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Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zürich (Europe): Seasonal variation and source allocation

Geir Legreid^a, Jacob Balzani Lööv^b, Johannes Staehelin^b, Christoph Hueglin^a, Matthias Hill^a, Brigitte Buchmann^a, Andre S.H. Prevot^c, Stefan Reimann^{a,*}

^a*Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution and Environmental Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland*

^b*Institute for Atmospheric and Climate Science, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland*

^c*Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

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Abstract

Twenty-one oxygenated volatile organic compounds (OVOCs) were measured in four seasonal campaigns at an urban background site in Zürich (Switzerland) with a newly developed double adsorbent sampling unit coupled to a gas chromatograph–mass spectrometer (GC–MS). In addition, selected non-methane hydrocarbons (NMHCs) were measured, as well as formaldehyde in the summer and winter campaign. The most abundant compound measured in all seasons was ethanol, with peak values of more than 60 ppb. Its seasonal variation with a lower mean value in summer compared to that in winter implied mostly anthropogenic sources. In contrast, compounds with additional biogenic sources, or compounds known to be produced in the troposphere by oxidation processes, had seasonal maxima in summer (e.g. methanol, acetone, formaldehyde, methacrolein and 2-butenone (methyl vinyl ketone, MVK)).

For the OVOCs it was estimated that local sources contributed 40% and 49% to the mixing ratios of the measured compounds in summer and in winter, respectively. Combustion was estimated to contribute 75% to these local sources independent of the season. About 50% of both the OVOC and NMHC levels in Zürich could be explained by the regional background, which included regional biogenic and anthropogenic sources in addition to secondary production. Industrial sources were identified for acetone, butanone (methyl ethyl ketone, MEK), *n*-propanol, iso-propanol, *n*-butanol, ethyl acetate and butyl acetate.

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1. Introduction

Volatile organic compounds (VOCs) and nitrogen oxides (NO_x) are important precursors for the production of ozone (O₃) and secondary organic aerosols during summer smog episodes (Odum et al., 1996, 1997; Atkinson, 2000). Several primary

*Corresponding author. Tel.: +41 44 823 5511; fax: +41 44 621 6244.

E-mail address: stefan.reimann@empa.ch (S. Reimann).

as well as secondary air pollutants formed in summer smog are known to be toxic to humans, animals and plants, and efforts are required to reduce their concentrations (Altshuller, 1978; Heck et al., 1984). Oxidized VOCs (OVOCs) are an important fraction of the VOCs and are primarily emitted by vehicular transport, solvent usage, industry and biogenic sources (Placet et al., 2000; Sawyer et al., 2000; Legreid et al., 2007b). Furthermore, several OVOCs are produced by oxidation processes in the troposphere (Atkinson, 2000).

Carbonyls (aldehydes and ketones), being one of the most abundant group of OVOCs in urban air, have been measured in several studies during the last decades (Hewitt, 1999). Formaldehyde, acetaldehyde and acetone were reported to be among the most abundant OVOCs in urban environments (Granby et al., 1997; Bakeas et al., 2003). Alcohols have not frequently been measured, but were included in urban campaigns in Boulder, USA (Goldan et al., 1995), in Stockholm, Sweden (Jonsson et al., 1985), in Sao Paolo, Brazil (Nguyen et al., 2001) and in Wuppertal, Germany (Niedojadlo, 2001). In Stockholm, large amounts of ethanol and iso-propanol were suspected to originate from window wiper fluid, whereas in Sao Paolo the influence of ethanol as replacement of gasoline in vehicles was studied. Niedojadlo (2001) also measured butyl acetate in Wuppertal, and discovered large industrial emissions. Furthermore, methyl-tert-butyl-ether (MTBE), a gasoline additive, has been detected in exhaust gas in studies from Europe and USA (Poulopoulos and Philippopoulos, 2000; Schade et al., 2002; Legreid et al., 2007b).

The most recent studies related to source identification of OVOCs and their emission strength in urban areas in Asia have been published by Zhao et al. (2004) and Kim et al. (2005), using factor analysis and positive matrix factorization, respectively. In Europe, Borbon et al. (2004) presented 4 years of measurement data of 50 non-methane hydrocarbons (NMHCs) and 17 OVOCs from a rural site in Eastern France, but the sample frequency was limited to two samples a week. For Zürich (Switzerland), Staehelin et al. (2001) used a principal component analysis (PCA) to determine the proportion of motor traffic emissions to the ambient air concentrations of 58 NMHCs. The data was collected from 1 year of continuous measurements, but no individual OVOCs were measured.

In this study a recently developed instrument for OVOC analysis (see Section 2.1) is applied. Section 3

contains the results from four one-monthly seasonal measurements of OVOCs and selected NMHCs from an urban background site in Zürich in 2005 and 2006. The measured compounds are discussed in relation to their relative abundances, as well as daily and annual cycles. In addition, anthropogenic sources are quantified by a source-tracer-ratio method (see Section 2.2) and their relative importance is discussed.

2. Methods

2.1. Measurements

The sample location in Zürich city centre is situated in a small park area (Kasernenhof) surrounded by busy streets within a residential area, and is regarded as an urban background site. Possible anthropogenic emissions from non-tailpipe OVOC sources include gasoline and solvent evaporation, residential heating and small industrial enterprises within the proximity of the site. At this site continuous measurements of O₃, nitrogen oxides (NO + NO₂), PM₁₀ and sulphur dioxide (SO₂) are performed by Empa within the Swiss national air pollution monitoring network (NABEL, 2006).

Air samples for OVOC analysis were taken from the main inlet of the measurement station by a 8 m × $\frac{1}{4}$ " PFA sampling line equipped with a 0.5 µm silcotreated inlet filter (Restek Corp.) for removal of particulate matter. This line was continuously flushed with 0.5 l of air per minute. In order to prevent producing aldehyde as an artefact during sampling (Northway et al., 2004), 10 ml min⁻¹ of 20 ppm NO was added to the air stream after 15 July 2005. Thereby, NO reacts rapidly with O₃ but not with the OVOCs (Komenda et al., 2003) and the produced NO₂ can be seen as non-reactive on the time scale of 0.5 min (i.e. the time which the air was in the sampling line). Every 50 min a sample of 350 ml was taken during 6 min.

