Response to reviewer comments on the manuscript by Kalafut-Pettibone et al. “Size-resolved aerosol emission factors and new particle formation/growth activity occurring in Mexico City during the MILAGRO 2006 Campaign”

ACP-2011-77

The authors would like to thank each of the reviewers for their detailed efforts. We received similar comments from both reviews and have addressed these comments, resulting in a much improved manuscript.

In response to the major comments, we have considered an alternate processing method for the APS data used within the manuscript. We have also recalculated the emission factors excluding certain hours of the day as described in detail below. During the recalculation, we found an error in Figure 8 and have since corrected this error.

Reviewer #1: This paper describes concentration measurements of particle number and volume and CO2 at a site in Mexico City during MILAGRO 2006. The measurements are used to estimate primary emissions factors of particle number and volume concentrations as a function of carbon mass concentration. There are many uncertainties associated with this approach, but I think that the authors have been quite thorough and discussed most of them. The extension of their approach to the measurements from the NASA DC-8 sampling the Mexico City urban plume is interesting. I have a concern about the treatment of the APS measurements and a few minor comments.

Comment 1 (Page 6662, lines 1-20)- It has been observed before that the number distribution obtained from the APS drops at smaller sizes in a manner inconsistent with other measurements. In particular, this reviewer has found that the number concentrations observed with the APS in the lowest three channels are lower than when compared with numbers from a SMPS and optical methods; the discrepancy associated with the first channel being the greatest and that associated with the third channel being the least. Unfortunately, I am unaware of a paper that deals specifically with this issue, but I believe there are others who have observed a similar result. An example of the ability of the APS to compare with a SMPS and a FSSP300 (an optical probe) when the first three channels of the APS are removed can be found in Figure 2a of Leaitch et al. (ACP 2010). The point of this comment is that by applying a factor of 2.86 to all sizes of the APS, which is what I understand you to have done, your volume estimates may be biased significantly high for particles >500 nm.

The reviewer is correct that the Aerosol Particle Sizer has this size dependent detection efficiency, and in our manuscript, we did not make a correction for this efficiency. We did, however, correct for inlet transmission; this ranged from 93% transmission at 500 nm to 33% transmission at 2.5 microns. We also shifted the APS data to a (smaller) equivalent mobility diameter using a density of 1.43 g cm^{-3}. After application of these transmission efficiencies and the density shift, two important mismatches in our Mexico City data were notable when doing instrument-to-instrument validation checks. The first mismatch was between the SMPS and the APS, with the ratio between the distributions as 0.35 (APS / SMPS) at 480 nm (corresponds to 574 nm aerodynamic diameter). The second mismatch was that the total reconstructed mass [(SMPS volume + APS volume) x density] was lower than it would need to be for comparison with nearby $PM_{2.5}$ continuous mass measurements.

Given these two pieces of information in the original manuscript, and no size dependent information on APS counts (the only other comparison we used on the APS efficiency was nephelometer scattering, this also supported an increase in the APS concentrations). The decision was made to make the correction (of multiplying by 0.35^{-1} or 2.86) to all sizes and to note the increased uncertainty that this created in the APS portion of the size distribution and the volume emission factor (line 25, page 6668 of original manuscript). This had the advantage of bringing the APS in better agreement with the SMPS, of improving correlation with the nephelometer, and reducing bias between SMPS+APS reconstructed mass and network $PM_{2.5}$ measurements. It had the disadvantages noted by the reviewers – it is difficult to quantify the accuracy of the adjustment, and it is likely an

over adjustment for larger particle sizes. That the adjustment is too large at some sizes (i.e. 1 micron and higher) is perhaps supported by comparison of our emission factor to that of published impactor-based size-resolved mass emission factors (Robert, M.A., C. A. Jakober, S. VanBergen, and M. J. Kleeman, JAWMA (2007), 57, pp1414-1428). In those measurements, the contribution to the emission factor at 1 micron is small. However, comparing the advanced engines tested by Robert et al. with the range of combustion processes is Mexico City is probably not valid.

