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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 comments. We recognize that the request for a more detailed description of the methods and discussion of results is justified, and revised the manuscript correspondingly, along with other corrections.

Specific comments

The sentence “Sulfur dioxide (SO₂) has also become a local problem in the northern parts of the city” should be deleted since last Quality Air report that SO₂ has a de-

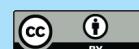
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creasing trend since 1990 with a 88% of reduction. Besides, this study is related with the Sotheastern area.

The referee is right in the aspect that the daily average in SO₂ has decreased. However, short lasting plumes with high concentrations, which are not visible in the daily average, have been occurring recently and are thought to affect human health. Therefore, we decided to leave the sentence, revising the wording to avoid confusion.

Methods Sampling How many grab samples were taken by year? Which was the frequency? Describe over what period of time the "grab" sample was obtained. Was it three hours? This (3h) would be an integrated sample given the variability of hydrocarbon concentrations in an urban area. Was the flow rate regulated?

The information is provided in the new version of the manuscript.

Was the meteorology measured at the site?

Yes, we have all common meteorological variables available in 1 hour resolution. Actually, as stated in section 2.2.1, we used them for explanatory data analysis, but then decided not to report these results since they are beyond the scope of this paper.

On the other hand in the reference of Sosa et al (2008), canisters were used for sampling, and it seems that it is not the case in this research. A better explanation is necessary.

The information is provided in the new version of the manuscript.

There is insufficient description of the sampling site and possible local influences, what kind of industries, main avenues, what is CENICA?

The information is provided in the new version of the manuscript.

Although other studies are cited for analysis, a discussion of measurement uncertainty is needed, as well as detection limits and results of reference materials analysis.

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The information is provided in the new version of the manuscript.

On page 3326, authors say that newer profiles determined in Guanajuato were included. Then, it is necessary to describe these profiles, and the differences with the previous profiles published, since the results could be very sensitive to the new profiles.

The profiles together with their uncertainties, as well as a short description of the experiment, is provided now in the supplementary information.

On the other hand, although this profiles are newer than other published, neither the fuels used in Guanajuato (gasoline and diesel) are the same than in Mexico City, nor the vehicle fleet is similar. Then it could be questionable the use of those profiles.

We agree with the referee that vehicle fleet and fuel composition can not be expected to be the same in two different cities. In this case, however, we think that Guanajuato and Mexico City are comparable, as described in the following paragraphs. Furthermore, we think that it is reasonable to assume that the Guanajuato profiles are less different to today's vehicle exhaust profiles in Mexico City, than Mexico City profiles taken in 1998 to recent profiles. Of course, this latter hypothesis cannot be proven unless more recent vehicular profiles can be measured in Mexico City.

Comparison of vehicle fleets of Guanajuato and Mexico City

1) Fuel composition

In Mexico City, the fuel composition for cars in 1996 was 4% diesel and 95% gasoline and 1% other (Inventario de Emisiones de Contaminantes Criterio de la Zona Metropolitana del Valle de Mexico 2006, <http://www.sma.df.gob.mx/sma/index.php?opcion=26id=501>). The fuel composition determined in the Barretero tunnel was 91% gasoline cars, 4% diesel trucks / buses, 5% gasoline motorbike (see also updated supplementary information).

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2) Fleet age

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Figures 1 and 2 at the end of this comment show the distributions of vehicle age in Mexico City and in the State of Guanajuato, respectively. Although in Mexico City there is a stronger tendency towards newer cars, the general shapes of the distributions are similar.

It is important to define the uncertainties of these profiles since they are important data for CMB application.

Information added in the supplementary information

Which were the fitting species (all of them?). Were Sensitivity tests performed?

As we describe now in the new version of the manuscript, the fitting species were all quantified ones but propylene and o-xylene (because of their high photochemical reactivities). From the remaining compounds, the model was allowed to omit up to one further compound, if this improved the fit. Thus, the model algorithm itself takes care of sensitivity.