The OVOCs were collected on a two-stage adsorbent system connected to a gas chromatograph with mass spectrometer (GC-MS Agilent HP 6890/HP 5973N). The water removal was performed on the sampling trap (0.6 g of Hayesep D (Supelco)) at room temperature. The hydrophobic nature of the adsorbent allowed most of the water to pass the trap, and the remaining humidity was removed by dry helium flushing. Thereafter, the compounds were refocused on a microtrap (14 mg of Hayesep D) at -40 °C to improve the separation of the

compounds on the analytical column. For further details, see Legreid et al. (2007a, b). The accuracy and precision calculated from intercomparison measurements were 3–25% (*n*-butanol: 37%) and 1–5%, respectively. This intercomparison was a part of the European project ACCENT, subgroup Quality Assurance (QA) and was performed at the SAPHIR smog chamber in January 2005. Methanol was only recovered at 60%, and this was corrected for in the following measurement campaigns. The detection limit for each compound was calculated as three times the standard deviation above the noise of five consecutive zero air samples. The sample error was calculated as the combined error of the given uncertainty in the calibration gas mixture and the uncertainty in the calibration. The latter was calculated from the analysis of five standards and five blanks and the reported value was calculated for the median value during the respective measurement campaign (Table 1). The calibration of the instrument was performed once per day by the analysis of a standard gas mixture (Apel & Riemer Environmental Inc., USA), with about 400 ppb mixing ratio of the compounds. A calibrated sample loop was used to dilute the standard with air from a zero-air generator (Parker Inc.). The system was in operation during 4 measurement campaigns in spring (18.03.05–18.04.05), summer (01.07.05–01.08.05), autumn (10.11.05–30.11.05) and winter (19.12.05–01.02.06). After discarding data during instrument start-ups and during instrument failure, a total of almost 2500 samples were further analysed as described below.

In addition, formaldehyde has been measured using an instrument with the Hantzsch chemistry fluorimetric detection technique according to Junkermann and Burger (2006), a further development of the Aero Laser AL4021 (Hak et al., 2005). The calibration was performed by using liquid standards (range 3–4 ppb), and the gas phase concentration was calculated from the enrichment factor between gas and liquid flows in the stripper. For more details see Balzani (2007).

2.2. Source-tracer-ratio method

To estimate the contribution of the different sources to the abundance of OVOCs and NMHCs in Zürich, a source-tracer-ratio method was applied (Millet et al., 2005). This method assumes that there is a characteristic ratio for each compound to a source-specific tracer. To eliminate the influence of

distant sources, a background subtraction was performed as follows. Firstly, the large-scale background was defined as the seasonal 0.1 quantile of the mixing ratio measured at the high alpine site Jungfrauoch. Measurements at Jungfrauoch were performed with the same instrument as in this study (Legreid et al., 2007a). Thereafter, the regional background was defined as the daily running 0.1 quantile and was subtracted from the data. The regional background represents the daily accumulation and is probably an overestimation. Data collected during two periods in winter with strong inversion were excluded from the source apportionment. The obtained data set was representative for the locally emitted pollutants, and the next step was to identify possible sources.

The sources taken into consideration to potentially contribute to atmospheric OVOCs were road traffic, residential heating, industry, evaporation and biogenic, as well as secondary production (i.e. oxidation of NMHCs). Road traffic and stationary combustion (i.e. room heating) could not be reasonably separated due to similar diurnal cycles and lack of specific tracers. This was also the case for secondary and biogenic sources due to similar influencing factors (temperature and radiation). The total concentration $[X]_i$ for each compound can then be explained as

$$[X]_i = [X]_{i,0} + [X]_{i,\text{comb}} + [X]_{i,\text{industry}} + [X]_{i,\text{other}}, \quad (1)$$

where $[X]_{i,0}$ is the background mixing ratio (consisting of regional and large-scale background), $[X]_{i,\text{comb}}$ the contribution of the combustion sources (mobile and stationary), $[X]_{i,\text{industry}}$ represents the industrial emissions and $[X]_{i,\text{other}}$ the other sources (biogenic, evaporative and other unidentified sources). Fig. 1 provides an overview of the applied method.

The contribution of combustion sources was determined using CO as the tracer. In Europe this compound is almost exclusively emitted from anthropogenic combustion processes and dominated by vehicle exhaust in urban regions in summer (Possanzini et al., 1996; Kuhlwein et al., 2002; EMEP, 2005). CO has a long tropospheric lifetime and is not significantly degraded within the time-frame of transport from the sources to the measurement site on regional scale. All of the measured OVOCs are reported to be emitted from combustion sources (Schauer et al., 1999; McDonald et al., 2000;

Table 1
Mixing ratios [ppb] measured in Zürich during seasonal campaigns in 2005/2006

