

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Can Positive Matrix Factorization identify sources of organic trace gases at the continental GAW site Hohenpeissenberg?

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Received: 24 February 2014 – Accepted: 7 March 2014 – Published: 25 March 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

ACPD

14, 8143–8183, 2014

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Abstract

From the rural Global Atmosphere Watch (GAW) site Hohenpeissenberg in the pre-alpine area of Southern Germany, a dataset of 24 C₂–C₈ non-methane hydrocarbons over a period of seven years was analyzed. Receptor modeling was performed by Positive Matrix Factorization (PMF) and the resulting factors were compared to literature source profiles. Photochemical aging during transport to the relatively remote site violates the PMF prerequisite of mass conservation from source to receptor. However, previous studies showed plausible results with this method at remote sites; the applicability and restrictions of the PMF model to such a remote dataset and the influence of photochemical processing on the interpretability of the results are discussed. A six factor solution showed a high stability and the most plausible results. In addition to biogenic sources and remote sources of very stable compounds – reflecting the continental background – four additional anthropogenic factors were resolved that could be divided into two short- and two long-lived patterns from evaporative sources and incomplete combustion processes, respectively. A method to increase the uncertainty for each individual compound by including photochemical reactivity did not improve the results, but decreased the stability of the model output. The contribution of the different source categories at the site over the entire period was, in decreasing order: remote sources, long-lived evaporative sources, residential heating and long-lived combustion sources, short-lived evaporative sources, short-lived combustion sources, and biogenic sources. Despite a low overall impact, biogenic sources played an important role during summer, in particular in terms of reactivity.

1 Introduction

Tropospheric ozone is an environmental pollutant that causes adverse effects to vegetation, e.g. by reducing and altering physiological processes and plant growth (Matyssek et al., 2010; Nunn et al., 2005), and to humans, where respiratory diseases

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source categories is necessary (Badol et al., 2008). Several receptor models such as principal component analysis/absolute principal component scores (PCA/APCS) (e.g. Chan and Mozurkewich, 2007; Guo et al., 2004, 2006), chemical mass balance (CMB) (e.g. Badol et al., 2008; Na and Kim, 2007), or UNMIX (e.g. Jorquera and Rappenglück, 2004; Olson et al., 2007) were used for source apportionment. In particular Positive Matrix Factorization (PMF) (e.g. Lingwall and Christensen, 2007; Paatero, 1997, 1999), a multivariate mathematical receptor model, has been shown to be quite reliable at identifying and quantifying source categories. But most studies investigating NMHC composition were concentrated in urban metropolitan areas with mainly anthropogenic emissions (e.g. Brown et al., 2007; Leuchner and Rappenglück 2010; Na and Kim, 2007).

Yuan et al. (2012) stressed the importance of different reactivity of the NMHC compounds and the impact of photochemical aging on the interpretability of the resolved source profiles that has not been considered in most of the studies applying PMF. The impact of photochemical processing increases with longer transport times from source to receptor which emphasizes the importance of considering this factor at remote sites. Only a few studies have applied PMF receptor modeling at remote sites with a focus on the global or continental background. Lanz et al. (2009) and Sauvage et al. (2009) used PMF analysis for reactive species such as NMHC at remote sites in Switzerland and France despite the PMF assumption of mass conservation from source to measurement site.

In the current work, NMHC data from the GAW global site Hohenpeissenberg, Southern Germany, was used to quantify the impact of different source categories as well as their seasonal contributions at this rural site with PMF analysis. One main objective of this study was to test and discuss whether PMF as a statistical tool is actually capable of reliably identifying the main sources of reactive trace gases at the remote site despite the mass conservation assumption. Limitations of the PMF model at remote sites will be discussed along with the results of the PMF model.

2 Methods

2.1 Experimental setup

The GAW Observatory Hohenpeissenberg is located about 70 km southeast of Munich (47°48' North, 11°02' East) at 980 m a.s.l. on top of a hill which is about 300 m above the surrounding countryside (approx, 70 % pasture and 30 % forest). Sample air was routinely measured daily at 01:00 CET (41 % of data) and 13:00 CET (48 %), however, 11 % of the data were measured at other times of the day. At 13:00 CET, the site was generally in a vertically fully developed mixed-layer and local emissions may have affected measurements only low to moderately. For this analysis only the 13:00 CET data were used to minimize the influence of local sources and shallow boundary layer conditions during nighttime as well as to ensure the homogeneity of the dataset.

C₂-C₈-NMHC were measured with an on-line GC-FID system. It consisted of a 3600 CX Varian gas chromatograph combined with a flame ionization detection (FID) system until January 2008 and was then replaced by a Varian CP-3800 GC-FID. The air intake was 17 m above the ground, and 2 m above a flat roof which was about the same height as the nearby forest canopy (> 10 m distance). The intake was a downwards-facing glass-funnel connected to a permanently flushed glass-manifold (375 L min⁻¹, 8 m length, 4 cm I.D.). The GC sampling unit was connected to a port on the manifold via a 1/16" Sulfinert line (Restek, length: 2 m, 0.96 mm I.D., 50 mL min⁻¹) such that an overall residence time in the lines of 3.5 s was achieved. After the port, the sample gas passed a filter for aerosol and ozone removal (PTFE filter holder: 25 mm I.D., Metron Technology, PTFE coated glass fiber filter, Fiberfilm, Pall Life Sciences, impregnated with sodium thiosulfate (Na₂S₂O₃), backed by a PTFE-membrane filter, 20–30 μm pores, Metron Technology), and further downstream a stainless steel-screen (10 μm pores, VICI). A custom-built sampling and gas flow system was used comprising a moisture trap at 228 K (0.5 m 1/8" Sulfinert, Restek), a VOC trap using cryo-adsorption on glass beads (87 K adsorption, 403 K desorption) (SPT-type by Varian, installed in custom built LN₂ dewar), a sample volume determination by measuring

