organic compounds (VOCs) and nitrogen oxides (NO_x), which are key species in the processes leading to the production of tropospheric ozone and secondary organic aerosols (SOA) (3–5). In these processes, oxygenated VOCs

(OVOCs), which include carbonyls, ethers, alcohols, organic acids, organic peroxides, and esters, play a crucial role both as primary and secondary pollutants. In addition, several OVOCs are toxic to human health and the environment, an example being acrolein, which is a highly toxic herbicide that is also produced during the combustion process (6).

Exhaust emissions from fossil-fuel driven vehicles are described by emission factors (EFs), which are defined as the emitted mass of a certain compound per driven distance. The EFs depend on many factors, such as fuel type, size and type of engine, driving conditions, and road gradient (7, 8). EFs of single vehicles (or engines) can be determined from dynamometric or engine tests. This allows investigation of how driving cycles influence the emissions of different types of vehicles and provide the basis of road traffic emission models (9–14). Information on emissions from large and representative samples of vehicle fleets have been obtained from measurements in road tunnels (1, 2, 15–22) or on busy streets (23–25). These studies have been used to evaluate the results of road traffic emission models for particular conditions (mainly emissions for highway driving conditions) (26, 27). Furthermore, road tunnel measurements can be used to investigate the impact of reduction measures and new technologies (i.e., catalytic converters) if repeated measurements are made in the same tunnel (2, 19, 22, 28).

Contrary to legally constrained compounds (i.e., NO_x, carbon monoxide (CO), and total VOCs), information on emissions of individual organic species is still incomplete. While reliable information on emissions of many NMHC species is available from dynamometric test measurements (9, 29), data for OVOC species is limited. However, OVOC data is available from several tunnel campaigns, which were, in part, undertaken to study the impact of alternative fuels containing oxygenated additives such as ethanol and methyl-tert-butyl ether (MTBE) (2, 15, 17, 30).

In this study, measurements of selected OVOCs and NMHCs, obtained in 2004 in the Gubrist tunnel (Switzerland), are used to evaluate their emissions under highway conditions. Results are compared with those of other studies, in particular with OVOC data from the same tunnel in 1993 and NMHC data from 1993 and 2002.

Experimental Section

The Gubrist tunnel is part of the highway in the northwest area of Zurich connecting three of the largest cities in Switzerland. It has one bore for each direction, with a total length of 3270 meters and a cross section of 48 m². There is a 100 km/h speed limit in the tunnel. The ventilation system was turned off during the measurements and the tunnel was passively ventilated through the piston effect of the passing vehicles. Two air velocity monitors were mounted 150 meters inside the entrance and exit of the tunnel, providing 5 min average values for the air velocity. Automatic loop detectors measured the traffic density, composition, and speed, averaged over 5 min intervals. Air sampling points were situated at both ends of the tunnel in the slightly ascending bore, with a road gradient of 1.3%. Samples for the OVOCs were taken only at the exit of the tunnel, 10 meters before the tunnel opening, and 1.5 meters above the road level. The entrance sampling point was situated 200 meters inside the tunnel, also 1.5 meters above the road level.

The main sampling line consisted of a 4 meter long, 1/4 inch diameter PFA sampling tube equipped with a 1 μm PTFE supported inlet filter (Whatman Inc, Florham Park, NJ) for removal of particulate matter, and was continuously flushed at 4 liters per minute. From the main sampling tube a 3

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meter long, 1/4 inch diameter PFA line was connected to the instrument. Every 50 min a 45 mL sample was acquired over a 4 min time interval. The samples were collected on a double adsorbent system connected to a gas chromatograph–mass spectrometer (GC–MS Agilent 6890– 5973N). The water removal was performed by collecting the samples on an adsorbent trap containing 0.6 g of 40–60 mesh Hayesep D, a polydivinylbenzene polymer, at room temperature. After sampling, the adsorbent was flushed with 400 mL of dry helium to remove residual humidity. To ensure good separation of the compounds, they were thermally desorbed (180 °C) onto a refocusing trap (30 mg Hayesep D) and cooled to –40 °C with Peltier elements. The compounds were rapidly desorbed from this trap (180 °C) and transferred through a heated fused silica line onto the gas chromatograph. The chromatographic separation was performed on a 25 m × 0.32 μm CP-Porabond U column (Varian Inc., Palo Alto, CA) with 7 μm film thickness. Initially, the temperature was held at 40 °C for 2 min, and then increased rapidly to 120 °C at a rate of 20 °C/min, and then to 200 °C at a rate of 5 °C/min, where it was held constant until the end of the run. Individual compounds were detected by operating the mass spectrometer in single ion monitoring (SIM) mode, for an improved signal-to-noise ratio. The compounds were identified by their mass spectra and quantified using a 24-compound OVOC standard gas mixture in the range of 350–450 ppb (Apel & Riemer Environmental Inc., Broomfield, CO), and a 30-compound VOC standard gas mixture in the range of 1–10 ppb (National Physical Laboratory, UK). Calibration was performed three times a day by filling a calibrated sample loop (127 μL), which was flushed with helium onto the adsorbent trap. The system was run for a period of 20 days, with approximately 12 days of good quality data collected.