	Spring 2005					Summer 2005					Fall 2005					Winter 2005/2006					
	Median	Mean	IQR	DTL	Error	Median	Mean	IQR	DTL	Error	Median	Mean	IQR	DTL	Error	Median	Mean	IQR	DTL	Error	
Formaldehyde	NA	NA	NA	NA	NA	1.98	2.35	1.56–2.76	NA	NA	NA	NA	NA	NA	NA	NA	1.66	1.83	1.14–2.34	NA	NA
Acetaldehyde	NA	NA	NA	NA	NA	0.62	0.80	0.44–1.10	0.028	0.151	0.35	0.45	0.23–0.57	0.049	0.027	0.65	0.82	0.41–1.21	0.060	0.038	
Propanal	NA	NA	NA	NA	NA	0.09	0.12	0.07–0.15	0.005	0.010	0.10	0.11	0.08–0.13	0.030	0.013	0.10	0.12	0.07–0.16	0.009	0.007	
Butanal	NA	NA	NA	NA	NA	0.04	0.05	0.03–0.06	0.003	0.004	0.02	0.02	0.01–0.03	0.008	0.004	0.04	0.04	0.02–0.06	0.009	0.004	
Pentanal	NA	NA	NA	NA	NA	0.03	0.03	0.02–0.04	0.002	0.003	0.02	0.02	0.01–0.03	0.003	0.002	0.02	0.02	0.01–0.03	0.009	0.003	
Hexanal	NA	NA	NA	NA	NA	0.05	0.06	0.04–0.07	0.001	0.005	0.02	0.03	0.01–0.03	0.002	0.002	0.02	0.02	0.01–0.02	0.008	0.003	
Benzaldehyde	NA	NA	NA	NA	NA	0.02	0.02	0.01–0.02	0.013	0.006	0.01	0.01	0.01–0.02	0.009	0.003	0.02	0.02	0.01–0.02	0.023	0.008	
Acrolein	0.07	0.08	0.05–0.10	0.009	0.002	0.05	0.06	0.03–0.07	0.004	0.006	0.06	0.09	0.04–0.11	0.009	0.006	0.12	0.14	0.07–0.21	0.007	0.008	
Methacrolein	0.01	0.01	0.01–0.02	0.002	0.000	0.03	0.04	0.02–0.05	0.001	0.003	0.01	0.01	0.01–0.01	0.001	0.001	0.01	0.02	0.01–0.02	0.003	0.001	
MTBE	0.10	0.14	0.06–0.17	0.000	0.001	0.13	0.18	0.09–0.22	0.000	0.011	0.09	0.15	0.05–0.21	0.000	0.007	0.07	0.09	0.04–0.11	0.000	0.004	
Acetone	1.45	1.66	0.96–2.12	0.060	0.013	1.81	2.12	1.40–2.55	0.034	0.137	0.95	1.24	0.71–1.57	0.040	0.058	0.88	1.17	0.60–1.62	0.017	0.046	
MVK	0.03	0.03	0.02–0.04	0.020	0.003	0.06	0.08	0.04–0.09	0.009	0.009	0.03	0.03	0.02–0.04	0.007	0.004	0.03	0.03	0.02–0.05	0.007	0.003	
MEK	0.19	0.24	0.14–0.32	0.002	0.002	0.16	0.20	0.11–0.25	0.001	0.011	0.15	0.17	0.10–0.23	0.004	0.011	0.16	0.22	0.10–0.32	0.003	0.009	
Methanol	1.83	2.18	1.26–2.84	0.121	0.043	3.05	3.18	2.15–3.97	0.061	0.391	0.86	1.11	0.56–1.33	0.086	0.066	0.97	1.21	0.67–1.62	0.102	0.045	
Ethanol	4.42	6.87	2.84–8.62	0.123	0.021	2.57	3.94	1.62–5.22	0.055	0.130	4.97	7.61	2.61–9.22	0.053	0.249	5.90	7.53	3.81–9.22	0.046	0.296	
Isopropanol	0.52	0.86	0.25–1.03	0.006	0.004	0.38	0.51	0.23–0.65	0.003	0.034	0.79	1.13	0.45–1.49	0.026	0.049	0.72	1.00	0.46–1.21	0.003	0.040	
Propanol	0.06	0.08	0.03–0.12	0.008	0.002	0.02	0.03	0.01–0.04	0.004	0.003	0.04	0.06	0.02–0.07	0.003	0.003	0.06	0.08	0.03–0.11	0.011	0.006	
MBO	0.06	0.08	0.04–0.10	0.000	0.001	0.08	0.11	0.05–0.14	0.000	0.006	0.13	0.18	0.08–0.23	0.000	0.009	0.14	0.16	0.08–0.21	0.000	0.005	
Butanol	0.01	0.01	0.01–0.01	0.020	0.003	0.02	0.07	0.01–0.04	0.011	0.004	0.03	0.04	0.02–0.05	0.000	0.002	0.02	0.06	0.01–0.03	0.013	0.021	
Methylacetate	0.05	0.06	0.04–0.07	0.004	0.001	0.04	0.05	0.03–0.06	0.003	0.005	0.05	0.06	0.03–0.07	0.000	0.003	0.06	0.07	0.04–0.11	0.006	0.004	
Ethylacetate	0.17	0.24	0.09–0.30	0.000	0.003	0.13	0.19	0.08–0.23	0.000	0.013	0.20	0.28	0.11–0.35	0.000	0.015	0.20	0.25	0.10–0.33	0.000	0.010	
Buthylacetate	0.07	0.10	0.03–0.13	0.000	0.001	0.04	0.06	0.02–0.08	0.000	0.004	0.10	0.15	0.06–0.19	0.000	0.006	0.08	0.13	0.04–0.18	0.003	0.005	
Butane	0.88	1.03	0.60–1.34	0.002	0.002	0.57	0.68	0.40–0.86	0.001	0.035	1.09	1.45	0.73–1.97	0.004	0.063	1.02	1.20	0.79–1.48	0.002	0.048	
1,3-Butadiene	0.06	0.07	0.04–0.09	0.000	0.001	0.06	0.07	0.04–0.09	0.001	0.002	0.06	0.08	0.03–0.13	0.000	0.004	0.08	0.09	0.05–0.12	0.000	0.003	
Isoprene	0.07	0.08	0.05–0.10	0.000	0.002	0.12	0.16	0.08–0.18	0.000	0.006	0.06	0.08	0.03–0.11	0.000	0.002	0.05	0.06	0.03–0.07	0.000	0.002	
Benzene	0.37	0.41	0.28–0.50	0.001	0.003	0.20	0.23	0.15–0.29	0.000	0.014	0.38	0.48	0.26–0.62	0.001	0.031	0.68	0.75	0.41–1.02	0.001	0.029	
Toluene	1.18	1.46	0.78–1.76	0.003	0.340	1.12	1.43	0.84–1.89	0.001	0.043	1.28	1.70	0.74–2.42	0.002	0.078	0.99	1.25	0.66–1.61	0.002	0.048	
Ethylbenzene	0.22	0.26	0.17–0.30	0.005	0.033	0.18	0.21	0.14–0.26	0.001	0.006	0.19	0.25	0.11–0.35	0.001	0.008	0.17	0.21	0.12–0.28	0.000	0.007	
<i>m,p</i> -Xylene	0.59	0.72	0.43–0.86	0.008	0.446	0.49	0.58	0.36–0.74	0.001	0.026	0.61	0.80	0.33–1.14	0.030	0.080	0.50	0.66	0.33–0.85	0.000	0.023	
<i>o</i> -Xylene	0.21	0.25	0.15–0.30	0.026	0.020	0.20	0.25	0.15–0.32	0.005	0.009	0.23	0.30	0.13–0.42	0.000	0.009	0.21	0.25	0.14–0.33	0.001	0.008	

The median, mean, IQR and measurement error are listed for each season as also for all measurements. IQR, interquartile range; DTL, detection limit; NA, not available.

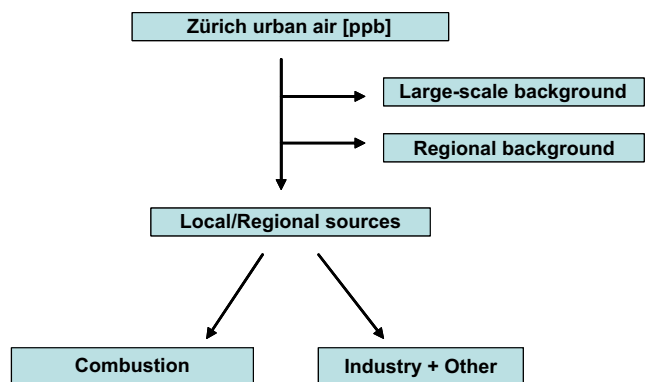


Fig. 1. Step by step source allocation of summer data (compare text).

Schauer et al., 2001; Schauer et al., 2002). Assuming no other sources for CO, the contribution from combustion sources for each compound was calculated by an approach presented by Millet et al. (2005) using Eq. (2). This was done separately for summer and winter data.

$$[X]_{i,\text{comb}} = [\text{CO}]_i \left(\frac{X}{\text{CO}} \right)_r, \quad (2)$$

where $(X/\text{CO})_r$ is the characteristic emissions ratio for each compound X to CO after subtraction of background for both X and the tracer CO. However, this ratio cannot be retrieved by simple linear regression since the influence of other sources than combustion can bias the results. Instead, the ratio is obtained by varying the $(X/\text{CO})_r$ over a range of possible values, and for each value the coefficient of determination (R^2) between the residuals $([X]_i - [X]_{i,0} - [X]_{i,\text{comb}})$ and CO is calculated. As an example, Fig. 2 shows the R^2 for residual benzene plotted against the ratio $(\text{benzene}/\text{CO})_r$. The minimum in Fig. 2 represents the optimum ratio $(\text{benzene}/\text{CO})_r$ describing the contribution from combustion sources.

