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volatile hydrocarbons**

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Factor analytical modeling of C₂–C₇ hydrocarbon sources at an urban background site in Zurich (Switzerland): changes between 1993–1994 and 2005–2006

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Abstract

Hourly measurements of 13 volatile hydrocarbons (C₂–C₇) were performed at an urban background site in Zurich (Switzerland) in the years 1993–1994 and again in 2005–2006. Changes in hydrocarbon profiles and source strengths were recovered by positive matrix factorization (PMF). Eight and six factors could be related to hydrocarbon sources in 1993–1994 and in 2005–2006, respectively. The modeled source profiles were verified by hydrocarbon profiles reported in the literature. The source strengths were validated by independent measurements, such as inorganic trace gases (NO_x, CO, SO₂), methane (CH₄), oxidized hydrocarbons (OVOCs) and meteorological data (temperature, wind speed etc.). Our analysis suggests that the contribution of most hydrocarbon sources (i.e. road traffic, solvents use, and wood burning) decreased by a factor of about two to three between the early 1990s and 2005–2006. On the other hand, hydrocarbon losses from natural gas leakage remained at relatively constant (–20%) concentration levels. The estimated emission trends are in line with the results from different top-down approaches reported for other European cities. Their discrepancies to national emission inventories are discussed.

1 Introduction

Air pollutants can have adverse impacts on human health, most notably on the respiratory system and circulation (Nel, 2005), acidify and eutrophicate ecosystems (Matson et al., 2002), diminish agricultural yields, corrode materials and buildings (Primerano et al., 2000), and decrease atmospheric visibility (Watson, 2002). Organic pollutants are very complex regarding their composition, properties and chemical processes. Organic gases and particles can both be directly emitted into the atmosphere, e.g. by fossil fuel combustion, or secondarily formed and decomposed there by chemical reactions and/or gas-to-particle conversions (Fuzzi et al., 2006). Volatile organic compounds (VOCs) have several important impacts: while only some of them are toxic to humans,

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e.g. benzene (WHO, 1993), or relevant greenhouse gases, e.g. methane (Forster et al., 2007), all VOCs are oxidized in the atmosphere and most are thereby involved in the formation of secondary pollutants, such as ozone (O₃), and secondary organic aerosol (SOA). Ambient VOC measurements got special attention since the 1950s due to summer smog phenomena, first and foremost due to high O₃ levels in the Los Angeles basin (Eggertsen and Nelsen, 1958). The identification and quantification of VOC sources is therefore a necessary step to mitigate air pollution.

Receptor models were developed to attribute measured ambient air pollutants to their emission sources. Depending on the degree of prior knowledge of the sources, a chemical mass balance (CMB; composition of the emission sources is known), a multivariate receptor model (no *a priori* knowledge) or a hybrid model in between these extreme cases is most appropriate (Christensen et al., 2006). The first multivariate source apportionment studies were about the elemental composition of particulate matter (e.g. Blifford and Meeker, 1967). In contrast to organic species, they do not react in ambient air. Given that their sources emit those elements in constant proportions over time, the calculated receptor profiles can directly be related to sources. Receptor models have also been applied to speciated organic data since detailed information about the chemical composition of volatile and semi-volatile organic compounds is available, provided e.g. by high-resolution gas-chromatography (Schauer et al., 1996) or aerosol mass spectrometry (Lanz et al., 2007). However, the fundamental assumption of non-reactivity or mass conservation (Hopke, 2003) can be violated and the calculated factors may not always be directly related to emission profiles but have to be interpreted as aged profiles (depending on the selected species and measurement location). Therefore, a flexible model such as positive matrix factorization (PMF; Paatero and Tapper, 1994) is favorable to model VOC concentration matrices. Furthermore, PMF modeling allows for any changes (e.g. local differences) in the nature of the VOC sources. The PMF2 program (Paatero, 1997) uses a stable algorithm to estimate source strengths and profiles from multivariate data sets (bilinear receptor-model). Miller et al. (2002) concluded for simulated data that PMF was superior in recovering VOC source profiles

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compared to other receptor models based on standard CMB (Winchester and Nifong, 1971), principal component analysis (Blifford and Meeker, 1967) or UNMIX, a multivariate receptor model developed by Henry (2003). Also Jorquera and Rappenglück (2004) found PMF resolved VOC profiles more reliable than profiles resolved by UNMIX, while Anderson et al. (2002) found the results of the two models to be in good agreement. Further evidence that bilinear unmixing by PMF2 can be used to model VOC data was provided for the Texas area (Buzcu and Frazier, 2006), where for certain emission situations (e.g. wind directional dependencies of point sources etc.) an enhanced PMF was favorable (Zhao et al., 2004).

Due to the environmental problems mentioned above, abatement strategies have been developed and implemented for the reduction of VOC emissions. In fact, the sum of non-methane VOCs at an urban background location in Zurich (Switzerland), as an example, decreased by -50% from the late 1980s to the early 1990s and again by -30% from the early 1990s to today (Fig. 1). For 1993–1994, about 20 volatile hydrocarbon species were determined at Zurich-Kaserne by hourly resolved gas-chromatography (GC-FID). For 2005–2006, more than 20 hydrocarbons were measured again at the same site (13 of them were measured during both periods and are summarized in Table 1 and Fig. 2). By PMF modeling of hydrocarbon observations in 1993–1994 and in 2005–2006 we describe the underlying factors of each data set. The factors recovered by multivariate PMF modeling are related to hydrocarbon source profiles and source strengths. This attribution needs to be verified by means of collocated measurements (inorganic trace gases, oxidized hydrocarbons, meteorology), by time series analysis of the source strengths as well as by published VOC profiles and emission factors from the literature. The decrease in ambient VOC concentrations between the early 1990s and today (2005–2006) is explained by comparing the factor analytical results for both data sets. The contribution of different emission sources to this trend is discussed.

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2 Methods

2.1 Measurements

2.1.1 Hydrocarbon measurements

The measurements at Zurich-Kaserne (410 m a.s.l.) represent an urban background site in Zurich, Switzerland. It is located at a public backyard near the city center. The earlier VOC measurements in 1993–1994 were presented by Staehelin et al. (2001). The time spans in this study included 4 June 1993 to 6 October 1994 and 4 June 2005 to 6 October 2006.

18 hydrocarbons were measured quasi-continuously in Zurich between 1993 and 1994: first, ambient air was passed through a Nafion Dryer to minimize its water content and was then extracted from hydrocarbons using an adsorption-desorption unit (VOC Air Analyzer, Chrompack) equipped with a multi-stage adsorption tube at -25°C . The flow of air through the trap was 10 ml min^{-1} and the trapping time was 30 min, yielding a total volume of 300 ml of sampled air. Then the trap was heated to 250°C for transferring the VOCs to a cryo-focussing trap (Poraplot Q), held at -100°C . Finally, concentrated VOCs were passed onto the analytical PLOT column ($\text{Al}_2\text{O}_3/\text{KCl}$, $50\text{ m}\times 0.53\text{ mm}$, Chrompack) by heating to 125°C . The analysis was performed by gas chromatography-flame ionization detection (GC-FID, Chrompack). Calibration was performed regularly by diluting a commercial standard with zero air to the lower ppb (parts per billion by volume) range.

22 hydrocarbons were measured quasi-continuously in 2005–2006: First, ambient air was passed through a Nafion Dryer to minimize its water content and was then extracted from hydrocarbons using an adsorption-desorption unit (Perkin-Elmer, TD), equipped with a multi-stage microtrap held at -30°C by means of a Peltier element. The flow of air through the trap was 20 ml min^{-1} and the trapping time was 15 min, yielding a total volume of 300 ml of sampled air. After flushing with helium to reduce the water vapor content the trap was rapidly heated to 260°C for desorption of the hy-

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drocarbons onto the analytical PLOT column ($\text{Al}_2\text{O}_3/\text{KCl}$, 50 m \times 0.53 mm, Varian). The analysis was performed by gas chromatography-flame ionization detection (GC-FID, Agilent 6890). Calibrations were performed regularly using a standard which contains the analyzed hydrocarbons in the lower ppb range (National Physical Laboratory, UK).

13 hydrocarbon species were measured in both data sets (summarized in Table 1 and Fig. 2) and used for the statistical analysis. Ethane measurements were not quantitatively determined in 1993–1994, but we can assume (based on comparisons with quantitatively measured compounds) that the reported signals are proportional to the real concentrations and therefore do not influence the PMF analysis.

2.1.2 Ancillary data

About 20 different, hourly resolved OVOCs are available at Zurich-Kaserne for campaigns in summer 2005 and winter 2005/2006. The measurements were performed by GC-MS (gas chromatograph with mass spectrometer) and summarized in Legreid et al. (2007a). Inorganic trace gases (NO_x , CO, SO_2), meteorological parameters (temperature, wind speed etc.), methane (CH_4), and t-NMVOC were measured by standard methods (Empa, 2006). Measurements of t-NMVOCs are performed continuously by a flame ionization detector (FID) (APHA 360, Horiba). For separation between CH_4 and t-NMVOCs the air sample is divided into two parts. One part is directly introduced into the FID, while the second part is lead through a catalytic converter to remove the NMVOCs. The outcome of both lines is measured alternately and the t-NMVOC concentration is calculated from the difference of the two measurements.

