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Atmospheric
Chemistry
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Discussions

Interactive comment on “Measurements and receptor modeling of volatile organic compounds in south-eastern Mexico City, 2000–2007” *by* H. Wöhrnschimmel et al.

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General comments

The authors sincerely acknowledge the referee’s critical comments. We recognize that the methods were not sufficiently described in the original manuscript, and we have improved this part in the new version. Furthermore, we took the referee’s critical observations as an opportunity to improve the model software according to the referee’s suggestions, and do a reanalysis of the data. Some of the results and interpretations have changed; in particular, one originally proposed source (FOOD) of the source contribution analysis became obsolete, and also some trends in source contributions have

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changed. In this process we also realized some additional limitations of the methodology, which are duly discussed in this recent version of the manuscript.

Specific comments

the manuscript has severe shortcomings and the uncertainty is not estimated so there is not way to judge the reasonableness of the input data,and hence no way to evaluate the final results.

The manuscript was revised and information on measurement uncertainties added.

There are numerous editorial errors that need to be corrected.

The manuscript was revised for editorial errors.

there should be more discussion about the overall composition of the VOC

Additional discussion, in particular on photoreactive VOC, has been included.

it is important to include the uncertainty of the measurements for both ambient and emission profiles. The manuscript does not show unambiguously how errors were used in different parts of the work, nor what their signal-to-noise ratios were in the experimental work. This is important when using receptor models as the uncertainty plays an important role in calculations.

Information was added on measurement uncertainties, for both ambient concentrations and emission profiles. Their role for CMB analysis is now discussed.

Authors did not mention on how important the inclusion of uncertainty is to the whole process, it is claimed that they represent "the standard deviation of the average value". For most variables, this "std-dev of average" is higher that the average itself. I wonder if the std-dev showed in table 1 represents the variability of the compounds for the whole period, which is different from what is used in the model. Overall, using so uncertain data base in CMB appears questionable or perhaps outright wrong.

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In the corrected manuscript we now emphasize more the importance of uncertainties for the analysis. The wording in the original manuscript was by no means intended to imply that the standard deviation of the measurements could be taken as a measure of uncertainty, rather than variability. In fact, the standard deviation (variability) is high, due to the typical log-normal distribution of the measurement data along the whole measurement period. For CMB, the uncertainty has been derived separately from laboratory exercises, and is explained in the last version of the manuscript.

Authors need to convince the reader that using less than 50% of the total mass, which is approximately the percentage of the 13 species in the VOC total mass, is valid to apply CMB.

The referee is right that it would not be appropriate to use 50% of VOC mass to analyze source contribution to total VOC (100%). Therefore, we investigate in our analysis the source contribution of sources to the sum of 13 species, not to the sum of all possible species. This has been emphasized more explicitly in the revised wording.

To have a better apportionment of sources it is necessary to have other key compounds that are important to trace specific sources. Authors analyzed 13 chemical species (ethane, propane, propylene, butane, acetylene, pentane, hexane, heptane, benzene, octane, toluene, nonane, o-xylene) that accounts for 50% of total VOC mass. This must be some form of artifact. When used in CMB, such an artifact invalidates the results entirely. Together, propane and butane account for more than 60% of the 13, it is highly likely that this fact bias the source apportionment results, giving an overestimation of the LPG contribution.

As stated above, the analysis carried out is not intended to explain the source-contributions to total VOC. The referee is right that for such endeavor there are species missing. The limitation to 13 species is a drawback of the study, however, it provides crucial information on source contribution to the selected compounds, among them the toxic BTX. We emphasize in the revised conclusions section the need for long term

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measurements with an extended number of species.

Authors claim that this source [LPG] has a median contribution of 68% at night, 60% during the day and 42% in the evening. How the authors can explain this? If they mentioned that this is due to leakages and why this is more important at night.

Model results are in agreement with what we expected from our knowledge on emission sources in Mexico City. Leakages from stationary LPG tanks are supposed to happen continuously, while vehicle exhaust emissions occur mainly during the day. Therefore LPG is relatively more important during the night. The reason for a still high contribution of 60% in the morning (not “during the day”, as the referee states) is that LPG gets accumulated during the night in the stable boundary layer, whereas vehicle emissions just start to increase with the morning rush hour. Comments to clarify this relation have been inserted in the manuscript.

They also mentioned a higher increase in November to February with 70%, claiming that this is due to usage of LPG for heating, but in Mexico which percentage of the population have such a heating systems? It is more likely that people use electricity rather than LPG heating systems.

In common Mexican homes there is no heating of the rooms. When we mention heating, we mean heating water, and this is done in 8 out of 10 homes in central Mexico with LPG. The corresponding comments have been inserted into the manuscript.

According to previous reported results in the area, the proportions of LPG-related species are in disagreement, how can the authors explain these results? Is this reflected in the CMB results, i.e. lower contribution of LPG during the afternoon period?

As stated in the text, the differences in source contribution results with regard to previous studies can be explained by the regional variability of source contributions within the urban area, also at the same time of day.

