

Characterization of Aerosols Containing Zn, Pb, and Cl from an Industrial Region of Mexico City

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Received December 6, 2007. Revised manuscript received June 16, 2008. Accepted July 21, 2008.

Recent ice core measurements show lead concentrations increasing since 1970, suggesting new nonautomobile-related sources of Pb are becoming important worldwide (1). Developing a full understanding of the major sources of Pb and other metals is critical to controlling these emissions. During the March, 2006 MILAGRO campaign, single particle measurements in Mexico City revealed the frequent appearance of particles internally mixed with Zn, Pb, Cl, and P. Pb concentrations were as high as 1.14 $\mu\text{g}/\text{m}^3$ in PM₁₀ and 0.76 $\mu\text{g}/\text{m}^3$ in PM_{2.5}. Real time measurements were used to select time periods of interest to perform offline analysis to obtain detailed aerosol speciation. Many Zn-rich particles had needle-like structures and were found to be composed of ZnO and/or Zn(NO₃)₂·6H₂O. The internally mixed Pb–Zn–Cl particles represented as much as 73% of the fine mode particles (by number) in the morning hours between 2–5 am. The Pb–Zn–Cl particles were primarily in the submicrometer size range and typically mixed with elemental carbon suggesting a combustion source. The unique single particle chemical associations measured in this study closely match signatures indicative of waste incineration. Our findings also show these industrial emissions

play an important role in heterogeneous processing of NO_y species. Primary emissions of metal and sodium chloride particles emitted by the same source underwent heterogeneous transformations into nitrate particles as soon as photochemical production of nitric acid began each day at ~7 am.

Introduction

Particulate air pollution is correlated with increased morbidity and mortality through cardiovascular and pulmonary effects (2). Although relatively little is known about the specific chemical constituents responsible for the adverse health effects, metal-containing particles are implicated in a number of studies (3–5). The solubility of metal ions present in particles affects their mobility in the human body while their oxidation state greatly affects their toxicity (5). Other factors such as particle size and shape determine how deep into the respiratory tract a particle may travel. Smaller particles with a compact morphology penetrate deeper into the lungs where they are more likely to be retained by the body (6–8). Anthropogenic particles created by high temperature processes (e.g., combustion and ore processing) possess many of the properties responsible for adverse health effects.

In urban areas, anthropogenic sources of submicron metal-containing particles are plentiful. For example, the burning of fossil fuel leads to the association of Ni and V within particles (9). Prior to 2000, tetra-ethyl-lead was used as a gasoline additive in many countries and resulted in traffic related emissions of submicron lead particles (10). In industrial areas, smelting produce particulate emissions rich in heavy metals (11). Combustion of municipal waste produces submicron particles composed of Zn, Pb, and Cl as well as numerous other metals (12). Zn and Pb are often found to be internally mixed in particles detected in different geographic locations (10). Dust particles are predominantly supermicrometer sizes and when stirred up through anthropogenic activities (such as construction and/or vehicular traffic), they effectively transport metals into the atmosphere (13). Each of these metal sources emits particles with unique compositions which can ideally be identified using the appropriate combination of analytical techniques.

To characterize metal-containing particles in the Mexico City metropolitan area (MCMA), an extensive suite of aerosol measurement and sampling techniques was used. In the past decade, several field studies in MCMA have employed a variety of instrumentation to address particulate pollution and air quality issues (14–17). Researchers found the northern part of the city is characterized by high concentrations of industrial emissions, in particular, Zn- and Pb-containing particles (14, 17, 18). Notably, blood Pb levels in children in the northeastern part of the city were 10.9% higher than children in the southwestern region (19). The elevated metal concentrations in the northern MCMA have been generally attributed to industry, and the exact identity has not been determined.