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2.2 Data analysis and preparation

2.2.1 Unmixing multivariate observations

Linear mixing of observable quantities is the basis to all receptor models and can be represented by the following equation (Henry, 1984):

$$5 \quad \mathbf{x}_i = \mathbf{g}_i \mathbf{F} + \mathbf{e}_i, \quad (1)$$

where \mathbf{x}_i represents the i -th multivariate observation (vector of m variables) and is approximated by linear combinations of the loadings or source profiles (\mathbf{F}) and scores or source strengths (\mathbf{g}_i) up to an error vector \mathbf{e}_i . Chemical mass balance models were designed for estimation of source strengths, \mathbf{g}_i (a p -dimensional vector), for given numerical values of \mathbf{F} , representing a $p \times m$ -matrix of the source profiles, and a specified number of assumed factors or sources p . Multivariate receptor models, on the other hand, are most useful when very little or no prior knowledge about the sources is assumed. In such a case, both \mathbf{g}_i and \mathbf{F} have to be estimated, and p has to be determined by exploratory means. Paatero and Tapper (1994) have proposed to solve Eq. (1) by a least-square algorithm minimizing the uncertainty weighted error (“scaled residuals”):

$$15 \quad e_{ij}/s_{ij} = (x_{ij} - g_{ip} f_{pj})/s_{ij} \quad (2)$$

The associated software PMF2 (Paatero, 1997) minimizes the sum of $(e_{ij}/s_{ij})^2$ (called Q) for all samples $i=1 \dots n$ and all variables $j=1 \dots m$. In practice, an enhanced Q is to be minimized, accounting e.g. for penalty terms that ensure a non-negative solution to Eq. (1). This approach implicitly assumes that uncertainties, s_{ij} , for each element of the multivariate data set, x_{ij} , are known. For VOC species, an ad hoc uncertainty calculation has been suggested by Anttila et al. (1995) and was used in many studies (e.g. Fujita et al., 2003, and Hellén et al., 2006):

$$20 \quad s_{ij}^2 = 4 (DL)_j^2 + (CV)_j^2 x_{ij}^2, \quad (3)$$

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where DL represents the detection limit (as an absolute concentration value) and the coefficient of variation, CV , accounts for the relative measurement error determined by calibration of the instruments. The DL s equal five times the baseline noise of the species' chromatograms, whereas the CV s are the relative standard deviations of six repeated measurements of a real-air standard in the range of ambient concentrations. Following this method, both DL and CV are species-specific and given in Table 1 for the present hydrocarbon data sets.

2.2.2 Model specifications and reactivity

For the presented results, the PMF2 program was run with default settings (robust mode, central rotation induced by $f_{peak}=0$, outlier thresholds for the scaled residuals of -4 and 4), but the error model ($EM=-14$) was adjusted for ambient data. A relatively high modeling uncertainty of 10% was assumed as the atmospheric lifetimes (due to reactions with OH radicals) of the considered VOC species vary widely: from 0.6 days (propene) to 55 days (ethane). We assumed that the VOC variability at the urban site Zurich-Kaserne is generally driven by source activities rather than by ageing of the compounds; VOC transport time from source to receptor was assumed to be less than 0.5 day on average, which is smaller than the lifetime of propene, the most reactive compound analyzed in the study. Furthermore, we have imposed an aged VOC profile – averaged during a high pressure episode at a remote location (Rigi-Seebodenalp, 1030 m a.s.l., about 40 km Southeast of Zurich) – on the Zurich-Kaserne data by using a hybrid receptor model in between CMB and PMF following the approach described in Lanz et al. (2008). The resulting source contributions indicated that down-mixing of aged air masses is not a relevant process that influences VOC variability at this location.

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2.2.3 Missing values

In 1993–1994, missing ethane and ethyne concentrations had to be imputed for $n=3450$ and $n=1500$ samples, respectively ($\sim 5\%$ of data matrix). Row-wise deletion of those missing values would have caused a loss of 50% of the data. We instead have used the k -nearest neighbor (*knn*) method to estimate those missing values (function *knn* of the EMV package in R, The R Foundation for Statistical Computing; www.r-project.org). Additional VOCs were considered for the nearest-neighbor calculations (e.g. 2,2,4-trimethylpentane, 2-methylpropene, and heptane). Advantages of data imputation by multivariate nearest neighbor methods in the field of atmospheric research were evaluated by Junninen et al. (2004): they are particularly important for practical applications as they are fast, perform well, and do not generate new values in the data. We calculated (by repetitively and randomly assigning missing values to known values) that the relative uncertainty of this imputational method is about 48% (1σ) for ethane and about 32% (1σ) for ethyne. Calculating the uncertainty matrix, the imputed concentration values of ethane and ethyne were multiplied by 0.96 (2σ) and 0.64 (2σ), respectively, and the square of this product was added to the error as stated by Eq. (3):

$$s_{ij}^2 = 4(DL)_j^2 + (CV)_j^2 x_{ij}^2 + (2\sigma x_{ij})^2, x_{ij} \text{ imputed} \quad (4)$$

In summary, this additional term down-weights the imputed values by a factor of about 10. Even though the imputed values have a minor weight in the minimization algorithm of PMF2, factors characterized by ethane or ethyne for the 1993–1994 data should nevertheless be carefully interpreted.

2.2.4 Outliers in the data (local contamination)

Propane peaks up to 400 ppb (2005–2006) and 200 ppb (1993–1994) could be observed and were most probably caused by local barbecue events. We have defined extreme observations to be larger than $\mu + \sigma$ (2005–2006) and $\mu + 2\sigma$ (1993–1994):

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About 70 samples were identified and excluded from both data sets in order to not distort the factor analysis. A detailed inspection of the deleted samples revealed that these propane peaks mostly occurred on/before weekends and holidays during the summery season, supporting the hypothesis of local barbecue emissions in the public backyard surrounding the measurement site. In 2005–2006, a threshold of σ rather than 2σ was needed to identify a similar fraction ($\sim 1\%$) of contamination type outliers.

2.2.5 Robustness of the PMF solution

In order to test the robustness of the presented results, we made additional PMF runs with 21 hydrocarbons available since 2005 (the sum of butenes was deleted column-wise from the data matrix due to its abundant missing values). Isoprene and 1,3-butadiene were found to determine two additional factors almost alone due to their distinct temporal behavior in ambient air: both VOCs are rapidly removed by radical reactions. Their atmospheric lifetime is in the order of minutes to hours and these compounds therefore change the variability structure of the data matrix. However, isoprene and 1,3-butadiene accounted for less than 1% of the total concentration (in ppb) given by the 22 hydrocarbons retrieved since 2005 at Zurich-Kaserne. Therefore, the exclusion of these latter compounds does not influence the representativeness, but yields robust results. On the other side, aromatic C_8 hydrocarbons, which were highly correlated ($R > 0.97$), summed up to considerable concentrations, but did not alter the variability pattern in the data (see Sect. 3.5.1).

3 Results and discussion

3.1 Determination of the number of factors (p)

The determination of the number of factors p is a critical step for receptor-based source apportionment methods, especially for multivariate models, where very little

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prior knowledge about the sources is assumed. Mathematically perfect matrix decompositions into scores and loadings do not guarantee that the solutions are physically meaningful and can be interpreted. Here, we followed the philosophy that an appropriate number of factors has to be determined by means of interpretability and physical meaningfulness as already proposed earlier (e.g. by Li et al., 2004; Buset et al., 2006; Lanz et al., 2007 and 2008). Mathematical diagnostics are however indispensable to corroborate the chosen solution and to describe the mathematical aspect of its explanatory power.

For the recently (2005–2006) measured VOCs, up to 6 factors can be interpreted. A detailed discussion of the interpretation of the 6-factorial solution can be found in Sects. 3.3 and 3.4. Choosing 5 and less factors coerces two profiles (attributed to “solvent use” and “gasoline evaporation”; see Sect. 3.3). On the other hand, by choosing 7 factors and more, a factor splits from the “gasoline evaporation” factor (the sum of two split contributions is very similar to 6-factorial gasoline source, $R=0.97$). We therefore consider the 6-factorial solution for further analyses of the VOC sources in 2005–2006. For the earlier VOC series (1993–1994), we have most confidence in the 8-factorial solution: when assuming 8 factors, for each of the 6 factors found in 2005–2006 a similar factor is found as in the earlier measurements (plus a toluene source and an additional, combustion-related source). This can not be observed for solutions where more than 8 factors or less than 8 factors were imposed.

The data sets from 1993–1994 and 2005–2006 had to be described by a different number of factors each (eight and six, respectively) in order to account for the different emission situations: two factors were absent in the 2005–2006 data, which can be explained by policy regulations (see Sects. 3.4 and 4).

3.2 Mathematical diagnostics

More than 93% and 96% of the variability of the VOC species could be explained on average by the 6-factorial model (2005–2006) and the 8-factorial model (1993–1994), respectively (see concept of explained variance; Paatero, 2007). Using the proposed

model we can further explain on average 97% and 99% of the VOC concentrations (in ppb) measured in 2005–2006 and 1993–1994, respectively. For both models, less than 1% of all data points (about 100 000 for both data sets) exceeded the model outlier thresholds for the scaled residuals and were down-weighted (Sect. 2.2). The Q -value, the total sum of scaled residuals, equals 11 275 in the robust-mode for the 1993–1994 data ($n=7606$, $p=8$). For 2005–2006 ($n=8912$, $p=6$), this value is 70 018. Thus, for both data sets the calculated Q is in the order of the expected Q , estimated by $mn-p(m+n)$ as a rule of thumb. The scaled residuals for each species and both data sets are approximately normally distributed $N(0, \sigma_j)$.

3.3 Hydrocarbon profiles and first-guess attribution to emission sources

In this section, the factor profiles as retrieved by PMF for 1993–1994 and 2005–2006 are summarized (Table 2) and discussed. We introduce a tentative attribution of PMF factors to emission sources based on *a priori* knowledge such as published source profiles. The factors underlying the recent measurements (Fig. 3) and the ones explaining the earlier VOC data (Fig. 4) are compared with each other, with reference profiles found in the literature, and with profiles reported in Staehelin et al. (2001).

The factors for the recent data (2005–2006) were sorted on the basis of explained variance (Paatero, 2007). The factors calculated for the earlier data (1993–1994) were rearranged according to the order of the factors retrieved from the recent data (2005–2006).

3.3.1 Profiles for the years 2005-2006

The variability described by factor 1 is dominated by contributions of (iso-)pentane, isohexanes, (iso-)butane and it includes toluene and benzene (Fig. 3). This feature is shared by gasoline evaporation as well as gasoline combustion as can be deduced from the VOC profiles reported in Theloke and Friedrich (2007). In fact, the first PMF computed factor correlates well with the following reference profiles found

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therein: two-stroke engine, urban mode, warm ($R=0.94$, $n=13$) and cold start phase ($R=0.94$, $n=13$) as well as with gasoline evaporation ($R=0.97$, $n=7$). Thus, based on its fingerprint alone factor 1 could be related to gasoline combustion and/or gasoline evaporation. A more specific interpretation of this first factor is given in Sect. 3.4.1.

5 In factor 2, prominent toluene, isohexane and isopentane contributions can be observed and most of the toluene (61%), isohexanes (52%), hexane (48%), pentane (40%) and isopentane (40%) variability is explained by the second factor. This factor is only weakly influenced by the variability of combustion related C_2 – C_4 hydrocarbons (<10%). We therefore attribute this factor to solvent use.

