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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 #1

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Hernandez et al present trends in ozone precursor emissions and measured ozone levels in three urban areas in Mexico: Monterrey, Mexico City, and Guadalajara. This is an important research topic because, while there has been a long history of ozone trends analysis in the EU and US, there has been relatively little published on trends in other parts of the world. The paper itself needs some revisions before it is suitable for publication in ACP. Please see comments below.

Overarching comments: Trends in emissions of ozone precursor: The authors need to more fully explore trends in ozone precursor emissions and discuss how the trends

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shown were derived. They provide some citations but don't address how reliable these sources are and whether there have been methodological changes over time in the emissions estimates that might impact the calculated emissions trends. Since these trends are later used to explain resulting ozone trends, they are a fundamental basis of the paper and need more discussion and exploration. In addition, Duncan et al., 2016 analyzed NOx trends in these three metro areas based on satellite NO2 column measurements between 2005-2014. The NOx trends reported by Duncan et al do not match those reported by the authors in Fig 1a. For instance, Duncan et al (Table S9) found that NO2 had decreased in Guadalajara in this period while Fig 1a suggests that the increased. Additionally, Duncan found that NO2 in Monterrey increased 8x more than NO2 in Mexico City while Fig 1a shows them increasing at similar rates. The authors should compare their results with Duncan et al and use this to explore uncertainties and limitations in in the emissions trends shown in Fig 1a.

Incomplete coverage of past trends work: In the introduction and throughout the paper the authors have a haphazard presentation of past trends work. One of the largest long-term ozone monitoring networks is located in the United States and yet the authors fail to cite any of the numerous studies looking at trends of US ozone (a subset of US trends references are listed at the end of the review). Rather, the authors inexplicably try to understand Monterrey O3 trends by comparing them to studies from London, Tokyo and other far off places with little in common meteorologically or emissions-wise to Mexico. While it is worth discussing broadly the ozone trends across the Northern Hemisphere, the authors have a huge gap in this exploration because they don't include any work from the US. Additionally, when trying to explain/understand O3 phenomena in Mexico, the authors should try to make comparisons to locations that have similar meteorological or emissions change drivers. Instead, the comparisons and reported trends from the literature are discussed in a disjointed way and don't provide an overall picture or provide context for the Mexican trends work presented here.

Lack of transparency of O3 metrics discussed: In the introduction, the authors cite

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numerous trends studies and say that ozone has changed by XX ppb but their description leaves out what metrics are being used. A 5 ppb change in annual average O3 would mean something completely different than a 5 ppb change in 5th percentile or 95th percentile O3. Additionally, O3 calculated using all hours versus O3 calculated using daily max (1-hr or 8-hr) will behave quite differently. In order for the reader to fully understand the literature that is being cited, the authors must provide information on which metrics the studies investigated. In addition, while the results in this paper do generally state the metric used, the authors switch between metrics (monthly avg – all hrs, annual avg – all hrs, 1-hr daily max values) without providing the reader with any information on why different metrics were used or how they might relate to each other. The authors need to provide more context in their own results about the meaning of each metric and what it reveals about O3 changes.

Specific comments: Line 43: add ", methane" between "CO" and "and volatile organic compounds".

Line 87-92: It would be helpful if the authors provided some basic background information on the relationship between emissions of NOx and VOC and O3. For instance explaining the conditions under which NOx increases versus decreases O3 concentrations.

Line 142-143: But didn't the authors state that previous trends work had been conducted for Mexico City and Guadalajara?

Lines 176-178 and 180-186: These appear to be results which are stuck in the middle of the methods section. I suggest moving these to the results section.

Lines 195-199: Were new and old instruments ever co-located to inter-compare the measurements? Just following QA procedures is probably not sufficient to control for changes in O3 data due solely to different measurement techniques.

Line 267: GPE had a higher max value than STA according to numbers reported in the

following paragraphs.

Line 276: It would be more accurate if this sentence read: “Reaction with O3 rapidly converts NO to NO2”.

Line 287: Here the authors switch from data using all hours (and daily averages) to daily max 1-hr O3 values. They should note the switch and explain the importance of the different metrics.

Line 288: Is this significant? If so state p-value.

Line 289: Here you state that changes 0.79 ppb/yr are “large” but on line 38 you referred to a change of 0.76 ppb/yr as “gradual”. Be consistent with characterization of these trends.

Line 290: the authors should state the magnitude and direction of the trend at STA is before discussing causes.

Line 315: What are the daily O3 profiles normalized to? It is not clear what calculations were performed here.

Lines 315-326: It would be interesting if the authors could discuss whether AVd has changed over time.

Lines 329-338: In contrast, the maximum O3 concentrations in the US usually occur in June-August. It would be good to note this difference.

Line 355: The authors state that AVs are similar to those recorded in the US but they have provided no information about the US with which to make this comparison.

Line 371: Are monthly averages calculated using all hours or just daytime max values?

Lines 381-389: Duncan et al can provide NO2 trends at many more locations than just Toronto. Also the US EPA publishes trends reports which include trends in emissions which could be used for comparison.

Lines 444-448: This explanation does not fit with the current literature. The most dramatic weekend/weekday effects have been observed in Southern California under VOC limited conditions, so VOC limitation would not explain the lack of a weekend/weekday effect.

Lines 4851-456: Past work (Simon et al, Cooper et al) has shown that O3 trends are much more pronounced at high percentiles than at average levels, so an annual average may not be a very good metric to use to see long-term trends.

Lines 458-464: Zheng et al and Camalier et al have analyzed the impact of inter-annual meteorological variation on O3 trends. These studies should be cited and discussed.

Lines 466-475: The explanation linking O3 trends to emissions trends does not follow logically and is in contrast to results presented by Duncan et al.

Tables 3 and 4: Are O3 statistics based on hourly O3 data or some other averaging period/daily max period. Please clarify in text and table headings.

Fig 1a: Text should describe how this figure was created from the data sources listed. Do different data sources/years use consistent methodologies?

Fig 3: The label for panel d is missing

Figure 8: How were 95% CIs constructed? Were they based on all daily values? Or on variation among sites in annually averaged profiles? In either case, these confidence intervals look VERY small, I think there is an error in the plotting. It is hard to believe that there would be so little day to day or site to site variability.

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