The research presented herein was carried out during the Megacity Initiative: Local and Global Research Observations (MILAGRO) field study held in March 2006 (see <http://mce2.org/>). As part of the MILAGRO study, a sampling site (T0) was established in northern MCMA and was impacted by industrial, vehicle, and residential emission sources (20). Single particle mass spectrometry was used to identify a unique period with a high abundance of Zn and Pb particles on March 24, 2005. Detailed studies using complementary techniques provide information on particle chemistry, metal speciation, size, mixing state, and morphology of metal-

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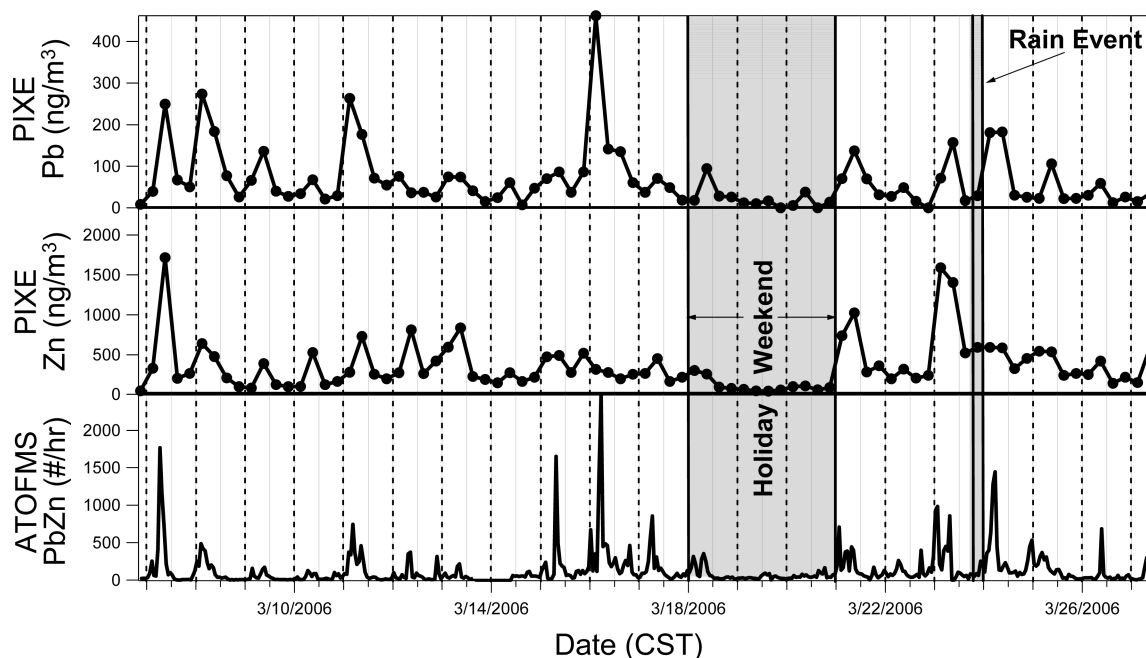


FIGURE 1. Time series of unscaled ATOFMS counts of Zn- and/or Pb-containing particles compared with the PIXE bulk mass concentrations of Zn and Pb. The major and minor tick marks occur at 12 am and 12 pm, respectively. PIXE data are shown for 0.36–2.5 μm particles.

containing particles along with quantitative mass loadings. Spatial, temporal, physical, and chemical information on these particles suggests they were produced by local waste incineration. Single particle mass spectrometry and electron microscopy provide unique information that is used to show not only the concentration and source of these industrial emissions, but also insight into the atmospheric processing these particles undergo after they are emitted. Microscopy and spectro-microscopic techniques provide morphology and oxidation state information that is crucial for elucidating the potential environmental effects of these particles.

Experimental Section

Sampling site T0 was located in the northern part of MCMA at the “Instituto Mexicano del Petroleo” (IMP) at 19°29'23.60 N, 99°08'55.60W and 2200 m above sea level. The site was surrounded by industrial and residential areas as well as roads with intensive traffic (16). A number of complementary techniques were used in this study. The aerosol time-of-flight mass spectrometer (ATOFMS) measures real-time single particle size and composition with hourly time resolution. Computer controlled scanning electron microscopy with energy dispersive X-ray analysis (CCSEM/EDX) provides quantitative information on thousands of the substrate collected particles. Scanning transmission X-ray microscopy with near edge X-ray spectroscopy (STXM/NEXAFS) provides off-line molecular speciation of individual particles. Proton induced X-ray emission (PIXE) yields time-resolved bulk mass concentrations of $Z > 23$ elements with a 6 h time resolution. A more detailed description of these techniques is presented in the Supporting Information.