Table 1. Why the number of data of each VOC is different? Why the n of the sum of VOC is around 20% lower than the data for the individual compounds. Did the instrument failed? How it could fail for toluene and not for benzene? This is very unclear.

In some cases, concentrations could not be quantified when the peaks of two neighbouring species in the chromatogram overlapped. In other cases, we have no explanation for the relative small difference in n. In any case, we had no reason to invalidate the whole sample, except for CMB analysis.

Only complete data sets should be used for modeling.

This has been done.

Figure 1. It is confused. Why all data is 00:00-24:00. How many intervals are? It

seems that there are only three intervals: night, morning and evening. Are there other intervals to say in all data that they have an entire day? How was averaged "all data"?

"All data" contain measurements evenly distributed across the 24 hours of the day. The averaging was done for samples in which all species were quantified and which lied in the respective time interval. The wording has been adapted at various parts of the manuscript to improve clarity about procedure.

The analysis of VOC trends is really short and I think that a more detailed analysis could be done. Is there some explanation about the differences among the years?

We consider a further analysis of VOC trends beyond the scope of this paper, since the focus is source contribution.

Toxicity was noted in relation to Benzene, but no information was given on whether exposure at the levels measured would be a problem at the site. Maybe it could be included an analysis at different hours, different months, that could give a final conclusion about this issue.

This issue is now commented with more detail in the conclusions section

Are the reactive VOCs concentrations high or low, by what criteria?

A valuation of reactivity has been included in the manuscript, providing a comparison of propylene concentrations with measurements in other urban areas.

The authors claimed in the introduction that the ozone levels are VOC sensitive, how the results are related with this situation?

Our measurements do not provide sufficient information in order to evaluate VOC sensitivity (nor were they intended to do so). Therefore, a discussion of VOC sensitivity is beyond the scope of this paper, however, future measuring and modeling work can build on these results. A comment on this has been added to the conclusions section.

Table 2. Page 3328. It would be useful the addition of a column with the decreasing

percentage of all species to clarify the trends.

Done

Figure 2 The cyclic annual patterns should be discussed deeply. How is the seasonal variation?, Which are the differences between the rainy and the dry-warm season? Is there some influence of the relative humidity or rain?

We have included possible hypotheses for the observed differences between the rainy and the dry-warm seasons. We think, however, that a deeper analysis of these questions is beyond the scope of our paper.

Figure 3. What is mid 2000? June?. Page 3329.

We revised the previously ambiguous wording.

"Reductions did not occur homogeneously over the day or for each VOC species in the same way. How do you explain the differences? The discussion about the species in the supplementary information is important.

The discussion on this topic has been extended

Taking into account that source activities are not homogeneous over the MCMC, it is not possible that some local sources were responsible of the high contribution of the LPG. This result should be discussed.

We agree that the validity of the source apportionment is limited to South-Eastern Mexico City, and that the results have no general validity for the whole urban area. We revised the wording to make sure that this limitation becomes clear to the reader.

Table 4. Although b translate to a yearly rate of change with the formula in page 3325. It would be convenient to add a column with these results.

Done

About weekends it is not clear why VOC concentrations are lower since Saturdays are

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the days with more traffic and higher concentrations of ozone.

We reanalyzed the data, applying the suggestions from referee 1. The results are slightly different. Among others, also the weekend effect got more consistent with expectations, now vehicle exhaust is significantly lower only on Sundays.

If LPG is the main source of VOCs, why the total VOC are lower in weekends when people is at home and use this fuel? More discussion is needed.

In our manuscript, we limit our discussion to the weekend effect of vehicular emissions. We do not discuss total VOC or LPG. However, when computing the weekend effect of LPG, no significant differences turn out. Actually this is not against our expectations, since food preparation and the use of warm water can be assumed to occur all days more or less the same.

How is explained that trends of LPG contributions are similar to exhaust contributions if they are independent sources?

Why should the independence of source exclude the possibility of similar trends? No causality is necessary for this.

There is no comparison with other countries.

We think this is beyond the scope of this article

The authors need to make the information relevant to the reader and discuss (and justify) the implications of the results.