In our opinion, the potential reasons for the mismatch between APS and SMPS can be divided into four categories. **First**, as noted by the reviewers, there is a known counting efficiency bias in the APS at sizes less than about 1.3 microns. For example, counting efficiencies are documented in Leinert and Wiedensohler (Leinert, S., and A. Wiedensohler, J. Aerosol Sci (2000), Vol. 31, Suppl. 1, ppS404-S405) which state a transmission of 58% at 0.51 microns (aerodynamic diameter) to 90% at 1 micron. Since we are evaluating overlap at mobility diameter of 0.48 microns, we are using counts at aerodynamic diameter of 0.57 microns, and the counting efficiency is significantly different from 100%. **Second**, the effective density of 1.43 used in this work reflects the bulk density of the aerosol components (combined in a mass weighted average according to AMS measured mass), which may not be equal to the effect density of the particles needed for the conversion between mobility and electrical mobility. Studies have shown size-dependent effective densities, effective densities of less than unity in combustion environments, and increases in effective density as the result of photochemical aging (Geller, M.D., S. Biswas, and S. Sioutas, Aerosol Science and Technology (2006), 40,

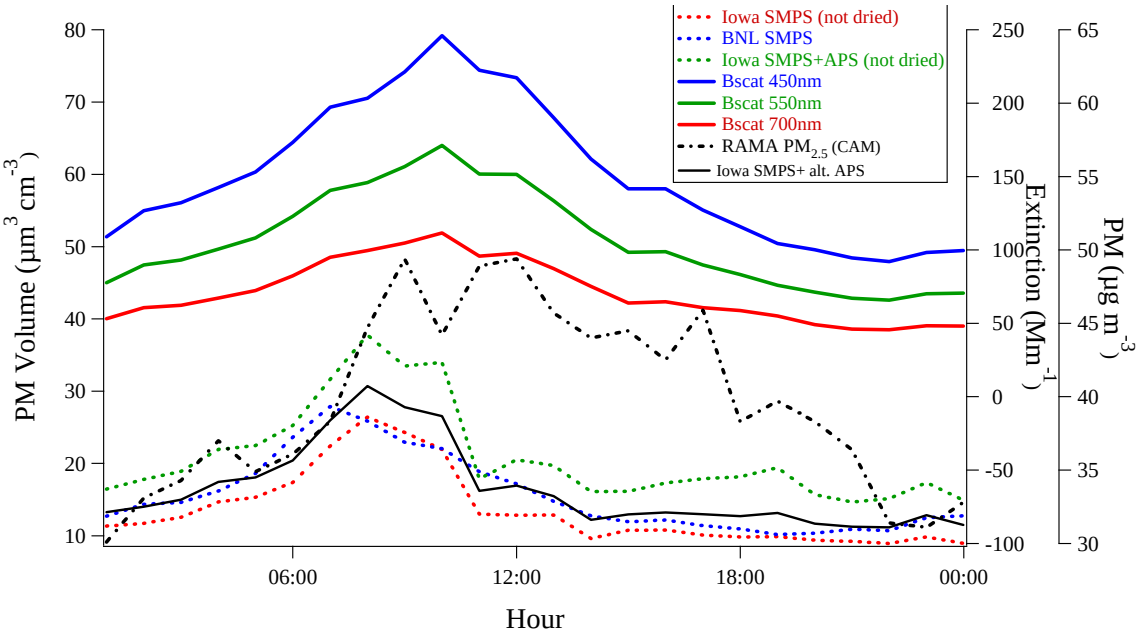
pp709-723). A size and temporally varying effective density could explain the scatter that we observed in the SMPS-APS overlap when a fixed effective density was assumed. Given the reviewer comments and the published work on effective density, we examined the APS-SMPS mismatch for a diurnal pattern, and a diurnal pattern exists (APS / SMPS at 480 nm at a minimum from 10 PM – 9 AM and at a maximum from noon- 4 PM. Such a pattern is consistent with effective densities of <1 from combustion and increases due to photochemical processing. Unfortunately, we do not feel we have sufficient information to perform a time-varying correction. This potential difficulty should be taken into account in future deployments of mobility and aerodynamic diameter instruments in Mexico City or other large urban areas. **Third**, there are transmission problems for liquid aerosols at larger sizes, as documented in Peters and Volcken (2005). These are thought not to influence our measurement result due to the low RH values in Mexico City. **Fourth**, there are possible causes of error that could be size independent, such as flowrate errors in the APS. The aerosol flowrate to the SMPS was routinely checked during the field campaign and was within our tolerance of 1 LPM ± 0.1 LPM. Therefore, this is probably not a root cause of the mismatch.