Compounds with a distinct difference in the ratio to CO on working days compared to weekends, were assumed to have substantial industrial sources (Steinbacher et al., 2005; Wang et al., 2005). In the case of Zürich the industries were assumed to be represented by nearby small-scale industries since there is no large emitting industry (such as chemical production or power plants) in the vicinity. As an example the weekday/weekend correlation between butyl acetate and CO is shown in Fig. 3. Similar behaviour was found for acetone, MEK, ethyl acetate, butyl acetate, iso-propanol, *n*-propanol and *n*-butanol. To obtain the characteristic emissions

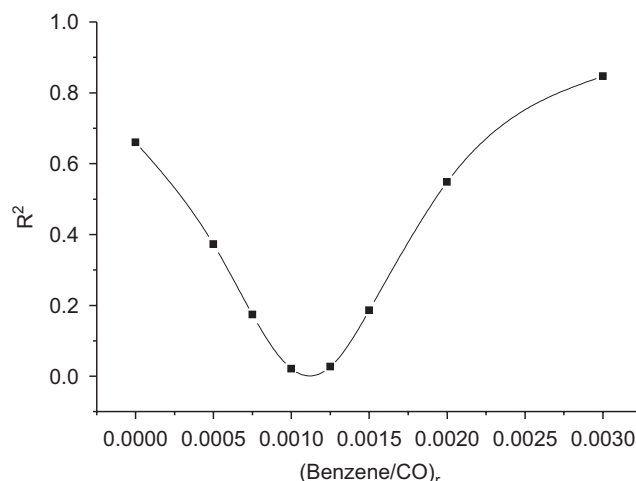


Fig. 2. Plot for estimation of the combustion ratio to CO for benzene in winter applying the method described by Millet et al. (2005) (see text).

ratio (X/CO) for road traffic, only the weekend data were considered. The derived road traffic emissions ratio was then used to calculate the road traffic contribution on all days, and the excess concentration of the compound X was attributed to industrial sources. In summer enhanced mixing of the air masses and stronger evaporative, biogenic and secondary sources masked the weekday/weekend differences, and made it thereby impossible to isolate the industrial emissions. Therefore, during summer industrial sources have been included in the categories “combustion” and “other sources.”

In summer the residual term was assumed to additionally originate from biogenic emissions, secondary production and evaporation, which were all incorporated in “other sources.” Some of these sources would also to some extent be explained by the regional background. Note that the used procedure is not suitable to describe chemical degradation when important at local scale. This especially could impact compounds with very low tropospheric lifetimes.

3. Results and discussion

3.1. Seasonal variation

In Table 1 the measured OVOCs and NMHCs from Zürich are listed as their seasonal median, mean and interquartile range (IQR: 25–75% quartiles) from the four seasonal campaigns. In total, 50% of the measured concentrations were alcohols, 16% aromatics, 15% aldehydes, 9% ketones, 2%

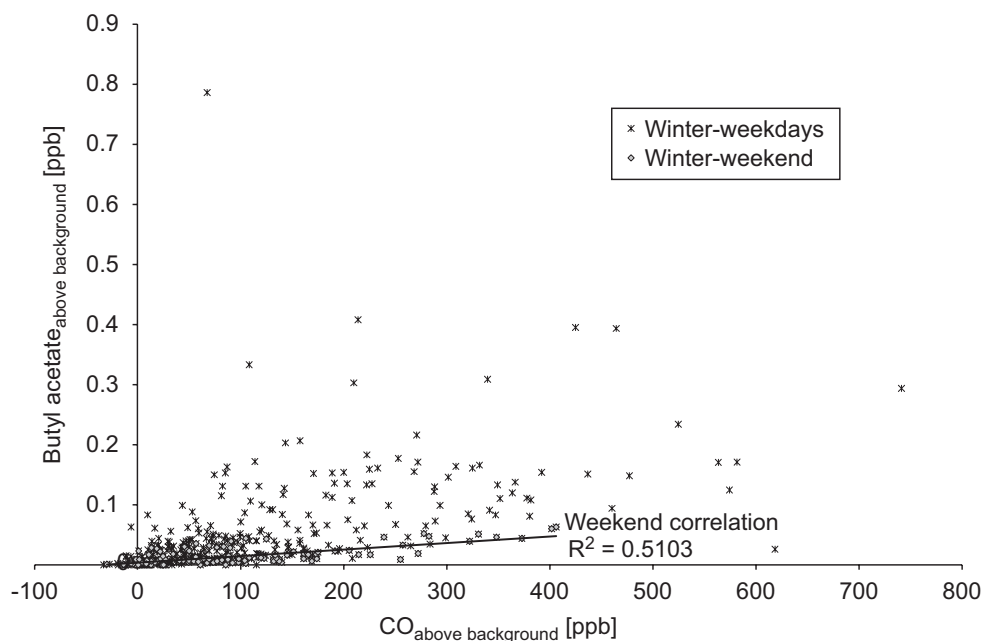


Fig. 3. Butyl acetate mixing ratios versus carbon monoxide (CO) in winter. Data separated into weekdays and weekends. (Note that the daily running 0.1 quantile is subtracted for both butyl acetate and CO, which cause the negative values).

esters, 7% butane/1,3-butadiene/isoprene and 1% MTBE. The most abundant OVOC measured was ethanol, which had the highest average annual mean mixing ratio of all the OVOCs with 6.6 ppb and with maximum values of more than 60 ppb. Ethanol is a main component of window wiper fluids, and therefore our finding confirms results from studies performed in a Swiss tunnel (Legreid et al., 2007b) and in the city centre of Stockholm, Sweden (Jonsson et al., 1985). The second most abundant OVOC measured was formaldehyde (1.83 ppb), followed by methanol (1.80 ppb) and acetone (1.45 ppb).

Methanol was the compound with the largest relative increase from winter to summer with 2.6 times higher median mixing ratio in summer (i.e. 1.21–3.18 ppb). This can be explained by the strong biogenic sources for methanol (Jacob et al., 2005), which also accounts for the elevated mixing ratio for isoprene (2.5 ×), hexanal (2.4 ×) and acetone (2.0 ×). Furthermore, products from the tropospheric oxidation of isoprene (Apel et al., 2002) also showed elevated mixing ratios in the summer compared with winter (i.e. methacrolein (2.0 ×), methyl vinyl ketone (MVK) (2.0 ×) and formaldehyde (1.2 ×)). On the contrary, benzene, which is exclusively emitted from anthropogenic sources, showed much higher mixing ratios in winter compared to summer (3.4 times higher median mixing

ratio). Larger winter values were also found for the mainly anthropogenic emitted compounds propanol (3.1 ×), ethanol (2.3 ×) and acrolein (2.3 ×).

