

# Use of X-ray Absorption Spectroscopy To Speciate Manganese in Airborne Particulate Matter from Five Counties Across the United States

Saugata Datta,<sup>†</sup> Ana M. Rule,<sup>\*,‡</sup> Jana N. Mihalic,<sup>‡</sup> Steve N. Chillrud,<sup>§</sup> Benjamin C. Bostick,<sup>§</sup> Juan P. Ramos-Bonilla,<sup>‡</sup> Inkyu Han,<sup>‡</sup> Lisa M. Polyak,<sup>‡</sup> Alison S. Geyh,<sup>‡</sup> and Patrick N. Breyse<sup>‡</sup>

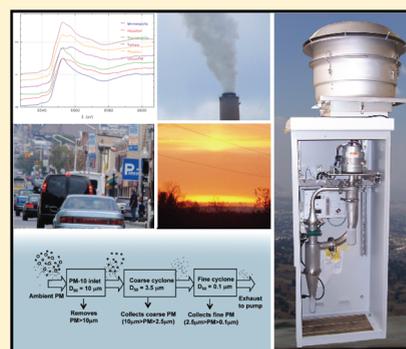
<sup>†</sup>Kansas State University, Department of Geology, Manhattan, Kansas 66506, United States

<sup>‡</sup>Johns Hopkins Bloomberg School of Public Health, Department of Environmental Health Sciences, Baltimore, Maryland 21205, United States

<sup>§</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York 10964, United States

## Supporting Information

**ABSTRACT:** The purpose of this study is to characterize manganese oxidation states and speciation in airborne particulate matter (PM) and describe how these potentially important determinants of PM toxicity vary by location. Ambient PM samples were collected from five counties across the US using a high volume sequential cyclone system that collects PM in dry bulk form segregated into “coarse” and “fine” size fractions. The fine fraction was analyzed for this study. Analyses included total Mn using ICP-MS and characterization of oxidation states and speciation using X-ray absorption spectroscopy (XAS). XAS spectra of all samples and ten standard compounds of Mn were obtained at the National Synchrotron Light Source. XAS data was analyzed using Linear Combination Fitting (LCF). Results of the LCF analysis describe differences in composition between samples. Mn(II) acetate and Mn(II) oxide are present in all samples, while Mn(II) carbonate and Mn(IV) oxide are absent. To the best of our knowledge, this is the first paper to characterize Mn composition of ambient PM and examine differences between urban sites in the US. Differences in oxidation state and composition indicate regional variations in sources and atmospheric chemistry that may help explain differences in health effects identified in epidemiological studies.



## INTRODUCTION

Numerous epidemiological and toxicological studies have found associations between increases in morbidity and mortality for respiratory and cardiovascular illness and elevated concentrations of ambient particulate matter (PM).<sup>1–3</sup> Airborne PM is a complex mixture that includes particles in a wide range of sizes and with varying composition. The National Research Council<sup>4</sup> identified the need to better understand the relationship between toxicity and the size and composition of PM as an important research priority. PM composition is known to vary by location<sup>5–7</sup> depending on various factors including local sources.<sup>8,9</sup> For example, a recent paper by Han et al.<sup>10</sup> found that elevated ratios of particle bound PAH (p-PAH) to black carbon (BC) were useful in examining local combustion sources beyond motor vehicles, such as coal power plants and petrochemical facilities. There is also growing evidence that PM composition and characteristics are related to health effects and that metals are an important determinant of toxicity.<sup>11–13</sup> Physical and chemical characteristics of PM that may affect toxicity include particle size, chemical composition (including metals), solubility of different compounds,<sup>14</sup> and oxidation state of elements.<sup>15</sup>

While the oxidation state(s) and solubility of metallic compounds in PM have been shown to affect uptake, transport, and mechanistic pathways,<sup>16–18</sup> little is known about how these potentially important determinants of PM toxicity vary by location. Synchrotron-based X-ray absorption spectroscopy (XAS) is a well established method for the determination of oxidation state and coordination chemistry of metals in minerals and soils.<sup>19</sup> However, this technique is only recently gaining widespread use in the analysis of ambient air samples, where metal compounds represent a tiny fraction of the total mass.<sup>20–24</sup> Consequently, there is a need to define the best procedures and protocols for the collection of air samples to be analyzed using XAS techniques, as well as to establish and optimize analysis parameters for different types of air samples.