CO data was acquired by means of two commercial CO monitors based on the nondispersive infrared (NDIR) technique (Horiba 350E). The CO monitors were mounted at both the exit and entrance of the tunnel. The sampling frequency was 5 min. Carbon dioxide (CO₂) was monitored at the tunnel entrance and exit by two Li-6262 infrared H₂O/CO₂ analyzers (LI-COR). CO and CO₂ results will be published in a separate paper (Vollmer et al., ref. 31).

The average emission factors were calculated using eq 1:

$$EF_{\text{fleet}} = \frac{\Delta C_p \times V_{\text{air}} \times t_{\text{sample}} \times A_{\text{tunnel}}}{n_{\text{vehicles}} \times l_{\text{tunnel}}} \quad (1)$$

where EF_{fleet} is the mean emission factor per vehicle for a given compound expressed as emitted mass per traveled distance, ΔC_p is the mixing ratio difference for a compound between the measurements at the tunnel exit and its entrance mixing ratio (see next paragraph), V_{air} is the air velocity in the tunnel, t_{sample} is the air sampling period for the chemical analyses, A_{tunnel} is the tunnel cross section, n_{vehicles} is the number of vehicles passing the tunnel in the sampling period, and l_{tunnel} is the length of the tunnel between the sampling points. The data was synchronized by assigning each sample to the next 5 min interval to obtain the best overlap with the traffic data. For the calculation of the EFs only periods with traffic densities above 20 vehicles per 5 min and air velocity above 2 m/s were used in order to restrict the analysis to situations with a steady air flow and pollution transport in the tunnel. The EF was calculated for each sample, and all EFs above the mean plus 3 times the standard deviation were removed as outliers. The uncertainty for each compound was defined as the 95% confidence interval for the EFs. Inherently, the reported uncertainty includes not only the analytical measurement error, but also the uncertainty caused by the statistical analysis, including variation in fleet composition, driving pattern, and meteorological conditions.

Mixing ratios of the OVOCs at the entrance were estimated based on the assumption that the ratios between the OVOC and CO₂ mixing ratios at the entrance and at the exit of the tunnel were identical. This is reasonable since the mixing ratio at the entrance is largely influenced by road traffic, as the entrance sampling point is located approximately 200 meters inside the tunnel, and the air flow into the tunnel is mixed with air from the opposite tunnel bore. This assumption was supported by the 3 times greater mixing ratio of CO at the tunnel entrance compared to the CO values reported from a nearby urban location (Zürich). This allowed an estimation of the entrance mixing ratio for the VOCs ($C_{\text{VOC,entrance}}$) to be calculated on a sample-to-sample basis using eq 2, where $C_{\text{VOC,entrance}}$ and $C_{\text{VOC,exit}}$ are the mixing ratios for the measured VOCs at both ends of the Gubrist tunnel, and $[\text{CO}_2]_{\text{entrance}}$ and $[\text{CO}_2]_{\text{exit}}$ are the CO₂ mixing ratios at the same locations:

$$C_{\text{VOC,entrance}} = \frac{C_{\text{VOC,exit}} \times [\text{CO}_2]_{\text{entrance}}}{[\text{CO}_2]_{\text{exit}}} = > \Delta C_p = C_{\text{VOC,exit}} - \left[\frac{C_{\text{VOC,exit}} \times [\text{CO}_2]_{\text{entrance}}}{[\text{CO}_2]_{\text{exit}}} \right] \quad (2)$$

For the distinction between EFs for heavy duty vehicles (HDV) and light duty vehicles (LDV), a linear regression model according to eq 3 was used:

$$EF_{\text{fleet}}(t) = EF_{\text{LDV}}(1 - f_{\text{HDV}}) + EF_{\text{HDV}}f_{\text{HDV}}(t) + \epsilon(t) \quad (3)$$

where f_{HDV} is the fraction of HDVs passing the tunnel in a given measurement interval and $\epsilon(t)$ is the random error. The information on vehicle categories (LDV and HDV) was obtained from traffic count measurements with average values for every 5 min. LDVs are less than 6 meters long, which include small vans, cars and motorcycles, whereas HDVs are longer than 6 meters, including trucks, buses and larger vans.