Given these factors discussed above, for the revised manuscript, we completed a second round of data processing using the original transmission efficiencies, the counting efficiencies from Leinert and Wiedensohler, and NOT using any additional correction. We have left the values from the manuscript as the "base" result of the paper, but we use the results of this alternate data processing in the discussion section.

The ratio of the alternate to base counts and emission factors are:

542 – 560 nm	0.49
560 – 750 nm	0.45
750-1000 nm	0.39
1000 and above	0.35

When the alternate treatment is used, the average APS volume decreases by approximately 5 $\mu m^3\ cm^{-3}$, and the correlation between nephelometer extinction and SMPS + APS volume decreased (R^2 for alternate processing was lower than R^2 for base), and the reconstructed mass is systematically below that of the RAMA network in the alternate data processing.



Alternate version of Figure 5. The alternate APS+SMPS volume has been added to the figure to show the comparison between the two treatments and is labeled 'Iowa SMPS+ alt. APS'.

Comment 2 (Page 6671 and Figure 8)- Your technique has validity when the correlation of CO_2 and particle number is very high. But when the correlation is lower, other factors besides emissions are strongly influencing your results. Since that correlation is near zero for your daytime points (Fig. 4), is it valid to include the daytime points at all; you note that most of the points (86%) are in the hours from 00:00-12:00 and 21:00-24:00. Indeed is it valid to include any points with a correlation of say <0.9 in your overall average?

Figure 4 in the original manuscript shows the correlation between total number and total CO_2. However, the fitting of the emission factor is not done using the raw signals, but rather is done using the peaks that exist above an urban background. We do see periods when small peaks in CO_2 do exist during afternoon hours, superimposed on a noisy background. These form valid emission factors, but the emission factors from the individual peaks require more averaging to yield a meaningful estimate of the emission factors. The fact that emission factors can be recovered (potentially) during all hours of the day is perhaps an advantage. In addition, while a user selected cutoff for the peak threshold is needed in the method, a user-selected cutoff of correlation or time of day is not needed. This is perhaps another advantage. It should be noted that the correlation coefficients between peaks (e.g. number peak heights vs. CO_2 peak heights) do not drop to the low values shown in figure 4; these correlation coefficients are usually higher than the correlation coefficients between the data themselves without the background subtraction.

Furthermore, the problem with these periods is not primarily the low correlation between the signals, but the fact the signals approach the CO_2 threshold, and errors begin to become dominant relative to signal.

As to whether it is "valid," we respectfully interpret this question as asking whether it is useful to apply the technique during periods of low correlation between number and carbon dioxide. For it to be useful, at least two conditions must be met. First, the technique would need to be able to detect changes in the underlying emission factor as a function of time of day if they were over a certain magnitude. Second, uncertainty in these emission factors would need to be treated appropriately. We believe that, given sufficient sampling time, real differences in the emissions (or the atmospheric processing of the emissions) could be detected by this method. And while the uncertainty treatment we have applied is very simple (95% confidence interval on the mean using the standard deviation of the emission factors), more sophisticated error models could be employed to improve the relative weightings of various emission factors in the averaging process.

Please note that we discovered an error in figure 8; the new version of figure 8 is shown below and the magnitude of the emission factor differences between different times of day are reduced.

Finally, please see the response to reviewer 2 comment 1 regarding the exclusion of different hours and how this affects the overall emission factor.

Comment 3 (Table 2)- Mention in the header that the conversion of CO_2 mixing ratio to a mass concentration is done at the lower elevation (pressure) and higher temperatures associated with your measurement site.

Table 2 contains average values for the ground-based measurements only. The conversion from CO_2 mixing ratio to mass concentration is done using the temperature and pressure as measured simultaneously (and adjacent) to CO_2 mixing ratio, and therefore a CO_2 mass concentration is determined for each measurement of mixing ratio. Because the conversion from mixing ratio to mass concentration was not done using one temperature and pressure after the average mixing ratio was determined, the header wording was retained. However, this is clarified in sentence 4 of Section 4.1 which reads "The conversion from CO2 mixing ratio to mass concentration was done continuously using simultaneous measurement of pressure and temperature as measured adjacent to the CO2 monitor."

Comment 4 (Abstract)- Define T0 and MCMA.

Both terms have been defined in the abstract, and again at the first use in the main body of the text.

Comment 5 (Page 6654, lines 22-24)- "which can also nucleate…"- is this different from the homogeneous nucleation mentioned on line 15?