Results and Discussion

Historically, the high concentrations of Zn and Pb particles in the northern MCMA have broadly been attributed to industrial processes (14, 16, 17). The time series derived from the ATOFMS and PIXE data presented in Figure 1 show episodes of particles containing Pb and Zn were common throughout the study. Table 1 shows the average, maximum, and minimum concentrations for Zn and Pb in the PM_{10} and

TABLE 1. Twenty-four Hour Average PM_{10} and $\text{PM}_{2.5}$ ($\mu\text{g}/\text{m}^3$) for Pb and Zn Determined between March 6 and 30

	Pb PM_{10}	Pb $\text{PM}_{2.5}$	Zn PM_{10}	Zn $\text{PM}_{2.5}$
average	0.22	0.15	0.50	0.34
min	0.06	0.01	0.14	0.04
max	1.14	0.76	1.4	0.49

$\text{PM}_{2.5}$ size ranges determined with high volume filters. The highest PM_{10} levels for Zn and Pb were 1.4 and 1.14 $\mu\text{g}/\text{m}^3$, respectively, with the majority of the Pb mass in $\text{PM}_{2.5}$. The episodes of Pb and Zn particles usually occurred between the night and mid morning (12–10 am CST). Calculated back trajectories indicate that during these periods the air masses originated from the industrial region of the city, north of the sampling site (20). Previous studies have attributed the source of the high Zn and/or Pb concentration to industrial emissions (14, 17, 18). The source assignment of industrial emissions is supported by the low concentrations of these particles during the holiday weekend of March 18–20 as highlighted in Figure 1.

On March 24, 5:15–5:30 CST the ATOFMS measured a peak in the percentage of particles containing Zn and Pb as indicated in Figure 1. This paper focuses on this episode, serving as a representative event that occurred nearly every day of the study. This particular event followed a heavy rainfall that significantly decreased the background aerosol concentrations, thus increasing the ability to study the industrial plumes microscopically.

Particle Classification. A rule based classification scheme showed that following the heavy rain event, the number percentage of particles containing Pb or Zn was 61% (by ATOFMS) to 73% (by CCSEM/EDX). The classification scheme shown in Figure 2 and detailed in the Supporting Information, was motivated by the observation that the majority of particles contained Pb, Zn, Fe, and/or Na. Particles were first separated into those containing metals ($\text{Me} > 0$) or no metals ($\text{Me} = 0$). The metal-containing particles were further separated into two classes; those containing Zn and/or Pb ($\text{Me} > 0$, $\text{ZnPb} > 0$), and those without Zn or Pb ($\text{Me} > 0$, $\text{Pb} = 0$, Zn

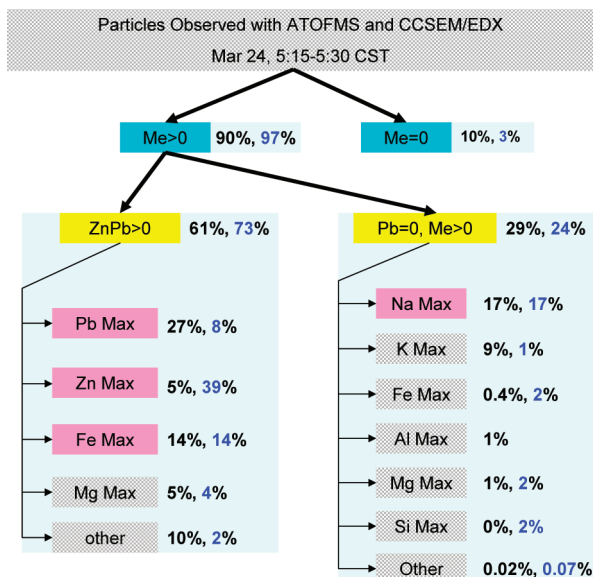


FIGURE 2. Rule based classification from ATOFMS and CCSEM/EDX data. Percent of particles in a class out of the total number of analyzed particles is indicated in black (ATOFMS) and blue (CCSEM/EDX). Pb or Zn in particles is indicated by $ZnPb > 0$. The size range analyzed for both instruments was approximately $0.2\text{--}2\ \mu\text{m}$.

