

***Interactive comment on “Factor analytical modeling of C<sub>2</sub>–C<sub>7</sub> hydrocarbon sources at an urban background site in Zurich (Switzerland): changes between 1993–1994 and 2005–2006” by V. A. Lanz et al.***

V. A. Lanz et al.

Received and published: 21 February 2008

We are grateful to Bo Larsen for providing valuable comments on our article. They are surely helpful to improve several aspects of the manuscript.

*Comment 1: Most critical is the issue of VOC reactivity, which the authors have addressed in a rather simplistic way. The use of a 10% uncertainty for all VOCs is arbitrary, and it is certainly not convincing that such a small uncertainty is sufficient to address the incomplete conformity with some of the basic assumptions for PMF (the non-reactivity issue and the issue of a constant source profiles over the complete time*

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*range of the modeled period are the two critical ones for this study). Additional PMF computations should be carried out with a range of uncertainties and the effect on the SCEs should be discussed (this is a rather easy job, and will strengthen the conclusion of the paper significantly). An approach has been described in the literature by which the reactivity of the individual VOC is taken into account for estimation of the uncertainties (Latella et al., 2005; Junninen et al., 2005), which should be taken into consideration, and at least cited in the modified version of the manuscript. Simple calculations based on ozone concentrations at the site will show, that that the compounds included in the present study have atmospheric lifetimes at the measurement site that varies with at least a factor of 10. This should be used somehow, for the estimation of uncertainties in modified version of the manuscript.*

The idea of weighting species within factor analysis based on to their photochemical stability (Latella et al., 2005; Junninen et al., 2005) is very interesting and will be mentioned in the chapter on reactivity (sect. 2.2.2). There is no doubt that the procedure as described in Latella et al. (2005) and applied to data from Bresso was beneficial. For the situation described here, however, this approach has only a limited influence on the results as outlined below:

The correction factors for the present VOC data (sticking to the idea of Latella et al., 2005) were calculated assuming an average transport time from source to receptor of 4 hours and a typical OH concentration of  $0.8 \cdot 10^{-6} \text{ cm}^{-3}$  (Seinfeld and Pandis, 1998), which however represents an overestimation for winter and night time. The correction factors were found to lie between 0.89...1.00 for the hydrocarbons in question (except for propene, where a factor of 0.66 can be calculated). Dividing the analytical uncertainty (eq. 3) by these correction factors and allowing a modeling uncertainty of 10% yields changes in the relative mean SCEs (source contribution estimates) that are smaller than 1% for each factor in 2005-06 and less than 4% for the factors of 1993-94.

Several reasons can explain this low influence on our PMF solutions: VOC measure-

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ments were performed close to sources, the limited reactivity of the hydrocarbons, inclusion of wintertime samples etc.

Furthermore, there are substantial differences between our study and the study in Bresso: *e.g.*, we did not include the most reactive substances (neither 1,3-butadiene nor isoprene nor butenes) as they were not determined in Zurich during the earlier period (1993-1994). [Remark: in fact, in the earlier Zurich data the strongest trend (+3.98%) in the rel. mean SCEs can be observed for the “fuel combustion” source (factor 6), as its loading of propene (clearly the most reactive compound in our study) was almost as high as ethene (the highest peak in factor 6). This is different for the 2005-06 data, where the propene loading in factor 6 accounted only half of the ethene intensity]. Evenly important, we measured the VOCs in the city center of Zurich, whereas Bresso is in the outskirts of Milan, at a distance of about 7 km from the city center. We can assume that transport time from the main sources is smaller than the lifetime of the most reactive substance (as already mentioned in the original manuscript; p. 914, lines 16-18), which may actually be different for the Bresso study. Unlike Latella et al. (2005), we investigated VOC sources based on year-long data, and as can be derived from Figs. 7 and 10, the highest contributions of many sources often coincided with thermal inversions, which typically occur most frequently in wintertime (when radical levels are low). These accumulations of VOCs emitted into the shallow boundary layer probably drive the variability in the data more than VOC removal by radical reactions. The Bresso study took place in September.