10 Given the hydrocarbon fingerprint only, factor 3 (propane and butane) and factor 4 (ethane) could be related to many different sources (natural gas distribution and/or combustion, gas grill emissions, petrol gas vehicles etc.). Because benzene and toluene do not influence this third factor, we tend to attribute these factors to gas leakage or a “clean” combustion source. Furthermore, factor 4 is dominated by ethane and potentially could also represent an aged background profile; ethane is the longest lived species considered in this study. In the Northern Hemisphere, ethane and propane are principally related to natural gas exploitation (Borbon et al., 2004), but the presence of background ethane needs to be considered as well. Additional analyses of the source strengths are necessary for further interpretations (Sect. 3.4.3.).

20 The hydrocarbon profile of factor 5 is similar to a wood burning profile from a flaming stove fire, which is characterized by ethene and ethyne as can be derived from Barrefors and Petersson (1995) (Fig. 5). Further, factor 5 is also correlated ($R=0.75$, $n=9$) with the one reference profile for wood combustion provided in Theloke and Friedrich (2007). According to both studies, more benzene than toluene is emitted by wood fires ranging from 3:1 ppb/ppb to 8:1 ppb/ppb. This latter value is close to a ratio of 6:1 ppb/ppb in factor 5 (2005–2006). Further, the sum of iso-hexanes is enhanced in factor 5, which is possibly due to furan derivatives. Furan is released by wood smoke (Olsson, 2006). Note that the iso-hexanes measured in 1993–1994 only included 2-methylpentane and 3-methylpentane, which are not likely to interfere with

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furan derivatives. This would explain the absence of the sum of isohexanes in the wood burning profile computed for the ancient data (Fig. 4). All these findings suggest that factor 5 can be related to wood burning.

Factor 6 is closest ($R=0.82$, $n=13$) to the profile measured for diesel vehicles in the urban mode and warm phase within the database compiled by Theloke and Friedrich (2007; source profiles representing 87 different anthropogenic emission categories in Europe). As observed for wood fires, gasoline and diesel powered vehicles typically release more alkenes (ethene, propene, etc.) than alkanes (ethane, propane, etc.) as well, but the latter sources emit more toluene than benzene (Staehelin et al., 1998). Increasing toluene-to-benzene ratios during the last decade can be derived from emission factors as calculated from a nearby tunnel study: while this ratio was 2:1 [$\text{mg km}^{-1} / \text{mg km}^{-1}$] in 1993 (Staehelin et al., 1998), a ratio of 5:2 [$\text{mg km}^{-1} / \text{mg km}^{-1}$] was reported for the year 2004 (Legreid et al., 2007a). Let both species be emitted into an air volume of unity at a distance of unity: we then can also say that the ratio toluene:benzene increased from about 1:1 ppb/ppb to 2:1 ppb/ppb from the early 1990s until today. This change is perfectly represented by factor 6 (comp. 1993–1994 vs. 2005–2006). The large ratio isopentane-to-pentane as found in factor 6 (namely 10:1) is shared with diesel reference profiles, where a ratio up to 7:1 can be calculated (Theloke and Friedrich, 2007). All in all, we interpret factor 6 as fuel combustion with significant contributions from diesel vehicles.

3.3.2 Profiles for the years 1993–1994

In this section, the PMF retrieved hydrocarbon profiles from 1993–1994 are compared with the factors for the recently measured data (2005–2006) and with the factor analytical results of a precedent study carried out by Staehelin et al. (2001).

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Comparison with recent data (2005–2006).

Five very similar factors ($R > 0.90$) as found for 2005–2006 (Sect. 3.3.1) can be recovered from the 1993–1994 data (both data sets analyzed by bilinear PMF2). Based on the correlation coefficient, R , factors 2a, 2b, and 7 seem to be missing in the recent data (2005–2006) and the most dramatic change can be observed for the organic solvents that were separated in the earlier data (1993–1994; represented by factor 2a and factor 2b) (Table 2 and Fig. 4).

In 1993, toluene showed a different temporal variability than the other potential organic solvents (iso-pentane, n-pentane, iso-hexanes, and n-hexane) and emerges as a distinct factor. Both factor 2a and 2b virtually only explain the variability of potential solvents (Fig. 6). The distinct temporal behavior of toluene (with increased concentrations at night) is probably due to the local printing industry that was active in the 1990s but was not continued after or uses other solvents. Also Staehelin et al. (2001) identified a distinct toluene source (see Sect. 3.4). It is possible that asphalt works are represented by factor 2b as well. The addition of factor 2a and 2b (1993–1994) however yields a factor with similar loading proportions of toluene, iso-hexanes and iso-pentanes as found for solvents in the recent data (2005–2006).

In terms of R , factor 7 is closest to two stroke-engines ($R = 0.74$, $n = 13$) within the reference data base provided by Theloke and Friedrich (2007). However, relatively prominent ethyne and isohexanes contributions (compared with other types of engines found in Theloke and Friedrich, 2007) point to gasoline driven vehicles without catalytic converters, which still accounted for about 30% of the Swiss fleet in 1993–1994 (Staehelin et al., 1998).

Comparison to Staehelin et al. (2001).

Staehelin et al. (2001) also analyzed the Zurich-Kaserne 1993–1994 data by non-negatively constraint matrix factorization. All six factors mentioned therein correlate

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well ($R > 0.80$) with the PMF computed profiles for the 1993–1994 data (Table 3). Sources dominated by single VOC species (toluene and propane source) are here also represented by one single PMF factor. The relation of the other factors is however more ambiguous, but for the reasons discussed below it can not be expected that the results of the two studies are in perfect agreement:

Unlike PMF2, the algorithm used in the precedent study was based on alternating regression. Similar to the considerations by Henry (2003), it was also assumed by Staehelin et al. (2001) that the VOC sources can be identified by the geometrical implications of the receptor model Eq. (1), i.e. there are samples in the data matrix that represent single-source emissions, defining the vertices of the solution space projected onto a plane (and thereby providing starting points for the unmixing algorithm). Contrary to this proceeding, the PMF2 algorithm is started from random initial values by default. In contrast to the present study, Staehelin et al. (2001) included inorganic gases and t-NMVOC in the data matrix. By expanding the data matrix its variability structure was altered and factors dominated by inorganic SO_2 and NO_x as well as t-NMVOC were identified. Different sources may have been coerced as e.g. SO_2 is emitted by several source types (wood burning, diesel fuel combustion etc.), and as activities of non- SO_2 emitting sources can be correlated with the SO_2 time series by coincidence or due to strong meteorological influence. Instead, we suggest using the inorganic gases and sum parameters (t-NMVOC) as independent tracers to validate our factor interpretation. Furthermore, wood burning was not considered as potentially important emission source by Staehelin et al. (2001).

3.4 Source activities and validation of hydrocarbon sources

In this section, the hydrocarbon factors are attributed to emission sources based on comparisons with other, indicative compounds and meteorological data measured at the same site. Before the factors are discussed individually, we will first give a brief overview of the correlation of computed source activities with independently measured trace gases at the same location. The correlation coefficients are summarized in Ta-

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ble 4. A positive correlation between a hydrocarbon and a trace gas can occur because they were emitted by the same source or because they were released by different sources showing similar time evolution (as both reflect human activities). However, an evaporative source, as an example, may also be correlated with tracers of combustion (e.g. NO_x) by coincidence; this clearly impairs the explanatory power of interpretations that are exclusively based on correlation.

Most evident is the high correlation of both the fuel combustion and wood burning factor with both nitrogen oxides (NO_x) and carbon monoxide (CO) found for both data sets (1993–1994 and 2005–2006). The factor interpreted as gasoline evaporation shows higher correlations with t-NMVOC than with combustion tracers, supporting that factor 1 represents a non-combustion source. Also factors that have been associated mainly with solvent use (factor 2 in 2005–2006; factors 2a and 2b in 1993–1994, see Sect. 3.3) are more strongly correlated with t-NMVOC than with the combustion tracers CO, NO_x , and SO_2 . The factors dominated by ethane (factor 4) show activities that are closest to sulphur dioxide (SO_2), which may point to a source active in winter, combustion of sulphur-rich fuel or long-range transport. Methane (CH_4) is strongest correlated with the “propane” factors; this discussion will be continued in more detail (Sect. 3.4.3).

3.4.1 Traffic-related sources

Gasoline evaporation.

Modeled gasoline evaporation sources (factor 1) in 1993–1994 and in 2005–2006 are positively correlated with temperature $R=0.45$ and $R=0.30$ (Fig. 7), respectively, while the other factors (related to road traffic) show a different seasonal behavior, typically anti- or uncorrelated with temperature. In several cases, positive deviations from the linear regression slope (scores vs. temperature) coincide with low wind speed (Fig. 7), which is indicative for thermal inversions and pollutant accumulation (e.g. in February 1994, October 2005, and January 2006). This general dependence suggests that factor 1 in both data sets represents gasoline release via evaporation, during cold

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starts and re-fueling rather than by warm-phase combustion. A positive correlation with temperature might also be due to a combustion-related gasoline source that is active in summer (e.g. from ship traffic or from engines used at road works), but is rather unlikely due to relatively low correlations with the inorganic combustion tracers (Table 4).

The comparison of the PMF calculated gasoline factor with methyl-tert-butyl-ether (MTBE) measured during two campaigns in 2005–2006 provides further evidence for an evaporative gasoline loss. Pouloupoulos and Philippopoulos (2000) reported MTBE exhaust emission particularly during cold start and from evaporation. This is in agreement with other studies (e.g. MEF, 2001). Further, MTBE is neither synthesized in Switzerland nor formed secondarily in the atmosphere, but exclusively used as a gasoline additive with concentrations between 2% and 8% per volume (BAFU, 2002). The gasoline factor is strongly correlated with MTBE in summer as well as in winter (Fig. 8) and, therefore, likely represents evaporative gasoline loss and cold start phases. The slightly higher correlation found in summer ($R=0.81$) compared to winter ($R=0.71$) is most probably due to larger temperature differences between day and night, which determine the amplitude of evaporative gasoline loss.

Gasoline and diesel fuel combustion.