($= 0$). The label “max” indicates that those particular metals made up the maximum signal out of all of the elements analyzed.

The percentages shown in black and blue in Figure 2 represent the relative number of particles classified for the CCSEM/EDX and the ATOFMS data sets, respectively. Figure 2 shows that, a majority of the particles, 61–72% by number, contained Pb or Zn, leaving a $PbZn = 0$ class mixed with other metals including Na, Pb, Zn, K, Cu, Cr, and Cd; 3 and 12% of the $Me > 0$ particles contained the health relevant metals Cd and Cr. The two data sets were in excellent agreement for the Na-max, Fe-max, and Mg-max particle classes. In general, the CCSEM/EDX and ATOFMS results agreed except for the higher percentages of the K max and Pb max classes given by the ATOFMS, reflecting the enhanced sensitivity of the ATOFMS toward these metals. In fact, 80% of the Pb max particles were internally mixed with Zn, so it is likely that many Zn-rich particles detected by the CCSEM are actually contained in the ATOFMS Pb max class.

Particle Mixing State and Source Profiles. The chemical mixing state of a particle describes which chemical species are contained in the same particle. Mixing state information from ATOFMS and CCSEM are presented in the Supporting Information while the most salient findings are reported here. ATOFMS and CCSEM/EDX showed that $ZnPb > 0$ particles are internally mixed with Cl, Na, K, P, S, and a multitude of other elements. This mixing state can be directly compared to source mixing states measured in previous source characterization studies. Tan et al. (2002) compared single particle mass spectra of particles collected from nonferrous smelters and municipal waste incinerators and showed that these two sources had many common elemental markers with the exception of P and Cl which were more abundant in incineration (21). Figure 3 compares the $Me > 0$ particles reported here with the source samples from municipal waste incineration and copper smelting from Tan et al. (21). The $Me > 0$ and nonferrous smelter particles did have sulfur at $m/z = -32$ and -64 in common, a marker not reported for incineration by Tan et al. However, the dot product of the percent contribution vectors shown in Figure 3 is 0.88 between incineration and $Me > 0$, while it is 0.53 between $Me > 0$ and nonferrous smelting. The best match with the

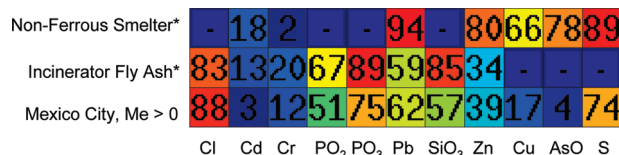


FIGURE 3. Comparison of MCMA aerosol on Mar 24 from 5:15–5:30 am with two industrial sources. The color is proportional to the percentage of particles in the sample given on the vertical axis containing a particular marker indicated by the horizontal axis; this percentage is also indicated inside of each box. Mexico City metal aerosol more closely matches waste incineration than smelting. Key elemental tracers include Pb, Zn, Cl, and P. The ATOFMS data used for this figure is the “ $Me > 0$ ” particle set defined in Supporting Information Table S1. (* Source data obtained from Tan, 2002 (21).)

$Me > 0$ particles from Mexico City is with incineration, with the key elemental tracers P and Cl both abundantly present in each sample.

The mixing state analysis is further supported by PIXE measurements from which we have applied a factor analysis to extract an industrial factor showing strong contributions from Pb, Zn, Cr, and Cl. As shown in Supporting Information Table S2, the strongest associations within the industrial factor were, from weakest to strongest, between Cl, Na, Zn, Pb, Cr, and P. This was similar to the mixing state identified by the ATOFMS and CCSEM/EDX. Furthermore, many of these elements were key markers distinguishing incineration from smelting in the work of Tan et al. (21). However, the PIXE factor analysis was unable to identify associations with nitrogen and carbon. Thus, as described below, other complementary methods are used to obtain a more complete picture.