Finally, it should be noted that the calculated profiles for the receptor site Zurich-Kaserne (*e.g.* wood burning, traffic emissions) could be directly related to measured source profiles from the literature. Thus, the assumption that the typical transport time from source to receptor is smaller than the atmospheric lifetime of the most reactive species (p. 914, line 16-18) seems to be justified. As shown for organic aerosols (Lanz et al., 2007), it can actually be meaningful to interpret PMF factors as secondary and differently aged profiles. The same could potentially hold true for more volatile organ-

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ics (VOCs) as well, but was not necessary here as we measured close to the VOC emission sources (and the chosen substances are not formed secondarily in the atmosphere).

Generally, the PMF solutions of the presented data were found to be stable with respect to different uncertainty specifications. In particular, the source contribution estimates (SCEs) are rather insensitive to different modeling uncertainties. This can be shown by increasing the relative modeling uncertainties from 5% up to 35%:

Changes in the rel. mean SCEs (2005-2006) as a function of **modeling uncertainty**

	<b>0.05</b>	<b>0.10</b> (ref.)	<b>0.15</b>	<b>0.20</b>	<b>0.25</b>	<b>0.30</b>	<b>0.35</b>
factor 1	-0.4%	0.0%	0.4%	0.8%	1.2%	1.4%	1.6%
factor 2	0.5%	0.0%	-0.7%	-1.1%	-1.6%	-1.8%	-2.1%
factor 3	-0.1%	0.0%	0.2%	0.3%	0.4%	0.5%	0.5%
factor 4	0.0%	0.0%	-0.1%	-0.2%	-0.2%	-1.3%	-1.3%
factor 5	-0.2%	0.0%	0.1%	0.1%	0.1%	1.2%	1.1%
factor 6	0.1%	0.0%	0.0%	0.1%	0.1%	0.2%	0.2%

For the recent Zurich data (2005-06), the largest change due to increasing the modeling uncertainty from 5% to 35% is observed for the rel. mean SCEs of factor 2, namely -2.6% (see Table above). For the earlier data, the SCEs are not very sensitive to modeling uncertainties neither: in analogy to the case described above, the largest change can be observed for factor 4 (1993-94), namely +5.6%. Please note that factor 4 is dominated by ethane (and ethyne), both of which were partially imputed. It is plausible that imputed species are more sensitive to increases of modeling uncertainties, as the fraction of their imputational uncertainties relative to their total uncertainty estimates is decreased.

We will briefly summarize these latter findings in the revised version and also add a sentence like “uncertainty due to radical reactions has not been accounted for individ-

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ual species (as e.g. in Latella et al., 2005) because the corresponding calculations showed only minimal effects on resulting source strengths even for the factors with the most reactive species.”.

*Comment 2: It is a strong point in this study, that the exactly same chromatographic column was used for separation of VOCs, which should be stressed in the abstract and the introduction. In the chapter on chromatography, it should be further discussed, that modern techniques for VOC analysis use two GC columns and heart-cutting techniques in order to separate potential, co-eluting interferences. This means, that although the obtained concentrations for some compounds in the present study might be overestimated, they are at least comparable from 1994-1995 to 2005-2006.*

We will mention this point in the abstract and introduction. In the chapter on chromatography (sect. 2.1.1), we will also add the following sentence: “The chromatographic column for separation of the VOCs is identical for the two measurement periods. This is an advantage for the comparison of the two data sets, although newest developments use two-dimensional gas chromatography (GCxGC) to separate overlapping peaks (e.g. Bartenbach et al., 2007.)”.