3.2. Diurnal variation

Fig. 4 shows the diurnal cycles of trace gases in Zürich, measured simultaneously with the OVOCs during the campaigns. For primarily emitted pollutants such as CO, SO₂, benzene and toluene the anthropogenic emissions and meteorology determine the diurnal cycles. At night (until about 05:00), mixing with cleaner air masses from the surrounding areas and lower emissions reduce the mixing ratios. Chemical reactions and deposition can for some compounds (such as O₃) play an important role as well. Thereafter, traffic emissions lead to local maxima in the morning, which is found for the anthropogenic pollutants NO_x, benzene and toluene (mainly from traffic). The following rapid decrease is due to the break-up of the nighttime inversion and vertical mixing with the residual layer, which is enriched in O₃ (see O₃ diurnal cycle). In the evening the build-up of the inversion and continuous emissions into the urban air, lead to another maximum for the pollutants.

The morning peak in winter appears 1–2 h later than in summer due to later break-up of the inversion, which can also be identified in the O₃

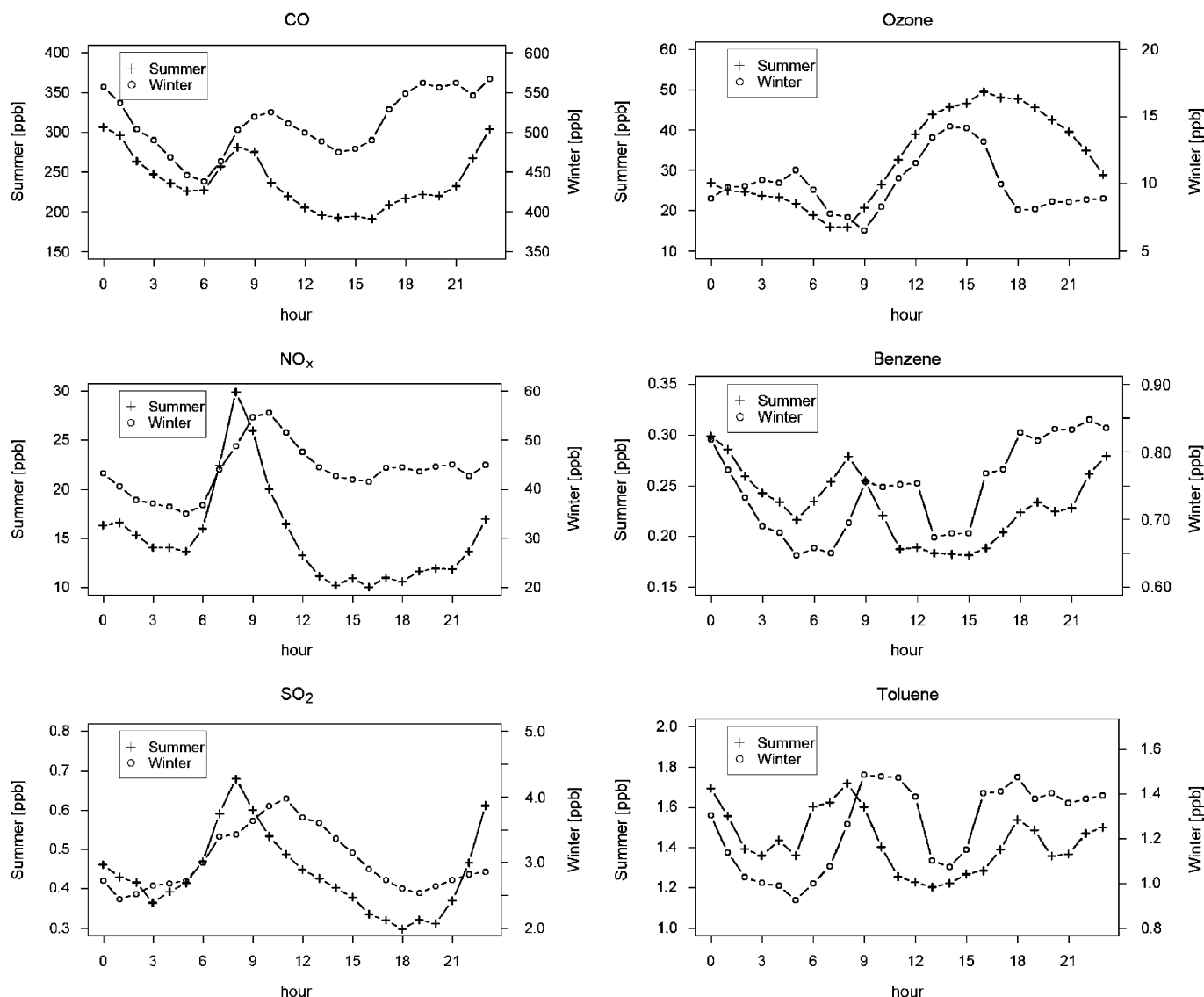


Fig. 4. Average diurnal cycles of CO, NO_x, SO₂, benzene, toluene and ozone in Zürich during the summer and winter campaigns. (Note the different scales for summer and winter.)

diurnal cycle. The 6 times higher morning peak increase for SO₂ in winter compared to that in summer is an indication of stationary combustion sources. In Zürich oil burners are frequently used for room heating, and they are known to emit more SO₂ than traffic sources due to the higher sulphur content in oil compared to gasoline. On the other hand, SO₂ emissions in summer are probably mostly caused by road traffic.

Fig. 5 shows the diurnal variations for isoprene, MVK, methanol, acrolein, iso-propanol and MTBE in summer and in winter. All these compounds were identified in traffic exhaust emissions measured recently in a road tunnel close to Zürich (Legreid et al., 2007b). As for the trace gases discussed in Fig. 4 the late evening maximum for all compounds

in summer was due to the build-up of an inversion layer during stable meteorological conditions and the continuous emissions into the shallow boundary layer. Iso-propanol and MTBE had additional maximum values in the morning parallel to the emissions of NO_x, CO, benzene and toluene (Fig. 4), which are compounds related to vehicle exhaust. Iso-propanol emissions have been observed from window wiper fluids in Stockholm (Jonsson et al., 1985) and in the Gubrist tunnel close to Zürich (Legreid et al., 2007b), but could also originate from small-scale industrial sources like printing shops. MTBE is used as a gasoline additive in Switzerland with concentrations between 2% and 8% per volume. Pouloupoulos and Philippopoulos (2000) reported MTBE exhaust emissions particularly