Results and Discussion

Figure 1 shows the air velocity, vehicle speed, traffic density, and CO₂ mixing ratio at the tunnel exit. The air velocity varied between 0 and 10.3 m/s and directly depended on the traffic density and speed of the vehicles. During the commuter traffic hours, the air velocity increased with the traffic density, and then slightly decreased when the traffic density was at its highest due to obstruction by the traffic. The maximum air velocity was reached on weekdays, due to the higher number of HDVs. On the weekend (4/12/04 and 5/12/04), the HDV counts were considerably lower than during the weekdays, which is a result of Swiss legislation banning goods transport over the weekend. Only a small number of buses were observed on these days. Since the proportion of diesel fuelled LDVs in Switzerland is low (2004: 9.1%, ref 31), most of the diesel emissions originated from the HDVs. The CO₂ mixing ratios at the tunnel exit also followed the traffic density with morning and afternoon peaks on weekdays. The maximum mixing ratio for CO₂ was lower at the weekend due to less traffic overall.

Figure 2 shows the measured mixing ratios of selected OVOCs (panel A) and NMHCs (panel B) at the exit of the Gubrist tunnel. Mixing ratios of OVOCs exhibited a diurnal cycle on work days with a morning peak between 0630 and 0900 AM and an evening peak between 0400 and 0630 PM. The lowest mixing ratios occurred, as expected, during the night. This clearly follows the pattern in the traffic counts shown in Figure 1, with low vehicle counts during the night and increased vehicle density during commuter traffic hours. On weekend days, the mixing ratios of the OVOCs showed

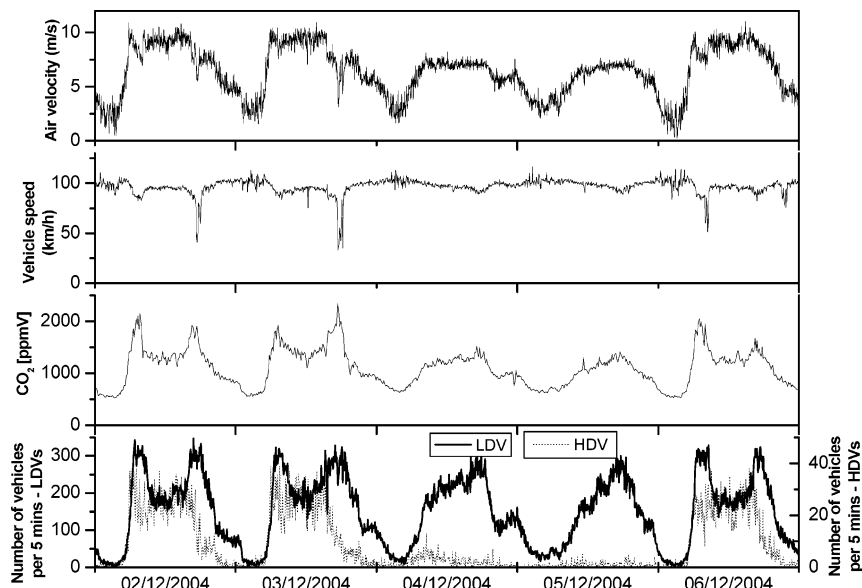


FIGURE 1. Air velocity, vehicle speed, CO₂ mixing ratio (37), and traffic density at the tunnel exit. LDVs: light duty vehicles (length < 6 m) and HDVs: heavy duty vehicles (length > 6 m).