No. The purpose of this sentence is to illustrate the competition between nucleation and condensation for low volatility gas phase species. For clarity, this sentence has been

reworded to read “Primary and secondary particles vie for growth through condensation of low volatility gas phase species, which can also homogeneously nucleate to form new particles as previously mentioned.”

Comment 6 (Page 6655, line 12)- the largest “megacity” is also the largest city in NA?

Yes. The text has been changed to read “Mexico City is the largest city in North America, …”

Comment 7 (Page 6656, line 3)- define MCMA

All acronyms have been defined in the abstract and again at the first use in the main body of the text.

Comment 8 (Page 6656, line 22)- particleS

An ‘s’ has been added to the end of ‘particle’ to read “freshly nucleated particles are…”

Comment 9 (Page 6657, lines 9-10)- you mean volume-controlled growth?

Yes. Here we are referring to the findings of Kleinman et al. (2009), and chose the term ‘volume growth’ to be consistent with the terminology used in the cited publication. The “volume growth law” ($dD_p/dt \sim D_p$) as described by Kleinman et al. describes the volume controlled case where larger particles grow in diameter faster than smaller ones.

Comment 10 (Page 6659, lines 13-15)- Potentially it could if there were significantly different slopes within your # to CO2 correlation plot, but only one slope is evident in your figure 4, excluding of course the new particle events.

We agree. During data analysis, multiple plots of number vs. CO2 were created to compare data from different time periods (for example, separating high traffic time periods from non-rush hour time periods), however one slope was evident.

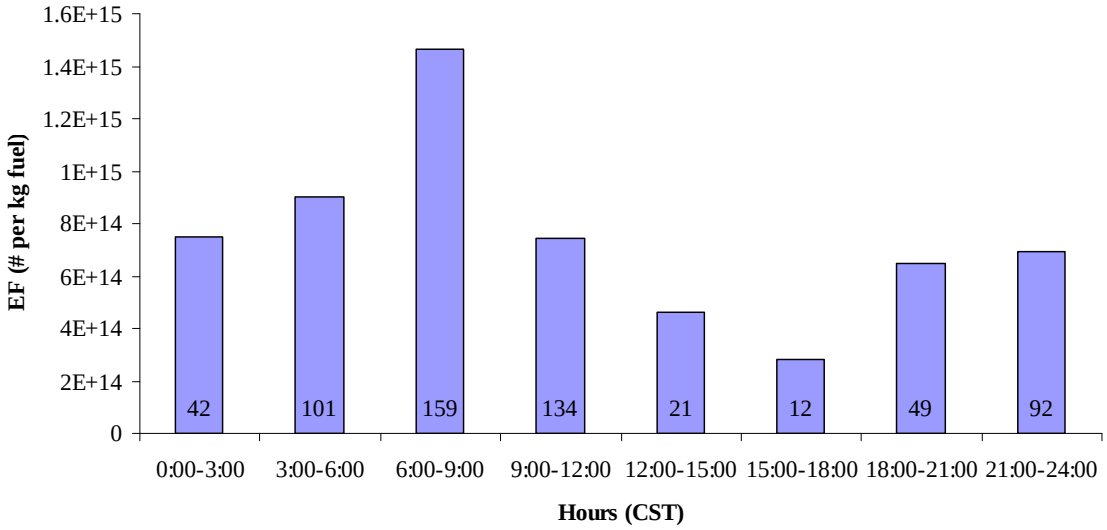
Comment 11 (Page 6662, line 1)- To enable rather than To improve. They are not comparable otherwise.

Correction made.