How is explained the weekend lower levels if most of the contribution come from the

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LPG?

As stated in the text, the weekend effect becomes visible in the modeled source contributions of vehicle exhaust.

Authors need to include the validation of their database for the CMB results, as the results do not sound reasonable.

Authors hope that with the above mentioned extended discussion of performance measures the needs for validation are satisfied.

They need to mention how they decide the source profiles and number of fitting species.

Done

How it can be explained that all sources reported (LPG, EXHAUST, HOTSOAK, SOLVENT and FOOD) are higher during the evening, if the important activities in the urban area take place in the morning, especially vehicular emissions and LPG handling, which as been reported by several authors,

We are not aware at which part of the manuscript (text, figures or tables) we stated such observation. From Fig. 4 of the original manuscript it can be seen that relative contributions of EXHAUST, HOTSOAK, SOLVENT and FOOD increase with time of day, wheras the relative contribution of LPG decreases. No statment has been made of a diurnal variation of absolute source contributions.

On the other hand, seems that the model has not sensitivity to differentiate HOTSOAK, SOLVENT AND FOOD as the results are quite similar at different time of the day.

Similarity alone is not yet a reason if or if not the model has sensitivity to differentiate those sources. A criterion is if the specific sources are detectable (t-value > 2). Another indicator that the model can distinguish the sources are their very different source profiles, so that an erroneous source selection is not likely.

Authors use erroneously the term source activity throughout the document, do they mean contribution of the source?

The terms “source activity”, “source strength” and “source contribution” are synonymously used in the literature. To make it easier for the reader, we now point out this equivalence in the beginning, and than limit ourselves to use the term source contribution.

The main assumptions on which CMB models rely are: (a) all the sources, contributing significantly to a receptor site, have been identified and have had their emissions chemically characterized (b) chemical species do not react with each other, i.e. They add linearly. In this sense authors should not use xylene as a fitting specie,

The model has been run again without xylene as a fitting species.

(c) compositions of source emissions are constant over the period of ambient and source sampling (d) the number of sources is less than the number of chemical species (e) the source compositions are linearly independent of each other (f) measurement uncertainties are random, uncorrelated and normally distributed The two fit indices, R^2 *and* χ^2*, are considered by the US EPA as primary performance measures of an EFWLS solution, along with the percent mass accounted for %mass, although the latter one can be misleading when the total mass concentration that has been measured for the VOC of the ambient sample is small, as is the case in this study.*

The %Mass reported refers to Σ_{13}VOC (modeled) / Σ_{13}VOC (measured), not total VOC.

The fraction FracEst of those source contributions that have acceptably large projection lengths in the eligible space is another primary performance measure that has been established by the US EPA so as to validate the well-conditioning of the least squares system being solved.

The criterion of minimum projection into eligible space has been included in the model and is reported as such. Model results with sources that do not comply with this crite-

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rion are discarded from further analysis.

Each T-statistic ratio Tstatj, is an additional performance measure, established by the US EPA, as an indicator of whether j source contribution is below detection limit or not. Low T-statistic values for several source contributions may be caused by collinearity among their profiles; the presence of collinearity could be uncovered in this case by the source contribution's projections in a properly adjusted eligible space.

The criterion of t-statistics has been included in the model and is reported as such. Model results with sources that do not comply with this criterion are discarded from further analysis.

Finally, each ratio (Res/Uncer)i is also an additional performance measure, established by the US EPA, which specifies the number of uncertainty intervals by which the calculated and measured concentrations of i species differ.

We have not used this criterion, since no analysis is reported on the species level

In general, authors mentioned only the primary performance measures and do not mentioned the other at all. I question whether the single paragraph is sufficient background for their methodological application.

See above.

Neither the instruments used for ambient samples nor the analytical techniques or the methodology to run the receptor model are mentioned in the manuscript. References are given where this information can be found, especially for emission profiles. It would be opportune to give at least a brief summary, though.

Done.

I do not find adequate to put a personal communication as a reference for a new profile for vehicle exhaust determined in Guanajuato, as this should be describe, how do they account for changes in vehicle technology and fuel characteristics, this will be *interesting.*

Now more details on the new and previously unpublished profiles are provided in the supplementary information.

How were gasoline catalytic vs. noncatalytic profiles discerned from each other? Why diesel was not take into account?. Give more detail about the CMB results (uncertainty, apportionement for individual species if any).

In Mexico, all cars must have catalytic converters. The distinction between gasoline and diesel was not possible, given the limited number of 13 quantified species. Therfore, EXHAUST means the sum of gasoline and diesel exhaust.

It was confusing, as authors state in the abstract that VOC species were decreasing during this period and in the introduction the mentioned that air pollution increase, and that in Mexico ozone formation is VOC-limited, so authors should clarify this.

The wording has been revised for clarity

In the introduction the toxicity of some VOC as well a debate on the LPG contribution. Would it not be possible and advisable to discuss the findings on this regard in the Conclusion?

Done.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C6013/2010/acpd-10-C6013-2010-supplement.zip

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3319, 2010.