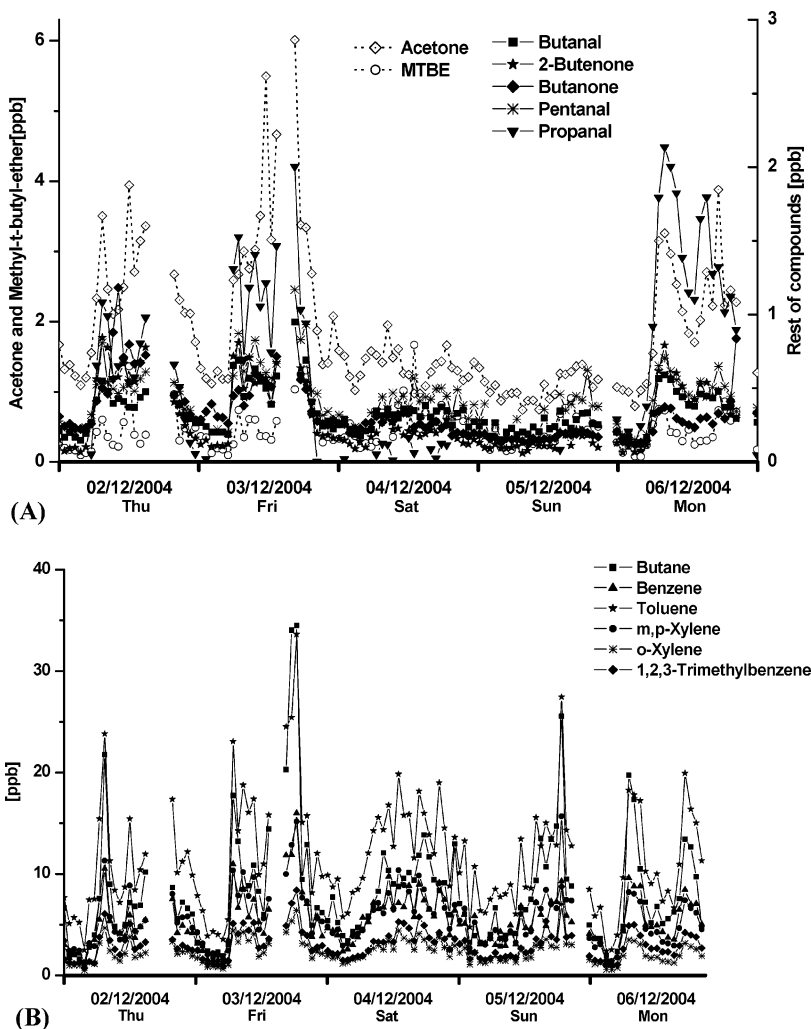


FIGURE 2. Mixing ratios for selected OVOCs (panel A) and NMHCs (panel B) at the exit of the Gubrist tunnel.

a more gradual increase during the day and had a lower maximum value than during the week (Figure 2, panel A). For the NMHCs (Figure 2, panel B) the trend was similar, but with the difference that the maximum values on Saturday

and Sunday were not significantly lower than during the week. This can be explained by the fact that the gasoline-fueled LDVs are predominantly responsible for the NMHC emissions, in contrast to the OVOCs, which are mainly emitted

TABLE 1. Mixing Ratios of VOCs Estimated from Parallel CO₂ Measurements at the Entrance Compared with the Urban Background in Zurich during the Same Season and Measured Mixing Ratios at the Tunnel Exit

compounds	entrance mixing ratio estimated from CO ₂ measurements (ppbV)		urban background measured in Zürich 1 year later (ppbV)		measured mixing ratio at tunnel exit (ppbV)		
	1. quartile	3. quartile	1. quartile	3. quartile	mean	min	max
acetaldehyde	1.78	6.45	0.23	0.57	14.3	bd	170
propanal	0.08	0.40	0.08	0.13	0.59	bd	2.13
butanal	0.11	0.17	0.01	0.03	0.30	0.04	0.95
pentanal	0.14	0.21	0.01	0.03	0.40	bd	1.29
hexanal	0.08	0.16	0.01	0.03	0.27	bd	0.76
benzaldehyde	0.42	0.60	0.01	0.02	1.09	0.38	3.95
acrolein	0.41	0.87	0.04	0.11	1.47	0.04	3.76
MTBE	0.14	0.27	0.05	0.21	0.47	0.08	3.94
acetone	0.70	1.21	0.71	1.57	3.20	0.62	65.7
MVK	0.09	0.21	0.02	0.04	0.34	0.05	1.67
MEK	0.10	0.19	0.10	0.23	0.34	0.12	2.07
ethanol	4.57	15.81	2.61	9.22	53.7	1.63	1272
isopropanol	1.03	3.64	0.45	1.49	14.4	0.38	310
<i>n</i> -propanol	0.06	0.12	0.02	0.07	0.29	0.07	3.37
isobutanol	0.01	0.03	0.00	0.00	0.07	bd	0.58
methyl acetate	0.02	0.05	0.03	0.07	0.08	bd	0.40
ethyl acetate	0.04	0.14	0.11	0.35	0.21	0.03	1.53
butyl acetate	0.06	0.12	0.06	0.19	0.21	0.05	1.12
butane	2.04	4.16	0.73	1.97	7.41	0.37	40.9
1,3-butadiene	0.65	1.09	0.03	0.13	1.88	0.12	4.94
isoprene	0.40	0.80	0.03	0.11	1.42	0.03	7.41
benzene	1.63	2.71	0.26	0.62	4.81	0.53	21.5
toluene	2.92	5.72	0.74	2.42	9.71	0.81	59.8
<i>m,p</i> -xylene	1.62	2.78	0.33	1.14	4.86	0.59	26.3
<i>o</i> -xylene	0.66	1.15	0.13	0.42	2.02	0.21	11.4
1,2,4-trimethylbenzene	0.99	1.55	0.02	0.07	2.76	0.51	10.5

