**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Determination of particulate lead during MILAGRO/MCMA-2006 using Aerosol Mass Spectrometry" *by* D. Salcedo et al.

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We thank the referee for the useful comments that allowed us to improve the manuscript.

Specific comments (P-page, L-line):

R2.1) As described in Introduction (first paragraph), Pb is important issue for human health. Can authors suggest anything about this issue from the results of this study?

We added the following paragraph to the conclusions section:

"Figure 1 suggests that levels of particle Pb in and around the MCMA probably remain

within the Mexican standard and within the more strict US standard; with the exception of some specific sites located in the North, including the PEMEX site, which shows Pb concentrations larger than the US standard level. Efforts should be made to identify the specific Pb emitters that cause these large local Pb concentrations in order to reduce the risk of Pb health effects on the population exposed."

R2.2) Pb has a similar diurnal cycle to that of black carbon (P2599/L21) but does not correlate to black carbon (P2600/L6). Is this correct? If so, some explanation would be helpful to understand their relation.

See response to R2.3 below.

R2.3) If Pb has a similar diurnal cycle to that of HOA because of meteorological condition (section 3.6, first paragraph; P2599/L21), Pb may not need to be coemitted or emitted near by the HOA sources (P2600/L16); i.e., the correlation between Pb and HOA could be explained by their diurnal cycle.

The diurnal cycles are averaged hourly concentrations during all the campaign and provide information regarding the daily variability of the pollutant concentration. The similar diurnal cycles for BC, HOA and Pb indicate that they are all primary pollutants, with emissions during the night and early morning into a shallow boundary layer (BL). During the late morning and afternoon, the BL height increases, resulting in lower concentrations due to greatly increased vertical dilution. This is the strength of the conclusions that can be extracted from the fact that the diurnal cycles are similar, i.e. the sources are located in the urban area and emit at similar times. As the referee mentions, the fact that BC, HOA and Pb have similar diurnal cycles does not imply that they are coemitted or that they have near sources.

On the other hand, the correlation of the actual time series for each day or for specific events can in principle provide stronger information about whether the sources of two pollutants could be the same or be located in close proximity. When looking closely at the time series, we did not observe any correlation between BC and Pb; but we ob-

served that some Pb plumes appear to be accompanied by HOA. Because the plumes are short, we think that some source may be emitting both Pb and HOA, or that the two may be emitted by nearby sources.

R2.4) Fig.13 suggests that the sources of PbCl+ differ from those of PbS+. However, Figs. 10, 12, and S11 suggest they have similar sources or time series. Although authors mentioned that "This is because the CFA result for PbCl+ is highly affected by 3 or 4 large peaks, while RWP roses are more sensitive to the median (P2602/L2)", it is not clear for me where is the most likely sources of PbCl+ and PbS+.

Fig 10, 12, and S11 suggest that the time series of PbCl+ and PbS+ have some similarities, but also some large differences. All figures are showing multiple days and some large differences may be hard to appreciate. For example Fig. 10 shows very different time series for the two sets of ions for March 24-26. These differences are exploited by the CFA method, which also uses more complete information (back-trajectories calculated from three-dimensional WRF wind fields) than the RWP method which only uses the winds at T0. We have changed the text to more properly reflect these facts to:

"This is because the CFA method uses more complete information (back-trajectories calculated from three-dimensional WRF wind fields) and is more influenced by some large peaks, vs. than the RWP method which only uses the winds at T0 and is more sensitive to the median."

R2.5) (P2598/L17) "It is also interesting to note that, although the times series of PbCl+ and PbS+ are similar, they are not identical; the differences are probably caused by differences in lead speciation depending on the source." This sentence is not clear. Please explain the exact meaning of "differences in lead speciation depending on the source."

We changed the sentence to "the differences are probably caused by particles with different lead composition depending on their source."

C2236

R2.6) (P2599/L6) "This result implies that lead species that generate PbCl+ and PbS+ ions (and/or species that are co-emitted with those), account for most, but not all of the variability of the Pb during this period." If PbCl+ and PbS+ account for most (although not all) of variability of the Pb, why are the source regions of Pb, PbS+, and PbCl+ quite different in Fig. 13?

We disagree with the reviewer statement about the source regions being quite different. As already discussed in the text, the source regions of PbS+ and PbCl+ in Fig. 13 are consistent with the S and N source regions found for Pb, respectively. On the other hand, the CFA plot for Pb shows an additional source E of the city which does not appear on the PbS+ and PbCl+ maps. This is consistent with the influence of additional sources of Pb beyond those which produce the PbS+ and PbCl+ signals. Also consistent is the statement within the text that the linear combination of PbS+ and PbCl+ does no account for all the variability in the Pb time series.

R2.7) PbCl has melting points of 934C but the AMS has 600C of vaporizer. Although PbCl and PbCl+ may not be identical, can PbCl+ be ionized so quickly?

In the paper we do not claim that the source of PbCl+ in the particles is PbCl2, it is only stated as a possibility (see also response to R1.8). It is also possible that other more volatile species (perhaps mixtures of metal compounds) are producing these signals. What matters in terms of AMS detection is that the vapor pressure is sufficient so that evaporation and ionization are possible in a few seconds. Future laboratory work should explore these timescales for different species and their relationships to species' melting and boiling points.

R2.8) P2600/ L16; "does not" typo

Corrected.

R2.9) Table 1. What does "m" mean?

"m" is the slope of the fits. This has now been specified in the text and table caption.

C2237

R2.10) Fig.1. Size range of PIXE is not shown properly.

Corrected.

R2.11) Fig.7. It will be better to have panel number (e.g., A, B, ..) and caption for each image. Relation between ""open" or "closed" Pb signal = sum of both fraction" and the arrow below the text is unclear.

Each "panel" already has a small caption. We prefer to not break the image further as the whole schematic is working together to make a point. We have changed the caption of Fig. 7 to more clearly explain the figure:

"Diagram of the adsorption/desorption model used to calculate the 'input' total Pb signal. Given a constant input of 5 ug/m3 (lower left), the beam blocking device modulates the incoming signal (lower right). For fast desorbing Pb components, this modulation fully separates the 'open' signal from a 'closed' background (upper left). For the slow desorbing Pb components, the detection of the sampled Pb is nearly independent of the modulation (upper right) and the total measured signal is the sum of the 'open' and 'closed' fractions."

R2.12) Fig.12. In panel B, the date starts from "15/09/06", although caption says 14, March.

Corrected.