

Supplementary Information for:

**Determination of particulate lead using Aerosol Mass Spectrometry:
MILAGRO/MCMA-2006 observations**

D. Salcedo¹, T.B. Onasch², A.C. Aiken^{3*}, L.R. Williams², B. de Foy⁴, M.J. Cubison³, D.R. Worsnop², L.T. Molina^{5,6}, and J.L. Jimenez³

¹*Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Cuernavaca, México*

²*Center for Aerosol and Cloud Chemistry, Aerodyne Research, Billerica, MA, USA*

³*Cooperative Institute for Research in the Environmental Sciences (CIRES) and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA*

⁴*Department of Earth and Atmospheric Sciences, Saint Louis University, Saint Louis, MO, USA*

⁵*Molina Center for Energy and the Environment, La Jolla, CA, USA*

⁶*Earth Atmospheric and Planetary Sciences Department, Massachusetts Institute of Technology, Cambridge, MA, USA*

** Now at ETH-Zurich, Switzerland*

Fig. S1. Topographical map of the Mexico City Metropolitan Area and surrounding region indicating the approximate location of measurements sites. The division and limits of the Federal District are shown in black.

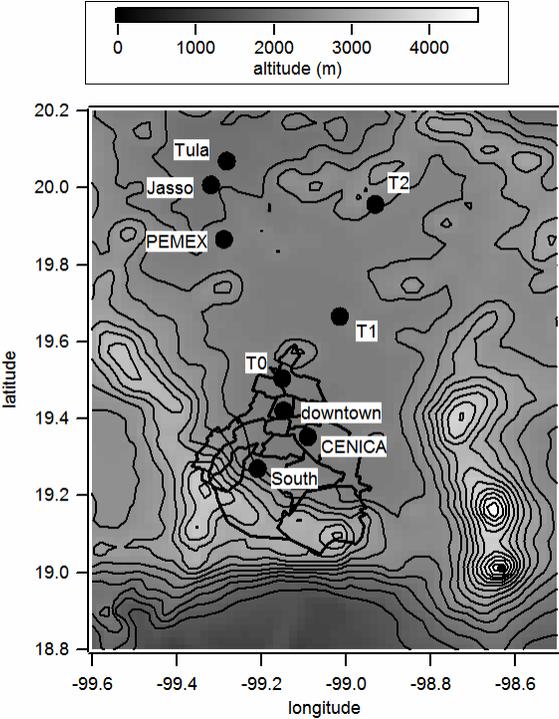


Fig. S2. 2.5 minute averaged open V and W mass spectra at m/z 206, 207, 208 at a time period with high Pb signal at T0 (as marked in Fig. 6). Black lines and circles correspond to the HR-AMS raw signal. Grey lines are modified Gaussian functions that represent the signal of individual ions whose exact mass is indicated by the vertical black lines. The height of the vertical lines corresponds to the peak height of the modified Gaussian functions. Red lines are the sum of the individual ion peaks and represent the fitted total signal at the given nominal m/z .