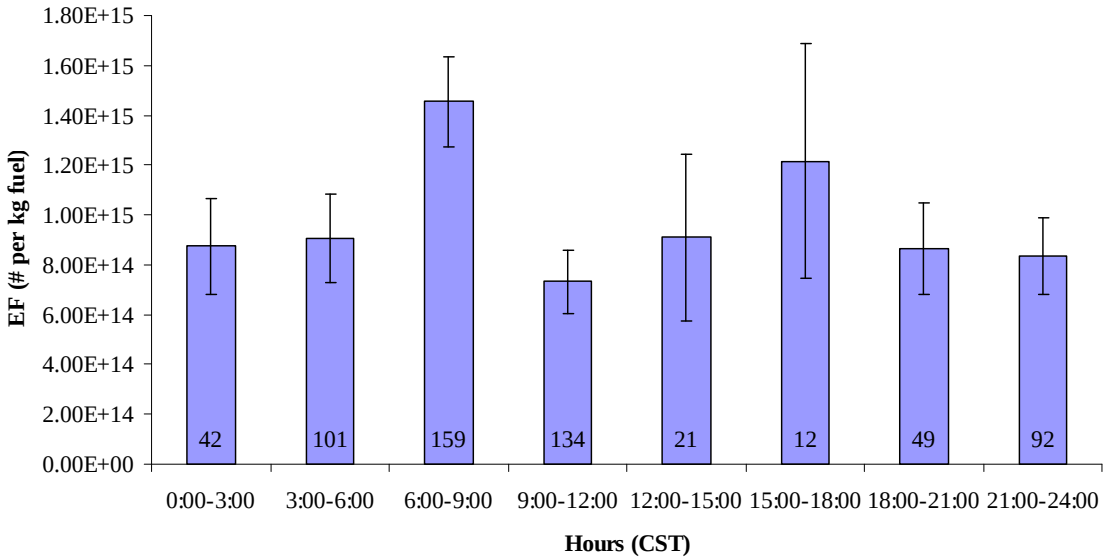
Comment 12 (Page 6671, lines 12-14)- You discuss here that including the apparent new particle formation events (Table 3) does not impact your emissions factors. Then you point out that afternoons have lower emissions factors as well as fewer identified points. Do you believe the sources were the same from day to night?

We identified and corrected an error in the construction of figure 8. The original emission factors were correct, but their diurnal averaging was in error. The original error caused emission factors with lower numbers of peaks (e.g. 15:00-18:00 hours) to be erroneously low. In the corrected version of figure 8, the emission factors are more consistent as a function of time of day. The exception is that the period from 06:00 to 09:00 has emission factors approximately 40% higher than other periods. It is not known whether this is a atmospheric phenomenon (e.g. aerosol dynamics, or changes in the area

of influence as the wind speed and mixing height change through the day), or whether this is an artifact of the measurement and data reduction technique. Collocated CO_2 and size distribution measurements at a faster time resolution would help resolve this question.



OLD Figure 8



Revised Figure 8. Average emission factor versus time of day. The numbers on the graph represent the total number of CO2 peaks that went into the calculation of the emission factor for each 3 h period.

Reviewer #2: This manuscript provides size resolved emission factors between 11 nm and 494 nm for a polluted urban area in Mexico City. The emission factors are based on a correlation between particle number and CO2 concentrations during the MILAGRO field campaign in March 2006. Size resolved emission factors for Mexico City is an important contribution to both climatic and health related research areas. The method used for calculating the emission factors in this manuscript is likely associated with large uncertainties, in particular due to the large separating distance between the particle and CO2 measurements. However, the authors are aware of this issue when discussing the results. The emission factors are applied to a plume measured from aircraft above the city with some interesting results, even though this section needs to provide some more information. The manuscript is clearly organized and in general well written. However, I

have some comments that need to be addressed before the manuscript can be considered for publication.

Comment 1- The first comment concerns the data used for calculating the emission factors. Figure 4a illustrates that the correlation between particle number and CO2 concentration is high in the morning between 04:00 and 12:00. This period also has most significant CO2 peaks and therefore this time period dominates in amounts of data used for calculating the factors, according to Fig. 8. However, a relatively large amount of data is used also from other periods of the 24 hours when the correlation is not very impressive. Why are data from these other periods included when calculating the emission factors? Would the emission factors have significantly different numbers if only data measured between 04:00 and 12:00 were included?

The recovery of the emission factor was repeated excluding data from 10:00 to 18:00, the hours with most variable correlation coefficient. It was also repeated using only data from 04:00 to 10:00. (The period from 10-12 AM often has some boundary layer ventilation and possible new particle formation, which are perhaps more problematic in terms of recovering a CO_2-based emission factor).

The effect of excluding data from 10 AM – 6 PM caused small increases and decreases in the SMPS size range, with the largest change in any bin of 6%. In the APS size range,

excluding data from 10 AM – 6 PM caused a decrease in the emission factor in all size bins, of up to 25% in magnitude.

The effect of performing data analysis only on data from 4 AM to 10 AM was an increase in the emission factor in all size ranges of the SMPS, with a magnitude of up to 20%. In the APS size range, the effect of including only this data subset was to decrease the emission factor in all size bins, by a magnitude of up to 18% for sizes between 0.5 and 1.8 microns, and a 32% decrease from 1.8 to 2.5 microns.