As for gasoline evaporation, factors representing fuel combustion were also found in both data sets (factor 6). They exhibit a bimodal daily cycle with peaks in the morning around 07:00 a.m. and in the evening at 09:00 p.m. in both data sets, as shown in Fig. 9 for the recent case (2005–2006). Typically, this temporal behavior is much more prominent on working days. A very similar pattern as found here was also reported for particulate emissions from incomplete fuel combustion at Zurich-Kaserne (Lanz et al., 2007). The strong dependence of the day of the week further supports findings based on the hydrocarbon fingerprint of this factor (Sect. 3.3): diesel exhaust is a major contributor. A large fraction (~66%, deduced from BAFU, 2000) of diesel-related total

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hydrocarbons in 2000 was caused by the heavy-duty fleet (transport of goods), which is not allowed to drive on weekends. Also commuter traffic is at a minimum, but the share of diesel passenger cars was and is still comparatively low in Switzerland (~10%, HBEFA, 2004) compared to its neighboring states, as diesel taxes are relatively high and petroleum taxes rather low (Kunert and Kuhfeld, 2007). Note that the same diurnal behavior was also found for other factors (e.g. solvents use; Sect. 3.4.4), but neither for ethane and propane sources (Sect. 3.4.3) nor for wood burning (Sect. 3.4.2).

Other traffic-related sources.

In 1993–1994, a similar factor to the gasoline evaporation source can be found (see Sect. 3.3.2), but due to the absence in 2005–2006 we hypothesize that this factor represents gasoline combustion by cars without catalytic converters (factor 7, 1993–1994). Recall that the fraction of non-catalyst vehicles was still in the order of one third of all passenger cars in the early 1990s (Sect. 3.3.2) and emissions were higher than from engines equipped with a catalytic converter. Today, this fraction is negligible: a large decrease in t-NMVOC (as well as in NO_x) was found in measurements of the Gubrist tunnel, which is located in the surroundings of Zurich (Colberg et al., 2005). Such tunnel studies do not cover cold start emissions and the large decrease was mainly attributed to the introduction of catalytic converters in the Swiss gasoline fleet. Therefore, no such factor could be resolved for the recently measured hydrocarbons (2005–2006). We will label this factor “earlier traffic source”.

3.4.2 Wood burning

Unlike the evaporative gasoline loss described in Sect. 3.4.1, factors representing wood burning activities are typically anti-correlated with temperature (i.e. increased domestic heating when outdoor temperatures are lower) and accumulate strongest during winter months that frequently are associated with temperature inversions (November to

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February; Ruffieux et al., 2006) (Fig. 10). For this latter hydrocarbon source, no significant difference between daily emission pattern on working and non-working days can be observed (also when the data of different seasons are analyzed separately). It has been suspected that wood is mainly used for private, supplementary room heating in winter (Lanz et al., 2008), which is not connected to working days.

3.4.3 Ethane and propane sources

The ethane (2005–2006) and propane (1993–1994 and 2005–2006) dominated factors generally exhibit a diurnal pattern different from other hydrocarbon sources, i.e. a bimodal daily cycle with maxima in the morning and late evening as found for fuel combustion (Sect. 3.4.1). In contrast, the diurnal patterns of the propane and ethane dominated factors are generally characterized by an early morning maximum and a mid-afternoon minimum, which was observed for measured methane as well. This behavior is shown for the 1993–1994 and 2005–2006 data in Fig. 11. Generally such a behavior is interpreted as accumulation during the night under a shallow inversion layer followed by reducing concentrations as the boundary layer expands during the morning and early afternoon (e.g. Derwent et al., 2000). Concentrations are therefore highest when the boundary layer depth is smallest and lowest when the boundary layer depth is highest. This implies that these emission rates must be reasonably constant between day and night. The medians between midnight and 04:00 a.m. (small traffic contribution) increase linearly for the propane and ethane factor, but also for measured methane in 2005–2006 (Fig. 11): an emission ratio for methane:ethane:propane of about 180:3:1 can be deduced. Natural gas leakage is an obvious candidate for the main urban source of these hydrocarbons, especially as a compositional ratio (per volume) of $190(\pm 129):3.7(\pm 0.8):1$ (methane:ethane:propane) can be deduced for transported natural gas in Zurich (Erdgas Ostschweiz AG, Zurich, 2005/2006, unpublished data). The uncertainties mainly reflect the variable gas mix, but also year-to-year variabilities. Natural gas consumption in [GWh] increased by 50% from 1992 to 2005 in Switzerland; it is typically more than four times higher in winter than in summer, which

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would explain its correlation with SO₂. For the early data (1993–1994), the presence of ethyne (Fig. 6) and a weak bimodal daily cycle (Fig. 11) point to the possibility that the ethane factor was then also influenced by incomplete combustion, possibly from residential (gas or oil) heating due to its yearly trend similar to that of wood burning (Fig. 10). It finally has to be noticed that factors 3 and 4 in both data sets predominantly explain the variability (>60%) of ethane and propane, respectively. The normalized loadings of other hydrocarbons than ethane and propane (e.g. butane in the “propane” factor from 2005–2006) do not represent their explained variability, but are, in other words, partially floating species within the mentioned factors.

Due to their relatively long atmospheric lifetimes (days to weeks), propane and ethane (also from other sources than gas leakage) tend to accumulate in the air. Therefore, we can not completely rule out that the factors “ethane” and “propane” may also represent aged VOC emissions as suspected by Buzcu and Fraser (2006). However, given the seasonal and diurnal patterns of those factors (Fig. 10 and Fig. 11) the contribution of processed VOC source emissions can not be of a major importance: for aged and secondary organic aerosols (SOA) with similar lifetimes (days to weeks as the considered hydrocarbons) Lanz et al. (2007 and 2008) have calculated increasing concentrations in the early after-noon (due to elevated photochemical activity) and only a slight enhancement of their mean concentrations in the winter ($5.3 \mu\text{g m}^{-3}$) compared to summer ($4.4 \mu\text{g m}^{-3}$), as stronger accumulation and partitioning of volatile precursors outweigh less solar radiation in wintertime (Strader et al., 1999). Furthermore, ethane and propane concentrations reported for European background air exhibit different levels and time trends than the factors as calculated for the urban background here (also see Sect. 4). Firstly, the ethane factors, as an example, showed 3–8 times higher concentrations than reported for ethane in Finnish background air (Hakola et al., 2006). Note that ethane is decomposed faster at mid latitudes than in Polar air (due to the temperature dependence of the ethane-OH reaction rate constant and [OH] levels). Secondly, we estimated that ethane and propane dominated factors, most likely representing natural gas leakage, slightly decreased by a factor of 1.3 from 1993–1994

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to 2005–2006, whereas background ethane and propane showed increasing trends between 1994 and 2003 (Hakola et al., 2006). We therefore conclude again that the hydrocarbon concentrations measured at the urban background of Zurich-Kaserne can not be significantly influenced by aged background air (also see Sect. 2.2.2).

5 3.4.4 Solvent usage

Acetates (belonging to the class of OVOCs) are commonly used solvents in industry (Legreid et al., 2007b). Also Niedojadlo et al. (2007) measured elevated acetate concentrations close to industries in Wuppertal (Germany). A strong correlation was found between the sum of acetates (methyl-, ethyl, and butyl-) measured during two campaigns in 2005–2006 and the calculated solvent factor for 2005–2006 (Fig. 12). Lower correlation of acetates in summertime ($R=0.61$) than in wintertime ($R=0.70$) is possibly due to secondary formation of acetates in the atmosphere, which is triggered by photochemistry. Further note that factor 2 was derived for two years of data; it nevertheless seems representative of weekly to daily variability of this hydrocarbon source.

15 3.5 Source contributions

Average source contributions as absolute concentrations [ppb] and relative [%] to the total mixing ratio of the 13 hydrocarbons were calculated for both data sets and summarized in Table 5.

3.5.1 Representativeness of the 13 hydrocarbons

20 The concentrations of the 13 hydrocarbons considered in this study accounted on average for 80–90% of the sum of all 22 NMHC species measured at this site since 2005. Aromatic C_8 hydrocarbons (*m,p*-xylene, *o*-xylene, and ethylbenzene) represent a major fraction of that difference, accounting for more than 6% of the total concentration [ppb] of the 22 NMHCs. They were not measured in 1993 and 1994. A PMF analysis of the
25 extended data set (2005–2006; comp. Sect. 2.2.5) revealed that those latter aromatics

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will be attributed to solvent use (60%), fuel combustion (30%), gasoline evaporation (5%), and wood burning (3%). The NMHCs plus the oxidized VOCs measured during three campaigns sum up to 73%–91% of the t-NM VOC concentrations determined by FID. For the earlier data (1993–1994), we estimate that NMHCs accounted for 62% and OVOCs for 13% of t-NM VOC (FID) on average. Today (2005–2006), the relative contributions to t-NM VOCs of the two measured classes is still 75% on average, but somewhat shifted towards the OVOCs (17%). Unlike the hydrocarbons used in this study, most OVOCs can be both directly released into the atmosphere or formed there secondarily. Furthermore they can be of anthropogenic as well as biogenic origin (Legreid et al., 2007b). We therefore conclude that the 13 hydrocarbons used in the present study are representative for primary and anthropogenic hydrocarbon emissions in Zurich.

3.6 Hydrocarbon emission trends (1993–1994 vs. 2005–2006)

For most hydrocarbon sources (road traffic, solvent use, and wood combustion) decreasing contributions by a factor 2–3 between 1993–1994 and 2005–2006 were modeled (Table 5 and Fig. 13). This trend is also reflected by the decline of t-NM VOC measurements (Fig. 1) and vice versa. However, for ethane and propane sources (mainly city gas leakage), no such strong negative trend was found. In contrast, propane and ethane sources only decreased by a factor of 1.3 (but its consumption increased about 1.5 times). In Switzerland, steering taxes of about 2 Euro per kg VOC were enforced in 1998. They are based on a black list of about 70 VOC species (e.g. toluene) or VOC classes (e.g. aromatic mixtures). Unlike most VOCs used in or as solvents, propane and ethane are not part of the black list (VOCV, 1997). This might explain the different trends for gas leakage hydrocarbons versus other sources. These results are in agreement with relatively constant methane concentrations measured in 1993–1994 and 2005–2006: ethane (1%–6%) and propane (~1%) are minor components of natural gas, which predominantly consists of methane (>90%). On the other hand, methane is emitted by other sources as well (e.g. incomplete combustion of fossil and non-fossil

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materials) and therefore no perfect correlation can be expected.