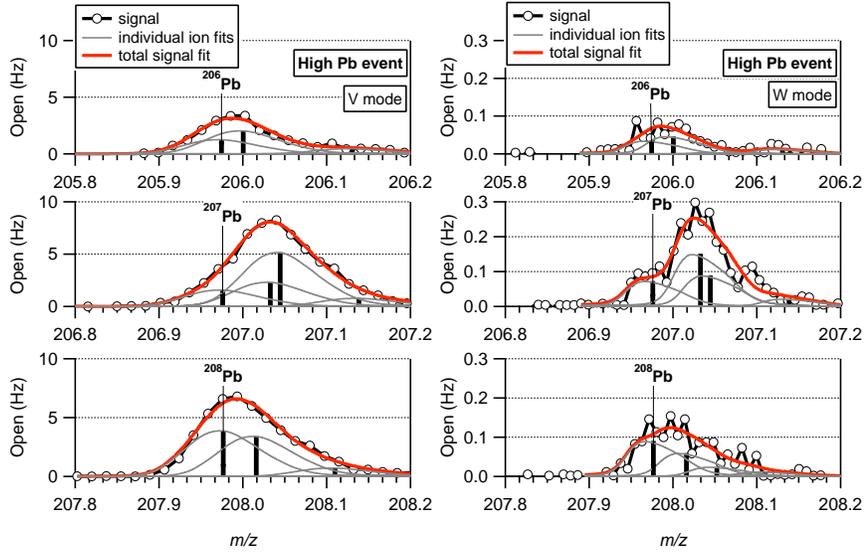


Fig. S3. 2.5 minute averaged open V and W mass spectra at m/z 103, 103.5, and 104 at a time period with high Pb signal at T0 (as marked in Fig. 6). Black lines and circles correspond to the HR-AMS raw signal. Grey lines are modified Gaussian functions that represent the signal of individual ions whose exact mass is indicated by the vertical black lines. The height of the vertical lines corresponds to the peak height of the modified Gaussian functions. Red lines are the sum of the individual ion peaks and represent the fitted total signal at the given nominal m/z .

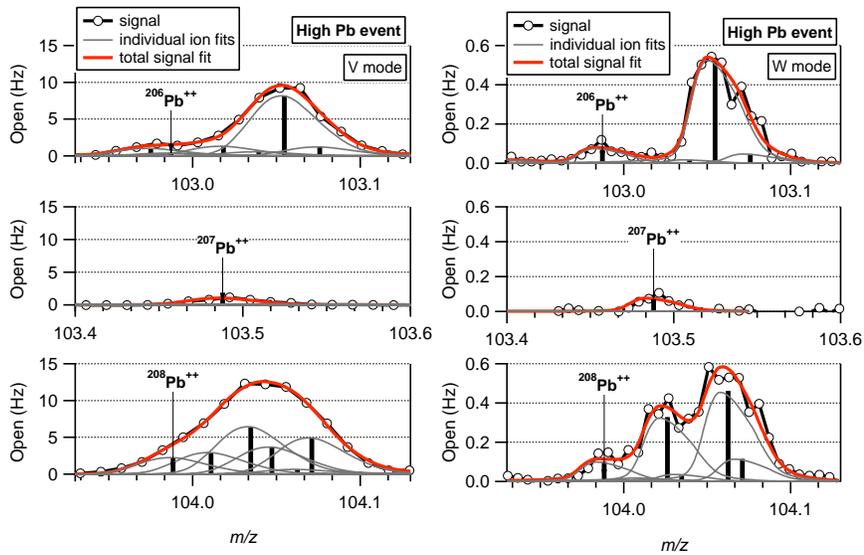


Fig. S4. Scatter plots showing correlations between the singly and doubly charged lead ions at T0. V and W from open and closed spectra signals are shown. Lines correspond to linear fits to the data.