Elements in ambient PM samples which have been examined using XAS include iron,<sup>22,24,25</sup> sulfur and nickel,<sup>26</sup> chromium,<sup>23</sup> zinc,<sup>21</sup> arsenic,<sup>27</sup> and manganese.<sup>21,28,29</sup> Of those metals, manganese (Mn) is of particular interest as it is a known

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Table 1. Description of the Five Monitoring Sites

County, state	Sacramento, CA	Maricopa, AZ	Anoka, MN	Harris, TX	Pinellas, FL
EPA land use description	residential	residential	commercial	residential	residential
sampling period (days)	Jan–Mar 2008 (54)	Jun–Jul 2008 (42)	Sep–Oct 2008 (32)	Jan–Feb 2009 (36)	Apr–May 2009 (41)
coordinates	38.683285, −121.164433	33.483904, −112.1426	45.137629, −93.207783	29.669944, −95.12851	27.98625, −82.78212
distance to nearest highway	2.5 km to SE US-50 and 6 km to NW I-80	1.5 km to E I-17	1.5 km to E I-35W	5 km to SW I-45	1.5 km to E Rd-1
traffic counts per day (truck counts; %) <sup>a</sup>	147 500 (10.5%)	170 945 (N/A)	137 000 (5.3%)	209 934 (10.9%)	87 500 (3.6%)
total Mn ( $\mu\text{g}_{\text{Mn}}/\text{mg}$ ) <sup>b</sup>	0.1371 $\pm$ 0.0413	0.6768 $\pm$ 0.4308	0.0613 $\pm$ 0.0127	0.0769 $\pm$ 0.0041	0.0195 $\pm$ 0.0020
estimated annual PM <sub>2.5</sub> emission (tons) <sup>c</sup>					
chemical and pharmaceutical	5	15	25	4848	80
electric and gas generating facilities	93	181	719	1482	4239
petroleum, refinery facilities	21	23	742	3388	27
total	613	1133	2870	10 550	4691

<sup>a</sup>Traffic counts on highways obtained from local state agencies. See list of references in Supporting Information. <sup>b</sup>Total Mn concentrations obtained by ICP-MS. <sup>c</sup>Estimated annual PM<sub>2.5</sub> emissions are obtained from the National Emission Inventory (US EPA) within a 75 km radius of each monitoring site. Detailed estimated Mn PM<sub>2.5</sub> emissions are summarized in Supporting Information Table S1.

toxicant to the central nervous system and its toxicity is dependent on oxidation state and speciation (determinants of solubility).<sup>30</sup> While Mn is an essential element and necessary for maintaining good health, long-term inhalation exposure has been linked to the development of an irreversible Parkinson-like disease known as manganism.<sup>31</sup>

Sources which contribute to airborne Mn are both natural and anthropogenic. Mn is one of the most abundant elements in soils<sup>32,33</sup> which would be expected to contribute to Mn in airborne particles larger than about 2  $\mu\text{m}$ .<sup>34</sup> In contrast, industrial processes, such as battery and electronics manufacturing and steel production, and occupations, such as welding, generate smaller particles that penetrate deep inside the lung. In addition, in areas where the fuel additive MMT (methylcyclopentadienyl-manganese-tricarbonyl) is used, Mn is a component of motor vehicle exhaust. Riders of subways have been shown to be exposed to elevated levels of Mn due to the wear of tracks and other metal components of subway cars.<sup>35–38</sup> Though Mn can be found in at least seven different oxidation states,<sup>39</sup> only the +2, +3, and +4 oxidation states have been identified in mammalian tissues.<sup>30</sup> Toxicological studies suggest that Mn(III) is more cytotoxic than Mn(II).<sup>12,40</sup> Additionally, the form of manganese (characterized by both oxidation state and solubility) determines differences in bioaccumulation and affects the kinetics of Mn throughout the body.<sup>15,41</sup> For example, the bioaccumulation of Mn measured in rat tissues following Mn inhalation exposure was found to be dependent on the form of Mn in the exposure: rats exposed to Mn sulfate (Mn(II), soluble) had lower lung Mn concentrations and higher olfactory bulb concentrations than rats exposed to Mn tetroxide (Mn(II/III), insoluble).<sup>16</sup> Therefore, an adequate characterization of manganese in PM should involve determination of oxidation states, as well as speciation.

In this study, we used XAS analysis to determine Mn speciation in ambient air samples collected from five counties across the US: Sacramento (CA), Maricopa (AZ), Pinellas (FL), Anoka (MN), and Harris (TX). The XAS spectra obtained allow the identification of Mn species in PM samples containing low concentrations of Mn that have not been altered by extraction techniques, the ability to distinguish between compounds of the same metal and between different compounds with the same oxidation state, as well as a semiquantitative determination of oxidation states present in

each sample. To our knowledge, this is one of the few studies to describe Mn oxidation states and speciation in airborne PM and the first study to describe how these potentially important determinants of PM toxicity vary by location in the US.

## MATERIALS AND METHODS

**Sample Collection.** Ambient PM samples were collected from multiple locations across the US as part of the Johns Hopkins Particulate Matter Research Center (JHPMRC). Research conducted by the JHPMRC was designed to explore the relationship between health effects and exposure to ambient PM of differing composition. The sample locations chosen for PM collection were identified by JHPMRC epidemiologists as representing higher or lower risk from PM exposure. The rationale for the selection of the counties is explained in detail elsewhere.<sup>7,11</sup> Briefly, nation-wide mortality and Medicare hospitalization data were analyzed together with PM data from EPA's nationwide monitoring network to establish risks of mortality and morbidity from PM by county. On the basis of this data, we selected counties with the highest and lowest risks for cardiovascular and respiratory disease hospitalizations by region.