3.6.1 Traffic-related sources and solvent use

The EMEP (Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) emission inventory for Switzerland (1993 versus 2004) suggests that the most dominant sources, i.e. solvent use (115 Gg or 55% of t-NMVOA 5 C in 1993) and road transport (63 Gg or 30% of t-NMVOA C in 1993) decreased by a factor of two and three, respectively (Vestreng et al., 2006). Roughly the same relative decrease for road traffic and solvent use can be deduced from the data presented in Table 5 and Fig. 13. However, we estimate that traffic is still an important VOC 10 emission source accounting on average for 40% (1993–1994) and 29% (2005–2006) of the measured hydrocarbon concentrations. In contrast, solvent usage contributed on average only to about 20% of the ambient hydrocarbon concentrations measured at Zurich-Kaserne.

For the 1993–1994 data Staehelin et al. (2001) have also found that road traffic 15 contributes at least twice as much to ambient VOC concentrations than solvents, which is in line with our findings. Thus, both studies disagree with the official Swiss emission inventory which claims that road traffic is a minor VOC source (contributing less than 20% to total VOCs, while solvent use would account for more than 50%; BAFU 2007). Vehicle emissions were limited by law since the 1980s, propagating the use of catalyst 20 converters. Generally, road-traffic sources diminished by a factor of nearly three between 1993–1994 and 2005–2006 (Fig. 13). However, the fuel combustion factor (strongly influenced by diesel contributions) only decreased by a factor of 1.3. For the diesel fleet, no catalysts have been enforced yet. This would also explain its rather similar hydrocarbon fingerprint found in 1993–1994 and in 2005–2006 (Sect. 3.3). On 25 the other side, gasoline evaporation showed a decrease by a factor of 2.2. We can explain this reduction of evaporative loss by the introduction of vapor recovery systems at Swiss gasoline stations during the late 1990s.

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3.6.2 Other trends

It is interesting to note that the modeled maximum wood burning emission in winter (January 2006 vs. February 1994) decreased by less than a factor 1.5, while modeled annual emissions decreased by a factor of 2.4. Therefore, the decrease of wood burning VOCs mainly results from reduced emissions in spring, summer, and autumn, potentially caused by changes in agricultural and horticultural management.

4 Conclusions

Underlying factors of two year-long data sets of volatile hydrocarbons (C_2 – C_7) were described by multivariate receptor modeling (PMF) and related to different sources: fuel combustion, gasoline evaporation, solvent use, wood burning, and natural gas leakage. With different numbers of factors for the 1993–1994 ($p=8$) and 2005–2006 ($p=6$) data we accounted for the different emission situations prevailing in the two periods and thereby higher comparability between the factor analytical results was achieved. In contrast to a traditional CMB based analysis, no source profiles are imposed within the PMF approach to calculate the source activities, and the profiles are estimated as well. In this way, we allowed for any changes in the nature and number of VOC source profiles, which obviously represents an advantage of an analysis based on PMF. We furthermore have provided evidence that yearly PMF factors are representative for short-term source variability (days to weeks) by comparing factor scores to tracer OVOCs (methyl-tert-butyl-ether and acetates). We however can not rule out that sources emitting widely variable hydrocarbon proportions, e.g. wood combustion (depending on burning conditions, temperatures etc.), may be underestimated by linear factor analysis.

To our knowledge it was not reported before that the number of dominating emission sources changed over time, which is however plausible due to large emission reductions. The disappearance of a factor representing spark emissions of gasoline road

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traffic is in accordance with the measurements of a nearby road tunnel (Gubrist) showing the successful introduction of catalytic converters in the Swiss road traffic fleet.

Hydrocarbons from combustion sources (road traffic and wood burning) as well as solvent use decreased by a factor of two to three, while factors that mostly represent natural gas leakage remained at relatively constant levels between 1993–1994 and 2005–2006. This general result is in line with conclusions drawn by Dollard et al. (2007) for similar sites (urban background) in the United Kingdom: while ethane concentrations pointing to natural gas leakage remained at constant levels between 1993 and 2004, a yearly decrease by –15% and –28% could be observed for vehicle exhaust tracing ethene and propene, respectively. A decrease of road traffic emissions by factor of 2.8 during 12 years as estimated in this study is therefore also in line with findings from other European urban background locations. Note that the loss of natural gas relative to its transported amount also decreased by more than a factor of two as its consumption increased by 50% between 1992 and 2005.

In agreement with Niedojadlo et al. (2007; CMB analysis of ambient hydrocarbons in a German city), we also found that solvent use is over-represented in European (Vestreng et al., 2006) as well as national (BAFU, 2007) emission inventories. We hypothesize that solvent VOCs used for industrial purposes were substituted by less toxic and oxidized VOCs; the proportion of OVOCs to t-NMVOCs measured at an urban background in Switzerland (Zurich-Kaserne) increased by 4% between 1993–1994 and 2005–2006. However, we believe that the disagreement between bottom-up (i.e. emission inventories) and top-down approaches (i.e. modeling sources from field measurements) can only be partly explained by the fact that a certain amount of VOCs used in solvents are oxidized species; this aspect can not be covered by studies with a main focus on hydrocarbons. A minor issue is also the reduced transmission efficiencies for long-chained and oxidized hydrocarbons that may adsorb on the surface of the inlet tubes to a greater extend. More importantly, many city centers in Europe and North-America today predominantly harbor service sectors, while manufacturing industries moved to suburban or remote places, which would indicate that Zurich is biased to-

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wards traffic emissions.

Acknowledgements. The OVOC measurements were supported by the Swiss Federal Office for the Environment (FOEN). We thank U. Lohmann, A. Prévôt and H. Hellén for their valuable comments and suggestions which improved this paper. The earlier hydrocarbon data were provided by AWEL (Kanton Zurich's Department for Waste, Water, Energy, and Air). The current VOC data are measured within the National Air Pollution Monitoring Network (NABEL). We are grateful to M. Hill for supporting the VOC measurements.

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Table 1. Mean concentrations and standard deviations [ppb] of the 13 considered hydrocarbon species for the years 2005–2006 ($n=8912$) and values for 1993–1994 ($n=7606$) in brackets. Detection limits (*DL*, in ppt) and the relative measurement error (coefficient of variation, *CV*) for each hydrocarbon species as used for PMF are also given. *Ethane and ethyne concentrations in 1993–1994 were partially imputed.

species	synonym	formula	mean conc. [ppb]	std. dev. [ppb]	<i>DL</i> [ppt]	<i>CV</i> [rel.]
ethane	dimethyl	C ₂ H ₆	2.34 (3.03)*	1.32 (2.17)	10 (15)	0.02 (0.05)
ethene	ethylene	C ₂ H ₄	1.85 (3.03)	1.38 (2.54)	10 (15)	0.02 (0.05)
propane	n-propane	C ₃ H ₈	1.25 (1.43)	0.87 (0.89)	7 (10)	0.02 (0.05)
propene	propylene	C ₃ H ₆	0.42 (0.90)	0.32 (0.76)	7 (10)	0.02 (0.05)
ethyne	acetylene	C ₂ H ₂	1.13 (3.87)*	0.74 (3.09)	10 (8)	0.03 (0.05)
isobutane	2-methylpropane	C ₄ H ₁₀	0.59 (0.94)	0.44 (0.72)	5 (8)	0.02 (0.10)
butane	n-butane	C ₄ H ₁₀	0.99 (2.76)	0.78 (2.04)	5 (8)	0.03 (0.10)
isopentane	2-methylbutane	C ₅ H ₁₂	1.24 (2.96)	1.02 (2.32)	5 (7)	0.03 (0.10)
pentane	n-pentane	C ₅ H ₁₂	0.48 (0.94)	0.35 (0.68)	4 (7)	0.03 (0.10)
isohexanes (sum)	2-methylpentanes	C ₆ H ₁₄	0.86 (1.17)	0.68 (0.96)	3 (7)	0.03 (0.08)
hexane	n-hexane	C ₆ H ₁₄	0.13 (0.29)	0.16 (0.23)	3 (6)	0.03 (0.10)
benzene	benzol	C ₆ H ₆	0.38 (0.95)	0.27 (0.68)	3 (5)	0.03 (0.05)
toluene	methylbenzene	C ₇ H ₈	1.37 (2.57)	1.15 (2.37)	3 (4)	0.03 (0.05)

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Table 2. Comparison of the 8-factorial PMF (1993–1994 data) with the 6-factorial solution for 2005–2006. A total of 13 hydrocarbons ($n=13$) were considered for the PMF analysis. The comparison is based on the correlation coefficient: $0.7 \leq R < 0.8$, $0.8 \leq R < 0.9$, and $0.9 \leq R \leq 1.0$.

PMF factors 1993–1994		factor 1 ("gasoline evaporation")	factor 2a ("non-toluene solvents")	factor 2b ("toluene")	factor 3 ("propane")	factor 4 ("ethane")	factor 5 ("wood burning")	factor 6 ("fuel combustion")	factor 7 ("earlier traffic source")
2005–2006 PMF factors	factor 1 ("gasoline evaporation")	0.92	0.38	-0.14	-0.20	-0.16	-0.20	-0.31	0.71
	factor 2 ("solvents")	0.42	0.78	-0.20	-0.14	-0.22	-0.21	-0.20	0.34
	factor 3 ("propane")	0.13	-0.40	-0.14	0.94	0.03	-0.08	-0.08	-0.16
	factor 4 ("ethane")	-0.15	-0.27	-0.06	0.10	0.94	-0.05	0.17	-0.17
	factor 5 ("wood burning")	-0.28	-0.19	-0.13	-0.09	0.22	0.97	0.43	0.10
	factor 6 ("fuel combustion")	-0.24	-0.28	0.12	-0.09	-0.25	0.42	0.90	-0.36

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Table 3. Comparison of the 8-factorial PMF (1993–1994 data) with factors reported in literature (Staehelin et al., 2001). A total of 12 hydrocarbons ($n=12$) were considered in both studies. The comparison is based on the correlation coefficient: $0.7 \leq R < 0.8$, $0.8 \leq R < 0.9$, and $0.9 \leq R \leq 1.0$.