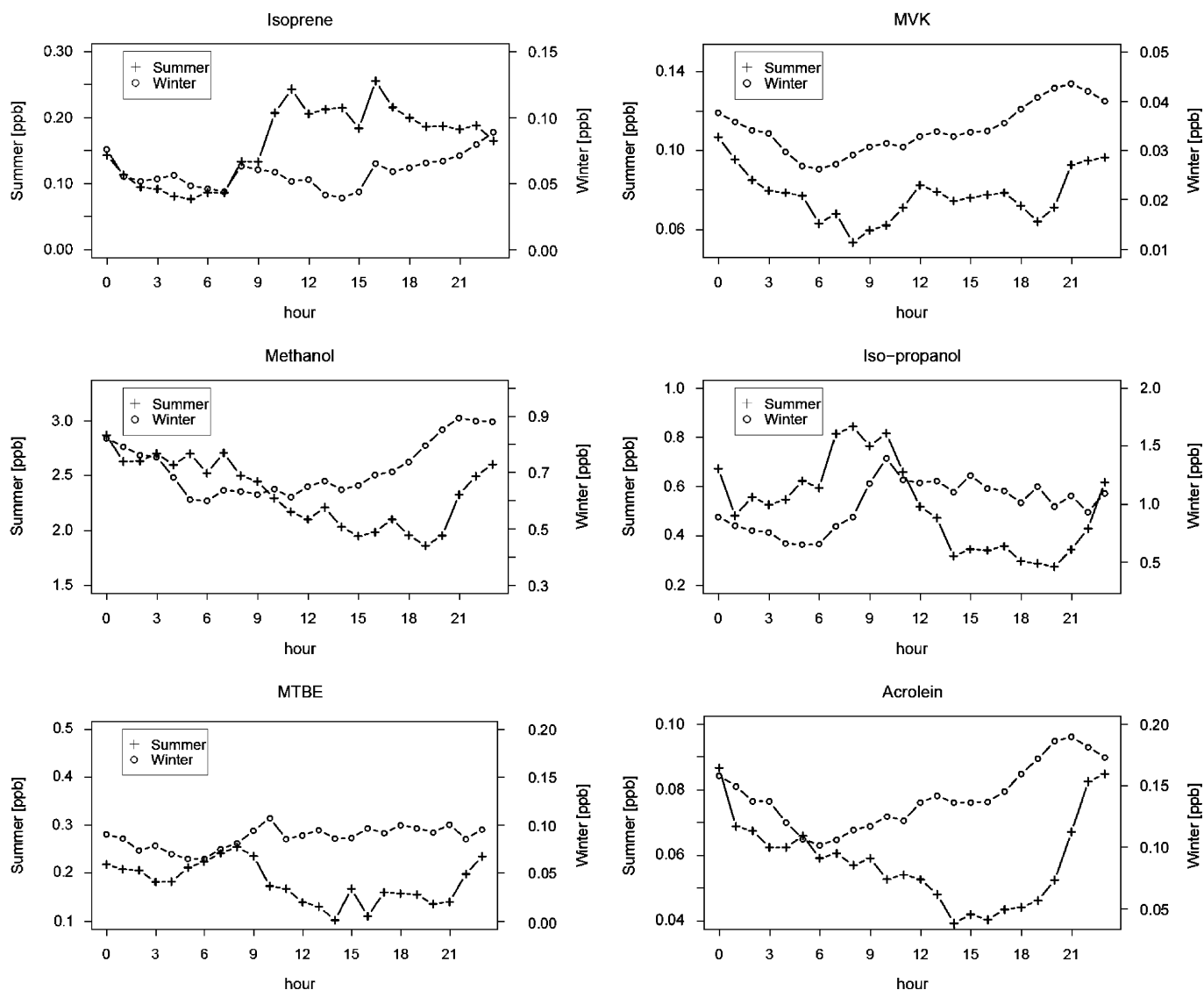


Fig. 5. Average diurnal cycles of isoprene, MVK, methanol, acrolein, iso-propanol and MTBE in Zürich during the summer and winter campaigns. (Note the different scales for summer and winter.)

during cold start and from evaporation. The summer values of isoprene are most probably explained by biogenic emissions as reflected in the diurnal cycle. Temperature and photosynthetically active radiation (PAR) are the main factors controlling the emissions of isoprene (Guenther et al., 1993). However, in urban environments a part of the emissions could also be due to traffic exhaust emissions (Reimann et al., 2000; Borbon et al., 2004). In fact, by closer inspection of the isoprene diurnal cycle, two small peaks can be seen at rush traffic hours at 8 AM and 4 PM.

MVK is a product from the photooxidation of isoprene and has a local maximum in summer around noon. The relative increase of the MVK

mixing ratio from the morning low to the daytime high is about 50% in summer. In winter, the MVK mixing ratio follows the CO mixing ratio quite closely, suggesting combustion sources for this compound. This has also been observed in other studies (Schauer et al., 1999, 2001, 2002). In contrast to the traffic related primary air pollutants, methanol shows no distinct late morning maximum. This suggests that even in an urban environment biogenic sources for methanol are dominant, which is underlined by the much higher mixing ratios in summer. From other studies methanol have also been reported to originate from biomass burning, both directly and secondarily from tropospheric oxidation processes (Holzinger et al., 1999; Holzinger et al., 2005).

3.3. Source identification using a source-tracer-ratio method

3.3.1. Summer campaign

The results of the source allocation for the summer campaign using the source-tracer-ratio method described in Section 2.2 are shown in Table 2. Acetaldehyde, butanal, pentanal and acetone were the compounds with the highest relative contribution from the large-scale background (see Table 2), which can be explained by their secondary production from the oxidation of NMHCs (Atkinson, 2000). In fact, for acetaldehyde the large-scale background (41%) was the most important contribution to its mixing ratio in Zürich. This compound has been measured throughout the atmosphere and has been found even in the Arctic at levels over 200 ppt (Boudries et al., 2002). At other remote locations in the northern hemisphere mixing ratios of 200–400 ppt have been observed (Wisthaler et al., 2002; Singh et al., 2004). The main portion of the other aldehydes was explained by the regional background. The regional background

probably includes more distant emissions as well as secondary production. Combustion explains less than 30% of the aldehydes mixing ratio in summer. The unsaturated aldehydes acrolein and methacrolein showed a different behaviour with negligible large-scale background due to their relatively low lifetime of less than a day. Acrolein was the aldehyde with the highest relative emission from combustion, whereas methacrolein had an important contribution from other sources, which in this case probably was dominated by secondary production from the oxidation of isoprene.

Apart from direct emissions, ketones (i.e. acetone, MEK, MVK) can also be produced by secondary formation in the atmosphere (Atkinson, 2000). Furthermore, the atmospheric lifetime of acetone is about 1 month. The combination of these two effects explains the relatively large amount of acetone in the large-scale background. Relatively high mixing ratios of acetone (0.5–1.1 ppb) have also been observed by other groups measuring this compound at remote locations (Boudries et al., 2002; Wisthaler et al., 2002; Holzinger et al., 2005; Schade and Goldstein, 2006). In summer large sources from vegetation have been reported for acetone (Goldstein and Schade, 2000; Jacob et al., 2002; Fall, 2003). In our study, these were incorporated in both the large-scale and the regional background, which explained in total 78% of the measured acetone mixing ratio in summer. MVK is a degradation product from isoprene, and MEK is an industrial solvent and also a secondary trace gas. Both compounds had a low large-scale background in this study, but could to a greater extent be attributed to the regional background. For MVK this can be explained by high regional atmospheric production in combination with the relatively low atmospheric lifetime of less than a day. MEK has an atmospheric lifetime of about 10 days, but low atmospheric production. Its regional background is probably explained by industrial sources due to its use as solvent in the manufacturing industry (EPA, 1994). MTBE could mainly be attributed to combustion due to its use as a gasoline additive in Switzerland. This compound is toxic and water soluble, which makes it a threat to drinking water sources.