Ambient PM samples were collected using a high volume sequential cyclone system (HVSCS), designed by Center researchers, that segregates ambient PM roughly into coarse PM (between 3 and 10  $\mu\text{m}$ ) and fine PM (between 0.1 and 3  $\mu\text{m}$ ) fractions. The design and operation of the HVSCS has been described in detail elsewhere.<sup>42</sup> Briefly, this cyclone system collects size fractionated PM in dry powder form. Each sample consists of between 300 and 1500 mg, which represents PM collected over a sampling period of 4 to 6 weeks. The HVSCS collects PM using inertial forces and does not require collection media (e.g., filters), removing any matrix effects associated with extracting PM from the media. PM was removed weekly from the cyclone collection cup using a PVC spatula designed for the purpose. The collected bulk PM was transferred to an amber glass vial and stored at 4 °C under Argon until analysis. Sample portions were weighed using a Mettler Toledo T5 Microbalance (Mettler Toledo, Columbus OH). Samples were parsed out for chemical and physical characterizations and later instillation in mouse toxicological studies. Although this is an unusual sample of airborne PM, the technique has been successfully applied to PM collected on

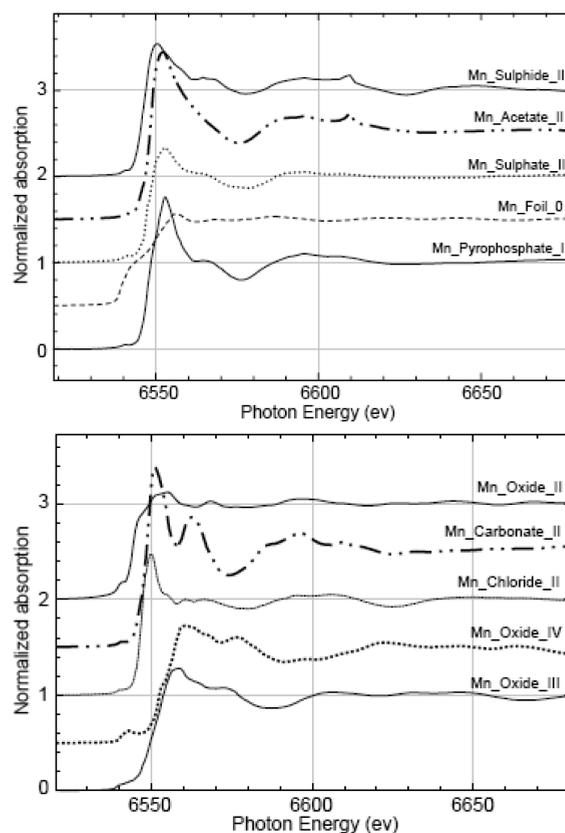
different media such as impaction surfaces<sup>22</sup> and Teflon filters.<sup>23</sup>

Samples represent five spatially and temporally different areas of the US. The areas and dates of sample collection are shown in Table 1. All PM samples except one were collected in areas designated by the EPA as residential, away from obvious point or strong mobile sources. Only the Anoka site was designated a commercial site, located at the edge of a small airfield. Synchrotron analysis was performed directly on the dry bulk PM, without any pretreatment or dissolution to avoid altering oxidation states. The results presented in this manuscript were obtained from the fine fraction samples, which exclude crustal elements and are likely to penetrate deep in the respiratory tract.

**Sample Analysis.** *Total Metal Analysis (ICP-MS).* Total Mn analysis was conducted, using inductively coupled plasma mass spectrometry (ICP-MS), to provide information on total Mn content of each PM sample. Results of this analysis were used to inform the selection of XAS beamlines. Five replicates of approximately 300  $\mu\text{g}$  of PM were weighed using a Mettler Toledo T5 Microbalance (Mettler Toledo, Columbus OH). PM was transferred from the vial to a tared small square (1 cm  $\times$  1 cm) Kimwipe tissue (Kimberly Clark Professional, Dallas TX) to reduce sample loss during transfer from the microbalance to the digestion vessel. The entire Kimwipe square including the PM was then transferred to a 5 mL Teflon microwave digestion vessel (Savillex Corporation, Eden Prairie MN). Samples were digested in  $\text{HNO}_3$  and HF (optima grade, Fisher Scientific, Columbia MD) using a Mars5 Xpress microwave system (CEM Corporation, Matthews NC). NIST Standard Reference Materials (NIST, Gaithersburg MD) SRM 2709 (agricultural soil) and SRM 1648a (urban particulate matter) were analyzed to ensure accuracy and precision of the sample digestion method and handled in the same manner as the PM samples. Reagent blanks for each batch included a small square of Kimwipe.

ICP-MS analysis was performed using an Agilent 7500ce ICP-MS (Agilent Technologies, Santa Clara CA). An internal standard, scandium, was added to each sample and calibration standard to correct for internal drift. Duplicate 8-point calibration curves were generated for each run. If values were within  $\pm 5\%$ , the run was allowed to proceed. Quantification was done by external and internal standardization. The output was converted into a mass per unit mass of PM and blank corrected. Results were adjusted on the basis of the recovery efficiency of either SRM1648a or 2709 ran in triplicate for each individual digest batch.