In addition to source identification, the mixing state may also be used to obtain more detailed chemical composition. ATOFMS shows that the Zn and Pb particles were found to be mixed with carbonaceous species such as elemental carbon (EC), aromatics, other metals, and organic species such as the oxalate ion. The ATOFMS spectra showed that at least 40% of the Pb and Zn particles were mixed with soot/EC supporting the assertion that they were generated from combustion. In Supporting Information Figure S2, it is shown that the nonmetal ($Me = 0$) class present in this industrial plume had a distinct aromatic hydrocarbon signature with 75% of these particles containing aromatic markers and 8% of these particles containing Cl. Furthermore, 13–15% of the Pb- and Zn-containing particles were found to be internally mixed with aromatic hydrocarbons in addition to chloride. The variability and extent of particle mixing with other species (including Mn and Cu) is further quantified in the Supporting Information (Figures S1–S4).

Particle Morphology. Morphology is an important microphysical trait that relates to particle aerodynamic behavior, possible health effects (2), speciation (3), phase, formation mechanism, and source identification. The SEM images shown in Figure 4 illustrate the morphology of metal rich particles typical for this study. Nonspherical, needle-like Zn- and Pb-containing particles (panels A, B, and C), as well as spherical Zn particles containing PbFe and Mn (not shown) were detected. Figure 4a shows Zn-containing particles internally mixed with soot, which is consistent with ATOFMS results indicating that at least 40% of the Zn-containing particles were mixed with elemental carbon. SEM/EDX analysis confirmed that the needle like structures shown in Figure 4c were mostly composed of Zn and O with only minor amounts of other elements suggesting a similarity to previously reported tetrahedral ZnO particles (22). ATOFMS optical measurements also indicated that the particles containing Zn and Pb were nonspherical with effective densities that exceeded $2.4\ \text{g/cm}^3$ (23). A high abundance of cubic

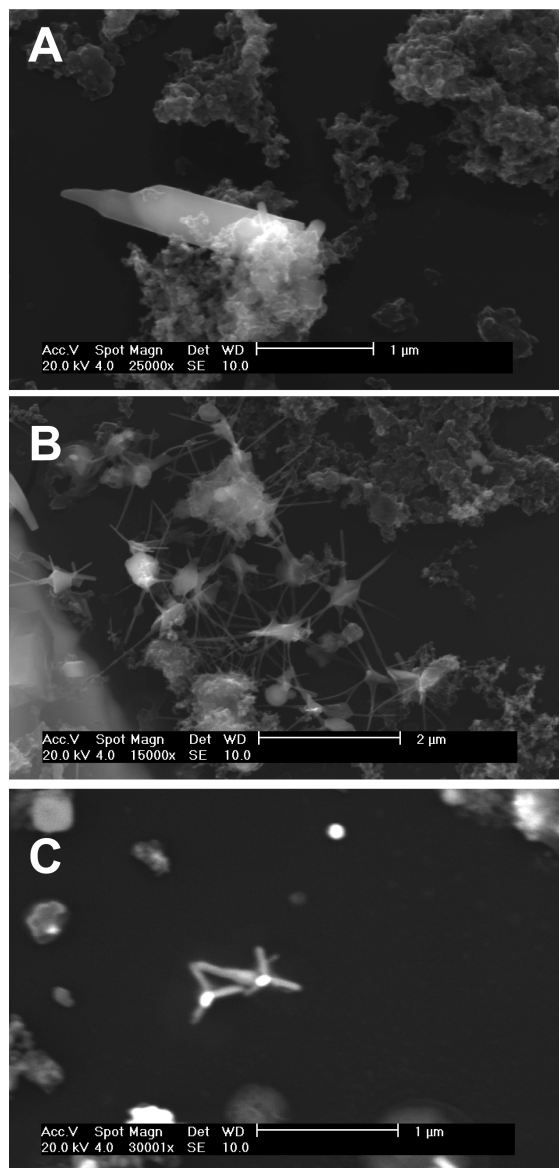


FIGURE 4. Images illustrating the morphology of metal containing particles observed in Northern Mexico City. (A) Zn containing crystal attached to soot; (B) Needle-like particles containing Pb, Zn, and Cl; (C) Tetrahedral Zn containing particles with compact Pb rich particles.