	measured mixing ratio at entrance (ppbV)		parallel measurements in Zürich (ppbV)	
carbon monoxide (CO)	0.962	1.873	0.303	0.682

by diesel-fueled HDVs (2, 32) (also confirmed by this study, see below).

In Table 1 the estimated entrance mixing ratios, calculated using the CO₂ method, are compared to measured mixing ratios from an urban background station in Zürich (situated within 10 km of the tunnel) during the same season. When comparing the two data sets using the interquartile range, most of the compounds showed estimated mixing ratios at the tunnel entrance to be higher in comparison with the measured mixing ratios in Zürich. This is reasonable since the entrance mixing ratio is also influenced by the number of vehicles entering the tunnel and exiting the other tunnel bore. Exceptions are the esters, propanal, butanone, and acetone, whose potentially local industrial emissions in Zürich disturb the comparison. For propanal, butanone, and acetone, this could also be caused by the high tropospheric background mixing ratio, which makes it difficult to accurately determine the appropriate entrance mixing ratio. This gives an increased uncertainty for these compounds.

The compounds with the highest mixing ratios were ethanol and 2-propanol, followed by acetaldehyde and acetone (Table 1). Formaldehyde, the most abundant OVOC measured in other studies (1, 2), was not measured by the method applied in this work. On wet cold days, high mixing ratios of ethanol and isopropanol were found. Both of these compounds are major components of windscreen wiper fluids, and thus were expected to be related to extensive windscreen cleaning. On these days mixing ratios of acetaldehyde and acetone were also up to 15 times higher than on dry days with similar traffic density. This increase may have been caused by enrichment in water droplets transported into the tunnel and evaporated during their residence time in the tunnel. Enrichment of acetaldehyde in rain and fog

has been reported from several studies (e.g., Levsen et al. and Grosjean et al. (33, 34)). This effect could also have been responsible for the elevated acetone mixing ratios, as acetone has a higher Henry's law constant (23.5 M/atm) than acetaldehyde (11.4 M/atm).

The largest EF of the quantified OVOCs, which is attributed exclusively to exhaust emissions, was acrolein, with an average mixing ratio at the tunnel exit of 1.39 ppb. In fact, acrolein is one of the most abundant aldehydes in the atmosphere (approximately 13% of total atmospheric aldehydes, ref 6) and originates mostly from the combustion of fossil fuel. Of the compounds measured in the Gubrist tunnel, the alcohols were the most prominent group comprising 54% of total measurements, followed by the NMHCs with 28%, the aldehydes with 15%, and the ketones with 3%. The esters and MTBE each represented 0.4% of the measured compounds. The organic acids and difunctional carbonyls were not measured, but other studies found only small amounts of these compounds in exhaust gas (35, 36).

In Table 2 the EF's for the measured compounds are listed together with EF's reported from other studies. The alcohols and the aromatic compounds dominated with 38 and 37% of the total EF's respectively. The aldehydes contributed with 12%, the ketones 3.0%, and MTBE 0.6%. Ethanol had the highest single EF with 10 mg/km, followed by toluene (5.0 mg/km) and isopropanol (3.3 mg/km). Of the other OVOCs, acetaldehyde was the most prominent at 2.4 mg/km, followed by acetone (0.78 mg/km), and benzaldehyde (0.64 mg/km).