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the pressure increase in an evacuated reference volume, and the corresponding Valco (VICI) switching valves mounted in a temperature controlled compartment at 293 K. After sampling for 20 min, the cryo-trap was dry-purged by helium at 15 mL min^{-1} for 15 min. The adsorbed NMHC were then thermally desorbed in a helium carrier gas flow at 5 mL min^{-1} injected and separated on a PLOT column ($\text{Al}_2\text{O}_3/\text{KCl}$, $50 \text{ m} \times 0.53 \text{ mm}$ I.D., Chrompack, the Netherlands). After an initial isothermal phase (313 K for 2 min), the GC column was heated in two phases, first to 345 K (4 K min^{-1}), then with a rate of 6 K min^{-1} to 473 K. This temperature was kept for 33.7 min. The end of the column extended to the FID system, where the separated compounds were identified. This system was regularly checked and calibrated with helium (zero gas), calibration gas by NPL (certified mixtures of a few ppb in nitrogen of some 30 NMHC), and different reference gases holding synthetic and whole air mixtures in pressurized cylinders (see metadata at WDCGG, 2013).

A more detailed description of measurement, integration, and error assessment was published by Plass-Dülmer et al. (2002). For this study mixing ratios of 24 substances over the course of seven years from 2003 to 2009, measured daily, were used. An individual uncertainty for each compound and each measurement comprising systematic uncertainty contributions and random factors was estimated and assigned to each value. It considers blank values, peak integration errors (including insufficient chromatographic separation) and detection limit, calibration uncertainties and random fluctuations in the system response (Plass-Dülmer et al., 2002).

2.2 Positive Matrix Factorization (PMF) model description

Next to Chemical Mass Balance (CMB), UNMIX, and PCA (principal components analysis), Positive Matrix Factorization (PMF) has become an accepted and regularly used tool for receptor modeling. In this study, factor analysis was conducted with PMF 3.0 (US-EPA, 2011). Positive Matrix Factorization determines the number of source factors ρ , a species profile f for each factor, and the amount g that each factor contributes to

each sample.

$$\mathbf{X}_{ij} = \sum_{k=1}^p \mathbf{g}_{ik} \times \mathbf{f}_{kj} \quad (1)$$

In PMF Eq. (1) is solved by decomposing the matrix \mathbf{X}_{ij} of measurement data, with i the number of samples and j the number of the different chemical species, into two matrices, factor contributions, and factor profiles. Both factor contributions and factor profiles can then be analyzed.

There are natural and logical physical conditions for such a model: the original data have to be reproduced by the model, the predicted source compositions and contributions must be non-negative, and the sum of the predicted mass contributions for each source must be less than or equal to the total measured mass for each substance (Hopke, 2003).

The multilinear engine ME-2 (Paatero, 1999) gives PMF the ability to solve multilinear problems and implement constraints like the replacement of missing values and individual weighting of data points by associating an uncertainty value U_{ij} to each point. The object function (Eq. 2) is then minimized using these uncertainties (Norris et al., 2008).

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{\mathbf{X}_{ij} - \sum_{k=1}^p \mathbf{g}_{ik} \times \mathbf{f}_{kj}}{U_{ij}} \right]^2 \quad (2)$$

PMF 3.0 also gives the opportunity to test the stability and uncertainty of the computed solutions by using a bootstrap technique. It also provides a tool called Fpeak to control the rotations of the different factors (Norris et al., 2008).

Several studies have compared PMF, CMB, PCA, and UNMIX (Anderson et al., 2002; Miller et al., 2002; Paatero and Tapper, 1994; Willis, 2000) and found limitations and advantages of the different models. Some of the advantages of PMF are the good performance not only with simulated data, the non-negativity constraint, and the possibility of individual treatment for single data points.

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Various studies have shown that PMF provides physically reasonable results for source identification of NMHC in environments located in proximity to the sources (e.g. Buzcu and Fraser, 2006; Lanz et al., 2008; Leuchner and Rappenglück, 2010) or particulate matter (e.g. Santoso et al., 2008; Tauler et al., 2009; Yue et al., 2008). But as receptor models are only mathematical models, they do not use pollutant emissions, chemical transformation mechanisms, or meteorological data to identify and quantify the sources at a receptor location. It is difficult to use PMF for data from remote sites, because with chemical reactions during the transport of air masses (Atkinson and Arey, 2003) and the effects of mixing (Parrish et al., 2007) the presumed mass conservation from source to measurement site, necessary for using receptor models (Hopke, 2003), is not given. Despite these limitations, PMF has been used for remote VOC data (Lanz et al., 2009; Sauvage et al., 2009) and obtained reasonable results. However, it needs to be considered that not only emission profiles but also their different aging determine the factor solutions of PMF.

