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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of emissions of VOCs and NO_x on trends of ground-level O_3 in Mexico during 1993–2014: Comparison of Monterrey with Mexico City and Guadalajara" *by* Iván Y. Hernández Paniagua et al.

Anonymous Referee #2

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This paper by Hernandez Paniagua deals with a very important topic of ground level ozone (O3) and its trend in Monterrey, Mexico (MMA) from 1993-2014. It also presents comparison of O3 trend with other big metropolitan areas in Mexico namely Mexico City (MCMA) and Guadalajara (GMA). While the topic is very important for both air quality and human health, the paper needs some revisions before it is suitable for publication in ACP.

Major Comments:

The paper as it stands is not fully digested. This is one of the major weakness of the pa-

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per. It could be significantly concise and coherent without losing any of the messages. A lot of figures could be moved to the supplemental section. For example Figures 3, 4, 5, and to some extent 6 do not really add much to the paper. Similarly, sections describing measurements at MCMA and GMA could be moved to the supplemental section as these measurements are not really different from MMA. On the other hand, the paper will benefit by expanding the analysis section.

There are also comparisons with places around the world that is not very relevant for MMA. While it is important to compare the results with measurements made at other places around the world, these locations need to be very carefully selected. O3 levels depend not only on the emissions of precursors but also the availability of the sunlight. The locations selected in the paper are from everywhere in the world from Canada to Japan, Cyprus to Saudi Arabia. These places do not have similar climate and very likely different emission scenarios and as a result not suitable candidate sites for comparison. Surprisingly there were no comparison being made with any locations in United States which likely has places with similar climate and emission sources (at least in terms of vehicular fleet make up). I suggest the other make a more selective comparison.

Despite the paper claiming it as a study of "impact of emissions of VOCs and NOx on trends of ground level O3", there is very little analysis of emissions of VOCs and NOx in the paper. The only analysis presented is the trend in VOC and NOx emission inventory in MMA, GMA and MCMA (Fig. 1). And, Fig. 1 is mainly used in the introduction and not interpreting the observed trends. It is misleading to claim it as the study of "impact of emissions" as it stands. I suggest the authors, present analysis of NOx and VOCs (CO) measurements and attempt to make connections between VOCs, NOx and O3. A more suitable title for the current paper would be "Trends of ground level O3 in Monterrey, Mexico during 1993-2014: Comparison with Mexico City and Guadalajara". The lack of NOx and VOCs trend makes most of the current conclusion seem more like speculations.

There are too many different O3 metrics being used in the paper and the authors constantly switch between them. There is no rationale being presented for why a certain metric is being used. I suggest the authors minimize the number of metric being used if possible or justify the use of different metrics in terms of what it reveals about O3 in MMA.

Specific Comments:

Line 23: Why is larger AVd observed at polluted sites close to industrial areas? O3 being a secondary pollutant should show larger AVd at downwind sites? In fact, the largest AVd is observed at STA which is furthest away from the industrial areas.

Line 30: GPE is described as highly populated area downwind of an industrial area in Table 1. So, GPE qualifies as site with largest and smallest seasonal cycle (AVs).

Line 70: Introduction: The introduction switches between O3 trend in rural background and urban areas. I suggest the authors focus solely on the urban areas as this is the focus of this particular paper.

Line 133-135: Based on Figure 14, O3 has gone up in MMA by only around 20-25% and decreased in GMA.

Line 172-186: This section belongs to the results and discussion section. These could be used to explain some of the observations rather than keeping it in the methodology section. Further, I suggest figures 3 and 4 be moved to a supplemental section to make the paper more concise.

Line 188: What is the time resolution of these measurements?

Line 204-235: Section 2.2 and 2.3: I suggest moving these sections to the supplemental as well. Most of the analysis focuses on the MMA and these two sections only describe the locations and measurements at MCMA and GMA. These measurements are not different from MMA. A reference sentence at the end of MMA measurement section would be sufficient.

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Line 237: Section 2.4: I suggest the author expand this section to describe all the methods used in the analysis of the data. Please add a brief description for (i) openair package for R, (ii) MAKESENS 1.0 macro, (iii) Seasonal Trend Decomposition technique. Please include how do they work or what is being done in each of these program and what are the advantages of such an analysis to reveal changes in O3?

Line 238: I suggest that figure 5 be moved to the supplemental section.

Line 265: It would be better to show 5, 50 and 95th percentile line for the data in Figure 6 than all the data.

Line 270: Add "(see Figure 8)" behind "(winter)".

Line 276: Reaction of O3 with NO to form NO2 is only a part of the null Ox cycle. Please include the full Ox cycle.