NaCl particles were also observed to be internally and externally mixed in the same samples as the metal rich particles, indicating they were likely produced by the same source.

Speciation and Phase of Zn- and Pb-Containing Particles.

Using STXM/NEXAFS, two major particle classes were distinguished from one another based on morphology and NEXAFS spectra. Representative STXM images are shown in Figure 5. Particles shown in Figure 5a (type A) were found to be internal mixtures of Zn, EC, and K, whereas particles in Figure 5b (type B) were found to be needle-like Zn particles discussed previously (22). The presence of EC and K in type A was confirmed with the corresponding carbon K-edge NEXAFS spectra.

To elucidate the chemical speciation of Zn-containing particles, the Zn L-edge NEXAFS spectra of ZnO, ZnS, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , ZnSO_4 standard reference materials were measured for comparison with particles of types A and B. Representative normalized Zn L-edge NEXAFS spectra for both particle classes and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZnO standards

are shown in Figure 5. The spectra in Figure 5a and b correspond to the average spectrum collected over six single particles located in different regions of the substrate. ZnS, ZnSO_4 , and ZnCl_2 standards did not match the spectra of the Zn-containing particles. The similarities in the spectra of the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZnO particles with those of particle types A and B, provide chemical identification of these two types. While the spectrum of particle type B matches well with that of ZnO, small deviations between the spectra of particle type A and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are observed at ~ 1025 eV and ~ 1050 eV. These deviations may arise due to the presence of minor amounts of other Zn compounds and/or unidentified components in the ambient particles.

Heterogeneous Chloride-to-Nitrate Chemistry. Different emission sources are expected to be associated with specific particle chemistry and morphology. Waste incineration, has been shown to emit Pb, Zn, and Na chloride particles (12, 24, 25). Nearly 100% of the Pb and Zn particles contained Cl (Supporting Information Figure S2). Furthermore, ZnCl_x and NaCl_x clusters were common in the ATOFMS spectra. Particles containing chloride can undergo atmospheric processing where the chloride is displaced by nitrate:



where M represents Zn, Pb, Na, or K. The CCSEM/EDX and ATOFMS show the Zn and Pb particles were internally mixed with Cl and NO_3 . As shown in Figure 6, the ATOFMS measured a strong temporal anticorrelation between nitrate and chloride for Pb-, Zn-, and Na-containing particles. Each morning, the initial spike of chloride containing particles was followed by the appearance of the same particles enriched in nitrate and depleted in chloride. The reaction started at approximately 7 am each morning and peaked at ~ 12 – 2 pm each day. The ZnCl_2 and NaCl particles began to be transformed to $\text{Zn}(\text{NO}_3)_2$ and NaNO_3 particles as soon as the HNO_3 began to form in the mornings (27). Thus, the displacement reaction shown in R1 explains the $\text{Zn}(\text{NO}_3)_2$ particles observed with the STXM/NEXAFS.

The extent of chemical processing may be different because particles contain different amounts of reactive chloride. CCSEM/EDX and ATOFMS show that Cl is present in over 70% of Zn- and Pb-containing particles (Supporting Information Figure S2) whereas “Pb max” particles contain larger amount of Cl compared to the “Zn max” particles (Supporting Information Figure S4). Also, all of the $\text{PbZn} > 0$ particles contained Na, therefore the chloride was also associated with Na within these same particles. Because these industrial particles represented as much as 73% of the total particles during morning hours, their presence can strongly influence the chemistry of aerosols in the MCMA as demonstrated in Figure 6.

Sources of Metal-Containing Particles in Mexico City.