Compared to the measurements performed in the same tunnel by Staehelin et al. (1998) in 1993 (21), a large reduction in mixing ratio was found for both OVOCs and NMHCs. Acetaldehyde has been reduced by 30%, propanal by 63%, acrolein by 77%, and 2-butenone by 25%. This is due to

TABLE 2. Emission Factors (EFs) from Measurements in the Gubrist Tunnel in 2004 Compared with Results from Other Studies^a

compounds	Gubrist 2004 (mg/km)	number of measurements for EF-calculation	Gubrist 2002 (mg/km)	Gubrist 1993 (mg/km)	Stockholm	Caldecott, 1999	Tuscarora, 1999 (mg/km)
					1998/1999 (mg/km)	(mg/km) ^a	(RSD)
acetaldehyde	2.40 ± 0.39	138		3.44	3.1 ± 0.8	1.31 ± 0.14	2.19 (31)
propanal	0.16 ± 0.02	156		0.45	0.47 ± 0.2	0.14 ± 0.02	0.33 (38)
butanal	0.12 ± 0.01	221			0.41 ± 0.10	0.10 ± 0.02	0.19 (50)
pentanal	0.18 ± 0.01	204				0.05 ± 0.02	0.35 (37)
hexanal	0.13 ± 0.01	100			0.46 ± 0.08	0.05 ± 0.02	0.21 (74)
benzaldehyde	0.64 ± 0.04	202			3.8 ± 0.7	0.81 ± 0.10	0.44 (66)
acrolein	0.42 ± 0.05	97		1.82		0.19 ± 0.02	0.41 (31)
MTBE	0.21 ± 0.01	214					
acetone	0.78 ± 0.09	215		1.72	1.4 ± 0.6	0.67 ± 0.07	2.14 (38)
MVK	0.14 ± 0.01	219			0.2 ± 0.5	0.10 ± 0.02	0.46 (45)
MEK	0.14 ± 0.01	220		0.18			
ethanol	10.03 ± 2.07	214					
isopropanol	3.31 ± 0.74	201					
n-propanol	0.09 ± 0.01	218					
isobutanol	0.03 ± 0.005	136					
methyl acetate	0.03 ± 0.01	117					
ethyl acetate	0.10 ± 0.01	205					
butyl acetate	0.13 ± 0.01	193					
butane	2.23 ± 0.10	219	2.6 ± 0.4	11.28			
1,3-butadiene	0.57 ± 0.02	182					
isoprene	0.51 ± 0.03	181					
benzene	2.13 ± 0.09	220	2.7 ± 0.3	13.69	17.3 ± 0.3		
toluene	4.99 ± 0.25	221	6.4 ± 0.8	26.27	67.3 ± 1.0		
m,p-xylene	2.91 ± 0.14	221	4.0 ± 0.5	15.49	48.6 ± 0.8		
o-xylene	1.20 ± 0.06	221	1.8 ± 0.2	7.76	19.6 ± 0.4		
1,2,4-trimethylbenzene	1.84 ± 0.07	221		5.04			
road gradient	1.30%		1.30%	1.30%	-0.036	4.20%	0-0.3%
average speed (km/h)	93		90	93	70	60	55
average traction, heavy duty vehicles	5.5%		7%	9%	5%	0.10%	60%

^a Calculated from emission factors in mg/L assuming a LDV consumption of 14.2 L/100 km (39).