PMF factors 1993–1994		factor 1 ("gasoline evaporation")	factor 2a ("non-toluene solvents")	factor 2b ("toluene")	factor 3 ("propane")	factor 4 ("ethane")	factor 5 ("wood burning")	factor 6 ("fuel combustion")	factor 7 ("earlier traffic source")
1993–1994 Staehelin et al.	factor 1 ("Comb")	-0.10	-0.22	-0.07	-0.15	0.61	0.97	0.51	0.24
	factor 2 ("Evap")	0.95	0.39	-0.12	-0.18	-0.02	-0.2	-0.25	0.77
	factor 3 ("SO ₂ ")	0.16	-0.48	0.01	0.29	0.86	0.74	-0.03	0.32
	factor 4 ("Tol")	-0.05	0.00	0.97	-0.16	-0.19	-0.13	0.06	-0.03
	factor 5 ("NM")	0.29	-0.06	0.02	0.00	0.84	0.40	-0.28	0.73
	factor 6 ("Pr")	-0.16	-0.31	0.07	0.99	-0.02	-0.13	0.09	-0.23

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Table 4. Correlation of measured trace gases (NO_x , CO, CH_4 , and SO_2) and total non-methane VOC, NMVOC, with the PMF calculated factors for 2005–2006 ($n \sim 8900$ samples) and 1994–1995 ($n \sim 7600$ samples). $0.7 \leq R < 0.8$, $0.8 \leq \mathbf{R} < 0.9$, and $0.9 \leq \underline{\mathbf{R}} \leq 1.0$.

	NO_x	CO	SO_2	CH_4	t-NMVOC
<i>PMF factors 2005–2006</i>					
factor 1 (“gasoline evaporation”)	0.64	0.63	0.24	0.39	0.72
factor 2 (“solvents”)	0.69	0.64	0.22	0.47	0.80
factor 3 (“propane”)	0.75	0.77	0.67	0.67	0.65
factor 4 (“ethane”)	0.29	0.42	0.54	0.46	0.21
factor 5 (“wood burning”)	0.66	0.80	0.58	0.64	0.56
factor 6 (“fuel combustion”)	0.76	0.84	0.59	0.53	0.71
<i>PMF factors 1993–1994</i>					
factor 1 (“gasoline evaporation”)	0.55	0.58	0.32	0.32	0.65
factor 2a (“non-toluene solvents”)	0.71	0.76	0.45	0.45	0.77
factor 2b (“toluene”)	0.67	0.64	0.44	0.43	0.73
factor 3 (“propane”)	0.59	0.54	0.60	0.64	0.45
factor 4 (“ethane”)	0.64	0.64	0.72	0.60	0.42
factor 5 (“wood burning”)	0.87	0.89	0.75	0.64	0.71
factor 6 (“fuel combustion”)	0.88	0.91	0.64	0.58	0.83
factor 7 (“earlier traffic source”)	0.61	0.66	0.28	0.31	0.76

Table 5. Summary of hydrocarbon source apportionments for both periods 1993–1994 and 2005–2006 and all factors. Factor grouping to classes of hydrocarbon sources.

		mean rel. contr. [%]	median contr. [%]	1. quart. [%]	3. quart. [%]	mean conc. [ppb]
<i>PMF factors</i>						
<i>2005–2006</i>						
factor 1	“gasoline evaporation”	13	13	8	18	1.7
factor 2	“solvents”	20	20	13	27	2.6
factor 3	“propane”	14	14	10	18	1.8
factor 4	“ethane”	21	19	13	27	2.8
factor 5	“wood burning”	16	15	10	20	2.1
factor 6	“fuel combustion”	13	13	9	17	1.7
<i>total explained mass conc.</i>	97%					
<i>average total conc.</i>	13.2 ppb					
<i>1993–1994</i>						
factor 1	“gasoline evaporation”	15	13	9	18	3.7
factor 2a	“non-toluene solvents”	10	9	8	11	2.2
factor 2b	“toluene”	8	7	9	23	2.0
factor 3	“propane”	8	7	13	27	2.0
factor 4	“ethane”	17	15	9	23	4.2
factor 5	“wood burning”	17	17	12	22	4.2
factor 6	“fuel combustion”	11	11	8	13	2.7
factor 7	“earlier traffic source”	15	14	9	19	3.7
<i>total explained mass conc.</i>	99%					
<i>average total conc.</i>	24.8 ppb					
<i>Source groups</i>						
<i>2005–2006</i>						
factor 1, 6	road traffic	29	27	18	38	3.8
factor 2	solvent use	20	20	13	27	2.6
factor 5	wood burning	13	13	9	17	1.7
factor 1, 2	gas leakage	36	36	23	45	4.7
<i>1993–1994</i>						
factor 1, 6, 7	road traffic	40	38	26	50	9.9
factor 2a, 2b	solvent use	18	17	13	21	4.5
factor 5	wood burning	17	17	12	22	4.2
factor 1, 2	gas leakage	24	22	13	33	6.0

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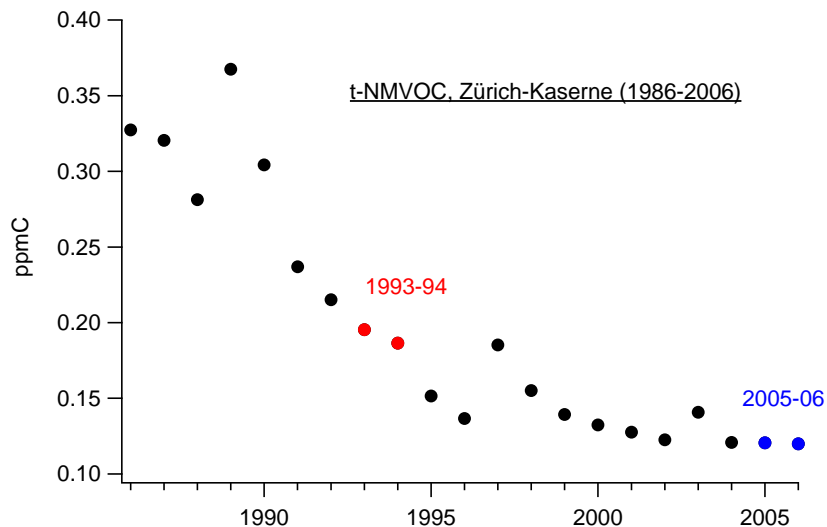


Fig. 1. Total concentrations [ppmC] of non-methane volatile organic compounds (t-NMVOC) at an urban background site (Zurich, Switzerland) measured by a standard FID (flame ionization detector). Speciated VOC data is available for 1993–1994 and since 2005 (red and blue points).

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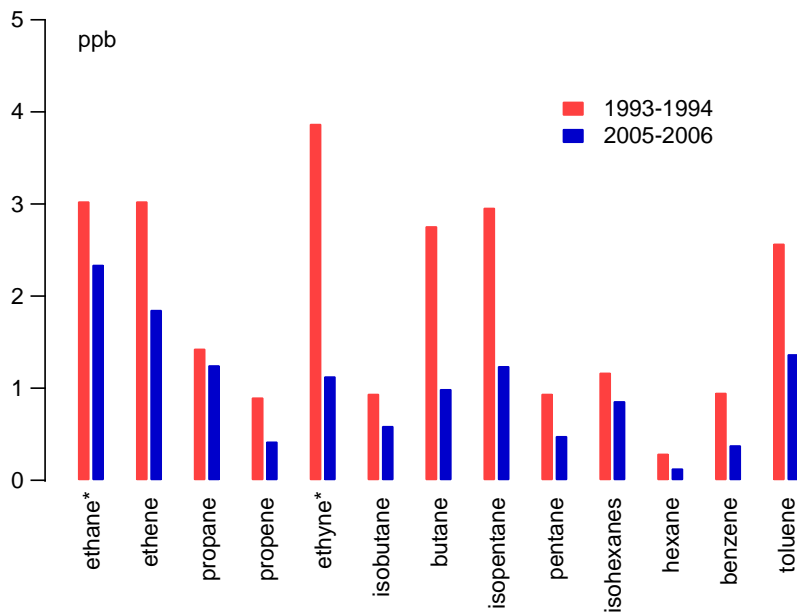


Fig. 2. Averaged values for the 13 hydrocarbons measured in 1993–1994 (red) and in 2005–2006 (blue) at Zurich-Kaserne. *Ethane and ethyne measurements in 1993–1994 were partially imputed (see text, Sect. 2.2.3).

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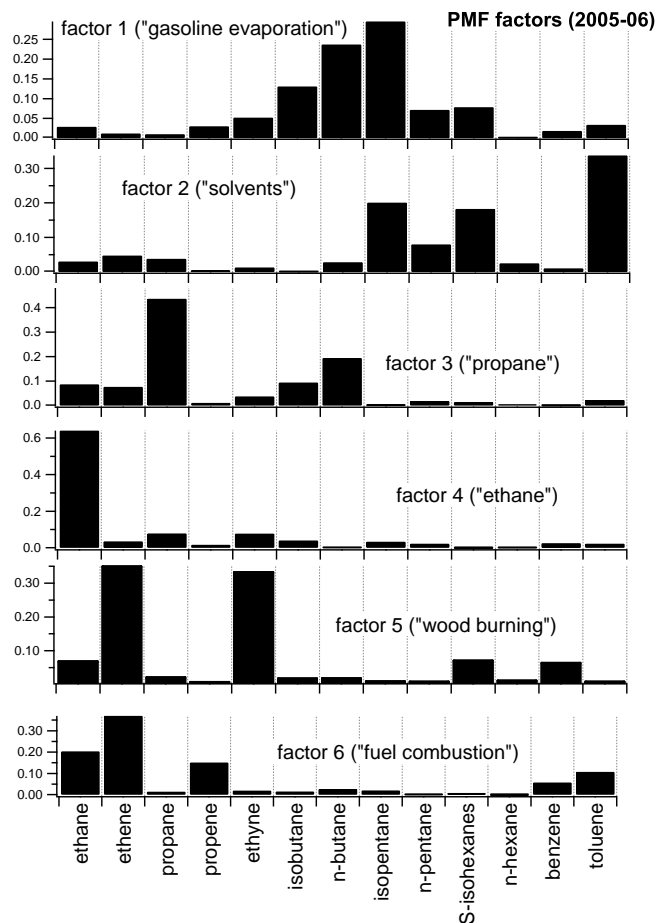


Fig. 3. The profiles of the 6-factorial PMF solution calculated for the recently measured hydrocarbon data (2005–2006). Each profile's loadings were normalized to a sum of unity.