These changes are within the uncertainty of the method.

Comment 2- Figure 4 gives no information on variation of the correlation coefficient with particle diameter. Since the presented emission factors are size-resolved, some information on this issue would be valuable. That might provide information on whether primary aerosol emission is absent in any particle size range. A contour plot showing the average correlation coefficient as a function of particle diameter and time intervals (as in Fig 4a) would be an interesting addition to Fig. 4.

The correlation analysis was repeated for 11 size bins. A 3D plot of the median correlation coefficient was made and will be included in the manuscript at figure 4c. It shows relatively high correlation for all sizes and times of day except for ultrafine particles in the afternoon and super micron particles in the early evening. The high correlation during the midday is due to simultaneously decreasing CO_2 and particle

concentrations at sizes greater than about 70 nm. The blue colors show an anticorrelation between ultrafine particles and CO_2 in the afternoon.

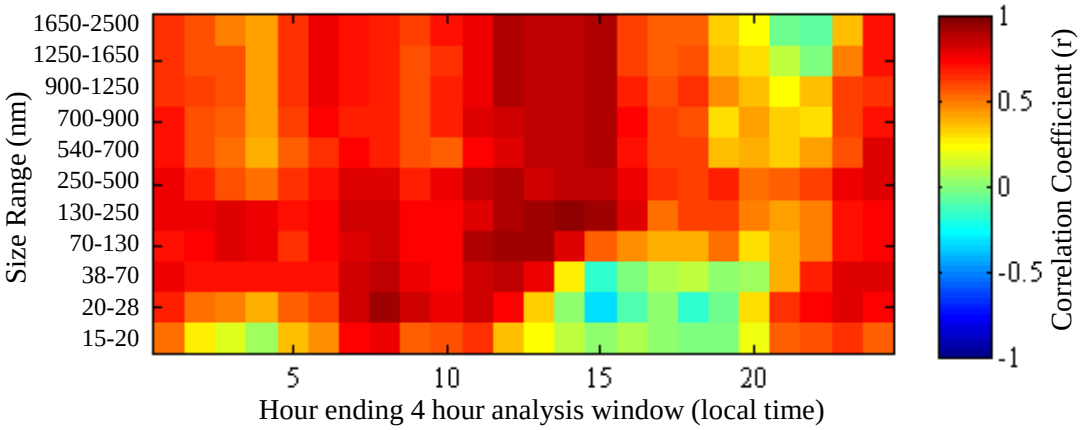


Figure. Correlation coefficient for various size ranges. Local time (x axis) is the last hour of a 4 hour time window over which correlation with CO2 is analyzed. E.g. hour 15 shows correlations from 11:00 until 15:00.

Comment 3- Does the correlation between particle number and CO2 concentration break down in the afternoon also on days with no ultrafine growth events, and if so, do the authors have any explanation for this pattern?

The correlation plot shown above was created for all days (as shown) and excluding the nucleation days. The appearance is nearly identical and the anticorrelation at hour 15 (which is for 11:00 -15:00) does not disappear, but decreases in absolute value slightly.

We believe that the decrease in the correlation between particle number and CO2 in the afternoon is related to the general diurnal wind patterns that are observed in Mexico City.

The Mexico City basin experiences rapid boundary layer growth and ventilation in the afternoon as a result of its geographical setting (Banta 1985; Jauregui 1988; Fast et al. 2008). The air mass existing above the morning boundary layer has a different particle number to CO_2 signature, and therefore when the boundary layer is diluted with this air mass the correlation decreases.

Comment 4- Section 4.6 is interesting but needs some more clarification. First of all, some information on the boundary layer depth during the flight is necessary. The aircraft measurements were performed "at an altitude of ~2.5 km a.s.l., or <1km above ground". It should be stated that these observations were made in the boundary layer, if this was the case. What information is available of the mixed layer depth during the flight, either from direct measurements during this campaign or from earlier studies of the mixed layer in Mexico City at a similar time of day and time of year? In this section, the authors speculate that "there is a source of particles during plume aging that significantly increases particle number while leaving CO_2 unchanged". Did particle number increase with increasing photochemical age in the plume or did the particle number decrease less than CO2 did? Was new particle formation observed at the T0 site on this day? It says on page 6677 on lines 2-3 regarding Fig. 11c that "the photochemical ages, calculated by the measured benzene/toluene ratio, are shown". It is not obvious to me from Fig. 11c (or the text) how I can read that information from the plot.