2.3 Data treatment

A total of 2335 valid day (13:00 CET) measurements of 24 substances per measurement were available for the investigated time span of which 345 values of individual substances were missing (0.6% of the entire dataset). There are different ways to treat these data. PMF 3.0 provides the option to exclude the entire sample. In that case a loss of 15% of the sample data would have occurred. To avoid such a high loss of data, the missing values were replaced by the respective species geometric mean and the corresponding uncertainties were set to four times the geometric mean according to Sauvage et al. (2009). Five different treatments of missing value replacement and uncertainty assessment were performed as described below and shown in Table 1.

Values greater than zero, but below the specific detection limit, were replaced by half the detection limit. The uncertainty for zero values and values below the detection limit was set to the specific detection limit (Sauvage et al., 2009). Fpeak values, indicating

the degree of rotation of the solutions, were varied between 5.0 and -5.0 in steps of 0.1.

The remote character of the research site at Hohenpeissenberg implies that only a few substances were emitted locally, but rather transported from their sources. During the transport time photochemical reactions occur and the original emission pattern is altered, due to different photochemical reactivity of the compounds (Atkinson, 2000, 2008). However, PMF assumes inertness of the substances; it cannot integrate reactivity into the model. Sauvage et al. (2009) proposed a method to integrate photochemical reactivity into the overall uncertainty to compensate this limitation of PMF. For each compound a potential error $E_{j(\text{reactivity})}$ was computed with Eq. (3) assuming pseudo first-order reaction kinetics and photochemical reactivity mainly driven by OH radical reactions.

$$E_j(\text{reactivity}) = \mathbf{X}_{ij}(1 - e^{-k_j[\text{OH}]\tau}) \quad (3)$$

k_j is the second-order rate constant of the reaction between the substance j and OH (Atkinson and Arey, 2003), τ is the source-receptor time of transport. [OH] is the seasonally and spatially averaged OH concentration published by Spivakovsky et al. (2000). The overall uncertainty s_{ij} for the PMF modeling was then computed following the ISO guide rule for uncertainty (ISO 13005, according to Sauvage et al., 2009) (Eq. 4) and used for PMF computations.

$$s_{ij} = 2\sqrt{\left(\frac{\mathbf{U}_{ij}(\text{measure})}{2}\right)^2 + \left(\frac{E_j(\text{reactivity})}{\sqrt{3}}\right)^2} \quad (4)$$

This interpretation, however, needs some more modification. The PMF results in factors which correspond to the prevailing factors determined at the receptor site and which are different from pure emission profiles. Instead, they may be seen as aged source profiles with an aging corresponding to some mean transport time from many diverse source locations to the receptor site. Accordingly, the resulting factors are uncertain

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as well as the plausible explanation of the source categories by expert knowledge of the authors.

At the GAW site Hohenpeissenberg other trace gases have also been measured (Gilge et al., 2010). Resolved factors can be compared to these independent measurements to verify the apportionment of the source when the hydrocarbons and the trace gas are emitted from the same source or at the same time but by a different source. Thus, the contributions of factors resolved by PMF were correlated to the additional trace gases NO, NO₂, SO₂, CO, and NO_y. Since sometimes correlations can also be coincidental, Lanz et al. (2008) suggested that these correlations can add evidence to the source apportionment of the factors, but should not be used as the only basis for the attribution of sources.

Carbon monoxide (CO) is a product of incomplete combustion, its main sources are traffic emissions, but it is emitted by all incomplete combustion processes. The nitrogen oxides NO and NO₂ are mainly emitted by combustion engines, NO_y is the sum of oxidized nitrogen species containing NO, NO₂, PAN and alkyl nitrates, HNO₃ and others. The main sources of sulfur dioxide (SO₂) emissions are power plants burning fossil fuels for energy generation but also households to a minor extent (UBA, 2011). Only if a resolved source profile correlated with one or more of the other trace gases, it was mentioned in the text.

PMF 3.0 provides a bootstrap function that selects blocks of input samples and creates new input files from them. These files have the same dimensions as the original input files. Then PMF is run and the resulting factors are mapped to the base factor they correlate with best. In this study, 200 bootstrap runs were performed on the base of the final solution with six factor profiles.

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3 Results and discussion

3.1 Determination of the number of factors

The calculated Q values of four different factor solutions with five to eight factors and other diagnostic parameters are shown in Table 2. The values decreased with increasing number of factors, due to a better explanation of the variability of the measured NMHC mixing ratios by a higher number of factors, and lower global minima of the object functions. All scaled residuals should be within $\pm 3\sigma$ (Willis, 2000) and symmetrically distributed. With this dataset all solutions from five to eight factors had normally distributed residuals. The number of residuals beyond three standard deviations decreased for an increasing number of factors (Table 2) down to four for 20 factors. An F_{peak} value of 0.0 showed the lowest Q values for all solutions displayed in Table 2, additional rotation of the factors did not improve the results. Coefficients of determination of modeled to measured mixing ratios and the mean ratio were high for all solutions and increasing with the number of resolved factors from 0.86 (R^2) and 0.97 (ratio), respectively, with five to 0.89 and 0.98, respectively, with eight factors.

An indication for an appropriate number of factors is the stability of the factors after performing the analysis at least five times with the same parameters but randomized starting points. No multiple solutions should be found (Hopke, 2003). In this analysis the tested five, six, seven, and eight factor solutions were very stable and showed the same distribution of factors for all five computations (not shown here).

On the basis of these statistical indicators no final decision about the optimal number of factors could be made. Thus, it remained a process based on plausibility arguments mainly by checking the resulting factors vs. reasonable source or aged source profiles (cf. Sect. 3.2), also in comparison to previous studies (Lanz et al., 2008, 2009; Sauvage et al., 2009). Careful consideration led to the decision of choosing six factors as the most reasonable.