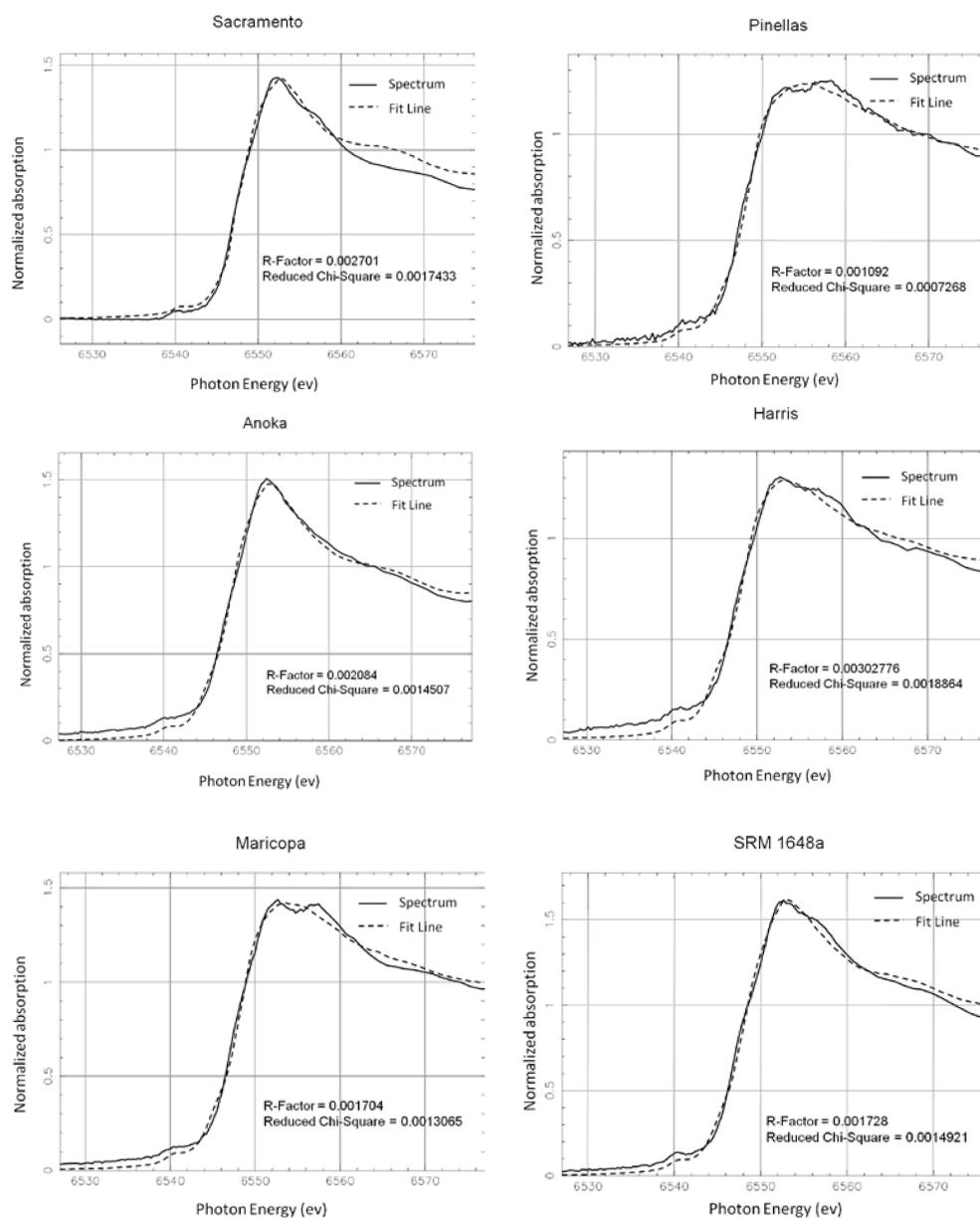
**XAS Analyses: Reference Compounds and Sample Preparation.** Ten reference Mn compounds were analyzed for use as model spectra to assist in interpretation of the PM spectra (Figure 1). Standards were chosen on the basis of their possible presence in the air and their stability in an oxidizing environment. All reference compounds were purchased from established chemical distributors (Fisher Scientific, Sigma-Aldrich, and Pfaltz & Bauer). Reference compounds included  $\text{Mn}^0$  foil, Mn(II) acetate, Mn(II) sulfate, Mn(II) oxide, Mn(II) chloride, Mn(II) pyrophosphate, Mn(II) sulfide, Mn(III) oxide, and Mn(IV) oxide. Solid or coarse standards were prepared for analysis by grinding with a mortar and pestle. Once a fine powder had been obtained, a uniform thin layer of material was brushed onto a piece of tape, which was then folded to ensure homogeneous powder distribution when presented in front of the X-ray beam.



**Figure 1.** Spectra of the 10 reference standard materials used for linear combination fitting (LCF) analysis. Individual spectra are offset for presentation purposes.