The measurements during this flight were made within the boundary layer, and this information has been noted in the text. March 11 was not classified as a new particle

formation event day. In the plume, particle number increases with increasing photochemical age. The sentence on page 6677 (line 3) that states "The photochemical ages, calculated by the measured benzene/toluene ratio, are shown in the figure and range from 2-15 h (referenced to 0 h set using the benzene/toluene ratio at 14:19)" is misleading as written. For clarity regarding the information in Figure 11c, the wording has been revised to read "Figure 11c shows the volume distributions normalized to the CO_2 increment above the baseline concentration. The four different traces shown on the graph are labeled according to the time that the DC-8 made the corresponding measurements (14:19, 14:21, 14:23, and 14:25). Rather than referring to each of the four traces by the time the measurement was made, it is informative to interpret the excess volume changes as a function of photochemical age. The photochemical age is not explicitly shown in Figure 11c. The photochemical age as calculated for the measurements made at 14:19 was set to 0 hours at a point of reference. Based on this information, the photochemical age of the measurement at 14:21 is 2 hours, 12.8 hours at 14:23, and 15 hours at 14:25".

Minor comments:

Page 6653, line 11: "The uncertainty of the number emission factor" sounds better to me.

The suggested revision was made.

Page 6653, line 20: It is a bit unclear here what "this" refers to in "this emission factor was applied to". I would suggest "the determined emission factor was applied to".

Thank you. The sentence was reworded as suggested for clarity.

Page 6653, same line: In my opinion the abstract must give information that can be understood by the reader without looking things up in the manuscript. If the authors want to use the expression "MCMA plume" in the abstract, there must be some very brief information on what the MCMA plume is.

All acronyms have been defined in the abstract and again at the first use in the main body of the text.

Page 6656, line 8: Remove ' from "3 of 10'days sampled"

Correction made.

Page 6656, line 15: Please write "The mass size distribution", if that is what you mean.

Correction made.

Page 6656, line 18: The first time "MILAGRO" is mentioned it should be written that it stands for "The Megacity Initiative: Local and Global Research Observations".

All acronyms have been defined in the abstract and again at the first use in the main body of the text.

Page 6668, line 24: "has a potential error of approximately 1.5" is better.

Correction has been made.

Page 6671, line 23: change "21:000" to "21:00".

Correction made.

Page 6672, line 1: What point do the authors want to make with "These directions correspond to an industrial area with many SO2 point sources", when discussing wind directions with combined number and CO2. Since SO2 is closely associated with sulfate and secondary aerosol, the sentence above is a bit confusing for the reader.

The sentence reading "These directions correspond to an industrial are with many SO2 point sources (to the west), Vallejo Ave. (to the west), Eje 4 Ave. (to the south) and Eje Central Ave. (to the northeast)" was added only to provide the reader with information about the area surrounding the site which we felt was relevant when discussing the wind directional dependence.

Page 6673, line 3: There should be a space between "colleagues" and "2005" in "Geller and colleagues(2005)"

Correction made. Thank you.

Page 6674, line 25: add "a.s.l." to "2530 m altitude". Otherwise one might get the impression that the measurement took place in the free troposphere.

Corrected.

Page 6675, line 13: The reference Warneke (2007) must be added to the reference list.

The reference has been added.

Page 6676, lines 18 and 27 and Fig. 11a-c: Why are the authors suddenly expressing time in UTC after been using CST on page 6675?

Thank you for catching the inconsistency, which was an oversight. All times in the document have been converted to CST.

Page 6676, lines 20-21: Change to "measured particle concentrations are well…"

Correction has been made.

Page 6677, line 25: Add a space between "Kleinman et al." and "2009".

Correction has been made.

Page 6679, line 4: "uncertainty of the number emission factor" sounds better to me.

Sentence was revised as suggested.

Page 6679, line 12: "parameters of N 1.65 x…" sounds strange. "parameters of N equal to 1.65 x…" would be better.

Thank you. Revision was made as suggested.

Page 6703: Please mark the two subplots in Fig. 9 with a) and b), respectively, and use these notifications in the figure caption to describe the two cases.

The subplots on Figure 9 have been marked with a) and b), and the following sentence has been added to the caption for clarity: “Panel a) provides a comparison on a log-linear plot, and panel b) shows the same comparison on a log-log scale.