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3.2 Source apportionment

In the following, the six factor solution (Fig. 1) will be discussed and compared to alternative solutions with five, seven, and eight factors. In addition, the apportionment to source categories and the interpretation of chemical aging for the respective factors will be performed by comparison to source profiles throughout the literature. Because of the complexity of the atmospheric system with transport, mixing, and chemistry, each individual factor can not be attributed exclusively to one source category. The factors should be seen as more or less aged profiles originating from different groups of sources (Sauvage et al., 2009). For a better attribution to source categories, the annual courses (Fig. 2) including the winter–summer amplitude of the retrieved profiles were compared to the seasonal change of OH at the site. Based on the continuous OH-radical measurements at Hohenpeissenberg, this effect accounted for an amplitude of about 7, e.g. short lived compounds emitted at constant rates throughout the year and with fairly homogenous spatial distribution, like vehicular exhaust, would be factors of about 7 higher in winter than in summer. However, there are effects that might potentially disturb this rather simple relation. The generally lower height of the mixed layer in winter might lead to less dilution and consequently higher winter–summer ratios. This, however, is valid only for those measurements that were performed within the mixed layer. On the other hand, in winter during daytime the site was frequently above the mixed layer and thus decoupled from the emissions at ground. Both effects are expected to partly compensate each other. In addition to a change of composition patterns during transport, emission profiles in literature vary due to measurement uncertainty associated with the use of different techniques, e.g. on-line or canister samples, the number of substances measured, the experimental set-up and associated conditions, and the published units. These variations made direct quantitative comparisons of the profiles difficult, but allowed a qualitative assessment for identification of possible source profiles.

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Figure 1 shows the absolute and relative contributions of substances to the six factor solution. Absolute values are the mixing ratios of each substance that PMF apportioned to each factor. Relative contributions are the fractions of each substance contributing to each factor, therefore, the sum of all factors for each substance is 1.

3.2.1 Biogenic sources

Factor I explained 34 pptv of the measured isoprene which was the only biogenic NMHC measured. On the absolute scale ethane (49 pptv), ethene (21 pptv) and isopentane (14 pptv) also contributed considerably to this factor, but due to the small total amount of isoprene, 94 % of it was explained by this factor in contrast to only about 4 % of the total amount of ethane and ethene. Since isoprene is the only substance in this study that is almost exclusively produced by plants, this factor is apportioned to biogenic sources. The high reactivity and short life-time of isoprene in the atmosphere exclude distant sources. Small amounts of ethene found in this factor might also be of biogenic origin, since ethene is an important plant hormone (Fall, 1999). Factor I was the only factor with a distinct maximum in summer (Fig. 2). Since isoprene emissions depend on the photosynthesis of plants, temperature, and solar radiation (Fuentes and Wang, 1999), the maximal source strength of the highly reactive diene and thus the maximal mixing ratios could be found in July despite higher photochemical reactivity and higher mixing during this time of year. The ethane contribution to this factor might have derived from biomass burning (Stein and Rudolph, 2007) with a maximum during the summer.

Similar profiles for this factor, including amounts of ethane, *n*-pentane and isopentane were also found by Sauvage et al. (2009) for three remote sites in France. The alkane contributions in this factor could be attributed to artifacts from the PMF model or to temperature related emissions like evaporation from fuel.

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3.2.2 Short-lived incomplete combustion sources

Factors II and III both showed a large contribution of short-lived substances. Factor II contained rather short-lived (< 1 day) alkenes such as ethene (133 pptv, 27%), propene (46 pptv, 79%), 1,3-butadiene (6 pptv, 90%), and some butenes, typical for incomplete combustion processes. The winter–summer amplitude (Fig. 2) of about 9 was quite consistent with the seasonal OH change of 7 indicating constant emissions throughout the year with possibly larger fetch areas for the short-lived compounds during winter due to the longer life-time. Due to these constant emissions and the following comparison to emission profiles, this factor was referred to as short-lived combustion sources mainly from vehicular exhaust.

Literature profiles of vehicle emissions show similarly high contributions of ethene, propene, isopentane, benzene, toluene and xylenes (e.g. Friedrich and Obermeier, 1999; Hellen et al., 2003; Sagebiel et al., 1996; Thijssen et al., 1999). Sauvage et al. (2009) provided a vehicle exhaust factor very similar for one of the French remote sites.

Factor II correlated well with NO₂ ($r = 0.84$), NO (0.75), NO_y (0.73), and CO (0.66), all associated with traffic emissions.

3.2.3 Short-lived evaporative sources

Factor III explained large parts of the measured toluene (63 pptv, 55%), ethylbenzene (11 pptv, 60%), and *m* + *p*-xylene (23 pptv, 65%). Alkanes such as pentanes, *n*-hexane, and *n*-heptane also contributed to this factor. The life-times of the compounds were in the short- to medium-lived range of 1–4 days. The aromatics were the only substances measured in this study that are found in evaporative solvent emission profiles, e.g. in paint or wood coating. The winter–summer amplitude of about 3.6 (Fig. 2) indicated stronger emissions during the summer, typical for evaporative sources dependent on temperature such as solvents and fuel evaporation. This factor is thus further referred to as short-lived evaporative sources, additionally containing

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some medium-lived combustion compounds, which is shown also by its correlation with combustion tracers NO₂ ($r = 0.74$), NO (0.74), and NO_y (0.75).