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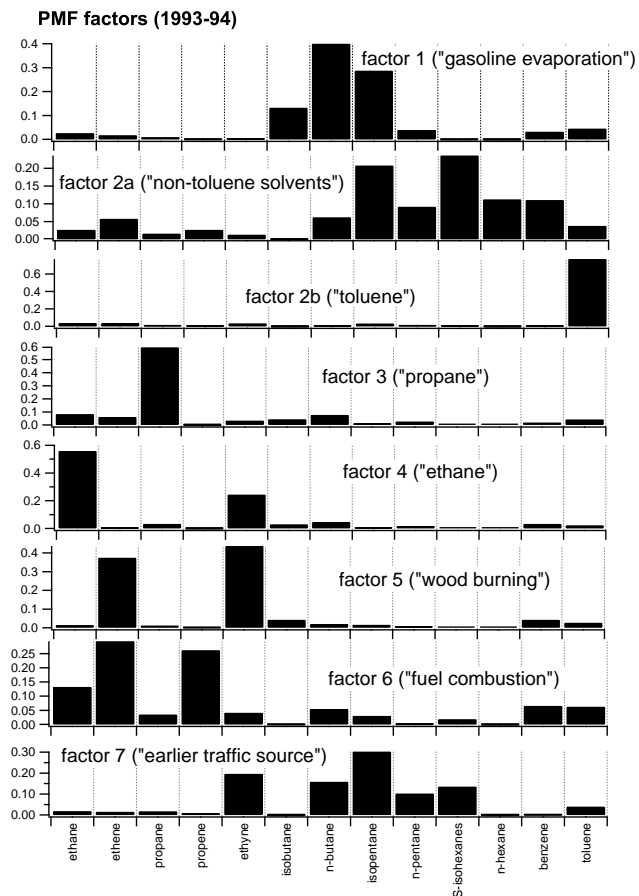


Fig. 4. The profiles of the 8-factorial PMF solution calculated for the earlier hydrocarbon data (1993–1994). Each profile's loadings were normalized to a sum of unity.

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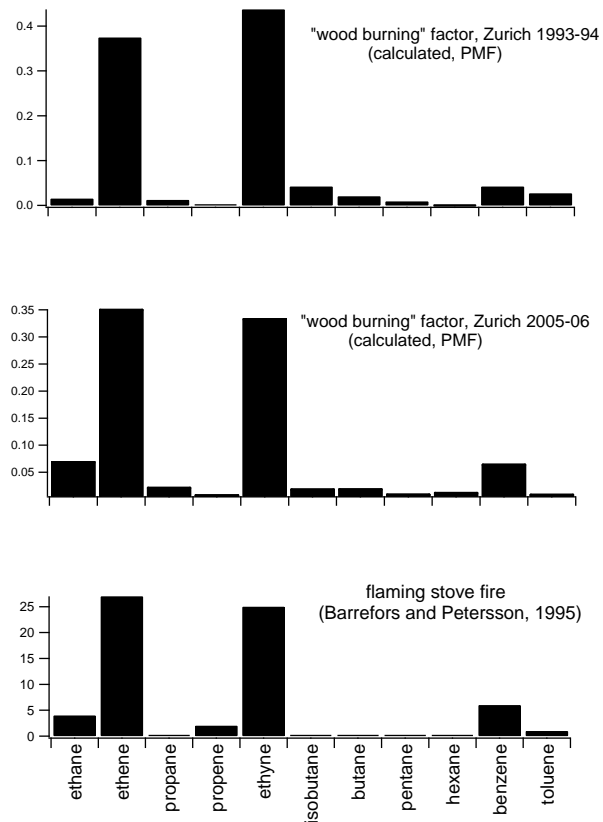


Fig. 5. Wood burning profiles calculated by PMF (1993–1994, 2005–2006) and from the literature (Barrefors and Petersson, 1995). The PMF loadings are normalized to unity. The measured profiles are given in % volume of total VOC (no isohexanes were determined).

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Explained variance [%] by factor 2a and factor 2b (1993-1994)

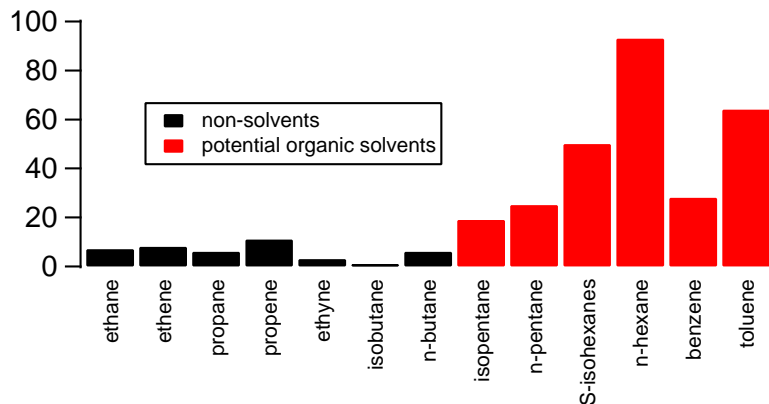


Fig. 6. Explained variance by factor 2a (“non-toluene solvents”) and factor 2b (“toluene”) for the 13 hydrocarbons considered for this study. Non-solvents comprise C_2 – C_4 hydrocarbons ethane, ethene, propane, propene, ethyne, isobutene and butane. C_5 – C_7 hydrocarbons isopentane, n-pentane, isohexanes, n-hexane, benzene and toluene are potential organic solvents.

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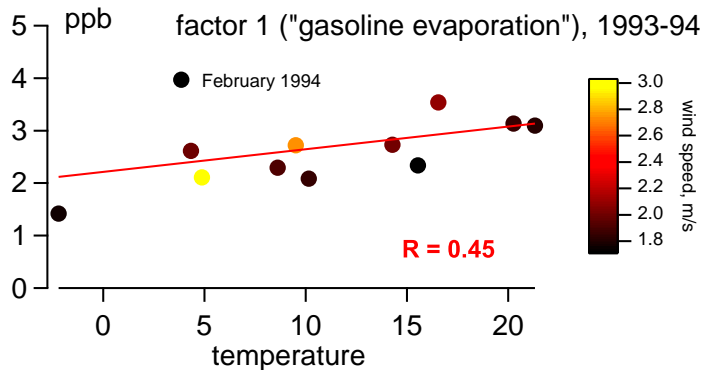
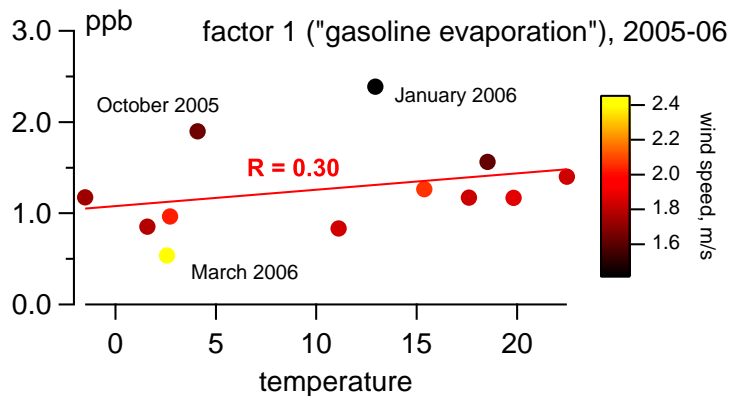


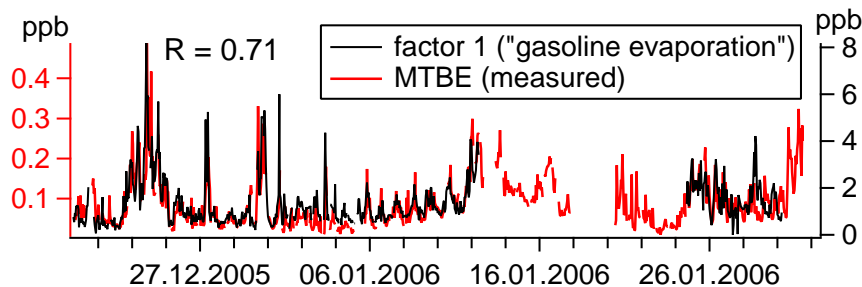
Fig. 7. Monthly median scores of the gasoline factors (PMF retrieved), temperature and wind speed for the years 1993–1994 (bottom) and 2005–2006 (top). Positive deviations from the regression slope scores vs. temperature represent months characterized by frequent thermal inversions: February 1994, October 2005, and January 2006.

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apportionment of
volatile hydrocarbons**

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Winter: 19 December 2005 - 1 February 2006 (n=594)



Summer: 1 July - 1 August 2006 (n=340)

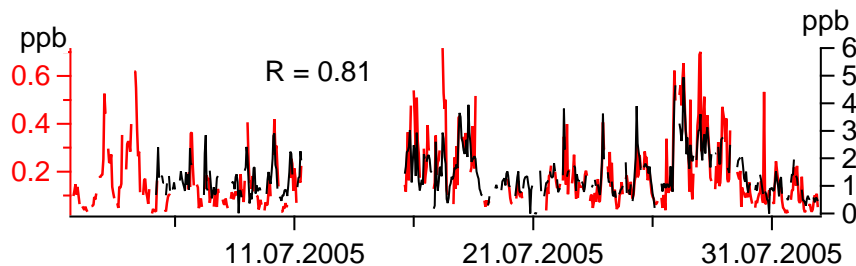


Fig. 8. Factor 1 ("gasoline"; black) versus measured methyl-tert-butyl-ether (MTBE, red) for the summer 2005 (bottom) and winter 2005/2006 (top). MTBE was measured at the same time during two campaigns.

