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## ***Interactive comment on “Physical and chemical properties of the regional mixed layer of Mexico’s Megapolis – Part 2: Evaluation of measured and modeled trace gases and particle size distributions” by C. Ochoa et al.***

**Anonymous Referee #1**

Received and published: 8 June 2012

The manuscript compares meteorology parameters, concentration of some gases and speciated particle size distributions measured at a high altitude mountain site 60km from Mexico City, with values of the same variables simulated with the WRF-Chem chemical transport model. The objective of this comparison is never clearly stated in the manuscript; however, I assume that the main reason for the study is to validate the model. The topic is of interest for the atmospheric community given the wide use of the model. However, I have some objections regarding the methods used in this study. Below, are my comments.

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## MAJOR ISSUES:

For the measurements-model comparison, ten days were chosen, which presented clear skies and did not have clear influence from biomass burning. Those days were classified according to the origin of the air mass during the previous 24h into groups of 6 (WNW), 2 (E) and 2 (SW) days. For each group, hourly diurnal averages were calculated; the correlation coefficient (Pearson's  $r$ ), and the average difference between the averages of the simulated and measured data was used to evaluate the predicted trends of the model in comparison with the measurements.

Why did the authors compared the hourly diurnal averages instead of comparing the hourly data directly, as is more often done? The authors should justify this choice in the manuscript. I am especially concerned with the E and SW days, because only two days were averaged. Is it really possible to obtain statistically relevant data averaging only two data points?

The fact that hourly averages of the data are being used, means that each point being compared has a standard deviation associated. This standard deviation is partly due to uncertainties in the measurements/simulations, as well as due to the natural daily variability (which, as usually occur in atmospheric measurements, might be quite large). This increased standard deviation complicates the interpretation of the comparisons and should be taken into account; however it is not even mentioned in the manuscript. Just by looking at the absolute differences in figures 3 and 4, it is impossible to know how much of them is caused by uncertainties/variability in the data, and how much is really due to the inaccuracy of the model. For example, in P9825, L15, a difference of 50%-80% between modeled and measured CO concentrations is described. However, part of that difference might fall within the natural daily variability. The manuscript should include a description on the measurements error, daily variability and standard deviations of the averages being compared. Also, all these parameters should be taken into account during the description and discussion of the comparisons.

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Furthermore, the Pearson's  $r$  analysis is, in general, not a good choice when comparing data with significant standard deviations associated, as in this case. I suggest to include, scatter plots of the data shown in figures 3 and 4, showing the standard deviations and best linear fits (which should be calculated with a robust method, in order to take into account uncertainties in  $x$  and  $y$  variables). This would make it easier to visually demonstrate the quality of the correlations. These figures could be included as supplementary material.

Another major issue that is not addressed properly in the manuscript is the emission inventory used for the region being simulated. As it is mentioned in the introduction, the air masses affecting Altzomoni might have other sources of pollutants in addition to Mexico City, such as the major population centers of Puebla, Cuernavaca, and Cuautla (P9816, L25-28). Also, a recently published paper (Salcedo, D., et al. Sci. Tot. Environ. 414, 417, 2012) showed that pollutant concentrations in the neighboring state of Morelos (where Cuernavaca and Cuautla are located) might be quite high; however, the emission inventory for Morelos is not very detailed. In P9820, L3-6, it is mentioned that the emission inventory described by Fast et al. (2009) was used. However, this emission inventory was developed for the Mexico City Metropolitan Area. What about the other urban areas (Puebla, Cuernavaca, Cuautla)? What was used for them? In this respect, I am concerned with the statement in P9820, L10-12: "Baumgardner et al. (2009) reported that in the area to the east of Mexico City there are no major sources of anthropogenic pollutants, although the small villages in this region may have some minor impact". On one hand, the authors are contradicting themselves, given that in the introduction of the manuscript Cuernavaca, Cuautla and Puebla are described as major population centers along with Mexico City (P9816, L25-27). On the other hand, the statement is probably not accurate given the size of the population and the relatively large industrial activity that exists in the states of Puebla and Morelos. Because of all of the above, the emission inventories of the region being simulated must be clearly described and supported in the manuscript. Also, a discussion is missing of the effects of the error in the emission inventory on the differences observed between

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measurements and simulations. For example, I wonder if the underestimation of O3 concentrations might be caused by not considering Puebla, Cuautla and Cuernavaca as important sources of precursors.

#### OTHER IMPORTANT ISSUES:

P9816, L17. "It is the primary objective of the study described herein, to extend the evaluation by Baumgardner et al. (2009) who looked at the physical and chemical properties of 20 the regional mixed layer of Mexico's Megapolis during the MILAGRO project." The objective of the study is to extend the evaluation of what? With what purpose? The objectives of the manuscript are not clearly described, nor justified, in this or any other statement in the manuscript.