Numerous industrial emission sources exist in northern Mexico City. The emissions inventory for the immediate area (within 5 km) obtained by the Secretary of the Environment of the Government of the Federal District (SMA/GDF) indicates that metallurgical sources release a substantial fraction of the $\text{PM}_{2.5}$ compared to other industries. While smelting could be a source of some of the particles observed here, previous studies do not report large amounts of Cl associated with smelter emissions. However, Dall’Osto et al. have reported such associations with chloride in a recent study of steelworking (26). Earlier metallurgical source studies also noted high SO_2 concentrations within smelter plumes. Such plumes of SO_2 were not reported for MCMA where only weak correlations were observed among SO_2 , Zn, and Pb. Zn- and Pb-containing particles identified by ATOFMS in this study also came from the northeast (20), and were not correlated with SO_2 gas phase concentrations. One caveat to this is that a high percentage of the $\text{Me} > 0$ particles observed

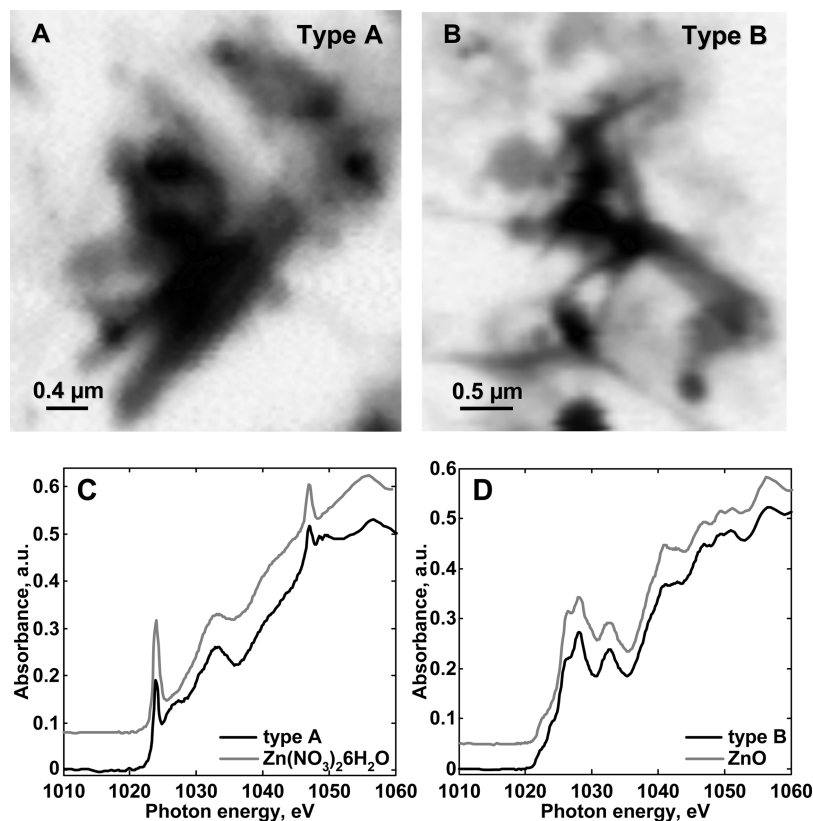


FIGURE 5. Upper panel: single energy (1024 eV) STXM images of two types of Zn containing particles observed in Northern Mexico City. (A) Zn-containing crystals internally mixed with elemental carbon; (B) - Needle-like Zn-containing particles. Lower panel: representative Zn L-edge normalized NEXAFS spectra for (C) particle type A and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ standard and (D) particle type B and ZnO standard.

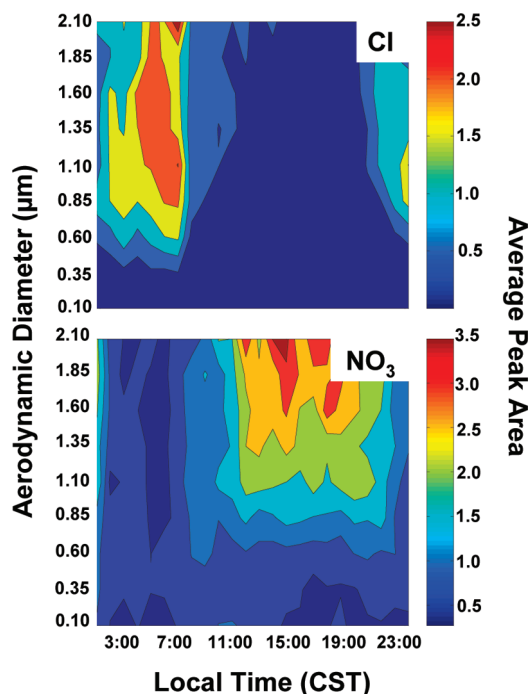


FIGURE 6. Average peak area for Cl and NO_3 as a function of time and size for Pb- and Zn-containing particles mixed with Cl. This demonstrates the displacement of chloride by nitrate within individual Pb and Zn particles.