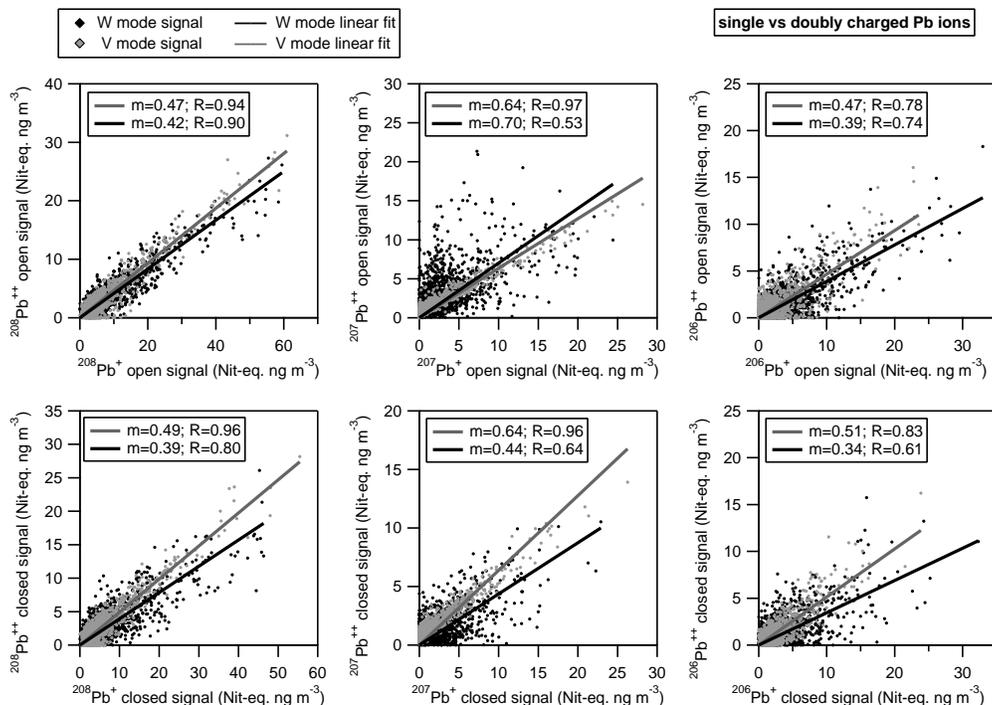


Fig. S5. Time series of 2.5 averaged V open and closed signals for $^{208}\text{Pb}^+$ ions for a time period of alternating ambient (closed symbols) and concentrator sampling (open symbols) at T0.

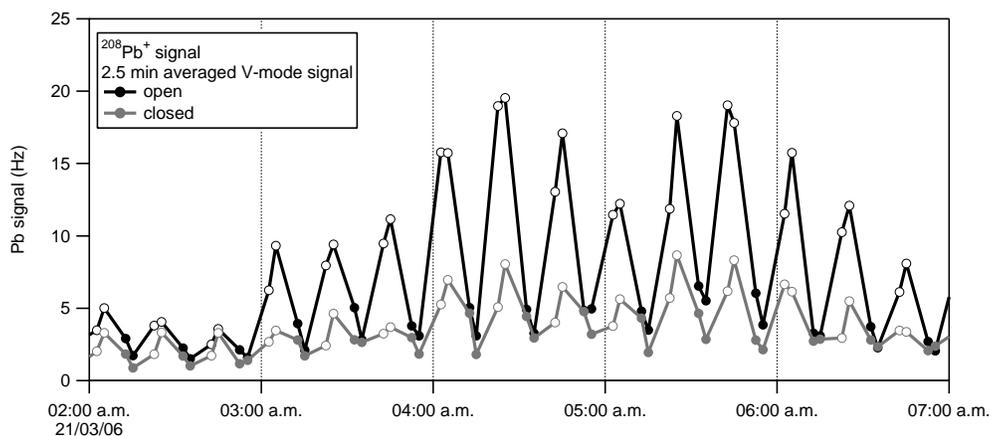


Fig. S6. Laboratory measurement of the ionization efficiency of Pb relative to NO_3 (RIE_{Pb}) using size selected $\text{Pb}(\text{NO}_3)_2$ particles: (red line and circles) laboratory measured Pb^+ in open, (black line and circles) laboratory measured Pb^+ in closed. The same model used for the field data is applied to the laboratory data in order to determine the actual Pb^+ input: (yellow line and circles) modeled incoming Pb^+ , (dashed black line and circles) modeled Pb^+ in closed. Panel (a) shows data for a vaporizer temperature of 630°C . The model gives a smaller fraction in the slowly vaporizing component, consistent with the lower Pb^+ signal in closed relative to open. Panel (b) shows data for a vaporizer temperature of 548°C , yielding a higher closed Pb^+ signal and a larger slowly vaporizing fraction in the model. $\text{Pb}(\text{NO}_3)_2$ decomposes at 270°C . The faster vaporizing component may be flash vaporized $\text{Pb}(\text{NO}_3)_2$, while the slowly vaporizing component may be a decomposition product with a higher melting temperature, e.g., PbO (melting point 888°C).