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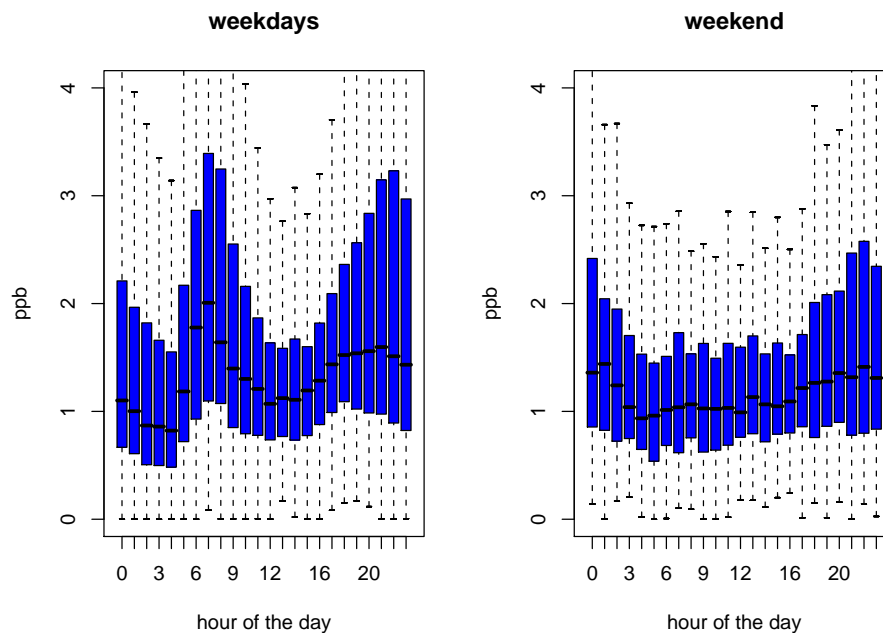


Fig. 9. Hourly boxplots of the modeled “fuel combustion” factor (2005–2006) for weekdays (Monday–Friday; left) and weekends (Saturday and Sunday; right).

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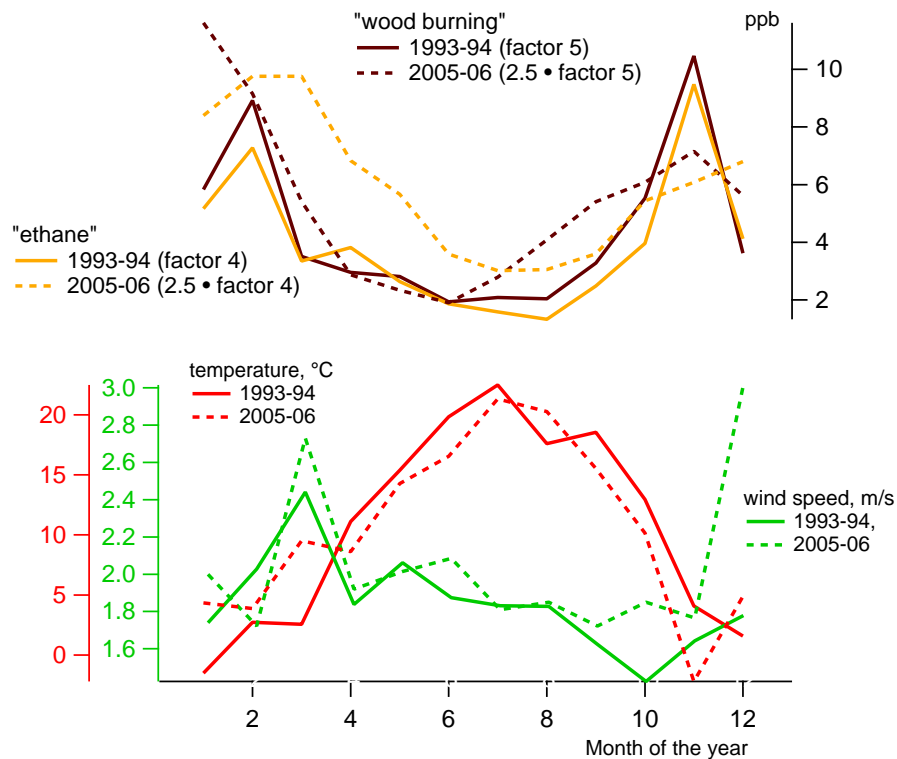


Fig. 10. Factors representing wood burning (brown) and the “ethane” factors (orange), measured temperature (red) and wind speed (green) as monthly medians in 1993–1994 and 2005–2006 (dashed).

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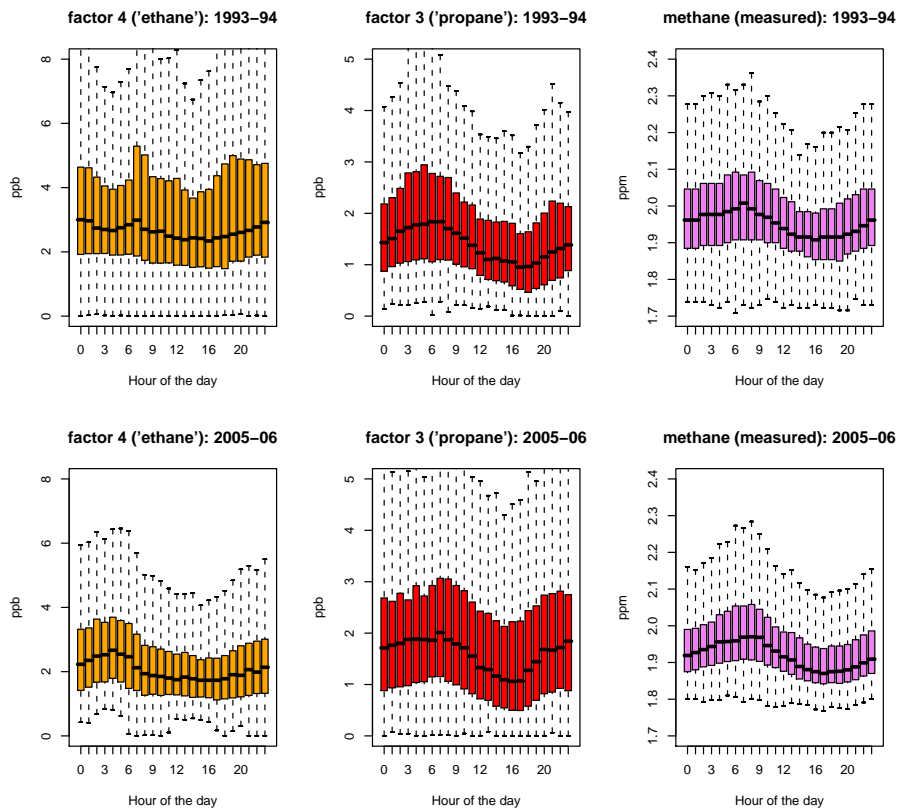


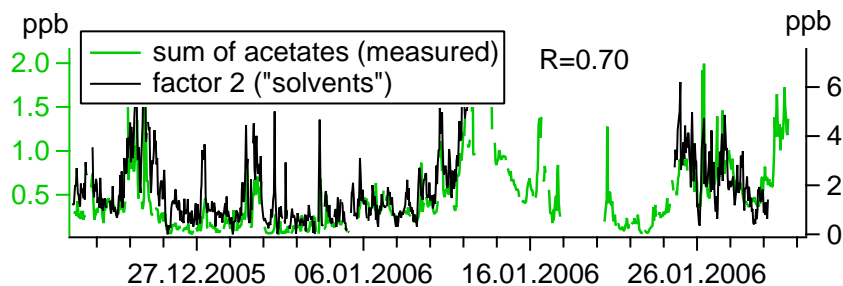
Fig. 11. Hourly boxplots of factors dominated by ethane (left) and propane (middle), measured methane (right) for 1993–1994 (top) and 2005–2006 (bottom).

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Winter: 19 December 2005 - 1 February 2006 (n=594)



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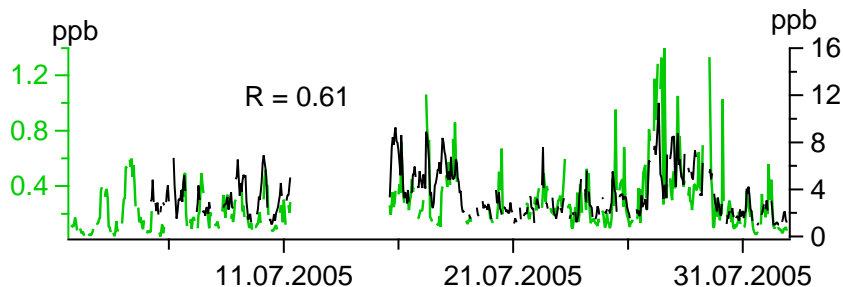


Fig. 12. The correlation between the “solvent use” factor and the sum of measured organic acetates (green) are shown as well. The sum of measured acetates comprises methylacetate, ethylacetate and butylacetate, measured during two campaigns.

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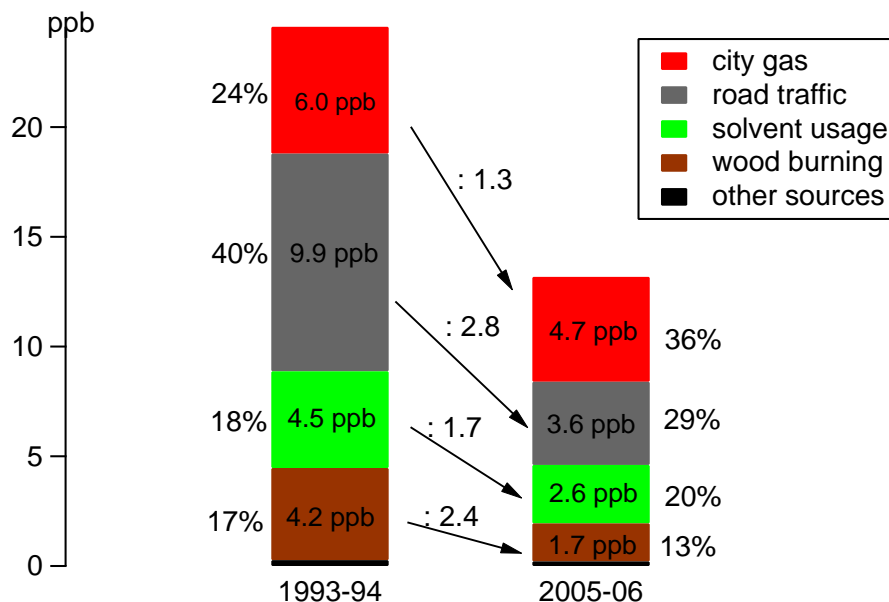


Fig. 13. Bar chart showing the relative [%] and absolute [ppb] source contributions for 13 hydrocarbons at Zurich-Kaserne (urban background) for 1993–1994 and 2005–2006. Factors were grouped to source classes as listed in Table 5.

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