in our study did contain primary sulfur markers at m/z -32 (S^-) and -64 (S_2^-) (Figure 3). Nevertheless, since the time trends and indicated source direction of the Cl particles reported by Salcedo et al. (27) and Johnson et al. (18) are

similar to those observed for the Zn/Pb/Cl-containing particles studied here, it is highly likely that the chloride particles observed in these previous studies came from the same source.

Municipal and hazardous waste incineration have been shown to emit Pb, Zn, and Cl particles (21, 28–31). For this source, the Cl is primarily from the burning of plastics such as polyvinyl chloride and paper, whereas the Pb and Zn can be produced from a variety of waste materials. Electronic waste represents a good example of a waste stream that contains an abundance of these three elements. The PIXE, ATOFMS, and CCSEM/EDX analyses presented here indicate these elements are internally mixed, while associations with carbonaceous material suggest these particles result from combustion. ATOFMS identified organic particles that contained an abundance of aromatic markers that may indicate the presence of diphenyl or other similar aromatic compounds typical for incineration emissions. Incineration is not currently listed in the emissions inventory for the MCMA; however, multiple waste incinerators exist in the northern part of Mexico City (20).

A combination of techniques was used to probe the mixing state, morphology, oxidation state and heterogeneous chemistry of Zn- and Pb-containing particles. A time series analysis indicates metal-rich particles peaked at the sampling site during the early morning hours. This is consistent with previous studies showing high Zn and Pb concentrations correlated with early morning air masses from the northeastern MCMA. Evidence of industrial incineration was supported by the time series data showing the lowest metal particle concentrations during a holiday weekend. Direct comparison of our data with single particle source samples from waste incineration supports incineration as the most probable source of these particles. Moreover, three different

techniques confirmed that many of the ZnCl-rich particles were mixed with EC, which additionally supports combustion as the source of these particles.

Complementary ATOFMS, CCSEM/EDX, and PIXE data show that particles containing Zn and/or Pb are mixed with Cl and nitrate. ATOFMS measured the conversion to metal nitrate particles immediately following the metal-chloride particle spikes. The time lag of nitrate behind chloride suggests a heterogeneous displacement reaction of metal chlorides with nitric acid. This assertion is supported by STXM/NEXAFS results showing Zn rich particles composed of $Zn(NO_3)_2 \cdot 6H_2O$. Because these particles sometimes dominated number concentrations in the 0.2–1 μm range, this heterogeneous chemistry may be an important source of submicron nitrate mass while impacting the gas phase NO_y budget.

The frequent observation of these metal-rich particles in an urban area with a high population density also has important implications for health effects. The largest fraction of the Pb-containing particles is less than 2.5 μm , meaning that these particles may be efficiently inhaled. Also, there may be important health ramifications if salts such as $Pb(NO_3)_2$ are formed because lead nitrate is soluble, and therefore more mobile within the human body.

Acknowledgments

We thank the individuals who helped out at the T0 site. The UCSD, the MIT, and the MCE² groups acknowledge support provided by the U.S. National Science Foundation (ATM-0528227), the Atmospheric Science Program of the office of Biological and Environmental Research (ASP/OBER) of the U.S. Department of Energy (DOE), (grant DE-FG02-05ER63980). The PNNL and the LBNL research groups acknowledge support provided by ASP/OBER DOE. The AUMA research group acknowledges support provided by Mexican Comision Ambiental Metropolitana, The CCSEM/EDX and PIXE particle analyses were performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research at Pacific Northwest National Laboratory. PNNL is operated by the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RL0. STXM/NEXAFS experiments at the ALS were partially supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231.

Supporting Information Available

Details regarding experimental procedures, rules based particle classification, and single particle mixing state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES7030483