TABLE 3. Emission Factors for LDVs and HDVs Determined by Linear Regression

compounds	Gubrist 2004 (mg/km)		Gubrist 2002 (mg/km)		Gubrist 1993 (mg/km)	
	LDV	HDV	LDV	HDV	LDV	HDV
acetaldehyde	2.1 ± 0.6	5.3 ± 6.6			2.3 ± 1.1	14.6 ± 5.1
propanal	0.08 ± 0.03	1.10 ± 0.30			0.18 ± 0.45	3.1 ± 2.0
butanal	0.11 ± 0.01	0.31 ± 0.11				
pentanal	0.16 ± 0.01	0.45 ± 0.16				
hexanal	0.07 ± 0.02	0.60 ± 0.19				
benzaldehyde	0.64 ± 0.06	0.75 ± 0.70				
acrolein	0.36 ± 0.07	0.71 ± 0.77			1.3 ± 0.4	7.2 ± 1.6
methyl-t-butyl-ether	0.24 ± 0.02	-0.18 ± 0.24			0.06 ± 0.05	0.27 ± 0.25
acetone	0.57 ± 0.13	3.94 ± 1.54			1.1 ± 1.8	8.0 ± 8.1
2-butenone	0.08 ± 0.01	0.93 ± 0.13				
butanone	0.11 ± 0.02	0.64 ± 0.19			0.08 ± 0.44	1.2 ± 2.0
ethanol	6.6 ± 2.8	58.8 ± 33.7				
isopropanol	2.0 ± 0.4	2.5 ± 5.3				
1-propanol	0.08 ± 0.02	0.32 ± 0.24				
isobutanol	0.02 ± 0.01	0.06 ± 0.08				
methyl acetate	0.03 ± 0.01	0.08 ± 0.10				
ethyl acetate	0.07 ± 0.02	0.52 ± 0.18				
butyl acetate	0.12 ± 0.02	0.31 ± 0.20				
butane	2.4 ± 0.2	-0.9 ± 1.9	2.7 ± 0.3	0 ± 3	9.7 ± 5.3	27.3 ± 27.1
1,3-butadiene	0.56 ± 0.04	0.8 ± 0.5			1.6 ± 0.2	-1.6 ± 1.1
isoprene	0.55 ± 0.04	0.0 ± 0.5				
benzene	2.3 ± 0.1	-1.3 ± 1.8	3.3 ± 0.2	0.7 ± 1.6	10.3 ± 6.2	20.9 ± 34.1
toluene	5.7 ± 0.4	-4.7 ± 5.0	8.7 ± 0.5	1 ± 5	20.4 ± 6.9	33.1 ± 35.0
m,p-xylene	3.3 ± 0.2	-2.2 ± 2.6	4.2 ± 0.3	1 ± 3	10.8 ± 3.0	27.2 ± 15.3
o-xylene	1.3 ± 0.1	-0.8 ± 1.1	1.9 ± 0.1	0 ± 2	4.8 ± 0.6	6.3 ± 2.9
1,2,4-trimethylbenzene	2.0 ± 0.1	0.2 ± 1.4			4.6 ± 1.1	9.6 ± 5.5

improved engine technology for both LDVs and HDVs, and the increased fraction of LDVs with catalytic converters, up from approximately 67% in 1993 to 93% in 2002 and 95% in 2004 (31). The emission factors for the aromatic hydrocarbons (benzene, toluene, xylenes) in the Gubrist tunnel show a

continued decreasing trend compared to those estimated from the same tunnel in 2002 (22) (-21 to -34%) and 1993 (-63 to -85%) (see Figure 2). This is mainly due to the higher proportion of Euro-3 and Euro-4 vehicles in the Swiss fleet in addition to the increased fraction of LDVs with catalytic

converters, i.e., the continuous phase-out of large emitters with no catalytic converter. Butane shows a lower reduction (−14%) since 2002. However it was the most volatile NMHC measured and, therefore, predominantly emitted by evaporation and not through vehicle exhausts. This is consistent with results from dynamometric measurements in a study based on European driving cycles by Ahlvik et al. (32), where approximately 4 times higher emissions of butane were reported from evaporation than from exhaust gas.

Compared to values reported from a tunnel study in Stockholm from 1999 (16), the emission factors for OVOCs and aromatic hydrocarbons were lower by 22 to 83% and 88 to 94%, respectively. The much smaller emissions in Switzerland are, again, expected to be due to a different fleet composition, with more catalyst equipped vehicles in this study, 95%, compared to 60% in Stockholm. The higher difference in the emission factors for the aromatic compounds than for the OVOCs can be related to the fact that diesel HDVs, which are predominantly responsible for the OVOC emissions, have no catalytic converters.

Values reported from the U.S. are for two tunnels with totally different fleet composition, one with 0.1% HDVs (Caldecott) (1) and the other with 60% HDVs (Tuscarora) (2). The emission factors from Caldecott are lower than the values reported in this study, due to the lower emissions of OVOCs from LDVs in comparison with HDVs. Benzaldehyde is the only exception with a larger emission factor in the Caldecott study. A possible explanation for this could be the lower emissions of the benzaldehyde precursor toluene from HDVs. The ratio of catalyst equipped LDVs from the study in Caldecott was 94%. A greater number of HDVs might explain the elevated emission factors for the OVOCs in the Tuscarora tunnel. However, the EF for acetaldehyde and benzaldehyde were found to be higher in the Gubrist tunnel compared with the Tuscarora tunnel.

The EFs separated for LDVs and HDVs by regression (see eq 3) are shown in Table 3. Generally, the results of the EFs of HDVs have much larger uncertainties due to the low fraction of HDVs in the tunnel. The highest fraction of HDVs was 21%, and the extrapolation to 100% is connected with a substantial uncertainty. This explains the slightly negative (statistically insignificant) EFs for several compounds as also reported in other studies (19, 21). For ethanol and isopropanol, the regression is not performed due to the high scatter in the data.

