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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evolution of anthropogenic pollution at the top of the regional mixed layer in the central Mexico plateau" *by* D. Baumgardner et al.

Anonymous Referee #2

Received and published: 24 March 2009

Review of Evolution of anthropogenic pollution at the top of the regional mixed layer in the central Mexico plateau by Baumgardner et al.

General Comments:

This manuscript describes measurements made at a mountain site Southeast of Mexico City. The measurements are unique, and the clear changes in the levels of pollution when the mixed layer reaches the height of the site are of interest. The measurments made at this site complement the urban and aircraft measurements made during the same period. Unfortunately the analysis only focuses on only three days of the study. This short time period is insufficient to make some of the broad conclusions in the

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manuscript. For this and the other reasons detailed below, it is recommended that this paper undergo a major revision before acceptance into ACP.

Specific Comments:

The title of the manuscript does not describe the contents of the manuscript well. It is suggested that the authors replace “Evolution” with “Measurments”.

Intercomparison of instrumental data needs to be done: For some of the data there are clearly discrepancies between measurements. For example: The PM_1 mass derived from the OPC in the easterly case peaks at about 7 μ g m^{-3}. The AMS measured organics (ignoring other species) during the same time period reach over 70μg m^{-3}. One would expect that the measurements would not necessarily agree, but a factor of 10 discrepancy between the measurements requires investigation and intercomparison. This could (and should) be done for more than just the 3 days of this study. This could even be placed in supplementary information if the authors would prefer that.

3 days of data are not sufficient for general statements: The conclusions of this paper are based on 1 day of measurements for each flow direction, and in the opinion of this reviewer that simply not sufficiently long enough of a measurment period to make general statements about aerosols coming from the east vs southeast vs southwest. e.g pg 3266 line 10 (abstract): “the highest concentrations of CO, O_3 and aerosol particles were from the east, decreasing as flow shifted to the southeast then southwest”. On page 3280, the statements about the 1 day and 1 night averages of the mass fractions of OM and SO_4 are compared to month-long measurements from a groundsite. It would be more appropriate to compare similar timescales. It is quite likely that there are days or times of the day when the mass fraction of OM at a city measurement site exceeds 60 percent, but on a month long timescale this will average out. If a quantitative comparison to Mexico City datasets is desired, then the authors need to look at more than 3 days of data in order to do such a comparison. Data can be filtered by wind direction, or back trajectories.

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CO background subtraction and OM/CO ratios: It is not clear from the manuscript whether the background CO concentration was subtracted from the CO when doing the analysis of pollutant to CO. If this was done, the corresponding background CO used needs to be explicitly stated in the text, if it was not done it needs to be. There is significant sensitivity in the OM/CO ratio in the choice of background CO. Additionally, the ratio of SO_4/CO (pg 3281 lines 2-11) is flawed since SO_4 and CO generally come from different sources, and consequently CO is not a conservative tracer for emissions of sulfur compounds. The increase in the SO_4/CO ratio can also be explained by changes in the relative mixing of a regional SO4 rich plume with an urban higher CO plume.

Later in the manuscript the OM/CO ratio is inverted, and a discussion of CO/OM is performed (discussion starts on pg 3281 line 26). First, it would be beneficial to choose one or the other, the ratios contain the same information. Second the discussion makes no mention of the effect that secondary organic aerosol formation would have on this ratio. Several studies (e.g. Volkamer et al. (2006), Kleinman et al. (2008), DeCarlo et al. (2008)) have shown significant secondary production of organic aerosol in this region. The relationships seen here could be explained by primary emissions followed by secondary formation, and do not necessarily point to one source of aerosol versus another. Further analysis of the AMS data (e.g. m/z 60) could provide some insight into whether there was significant burning influence at this site. Without consideration of secondary formation and other complementary data, the conclusion of the source type by the CO/OM slopes are far from robust.

Other Comments:

Background section is quite informative on the history of measurements in Mexico City, but does not discuss the many papers which have been recently published on the MILAGRO campaign which would serve to put this study in better context.

Discussion of SO_4 mass fraction on page 3280 can also be explained by sulfate being a

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regional component of aerosol as shown in previous studies e.g. Salcedo et al. (2006) and DeCarlo et al. (2008). The authors should consider this in their discussion of the increasing MF of SO_4 at night.