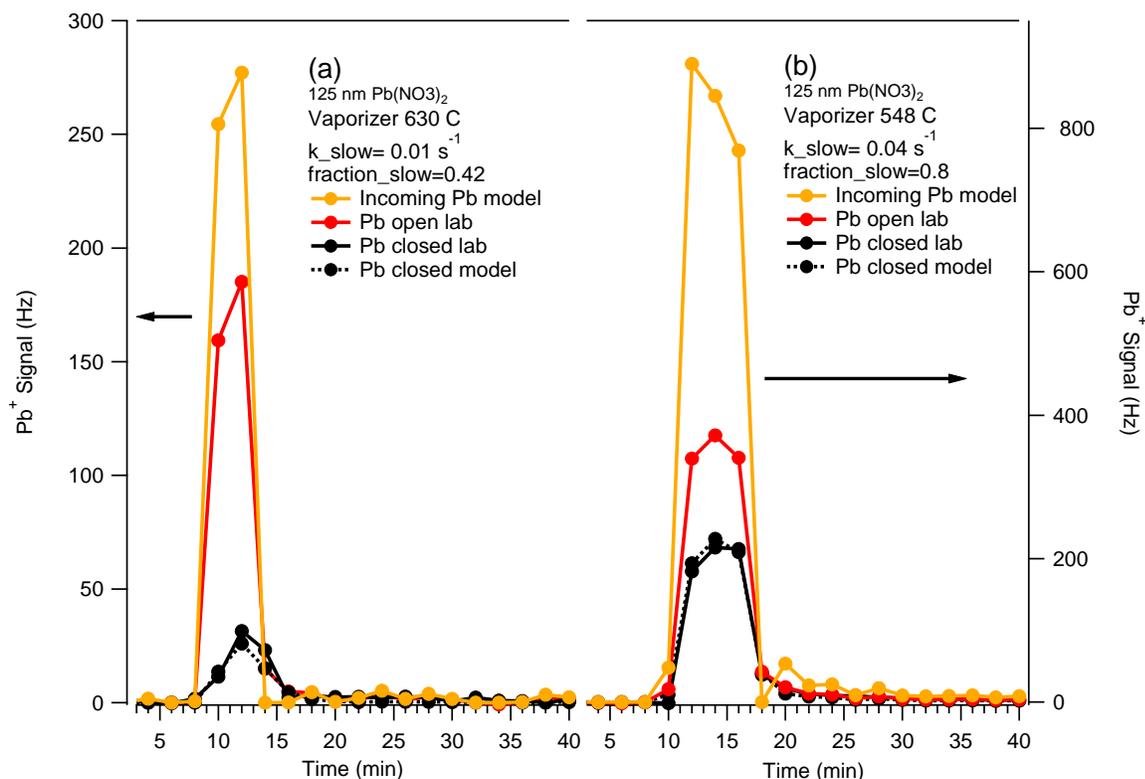


Fig. S7. 2.5 minute averaged open and closed V and W mass spectra at m/z 238, 239 and 240 corresponding to PbS ions. Black lines and circles correspond to the HR-AMS raw signal. Grey lines are modified Gaussian functions that represent the signal of individual ions whose exact mass is indicated by the vertical black lines. The height of the vertical lines corresponds to the peak height of the modified Gaussian functions. Red lines are the sum of the individual ion peaks and represent the fitted total signal at the given nominal m/z .