3.2.4 Residential heating and long-lived incomplete combustion sources

In comparison to Factors II and III, the compounds in Factors IV and V exhibited longer atmospheric life-times. Large parts of the alkynes acetylene (216 pptv, 49 %) and propyne (8 pptv, 56 %) were explained in Factor IV that also contained ethene (287 pptv, 58 %), benzene (65 pptv, 48 %) and toluene (23 pptv, 21 %) that are typical compounds emitted by residential heating and other incomplete combustion processes, in particular from road traffic. The major compounds resembled in this factor had atmospheric life-times of 1–10 days. Only a few source profiles for domestic combustion emissions were found in literature. A wood burning profile by Friedrich and Obermeier (1999), adjusted to the substances measured for this study, showed a similar composition to Factor IV, as does a “residential heating” profile by Klemp et al. (2002) and Mannschreck et al. (2002). Ethene and acetylene contributions of the literature profiles differed from those found in Factor IV. These differences indicated that not only wood burning but also other sources contributed to this factor. Similar profiles to Factor IV were found by Lanz et al. (2008) and Sauvage et al. (2009), who attributed the French profiles to hot water generation and building heating by burning fossil fuels and wood. The benzene/toluene ratio for those French sites was 2, for Mannschreck et al. (2002) 3.2, and for Factor IV 2.7. The winter–summer ratio was very high with an amplitude of 15.8 (Fig. 2) indicating a much higher source strength in winter than in summer according to a higher heating demand during the cold season. The shorter-lived compounds such as ethene and some of the aromatics possibly had larger fetch areas during winter due to the longer life-times at lower temperatures contributing to this large winter–summer spread. Factor IV correlated well with the combustion tracer CO ($r = 0.87$). A correlation to SO₂ (0.62) was found for this factor, which is reasonable, since household emissions contribute to SO₂ in the atmosphere (UBA, 2011).

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days) that underline the background character of this factor. Hellen et al. (2003) provided a measured profile attributed to distant sources in Finland that showed a similar composition. Sauvage et al. (2009) identified a remote source factor with high ethane loadings and amounts of propane in France and Lanz et al. (2008) found an ethane factor. These findings led to the conclusion that this factor represented the European NMHC background. Factor VI did not correlate well with any of the additional trace gases.

3.2.7 Seasonality and total contributions

The winter–summer amplitude was already used for better attribution of source categories to the individual factors in the previous sections (Fig. 2). The total monthly variation of factorial NMHC mixing ratios is summed in Fig. 3. The maximum was encountered in February (7.1 ppbv), the minimum in July (1.8 ppbv). During fall and winter, chemical reaction rates decreased due to lower OH concentrations as a consequence of lower UV light available and lower temperatures. Thus, the NMHC were not depleted as rapidly as during the summer months.

Within this dataset, biogenic sources only contributed to the measured and modeled NMHC in summer, but are responsible for 20 % of the total modeled amount of hydrocarbons in July. Due to the high reactivity of isoprene, this overall small factor plays an important role in atmospheric processes in summer. All anthropogenic factors (Factors II–VI) were more or less consistent with the annual variation of OH, depending on the seasonal source strengths of the individual factors as discussed in the previous chapters. Due to massive summer depletion, the short-lived combustion (II) and long-lived evaporative (V) compounds had factor 7–9 higher mixing ratio contributions in winter than in summer, although their atmospheric turn-over remained the same all over the year. The remote factor VI containing only long-lived hydrocarbons dominated throughout the year with more than 50 % abundance in May. The substances contributing to the short-lived Factor II were expected to be enhanced in winter due to cold start emissions of vehicles (Borbon et al., 2004) and higher use of heating functions in vehicles

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(winter/summer = 9). Contrary, short lived evaporative emissions were driven by temperature and much enhanced in summer (Factor III). The residential heating Factor IV showed the most pronounced maximum in winter as expected. The annual course of Factor V showed fairly constant emissions such as leakage from natural gas, LPG, and vehicular carburetors, rather than temperature dependent evaporation.

The absolute contributions of Factor VI had their minimum in July/August and the maximum in March, however, later than e.g. Factors IV and V. The annual mixing ratio variability followed the OH abundance with a lag caused by the very slow reaction rate constant of ethane (Plass-Dülmer et al., 2002).

Over the entire seven year period remote sources contributed most to the NMHC volume (Fig. 4a) and mass at the remote site (31.3 vol%, 25.8 mass%) followed by long-lived evaporative sources (24.6 vol%, 25.4 mass%). Residential heating/long-lived combustion sources accounted for 23.4 vol% (21.0 mass%), short-lived evaporative sources for 11.3 vol% (17.8 mass%), and short-lived combustion sources for 6.0 vol% (5.9 mass%), respectively. The smallest fraction was attributed to biogenic sources (3.5 vol%, 4.0 mass%), but mainly emitted in summer, being an important precursor to ozone formation. Weighted with the corresponding OH reaction rate constants, the mean OH-reactivity of the factors was as follows (Fig. 4b): biogenic – 24.2 %, short-lived combustion – 22.5 %, residential heating – 20.6 %, short-lived evaporative – 15.1 %, remote sources – 9.0 %, long-lived evaporative – 8.5 %. Despite low volume and mass fractions the biogenic isoprene factor has the highest contribution for the total reactivity. The impact is even higher during maximum emissions in the summer.