The same procedure could not be used for the PM samples, since the vast majority of the sample on the tape never interacts with the X-ray beam, thus wasting the limited amount of PM that was collected from each site. Consequently, a sample holder was specifically designed to minimize PM use and optimize sample exposure to the X-ray beam. The sample holder consisted of a 50  $\times$  50 mm square made from 1 mm thick acrylic in which a 10  $\times$  1 mm slot has been cut to contain the bulk PM sample. To minimize losses due to static electricity while PM sample was transferred into the slot, the sample holder was placed on top of a Polonium-210 antistatic strip (2U500, NRD, LLC NY) covered with aluminum foil. PM was transferred to the sample holder using an antistatic microspatula. Once the PM sample was deposited in the slot, it was removed from the Po strip and held in place between 2 pieces of adhesive tape (Scotch Magic, 3M, St. Paul, MN) taped to either side of the slot. The new sample holder requires ca. 25 mg of bulk PM and presents a homogeneous sample in front of the X-ray beam.

**XANES Analysis of PM Samples.** Characterization of Mn in fine PM samples was carried out using bulk Mn K-edge X-ray absorption near edge structure (XANES) at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory in New York. XANES involves the analysis of energies immediately surrounding the absorption edge and can give detailed information on oxidation states. Analysis of XANES allow for the characterization of samples containing low concentrations of elements and for the determination of the chemical structure and association of elements involved.

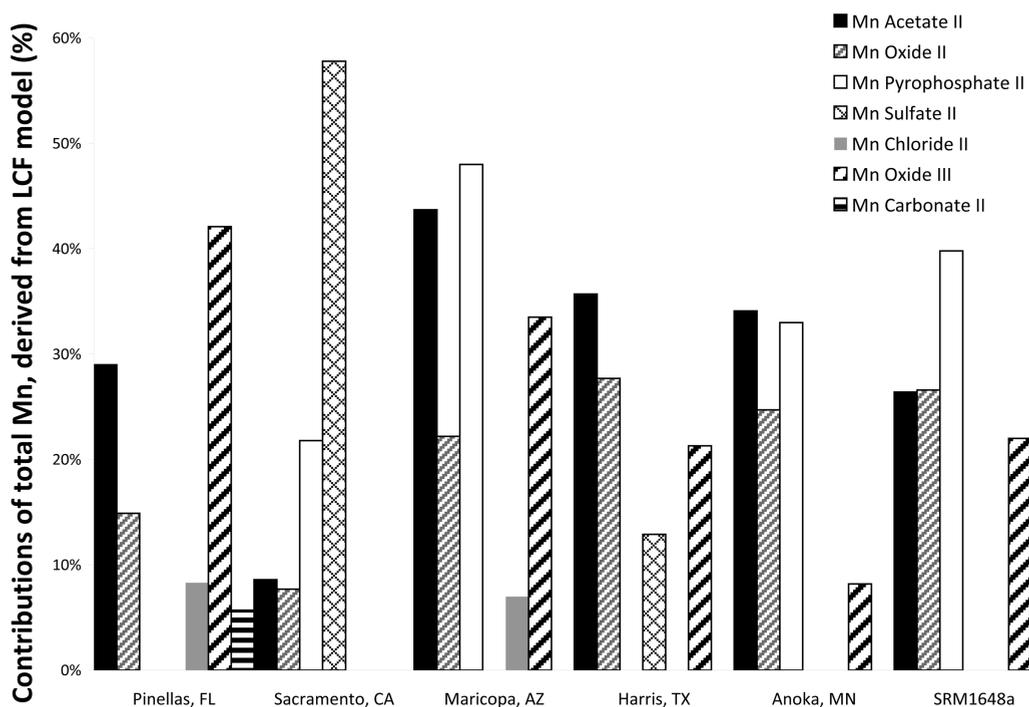


**Figure 2.** Sample spectrum and linear combination fitting of each of the samples from five counties and SRM 1648a, along with R-factor and reduced Chi-square values for individual fit. Refer to Figure 3 for percent contribution of each standard spectrum to each of the fits.

PM samples were analyzed at high resolution beamlines X19A and X11A, which are both equipped with Si(111) double-crystal monochromators for energy selection, and 13-element solid state Ge detectors especially suited for detecting low concentrations of metals. The storage ring operated at 2.8 GeV at currents of ca. 250 mA. PM sample spectra were recorded in fluorescence mode at a 45° angle to the incident beam; fluorescent intensity was normalized to the intensity of the incident X-ray beam ( $I_0$ ). Spectra of a Mn metal foil were collected concurrently with all samples and used for energy calibration and alignment. Spectra were collected from 200 eV below to 900 eV above the Mn K-edge (6539 eV). Three or four scan-region boundaries were defined; different step sizes were assigned to each region, and counting time per step was varied between 0.5 and 8 s for optimized signal/noise ratio in the region of most interest. Twelve to fifteen scans of each sample were obtained to improve signal-to-noise ratio. The sample holder described above was optimized for the

dimensions of both beamlines (10 × 1 mm maximum). Due to limited beam time availability, additional scans of some reference materials were repeated with an 8 element detector at beamline X10C.