Alcohols had a small relative contribution from the large-scale background except for methanol with 11%. Methanol has a long lifetime of 12 days and has consequently been found in relatively high quantities (0.3–1.2 ppb) at distant locations

Table 2
Source allocation for OVOCs in summer

	Local sources		Background	
	Combustion (%)	Other sources (%)	Regional (%)	Large scale (%)
Formaldehyde	12	15	60	13
Acetaldehyde	19	16	25	41
Propanal	19	12	56	13
Butanal	12	12	49	26
Pentanal	18	13	42	26
Hexanal	29	11	49	11
Benzaldehyde	31	9	50	10
Acrolein	34	9	52	4
Methacrolein	16	20	61	2
Methyl-tert-butyl-ether	50	6	43	2
Acetone	9	14	48	30
MVK	12	26	55	6
MEK	20	13	59	8
Methanol	18	8	63	11
Ethanol	55	11	32	1
Isopropanol	43	17	37	3
Propanol	41	23	33	4
2-Methyl-3-buten-2-ol	50	8	39	3
Butanol	17	69	14	NA
Methyl acetate	28	7	48	16
Ethyl acetate	35	23	40	2
Butyl acetate	35	26	36	3

The local sources describe the daily accumulation (see Section 3.2).

(Singh et al., 2000; Boudries et al., 2002; Wisthaler et al., 2002; Singh et al., 2004). It has been reported to mainly originate from biogenic sources (Jacob et al., 2005; Schade and Goldstein, 2006), but also from secondary production in altered biomass burning plumes (Holzinger et al., 2005). The other alcohols, except *n*-butanol, could mainly be explained by combustion processes, either from vehicle or industrial emissions. The high relative contribution of the combustion source to ethanol and iso-propanol can be explained by their usage in window wiper fluids. For *n*-butanol industrial sources were shown to be dominant in winter (see below), which in summer were included into the fraction of “combustion” and “other sources.”

The esters (methyl acetate, ethyl acetate and butyl acetate) were mainly attributed to the regional background. These compounds are common solvents in the industry, and ethyl acetate and butyl acetate are also used in industrial food production. In addition, methyl acetate has a considerable contribution from the large-scale background, which can be explained by its stability with a lifetime of about 30 days due to the reaction with OH radical. It is produced in the atmosphere from the oxidation of MTBE (Smith et al., 1991; Tuazon et al., 1991) and tert-amyl methyl ether (TAME) (both gasoline additives, Smith et al., 1995), and is also found in air from landfills (Fernandez-Martinez et al., 2001).

In Table 3 the contributions of the background and regional sources to NMHC concentrations in summer in Zürich are shown. Generally, the NMHCs have a low contribution from the large-scale background (0–5%), and again the compound with longest lifetime (benzene) had the highest contribution. Most of the NMHCs were mainly explained by regional background, which could originate from distant road traffic and industrial sources. The exceptions were 1,3-butadiene and isoprene due to their low lifetimes of only a few hours in summer. In the case of 1,3-butadiene local industry could be important, which was also suspected from a study in France (Borbon et al., 2004). The high fraction of other sources explaining the isoprene emissions were most likely of biogenic origin as estimated for European conditions by Simpson et al. (1995).

Fig. 6 shows the summary of the source profiles for the OVOCs and NMHCs in summer in Zürich obtained from the source-tracer-ratio method. The large-scale background was much higher for the

Table 3
Source allocation for NMHCs in summer

	Local sources		Background	
	Combustion (%)	Other sources (%)	Regional (%)	Large scale (%)
Butane	34	6	58	2
1,3-Butadiene	26	55	18	1
Isoprene	8	66	26	0
Benzene	31	5	59	5
Toluene	23	16	60	1
Ethylbenzene	25	9	64	1
<i>m,p</i> -Xylene	31	8	61	1
<i>o</i> -Xylene	29	10	60	1
1,2,4-Trimethylbenzene	35	27	37	1

OVOCs compared to the NMHCs due to secondary production of the important compounds acetaldehyde, acetone and methanol. The regional background was the largest contributor for both groups of compounds with 50% and 56% contribution to the OVOCs and NMHCs, respectively. The main local source was combustion, which explained about one-quarter of the mixing ratios for both groups of compounds. Other sources in summer could be emissions from biogenic sources, from industry (explained in winter 4% of the OVOC emissions) and households.

3.3.2. Winter campaign

The relative contributions to the OVOC mixing ratios from the various sources in winter are shown in Table 4. For the majority of the aldehydes, the relative contribution from the large-scale background was higher in winter than in summer. This might reflect the longer atmospheric lifetimes in this season. Lower biogenic sources were the most likely reason for the reduced contribution of the regional background for acetaldehyde, butanal and hexanal. The combustion source contribution increased for all aldehydes in winter compared to summer, which is probably due to elevated emissions from stationary combustion sources like oil burners and stoves. The fuel for these units are similar to diesel, and diesel-fuelled vehicles are known to emit more oxygenated compounds than gasoline-fuelled vehicles per litre of fuel (Schauer et al., 1999, 2002; Legreid et al., 2007b).

MTBE has the same contribution from combustion sources in winter as in summer since it is solely emitted from gasoline vehicles. In winter the ketones

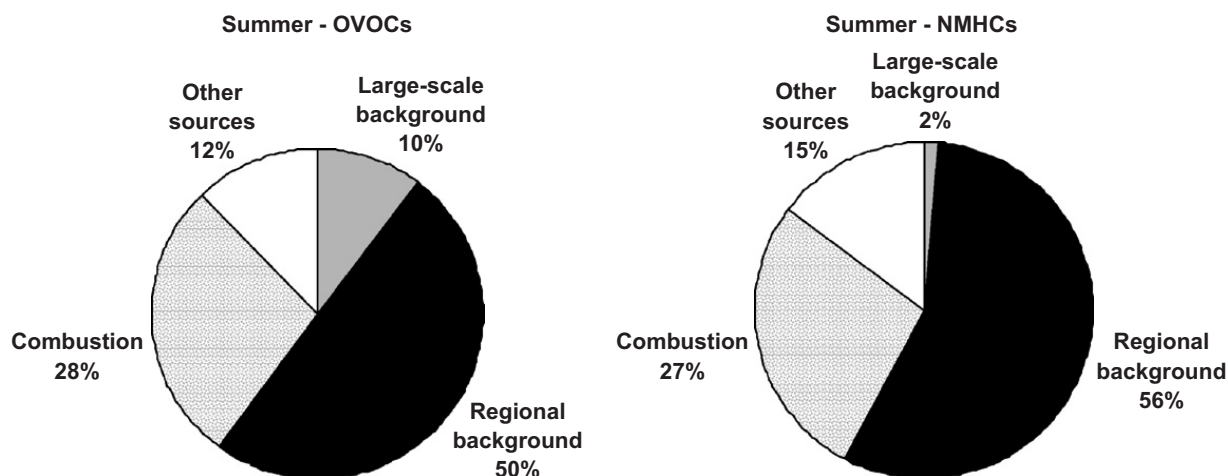


Fig. 6. Source profile for OVOCs and NMHCs in Zürich in summer. (Other sources mean local biogenic sources, solvent use or locally produced secondary compounds.)