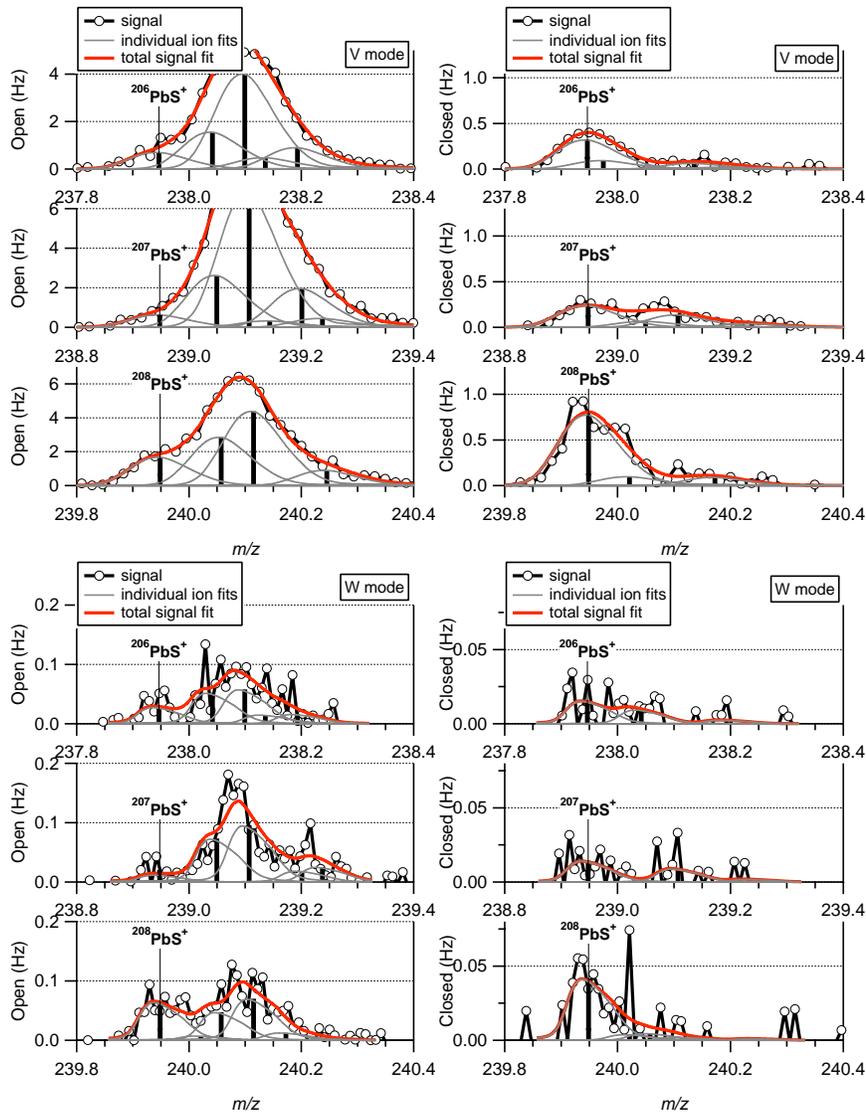


Fig. S8. 2.5 minute averaged open and closed V and W mass spectra at m/z 241, 242 and 243 corresponding to PbCl ions. Black lines and circles correspond to the HR-AMS raw signal. Grey lines are modified Gaussian functions that represent the signal of individual ions whose exact mass is indicated by the vertical black lines. The height of the vertical lines corresponds to the peak height of the modified Gaussian functions. Red lines are the sum of the individual ion peaks and represent the fitted total signal at the given nominal m/z .

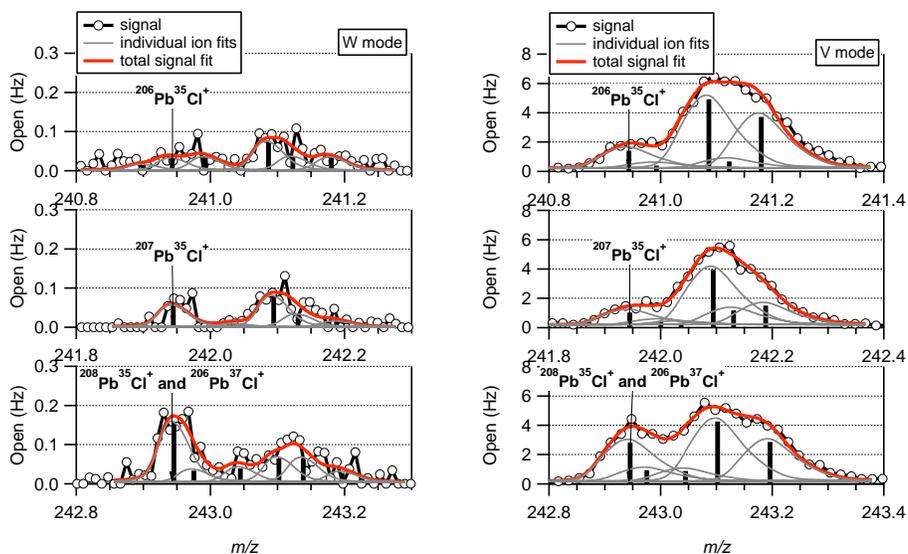


Fig. S9. Scatter plots of PbS^+ and PbCl^+ isotopic ions when the HR-AMS was sampling through the concentrator. V and W from open and closed spectra signals are shown. Black lines correspond to the expected isotopic ratio.