**Statistical Analysis. Linear Combination Fitting.** An average spectrum of each sample was composed of up to 15 scans to improve the signal/noise ratio. Data reduction of the XAS spectra involved energy calibration, background subtraction, and normalization. Analyses were performed using linear combination fitting (LCF) with Athena software<sup>43</sup> within an energy range of -20 eV below to +30 eV above the edge. LCF is a method for the semiquantification of oxidation states.<sup>21,44</sup> LCF reconstructs the sample spectrum using a combination of selected model spectra, and reports goodness of fit parameters (R-factor and reduced  $\chi^2$ ) along with the percent that each model contributes to the fit. The accuracy of this method depends on how well the spectra of the chosen



**Figure 3.** Percent contributions of each standard spectrum to the fit obtained for the five counties and SRM 1648a, obtained from LCF analysis.

reference compounds represent the components in the samples.<sup>43</sup>

Every PM sample spectra was fitted to the maximum number of standard spectra; the combination of standards that resulted in the best fit (smallest R-factor and reduced  $\chi^2$ ) was chosen as the most likely representation of the sample. Combinations that explained less than 5% of the fit were not considered.

## RESULTS

**Total Metals Results.** Total Mn concentrations analyzed by ICP-MS for each sample are reported in Table 1 and Figure S1 in the Supporting Information. Recovery of Mn from SRM standards was within  $\pm 25\%$  of their certified concentrations of  $0.790 \pm 0.044 \mu\text{g}/\text{mg}$  for SRM 1648a (mean recovery =  $1.012 \pm 0.016 \mu\text{g}/\text{mg}$ ) and  $0.538 \mu\text{g}/\text{mg}$  for SRM 2709 (mean recovery =  $0.673 \pm 0.16 \mu\text{g}/\text{mg}$ ). All sample values were adjusted according to the SRM recovery in each individual digest batch. Mn concentration in the five counties range from  $0.020 \mu\text{g}/\text{mg}$  (Pinellas) to  $0.68 \mu\text{g}/\text{mg}$  (Maricopa).

**XANES Results.** Spectra of the ten Mn reference compounds are shown in Figure 1. A visual review indicates distinct spectral features for each Mn compound such as the small pre-edge peak for Mn(IV) oxide, the large postedge oscillation in Mn(II) carbonate, the taller peak in the near-edge oscillation of Mn(II) acetate, and the distinct shift in energy between the absorption edges of the different oxidation states (for example, Mn(II) compounds occurring before Mn(IV) compounds).

Reduction and fitting of XANES spectra from the five samples and the NIST SRM 1648a analyzed in this study are shown in Figure 2. The dotted lines in the figure represent the LCF curves, which closely follow the original spectrum. The fact that they do not perfectly match suggests that the standards available to construct each LCF curve do not fully explain the sample spectra and that small amounts of other Mn species may

be present. Percent contributions of each standard to the fits are shown in Figure 3.

Differences in oxidation states and speciation between samples can be described from the relative proportions obtained from the LCF curves (Figure 3). For example, our results indicate that Mn(III) oxide predominates in the Pinellas, FL sample (42%), contributes significantly to Maricopa, AZ and Harris, TX samples (33% and 21%, respectively), constitutes a small percentage (8%) of the Anoka, MN sample, and is absent from the Sacramento sample. Mn(II) acetate is present in all 5 samples, contributing between 8 and 40% of the total Mn, and is the predominant species in Harris, TX and Anoka, MN with  $\sim 35\%$ . The second most dominant form is Mn(II) oxide, which is also present in all our samples, and has the smallest proportion in the Sacramento, CA sample (8%). Mn(II) pyrophosphate was found in Sacramento (21%), Maricopa, AZ (48%), and Anoka MN (33%) and was absent from Pinellas, FL and Harris, TX. Finally, Mn(II) sulfate was only present in Sacramento, CA (58%) and Harris, TX (12%), and Mn(II) chloride was marginally present in the samples from Pinellas, FL (8%) and Maricopa, AZ (7%).

Of the five county spectra, only samples from Pinellas (FL) and Maricopa (AZ) show the presence of a doublet peak after the absorption edge (Figure 2). This doublet could not be explained by our library of standards. On the basis of our standard data and on that reported in the literature,<sup>45,46</sup> the second mode of the doublet likely coincides with the energy associated with either presence of Mn(III) or Mn(IV) oxidation state, which is also consistent with these two samples having more mineral/crustal inputs than the other samples as reflected by their higher Mn, Ti, and Al concentrations (Figure S1 in Supporting Information).

Finally, the NIST standard SRM1648a analyzed as part of our quality control measures was in good agreement with that reported in the literature<sup>47</sup> (Figure S2 in Supporting Information).