3.3 Comparison to alternative factor solutions

In Fig. 5 the additional factors that were resolved in the seven and eight factor solutions and one different factor for the five factor solution are shown. In general, all factors of the six factor solution could also be found in these alternative computations. For the five factor computation considerable differences to the solution above could be found in Factors II, IV, and V. Factor II also contained large amounts of ethane, smaller amounts

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Table 1. Different treatments of missing values, values below the detection limit, and zero values.

#	Treatment
1	missing values replaced by species median; corresponding uncertainties set to four times the species median
2	missing values replaced by geometric mean; corresponding uncertainties set to four times the geometric mean
3	additional to 2: values below detection limit (dl) set to half the detection limit; corresponding uncertainties set to detection limit
4	additional to 3: zero values set to half the detection limit
5	additional to 3: uncertainty of <i>n</i> -hexane increased by 20%

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Table 3. Mean values of calculated uncertainties for assumed time of reaction with OH of 0 h and 36 h.

Compound	Average uncertainty [%]	
	0 h	36 h
ethane	7.1	8.0
ethene	11.0	56.3
propane	6.2	13.5
propene	12.6	82.7
isobutane	6.9	21.6
acetylene	21.0	25.2
<i>n</i> -butane	26.0	39.2
1-butene	29.3	92.4
isobutene	16.9	96.2
<i>cis</i> -2-pentene	39.1	105.3
isopentane	11.2	33.8
<i>n</i> -pentane	6.8	32.4
propyne	33.5	55.1
1,3-butadiene	43.6	108.9
2-methylpentane	15.0	42.8
3-methylpentane	25.7	48.9
<i>n</i> -hexane	18.3	45.3
isoprene	33.3	115.8
<i>n</i> -heptane	12.9	48.4
benzene	8.6	16.3
toluene	10.9	44.8
ethylbenzene	30.7	59.5
<i>m</i> + <i>p</i> -xylene	25.2	72.8

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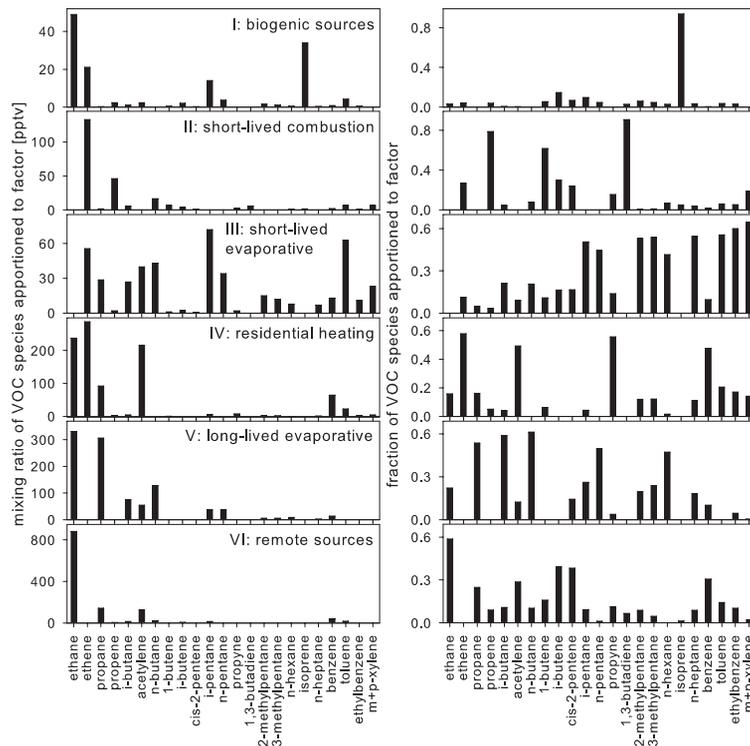


Fig. 1. Source composition profiles for the six factor solution calculated by PMF, left: mixing ratio of each species apporportioned to each factor [pptv], right: relative fraction of each species to the overall species mixing ratio. Note that the scales for each subplot are different due to large variations in absolute mixing ratios.

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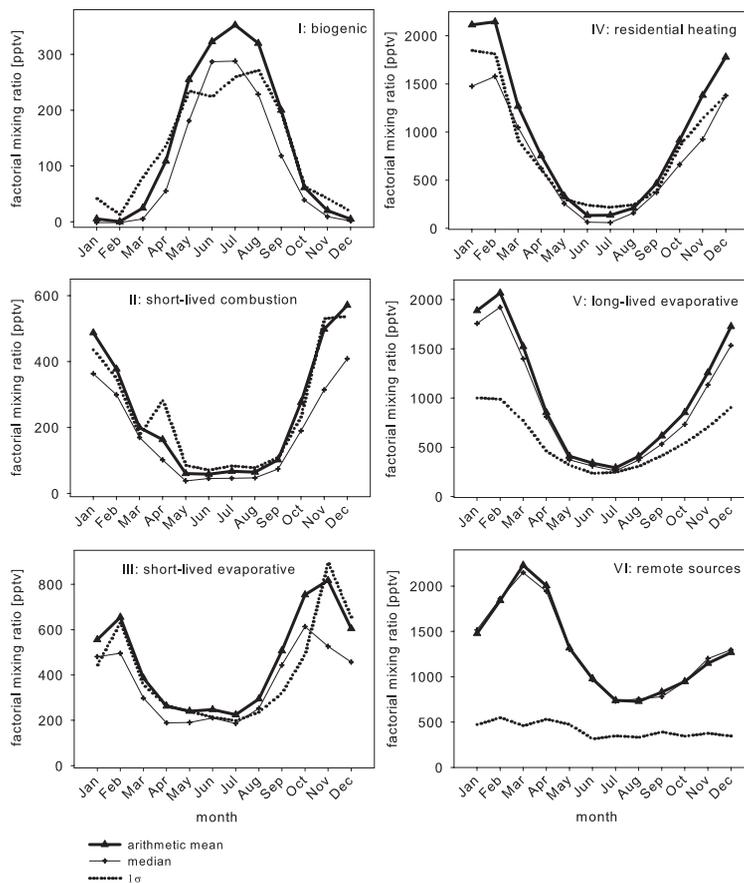


Fig. 2. Annual pattern of the mean, median, and standard deviation of the factorial mixing ratio [pptv] of the respective source category.