*Comment 3: On page 914 you interestingly conclude that down-mixing of aged air masses is not a relevant process in this study. Please explain in more detail the approach you followed with the hybrid model.*

For this analysis, we considered the concentrations of 9 volatile hydrocarbons (butane, 1,3-butadiene, benzene, ethylbenzene, isobutene, isopentane, hexane, m/p-xylene, and toluene), four inorganic gases (NO, NO<sub>2</sub>, CO, SO<sub>2</sub>) and ozone. . . as well as different subsets of these quantities. Those gases are routinely measured at both the “Zurich-Kaserne” and “Rigi-Seebodenalp” site. An aged profile was determined by averaging the measurements at the remote site (Rigi-Seebodenalp, 47°04'03" / 8°27'48" - 1031 m a.s.l.) during a week-long high-pressure episode in 2005. This profile was

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fixed and imposed on the factor analytical solution for the urban data (Zurich-Kaserne, 47°22'39" / 8°31'50" - 410 m a.s.l.) spanning the same time interval. While the aged profile was frozen during the iterative (hybrid) model fit,  $n=1, 2, \dots$  factors were allowed to evolve freely within a non-negative subspace. The computations were carried out using the multilinear engine program, ME-2, designed by Paatero (1999). We have lately described the technical details of such an approach (Lanz et al., 2008). The resulting scores of the imposed profile (enriched with stable and secondary species) did however not show the typical, strong increase during early morning hours as expected for chemically stable and secondary pollutants. Such increases were ascribed to vertical down-mixing of air from the nocturnal residual layer to the surface air of the planetary boundary layer (e.g. McKendry et al., 1997). We therefore concluded that highly aged and processed air masses do not significantly influence the variability in the VOC profiles here. In the revised manuscript, these details on the hybrid approach will be mentioned.

*Comment 4: There is not given adequate reference to relevant receptor modeling studies already published in literature by other research groups (only Christensen; 2006 is cited), and the reviewer remains in doubt, if the authors are aware of the pioneer work carried out in the early nineties on hybrid receptor models. As an intermediate between factor analysis and CMB, a method called target transformation factor analysis (TTFA) has been used (Hopke, 1988). Another application of a hybrid receptor model (COPREM) was developed in the early 90ties by Wählín (Wählín, 1993, Lee et al., 1999, Wählín et al., 2001; Wählín, 2003).*

We include these important papers by Wählín (COPREM) and Hopke (TTFA) in the revised article.

*Comment 5: Throughout the paper distinguish CMB from multivariate receptor models. It would be more adequate to distinguish CMB from PMF by its use of authentic source*

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profiles as opposed to estimated Factors. Indeed CMB is also a multivariate model. On page 909 and page 910 there is a misconception; CMB does not “recover” VOC profiles.

We will follow the referee’s suggestion.

*Comment 6: There is a problem with the chemical nomenclature used in the paper, which makes it difficult to understand. To solve this, simple IUPAC names should be used throughout the text. Isohexanes (sometimes called iso-hexanes), isohexanes (sum), isopentane, isobutene, are all ambiguous names.*

We will change the nomenclature according to IUPAC throughout the modified paper.

*Comment 7: Based on the explanation given on P 912 it is not possible to understand, how quantitative Ethane data was obtained for the period of 1993-1994. Did the authors reintegrate old chromatograms?*

Please consider our reply to anonymous referee 2 (comment 1)

*Comment 8: Give a reference to the “rule of thump” P918 L 8.*

“If the errors are estimated properly, then the theoretical value of  $Q$  should be approximately equal to the number of degree of freedom, or approximately equal to the total number of data points” (Li et al., 2004). The degrees of freedom equal the number of independent observations ( $mn$ , i.e. the number of matrix elements in  $\mathbf{X}$ ) minus the number of estimated parameters ( $pm+pn$ , i.e. the number of matrix elements in the estimated matrices  $\mathbf{G}$  and  $\mathbf{F}$ ),  $mn-p(m+n)$ , which is approximately  $mn$  for large data matrices and few factors.

*Comment 9: The paper needs a careful linguistic review. At points it is not easy to understand what the authors mean (e.g. Page 909 Line17-20; Page 911 L 9-13; Page*

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912 L6-9; P914 L19; P915 L4-5; P917 L9-13 Page 915 L 17, should read Eq. 4)

We will carefully check the wording of the passages listed by the reviewer.

#### References:

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