## DISCUSSION

We were able to characterize manganese oxidation states and differentiate between compounds contained in samples of ambient PM collected in five counties across the US. The XAS spectra we obtained allow for the identification of Mn species in bulk samples of fine PM that contain relatively low concentrations of Mn as compared to soil or mineral samples typically analyzed via XANES spectra. Since our samples are composed of particles smaller than  $3\ \mu\text{m}$ ,<sup>42</sup> soil resuspension is not expected to have a major contribution, and therefore, the contribution of natural sources and crustal elements expected in our samples is low, which might explain the absence of Mn(IV) compounds in our samples. On the other hand, the fact that an unexplained doublet peak is present in the Maricopa, AZ and Pinellas, FL sample spectra together with the observation that these two samples have higher crustal elements such as Mn, Ti, and Al concentrations is consistent with these two samples having more of a crustal influence; literature review<sup>45,46</sup> also suggests the doublet might be associated with Mn(IV) oxides which can be important in mineral and crustal sources. However, a study of Asian samples impacted by resuspended dust<sup>21</sup> did not find any evidence of Mn(IV) compounds in their samples.

Our results (Figure 3) indicate that Mn(II) oxide (MnO) is present in all samples (8% to 28% of total Mn). MnO is a basic oxide that is insoluble in water but dissolves in acids. It is readily assimilated by living organisms, which explains its use as a component of fertilizer and feed additives. Many thousands of tons<sup>49</sup> are produced annually for this purpose.<sup>49</sup> It is also used in the production of specialty ceramics and glasses for electronic applications, in ferrites and thermistors, and for making welding rod fluxes and high-purity Mn chemicals, which likely explains our widespread findings.

The more reactive Mn(III) oxide ( $\text{Mn}_2\text{O}_3$ , insoluble) is used for the preparation of electronic materials such as ceramic magnets and semiconductors.<sup>49</sup> Mn(III) oxide was found in relatively high proportions (21–42%) in Harris, TX, Maricopa, AZ, and Pinellas, FL samples and contributes little to the Anoka, MN sample (8%), and it was absent from the Sacramento CA sample. It was the most dominant species in Pinellas, FL (42%), which is a major producer of electronics components,<sup>50</sup> as are Maricopa, AZ (34%) and Harris, TX (21%).

Mn(II) acetate is also present in all five samples, where it contributes between 8% and 40% of the total Mn. It predominates in Harris, TX and Anoka, MN with ~35%. Mn(II) acetate (soluble) is used as a desiccant and a catalyst in textile dyeing, feed additives, food packaging, and paints and varnishes and as fertilizer.<sup>32,50</sup> The widespread use of Mn(II) acetate in industry might explain our findings. Additionally, Mn acetate is expected to be higher in places where there are significant sources of hydrocarbon emissions, which is the case of Harris and in our case Anoka, due to the proximity to the airport. The significant proportion of acetates found in all our samples suggests that organic ligand-bound metals are not easily oxidized and can remain in PM even when sampled at high flow rates and for extended periods of time.

Mn(II) pyrophosphate was found in Sacramento, CA (21%), Maricopa, AZ (48%), and Anoka, MN (33%) counties. Mn pyrophosphate ( $\text{Mn}_2\text{P}_2\text{O}_7$ ) compounds are used as catalysts, reactants in ionic conditions, ceramic dye pigments, ionic conductors, and superphosphate fertilizers.<sup>51</sup> The inorganic

pigment known as manganese violet (a manganese ammonium pyrophosphate complex) has nearly ubiquitous use in cosmetics and is also found in certain paints.<sup>33</sup> Sacramento, Maricopa, and Anoka counties are all heavily industrialized (Tables 1 and S1, Supporting Information). Investigation into the possible sources of this compound is ongoing.

Mn(II) sulfate was the predominant species in the Sacramento, CA sample (58%) and was also present in Harris, TX (13%). Mn(II) sulfate is commercially one of the most important Mn products. It is the precursor to manganese metal production and other chemical compounds such as fungicides and pigments,<sup>49</sup> and Mn-deficient soil is remediated with this salt. Additionally, some metals emitted from incinerators as chlorides can be transformed to sulfate in the atmosphere in the presence of water and acid conditions.<sup>52</sup> California is one of the states with the largest number of manufacturing plants that use Mn,<sup>33</sup> which could help explain the Mn sulfate found in Sacramento county. The only other sample with Mn(II) sulfate was Harris, TX where it contributes 13% of total Mn. As a world leader in petrochemical, chemical, and metal manufacturing industries, the air in Harris, TX has many potential sources of Mn (Table S1, Supporting Information).

Mn(II) chloride was only marginally present in our Pinellas, FL (8%) and Maricopa, AZ (7%) samples. Mn(II) chloride is mainly used in the production of dry cell batteries. It is also the precursor to the antiknock compound MMT.<sup>49</sup> As mentioned before, metals emitted from incinerators as chlorides are transformed in the presence of water and acidity in the atmosphere, where HCl can evaporate from the particles allowing for  $\text{Cl}^-$  replacement by sulfate, nitrate, or acetate. This might explain why we did not find an abundance of Mn(II) chloride in our samples.