The results of the regression show that for many OVOCs, the EFs of HDV are significantly larger than those of LDVs such as for propanal, butanal, pentanal, hexanal, acetone, 2-butenone, butanone, ethyl acetate, and butyl acetate. This was also found by Staehelin et al. (21) from measurements obtained in 1993 for some of the compounds. Dynamometric tests have also shown higher emissions of OVOCs from HDVs in comparison to LDVs (35, 36). MTBE is the only OVOC which has a significantly higher EF from LDVs which is expected due to this compound being added to gasoline (Swiss regulation: max. 15%, usual range: 2–10%) but not to diesel. For some of the OVOCs, the EFs are not significantly different due to high uncertainty for the HDV EFs. The highest uncertainty was found for acetaldehyde, caused by the previously discussed factors on cold, rainy days. For both vehicle classes (LDVs and HDVs), the OVOC emission factors in the Gubrist tunnel were lower in 2004 than in 1993. Butanone is the only exception with approximately the same EF. For all the measured NMHCs, except 1,3-butadiene, the regression results yield higher EFs from the LDVs than from the HDVs. This is also shown for the majority of compounds from dynamometric tests (35, 36). However, the EFs for butane reported from these dynamometric tests were lower for the LDVs than for HDVs. The opposing result obtained

TABLE 4. Estimate of the Yearly Road Traffic Emissions of the Quantified OVOCs from Measurements in the Gubrist Tunnel, and the Reported NMVOC Values for the EU-15 Countries and Switzerland^a

compounds	emission (kt/year)		
	Switzerland	EU-15	Switzerland*
acetaldehyde	0.10	5.54	0.15 ± 0.025
propanal	0.011	0.65	0.01 ± 0.001
butanal	0.006	0.37	0.01 ± 0.0004
pentanal	0.010	0.58	0.01 ± 0.001
hexanal	0.005	0.30	0.01 ± 0.001
benzaldehyde	0.03	1.53	0.04 ± 0.002
acrolein	0.02	1.24	0.03 ± 0.003
MTBE	0.02	0.89	0.01 ± 0.001
acetone	0.07	4.27	0.05 ± 0.006
MVK	0.010	0.59	0.01 ± 0.001
MEK	0.008	0.44	0.01 ± 0.001
ethanol	1.00	57.5	0.63 ± 0.130
isopropanol	0.37	21.4	0.21 ± 0.047
propanol	0.007	0.39	0.006 ± 0.001
ethyl acetate	0.006	0.33	0.002 ± 0.0004
butyl acetate	0.007	0.39	0.006 ± 0.001
sum OVOC	1.68	96.5	
sum NMVOC	28.0	2555	

^a Values calculated from the reported EFs in Table 3 and the annual driven distance for the total fleet in Switzerland.

from the Gubrist tunnel is probably due to evaporation effects as mentioned earlier.

The Swiss and European (EU-15, i.e., the 15 countries belonging to EU before 2004) traffic emissions of the quantified OVOCs have been approximately estimated (Table 4) by using the ratio of the measured OVOCs with concurrently measured CO₂ at the tunnel exit. The slope for the linear regression line from the CO₂ and OVOC data was multiplied with the total CO₂ emissions from road transport for Switzerland (37) or EU-15 (38), respectively. Using this approach, it was assumed that the OVOC to CO₂ ratio represented the average fleet under highway driving conditions. This is most likely a lower limit for the emissions, since congested driving, as well as cold starts, are not included. All OVOC data were used for this estimation including data from days with elevated mixing ratios for some compounds due to the utilization of windscreen wiper fluid. This explains the lower values obtained from the approach using the calculated EFs multiplied with the total annual driven distance for the Swiss fleet. These values are also shown in Table 4, and they are in most cases almost identical with the values calculated from the CO₂ emissions. For Switzerland the estimated OVOC emissions contribute to approximately 6% of the total road traffic VOC emissions, for EU-15 this fraction is approximately 4%. The principal OVOCs are ethanol and isopropanol, the main components of windscreen wiper fluid, which account for more than 80% of the total OVOC emissions measured in this study. In 2004 the total LDV fleet in Switzerland was approximately 3.8 million vehicles, which gives an emission per vehicle of 0.6 liter of ethanol per year, assuming no other ethanol source.

The studies in the Gubrist tunnel have confirmed that the emissions of OVOCs and NMHCs from road transport have been reduced significantly with improved engine technology. There is still a need for more studies regarding the impact of the compounds in windscreen wiper fluids, and this may become even more important as emissions from combustion engines are expected to be reduced further.

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