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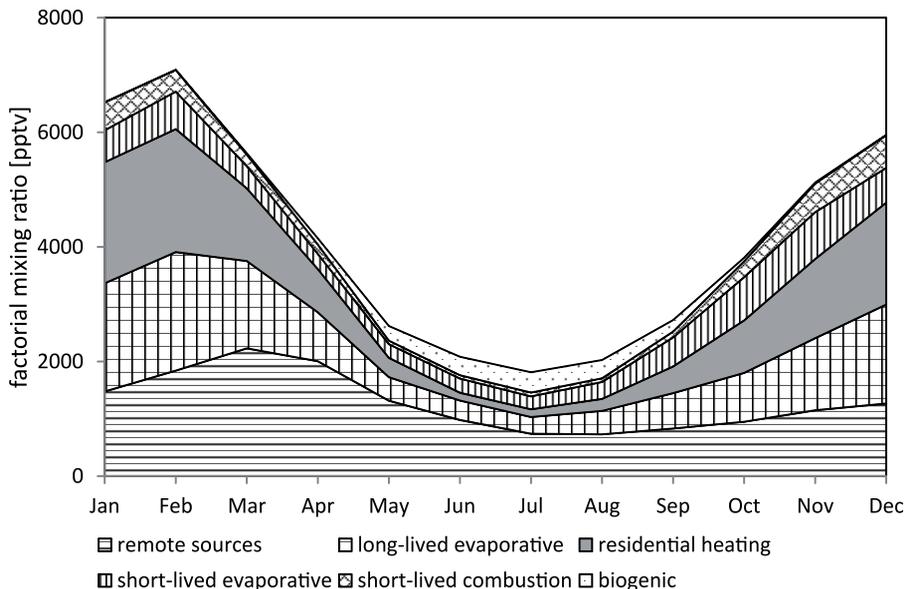


Fig. 3. Mean monthly variability of the contributions from the six factors.

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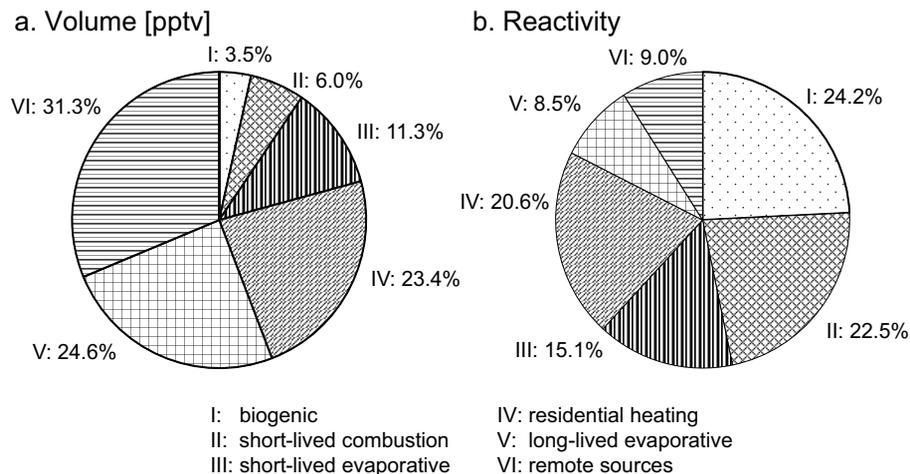


Fig. 4. Contributions of individual factors, left: to the total amount of modeled NMHC [pptv], right: to the total OH reactivity of modeled NMHC [pptcm³ molec⁻¹ s⁻¹].

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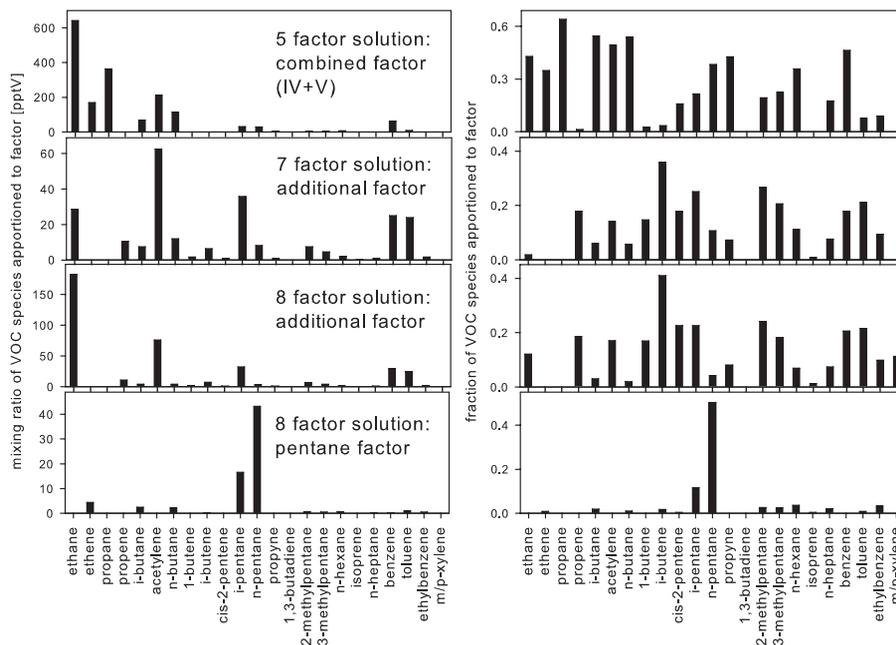