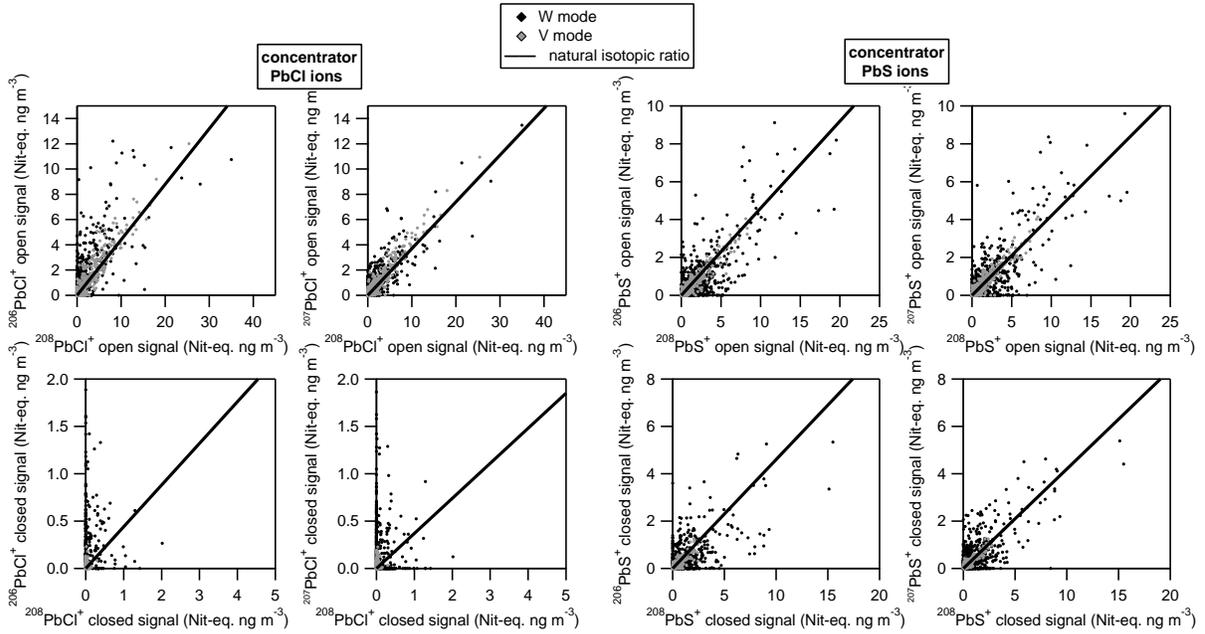


Fig. S10. The lower panel shows the time series of the open Pb^+ signal when sampling through the concentrator (black lines and circles), and the reconstructed signal as a linear combination of PbS^+ and PbCl^+ signals (shaded stacked areas). The upper panel shows the relative residual of the fit $((\text{fit} - \text{field data})/\text{field data})$.

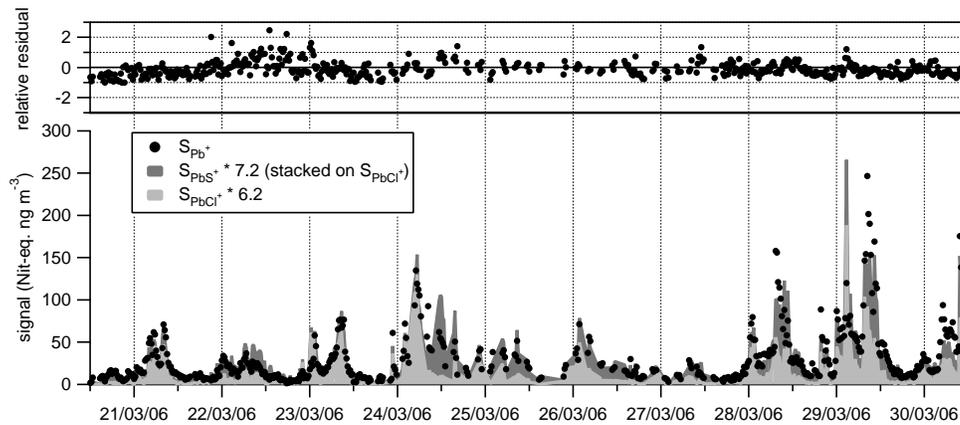


Fig. S11. Wind rose using Radar Wind Profiler for 0 to 500 m of the boundary layer for $^{208}\text{PbS}^+$ and $^{208}\text{PbCl}^+$ open signals at T0. Shown in blue is the data for low signal levels ($< 3 \text{ Nitr.-eq. ng m}^{-3}$) and in red, data for high signal levels ($> 3 \text{ ng Nitr.-eq. ng m}^{-3}$).