Section 2.1 and Table 1. The time resolution of all measurements should also be indicated. Only for the AMS is time resolution mentioned.

P9825, L3-7. Water mixing ratio for E and SW days is described, but no for WNW days. Why?

P2825, L9-27 and Fig. 4a. The description of the CO trends is confusing and not accurate. "Looking at Fig. 4a we see that from midnight to midday, the model reproduces the measurements of CO quite well when the air masses originate from the E or SW with excellent agreement in absolute values as well as the general trends." This statement might be true for E days in the general trend; although I disagree for the absolute values, because the model predicts concentrations 40% larger than the measured ones during the first hours of the day. In the case of SW days, the trends and absolute values of measured and simulated CO concentrations are quite different. For example, the measured values show a minimum at 9AM that is not seen in the simulated values. "The CO predicted by the model, in the WNW air mass, overestimates CO by an average of ca. 0.05 ppm throughout the day, with the exception of one hour at 14:00 when the measurements spike and exceed the model by 80 %." In fact, according to Fig 4a for WNW days, the model line (dashed black) is always below the

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measured line (continuous black), with the exception of one hour at 9AM. "Comparing Figs. 2 and 4b, both atmospheric species begin to increase as the RML approached the altitude of the research site and reach their maximum values at the same time. The secondary peaks that are prominent in the measured CO are not as sharp in the trends of CN but inflections in the trends are still noticeable." I suggest to include a figure (as a supplemental material if necessary) directly comparing CN and CO traces in order to visually show the similarities.

P 9826, L10-24. "The O3 is underestimated by the model throughout the 24 h period regardless of the air mass origin (Fig. 4c). When the model results are shifted two hours later with respect to the measurements, the correlations are all positive and significant at the  $P < 0.01$  level (Table 3), indicating good agreement in trends even though the absolute values are on average more than 0.02 ppm less than observed." According to Table 3, only SW days have a positive significant correlation coefficient (0.598); WNW and E days have a correlation coefficient equal to 0.136 (not in bold, i.e. not statistically significant) and -0.601 (negative), respectively. Although the correlation coefficient for E days is statistically significant, a negative correlation cannot be considered "good agreement". Hence, Table 3 does not show a good agreement in O3 trends for all days as is stated in the manuscript. In fact, good agreement in O3 between measurements and model is mentioned several times in the manuscript (for example P9830, L19-21 and P9831, L9-11), and is used as a justification to reach some of the conclusions of the study. Given the arguments above, authors should revise the manuscript removing the references to the "O3 good agreement", and check if their conclusions still hold.

P9830, L19-24. "The temperature and water vapor mixing ratios were well correlated regardless of air mass origin, as was the ozone. The CO was very well correlated prior to the arrival of the RML but the significant underestimation by the model after that time causes the correlation coefficients to decrease." As mentioned above, the statements related to O3 and CO are not justified.

P9837, L25. "The fidelity of the model, validated by the measurements, is generally

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quite good. . ." This statement is too general, and not quantitative or descriptive at all. Also, it contradicts most of the discussion, which describes all the differences in CO, O<sub>3</sub>, AP and PSDs observed.

#### MINOR CORRECTIONS AND SUGGESTIONS:

Fig 1. Because the urban areas of Cuernavaca, and Puebla are also mentioned in the text, they could also be included in the map.

P9816, L26. Should be "Cuernavaca"

P9817, L5-20. "In the following presentation we describe observations of diurnal trends in the mass size distributions of sulfate, nitrate, ammonium and organic matter and compare these observations with simulations from the WRF-Chem model." This description of the manuscript does not agree with the title, nor with the content of the manuscript, which also include modeled trace gases.

P9817, L13-18. I suggest to make reference to Fig. 1, where the position of the site is marked in a map. Also, it might be helpful to have the relative altitude with respect to the MCMA, rather than only meters above sea level.

P9817, L23. "AGL" should be "a.g.l." in order to be consistent with the rest of the document, where the latter is used.

Fig 2. The wording of the label and the text describing the figure is very confusing.

Table 3. What do the dashes in the error column mean?

P9824, L25. Should be "...temperature and water mixing ratios".

P9825, L21. It should be "4a" (?)

P9828, L14. "a decrease" would be more accurate than "a shift".

Table 3. Use WMR, instead of MR for water mixing ratio. Also, define MR (or WMR) in the text and/or the table caption/footnote.

P9830, L20. Should be ratios instead of "rations".

Fig 9 label. "RMA" should be "RML" (?)

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