



Determination of particulate lead during MILAGRO / MCMA-2006 using Aerosol Mass Spectrometry

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We report the first measurements of particulate lead (Pb) from Aerodyne Aerosol Mass Spectrometers, which were deployed in and around Mexico City during the Megacity Initiative: Local and Global Research Observations (MILAGRO) / Mexico City Metropolitan Area 2006 (MCMA-2006) field campaigns. The high resolution mass spectrometer of one of the AMS instruments (HR-AMS) and the measured isotopic ratios unequivocally prove the detection of Pb in ambient particles. A substantial fraction of the lead evaporated slowly from the vaporizer of the instruments, which is indicative of species with low volatility at 600°C. A model was developed in order to estimate the ambient particulate Pb entering the AMS from the signals in the “open” and the “closed” (or “background”) mass spectrum modes of the AMS. The model suggests the presence of at least two lead fractions with ~25% of the Pb signal exhibiting rapid evaporation ($1/e$ decay constant, < 0.1 s) and ~75% exhibiting slow evaporation (~ 2.4 min) at T0 and a different fraction (70% prompt and 30% slow evaporation) at a site northwest from the metropolitan area (PEMEX32 site). From laboratory experiments with pure Pb(NO₃)₂ particles, we estimated that the Pb ionization efficiency relative to nitrate (RIEPb) is 0.5. Comparison of time series of AMS Pb with other measurements carried out at the T0 urban supersite during MILAGRO (using Proton Induced X-ray Emission (PIXE), Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) and single-particle counts from an Aerosol Time-of-Fight Mass Spectrometer (ATOFMS)) shows similar levels (for PIXE and ICP-MS) and substantial correlation. During part of the campaign, sampling at T0 was alternated every 10 minutes with an Aerosol Concentrator, which enabled the detection of signals for PbCl⁺ and PbS⁺ ions. PbS⁺ displays the signature of a slowly evaporating species, while PbCl⁺ appears to arise only from fast evaporation, which is likely due to the higher vapor pressure of the compounds generating PbCl⁺. This is consistent with the evaporation model results. Levels of particulate Pb measured during MILAGRO at T0 were similar to previous studies in Mexico City. Pb shows a diurnal cycle with a maximum in the early morning, which is typical of primary urban pollutants. Pb shows correlation with Zn, consistent with previous studies, while the sources of Pb appear to be at least partially disjoint from those of particulate chloride. Back trajectory analysis of the T0 Pb data suggests the presence of sources inside the urban area SSW and N of T0, with different chemical forms of Pb being associated with different source locations. High signals due to particulate lead were also detected in the PEMEX site; again, no correlation between Pb and chloride plumes was observed, suggesting mostly different sources for both species.