Line 278: Ox cannot have a minimum value of 0. This would require both NO2 and O3 to be 0. It is very likely a measurement error or lack of measurements. I suggest the authors employ some kind of data filtering. There are also instances where Ox is lower than O3 which is again not possible.

Line 282-285: It would be very helpful to include trends in measured NOx and CO to interpret the observed trends in O3 and Ox. This would also be in line with the title of the paper.

Line 287: Please add description of how the data is de-seasonalised.

Line 289: A NOx trend would also help justify this statement regarding increased localized industrial emissions.

Line 290-292: Isn't this the further study to connect emissions with O3?

Line 298: It is surprising that new vehicles are only limited to the city center or the impact of new vehicles are only seen there. Is there some kind of restrictions on the age limit of vehicle that can enter the city center? Else you should see the benefit over

the whole MMA unless the industrial emissions are offsetting the vehicular emissions.

Line 305: Is there seasonality in rush hour or is the observed shift in O3 dip due to change in time i.e. day light saving?

Line 315: How is the normalization performed? Do you subtract the mean O3?

Line 318: All the sites show lowest AVd in winter not just SNN.

Line 318-320: Please justify this statement or add a reference. This statement seems to be misplaced. The lowest AVd during winter is likely due to availability of less sunlight and subsequent slower photochemistry as shown in Section 3.3 and not due to inflow of VOC and NOx laden air masses. These should instead enhance O3 production resulting in larger AVd.

Line 340: It is hard to see what is going on in Figure 10. Please consider adding a second panel focusing only on one of the years.

Line 341: How does reduced rainfall decrease O3 levels? In line 345-346, it is mentioned that frequent rain storms suppresses O3 levels in late summer and early autumn. These two statements are contradictory.

Line 359: What is the benefit of calculating AVs. It is currently not clear. One could do a similar trend analysis without calculating AVs.

Line 364: How did NOx and CO change during the economic crisis? A large decrease in NOx was observed in US and Europe during the last recession (Castellanos et al., 2012, Russell et al., 2012). Do you see similar decrease in NOx as well?

Line 376: Please see previous comments regarding NOx trend.

Line 385: Please see previous comments regarding new vehicle being limited to city centers.

Line 399: Why would accumulation or stagnation of air mass not result in an increasing

trend? If more O3 and precursors are coming in from nearby places, then O3 should go up?

Line 400: Figure 4 does not show stagnation at STA.

Line 423: SNB has growth rate of -0.06 ppb not SNN.

Line 437: Please add p value.

Line 431: Are there any sites upwind of the MMA industrial area? This would help interpretation of the data.

Line 442: Figure 1 shows largest emissions for GMA in recent years. This contradicts the statement being made about Figure 1 describing the magnitude of AVd s in three cities.

Line 445-448: The statement regarding weekend effect is not clear. Figure 13 does not differentiate between weekday and weekend. It is not clear whether NOx or VOCs decrease during the weekend. So, the statement regarding why no differences in O3 is observed between weekday and weekend is not appropriate.

Line 450: Section 3.7: I suggest the authors consolidate the trend in O3 in the three metropolitan areas to the observation based only on the trend line. A statement regarding why the trend line is more appropriate than randomly choosing the start and end data to get the reduction/increase in O3 is justified.

Line 462: Why is there such a large variance in the annual averages?

Line 471: Figure 1 shows both VOCs and NOx are going up for MCMA not going down. So, why is O3 going down with both the precursors going up?

Line 487: Which standard is used for Table 5, new or the old one? If it is a mixed of two then, the data is not directly comparable. I suggest using the new O3 standard for all years.

Line 493: It is hard to evaluate the statement without not knowing what is represented in table 5. 2012 and 2013 showed a significant reduction in number of days exceeding the standard. Then, there is a big jump in 2014. If the big jump in 2014 due to the change in the standard, then it is kind of misleading to say "recommended that more stringent emission controls are introduced in order to improve air quality within the MMA".

Table 3: I suggest moving it to the supplemental section.

Table 5: Which standard is being used to calculate these exceedances?

Figure 2: Please remove the wind rose plot from OBI and add predominant wind direction for each site as a single arrow for each site.

Figure 9: Legend is missing STA. There are two GPE s instead.

Figure 10: Please add a zoom into one of the years.

References:

Castellanos, P. and Boersma, K. F.: Reductions in nitrogen oxides over Europe driven by environmental policy and economic recession, Scientific Reports, 2, 265, 1–7, doi:10.1038/srep00265, 2012.

Russell, A. R., Valin, L. C., and Cohen, R. C.: Trends in OMI NO2 observations over the United States: effects of emission control technology and the economic recession, Atmos. Chem. Phys., 12, 12197-12209, doi:10.5194/acp-12-12197-2012, 2012.

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