We revised the manuscript thoroughly and hope that the improvements made satisfy the requirements of the referee.

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

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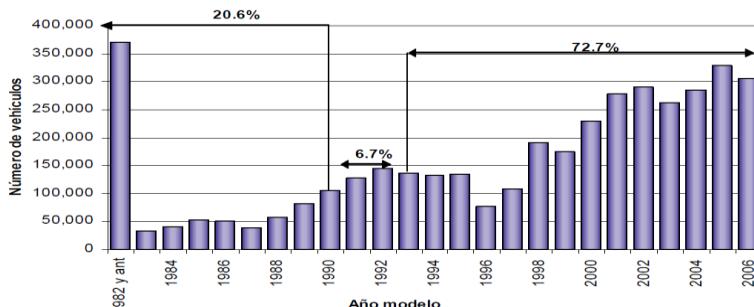
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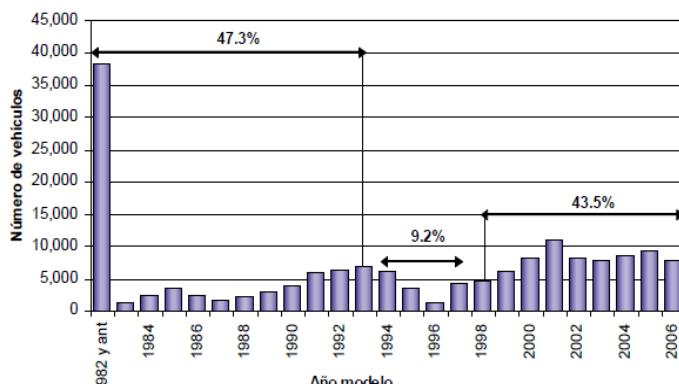
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Gráfica 4.3.1 Vehículos a gasolina por año modelo y tecnología



Gráfica 4.3.2 Vehículos a diesel por año modelo y tecnología

Fig. 1. Data for the MCMA. From Inventario de Emisiones de Contaminantes Criterio de la Zona Metropolitana del Valle de Mexico 2006. <http://www.sma.df.gob.mx/sma/index.php?option=26&id=501>

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Figura 3.27 Distribución de la flota vehicular por año-modelo.

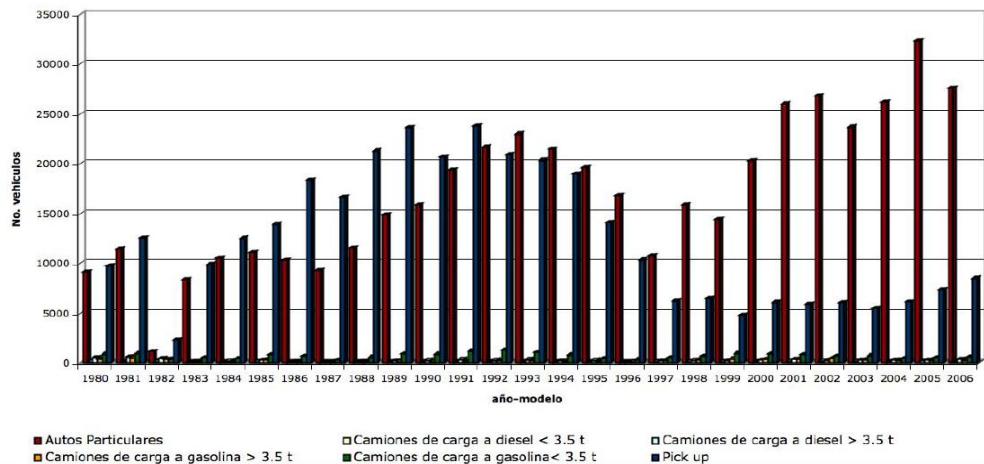


Fig. 2. Data for the State of Guanajuato. From *Inventario de emisiones Guanajuato 2006*, http://ecologia.guanajuato.gob.mx/documentos/inventario_emisiones_2006.pdf

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