There are very few studies that we are aware of that have analyzed ambient PM for Mn chemistry. For example, Wang et al.<sup>29</sup> sampled urban and agricultural areas in China and analyzed for Mn in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  samples by comparing it to reference Mn(II) and (IV) materials. By visual inspection of the spectra, Wang et al. concluded that Mn was present in divalent form in their samples and from those two standards conclude that probably sulfate and other compounds of divalent Mn are present. Ohta et al.<sup>21</sup> analyzed Fe, Mn, and Zn in 6-stage size-segregated PM from four cities across Asia to track airborne transport of aeolian dust. They compared XAS spectra to one standard of each Mn valence state (II, III, IV) and normalized by total Mn for the comparison. Ohta et al. found Mn(II) and (III) in all their samples, with none containing Mn(IV). Differences in composition were not analyzed in that study. Ressler et al.<sup>53</sup> sampled PM directly from the exhaust of vehicles running with MMT-added gasoline and found that Mn(IV) oxide, Mn(II) sulfate, and Mn(III) phosphate were the principal components of the exhaust, which vary in proportion depending on vehicle, driving cycle, and mileage accumulation. Further analysis<sup>20</sup> revealed evidence of Mn species formation in the exhaust of vehicles. These last two studies sampled PM at the vehicle's exhaust and thus cannot be directly compared to our results of ambient samples that may/probably have undergone photochemical modifications.

Other studies have applied XAS and LCF analysis to ambient PM samples focusing on different elements. Majestic et al.<sup>22</sup> examined L-edge iron oxidation states in size-fractionated PM samples collected from three US cities and showed that >60% Fe was in the form of Fe(II) and varied little among size fractions or with aging. Werner et al.<sup>23</sup> used micro-XANES to

speciate chromium in airborne PM<sub>2.5</sub> from three sites in the Sacramento Valley and found that Cr(III) was the dominant form, with the more toxic Cr(VI) found only in the most urban site; Cr(OH)<sub>3</sub> and a Cr–Fe phase were found to be the dominant species. Of the studies described above, Wang et al.<sup>29</sup> also analyzed for Cr, Cu, and Zn, and Ohta et al.<sup>21</sup> analyzed Fe and Zn.

The spectra from the five county samples could not be fully reproduced with any combination of the reference spectra that were included in the linear combination fits. This indicates the presence of additional Mn species and compounds that cannot be conclusively determined from the present analysis. Other Mn species that might be present in our samples include birnessite, which is a byproduct of potassium permanganate oxidation used in chemical processes and water purification, and Mn gluconate, used in pharmaceutical production, as well as a small fraction of mineral aerosols, asphalt, and cement, that could be present in the smaller particle sizes of resuspended aerosols from vehicular traffic. We chose standard compounds that are relevant to ambient aerosol and stable in an oxidizing environment in order to account for as much of the spectra as possible.

This notwithstanding, results of the LCF analysis were satisfactory to describe differences in composition between samples and complement other speciation reported in the literature for Mn characterization of ambient PM.<sup>21,29</sup>

It is possible that the oxidation of metals vary depending on the length of sampling and meteorological conditions during sampling. Some ways this might happen is during periods of high humidity and postdeliquescence oxidation by ozone, dissolved oxygen, or hydrogen peroxide. In these cases, soluble Mn will likely become sulfate, nitrate, or acetate (from small aldehyde oxidation) as fine particles age.<sup>52</sup> This is a limitation of all integrated air sampling studies in which samples are collected for extensive periods of time; we hope to address this in the future by collecting samples side by side for different times to assess how weather changes oxidation states of different metals.

Synchrotron-based analyses have been extensively applied in soil and mineral sciences but are only recently gaining widespread use in the study of particulate matter in ambient air. A search of the literature returns only a handful of papers that are using XAS to analyze air samples. Consequently, there is a need to define the best protocols for the collection of air samples to be evaluated using XAS techniques, as well as to optimize analysis parameters for different types of air samples. Some of the optimizations might include XAS analysis of aqueous or acid leachate that would contain minor species to complement the LCF fits.

To our knowledge, this is the first study to demonstrate that there are large differences in the contribution of Mn compounds to total Mn in samples collected from locations across the US. For example, Mn acetate, although present in all samples, contributed more than 40% to the Maricopa sample and less than 10% to the Sacramento sample. Conversely, manganese oxide II contributed almost 60% to the Sacramento sample but was not found at all in Pinellas, Maricopa, or Anoka samples. Future studies will explore differences in other elements and how the oxidation of metals varies depending on the length of sampling and atmospheric conditions. Differences in composition<sup>48</sup> of the five counties sampled for this study reflect regional variations in sources and atmospheric

chemistry and may eventually help explain differences in health effects found by epidemiological and toxicological studies.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

One table (Table S1) of additional references for the traffic counts contained in Table 1 and two figures (Figures S1 and S2). This information is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Address: Johns Hopkins University, Bloomberg School of Public Health, Department of Environmental Health Sciences, 615 N. Wolfe Street, E-6618 Baltimore MD 21205; e-mail: [arule@jhsph.edu](mailto:arule@jhsph.edu).

### Notes

The authors declare no competing financial interest.

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