Atmos. Chem. Phys. Discuss., 8, S211–S215, 2008
www.atmos-chem-phys-discuss.net/8/S211/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Factor analytical modeling of C_2–C_7 hydrocarbon sources at an urban background site in Zurich (Switzerland): changes between 1993–1994 and 2005–2006" *by* V. A. Lanz et al.

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Received and published: 15 February 2008

The paper compares an old (1993-1994) dataset with a new (2005-2006) dataset on C2-C7 VOCs using a modern statistical approach, and obtain very interesting results, which are fitting nicely into the Atmos.Che,.Phys.Discuss. and thus, should be published as soon as possible. Besides minor linguistic problems, there are a number of weak points in the investigation that deserve to be addressed in the modified version of the manuscript.

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Discussion Paper

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 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

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.

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.

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

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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 Wåhlin (Wåhlin, 1993, Lee et al., 1999, Wåhlin et al., 2001; Wåhlin, 2003).

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 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.

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.

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

Give a reference to the 'rule of thump' P918 L 8.

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

Check list:

1)Does the paper address relevant scientific questions within the scope of ACP. Yes

2) Does the paper present novel concepts, ideas, tools, or data. Yes

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3) Are substantial conclusions reached. Yes

4) Are the scientific methods and assumptions valid and clearly outlined. Partly; see expanations

5) Are the results sufficient to support the interpretations and conclusions. Yes

6) Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results). Partly; see explanations

7) Do the authors give proper credit to related work and clearly indicate their own new/original contribution. I don't hink so; see explanation.

8) Does the title clearly reflect the contents of the paper. Yes

9) Does the abstract provide a concise and complete summary. Yes

10) Is the overall presentation well structured and clear. Yes, like a Swiss clock ;-)

11) Is the language fluent and precise. Needs some improvements; see explanations.

12) Are mathematical formulae, symbols, abbreviations, and units correctly defined and used. Yes, with the exception of the non-IUPAC names; see explanation

13) Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated. Yes, if the Editor does not have a problem with the many figures. They are all relevant and clear.

14) Are the number and quality of references appropriate. OK; See point 7)

15) Is the amount and quality of supplementary material appropriate. Yes.

Relevant references:

Hopke PK.Target Transformation Factor Analysis as an Aerosol Mass Apportionment Method: A Review and Sensitivity Analysis, Atmos Environ 1988; 22:1777-92.

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Junninen H, Borbon A, Astorga C, Locote N, Larsen BR. Source Apportionment of Ozone Precursor VOCs in Urban Atmospheres by Receptor Modeling. In: Proceedings of the 5th International Conference on Urban Air Quality, UAQ 2005, March 29-31, Valencia (Spain). Eds Sokhi, RS. Millan MM, and Moussiopulos N. CD-ROM, ISBN I-898543-92-5, University of Hertfordshire.

Lee E, Chan C, Paatero P. Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. Atmos. Environ. 1999;33: 3201-12

Latella A, Stani G, Cobelli L, Duane M, Junninen H, Astorga C, Larsen BR. Semicontinuous GC analysis and receptor modelling for source apportionment of ozone precursor hydrocarbons in Bresso, Milan, 2003. J. Chromatography A. 2005; 1071:29–39

Wåhlin, P. A multivariate receptor model with a physical approach. In: Heidam, N.Z. (Ed.), Proceedings of the Fifth International Symposium on Arctic Air Chemistry. 1993. NERI Technical Report No. 70. Roskilde; Denmark.

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Wåhlin, P. COPREM - A multivariate receptor model with a physical approach. Atmos Environ 2003; 37:4861-7.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 907, 2008.