Fig. 5. Source composition profiles of alternative solutions calculated by PMF, left: mixing ratio of each species apporportioned to each factor [pptv], right: relative fraction of each species to the overall species mixing ratio.

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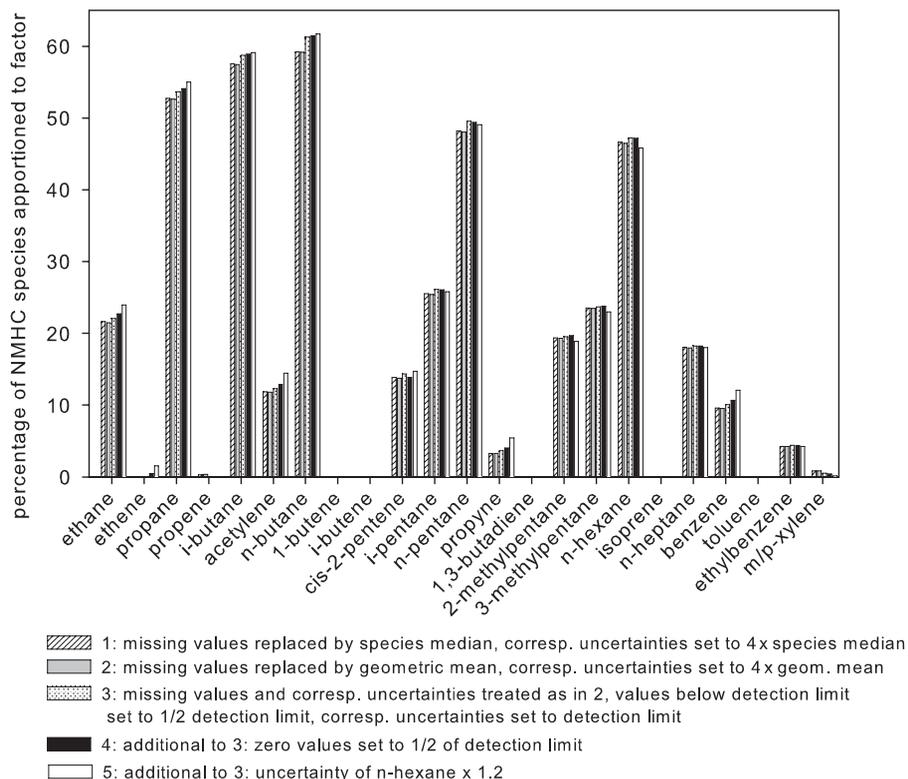


Fig. 6. Composition profiles of Factor V, showing the relative contribution of each substance to the factor, for five different treatments of missing and small values (see Table 1).

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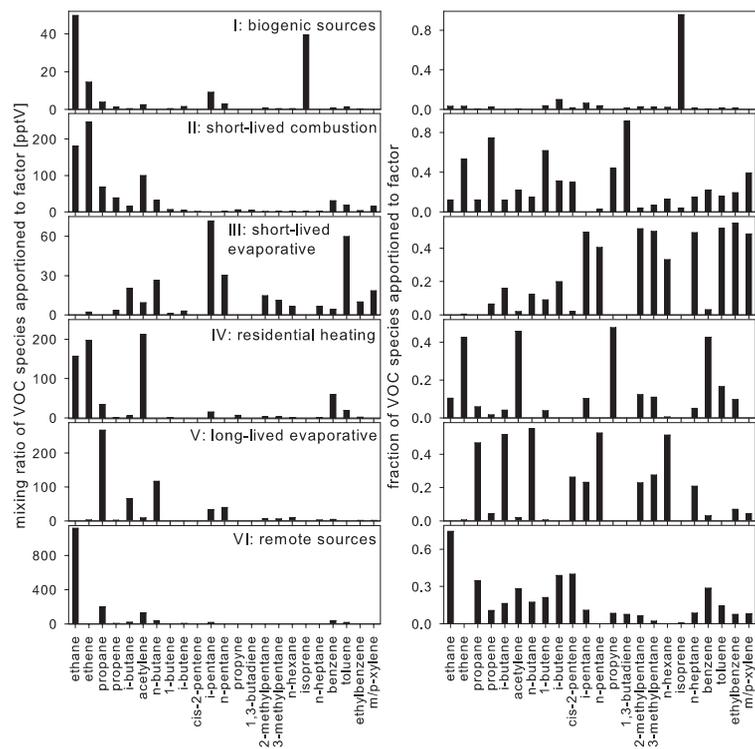


Fig. 7. Source composition profiles for the six factor solution calculated by PMF, assumed reaction time: 36 h, for isoprene: 0 h. left: mixing ratio of each species apportioned to each factor [pptV], right: relative fraction of each species to the overall species mixing ratio.

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