Table 4
Source allocation for OVOCs in winter

	Combustion (%)	Industry (%)	Other sources (%)	Regional background (%)	Large-scale background (%)
Formaldehyde	19		11	63	7
Acetaldehyde	36		6	4	55
Propanal	26		5	53	16
Butanal	29		5	6	61
Pentanal	39			49	12
Hexanal	36			28	36
Benzaldehyde	43			41	17
Acrolein	41		7	45	7
Methacrolein	49		0	42	9
Methyl-tert-butyl-ether	50			46	4
Acetone	16	16		17	52
MVK	29		8	46	16
MEK	15	18		49	18
Methanol	26		13	−4	65
Ethanol	41		15	44	1
Isopropanol	38	17		42	3
Propanol	13	32		53	2
2-Methyl-3-buten-2-ol	48			49	3
Butanol	30	14		57	NA
Methyl acetate	27		10	42	21
Ethyl acetate	16	34		45	5
Butyl acetate	9	32		57	2

have a higher contribution from the large-scale background than from the regional background. This might be explained by the increased lifetime, and in the case of acetone and MVK the reduced contribution of the regional background is due to lower emissions from biogenic sources (acetone) and regional secondary production (MVK and acetone) in wintertime. The combustion sources for these two

compounds were elevated in winter for the same reason as for the aldehydes. MEK had an additional contribution from industrial sources, reflecting its use as an industrial solvent (EPA, 1994).

With the exception of methanol, a negligible contribution from the large-scale background was observed for the alcohols in both winter and summer. Methanol has a much higher relative

contribution from the large-scale background due to the longer lifetime and lower contribution of regional biogenic emissions during the winter. The other alcohols have a somewhat higher contribution from the regional background and lower influence from the combustion sources except for *n*-butanol, for which almost half of the mixing ratio was explained by a local industry source in winter. Methyl acetate has a very similar source pattern in winter as in summer. Ethyl and butyl acetate had a distinct weekday/weekend difference in the ratio to CO, which was explained by local industrial sources like printing shop and small industries (Niedojadlo, 2001).

Table 5 shows the estimated NMHC contributions to the measured mixing ratios. Both butane and benzene have a higher fraction explained by the large-scale background in winter than in summer, due to the longer atmospheric lifetime in this season. The more reactive NMHCs have negligible amounts in the large-scale background, and are

mainly explained by the regional background. Combustion has a larger relative importance in winter than in summer due to more intensive stationary combustion and cold-start emissions from mobile sources.

Fig. 7 shows the summary of the source profiles for the OVOCs and NMHCs in Zürich in winter. Compared to summer, the contribution of both the regional and large-scale background was lower for the OVOCs, whereas the contribution of the combustion is elevated. This is due to lesser biogenic emissions and secondary production combined with higher emissions from stationary and mobile combustion. A similar pattern is found for the NMHCs, but for these compounds the large-scale background is elevated compared to summer.

4. Conclusions

Four seasonal campaigns where OVOCs and selected NMHCs have been measured in Zürich

Table 5
Source allocation for NMHCs in winter

	Local sources			Background	
	Combustion (%)	Industry	Other sources (%)	Regional (%)	Large scale (%)
Butane	34		3	53	9
1,3-Butadiene	41		12	45	2
Isoprene	46		22	32	0
Benzene	31		4	52	13
Toluene	47			52	1
Ethylbenzene	32		6	60	1
<i>m,p</i> -Xylene	48			51	1
<i>o</i> -Xylene	47			53	1
1,2,4-Trimethylbenzene	39			58	3

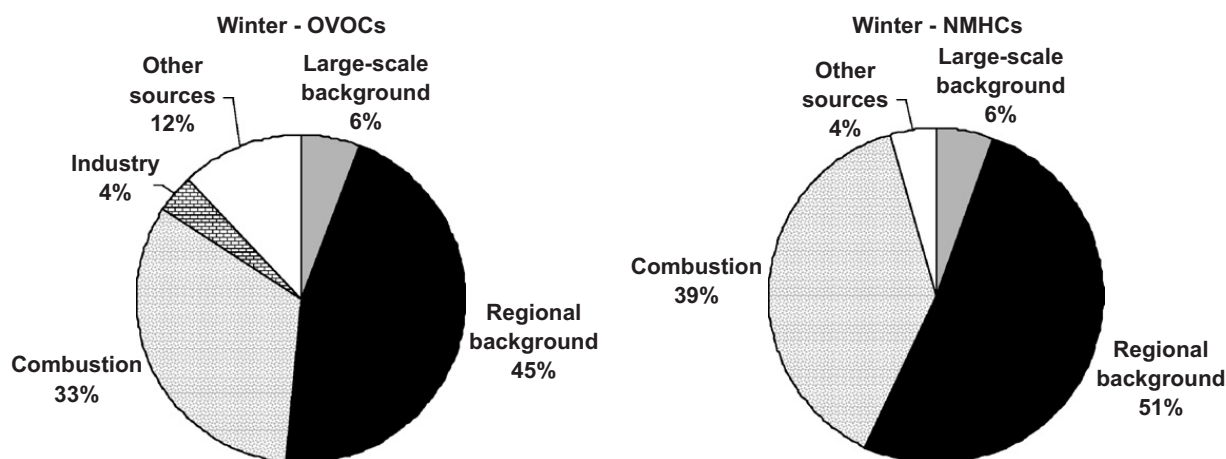


Fig. 7. Source profile for OVOCs and NMHCs in Zürich in winter.

have been presented in this paper. The collected data are unique since they represent the first dataset with a large number of OVOCs from one European urban site during all seasons. Ethanol was the compound with the highest mixing ratios at all seasons. There was a clear annual cycle for compounds known to be emitted from biogenic sources in summer. This resulted in more than two times higher mixing ratios for methanol, isoprene, hexanal and acetone in summer compared to winter, which implies that biogenic sources are dominant for these compounds. Oxidation products of isoprene were also elevated in summer due to atmospheric production. This was the case for methacrolein and MVK which both had two times higher mixing ratios in summer. Other compounds like ethanol, propanol, acrolein and benzene showed an opposite trend due to more intensive stationary combustion in winter. By the source-tracer-ratio method, combustion was estimated to be the main local source during both seasons, with 28% in summer and 33% in winter. For the measured NMHCs, combustion explained 27% and 39%, respectively. Overall, the main contributions to measured concentrations were explained by the regional and large-scale background.

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