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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vertical distribution of ozone and VOCs in the low boundary layer of Mexico City" *by* E. Velasco et al.

Anonymous Referee #1

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General Comments:

This paper describes measured profiles of volatile organic compounds obtained in Mexico City during the 2006 MILAGRO field campaign. The measurements, especially the VOCs, are very useful for evaluating air quality models and for determining whether emission inventories are consistent with measurements. However, the paper would have been strengthened considerably by collaborating with scientists performing either of these activities and by utilizing a few key measurements made by other MILAGRO scientists to aid in their analyses..

Specific Comments:

1) While it is important to report key measurements in the literature needed to improve

our understanding of oxidant chemistry, it is insufficient to present the data itself without sufficient analyses and discussion that puts the data into the proper context. In general, the limited analyses the authors present do not shed much new information on chemical evolution in Mexico City or in urban boundary layers.

2) The primary analysis of plotting all the profiles on the same plot is flawed and makes interpreting the results difficult. While the measurements indicate a consistency from one day to the next, there are significant differences that show up as anomalies in the contour plots that likely result from either different meteorological conditions, different emission rates on a particular day, from other processes, or a combination of various processes. Segregating the vertical profiles into types of days would have provided a more "clearer" picture of the evolution of the trace gases in the boundary layer. Also putting measurements from different sites (and from different periods) also complicates the interpretation since they would be influenced by different local emissions and transport patterns. I suggest also separating the sites in the analysis as well.

3) As the authors point out, an interesting feature of Mexico City is that the CBL does not grow in a classic manner. Instead, the CBL grows slowly in the morning and then grows rapidly shortly before noon. It is possible that this CBL feature affects photochemistry in some way since precursors are trapped in a relatively shallow layer for a long period of time during daylight. The observed chemical profiles, coupled with a simple theoretical model or column model driven by this observed CBL depth could have provided some answers.

4) A description of the chemical profiles at night is an interesting part of this paper. The temperature profiles indicate a shallow layer near the surface in which emissions are mixed into. Ozone is titrated by NO within this layer. However, most of the VOCs shown in Fig. 6 are complicated and not as simple as described by the authors. This is probably the result of merging the results from all days into one plot. At times the highest concentrations are adjacent to the ground close to the emissions sources, but at other times the peak concentrations are significantly above the surface and it is not

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apparent why this occurs. As stated in 2), segregating the data may provide a clearer picture of what is going on at night in the BL. It would have be useful to have another 50 m of measurements to get above the nocturnal BL and provide a strong vertical gradient depth. Please describe in section 2 why in the pre-field campaign planning the VOC measurements were limited to 200 m AGL.

5) As described in some of the minor comments, the analysis and conclusions drawn in the paper would have been strengthened by utilizing a few other key MILAGRO measurements to supplement those collected by the authors.

Technical comments:

1) Abstract, line 9: Normally one does not consider ozone in the nocturnal residual layer to be “trapped”. Ambient winds could transport this material out of the valley leaving background concentrations aloft that remain relatively constant since little NO titration occurs aloft. Also the reference to the “shallow unstable layer” at the ground at night is a bit confusing without reading the text. Normally one assumes the BL within a few hundred meters of the surface is stable, albeit at a different than further aloft. In the text the authors describe some urban processes to explain the apparent unstable conditions at the surface. This finding should be elaborated further in the abstract.

2) Introduction: the first two sentences are awkward and should be re-written.

3) Page 3, line 3 from bottom: This sentence is awkward, suggest changing to “There were three objectives of this study including 1) to investigate Ĕ , 2) to determine Ĕ, and 3) to provide Ĕfor air quality models.”

4) Page 4, lines 3 and 4 from bottom: Please include some information on what “old” and “new” are.

5) Page 5, lines 1 and 2: How were the profiles similar? Where the average values similar to the ones obtained here? The emission inventories indicate large variations across the city that would suggest differences in measured VOCs, so the statement that

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the profiles were similar is a bit surprising and should be elaborated. Why not include some information on differences in the emission rates at the sites, as determined by the emission inventory?

6) Page 6, end of section 2. It would be useful to include a table that includes the times and days of the profiles obtained during MILAGRO. The generalizations made by the authors later depend on the ambient meteorology that varies from day to day. So it is not known if profiles were not made on one or more key days.

7) Page 7, first paragraph: I assume that what is plotted in Fig. 2 is a simple interpolation of all the profiles. Did some of the profiles on different days occur at the same time? If so, how does the interpolation handle that? Is an average taken?

8) Page 7, near the bottom: The authors should do a literature search on computing the Richardson number from tethersonde platform. I'm not sure that computing secondary quantities from a profile that will vary somewhat as the tethesonde ascends and descends is appropriate. A reference to another work that computes Richardson number from tethersondes is needed and a brief discussion of the uncertainties is warranted.

9) Page 9: The authors mention that the tethersonde measurements cannot determine what is happening in the upper part of the CBL during the late afternoon. However, there were rawinsondes made at 18 and 00 UTC each day during MILAGRO that could be used to supplement their measurements aloft. The two measurements are not that far apart. Coupling the measurements would provide a more complete picture of CBL evolution.

10) Page 10, third line of 3.2: This sentence is awkward. Suggested changing to "While our measurements were not able to describe the diurnal and spatial variations of the boundary layer winds in Mexico City, they provide a glimpse of the winds in the lower boundary layer over the southeastern portion of the city as long as the wind speeds were low enough to safely launch the tethered balloon."

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11) Page 10, line six of 3.2: It looks like the winds were more variable with both northerly and westerly winds (not just northerly) at that time.

12) Page 10, line 13 of 3.2: The authors state that the wind tend to blow out of the north. However, it is not known if the profiles are representative during the period. Where more profiles taken on days with northerly winds aloft, so that the results are biased in some way?

13) Page 10, last sentence of section 3.2: There were at least two periods during MILAGRO in which the ambient winds were strong as a result of strong troughs. Were profiles made at that time and how do they correspond to the other measurements. There seem to be, but it is difficult to separate out those periods given the way the profiles are plotted in Fig. 2.

14) Page 12, line 4: Do the authors mean that the ozone concentrations in the shallow BL were typically 35 ppb and the concentrations aloft in the residual layer were typically 50 ppb? It sounds like the text is backward.

15) Page 13, end of section 3.4: As described by several studies in Mexico City, transport would also play a large role in producing day-to-day variations in ozone at a single site.

16) Page 13, end of first paragraph of section 3.5. The first author is referencing himself for a personal communication. This should be eliminated. Either provide the material or eliminate it from the text.

17) Page 13, line 5 of paragraph 2 of section 3.5: Change “contributes” to “likely contributes”.

18) Page 15: It would seem logical to mention that many aircraft made VOC measurements aloft above the city. But they could not fly close to the surface; therefore, the present measurements fill in a gap in the data.

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