The abstract and conclusions state that the regional emissions rapidly erase the Mexico City plume, are not demonstrated in this paper. The Mexico City plume is not considered in the analysis presented here. The reader has no context by which to interpret this statement. If the authors want to make such a comparison, then plumes from the Mexico City area need to be considered and compared in this manuscript.

pg 3279 lines 8-11: "On the days with flows from the southeast and south west, the gas and particle concentrations remain approximately constant as the rate of dilution by mixing and entrainment is balanced by a constant flow of new material arriving from the sources of pollution." Is more of a hypothesis, rather than a conclusion, as there is no context to show that this is in fact happening. In addition, this statement implies that there is no secondary formation occuring and that the relative balance of pollutants comes only from consistent mixing and dilution. This should be demonstrated if it is the case.

pg 3281 line 20-25: This is a confusing statement. O_3 is a secondary pollutant, as is much of the particulate mass (e.g. Volkamer et al. 2006). Additional sources of these pollutants could still be primary, or are the authors refering to secondary sources? Please clarify this.

pg 3282 line 9: The use of a single factor of 1.8 for the OM/OC value for different source types is problematic. While 1.8 could be appropriate for a bulk average OA, different sources have different OM/OC values. Turpin and Lim (2001) and Aiken et. al. (2008) gives OM/OC values for several types of aerosol, and the authors are encourages to use more source specific OM/OC values to adjust the lines.

pg 3282 line 25 and continuing: Ammonium and sulfate have many other sources besides fires. In particular for sulfate the Popocateptl volcano near the measurement

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site is a quite large sulfur source for the region. Yet this is not discussed as a possible source for some of the sulfate in the measurements. Ammonium is also associated with agriculture and farming and not only with fires. Do the back trajectories point towards agricultural areas? The authors need to consider all sources of a particular pollutant in this discussion.

pg 3283 line 3-14: The EBC measurement may be influenced by biases due to high organic aerosol loading. Lack (2008) and Cappa (2008) discuss this bias as seen in the field and reproduced in the lab, and this may account for some of the changes in the EBC/CO slope. It is suggested the authors discuss this potential influence on this analysis in the subsequent revision.

Figure 12 D: For the Southwesterly case, the measured SSA is quite low here. There is no discussion of this. Is this real. Do the authors have an explanation for the values shown here? The corresponding pie charts in Figure 13 suggest that the SSA should not be as low as it is.

Technical Comments:

pg 3266 line 12, and several places throughout the manuscript: CN concentration should be 10^3 not 10^{-3}.

pg 3266 line 13: Ions are incorrect they should read: SO_4^{2-} and NO_3^-

pg 3270 line 5-9: What collection efficiency was used for the AMS data?

pg 3271 line 1: The authors state the AMS was calibrated twice. On what dates, were the calibrations done reasonably close to the days focused on for this manuscript? Does this justify the 14

pg 3271 line 15: How was it determined that there was “no influence from local biomass burning...” was there some criteria used to determine this?

pg 3272 line 9: suggest replacing “diurnal averages” with something more appropriate,

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such as “daily timeseries”. Diurnal averages implies that multiple days were averaged together to determine the diurnal pattern.

pg 3272 line 17: “averages” implies single value, should replace with something such as “trends”.

pg 3272 line 25: “time” should read “times”

pg 3274 line 21: “1023.25” should read “1013.25”

pg 3275 line 11: density of 1.9 g cm^{-3} is extremely high considering the pie charts given in figure 13. What density was used for the individual species measured with the AMS?

pg 3275 line 29: AMS data missing due to data system, or from Figure 10, a power outage? Is it both? Please be consistent.

pg 3276 lines 10, 21, 22: Ionic species are not written correctly they should be: SO_4^{2-}, NO_3^-, NH_4^+

pg 3277 line 1-11: What are the associated errors with the FTIR measurement. Table 2 does not list this as it does for other instruments. Are the percent differences significant? For example how significant is the difference in carboxylic acids 14 vs 5 percent (line 6)?

pg 3280 line 5: Remove the extra C in MCMA.

pg 3281 line 7: are the low OM/CO values found after a background of OM and CO were subtracted?

Figure 1: This figure comes from a measurement campaign in 1991, and is better suited as supplementary material, than a figure for this manuscript.

Figure 2: Only one axis for the O_3 and CO data would be beneficial to interpret and compare the data.

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Figures 7,8,9,10,12,14,15: When the paper is printed, there is very little contrast between the blue and black traces, It would be helpful to use a lighter blue color, or another color with more contrast. It is often difficult to tell these traces apart.

Figures 7,10,14,15: Suggest removing data points when data does not exist, instead of setting them to 0.

Figure 14 legend: Suggest removing “diurnal”

References:

Aiken, A. C. et al. (2008). O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry. Environ. Sci. Technol. 42(12): 44788211;4485

Cappa, C. D., et al. (2008). Bias in filter-based aerosol light absorption measurements due to organic aerosol loading: Evidence from laboratory measurements. Aerosol Sci Tech. 42: 1022-1032.

DeCarlo, P. F., et al. (2008). Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign. Atmos. Chem. Phys. 8(14): 4027-4048.

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Salcedo, D., et al. (2006). Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite. Atmospheric Chemistry and Physics 6: 925-946.

Volkamer, R., et al. (2006). Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. Geophysical Research Letters 33(L17811).

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 3265, 2009.